Chinese Journal of Physics

February 2014

Part II

Special Issue on ‘Ultrafast Intense Laser Science’

Published by

The Physical Society of the Republic of China
Taipei, Taiwan, R.O.C.
Http://PSROC.phys.ntu.edu.tw/cjp
CONTENTS

Preface .......................... See Leang Chin, Shih-I Chu, Sheng Hsien Lin, and Jyhpyng Wang  i

Atom
Probing and Controlling Autoionization Dynamics with Attosecond Light Pulses in a Strong
Dressing Laser Field .......................... Wei-Chun Chu, Toru Morishita, and C. D. Lin 301

Effect of Ionization on the Wavelength Scaling of High Harmonic Generation Efficiency ....
................................. Jun Dai, Zhinan Zeng, Candong Liu, Ruxin Li, and Zhizhan Xu 320

Semi-Classical Methods in Non-Sequential Double Ionization ..............................
................................. Allan S. Johnson, André Staudte, and D. M. Villeneuve 329

Nonperturbative Atomic Dynamics: Population Trapping and Polarization Response in Strong

High-Order Harmonic Generation Driven by Two-Color Laser Fields ........................
................................. Guihua Li, Jiping Yao, Chaojin Zhang, Bin Zeng,
..... Wei Chu, Jielei Ni, Jing Chen, Zhinan Zeng, Ruxin Li, Ya Cheng, and Zhizhan Xu 366

Quantum Orbits: a Powerful Concept in Laser-Atom Physics ... Wei Quan, XuanYang Lai,
..... YongJu Chen, ChuanLiang Wang, ZiLong Hu, XiaoJun Liu, XiaoLei Hao, Jing Chen,
..... Elvedin Hasovic, Mustafa Busuladzic, Dejan B. Milosevic, and Wilhelm Becker 389

Numerical Simulations of Attosecond Streaking Time Delays in Photoionization ...........
................................. Jing Su, Hongcheng Ni, Andreas Becker, and Agnieszka Jaroñ-Becker 404

Filamentation
Laser Air Photonics: Covering the “Terahertz Gap” and Beyond ............................
................................. Benjamin Clough, Jianming Dai, and X.-C. Zhang 416

Supercontinuum Generation in Barium Fluoride Using Bessel Beams ......... Krithika Dota,
..... Jayashree A. Dharmadhikari, Deepak Mathur, and Aditya K. Dharmadhikari 431

Dynamics and Kinetics of Laser-Filament Plasma in Strong External Electric Fields and
Applications ......... Takashi Fujii, Alexei Zhidkov, Megumu Miki, Kiyohiro Sugiyama,
..... Naohiko Goto, Shuzo Eto, Yuji Oishi, Eiki Hotta, and Koshichi Nemoto 440

Intensity Clamping During Femtosecond Laser Filamentation ............................ Weiwei Liu 465

Controlling Laser Filamentation Induced Strong THz Fields ..............................
................................. M. Massaouti and S. Tzortzakis 490
Ionic Valence Change of Metal Ions in Solution by Femtosecond Laser Excitation Accompanied by White-Light Laser ........................................................... Nobuaki Nakashima, Ken-ichi Yamanaka, Ayaka Itoh, and Tomoyuki Yatsuhashi 504


Laser Fusion
Nuclear Fusion Driven by Coulomb Explosion of Deuterated Methane Clusters in an Intense Femtosecond Laser Field .................................................. Jiansheng Liu, Haiyang Lu, Zili Zhou, Cheng Wang, Hongyu Li, Changquan Xia, Wentao Wang, Yi Xu, Xiaoming Lu, Yuxin Leng, Xiaoyan Liang, Guoquan Ni, Ruxin Li, and Zhizhan Xu 524

Laser Technology

Review of Multi-Frequency Raman Generation ................................................. D. Strickland 546

Molecule
Atomic and Molecular Photoelectron Holography in Strong Laser Fields .................... Xue-Bin Bian and André D. Bandrauk 569


Nonadiabatically Coupled π-Electron Rotation and Molecular Vibration in Aromatic Molecules Excited by Polarized UV/Vis Laser Pulses .................................................. Manabu Kanno, Yukari Ono, Hirohiko Kono, and Yuichi Fujimura 617

Fragmentation of Hydrocarbon Molecules in Intense Laser Fields Studied by Coincidence Momentum Imaging: a Review .................................................... Bosi Yang, Li Zhang, Huailiang Xu, Ruxin Li, and Kaoru Yamanouchi 652

Cumulative Author Index .................................................................................. 675

Covered in Citation Index
Abstracts Covered in Physics Abstracts and Chemical Abstracts
Contents Covered in Current Contents/PC&ES, SciSearch and Research Alert
©Copyright by The Physical Society of the Republic of China, 2014
PREFACE

This special issue presents review and original papers written by many top specialists working at the forefront of ultrafast intense laser science. The subjects range from the physics of atoms and molecules in an intense laser field, femtosecond laser filamentation as well as modern laser technology and laser fusion. These include theories and experiments on high harmonic generation, attosecond physics, laser fusion, supercontinuum generation, filament induced lightning, filamentation control and applications, THz in air filament, filament chemistry in liquids. They are organized into the following categories, namely, atoms, molecules, filamentation, laser technology and laser fusion. In each category, the papers are organized in alphabetical order according to the name of the first author. This special issue should be useful for those working in the field and those who would like to get into the field. To this end, we would like to thank all the authors for their kind and enthusiastic support.

The co-editors
See Leang Chin, Laval University, Canada
Shih-I Chu, National Taiwan University, Taiwan and University of Kansas, USA
Sheng Hsien Lin, National Chiao Tung University, Taiwan
Jupyter Wang, Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan
Review

Probing and Controlling Autoionization Dynamics with Attosecond Light Pulses in a Strong Dressing Laser Field

Wei-Chun Chu,1,2,* Toru Morishita,3 and C. D. Lin1
1J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66056, U. S. A.
2Max Planck Institute for the Science of Light, Günther-Sharpovsky-Straße 1, 91058 Erlangen, Germany
3Department of Engineering Science, The University of Electro-Communications, 1-5-1 Chofu-ga-oka, Chofu-shi, Tokyo, 182-8585, Japan
(Received September 18, 2013)

We review the theoretical investigations of the autoionizing wave packet excited by an isolated attosecond pulse and dressed by a time-delayed intense laser pulse. The few-level model is described and the applications in photoemission and photoabsorption are given. For the three-level, resonantly coupled system, the main features are explained by the Rabi oscillation modulated in the dressing field. For such a system, by precisely controlling the intensity and the time delay of the dressing pulse, we show the shaping of the attosecond pulse when propagating in a gas medium. A more sophisticated multi-level system with coupling terms involving continuum states is also developed, in which the importance of the continuum-continuum coupling is evaluated with the help of an ab initio calculation.

DOI: 10.6122/CJP.52.301 PACS numbers: 32.80.Qk, 32.80.Zb, 42.50.Gy

I. INTRODUCTION

Atomic and molecular physics deals with systems in the quantum mechanical spatial and temporal scales. These quantum systems are traditionally studied by energy-domain measurements with highly developed spectroscopic tools. The absolute domination of the energy-domain measurements has changed in the past two decades as the ultrafast tools have acquired better precision, stability, and efficiency over time. One of the most remarkable ultrafast technologies in recent years is the emergence of reliable, table-top light sources in the attosecond timescales in the forms of attosecond pulse trains (APTs) and isolated attosecond pulses (IAPs), which are enabled by the high harmonic generation (HHG) in noble gases [1, 2]. These light sources have now become indispensable tools for the measurement and control of ultrafast electronic dynamics in quantum systems. In this article, we limit ourselves to the use of IAPs for their absolute short timescales and the broadband features, while thorough introductions to the APTs can be found in extensive review articles [3, 4].

Using extreme ultraviolet (XUV) IAPs synchronized with intense infrared (IR) pulses to

*Electronic address: wei-chun.chu@mpl.mpg.de
detect electronic dynamics was demonstrated in 2001 for the first time in the photoelectron emission of krypton atoms [5], and the general method has since been applied to study many atomic and molecular processes, including electron tunneling [6], autoionization [7–10], ac Stark effect [11], and dissociation [12] and ionization [13] of molecules.

Autoionization is a fundamental electron correlation effect in quantum systems. With the typical timescale of a few to a few hundreds of femtoseconds, the excited autoionizing state (AIS) decays to the degenerate background continuum, leaving an asymmetric resonance shape in the photoemission (photoelectron) spectroscopy (PES) or photoabsorption spectroscopy (PAS), which has been characterized by Fano with a simple formula [14]. Physicists have long been observing “Fano resonances” in spectroscopy, most commonly in synchrotron radiations for high precision measurements. The asymmetry and the width of the lineshape are determined by the fraction of the metastable-state quantum pathway and the lifetime of the metastable state, respectively, in a photoionization event. The theory thus connects the spectral measurement to the dynamics of the autoionization process.

Along the development of mode-locked lasers and strong field physics [15], autoionizing systems in strong coupling fields, in analogy to the condition for the electromagnetically induced transparency (EIT) done in bound excited states [16], have been carried out in numerous theoretical reports [17–20] and experiments [21, 22]. The EIT effect has been well established and become the base of a number of modern optical techniques [23] and can readily explain the main features in the coupled autoionizing systems. However, the pulses therein were still considered long compared to the autoionization process and could not resolve the dynamics directly. The direct time-domain measurement of autoionization was infeasible until the recent breakthrough in attosecond light sources and in related ultrafast techniques. For an IAP-excited AIS, the time evolution and the general behavior of the unperturbed wave packet has been treated numerically [24, 25]. In the XUV+IR configuration, by utilizing the IR simply to deplete the AIS or to “streak” [26–28] the photoelectrons, the time-domain studies in autoionization were performed theoretically [29, 30] and experimentally [7, 8], where the AIS lifetimes could be retrieved. However, such studies did not capture the strong coupling between resonances that were emphasized in Refs. [17–22], and thus limited the capability of the dressing field to effectively manipulate the autoionizing system. Beside the models, ab initio calculations have also been employed for the time-domain experiments for autoionization [31, 32]; however, they are usually numerically expensive and hard to be extended to more complex systems.

Our goal in this article is to review the development and application of the few-level model which considers the ultrafast coupling between autoionizing states using a synchronized pair of pulses—an IAP and a few-femtosecond intense laser pulse [33–36]. The wave packet evolving in time is simulated, which returns the PES or PAS comparable to experimental measurements. In all scenarios, the ability to control the autoionizing wave packet relies on time-resolving the dynamics of autoionization, the Rabi oscillation, and the evolution of the pulses. The treatment of the continuum states in such an attosecond wave packet needs to go beyond earlier approaches [17–20], which would then trigger spectral features unexpected previously.

The article is organized in the following way. In Sec. II, the EIT-like coupled au-
toionizing system is presented. The model for the wave packet evolution is described, which provides the fundamentals for spectroscopic calculations. Sec. III introduces the PES in this model and demonstrates an attosecond time-delayed PES of the 2s2p\(^1\)P resonance in helium dressed by a strong laser pulse. In Sec. IV, the simulation for PAS is illustrated and demonstrated in the same system. Comparison is made against the simulation with long pulses, which recovers the typical EIT features. In Sec. V, propagation of the IAP is then considered for the realistic pulse reshaping. A remarkable enhanced resonant part of the IAP was theoretically predicted. While the above sections deal with the three-level system, Sec. VI extends the model to include multiple AISs and the coupling involving continuum states, with the help by the \textit{ab initio} calculation. The retrieval of the atomic structure is shown possible in the presence of such coupling terms. In all sections, for the model description, atomic units (a.u.) are used unless otherwise specified, and for applications, electron Volts (eV) are used for energy and femtoseconds (fs) are used for time unless otherwise specified.

II. THREE-LEVEL WAVEFUNCTION

Three-level systems coupled by laser fields are most notably studied for coherent population trapping (CPT) \cite{37, 38} and the EIT effect \cite{16, 23}. It is common to solve the time-dependent Schrödinger equation (TDSE) for the coherent quantum state of the system in terms of the atomic eigenstates. With intense laser pulses, as what this article concerns, the field is treated classically. Our intention is to calculate the time-evolution of the wavefunction for the Hamiltonian of the system specified by a given set of atomic parameters and the external field.

For coupled AISs, as differing from coupled bound states, the continuum states associated to the AISs are included in the total wavefunction as in Refs. [17–20] and illustrated in Fig. 1. The wavefunction can be generally written in the form of

\[
|\Psi(t)\rangle = e^{-i\epsilon_g t}c_g(t)|g\rangle + e^{-i\epsilon_c t}\left[c_{b_1}(t)|b_1\rangle + c_{b_2}(t)|b_2\rangle\right] + \int c_{\epsilon_1}(t)|\epsilon_1\rangle d\epsilon_1 + \int c_{\epsilon_2}(t)|\epsilon_2\rangle d\epsilon_2,
\]

where \(|g\rangle\) is the ground state, \(|b_1\rangle\) and \(|b_2\rangle\) are the bound configurations of the two Fano resonances, and \(|\epsilon_1\rangle\) and \(|\epsilon_2\rangle\) are the two groups of continuum states associated with \(|b_1\rangle\) and \(|b_2\rangle\), respectively. The energy levels of the three bound states are \(\epsilon_g\), \(\epsilon_{b_1}\), and \(\epsilon_{b_2}\), respectively, and \(\epsilon_c \equiv \epsilon_g + \omega_X\) is the central energy of the excited wave packet, with the XUV central frequency \(\omega_X\) factored out of the excited wave packet. Note that the \(|b\rangle\) and \(|\epsilon\rangle\) states are not eigenstates of the atomic system, but rather a convenient choice where autoionization can be visualized. With the XUV+IR setup, the \(|b_1\rangle-|\epsilon_1\rangle\) resonance is directly excited by the XUV from the ground state, when the \(|b_1\rangle\) and \(|b_2\rangle\) AISs are coupled by the IR field. The coupling scheme is plotted in Fig. 1 schematically. The XUV field is expressed in the envelope form as \(E_X(t) = F_X(t)e^{i\omega Xt} + F_X^*(t)e^{-i\omega Xt}\), but the IR field \(E_L(t)\)
FIG. 1: Schematics of the coupled three-level autoionizing system. The XUV IAP excites the wave packet around the $|b_1\rangle-|\epsilon_1\rangle$ resonance, while the intense IR pulse couples it to the other AIS.

is kept in its numerical form because it may be a few-cycle pulse. The XUV envelope $F_X(t)$ is a smooth function of time against the fast oscillation with the carrier frequency $\omega_X$. It is in general complex and it contains any extra phase additional to the carrier phase.

Taking only the electric dipole terms in the light-matter interaction, the Hamiltonian of the system is written as

$$H(t) = H_A - D \cdot E(t), \tag{2}$$

where $H_A$ is the atomic Hamiltonian determined by the field-free atomic structure, $D$ is the dipole operator, and $E(t)$ is the total external field. The off-diagonal terms of $H_A$ in the current basis, $V_{b_1\epsilon_1} = \langle b_1 | H_A | \epsilon_1 \rangle$ and $V_{b_2\epsilon_2} = \langle b_2 | H_A | \epsilon_2 \rangle$, are responsible for the autoionization. By solving TDSE with this Hamiltonian, the coupled equations for the coefficients in Eq. (1) are obtained. For the system in concern, the following representations and approximations are then made to simplify the model: (1) Standing wave representation is taken for the basis set, so all the matrix elements in the Hamiltonian are real. The use of such basis is conventional and does not impose any physical restriction. (2) The AISs are assumed to be far above the ionization threshold compared with their widths, where the scattered electrons have almost constant momentum across the AISs. As a consequence, the atomic parameters can be viewed as constants estimated at the resonance frequencies, i.e., $V_{b_1\epsilon_1} = V_{b_1\epsilon_b_1} \equiv V_{b_1}$, $D_{g\epsilon_1} = D_{g\epsilon_b_1} \equiv D_{g1}$, and so on. This approximation is good in many autoionizing systems; for example, the $2s2p(1P)$ resonance in helium is 35 eV above the binding energy compared to its width of 37 meV. (3) Rotating wave approximation is applied to the XUV since its photon energy is roughly on resonance with the AISs within a confined bandwidth. (4) By assuming that the continuum state coefficients evolve slowly in time, we employ adiabatic elimination (AE) for them. With these assumptions, we arrive at the self-contained equation of motion (EOM) for the bound part of the wavefunction,
given by

\[
\begin{align*}
i\dot{c}_g(t) &= - F_X(t) \bar{D}_{gb_1} c_{b_1}(t) - i |F_X(t)|^2 j_{gg} c_g(t), \\
i\dot{c}_{b_1}(t) &= - F_X^*(t) \bar{D}_{gb_1} c_g(t) - (\delta_1 + i\kappa_1) c_{b_1}(t) - E_L(t) D_{b_1 b_2} c_{b_2}(t), \\
i\dot{c}_{b_2}(t) &= - (\delta_2 + i\kappa_2) c_{b_2}(t) - E_L(t) D_{b_1 b_2} c_{b_1}(t),
\end{align*}
\]

where \( j_{gg} \equiv \pi |D_{g1}|^2 \) is the broadening of the ground state by the field, \( \delta_1 \equiv \epsilon_e - \epsilon_{b_1} \) and \( \delta_2 \equiv \epsilon_e - \epsilon_{b_2} \) are the detuning of the XUV to the AISs, \( \Gamma_{b_1} = 2\kappa_{b_1} = 2\pi|V_{b_1}|^2 \) and \( \Gamma_{b_2} = 2\kappa_{b_2} = 2\pi|V_{b_2}|^2 \) are the resonance widths, and \( \bar{D}_{gb_1} \equiv D_{gb_1} - i\pi V_{b_1} D_{g1} \) is the composite dipole matrix element between \( |g\rangle \) and \( |b_1\rangle \) consisting the direct and indirect paths. Note that \( \bar{D}_{gb_1} \) is complex although the individual dipole matrix elements are real in the standing wave representation. The Fano lineshape parameter \( q \equiv \bar{D}_{gb_1}/(i\pi V_{b_1} D_{g1}) \) is determined exclusively by the atomic structure parameters \( D \) and \( V \) and already embedded in the coupled equations. The bound part of the wavefunction is carried out without any numerical treatment for the continuum coefficients. The required input parameters are the \( D \) and \( V \) values which are totally determined by the atomic structure, and the external field parameters. Up to this point, the model can deal with problems with long pulses where their narrow bandwidths are viewed as energy points in the spectrum, and the wave packet has negligible portion of the continuum states, as shown in Refs. [17–22].

With the use of ultrashort pulses, when the pulse length gets comparable to or even shorter than the autoionization, the bandwidth covers an energy range comparable to or wider than the resonance width. This means that the short pulse excites a considerable portion of the continuum states around the AISs, and the evolving wave packet has to include the continuum part. To this end, the continuum state coefficients are calculated by bringing in the original coupled equations,

\[
\begin{align*}
i\dot{c}_{e_1}(t) &= (\epsilon_1 - \epsilon_g - \omega_X) c_{e_1}(t) + V_1 c_{b_1}(t) - F_X^*(t) D_{g1} c_g(t), \\
i\dot{c}_{e_2}(t) &= (\epsilon_2 - \epsilon_g - \omega_X) c_{e_2}(t) + V_2 c_{b_2}(t),
\end{align*}
\]

where all the bound state coefficients therein have already been solved in Eqs. (3)-(5). The recovery of the continuum state coefficients is an iteration process which “corrects” the zeroth order solution that is only used in the AE. Note that the solution at each energy point in Eqs. (6) and (7) is independent of other energy points, so the precision of the solution is irrelevant to the energy range and the energy resolution taken in the computation. Up to here the total wave function of this atomic system is calculated, where all observables can be derived accordingly.

### III. PHOTOEMISSION

For photoionization events, PES, PAS, and photoion spectroscopy are all common measurements. In PES, with various detection angles against the polarization direction, the scattered electrons in momentum space are recorded. Let the excited part of the wave packet in Eq. (1) be denoted by \( |\Psi_E(t)\rangle \). The momentum distribution of the detected
scattered electrons can then be written as \( P(\vec{k}) = |\langle \psi_k^{(-)} | \Psi_E(t_f) \rangle|^2 \), where \( P(\vec{k}) \) is the probability density in the momentum space, \( |\psi_k^{(-)} \rangle \) is the momentum eigenstate with the incoming boundary conditions, and \( t_f \) is the time of the detection, which should be very large in the atomic timescale. The momentum eigenstates can be written in the coordinate space as the expansion of the scattering partial waves, in the energy-normalized form of

\[
\psi_{\vec{k}}(\vec{r}) = \sqrt{\frac{2}{\pi k r}} \sum_{lm} i^l e^{-in} u_l(kr) Y_l^m(\hat{r}) Y_l^{m*}(\hat{k}),
\]

(8)

where \( u_l(kr) \) are the radial waves and \( Y_l^m \) are the spherical harmonics of angular momentum \( l \) and magnetic quantum number \( m \). By removing the azimuth dependence, \( P(\vec{k}) \) is given in spherical coordinate by

\[
P(\epsilon, \theta) = \left| \sum_l \sqrt{\frac{2l + 1}{4\pi}} \frac{e^{im}}{r} c_{l}(t_f) P_l(\cos \theta) \right|^2,
\]

(9)

where \( \epsilon = k^2/2 \) is the kinetic energy, \( \theta \) is the polar angle with regard to polarization, \( c_{l}(t_f) \) are the final continuum state coefficients, and \( P_l(\cos \theta) \) are Legendre polynomials.

In the three-level autoionizing system, the two resonances dominate two different partial waves, and their energy spectra can be simulated separately. An angular-integrated spectrum is given by \( P(\epsilon) = \sum_l |c_{l}(t_f)|^2 \) where \( c_{l}(t) \) is the corresponding continuum state coefficients simulated as described in Sec. II. In principle, \( t_f \) should be infinitely large when all the dynamic processes are over. Practically, it is set after the external fields and must be much larger than the decay lifetimes of the AISs, since the decay processes are exponential without a definite end. For example, the \( 2s2p(1P) \) AIS in helium has a lifetime of 17 fs, and \( t_f \) can be set 200 fs later than the end of the external field, at which time the wave packet is finalized in the energy or momentum space [25]. For systems of longer decay lifetimes, a technique to reduce the total calculation time is to project the wave packet right after the end of the external field onto the atomic eigenstates, at which point the eigenstate coefficients will not change anymore (except the regular phase rotation). This technique is based on Fano’s configuration theory for autoionization [14] and was described in details in Ref. [33].

For demonstration, we simulate the PES of the \( 2s2p(1P) \) resonance (referred as \( 2s2p \) hereafter) of helium where the “IR” pulse couples this resonance to the \( 2s^2(1S) \) resonance (referred as \( 2s^2 \) hereafter). The 500 as XUV is weak and centered at \( 2s2p \), which linearly excites a broadband autoionizing wave packet. It is much shorter than the 17-fs decay lifetime of \( 2s2p \) and instantaneously initiates the autoionizing wave packet. The coupling laser pulse (wavelength is 540 nm, pulse length is 7 fs in FWHM, peak intensity is \( 1.5 \times 10^{12} \) W/cm\(^2\)) is actually in the visible wavelength in order to resonantly couple the two AISs. The time-delayed PES is plotted in Fig. 2. The time delay \( t_0 \) is defined positive if the XUV comes before the IR. In the spectrogram [Fig. 2(a)], the lineshape remains the same for \( t_0 < 0 \), but suddenly flips its shape from left to right when \( t_0 \) increases to around 6 fs.
FIG. 2: Time-delayed PES at the 2s2p resonance. (a) Spectrogram for time delays between -15 to 55 fs. (b) PES at $t_0 = 6$ fs which displays a horizontally inverse image of the original Fano lineshape additional to an overall reduction. The corresponding time delay is indicated in (a) by the dashed black line. The original lineshape in the laser-free condition is shown in the background for comparison.

When $t_0$ further increases and becomes large compared to the 17 fs lifetime of 2s2p, the resonance gradually returns to the original lineshape. The dramatic flipping at 6 fs can be understood by the Rabi oscillation between the two AISs. At $t_0 = 6$ fs, the total dressing field after the XUV pulse has a pulse area of 2π, which means once 2s2p is pumped by the XUV, the electrons therein go through one Rabi cycle through 2s and back to 2s2p, where the phase of this oscillating part in the wave packet changes by π. This phase shift has the same effect of changing the sign of $q$ and making a mirror image of the lineshape. At the same time, the signal strength drops because for such an autoionizing system, the excited states decay to the continuum all the time, and the population is lost during the Rabi oscillation. The PES for the 2s2($^1S$) resonance versus the time delay, which we do not show here, also supports this conclusion [33]. The simulated result by this model compared to a recent measurement [8] has been reported [33].
IV. PHOTOABSORPTION

In the same XUV+IR coupling system, the measurement can also be made in PAS. Attosecond transient absorption (ATA) [39] has been one of the most rapidly developing fields in ultrafast optics. Other than the instrumental concerns and the experimental setup, there are some advantages of the PAS over the PES measurements, such as the access to both the ionized and the neutral species, and the higher energy resolution in spectrometers up to 20 meV at 60 eV as demonstrated in the recent experiment [10]. In measuring autoionizing systems, the lineshape observed in high precision for different time delays would be especially informative of the wave packet dynamics.

In the following we introduce the calculation of PAS based on a given external field and the induced total electronic dipole. The response function $S(\omega)$ is defined as the probability density of the energy that the atomic system absorbs from the field [40]:

$$\Delta U = \int_0^\infty \omega S(\omega) d\omega,$$

where $\Delta U$ is the total energy transferred from the field to the atomic system. Following the Hamiltonian in Eq. (2), $S(\omega)$ is given by

$$S(\omega) = -2\text{Im}\left[\tilde{D}(\omega)\tilde{E}^*(\omega)\right],$$

where $D(t)$ is the total electric dipole moment of the atomic system, and the Fourier transform is defined by $\tilde{f}(\omega) = \frac{1}{\sqrt{2\pi}} \int e^{-i\omega t} f(t) dt$. The response function has the same dimensionality of the PES probability density $P(\epsilon)$ presented in Sec. III. Both $S(\omega)$ and $P(\epsilon)$ display the spectral lineshapes of Fano resonances.

For the autoionizing system described by in Eq. (1), the dipole moment $D(t)$ is given by

$$D(t) = e^{i\omega_X t} u_X(t) + u_L(t) + c.c.,$$

where the XUV and IR frequency components are separate and given by

$$u_X(t) = D_{gb_1} \chi^* c_{b_1}^\dagger(t) c_g(t) - i F_X(t) j_{gg} |c_g(t)|^2,$$

$$u_L(t) = D_{b_1 b_2} c_{b_2}^\dagger(t) c_{b_1}(t).$$

Because of the separation of the XUV and the IR frequency components in Eq. (12), the PAS can be simulated for only the XUV or IR part of the spectrum. In the current XUV+IR scheme, the IR interacts only with the top two levels, while the overall excitation of these levels is limited by the XUV intensity that is much weaker than the IR. As a consequence, the absorption of IR is negligible compared with the IR pump in most cases in the sense of pulse shaping, unless a very optically thick medium is present. The IR absorption in such a scheme is discussed in Ref. [34], while we deal with only the XUV absorption here. The
The cyan color in (a) indicates the negative absorption, or emission, induced by the dressing field. In (b), the spectrum at $t_0 = 6$ fs shows an upside-down image to the original Fano lineshape in the laser-free condition. Note that the peak of the Fano profile is turned to an emission line by the dressing laser.

response function has a straightforward connection to the commonly used absorption cross section, given by

$$\sigma(\omega) = \frac{4\pi\alpha\omega S(\omega)}{|\tilde{E}(\omega)|^2},$$

for the linear cases before the propagation effect comes in.

In Fig. 3 we show the simulated response function in the PAS result, for the same system introduced in Sec. III. The spectra in Fig. 3 and Fig. 2 have the same dimensionality and can be directly compared to each other. As seen in the figure, the overall dependence on the time delay is almost the same as the PES result, except that there are some negative signals at $t_0 = 6$ fs at the resonance and in the fringes at larger delays above the resonance energy. These negative values represent the emission of the XUV, which cannot be found in typical EIT measurements. This extraordinary phenomenon can again be explained by the Rabi oscillation as in the PES case. The original Fano lineshape represents the interference between the dipole stored in the continuum electrons and the dipole stored in the bound
electrons. At $t_0 = 6$ fs, as the bound electrons go through the $2s2p-2s^2-2s2p$ Rabi cycle, they gain an additional $\pi$ phase shift. It means that between the two interfering paths, only the bound but not the continuum path changes. The field generated by the coherent sum of the two dipole components, with one of them shifted phase by $\pi$, carries the spectral pattern where the constructive and destructive parts of the interference swap. This results in the upside-down lineshape and forms an emission peak at the resonance energy.

In order to elucidate how such an ultrafast three-level coupling differs from the typical EIT system, we conduct an additional simulation with a 50-fs long dressing field. The pulse length is considerably longer than the 17-fs decay lifetime of $2s2p$. Fig. 4 shows the time-delayed PAS of the XUV in this dressing field. The most obvious feature in the spectrogram is the splitting of the absorption peak, whose separation distance changes with the time delay. The separation reaches maximum at $t_0 = 15$ fs as shown in Fig. 4(b). The separation there of about 3.5 eV is the same as the Rabi frequency of the dressing field, which is expected as the Autler-Townes doublet [41] in such an EIT scheme. As the dressing pulse temporally shifts away from the XUV, the absorption profile returns to the single-peak shape. It suggests that the whole XUV-excited wave packet “sees” a stable dressing field most strongly at $t_0 = 15$ fs, when the existence of the $2s2p$ within its lifetime is mainly at the peak of the dressing pulse. This type of adiabatic control utilizes the time delay

FIG. 4: Same as Fig. 3 but for the longer (50 fs) dressing field. The spectrum at $t_0 = 15$ fs is shown in (b) where the Autler-Townes splitting is the largest.
between the XUV and the IR to turn on or turn off the EIT effect and has been carried out experimentally in Ref. [22].

V. PROPAGATION EFFECT

The linear absorption of light across a gas medium can be described by Beer’s law [42], i.e.,

\[ T(\omega) = T_0(\omega) \exp[-\rho L \sigma(\omega)], \]  

(16)

where \( T_0(\omega) \) and \( T(\omega) \) are transmission spectra before and after the gas medium of number density \( \rho \) and propagation length \( L \). The absorption cross section \( \sigma(\omega) \) represents the rate of absorption which does not change along the path of light. On the contrary, in the nonlinear regime, the absorption is strongly dependent on the instantaneous electric field, and the cross section evolves over the distance where the light pulse reshapes itself. In such cases, Maxwell equation has to be applied.

Similar to the consideration in Sec. IV, we focus on the propagation of the XUV where the IR is assumed to propagate without change across the medium. Applying loosely focusing condition which is typical in ATA spectroscopy, we assume that the electric field is transverse to the pulse propagation in the forward \( z \) direction. Using the coordinate transformation \( t' = t - z/c \), the Maxwell equation can be simplified to the first-order form of

\[ \frac{\partial E(z, t')}{\partial z} = -\frac{\rho}{2 \varepsilon \varepsilon_0} \frac{\partial D(z, t')}{\partial t'}. \]  

(17)

At each spatial point, the total wavefunction and the dipole oscillation in time is calculated in the given external field, which then determines the field at the next point, from the front to the rear end of the medium. Taking only the XUV field into account, the envelope of the XUV is propagated by

\[ \frac{\partial F_X(z, t')}{\partial z} = -\frac{\rho}{2 \varepsilon \varepsilon_0} \left[ \frac{\partial u_X(z, t')}{\partial t'} + i \omega_X u_X(z, t') \right], \]  

(18)

where \( u_X(t) \) represents the envelope of the XUV dipole, given in Eq. (13).

In Sec. IV, the emission peak of the XUV is induced by a precisely controlled dressing-field. It is shown as the negative absorption in the response function, or equivalently, in the single-atom absorption cross section. However, a negative absorption rate cannot sustain itself physically in an actual medium, or it would become singular at certain spatial point. Thus, it is interesting to simulate this emission peak and to study its behavior in the medium with actual propagation effects. With the same helium system and the same field parameters in Sec. III, we assume a gas medium of the pressure of 25 Torr at room temperature, which is equivalent to the number density of \( 8 \times 10^{17} \) cm\(^{-3}\). Simulation carried out up to the propagation distance of \( z = 2 \) mm is shown in Fig. 5, where the general trend
along the path and the detail spectral shapes at 1 and 2 mm are shown in Fig. 5(a) and Fig. 5(b), respectively. It shows that in contrast to the Beer’s law, the emission part of the propagating spectrum does not (and cannot) grow exponentially. Instead, it remains the height along the propagation, while the background signal around it drops exponentially, as clearly seen by the $z = 1$ and 2 mm spectra in Fig. 5(b). This remarkable case exemplifies
the redistribution of the XUV photons controlled by the IR dressing pulse, while the total XUV energy attenuates along the propagation in the medium regardless of the appearance of the IR.

As shown in Fig. 3, in the single-atom calculation, a strong modulation of the emission peak lies on the time delay of the laser pulse. In the macroscopic simulation here, in order to emphasize this modulation at the resonance, we assume a spectrometer with the energy resolution of $\Delta \epsilon = 40$ meV at the resonance position at 60.15 eV. By collecting the transmitted XUV within this $\Delta \epsilon$ interval, the total yield at the exit of the medium ($z = 2$ mm) is plotted against the time delay in Fig. 5(c). As predicted by the single-atom case, the strongest emission occurs at $t_0 = 6$ fs, which is clearly higher than the incident light, i.e., the XUV experiences a gain at the resonance frequency in the medium. As the time delay moves away from this optimal value, the XUV starts to be absorbed. With large temporal separation between the pulses, the level of absorption rises back to that of the original Fano lineshape. The variation of the emission yield along the time delay, specified by the 40-meV spectral window, shows a strong manipulation on a broadband attosecond pulse, in both the energy domain and the time domain. Further discussions and demonstrations for the intensity dependence is given in Ref. [35].

VI. CONTINUUM-CONTINUUM COUPLING

The IR coupling in the model illustrated in Fig. 1 is between the bound states for taking only the first-order transition, where the coupling involving any continuum state is neglected. However, if we widen the bandwidth of an ultrashort coupling pulse that covers a continuum with a number of embedded bound states, the collective transition to the continuum will increase, but the transition to the bound states will stay the same since it is already confined by the resonances’ own widths. Consequently, neglecting the coupling through continuum states, i.e., bound-continuum coupling and continuum-continuum (C-C) coupling, is not appropriate once the pulse becomes shorter. To bring such coupling into the model and to test its validity, we employ an \textit{ab initio} two-active-electron (TAE) TDSE calculation [43, 44] as a virtual experiment to calibrate the model. The TAE-TDSE method describes the time evolution of the two-electron wavefunction in space in the nuclear potential. It then projects the total wavefunction onto the eigenstate wavefunctions with the correct scattering boundary conditions to obtain the energy spectrum for each partial wave. To conduct a realistic calibration for the model, the size of the system in Sec.II is further expanded so that each symmetry in the coupling possesses multiple AISs. The coupling scheme is plotted in Fig. 6.

The total wavefunction of the system in Fig. 6 is given by

$$|\Psi(t)\rangle = e^{-i\epsilon g t}c_g(t)|g\rangle + e^{-i\epsilon_C t} \left[ \sum_m c_m(t)|m\rangle + \sum_n c_n(t)|n\rangle \right]$$
$$+ \int c_{\epsilon_1}(t)|\epsilon_1\rangle d\epsilon_1 + \int c_{\epsilon_2}(t)|\epsilon_2\rangle d\epsilon_2 .$$

(19)
FIG. 6: Schematics of the IR coupling between two groups of Fano resonances that are excited by a XUV IAP. Both the bound and the continuum parts of the resonances are coupled by the IR.

To simplify the calibration with the TAE-TDSE, we limit the XUV intensity to avoid second-order excitation. In such a condition, the ground state coefficient $c_g(t) = 1$ is a constant of time. By taking into account all the dipole matrix elements including the ones involving continuum states and applying AE for the continuum, the coupled equations for the bound states are

$$i \dot{c}_m(t) = - F_X^*(t) \bar{D}_{gm} - (\delta_m + i \kappa_m) c_m(t) - E_L(t) \sum_n \bar{D}_{mn} c_n(t),$$  \hspace{1cm} (20)

$$i \dot{c}_n(t) = - i F_X^*(t) E_L(t) j_m - (\delta_n + i \kappa_n) c_n(t) - E_L(t) \sum_m \bar{D}_{mn} c_m(t),$$  \hspace{1cm} (21)

where

$$\bar{D}_{gm} \equiv D_{gm} - i \pi D_{g\epsilon_m} V_m,$$  \hspace{1cm} (22)

$$D_{mn} \equiv D_{mn} - \pi^2 V_m D_{\epsilon_m \epsilon_n} V_n - i \pi (V_m D_{\epsilon_m n} + D_{m \epsilon_n} V_n)$$  \hspace{1cm} (23)

are the complex composite dipole matrix elements incorporating the continuum states. All the atomic structure parameters in Eqs. (20)-(23) are labelled in the same way as in the three-level system in Sec. II but with the $|m\rangle$ and $|n\rangle$ states replacing $|b_1\rangle$ and $|b_2\rangle$ respectively. One can see that the IR coupling with the continuum states comes into the terms of $D_{\epsilon_m \epsilon_n}$, $D_{\epsilon_m n}$, and $D_{m \epsilon_n}$ in Eqs. (22) and (23) and thus contributing to Eqs. (20) and (21).

To retrieve the continuum state coefficients by iteration, all continuous dipole matrix elements have to be kept in the original coupled equation. With mutual coupling terms between the two background continua, the final continuum state coupled equations are
given by

\[ i\dot{c}_1(t) = -F_X^*(t)D_{ge_e} - \delta_{\epsilon_1}c_{\epsilon_1}(t) + \sum_m V_m c_m(t) - E_L(t) \left[ \sum_n D_{\epsilon_1 n} c_n(t) + \alpha_{\epsilon_1}(t) \right], \]  

(24)

\[ i\dot{c}_2(t) = -iF_X^*(t)E_L(t)j_{ge_2} - \delta_{\epsilon_2}c_{\epsilon_2}(t) + \sum_n V_n c_n(t) - E_L(t) \left[ \sum_m D_{mc_2} c_m(t) + \alpha_{\epsilon_2}(t) \right], \]  

(25)

where

\[ D_{\epsilon_1 n} \equiv D_{\epsilon_1 n} - i\pi D_{\epsilon_1 \epsilon_n} V_n, \]  

(26)

\[ D_{mc_2} \equiv D_{mc_2} - i\pi V_m D_{\epsilon m \epsilon_2}, \]  

(27)

\[ \alpha_{\epsilon_1}(t) \equiv \pi D_{\epsilon_1 \epsilon_2} \dot{c}_{\epsilon_2}(t)|_{\epsilon_2 = \epsilon_1}, \]  

(28)

\[ \alpha_{\epsilon_2}(t) \equiv \pi D_{\epsilon_1 \epsilon_2} \dot{c}_{\epsilon_1}(t)|_{\epsilon_1 = \epsilon_2}. \]  

(29)

For each value of \( \epsilon_1 \), the evolution of \( c_{\epsilon_1}(t) \) has the coupling term of \( c_{\epsilon_2}(t) \) only at \( \epsilon_2 = \epsilon_1 \), which means all the \( \epsilon_2 \) continuum states together have a collective effect approximated by \( \alpha_{\epsilon_1}(t) \), and the same applies to \( c_{\epsilon_2}(t) \) too. The \( \alpha \) functions are evaluated by Eqs. (28) and (29) with the \( c(t) \) coefficients calculated by Eqs. (24) and (25) without the \( \alpha \) functions themselves, i.e., they are added iteratively. These terms minimize the numerical burden and consider the C-C coupling at the same time. With the complete wavefunction, the PES for the two continua are \( P_1(\epsilon) = |c_{\epsilon_1}(t_j)|^2 \) and \( P_2(\epsilon) = |c_{\epsilon_2}(t_j)|^2 \) as explained in Sec. III.

In the following we take the same example system, the \( 2s2p \) resonance in helium, for demonstration. The TAE-TDSE calculation is taken as a virtual experiment to calibrate the present model. With the XUV (central frequency is resonant with \( 2s2p \), FWHM pulse length is \( 690 \) fs, peak intensity is \( 10^9 \) W/cm\(^2\)) and the laser (wavelength is \( 540 \) nm, FWHM pulse length is \( 4 \) fs, peak intensity is \( 5 \times 10^{11} \) W/cm\(^2\)) pulses, both with zero carrier-envelope phase, the TAE-TDSE result shows the first three partial waves—\( s \), \( p \), and \( d \)—are the dominant ones in the PES. Thus, in the model, a third continuum is added alongside Eqs. (24) and (25), and all the atomic parameters are adjusted to fit the PES by TAE-TDSE. In Fig. 7, the three dominant partial waves for zero delay between the two pulses are shown in the PES, which achieve a good agreement between the two calculations. The original Fano lineshape, displayed as a reference, is calculated as the \( p \)-wave PES in the laser-free condition. With the laser turned on, the strength of the \( p \) wave drops down, while both the \( s \) and \( d \) waves rise up, showing the laser transition from the \( 2s2p \) resonance and its background to other symmetries. The two \( s \)-wave resonances, identified as \( 2s^2 \) and \( 2p^2(1S) \) (referred as \( 2p^2 \) hereafter), are well reproduced by the model. Certain signal depletion appears in the model relative to the TAE-TDSE calculation as the result of the laser ionization, which is not considered by the model due to the lack of reliable treatment for strong-field ionization so far.

In Fig. 7, the \( s \)-wave PES has a flat signal strength between \( 2s^2 \) and \( 2p^2 \). Considering the laser bandwidth of about \( 1 \) eV counted after the XUV excitation, the middle part of this
flat signal must be the contribution by the C-C transition from the background parts of the $p$ wave. To draw a detail account of the C-C coupling, we plot the $s$-wave PES with various time delays in Fig. 8. At $t_0 = 0$, the XUV is on top of the maximum field of the laser. As seen in the figure, once the laser lags behind the XUV, as shown at $t_0 = 0.3$ fs, the signal between $2s^2$ and $2p^2$ decreases significantly to about half of its original strength. As the laser lags more, the signal further decreases, but the speed slows down, until at $t_0 = 0.5$ fs the signal drops to nearly zero. Meanwhile, the $2s^2$ and $2p^2$ resonance peaks stay strong and are just slightly changed by the time delay. This contrast between the background and resonance parts of the signal suggests that the C-C coupling by the laser only happens at the beginning of the XUV excitation. Once the autoionizing wave packet is formed by the XUV excitation, the bound state electrons and the photoelectrons are all spatially near the atomic core. The photoelectrons, represented by the continuum states, can thus be coupled by the laser and transferred to other symmetries at this moment. However, if the XUV overlaps the zero field of the laser, the photoelectrons are scattered far away from the core and free from the laser coupling. In principle these “free” electrons are still controlled by the laser through streaking, but in the current case the intensity is low enough to neglect streaking. This observation supports the claim that the C-C coupling is important in a very short period after such a broadband wave packet is formed, which contradicts the common assumption that the C-C coupling is negligible in laser-coupled systems.
FIG. 8: PES for the $s$-wave with various time delays ($t_0$) calculated by TAE-TDSE and the present model. In both calculations, the signal in the middle between the two resonances attenuates dramatically along $t_0$, and drops to nearly zero at $t_0 = 0.5$ where the XUV is on top of the zero laser field.

VII. CONCLUDING MARKS

We have reviewed the few-level model for the autoionizing wave packet excited by an XUV IAP and dressed by an intense dressing field. For the simplest case, the three-level model is described where the total wavefunction, including the broadband continuum components, is constructed. Taking the resonantly coupled $2s2p(1P)$ and $2s2(1S)$ resonances in helium as an example, the PES and PAS are simulated, where the spectral features are manipulated by the intensity and time delay of the IR and analyzed by the Rabi oscillation between the resonances. By taking into account the propagation effect, with specific dressing field parameters, an emission peak of the XUV at the resonance energy can be stabilized in the medium in the millimeter distance scale, which demonstrates an ultrafast control over an attosecond pulse. In a more complex model where multiple resonances and the coupling with continuum states are considered, the calibration of the model by an ab initio calculation suggests that the continuum-continuum coupling has an essential contribution in the ultrafast XUV+IR scheme, especially at the beginning of the photoionization.

Attosecond light sources have renewed the interests in autoionizing systems, where certain recent experiments have been carried out beyond the scope of this review, such as the autoionization in molecular Rydberg states [45], the two-photon coupling between the AISs through an intermediate state [46], and continuous shift of the asymmetry of Fano resonances by an intense laser field [10]. With the rapid ongoing development, the demand for insightful and efficient models are expected to keep rising.
Acknowledgements

This work was supported in part by Chemical Sciences, Geosciences and biosciences Division, Office of Basic Energy Sciences, Office of Science, U. S. Department of Energy. T. M. was supported by Grants-in-Aid for Scientific Research (A), (B), and (C) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. W.-C. C. thanks G. Sansone for discussions on transient absorption spectroscopy, and T. Pfeifer and C. Ott for discussions on the continuum-continuum coupling of autoionizing states.

References

Review

Effect of Ionization on the Wavelength Scaling of High Harmonic Generation Efficiency

Jun Dai, Zhinan Zeng,* Candong Liu, Ruxin Li,† and Zhizhan Xu‡

State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China

(Received August 30, 2013)

The physical origin of the recently reported wavelength scaling law of high harmonics generation (HHG) yield [Tate et al., Phys. Rev. Lett. 98, 013901 (2007); Shiner et al., Phys. Rev. Lett. 103, 073902 (2009)] is not fully understood. We re-investigate theoretically the wavelength (from 800 nm to 2000 nm) scaling of HHG yield in atoms with different soft-core Coulomb potentials. It is found that the power $x$ of the wavelength scaling $\lambda^x$ surprisingly oscillates in the region $-3.63 \sim -6.32$. A similar oscillation is found in the wavelength scaling of ionization ratio upon the ionization potential, indicating that the wavelength scaling of HHG yield is closely relevant to the ionization. The origin of this oscillation in ionization is also identified.

DOI: 10.6122/CJP.52.320 PACS numbers: 42.65.Ky, 32.80.Rm, 32.80.Fb

HHG in atoms and molecules is a primary approach for table-top coherent sources in the extreme ultraviolet (XUV) region. To pursue a shorter wavelength emission, a longer wavelength laser driver is desirable according to the well-known cutoff law of HHG, i.e. the highest photon energy is approximately $I_p + 3.17U_p$ [1, 2], where $I_p$ denotes the ionization potential of the target atom, $U_p = F_0^2 / 4\omega^2$ is the ponderomotive energy, $F_0$ is the peak electric field and $\omega$ is the angular frequency. A longer wavelength pulse can push the cutoff to higher photon energy, since $U_p$ increases quadratically with the wavelength $\lambda$. This wavelength scaling law and the favorable phase matching conditions motivated the HHG experiments using intense mid-infrared laser pulses [3–6] and the water-window HHG have been demonstrated recently by several groups [7–9].

The major concern in the HHG driven by longer wavelength laser pulses is the efficiency. It has been commonly assumed that the wavelength scaling of HHG yield is $\lambda^{-3}$ [10]. However, a more rapid decrease in HHG yield as $\lambda^{-5-6}$ over the wavelength range of 800–2000 nm was revealed using the time-dependent Schrodinger equation (TDSE) and the strong field approximation calculations [11–15]. More recently the first experimental measurement [16] at the single-atom level showed that the wavelength scaling is $\lambda^{-6.3\pm1.1}$ in Xe and $\lambda^{-6.5\pm1.1}$ in Kr over the wavelength range of 800–1850 nm. In addition, the wavelength dependence was found not smooth on a fine $\lambda$ scale, but exhibiting fluctuations due to

*Electronic address: zhinan_zeng@mail.siom.ac.cn
†Electronic address: ruxinli@mail.shcnc.ac.cn
‡Electronic address: zzxu@mail.shcnc.ac.cn
quantum-path interference [12–14]. The change of wavelength scaling with the ionization potential for single atom response was observed by M. V. Frolov et al. [13] for the first time. Popmintchev et al. [9] confirmed this behavior in a large ensemble of atoms and under phase matching conditions. Furthermore, Ref. [15] reported that the harmonic yield is nearly independent of the driving laser wavelength when the target atoms are irradiated simultaneously by an XUV pulse with the cut-off energy and ionization yield fixed.

So far, the reported wavelength scaling $\lambda^x$ of HHG yield was obtained mainly for several typical target atoms, i.e. He, Ar, Xe and Kr. The yield of the high harmonics can be simply written as $|\langle \Psi_0 | \vec{r} | \Psi_c \rangle|^2$, where $\Psi_0$ is the fundamental state of the atom and $\Psi_c$ is the return electron (continuum state). For the return electron wavepacket, the $\Psi_0$ looks like a $\delta$ function. For longer wavelength pulse, the return electron wavepacket will expand much larger and reduce the harmonic yield as $\lambda^{-3}$. Also, longer wavelength will increase the photon energy as $\lambda^2$. That means if we sum the harmonic yield within the frequency region of $\Delta E$, the $\Delta E$ will also increase as $\lambda^2$ when the laser wavelength is increased. But in previous work, the $\Delta E$ is kept constant. So the summed harmonic yield will decrease as $\lambda^{-2}$. Then, it can be understood that $\lambda^{-3}$ is from the spread of the ionized wavepacket and $\lambda^{-2}$ arises from the $U_p$ quadratically increasing with $\lambda$. It is not understood where the factor in addition to $\lambda^{-5}$ comes from and why the power $x$ varies for different atoms. In this work, we theoretically investigate the dependence of the HHG yield on $\lambda$ using atoms of different ionization potentials. It is found that the power $x$ of the wavelength scaling $\lambda^x$ surprisingly oscillates in the region $-3.63 \sim -6.32$ when the ionization potential is varied. A similar oscillation is found in the wavelength scaling of ionization ratio upon the ionization potential, indicating that the wavelength scaling of HHG yield is closely relevant to the ionization.

We first numerically solve the 1D TDSE in the length gauge for a linearly polarized laser field, and the TDSE is treated in a single-active electron approximation (SAE) [17] with spin-orbit coupling neglected,

\[
i \frac{\partial \psi(z,t)}{\partial t} = \left[ -\frac{1}{2} \nabla^2 + V_{\text{soft}}(z) + z * E(t) \right] \psi(z,t)
\]

where $E(t) = E_0 f(t) \sin(\omega t)$ denotes the laser electric field, with $E_0$ the peak amplitude and $f(t)$ the envelope. The atom is subjected to an 8-cycle flat-top laser pulse, which is switched “on” and “off” in a half cycle. The peak intensity of driving laser field is fixed at $1.6 \times 10^{14}$ W/cm$^2$, and a variation of $\lambda$ over a range of 800–2000 nm is adopted.

We employ the soft-core Coulomb potential $V = -1/\sqrt{x^2 + C}$ to describe the target atom, where $C$ represents the softening parameter. In the calculations, we vary the softening parameter $C$ from 0.8 to 1.4 by an interval $\Delta C = 0.005$, corresponding to a change in the ionization potential from $-0.735$ a.u. to $-0.582$ a.u., and study how the $\lambda$ scaling of HHG yield changes with respect to the ionization potential. The harmonic spectrum is obtained from the direct Fourier transform of the dipole acceleration, and the integrated HHG yield is defined in a fixed energy interval from 20–50 eV. Fig. 1 shows that the power $x$ of the wavelength scaling $\lambda^x$ are $-4.77$, $-4.86$ and $-5.13$ for the ionization potential of $-0.735$ a.u., $-0.670$ a.u. and $-0.621$ a.u., respectively.
One of the main results of this work is the evolution of power $x$ of HHG yield upon the ionization potential, as shown in Fig. 2. A surprising oscillation of the power $x$ around $-5$ can be seen. The maximum and minimum values of the power $x$ are $-3.63$ at $I_P = -0.638$ a.u. and $-6.32$ at $I_P = -0.706$ a.u., respectively. When the ionization potential is deeper than $-0.621$ a.u., the separation of the adjacent peaks of the power $x$ are $I_{P_1} = 0.013$ a.u., $I_{P_2} = 0.025$ a.u., $I_{P_3} = 0.029$ a.u. and $I_{P_4} = 0.032$ a.u., respectively. The oscillation of the power $x$ slows down with the decrease in the ionization potential, i.e., the period of the oscillation is becoming larger and larger. When the ionization potential proceeds less than $-0.621$ a.u., it is noticed that the ionization ratio (In our TDSE simulation, “ionization ratio” is defined as $P(t) = 1 - \|\psi(t)\|^2$, where $\psi(t)$ is the time-dependent wavefunction.) in the case of the 2000 nm is as high as 24%.

To analyze the remarkable phenomena shown in Fig. 2, we calculate the corresponding $\lambda$ scaling of the ionization ratio upon the ionization potential. The ionization ratio as a function of the ionization potential for different $\lambda$ from 800 to 2000 nm is shown in Fig. 3 (a). The $\lambda$ scaling of the ionization ratio are presented in Fig. 3 (c), in which an oscillation similar to that shown in Fig. 2 can be seen. A detailed comparison of Fig. 3 (b) (reproduced from Fig. 2) and (c) tells us that two oscillation curves match each other very well, with every peaks (labeled by the red dashed lines) and valleys (labeled by the blue dashed lines) appearing at the same values of the ionization potential, until that the ionization potential is approaching $-0.621$ a.u. and beyond. The very low ionization potential leads to a large
FIG. 2: The power $x$ of wavelength scaling $\lambda^x$ of the integrated HHG yield as a function of the ionization potential from $-0.735$ a.u. to $-0.582$ a.u.. $I_{p1} = 0.013$ a.u., $I_{p2} = 0.025$ a.u., $I_{p3} = 0.029$ a.u. and $I_{p4} = 0.032$ a.u. denote the interval of the adjacent peaks of the oscillation curve.

ionization ratio and the depletion of the ground state, the wavelength scaling law would therefore change considerably.

We also calculate the photoelectron spectra (PES) of different ionization potentials. The results obtained using the TDSE solved with the method of Ref. [18] for the 2000 nm pulse are shown in Fig. 4. One can see a complicated interference pattern. In the calculation, all the PES for different ionization potentials are from the absorbed wavefunction, which means that the integration of the PES of each ionization potential is the ionization ratio shown in Fig. 3 (a). As pointed out recently by H. R. Reiss [19], that the PES is affected by two factors, the momentum factor $F(p)$ and the generalized Bessel function $J_n(u, v)$, which lead to the complicated interference fringes. In the momentum factor, $p = n\omega - E_B - U_p$ and $E_B$ is the ionization potential of the atom. We think that the complicated interference pattern in Fig. 4 can also be explained by these two factors. Because of the interference pattern shown in Fig. 4, the ionization ratio in Fig. 3 (a) for all the driving laser wavelengths do not increase monotonically with the ionization potential, with considerable fluctuations appearing in the evolution curves. Many peaks and valleys appear on the curves, but at different values of the ionization potential for different laser wavelengths.

Now we can explain the observed oscillation in the power $x$ of the wavelength scaling $\lambda^x$ of the ionization ratio and the HHG yield. If we define the scaling law represented by the smooth curves as “normal”, the fluctuation of the curves will make the scaling law “abnormal”. For example, if a peak appears at $I_p = -0.656$ a.u. for the 800 nm wavelength, but no peak showing up here for the 2000 nm wavelength, then the power $x$ in the scaling
FIG. 3: (a) Ionization ratio as a function of the ionization potential for different laser wavelength from 800 nm to 2000 nm. (b) The same as Fig. 2. (c) The power $x$ of the wavelength scaling $\lambda^x$ of the ionization ratio as a function of the ionization potential. The red and blue dashed lines are used to label the peaks and valleys of the oscillation curves, showing a good matching in two scaling laws.
FIG. 4: The photoelectron energy spectrum as a function of the ionization potential, calculated by using the TDSE and a 2000 nm driving laser pulse. Complicated interference structures appear.

law will be smaller than the normal value. But if a peak appears at \( I_p = -0.670 \) a.u. for the 2000 nm wavelength, but no peak showing up there for the 800 nm wavelength, then the power \( x \) in the scaling law will be larger than the normal value. Consequently, the oscillation of the power \( x \) of the wavelength scaling \( \lambda^x \) appears.

Further investigation using a 3D TDSE is performed also. For the 3D model, we use the helium atom model [20] to do the calculation. The soft core model is written as [21]

\[
V = -\frac{1}{r} \left( 1 + e^{-2.505r} \right)
\]

(2)

\[
r = \sqrt{\rho^2 + z^2 + C}
\]

(3)

where \( \rho \) and \( z \) are radial and axial variables in the cylindrical coordinate.

The power \( x \) as a function of the ionization potential is shown in Fig. 5 (a). When the ionization potential is deep, e.g. \(-0.8 \) a.u., the center of the oscillation of the power \( x \) is about \(-6 \). With the decrease of the ionization potential, the center of oscillation moves to \(-5.5 \) gradually. This is similar to the results obtained with the 1D model that the center of the oscillation increases with the decrease of the ionization potential. When the ionization potential is around \(-0.5 \) a.u., the ionization ratio becomes larger and the power \( x \) begins to decrease. In comparison with the results of 1D model, the power \( x \) obtained by 3D TDSE is more sensitive to the change in the ionization potential. We speculate that two additional dimensions will induce more complex interference for the electron wavepacket. Fig. 5 (b) shows in more details a part of the curve for the atomic potential between \(-0.7 \) a.u. and \(-0.6 \) a.u. Although the fluctuation of the power \( x \) is more sensitive to the atomic potential in the 3D TDSE simulation, we can draw the same conclusion as that of the 1D TDSE simulation from Fig. 5 (b). Two curves match each other very well, with every peaks (labeled by the red dashed lines) and valleys (labeled by the blue dashed lines) appearing almost at the same values of the ionization potential.
FIG. 5: (a) The power $x$ of the wavelength scaling $\lambda^x$ of the integrated HHG yield as a function of the ionization potential, obtained by using the 3D model. The ionization potential changes from $-0.861$ a.u. (close to He atom) to $-0.490$ a.u. (close to H atom). (b) Enlargement of (a) between $-0.7$ a.u. to $-0.6$ a.u.. The red and blue dashed lines are used to label the peaks and valleys of the oscillation curves.

The 3D TDSE calculation results for different noble gas are Ne (0.7928 a.u., $x = -5.4$), Ar (0.5794 a.u., $x = -5.6$), Kr (0.5147 a.u., $x = -5.8$), and Xe (0.4460 a.u., $x = -7.2$), respectively. The laser intensity was assumed to be $1.6 \times 10^{14}$ W/cm$^2$ except
that for Xe is $8 \times 10^{13}$ W/cm$^2$. In the previous work, the power $x$ are $-5.5$ for Ar (obtained theoretically) [12], $-6.5 \pm 1.1$ for Kr (obtained experimentally at laser intensity of $1.3 \times 10^{14}$ W/cm$^2$) and $-6.3 \pm 1.1$ for Xe (obtained experimentally at laser intensity of $8 \times 10^{13}$ W/cm$^2$) [16]. According to our calculations, if the laser intensity is $1.6 \times 10^{14}$ W/cm$^2$, the power $x$ will become larger when the atomic potential is smaller than 0.5 a.u. at which the ground state is depleted too much. Actually, the atomic potential has the discrete nature. It is difficult to observe experimentally and directly the oscillation of power $x$ found in this work. But some effects due external fields may be used to test the prediction, e.g. Stark or Zeeman effects, due to which the energy level of the atom will shift.

We should point out that, based on the TDSE simulation, it is impossible to obtain the accurate value of the power $x$ for each noble gas, because it is difficult to model a true atom accurately. For example, the power $x$ reported in Ref. [12] for the hydrogen is $-4.8$, but the analytic result reported in Ref. [22] is $-5.2$. The difference in the absolute values of the power $x$ reported in different works is related to the difference in the modeling. In this work, we do not attempt to obtain the accurate value of the power $x$ for each noble gas, while we attempt to understand why the power $x$ is so strange, e.g. it is not an integer as reported in previous works. By taking the effect of ionization into account, we can now understand where the factor in addition to $\lambda^{-5}$ comes from and why the power $x$ varies for different atoms in previous investigations. Ionization potential is found to play an important role in the wavelength scaling law. The curve of ionization ratio as a function of ionization potential is not a smooth one. For a special ionization potential, e.g. Ar or He, the power in the scaling law may be smaller or larger than the “normal” value.

In conclusion, the wavelength scaling of the HHG yield for atoms with different ionization potential has been investigated. It is found that the power $x$ of wavelength scaling $\lambda^x$ exhibits a surprising strong oscillation which slows down gradually with increasing ionization potential. We also explore the wavelength dependence of the ionization ratio as a function of ionization potential. It shows a remarkable oscillation similar to the wavelength scaling of the HHG yield, in which every peak and valley accurately match each other. The effect of ionization potential is also investigated with the 3D model. The oscillation of the power $x$ is more sensitive to the change in the ionization potential. We think it can be attributed to the more pronounced electron wavepacket interference in the 3D model. However, the relationship among the ionization ratio and HHG yield scaling, and the ionization potential is still a subject need to be explored further. Furthermore, the single-active electron approximation is considered in the present work. If multiple electrons are considered, some additional effects may affect the wavelength scaling greatly, e.g. Cooper minima, electron correlation effects [22].

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants No. 11127901, No. 61221064, No. 11134010, No. 11227902, No. 11222439, No. 11274325, and No. 61108012), the 973 Project (Grant No. 2011CB808103), and Shanghai
Commission of Science and Technology (Grant No. 12QA1403700). and Shanghai Supercomputer Center.

References

Review

Semi-classical Methods in Non-Sequential Double Ionization

Allan S. Johnson, André Staudte and D. M. Villeneuve*

Joint Attosecond Science Laboratory,
National Research Council of Canada and University of Ottawa,
100 Sussex Drive,
Ottawa ON K1A 0R6, Canada
(Received September 17, 2013)

Non-sequential double ionization of an atom in an intense laser field is a prototypical problem in multi-body strong field interactions. To examine non-sequential double ionization, an often used approach is the semi-classical method, by which initial conditions are set according to quantum expressions and the ensuing dynamics modelled classically. Here we present a comparative study of quantum and semi-classical methods in the single active electron approximation. We show that semi-classical methods over-estimate the kinetic energy of rescattered electrons by up to 150%. We further show that the return time of the recolliding electrons deviates between quantum and semi-classical methods at low intensities, and that the deviation is attributable to the choice of the initial tunnelling position.

DOI: 10.6122/CJP.52.329 PACS numbers: 71.27.+a, 73.23.Hk, 34.80.Dp

I. INTRODUCTION

The three step model of electron recollision in strong laser fields has become one of the linchpins of strong field physics [1, 2]. In its canonical formulation, an electron tunnels out of an atom or molecule in the presence of a strong laser field, propagates in the presence of said field, and finally returns with a kinetic energy of up to \(3.17U_p + I_p\), where \(U_p\) is the ponderomotive potential of the field and \(I_p\) is the ionization potential [3]. While the three step model has been tremendously successful, explaining high harmonic generation and angular structure in above threshold ionization electrons, only recently has the three step model moved significantly outside the single active electron approximation, with new models for rescattering in complex systems [4]. The notable exception is non-sequential double ionization (NSDI) [5–7], which forms a prototypical multi-body strong field problem [8]. Here, the recolliding electron causes a second electron to detach in a highly correlated process. This is thought to proceed by a variety of mechanisms, including "knock-out" e-e collisions [9, 10], recollision excitation with subsequent ionization (RESI) [11, 12], and formation of transient doubly excited states [13, 14]. NSDI was one of the earliest successes of the 3 step model, and has accordingly been thoroughly studied for over ten years, and

*Electronic address: david.villeneuve@nrc.ca

great success has been obtained treating the problem with semi-classical methods [4]. Semi-classical methods are widely used, as full quantum treatments are extremely computational demanding and have thusfar only been possible at wavelengths of 400nm, while almost all experiments have been performed at 800 nm [15]. Semi-classical methods begin by setting initial conditions according to a mixture of analytic quantum theories and statistical ensembles [8], and then propagating the system using classical mechanics. These models have successfully recreated such features of NSDI as the enhanced probability [16], recoil ion momenta distributions [17], and electron correlation patterns [18].

Despite these successes, the problem of NSDI is far from completely understood. Recent studies have shown a variety of interesting new phenomena not previously observed, including new effects occurring at low intensities [19, 20] and modified correlation spectra with single cycle laser pulses [12, 14]. While one might expect these new phenomena to require a more complete quantum treatment as the effects of cycle averaging are removed and the energy of the recolliding electron decreases below the threshold for ionization, thus far semi-classical modelling has been sufficient to describe most of the observed effects [14, 16, 21, 22]. This raises the interesting question of when semi-classical methods can be expected to fail, if not when intuitively it would seem the quantum structure of the ion would dominate dynamics. To that effect, we have performed a comparative examination between full quantum and semi-classical models for the first two steps of NSDI - ionization and propagation of the first electron. By examining the kinematics of the recolliding electron, we identify when the quantum structure of the target is likely to influence NSDI. Incredibly, we find that despite its successes, semi-classical models deviate significantly from a full quantum treatment across a broad range of conditions. In particular, semi-classical methods systematically over-estimate the maximum recollision energy of the electron at low intensities by up to a maximum of 150%. Furthermore, at low intensities the time of recollision is also incorrectly modelled by the semi-classical method, leading to recollision taking place in the presence of a strong field instead of around a zero-crossing. Our results suggest that semi-classical methods must be looked at carefully when used to model NSDI at low intensities.

II. METHODS

In order to compare semi-classical methods with a full quantum treatment and to be able to present the results clearly, we perform simulations in the one dimensional, single active electron approximation. It is straightforward to use fully 3D classical calculations, and 3D quantum calculations. However the essence of what we are trying to demonstrate can most easily be seen in 1D.

Semi-classical methods employ Newton’s equations to predict the trajectory of electrons in the presence of a Coulomb potential (due to the ion) and of a time-varying electric field in the dipole approximation (due to the laser field). For intensities below $10^{16}$ W/cm$^2$, the magnetic field associated with the laser field can be neglected. Several approximations must be made; for example, the singularity associated with the Coulomb potential leads
to unrealistic accelerations and velocities, and a softened potential is used [23, 24]. The electron can quantum-mechanically tunnel through the potential barrier, even though it does not have sufficient energy to do so classically; therefore in semi-classical calculations the electron must be placed outside the barrier at a position that mimics the position at which the wave function exits the potential barrier as shown in Fig. 1.

![Atomic Potential Plus Laser](image)

**FIG. 1:** Illustration of the tunneling barrier representing ionization of an atom in an intense laser field. The dashed curve shows the ionic potential plus the potential of the laser electric field. The fine dotted line at $V(x) = -0.5$ represents the energy of the eigenstate. The ionic potential has been reduced by the laser field, allowing some of the bound electronic wave function at the origin to tunnel out into the continuum. With a classical model, tunneling cannot occur. Instead, the initial condition of the “tunnelled” electron is set at the exit of the classically forbidden region, marked by the circle.

For the initial position of the electron, we choose to place it at the point where it exits the classically forbidden tunnelling region. This position is commonly defined using a zero-range potential as $x_0 = I_p/E_0$, or using a Coulomb potential as

$$x_0 = \frac{I_p + \sqrt{I_p^2 - 4E_0 \cos(\omega t_0)}}{2E_0 \cos(\omega t_0)}$$  \hspace{1cm} (1)$$

where $I_p$ is the ionization energy, $E_0$ is the peak electric field strength, $\omega$ is the angular frequency of the laser field and $t_0$ is the time of birth into the continuum. Electrons are given a zero initial velocity. These initial conditions are typical for semi-classical models [4, 8, 12, 14, 16, 21]. The electrons are propagated over a full cycle in the presence of the cosine laser field and a softened Coulomb potential by solving Newton’s equations using a
fourth order Runge-Kutta method. We use the softened potential

\[ V(x) = -\frac{1}{\sqrt{x^2 + I_p^2}} \]  

so that the minimum value of the potential, at the origin, is \(-I_p\). This form of softened potential is widely used across classical and semi-classical simulations [8, 25–28]. From the classical trajectories the time at which the electron returns to the origin and the kinetic energy at return can be determined, while the probability of a trajectory is determined via the ADK tunneling rate at the time of birth \(t_0\). One-hundred and eight trajectories were sampled for each different intensity.

For the quantum simulations, we numerically solve the Schrödinger equation using the split operator method with the following Hamiltonian:

\[ H(x, t) = \frac{p^2}{2m} + V(x) + xE(t), \]  

where \(V(x) = -\frac{1}{\sqrt{x^2 + \alpha^2}}\) with \(\alpha\) chosen such that the energy of the initial eigenstate of \(V(x)\) is \(-I_p\), and the time dependent laser electric field (shown in Fig. 2) is defined as

\[ E(t) = \begin{cases} E_0 \cos^2(\omega t), & t_s < t < 0 \\ E_0 \cos(\omega t), & 0 < t < t_f \end{cases}. \]

The cosine squared field is used for the initial quarter cycle in order to ensure a smooth turn on. Comparative simulations have been performed which show this does not affect the returning recollision energy or time significantly, but does decrease numerical artifacts. Simulations begin at \(t_s = -\frac{\pi}{2\omega}\) and end at \(t_f = \frac{5\pi}{2\omega}\). The initial ground state wave function \(|\Psi(0)\rangle = |\Psi_g\rangle\) is the lowest eigenstate of the field-free potential \(V(x)\). To isolate the recolliding trajectories, we define the continuum wavefunction \(|\Psi_c(t)\rangle\) by

\[ |\Psi_c(t)\rangle = (1 - |\Psi_g\rangle\langle \Psi_g|)|\Psi(t)\rangle. \]

which is the full wavefunction minus the projection onto the bound state, in analogy with earlier studies isolating the recolliding wavepacket contribution [29]. We propagate the full wavefunction for the first half cycle, but at \(t = \frac{\pi}{2\omega}\) we remove the ground state and consider only the continuum wavefunction by using the projection operator considered above.

We employ a spatial window to isolate that portion of the continuum wave function near the origin, corresponding to the position of the ionic core. A window function is applied to the continuum wavefunction around the origin, and the resulting truncated wavefunction is Fourier-transformed to the momentum representation, i.e.

\[ \Phi_R(p, t) = \int g(x)\Psi_c(x, t)e^{-ipx} \, dx \]

where \(g(x) = e^{-\frac{x^2}{2\sigma^2}}\), and \(\sigma\) is chosen to cover the ground state wavefunction. In the results presented here, \(\sigma = \sqrt{10}\) a.u., and \(g(x)\) is truncated outside of \(x \in [-10, 10]\). The window function and the initial ground state are shown in Fig. 3.
FIG. 2: Illustration of the laser electric field used in the quantum calculation. The first quarter-cycle has a smooth turn-on. At time $t = \frac{\pi}{2\omega}$, the bound state wave function is projected out to isolate the continuum portion of the wave function.

FIG. 3: Initial ground state wavefunction (solid line) and Fourier transform window (dashed line) in the spatial domain. The transform window is sufficiently broad to cover the ground state region without including significant continuum dynamics.
At this point the positive momentum components of the wavefunction are discarded, leaving only the trajectories which correspond to those turned by the laser field. From here the distribution of kinetic energies is calculated by applying the kinetic energy operator \( K = \frac{p^2}{2m} \). By performing this algorithm for each time step, the recollision energy as a function of return time is mapped out. We are particularly interested in the mean energy as a function of time, as this should correspond to the classical trajectories in accordance with the Ehrenfest theorem.

III. RESULTS

In order to compare the predictions of the two models, we first examine their results in a regime where both semi-classical methods and the canonical three step model are known to give accurate results. Figure 4 shows results obtained at a peak intensity of \( 2.2 \times 10^{14} \) W/cm\(^2\), a wavelength of 800 nm, and \( I_p = 15.8 \) eV, corresponding to argon and a Keldysh parameter of 0.77. The agreement between the mean recollision energy from the Schrödinger equation (in blue) and the Semi-classical Model (in green) is excellent for the long trajectories. Both predict a maximal return energy around the zero crossing of the field at 270\(^\circ\), and the two methods' prediction for maximal return energy of 62.5 eV is very close to the value of \( 3.17U_p + 1.3I_p = 62.3 \) eV determined from the more sophisticated fully quantum mechanical version of the three step model [30]. The most significant deviation is for the short trajectories in the semi-classical model; these trajectories are found to be born very far from the nucleus close to the field zero, and accelerated through the next subsequent half-cycle to recollide with high kinetic energy. While these trajectories have a vanishing probability relative to the long trajectories, they illustrate a potential problem with the semi-classical method which we shall see becomes significant at low intensities.

Figure 5 shows the maximum recollision energy as determined by the Schrödinger equation, semi-classical model and the canonical three step model. At high intensities, the agreement between all three models is excellent. The agreement applies even into the multiphoton regime and, for the Schrödinger equation and three step model, well into the over-barrier ionization regime (not shown), far beyond where the 3 step model might be thought to apply.

Below \( 1 \times 10^{14} \) W/cm\(^2\) however, the models begin to deviate severely. While the semi-classical model systematically over-estimates the return energy at all intensities, at lower field strengths the deviation becomes severe. In order to remove the influence of short trajectories with vanishing probabilities, we consider only return trajectories that have a relative probability of greater than \( 10^{-6} \). The results here are unchanged varying this cutoff up to \( 10^{-3} \). The increasing deviation at low intensities is due to the increasingly significant contribution from the short trajectories as the intensity becomes lower. An examination shows that while at high intensities a sharp cutoff in return energy can be seen, at low intensities the semi-classical model predicts a slow decrease in the probability of ever more energetic electrons. Below \( 2 \times 10^{13} \) W/cm\(^2\) no recollision is found to occur. Conversely, the full quantum treatment predicts lower return energies than the three step model at
FIG. 4: The recollision energy vs. the time of return (given in units of $\omega t$ and expressed in degrees) for the various models at an intensity of $2.2 \times 10^{14}$ W/cm$^2$. The dashed line shows the mean energy of the recolliding wavepacket from the 1D Schrödinger equation. The solid line shows the return energy from the semi-classical model. At this intensity, both models agree well with the canonical model, except for the low-probability short trajectories.

low intensities, as the increasingly weak field is no longer sufficient to draw the wavepacket away from the ionic core. The qualitatively different behaviour between the fully quantum mechanical and semi-classical calculations leads to the semi-classical model predicting a recollision energy 2.5 times that of the quantum case at the lowest intensities.

In addition to the semi-classical model incorrectly predicting the maximal return energy, at low intensities we also see a significant error in predictions of the return time. Figure 6 shows a comparison between energy vs. return time for the semi-classical model and the Schrödinger equation at a low intensity of $6 \times 10^{13}$ W/cm$^2$, a particularly interesting regime for NSDI where the recolliding electron is not expected to have sufficient energy to trigger a RESI process. We immediately see that while the Schrödinger equation predicts that short trajectories occur throughout the first half cycle after birth, the semi-classical model predicts all recollisions occur two half cycles after ionization, recolliding against the action of the field. Unlike at high intensities, the short trajectories now have comparable probability to the long trajectories in the semi-classical model. As time of birth is thought
FIG. 5: The maximum recollision energy as a function of intensity given by canonical formula $3.17U_p + 1.3I_p$, full solution to the 1D Schrödinger equation and the semi-classical method. The agreement between the three models is excellent at high intensities but deviates at low intensities.

to be a major, if not primary determinant of the electron correlation in NSDI, this deviation suggests semi-classical methods might well break down completely at low intensities. These trajectories are now relegated to the third half cycle of the field by virtue of being born so far into the continuum that even acceleration through an entire half cycle is not sufficient to return them to the core within that half cycle. This error is thus attributable purely to the tunnelling step.

Another feature of the full Schrödinger equation solution which is not captured by the usual semi-classical method is the spread of energies in the recolliding wavepacket. For the semi-classical model, only a single kinetic energy is predicted, but the quantum model predicts a range of kinetic energies at any one time. In Fig. 7 we plot the standard deviation of the kinetic energy of the recolliding wavepacket, at its most energetic time of return, as a function of the intensity. The variance in the energy is seen to be quite significant, particularly at low intensities where only a few additional eV of energy might be necessary to allow the formation of doubly excited states or trigger a RESI process. Indeed we see that even at $4 \times 10^{13}$ W/cm$^2$, a simple estimate of the recollision energy as the mean plus the standard deviation gives 28.8 eV, enough to form a doubly excited state in argon [31].
FIG. 6: The recollision energy vs. the time of recollision (given in phase of optical cycle in degrees) for the two models at an intensity of $6 \times 10^{13}$ W/cm$^2$. The dashed line shows the mean energy of the recolliding wavepacket from the 1D Schrödinger equation. The solid line shows the return energy from the semi-classical model. The two models now diverge heavily in terms of predicted return time as well as energy. Note that interference structures are also increasingly significant in the quantum model.

Modelling this spread in energies should be possible in semi-classical methods by sampling a variety of initial momenta parallel to the laser field.

IV. CONCLUSIONS

We have shown that semi-classical methods, widely used in analysing NSDI, deviate from a full quantum treatment in a variety of important ways. The semi-classical model systematically overestimates the recollision energy, with the deviation increasing at lower intensities. Furthermore, the semi-classical model, while correctly determining the recollision time at higher intensities, gives highly skewed results at lower intensities, and generally performs poorly handling the short trajectories. Finally, the semi-classical model as it is usually implemented does not capture the spread of energies seen in the quantum treat-
FIG. 7: The standard deviation of the distribution of kinetic energy of the recolliding wavepacket as a function of intensity. The standard deviation is taken at the time of recollision corresponding to the highest mean kinetic energy. As can be seen, there are significant energy contributions above the mean at all intensities.

This spread of energies is quite significant, particularly at low intensities where the different NSDI mechanisms are expected to become very sensitive to the return energy. In particularly this spread in energies can be expected to shift the cut-off for both knock-out collisions and RESI, as well as enable the formation of doubly excited states across all experimentally studied regimes. Our results point towards the necessity of quantum treatments at low intensities, as well as indicating that semi-classical methods should in future sample a variety of momenta parallel to the field at intermediate intensities in order to mimic the spread of return energies. At present the widely used semi-classical treatments risk giving incorrect results at intensities below the recollision knock-out regime.

References

Nonperturbative Atomic Dynamics: Population Trapping and Polarization Response in Strong Laser Fields

V. Yu. Kharin,1,2 A. M. Popov,1,2,* O. V. Tikhonova,1,2 and E. A. Volkova1

1Institute of Nuclear Physics, Moscow State University, 119991, Moscow, Russia
2Physics Department, Moscow State University, 119991, Moscow, Russia

(Received September 1, 2013)

The population trapping in highly-excited atomic/molecular states under intense femtosecond laser pulse action is studied. Two different mechanisms, namely interference stabilization and Kramers-Henneberger stabilization, are responsible for such a trapping. The implication of the atomic dynamics driven by laser field in the nonperturbative limit of ionization to the determination of the strong-field polarization response is discussed.

DOI: 10.6122/CJP.52.340 PACS numbers: 32.80.Rm, 32.80.Fb, 42.50.Hz

I. INTRODUCTION

Strong-field stabilization (or population trapping) of atoms in high-intensity laser field is the phenomenon that attracts attention of scientists during the last decades. The phenomenon was discovered, first theoretically [1, 2] and only later several attempts were made to observe it in experiments [3–7].

Two main types of atomic stabilization can be distinguished: the interference stabilization (IS) of Rydberg atoms [1, 8, 9] and the Kramers-Henneberger (or adiabatic) one [2, 10]. The physical reason of both types of the stabilization is the formation of so-called “dressed states” that characterize an atom in the presence of a strong field. They appear to differ dramatically from the field-free atomic eigenstates. In the case of interference stabilization the observed ionization suppression can be interpreted as a result of the coherent repopulation of neighboring Rydberg states by Raman transitions and further destructive interference of the transition amplitudes from the repopulated states to the continuum. If the repopulation occurs mostly by Raman Λ-type transitions via continuum, one deals with Λ-type stabilization [1, 8], while the resonant involving of the low-lying bound states corresponds to so-called V-type transitions and V-type stabilization [9]. The threshold of the interference Λ-type stabilization phenomenon can be estimated as

\[ \varepsilon_0 / \omega^{5/3} > 1, \]

where \( \omega \) is the laser frequency and \( \varepsilon_0 \) is the amplitude of the laser’s electric field strength [1]. For the Ti:Sapphire laser (\( h\omega = 1.55 \) eV) condition (1) is fulfilled for laser intensities

*Electronic address: alexander.m.popov@gmail.com
Another mechanism of ionization suppression widely discussed is the Kramers-Henneberger (KH) stabilization [2, 10]. This model of stabilization is usually related to ionization dynamics of non-excited atoms or negative ions. Such a stabilization regime is found to arise due to a significant reconstruction of the energy structure and eigenstates of the system in the presence of the electromagnetic laser field that seems to be rather different in comparison to the repopulation of Rydberg levels caused by Λ- or V-type transitions. In the case of KH stabilization a new “dressed” potential completely different from the field-free atomic one appears in the strong field region, and a system in a laser field reveals essentially new features originating from the formed “dressed atom” – namely, the Kramers-Henneberger atom. Typically the KH stabilization appears to exist in the high-frequency limit \( \omega > I_i \) (\( I_i \) is the ionization potential) [2, 10]. In [11] it was predicted that in multiphoton regime of ionization the formation of the KH atom will take place only if the laser intensity will exceed the barrier suppression value \( I > I_{BSI} \). For most atoms the barrier suppression intensity \( I_{BSI} \) is about \( 10^{14} \) W/cm\(^2\) or little bit more.

The possibility of IS for the atom in the ground atomic state which is coupled with the continuum by the multiphoton transition was proposed in [12] and studied theoretically in detail in [13]. The key element of such interpretation is the multiphoton resonance of the ground state and a set of high-lying Rydberg states AC Stark shift taking into account, and then the IS of population trapped in excited Rydberg states.

Independently, the same idea of population trapping in Rydberg states was suggested in [14–16] for interpretation of experimental results on the strong – field ionization yields in atoms of noble gases and molecules, respectively. It was found that in a certain intensity range below the saturation intensity, the ion yield would decrease subtly before increasing again. This was explained by the dynamic resonance of the ponderomotively shifted Rydberg states resulting in population trapping. Numerical analysis of the population trapping of Xe atoms was found in qualitative agreement with experimental data obtained by S. L. Chin group [17].

The trapping of population in highly excited Rydberg states was also observed in recent experiments with He atoms irradiated by Ti-Sa femtosecond laser pulse [18]. The authors of this paper proposed the model of the frustrated tunnel ionization. In accordance with this theoretical model the capture to highly excited states take place as a result of the recombination process on parent ion during the turn-off time of the laser pulse caused by the Coulomb interaction with the atomic core. Such a temporal dynamics is in contradiction with the model based on IS phenomenon where the population of excited Rydberg states is found to be pronounced already at the first ramp of the laser pulse as soon as the field amplitude becomes close to its peak value [19].

Recently it was pointed out that population trapping in high-lying Rydberg states can contribute significantly to the polarization response at the fundamental frequency during the self-focusing and filamentation of strong laser pulses [20, 21] and for generation of THz radiation in filaments [22].

The aim of this paper is to present the overview of recent data on the stabilization and population trapping phenomena for different quantum systems in a wide range of laser pulse
parameters and to analyze the contribution of the trapping to the polarization response in the different regimes of ionization.

II. THE MODEL

We performed numerical simulations for a quantum system in single-particle approximation. In the nonrelativistic case, the dynamics of the quantum system in the presence of the electromagnetic wave field is given by the equation

\[ i \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{1}{2} \nabla^2 \psi(\vec{r}, t) + V(r) \psi(\vec{r}, t) + W(\vec{r}, t) \psi(\vec{r}, t) \]  

(2)

where \( V(r) \) is the central single-particle potential and \( W(\vec{r}, t) \) is the operator of the interaction of atomic system with external electromagnetic field. In the dipole approximation, the operator can be represented as

\[ W(\vec{r}, t) = -\vec{d} \cdot \vec{\varepsilon}(t) \]  

(3)

where \( \vec{\varepsilon}(t) \) is the electric field strength of electromagnetic wave and \( \vec{d} \) is the operator of dipole moment. We assume that the electromagnetic wave is linearly polarized and vector \( \varepsilon \) is directed along the z axis. We also assume that the laser pulse has a smoothed trapezoidal shape with duration of edges \( t_f \) and duration of plateau \( t_p \). In the calculations, the durations of edges are several periods of the wave electric field \( T = 2\pi/\omega \). Different frequencies of laser radiation from mid IR to UV band corresponding to various regimes of photoionization were under the study. The technique of numerical integration of the time-dependent Schrödinger equation (TDSE) was discussed in detail in [23].

III. DISCUSSION

III-1. Stabilization of atoms in Ti-Sa laser field

Let us discuss first our recent investigations of the dynamics of a Hydrogen atom in low-frequency Ti-Sa laser pulses performed by direct numerical solution of the TDSE with the atom-field interaction. Initially the atom is supposed to be in its ground state. The main result obtained in these calculations is presented in Fig. 1 and demonstrates the nonmonotonous dependence of the ionization and excitation [38] probabilities of the Hydrogen atom versus laser intensity. Both curves are seen to reveal a lot of maxima and minima changing each other with each ionization minimum being accompanied by maximum of the excitation and enhancement of trapping the population in high-lying Rydberg states. The maxima observed on the excitation curve are seen to be separated by approximately the same value of laser intensity equal to \( \Delta I \approx 2.25 \times 10^{13} \text{ W/cm}^2 \), which exactly corresponds to the condition that the ponderomotive shift of the ionization threshold \( U_{pond} = \varepsilon_0^2/4\omega^2 \) changes the photon energy \( h\omega, \Delta U_{pond} = \omega \). A single oscillation of the excitation probability is presented in details in Fig. 2. To understand the physical reason of such behavior observed
for the excitation it is very useful to analyze the energy spectrum of photoelectrons obtained for intensities corresponding to the maximum and minimum on the curve on Fig. 2. The typical photoelectron spectrum demonstrates a lot of ATI peaks separated by $\hbar \omega$. The main change of the spectrum with growing laser intensity consists in a shift of the positions of the ATI peaks to lower energies and the occurrence of the channel closing effect [24]. Fig. 3 demonstrates the dependence of positions of several first ATI peaks on the peak laser intensity. The channel closing is clearly demonstrated and the change of the multiphoton order of the ionization process is seen to take place as soon as the peak laser intensity is increased by $2.25 \times 10^{13}$ W/cm$^2$. As can be seen from Fig. 3 the intensity $7.5 \cdot 10^{13}$ W/cm$^2$ providing almost the maximum of excitation probability corresponds to the case just after closing of the 12-th channel when 13 photons are needed to be absorbed to go to the continuum. In this situation the energy of the first ATI peak is little smaller 1.5 eV and absorption of 12 photons leads to the transition to closely-situated high-lying Rydberg states that can be efficiently populated. In contrast, for laser intensity $9 \cdot 10^{13}$ W/cm$^2$ the 13 photon transition to the continuum provides the first ATI peak at the energy $\approx 0.5$ eV and the absorption of 12 photons or less gives the possibility to populate only low-lying states with binding energy around 1 eV and rather low principal quantum numbers.

![FIG. 1: Probabilities of ionization (1) and excitation (2) of a Hydrogen atom in dependence on the laser intensity for the Ti-Sa laser for the smoothed trapezoidal pulse with ramps and plateau durations of two and ten optical cycles, correspondently. The arrows label the intensity values of $7.5 \times 10^{13}$ W/cm$^2$ and $9 \times 10^{13}$ W/cm$^2$, corresponding to the maximum and minimum values of excitation probability.](image_url)

The scheme of the multiphoton transitions into the continuum and possible excitation channels is presented in Fig. 4. Since for intensity $9 \cdot 10^{13}$ W/cm$^2$ there are only several bound state resonantly coupled with the ground one, the excitation probability is expected
FIG. 2: The detailed structure of one oscillation of the excitation probability versus the laser intensity.

FIG. 3: Energies of several first ATI peaks of the photoelectron spectra in Hydrogen in dependence on the laser intensity. Solid curves correspond to the theoretical calculations taking into account the Stark shift of the continuum boundary.

to be suppressed in this case. Indeed, Fig. 5 demonstrates the dramatic difference of the population of excited states for the two considered laser intensities. For intensity $7.5 \cdot 10^{13}$ W/cm$^2$ the high-lying Rydberg states with $n = 7–10$ are predominantly populated and the
total probability of excitation appears to be much higher than in the case of intensity $9 \times 10^{13}$ W/cm$^2$ when only several bound states with $n = 3–5$ are found to be populated but with relatively small probability. As a result, the multiphoton resonance coupling between the ground state and a band of close neighboring high Rydberg levels is found to be accompanied by dramatic enhancement of excitation and trapping the population in Rydberg states. The reason of the observed population trapping consists in the repopulation of the resonantly coupled Rydberg band by Raman $\Lambda$-type transitions via the continuum that are very efficient in a strong field and results in the significant suppression of the ionization process. The evidence of the found $\Lambda$-type transitions is clearly demonstrated by Fig. 6, where the distribution of the bound states over angular momentum is presented for two laser intensities corresponding to two local maxima of the excitation probability. For lower of the two intensities the 12-photon absorption and further $\Lambda$-type transitions result in the predominant population of states with only even orbital numbers while for intensity $10^{14}$ W/cm$^2$ 13 photon are needed to excite the high-lying Rydberg states and a set of odd orbital states are found to be mainly populated due to $\Lambda$-type transitions.

**FIG. 4:** The scheme of multiphoton transitions into the continuum for intensities $7.5 \times 10^{13}$ W/cm$^2$ and $9 \times 10^{13}$ W/cm$^2$ corresponding to high (a) and low (b) level of excitation probabilities.

It should be emphasized that the observed enhancement of the excitation means the suppression of ionization and is seen as non-monotonous character and a number of local minima on the dependence of the ionization probability on the laser intensity. Moreover, in a strong field limit the residual bound probability appears to remain at several percents providing the asymptotic value of the ionization probability less than unity. It is also important that the population of excited Rydberg states is found to be pronounced already at the first ramp of the laser pulse as soon as the field amplitude becomes close to its peak value. This fact is clearly demonstrated by Fig. 7. It is seen that rather small part of the population comes back to the bound states during the turn-off of the pulse.

Similar simulations were performed for a single-electron atom with the ionization potential $I = 7.58$ eV, which corresponds to that of silver atom. The single-electron model of a silver atom was discussed in detail in [11, 23]. The probabilities of ionization and excitation as functions of the Ti:Sa laser intensities below the barrier-suppression ionization threshold ($I < I_{BSI} \sim 10^{14}$ W/cm$^2$) are presented at Fig. 8. For weak fields, when the Stark
FIG. 5: The population of Rydberg states of the Hydrogen atom with different principal quantum numbers obtained for the laser pulse with ramps and plateau durations of two and ten optical cycles correspondently with peak intensities $7.5 \times 10^{13}$ W/cm$^2$ (1) and $9 \times 10^{13}$ W/cm$^2$ (2).

FIG. 6: Distribution of population all bound states in the angular momentum arising after interaction with a laser pulse with ramps and plateau durations of two and ten optical cycles and with peak intensities (1) $7.5 \times 10^{13}$ W/cm$^2$ (1) and (2) $9 \times 10^{13}$ W/cm$^2$ (2).
FIG. 7: The temporal population of the excited Rydberg states (1) and continuum (2) for the laser pulse with ramps and plateau durations of two and ten optical cycles correspondently with peak intensity $7.5 \times 10^{13}$ W/cm$^2$.

shift of the continuum can be neglected, the ionization is six-photon. In the intensity range below $5 \times 10^{12}$ W/cm$^2$, the obtained dependences correspond to the lowest perturbation theory order. For stronger fields ($I \geq 10^{13}$ W/cm$^2$), the dependences demonstrate the nonmonotonous behavior. The probability of excitation is found to be an oscillating function of the laser intensity with period $\Delta I \approx 2.2 \times 10^{13}$ W/cm$^2$ that almost coincide with the period found for Hydrogen atom. The value of excitation probability $w^*$ was found to change from 0.02 to 0.3 in the intensity range $10^{13}$–$10^{14}$ W/cm$^2$. For a silver atom in the Ti: Sapphire laser field, the Keldysh parameter is $\gamma = 1$ for a radiation intensity of $\sim 3.5 \times 10^{13}$ W/cm$^2$. Therefore, even for $\gamma \leq 1$ (tunneling ionization regime), the role of the excited states of the atomic spectrum is important. The distribution of the bound states over angular momentum for different values of laser intensity is similar to that found for Hydrogen atom and clearly proves the existence of $\Lambda$-type transitions being responsible for the stabilization.

Thus, the evidence of the interference stabilization in the Ti–Sa laser field was confirmed and the trapping of population in highly-excited Rydberg states due to $\Lambda$-type transitions was found. The multiphoton resonance coupling between the ground and a set of high-lying states was demonstrated to result in the suppression rather than the enhancement of ionization as it could be properly expected. Recent experimental data on population trapping in Rydberg states in Helium atoms [25] are found to be in agreement with theory of interference stabilization.
III-2. Stabilization of atoms in mid IR laser field

The calculations were performed for a Silver atom and for the mid-IR field with the photon energy $\hbar \omega = 0.4$ eV. The laser pulse had a smoothed trapezoidal shape with front and plateau durations $t_f = 2T$ and $t_p = 5T$, respectively. For the defined value of the laser frequency the pulse duration was $\approx 90$ fs, that is even more in comparison with the pulse durations of the Ti-Sa laser used in previous sections.

The probabilities of the ionization $w_i(I)$ and excitation $w^*(I)$ of atomic states calculated by the end of the laser action are presented in Fig. 9. First, we would like to note, that in the case under consideration the intensity is below the barrier suppression limit. As the Keldysh parameter $\gamma = \omega \sqrt{2I/\varepsilon}$ is equal to unity for the laser intensity $I \approx 4 \cdot 10^{12}$ W/cm$^2$, almost all the calculations were performed in the tunnel (but not above barrier) regime of ionization. Nevertheless, the resonances on the dependence $w^*(I)$ are still pronounced. The probability to find the atom in excited states is rather high and reaches the value up to 5 – 6 percents for the intensity range $2 - 3 \cdot 10^{13}$ W/cm$^2$. All this population is trapped in highly excited (Rydberg) states coupled with the continuum by single photon transitions. This effect is similar to that observed experimentally in [16, 18, 25]. The reason of the observed population trapping for mid IR frequency range also consists in multiphoton resonance population of the Rydberg states near the continuum boundary [39] and further repopulation of these states by Raman $\Lambda$ - type transitions via the continuum that are very efficient in a strong field and result in the significant suppression of the ionization process. The proof of the found $\Lambda$ - type transitions is clearly demonstrated by Fig. 9 and Fig. 10, where the distributions of the bound states over principal quantum number and angular
momentum are presented for two laser intensities corresponding to two local maxima of the excitation probability. For the intensity of $2 \times 10^{13}$ W/cm$^2$ the even-photon absorption and further $\Lambda$ - type transitions result in the predominant population of bound states with only even orbital quantum numbers while for intensity $2.7 \times 10^{13}$ W/cm$^2$ odd - photon are needed to excite the high-lying Rydberg states and a set of odd orbital states are found to be mainly populated due to $\Lambda$ - type transitions. In the case of the intermediate value of the laser intensity $2.2 \times 10^{13}$ W/cm$^2$ the multiphoton resonance between the ground and the group of high-lying Rydberg states is not pronounced that results in the significant decrease of the population of bound states near the continuum boundary. We should also note, that the population is trapped only in the states with binding energy less than $\hbar \omega$.

![FIG. 9: Probabilities of ionization (1) and excitation (2) of a silver atom in dependence on the laser intensity of mid – IR laser pulse ($\hbar \omega = 0.4$ eV) with ramps and plateau durations of two and five optical cycles.](image)

### III-3. Interference stabilization of heteronuclear molecules

An interesting question that hasn’t been studied yet in detail and remains still open is whether the interference stabilization against dissociation is possible for molecules and what are the conditions for dissociation suppression to take place. Since the interference stabilization is strongly accompanied by the repopulation of highly excited levels, it is also very important to investigate the dynamics of the bound vibrational wave packet formed in a presence of a strong field.

Due to the laser parameters chosen in our calculations we used the Born-Oppenheimer approximation with only one (ground) molecular potential surface. The time-dependent Schrödinger equation for the nuclear subsystem of the molecule interacting with the laser
FIG. 10: Distribution of population of all bound states over the principal quantum numbers (a) and the angular momentum (b) arising after interaction with a mid – IR laser pulse ($\hbar \omega = 0.4$ eV) with ramps and plateau durations of two and five optical cycles and with peak intensities (1) $2 \times 10^{13}$, (2) $2.2 \times 10^{13}$, (3) $2.7 \times 10^{13}$ W/cm$^2$.

pulse can be written in the dipole approximation as follows:

$$i\hbar \frac{\partial \psi(\vec{R}, t)}{\partial t} = -\frac{\hbar^2}{2\mu} \Delta \psi(\vec{R}, t) + \left[ V^{(eff)}(R) - q\overline{\varepsilon}(t)\vec{R} \right] \psi(\vec{R}, t).$$  \hspace{1cm} (4)

Here $R$ is the internuclear distance, $\mu$ stands for the reduced mass of the system; $V^{(eff)}(R)$ is the effective potential determining vibrational motion; $\varepsilon$ is the linearly polarized laser field,
$q$ is the effective charge of the system which determines the dipole moment of the nuclear subsystem in the own frame of reference of the molecule. In our approach we consider the direct action of the laser field on the nuclear subsystem of the molecule without involving any electron transitions. To describe the potential energy of interaction, the Morse potential curve has been chosen.

$$V^{(\text{eff})}(R) = D \left( \exp \left( -2\alpha \frac{R - R_0}{R_0} \right) - 2 \exp \left( -\alpha \frac{R - R_0}{R_0} \right) \right). \quad (5)$$

Here $D$ denotes the dissociation potential; $R_0$ is the equilibrium internuclear separation, $\alpha$ is the steepness of the potential curve which provides the value of the bottom vibrational quantum $\hbar \Omega \approx 0.1$ eV. In our calculation we took $R_0 = 2.5$ Å, $D = 1.3$ eV, $\alpha = 5$, $\mu = 16$ at. units, $q = 1$.

Following to [26] the equation (4) has been solved numerically with the initial condition corresponding to the superposition of two rather highly-excited vibrational states in the potential (5) and zero initial rotational quantum number:

$$\psi|_{t=0} = \frac{1}{\sqrt{2}} (\phi_{v=37}(R) + \phi_{v=39}(R)). \quad (6)$$

We assumed the laser pulse envelope had smoothed trapezoidal shape and the energy of laser quantum $\hbar \omega$ equal to 0.1 eV. These parameters correspond to single-photon coupling of each of initially populated states with the vibrational continuum. The laser intensity is chosen not to be very high to provide the validity of the single potential surface approximation.

One of the most interesting results obtained in our calculations consists in the suppression of the dissociation process of the molecule found in a strong field regime. The observed dependence of dissociation probability on the laser intensity is presented on Fig. 11 (solid curve). For high intensities the dissociation probability is found to deviate dramatically and appears to be much lower in comparison to predictions of the generalized perturbation theory (dashed curve). The obtained dissociation probability seems to tend to the saturation at the level less than unity. The physical nature of the found stabilization phenomenon is also supposed to arise from the interference stabilization mechanism. To demonstrate this fact more evidently the dissociation probability of the system is calculated in dependence on time during the laser pulse action for various laser intensities and is presented on Fig. 12. Since two highly excited states are populated initially, in a weak field regime we normally see the linear growth of dissociation probability with time accompanied by some oscillations corresponding to the energy difference between these two states. This result obtained in a weak field case is fully consistent with the perturbation theory. However for intensities above $4 \times 10^{12}$ W/cm$^2$ the dynamics of dissociation process changes and is found to be characterized by the bi-exponential decay due to transitions into vibrational continuum (see curves 3, 4). This fact is a clear evidence of the strong reconstruction of the eigenstates of the system in a presence of the strong field and the formation of the “dressed” states. Some of these states appear to be rather resistant to the dissociation process. This picture is very similar to the phenomenon of interference stabilization observed in the case of ionization of Rydberg atoms.
FIG. 11: Probability of dissociation of the molecule as a function of laser intensity. Generalized perturbation theory (1) and numerical TDSE solution (2).

FIG. 12: Probability of dissociation of the molecule as a function of time for different laser intensities: 1 TW/cm² (1), 4 TW/cm² (2), 9 TW/cm² (3), and 15 TW/cm² (4). The pulse envelope is presented as dashed curve.

The observed dissociation suppression is found to be accompanied by the trapping of the significant part of population in bound vibrational states. The population of different vibrational states calculated for low and high intensities at the end of the laser pulse is presented on Fig. 13. The peaks located at $v = 37$ and $v = 39$ correspond to initially populated states. As one can see, the field-induced repopulation of various vibrational states is strongly pronounced for high laser intensity. The population of highly-excited (in comparison to initial ones) states results from the Raman Λ-type transitions via the vibrational continuum. The population of lower-lying states is caused by the so-called V-type
transitions and can be characterized by a number of peaks separated by the energy of the laser quantum well seen in the distribution (Fig. 13, circles). Thus, in a strong field regime the suppression of dissociation of a molecule is found to take place due to the interference stabilization mechanism and trapping of population in excited bound vibrational states is observed to result from the Raman Λ- and V-type transitions.

FIG. 13: The population of vibrational bound states calculated at the end of the laser pulse for weak field (laser intensity 0.1 TW/cm²) – triangles and for strong field (laser intensity 15 TW/cm²) – circles.

III-4. Kramers-Henneberger regime of stabilization

In this chapter another one type of stabilization of atomic systems in strong laser fields, namely the Kramers – Henneberger (KH), is discussed. This type of stabilization appears to exist for atoms in the ground state in the case of single-photon coupling with the continuum. It should also be noted that, in high-intensity laser fields with a nonperturbative regime of ionization during laser pulse action, one may very tentatively speak of the population of particular atomic states assuming a definite basis set of atomic states of the discrete spectrum and continuum. Use of the basis set of a free atom in this case is, generally speaking, incorrect because a strong radiation field produces a significant modification of atomic states and leads to the formation of a “field-dressed” atom. In the case under consideration these states for a field-dressed atom are represented by those of the Kramers–Henneberger (KH) atom [27, 28]. States of the discrete spectrum in the KH potential may correspond to states of the continuum in the basis set of a free atom and vice versa, states in the continuum of the KH potential may correspond to states of the discrete spectrum of a free atom.

To demonstrate the KH regime of stabilization we analyze the interaction of a silver
atom with UV radiation ($\hbar\omega = 9.0$ eV, $\tau_f = 5T$, and $\tau_p = 10T$), where the ground state and all excited states are coupled to the continuum by single-photon transitions. For this case, the probability of ionization $w_i(I)$ as a function of the radiation intensity is presented in Fig. 14, while the excitation of states in the discrete spectrum can be ignored. An important feature of the $w_i(I)$ curve is the presence of an interval of intensities ($I > I^* \approx 4 \times 10^{15}$ W/cm$^2$) corresponding to stabilization of the quantum system with respect to the ionization process. In this case, stabilization can be treated in terms of the KH formalism [28] and the threshold of this regime can be determined from the condition $\varepsilon/\omega^2 > a$, where $a = 3–4$ is the characteristic size of a silver atom. In this regime, up to 20% of the population still trapped in the bound ground state.

We should mention also that the KH type of stabilization is also can be observed in the multiphoton limit of ionization in the fields above the barrier-suppression threshold. Such situation was studied in detail in [19]. It seems that in the case of barrier-suppression ionization, the electrons will rapidly (for times on the order of half the optical cycle) transfer to the continuum state, and the residual nonionization (excitation) probability in barrier-suppression fields should be vanishingly small. However, the residual probability to find the atom in the bound (Rydberg) state is still $\sim 4–8\%$ in superatomic atomic fields. In this case, unlike intensity range $I < I_{BSI}$ where the strongly nonmonotonic dependence $w^*(I)$ was observed, caused by the closing of ionization channels and the resonance population of a group of Rydberg states stable with respect to ionization, the dependence of the population trapped in Rydberg states $w^*(I)$ on the laser intensity in barrier-suppression fields behaves differently (see Fig. 15). In this intensity range, the dependence is smooth and resonances

![Figure 14: Plot of the probability of ionization $w_i$ for a model silver atom in the field of UV radiation with photon energy $\hbar\omega = 9.0$ eV and with ramps and plateau durations of five and ten optical cycles.](image-url)
are absent. The analysis of photoelectron energy spectrum [11, 19] demonstrates the absence of the channel closing effect and the coincidence of the peaks position with that following from the assumption that the “dressed” atom exists in a form of KH atom.

![Figure 15](image_url)

**FIG. 15:** Dependence of the excitation probability of a model silver atom on the Ti-Sa laser intensity in fields lower and higher than the barrier-suppression threshold $I_{BSI}$ with ramps and plateau durations of two and ten optical cycles correspondently.

Thus, in barrier-suppression fields ($I > I_{BSI}$) the system is stabilized: a considerable part of the electron density forms a Rydberg wavepacket stable with respect to ionization. However, the stabilization mechanism of an atom in barrier-suppression fields differs from the interference mechanism. It is known that the spectrum of atomic states in a superatomic-intensity electromagnetic field considerably changes and a dressed atom is produced in the form of a KH atom [28]. In the case of the silver atom, as mentioned above, superatomic intensities are achieved above $I_{BSI} \approx 10^{14}$ W/cm$^2$.

**III-5. Polarization response of a quantum system in a nonperturbative limit of interaction with a laser field**

The creation of laser sources more than fifty years ago made it possible to reach the intensities $10^{10} \div 10^{12}$ W/cm$^2$ in the optical frequency band and to observe a lot of nonlinear effects. To understand the physics of these effects it is necessary to determine the polarization response of the medium to an external high-intensity electromagnetic field. For example, to describe the phenomenon of the self-focusing of electromagnetic radiation the value of the response at the frequency of the acting field should be calculated. The generation of harmonics of the incident radiation is determined by the response at the harmonics of the fundamental frequency. It is important to note that for the above mentioned intensity range the electric field in an electromagnetic wave is two or three orders
of magnitude smaller than the atomic field value. Therefore, to perform the analysis of the atomic response to the external action, it is possible to use the quantum mechanical perturbation theory and the expansion of the response in powers of the field. For example, to describe correctly the self-focusing effect of the radiation, it is necessary to take into account the nonlinear susceptibilities of all odd-orders (except the first one) of the fundamental frequency. If the perturbation theory is valid the main contribution to the nonlinear response gives the cubic susceptibility of the medium. Nonlinear susceptibilities of the fifth and higher odd orders give additional (small) contribution to the nonlinear response at the frequency of the acting field.

Thus, using the proposed approach, the atomic response at the field frequency can be expressed as a series:

\[
d_\omega = \chi^{(1)}(\omega)\varepsilon_\omega + \chi^{(3)}(\omega)\varepsilon^3_\omega + \ldots,
\]

where \(\chi^{(1)}(\omega)\) is the linear and \(\chi^{(3)}(\omega)\) is the cubic nonlinear susceptibility component, respectively, at the radiation field frequency. Similarly, for analysis of the third-harmonic generation (at the triple frequency), we have

\[
d_{3\omega} = \chi^{(3)}(3\omega)\varepsilon_\omega = \chi^{(3)}(3\omega)\varepsilon^3_\omega + \chi^{(5)}(3\omega)\varepsilon^5_\omega + \ldots
\]

where \(\chi^{(3)}(3\omega)\) and \(\chi^{(5)}(3\omega)\) are the cubic and fifth-order nonlinear susceptibilities, respectively, at the third harmonic frequency. All above mentioned susceptibilities can be calculated in the frames of quantum-mechanical perturbation theory.

The appearance of high-power (terawatt) pulsed lasers capable of generating radiation with electric field strength comparable to (or even greater than) the intra-atomic values and a pulse duration of several tens of femtoseconds makes it of special importance to investigate nonlinear processes in this new range of laser radiation parameters. However, under these conditions, quantum-mechanical perturbation theory is no longer applicable to the description of atomic dynamics in the field of laser radiation and, hence, expansion in powers of the field intensity cannot be used for calculating atomic susceptibilities. Therefore, the determination of atomic response in such a nonperturbative limit is one of the most important problems of modern nonlinear optics and atomic physics.

On the other hand, within a pulse several tens of femtoseconds long, particles in a gaseous medium experience no mutual collisions. This implies that the polarization response of the medium may be calculated by studying the dynamics of a single atom or molecule in the field of a high-intensity ultrashort laser pulse. At present, this problem can be numerically solved from first principles, by the direct integration of a nonstationary Schroedinger equation that describes the dynamics of an atom (molecule) of a gas phase in the electromagnetic wave field [29]. This approach was recently developed in a number of papers [20, 21, 31–33].

The polarization response of an atomic system can be calculated from the wave function of the system \(\psi(\vec{r}, t)\) obtained as a result of solution of TDSE:

\[
\langle d_z(t) \rangle = -\int r \cos(\theta) |\psi(\vec{r}, t)|^2 d^3r,
\]

\( (9) \)
where $\theta$ is the angle between the electric field vector $\vec{\varepsilon}(t)$ (oriented along axis OZ) and the electron radius-vector $\vec{r}$. Note that the dipole moment arising in the case under consideration is directed along the radiation polarization vector.

Then, using expansions of $\varepsilon(t)$ and $\langle d_z(t) \rangle$ into Fourier integrals

$$\varepsilon_\Omega = \frac{1}{\sqrt{2\pi}} \int \varepsilon(t) \exp(-i\Omega t) dt, \quad (10)$$

$$d_\Omega = \frac{1}{\sqrt{2\pi}} \int \langle d_z(t) \rangle \exp(-i\Omega t) dt \quad (11)$$

it is possible to determine the spectral expansion $d_\Omega(\varepsilon_\Omega)$ of the polarized response, calculate from first principles the susceptibility at various frequencies, determine the domains of applicability of the method of response expansion in powers of the field, and analyze contributions to the response from various atomic states in the discrete spectrum and continuum for the strong field limit, where the expansion in powers of the field is definitely incorrect.

It is more convenient to perform the calculations of the atomic response to apply the Ehrenfest theorem and to calculate first the acceleration

$$\langle a_z(t) \rangle = -\varepsilon(t) - \left\langle \frac{\partial V}{\partial z} \right\rangle, \quad (12)$$

and then using the expression $d_\Omega = a_\Omega / \Omega^2$ to obtain the spectral component of the polarization response $d_\Omega$.

Let us first consider the results of calculations of the nonlinear susceptibility of silver atoms in IR field with a photon energy of $\hbar\omega = 1.5$ eV, which approximately corresponds to the radiation of a Ti:Sapphire laser. For this analysis, the wavefunction $\psi(r, t)$ determined by direct numerical integration of the nonstationary Schroedinger equation (1) has been used to calculate the acceleration via Eqs. (12) for various laser intensity values.

Figure 16 demonstrates the typical results of these calculations for two radiation intensity values. Note that the case of a lower intensity ($3 \times 10^{12}$ W/cm$^2$) corresponds to a regime of perturbation theory where the ionization and excitation probabilities are much less unity. The opposite situation takes place for a greater intensity ($1.5 \times 10^{13}$ W/cm$^2$), where the ionization probability increases up to 0.90. As a result, the acceleration amplitude increases with time and application of the perturbation theory for calculations of the polarization response becomes impossible.

The functions were decomposed into Fourier integrals. Figure 17 shows these spectral expansions for two values of laser intensity. The curves reveal clearly pronounced maxima at $\Omega$ values corresponding to odd harmonics of the laser radiation frequencies, $\Omega_{2n+1} = (2n+1)\omega, (n = 0, 1, 2, \ldots)$. Then, it is possible to calculate nonperturbatively the polarization response at $\Omega_{2n+1}$, and to determine the limit of the validity of the perturbation theory.

Figure 18 shows a plot of the polarization response $d_\omega$ at the fundamental frequency versus spectral value of the electric field $\varepsilon_\omega$ (or radiation intensity $I$). In relatively weak fields, when the atom under laser action remains predominantly in the ground state, the
FIG. 16: Temporal variation of the (solid curves) quantum-state average acceleration of a model silver atom and (dashed curves) electric field strength $\varepsilon$ (b) for radiation with photon energy $h\omega = 1.5$ eV and intensity (a) $3 \times 10^{12}$ and (b) $1.5 \times 10^{13}$ W/cm$^2$.

obtained dependences are adequately described by expression (7), which take into account the linear and cubic terms in powers of the field strength. However, as the field intensity increases above $5 \times 10^{12}$ W/cm$^2$, the polarization response saturates, then decreases, and eventually changes sign to become negative. This behavior implies that, as the radiation intensity increases, the properties of the medium change from focusing to defocusing, which leads in practice to filamentation of the radiation.

The detailed analysis of the contribution of different atomic states to the nonlinear
FIG. 17: Spectral expansions of electron acceleration (solid curves) during laser pulses with photon energy $\hbar\omega = 1.5$ eV and intensity (a) $3 \times 10^{12}$ and (b) $1.5 \times 10^{13}$ W/cm$^2$. Dashed curves correspond to the spectral expansion of a laser pulse.

atomic susceptibility $\chi(\omega, \varepsilon_\omega)$ plotted in Fig. 19 (curve 1) was performed in [31, 32]. It was found that, under the studied conditions, the contribution from low-lying excited atomic states to the total atomic susceptibility is negligibly small and the $\chi(\omega, \varepsilon_\omega)$ is determined mainly by free electron plasma component and population trapped in high-level Rydberg states. Hence, saturation of the response and the change in its sign is undoubtedly related to the photoionization and stabilization of highly excited atomic states. Which particular mechanism of trapping atoms in the highly excited states (interference stabilization or
FIG. 18: Plot of the polarization response $d_\omega$ of a model silver atom at the fundamental frequency $\omega$ vs spectral value of the electric field $\varepsilon_\omega$ (or radiation intensity $I$). The inset shows the region of small fields on a greater scale, which can be used to determine the limits of applicability of the expansion of polarization in powers of the field strength. Dashed line corresponds to Eq. (7) that takes into account the linear and cubic terms of expansion.

KH atom formation) is not important due the fact that Rydberg atoms contribute to the response like the continuum states.

As the susceptibility of free electron and high-lying Rydberg states is $\chi_e(\omega) = -1/\omega^2$ [34] and increases dramatically in low-frequency domain the role of the effects of the ionization and population trapping is expected to grow up significantly in mid-IR frequency band and dominate in comparison with the contribution of Kerr effect even for significantly low value of ionization probability. The calculated dependence of the susceptibility at the fundamental mid IR frequency $\chi(\omega, \varepsilon_\omega) = d_\omega(\varepsilon_\omega)/\varepsilon_\omega$ is shown in figure 20. In relatively weak laser fields up to $5 \times 10^{12}$ W/cm$^2$, when the atom remains dominantly in the ground state, the value of susceptibility is approximately constant and corresponds to the static value for the silver atom. However, for higher intensities one first observes the decrease of the polarization response, after which it changes sign and becomes negative for intensities larger than $8 \times 10^{12}$ W/cm$^2$. The change of the response sign can be caused by the population of high-lying Rydberg and continuum states only. Indeed, the susceptibility of a free electron gas (collisionless plasma) per one electron, is determined by the expression $\chi_e(\omega) = -1/\omega^2$. This value for a photon of mid-IR laser radiation with $\hbar \omega = 0.4$ eV is more than two orders of magnitude larger than the linear atomic susceptibility $\chi^{(1)}(\omega)$ of a silver atom. Therefore, even at a degree of gas ionization of about 1 %, the contribution of free electrons in the continuum to the polarizability of the medium is expected to be dominant. That is the situation observed in our calculations: the ionization probability per
FIG. 19: Plots of the (1) total susceptibility $\chi(\omega, \varepsilon_\omega) = d_\omega(\varepsilon_\omega)/\varepsilon_\omega$ of a model silver atom at the radiation field frequency, (2) contribution due to Rydberg atoms, and (3) contribution due to electrons in the continuum and low-lying excited atomic states vs. spectral value of the electric field $\varepsilon_\omega$ (or radiation intensity $I$).

pulse for silver atoms at the intensity of $8 \times 10^{12} \text{ W/cm}^2$, when the response changes the sign, is about $\sim 0.01$.

FIG. 20: The dependences of the susceptibility of model silver atoms $\chi(\omega) = d_\omega(\varepsilon_\omega)/\varepsilon_\omega$ at the fundamental frequency for the mid IR laser radiation.
Another situation appears to exist for high-frequency (UV) radiation, when the ground state coupled to the continuum by single-photon transitions. Figure 21 shows the results of calculating the total susceptibility $\chi(\omega, \varepsilon_\omega)$ and the contributions from neutral atoms and electrons in the continuum for the case under consideration. Important feature of the obtained dependence is that the atomic susceptibility is negative even in weak fields and its absolute value is even greater than that of free electrons. Indeed, for single-photon transitions between the ground state and continuum, the linear atomic susceptibility $\chi_g^{(1)}(\omega)$ is given by

$$\chi_g^{(1)}(\omega) \approx \int |dE_g|^2 \cdot \frac{2(E - E_g)}{(E - E_g)^2 - \omega^2} dE,$$

(13)

where $E_g < 0$ is the atomic ground-state energy and $E$ is the electron energy in the continuum. As can be seen from (13), a narrow energy interval near $E = E^* = \omega - |E_g|$ dominantly contribute to the integral. Since the square modulus of a matrix element of the dipole operator $|dE_g|^2$ for a Coulomb spectrum is a monotonically decreasing function of the energy, the integral in Eq. (13) is negative and, hence, $\chi_g^{(1)}(\omega) < 0$. A detailed analysis of susceptibility (13) for a hydrogen-like system was carried out in [35]. In particular, for the initial s state of the atom expression (13) can be expanded in the high-frequency limit $(\omega \gg |E_g|)$ as

$$\chi_g^{(1)} = -\frac{1}{\omega^2} - \frac{4}{3n^3\omega^4} + \ldots,$$

(14)

where $n$ is the principal quantum number of the initial state. In this expansion, the first term describes the susceptibility of the free electron and the second term is an additive, which is also negative and rapidly decreases in absolute value with increasing of laser frequency and principal quantum number of the initial state.

In view of the above considerations, the ionization process and the appearance of free electrons must lead to a growth in susceptibility with increasing intensity in agreement with our calculations (see Fig. 21). In the region of stabilization ($I > I^* \approx 4 \times 10^{15}$ W/cm²), where the probability of ionization decreases with increasing radiation intensity, the susceptibility keeps growing so as to approach the value corresponding to the susceptibility of free electrons. This implies that the susceptibility of neutral atoms at intensities significantly exceeding the stabilization threshold $I^*$ almost coincides with the susceptibility of free electrons. This behavior of the atomic susceptibility can be explained in the frames of the KH formalism. Indeed, in the region of $I > I^*$, the potential of a field-dressed atom (KH atom) acquires an additional dichotomic structure, the size of which is determined by the amplitude of oscillations of free electrons, $a_e = \varepsilon/\omega^2$, in the electromagnetic wave field. The spatial size of this structure increases with intensity, which leads to a decrease in the potential of ionization of the field-dressed atom, which becomes significantly lower than the photon energy. As a result, oscillations of the atomic electron become quasi-free. The results of our previous analysis of the susceptibility of a field-dressed atom [36] also confirmed that the susceptibility of a KH atom is close to that of a free electron. The significant contribution to the atomic response of the bound states of the KH atom was demonstrated also in recent paper [37].
FIG. 21: Plot of the total susceptibility $\chi_\omega$ at the fundamental frequency (curve 1), contribution due to neutral atoms (curve 2), and contribution due to electrons in the continuum (curve 3) for a model silver atom in the field of UV radiation with photon energy $\hbar\omega = 9.0$ eV (dashed line indicates the level of susceptibility determined by free electrons).

IV. CONCLUSIONS

In conclusion, we have found that population trapping in strong laser field is a sufficiently general phenomenon occurring both in atoms and in molecules. This trapping is the result of ionization (or dissociation) suppression or stabilization phenomenon. Two different types of stabilization were distinguished in our study. One of them, interference stabilization (IS) can be observed either if one prepares in advance atoms or molecules excited to a set of closely located (Rydberg or vibrational) levels in processes of direct multiphoton ionization or dissociation from ground levels. In the last scheme of experiments, under proper conditions, ionization or dissociation can be accompanied by an efficient population of highly excited bound levels, at which the IS effect can occur. Stabilization occurs most efficiently when the multiphoton resonance appears between the ground state of the atom a group of Rydberg states near the continuum boundary. In stronger (barrier-suppression) fields, the atomic spectrum of the system drastically changes, resulting in the disappearance of a nonmonotonic dependence of the ionization probability on the radiation intensity caused by the closing of ionization channels: a dressed atom appears, which is stable with respect to ionization, as follows from the KH formalism.

The nonperturbative strong-field atomic dynamics should be taken into account in determination of the polarization response and atomic susceptibilities. Our numerical calculations of the polarization response clearly demonstrate limitations of the approach based on the quantum-mechanical perturbation theory and on the expansion of this response in
powers of the electric field strength and the introduction of nonlinear susceptibilities of various orders. In the case of IR radiation, the electron dynamics in atoms already at the intensity in excess of $3 \times 10^{12}$ W/cm$^2$ has a significantly nonperturbative character and cannot be adequately described by the quantum-mechanical perturbation theory. In particular, in the nonperturbative regime, the most important effects contributing to the polarization response at the fundamental frequency are related to electron transitions from the initial state to the continuum and to the population of high-lying (Rydberg) states. These processes change the sign of the atomic response and are responsible for the filamentation of ultrashort high-intensity laser pulses in various media. Due to the fact that the susceptibilities of Rydberg states of atoms and free electrons are close, it is apparently a very difficult experimental task to reveal contributions related to the ionization and excitation of Rydberg states. In the barrier-suppression regime of ionization, it is convenient to study the problem using a basis set of states of the KH atom. This approach makes it evident the ambiguous character of dividing atomic states into those belonging to states in the continuum and discrete spectrum, since for the dichotomy structure of KH potential, bound states of KH atom seem to be continuum states of field-free atom and vice versa.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Grant No. 12-02-00064 and 14-02-31114). Numerical integration of the Schrödinger equation was performed on the SKIF-MGU Chebyshev and Lomonosov supercomputers.

References


[34] N.B. Delone and V.P. Krainov, Multiphoton processes in atoms (Berlin: Springer-Verlag) section 2.4 (1993)


[38] The probability of excitation is the total probability of the population of all the bound states except of the initial (ground) one.

[39] In our case the number of photons coupling the initial ground state and high-level Rydberg states is about 20 and even more.
Review

High-Order Harmonic Generation Driven by Two-Color Laser Fields

Guihua Li,1,2 Jinping Yao,1,∗ Chaojin Zhang,1,3 Bin Zeng,1 Wei Chu,1 Jielei Ni,1 Jing Chen,4,5 Zhinan Zeng,1 Ruxin Li,1 Ya Cheng,1 and Zhizhan Xu1

1State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China
2University of Chinese Academy of Sciences, Beijing 100049, China
3School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, China
4Key Laboratory of High Energy Density Physics Simulation, Center for Applied Physics and Technology, Peking University, Beijing 100084, China
5Institute of Applied Physics and Computational Mathematics, Beijing 100088, China

(Received November 2, 2013)

In the past three decades, high-order harmonic generation (HHG) has attracted much attention due to its promising applications on creating table-top coherent extreme-ultraviolet (EUV/XUV) or X-ray sources, synthesizing attosecond pulses, probing electron dynamics and making “molecular movies”, etc. We review our recent experimental and theoretical progresses in HHG driven by two-color laser fields, including broadening of XUV supercontinuum, generation of isolated attosecond pulses (IAPs), selection of long or short quantum trajectories, enhancement of HHG yield, creation of wavelength-tunable, bandwidth-controlled XUV emission, etc.

DOI: 10.6122/CJP.52.366 PACS numbers: 42.65.Ky, 42.65.Re

I. INTRODUCTION

In the past three decades, significant advances in high-order harmonic generation (HHG) have opened up a wide range of potential research opportunities in physics, biology, chemistry, material science, etc. From the well-known simple-man model [1], HHG can be intuitively understood as the subsequence of three steps. The electron first tunnels through the barrier formed by the combined action of Coulomb potential and the driving laser field (ionization), then it oscillates in the laser field (propagation), and finally it may recombine with the parent ion and emit a photon with an energy equal to the ionization potential plus the kinetic energy obtained from the laser field (recombination). In this way, HHG provides table-top ultrafast extreme-ultraviolet (EUV/XUV) or X-ray sources with high temporal and spatial coherence, which not only motivates its potential applications on

∗Electronic address: jinpingmrg@163.com
nanolithography [2], high-contrast X-ray microscopy [3], ultrafast electron spectroscopy [4–6], bio-imaging [7, 8] and so on, but also paves a way for spanning from femtosecond chemistry to attosecond physics [9]. Furthermore, the inherent pump-probe property during HHG process makes itself a tool for investigation of light-matter interaction in the strong field regime. For example, we can retrieve the information of molecular structures [10, 11] and dynamics [12–14] from HHG, which makes an important step towards the dream of making “molecular movies” with attosecond temporal and sub-angstrom spatial resolutions.

Based on the expectations mentioned above, considerable efforts have been devoted to extending the cutoff energy of HHG, improving HHG yield, shortening the duration of isolated attosecond pulses (IAPs), controlling XUV or X-ray emission (e.g., polarization, central wavelength and bandwidth, etc.). It is well known from the simple-man model [1] that the three processes involved in HHG all depend strongly on the waveform of the driving laser field, which offers us an opportunity to manipulate HHG as well as electron wavepacket dynamics with a great flexibility. A simple, straightforward method to waveform shaping is to control carrier-envelop phase (CEP) of few-cycle laser pulses [15]. However, the creation of few-cycle, high-energy laser pulses is now still a challenge for most laboratories; on the other hand, the limited waveform-control capability makes this approach difficult to enable a full control of HHG. Another technique is to tailor the shape of driving pulses with sub-cycle resolution and attosecond precision by a 1.5-octave three-channel optical field synthesizer and their attosecond sampling [16]. However, the employment of sophisticated waveform tailoring system often leads to increased complexity of the experimental setup, limited driving pulse energies, and extra optical losses. Two-color field technique [17–19] effectively combines the advantages of two methods as we will show below. It is not only simple but also highly flexible for experimental implementation.

The review focuses on the generation and manipulation of high-order harmonics in a two-color laser field. We firstly give an intuitive picture on manipulation of HHG with a two-color laser field. And then we will discuss the advantages of two-color field scheme on broadening of XUV supercontinuum, shorter attosecond pulse generation, selection of long or short quantum trajectories, enhancement of HHG yield, and the creation of wavelength-tunable, bandwidth-controlled XUV emission due to its ability of sub-cycle control for electron wavepackets. Finally, we give a summary and the future outlook about HHG in the two-color field.

II. MANIPULATION OF HHG WITH A TWO-COLOR LASER FIELD

The key point of manipulating HHG with a two-color laser field is to control the electron wavepacket dynamics, including tunnel ionization of electron, propagation of electron in the laser field and its recombination with parent ions. In this section, we will provide a basic picture on how two-color laser field affects three processes above.

First, tunnel ionization, as the first step as well as a fundamental process of HHG, is highly sensitive to the waveform of driving pulses due to its exponential dependence on the laser intensity [20]. By superposing a weak control field at another wavelength onto an
intense laser field, the waveform of the driving field will be tailored on sub-cycle time scale. The broken symmetry of the laser field enlarges the difference of ionization rate as well as HHG yield between the adjacent half optical periods. Therefore, a shaped laser pulse allows for sub-cycle manipulation of HHG, leading to the enhancement of XUV emission in some half cycles and the weakening of XUV emission in some other half cycles.

In the next two processes (i.e., propagation and recombination) of HHG, the waveform of driving pulses determines the electron trajectory, the excursion time in the laser field and the kinetic energy obtained from the laser field. Therefore, by using a waveform-controlled laser field, we can extend cutoff energy of HHG, broaden and tune the spectrum of XUV supercontinuum, and select quantum trajectories. To give a clear view, we depict schematic diagrams of HHG in one-color and two-color laser fields, as shown in Figs. 1(a) and (b) respectively. In Fig. 1(a), there are three electron trajectories contributing to HHG, originated from the electrons ionized at the time 1, time 2, and time 3. Because the central half cycle of the optical pulse is much more intense than any other half cycles, the electron ionized at time 2 will gain more energy upon the recollision than all the electrons ionized at the other times. Hence, we will obtain an attosecond pulse train, with the pulse 2 having the highest photon energies. Then, we can place a metal foil to block all these two-pulses composed of the low-energy photons, only part of the pulse 2 is allowed to pass through due to the higher photon energies it carries. In the spectral domain, it corresponds to an XUV supercontinuum spectrum. Therefore, in order to obtain IAPs, we need to have a few-cycle driving pulse with an intense central half cycle, but relatively weak neighboring half-cycles. The contrast between the central half cycle and the neighboring cycles will determine the bandwidth of supercontinuum emission and the pulse duration of attosecond pulses.

Fortunately, the synthesis of two-color fields provides us an effective method to enhance the contrast between the central half cycle and the neighboring half cycles. As shown in Fig. 1(b), if we add a second harmonic wave upon the fundamental wave, we can effectively enhance the central peak, and suppress these two neighboring peaks, which is equivalent to shortening of pulse duration. In this case, we can obtain broader supercontinuum spectra and shorter attosecond pulses due to the modified electron trajectories (See red dashed line in Fig. 1(b)).

III. ADVANTAGES OF HHG IN A TWO-COLOR LASER FIELD

III-1. The broadening of XUV supercontinuum and generation of IAP

Generally, HHG inherently produces attosecond pulse trains separated by about half optical period of the driving laser field. Therefore, to achieve IAPs desired for a lot of applications, it is necessary to gate the driving pulses or the harmonic emission itself, making the HHG process periodically occurring in a multi-cycle regime can be virtually reduced to only once. By gating the driving field with CEP-stabilized, few-cycle laser pulses, one has broken through the 100-as barrier [21]. However, up to now, the achievement of few-cycle, high-energy laser pulses is still a challenge for most laboratories, which hampers the widespread use of attosecond technology. The commercial availability of multi-cycle, high-energy laser
system motivates us to explore other methods, such as multi-color field synthesis [17, 22], polarization gating [23], double optical gating (DOG) [24], phase matching gating [25], etc., which are capable to gate HHG itself on a sub-cycle time scale. In this review, we focus on the two-color field scheme. As compared to one-color laser field, the two-color synthesized field provides us more parameters (e.g., wavelength ratio, intensity ratio, time delay, relative angle of polarization planes, etc.) to control electron wavepackets, leading to high flexibility of experimental implement. In this section, we will show the capability
of two-color field for broadening XUV supercontinuum and shortening attosecond pulses.

**A. Parallel-polarized two-color field scheme**

The parallel-polarized two-color field is a common and simple waveform shaping method. In the scheme, the main field and the control field have the same polarization direction, and thus the polarization of their synthetic field is time independent, which means the electron travels along a one-dimensional (1D) path. However, taking advantage of the simple technique, we can significantly extend XUV supercontinuum spectrum and break through the bottleneck of 100 as due to the high sensitivity of HHG on the laser waveform [19]. Figure 2(a) shows electric fields of the 6-fs, 800-nm pulse (dashed line), the two-color pulses composed of 800-nm and 400-nm pulses at zero delay (dashed dotted line), and at the time delay of $-166.7$ as (solid line). In our simulation, the single-atom response of HHG is calculated using the Lewenstein model [26, 27] based on a single-active-electron approximation. It should be pointed out that all simulated spectra shown in the review are obtained by the method. The calculated HHG spectra in the three driving fields are shown in Fig. 2(b). Clearly, the minor difference of the three laser fields leads to the dramatic change of HHG spectra. The XUV supercontinuum spectrum produced by the single 6-fs pulse alone shows a bandwidth of approximate 30 eV. In this case, although a single attosecond pulse is generated, its temporal profile shows two subpulses with comparable peak intensities, and each subpulse is longer than 100 as, as shown by curve III of Fig. 2(c). A significantly broadened XUV supercontinuum with a spectral width of $\sim 75$ eV can be achieved by superposing the weak frequency-doubled pulse onto the fundamental pulse with a zero time delay. Surprisingly, XUV supercontinuum is dramatically broadened to 148 eV when we introduced a relative phase shift of $t_0 = -166.7$-as between two-color pulses. The ultra-broad XUV supercontinuum can support an isolated 65-as pulse even without any phase compensation, as shown by curve II of Fig. 2(c). Furthermore, if all the phase dispersion over the spectral width of 148 eV can be properly compensated for, an isolated 23-as pulse with a clean temporal profile could be theoretically predicted [See curve I of Fig. 2(c)]. Therefore, parallel-polarized two-color field with the optimized delay offers an effective method to obtain extremely broad XUV supercontinuum as well as IAPs close to an atomic unit under the conditions available in quite a few laboratories around the world. This surprising result gave us a lesson that the electron motion is very sensitive to the waveform of light field.

Additionally, with the method, it has been experimentally demonstrated the generation of the XUV supercontinuum in argon with a two-color laser field consisting of an intense 7-fs, 800-nm pulse and a relatively weak 37-fs, 400-nm pulse [28]. By controlling the relative time delay between the two laser pulses, one has observed both enhanced HHG and spectral broadening of the supercontinuum.

**B. Orthogonal-polarized two-color field scheme**

Furthermore, we extended this technique into the orthogonal-polarized two-color laser field. As compared to parallel-polarized two-color field, the driving pulse composed of orthogonal-polarized two-color field has a rapid varying polarization on sub-cycle time scale, and thus it can effectively control electron wavepacket (e.g., its traveling path, the recolliding direction, etc.) in two-dimensional (2D) space. Actually, the orthogonal-polarized
FIG. 2: (a) Electric fields of the single 6-fs pulse (dashed line), the two-color pulses without a time delay (dashed dotted line), and with a $-166.7$-as time delay (solid line). (b) The spectra of the XUV supercontinuum generated with the single 6-fs pulse (dashed dotted line), the two-color pulses without a time delay (dotted line), and with a $-166.7$-as time delay (solid line). (c) The temporal profiles of the attosecond pulses generated from the XUV supercontinuum of 148 eV spectral width with (red dashed line) and without (blue solid line) phase compensation. For comparison, the attosecond pulse generated by the single-color 6 fs pulse without phase compensation is shown as black solid line.
two-color field scheme can be recognized as a combined version of parallel-polarized two-color field technique and polarization gating technique. Therefore, in principle, it should be easier to broaden XUV supercontinuum emission as compared to the parallel-polarized two-color field.

As an example, we theoretically demonstrated the generation of XUV supercontinuum in an orthogonally polarized two-color laser field synthesized by two sinusoidal pulses at 800-nm and 1300-nm wavelengths, both with a pulse duration of 9-fs and an equal peak intensity [29]. As shown in Fig. 3(a), the synthesized electric field shows an asymmetric, rapidly varying waveform and polarization in three-dimensional (3D) space. In the case, the electron born at certain moments can be driven back to its parent ion after traveling along a curved trajectory in a plane perpendicular to the beam propagation direction, while the electron at some moments can never revisit the parent ion and thus it does not make any contribution to HHG. The $x$ and $y$ components of HHG spectra generated by the driving field are shown in Fig. 3(b). In order to give a clear view, we purposefully shift the $y$ component of the HHG spectrum to lower location. The $x$ component of the HHG spectrum [the upper curve in Fig. 3(b)] shows a smooth XUV supercontinuum covering almost the entire plateau region. In contrast, in the lower curve in Fig. 3(b), significant spectral modulation appears in the low energy range, indicating the existence of multiple electron recolliding events capable of contributing to the generation of low-order high harmonics polarized in the $y$ direction. The spectral modulation originates from the interference between the low-order harmonics emitted at different times. By performing inverse Fourier transformations of the XUV supercontinuum from 25 eV to 325 eV, we obtained the electric fields of the attosecond pulses in 3D space and their corresponding temporal envelopes, as shown in Figs. 3(c) and (d), respectively. Clearly, the supercontinuum in the spectral range can synthesize an attosecond pulse train and each attosecond pulse in the pulse train shows different polarization states, which is determined by the moving direction of the electron at the moment of recombination. The unique property opens up a new avenue to control the polarization of attosecond pulses using the orthogonal-polarized two-color field [30]. On the other hand, it can trigger a series of interesting phenomena in molecular HHG, where the conversion efficiency of HHG critically depends on the angle between the laser polarization direction and the molecular axis [31]. In other words, the sensitivity of the molecular HHG to the angle between the moving direction of the recolliding electron and the molecular axis provides an additional way to further confine the temporal window of HHG and eliminate undesirable satellite attosecond pulses shown in Figs. 3(c) and (d).

Based on the above consideration, we employed the technique of the orthogonal-polarized two-color field to molecular HHG [32]. Figure 4(a) shows HHG spectra of argon (Ar) generated by the driving field consisting of a 9-fs, 800-nm, $x$-polarized pulse and a 15-fs, 1300-nm, $y$-polarized pulse. Obviously, both the $x$ and the $y$ components of the HHG spectrum of Ar show smooth XUV supercontinuums in the spectral range of 80–100 eV. However, in the low-energy range, especially in the $y$ component, there is a significant spectral modulation originating from the interference between the attosecond pulses emitted at different times. This property can be seen more clearly from the temporal profiles of the high harmonics in the spectral range of 50–100 eV, as shown in Fig. 4(b). We noted
FIG. 3: (a) 3D plot of the orthogonally polarized two-color laser field; (b) $x$ and $y$ components of the high-order harmonic spectrum produced in the orthogonal-polarized two-color field; (c) 3D plots of electric fields of attosecond pulses generated by Fourier syntheses of the harmonics in the spectral ranges of 25–325 eV and (d) corresponding pulse envelope.

that the pulse train contains two single attosecond pulses, namely, a main pulse released at about $0.3T$ and a weak one at $\sim 2.5T$, where $T$ is the period of an 800 nm pulse. In addition, it was also found that the polarization directions of the two pulses were different, implying that the electrons return to the vicinity of cores with varying incident angles due to the change of the polarization direction of the synthesized field with the time. The main pulse polarizes along the direction of $\sim 45^\circ$ with respect to $x$ axis, while the satellite pulse polarizes along the $y$ direction. When the interaction medium is switched to molecular nitrogen ($N_2$) from Ar, the case will be different. Figures 4(c) and (d) show HHG spectra of $N_2$ with the molecular axis oriented at $45^\circ$ with respect to $x$ direction and the attosecond pulses synthesized by harmonics in the same spectral range, respectively. Comparing to the HHG in Ar, both $x$ and $y$ components of HHG spectra in $N_2$ become smoother in the low-order harmonics and the weak satellite pulse generated at $\sim 2.5T$ disappears. The reason is that, when the molecular axis is along the moving direction of the recolliding electron (i.e., the polarization direction of the main attosecond pulse), the electron ionized from the
highest occupied molecular orbital (HOMO) of N\textsubscript{2} has the highest probability to recombine with its parent ion \cite{33}. In this case, the efficiency of HHG corresponding to the main attosecond pulse reaches its maximum, while the efficiency of HHG corresponding to the \(y\)-polarized satellite pulse is effectively reduced. In this way, the undesirable satellite pulse is eliminated. Therefore, by means of the sensitivity of HHG on the molecular orientation, the rapid variation of moving direction of the recolliding electron in the orthogonal-polarized two-color laser field can be employed for further confining the temporal window of HHG and isolating single attosecond pulse from attosecond pulse train.

FIG. 4: \(x\) (solid line) and \(y\) (dotted line) components of high-order harmonic spectra from (a) Ar and (c) N\textsubscript{2} aligned at 45\(^\circ\) with respect to \(x\) axis in the orthogonal-polarized two-color field; (b) and (d) are the corresponding electric fields of attosecond pulses synthesized by the harmonics in spectral range of 50–100 eV.

**C. Broad supercontinuum generation in multi-cycle laser fields**

Although both parallel- and orthogonal-polarized two-color field schemes can dramatically extend the bandwidth of XUV supercontinuum spectra, they usually require at least one ultrashort pulse with the pulse duration of 1-2 optical cycles in order to create sub-100as IAPs. The energy loss caused by the pulse compression largely reduces the output energy of IAPs. Therefore, considerable effort has been devoted to generating IAPs.
with multi-cycle pulses directly from the chirped pulse amplifier. Currently, several methods have been proposed for broadening XUV supercontinua in the long pulse regime, e.g., DOG [24], generalized double optical gating (GDOG) [34], adding a nonlinear chirp on the multi-cycle driving field [35], etc.

We found a simple method to generate sub-100as IAPs by use of a multi-cycle two-color laser field [22]. Theoretical simulation demonstrated that the supercontinuum spectrum was significantly broadened by optimizing the time delay and the angle of polarization planes between two multi-cycle, linear-polarized laser fields. In Fig. 5(b), we can clearly see an extremely broad XUV supercontinuum with the bandwidth of 180 eV when the polarization between an intense 800-nm, 25-fs laser pulse and a relatively weak 1400-nm, 43-fs laser pulse is arranged at an angle of $\sim 73$ degree and the time delay is adjusted at 3.63 fs. In contrast, in the case with either 800-nm or 1400-nm one-color field, no observable supercontinuum is generated in the multi-cycle regime. Figure 5(a) illustrates the driving field consisting of 800-nm and 1400-nm pulses. The $x$ component of synthesized field is a one-color field at 800 nm, while the $y$ component is a two-color field composed of 800 nm and 1400 nm laser pulses and exhibits a high asymmetry. Due to this reason, polarization state of the synthesized field rapidly changes within an optical period, which allows us to purposely manipulate the free electron trajectories contributing to HHG. Furthermore, the ultra-broad supercontinuum generated by the synthesized field can support a $\sim 73$-as IAP even without any phase compensation when the long trajectory is removed, as shown in Fig. 5(c). The ability of the two-color field scheme to generate sub-100as IAPs in the multi-cycle regime relaxes the requirement of attosecond pulse generation for pulse duration of laser system and avoids the energy loss of the pump pulse caused by a complex compressing device. Consequently, it holds great potential for generation of stronger and shorter IAPs in the future.

More interestingly, we experimentally generated EUV supercontinuum with a high-energy, multi-cycle, one-color laser field [36]. The experimental setup is sketched in Fig. 6(a). The 11-mJ, 35-fs, 800-nm laser pulses directly from the laser system (Legend Elite Cryo PA, Coherent Int.) are focused by $f = 100$ cm lens into 30-mbar Krypton. HHG spectra are detected by home-made X-ray grating spectrometer equipped with a X-ray CCD (Princeton Instruments, 1340 $\times$ 400 imaging array PI:SX 400). A long filament channel can be clearly seen at the both sides of the gas cell, as shown in inset of Fig. 6(a). It is noteworthy that although our gas cell is only 10-mm-long, there are two holes drilled by the driver laser pulses at the two ends of the cell through which leakage of krypton gas inevitably occurs. Actually, the leaking gas from the holes could form a favourable density distribution of the krypton gas outside the gas cell for inducing filamentation and self-compression of the driver pulses. By performing a SHG-FROG measurement, we retrieved the temporal intensity and phase of the driving pulse coming out from gas cell, as illustrated in Fig. 6(b). Apparently, the driving pulses are split into several intensity spikes at the end of the filament due to propagation effects. In fact, at different interaction lengths, the waveform of the driving pulses could be different. Both the pulse shaping naturally occurring in the interaction region and propagation effects involved in HHG lead to EUV supercontinuum generation in the high-energy, multi-cycle, one-color laser field. Figure 6(c) shows a typical
FIG. 5: (a) $x$ and $y$ components of the synthesized laser field; (b) Harmonic spectra generated with the 800-nm laser field (dotted curve), 1400-nm laser field (dashed curve), and their synthesized field (solid curve); (c) Envelope of attosecond pulses obtained by performing inverse Fourier transformation for the supercontinuum from 200 eV to 380 eV after removal of the long trajectory.
single-shot HHG spectrum with photon energies spanning from 35 eV to 50 eV, which can support a $\sim 270$-as IAP by assuming a flat phase. This new technique greatly simplifies the experimental setup of attosecond pulse generation and efficiently utilizes the driving pulses, so it is a promising way for generating intense attosecond pulses. These advantages will have important implementations for attosecond science and technology.

FIG. 6: (a) Schematic of the experimental setup; (b) Retrieved temporal intensity (solid line) and phase (dashed line) of driving pulses coming out from gas cell; (c) Single-shot supercontinuum spectrum generated by $\sim 35$-fs, 11-mJ laser pulses.

III-2. The selection of single quantum trajectory

The employment of two-color field can create spectrally smooth XUV supercontinua by selecting long or short quantum trajectory in HHG, leading to clean temporal profiles of IAPs. When a 64-fs, 2400-nm control pulse is superposed onto a 6-fs, 800-nm main pulse, the short quantum trajectory is selected while HHG from long trajectory is effectively suppressed [37]. In order to give a clear view, Figs. 7(a) and (b) indicate the classical analysis and time-frequency analysis for HHG driven by the two-color field above. Figure 7(a) shows the synthesized electric field (dashed line), the electron return kinetic energy (solid line) as a function of time calculated by classical three-step model [1], and the tunnel ionization rate calculated by Ammosov-Delone-Krainov (ADK) model (gray filled curve) [20]. Obviously, one can see that the electrons tunnel-ionized around time $t_{\text{max}}$ will recombine with the ions with the highest return energies. A remarkable feature shown in Fig. 7(a) is that, almost all of the electrons tunnel-ionized around the time $t_{\text{max}}$ are actually freed from a binding state at those moments on the “short trajectory” side. This implies that the major contribution
of HHG is from the short quantum trajectory. The corresponding time-frequency analysis shown in Fig. 7(b) provides further evidence for the selection of short trajectory in the two-color field.

We also found that not only the short trajectory but also the long trajectory can be selected using the two-color field schemes [19]. When a two-color laser field synthesized by a 6-fs, 800-nm main pulse and a 21.3-fs, 400-nm control pulse with the time delay of $-166.7$ as is employed for HHG, the dominant quantum trajectory contributing to HHG will be switched to the long trajectory from the short trajectory. Its direct evidence can be obtained with the classical calculation and time-frequency analysis, as shown in Figs. 7(c) and (d), respectively. In Fig. 7(c), we can clearly see that most of the ionized electrons that could contribute to the XUV supercontinuum generation actually travel along the long trajectory before they recombine with their parent ions. This reveals the mechanism of the formation of the smooth spectral profile of the ultra-broad XUV supercontinuum we
observed in Fig. 2(b) (curve III).

III-3. The generation of narrow-bandwidth, wavelength-tunable XUV emission

Typically, high-order harmonic emission consists of a few rapidly decreasing harmonics followed by a plateau with a sharp cutoff, so that HHG spectrum always covers a broad spectral range with comparable intensity due to its nonperturbative nature. However, wavelength-tunable XUV radiation with a narrow spectral bandwidth is of potential importance in many fields such as the resonant excitation of atoms and molecules by XUV pulses, the seeding of XUV or X-ray free electron laser, and so on. In order to create this kind of coherent light source via HHG, a series of methods have been explored. The most straightforward method is to use a filter, grating or monochromator to spectrally select the desirable spectral components of the input beam [38–40]. However, these optical elements usually induce extra loss in the XUV regime. Another approach to obtain narrow-bandwidth XUV radiation from HHG is to precisely control the phase matching by carefully tailoring the shape of driver pulses in a feedback system [41] or by performing quasi-phase-matching technique [42]. However, these methods based on phase matching are usually complex and difficult to implement. Fortunately, HHG driven by a two-color laser field shows great potential to select and control high-order harmonic spectrum, allowing for direct generation of narrow-bandwidth, tunable XUV emission in HHG by two ways as follows. This will be discussed in detail in the section.

One strategy is to selectively enhance single or several harmonic orders by manipulating the electron wavepacket with the two-color field. We theoretically demonstrated the selective enhancement of HHG in two-color laser fields consisting of a 3-fs, 800-nm laser pulse with a laser intensity of $3 \times 10^{14}$ W/cm$^2$ and a 64-fs, 400-nm laser pulse with a laser intensity of $1 \times 10^{14}$ W/cm$^2$ [43]. Figure 8(a) shows HHG spectra calculated at time delay of 0.75 fs, 1 fs, 1.25 fs, 1.5 fs, 1.75 fs and 2 fs. Interestingly, although these HHG spectra show nearly the same cutoff energies at $\sim 200$ eV, a phenomenal enhancement of the XUV radiation with a bandwidth ranging from 3 eV to 10 eV can be observed at different positions of each HHG spectrum. For each time delay used in our simulation, the enhancement factor is almost one order of magnitude. The central frequency of the enhanced XUV radiation can be continuously shifted from the beginning of HHG plateau to the cutoff region by scanning the time delay, leading to a wide tuning range spanning from $\sim 50$ eV to $\sim 150$ eV. Furthermore, the selectively enhanced HHG gave rise to a bandwidth-controllable XUV supercontinuum in the plateau region, facilitating generation of intense isolated attosecond pulses. Further investigation revealed this enhancement effect is a result of the modified electron trajectories in the complex optical waveform offered by the two-color laser field. Figure 8(b) illustrates the electric field of the two-color laser pulse with the 1.5-fs time delay (dashed curve), the electron return energy as a function of its ionization time calculated by the classical three-step model (solid curve) [1] and the ionization probability (grey filled curve) calculated by the ADK model [20]. Obviously, the waveform of the two-color laser field fundamentally deviates from that of a single-color laser field, particularly evidenced by the two pits A and B presented in the two-color laser field. The electric field approaches zero near these two pits. Because of these two pits, the electron return energy curve as a
function of time (solid curve) in Fig. 8(b) also shows two pit-like structures, as indicated as
the pits C and D. Since the tunnel ionization is a highly nonlinear optical process which is
very sensitive to the strength of the electric field, the strongest ionization of the Ar atom
occurs at a time corresponding to the maximum peak electric field. Therefore, most of
the ionized electrons which contribute to selectively enhanced XUV radiation will travel
along the folded electron trajectory with the pit C. On the other hand, the folded region
of electron trajectory corresponds to the comparable return kinetic energy, and thus the
constructive interference between XUV radiation from the folded trajectory leads to the
selective enhancement of HHG.

Although the two-color field scheme above provides a simple, all-optical approach
for finely control of HHG spectra (i.e., central wavelength and bandwidth), it requires
the nearly single-cycle laser field. In order to relax the experimental requirement, we
further investigated narrow-bandwidth, tunable HHG in a three-color laser field [44]. The
enhancement of HHG in a selected spectral range was observed due to the modified electron
trajectory in the shaped laser field consisting of a 5-fs, 800-nm pulse, a 15-fs, 2000-nm
pulse and a 25-fs, 2200-nm pulse. Particularly, recently the selective enhancement of a
single harmonic has been experimentally demonstrated by using a three-color laser field
synthesized by the 800-nm main pulse and two control pulses at 400 nm and 267 nm with
perpendicular polarizations [45].

The other strategy is to confine HHG occurring in a narrow spectral range. The
trick of the technique is that only the electron born at a specific time can come back
and recombine with the ion, contributing to HHG. For these electrons, they carried a fix
amount of kinetic energy so that they can only release photons with a fixed energy upon
recollision. In this way, we can create narrow-bandwidth HHG spectra with a high contrast
(i.e., the ratio between the selected harmonics and the adjacent harmonics). Theoretical
investigation demonstrated that an orthogonal-polarized two-color laser field has the ability
to gating HHG in spectral domain [46, 47]. In our simulation [46], the driving field is
synthesized by an intense 10-fs, 1500-nm pulse polarized in x direction and a relatively
weak 40-fs, 2400-nm pulse polarized in y direction. When the intensity of 1500-nm laser
pulse is $6 \times 10^{14}$ W/cm$^2$, and the amplitude ratio $A$ and time delay between the 2400-nm
and 1500-nm laser pulses are set to be 0.5 and $\sim 2.17$ fs, respectively, the evolution of the
synthesized electric field in 3D space is shown by green curve in Fig. 9(a). Clearly, in the
superposing region of the two laser fields, the polarization state of laser field exhibits a rapid
and complex variation within an optical cycle. Surprisingly, both $x$- and $y$-components of
harmonic spectra show a peak around 270 eV, as shown in Fig. 9(b). In this way, XUV
radiation with a bandwidth of $\sim 4$ eV is well selected from the broad plateau region of the
HHG spectrum. The selected harmonics are about two orders of magnitude stronger than
the adjacent harmonics. To give a clear demonstration, the harmonic spectra polarized in
both $x$ and $y$ directions are shown in linear scale (see inset of Fig. 9(b)). We can clearly
see that in the $y$ direction, the spectrum of the selected XUV radiation shows a smooth
profile, which allows us to synthesize isolated pulses with the sub-cycle duration. However,
the XUV radiation in the $x$ direction, which has broad spectrum with deep modulations,
is more than one order of magnitude weaker than that in the $y$ direction. Furthermore, we
found that the central wavelength of the narrow-bandwidth XUV emission can be tuned in an extremely broad range by adjusting the laser intensity of 1500-nm pulses or the amplitude ratio $A$ of two laser fields, as shown in Figs. 9(c) and (d), respectively.

Why is HHG confined within a narrow spectral range? In order to gain the insight into the physics underlying the narrow-bandwidth HHG, we perform classical analysis based on the three-step model of HHG [1]. Figure 10(a) shows the minimum returning distance of electron (blue solid curve) and its returning kinetic energy (red dashed curve) as a function of the time.
FIG. 9: (a) 3D plot of the driving field synthesized by a 1500-nm, 10-fs laser field polarized in the $x$ direction and a 2400-nm, 40-fs laser field polarized in the $y$ direction. The amplitude ratio ($A$) and time delay between the two laser fields are 0.5 and $\sim 2.17$ fs, respectively. (b) The $x$ (red curve) and $y$ components (black curve) of high-order harmonic spectra generated by the synthesized field in (a). Inset: High-order harmonic spectra in a linear scale. High-order harmonic spectra obtained (c) at different intensities of 1500-nm pulses and (d) at different amplitude ratios ($A = 0.2–0.7$) between 2400-nm and 1500-nm pulses.

of birth time (i.e., the time at which the electron is tunnel ionized). It can be seen that only the electron born at $t_0$ (indicated by a red dot) can accurately return to its parent ion (i.e., its displacement from ion approaches zero), while electron born before or after $t_0$ has a rapidly increasing displacement. When the displacement is so large that electron cannot recombine with parent ion, HHG will terminate. The dominant contribution to HHG comes from the electrons born within a small temporal window centered at $t_0$, as indicated by the rectangle (shaft-gradient color filled) in Fig. 10(a), and these electrons obtained almost the same kinetic energy in the laser field, leading to narrow-bandwidth XUV emission. For better understanding the electron motion in the specific laser field, in the Figs. 10(b)–(d), we depict 2D classical trajectories for the electrons born at $t_0$-50as, $t_0$, and $t_0$+50as, respectively. The electron born at $t_0$ comes back to its initial position (the initial position is indicated by the red solid dot) at $t_r$ along a curved trajectory [see Fig. 10(c)] and then a high energy photon can be generated when the electron is captured by the parent ion. We
also notice that the recolliding electron moves in a direction nearly parallel to the \( y \)-axis, as indicated by the red arrow in Fig. 10(c). Accordingly, the birth time \( (t_0) \) and the return time \( (t_r) \) of the electron are indicated by the black dots and black squares in Fig. 9(a), respectively. As shown in Fig. 9(a), since the recolliding electron is born near the peak of the electric field, and then recombines with its parent ion when the strength of electric field is near zero, the polarization direction of high-order harmonic emission can be considered to be the same as the moving direction of the recolliding electron (i.e., the high-order harmonic emission from the trajectory is polarized almost along the \( y \)-axis). When the electron is ionized 50 as before or after \( t_0 \), the minimum distances between the return electrons and its parent ion reach up to \( \sim 50 \) atomic units (a.u.), as illustrated in Figs. 10(b) and (d), respectively. Therefore, in these two cases, harmonic emission will significantly decrease or even terminate because of a great drop in recombination probability. The classical analysis above clearly reveals that the constructed laser field realizes the attosecond control of electron dynamics. In this way, only the electron from a single trajectory can come back with a fixed kinetic energy and recombine with the ion so that HHG only efficiently occurs in a narrow spectral range.

Furthermore, we extended the technique to molecular HHG [47]. It was found that the peak intensity of narrow-bandwidth XUV emission strongly depends on molecular alignment angles. Therefore, this technique not only has important applications in XUV nonlinear optics, but also may provide us an alternative method for extracting the structural information of molecular orbitals.

III-4. The enhancement of HHG yield

The low yield of HHG largely limits its widespread use in many fields. Therefore, considerable effort has been devoted to developing efficient harmonic conversion techniques. By loosely focusing a high-energy laser pulse into a long gas cell or gas jet, HHG in the absorption-limited regime has been obtained under the optimized phase matching condition [48, 49]. In order to further enhance HHG yield, one also proposed some new techniques, such as the synthesis of two-color field [28, 50, 51], quasi-phase matching [42], mixture of two gases with different ionization potentials [52, 53] and preparation of excited state atom [54]. In the review, we mainly focus on two-color field scheme. It has been experimentally demonstrated that the employment of both parallel-polarized and orthogonal-polarized two-color field can effectively enhance HHG yield [28, 50, 51]. Particularly, by applying a second harmonic with a high intensity, high-order harmonics are more than two orders of magnitude stronger in the orthogonal-polarized regime as compared to one-color field [50]. Very recently, it was demonstrated that the generation of intense isolated attosecond pulses with the energy up to 1.3 \( \mu \)J by combing a two-color field scheme and an energy-scaling method of HHG [51].

However, as mentioned in section II, the trick of the two-color field technique to dramatically extend supercontinuum spectra is to enhance the intensity contrast between the central half cycle and the neighboring half cycles. In this way, HHG yield corresponding to the supercontinuum is usually significantly lower than that produced by the one-color driving field because of the relatively low ionization rate for those electrons of the highest
kinetic energy upon recombination [19, 22]. In order to address the problem, we replaced the cosine-waveform by a sine-waveform counterpart in order to create a better waveform of two-color laser field by which both supercontinuum emission and IAPs were significantly enhanced [55]. It is well-known that when a sine-waveform few-cycle pulse is used, then two attosecond pulses will be generated in the laser field. In this case, because these two pulses have comparable photon energies, spectral filtering cannot be applied for selecting out an isolated attosecond pulse. However, one may recognize that these two attosecond pulses generated by the sine-waveform few-cycle field will have different intensities because of the different tunnel ionization ratios within different half cycles. Moreover, the shorter the duration of the few-cycle driving pulse with a sine-waveform, the greater the difference between the ionization ratios of the recombination electrons giving rise to the two attosecond pulses, and consequently, the intensities of the two attosecond pulses themselves. This is why in the experiment of generating $\sim 80$-as pulses [21], a CEP of $70^\circ$ is chosen for the near-single-cycle ($\sim 3.3$ fs) driving pulse. The focus of our work was to extend this strategy to few-cycle pulses with relatively long temporal durations (e.g., $\sim 5$ fs) by adding a control
field. From a technical point of view, a $\sim 5$-fs few-cycle pulse will be more easily generated and manipulated than a near-single-cycle 3.3 fs pulse. The new waveform-controlled two-color laser field leads to intense IAPs. The numerical simulation demonstrated that when a weak 15-fs, 1600-nm control pulse was superposed on the intense 5-fs, 800-nm main pulse and both pulses were sine waveform, the efficiency of the HHG is boosted by approximately two orders of magnitude as compared to that in the case that both pulses are cosine waveform, as shown in Fig. 11(a). In the inset of Fig. 11(a), we can clearly see that in the sine-waveform two-color field, the electrical field which ionized the electrons with the high kinetic energy upon recombination is strong, that leads to a high tunneling ionization rate as well as HHG yield. In spite of the fact that there is another trajectory that electrons can gain high kinetic energy, the ionization rate is much lower due to the broken symmetry of the driving field. In contrast, in the cosine-waveform two-color field, high-energy recolliding electron contributing to HHG is born at the moment when the electric field is relatively weak, resulting in the low HHG yield due to the high sensitivity of tunnel ionization to the laser intensity.

Temporal profiles of attosecond pulses are obtained by performing inverse Fourier transforms for the XUV supercontinua generated with sine- and cosine-waveform driving pulses, as shown in Fig. 11(b). Clearly, the intensity of attosecond pulses generated with the sine-waveform two-color pulse is almost two orders of magnitude stronger than that with the cosine-waveform pulse in the case without any phase compensation. The satellite pulses are about two orders of magnitude weaker than the main pulses. Further phase compensation using XUV chirped mirrors or metal foils with an opposite sign of dispersion slope would lead to near-transform-limited attosecond pulses with the duration of less than 50 as. Therefore, the sine-waveform two-color field offers a promising method to create intense attosecond pulses by significantly enhancing ionization rate of high-energy recolliding electron contributing to the XUV supercontinuum.

IV. CONCLUSIONS AND OUTLOOK

In this work, we have reviewed our main achievements on HHG driven by two-color laser fields. It was demonstrated that two-color field can effectively manipulate ionization, propagation and recombination processes involved in HHG due to its unique ability to control electron wavepackets on the sub-cycle time scale and the sensitivity of HHG on the pulse waveform. Both theoretical and experimental studies in the last a few years have revealed the advantages of two-color field scheme for broadening XUV supercontinuum, creating shorter IAPs, selecting single quantum trajectory, controlling wavelength, bandwidth, polarization and yield of HHG. These investigations will help to motivate the widespread use of HHG in many fields, such as attosecond nonlinear optics, molecular imaging, nanolithography, X-ray microscopy, etc.
FIG. 11: (a) Comparison of HHG spectra generated in two-color driving pulses with cosine (dashed line) and sine waveforms (solid line). The corresponding electric fields are shown in inset. (b) Temporal profiles of HHG spectra generated by cosine-waveform pulses without (solid line) and with phase compensation (dashed line), by sine-waveform pulses without (dotted line) and with phase compensation (dash-dotted line).

Acknowledgements

This work is supported by the National Basic Research Program of China (Grant Nos. 2011CB808100, 2014CB921300), National Natural Science Foundation of China (Grant Nos. 11127901, 11134010, 61221064, 61275205, 11274050 and 11204332) and the Program of Shanghai Subject Chief Scientist (11XD1405500). We acknowledge the contributions of Xiaohong Song, Yongli Yu, Yuxi Fu, Hui Xiong, Han Xu, Haisu Zhang, Chenrui Jing, Hongqiang Xie et al.
References

Quantum Orbits: a Powerful Concept in Laser-Atom Physics

Wei Quan, XuanYang Lai, YongJu Chen, ChuanLiang Wang, ZiLong Hu, XiaoJun Liu, XiaoLei Hao and Jing Chen, Elvedin Hasović, Mustafa Busuladžić, Dejan B. Milošević, and Wilhelm Becker

1State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China
2University of Chinese Academy of Sciences, Beijing 100080, China
3HEDPS, Center for Applied Physics and Technology, Peking University, Beijing 100084, China
4Institute of Applied Physics and Computational Mathematics, P. O. Box 8009, Beijing 100088, China
5Faculty of Science, University of Sarajevo, Zmaja od Bosne 35, 71000 Sarajevo, Bosnia and Herzegovina
6Medical Faculty, University of Sarajevo, Cekalusa 90, 71000 Sarajevo, Bosnia and Herzegovina
7Academy of Sciences and Arts of Bosnia and Herzegovina, Bistrik 7, 71000 Sarajevo, Bosnia and Herzegovina
8Max Born Institute for Nonlinear Optics and Short-Pulse Spectroscopy, Max-Born-Str. 2a, 12489 Berlin, Germany

(Received October 3, 2013)

Additional support for the concept of “quantum orbits” is presented that emphasizes in particular the importance of “long orbits” where the time between ionization and rescattering may be many periods of the laser field. Two examples are discussed, above-threshold ionization by an elliptically polarized laser field and intensity-dependent enhancements of certain spectral regions within the backscattering plateau, where we compare experimental data and the theoretical quantum-orbit simulations. In both cases, good agreement is obtained.

DOI: 10.6122/CJP.52.389 PACS numbers: 33.80.Rv, 33.80.Wz, 42.50.Hz

I. INTRODUCTION

Atoms irradiated by intense laser fields that are strong enough to liberate one or several electrons have presented an enormous challenge to theory. The electron interacting
with either the Coulomb field without the laser field or with the laser field without the Coulomb field allow for analytical solutions, but the combination of the two fields has resisted any straightforward analytical attack. Of course, with currently available computing power solution of the time-dependent one-electron Schrödinger equation has become standard. But if there is more than one electron then even today’s computing facilities quickly reach their limits. Moreover, solutions of the TDSE call for an interpretation just like real experiments.

It is here where the theory of “quantum orbits” comes in. It derives from the strong-field approximation (SFA) [1, 2], which accounts for the Coulomb interaction only in the initial bound state of the electron, or from the improved SFA (ISFA), which includes exactly one additional interaction of the liberated electron with the binding potential [3, 4]. This is analogous to the first term of the Born series. The ISFA allows the analysis of rescattering processes, which are central to current strong-field physics and have, via the process of high-order harmonic generation (HHG), opened the door to attosecond science [5]. Here, we will restrict ourselves to above-threshold ionization (ATI), but HHG and other processes such as field-assisted electron-atom scattering or nonsequential double ionization can be and have been treated along the same lines [6].

Quantum orbits provide a good approximation under conditions where the electron can be envisioned as being liberated by the process of tunneling through the time-dependent barrier that is formed by the binding potential plus the electron-field interaction \( r \cdot E(t) \). Actually, it does not matter exactly how the electron gets out of the atom, as long as it makes sense to assume that this happens at a fairly well-defined time and position. The quantum orbits then depict the electronic trajectory from this point, the “exit of the tunnel,” toward the detector at infinity within the limitation pointed out above: at most one interaction with the potential. Otherwise, they are much like classical trajectories. However, they are complex in consequence of their origin via tunneling and they interfere if more than one orbit leads from the initial bound state to the final plane-wave state. The (I)SFA and quantum orbits allow one directly to calculate approximations to individual S-matrix elements, which are specified by the asymptotic momentum \( p \) of the electron in its final state. This is in contrast to solution of the TDSE, where first the wave function has to be computed in its entirety and to be stored, before such matrix elements can be evaluated.

Usually, there are many different quantum orbits that lead from the same initial into the same final state. They can be characterized by the length of their “travel time,” that is, by the difference between the time when the electron has its final recollision with its parent ion and the time when it is liberated by tunneling. Formally, there are orbits with longer and longer travel times, limited only by the duration of the laser pulse. It is tempting to assign some physical reality to the quantum orbits and also to these “longer orbits.” In this paper, we review two recent experiments and their quantum-orbit interpretations, which provide additional support for their physical significance.

In the next Section, we briefly review the concept and the formalism of quantum orbits. Thereafter, we focus on the two recent examples: ATI by an elliptically polarized laser field where the dominant contribution comes from orbits with travel times longer
than that of the shortest two orbits [7], and the intensity-dependent enhancements in ATI spectra of molecules [8]. The paper is terminated by our conclusions.

More detailed reviews of the theory and applications of quantum orbits can be found in Refs. [9–11]. We use atomic units such that \(|e| = m = \hbar = 1\) throughout the paper.

II. QUANTUM ORBITS

Quantum-orbit theory starts from the strong-field approximation (SFA) for “direct” electrons, i.e. those that after they have been liberated from their parent ion do not interact with it any more, or from the “improved” strong-field approximation (ISFA), which allows for one such interaction. The latter corresponds to the first-order Born approximation for the liberated electron revisiting the ion. The ionization amplitude is the sum of the “direct” amplitude

\[
M^{(0)}_p = \int_{-\infty}^{\infty} dt' \langle \psi^V_p (t') | r \cdot E(t') | \psi_0 (t') \rangle
\]

and the rescattering amplitude

\[
M^{(1)}_p = \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \langle \psi^V_p (t) | V U^V(t, t') r \cdot E(t') | \psi_0 (t') \rangle.
\]

The final state is a Volkov state

\[
\langle r | \psi^V_p (t) \rangle = (2\pi)^{-3/2} e^{i[p + A(t)] \cdot r} \times \exp \left( -\frac{i}{2} \int d\tau [p + A(\tau)]^2 \right)
\]

with asymptotic (drift) momentum \(p\), and the ISFA amplitude (2) contains the corresponding Volkov time-evolution operator \(U^V(t', t)\). While the times \(t'\) and \(t\) are, of course, just integration variables, we will see below that it is suggestive to interpret them as the times of ionization and recollision, respectively.

Henceforth, we will focus on the ISFA amplitude (2). It is convenient to expand the Volkov time-evolution operator in terms of the Volkov states (3),

\[
U^V(t, t') = \int d^3 k |\psi^V_k (t)\rangle \langle \psi^V_k (t')|,
\]

which is here given in length gauge. The ISFA amplitude then has the structure

\[
M^{(1)}_p = \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \int d^3 k e^{iS_p (t, t', k)} m_p (t, t', k)
\]

where \(m_p (t, t', k)\) combines various slowly varying factors, which are not relevant for the subsequent discussion. (One may note that the function \(m_p\) is dependent of the gauge
adopted for the description of the laser field and that it is a constant for a zero-range potential). The decisive factor is the exponential of the action

\[ S_p(t, t', k) = -\frac{1}{2} \int_t^{t'} d\tau [p + A(\tau)]^2 - \frac{1}{2} \int_t^{t'} d\tau [k + A(\tau)]^2 + \int_{-\infty}^{t'} d\tau I_p, \]

(6)

which combines terms of the Volkov functions and the initial state. The action is written in a suggestive form that recalls the simple-man rescattering picture: the field-free initial state with ionization potential \( I_p \), for times between \(-\infty\) and \( t' \), propagation in the Coulomb-free continuum in between the ionization time \( t' \) and the recollision time \( t \), and Coulomb-free propagation towards the detector with the final drift momentum \( p \) thereafter.

There are essentially two possibilities to evaluate the amplitude. One method is limited to monochromatic sinusoidal plane-wave fields. One may then expand the action \( S(t, t', k) \) in a product of series of Bessel functions. One of the two temporal integrals can be carried out analytically and yields the \( \delta \) function

\[ \delta (p^2/2 - I_p - U_p - n\omega), \]

(7)

which expresses energy conservation with the absorption of \( n \) photons with energy \( \hbar \omega \) from the laser field. Here, \( U_p = \langle A^2(t) \rangle /2 = I/(4\omega^2) \) denotes the ponderomotive energy \( (\ldots) \) is the average over one period of the field and \( I \) its intensity; for a linearly polarized field with the vector potential \( A(t) = k A_0 \cos(\omega t + \phi) \) we have \( U_p = A_0^2/4 \). Actually, since the description relies on a classical external field, there are no photons. The term \( n\omega \) with \( \omega = 2\pi/T \) and \( T \) the period of the field reflects the temporal periodicity of the field environment. The remaining temporal integral and the sums have to be carried out numerically.

The alternative is an evaluation of the integrals over \( t \) and \( t' \) by the method of steepest descent (stationary phase). To this end, we determine the stationary points of the action (6), which are given by the solutions \((t, t', k)_s\) of \( \partial S/\partial t = \partial S/\partial t' = 0 \) and \( \partial S/\partial k = 0 \), i.e. by the solutions of the so-called saddle-point equations [12]

\[ [k + A(t')]^2 = -2I_p, \]  

(8a)

\[ (t - t')k = -\int_t^{t'} d\tau A(\tau), \]  

(8b)

\[ [k + A(t)]^2 = [p + A(t)]^2, \]  

(8c)

which physically describe energy conservation at the time \( t' \) of ionization, return of the electron to its parent ion at the time \( t \), and elastic scattering at this time into the final state with drift momentum \( p \). The only numerical work consists in the solution of the saddle-point equations (8). However, this may be not completely straightforward, especially if the laser field has significant ellipticity. For fixed asymptotic momentum \( p \), Eqs. (8) have more than one solution, and we number them by the index \( s \). Given these solutions \((t, t', k)_s \) \( (s = 1, 2, \ldots) \), the saddle-point approximation to the amplitude is

\[ M_p^{(1)} = \sum_s \left( \frac{(2\pi i)^5}{\det(\partial^2 S/\partial q_j^{(s)} \partial q_k^{(s)})_{j,k=1,\ldots,5}} \right) e^{iS(t, t', k_s)}, \]  

(9)
FIG. 1: (Color online) Graphical determination of the rescattering time $t$ from the given ionization time $t'$. The return condition $x(t) = 0$ can be written in the form $F(t) = F(t') + (t - t')F'(t')$ [10] where $F(t) = \int_t^{t'} d\tau A(\tau)$ is represented by the (blue) sinusoidal curve. The return condition requires to put the tangent to the curve $F(t)$ at the ionization time $t'$. The subsequent intersection ($t > t'$) of the tangent with the curve $F(t)$ determines the rescattering time. Two examples are given: The ionization time $\omega t' = 108^\circ$ determines the rescattering time for the situation where the return energy assumes its maximum of 3.17 $U_p$ (pink tangent). There is only one solution for the rescattering time in this case. The ionization time $\omega t' = 99^\circ$ determines three solutions for the rescattering time (yellow tangent), and ionization times closer and closer to 90° lead to more and more such solutions.

where $q_i^{(s)}$ ($i = 1, \ldots, 5$) combines the five variables $t_s, t'_s$, and $k_s$. Actually, the sum over $s$ runs only over a subset of all solutions of the saddle-point equations, namely those through which the original multidimensional integration contour must be routed. We notice that owing to Eq. (8a) the solutions $(t, t', k)$ must be complex. It is interesting to note that the quantum-orbit representation of the rescattering amplitude is a realization of the quantum-mechanical path integral [10].

The purpose of the present paper is to review recently obtained additional support for the physical relevance of the concept of quantum orbits, especially for the significance of the so-called “longer orbits.” As already mentioned, for fixed drift momentum $p$, the saddle-point equations may have more than one relevant solution for $t, t'$, and $k$. This can easily be seen (cf. Fig. 1). Their contributions must be included, in general, to obtain a quantitatively good approximation to the amplitude (2). However, in two cases their contributions are even qualitatively crucial: for elliptical polarization and for the description of the so-called intensity-dependent enhancements within the rescattering plateau. In the first case, the dominant contribution to the ionization amplitude is not provided by the two shortest orbits (as is normally the case) but originates from longer orbits. In the second case, the enhancements only come about by the coherent superposition of the contributions of very many long orbits. We shall discuss recent measurements for elliptical polarization that confirm this point [7], and new results regarding the existence of the afore-mentioned enhancements in molecules [8] where it had been in question. The origin of the longer orbits is explained in Fig. 1; an illustration of the shortest and some longer quantum orbits for elliptical polarization is given in Fig. 2.
FIG. 2: (Color online) Real parts of quantum orbits in an elliptically polarized laser field with ellipticity $\xi = 0.36$. The field ellipse is depicted in the upper right corner of the figure. The position of the ion is marked by the black dot at the origin. The orbits start at the respective “tunnel exits,” which are given by $\text{Re}(x(\text{Re}t'))$, and are located away from the position of the ion, mostly in the direction of the major axis of the elliptically polarized field. Depending on the direction of the field at the time $t'$ of ionization, the tunnel exit can be on either side of the ion. Some typical orbits are presented, which become more and more complicated as the travel time increases. All orbits shown have the same drift momentum, which is the momentum at the detector outside the field. Note the different scale of the two axes.

III. LONGER ORBITS FOR AN ELLIPTICALLY POLARIZED LASER FIELD

Within the simple-man model [13], the electron is usually assumed to start its orbit at the “exit of the tunnel” with zero velocity. However, for elliptical polarization, if it starts with zero velocity it will not, in general, revisit the ion: if it does revisit in the direction of the major axis at the time $t$, it will be off in the direction of the minor axis. Formally, this can be seen from the saddle-point equations (8). Consider the limit $I_p = 0$, which corresponds to the simple-man model, and a specified final momentum $p$. For linear polarization in the $x$ direction, Eq. (8b) requires that $k_y = k_z = 0$. The remaining three equations (8) are then solved in terms of the three variables $t, t', k_x$, and the initial velocity is $v_x(t') \equiv k_x + A_x(t') = 0$. For elliptical polarization in the $(x, y)$ plane, we have $k_z = 0$, and the remaining four equations are solved in terms of the four variables $t, t', k_x, k_y$. However, it is no longer possible that the initial velocity be zero since we cannot have, in general, that both $v_x(t') = k_x + A_x(t') = 0$ and $v_y(t') = k_y + A_y(t') = 0$.

However, while such a nonzero initial velocity does allow the electron to revisit the parent ion, the weight of such an orbit will be substantially reduced. Therefore, rescattering processes continue to occur for elliptical polarization but at reduced yields. Another consequence is: for linear polarization, normally the shortest orbits dominate the ionization
Experimental [(a), (b), and (c)] photoelectron spectra of Ar, Kr, and Xe along the major polarization axis for elliptically polarized laser pulses with wavelength of 800 nm, intensity of $7.0 \times 10^{13}$ W/cm$^2$, and ellipticities $\xi = 0, 0.07, 0.14, 0.21, 0.29, \text{and} 0.36$ from top to bottom. The spectra are normalized to unity at zero energy. (d)–(f): Ratios of the electron yields for various low-energy intervals over one high-energy interval as functions of the ellipticity. For details, see the text.

amplitude. The contributions of the longer orbits are increasingly suppressed by quantum-mechanical wave function spreading. They cause some modifications of the spectrum but do not qualitatively change it. (An exception is provided by the intensity-dependent enhancements, which will be considered in the next Section.) This is different as soon as the polarization is sufficiently elliptical. Then, those orbits have the highest yield that require the smallest magnitude of the initial velocity in order to revisit. Those are not necessarily the shortest orbits [14] because the longer the travel time is the smaller is the transverse initial momentum that is required in order that the electron revisit the ion [14]. This can also be realized by inspection of the orbits of Fig. 1.

Experimental evidence for substantial contributions of longer orbits in ATI with elliptical polarization was presented in Ref. [10], but no quantitative comparison with quantum-orbit theory was attempted. Here we will report the results of recent measurements and
compare them with theory [7].

Figure 3 exhibits experimental ATI spectra along the major polarization axis for the three rare gases Ar, Kr, and Xe for ellipticities up to $\xi = 0.36$. After normalization in order to compensate the general decrease with increasing ellipticity the spectrum of the direct electrons is all but independent of ellipticity, and the onset of rescattering is very clearly visible. Our goal is quantitatively to support the quantum-orbit picture. To this end, we plot the ratios of the electron yields in four adjacent energy windows in the beginning and the middle of the plateau over the yield in a high-energy window as a function of ellipticity. Each window is defined so as to contain two ATI peaks. The windows extend from 17.0 to 20.1 eV, from 20.1 to 23.2 eV, from 23.2 eV to 26.3 eV, and from 26.3 to 29.4 eV, and the ratio is formed with the yield in the window from 37.0 to 40.1 eV. Since the rescattering plateau is more like an inclined plane, all of the ratios are larger than unity. Since the inclination of the plateau becomes stronger when the ellipticity is higher, the ratios increase strongly with increasing ellipticity.

In Fig. 4 we compare the experimental data with the quantum-orbit theory reviewed in the preceding Section. For simplicity, we took a zero-range potential to bind the electron to the ion in place of a Coulomb-like potential. This renders the description of the direct electrons unreliable; so the reader should ignore the discrepancy between the spectra in
Figs. 3(a) and 4(a) for energies below about 10 eV. We will focus on the rescattered electrons and calculate, for argon, the same ratios as in Fig. 3. The results are plotted in panel (b), which should be compared with Fig. 3(d). The agreement is quite good. The calculation was based on including the first 20 pairs of quantum orbits. Now, in order to assess the significance of the contributions of the longer orbits, we repeat the calculation including only the first pair of orbits. The result is shown in Fig. 4(c). Clearly, the good agreement is gone, definitely for the low-energy ratio. This proves a substantial contribution of the longer orbits especially to the low-energy part of the rescattering plateau. Finally, in Fig. 4(d) we plot the ratio of the two ratios in (b) and (c), which roughly gives the number of the contributing pairs of orbits. It goes up from unity for small ellipticity and high energy to 5 or 6 at large ellipticity and low energy. This confirms that the long orbits are especially important for the low-energy part of the plateau [14]. Similar conclusions were drawn from SFA simulations of nonsequential double ionization [16] as well as from completely classical trajectory calculations [17].

IV. INTENSITY-DEPENDENT ENHANCEMENTS OF GROUPS OF PEAKS IN THE RESCATTERING PLATEAU

The rescattering plateau has an essentially classical origin: backscattering allows the electron an additional acceleration by a full half cycle of the laser field, which leads to a maximal classical energy of $10 U_p$. However, the plateau also exhibits a fascinating feature, which appears to be of quantum origin: in some cases, if the laser intensity is raised by as little as a few percent, the yield of a group of peaks within the plateau may rear up by almost an order of magnitude [18, 19]. Typically, this may happen in the middle part of the plateau, for energies between 6 and 8 times the ponderomotive energy $U_p$. The physical origin of this phenomenon is still controversial. Essentially, two different mechanisms have been proposed.

The effect is reminiscent of an intensity-dependent resonance. Indeed, it was suggested that it is due to a multiphoton resonance with an intensity-dependent excited bound state [20–23], much like the well-known Freeman resonances in the low-energy region [24]. A different mechanism – and the one that we will here pursue – is in the context of the strong-field approximation and the quantum-orbit picture. At first sight, it appears that quantum orbits are unable to generate these very sharply defined features, because each individual orbit depends very smoothly on the laser intensity and the electron energy. However, on closer inspection it turns out that the effect comes about by constructive interference of a large number of quantum orbits with the same final energy, which by necessity then have a very long travel time, as we call the time $t - t'$ between rescattering and ionization [11, 15, 25–30]. The conditions for such a constructive interference are satisfied near channel closings (CCs), i.e. if the parameter

$$\eta \equiv (I_p + U_p)/\omega$$

has an integer value $n$ with $n > n_{\text{min}} = [I_p/\omega]$ and $[x]$ the largest integer contained in $x$. 
FIG. 5: (Color online). Measured photoelectron energy spectra in the direction along the laser polarization as functions of the laser intensity for the three gas targets Ar, N$_2$, and O$_2$, from left to right. The spectra are recorded with 30 fs, 800 nm laser pulses. The laser intensity is displayed in multiples of $10^{13}$ W/cm$^2$. Note that $2U_p = 9.56$ eV at $8 \times 10^{13}$ W/cm$^2$. Argon displays two well-defined enhancements in the energy region of 25 to 30 eV at about $8 \times 10^{13}$ W/cm$^2$ (area A) and between 35 and 45 eV at about $9\times 10^{13}$ W/cm$^2$ (area B), N$_2$ exhibits an analog of the enhanced area B in area C, while for O$_2$ no enhancements are visible. The 10$U_p$ cutoff of the backscattering plateau is clearly visible.

FIG. 6: (Color online). Calculated spectra for Ar, N$_2$, and O$_2$. The laser intensity is also displayed in terms of the parameter $\eta = (I_p + U_p)/\omega$ [Eq. (10)] to demonstrate the channel-closing effect. Parameters in the simulation are chosen in accordance with the experiments. The areas labeled A, B, and C approximately correspond to those in Fig. 5.
When the laser intensity varies such that a CC is passed, the minimum number of photons required for ionization changes by one. (We refer to the intensity, for which \( n = \eta \) by \( I_\eta \).) Just above a CC, intermediate states with very low momenta allow the electron many times to revisit its parent ion. The sensitive dependence on the laser intensity, which is absent from each individual quantum orbit, comes about by the interference of a large number of them, each corresponding to rescattering at one of these revisits. A closely related explanation invokes the so-called threshold anomalies in the detachment of electrons bound by short-range potentials [31, 32], see also Ref. [11].

Both explanations are capable of reproducing the data quite well. This appears surprising since the first mechanism crucially depends on the existence of excited bound states, which are completely absent from the latter. On the other hand, the assumption of an “effective continuum threshold” in the context of the SFA may provide a description that captures essential aspects of Rydberg states [26].

Multiphoton ionization of molecules has come a long way since the first attempts to confirm the \( I^N \) behavior of the total ionization rates [33]. Here we will present measurements of ATI spectra in \( \text{N}_2 \) and \( \text{O}_2 \) (and compare them with \( \text{Ar} \)) that exhibit noticeable enhancements in \( \text{N}_2 \) but not in \( \text{O}_2 \) and describe them in terms of the molecular SFA [34] and ISFA [35]. The presence or absence of these enhancements in molecules still is an open issue. Cornaggia [36] observed enhancements in \( \text{H}_2 \) but not in more complicated molecules.

The spectra were recorded with 30-fs laser pulses with a center wavelength of 800 nm. Details of the experimental setup can be found in Ref. [37, 38]. Figure 5 displays photoelectron energy spectra in the laser polarization direction for \( \text{Ar}, \text{N}_2, \) and \( \text{O}_2 \) at various intensities as given in the caption. For each intensity, the spectrum was separately normalized in order to compensate the general increase of the yield with increasing intensity. We notice two kinds of structures in Fig. 5: first, there are intensity-dependent structures such as the 10\( U_p \) cutoff, which marks the end of the plateau. Second, there are horizontal structures, which set in at certain well-defined intensities. They are marked by the letters A, B, and C. These we associate with the intensity-dependent enhancements [15, 18, 19] of groups of peaks within the backscattering plateau. They rise rather suddenly at a certain intensity and die out rather slowly when the intensity further increases. The group of peaks concerned remains the same throughout this process. Quantum-orbit theory predicts that the enhancements start at the CC intensities \( I_\eta \) [defined above below Eq. (10)]. For argon, the relevant CC intensities are \( I_{13} = 7.34 \times 10^{13} \text{ W/cm}^2 \) and \( I_{14} = 9.94 \times 10^{13} \text{ W/cm}^2 \), for \( \text{N}_2 \) they are \( I_{13} = 7.64 \times 10^{13} \text{ W/cm}^2 \) and \( I_{14} = 10.2 \times 10^{13} \text{ W/cm}^2 \). Corresponding spectra at selected fixed intensities can be found in Ref. [8]. The areas B for argon and C for \( \text{N}_2 \) qualitatively correspond to each other, which confirms the existence of the intensity-dependent enhancements in \( \text{N}_2 \). However, any such structures are distinctly absent in \( \text{O}_2 \). These two observations are the most important message of Fig. 5.

Can we understand the absence of the enhancements in \( \text{O}_2 \)? Indeed, if resonance with ponderomotively upshifted Rydberg states were responsible for the enhancements the different behavior of \( \text{N}_2 \) and \( \text{O}_2 \) would be hard to understand, in view of the close similarity of the respective Rydberg states (Freeman-type resonances have been identified in both molecules [39, 40]). To answer the question, we carry out quantum-orbit calculations along
the lines of Ref. [35]. Molecular SFA simulations depend on the gauge employed for the
description of the laser field. We use the so-called dressed length gauge, which quite well
reproduces the suppression of the low-energy yield in O$_2$ compared with N$_2$ [41].

Since we are concerned with electron energies above the direct-electron cutoff of $2U_p$, we
need to evaluate the rescattering amplitude (2). Molecular information enters this
expression via the rescattering potential $V$ and via the ground-state wave function $|\psi_0(t')\rangle$.
The potential is modeled by the superposition of target-specific atomic scattering potentials
and the wave function has the form of a linear combination of atomic orbitals (LCAO) [30]

$$
\sum_a c_a \left[ \psi_a^{(0)}(\mathbf{r} + \mathbf{R}_0/2) + (-1)^{l_a-m_a+m_\lambda} \psi_a^{(0)}(\mathbf{r} - \mathbf{R}_0/2) \right],
$$

(11)

Here $\mathbf{R}_0$ denotes the relative nuclear coordinate and $l_a$ and $m_a$ the orbital and magnetic
quantum numbers while the functions $\psi_a^{(0)}(\mathbf{r})$ are Slater-type orbitals and $m_\lambda$ is the projection
of the orbital angular momentum on the internuclear axis. Compared with rescattering
off a single atom, the two-center situation will generate the additional factor

$$
M_p^{(1)} \propto \begin{cases} 
\cos(\mathbf{k} \cdot \mathbf{R}_0/2) \cos((\mathbf{p} - \mathbf{k}) \cdot \mathbf{R}_0/2) & \text{for even } l_a, \\
\sin(\mathbf{k} \cdot \mathbf{R}_0/2) \cos((\mathbf{p} - \mathbf{k}) \cdot \mathbf{R}_0/2) & \text{for odd } l_a.
\end{cases}
$$

(12)

For the longer orbits, the intermediate momentum $\mathbf{k}$ is small (cf. Fig. 1). Hence, this factor
crucially depends on the orbital angular momentum $l_a$. For N$_2$, the initial highest occupied
molecular orbit (HOMO) is $3\sigma_g$, which is a linear combination of $s$ and $p$ states with almost
equal weights. In contrast, for O$_2$ its initial HOMO is made up only of $p$ states. Therefore,
for O$_2$ the contribution of the long orbits will be much reduced in comparison with N$_2$.

We find this confirmed by the calculational results, which are presented in Fig. 6. Indeed, for O$_2$ we find the entire plateau much weaker than for N$_2$ and there is hardly
any trace of enhancements. The agreement with the experimental data of Fig. 5 is quite
satisfactory. The fact that the experimentally observed existence of the intensity-dependent
enhancements in N$_2$ and their absence in O$_2$ can be reproduced by quantum-orbit theory
lends further support to the physical significance of quantum orbits and, especially, to that
of the longer orbits.

V. CONCLUSIONS

Quantum orbits are a physically appealing and also a very powerful tool, which is
able to describe a multitude of laser-atom phenomena. An unavoidable consequence of the
derivation of the expansion into quantum orbits from the strong-field approximation is
the fact that there are many quantum orbits contributing to a given amplitude, which
take a longer and longer time between ionization and rescattering. However, the physical
significance of these long orbits appears questionable, since they disregard the Coulomb
potential except in the very process of rescattering. Whenever a classical recolliding electron
passes its parent ion at a short distance, it will be attracted by the Coulomb field and
significantly deflected from its original course. Especially the motion transverse to the laser polarization, whose momentum is conserved in the ISFA except in the recollision, is strongly affected and will have little in common with the trajectory without the Coulomb field. This seems to imply that the longer orbits – where the crucial interaction with the Coulomb potential occurs at the occasion of not the first but a subsequent revisit – are void of physical significance.

However, this is not necessarily the case in the quantum description. In this paper, we presented additional support for the quantum-orbit description. First, whenever long and very long orbits play a substantial role, then quantum-orbit theory trivially predicts that the effect in question, such as the intensity-dependent enhancements discussed above, will go away for short pulses. Indeed, this has been observed for the ATI enhancements [42]. Second, we investigated these enhancements for the case of molecules, found them to exist for N₂ but not for O₂, and successfully described the experimental data in terms of quantum-orbit theory. We emphasize again that the intensity-dependent enhancements appear to be a quantum effect, which is inaccessible to classical modeling. We also considered above-threshold ionization by an elliptically polarized laser field. In this case, quantum-orbit theory predicts that the spectrum is qualitatively dominated by substantial contributions of longer orbits. We found this confirmed and obtained good agreement when we compared our experimental spectra with the quantum-orbit simulations.

The exact reason of why the quantum-orbit description of the effects here described works so well remains unclear. This is puzzling because the description crucially depends on the longer orbits, which appear to have so little in common with classical Coulomb-affected trajectories. On the other hand, the ISFA can be evaluated without recourse to the quantum-orbit expansion as briefly discussed above around Eq. (7). In this context, near channel closings the integration over the travel time has to be extended over very many periods of the field while away from CCs at most two periods normally suffice. Quantum orbits are a very convenient tool for the calculation as well as for the interpretation, but their use is not mandatory. In the frame of the finite-range quasi-energy method, the enhancements occur as well and are subsumed under the term “threshold anomalies” [31, 32]. Finally, we mention that all of the Coulomb-related complications are absent for the otherwise closely related case of multiphoton detachment of negative ions. In this case, the quantum-orbit expansion is a quantitatively reliable tool, see e.g. Ref. [43].

VI. ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (Nos. 2013CB922201 and 2011CB808102) and NNSF of China (Nos. 10925420, 10904162, and 11174330, and 11274050). Sponsorship has also been provided by the Alexander von Humboldt Foundation and funding by the German Federal Ministry of Education and Research in the framework of the Research Group Linkage Program.
References

[12] We treat the term \( \exp \left[ \mathbf{A}(t) \cdot \mathbf{r} \right] \) as slowly varying.
Numerical Simulations of Attosecond Streaking Time Delays in Photoionization

Jing Su, Hongcheng Ni, Andreas Becker, and Agnieszka Jaroń-Becker

JILA and Department of Physics, University of Colorado, Boulder, CO 80309-0440, USA

We present results of numerical simulations and theoretical classical analysis of time delays with respect to the instant of ionization in a numerical streaking experiment. These results confirm our previous interpretation of the streaking time delay as a finite-range and field-weighted time delay. We show that in the streaking experiments the time delay strongly depends on the parameters of the streaking field. Consequently, the streaking time delay is accumulated over a finite range in space, which the emitted electron probes after its transition into the continuum until the streaking pulse ceases. Moreover, we confirm by results of our numerical simulations that the streaking time delay can be understood as a sum (or integral) over field-free time delays weighted by the relative instantaneous field strength during the propagation of the photoelectron.

DOI: 10.6122/CJP.52.404 PACS numbers: 33.80.Rv, 33.80.Wz

I. INTRODUCTION

Recently, applications of attosecond (1 as = 10^{-18} s) pulse technology led to the analysis of the question whether or not an electron is emitted instantaneously from an atom, molecule or solid upon the absorption of an extreme ultraviolet (XUV) laser photon [1–3]. One approach to observe this ultrafast dynamics of the photoelectron is the so-called attosecond streak camera technique [4]. In this approach due to the interaction with a second weak streaking pulse at a near-infrared wavelength, which is superimposed to the ionizing XUV laser pulse, the momentum of the photoelectron is modulated. Neglecting the long-range Coulomb interaction between the photoelectron and the residual target ion the momentum of the photoelectron is given by

$$ k_f^{(0)}(t_i) = k_0 - A_s(t_i), $$

where $k_0 = \sqrt{2(\omega - I_p)}$ is the asymptotic momentum without application of the streaking pulse and $A_s(t_i)$ is the vector potential of the streaking field at the instant of transition of the photoelectron into the continuum $t_i$, which we denote here also as the time of ionization.

In the reported experimental data [1, 2], an oscillation of the photoelectron momentum as a function of the delay between the XUV and the near-infrared laser pulses has been observed, as expected from Eq. (1). However, the observations also revealed temporal offsets $\Delta t_s$ in the oscillations as compared to the vector potential $A(t_i)$, i.e.,

$$ k_f(t_i) \simeq k_0 - \alpha A_s(t_i + \Delta t_s), $$

(2)
where $\alpha$ is a fitting parameter. These temporal offsets were first interpreted as delays in the emission of the photoelectron. However, theoretical works, e.g., [5–19], showed that on the attosecond time scale of these observations a detailed analysis of the effect of the Coulomb potential on the photoelectron as well as the coupling between the Coulomb potential and the streaking field needs to be taken into account. It was expected that the observed temporal offsets are, at least partially, related to the well-known Wigner-Smith (WS) time delay [20, 21]. The latter denotes the time delay of an electron propagating in a potential towards infinity as compared to a freely propagating electron. A concern with this interpretation is related to the fact that the WS time delay does diverge for a long-range interaction, such as the Coulomb potential [21–23]. Theoretical work therefore focused on the role of short- vs. long-range part of the Coulomb potential itself as well as during the coupling between the Coulomb potential and the streaking field (e.g., [9–13]).

Recently, we reported [24] results of numerical simulations and a classical analysis, which revealed the following aspects in the interpretation of the observed temporal offsets: First, we found that the temporal offsets are related to the propagation of the photoelectron over a finite range in time and space instead of its propagation towards infinity, as assumed in the WS time delay. Thus, according to our interpretation any previously expressed concerns regarding the divergence of the temporal offsets are unnecessary. Furthermore, we proposed that — based on an approximate formula derived in a classical analysis — the temporal offsets can be interpreted as a sum of piecewise field-free time delays weighted by the instantaneous streaking field strength relative to the field strength at the transition of the photoelectron into the continuum.

The intention of this invited paper is to review the above aspects of the temporal offsets and support our interpretation by further results of numerical calculations. To this end, we first outline the model used in the present simulations of a streaking experiment as well as the numerical techniques applied to solve the time-dependent Schrödinger equation (TDSE). Using a short-range Yukawa potential centered at a distance to the center of a Coulomb potential. Since the photoelectron is initially located in the ground state of the Coulomb potential, we can test by variation of the location of

II. NUMERICAL SIMULATIONS

As mentioned in the introduction, our results in a previous report [24] indicate that the temporal offsets in numerical simulations of streaking experiments are related to the propagation of the photoelectron over a finite range in time and space after its transition into the continuum upon interaction with the XUV laser pulse. To substantiate this interpretation, we consider a model system in which we add a short-range potential at a distance to the center of a Coulomb potential. Since the photoelectron is initially located in the ground state of the Coulomb potential, we can test by variation of the location of
the short-range potential and/or by variation of the parameters of the streaking pulse how this additional potential does influence the temporal offset \( \Delta t_s \) in the numerically obtained streaking patterns. In order to vary the location of the additional short-range potential over a large region in space, we needed to use a large space-time grid in each of our numerical simulations. In view of the numerical effort to obtain precise results on the attosecond time scale as well as the number of simulations performed we restricted our analysis to a 1D model, which is well justified by noting that for a linearly polarized laser pulse the final momentum of the photoelectron is streaked along the polarization direction [c.f., Eq. (1)].

Previously, we considered Gaussian potentials of various strength as additional short-range potentials [24]. In order to show that our conclusions are independent of the form of the model potential, we used in the present set of numerical simulations the following 1D potential (Hartree atomic units, \( e = m = \hbar = 1 \) are used):

\[
V_{\text{CY}}(x) = -\frac{Z_1}{\sqrt{x^2 + a_1}} - \frac{Z_2 e^{-\sqrt{(|x| - x_0)^2 + a_3/b}}}{\sqrt{(|x| - x_0)^2 + a_2}}. 
\] (3)

The potential \( V_{\text{CY}}(x) \) consists of a Coulomb potential with an effective charge \( Z_1 = 4.0 \) and a soft-core parameter \( a_1 = 3.0 \), and an additional Yukawa potential with \( Z_2 = 3.0 \), \( a_2 = 2.0 \), \( a_3 = 1 \times 10^{-5} \), and \( b = 5.0 \) centered at a distance \( x_0 \) from the center of the Coulomb potential at \( x = 0 \). The strength of the Yukawa potential is chosen to be comparable to that of the Coulomb potential to avoid any concerns regarding the influence of this additional potential on the observed temporal offsets. As we will show below [see e.g., Fig. 1(b)] the effect of the present Yukawa potential is indeed substantial enough to draw conclusions. We have chosen the electron to be initially located in the ground state of the Coulomb potential, which has an energy of \(-1.9448\). We have tested that this initial state is not affected by the additional Yukawa potential as long as the center of the Yukawa potential is located at distances of \( x_0 \geq 50 \).

In our streaking simulations we have numerically solved the corresponding TDSE

\[
i \frac{\partial \Psi(x, t)}{\partial t} = \left[ \frac{p^2}{2} + V_{\text{CY}}(x) + (E_{\text{XUV}}(t) + E_{\phi}(t)) x \right] \Psi(x, t),
\] (4)

with the momentum operator \( p \). The electric fields of both the XUV, \( E_{\text{XUV}}(t) \), and the streaking laser pulse, \( E_{\phi}(t) \), are represented as

\[
E(t) = E_0 \sin^2(\pi t/T) \cos(\omega t + \phi),
\] (5)

where \( E_0 \) is the peak amplitude, \( T \) is the pulse duration, \( \omega \) is the central frequency, and \( \phi \) is the carrier-envelope phase (CEP) of the respective field. The TDSE was solved on a sufficiently large grid in space and time using the Crank-Nicolson method. We confirmed that in all simulations the outgoing wave packet stays on the grid until both pulses ceased.

The momentum distributions were obtained by spatially separating the ionized wave packet from the total wave function, which is possible due to the long propagation times used in our simulations, and then performing a Fourier transform. By varying the delay \( t_i \).
between the XUV and the streaking pulses we obtained the streaking trace as the expectation value of the final momentum of the photoelectron $k_f$ as a function of $t_i$ (e.g., see Fig. 1). As expected, the distributions have a temporal offset or delay $\Delta t_s$ with respect to the vector potential (red dotted line) at $t_i$. The comparison of the streaking traces obtained in simulations with (green dashed line) and without (blue solid line) the additional Yukawa potential shows that the Yukawa potential has a substantial effect on the temporal offset. We then extracted $\Delta t_s$ by fitting the momentum trace to the expression in Eq. (2) using the least-square method for the fitting parameters $\alpha$ and $\Delta t_s$.

### III. INTERPRETATION OF STREAKING TIME DELAYS

In order to interpret the results of our numerical simulations, presented below, we also performed a classical analysis of the streaking process. To this end, we model the propagation of an electron in the continuum by Newton’s equation [25]:

$$\frac{dk}{dt} = -E_s(t) - \frac{dV}{dx}. \quad (6)$$
By multiplying $dx$ to both sides and then integrating, the solution for the asymptotic momentum of the electron at $x \to \infty$ is given by [24]

$$k_f(t_i) = \sqrt{k_0^2 - 2 \int_{t_i}^{T} E_s(t)k(t)dt},$$

(7)

with $k_0 = \sqrt{2(\omega - I_p)}$ and $t_i$ as the time delay of photoelectron emission. We note that in Eq. (7) the integral over time is effectively limited by the end of the streaking pulse since $E_s(t)$ appears as a factor in the integrand. We then equal this result to the streaking formula, Eq. (2),

$$k_f(t_i) \approx k_0 - \alpha A_s(t_i + \Delta t_s)$$

$$\approx k_0 - \alpha A_s(t_i) + \alpha E_s(t_i)\Delta t_s$$

(8)

to get [for $E_s(t_i) \neq 0$]

$$\Delta t_s \approx \frac{\alpha A_s(t_i) + \sqrt{k_0^2 - 2 \int_{t_i}^{T} E_s(t)k(t)dt} - k_0}{\alpha E_s(t_i)}.$$  

(9)

We note that in the above approximation the time delay depends on the choice of the initial position $x_i$ and the parameter $\alpha$. We have chosen $x_i$ to be the expectation value of the electron position in the initial state, i.e., $x_i = 0$ for $V_{CY}(x)$. Furthermore, we determined $\alpha$ such that $\Delta t_s$ remains approximately constant while varying $t_i$ typically over the central cycle of the streaking pulse (see Fig. 2 in Ref. [24]).

### III-1. Finite-range time delays

As mentioned above, the integral in Eq. (7) is limited by the instants of transition of the photoelectron into the continuum, $t_i$, and the end of the streaking pulse, $T$. Thus, according to our classical analysis the observed time delay is accumulated during the propagation of the photoelectron over this finite time interval. For this reason, the range of the potential that has to be taken into account is well determined and limited, since the photoelectron propagates over a finite distance in space from $t_i$ to $T$. This is in contrast to the WS time delay, which accounts for the full range of the potential, i.e., for a long-range Coulomb potential in 1D up to $x \to \infty$. Thus, due to the finite limits in our classical analysis the temporal offset $\Delta t_s$ does not diverge (for a streaking pulse with finite pulse duration), in agreement with the observations in the experiment and in contrast to the assumption that a (diverging) WS time delay is part of the observed temporal offset.

To test this conclusion from our classical analysis we performed a series of numerical simulations using the model potential, Eq. (3), by varying the position of the Yukawa potential with respect to the center of the Coulomb potential. In the first set of calculations we have chosen a 6-cycle streaking pulse at 800 nm with a peak intensity of $I_s = 1 \times 10^{12}$ W/cm², and a CEP of $\phi_s = -\pi/2$. To photoionize the electron, we used an XUV pulse with $I_{XUV} = 1 \times 10^{15}$ W/cm², $\omega_{XUV} = 100$ eV, $\tau_{XUV} = 600$ as, and $\phi_{XUV} = -\pi/2$. Quantum
results in Fig. 2 (blue open circles) confirm our expectation that only a finite range of the combined Coulomb-Yukawa potential takes effect in a streaking experiment, since the streaking time delay remains constant if the Yukawa potential is located at far distances, here $x_0 \gtrsim 650$. We have checked that the constant time delay for $x_0 \gtrsim 650$ is equal to the streaking time delay obtained without the additional Yukawa potential. These results clearly show that the obtained time delays do not account for the presence of the Yukawa potential, if it is located at far distances from the location of photoemission of the electron.

Furthermore, our classical predictions from Eq. (9) for $\Delta t_s$ (green solid lines) agree very well with the TDSE results (blue open circles). From Eq. (9), we see that $\Delta t_s$ depends on the coupling between the streaking field and the potential and, thus, on both the parameters of the streaking field $E_s(t)$ and the shape of the potential. Thus, we expect that the streaking time delay can be indeed interpreted via the classical dynamics of the photoelectron in the combined potential of the Coulomb and streaking fields over a finite range in time and space until the streaking pulse ceases at $t = T$.

To further confirm these expectations we performed further sets of numerical simulations. In these simulations we varied the XUV photon energy (Fig. 3) or the shape and length of the streaking pulse (Fig. 4), respectively. We varied these two laser parameters in order to change either the momentum or the propagation time of the photoelectron until the streaking pulse ceases. With both changes we therefore control the propagation distance of the photoelectron while the streaking pulse is present. In the first of the two sets of simulations we used a 8-cycle, 800 nm streaking pulse with an intensity of $I_s = 1 \times 10^{12}$ W/cm$^2$, and a CEP of $\phi_s = -\pi/2$. In the second set we applied a 3-cycle, 800 nm streaking pulse with the same peak intensity and CEP and an additional pedestal. The form of the latter field envelope was given by
FIG. 3: (Color online) (a) Difference in the streaking time delay (blue solid line with open circles) obtained with and without Yukawa potential as a function of XUV central frequency. Assuming the electron is ionized at the peak of the streaking field, we show the signs (red plus or minus symbols) of the streaking field at the instant when the electron wave packet arrives at the Yukawa potential for each of the data points. (b) Position of the electron wave packet at the end of the streaking field for the first five XUV frequencies used in this set of simulations [see panel (a)]. The Yukawa potential was located at the distance $x_0 = 700$, which is marked by a red dashed line. The wave packet is chosen to be liberated at the center of the streaking pulse and each wave packet is normalized to 1 for the sake of comparison. Laser parameters are given in the text.

\[
E_{\text{env}}(\beta_p, T_p) = \begin{cases} 
E_0 \sin^2(\pi t/T_s) & 0 \leq t \leq T_s/2, \\
(1 - \beta_p)E_0 \sin^2(\pi t/T_s) + \beta_p E_0 \cos^2 \left[ \frac{\pi(t-T_s/2)}{T_s+2T_p} \right] & T_s/2 \leq t \leq T_s, \\
\beta_p E_0 \cos^2 \left[ \frac{\pi(t-T_s/2)}{T_s+2T_p} \right] & T_s \leq t \leq T_s + T_p, \\
0 & \text{else},
\end{cases}
\]

in which $\beta_p = 0.2$ and the length of the pedestal is determined by $T_p$. For the XUV parameters, we have chosen $I_{\text{XUV}} = 1 \times 10^{15}$ W/cm$^2$, $\tau_{\text{XUV}} = 600$ as, $\phi_{\text{XUV}} = -\pi/2$ as in all simulations, and $\omega_{\text{XUV}} = 100$ eV for the latter set.

In Fig. 3 (a), we present the difference between the streaking time delays obtained with and without the Yukawa potential as a function of the XUV central frequency. To relate the streaking time delay to the propagation distance of the photoelectron during the presence of the streaking pulse, we show in panel (b) the normalized ionized wave packet at the end of streaking pulse as a function of $x$ for the five lowest XUV photon energies considered in this set of simulations. As a reference, the position of the Yukawa potential is marked by a red dashed line. We find, as expected, that the difference between the time delays obtained with and without the additional short-range potential does equal zero, when the ionized wave packet does not reach the location of the Yukawa potential until the streaking pulse ceases, i.e., for $\omega_{\text{XUV}} \leq 80$ eV in the present set of simulations. For
larger XUV photon energies, the two time delays deviate due to the influence of the Yukawa potential, which is then reached by the ionized wave packet.

The same conclusion can be drawn from the results in Fig. 4, in which we present the streaking time delays with and without the Yukawa potential as a function of the pedestal length [c.f., Eq. (10)]. In this set of simulations the wave packet reached the location of the Yukawa potential at $x_0 = 700$ for streaking pulses with a pedestal length of $T_p \gtrsim 200$. Clearly, the two streaking delays deviate for a longer pedestal, which again confirms our interpretation of a finite-range time delay, in which the range is determined by the propagation distance of the photoelectron until the end of the streaking pulse.

III-2. Field-weighted time delays

As mentioned at the outset, using further approximations our classical analysis provides another interesting interpretation in the form of field-free time delays. To this end, we note that the momentum shift $k_f(t_i) - k_0$ in Eq. (7) is usually small. We can therefore expand the square root to first order and by setting $\alpha = 1$ we obtain

$$\Delta t_s \simeq \frac{1}{E_s(t_i)} \int_{t_i}^{T} E_s(t) \left(1 - \frac{k(t)}{k_0}\right) dt,$$

or by rewriting the integral as a sum

$$\Delta t_s \simeq \frac{1}{E_s(t_i)} \sum_{j=1}^{N} E_s(t_j) \Delta t^{(j)},$$

with

$$\Delta t^{(j)} = \left(1 - \frac{k(t_j)}{k_0}\right) \delta t,$$
FIG. 5: (Color online) (a) Time delays $\sum_j \Delta t^{(j)}$ and $\sum_j \Delta t^{(j)}_{\text{field-free}}$ as a function of the XUV central frequency. The time delays were calculated using the back-propagation method introduced in [22, 23] for an electron propagating in the Coulomb+Yukawa potential ($\sum_j \Delta t^{(j)}_{\text{field-free}}$, blue solid line with circles) and an electron propagating in the combined potential of the streaking and Coulomb+Yukawa fields ($\sum_j \Delta t^{(j)}$, green solid line with stars). (b) Relative difference between the two time delays as a function of the XUV central frequency. All calculations were performed with the same laser parameters as in Fig. 3, while the XUV pulse was applied at the peak of the streaking field in the forward-propagation step.

where we assumed that the streaking field and the electron momentum are approximately constant in the time interval $[t_j, t_j + \delta t]$, i.e., $E_s(t) \approx E_s(t_j)$ and $k(t) \approx k(t_j)$ in the corresponding time interval.

We note that Eq. (13) is the classical expression for the time delay accumulated by the photoelectron in the combined potential of the Coulomb and the streaking fields as compared to the propagation of a free photoelectron in the corresponding region $[x_j, x_j+\delta x]$. Thus, this expression is similar to that for the (classical) WS time delay with the important difference that the expression in Eq. (13) relates to the propagation over a piecewise finite distance while the WS time delay accounts for the propagation to infinity.

We further note that for a weak streaking field the time delay $\Delta t^{(j)}$ can be well approximated by neglecting the influence of the streaking field on $k(t)$ as [22, 23]:

$$\Delta t^{(j)} \approx \Delta t_{\text{field-free}}^{(j)} = \left(1 - \frac{k_{\text{field-free}}(t_j)}{k_0}\right) \delta t.$$  \hspace{1cm} (14)

To show this we compare in Fig. 5 results for $\sum_j \Delta t^{(j)}$ and $\sum_j \Delta t_{\text{field-free}}^{(j)}$ for typical laser parameters used in the present streaking simulations. The corresponding time delays were obtained using the back-propagation method introduced in Refs. [22, 23]. It can be clearly seen from the results that the streaking field has negligible influence on this time delay.
Using this additional approximation the streaking time delay finally yields:

\[ \Delta t_s \simeq \sum_{j=1}^{N} \frac{E_s(t_j)}{E_s(t_i)} \Delta t_{j,\text{field-free}}. \tag{15} \]

As mentioned above, \( \Delta t_{j,\text{field-free}} \) is the finite-range piecewise field-free time delay that the electron accumulates during its propagation in the time interval \([t_j, t_j + \delta t]\) and over a related finite region \([x_j, x_j + \delta x]\) of the potential \(V(x)\) as compared to the propagation of a free particle over the same distance in space.

Predictions based on Eq. (15) (red dashed line) are in good agreement with those of the full TDSE results as well as those based on Eq. (9), as exemplified in Fig. 2. Thus, we can give the following interpretation: The observed streaking time delay is neither the WS time delay nor the simple sum of finite-range piecewise field-free time delays. Instead, it can be understood as a field-weighted time delay, in which the piecewise field-free time delays are weighted by the streaking field strength present when the electron wave packet propagates over the corresponding part of the potential.

We finally point out that the influence of the instantaneous field strength on the observed time delay can be also seen from the results in Fig. 3(a). To this end, we note that according to our interpretation the difference between the streaking time delays with and without the additional Yukawa potential, as presented in Fig. 3(a), is approximately given by the contribution to the streaking time delay caused by the presence of the Yukawa potential as:

\[ \Delta t_s^Y(x_0, \omega_{\text{XUV}}) \simeq \frac{E_s(t_Y)}{E_s(t_i)} \Delta t_{Y,\text{WS}}, \tag{16} \]

where \(t_i\) and \(t_Y\) are the instant of ionization and the time instant at which the electron reaches the Yukawa potential, respectively, and \(\Delta t_{Y,\text{WS}}\) is the WS time delay induced by the Yukawa potential. Since \(E_s(t_i) > 0\) in the present simulations and one can show that \(\Delta t_{Y,\text{WS}} < 0\), we expect that the sign of the time delay difference should be opposite to the sign of the instantaneous field strength as the photoelectron reaches the Yukawa potential. The latter were retrieved from the actual numerical simulations and are marked in Fig. 3(a) for each of the simulations. It is seen that our expectation of a difference in sign between the time delay difference and the instantaneous field strength is indeed confirmed.

IV. CONCLUSIONS

In summary, we presented numerical simulations of streaking experiments using a model system consisting of a 1D Coulomb potential and an additional short-range Yukawa potential at a distance to the center of the Coulomb potential. By varying the location of the Yukawa potential and the field parameters of the streaking pulse we were able to confirm two aspects of the streaking time delay, which we proposed in a previous report [24]. First, the streaking time delay is accumulated by the photoelectron after the transition into
the continuum over a finite range in time and space until the streaking pulse ends. Next, the streaking time delay can be understood as a sum of piecewise field-free time delays weighted by the instantaneous field strength during the propagation of the photoelectron in the potential.

Acknowledgments

J.S. and A.B. acknowledge support by a grant from the U.S. Department of Energy, Division of Chemical Sciences, Atomic, Molecular and Optical Sciences Program. H.N. was supported via a grant from the U.S. National Science Foundation (Award No. PHY-0854918). A.J.-B. was supported by grants from the U.S. National Science Foundation (Award No. PHY-1125844 and Award No. PHY-1068706). This work utilized the Janus supercomputer, which is supported by the National Science Foundation (award number CNS-0821794) and the University of Colorado Boulder. The Janus supercomputer is a joint effort of the University of Colorado Boulder, the University of Colorado Denver and the National Center for Atmospheric Research. Janus is operated by the University of Colorado Boulder.

References

Review

Laser Air Photonics: Covering the “Terahertz Gap” and Beyond

Benjamin Clough,1 Jianming Dai,1,2 and X.-C. Zhang1,2,*

1 Center for Terahertz Research, Rensselaer Polytechnic Institute, Troy, New York 12180, USA
2 Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China

(Received October 28, 2013)

Laser air photonics involves the interaction of high-peak-power femtosecond laser pulses with air. Through the ionization process, the very air that we breathe is capable of generating terahertz (THz) electromagnetic field strengths greater than 1 MV/cm, useful bandwidths of over 100 THz, and highly directional emission patterns. Following the ionization of air, the emitted air-plasma fluorescence or acoustics can serve as an omnidirectional, broadband, THz wave sensor. Frequencies lying within the THz band were historically termed the “THz gap,” due to the relative difficulty for generating and detecting the radiation at these frequencies. Here we review significant advances in laser air photonics that help to close this “gap,” enabling ultra-broadband THz wave generation and detection through nonlinear optical processes. Research opportunities and applications including non-destructive evaluation, material characterization, and feasibility for remote sensing, are discussed.

DOI: 10.6122/CJP.52.416 PACS numbers: 42.65.-k, 52.38.-r, 52.20.Fs, 52.50.Sw

Plasma is regarded as the fourth state of matter [1] because it exhibits unique characteristics that set it apart from solids, liquids, and gases. A bolt of lightning, the glow of the Northern Lights, and our night-lit stars all stem from plasma formation. When a laser pulse is focused into a gas with intensity above a critical value near $10^{14}$ W/cm$^2$, the gas is ionized, yielding positively and negatively charged particles, or plasma [2]. High-energy pulsed lasers capable of ionizing ambient air or select gases were once only available at large-scale scientific facilities. Although pulsed CO$_2$ lasers capable of ionizing air have been in use since the 1970s, the optical pulse durations were insufficiently short for terahertz (THz) wave generation. More recent advancements in laser technologies have included self-mode-locked femtosecond Ti:sapphire oscillators, based on the Kerr effect, and high-power femtosecond Ti:Sapphire amplified laser systems, based on chirped pulse amplification (CPA) [3]. These technologies have allowed for critical intensities with pulse durations on the order of femtoseconds in commercial tabletop laser systems. This has substantially increased the interest in using laser air photonics within the THz science community.

Laser-induced gas-plasma can be used to generate intense, coherent, broadband, and highly directional THz waves through a nonlinear optical process [4–10]. Moreover, plasma in ambient air or other selected gases can be used as a THz wave sensor [11–16]. One technique, termed THz air biased coherent detection (THz-ABCD) [11, 12], provides superior bandwidth (0.1 to 40 THz), detection sensitivity (heterodyne method), and frequency

*Electronic address: zhangxc@rpi.edu
resolution (MHz). These parameters are important for the study of materials since many non-metallic molecular compounds exhibit vibrational and rotational resonances when stimulated by THz waves. Therefore, THz radiation can serve as a unique tool for non-invasive material classification, particularly since it easily penetrates many optically opaque materials such as paper, plastics, and clothing. By detecting THz radiation after its interaction with a material, absorption features at the resonant frequencies can be used as a unique spectral signature, or “fingerprint,” for its identification. It is clear that air photonics presents a unique technique for the generation and detection of THz radiation, but it remains desirable to seek sensing methods which could apply this powerful technology while overcoming existing limitations such as stand-off distance and limited detection geometries.

Plasma formed in gas through laser-atom/molecule interaction emits both fluorescence and acoustic waves. When the plasma is subject to a strong external electric field, both the intensity of fluorescence amplitude of the acoustic waves are increased by the transfer of kinetic energy from accelerated electrons to surrounding molecules through electron-electron, electron-ion, and electron-neutral atom collisions. THz radiation enhanced emission of fluorescence (THz-REEF) and THz enhanced acoustics (TEA) [13–18], are two techniques that utilize a dual-color laser field (800 and 400 nm pulses of light superimposed in space and time) to create air-plasma with asymmetric electron motion, making it possible to coherently detect broadband THz waves remotely. Amplitude and phase information obtained from the THz wave, can be used for performing THz spectroscopy of materials. These techniques can overcome large THz wave absorption by water vapor in air, and limited detection angles, by carrying THz wave information in the form of fluorescence or acoustic waves that are emitted in an isotropic manner.

The basic science and engineering of laser air photonics for wideband, high-field THz technology is just beginning. Here we review THz wave generation and detection techniques, sensing methodologies, applications for material classification, remaining challenges, and future opportunities for this rapidly evolving area of research that transcends the “gap” once existing between optics and electronics.

I. GENERATION AND DETECTION OF TERAHERTZ WAVES IN AIR

THz wave generation from intense laser-plasma interaction in air was first reported by Hamster et al. in 1993 [4]. At the time, single color (800 nm) sub-picosecond laser pulses were used, and the generation process was attributed to the ponderomotive force inside the plasma. In 2000, Cook et al. reported that higher intensity THz radiation could be emitted from laser-induced gas-plasma excited with both a fundamental pulse (800 nm) and its second harmonic (400 nm) [5]. The THz wave emission mechanism was attributed to the four-wave mixing (FWM) nonlinear optical process. At that time, several other groups became interested in this topic. Among them, Bartel et al. reported THz wave generation from gas-plasma with peak electric fields higher than 100 kV/cm, indicating promising applications of the gas-plasma THz wave source [6]. However, the physical process for THz wave emission remained under debate. In order to identify the basic mechanism, coherent
control experiments were performed which verified that FWM could be used to explain the THz wave generation process in a gas-plasma [19]. More importantly, using the FWM approximation, the detection of broadband pulsed THz waves with a laser-induced gas-plasma was successfully predicted and experimentally demonstrated [11]. In light of this, THz wave generation and detection with laser-induced gas-plasma have become attractive scientific research topics, and many groups worldwide have become involved [6–9, 14, 15, 20–29].

Laser air photonic systems differentiate themselves from other THz time-domain spectrometers by using ambient air or selected gases for the generation and detection of broadband pulsed THz waves [19, 30–32]. Fig. 1 (a) illustrates the schematic diagram for a THz-ABCD spectroscopic system in both transmission and reflection mode.

![Schematic diagram of a THz-ABCD spectroscopic system](image1.png)

**FIG. 1:** Schematic diagram of a THz-ABCD spectroscopic system in both transmission and reflection mode. The system can be converted from transmission to reflection mode by taking off the mirrors indicated with an enclosing dashed box. (b) Photograph of laser-induced air-plasma created after focusing the optical beam from left to right through a lens (left) and mounted nonlinear crystal (center) used for second harmonic generation. The bright horizontal line emits an intense, highly directional THz field to the right. PMT: photomultiplier tube; BS: beamsplitter; β-BBO: beta-barium borate.

A Ti:Sapphire regenerative amplifier is used as the laser source. Such a laser typically delivers laser pulses with millijoule pulse energy, femtosecond pulse duration, 800 nm center wavelength, and kilohertz repetition rate. The beam is split into pump and probe beams using a beamsplitter. The pump beam is focused through a beta-barium borate (β-BBO) crystal to produce the second harmonic at 400 nm. The mixed fundamental and second harmonic beams (ω and 2ω respectively) generate the ionizing plasma spot (center-right of Fig. 1 (b)) that emits intense, directional, and ultra-broadband THz radiation through a third-order nonlinear process [5]. Although four-wave-mixing (FWM) cannot completely describe the complex physical details [33–36], it remains a convenient framework for experimental results due to its simplicity. After interaction with a sample, the remaining THz energy and optical probe beam are recombined at the detection region, where an electric bias (Ebias) is applied to create a second harmonic local oscillator for coherent detection through DC-field-induced second harmonic generation [12]. Fig. 2 shows that the THz field
is proportional to the intensity of the fundamental pulse ($\omega$) above the ionization threshold for lower intensities, and is proportional to the square root of the second harmonic pulse ($2\omega$) [37]:

$$E_{THz} \propto \chi^{(3)} \sqrt{I_{2\omega} I_{\omega}}$$ \hspace{1cm} (1)

It is important to note that this relationship is only valid for relatively low peak laser power intensities, since FWM is an approximation in the perturbation region that is no longer valid when the laser intensity is very high.

![Graph showing dependence of THz field on fundamental pulse energy](image)

**FIG. 2:** Dependence of THz field on fundamental ($\omega$) pulse energy, with fixed second-harmonic ($2\omega$) pulse energy. (b) Dependence of THz field on second-harmonic pulse energy, with fixed fundamental pulse energy. The solid line and curve are the linear and square-root fits, respectively.

Similar to the widely used generation and detection of THz waves in electro-optic (EO) crystals by second-order optical nonlinearity [38–40], THz waves can be detected by the third-order optical nonlinearity in air or other selected gases [11, 31]. Fig. 3 (a) and (b) plot THz waveforms and spectra detected with laser-induced air-plasma using THz air-biased coherent detection (THz-ABCD) in comparison with the conventional EO method with a ZnTe crystal as the sensor. Using air as the sensor, the spectrum from 0.3 THz to over 30 THz sufficiently covers the “THz gap”. Using shorter laser pulses, THz peak fields may exceed 1 MV/cm, and the spectrum may extend beyond 120 THz [41]. As a comparison, the DC breakdown threshold for air is about 30 kV/cm.

The use of air to sense pulsed THz waves is a measurement of the THz field induced optical second harmonic light generated through a third-order nonlinear process that has been investigated extensively in the previous literature [12, 42, 43], and therefore details will not be presented here. The measured second harmonic intensity can be expressed as:

$$I_{2\omega}(\tau) \propto 2 \left[ \chi^{(3)} I_{\omega}(t) \right]^2 E_{bias} E_{THz}(t - \tau)$$ \hspace{1cm} (2)

Eq. (2) is the key description for detection. The linear dependence of $I_{2\omega}$ on $E_{bias}$ indicates heterodyne detection when $E_{bias}$ is treated as a local oscillator. The field induced second
Fig. 3: (a) Time-resolved THz signals generated and detected using dry nitrogen gas as compared to conventional EO crystal detection in ZnTe. The probe beam for air detection has energy of 85 μJ and pulse duration of 32 fs. (b) Corresponding spectra after Fourier transform.

Harmonic signal $I_{2\omega}$ is quadratically proportional to $\chi^{(3)}$ and $I_{\omega}(t)$, and linearly proportional to $E_{bias}$ and $E_{THz}(t-\tau)$. Fig. 4 (a) illustrates this concept where THz and optical pulses are focused together between modulated high-voltage-biased electrodes. The second harmonic induced by $E_{bias}$ acts as the local oscillator for heterodyne detection [12]. Fig. 4 (b) plots the detected second harmonic intensity as a function of normalized third order nonlinear susceptibility $\chi^{(3)}$ along with a quadratic fit [31, 44]. C₆H₁₄ provides more than 243 times the sensitivity compared with N₂ or air. Using gases with larger $\chi^{(3)}$, elevated pressure (effective $\chi^{(3)}$ is proportional to the number of molecules), and higher probe pulse energy can help to optimize the sensitivity of the air-plasma detector [31].

Fig. 4: (a) Basic concept of THz-ABCD: electrodes are placed at the geometric focus of collinearly focused THz and optical probe beams with a variable time delay. Second harmonic light is induced from the THz field and the local bias field $E_{bias}$. Modulating $E_{bias}$ allows for heterodyne detection for enhanced sensitivity. (b) Measured second harmonic intensity vs. third order nonlinear susceptibility $\chi^{(3)}$. All $\chi^{(3)}$ are normalized with respect to nitrogen.
II. THZ SENSING WITH AIR-PLASMA: FLUORESCENCE & ACOUSTICS

Intense, broadband, pulsed THz wave generation is achieved at remote locations by focusing two-color laser pulses into air at distances of tens of meters or even potentially hundreds of meters [29, 45, 46]. THz signals can be detected indirectly by observing THz radiation enhanced emission of fluorescence (THz-REEF), or THz enhanced acoustics (TEA). The THz spectroscopic “fingerprints” of materials can thus be carried to the operator via fluorescence (wavelength of 300–450 nm), or acoustic frequencies (10 Hz–140 kHz), due to their atmospheric transparencies. In the THz-REEF experiment, as shown in Fig. 5 (a), a THz pulse propagates through the plasma and the fluorescence is measured by a spectrometer. By increasing the kinetic energy of electrons through THz-field acceleration in the plasma, as illustrated in (b), fluorescence emission can be enhanced. Fig. 5 (c) plots the nitrogen fluorescence spectra with and without THz field imposed on the gas-plasma.

![Diagram](image-url)

FIG. 5: (a) Experimental geometry for THz-REEF from air-plasma using a single-color laser pulse. (b) Electron acceleration in the THz field and collision with neighboring molecules. (c) THz-enhanced fluorescence spectra of nitrogen gas-plasma under influence of 100 kV/cm peak field.

When two-color pulses (800 nm and 400 nm) create a plasma, the ionized electrons’ net drift velocity becomes a function of the relative phase between the pulses [34]. Electron motion can be symmetric, parallel, or anti-parallel to the THz wave polarization by changing the relative phase of the pulses. Once the THz pulse arrives, electrons are driven to move faster (if $E_{THz}(t)$ is anti-parallel to the initial velocity) or slower (if $E_{THz}(t)$ is parallel). The upper half of Fig. 6 shows the time-resolved air-plasma fluorescence for the parallel, symmetric, and antiparallel electron drift velocities as the THz pulse interacts with the plasma. In each scenario, there is fluorescence enhancement, but each contains unique “features” from either the increase or decrease in electron velocity (and therefore energy transfer) by the THz field [14]. The lower half of Fig. 6 shows the coherent THz waveform revealed in the fluorescence by subtracting the parallel curve from the antiparallel curve.

The THz-REEF signal thus allows for THz wave coherent detection, meaning air-plasma fluorescence can indirectly give information regarding a material. The omnidirectional nature of the fluorescence emission is a further advantage for THz wave detection.
FIG. 6: Time-resolved air-plasma fluorescence enhancement from THz wave interaction with antiparallel, symmetric, and parallel electron drift velocities with respect to the laser field, controlled by changing the relative phase between the $\omega$ and $2\omega$ optical pulses. Subtracting the parallel curve from the antiparallel curve removes the incoherent energy transfer by electrons after inelastic collisions and scattering at random directions. This reveals the THz waveform in the form of fluorescence modulation. The optical pulse leads the THz pulse in time for delay $t_d < 0$.

This method was demonstrated using air-plasma for both the THz wave emitter and detector [16]. THz-REEF has been used for sensing several explosive compounds in a transmission mode: nitroguanidine (NG), 2,4-dinitrotoluene (DNT), and octogen (HMX). Fig. 7 compares the absorbance information obtained using THz-REEF with that obtained using conventional EO sampling with ZnTe.

Although monitoring optical photons gives highly sensitive detection, UV from sunlight may easily saturate a sensitive photodetector such as a photomultiplier tube (PMT), making field measurements difficult. Therefore, it is useful to search for complementary sensing techniques.

A distinct acoustic pitch can be heard from laser-induced air-plasma as the gas is ionized at the repetition rate of the laser [47, 48]. Although the main component of audible sound is determined by the repetition rate of the amplified laser (typically on the order of kHz), much like a repetitive clap of the hands, a very broad range of acoustic frequencies corresponding to high harmonics, are emitted for each clap. When a pulse of THz radia-
FIG. 7: (Top) Absorbance signatures for pellet samples of explosives: NG, 2,4-DNT, and HMX (20% in polyethylene) using conventional EO sampling. (Bottom) Absorbance signatures obtained using THz-REEF. All samples tested were in a transmission geometry and identical samples were used for the respective methods. Curves are offset for clarity.

Fig. 8 shows acoustic pulses formed by focusing an 85 fs optical pulse into air. The acoustic pressure is enhanced by 10% for an incident peak field of 100 kV/cm. The air-pressure disturbance, lasting tens of microseconds, is recorded using a broadband microphone. The acoustic bandwidth extends from a few Hz to almost 1 MHz. Acoustic spectral components at integer multiples of laser repetition rate (1 kHz) are obtained using harmonics of a lock-in amplifier referencing the synchronized laser output. Measurements at the 100th harmonic (100 kHz) are favorable due to higher signal amplitude and lower ambient noise. The inset of Fig. 8 shows the experimental setup used for detection of THz
waves through sound. A pulsed laser and its second harmonic, with adjustable time delay $t_R$, create a plasma that emits acoustic pulses at the laser repetition rate. This plasma interacts with a THz pulse, with adjustable time delay $t_d$, and the acoustic amplitude has a linear dependence on the THz intensity (or quadratic dependence on the field) applied to the air-plasma [15].

As in the THz-REEF experiment, free electrons are accelerated or decelerated in the THz field depending on the THz polarity with respect to the electron drift velocity at their time of birth. Monitoring acoustic emission for parallel and antiparallel electron drift velocity reveals the acoustic enhancement from THz-field-accelerated electrons and their energy transfer released in the form of heat. Single-shot acoustic waveforms captured at various distances from the plasma show that even at 11 meters of acoustic propagation (test limit due to lab space), spectral content well into the ultrasonic region is still available for detection [49]. Acoustic measurements do not require direct line of sight, meaning useful data might be collected from an operator behind a barrier, using reflected or transmitted acoustic waves. In addition, the pressure attenuation is $1/r$ with radial distance, whereas the fluorescence intensity decays at $1/r^2$.

III. LASER AIR PHOTONIC APPLICATIONS

THz radiation generated and detected using laser air photonics remains a relatively young technique, but there exist a wide range of potential applications [50]. Some examples include linear and non-linear THz spectroscopy [51, 52], determination of the carrier-envelope (CE) phase of ultra-short (< 10 fs) laser pulses20, identification of materials [53, 54], THz-wave polarization control [25, 26], plasma diagnostics55, and remote THz generation and detection [14, 29, 45].
A THz-ABCD spectrometer using air or select gases as both THz emitter and sensor is capable of measuring material optical properties covering the entire “THz gap” and well beyond, if reflection geometry is used, for solid and liquid materials. In comparison with commonly used detection methods, gases do not exhibit either the phonon absorption seen in EO crystals, or carrier lifetime limitations as observed in photoconductive dipole antennas. Fig. 9 compares absorption spectra of ambient air containing 15% relative humidity between the air photonic THz-ABCD system and a conventional FTIR system, showing excellent agreement between the methods.

![Absorption spectra comparison](image)

**FIG. 9:** Spectroscopy data of water vapor absorption for THz-ABCD and FTIR systems. Measurements were independently performed under a relative humidity of 15%.

Typically, when performing a spectroscopic measurement, a short pulse of THz radiation containing a broad range of frequencies is allowed to pass through or reflect off a target material. After interaction with the sample, the remaining radiation can be analyzed to determine what frequencies were absorbed during the interaction. It is also possible to extract the index of refraction for the material for this broad range of frequencies in either transmission or reflection geometries with only two measurements (a reference measurement and sample measurement). Once the complex index of refraction is determined, the material’s absorption coefficient can be calculated.

Fig. 10 (a) shows a linear spectral measurement of $\alpha$-BBO in both transmission and...
reflection modes using a THz-ABCD spectrometer similar to the setup in Fig. 1 (a) [56]. The reference spectrum and transmitted spectra for both the o beam and the e beam are shown. The transmitted signal level in the range of 5–7 THz and above 10 THz for the o beam, and above 6 THz for the e beam, respectively, is as low as the noise floor due to the large THz wave attenuation by the crystal. Optical properties in these regions can only be revealed by performing measurements in reflection. The reference spectrum covers from 0.3 to over 20 THz with a dip around 18.3 THz due to the two-phonon absorption of the silicon beamsplitter depicted in Fig. 1 (a). The positions of sharp changes in reflected spectra are coincident with positions of those dips in transmitted spectra. Fig. 10 (b) plots absorption coefficients $\alpha_o$ and $\alpha_e$ and refractive indices $n_o$ and $n_e$ of the $\alpha$-BBO crystal.

![Graphs of THz spectra](image)

**FIG. 10:** (a) Measured transmitted and reflected THz spectra of a 0.3-mm-thick $\alpha$-BBO crystal and reference spectrum. (b) Absorption coefficients and refractive indices of the $\alpha$-BBO for both $e$ and $o$ crystal axis in the range of 0.3–10 THz. (Insets) Comparison between transmission (TR) and reflection (RL) measurements.

IV. CHALLENGES, LIMITATIONS, AND OPPORTUNITIES

Although laser air photonics technology has opened new possibilities for application, many areas remain for improvement. Remote sensing and standoff detection with THz waves could be considered one of the most challenging topics in THz sensing. Due especially to strong water vapor attenuation in the THz frequency range and insufficient THz power,
broadband THz sensing has been limited to short distances (a few centimeters). The generation of air-plasma near the target(s), through laser excitation, provides one approach to remote detection. The THz-ABCD method offers broadband sensing capabilities, but the THz-induced second harmonic signal cannot be collected from either a backwards or sideways direction. It is also necessary to provide a high voltage local oscillator bias that cannot be readily placed near the remote target for coherent detection.

While remote THz wave generation (> 100 meters) is realistic, coherent remote sensing remains extremely challenging. Currently, the only known solution is to use a two-color laser field to generate air-plasma near the target, measuring THz wave information indirectly through THz-field-induced changes in plasma fluorescence or acoustics. THz air-plasma detection through THz-REEF or TEA, in contrast to nearly all other THz wave sensing methods, enables omnidirectional signal collection, and significantly mitigates the problem of THz absorption by atmospheric moisture. Although both remote generation and detection have been demonstrated separately, it remains to combine these laboratory demonstrations to realize real world THz remote spectroscopy of explosives or other hazardous materials.

Using an intense laser with millijoule pulse energy for many practical applications is also a challenge. The focusing of high intensity optical pulses over long distances with precision, and practical control of the THz amplitude and phase at these ranges has not yet been demonstrated. While some applications such as battlefield monitoring or sensing in remote atmospheric locations may be feasible, public safety must also be considered. These limitations are motivation for improvements to this technology, and/or alternative solutions for remote THz spectroscopy. In the future, we will need to address scientific and technical concerns, provide guidelines and solutions to satisfy safety issues, and develop further approaches that make use of THz wave laser air photonic systems and their unique abilities. As a summary, Table I provides some advantages and disadvantages associated with air photonics for THz wave generation and detection.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emitter and sensor can be ambient air</td>
<td>Intense laser pulses are needed</td>
</tr>
<tr>
<td>Capable of MV/cm peak electric field strengths</td>
<td>Low optical-to-THz conversion efficiency</td>
</tr>
<tr>
<td>&gt; 100 THz bandwidths</td>
<td>Bulky, amplified laser systems required</td>
</tr>
<tr>
<td>Sensor does not suffer from phonon absorption</td>
<td>Intense optical radiation is not eye-safe</td>
</tr>
<tr>
<td>Emitter and sensor can be formed remotely</td>
<td>Critical alignment is necessary</td>
</tr>
<tr>
<td>THz can be detected through fluorescence or acoustic wave modulation</td>
<td>Lower sensitivity from the use of high-order nonlinearity</td>
</tr>
</tbody>
</table>
V. OUTLOOK & FUTURE PERSPECTIVES

Laser air photonics for THz wave technology remains an active area of research both scientifically and for practical uses, particularly geared towards sensing, identification, and material characterization. A further understanding of the science behind THz wave generation and detection mechanisms in laser-induced gas-plasmas is crucial to advancements in THz wave sources and sensors. Many parameters influence THz wave generation, manipulation, and detection, such as: optical energy, pulse duration, beam polarization, optical phase (in dual color excitation), plasma density, beam divergence angle, air turbulence, air density, and humidity. The study of THz wave generation and detection using lasers with higher powers and shorter pulse durations will push the envelope for THz field strengths and bandwidths. The success of broader impact on the sensor will come through the five S's: sensitivity, selectivity, simplicity, scalability, and stability. By focusing on these challenges, key applications in spectroscopy, non-invasive evaluation of materials, and imaging will continue to flourish. THz air-plasma systems are expected to provide orders of magnitude improvement in field strength, bandwidth, and sensitivity over commercial THz time-domain spectrometer (THz-TDS) systems available today. For example, recent progress in laser air photonics shows that a bandwidth covering the entire “THz gap,” and continuously stretching to the near-IR can be obtained [57].

In the future, laser air photonics may find alternative niche applications. The following “wish list” items may provide useful topics of study:

- Using compact oscillator lasers to replace amplified lasers for THz-ABCD
- Selecting alternative gases to increase generation and detection efficiency
- Studying plasma sensors for detecting other forms of electromagnetic radiation such as UV, microwave, X-rays, or gamma rays

Recent observations that THz radiation is able to modulate both the fluorescence and acoustics of laser-induced plasma in air, means that THz-REEF or TEA not only present feasible solutions toward remote THz wave detection, but also open exciting new areas of basic research. The fluorescence technique could, for example, exploit the Stark effect to directly measure rectified THz fields inside of a filament core, providing evidence of potentially enormous field strengths that are unable to couple out into free space. Furthermore, acoustic techniques could make it possible to study solids or liquids with high absorption coefficients by indirectly studying changes in a sample’s acoustic properties under illumination of high-field THz radiation. It is clear that pioneering direction, and growth in application, will require continued advances in laser air photonics technology.

Acknowledgements

This work was supported in part by the U.S. Office of Naval Research (ONR), the Defense Threat Reduction Agency (DTRA), National Science Foundation (NSF) under Grant
No. 0333314, and the U.S. Department of Homeland Security through the DHS-ALERT Center under Award No. 2008-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

The authors gratefully acknowledge assistance from Dr. Nicolas Karpowicz, Dr. Jingle Liu, Dr. Xaofei Lu, Dr. Karen Ho, and Dr. David Brigada.

References

[34] K. Y. Kim et al., Optics Express 15 (8), 4577 (2007).
Supercontinuum Generation in Barium Fluoride Using Bessel Beams

Krithika Dota,1,2 Jayashree A. Dharmadhikari,2
Deepak Mathur,1,2 and Aditya K. Dharmadhikari1

1Tata Institute of Fundamental Research,
1 Homi Bhabha Road, Mumbai 400 005, India
2Centre for Atomic and Molecular Physics,
Manipal University, Manipal 576 104, India

(Received August 20, 2013)

We investigate supercontinuum generation using femtosecond duration pulses in a 15 mm long barium fluoride crystal using an axicon-generated Bessel beam. Spectral profiles of the generated supercontinuum are measured using axicon lenses of different cone angles, and with two different incident beam diameters. Our measurements reveal that the spectral profile is, indeed, dependent on the distance between the crystal and the tip of axicon, and also on incident laser power. We observe both modulated and smooth spectral profiles as the axicon cone angle is changed. Our experimental observations manifest the variation of the input laser intensity along the propagation axis in the crystal. The spectrum is found to be smoothest when the crystal is kept in physical contact with the tip of the axicon. The spectral extent is broadest for the highest axicon cone angle.

DOI: 10.6122/CJP.52.431 PACS numbers: 42.25.Bs, 42.65.Jx, 52.38.Hb, 42.65.Sf

I. INTRODUCTION

Femtosecond supercontinuum generation is a visually spectacular effect and has been of interest for the past three decades [1, 2] and pioneering contributions have been made in the areas of femtosecond supercontinuum generation and filamentation nonlinear optics by Chin and coworkers [2]. The supercontinuum manifests itself in the light transmitted through a medium as a white disk surrounded by a distinct, concentric, rainbow-like conical emission, the low-divergence central part of which has come to be called the whitelight continuum or supercontinuum. There exist various mechanisms that seek to rationalize supercontinuum generation (SG): self-phase modulation [3]; ionization-enhanced SPM [3, 5], with additional contributions from the interplay of diffraction and instantaneous electronic Kerr nonlinearity [6]; stimulated Raman scattering; self-steepening; four-wave parametric processes; shock wave, group velocity dispersion, chromatic dispersion and band gap [7–11]. All such studies have considered the use of a Gaussian profile of the laser beam that is focused using a spherical lens. A Bessel beam, on the other hand, has a non-diffracting property that makes it suitable for longer distance propagation of optical energy than is possible with Gaussian or near-Gaussian beams. This affords an obvious advantage: it allows the Bessel beam to maintain a tight focus over distances larger than the conventional Rayleigh range. Another property that is important for propagation of femtosecond laser pulses is that the beam is “self-healing” in the sense that if the beam is partially obstructed it can re-form at a different location further along its propagation path [12–15]. Bessel beams
(or axicon beams) have attracted the attention of both theoreticians and experimentalists [16, 17] for a very long time but it is only relatively recently that the relative simplicity of using axicons to generate Bessel beams has begun to be practically appreciated, opening new opportunities for their application in parametric down conversion [18], waveguide writing [19], femtosecond laser filamentation [20], and stimulated Raman scattering [21]. Bessel beam filamentation in air and liquid has begun to be studied [22-26] and it has been demonstrated that the on-axis intensity distribution can be simply controlled by (i) changing the distance between the axicon and the sample under study, (ii) altering the bluntness of the axicon tip, and (iii) selecting the input beam size [27]. Theoretical simulations carried out to investigate dispersion-induced distortions of field distribution along longitudinal and transverse direction in a femtosecond laser beam generated using an axicon lens [28] have shown that dispersion increases laser pulse duration in the course of its propagation. A numerical study in K108 glass, focusing on supercontinuum conical emission, has predicted that conical emission first decomposes into speckles, followed by splitting into narrow rings as the pulse energy is increased [29].

In earlier work carried out in our laboratory with Gaussian beams of ~45 fs duration [30] we have demonstrated very efficient whitelight generation in BaF₂ and have reported results of systematic studies carried out under varying experimental conditions, such as laser energy, pulse duration, polarization, and external focusing [31]. The rate of change in electron densities within BaF₂ have also been obtained from such studies [32]. We have experimentally shown exercising control over the filamentation dynamics within a large BaF₂ crystal [33], and estimated six-photon absorption cross-section [34]. All the above mentioned work was carried out using Gaussian beam focused by a spherical lens. In the following we report results of experiments that we have conducted on supercontinuum generation using axicon lenses. Despite the above-noted resurgence of interest in supercontinuum generation using axicon-related studies, there continues to be a dearth of experimental data on axicon-generated supercontinuum generation in condensed media. In recent work [35] we carried out experiments that revealed the following aspects of axicon based filamentation: i) a higher incident laser energy is required for a filament as the axicon cone angles increases; (ii) the filament size is independent of whether an axicon or a spherical lens is used; and (iii) the distance between the tip of the axicon and the BaF₂ crystal is a crucial parameter that quantifies changes in periodicity of focusing-refocusing events within the crystal. In the following we extend these studies and report on the systematics of supercontinuum generation using femtosecond duration pulses in a 15 mm long barium fluoride crystal focused by an axicon-generated Bessel beam, including measurements of the spectral profile of the supercontinuum we generate using axicon lenses of different cone angles, using two different incident beam diameters. We present our results in the form of both images as well as spectra.

II. EXPERIMENTAL METHOD

Figure 1 is a schematic depiction of our experimental set-up used to investigate supercontinuum generation in a BaF₂ crystal (15 mm long) using axicon lenses of different
We utilized two separate Ti-sapphire lasers (Laser 1: 800 nm wavelength, 1 kHz repetition rate, with 7 mm diameter beam, 1 mJ energy and 40 fs pulse duration; Laser 2: 800 nm wavelength, 1 kHz repetition rate, with 10 mm diameter beam, 4 mJ energy and 35 fs pulse duration).

The beam from one or the other of these lasers was made incident on an axicon lens (we used different lenses with cone angles varying from 178° to 170°). Figure 2 shows the beam profile of the two lasers along with the beam profile of the Bessel beam generated using a 178° axicon; the profile has been measured using a CCD-based beam profiler. The Bessel beam profile is found to be identical for two incident laser beams (Laser 1 and Laser 2); we show only the beam profile obtained using Laser 2 in Fig. 2. The Bessel beam thus characterized was propagated through BaF$_2$ such that supercontinuum could be generated and measured. We employed a fibre-coupled spectrometer (Ocean Optics USB 2000) to quantify the spectral extent of the supercontinuum emerging from the crystal. Far-field images of the whitelight and conical emission obtained under different conditions were captured using a CCD camera coupled to a computer.

### III. RESULTS AND DISCUSSION

We probed supercontinuum generation using axicon lenses with different cone angles in BaF$_2$ with both the lasers (7 mm and 10 mm beam diameter). We made two types of measurements: one in which the incident input energy was kept constant and the distance between the axicon and the crystal was varied, and another in which the latter distance was
fixed and the input energy was varied. Figure 3 (top panel) shows typical supercontinuum spectra of the central portion of the transmitted beam; this was obtained as a function of distance using an axicon with 170° cone angle at a fixed input energy of 90 μJ. As the distance between the axicon and the crystal increases (5.5 cm to 9.5 cm), there is an increase in spectral width, particularly towards the blue side of the spectrum. Moreover, the axicon-generated supercontinuum spectrum begins to exhibit distinct peaks: the spectrum appears to be highly modulated, in contrast to the smooth continuum that is generally obtained using a spherical lens [36]. In the context of Gaussian laser beams, modulated axial supercontinuum has also been observed in sapphire [37] and water (along with the stimulated Raman scattering) [21]. Modulations are also observed in the spectrum when the supercontinuum is generated from a hollow fibre; these are usually attributed to a laser pulse undergoing self-phase modulation in the leaky modes (higher order modes) of the hollow fibre [38, 39]. In case of Bessel beam propagation a similar analogy may be made to rationalize the modulations in the spectra that we observe. Recently using a

FIG. 2: (Color online) Beam profiles of Laser 1 (left, top panel) and Laser 2 (right, top panel). The lower panel shows the beam profile of the Bessel-like beam generated 9 cm from the tip of an axicon with 178° cone angle.
short length sapphire crystal Majus and Dubietis [40] have demonstrated modulation-free supercontinuum using an axicon. This is attributed to the fact that the 3 mm crystal experiences no variation in the intensity of the central spot. We show an entirely different method to generate modulation free supercontinuum in a long sample using low cone angle axicon and low incident energy.

The middle panel of Fig. 3 depicts the supercontinuum spectra we obtained using a 175° cone angle axicon. Even though the extent of the supercontinuum is somewhat reduced, it is interesting to note the absence of modulations in the spectrum. Similarly in the case of 178° cone angle axicon the modulations are found to be completely absent. The intensity variation in the central spot is constant over a distance much larger than the crystal size. To ascertain this fact we have measured supercontinuum yield as a function of distance from the tip of the axicon. Figure 4 shows how the total supercontinuum yield depends on incident laser beam diameter and on axicon cone angle. Here the yield was taken to be the area under the supercontinuum spectrum over the wavelength range 600-900 nm (normalized, in each case, to the peak at 812 nm). It is clear that supercontinuum yield is constant as the crystal is translated along the laser propagation direction. Moreover, it appears that the axicon-generated supercontinuum depends on the input beam diameter that decides the depth of focus. For the 1 cm beam the depth of focus is larger than for the 7 mm beam. As is seen, for 1 cm beam diameter with 175° cone angle, we observe nearly constant supercontinuum generation up to a distance of 10 cm. The yield of supercontinuum generation is more in the case of the 7 mm beam compared to the 10 mm beam even though the incident energy is less.

We now discuss results obtained when the axicon is touching the crystal. Here, the supercontinuum is measured as a function of incident energy. Figure 5 shows the supercontinuum spectra obtained using cone angles of 170°, 175°, and 178°, with the barium fluoride crystal being kept in physical contact with the tip of the axicon in each case. The incident energy was varied from 27 to 340 μJ. At a fixed energy of 200 μJ the spectra are compared for the three axicons when the crystal was touching the tip of the axicon. The supercontinuum extent is seen to be distinctly wider in the case of 170° cone angle axicon compared to what is obtained with the other two axicon cone angles. Our results (Figs. 3, 5) are consistent with earlier observations in water [21]. Two transition regions were identified in this case: one is the “smooth” case in which the water sample touched the axicon tip and the second “sharp” case in which the sample is at some distance from the axicon tip. In the former, a transition occurred from a linear to a nonlinear regime in smooth fashion whereas in the latter the transition occurred abruptly. The sharp regime has been attributed to collapse of the Bessel beam initiated by a Kerr-driven (four wave mixing) process [41] which gives rise to localized enhancement of peak laser intensity that, in turn, results in relaxation of the condition for transverse momentum conservation.

An image of the generated supercontinuum is shown in Fig. 6 in which the left panel shows the image when a 170° cone angle axicon was used. Here, the central disc is the supercontinuum and the surrounding rings are the conical emission. Contrast this with the measured spectra of the central disc shown in Figs. 3 and 4.

In summary, we have carried out a systematic investigation of supercontinuum gen-
FIG. 3: (Color online) Supercontinuum generation at different distances between the BaF$_2$ crystal and the axicon tip, for cone angles of 170°, 175°, and 178°.
FIG. 4: (Color online) Supercontinuum yield at different distances (d) from the axicon tip obtained with beams from Laser 1 (red) and Laser 2 (black) for an axicon cone angle of 175°.

FIG. 5: (Color online) Whitelight spectra obtained using three different axicon cone angles at a fixed incident laser energy of 200 μJ with the BaF₂ crystal touching the axicon tip. Note the smoothness of the spectra (see text).

etration in a crystal of barium fluoride with femtosecond duration pulses using axicon lenses with different cone angles. Our results are presented in terms of images as well as spectra. With higher cone angle we observed modulations in the supercontinuum spectra. The input beam size is also found to have relevance in the yield of supercontinuum generation. By placing the barium fluoride crystal in physical contact with the tip of the axicon, we observed a smooth spectrum, with spectral extent being broader for higher cone angles.
FIG. 6: (Color online) Far-field images of the supercontinuum and conical emission obtained using cone angles of 170° (left image), 175° (centre image), and 178° (right image).

IV. ACKNOWLEDGMENTS

JAD thanks the Department of Science and Technology for assistance under the Women Scientists Scheme while DM acknowledges generous support as a J C Bose National Fellow.

References

Review

Dynamics and Kinetics of Laser-Filament Plasma in Strong External Electric Fields and Applications

Takashi Fujii,1,2,* Alexei Zhidkov,1 Megumu Miki,1 Kiyohiro Sugiyama,2 Naohiko Goto,1 Shuzo Eto,1 Yuji Oishi,1 Eiki Hotta,2 and Koshichi Nemoto1

1Electric Power Engineering Research Laboratory, Central Research Institute of Electric Power Industry, 2-6-1 Nagasaka, Yokosuka-shi, Kanagawa 240-0196, Japan
2Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama-shi, Kanagawa 226-8502, Japan
(Received November 13, 2013)

Physics of atmospheric laser-induced filaments in strong electric fields provides us with good instruments for the distant study and control of atmospheric and industrial high voltage discharges and accompanying processes. Dynamics and kinetics of laser filaments in strong non-uniform electric fields are studied both theoretically and experimentally with the high temporal and spatial resolution. Among others, a considerable reduction of the breakdown potential was found and was attributed to a filament-induced leader. Two breakdown modes, fast and slow, were found in 0.4 MV positive dc-voltage discharges activated by filaments. In the fast mode with duration order of a few microseconds, the filament may acquire the electrode potential and temporarily maintain it, becoming a leader. The slow mode with its duration order of 1 ms appears with a considerably smaller voltage reduction when the leader decays before the secondary streamer. Long, about a half of microsecond, non-uniform corona UV burst is observed after the laser-filament plasma appears nearby an electrode biased (positively or negatively) slightly higher than the corona discharge threshold. The effects of electron runaway in positive high-voltage-impulse discharges were studied. Strong hard ($\varepsilon > 100$ keV) x-rays being observed from impulse atmospheric discharges just before the breakdown were completely stopped with the use of the laser-filament plasma. Runaway electrons, generating such x-rays, disappear if the laser-filament plasma is ignited perpendicularly to the runaway nearby the positive electrode. These results are important to understand the filament physics, and also useful for the applications to laser triggered lightning, electric field measurement, protection of high-voltage facility and others.

DOI: 10.6122/CJP.52.440 PACS numbers: 52.38.Hb, 52.80.Mg, 52.25.Tx

I. INTRODUCTION

Recently, the laser filament plasma (LFP) [1–18], produced by intense ultra-short laser pulses, in strong external electric fields has attracted interest both in the physics of
streamer discharges [19, 20] and in various applications such as the discharge triggering [21–35], the generation of terahertz radiation [36, 37], and the measurement of electric fields in atmosphere [38–43].

Although atmospheric electricity is a subject of longtime study, there is still no practical use of its huge energy. For example, the extreme event such as lightning is out of human control. For control of lightning, laser-triggered discharge by filaments is of particular interest. However, the physics of laser filaments in strong non-uniform electric fields has yet to be understood. Initially, the laser-triggered discharge using long laser pulses in air has been studied for lightning protection of sensitive installations such as electrical power plants, chemical plants, and airports [44]. Recently, the femtosecond (fs)-pulse-laser-triggered discharge has been extensively studied [21–35]. However, conclusions based on those measurements are still ambiguous, and the physical picture of the process is obscure. The explanation of the breakdown physics based solely on the assumption of gas rarefaction with an increase in \( E/N \), where \( E \) is the electric field, and \( N \) is the density of molecules at the atmospheric pressure [26], cannot fully describe the discharge evolution: appearance of fast and slow discharge modes [34] and the breakdown potential reduction. Moreover, these phenomena strongly depend on the geometric relation between the filament and the electrode.

The dynamics of LFP, before the breakdown, is also surely important to understand filament physics. Besides, LFP may find various applications as a point source of radiation in atmosphere: a source that is very sensitive to atmospheric conditions including atmospheric electric field. An interesting phenomenon has been found in pioneering experiment [37] on the terahertz radiation of LFP: the intensity of the radiation is very sensitive to the external field strength. The UV radiation of LFP has been also found very sensitive to external field strength [38–43]: it increases nonlinearly with the applied voltage. The field dependency of UV emission may become a basis for the remote field measurements in the atmosphere. However, there are various effects which can also result in the LFP emission such as the secondary emission, strong corona, runaway electrons, and so on and, therefore, can change the emission dependency on the field strength. The LFP, itself, may also affect the field distribution in the vicinity of measurements. To make a practical tool, we have to prove the conformity between the emission signal and the external field strength and the ability to maintain it. Detailed studies of LFP behavior in the external fields of different configurations are necessary to understand whether such measurement can be calibrated or can provide only the relative field measurements.

Interest in the effect of electron runaway in the atmosphere has been growing in the last decade, mostly due to the strong x rays observed by aircraft, satellites and ground detectors associated with thunderstorms [45–48]. The observation of hard x rays and \( \gamma \)-rays in conventional high-voltage discharges in the laboratory [49, 50] has also been reported. However, so far, the physics of the formation of runaway electrons in air and their acceleration is unclear.

LFP can be an excellent tool to investigate discharge physics including the electron runaway, because it can produce space charges instantaneously to control the initiation of atmospheric ionization precisely.
In this paper, we overview the kinetics and dynamics of the LFP in external electric fields of various configurations and its applications, such as the control of high-voltage discharges, including electron runaway, and the dynamics of UV emission from LFP for the applications of remote field measurement.

II. FILAMENT PLASMA INDUCED BY HIGH-INTENSITY FEMTOSECOND LASER PULSES AND ITS DYNAMICS IN STRONG EXTERNAL ELECTRIC FIELDS

LFP is produced in air by femtosecond laser pulses via the laser field ionization (multiphoton and/or tunnel ionization) [51]. A fs laser pulse undergoes the Kerr self-focusing in air [2, 7]; its intensity increases until an LFP is produced. Diffraction of the laser pulse in the plasma prevents any further self-focusing. The parameters of LFP such as the electron density and temperature strongly depend on the energy of laser pulses and focusing conditions. The electron density in LFP is about $10^{16} - 10^{18}$ cm$^{-3}$ (see Ref. [1, 2, 12, 18]), and the electron temperature is low; it is estimated to be $\sim 0.5$ eV [18]. A comprehensive analysis of the laser-filament dynamics in air can be found in Refs. [14]. Recently, the emission of laser filaments at several kilometer altitudes has been detected [6], ionization channels have been also observed over a distance reaching 400 m [10]. In addition, Kasparian et al. observed an increase of the number of cloud-cloud discharges using laser filaments, which shows the presence of plasma at several kilometer altitude [35]. These results suggest that the distant application of LFP, such as remote measurements of electric field and laser triggered lightning, is possible.

Figure 1 shows an image of plasma generated by a laser beam, when the beam was focused by a spherical mirror with a focal length of 20 m. In the inset of Fig. 1, multiple filaments are observed as bright lines [52]. Typical transverse profiles of filaments, produced when the laser beam was focused by a spherical mirror with 10 m focal length, in air without an external field are given in Fig. 2 (a)–(c) [34]. Multiple filamentation with transversely non-uniform plasma is detected. The appearance of plasma due to the Kerr self-focusing is clearly seen after the pulse passes over 7 m from the spherical mirror. The plasma filament is not uniform in the direction of laser pulse propagation. Fig. 2 (d) shows the calculated electron density distribution along a single filament [34]; it has many peaks in this direction reflecting the process of laser pulse focusing and defocusing.

The LFP is not a conventional discharge plasma or laser-breakdown plasma. Even in a strong electric field, LFP is cold and the dissociation recombination reduces the LFP electron density quickly: $N_e = N_{e0}/[1 + \beta N_{e0}t]$, where $\beta \sim 2 \times 10^{-7}$ cm$^3$/s [20, 53] and $N_{e0}$ is the initial electron density in the filament. At $t \leq (\beta N_{e0})^{-1} \sim (5 - 500)$ ps, the LFP is dense, the Debye radius is smaller than a plasma size; electrons do not attach to oxygen molecules. [In this regime, the LFP acquires and maintains a minimal potential in its vicinity.] For $t > (\beta N_{e0})^{-1}$, the electron density loses the information on the initial value. Although the dissociation recombination reduces the plasma charge shortly ($\sim 100$ ns) [20], the electron density $N_e = 5 \times 10^{14}$ cm$^{-3}$, at which the electron attachment to molecules
becomes dominant and the density of negative ions rapidly grows, is much higher than that of electron avalanches preceding a natural breakdown. In this range, discharge between the electrode and LFP, electrons avalanches and streamers heat up plasma and change filament plasma dynamics. The filament can maintain an electrode potential necessary for the breakdown development and can become a leader, which leads to the filament-triggered breakdown.

III. NUMERICAL MODELING OF DYNAMICS OF LASER FILAMENT PLASMA IN EXTERNAL ELECTRIC FIELD

Dynamics of laser filament plasma in an external, near corona threshold field was studied by 2D3V particle-in-cell (PIC) simulation including elastic collisions e − M, e − e (M means molecules) and the kinetic approach following [54] with variable particle weights. The electron-electron collisions were included because they are dominant if the electron density exceeds $10^{14}$ cm$^{-3}$. Only five sorts of particles have been included: electrons, negative oxygen ions, positive oxygen and nitrogen ions, and meta-stable nitrogen molecules. Assuming the rapid association, $A + A + B^- \rightarrow A_2 + B$ where $B$ is an $O_2$ or $N_2$ molecule, we attributed the ions to $O_2^-$ and $O_2^+ = X^+$ and $N_2^+ = Y^+$. The weight of particles was calculated in the kinetic cells according to the balance equation [20]. For the electron part
FIG. 2: (Color online) Transverse filament images after (a) 6.5 m, (b) 7.9 m, and (c) 9.2 m propagation from the spherical mirror; (d) calculated longitudinal distribution of electron density for a laser pulse with a peak power $P = 100P_{cr}$ and 70 fs pulse width in air. [34]

$$\frac{dN_e}{dt} = \left[ \alpha_{ion}^X (E/N) N_X + \alpha_{ion}^Y (E/N) N_Y \right] N_e + \pi_P N_Y^2 - \left[ \beta_{DR}^X N_X + \beta_{DR}^Y N_Y \right] N_e - \nu_{Attach} N_X N_e$$

where $\alpha_{ion}^M$ is the ionization rate of $M$ molecule calculated with the sampling electron distribution in PIC, $\pi_P$ is the rate of Penning reaction; $\beta_{DR}^M$ is the dissociative recombination rate for $M$ ions, and $\nu_{Attach}$ is the electron attachment rate. In the ion part, the ion-ion recombination of positive and negative ions [20] was included as well. The UV emission was calculated using the simplified 2 level approximation with the sampling electron distribution from the PIC. In the present calculation the Penning and radiation effects were small.

We used Buneman scheme and calculated the electric field using pair of Maxwell equations:

$$\frac{\partial \vec{E}}{\partial (ct)} = \vec{\nabla} \times \vec{B} - 4\pi \vec{j}$$
$$\frac{\partial \vec{B}}{\partial (ct)} = -\vec{\nabla} \times \vec{E}$$
with the initial conditions found from a solution of Poison equation

\[
d^2 \phi / dx^2 = 0; \quad -\nabla \phi |_{\text{boundary}} = \vec{E}
\]

The simulation geometry is shown in Fig. 3. Results of the simulation for three different filament plasma shapes are shown in Fig. 4, 5, and 6.

![Simulation diagram](image)

**FIG. 3:** (Color online) Simulation area. The initial field is directed from the left to the right.

One can see that electric field strength in the case of needle filament plasma approaches to the critical field for the electron runaway [39]. As seen in Fig. 7, the ionization wave are formed in the both sides of the filament plasma and are typical both for the negative and positive streamers.

**IV. TRIGGERING AND GUIDING HIGH-VOLTAGE DISCHARGES (DISCHARGE CONTROL)**

In 1995, Zhao et al. [21] reported the laser triggered discharges using laser pulses with the pulse length of 200 fs. After that, Pepin et al. [25] succeeded in triggering and guiding large-scale leader discharges over distances of 3 m with a megavolt impulse using sub-joule ultrashort laser pulses. From 2002, Teramobile group has reported on long gap laser-triggered discharges using the filament plasma produced by mobile terawatt laser system [27]. They have demonstrated the laser triggered discharges in 4.5 m gap length.
FIG. 4: The $x$-(a) and $y$-(b) components of electric field near the laser filament plasma of cylindrical shape. Diameter of the filament is 0.5 mm. $E_x(0) = 29 \text{kV/cm}$, $a$ is the normalized field strength; $a(0) = 0.02$. [41]

FIG. 5: The $x$-component of electric field near the laser filament plasma of elliptical shape. The filament is $0.3 \times 1 \text{ mm}^2$.

with 2.2 MV negative impulse voltage using slightly focused femtosecond terawatt laser pulses [55]. They also tried to initiate the laser triggered natural lightning, and, finally, observed the sine of laser-triggered cloud-cloud lightning [35]. Recently, triggering and guiding of AC high voltage discharges has been performed using Tesla coil, which is promising for
FIG. 6: Dynamics of $x$-component of electric field near the laser filament plasma of needle shape. The filament is $0.1 \times 1 \text{ mm}^2$.

FIG. 7: Electron density in the laser filament plasma of needle shape. The filament is $0.1 \times 1 \text{ mm}^2$. 
a compact high voltage source [56–58].

However, in the case of natural lightning, the electric field may increase slowly before stroke. This phenomenon resembles the dc-discharge. An upward leader induced by lightning often has the positive polarity. Therefore, the study of the triggering and guiding of dc-high-voltage discharges is important for the operation with the natural lightning.

We have reported on temporally and spatially resolved measurements of dynamics of laser filaments in a strong electric field produced by positive dc voltages up to 0.44 MV for a gap length of up to 1 m, and their effects on the breakdown [34]. A typical time-integrated UV emission of the filament plasma in the external field without the breakdown, and that with the breakdown along the filament, are shown in Fig. 8. Bright emission between the grounded electrode and filaments, which may show the electron flow, is clearly seen. Other effects of plasma non-uniformity are illustrated in Fig. 9 by time-integrated discharge images. It is clearly seen in Fig. 9 (a) that the discharge stroke hops in the transverse direction. This indicates that the discharges occur via hopping between filaments having maximum electron density [32], which is also a sign of plasma non-uniformity as shown in Fig. 2. Figure 9 (b) shows a time-integrated plasma emission taken using the UV lens. Traces of electron avalanches can be seen from a location far from the electrode in both directions toward the electrode and toward the coronae.

Figure 10 shows dependency of the breakdown voltage versus the breakdown delay time for various distances between the laser filament and the 50-mm-spherical grounded electrode at a gap length of 0.6 m. Two completely different groups of discharges are observed. In Fig. 10, the first, which is called fast mode discharge, occurs after several microseconds from the laser shot with frequently the considerable breakdown voltage reduction. The second, called the slow mode discharge, occurs after more than several hundred microseconds from the laser shot without an essential breakdown voltage reduction. In the fast mode discharge, the maximal breakdown voltage reduction is $\sim 40 \%$ from the natural breakdown voltage, whereas it is only 4–10 % in the slow mode discharge. To investigate the fast and slow mode discharges, we have performed time-resolved measurements of plasma current and light emission.

Fig. 11 (a) shows a typical electrical current waveform along with the photodiode signal of laser shot. It demonstrates the typical behavior of the streamer breakdown. The first current signal shows that the primary streamer, installed near the high-voltage electrode immediately after the laser shot, reaches the grounded electrode after 3 $\mu$s from the laser shot. The estimated streamer speed is about $10^5$ m/s, which agrees well with the results of previous streamer measurements [20, 59, 60]. The rise of the main current pulse, which is attributed to the ionizing waves and the secondary streamer [59, 60], is seen after about 100 ns from the first current signal. Therefore, one may estimate the speed for the potential wave [20, 59] as close to $10^7$ m/s.

Fig. 11 (b) shows a temporally and spatially resolved image of plasma radiation in the fast mode discharge without an essential breakdown voltage reduction. Localized emission, corresponding to the first current and being shown in Fig. 11 (a), is observed 200-300 ns before the breakdown near the grounded electrode (position A). After several tens of nanoseconds, strong local emission is also observed at 150 mm from the high-voltage
FIG. 8: (a) Filament emission without discharge at 0.28 MV voltage, and (b) discharge along the filament at 0.30 MV voltage with a gap length of 0.6 m. [34]

electrode (position B). One can see that ionizing waves correlating with bright plasma emission appear and exist in the gap between position A and B. The estimated speed of the ionizing wave is about $10^7$ m/s, which agrees well with the measurement result in Ref. [60]. Appearance of a strong emission in position B can be attributed to the leader head.

The ionizing waves repeatedly appear in the plasma channel with strong field inducing the Ohmic heating of the plasma channel if the electron attachment rate in air plasma increases with the electric field [59, 60]. This is possible if the average field exceeds the critical value for air, $<E/N> \sim (2/3) \times 10^{-20}$ Vm$^2$. The fast mode discharge appears if the first streamer induces enough electrons from the grounded electrode to start the secondary streamer [20, 59, 60]. Moreover, the fast mode discharge with a considerable breakdown voltage reduction can occur only along with an artificial leader generated by the filament. The reduction of breakdown voltage is determined by the leader length in this case. Occurrence of the leader only in the fast mode discharge and the strong fluctuation of the breakdown voltage shown in Fig. 10 reflect a short lifetime of the filament-induced leader.
FIG. 9: (Color online) Photographs of laser-induced discharges in a 1-m-long gap taken using (a) a normal lens at a voltage of 0.4 MV and (b) a UV lens and a filter (blocking: 400–800 nm) at a voltage of 0.44 MV. No discharge is occurred up to 0.5 MV without laser filaments. [34]

FIG. 10: Dependency of the breakdown voltage on the breakdown delay time at various distances between laser beams and the 50-mm-diameter spherical grounded electrode at a gap length of 0.6 m. [34]

We attribute the slow mode discharge to a weaker emission of electrons from the grounded electrode, lower than that necessary for developing of the secondary streamer. For initiating a new primary streamer, the negative and positive ions should be distant by the external field at $\delta L \sim 1$ cm [20, 60]. With an ion mobility $\mu \sim 2 \times 10^{-4}$ m$^2$/Vs in
FIG. 11: (a) Electrical current and photodiode signal of laser shot and (b) image converter camera image of a fast mode discharge along with the experimental setup with an applied voltage of 0.275 MV on a 0.4 m-length gap using the 250-mm-diameter spherical grounded electrode. The self-breakdown voltage is 0.28-0.285 MV. [34]

air, it gives a time $T_{\text{slow}} \sim \delta L/\mu E \sim 0.5$ ms for $E = 0.5$ MV/m, which is typical for the experimental conditions.
V. LFP EFFECTS ON CORONA DISCHARGES

In this chapter, we discuss the dynamics of UV emission from LFP with a high spatial and temporal resolution when the electric field strength near the electrode surface only slightly exceeds the corona discharge threshold $\sim 30 \text{kV/cm}$ [39].

V-1. Experimental setup

The scheme of the experimental setup is shown in Fig. 12. Ti:Sapphire laser pulses ($\lambda = 800 \text{ nm}, \tau = 50 \text{ fs}, \text{energy} = 84 \text{ mJ}$) were focused by a concave mirror of 10 m focal length. A negative or positive high voltage was applied on a spherical high voltage electrode (HVE) with 250 mm diameter placed at the distance of 10.4 m from the focusing mirror. A high voltage was varied between 0 kV and $+400 \text{kV}$ or $-400 \text{kV}$. The optical axis of the laser pulse was set at 5 mm, 6.8 mm or 28 mm from the HVE. The fluorescence of LFP was collected by a telescope located 20 m far from the HVE. The fluorescence was detected by a spectrometer and by an ICCD camera. UV images of LFP were taken by another ICCD camera with UV lens and a filter placed at 4 m from HVE perpendicularly to the laser axis. A still camera with the UV lens and the filter was set with a film slightly beside the UV-ICCD camera.

![Experimental setup](image)

FIG. 12: (Color online) Experimental setup for investigation of corona bursts. [39]

V-2. Experimental results

V-2-1. Negative polarity

Images illustrating the voltage dependence and the temporal behavior of the negative corona at different voltages are shown in Figs. 13 and 14 in the presence of the LFP
positioned at 5 mm or 6.8 mm from the HVE surface. The corona discharges are caused by the LFP already at \( U = -200 \text{ kV} \), and become stronger at the higher applied voltages up to \( U \sim -400 \text{ kV} \). Visibly, there was no corona discharge in the absence of the LFP at any voltage applied up to \( U \sim -400 \text{ kV} \). The LFP induced corona discharges exhibit a complicated dynamics and spatial structure.

![UV-still images of the negative corona induced by LFP positioned at 5 mm from the HVE surface at several applied voltages from \(-100 \text{ kV}\) to \(-400 \text{ kV}\). [39]](image)

When the LFP appears below the HVE, the filament electrons move outwards. The recombination of the LFP is so rapid that the ions from the plasma cannot reach the electrode to cause the secondary emission: ion mobility is about \( \mu = 2.1 \text{ cm}^2/\text{V/s} \) [20] and the velocity is about \( 10^5 \text{ cm/s} \) at \( E \sim 50 \text{ kV/cm} \) and is surely too low for that: the process ceases in 1 \( \mu \text{s} \) as shown below. However, the LFP may affect the corona discharge via the UV flash which appears just after the creation of LFP and the consequent electron emission from the electrode. The latter assists the discharge developing between the LFP and the electrode.
Assuming that the electrode electric field does not change much along the LFP in the beginning, one can get the filament filed as $\sim 60$ kV/cm in the experimental conditions using the conventional estimation: $E_f = -\Lambda U_0 \cdot R_0 / R_f^2$, where $U_0$ is the electrode potential, $R_f$ is the filament position from the center of the electrode, $\Lambda$ is the geometrical field gain: for a cylindrical filament $\Lambda = 2$. In the absence of inelastic collisions, the LFP electrons would have acquired the average energy, $\bar{\varepsilon} \sim \sqrt{M/3m(eEl)}$, with $l$ the electron free-path and $M$ the ion mass. For the field in the experiment this value is about 1 keV. Therefore under the experimental conditions, an LFP electron is accelerated and loses its energy for the ionization and excitation till it forms a negative ion in the reaction: $O_2 + e \rightarrow O^- + O (\varepsilon_{\text{max}} \sim 8 \text{ eV})$. Then, the strong radiation ceases. The intensity of UV flashes depends on the field strength [38–43] and plays an important role in the LFP dynamics.

The UV radiation from the LFP may initiate the electron emission from the electrode. This results in the rapid discharge between the LFP, becoming a virtual anode, and the cathode. This can be seen in Figs. 13 and 14. If the breakdown appears swiftly, the electron density in LFP is high and the LFP acquires the cathode potential because its capacity is much lower than that of the cathode. As a result, the field at the LFP surface drastically changes: $E_f = -U_0 / D$. Since $D \sim 200 \mu \text{m}$ the field may become very high, $\sim 10 \text{ MV/cm}$. Apparently the real field is smaller because the electron density in LFP decreased so rapidly that the LFP cannot maintain the whole electrode potential. Nevertheless such a field is strong enough to provoke the streamer developing outward from the LFP.

Dynamics of the corona discharge in the case of $U_0 = -400$ kV is given in Fig. 14. One can see the two distinct regions. Figure 15 shows the temporal and spatial evolution of UV emission at the axis perpendicular to the laser filament through the center of the HVE obtained from the results shown in Fig. 14. As shown in Fig. 15, the UV emission...
spreads over 200 mm far from the electrode for about 100 ns. On the other hand, the emission at the filament position continuously increased in the first 100 ns. The velocity of the UV emission front was estimated to be 0.6 % of the speed of light. As seen from Figs. 14 and 15, the strong streamer radiation at a distance quite far from the electrode lasted for \( \sim 150 \) ns, and the post-plasma recombination radiation emitted for \( \sim 0.5 \) \( \mu \text{s} \). Such a long emission can be produced by a hot plasma; in our case the best fitting gives \( T_e \sim 10 \) eV and \( N_e \sim 10^{15} \text{ cm}^{-3} \) (from local kinetic simulations [20]). This velocity agrees well with the velocity of the streamers [19]. The two distinguished regions may just reflect (i) the radiation of the streamer heads, far from the electrode, and (ii) the radiation of recombining LFP.

The voltage dependence and temporal evolution of the UV spectra in the vicinity of LFP detected by the telescope is presented in Fig. 16 for the 313.6 nm, 315.9 nm, and 337.1 nm nitrogen lines (\( \text{N}_2 : \text{C}^3\Pi_u \rightarrow \text{N}_2 : \text{B}^3\Pi_g \)). The temporal evolution of the peak signal height of \( \text{N}_2 \) fluorescence well corresponds to that of the UV emission in the vicinity of LFP as seen in Fig. 15. One can find the strong dependence of the UV spectra on the external voltage. These UV spectra can be used for the electric field diagnosis.

**V-2-2. Positive polarity**

We have also tested the positive corona as shown in Fig. 17 and 18 upon positioning the LFP at 5 mm from the HVE surface. Again in the absence of the LFP, we observe no corona discharge. However, the LFP drastically changes the corona dynamics.
FIG. 16: (Color online) Fluorescence spectra of N$_2$ molecules and peak signal height of the N$_2$ fluorescence for the wavelengths of 313.6 nm, 315.9 nm, and 337.1 nm in the vicinity of the HVE and filament when the optical axis of the laser beam is set at 5 mm from the HVE surface for the negative polarity. (a) Fluorescence spectra of N$_2$ molecules at several applied voltages and background spectra (shown as BG) taken at a voltage of $-400$ kV without the LFP, (b) peak signal height of the N$_2$ fluorescence over background spectra as a function of applied voltage, (c) peak signal height of the N$_2$ fluorescence over background spectra as a function of the gate delay time of the ICCD camera with the applied voltage of $-400$ kV. The gate width and delay time of the ICCD camera for the experiments shown in (a) and (b) are 500 ns and 0 s, respectively. The gate width of the ICCD camera for the experiments shown in (c) is 50 ns. [39]
FIG. 17: (Color online) UV-ICCD images of the positive corona induced by LFP positioned at 5 mm from the HVE surface at several applied voltages from 100 kV to 400 kV. The gate width and delay time of the ICCD camera are 500 μs and 0 s, respectively. The gain of the ICCD camera is 250 for 100/300 kV and 50 for 400 kV. The maximal values of color bar are 3,000 for 100 kV/200 kV and 30,000 for 300 kV/400 kV. [39]

In the figures, one can see a scenario that is expectedly different from the scenario for the negative streamer. In this case one can expect a stronger effect of the LFP because the electrons from the plasma could reach the electrode: the necessary time is about 20 ns since electron mean velocity in air at the field strength $E \sim 30$ kV/cm is not high, about $2 \times 10^7$ cm/s [20]. However, the electron evacuation must be rapidly ceased when $U_0 R_0 / R^2 \sim U_f / D$ where $R$ is a distance between the center of HVE and the filament, and $U_f$ is the LFP potential; this process results in the strong initial UV emission from LFP. In the case of the positive polarity, the UV emission cannot provoke a discharge between the LFP and electrode; the UV emission may only pre-ionize air to stimulate the positive streamers as seen in Fig. 18 where the snapshots of the positive corona are presented.

VI. RUNAWAY ELECTRONS

In this chapter, we present and discuss the effects of the electron runaway in positive high-voltage-impulse discharges studied via detecting hard x ray spectra [61]. LFP is used to localize the source of runaway electrons. We will not consider the relativistic avalanches provoked by the cosmic rays in the atmosphere [62].
The effect of runaway electrons in gas discharges occurs in rather strong electric fields. For an electron to run away, it has to acquire kinetic energy from a field greater than the energy it lost by ionization, excitation, and dissociation of air molecules. The threshold field strength, $E_{RW}$, for $\sim 1-10$ eV energy electrons in the normal-pressure air is about $E_{RW} \sim 320$ kV/cm. However, the maximum field strength in the atmosphere is approximately $\sim 29$ kV/cm [20]; the typical field strength in a thunderstorm is $\sim 1$ kV/cm [63]. There is another way of allowing electrons to run away by increasing their free paths by reducing the air density, increasing their initial energy (cosmic rays), and/or by preheating the electrons. The joint effect of a strong electric field and preheated plasma likely results in the formation and acceleration of electrons in air at lower electric field strengths.

In our experiments, brass balls of 250 mm diameter were used as the high-voltage electrode (HVE) and the grounded electrode with a gap length of 0.45 m. Positive impulse voltage, which reached its maximum at $\sim 0.6$ μs, was applied on HVE. The charging voltage (CV) applied at the impulse generator was set at 650 or 750 kV. Ti:sapphire laser pulses with 70 fs duration and 90 mJ energy were focused by a concave mirror of 10 m focal length, placed at the distance of $\sim 10$ m from the electrodes, and LFP was produced in the gap. Cylindrical detectors, each composed of a NaI (Tl) scintillator and a photomultiplier tube (PMT), were used for measuring x rays signals from the sparks. The detectors were placed at about 3 m from the electrodes perpendicularly to the laser axis.

As shown in Fig. 19, the breakdown plasma channel is strongly convoluted and a lot of streamers generating from HVE are observed without using LFP. On the other hand, when LFP was produced at 5 mm from the HVE, the breakdown plasma channel is rather straight, and there is less number of streamers generating from HVE. This is also confirmed by detector signals showing the dark current (a small current before the breakdown) presented in Fig. 20. The voltage just before an x-ray burst was about 550 kV, and the electric field strength near the grounded electrode, according to [64], was about 10 kV/cm. Therefore, streamers resulting in the dark current can propagate only from the HVE.

More than 50% of all the discharges without LFP were accompanied by x ray bursts.
As shown in Fig. 20, the bursts, which should originate from the Bremsstrahlung radiation generated by runaway electrons in the positive electrode, always occur before the breakdown. The Bremsstrahlung radiation was always synchronized with the beginning of the dark current.

To evaluate the spectrum of x-rays, we used the absorption technique [49]: x-rays were detected with Pb or Al shields in front of the detector. The depletion of the signals with the attenuator thickness is shown in the inset of Fig. 21. The experimental data are fitted with the calculated results using a Monte Carlo-type code (Geant4) [65]. In the calculation, we assumed an x-ray energy distribution $\sim \exp(-\varepsilon_x/\varepsilon_{x0})$ with an exponential shape, where $\varepsilon_x$ is the x-ray energy and $\varepsilon_{x0}$ is a fitting parameter. The best fitting energy, $\varepsilon_{x0}$, lies in the range of 50–100 keV. The main graph of Fig. 21 shows calculated backward x-ray spectra from a massive brass target irradiated by monoenergetic electron beams with different energies. Each spectrum has also been fitted by an exponent of $\sim \exp(-\varepsilon_x/\varepsilon_{x0})$. By comparing these values of $\varepsilon_{x0}$ with that determined in the inset, one can see that the electron energy before interaction with the brass must be approximately 500–700 keV, which is close to the applied potential. These results suggest that the position of the source of runaway electrons should be near the surface of the negatively biased electrode.

The second evidence of the position of the runaway electron source was found with the use of the LFP before the breakdown as in [34, 39]. A laser pulse was shot at 0.5 ± 0.1 μs before voltage breakdown, which is the time that corresponds to the beginning of an
x-ray burst in the case of discharges without the laser irradiation. The formation of LFP at 5 mm from the HVE stopped the x-ray burst in 100% of the cases, as shown in Fig. 20, whereas LFP 5 mm from the grounded electrode did not strongly affect the burst. As shown in Fig. 20, an essential dark current were not observed. On the other hand, LFP may affect the propagation of avalanches and streamers starting from the HVE, as discussed in [39], making the ionization wave [34, 60] weaker during the development of streamer discharge. We accept the following scenario for the runaway formation in the case of the positive polarity. A positive streamer propagates from the HVE to the grounded electrode and initiates a weak discharge (see also [19]) generating a plasma channel: the small current growth before the x-ray burst is always seen, as shown in Fig. 20. The plasma channel in the vicinity of the grounded electrode is heated, forming a short, pin-shape leader. Such a leader with a considerable number of $\sim 1$ keV electrons can be a source of the electron runaway resulting in the x-ray burst from the opposite electrode. When the LFP was ignited, the small dark current decreased and no pin-shape leader is formed, which also supports the above scenario.

2D PIC simulations, including elastic collisions and plasma kinetics, show the possi-
FIG. 21: (Color online) Calculated backward x-ray spectra from a brass target produced by electron beams with energies ($\varepsilon_e$) of 300 keV, 500 keV, 700 keV, and 1.0 MeV. The inset is the measured depletion of x-rays after attenuators with a CV of 750 kV, shown by solid circles (T$_{room}$: 15–18 centigrade, RH: 40 ∼ 56%, P$_{atm}$: 992–1000 hPa) and triangles (T$_{room}$: 14–15 centigrade, RH: 45-58%, P$_{atm}$: 985–993 hPa), and calculated curves for several fitting parameters of x-ray energy ($\varepsilon_{x0}$). [61]

bility of the formation of such a leader with electron runaway [61]. The runaway electrons are likely produced from preheated, ∼ 0.1-1-mm-size leaders with the electron density of ∼ 10$^{14}$ cm$^{-3}$. The electrons can then be accelerated even by low-strength electric fields, $E < 30$ kV/cm.

VII. SUMMARY

The kinetics and dynamics of the LFP in external electric fields of various configurations are studied.

We have made time-resolved measurements of dynamics of plasma of laser-induced filaments in a strong external electric field for various field conditions and geometry. Two different discharge modes, fast and slow, have been found. Considerable reduction of breakdown voltage has been observed only in the fast mode. The non-uniform distribution of electron density along the filament strongly results in the discharge dynamics. The potential reduction appears when filaments induce the leader maintained by strong non-uniform field. We anticipate that the high predictability and well-determined position of the laser-filament
induced leader open a way of comprehensive study of leader-streamer physics.

We have performed the imaging and spectral measurement of UV from laser-filament plasma in an external field of different polarities produced by the spherical electrode. The field dependency of the UV emission has been shown to be useful at least for the relative field measurements (detection of field distribution). The discharges between the LFP and electrode plays the dominant role, and we have observed the long (tens of centimeters) positive and negative corona induced by the laser-filament plasma initiated by a femtosecond laser pulse in the vicinity of an isolated electrode without an initial corona. We have detected the different stages of the corona bursts: the initial UV flashes from the LFP; the UV flashes from discharge between the LFP as a virtual electrode and the real electrode; and UV from the streamer discharges. For the negative polarity, the UV emission peak observed at 15 cm far from the filament can be explained by the streamer developing at the velocity 0.6% of the speed of light.

The effects of electron runaway in positive high-voltage-impulse discharges have been investigated using the LFP to localize the source of runaway electrons. By measurement of the characteristics of x-ray bursts with and without LFP and via the numerical simulations, we have found that (i) sources of electron runaway are localized at the negative polarity electrodes even if this electrode is grounded. (ii) The runaway electrons in the discharges are likely produced from preheated, \( \sim 0.1-1\)-mm-size leaders with the electron density of \( \sim 10^{14} \text{ cm}^{-3} \), and formed on the surface of the electrode. The electrons can then be accelerated even by low-strength electric fields, \( E < 30 \text{ kV/cm} \). (iii) Those electrons acquire kinetic energies close to or probably even exceeding the potential difference between the electrodes resulting to produce the strong hard x rays.

The obtained results are very useful not only for understanding the filament physics but also for applications of filament such as discharge control, laser lightning rod, and remote measurement of electric field. In order to realize such applications, the control of filament is important. It was demonstrated that filaments can propagate well in adverse atmospheric conditions such as turbulence [66], foggy [67] or rainy [68] atmosphere partly due to the self-healing effect. However, precise control of the filament plasma position, which may depend on atmospheric conditions, has yet to be achieved. Thunder lightning can be occurred with much lower electric field (\( \sim 1 \text{ kV/cm} \)) than the theoretical value, but its mechanism is still unclear. The study of runaway electrons is surely useful for understanding the high energy physics in the atmosphere, which can lead to complete understanding of mechanisms of lightning. Recently, the runaway electron avalanche model, in which the runaway electron avalanche may pre-ionize air and initiate lightning, has been proposed to explain the phenomena. The necessary conformity of laboratory experiments and the field observation requires its further development.

In addition, huge amount of electricity is transported by using air as an electrical insulator. Since many electric power apparatuses use the air as an electrical insulator, discharge plasma in air is one of key issues in electric power industries. If we can simulate discharge characteristics, we can design and manage electric facilities far more efficiently. The LFP is the very attractive and flexible instrument for investigating plasma physics in air.
References

The femtosecond laser filamentation is commonly understood as the result of the dynamic balance between optical Kerr effect induced self-focusing and plasma defocusing effect. When the balance of these two processes is achieved, the laser intensity inside filament is not only stabilized along the propagation distance, but also almost invariant with the increase of the input laser energy. This special phenomenon is named intensity clamping. The intensity clamping represents one of the fundamental characteristics of the filamentation phenomenon. It governs the major evolution dynamics of the laser pulse propagation during the filamentation and impacts extensively the applications of the filamentation. This paper summarizes the main research results about the intensity clamping, including current understanding about the underlying mechanism of the intensity clamping, experimental evidences proving the intensity clamping and some recommended approaches to measure the clamped intensity. The paper also introduced some impressive effects brought by the intensity clamping in various applications, such as high stability of the fluorescence signal in remote sensing, beam-cleaning in short pulse production, etc. The effects are in fact in contrary to the common sense about the outcome of nonlinear interaction, which would be unstable under perturbation. Furthermore, the paper presents some methods to increase the clamped intensity inside the filament. At the end, some other effects that may arrest the beam collapse during the filamentation are briefly discussed. These effects mainly include the diffraction, the dispersion and high order Kerr effect.

DOI: 10.6122/CJP.52.465 PACS numbers: 42.65.Jx, 52.35.Mw, 42.25.Bs

I. INTRODUCTION

Femtosecond filamentation is a unique nonlinear optical phenomenon [1–7], during which ultrashort laser pulse could propagate over long distance with high intensity, overcoming nature diffraction and dispersion. Since the laser intensity is high enough, the optical medium will be ionized and a long plasma channel will be left behind the laser pulse. This plasma channel is often referred to as a filament. In condensed matters, the length and the diameter of the filament are about several millimeters and a few micrometers, respectively. While in gas media, such as air, the length of the filament may reach
hundreds of meters and the diameter is in the scale of a hundred micrometer. The suggested application of the filamentation ranges from lightening control, to remote sensing, to pulse compression, to weather control and THz generation, etc.

During the filamentation, plenty optical processes are involved, including dispersion, diffraction, self-focusing, ionization, Raman excitation, self-phase modulation, four wave mixing, Cherenkov radiation, etc. On the other hand, the scales of the space and time are widely spanned in the study of filamentation. For example, in time, the shortest laser pulse duration may reach sub-cycle, while the life time of the plasma channel could extend up to many microseconds. The studied electromagnetic wave frequency also covers broad range from UV, to visible, to IR and to THz. Furthermore, the filamentation can be observed in extensive transparent optical media such as liquids, glasses and gases. Since its application in atmosphere is particularly attractively, the dynamics of the interactions of ultrafast laser with aerosol, dust and turbulence are also important issues in the course of filamentation. All these concerns complicate the research about the filamentation. However, the understanding about the intensity clamping, a profound phenomenon occurs during the filamentation, provides a key to solve these challenges.

It has been widely accepted that the filamentation is mainly induced by two counteracting effects: one causes the contraction of the laser pulse during the propagation, while the other will lead to the diffraction of the beam. When the balance of these two processes is achieved, the laser pulse will neither diffract significantly nor collapse catastrophically, i.e., propagating in a self-guided form. This is the most simplified scenario of the filamentation process. Due to this balance, the laser intensity inside filament is not only stabilized along the propagation distance, but also almost invariable with the increase of the input laser energy. This special phenomenon is named intensity clamping. The intensity clamping represents one of the fundamental characteristics of the filamentation phenomenon and impacts extensively the applications of the filamentation. This paper is then aimed to give a brief review about the important research results about the intensity clamping.

II. PROOF OF INTENSITY CLAMPING

It is well known that the whole filamentation process starts with laser beam self-focusing induced by the intensity dependent refractive index, which is written as \( n = n_0 + \Delta n_{kr} \). Here \( n_0 \) is the linear index of refraction and \( \Delta n_{kr} = n_2 I \), the Kerr nonlinear index of refraction, \( n_2 \) and \( I \) being the coefficient of Kerr nonlinear index of refraction and the local intensity, respectively. For the self-focusing to occur, the transverse spatial intensity distribution of the pulse across the wavefront should not be uniform. Assuming a Gaussian CW beam, its intensity decreases radially from the center to the edges. Since the phase velocity is given by \( c = c_0 / n \) where \( c_0 \) is the light speed in vacuum, the central part of the beam propagates slower than the rest giving rise to a concave wavefront and the beam self-focuses.

However, different views have been brought forward to interpret the dominant effect balancing the self-focusing. Dated back to 1960s, when the filamentation was experimen-
tally observed as a serial of damage spots inside glasses by using nanosecond laser pulse, the efforts of retrieving the counteracting effect to self-focusing was limited to condensed matters due to the available low laser power. The masking of optical breakdown in condensed matters using long laser pulses however impeded the advancement of the understanding of the ‘filament’, and restricted the perspective for applications. For example, the role of plasma generation during the formation of the filament has not been extensively taken into account although it had been brought forward by Bloembergen in the early seventies [8, 9]. Owing to the development of the chirped pulse amplification (CPA) technique [10, 11], it has been possible to achieve femtosecond (fs) laser pulses with terawatt (TW) level peak power. Nonlinear phenomena during propagation of such intense ultrashort laser pulses become much more pronounced than for longer pulses. It is not only due to the high peak power, but also because of the short pulse duration that avoids the conventional optical breakdown [12–18], in which case the medium gets totally ionized through collision processes induced by the long pulse. Moreover, the filamentation could be conveniently observed in gas media [19], which normally require a few gigawatts (GW) laser power to exceed the self-focusing critical power. This revealed new attention to the research on the filamentation phenomenon.

The inspiring experiments were carried out to demonstrate the generation of filamentation over several tens of meters by propagating near infrared (∼800 nm) fs laser pulses [20–22]. Particularly, the researchers in Michigan University measured the pulse energy inside the generated filament in air. It was performed by reflecting the laser pulse at grazing angle of a glass slide, thereby avoiding the damage to the glass. The obtained results showed that the pulse energy contained inside a filament is roughly constant. They proposed that the defocusing effect of the self-generated plasma during the filamentation was the counteracting effect to balance the self-focusing. Numerical simulation was also performed based on this idea. The laser intensity was found to be clamped as a result of the plasma defocusing effect as shown in Fig. 1.

![Calculated intensity during the filamentation](image)

FIG. 1: Calculated intensity during the filamentation (solid line) and the linear propagation (dashed line), respectively. From [20].

In 1998, Brodeur and Chin stated that in order to explain the asymmetry broadening of the supercontinuum spectrum generated by the filamentation in condensed matters, the
contribution of the plasma formation to the refractive index has to been included in the self-phase modulation modeling as summarized in Fig. 2 [23]. They have further found the close correlation between the maximum blue frequency shift of the supercontinuum and the bandgap energy needed for the multiphoton excitation of electrons into the conduction in various condensed matters [24]. The results confirmed the crucial role of the plasma generation in sustaining the filament.

![Supercontinuum spectrum](image)

**FIG. 2:** Supercontinuum spectrum measured during filamentation (solid line) and obtained by numerical simulation with (dashed line) and without (dotted line) taking into account plasmas generation, respectively. From [23].

Since then, the essential role of plasma defocusing that leads to intensity clamping has become a hot topic in the community. It is worth noting that S. L. Chin’s group in Laval University has made tremendous contribution to the understanding of the intensity clamping.

Plasma generation takes place as soon as the laser intensity at the self-focus is high enough to generate a significant amount of free electrons in the medium. In fact, the major fundamental physics of filamentation is the same in all optical media, be they gases, liquids or solids. The difference lies in the detail of free electrons generation. In gases, it is tunnel/multiphoton ionization of the gas molecules inside the self-focal volume resulting in the plasma [25]. In condensed matters, it is the excitation of free electrons from the valence to the conduction bands [23] followed by inverse Bremsstrahlung and electron impact ionization [2] before the short pulse is over. The well-known type of optical breakdown of the medium (generation of a spark) by longer laser pulses in the picosecond and nanosecond regimes does not occur in the femtosecond self-focusing regime because there is not enough time to sustain cascade (avalanche) ionization. For example, at one atmospheric pressure, the mean free time of electron collision is \( \sim 1 \) ps. This time is longer than the fs pulse duration so that only tunnel/multiphoton ionization, an ‘instantaneous’ electronic transition process, is responsible for the generation of free electrons [25] even if the full pulse is
involved in the self-focusing. In condensed matters, some cascade ionization will contribute to the total number of free electrons. Its contribution strongly depends on the geometrical focusing condition. However, even in the case of extremely strong external focusing, not many cycles of collision can be involved, and it is too little to induce total ionization [21]. That is to say, in both gases and condensed matters, the plasma density induced by femtosecond laser pulses during self-focusing is only a tiny fraction (about $10^{-3}$) of the neutral density [23, 26].

Considering the ionization rate in gases when the filamentation takes place, it is generally written as

$$\frac{\partial N_e}{\partial t} = \sigma I^m (N_0 - N_e),$$

where $N_e$ denotes the free electron density inside the filament, $\sigma$ and $I$ represent the ionization cross section and the laser intensity, respectively. $N_0$ indicates the neutral molecule density. Because tunnel/multiphoton ionization is a highly nonlinear process and the electron density increases very rapidly with intensity, in Eq. (1) we approximate such an increase as being governed by an effective power law, where $m$ is the effective nonlinear order of ionization. In air, $m$ is about 8 [27]. Because $N_e \ll N_0$, Eq. (1) could be simplified as

$$N_e = N_0 \beta I^m,$$

(2)

$\beta$ is a proportional coefficient taking into account the cross section and temporal integral. On the other hand, the refraction index change due to the plasma generation can be approximated as

$$\Delta n_p = -\frac{\omega_p^2}{2\omega_0^2} (\omega_0, \text{the central frequency of the pulse})$$

(3)

Here the plasma frequency is given by $\omega_p = \sqrt{\frac{e^2}{\varepsilon_0 m_e N_e}}$, where $e$ and $m_e$ are the charge and mass of the electron, and $\varepsilon_0$ is the permittivity of free space. The effective index of refraction during the filamentation is thus:

$$n = n_0 + \Delta n_{kr} + \Delta n_p = n_0 + n_2 I - \frac{e^2}{2\varepsilon_0 m_e \omega_0^2} N_0 \beta I^m.$$  

(4)

Qualitatively, it means that the free electron term would quickly catch up with the Kerr term until they are equal; i.e. until $\Delta n_{kr} + \Delta n_p = 0$. At this point, Kerr self-focusing balances free electron defocusing. The laser beam, having now an index of refraction $n_0$, propagates at the linear speed $c$. There is no more focusing and the intensity is highest at this balancing point. This is the condition of intensity clamping. That is to say, during self-focusing of a powerful femtosecond laser pulse in an optical medium, there is a maximum intensity that self-focusing can reach. According to the concept of Eq. (2), Kasparian et al. has estimated that in air the clamped intensity the filamentation by 800 nm is around $5 \times 10^{13} \text{ W/cm}^2$ [28]. By substituting the wavelength dependent $n_2$, $\beta$ and $m$, the estimated
clamped intensity at 400 nm and 267 nm are $1.5 \times 10^{13}$ W/cm$^2$ and $3 \times 10^{12}$ W/cm$^2$, respectively [29].

Soon afterwards, experimental evidences of intensity clamping were demonstrated by S. L. Chin’s group. In 2000, Talebpour et al. found that the fluorescence spectrum from the excited species inside the filament has little contribution from the plasma continuum and the line broadening was less than that of the spectra radiated from a plasma generated by a long pulse [30, 31]. They concluded that the plasma density does not exceed some limiting value as a result of the defocusing by the electrons resulting from multiphoton ionization and the involvement of high order nonlinearities. Beck et al. advanced the work in this direction [32]. As indicated in Fig. 3, they studied the peak intensities of the strongest band heads of two band systems of N$_2$ fluorescence at 337 nm (open squares) and 391 nm (solid circles) as a function of the input pulse energy. The data were obtained at 0.63 Torr, 400 Torr and atmospheric pressure, respectively.

FIG. 3: Nitrogen fluorescence signal as a function of input laser energy at (a) 0.63 Torr, (b) 400 Torr and (c) 760 Torr. From [32].

In Fig. 3, the interpretation of the fluorescence signals as a function of the input laser energy at 0.63 Torr was referred to as the “vacuum case” since it is consistent with the geometrical focusing of the laser pulse without any deformation. The change in its slope in Fig. 3(a) is due to the depletion of neutral molecules in the focal volume. However, the characteristic change in slope of the band head strengths at high pressures (Fig. 3 b, c) occurred at a significantly lower pulse energy than in the “vacuum case”. The explanation given is such that the slope changing points at high pressures indeed correspond to the critical power of self-focusing. For higher laser energy, the filamentation takes place and the laser intensity is clamped. Therefore, the fluorescence signal change are mainly associated with the increase of the volume of the plasma column, but not the enhancement of the laser intensity which would give rise to much more steeper slope of the signal increase. Andreas et al. also explained the difference of two settings in energies of intensity clamping at 400 Torr and 760 Torr by the pressure dependence of $n_2$. Since $n_2$ is proportional to the medium density, the critical power for self-focusing will be inverse proportional to the gas
Further experimental evidences of intensity clamping were revealed by Liu et al. in condensed matters [33]. In this work, the dependence of the maximum positive frequency shift of the supercontinuum generated by the filamentation on the input laser energy. The results are demonstrated in Fig. 4 by using water as an example. It was found that the maximum frequency shift remains constant at pulse energies that generate single and multiple filamentation. The constant shift is due to the clamping of the peak intensity inside the filaments. The suggested analyzing procedure is the following.

\begin{equation}
\Delta \omega(z, t) = -\frac{\omega_0 z}{c} \frac{\partial n}{\partial t} - a \frac{\partial I}{\partial t} + b I^m (\text{after substituting Eq. (1)})
\end{equation}

\begin{equation}
= -a I_0 \frac{\partial f(t)}{\partial t} + b I_0^m f^m(t).
\end{equation}

$I_0$ is the peak intensity and $f(t)$ is the temporal shape function. $c$ is the speed of light in vacuum, $z$ is the propagation distance in the medium, $a = n_2 \omega_0 z/c$ and $b = \frac{e^2}{2\varepsilon_0 m c^2} N_0 \beta$ are positive and independent of time. The first summand in Eq. (7) represents a frequency shift due to the non-linear refractive index $n_2$ of the material, i.e. the interaction of the light with the bound electrons. If $n_2$ is positive, lower frequencies, red-shift $\Delta \omega_-$, are created in the leading edge and higher frequencies, blue-shift $\Delta \omega_+$, in the trailing edge of the pulse. The second summand appears due to plasma generation via multiphoton excitation in the condensed matters, i.e. the interaction of the light with free electrons, and causes
a blue-shift of the spectrum only. Note that the two summands have a different power dependence on the peak intensity $I_0$. Thus, the maximum blue frequency shift is expected to be dominated by the influence of the term arising from the non-linear index of refraction at low intensities and by the plasma contribution at high intensities, i.e.:

$$\Delta \omega_{+,\text{max}} \propto \begin{cases} -I_0 \min_t (\partial f(t)/\partial t) & : \text{at low peak intensities} \\ I_0^m & : \text{at high peak intensities} \end{cases} \quad (8)$$

where $\min_t (\partial f(t)/\partial t)$ denote the minimum value of the time derivative of the temporal shape function. One would expect according to Eq. (8) that the maximum frequency shift of the supercontinuum spectrum on the blue side is highly sensitive to changes in the peak intensity. Hence, constant frequency shift depict in Fig. 4(b) eventually reveals clamped laser intensity inside filament.

III. MEASURING CLAMPED INTENSITY

Fig. 3 and 4 represents qualitatively interpretation of the intensity clamping. Nevertheless, quantitative characterization of the laser intensity is essential not only for the study of intensity clamping, but also for understanding the underlying dynamic of the filamentation process. Due to the fact that the high laser intensity inside the filament is unsustainable by conventional measuring instruments, precise measurement of the spatio-temporal intensity distribution of the pulse in the course of the propagation is difficult. The interpretation of laser intensity still relies on numerical simulation to a large extent [1–7].

Different methods have been developed to measure the laser intensity inside a filament. In air, it could be roughly estimated by calibrating the grey level of the burn spot left by single-shot pulse on burn paper [34]. Alternative ways of determining the intensity inside a filament are offered by the observation of nonlinear interaction output outside the filament. For example, Lange et al. have sent a filamentating pulse into a noble gas cell and through investigating the cut-off frequency of the high order harmonic spectrum generated inside the noble gas cell, a value of $4.5 \times 10^{13}$ W/cm$^2$ was obtained for the laser intensity [35].

Another type of means is to make use of Eq. (2). Since $\beta$ and $m$ are constants for an individual medium and can be obtained in preparation experiment, the free electron density is the key information needed to be known in order to interpret the laser intensity inside the filament. Shadowgraph and holograph are two basic techniques to retrieve the free electron density via the measurement of the refractive index variance [36–38]. For example, Chen et al. has measured the free electron density of the filament generated in air and it is several $10^{16}$ cm$^{-3}$ [39]. In 2005, researchers at SIOM suggested so-called longitudinal diffraction technique to measure the plasma density variable inside a filament [39]. In this scheme, a probe beam was co-axially aligned with the filament. The far field diffraction pattern of the probe beam carried the information of the refractive index spatial distribution. According to Eq. (3), the free electron density is retrieved. In [39], the temporal evolution of the plasma density was even studied by this method. The above introduced methods need
a probe beam. It will complicate the experimental setup and require high quality beam alignment and very stabilized experimental environment.

Some probe-free measurement has been suggested. Liu et al. have demonstrated that the measurement of free electron density can be realized by characterizing the Stark broadening of the atomic fluorescence lines associated with the electron impact [40]. This relationship is as simple as:

\[ \Delta \lambda_{1/2} = 2\gamma \left( \frac{N_e}{10^{16}} \right), \]

where \( \Delta \lambda_{1/2} \) indicates the full width at half maximum (FWHM) of the electron impact broadening induced line width and \( \gamma \) is the electron impact parameter. Therefore, with prior knowledge of the value of \( \gamma \), one could calculate the electron density from the experimentally obtained line width. This method has been used in argon and air [40, 41]. A representative measurement result obtained for the filamentation in argon gas is shown in Fig. 5. It can be observed that the filament plasma density starts to increase from the distance of 93 cm. It reaches a plateau at 97 cm. The plasma density remains at a level of \( 6.5 \times 10^{-16} \text{ cm}^{-3} \) for 6 cm and begins to decline again from 103 cm. The plateau of the plasma density arises due to the intensity clamping phenomenon. By using the same method, Bernard et al. have investigated the clamped laser intensity as a function of the gas pressure [42]. As shown in Fig. 6, the measured free electron density is eventually proportional to the pressure, i.e. the initial neutral gas density. According to Eq. (2), it implies that the ionization probability is constant at different pressures. That is to say that the clamped intensity is independent to the gas pressure once the filamentation occurs. It is easy to understand because the intensity clamping requires \( \Delta n_{kr} + \Delta n_p = 0 \), and thus

\[ n_2 I = \frac{e^2}{2\varepsilon_0 m_e \omega_0^2} N_0 \beta I^m \]

Since the right hand and left hand sides of Eq. (7) are both proportional to the gas density \( N_0 \), the laser intensity satisfying Eq. (7) is independent on the gas density. A consequence of this phenomenon in vertical atmospheric propagation is that the filament size (diameter) will become larger and larger as the altitude increases because of the following reason. Since the critical power for self-focussing \( P_c \) is inversely proportional to \( n_2 \) and since \( n_2 \) is proportional to air density, the critical power for self-focussing increases as the pressure at higher altitude decreases. Hence, to obtain self-focussing at higher altitude, the input peak power of the pulse has to increase. But since the intensity is clamped at the value at sea level, the higher peak power of the pulse has to be contained inside a region with a larger diameter than that at sea level.

Xu et al. have studied the clamped laser intensity at various input laser peak power up to 1.5 TW [43]. The results are depicted in Fig. 7. In the experiment, three focusing lenses were used. Fig. 7 indicates that the intensity clamping phenomenon exist for TW level laser pumping. Further experiment suggests that even one further raises the input laser peak power by two orders of magnitude, the increase of the laser intensity inside the filament does not exceed 30% [44].
FIG. 5: Measure longitudinal plasma density distribution of a filament generated in air by $f = 100$ cm. From [40].

FIG. 6: Free electron density as a function of gas pressure. From [42].
Recently, Xu et al. have suggested another simple way to characterize laser peak intensity inside the filament in air [45]. The central idea is to measure the laser intensity dependent ratio of the signal strength of two nitrogen fluorescence lines, namely, 337 nm and 391 nm, which are assigned to the second positive band of $N_2 \left( C^3\Pi_u \rightarrow B^3\Pi_g \right)$ and the first negative band system of $N_2^+ \left( B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+ \right)$, respectively [10]. Because of distinct excitation mechanisms, the signals of the two fluorescence lines increase with the laser intensity at different orders of nonlinearity. An empirical formula has been deduced according to which laser peak intensity could be simply determined by the fluorescence ratio $R$ of 391 nm and 337 nm:

$$I_0 = 79 \times \left( \frac{2.6}{R} - 1 \right)^{-0.34} \times 10^{12} \text{ W/cm}^2. \quad (11)$$

According to Eq. (8), the measured laser intensity as a function of the input laser energy is shown in Fig. 8 for difference focal lengths. Fig. 8 indicates that the peak intensity clamps at $4 \times 10^{13}$ W/cm$^2$ when $f = 100$ cm. The clamping intensity increases with decreasing of focal length. Eventually, for the shortest focal length we have used ($f = 11$ cm), the clamping intensity is more than $1 \times 10^{14}$ W/cm$^2$. The important observation of Fig. 8 is such that the clamped intensity varies with the external focusing condition, which could also be seen in Fig. 7. Similar results have been present by Théberge et al. [46]. This has stimulated an approach to increase the laser intensity achieved inside the filament. However, as we will discuss later in this paper, the increase of the laser intensity by this method would not be unlimited.
IV. APPLICATION OF INTENSITY CLAMPING

The impact of the intensity clamping is extensive. From the fundamental physics point of view, because of the intensity clamping, all the laser energy cannot be constrained into a single self-focus. Evidences have shown that only about 10% of the total laser energy is embraced inside the filament. The rest laser energy forms broad low intensity robe surrounding the filament. This part of the laser energy forms the background energy reservoir [47–50]. It is important to emphasize that the background is not stationary. The dynamic energy exchange between the reservoir and filament preserves the long distance propagation of the filamentation. Also because of the intensity clamping, when the laser peak power well exceeds the critical power for self-focusing, the laser beam may evolve in the form of multiple re-focusing cycles [51–53], or break up into multiple filaments if perturbation exists in the intensity distribution of the laser beam [1–7]. In conclusion, the intensity clamping governs the major evolution dynamics of the laser pulse propagation during the filamentation.

In application, the most intuitive consequence of the intensity clamping might be the saturation of the outcome from the optical interaction happening inside the filament when the input laser energy keeps increasing. Fig. 3 and 4 are good examples for the obtained fluorescence strength and laser spectrum broadening. Fig. 9 is another example of the output saturation when the intensity clamping is applied in the laser ablation [54]. Fig. 9 illustrates that because of intensity clamping, when the laser peak power is higher than the critical power for self-focusing, further increase of the laser power cannot result in corresponding decrease of the number of the laser shots required to penetrate a metallic
sample. The results hint that the ablation rate will finally approach a stabilized value. Since the saturation point is identical to the critical power of self-focusing, the experimental technique implemented in Fig. 9 could be potentially used to measure the self-focusing critical power and the nonlinear refractive index.

FIG. 9: In air, number of laser pulses required to penetrate the aluminum foil as a function of pulse energy. From [55].

As discussed previously, the intensity clamping leads to the observation that the plasma density is generally only a small fraction of the neutral density during the filamentation. So, the optical radiation emitted from the filament contains little contribution of plasma continuum [30, 33]. Finger-print fluorescence spectra of molecules or atoms are therefore highly distinguishable (see Fig. 10). This clean fluorescence spectrum constitutes the basis of a new material analysis tool – Filament Induced Breakdown Spectroscopy (FIBS) [55]. Since linear diffraction of the laser beam will be overcome by the filamentation, remote detection of fluorescence can be realized. For the sake to demonstrate the application of FIBS, by using a beam sending telescope, filaments have been created at various distances up to 100 m through adjusting the relative distance between the divergent and convergent optical components [56, 57]. In this case, the location of the filament merged with geometrical focus. As displayed in Fig. 11, the recorded back scattered fluorescence signal shows unique invariable feature for distance longer than 30 m [56]. Note that there is a modulation of the result in the range from 60 m to 80 m. It could be explained by the presence of a strong ventilation exit near that region. Evidently, Fig. 11 is opposite to the linear optics principle, according to which the focus intensity is inversely proportional to the square of the focal length. It is due to the profounder phenomenon of intensity clamping
when filamentation occurs.

FIG. 10: Spectrum of the optical radiation emitted by (a) breakdown plasma produced by long pulse and (b) a filament in air, respectively. From [31].
Another benefit brought by the intensity clamping when applying the FIBS is the high stability of the fluorescence signal. Xu et al. have studied the stability of nitrogen fluorescence signal emitted from the filament as a function of propagation distance [57]. The results (Fig. 12) demonstrate that there exists a region where the fluorescence signal is highly stabilized. The measured root-mean-square (RMS) fluctuation of the signal within this range is at least one order of magnitude lower than that of the linear propagation case (dashed line in Fig. 12). With further numerical simulations, they have pointed out that this highly stabilized range is consistent with the intensity clamping zone, where the laser peak intensity is roughly constant. This has established one example of the highly self-stabilized outcome for nonlinear optical interactions taking place inside filament.

More examples of self-stabilized nonlinear interactions could be found in [58]. F. Théberge et al. have developed a method to generate tunable and stable few-cycles laser pulses in the visible spectrum by four-wave mixing process during the filamentation of a near-infrared and an infrared laser pulses in gases ($\omega_{4WM} = 2\omega_{NIR} - \omega_{IR}$) [59]. It is shown experimentally that the intensity clamping occurring inside the filament stabilize the energy fluctuation of the generated tunable pulse (see Fig. 13). This is contrary to the normal wisdom that any non-resonant nonlinear interaction will result in a large fluctuation of the signal/outcome as compared to linear interaction. We call this ‘filamentation nonlinear optics’.

In [59], the ultrashort 4WM pulses not only show a remarkable low energy fluctuation, but also possess an excellent mode quality. Fig. 14(a) shows the distorted NIR fluence signal as function of distances.
FIG. 12: Black squares (left label): Longitudinal distribution of nitrogen fluorescence signal at 357 nm; red circles (right label): RMS fluctuation of the measured nitrogen fluorescence signal as a function of propagation distance. Blue dashed line: the measured RMS fluctuation by the same detection setup under linear focusing condition. From [57].

FIG. 13: Time series of energy per pulse normalized over the mean energy for (a) the IR seed, (b) the NIR pulse, (c) the generated 4WM pulse for NIR pump power below the critical power for self-focusing ($P_{NIR} = 0.1P_{cr}$) and (d) the generated 4WM pulse for pump power above the critical power for self-focusing ($P_{NIR} = 2.5P_{cr}$). The root mean square (RMS) energy fluctuations are indicated on the right-hand side for the respective time series. From [59].

distribution before the filament and Fig. 14(b) shows the exceptional beam quality profile of the 4WM pulse generated through filamentation. The 4WM fluence distribution was smooth, centered on the propagation axis and similar to a symmetric Gaussian profile. The
parameters of the 4WM beam diffracting out of the filament are very similar to those of a near diffraction limited Gaussian beam whose $M^2$ value was measured to be less than 1.01 while the initial quality factor of the NIR beam was $M^2 = 1.3$. The excellent laser profile of the generated 4WM pulse is due to the spatial self-cleaning process occurring in the filament.

![Image](image-url)

**FIG. 14:** Distorted NIR fluence distribution used to generate the filament in air and (b) the far-field fluence distribution of the generated 4WM pulse. From [59].

Using a simplified numerical model of the self-focusing process, further light has been shed into the understanding about the physical dynamic of the beam self-cleaning behaviour [60]. As shown in Fig. 15(a), the initial laser beam is Gaussian with ten randomly distributed perturbations added into this smooth beam profile. In Fig. 15, the panel (b)–(d) present the beam profiles at various propagation distances at the pump wavelength of 800 nm. Comparing panels (b)–(c) with (a), one clearly see the continuous shrinking of the beam size due to self-focusing. On further propagation as depicted in Fig. 15(c), the profile of the central zone is evidently improved displaying an excellent beam quality at $z = 33$ cm. It is the manifestation of the self-cleaning behavior of the ultrashort laser pulse filamentation [59, 61]. The plots shown in Fig. 16 are the corresponding intensity distributions along $y = 0$ axis (indicated by white dot lines in Fig. 15). The interesting phenomenon illustrated by Fig. 16 is the gradual spread of the high frequency spatial modulations. The result in Fig. 16 implies that the intensity perturbation contained in the initial beam profile could be treated as high order spatial modes superposing on a fundamental mode. The self-focusing of the laser beam acts as a spatial filter. It focuses the fundamental mode toward the propagation axis, and produces a fundamental mode profile at the self-focus while the higher order modes diffract strongly. Therefore the propagation of higher order modes is mainly governed by the divergence without destroying the high beam quality at the self-focal region. These bring forth the observation of beam profile self-cleaning behavior.

Therefore, if one could sample only the filament core, the output would be very good in quality. This has been confirmed in studying the spatial profile of supercontinuum [60], third harmonic generation in air [58], pulse self-compression [62].
V. EFFORTS TO INCREASE CLAMPED INTENSITY

So far, we have demonstrated several applications of intensity clamping. In some cases, one may need to increase the laser intensity inside a filament to achieve higher interaction efficiency of optical process.

By the use of the calibrated side imaging technique, Théberge observed that the plasma column parameters and plasma density in the filament are strongly dependent on the external focusing and slightly dependent on the initial laser power as shown [46]. By using the semi-empirical model for the tunnel ionization rate of N$_2$ and O$_2$ molecules [14], they estimated from the measured plasma density that the clamped laser intensity inside the filament for the 10 cm focal length lens was $1.6 \times 10^{14}$ W/cm$^2$. For the 380 cm focal length lens, this value was $5.3 \times 10^{13}$ W/cm$^2$. However, for all the focal lengths explored in the experiment, the peak intensities saturate once the laser power is above the critical power for self-focusing. On the other hand, Kiran et al. studied the filamentation process under strong geometric focusing with numerical aperture up to 0.1 [63]. According to the numerical simulation, the peak intensity at the laser focus could be as high as $10^{15}$ W/cm$^2$. Liu et al. have further pointed out that this value may be overestimated since double

---

FIG. 15: Numerically simulated laser beam profiles at various propagation distances when the power. From [60].
ionization might need to be taken into account when the laser intensity exceeds $3 \times 10^{14}$ W/cm$^2$ [64]. By considering the double ionization in the analytical model, Liu et al. have shown that during the propagation of tightly focused femtosecond laser pulse with numerical aperture of 0.12, the peak intensity is clamped at a level of $5 \times 10^{14}$ W/cm$^2$ [64]. Ionin et al. have given a research on the influence of external focusing conditions on absolute energetic characteristics of third harmonic, the result shows that the intensity clamping still governs the THG efficiency for different numerical aperture magnitudes at higher laser powers [65]. Although improved peak intensity can be obtained in the filament core by use of tight focusing, under such condition the filament cannot be launched far away.

Another efficient way to change the external focusing is the so-called space-time focusing technique [66]. The laser was dispersed by a parallel pair of 1500 lines/mm gratings in the horizontal direction. It was then focused with a 100 cm focal length lens into the air. They have shown that by employing the spatio-temporal focusing technique, the peak intensity in the filamentation core can be effectively enhanced as compared to that allowed by a loose focusing geometry. In addition, the filamentation length is significantly shortened as a result of elongated pulse duration in the out-of-focus region. This technique could be of great interest in remote sensing for achieving better spatial (longitudinal) resolution and high signal-to-noise ratio while keeping the flexibility of being able to project the filament at long distances as recently experimentally confirmed by Zeng et al. at a distance of 22 m away [67]. It can also be useful for other important applications, such as high-order harmonic generation. Higher conversion efficiency and higher cutoff photon energies could be attainable due to the higher achievable peak intensity benefited from the temporal focusing
Lately, researchers have suggested intercrossing two filaments to realize energy coupling between two pulses in nitrogen gas. Kosareva et al. have demonstrated that when two filaments cross each other at an angle as small as 0.16°, two filaments merge together [68]. The peak intensity attained in the case of two filaments merging is just 1.3 times higher than that reached in a single filament. Stelmaszczyk et al. and Wu et al. have reported efficient white light generation in fused silica block and third harmonic generation in argon gas by dual filaments interaction, respectively [69, 70]. In the later work, the incident angle between two filaments is about 0.32°.

Recently, a theoretical work has studied the sub-cycle spatiotemporal dynamics of the laser transformation during filamentation by retaining the full electric-field of the laser pulse. The result predicts a sub-fs intensity spike, having intensity exceeding the clamping intensity by a factor of 3, can last for a short propagation distance in the filamentation process [71]. The theoretical prediction has been recently reproduced by Sun et al. [72]. The longitudinal distribution of the laser peak intensity inside a half meter long femtosecond laser filament in air was studied by measuring the signal ratio of two nitrogen fluorescence lines, 391 nm and 337 nm. As shown in Fig. 18, the experimental results reveal that laser peak intensity initially remains almost constant (~ 4.3 × 10^{13} W/cm^2) inside the filament. However, before the end of the filament, surprisingly the laser intensity undergoes dramatic increase. A maximum intensity as high as 2.8 × 10^{14} W/cm^2 could be reached. As discussed in [71], the experimentally observed sharp intensity increase shown in Fig. 3 could be attributed to the re-focusing of the reservoir energy at the end of the filament. In this
case, when the inward energy flow to the axis is faster than the energy divergence caused by
the plasma due to a shock formation, higher laser intensity could be obtained. It is worth
mentioning that the high intensity is only achieved in a very confined spatio-temporal area.
For example, in argon gas the duration of the created short pulse could be sub-cycle and
the diameter is only a few microns, which is around one order of magnitude less than the
diameter within the plateau region [71].

![Graph](image)

**FIG. 18:** Evolution of $R = S_{391nm}/S_{337nm}$ versus distance (black line, left label) and the retrieved
laser peak intensity according to Eq. (8) (red line, right label). From [72].

**VI. OTHER EFFECTS MAY BALANCE SELF-FOCUSBING**

Up to now, we have considered that the intensity clamping is mainly induced by
the dynamic balance between the optical Kerr effect caused self-focusing and the plasma
defocusing effect. However, some other scenarios have suggested intensity clamping without
ionization. That is to say that the balancing is achieved by effects other than plasma
defocusing. These effects include diffraction, dispersion and high order Kerr effect.

In 1960s, Chiao et al. proposed the self-trapping model based on a continuum wave
(CW) theory [73]. In this model, the natural diffraction was suggested to balance the
self-focusing. If the self-focusing effect is not strong enough to counteract the diffraction
effect, the consequence is a slowly divergent pulse, slower than that due to pure linear
diffraction. When the natural linear diffraction of the pulse is just balanced by self-focusing,
a laser beam can produce its own dielectric waveguide and propagate without any change
in the beam profile; i.e. the laser beam is self-trapped. Presumably, the filaments are
induced by the intense self-trapped beam. The critical balance between the self-focusing
and the natural diffraction is labeled as the so-called critical power for self-focusing [74]. Through the numeric solution of the Maxwell’s equations, for a non-paraxial parallel CW Gaussian beam, the critical power for self-focusing is given by: $P_c = \frac{3.77 \lambda_0^2}{8 \pi n n_0}$ [74], where $\lambda_0$ is the laser central wavelength. The critical power in condensed matters is about a few megawatts (MW) and in gas it is a few gigawatts (GW). The definition of critical power shows that it depends only on $n_2$, $n_0$ and $\lambda_0$ and is independent of the intensity. Subsequently, many investigations on this so-called self-trapped model were carried out with nanosecond (ns) and picosecond (ps) laser pulses in the 1970s. Later, people noticed that self-trapping solutions are not stable. A critical balance between the self-focusing and the natural diffraction is required. Any small perturbation would cause that the self-trapped beam either diffracts or self-focuses.

In 2004, M´echain et al. claimed stable non-ionizing channels extending over the distance of kilometers in air [75]. However, the recent researches have shown that the non-ionizing channels are those occurring after the plasma zone where the intensity is still high enough to produce self-focusing, which could balance the linear diffraction and induce the beam to have a very small divergence angle over a long distance as if it is still undergoing filamentation [76–78].

Group velocity dispersion (GVD) has also been suggested to be an effect to arrest the beam collapse due to self-focusing in condensed matters since GVD is much stronger in condensed matters than that in gases [79–81]. In the proposed scheme, the strong GVD in condensed matters may induce pulse splitting and reducing the peak power of the laser pulse during propagation, thus, weakening the self-focusing which is determined by the laser peak power. However, this mechanism is mainly applicable for the laser having lower power than the critical power for self-focusing. When the laser power is higher than the critical power for self-focusing, multiphoton ionization will play more important role than GVD to arrest the beam collapse [82].

In 2004, Kolesik et al. have proposed that the filamentation process in water can be interpreted as being due to the propagation of a dynamic nonlinear X waves resulted from the interplay between nonlinearity and chromatic dispersion [83]. Though experimental evidences have shown that the far-field and near-field laser intensity profile share some characteristics of X-wave, detailed numeric study has investigated the influence of these physical effects in the strongly nonlinear regime. The results demonstrated that the group velocity dispersion alone is insufficient to arrest collapse. The collapse is shown to be arrested mainly by plasma generation, but not by dispersion [82].

On the other hand, instead of plasma defocusing effect considered in conventional numerical study of the filamentation process, the high-order Kerr effect (HOKE) has been recently proposed as an alternative mechanism to arrest the self-focusing and inducing the filamentation phenomenon [84, 85]. Though there is still hot debate about the validity of HOKE model [84–86], the plasma generation will take place in both models. The difference lies in the quantities of the outcome parameters, including the plasma density and the filament radius. Particularly, researchers from the University of Arizona have pointed out recently that the well established plasma-defocusing model will give better prediction to
the quantity of the plasma density generated by the filamentation [87].

VII. SUMMARY

In conclusion, though there is still debate about the dominant mechanism inducing femtosecond laser filamentation, the dynamic balance between the optical Kerr effect and the plasma defocusing effect is more accepted as the major reason. The intensity clamping phenomenon is inherently given rise by this balance, leading to an almost invariable laser intensity during the filamentation. Therefore, the intensity clamping represents one of the fundamental characteristics of the filamentation and governs the self-transformation of the laser pulse during the nonlinear propagation. Due to intensity clamping, the output of the nonlinear interaction takes place inside a filament is high stabilized in view of the signal’s energy and the spatial mode. This phenomenon has constituted the significant advantages of the filamentation in various applications, ranging from remote sensing, to laser ablation, to self-pulse compression, to laser frequency conversion. Hence, current research focus about the intensity clamping lies on the application of this unique phenomenon, particularly, on the optimization of the clamped laser intensity clamping inside a filament. The main directions include increasing the clamped laser intensity and launch this highly stabilized laser intensity to remote distance. Throughout understanding about the fundamental physics of the intensity clamping will certainly inspire more innovative application and expand the context of the research of femtosecond laser filamentation.

Acknowledgement

This work is financially supported by National Basic Research Program of China (2014CB339802, 2011CB808100), National Natural Science Foundation of China (11174156) and the open research funds of State Key Laboratory of High Field Laser Physics (SIOM).

References

INTENSITY CLAMPING DURING FEMTOSECOND …

Controlling Laser Filamentation Induced Strong THz Fields

M. Massaouti\textsuperscript{1} and S. Tzortzakis\textsuperscript{1,2,*}

\textsuperscript{1}Institute of Electronic Structure and Laser (IESL),
Foundation for Research and Technology – Hellas (FORTH),
P.O. Box 1527, 71110 Heraklion, Greece
\textsuperscript{2}Department of Materials Science and Technology,
University of Crete, 71003 Heraklion, Greece

(Received September 17, 2013)

This article reviews recent advances on tuning intense THz pulses generated from 2-color femtosecond laser filaments in gases. In particular, extended tunability of the THz pulses is shown via filamentation molding and the use of cleverly engineered metamaterials and eutectics.

DOI: 10.6122/CJP.52.490 PACS numbers: 52.38.Hb, 42.65.-k, 81.05.Xj, 78.67.Pt

I. INTRODUCTION

During the past decade, thanks to the tremendous technological development in photonics and materials science, terahertz (THz) radiation became routinely accessible, opening new frontiers in several research fields, including chemistry \cite{1}, biology \cite{2}, medicine \cite{3} and materials science \cite{4}. The continuously increasing interest for terahertz waves and their applications is fostered by their non-invasive nature (1 THz=4.43 meV photon energy) and their ability to penetrate through many materials \cite{5}, which are usually opaque in the infrared and visible. Additionally, several physical and chemical processes, not accessible before, are closely related to the low frequency dynamic modes such as crystalline lattice or inter-molecular vibrational modes, hydrogen bonding stretches, large-scale motions of an entire macromolecule, which are lying in this low-frequency range.

Up to date, numerous techniques have been tested and developed as THz sources and many of them, such as photoconductive antennas and optical rectification, are widely employed in various laboratories around the world. Using techniques like electro-optic (e.o.) \cite{6} or photoconductive sampling \cite{7}, it is possible to coherently detect in the time domain the generated THz pulses, giving a direct access to the amplitude and more importantly the phase of the electric field. Yet, there is still a stumbling block for many applications in the THz regime due to the relatively low THz peak power that most of the existing techniques exhibit, with energies per pulse barely reaching the nano-Joule regime, while their further development is hindered by the lack of natural occurring materials exhibiting strong electric or magnetic response in the THz range.

*Electronic address: stzortz@iesl.forth.gr
In the past years, various table-top approaches have been followed in order to successfully scale up the strength of the THz pulse energy [8] with one of the most promising ones being the 2-color femtosecond filament plasma based THz source. This source is based on the use of amplified lasers where THz emission originates from the transverse plasma current which is formed by an asymmetric 2-color electric field filament. The 2-color filament induced plasma THz emission yields super-broadband spectra, reaching up to 200 THz [9], while extremely low-frequencies (< 0.1 THz) are produced [10]. Basically, this source produces a broadband electromagnetic THz radiation with electric field intensities up to 1 MV/cm [11], making it attractive for a wide range of experiments.

The aim of this review paper is to introduce the versatility of the 2-color femtosecond filament plasma based THz source through the tailoring of the plasma string which naturally governs the macroscopic properties of the emitted THz pulse. In addition, taking advantage of the broadband feature of the source and its ability to be combined with other synchronized optical pulses (covering a large spectral range of the E/M spectrum), we will present the ability to control the emitted THz wave through the use of artificially fabricated materials like THz metamaterials [12] and eutectics.

II. EXPERIMENTAL SYSTEM

In Figure 1 is shown the terahertz time-domain spectroscopic (THz-TDS) system developed in our group, which is based on a pump-probe coherent detection approach where intense, s-polarized THz pulses are generated through 2-color gas filaments. The setup uses a powerful amplified kHz Ti:Sa laser system delivering 35 fs pulses at 800 nm central wavelength and energy of 2.3 mJ per pulse. The initial beam is split in two arms (10% and 90% respectively). The most intense one, with energy equal to 1.3 mJ and a Gaussian beam profile with a diameter of 6.6 mm, is focused in ambient air with a positive lens of 200 mm focal length and partially doubled in frequency in a BBO crystal (50 μm thick) to produce a 2-color filament and subsequently, THz radiation. The optimum ratio between the fundamental and the second harmonic amplitudes is 9 to 1. The second arm, after being further attenuated is used for probing the THz-induced birefringence in an electro-optic (e.o.) crystal and monitoring the time profile of the THz electric field [13]. For the collection, collimation and refocusing the generated THz beam in the e.o. detection crystal, a set of four parabolic mirrors is used, as depicted in Figure 1. The whole setup is enclosed in a purged gas (e.g. N2) chamber for eliminating THz absorption from water vapor [14].

Using this THz setup, the electric field emitted from the 2-color filament is estimated to be up to 200 kV/cm for an input laser pulse energy of 1.3 mJ/pulse. In Figure 2 are presented two examples where the same emitted signal has been recorded with a thick ZnTe crystal (500 μm) and a thin GaP crystal (100 μm). The measured electric field inherently depends on the crystal thickness (phase matching between the two pulses) and the presence of optical phonon modes. Thus, although with a thin GaP crystal we are able to detect higher frequencies (up to 8 THz) compared to ZnTe (see Figure 2(b)) -which has optical
phonon modes at lower frequencies— a signal with higher signal to noise ratio is recorded in
the case of the ZnTe crystal (see Figure 2(a)) due to its thickness and its higher electro-optic
coefficient compared to the GaP crystal. By applying a Fourier transform to these electric
fields, one obtains the spectral distribution of the THz pulse (Figure 2(b)) and as one can
see, the detected THz pulse duration clearly depends on the properties of the e.o. crystal
used. We should note here that other techniques allowing a much broader band detection
[15], have revealed frequency components up to 30 THz, using similar sources.

An estimation of the THz peak electric field can be directly deduced from the time
domain trace, the measured energy and the estimation of the focused beam diameter. Using
a commercially available THz-sensitive pyroelectric detector (Gentec-EO, SPI-A-62THz),
we have measured the THz pulse energy to be 80 nJ for an input laser pulse energy of 1.3
mJ. In order to measure the diameter of our focused THz beam, a knife edge technique is
used where a razor blade is scanning across the focused THz beam and the respective THz
power is measured by the aid of the pyroelectric detector. For a Gaussian-like beam profile,
the extracted full width half maximum (FWHM) is equal to 205 μm and at 1/e² 435 μm.
This size corresponds to a diffraction limited spot for a THz beam at 1.7 THz, which is
in good agreement with the THz spectra presented above. Using the time trace measured
with the thin GaP crystal (Figure 2(b)) and the full bandwidth measurement of the energy,
the THz electric field is estimated to be equal to 200 kV/cm. One can scale up the energy

FIG. 1: Schematic representation of the THz-TDS experimental set-up.
content of the THz pulses using much higher input laser pulse energies (10 mJ) obtaining thus THz energies in excess of 1 μJ per pulse [11], hence opening the door to nonlinear THz optics and intriguing applications of high-field single-cycle THz pulses [16, 17].

III. TUNING THZ WAVES

III-1. Filamentation tailoring

The advantage of this source is not solely based on its intensity and broadband nature but also on using filaments which compared to the solid-state THz sources can be tailored, offering thus the possibility to tune the emitted THz pulses.

Microscopically, the generation of THz emission from a 2-color filament is the result of a transversal photocurrent. In a simplified view, one can describe the process like this: after the electrons get liberated at a certain velocity via the ionization process, they experience a drift from the remaining part of the laser electric field, which leads to a separation of charge in the transverse plane and the creation of a photocurrent [18]. The phase of the second harmonic field allows the projection of the photocurrent in any direction within the transverse plane. A direct consequence is that the technique offers a control on the polarization of the emitted THz pulse via the phase between the fundamental and its second harmonic [19–21].

Motivated by this microscopical picture, one could expect to achieve THz polarization control for short filament lengths via the accurate adjustment of the surrounding gas pressure. By changing the pressure, a wavelength dependent change of the refractive index is induced, which in turn will affect the phase of the synthesized laser field and consequently offer coherent control on the emitted THz pulse polarization. As shown in Figure 3, for relatively short plasma strings where the phase walk-off occurring in the plasma channel can be neglected, a π/2 polarization rotation of the emitted THz pulse is achieved over 650 mbar of the gas medium pressure with quasi constant THz power and linear pulse polarization. As demonstrated in [20], one can accurately predict the change in the polarization...
angle of the emitted THz pulses by just calculating the dispersion between the $\omega$ and $2\omega$ laser fields using the pressure dependent Sellmeier equation.

![Calculated phase variation](image)

FIG. 3: Detected THz power as function of nitrogen gas pressure (dots-line) and THz pulse polarization states at different pressure levels of N$_2$. The upper axis (blue on-line) represents the calculated phase variation.

![Thz beam polarization](image)

FIG. 4: (a) Normalized values of THz beam polarization state as measured for two different levels of input laser pulse energy in air, at atmospheric pressure. (b) The linear polarization (red curve) state of the THz beam pulse at low pressure in comparison to the circular polarized THz beam pulse (black curve) as recorded at 880 mbar in Xenon.

Nevertheless, at higher input laser pulse energies where the filament length is inherently longer, a degenerative behavior can be observed associated to the phase mismatch.
within the elongated source. This is also accompanied with the appearance of ellipticity in the polarization of the beam, as one can see in Figure 4(a), where THz normalized polarization diagrams are presented for two different levels of laser pulse input energy at atmospheric pressure air. The observed ellipticity simply arises from the birefringence of the filament itself [22]. Furthermore, it is known from the literature that the saturation intensities within the filament are much lower for gases with low ionization potential (e.g. Xenon (12.13 eV)) and the excess of input laser energy leads to an extension of the plasma length as was shown by numerical simulations [23]. Consequently, using a gas such as Xenon, we have been able to clearly extend the plasma length and thus increase the accumulated birefringence and obtain fully circularly polarized THz beams, as presented in Figure 4(b). This result is of main importance since circularly polarized THz light can be used for instance to study circular dichroism in various molecular and biological systems.

FIG. 5: (i) Fluorescence images of filament plasma string distributions, (a) asymmetric (b) symmetric double peaks, (c) uniform and (d) gradient, obtained under various experimental conditions and (ii) their respective electric field traces. In (iii) are shown the corresponding spectra of the uniform and gradient plasma recorded electric fields.

As we have seen, except the microscopical picture of THz generation through 2-color gas filaments, equally important is the macroscopic filament-THz propagation effect, which practically affects not only the polarization of the emitted THz pulses but also their bandwidth [24] and energy scale [10, 25]. In order to investigate how the THz field is modified for different plasma string distributions, we have followed the approach of filamentation tailoring. In most experimental situations, the highly dynamical nature of the filamentation process leads to a non-uniform plasma distribution with strong gradients along the propagation path. Furthermore, due to the high intensities reached within a filament, it is impossible to insert optics in order to gain control on the filamentation process. Consequently, one needs to find external means to obtain control on this process. For example,
the introduction of distortion in the laser beam wavefront can lead to the control of the electron density distribution, which in turn yields different THz waveforms [24]. The waveform recorded for diverse electron density distributions are presented in Figure 5(ii) along with a CCD picture of the respective plasma strings (Figure 5(i)). Hence various THz waveforms are produced offering wide tunability in terms of the spectral distribution. As observed in Figure 5(iii), the uniform plasma distribution offers a wider bandwidth and a different central frequency compared to the gradient case.

**FIG. 6:** (a) Schematic representation of the spatial and temporal arrangement of two independent plasma strings and (b) their respective fluorescence images along with the concatenated one as recorded with a CCD camera.

Following the same idea of plasma string tailoring we studied the effect of the extension of the length of the plasma string on the THz emission. In order to keep a uniform electron density distribution we used the approach of coherently linking two similar uniform filaments along the propagation axis (z axis on Figure 6(a)). This concatenation effect, which requires appropriate spatiotemporal adjustment of the 2 single filaments, results in the enhancement by one order of magnitude of the yielded THz pulse power and consider-
FIG. 7: Recorded THz signal for different spatial distributions of the two plasma strings and for each plasma string individually.

ably more than the strength of a single filament having an input laser energy equivalent to the sum of the two filaments (see Figure 7).

III-2. THz metamaterials

Another approach to control terahertz radiation is by using metamaterials which are specifically tailored for the THz regime [26]. Metamaterials are artificially fabricated materials composed of subwavelength structures, periodically arranged, exhibiting unique electromagnetic properties that cannot be found in nature. Up to date, a large variety of metamaterials have been designed and applied as manipulating devices of THz waves, including phase modulators [27], polarizers [4], absorbers [28, 29], and active frequency THz devices which can be controlled by light [30, 31].

Here we review two different schemes that allow the dynamic control of phase modulation [32] and resonance shifting [31] in the THz regime. Additionally, a self-organization approach for fabricating metamaterials will be presented, showing the potential of realizing simple subwavelength THz waveguides [33].

The first metamaterial is a classical metamaterial sample consisting of an array of split-ring-resonators (SRRs), fabricated from copper which are periodically arranged on top of a high resistivity GaAs substrate (670 μm). A sketch of the experimental approach, together with the exact dimensions of the SRR unit shell, is given in Figure 8. The metamaterial is designed so as to exhibit electric resonance response in the THz regime which can be dynamically tuned as photocarriers are injected within the GaAs substrate. The dynamic response of the metamaterial has been studied by placing the sample at the THz focus, at normal incidence and performing THz transmission measurements through the metamaterial sample as it is illuminated by an optical-pump laser beam (of central wavelength 800 nm) launched at 45° on the sample. The temporal synchronization of the THz
and the optical pump beams have been experimentally defined.

![Diagram](image)

**FIG. 8**: Graphic representation of the metamaterial sample and the experimental geometry of the laser and THz beams.

In Figure 9(a) are shown the recorded THz amplitudes for different levels of excitation fluence. In the absence of photocarriers, the non-excited sample exhibits a broad resonance which is a dipole-like resonance of the structure, related to the finite length of the metallic element along the electric field direction. By injecting photocarriers, an amplitude modulation of the resonance is observed. By performing theoretical calculations (Figure 9(c)), using a simple Drude model, the experimental observations are explained as a result of the change of conductivity of the GaAs substrate, where increasing amounts of charges finally screen the existing resonance. More interestingly, a frequency shift is observed towards higher values (up to 50 GHz) as photocarriers are injected within the substrate (see Figure 9(b), (d)). As electrons and holes are created under photo-excitation within the substrate (over one penetration depth; 1 μm at 800 nm), beyond the changes in the conductivity, the complex index of refraction is expected to change as well, contributing to the observed phase shift. More details on these experiments and corresponding numerical simulations can be found in Ref. [32].

The second case we will discuss here involves a specifically designed metamaterial for which t-gap metallic SRRs are deposited on a dielectric substrate (sapphire). In this case, the tunability of the metamaterial is achieved by incorporating silicon semiconductor islands on 2 out of the 3 gaps of the SRRs, as shown in Figure 10. Other than that the experimental approach is the same as previously only that this time the photoexcitation will affect only the 2 gaps. At high laser fluence levels, the photoexcited silicon islands will completely short-circuit the 2 gaps, leaving the metamaterial only with one and thus a completely different resonance mode.

This is indeed depicted in the experimental results shown in Figure 11(a), where the THz transmission spectrum is plotted as a function of the laser pump fluence. As the pump energy flux increases, the observed resonance at 0.76 THz starts to weaken while it
FIG. 9: (a) Experimental results of THz transmission spectra and (b) phase tenability as function of the energy flux of the laser pump beam. (c) and (d) present the respective theoretical results as extracted for different levels of carriers density within the GaAs substrate.

FIG. 10: Optical microscopy images of the hybrid metamaterial. (a) Large area of the metamaterial, (b) close view of the unit cell where the inclusions of photoconductive silicon within the gaps can be seen.

is significantly shifted to higher frequencies resulting to a new resonance peak located at 0.96 THz (red line). This corresponds to a fairly broadband blue-shift of 26% in the resonance frequency. As a comparison and for interpreting the experimental demonstrations, numerical simulations have been performed using the commercial software CST Microwave Studio which are overall in quite good agreement with the experimental observations (Figure 11(b)). The experimentally observed and theoretically calculated, broadband blueshift tunability of the resonance response of the hybrid THz metamaterial demonstrates the po-
tential of achieving ultrafast THz switches, opening thus, a new path to exploring more designs targeting greater flexibility for practical applications in the range of frequency-agile metamaterials [31].

FIG. 11: (a) Normalized transmission of the THz beam pulse, as measured experimentally, for different energy flux of the IR laser beam irradiating the metamaterial. A clear switch-effect of the resonance frequency appears at high photo-excitation levels. (b) Results of simulations for different values of silicon conductivity as calculated for the respective experimental values of the energy flux of pump beam.

Both of the aforementioned metamaterial designs have been fabricated following lithographic approaches where the desired THz response is achieved by designing properly metallic structures. An alternative way to have fascinating metamaterial properties and possibilities in the THz range, like negative refractive index [34], and/or manipulate the dispersion of THz waves in unique ways [35], is to use properly structured polaritonic materials.

FIG. 12: (a) Scanning electron microscopy (SEM) image of polished longitudinal section of the eutectic LiF/KCl. In bright phase are shown the long continuous LiF rods lattice embedded in KCl matrix (dark phase). (b) SEM image of the transverse cross-section of LiF/KCl eutectic sample grown at 2 mm/h pulling rate.

The third metamaterial system presented in this review paper is fabricated employing the eutectic directional solidification technique [36] which has been proven extremely suitable for achieving polaritonic metamaterial structures. Following this self-organization approach, a 2D periodic polaritonic system of long and continuous LiF rods embedded in
a KCl host has been fabricated (Figure 12). According to recent theoretical studies, an enhancement of E/M wave transmission through an epsilon-near-zero (ENZ) material is expected if dielectric cylinders are embedded in it [37], a transmission which is associated with subwavelength guiding effects. In the case of the eutectic polaritonic LiF/KCl system where, the KCl host shows an epsilon-near-zero (ENZ) response around 6 THz, ($\varepsilon_{KCl} \sim 0$), while the LiF has a dielectric-like response [38], with $\varepsilon_{LiF} = 15.5$ at $\sim 6$ THz, similar phenomena are expected.

![Figure 13](image)

**FIG. 13:** (a) THz transmission spectra, through a 60 m thick, LiF/KCl system, as recorded for a polarization of the THz electric field parallel (circles) and perpendicular (triangles) to the LiF rods lattice, (b) THz transmission through the sample as simulated using the CST Microwave studio.

In Figure 13(a) are presented the THz transmission spectra through a longitudinally sliced LiF/KCl eutectic as measured for two different orientations of the LiF rods to the incident THz electric field, within the frequency range between 3.0 and 8.0 THz. As one can clearly see, in the case of perpendicular polarization the eutectic system exhibits zero transmission between 4.3 THz to 6.2 THz. On the other hand, for parallel polarization, a broad transmission peak appears centered around 6 THz, at the frequency where the KCl host of the eutectic exhibits near-zero permittivity. Similar response is predicted from theoretical calculations (Figure 13(b)) indicating that the experimentally observed transmission peak at 6 THz is an enhanced transmission associated with Mie-resonances in the LiF rods and the ENZ response of the KCl host, at this frequency. An additional feature characterizing this resonant response is associated with an electric field which is strongly confined along the direction of the incident wave. As theoretically calculated and presented in Figure 14, the electric field amplitude of a plane wave of 6 THz frequency as propagating through a microstructured system with features similar to the experimentally studied one, is sub-wavelength waveguided within the microstructures of the ENZ eutectic material. These theoretical predictions along with the experimental observations show a new way for realizing simple sub-wavelength waveguides in the THz regime. More details on this work can be found in [33].
FIG. 14: The electric field amplitude distribution of a plane wave of 6 THz frequency, propagating in a KCl medium (left), LiF (middle) and in a matrix of KCl matrix doped with LiF rods (right), passing through a 15 μm slit.

IV. CONCLUSIONS

In this review, we have presented in details a source yielding ultrashort THz pulses with high peak intensity and broadband frequency spectrum. We have shown ways to tune the emitted THz pulses in terms of duration, strength and polarization by appropriately tailoring the filamentation process, the uniformity and length of the plasma string. One of the most interesting possibilities offered by this tunability is the generation of fully circularly polarized THz light, which will be of great interest in studies like circular dichroism or chirality. Finally, we have shown additional ways of controlling the THz fields using either dynamically controlled metamaterials or cleverly fabricated microstructures based on self-organization which open the way for future large-scale production of THz devices.

Acknowledgements

The authors acknowledge their colleagues that have contributed in parts of this work, J. M. Manceau, M. Kafesaki, C. M. Soukoulis and E. Ozbay and R. I. Merino for the fabrication of the hybrid metamaterials and the eutectic metamaterials respectively. This work was supported in part by the EU Marie Curie Excellence Grant “MULTIRAD” MEXT-CT-2006-042683, the FP7 programs LaserLab-Europe (grant no 284464), CHARISMA (grant
no 228330), ENSEMBLE (grant no 213669), NIMNIL (grant no 228637) and Aristeia “FTERA” (grant no 2570) co-financed by the European Union and Greek National Funds.

References

Review

Ionic Valence Change of Metal Ions in Solution by Femtosecond Laser Excitation Accompanied by White-Light Laser

Nobuaki Nakashima,1,2,* Ken-ichi Yamanaka,3 Ayaka Itoh,2 and Tomoyuki Yatsuhashi2

1Toyota Physical and Chemical Research Institute, Nagakute, Aichi 480-1192, Japan; Institute for Laser Technology, Osaka, 550-0004, Japan
2Department of Chemistry, Graduate School of Science, Osaka City University, Sumigoshi, Osaka 558-8585, Japan
3Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

(Received August 30, 2013)

Three lanthanide ions (Ln3+), Ln = Eu, Sm, and Yb, and two transition metals, Fe3+ and Ag+, were found to be reduced to the corresponding Ln2+, Fe2+, and Ag+ in methanol or aqueous solution upon irradiation with intense femtosecond laser pulses. The major excitation wavelength was 800 nm and single-photon-non-resonant with the electronic transitions of metal ion solutions. Laser pulses with wavelengths of 970, 1190, and 1930 nm were used for particular cases. Whenever the white-light laser was generated, the reductions were observed. The reduction mechanisms would be explained in terms of self-focusing, solvated electron formation followed by trapping the electron. The electron ejection under focused beam conditions in solution has been known to be accompanied by white-light laser. In the exceptional case of Fe3+ at 800 nm, two-photon excitation of the charge transfer state followed by the reduction would be operative. Fe2+ was detected even with an intensity lower than the threshold of the white-light laser generation.

DOI: 10.6122/CJP.52.504 PACS numbers: 82.50.Bc, 82.50.Pt

I. INTRODUCTION

Femtosecond filamentation, particularly with respect to phenomena in air and its applications, have been extensively studied and reviewed [1]. Many interesting applications have emerged, including rain making [2] and generation of mid-infrared pulses [3]. In this paper we introduce a chemical application in solution induced by femtosecond laser filamentation. Two of the authors found Eu2+ ion formation accompanied by white laser generation in Eu3+ ions in methanol [4] and subsequently found an Sm3+ →Sm2+ reaction [5]. The excitation wavelength of 800 nm was non-resonant with the electronic transitions of the 3+ metal ions. The reactions would be induced by electron ejection by femtosecond filamentation accompanied by white laser generation. We have suggested that these reactions are similar to those in radiation chemistry in solution [4]. In this context, it is worth pointing out two recent papers in relation to femtosecond filament chemistry. One of these studies

*Electronic address: nakashima@toyotariken.jp
found that carbon nano-particles form on the benzene/water interface under the generation of femtosecond laser plasma [6]. In the other paper, femtosecond filamentation was applied to cancer therapy, yielding ultra-high dose rates without any dose deposit in front or behind the target volume [7]. This paper will show that the metal ion reduction by femtosecond laser excitation is a general phenomenon by extending the reduction to a few metal ion systems. The metal ion reaction is a simple redox reaction; therefore, this study will provide fundamental characteristics of the chemical reactions induced by femtosecond filamentation in solution and in tissues.

We have added another lanthanide ion, Yb\(^{3+}\), and two transition metal ions, Fe\(^{3+}\) and Ag\(^{+}\). Reduced ions for all of the above systems have been distinctly observed with absorption, emission, and/or visual color changes under femtosecond laser irradiation. The reactions of Eu\(^{3+}\) in solution have a similarity with Eu\(^{2+}\) formation in optical glasses from Eu\(^{3+}\) by infrared femtosecond laser pulses. It has been suggested that an electron is ejected and that Eu\(^{3+}\) ions act as electron-trapping centers [8, 9]. The reactions between electrons and Eu\(^{3+}\) ions induced by femtosecond pulses are similar to those in radiation chemistry in solutions. Irradiation of γ-rays can produce an electron that will subsequently reduce Eu\(^{3+}\) to Eu\(^{2+}\) [10, 11]. The rate constants between the metal ions, including molecules, and electrons have been studied in detail and accumulated for more than 1500 examples in radiation chemistry [12, 13].

In this paper, we will try to clarify the following points.

i) To generalize metal ion reactions by femtosecond laser pulses, we adopt Yb\(^{3+}\) solution as the third example of lanthanide ions. The reaction of the Yb\(^{3+}\) system should be similar to those of the other two lanthanide ions, Eu\(^{3+}\) and Sm\(^{3+}\). These three ions have small oxidation potentials and fast rate constants with a solvated electron in common [12–14].

ii) We will try to extend the reduction to two transition metal ions: Fe\(^{3+}\) and Ag\(^{+}\).

iii) Multiphoton absorption followed by reduction would be included, because the inorganic systems have a charge transfer (CT) absorption band in the UV-Vis ranges. Redox reactions can be induced by the CT band excitation. The three lanthanide Eu, Sm, and Yb ions have photochemically active CT bands which are active for single as well as two-photon excitation [5, 15–18]. We have examined the reactions with femtosecond pulses with different wavelengths. The oxalate Fe\(^{3+}\) complex is used as one of the transition metal ion systems. The complex has been used for chemical actinometry [19, 20] and its photochemical mechanism has been extensively studied [21–24]. The CT band below 400 nm is known to be two-photon active for a 694.3-nm laser [25]. We will see that the oxalate Fe\(^{3+}\) complex is two-photon active for 800-nm femtosecond pulses in this paper. Pulses with a long wavelength of 1190 nm are used to suppress the two-photon chemistry, but multiphoton absorption could still occur. For organic molecules, multiphoton absorption of 5–7 photons occurs just below the intensity white-light laser generation [26, 27].

iv) The reductions are similar to the reactions in radiation chemistry, because the electron ejection is the primary step in both excitation methods. Many metal ion reductions including the ions treating here have been accumulated in the field of radiation chemistry [12–14]. In the present study we will consider an Ag\(^{+}\) system, because Ag\(^{+}\) re-
duction and Ag\(^+\) cluster and/or nanoparticle formation have been studied by \(\gamma\)-radiolysis [28 a]. It will be of interest to see whether similar reactions actually occur by femtosecond pulse excitation. It should be noted that Ag nanoparticle formation has been reported with femtosecond laser irradiation under high laser intensities, where solvent break down occurs [28 b]. We observed Ag nanoparticles under weak laser intensities, where white-light laser emission was barely visible. The reactions under the break down conditions should be compared with plasma induced reactions, while the present results would have some similarities with \(\gamma\)-radiolysis.

II. EXPERIMENTAL

For Yb\(^{3+}\) experiments, a linearly polarized femtosecond laser pulse with a central wavelength of 800 nm was used [29]. It was delivered from a Ti:sapphire laser system Alpha 100/XS, Thales Laser, at a repetition rate of 100 Hz. The transform-limited pulse had a duration of 43 fs. The pulse width was measured with a single-shot autocorrelator (Thales, TAIGA), and the total pulse energy was measured with a power meter (Gentec eo, PS-310B). Infrared pulses at central wavelengths of 970 and 1930 nm were converted from an 800-nm fundamental pulse using an optical parametric oscillator and amplifier (Quantronix, TOPAS). The spectral widths were about 40 nm for the 970-nm pulse and 80 nm for the 1930-nm one. The infrared pulses from the parametric converter were selected by reflecting it with several dielectric mirrors. The pulse width was estimated to be 130 fs. This value was obtained at 1.4 \(\mu\)m by a second order scanning autocorrelator (APE, PulseCheck). The cell contained 0.16 cm\(^3\) Yb\(^{3+}\) solution in a 2 (width) \(\times\) 4 (depth) \(\times\) 20 (height) mm\(^3\) quartz cell. Samples were degassed to avoid a back reaction due to air oxidation of Yb\(^{2+}\). The femtosecond laser beam was introduced in the direction of 0.4 cm depth, and absorption of Yb\(^{2+}\) was measured with a path length of 0.4 cm.

For Fe\(^{3+}\) and Ag\(^+\) experiments, 800-nm and 1190-nm pulses were used. The output of a mode-locked Ti:sapphire oscillator (Coherent, Vitesse), which was pumped by the second harmonic generation (SHG) of a continuous wave Nd\(^{3+}\):YVO\(_4\) laser (Coherent, Verdi), was amplified with a regenerative amplifier (Coherent, Legend), which was pumped by a Nd\(^{3+}\):YLF laser (Coherent, Evolution) [30]. The output of the amplifier (2.4 W, 100 fs fwhm, 1 kHz, 800 nm) was converted to 1190-nm pulses with a spectral width of 30 nm using an optical parametric amplifier (OPA) system (Coherent, OPerA). The averaged power of the laser pulse and the pulse energy were monitored with power meters (Gentec TPM310) with photo-diode (THORLABS PDA50B) combinations. The cell contained 0.3 cm\(^3\) 0.1–0.2 M of Fe\(^{3+}\) solution in a 5 (width) \(\times\) 10 (depth) mm\(^2\) quartz cell for 1190-nm pulses and in a plastic cell for 800-nm pulses.

A plano-convex lens with a focal length of 200 mm was used to focus the laser beam into a sample cell located 20 mm before the focal point for the Eu\(^{3+}\) system only [4], and at the focal point for other all systems. The product Yb\(^{2+}\) was detected by its absorption spectrum with a peak at 367 nm [17]. The Yb\(^{3+}\) complexes and its photochemistry have been described previously [17]. A solution of Fe\(^{3+}\) potassium ferrioxalate was prepared and the
formed Fe\(^{2+}\) ion was detected by the standard chemical actinometry method [20]. Briefly, after irradiation, the Fe\(^{2+}\) ion is complexed with 1,10-phenanthroline, which has a broad absorption spectrum peak at 510 nm with a molar extinction coefficient of \(1.1 \times 10^4\) M\(^{-1}\)cm\(^{-1}\). In the present study, the Fe\(^{2+}\) complex concentration was measured at 520 nm with spectrophotometers with a Biochrom CO7500 Colourwave and a Shimadzu UV 3600. For the 1190-nm experiments, potassium tris(oxalate)ferrate(III) trihydrate (K\(_3\)Fe\(_2\)(C\(_2\)O\(_4\))\(_3\)·3H\(_2\)O) (Wako Chemicals) and D\(_2\)SO\(_4\) were dissolved in D\(_2\)O in order to minimize the absorption of the excitation infrared pulse. Ag\(^{+}\) ion aqueous solution was prepared according to the literature [28], but the Ag\(^{+}\) concentration was \(5 \times 10^{-3}\) M with 0.01 M sodium polyacrylate, PANa (MW: 2100) and 0.13 M 2-propanol. The Fe\(^{3+}\) and Ag\(^{+}\) samples were air saturated.

### III. RESULTS

#### III-1. The third lanthanide ion reaction of Yb\(^{3+}\) → Yb\(^{2+}\) followed by Eu\(^{3+}\) → Eu\(^{2+}\) and Sm\(^{3+}\) → Sm\(^{2+}\) reactions

The energy levels of the three lanthanide ions and excitation wavelengths are shown in Fig. 1. The figure was constructed based on 4f electronic levels [14], the charge transfer (CT) states [31], and luminescence lifetimes [17, 32]. The ionic valence changes have been observed for Eu\(^{3+}\) and Sm\(^{3+}\) by femtosecond pulses with a wavelength of 800 nm [4, 5], and a Yb\(^{3+}\) ion system is further examined in this paper as the third active lanthanide ion by femtosecond pulses with 970 and 1930 nm in addition to 800 nm wavelengths. The major wavelength of 800 nm is non-resonant with the electronic levels for all cases, and the 970 and 1930-nm wavelengths are one photon and two-photon resonances with an electronic level of Yb\(^{3+}\). The CT states with the counter chloride ion are photo-reactive and locate in the UV region. If these levels are excited with a single photon and/or stepwise two-photon, each lanthanide system shows a reduction to Ln\(^{2+}\) [5, 15–18]. When we discuss the reduction of the lanthanide ions on irradiation with an intense laser pulse, we have to think about whether multiphoton excitation to the CT levels might be included or not.

Figure 2 shows the appearance of the Yb\(^{2+}\) spectra with a peak at 367 nm by irradiation with \(1.8 \times 10^5\) shots of 800-nm wavelength. The spectral shape of Yb\(^{2+}\) is the same as that produced by UV irradiation [17]. The Yb\(^{2+}\) is formed with 970-nm 130-fs pulses with \(1.8 \times 10^5\) shots in a pulse energy range of 3–40 \(\mu\)J and at 1930 nm with a single pulse energy of 4–10 \(\mu\)J. The femtosecond pulse with a central wavelength of 970 nm has a width of 40 nm; therefore, it can be a resonant wavelength with the \(2F_{7/2} \leftarrow 2F_{5/2}\) transition, and the 1930-nm pulse can be regarded as a two-photon resonant wavelength. The spectral width is 70 nm from 920 to 990 nm between the luminescent level of \(2F_{5/2}\) and the ground state of \(2F_{7/2}\). The central wavelength of the transition is 975 nm in CH\(_3\)OH with the molar extinction coefficient of 2.6 M\(^{-1}\)cm\(^{-1}\). No other 4f electronic excited state exists below the charge transfer state, which is shorter than 280 nm.

The following two points are derived from the results in Figure 3. i) The thresholds for the appearance of Yb\(^{2+}\) were 2–4 \(\mu\)J and there was no clear difference for the formation of Yb\(^{2+}\) between the excitation wavelengths of 800 and 970 nm. These results indicate
FIG. 1: Energy levels and excitation wavelengths of the lanthanide Ln$^{3+}$ systems. The major excitation wavelength 800 nm is non-resonant with the electronic levels, as shown by the longest vertical arrows. For the Yb$^{3+}$ system, 970 and 1930 nm are the resonant wavelengths. The photoreactive charge transfer (CT) levels are indicated with the gray areas in the UV region. The emission lifetimes in methanol are indicated.

FIG. 2: Yb$^{2+}$ absorption spectra appear around 367 nm by irradiating an Yb$^{3+}$ system of 0.1 M of YbCl$_3$·6H$_2$O with 0.5 M of 15-crown-5-ether in methanol with $1.8 \times 10^5$ shots of 800-nm and 43-fs pulses. The pulse energies are indicated.
that the formation efficiencies for the two wavelengths were almost the same for the input energy. ii) The slopes were about 1.7 for 800-nm pulse and 1.8 for 970-nm pulse from the absorbance values of Yb$^{2+}$ vs. laser intensity in the logarithmic scale.

**FIG. 3:** (a) Yb$^{2+}$ formation as absorbance at 367 nm for a 0.4 cm cell length after $1.8 \times 10^5$ shots of irradiation of 0.1 M of YbCl$_3 \cdot 6$H$_2$O with 0.5 M of 15-crown-5-ether in methanol. ○: At a wavelength of 800 nm with a duration of 43 fs; ■: at a wavelength of 970 nm with a duration of 130 fs. The arrow indicates the range where white-light laser was visually detectable with a pulse with a duration of 43 fs at 800 nm.

In order to reach the CT state ($< 280$ nm), three photons for 800-nm pulses are required; in addition, four photons for 970-nm pulses and more than seven photons for 1930-nm pulses are needed by multiphoton excitation. The conversion efficiency to Yb$^{2+}$ should be drastically reduced by going from the 800-nm excitation to 970- and 1930-nm excitations, if the multiphoton mechanism worked (for an additional discussion see section IV-2). The present observations do not support the multiphoton excitation to the CT levels. The efficiencies were not largely different between 800- and 970-nm excitations. Even at the 1930-nm pulse, Yb$^{2+}$ absorption was detectable at 4–10 μJ pulse excitation. The slopes of the formation of Yb$^{2+}$ did not support the expected orders if the multiphoton processes were operative. The low order might be expected for the resonant wavelengths at 970 nm. The slope of 1.8 did not support the one-photon plus three-photon absorption mechanism.

The white-light laser was visually observed on a white paper 20 cm behind the sample cell and the threshold was also around 3 μJ for both the 800- and 970-nm wavelengths. The spectrum of the white-light laser was essentially the same as that reported elsewhere [33]. The spectra have a $1/e^2$ width of about 50 nm at 3–10 μJ of irradiation energy and spread over the entire visible range at 20 μJ of laser energy.

The thresholds for the formation of Yb$^{2+}$ can be regarded as the same for the white laser generation. The generation of white-light laser is an indication of an electron injec-
tion [1, 33–35]. Immediately after the ejection the electron will be solvated to less than 1 ps to form e⁻sol as has been observed in the case of a solvent of water [36]. We conclude that the mechanism of Ln²⁺ formation is as follows, where the Ln = Eu, Sm, and Yb.

\[
\text{CH}_3\text{OH} \xrightarrow{\text{hv}} \text{CH}_3\text{OH}^+ + e^-_{\text{sol}}, \\
\text{Ln}^{3+} + e^-_{\text{sol}} \rightarrow \text{Ln}^{2+},
\]

(1)

where e⁻sol is an solvated electron by methanol.

**III-2. Fe³⁺ → Fe²⁺ as a first example of transition metal ions**

The photo-redox reaction of the Fe³⁺(C₂O₄)³⁻ complex in aqueous solutions has been used for chemical actinometry. Parker et al. first suggested the use of the Fe³⁺ to Fe²⁺ photo-redox reaction as a sensitive chemical actinometer [19], and its quantum yields have been studied in detail and summarized in the 254–436 nm range [20]. The accepted overall reaction is presented by the following scheme [21–24]:

\[
2[\text{Fe}^{3+}(\text{C}_2\text{O}_4]^3-) \xrightarrow{\text{hv}} 2[\text{Fe}^{2+}(\text{C}_2\text{O}_4]^2-) + 2\text{CO}_2 + \text{C}_2\text{O}_4^{2-}. 
\]

(2)

The reaction involves CT band excitation, dissociation to CO₂•⁻ radical/solvated electron (e⁻sol) ejection, and subsequent reactions of CO₂•⁻ radical and e⁻sol with the parent Fe³⁺ complex to reduce Fe³⁺ to Fe²⁺ by intermolecular electron transfer.

The absorption spectrum of the Fe³⁺(C₂O₄)³⁻ complex in acidic water has the CT band in the UV region with its shoulder at 280 nm with 5 × 10³ M⁻¹ cm⁻¹ as shown in Figure 4 [21]. The other band in the visible region, which is assigned to a d-d transition, is not clear in this figure because of its small coefficient of 1 M⁻¹ cm⁻¹. The photoproducts Fe²⁺ can be detected by forming an o-phenanthroline complex [20], which has a reasonably broad, strong absorption with 1.1 × 10⁴ M⁻¹ cm⁻¹ at 510 nm, as shown in Figure 4.

The pictures in Figure 4 show the color change of Fe³⁺(C₂O₄)³⁻ solution induced by irradiating 800-nm femtosecond pulses. The solution color was yellow before irradiation due to weak absorption starting at 400 nm for the 0.1 M K₃Fe³⁺(C₂O₄)₃ solution. After irradiation of pulses with an energy of 12 μJ/pulse and a duration of 100 fs, at 1 kHz for 5 min, followed by addition of o-phenanthroline, the red color appeared with an absorbance of more than 1.0 even at 540 nm. The detailed results are shown in Figure 5 with an absorbance Fe²⁺ complex under an irradiation energy in the range of 0.2–12 μJ/pulse 0.25–30 min. The vertical scale represents concentrations of Fe²⁺(o-phen)₃²⁻ and was normalized to absorbance at 520 nm for 1 cm cell length per 1 min. The dotted line has a slope of 2.0 for the log-log scale. A deviation from the line was seen before an energy of 10 μJ/pulse.

The dotted line has a slope of 2.0 for the log-log scale. Two-photon excitation to the CT state followed by reduction to Fe²⁺ would be the major reaction mechanism. In fact two-photon excitation to the CT state followed by reduction to Fe²⁺ has been reported by using a nanosecond ruby laser at 694.3 nm with a coefficient of 1.5 × 10⁻⁵⁰ cm⁴ s/photon [25]. The same mechanism would be operative at the present, long wavelength of 800 nm.

Figure 6 shows Fe³⁺ → Fe²⁺ conversion on irradiation with 1190-nm laser pulses. The absorbance of Fe²⁺ complex per at 520 nm one minute under an irradiation energy in
FIG. 4: The solid line is the absorption spectrum of Fe$^{3+}$(C$_2$O$_4$)$_3$$^{3-}$ in acidic water in the UV region with a light yellow color, and the broken line represents Fe$^{2+}$(o-phen)$_3$$^{2-}$ in the Vis region. Femtosecond pulse irradiation of the 0.1 M K$_3$Fe$^{3+}$(C$_2$O$_4$)$_3$ solution turns the yellow color to red. The dotted rhomboid is a guide for the sample cell. The vertical arrow with a broken line is a wavelength of two-photon absorption of a pulse at 0.8 μm.

FIG. 5: Fe$^{3+}$ → Fe$^{2+}$ conversion on irradiation with 800-nm, 100-fs laser pulses of 0.1 M K$_3$Fe$^{3+}$(C$_2$O$_4$)$_3$ aqueous solution. The vertical scale represents log (absorbance) at 520 nm for 1 cm cell length per 1 min of Fe$^{2+}$−o-phenanthroline complex and the horizontal scale is log (laser energy in a unit of μJ/pulse). An arrow with WL is a region of energy where white-light laser was visually observed and an arrow with BD shows an energy region where bright spots were occasionally observed visually.
the range of 1.3–12 μJ/pulse for 5–751 min is shown. The smallest absorbance value in the figure was observed as 0.00 in absorbance at 1.45 μJ of laser energy after 751 min irradiation; therefore, the maximum value would be 0.005/751 = 6.7 × 10^{-6} in absorbance per min. The reduction mechanism seems to be solvent ionization followed by the electron tarp reaction on the basis of two important differences from those for an excitation wavelength of 800 nm. i) A single straight line cannot fit most of the observed points, but a sharp drop is seen in an energy range lower than that where white-light laser is observable. A multiphoton excitation and reduction mechanism does not seem to support the present observation, though the three-photon energy corresponds to 397 nm and reaches the CT state. ii) A low conversion efficiency to Fe^{2+} from the input laser energy is observed and about 1/10 of that with an excitation wavelength of 800 nm at several micro Joule of laser energy. But it would not be low enough to explain them by the mechanism based on the three-photon absorption (for a detailed discussion see section IV-2).

FIG. 6: Fe^{3+} → Fe^{2+} conversion on irradiation with 1190-nm, 100-fs laser pulses of 0.1 M K_3Fe^{3+}(C_2O_4)_3 aqueous solution. An arrow with WL is a region of energy where white-light laser visually seen.

III-3. Ag^+ → Ag^+_n

Silver ions have been known to be reduced to Ag^+_n by γ-ray irradiation in aqueous solutions that contain sodium polyacrylate [28]. While Ag nanoparticle formation has been reported on irradiation with femtosecond laser pulses under high laser intensities, where solvent break down occurs [28 b], the present results were obtained under weak laser intensities, where white-light laser emission was barely visible. The reducing agent is the
hydrated electron by generated $\gamma$-radiolytically. The absorption spectra of the solutions vary from rose to green or blue depending on the size of the silver clusters. Aqueous solutions containing silver ions are good systems, because we can produce solvated electrons by femtosecond laser irradiation. Figure 7 shows preliminary results for the color change of an $\text{Ag}^+$ ion solution by femtosecond laser pulses.

Before irradiation a 0.3 ml solution in a 1-cm cell containing $6 \times 10^{-3}$ M $\text{AgClO}_4$, 0.01 M PANa, and 0.13 M 2-propanol has no absorption visible region. After 100-fs, 5-$\mu$J laser pulses at 1 kHz for 10 min, the color becomes dark brown with an absorption spectrum in the entire visible range with a broad hump around 450 nm. Interestingly, a kind of brown smoke in the cell was visible during the irradiation.

White-light laser was generated in a pulse energy range of 2–10 $\mu$J. This observation coincides with a report in which white-light laser was studied in the presence of silver clusters with 50-fs and 800-nm laser pulses with a focal lens of 170 mm with an energy higher than 3 $\mu$J/pulse [37]. A bright spark was seen occasionally, probably due to the cluster inducing a breakdown even at an energy of 5 $\mu$J/pulse. We observed $\text{Ag}^+_n$ absorption in the energy range of weak irradiation intensities, where white-light laser is generated. The absorbance-laser intensity in logarithmic scales gave a slope of about 1.5, though the absorbance data of $\text{Ag}^+_n$ fluctuated widely. The absorption spectrum in Figure 7 indicates that the $\text{Ag}^+$ solution would require at least three photons of an 800-nm pulse to reach an excited state of this system, but the slope of the formation of $\text{Ag}^+_n$ vs. the laser intensity was not three but about 1.5.
IV. DISCUSSION

IV-1. Reduction with $e_{\text{sol}}^-$ accompanied by white light laser

Three lanthanide ions ($\text{Eu}^{3+}$, $\text{Sm}^{3+}$, and $\text{Yb}^{3+}$) and two transition metal ions ($\text{Fe}^{3+}$ and $\text{Ag}^+$) have been found to be reduced to the corresponding ions by femtosecond laser pulses accompanied by white-light laser generation. The common mechanism through these reactions, including $\text{Fe}^{3+}$ at 1190 nm other than the case of a $\text{Fe}^{3+}$ system by 800-nm pulse excitation, is schematically depicted in Figure 8. The interaction and related phenomena between high intensity femtosecond laser beams and liquid media have been well studied [33–35]. Briefly, an input laser beam is converged by a focusing lens and nonlinear index $n_2$ of the medium. An electron is injected under a high intensity laser field and the electrons play a role of defocusing due to their low index of electron. A balance between the positive and low indexes maintains a small size of the high intensity region, which is called a filament. The peak intensity in the filament is clamped and kept at approximately $10^{13}$ W/cm$^{-2}$, which is high enough to ionize solvent and generates electrons. At the same time, the laser pulse becomes steep in the filament, resulting in self-phase modulation, i.e., the input laser energy is partly converted to white-light laser. Conversion to the white-light laser proceeds before laser induced bulk breakdown (BD) in the case of femtosecond pulse excitation unless there are tight focusing conditions. The ionization causes plasma-induced defocusing, followed by multiple refocusing, which has been clearly observed [35].

![Figure 8: Schematic diagram of the reduction of $\text{Me}^{3+} \rightarrow \text{Me}^{2+}$ and/or $\text{Ag}^+ \rightarrow \text{Ag}$ under IR femtosecond laser pulse accompanied by white-light laser.](image)

Once an electron is ejected, the surrounding methanol/water molecules relax it to the solvated electron, $e_{\text{sol}}^-$, and it can then be captured by $\text{Me}^{3+}$ and / or $\text{Ag}^+$. The scheme in Figure 8 is rewritten for each reduction system as in (1), (3), (4), and (5). The three lanthanide system has been described in (1). Ionization of water and relaxation to $e_{\text{sol}}^-$ would be the first step as in (3) for the $\text{Fe}^{3+}$ system at 1190-nm pulses and for the $\text{Ag}^+$ system.

$$\text{CH}_3\text{OH}/\text{H}_2\text{O} \xrightarrow{n\hbar\nu} \text{CH}_3\text{OH}^+ / \text{H}_2\text{O}^+ + e_{\text{sol}}^-,$$  

(3)

$$[\text{Fe}^{3+}(\text{C}_2\text{O}_4)_3]^3^- + e_{\text{sol}}^- \rightarrow [\text{Fe}^{2+}(\text{C}_2\text{O}_4)_3]^4-,$$  

(4)

$$\text{Ag}^+ + e_{\text{sol}}^- \rightarrow \text{Ag}, \text{Ag}^+ + \text{Ag} \rightarrow \text{Ag}^+ \text{Ag}_2^+, \ldots \rightarrow \text{Ag}_n^+. \quad \text{(5)}$$
We suggest Scheme (4), in which the parent oxalate Fe$^{3+}$ ion is reduced by $e^-_{\text{sol}}$ following Scheme (3). The reaction with $e^-_{\text{sol}}$ with [Fe$^{3+}$(C$_2$O$_4$)$_3$]$^{3-}$ in (4) has been discussed as a minor contribution to the photochemical one-photon reaction of [Fe$^{3+}$(C$_2$O$_4$)$_3$]$^{3-}$ with a high rate constant of $1.2 \times 10^{10}$ M$^{-1}$s$^{-1}$ [24]; in other words, (4) is an efficient reaction if $e^-_{\text{sol}}$ is present. It is notable that at least five 800-nm photons are required to be absorbed to ionize the media on the based on the band gap in methanol of 6.2 eV methanol [35] and in water of the $I_p$ of 6.5 eV [38].

After a solvent molecule is ionized, a few events follow. We estimate that about a half of the initially ejected electrons could react with the metal ions. Immediately after the ionization, the electron will be solvated to less than 1 ps to form $e^-_{\text{sol}}$ [36]. The next event would be geminate recombination between the parent cation and $e^-_{\text{sol}}$. Photoionization studies in neat water at room temperature have been performed in a picoseconds timescale. After the electron has been solvated, the geminate recombination occurs in roughly 60 ps with 40-50% of the electrons, in other words, 50–60% of $e^-_{\text{sol}}$ escape from the initial pair [40]. The escaped electron has a high possibility of reaction with metal ions. The reaction rate constants between metal ions and $e^-_{\text{sol}}$ have been accumulated in the field of radiation chemistry [12] and are $1-5 \times 10^{10}$ M$^{-1}$s$^{-1}$ for the present metal ions. The reaction time is 0.2–1 ns for the case of 0.1 M metal ion concentration. Major competing reactions would be $e^-_{\text{sol}} + \text{O}_2 \rightarrow \text{O}_2^-$ with $1.9 \times 10^{10}$ M$^{-1}$s$^{-1}$ [12], which is in 200 ns, and $e^-_{\text{sol}} + e^-_{\text{sol}}$ quenching with a rate constant of $1.1 \times 10^{10}$ M$^{-1}$s$^{-1}$, which will be in 100 ns time scale. These time scales are estimated assuming $[e^-_{\text{sol}}] \sim 9 \times 10^{-4}$ M based on 55% of initially generated electron of $10^{18}$ cm$^{-3}$ in filaments [34] and $[\text{O}_2] \sim 2.8 \times 10^{-4}$ M in an air saturated solution. As a conclusion, the major reaction would occur between metal ions and $e^-_{\text{sol}}$, and a half of the initially ejected electrons can be trapped by metal ions for the case of 0.1 M of a metal ion solution. To experimentally determine the trapping efficiency, we need information on the electrons ejected/unit filament, and the number of filaments, although we roughly estimated the efficiency of 0.2 for the case of Eu$^{3+}$ reduction [4].

IV-2. Two photon absorption followed by reduction

For the Fe$^{3+}$ system at 800-nm pulses, two-photon excitation to the CT state followed by the normal photochemical reaction of Scheme (2) proceeds. Formation of Fe$^{2+}$ was clearly observed with keeping the slope of two even in an energy range lower than the threshold laser intensity of white laser emission as in Figure 5.

At 800 nm, the conversion efficiencies of the reduced metal ion numbers divided by the input photon numbers were evaluated to be 0.052 for Fe$^{2+}$ formation from Figure 5. The input laser energy was measured to be absorbed by Fe$^{3+}$ solution by 10 % more than that by pure water. The single-photon photochemistry of Fe$^{3+}$ complex has the yields of 1.13 (392 nm)-1.14 (405 nm) [20]. The observed conversion efficiency of 0.052 is close to the expectation: 0.1(absorption of 800-nm laser pulse) $\times 1.13$ (yield of the excited CT state at 405 nm)/2(two-photon) = 0.057. It is very reasonable for the two photon chemistry. The two-photon coefficient was reported as $1.5 \times 10^{-50}$ cm$^4$/s/photon at 694.3 nm [25]. This value is equivalent to the molar extinction coefficient of 150 M$^{-1}$cm$^{-1}$ at 10$^{13}$ Wcm$^{-2}$. The absorbance at 10 $\mu$J of the 800-nm pulse was 0.05; therefore, the two-photon coefficient at
800 would be on the order of \(0.05 \times 10^{-50} \text{ cm}^4 \text{ s/photon}\), if the filament length was 0.1 cm.

The CT level of \([\text{Fe}^{3+}(\text{C}_2\text{O}_4)_3]^{3−}\) can be reached by three photon absorption of 1190-nm pulses and the CT state \(\text{Yb}^{3+}\) by three-photon absorption of 800-nm pulses; however, the results in Figures 3 and 6 cannot be explained in terms of the slopes of three. The order for the \(n\) th-multiphoton absorption and reactions sometimes go into behind the scene, in the intensity region where self-focusing of the laser beam occurs [26, 27]. In those organic molecules, the multiphoton absorption was clearly observed under the threshold of the white-light laser [26, 27]. The reduction due to two-photon absorption was observed well under the threshold of the white-light laser for the \(\text{Fe}^{3+}\) system by 800-nm pulse excitation.

IV-3. To \(\text{Fe}^{2+}\) at 1190 nm with an efficiency of \(10^{-3}\)

The efficiencies of the reduced metal ion numbers divided by the input photon numbers can be evaluated to be 0.001 for \(\text{Yb}^{2+}\) at 800 and 970 nm from Figures 2 and 3, and 0.0016 for \(\text{Fe}^{2+}\) at 1190 nm from Figure 6, in all cases at 10 \(\mu\)J/pulse. The same order of the efficiencies for the two different chemical systems is a good indication to hold the same reduction mechanism. The absorbance of 0.05 at 367 nm for \(\text{Yb}^{2+}\) in Figures 2 and 3 was obtained by \(1.8 \times 10^5\) shots irradiation of 10 \(\mu\)J/pulse. Using the molar extinction coefficient of 500 M\(^{-1}\)cm\(^{-1}\) and the excitation volume of 0.04 cm\(^{3}\), the produced \(\text{Yb}^{2+}\) was evaluated to be \(1.0 \times 10^{-8}\) mol and the input photons were \(1.2 \times 10^{-5}\) E (Einstein = mol photon). Therefore the conversion efficiency was on the order of \(10^{-3}\). There are two steps for the reduction. The first step is the formation of \(e_{\text{sol}}^{-}\) and the second one is the trapping reaction of \(e_{\text{sol}}^{-}\) by the metal 3+ ions. To reach the coincidence the efficiencies, the rate constants between the metal 3+ ions and \(e_{\text{sol}}^{-}\) should be similar. In fact, they are on the same order; \(1.5 \times 10^{10}\) M\(^{-1}\)s\(^{-1}\) for the oxalate \(\text{Fe}^{3+}\) system [24] and \(4.3 \times 10^{10}\) M\(^{-1}\)s\(^{-1}\) for \(\text{Yb}^{3+}\) aqueous solution [12].

If the mechanism of three-photon absorption followed by reduction worked for 1190-nm excitation, the efficiency at 1190 nm should be reduced to \(10^{-3}\) times of that of the two-photon absorption, according to the absorption cross section ratio between three photon \((\sigma^{(3)}I^2)\) versus two-photon one \((\sigma^{(2)}I)\), where the laser intensity \(I = 10^{13}\) W/cm\(^2\) \((3.8 \times 10^{31}\) photons cm\(^{-2}\)s\(^{-1}\) at 800 nm and \(5.7 \times 10^{31}\) photons cm\(^{-2}\)s\(^{-1}\) at 1190 nm, under 3 \(\mu\)J in 100 fs and 20 \(\mu\)m diameter). We adopt \(\sigma^{(3)}/\sigma^{(2)} \approx 10^{-35}\) photons\(^{-1}\)cm\(^2\)s according to a review about \(n\)-photon absorption on atoms [39]; therefore,

\[
\text{Crosssectionratio} = \frac{\sigma^{(3)}I^2(1190 \text{ nm})}{\sigma^{(2)}I(800 \text{ nm})} \approx 1 \times 10^{-3}.
\]

The observed efficiency ratio at 1190 nm vs. that at 800 nm was \(0.0017/0.052 \approx 0.03\), and is 30 times larger than that of the expected value of \(10^{-3}\) in Eq. 6. The high conversion to \(\text{Fe}^{2+}\) at 1190 nm can be another reason that suggests the reduction mechanism is not the three-photon absorption process but formation of \(e_{\text{sol}}^{-}\) followed by reduction. Although we may not directly apply a parameter in atoms to the \(\text{Fe}^{3+}\) complex, it is not unreasonable to indicate the low conversion efficiency by three-photon absorption mechanism.
V. CONCLUSIONS

The following points from the Introduction have been made clear. i) Yb$^{3+}$ system has been realized to show a reaction of Ln$^{3+} + e_{\text{sol}}^{-} \rightarrow \text{Ln}^{2+}$, which is similar with the Eu and Sm systems. Now three lanthanide ions, which have fast reaction rate constants of $e_{\text{sol}}^{-}$ in the literature [12–14] and have low redox potentials [41], show the same behavior. ii) We have succeeded in extending two transition metals of Fe$^{3+}$ at 1190-nm excitation, and Ag$^{+}$ at 800 nm. Whenever white-light laser is emitted, the reactions have been detected to Fe$^{2+}$ and Ag$^{+}$. iii) An Fe$^{3+}$ system by 800-nm excitation, Fe$^{2+}$ was detected even lower than the white laser threshold and was explained in terms of two-photon reaction. iv) Now we know that three lanthanide ions Ln$^{3+}$ (Ln = Eu, Sm, Yb) and two transition metals (Fe$^{3+}$ and Ag$^{+}$) were found to be reduced to the corresponding Ln$^{2+}$, Fe$^{2+}$, and Ag$^{+}$ by $e_{\text{sol}}^{-}$ generated by femtosecond laser pulses. These reactions are along the same lines as those in radiation chemistry, as we have already suggested when we observed the Eu$^{3+} \rightarrow \text{Eu}^{2+}$ reaction as the first example [4]. These reactions could be very general and the accumulated results in the radiation chemistry can be used as reliable references. We need to study more in detail, because there must be some differences in chemistry among femtosecond laser with white laser, laser induced break down, and γ-ray radiation. Recently, femtosecond filamentation has been applied to cancer therapy [7]. Studies on various chemical reactions by femtosecond filamentation would be helpful to understand the chemical reactions in cancer therapy.

Acknowledgements

This work was financially supported in part by a Grant-in-Aid (No. 23550030) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan to N.N.

References

Temperature-Dependent Supercontinuum Generation from Femtosecond Filamentation in an Aqueous CuSO$_4$-solution

X. W. Song, Z. Jin, Z. Q. Hao,* X. H. Zhang, and J. Q. Lin†

School of Science, Changchun University of Science and Technology, Changchun, 130022, China
(Received September 4, 2013)

Supercontinuum generation from laser filamentation in aqueous CuSO$_4$-solution is found to be strongly influenced by the solution temperature. The supercontinuum spectrum becomes broader as the solution temperature decreases from $65 \, ^\circ \text{C}$ to $5 \, ^\circ \text{C}$. Correspondingly, the conversion efficiency of fundamental laser pulse to supercontinuum generation increases from 41.9\% to 63.9\%.

DOI: 10.6122/CJP.52.519 PACS numbers: 52.38.Hb, 42.65.Jx, 42.65.Ky

I. INTRODUCTION

The propagation of intense femtosecond pulses in liquid that results in filamentation and spectral broadening has been studied for more than ten years [1–10]. The broaden spectrum of the pulse, called supercontinuum generation, extends from ultraviolet to infrared range, which can find many applications in white light LIDAR, spectroscopy, and interferometry. The supercontinuum emission can be obtained in many kinds of media, including gases, liquid and transparent solid material. Many researchers have investigated femtosecond filamentation in those media, and the sample used is not confined to pure material. It is found that the laser interaction with mixed samples, for example water doped with scattering polystyrene microspheres [11] or noble metal nanoparticles [12], show some unique characteristics of filamentation and supercontinuum generation. Recently, an aqueous solution of CuSO$_4$ has been used as an absorptive medium, because it has a strong absorption around 800 nm of the laser central wavelength as well as a high transmission on blue side, and finally a unique supercontinuum spectrum with a flat plateau in the visible range can be obtained [13].

Refractive index of a liquid and laser parameters are important factors that determine the characteristics of supercontinuum spectrum. In the case of solution, it is known that, in addition to the concentration of the solution which affects the index of refractive, the temperature also influences its refractive index [14]. On the other hand, the temperature variation will affect stability of laser-liquid interaction, especially under high repetition rate laser condition; therefore, the temperature is an essential parameter which has to be considered besides the solution concentration and the laser parameters if one wants to

*Electronic address: zqhao@cust.edu.cn
†Electronic address: linjingquan@cust.edu.cn

obtain a stable and efficient white-light source. However, up to now there are no reports of temperature-dependent filamentation or supercontinuum generation in liquid samples. In this paper, we studied experimentally the temperature effect on the supercontinuum generation induced by femtosecond laser pulses from a solution of CuSO\textsubscript{4}. The results show that the generated supercontinuum spectrum highly depends on solution temperature. Thus the supercontinuum generation can be optimized by means of temperature control, and it could be an easy method to get a flat and efficient supercontinuum spectrum to be more suitable for applications.

II. EXPERIMENTAL SETUP

The experimental setup for generating supercontinuum from CuSO\textsubscript{4} is illustrated in Figure 1. The laser employed in the experiment is an amplified Ti:sapphire femtosecond laser system that generates laser pulses at central wavelength of 800 nm, with the maximum pulse energy of 4 mJ, pulse duration of 50 fs, and repetition rate of 1 kHz. The linearly polarized femtosecond laser beam is loosely focused by a lens (lens L1, \( f = 400 \) mm) into a 4 cm long fused silica cuvette containing the solution of CuSO\textsubscript{4}. The pulse energy is adjusted with neutral density filters. The concentration of the solution in our experiment is chosen to be 0.035 mol/L. Another lens (lens L2, \( f = 50.8 \) mm) is used to collect the laser beam into an integrating sphere. A spectrometer (USB 4000, Ocean Optics) is used to record the supercontinuum spectra. In order to control the temperature of the solution, we attached a home-made thermoelectric cooler to the cuvette. The temperature of the solution can be controlled from 5 \( ^\circ \)C to 75 \( ^\circ \)C continuously.

![Experimental setup for temperature dependent supercontinuum generation.](image)

III. RESULTS AND DISCUSSIONS

Different from filamentation in air or solid, vapor bubbles will appear during the process of laser filamentation in liquid samples, and the bubbles greatly degrade the spectral repetitiveness of supercontinuum. Laser-induced vapor bubbles are mainly influenced by laser intensity at the repetition of 1kHz we used. We found that the vapor induced by a laser pulse will interact with the followed laser pulses, and in our case the influence of the bubbles on filamentation and supercontinuum generation can be reduced to a great extent.
when relatively low laser pulse energy of 10 μJ is used.

Figure 2 shows the spectra of the supercontinuum generated from laser filamentation in the aqueous CuSO₄ solution under conditions of different temperatures. We can see from the Fig. 2 that the temperature results in spectra with different degrees of spectral broadening. The supercontinuum spectrum mainly covers a spectral range of from 720 nm to 850 nm at temperature of 65 °C, and it spreads from about 450 nm to 950 nm which covers more than 500 nm at temperature of 5 °C. Lower solution temperature leads to a relatively wider spectral broadening and a stronger emission especially in the visible range, i.e. a higher conversion efficiency of supercontinuum generation.

![Supercontinuum spectra generated in the solution of CuSO₄ at different temperatures varying from 5 °C to 65 °C.](image)

In order to investigate the effects of temperature quantitatively, we define the conversion efficiency as the energy ratio of the continuum part (spectral range of < 785 nm and > 815 nm) except the fundamental part (spectral range of 785–815 nm) to the whole. As shown in Fig. 3, the supercontinuum conversion efficiency decreases linearly with the increase of the solution temperature. Under the condition of our experiments, at the temperature of 5 °C we got the highest conversion efficiency of 63.9%, and a broadened spectrum of supercontinuum which covers at least from 450 nm to 950 nm. The spectral intensity in the visible range at wavelength of 600 nm for example in the case of 5 °C is two orders of magnitudes higher than that in the case of 65 °C, and the corresponding conversion efficiency is more than 1.5 times higher than that at temperature of 65 °C.

It is known that the decrease of the temperature will result in an increase of the linear and nonlinear refractive index of the liquid sample, which would lead to a lower critical power for self-focusing, hence to a lower clamped intensity of filament. This would
give rise to a weaker interaction, and consequently a narrower SC emission is expected. However, our results show that the SC from CuSO$_4$ becomes broader as the temperature decreases, this behavior can be explained as the following. When filamentation forms in liquid with a high repetition rate laser as the case of our experiment, the laser would heat up the filament zone very efficiently, especially when an absorbing medium is used. This heating would induce some nonuniform heat flow in the filament region. This turbulence will perturb the focusing, thus the laser intensity in the filament zone, and this would reduce the intensity in the zone. The larger this perturbation is, the lower the intensity in the filament zone will be. A colder medium would dissipate heat more efficiently than a warmer one. Thus, when the liquid is colder, heat dissipation is more efficient. This leads to weaker turbulence, resulting in higher laser intensity in the filament zone. A higher intensity would give rise to more ionization, hence, more self-steepening, and consequently a broader SC spectrum is obtained.

Compared with supercontinuum from pure water, the overall intensity of the SC from CuSO$_4$ solution is lower, especially near the pump wavelength. This is due to that the SC is modulated by the transmission of CuSO$_4$ solution, whose transmission at shorter wavelength (400–600 nm) is high (80–90%), while its value sharply decreases to below 10% near the pumping wavelength [13]. Even though the efficiency of SC generation decreases in the case of CuSO$_4$, the use of the solution is favorable for a flat-plateau SC. Furthermore, the cooling of the CuSO$_4$ solution will, to some extent, compensate the loss of SC conversion efficiency.
IV. CONCLUSIONS

The effect of temperature on supercontinuum generation in the aqueous solution of CuSO$_4$ has been experimentally investigated. We have found that a lower solution temperature is favorable for a broader spectrum and higher conversion efficiency of supercontinuum, i.e. lower temperature enables more efficient supercontinuum generation. The underlying mechanism is attributed to that the lower temperature of the solution gives rise to a less turbulence in the filament zone. As a result, a lower temperature leads to a stronger nonlinear laser-sample interaction and consequently a stronger supercontinuum emission. The method of supercontinuum generation control via solution temperature as shown in this work offers another degree of freedom to get a flat and much more efficient supercontinuum emission besides the one via concentration control [13].

Acknowledgements

We would like to thank Prof. S. L. Chin from Laval University, Canada for fruitful discussions. This work was supported by 973 program under Grant No. 2013CB922404, the National Natural Science Foundation of China under Grant Nos. 11274053, 11074027, 61178022 and 11211120156, the Doctoral Program of Higher Education under Grant Nos. 20122216120009, 20122216110007 and 20112216120006, and Funds from Sci. & Tech. Dept. of Jilin Province under Grant No. 20130522149JH, 20111812.

References

Review

Nuclear Fusion Driven by Coulomb Explosion of Deuterated Methane Clusters in an Intense Femtosecond Laser Field

Jiansheng Liu, Haiyang Lu, Zili Zhou, Cheng Wang, Hongyu Li, Changquan Xia, Wentao Wang, Yi Xu, Xiaoming Lu, Yuxin Leng, Xiaoyan Liang, Guoquan Ni, Ruxin Li, and Zhizhan Xu

State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, P.O. Box 800-211, Shanghai 201800, China

(Received November 14, 2013)

We have made experimental studies on the generation of deuterium-deuterium fusion neutrons from intense Coulomb explosions (CE) of large-size (CD₄)₅ cluster jets under the irradiation of intense femtosecond laser pulses. By optimizing the propagation of a laser pulse in the cluster gas and the time delay between the laser pulse and the gas flow, the maximum neutron yield of 2.5 × 10⁵, which corresponds to a conversion efficiency of 2.1 × 10⁶ fusion neutrons per joule of incident laser energy, has been obtained with a 120-mJ, 60-fs laser pulse and cluster jets with an average molecular density of 3.6 × 10¹⁸ cm⁻³ and cluster radius of 7 nm. We have demonstrated that the neutron yields can be dramatically increased by using heteronuclear (CD₄)₅ clusters as compared with the similar sized homonuclear (D₂)₅ clusters. This enhancement is attributed to the significant increase in the deuteron kinetic energies due to energetic boosting and overrun effects during CE of heteronuclear clusters.

DOI: 10.6122/CJP.52.524

PACS numbers: 36.40.Gk, 52.50.Jm, 25.45.-z

I. INTRODUCTION

A cluster is a microscopic aggregation of 10²–10⁷ atoms (i.e., a few nanometers in radius) bound together by van der Waals forces. The interaction of a gas target composed of these kind of clusters with ultrashort intense laser pulses has attracted considerable attention in the last two decades since many fascinating phenomena have been observed such as strong absorption of laser energy, emission of laser harmonics, strong x-ray generation, and the production of very energetic and highly charged ions [1–3]. The latter has directly triggered the novel idea and implementation of table-top fusion neutron sources [4]. Possessing the properties of both solid and gas, clusters act as important targets which can bridge our knowledge of laser interaction with gas and solid. The generation of deuterium-deuterium (dd) fusion neutrons from Coulomb explosions of laser-heated clusters was firstly demonstrated by Ditmire et al. in 1999 and immediately arouse researchers’ intense enthusiasm because just by irradiating cryogenic deuterium cluster jets with a low-energy, compact and high-repetition-rate table-top laser (35 fs, 150 mJ), an efficiency of about 10⁵ fusion neutrons per joule of incident laser energy was achieved, which was close to the efficiency of large-scale laser-driven fusion experiments [4]. While blasting (D₂)₅ clusters with an
intense fs laser pulse, the electrons are stripped off the cluster, leaving the ions to explode violently from their mutual repulsion. The explosions are so violent that deuterons from neighboring clusters fuse and emit neutrons. Such kind of extremely short (sub-ns) bursts of fast neutrons could find wide applications in material science such as time-resolved study on radiation induced damage if the efficiency could be improved by 3 orders of magnitude [5, 6]. To that aim, quite a lot of work has been made to investigate the fusion dynamics in laser-cluster interactions, the characterization of fusion burn time and angular distribution of neutron emission, as well as to search for higher neutron yield [7–21]. The effects of the (D$_2$)$_N$ cluster size, the laser energies and focusing conditions have been investigated by Zweiback et al. to optimize the fusion neutron yields [8]. However, the average kinetic energies (KEs) of deuterons from explosion of (D$_2$)$_N$ clusters were reported to be located only in the range of 2.5–7 keV [7, 8, 14–16], which are still much lower than the optimal KEs in the range of 40–100 keV for efficient dd fusion.

Last and Jortner proposed an efficient mechanism for enhancing the deuterons’ KEs by using clusters of heteronuclear deuterium containing molecules e.g. (D$_2$O)$_N$ and (CD$_4$)$_N$ [10, 11, 13, 17, 18]. For heteronuclear clusters, the light deuterons can outrun heavy ions inside the cluster and experience much more violent Coulomb repulsion due to energetic boosting effect and therefore the deuterons’ KEs can be greatly enhanced. Moreover, a quasi-monoenergetic distribution of deuterons, suitable to induce dd fusion, can be generated due to this overrun effect. Our previous work has also indicated that the neutron yields from CD$_4$ clusters can be at least increased by 2 orders of magnitude compared with the same sized (D$_2$)$_N$ clusters [22]. In Ref. [13], Grillon et al. investigated the two origins of nuclear fusion driven by Coulomb explosion (NFDCE) of hetronuclear (CD$_4$)$_N$ clusters by using a low gas density of $2 \times 10^{17}$ cm$^{-3}$. In their experiments, the most probable KE of D$^+$ ions could be as high as 45 keV with the estimated cluster size of $2 \times 10^5$ molecules (14.4 nm). This result indicated the significant enhancement of deuteron KEs by CE of (CD$_4$)$_N$ clusters as compared to (D$_2$)$_N$ clusters. However, Owing to the low gas density, the maximum neutron yield reported by them was $\sim 8000$ at a laser intensity of $7 \times 10^{17}$ Wcm$^{-2}$, which corresponds to a conversion efficiency of $10^4$ neutrons per joule of incident laser energy. It is much lower than the maximum neutron conversion efficiency ($1 \times 10^5$/J) from NFDCE of (D$_2$)$_N$ clusters reported by Ditmire’s group [4].

In Ref. [15], Madison et al. gave a comparison between the NFDCE of (D$_2$)$_N$ and (CD$_4$)$_N$ clusters. In their experiments, at low laser energy of 100 mJ, the fusion neutron yield in (CD$_4$)$_N$ clusters is higher than in (D$_2$)$_N$ clusters just by a factor of 2. However, by increasing laser energy from 100 mJ to 10 J, the neutron yield in (CD$_4$)$_N$ clusters became lower than that in (D$_2$)$_N$ clusters. They attributed this reversal in the actual fusion yield from expectation to a slight degradation in the jet performance, which produced a lower (CD$_4$)$_N$ gas jet density. Recently, we have successfully demonstrated that the neutron yields can be dramatically increased by 50 times by using heteronuclear (CD$_4$)$_N$ clusters in comparison with the similar sized homonuclear (D$_2$)$_N$ clusters [23, 24].

In the following, we have made experimental studies of generation of dd fusion neutrons from intense Coulomb explosions of high-density large-size (CD$_4$)$_N$ cluster jets under the irradiation of superintense femtosecond laser pulses. A correlated study of neutron
yields, deuterons’ KEs and plasma channel formation diagnosed by a pump-probe interferometer allows us to optimize the coupling of laser-cluster interaction in order to produce very efficient nuclear fusion. The maximum efficiency of $2.1 \times 10^6$ fusion neutrons per joule of incident laser energy has been obtained with a 120-mJ, 60-fs laser and cluster jets with an average molecular density of $3.6 \times 10^{18} \text{ cm}^{-3}$ and cluster radius of 7 nm at a backing pressure of 84 bars. The comparison between $(D_2)_N$ and $(CD_4)_N$ clusters has been investigated with respect to the deuteron energy and neutron yield.

II. CLUSTER FORMATION AND DIAGNOSTICS

Although clusters can be produced in a number of ways, in laser-cluster interactions, clusters are generally produced by adiabatic expansion of gases through a conical nozzle into vacuum. When high-pressure gas flows into vacuum through a conical nozzle, due to adiabatic expansion these gaseous atoms or molecules cool and nucleate and can be held together by van der Waals forces into quite large-size clusters under appropriate conditions. As shown in Fig. 1(a), we have made a liquid nitrogen cooled pulsed valve to generate large-size clusters of deuterium or deuterated methane. Fig. 1 (b) shows a pulsed sonic gas jet with a conical nozzle. The throat diameter $d$ is 310 mm, the length $L$ is 26 mm, and the output diameter $D$ is 4.5 mm. The operation repetition of the jet is 1 Hz and the vacuum is $2 \times 10^{-3} \text{ Pa}$ which is good for cluster formation. The onset of cluster formation and size estimation in gas jets can be characterized by a widely used empirical Hagena parameter [25–27]

$$\Gamma^* = k\left[\frac{d}{\tan(\alpha)}\right]^{0.85}p_0T_0^{-2.29}$$

(1)

Where $d$ is the diameter in $\mu$m of the jet throat, $\alpha$ is the half angle of the conical nozzle, $p_0$ is the backing pressure in mbar, $T_0$ is the initial gas temperature, and $k$ is a constant that depends on the atomic species. The average number of atoms in a cluster is given as $<N> = 33(\Gamma^*/1000)^{2.35}$. The dependence of Hagena parameter on $p_0$ and $T_0$ indicates that high backing pressure and low gas temperature favors the production of large-size clusters. Although Hagena parameter gives a rough estimation of cluster formation and cluster size, it is not reliable to calculate the size of clusters generated by a gas jet by using Hagena parameter. In our experiment, Rayleigh scattering technique has been used to measure the intensity of scattering signal as a function of backing pressure and then the cluster size as function of backing pressure can be approximately calculated. Fig. 2 shows the measured scattering intensity of $(CD_4)_N$ clusters as a function of backing pressure from 10 to 80 bars. By a fitting procedure, the scattering intensity is proportional to $P_0^4$. At low pressure, we use the measured energy spectra of deuterons from laser-cluster interaction to calibrate the size of the $(CD_4)_N$ clusters [28]. The average size of $(CD_4)_N$ clusters at 80 bars is estimated to be 7 nm in radius.
FIG. 1: Liquid nitrogen cooled pulsed valve and conical nozzle to generate large-size clusters of deuterium or deuterated methane.

FIG. 2: Measured scattering signal of \((\text{CD}_4)_N\) clusters as a function of backing pressure from 10 to 80 bars.

### III. EXPERIMENTAL SETUP FOR LASER-CLUSTER INTERACTION

The experimental setup is shown in Fig. 3. A chirped-pulse-amplification Ti:sapphire laser system delivers 10-Hz laser pulses with the duration of 60 fs at the center wavelength of 800 nm into the chamber. The contrast ratio of the laser pulse is \(10^7\) on a time scale of 100
ps before the main pulse, preventing any pre-dissociation of the cluster in the experiments. The propagation effects of fs laser pulses in the cluster jets and the plasma channel formation are probed by splitting 5 percent of the laser beam and passing it perpendicularly across the plasma filament into a Michelson-type interferometer. The pump pulse which holds about 95% of the energy is tightly focused at 0.8 mm downstream from the nozzle exit by an f/4 off-axis parabolic mirror, yielding a maximum intensity of about $I_{\text{peak}} = 7 \times 10^{17}$ Wcm$^{-2}$ (120 mJ) in vacuum. The focusing depth $D_f$ (defined as the distance from the focal plane in vacuum to the gas jet axis) is arranged from −1.85 to 0.95 mm in order to investigate the propagation effect of incident laser, as well as to optimize the neutron production and KE of Deuterons. The neutrons are measured through a plastic scintillator coupled with a photomultiplier (PMT). Two detectors were used. One is home-made (ND-1), and calibrated by a neutron source in the institute of Chinese Academy of Engineering Physics (CAEP). The detection efficiency is calculated to be 0.31 pC per neutron, under the voltage supply of 2400 V. The other is bought from Saint-Gobian (BC-408), and the detection efficiency is measured according to ND-1 to be about 3.5 pC per neutron, under the voltage supply of 1200 V. The scintillator rod diameters are 127 mm and 180 mm for BC-408 and ND-1, respectively. The PMT was 2.5-ns fast response tube. The KEs of ions are measured through a 2.25-meter long time-of-flight spectrometer. Thanks to the high molecular polarizability of CD$_4$, large-size clusters can be produced even at room temperature by supersonic expansion of CD$_4$ gas into vacuum. However, in order to generate

FIG. 3: Experimental setup for fusion neutron generation from laser-cluster interaction. The plasma channel formation is probed by splitting 5 percent of the laser beam and passing it perpendicularly across the plasma filament into a Michelson-type interferometer. The energy spectra of ions are measured through a 2.25-meter-long time-of-flight spectrometer.
large-size deuterium clusters, the pulsed solenoid valve has to be operated at liquid-nitrogen temperature.

IV. OPTIMIZATION OF NEUTRON GENERATION

In order to drive efficient dd nuclear fusion, highly energetic D\(^+\) ions should be produced, which requires generation of large-size \((\text{CD}_4)_N\) clusters. On the other hand, efficient neutron generation greatly relies on the frequent collisions of D\(^+\) ions, which requires a high deuteron density and the deposition of laser energy into the cluster jets should also be optimized. Therefore, the pulsed solenoid valve is designed to be operated at a high backing pressure of 80 bars. The opening of the valve is triggered by a square electric pulse with duration of 1.1 ms. However, the cluster flow can last several milliseconds. It must be mentioned that evolutions of gas density and the cluster size are quite different. The gas densities at the leading (small delay time) and tailing edges of the cluster flow are very low while the cluster size increases as the time delay increases. By changing the time delay between the laser pulse and the gas flow as well as the backing pressure, we have measured the interferograms of the plasma filaments, KEs of D\(^+\) ions and neutron yields. Fig. 4 shows the typical interferograms of the plasma filaments at different time delays from 1.4 to 6 ms with a backing pressure of 80 bars. It can be seen that a long plasma channel with high electron density can be generated at a time delay of 3–4 ms. Using Abel inversion, the electron density as a function of plasma diameter at different positions along the plasma channel can be calculated. The D\(^+\) ion density, which is half of the electron density if the average charge state of C\(^{4+}\) is produced, is calculated as a function of the time delay and shown in Fig. 5(a). It is found that the average deuteron density is around \(1.2 \times 10^{19} \text{ cm}^{-3}\) at the time delays from 2 to 3.5 ms. In Fig. 5(a) we also show the measured average KEs of D\(^+\) ions which increase rapidly from 4 to 13 keV as the time delay increases from 2 to 3.5 ms. However, the average KEs increase slowly from 13 to 15 keV and saturate as the time delay continues to increase. This increasing trend of average KEs implies the time-varying formation process of \((\text{CD}_4)_N\) clusters and the largest clusters are produced at the tailing edge of the cluster flow [29].

From Fig. 4 we can find that a plasma channel with a length of \(\sim 2 \text{ mm}\) and radius of \(\sim 200 \mu\text{m}\) is produced only in the case of high-density cluster flow. It means that most of the laser energy is efficiently deposited into this plasma channel. The produced neutron yields at different time delays are simultaneously detected and shown in Fig. 5(b). The maximum yield of \(2.5 \times 10^5\) neutrons is detected at 4 ms of delay with deuteron density of \(1 \times 10^{19} \text{ cm}^{-3}\) and average KEs of 13.5 keV. Since the neutron yield is proportional to the squared density of the D\(^+\) ions’ and DD fusion cross section, the maximum neutron yield is determined by a trade-off between D\(^+\) ions’ density and average KEs. Considering the laser energy of 120 mJ, we have achieved a conversion efficiency of \(2.1 \times 10^6\) neutrons per joule of incident laser energy, which is roughly higher by 2 orders of magnitude than the results reported by Madison and Grillon et al. [13, 14]. By increasing deuteron density through the increase of the backing pressures from 44 to 84 bars, we have measured neutron
FIG. 4: Recorded interferograms of plasma filaments at different time delays from 1.4 to 6 ms.

FIG. 5: Measured densities and average KEs of D\(^+\) ions as a function of the time delay. (b) The measured densities of D\(^+\) ions and neutron yields as a function of the time delay.

yields as a function of time delay at different backing pressure from 44 to 84 bars, which are shown in Fig. 6(a). The optimized neutron yields and D\(^+\) ions’ average KEs as a function of backing pressure are shown in Fig. 6(b). Although D\(^+\) ions’ average KEs are close to saturation as the backing pressure increases to 84 bars, we do not see the saturation effect of neutron yield. It means the efficiency of neutron generation can still be increased, e.g. by employing a cryogenic jet to produce larger-size cluster flows with higher gas densities.

On the other hand, efficient neutron generation relies on the optimal deposition of laser energy into the dense gas region. Because the low-density gas at the edge of the gas
jet can greatly absorb the laser energy and influence the generation of fusion neutrons, the propagation effect of femtosecond laser pulses in cluster gas such as the ionization-induced defocusing and absorption of the laser energy by the clusters should be considered [30]. By changing the focal position related to the center of the gas jet, the neutron yield as well as the KEs of D$^+$ can be optimized. The focusing depth $D_f$ (defined as the distance from the focus plane to the gas jet axis) is arranged from $-1.85$ to $0.95$ mm. Six typical interferograms of the filaments and the non-axisymmetric-Abel-inverted electron density distributions are listed in Fig. 7 [31]. Here, the laser energy is 80 mJ, and the pulse duration is 60 fs. The maximum electron density is estimated to be $2.88 \times 10^{19}$ cm$^{-3}$ as shown in Fig. 7, so the neutral (CD$_4$)$_N$ gas density is approximated to be $3.6 \times 10^{18}$ cm$^{-3}$ provided that C$^{4+}$ is the highest ionization state in this condition. Simultaneously detected neutron yields, average KEs of D$^+$ ions and $N_{D^+}$ (total number of D$^+$ ions within filament) are shown in Fig. 8.

Two evident phenomena are observed in Fig. 7: the plasma filament length is restricted within 2.5 mm due to the laser attenuation; and the filament shape is modified by the ionization-induced defocusing effect. When $D_f$ is $-1.85$ and $-1.55$ mm as shown in Fig. 7(a) and 7(b), the filament with a conic shape is confined at edge of the gas jet. Large waist of the filament near the jet axis suggests low laser intensity, which leads to low KEs of the D$^+$ ions and thus limited neutron yields not exceeding $4.5 \times 10^4$ per shot as shown in Fig. 7(b). As focusing the laser pulse deeper into the gas jet with $D_f$ being $-0.95$ and $-0.60$ mm as shown in Fig. 7(c) and 7(d), the plasma defocusing effect starts to counteract the convergence of incident beam and results in a cylindrical-shaped plasma channel with a constant small diameter. Although $N_{D^+}^+$ is at low level as shown in Fig. 7(b), the KE of D$^+$ ions increases and obtains the maximum value of 17 keV when $D_f$ increases to $-0.60$ mm. Simultaneously, the maximum neutron yield of $1.9 \times 10^5$ neutrons per shot is obtained in this case. When $D_f$ increases further to $-0.05$ and 0.45 mm as shown in Fig. 7(e) and 7(f), the filament holds a swelled volume deep in the jet, resulting in obviously growing $N_{D^+}^+$ as...
FIG. 7: Interferograms of the plasma filaments at the backing pressure of 84 bars for six typical $D_f$ s (from $-1.85$ to $0.45$ mm) and the non-asymmetric-Abel-inverted electron density distributions. The locations of focal plane (f. p.) and gas jet axis are marked by dashed lines. The laser pulse propagates from the left to the right of the images.

shown in Fig. 8. However, the neutron yields decline by a large margin because most of the D$^+$ ions within the filament are less energetic owing to the weakened laser intensity caused by the greater laser absorption.

V. COMPARISON BETWEEN (D$_2$)$_N$ AND (CD$_4$)$_N$ CLUSTERS

As a comparison, we have measured the D$^+$ ion energy spectrum and neutron yield generated from the Coulomb explosion of (D$_2$)$_N$ clusters. The (D$_2$)$_N$ clusters are produced by using a supersonic gas jet, cryogenically cooled with liquid nitrogen at 100 K. At a backing pressure of 64 bars, the average cluster radius is estimated to be about 6 nm. The measured energy spectrum of D$^+$ ions is shown in Fig. 9(a). Also shown is the energy spectrum of D$^+$ ions from (CD$_4$)$_N$ cluster experiment at 84 bars of backing pressure and the average cluster size is estimated to be 7 nm. The average/maximum KEs of D$^+$ ions are 3.6 keV / 14.45 keV and 13.4 keV / 60 keV for (D$_2$)$_N$ and (CD$_4$)$_N$ clusters, respectively. The
maximum and average KEs of D$^+$ ions from (CD$_4$)$_N$ clusters are both increased by 3 times, compared with D$_2$ clusters with the similar radius. This enhancement shows explicitly the contribution of both the energetic boosting and the kinematic effects in the CE of the heteronuclear clusters [22, 32]. For the (D$_2$)$_N$ and (CD$_4$)$_N$ clusters, we detect the fusion neutron yield of 5 × 10$^3$ and 2.5 × 10$^5$ per pulse which corresponds to the efficiencies of 4 × 10$^4$ and 2.1 × 10$^6$ neutrons per joule of incident laser energy. The neutron yield is dramatically increased by 50 times, without considering the relatively low deuteron density of (CD$_4$)$_N$ clusters compared with the cryogenically cooled (D$_2$)$_N$ clusters. Fig. 9(b) shows the measured neutron yields from (D$_2$)$_N$ and (CD$_4$)$_N$ clusters respectively as a function of backing pressure from 44 to 84 bars.

A modified model based on the Coulomb explosion model is proposed to roughly estimate the nuclear fusion yields produced in the Coulomb explosion of (D$_2$)$_N$ and (CD$_4$)$_N$ clusters with irradiation of the intense laser pulses, by taking the attenuation of laser energy absorbed by the clusters with a log-normal size distribution into account [22, 33]. The neutron yield generated inside the heated plasma filament, as the sum of the intercluster fusion yield and beam-target fusion yield, is calculated as a function of laser-cluster parameters such as the cluster size, the laser energy, the focus spot radius and position. Only these parameters match with each other, can the neutron yield or the neutron conversion efficiency be maximized.

A comparison between the contribution of heteronuclear and homonuclear clusters to the fusion yield is made between (CD$_4$)$_N$ and (D$_2$)$_N$ with equal size $R_0$. Because of
FIG. 9: (a) Measured energy spectrum of D\(^+\) ions from (D\(_2\))\(_N\) and (CD\(_4\))\(_N\) clusters, respectively. (b) Measured neutron yields from (D\(_2\))\(_N\) and (CD\(_4\))\(_N\) clusters respectively as a function of backing pressure from 44 to 84 bars.

the boosting effect of multicharged carbon ions on the kinetic energy of deuterons and the accelerating effect on the deuteron velocity in the overrun process of deuterons relative to heavy carbon ions, the deuteron energy of (CD\(_4\))\(_N\) is highly increased compared to that of (D\(_2\))\(_N\) with the same cluster size. For example, the maximum and average deuteron energies of the (CD\(_4\))\(_N\) cluster are respectively 3.2 times and 4.6 times as high as those of the (D\(_2\))\(_N\) cluster. Furthermore in the energy spectrum of (CD\(_4\))\(_N\), a large number of deuterons locate close to the maximal energy due to the overrun effect of deuterons relative to heavy carbon ions, which facilitates high fusion efficiency. The dependence of nuclear reaction yield originating from Coulomb explosion of the two kinds of clusters on the cluster radius is presented in Fig. 10. The fusion yield increases conspicuously as the initial cluster size increases. For smaller cluster which produces lower deuteron energy, the beam-target reaction yield \(Y_{bt}\) is lower than the intercluster fusion yield \(Y_{ic}\). As the cluster size increases, \(Y_{bt}\) becomes comparable to \(Y_{ic}\). Eventually \(Y_{bt}\) exceeds \(Y_{ic}\) with further increase of cluster size. A clear relationship is obtained from the figure that the intercluster and beam-target \(dd\) fusion yield as well as the total fusion yield of (CD\(_4\))\(_N\) are accordingly improved by a magnitude of one or two orders compared to those of (D\(_2\))\(_N\) with the same cluster size. A qualitative agreement is obtained between our simulated and the measured results. It has been validated that heteronuclear clusters are a better candidate compared to homonuclear clusters for enhancing the total intercluster fusion yield because both a higher energy region and a higher proportion of deuterons distributing in the energy region can be created in the deuterated heteronuclear clusters.

In conclusion, we have experimentally demonstrated efficient generation of dd fusion neutrons from intense Coulomb explosions of high-density large-size (CD\(_4\))\(_N\) cluster jets under the irradiation of superintense femtosecond laser pulses. A correlated study of neutron yields, deuterons’ kinetic energies and plasma channel formation diagnosed by a
FIG. 10: Dependences of the nuclear reaction yield originating from cluster Coulomb explosion of $(\text{CD}_4)_N$ and $(\text{D}_2)_N$ on the cluster radius $R_0$. The dash, dot, solid lines represent the intercluster, beam-target and total fusion yield respectively.

pump-probe interferometer allows us to optimize the coupling of laser-cluster interaction in order to produce efficient nuclear fusion. By adjusting the time delay between the laser pulse and gas flow as well as the focusing condition, the neutron yield can be significantly increased. The comparison between $(\text{D}_2)_N$ and $(\text{CD}_4)_N$ clusters has been investigated with respect to the deuteron energy and neutron yield. It has been verified that the neutron yields can be dramatically increased by using heteronuclear $(\text{CD}_4)_N$ clusters as compared with the similar sized homonuclear $(\text{D}_2)_N$ clusters. This enhancement is attributed to the significant increase in the deuteron kinetic energies due to energetic boosting and overrun effects during CE of heteronuclear clusters.

This work was supported by the National Basic Research Program of China (Contract No: 2010CB923203, 2011CB808100), National Natural Science Foundation of China (Contract Nos: 11127901, 61221064, and 10974214), Shanghai science and technology talent project (12XD1405200), the State Key Laboratory Program of Chinese Ministry of Science and Technology, and the Cooperation in the Development and Application of Femtosecond Petta-watt Level Ultra-intense and Ultra-short Laser System (Grant No. 2011DFA11300).

References

Review

Intense Few-Cycle Infrared Laser Pulses at the Advanced Laser Light Source


1 Institut National de la Recherche Scientifique, Centre Énergie Matériaux et Télécommunications, 1650 Boulevard Lionel-Boulet, Varennes, Qc, J3X1S2, Canada
2 Joint Attosecond Science Laboratory, National Research Council and University of Ottawa, 100 Sussex Drive, Ottawa ON K1A 0R6 Canada
3 J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, KS 66506 USA

(Received December 7, 2013)

To push the generation of isolated attosecond pulses towards shorter XUV wavelengths (0.3 to 1 keV), intense few-cycle driving pulses are required whose center frequency is significantly red shifted compared to established Ti-Sa technology. A simple route for generating these pulses is demonstrated using an optical parametric amplifier (OPA). Its infrared (IR) multi-cycle laser pulses with millijoule of energy are spectrally broadened by nonlinear propagation in a hollow-core fiber (HCF) filled with Argon. For the OPA Signal wavelength ($\lambda = 1.4$ micron), chirped mirrors were used for dispersion compensation with a resulting pulse duration of 13.1 fs. For the OPA Idler wavelength at 1.8 micron, a new compression scheme has been developed with which 11.2 fs laser pulses have been characterized (1 cycle = 6 fs). Here, pulse compression is achieved through the combined effects of self-steepening during nonlinear propagation in the HCF followed by anomalous dispersion during linear propagation in fused silica.

DOI: 10.6122/CJP.52.537 PACS numbers: 42.65.Re, 42.65.Jx, 42.65.Yj

I. INTRODUCTION

The discovery of X-rays in 1895 by Dr. William Roentgen has been an important step towards major scientific breakthroughs in the last century. One can hardly imagine the development of society without the progress made in medicine by providing physicians with unique tools for X-ray diagnostics and treatments. In scientific research, X-rays are used for spectroscopic and structural characterization of atoms, molecules, biological structures and materials. Today, researchers from a broad diversity of scientific horizons anticipate using ultrashort X-ray laser pulses to probe dynamical processes with combined high spatial and high temporal resolutions. This quest motivates the construction of X-ray free electron laser (XFEL) facilities providing femtosecond X-ray laser pulses of high brilliance [1].

In parallel to the development of those infrastructures for ultrafast X-ray science...
research, there are major ongoing activities to develop table-top approaches [2–5]. Among them, X-ray sources based on the process of high harmonic generation (HHG) [6–9] provide the ultimate temporal resolution with a world record of 67 attoseconds pulse duration [10]. With those pulses, researchers now possess a unique metrology to probe ultrafast electronic dynamics [11–15]. Currently, this technology has been developed in the spectral range of 20 to 100 eV, which limits the temporal resolution but also important applications where higher photon energies are required [16]. So far, isolated attosecond pulses have been generated using Titanium-Sapphire (Ti-Sa) laser technology which is centered at 800 nm wavelength. Based on the three-step model introduced by Corkum in 1993 [17], the maximum photon energy obtained from HHG is given by \( I_p + 3.17 U_p \) with \( U_p \sim I \lambda^2_{\text{laser}} \), where \( I \) is the intensity and \( \lambda_{\text{laser}} \) the laser wavelength. From this simple formula, one may conclude that an ever increasing intensity would provide higher and higher photon energy. This is neglecting the fundamental coherent nature of HHG where the emission arises from the interference of the returning electron wavepacket with the bound atomic one. The latter must not be fully depleted by ionization, which will prevent emission, thus limiting the maximum intensity (I) that can be used. For helium, this intensity is in the range of \( 1 \times 10^{15} \) W/cm\(^2\), corresponding to a \( U_p \) of 60 eV at 800 nm. Thus, with Ti-Sa, the maximum photon energy expected is in the range of 200 eV. Phase matched HHG from helium using the capillary approach has been extended up to 150 eV [18]. Therefore, to further increase the maximum photon energy from HHG, one has to increase \( \lambda_{\text{laser}} \). This was first illustrated by Shan and Chang [19], followed by several groups [20–23] with now a maximum photon energy of 1.6 keV by using a driving laser field at 3.8 micron [24]. Despite this great progress, isolated attosecond pulses in the sub-keV spectral range have not yet been demonstrated. This requires the development of intense few-cycle infrared laser pulses.

In contrast to other research groups worldwide working on the development of few-cycle infrared laser sources [25–28], we have decided to develop this technology using spectral broadening of millijoule multi-cycle OPA laser pulses through propagation in a HCF filled with argon. Intense few-cycle pulses have been generated at both the Signal and Idler wavelengths [29–31]. The use of HCF to spectrally broaden pulses, followed by pulse compression at the output, was first introduced by Nisoli and co-workers for a Ti-Sa (800 nm) laser system [32]. In this proof of concept experiment, pulse compression was achieved using a prism pair. Nowadays, chirp mirrors allow the generation of 1.5 cycle pulses [33]. It is important to note that this development in the late 90s has been one of the key steps, together with carrier envelope phase stabilization [34, 35] and the attosecond streak-camera [36], to enable the generation and the characterization of attosecond pulses in 2001 [6].

II. METHODOLOGY

The long wavelength few-cycle laser sources (1.4 and 1.8 micron) have been integrated to the 800 nm, 100 Hz, 100 mJ, 35 fs, Titanium-Sapphire (Ti-Sa) laser beamline of the Advanced Laser Light Source (ALLS, located at INRS-EMT). Using an OPA based on parametric superfluorescence (He-TOPAS, Light Conversion), we convert 6 mJ from the
800 nm beamline to the Signal and Idler wavelengths, shown as red and blue lines in Figure 1.

FIG. 1: Experimental layout for the generation of intense few cycle infrared laser pulses. Millijoule level OPA pulses are broadened in a hollow-core fiber and subsequently compressed by chirped mirrors in the Signal spectral range. Idler laser pulses are compressed using the anomalous dispersion provided by 3 mm of fused silica.

Typical pulse energy is 1.3 mJ and 0.9 mJ, for the Signal and Idler respectively. By using different wavelength separators either Signal or Idler laser pulses can be selected for the experiment as shown in Figure 1. In both cases energy fluctuations of the OPA are about 3% RMS, and the laser pulse duration is about 60 fs. The beam is coupled into the HCF setup using an f = 1 m focusing lens. The fiber diameter is 400 μm with a length of 1 m. It is installed in a closed gas cell and supported on an aluminum V-groove. Typical pressure ranges from 1–2 bars are used and the fiber transmission efficiency is between 40% and 60% depending on the mode quality of the OPA. At the fiber output, the laser beam was collimated using an f = 1 m concave silver mirror. The confined propagation in the fiber provides conditions for nonlinear propagation where the light pulse itself modifies the medium properties through which it propagates. As a consequence the refractive index of the medium becomes intensity dependent and hence time dependent which causes a temporal variation of the instantaneous phase, known as self-phase modulation (SPM). Following the basic relations of Fourier transformation this temporal variation of the phase is associated with spectral broadening in the frequency domain. That means the HCF output spectrum is significantly broadened with respected to the input spectrum as can be seen in Figure 2.

After spectral broadening, the laser pulses have to be compressed in time, which is achieved in two ways; with chirped mirrors for the Signal [29] and using the anomalous dispersion of bulk material for the Idler [30, 37]. Those approaches are described in the next section. Replacing the OPA based on parametric superfluorescence by a white light seed version enabled to passively stabilized the carrier envelope phase of the Idler pulses [23,
Temporal characterization of the intensity profile of the few-cycle pulses has been achieved with a home built dispersion free second harmonic generation frequency resolved optical gating (SHG-FROG) [39]. To avoid dispersion we do not use a traditional beam splitter. Instead we divide the beam geometrically using a pair of 2 mm diameter pinholes that are separated by 4 mm. The resulting beams are delayed with respect to each other and focused in a non-collinear geometry with an f = 500 mm silver mirror. A very thin type I BBO crystal (Φ = 21°) of 10 μm thickness guarantees ultra broadband phase matching over the whole spectral bandwidth of our pulses.
III. RESULTS

First we describe results achieved when coupling the OPA Signal pulses into the HCF and subsequent compression with chirped mirrors. Because the spectral phase introduced by SPM can be approximated by a quadratic function (positive group velocity dispersion (GVD)), it can be compensated by negative GVD as provided by chirped mirrors. However, those mirrors were not commercially available in the Signal wavelength range and first had to be designed in collaboration with Femtolasers (Vienna, Austria). Each mirror consists of 73 alternating layers of SiO$_2$ and Nb$_2$O$_5$ to provide sufficient reflectivity (R > 99.5%) over a bandwidth ranging from 1000–1700 nm. This multi layer design provides a large GVD of $-300$ fs$^2$ (per roundtrip) and a third order dispersion (TOD) of $-15$ fs$^3$ at 1425 nm per single bounce. Fine tuning of dispersion was achieved by introducing small amounts of positive dispersive material like SF10 into the beam.

In Figure 3, we present the retrieved temporal intensity profile of the laser pulses. Those results have been obtained by combining one round trip on the chirped mirrors with $\sim 1.5$ mm of SF10. The fact that the obtained FWHM duration of 13.1 fs is only 1.07 times the Fourier limit (12.2 fs assuming flat spectral phase) proves the good compressibility of the broadband spectra at 1425 nm. At 1425 nm, 13.1 fs is less than 3 optical cycles, equivalent to about 7.5 fs at 800 nm. Moreover, we have calculated that 70% of the energy is concentrated in the central peak of the laser pulse temporal intensity profile. The direction of the time axis was determined by overcompensating the dispersion with one round trip on the chirped mirrors and added positive dispersion with SF10 windows.

![Figure 3: Retrieved intensity profile for the sub three cycle Signal laser pulses. Full width half maximum is 13.1 fs corresponding to 2.7 optical cycles.](image)

After discussing the established approach for pulse compression via spectral broaden-
In HCF followed by dispersion using chirped mirrors, we now describe a new compression scheme in the Idler spectral range which utilizes the anomalous dispersion of bulk material. The GVD and third order dispersion (TOD) curves for the glasses used in this setup are shown in Figure 4 from which one can deduce several things. First, bulk material like fused silica (FS) provides negative GVD predominantly in the Idler spectral range. Thus, it cannot be used to compress the Signal laser pulses to sub three cycle pulse duration. Second, CaF$_2$ exhibits the lowest absolute GVD and TOD in the spectral range of interest and hence was chosen as material for transmissive optics like lenses and cell windows. Third, regardless of the sign of GVD all glasses provide only positive TOD throughout the entire spectral range.

FIG. 4: GVD (a) and TOD (b) curves for the transmissive optics used in the setup. The negative GVD of FS in the anomalous dispersion regime can be utilized for sub-two cycle pulse compression if the positive TOD is compensated by self-steepening during nonlinear propagation in the fiber prior to linear propagation in the glass.

That means dispersion with bulk material will be limited by TOD which never becomes negative. Surprisingly, the compressed pulse of 11.5 fs shown in Figure 5 is very close to the transform limit of 10.1 fs. For the corresponding experimental spectrum of Fig. 2 one can calculate that the TOD of 3 mm FS and 1 mm CaF$_2$ (cell window at the HCF output) would broaden the pulse to about 14.9 fs which is much longer than the experimentally observed duration.

The explanation for this unexpected result, which cannot be provided by the bulk material alone, lies in the nonlinear propagation itself. SPM is not the only effect taking place in the fiber. Self-steepening is also present in which not only the gas medium is modified as function of laser pulse intensity but also the time dependent medium couples back to the temporal properties of the driving pulse causing an asymmetric power-spectral shape and phase. The later is the key ingredient for subsequent pulse compression with bulk material because the spectral phase asymmetry due to self-steepening opposes the
positive TOD component of the glass. This was confirmed through numerical simulations where experimental results were reproduced with a level of accuracy [30, 37].

IV. CONCLUSIONS

One of the motivations to develop intense few-cycle infrared laser pulses is to use the process of HHG to enable the generation of shorter XUV wavelengths (100 eV to 1 keV) laser pulses, with femtosecond to attosecond duration [16]. The establishment of such a table-top ultrafast X-ray source will open new scientific horizons by providing the ultimate temporal resolution to probe ultrafast processes in the condensed matter, enabling applications that are nowadays not possible. Among a large variety of possible applications, the water window spectral range (280 to 540 eV) is highly attractive for biological imaging [40], and the range of 700 to 900 eV is in high demand to study ultrafast demagnetization of ferromagnetic materials [41]. In addition to those applications, intense few-cycle infrared laser pulses provide high cut-off for low ionization potential atoms and molecules thus are ideal to perform HHG spectroscopy [23, 42, 43], and to control of molecular electronic dynamics in intense laser fields [44].

To conclude, we are convinced that this large variety of applications for intense few-cycle infrared laser pulses makes compression using the HCF approach very attractive for the ultrafast community considering that the only requirement is combine Ti-Sa systems with a commercially available OPA.
Acknowledgements

We are very grateful for the help and the time spent on the laser system by Mr François Poitras and Mr Antoine Laramée. The authors acknowledge the financial support of the Canada Foundation for Innovation, The Natural Sciences and Engineering Research Council of Canada, the Fonds de recherche du Québec - Nature et technologies, the Canadian Institute for Photonic Innovations, NanoQuébec, and Ministère du développement économique, de l’Innovation et de l’exportation (MDEIE) du Québec.

References

Review

Review of Multi-Frequency Raman Generation

D. Strickland

Department of Physics and Astronomy,
Guelph-Waterloo Physics Institute, University of Waterloo,
200 University Ave. W, Waterloo, Ontario N2L 3G1, Canada
(Received August 31, 2013)

To keep pushing the boundaries of ultrafast spectroscopy, high power optical pulses with sub-femtosecond durations must be synthesized. Although pulses with attosecond durations have been generated, the peak power remains low, and the spectral range is in the XUV. The technique of multi-frequency Raman generation shows promise as a simple method to generate visible or UV pulses with single femtosecond duration and sufficient power to drive nonlinear optical processes. In this paper, I review the progress made generating broad spectra by multi-frequency Raman generation and compressing the resulting electric field to generate high power, single femtosecond pulses.

DOI: 10.6122/CJP.52.546 PACS numbers: 42.65.Re, 42.65.Dr, 42.50.Gy, 32.80.Qk

I. INTRODUCTION

There are a number of different schemes to generate ever shorter, more intense optical pulses for nonlinear optics applications. The shortest pulse duration achieved to date, just 67 attoseconds, has been accomplished using high order harmonic generation (HHG) [1]. The pulses can be very short because HHG produces an extremely broad spectrum that is centered in the VUV. The drawback is that the HHG process is not very efficient (energy conversion efficiency to the harmonic < $10^{-6}$ [2]) resulting in the intensity of the ultrashort pulse being less than the pump pulse intensity and so is insufficient to drive nonlinear processes. On the other hand the process of multi-frequency Raman generation (MRG) can efficiently generate broad spectral bandwidths centered in the visible to UV. The shortest pulses generated by MRG to date were 1.6 fs in duration [3]. MRG produces many Raman orders spanning from the ultraviolet to the infrared. Trains of short pulses can be generated by properly phasing the coherently generated orders. Because the frequency spacing of Raman orders is significantly smaller than the frequency separation of harmonic orders the temporal separation of the pulses is correspondingly longer making it possible to isolate single pulses with standard nonlinear optics techniques.

HHG proceeds from very different physics than the perturbative nonlinear process of harmonic generation, where a nonlinear material polarization susceptibility $\chi^{(n)}$, of order n, corresponding to the nth harmonic, is driven by a single pump field [4]. At high pump intensities, HHG arises from what is now known as the three-step model [5]. When the laser intensity is high enough and the wavelength is long enough that the electron tunneling time is shorter than the laser period, the atom or molecule undergoes tunnel ionization. The
ejected ion is then accelerated in the oscillating laser field and returns to the atom with high kinetic energy that can be converted back into high-energy photons through recombination with the ion. The resulting spectrum is a large plateau of harmonics. As will be discussed in this paper, the multi-frequency Raman generation process also produces a large number of spectral orders, but, the high order process is still driven by the same $\chi^{(3)}$ Raman process that drives the first anti-Stokes order [6]. The process simply gets stronger as the pump intensity increases. As the Stokes and anti-Stokes orders are generated, they can then re-scatter off the material oscillation and create either higher or lower Raman orders. Once the orders are created they continue to mix with their nearest neighbor to generate Stokes and anti-Stokes in a multi-wave third order nonlinear process. The high order Raman process can start from a single pump pulse. The single pump pulse can generate the first Stokes field efficiently through the linear Stimulated Raman Scattering (SRS) process [6]. Once the two fields are sufficiently strong, they drive the $\chi^{(3)}$ nonlinear Raman process, which generates the first anti-Stokes (AS) order. The MRG process then cascades to higher orders from this initial scattering. The MRG process however gets significantly stronger if two intense pump pulses that have frequencies corresponding to pump and Stokes fields are used to drive the molecular oscillation [7].

As with HHG, for ultrashort pulses to be generated through the MRG process, the material polarization must be coherently driven and the scattering of the electric fields from the oscillation must be coherent. Along with this coherent interaction, the many fields must propagate through the medium requiring the nonlinear medium to have low dispersion. MRG with two-color pumping of the Raman oscillation has been extensively studied in three different temporal regimes. The adiabatic regime uses two equally strong pump pulses that both have durations longer than the coherence time of the Raman transition. It was shown theoretically that not only could you achieve the maximum coherence, that is $|\rho_{ab}| = 0.5$, by adiabatic pumping but that the resulting index of refraction of the nonlinear medium was $\sim 1$, resulting in the generation of a large number of phased Raman orders [8]. The 1.6 fs pulses have been achieved with adiabatic pumping. However, the ultrashort pulses were separated by 11 fs in a nanosecond long pulse train resulting in a peak power of 1MW [3]. The duration of the pulse train corresponds to the duration of the pump by the Fourier transform of the spectra. The low peak power of the pulses from adiabatic pumping is the drawback of this process. If the goal is to create ultrashort, high-intensity pulses, the pump pulses must be short so that the pulse train has only a few orders. This then leads to the next temporal regime, the transient regime, where the pump pulses have durations of the same order or less than the coherence time. Losev and Lutsenko showed theoretically, that with transient pumping a broader spectrum of Raman orders could be achieved compared to the steady state regime [9]. The total bandwidth could theoretically reach a level of 1.4 times the pump frequency. Unlike the adiabatic case, the Raman orders propagated with a phase mismatch given by the dispersion of the medium, which must be minimized to obtain a broad spectrum. Lastly MRG can be achieved in the impulsive regime, where the two colors are both present within the very large bandwidth of the ultrashort pump pulse [11]. In impulsive pumping, the pulse duration is then shorter that vibrational period of the molecular oscillation [11]. The Raman orders spectrally overlap each other forming a
continuous spectrum that can be compressed to generate single ultrashort pulses. To date, single pulses with 3.8 fs duration have been measured [12].

In this review paper, I will first summarize the work on stimulated Raman scattering, higher order Raman scattering and Coherent Anti-Stokes Raman Scattering (CARS) that led to the development of MRG. I will then describe the MRG studies in the three temporal regimes, where in each case the goal is to maximize both the conversion efficiency and the generated spectral width. I will also discuss the work done to coherently sum the Raman orders to generate ultrashort pulses, high intensity. I will conclude with very recent work on creating ultrashort pulses with stable Carrier Envelope Phase.

II. STIMULATED RAMAN SCATTERING

Although Raman and Krishnan discovered the linear inelastic scattering process back in 1928 [13], it took the discovery of the laser before any nonlinear optical process could be observed and so the nonlinear process of stimulated Raman scattering wasn’t observed until 1962 [14]. Jonathan White has written a very extensive review of Stimulated Raman Scattering (SRS) [15]. SRS was first observed by Woodbury and Ng, when they were studying Q-switching of a Ruby laser and detected frequency shifted radiation, but at the time they did not know what caused it [14]. They were using a Kerr cell filled with nitrobenzene and measured an output of ∼ 200 mJ at the ruby laser wavelength of 694.3 nm and also 30 to 40 mJ of radiation at 767 nm. The longer wavelength did not appear when the nitrobenzene was not in the cavity. What was striking about the observation was that the secondary emission was almost 20% as energetic as the primary laser radiation, yet linear Raman scattering has an efficiency of just ∼ 10^{-7}. Later that year, Woodbury and colleagues studied a number of liquids and noted that the shifts corresponded to known Raman shifts and that there was a laser energy threshold to go from an extremely weak signal at the shifted frequency to a signal strength of over 10% of the laser power [16]. One of these colleagues, R. W. Hellwarth then derived a phenomenological theory of SRS that derives the coherent gain of a Stokes field by annihilating a laser photon and creating a photon in the scattered mode, with the excess energy being taken up by a transition from an initial to final state of the medium [17]. In spontaneous Raman scattering the radiation is emitted in a dipole pattern, but in the case of SRS, where the Stokes field exhibits gain, the radiation is predominantly in the forward and backward direction of the driving laser field. Since these initial SRS studies a vast number of vibrational and rotational SRS experiments have been done in various gases, liquids and solids with the main application to generate tunable radiation across the optical spectrum that could not be achieved by lasers alone. References to these experiments can be found in the review by White [15].

Hellwarth pointed out that if there was a population inversion between the two levels of the material transition, then anti-Stokes orders would be generated by the medium giving up the excess energy [17]. Garmire and co-workers developed the theory of coherently driving molecular vibrations with two fields having frequencies separated by the natural molecular vibrational frequency, \( \omega_r \) [18]. The interaction of the field and the driven molec-
ular oscillation then amplifies the different components of the driving field. If the optical radiation field is comprised of three fields having frequencies of $\omega_0, \omega_0 + \omega_r, \omega_0 - \omega_r$, where $\omega_0$ is the pump frequency, then under certain phase matching conditions, the Stokes and anti-Stokes frequencies can experience gain through the linear and nonlinear polarization with a susceptibility of the form $\chi = \chi_1 + \chi^{(3)}E^2$. The authors also point out that the same third order nonlinear process can generate higher order Stokes and anti-Stokes radiation by interaction of fields at $\omega_0, \omega_0 - \omega_r$ and $\omega_0 - 2\omega_r$ and $\omega_0 + \omega_r, \omega_0 + 2\omega_r$ if sufficient intensity is reached in the first orders. The various Raman orders generated by the third order polarizability would radiate as cones in order to satisfy both energy and momentum matching. For this reason, only Stokes radiation, from the linear polarizability, was seen in the early SRS experiments where the Raman order was generated inside a laser cavity and so only on axis radiation could build up.

III. HIGH-ORDER ANTI-STOKES RADIATION

Shen and Bloembergen in 1965 presented a theory showing that in the forward direction and so ignoring the anti-Stokes radiation, that higher order Stokes radiation was generated in a sequential fashion if the radiation was assumed to be spatially uniform [19]. That is, as the first order Stokes radiation reached equivalent power as the pump, that the pump would therefore decrease and the second order Stokes would then be generated and so on as a function of propagation distance. In 1969, von der Linde, Maier and Kaiser improved on this theory by allowing the spatial profile of the radiation to be Gaussian [20]. In this case, they showed that at the end of the Raman cell a number of Stokes orders can be present and the number of orders increases with input laser intensity. This result was confirmed by their experiments using liquid CS$_2$ as the Raman medium. Their work also showed that the Raman conversion efficiency was optimum when the pulse duration was on the order of 1 ns so that the competing process of stimulated Brillouin scattering was not significant.

Liquid nonlinear media have higher Raman gain than gases, but they also exhibit much higher dispersion, which limits the generation of high order anti-Stokes (AS). The first SRS experiments in gases were done by Minck, Terhune and Rado, where they observed multiple Raman lines in H$_2$, D$_2$ and CH$_4$ [21]. Because of the low dispersion of the gases, the anti-Stokes radiation was also emitted axially. They observed up to the 4th AS line of the hydrogen vibrational transition at 4155.21 cm$^{-1}$ or 125 THz. By 1978, Wilke and Schmidt were able to cover the spectral range of 189 nm to 2064 nm by generating several Stokes and anti-Stokes orders in hydrogen gas, by pumping with an amplified dye laser having energy of $\sim 30$ mJ and pulse duration of 9 ns or with the frequency-doubled dye laser [22]. They followed up this experiment in 1979 and reached the shortest wavelength of 175 nm, which was the 5th anti-Stokes order of the frequency-doubled dye laser at 276.5 nm [23]. They generated the 8th anti-Stokes order at 195 nm from the fundamental radiation from the dye laser at 558 nm. The conversion efficiency from the nth to $(n + 1)$st order was always greater than 30% giving an energy of the 8th AS line of $\sim 30$ µJ. They studied the
pressure dependence on the power of the various AS lines and showed that the dispersion was responsible for optimizing the various orders. The generated total bandwidth of all the orders was greater than the pump frequency.

In 1983, Schomburg, Dobele and Ruckle reported generating up to the 13 AS order at a wavelength of 138 nm [24]. For this work, they built a dye laser that could generate over 100 mJ of energy in a 12 ns duration. The spectral maximum of the tunable dye laser was at 550 nm. They were able to measure the energy of the orders over 8 orders of magnitude to see the 13th AS order. They noted that the efficiency from one order to the next stayed high ~ 50% until the 8th order, but then drops to 20% for the higher orders because of the dispersion in the VUV.

Baldwin, Marangos and Burgess used an excimer-pumped dye laser to generate radiation further into the UV through high order Raman scattering [25]. The dye laser operated at a wavelength of 360.6 nm with a modest energy of 7.4 mJ in a pulse duration of 4 ns. With this modest energy they still achieved the 11th AS order at a wavelength of 136.2 nm showing that the Raman process is more efficient for higher frequency pumps.

Eimerl, Hargrove and Paisner developed a multi-wave theory for high order Raman generation that is valid when the Raman shift is small in comparison to the pump frequency and so the total generated bandwidth would still be less than the pump frequency [26]. In this theory, all orders, \( E_n \), that oscillate at frequency \( \omega_0 + n \Delta \omega \), where is \( \omega_0 \) is the pump frequency and \( \Delta \omega \) is the Raman transition frequency, are mutually coupled to each other through multiple four-wave parametric processes. To describe the interaction of the multiple fields and the material transition, they used Maxwell Bloch equations. In an analogous manner to resonant single field interactions that use a Rabi frequency of \( \Omega = \mu E/\hbar \) the authors defined a two-photon Rabi frequency as: \( \Omega e^{i\theta} = 2 \alpha_{12} E_r E_{r-1}^*/\hbar \), where \( \alpha_{12} \) is the transition polarizability. In the Bloch equations, the time derivative of \( \theta \) was added to the two-photon detuning of the two fields from the transition frequency. With the assumption of \( \omega_r \ll \omega_0 \), they could solve the equations exactly and found that the intensity of the nth order at the output was given by \( I_n(\xi) = I_0 \xi J_n^2(\xi) \), where \( \xi \) is the retarded time in the pulse, \( I_0 \) is the pump intensity, \( J_n \) is a Bessel function and the \( \{|\beta\rangle \) is the parametric gain parameter. This theory requires two inputs one at the pump frequency and one at the first Stokes. The experimental results to this date were for a single pump and so the second input is considered to come from SRS. The conversion efficiency of this theory agreed reasonably with the experimental results.

The multi-wave theory was improved by Hickman and Bischel in 1986 [27]. It assumes the transient regime where the pump pulse duration is short compared to the relaxation times of the Raman medium. Their theory matches the earlier theory of Eimerl and co-workers in the limit of \( \omega_r \ll \omega_0 \). The equations have to be solved numerically. They showed that the conversion efficiency to higher orders can be improved by increasing the input power of the Stokes radiation. Using input energies of 8 mJ and 0.8 mJ and pulse durations of 10 ns and 1 ns for the pump laser and first Stokes, respectively, with the Stokes pulse delayed by 5 ns from the peak of the pump, which is consistent with the input Raman pulse being generated through SRS and assuming that the relaxation times are infinite, the 8th AS order could be generated with a conversion efficiency of \( 10^{-3} \) compared to the
pump energy. This efficiency was improved by using a pump energy of 7.2 mJ and a Stokes energy of 1.6 mJ and thereby keeping the total input energy constant.

Through the 1970’s and into the 80’s, the work on high order anti-Stokes generation was about generating tunable radiation and extending the range of coherent radiation into the VUV for spectroscopic applications. Yoshikawa and Imasaka realized that in an analogous scheme to laser mode-locking, where ultra-short pulses are produced by phase-locking the spectral orders of the laser cavity, even shorter pulses could be produced by phase controlling the coherently produced multiple Raman orders [28]. They numerically modeled the process by using just 10 rotational lines from ortho-hydrogen and showed that Fourier transform limited pulses of 6.4 fs FWHM could be obtained. The pulses would be separated by 57 fs. They also showed that if it was possible to completely control the phases of 10 vibrational lines of hydrogen that the Fourier transform limited pulses would be just 1.4 fs, but the pulses would be separated by just 7.9 fs.

The advantage of using the rotational lines in H$_2$ rather than the vibrational lines is that the spectral spacing is closer allowing the temporal pulse spacing to be longer. This has two advantages. First there would be fewer pulses in the pulse train and so the peak power would be higher. Also the longer the time between pulses makes it easier to isolate a single pulse. Kawano, Lin and Imasaka used 100 ps pulses with energies up to 50 mJ at a wavelength of 827 nm from an amplified Ti:sapphire laser and generated up to the 15 AS rotational order [29]. They used elliptical polarization to maximize the rotational excitation. The 7th AS rotational line was stronger than the first AS vibrational line that occurs almost at the same wavelength.

The Imasaka group followed this experiment by measuring the MRG spectrum as a function of pulse duration using a femtosecond amplified Ti:sapphire system [30]. They varied the pulse duration by linearly chirping the pulse and kept the energy constant at 5 mJ. At a pulse duration of 800 fs they observed 40 rotational lines. This was the optimum condition. At longer pulse durations the Raman gain was lower because of the reduced pump intensity and at shorter pulse durations, the competing nonlinearity of self-phase modulation (SPM) caused a spectral continuum to appear and a decrease of Raman orders. These experiments are single pump experiments and so rely on generating the first Stokes radiation to then nonlinear mix to generate the other orders. They discussed that by pumping with a linearly chirped pump pulse that the Raman orders would also be created with a linear chirp. If the 40 rotational orders are to be phased to generate an ultrashort pulse, then the linear chirps on all the orders would also need to be corrected. If this can be done, then the Fourier transform of the total rotational MRG spectra produces sharp pulses of 0.6 fs FWHM surrounded by oscillating wings of 6.4 fs. The pulses would be separated by 57 fs in a pulse train given by the length of the pulse, which in this case was 1.2 ps.

This early work on high order anti-Stokes generation confirmed that the Raman gain increases with pump intensity, and pump frequency and that the generated bandwidth increases with lower dispersion. Recently, high order Raman scattering has been generated in hollow core photonic crystal fibers (HC-PCF). Photonic crystal fibers have the advantages of a very small area so the high intensity can be achieved with relatively low powers and
very low dispersion so the coherence length can be quite long [31]. Since fibers guide the light and the coherence length can be very long, the required Raman gain can be reduced and so further reducing the peak powers. Couny and colleagues used 12 ns long pulses at 1.06\mu m from a Nd:Yag laser, with just 40 kW peak power to pump a Kagome HC-PCF filled with hydrogen [32]. With linear polarization they observed 5 AS lines and 1 Stokes from vibrational excitation. With circular polarization driving the rotational transition, they generated 45 spectral components covering essentially the same total bandwidth. The group further investigated the transition from the steady state to the transient regime using a laser that generated pulses with a variable pulse duration [33]. They measured the threshold energy for detection of the first Stokes as a function of pulse duration. The plot of the experimental data showed an inflection point around 12 ns between two different linear slopes. The two different slopes matched the theoretical curves for steady state and transient Raman gain. This transition time between the two temporal regimes could be varied between 10 and 30 ns, by varying the gas pressure and the fiber length.

IV. COHERENT ANTI-STOKES RAMAN SCATTERING

So far the experimental work that we have considered used a single input pulse. However, the multi-wave theory assumes two inputs and the numerical modeling showed that increasing the Stokes input would increase the efficiency. Using two inputs was used early on. Maker and Terhune were the first to nonlinearly mix the laser pump and Stokes radiation [34]. They first generated the Stokes radiation in a cell containing a benzene derivative pumped with a Q-switched ruby laser that delivered 100mJ pulses with 30ns FWHM duration. After this cell, the peak powers in the beam were 50 kW at the pump frequency, 10kW at the first stokes, 50 W at the second stokes and less than 10 photons per pulse in the first anti-Stokes. The pump and first Stokes beam were then both focused into a second nonlinear Raman cell. The two beams were focused at the proper phase matching angle to generate the AS line. The generated power of the first AS line was then measured along its phase matching angle. They measured the AS power as a function of cell thickness, L, which showed a \( \sin^2(L) \) dependence indicative of the effect phase matching. They measured the AS power for a number of different liquids as the Stokes frequency was tuned by changing the benzene derivative in the first cell. These experiments demonstrated the resonant enhancement of the Raman transitions. The observation of the resonant enhancement led to a new type of spectroscopy, which was coined Coherent Anti-Stokes Raman Scattering (CARS) by Byer’s group [35]. Rather than using a weak Stokes signal as the second input frequency, spectroscopists realized that they could measure the Raman levels by using two different laser frequencies, typically provided by a tunable dye laser along with the pump laser radiation. CARS is now a well established spectroscopic technique [36]and more recently is used in microscopy [37]. I will not review this technique as the spectroscopy is concerned with understanding the media rather than generating the Raman orders. However the two techniques are linked because if a Raman medium is pumped by two fields, having a frequency separation given by the Raman transition,
then higher orders are efficiently generated and these orders extend the tunable range used by the spectroscopists. Because two laser fields are input, CARS is carried out at much smaller intensities than the higher order AS generation discussed above. In 1975, Chabay, Klauminzer and Hudson were using two dye lasers with energies less than 500 μJ and 6ns pulse duration operating at wavelengths of 490 nm and 515 nm and observed the third Stokes and the second anti-Stokes orders [38]. They dubbed the process higher-order Raman spectral excitation studies (HORSES). The higher orders radiated at angles imposed by phase matching. These pump energies are about three orders of magnitude smaller than in the single pump pulse experiments and so demonstrates the improved efficiency by using two pumps.

Mennicke, Mayer and Sinnott collinearly pumped a Raman cell containing liquid nitrogen with two lasers [39]. They used the 1 MW peak power output of a ruby pumped dye laser at 820 nm and the 10 MW peak power of the ruby laser itself at 694 nm. They observed up to the 5th AS order at a wavelength of 384 nm. They not only achieved more orders than Chabay and co-workers with the increased pump power, but the higher AS orders radiated collinearly with the pumps, even though the Raman medium is a liquid and so has significant dispersion. This work shows that collinear AS radiation can be generated if the Raman gain length is shorter than the phase matching coherence length.

In 1989 Inmasaka and co-workers generated 40 spectral orders by mistakenly allowing amplified spontaneous emission (ASE) to build up in the laser cavity and thereby provided two strong pumps that strongly drove the molecular polarization oscillation [7]. It was this experiment that made the authors realize that this technique was a candidate for ultrashort pulse generation [28]. They were using an excimer pumped dye laser to generate tunable UV by high order anti-Stokes Raman generation, when they observed that the process was strongly pronounced when the laser was tuned in such a way as to allow a strong amplified spontaneous emission (ASE) pulse. It turned out that the frequency separation between the ASE and the laser pulse was ~ 600 cm⁻¹ that corresponded to the frequency difference of the J = 1 to J = 3 rotational level (588.07 cm⁻¹) of hydrogen. This strong pumping of the rotational levels, with energy between 3 and 9 mJ caused a large number of orders separated by this energy spacing to be produced. Both vibrational stokes and anti-Stokes orders were generated as well as the numerous rotational Stokes and anti-Stokes orders. The orders were all collinear with the pumps.

In 1990, Schulz-von der Gathen and co-workers compared the high order AS generation in liquid nitrogen with and without a second pulse at the first Stokes frequency [40]. They referred to the comparison as SRS versus CARS. They showed an increase in efficiency for the high order generation as the input Stokes field energy was increased for a fixed pump energy of 80 mJ at 532 nm. They also demonstrated a decrease in pump threshold for a fixed Stokes field energy of 2 mJ. With the Stokes field present, they were able to increase the number of AS orders generated and achieved the 14th AS order.
V. MULTI-FREQUENCY RAMAN GENERATION

To achieve a wide band of Raman orders requires large Raman gain and minimal phase mismatch. MRG with two pumps has now been studied extensively in gases in the three temporal regimes. Gases are used because the dispersion is minimal. However large bandwidths have also been observed in solids because of their extremely high Raman gain. The phase matching is accomplished by having the two pump beams cross at a phase matching angle. The Raman orders then radiate at different phase matched angles. I will summarize the MRG work and the ultrashort pulse generation for these four regimes; gas media in the adiabatic, transient and impulsive temporal regimes; and solid media.

VI. ADIABATIC REGIME

The classical physics approach to describe SRS with both a linear and nonlinear susceptibility describes the scattering of the waves off a grating induced by the coupling of the two input waves. To achieve high orders, the nonlinear component must be as large as the linear component and the dispersion must be negligible. Harris and Sokolov showed that the molecular transition can be driven adiabatically to achieve the maximum coherence, that is $|\rho_{ab}| = 0.5$ [8]. A number of Raman sidebands are generated through mixing this coherence with the two driving fields. The most surprising outcome of their theory is that the side bands can be phased in such a way that reduces the material refractive index to near unity. This adiabatic theory of MRG is analogous to electromagnetically induced transparency (EIT) [41] or in the authors’ words “a broadening of the EIT theory”. Sokolov and Harris then use this theory and solve for the propagation of all the orders. They numerically solved the equations for hydrogen for the cases of phased states where the two pumps have frequencies closer together than the transition frequency, the resonant case when the frequency separation matches the Raman transition and the anti-phased where the detuning has the opposite sign. They showed that more orders were possible with phased states where the detuning corresponded to the AC Stark shift of the transition and all the fields propagate with near unity refractive index.

Huang, Chen and Kung [42] followed up the adiabatic theoretical treatment to include the effects of Doppler broadening, which reduces the maximum coherence and collisions that can reduce the negative effect of Doppler at high pressures. They compared the theory to experimental results of vibrational MRG carried out in room temperature $\text{H}_2$ at pressures ranging from $< 1$ to 1000 Torr. The agreement was excellent at 200 Torr. There was a discrepancy with the theory at the higher pressure that could not be explained, but both the experiment and theory showed many more orders at the higher pressure.

LeKien and colleagues theoretically studied adiabatic MRG for high-density hydrogen as a model for solid hydrogen [43]. The solid will have much higher Raman gain but also correspondingly higher dispersion because of the higher molecular density. Their numerical model predicted that the Raman orders would span the spectrum of 864 nm to 188 nm for pumps at 355 nm and 416 nm. If the Raman orders are properly phased, they would create
a pulse train of 0.3 fs separated by 7.9 fs.

Sokolov and colleagues experimentally confirmed their adiabatic theory with the experimental demonstration of vibrational Raman generation in molecular D$_2$, which showed that many more orders were generated when the two pumps were tuned to have phased molecular states [44]. The Stokes field was provided by a Nd:YAG laser at 1.0645 $\mu$m with an energy of 100 mJ and pulse duration of 12 ns. The pump laser radiation from a tunable Ti:sapphire laser was tuned through the transition at 807.22 nm with 7 mJ of energy and pulse duration of 16 ns. With the two input fields tuned to be on resonance or further apart, only the 4th AS order was observed, but with the two frequencies tuned to be less than the transition frequency of 89.8 THz by 700 MHz, 13 AS orders were observed. These results are shown in Figure 1.

![Pulse energies generated in the setup of (Fig. 1 in ref. 43) at $P = 72$ torr. The triangles show on-resonance generation ($\Delta\omega = 0$), the circles show generation by phased ($\Delta\omega = 500$ MHz) and the squares by anti-phased ($\Delta\omega = -200$ MHz) states of D$_2$. Figure reproduced with permission from ref. 43 © 2000 APS](FIG. 1.png)

The Harris group [45] also studied MRG in the adiabatic regime for a rotational transition in H$_2$. They found a large number of rotational Raman lines: 27 AS and 8 Stokes when again the two pump frequencies were closer together than the transition frequency corresponding to the phased molecular state. They found that under this condition, the Raman conversion efficiency was near unity with 70% of the pump laser depleted. Both lasers had 60 mJ of energy and transformed limited pulse durations of 17 and 14 ns.

Along with demonstrating large bandwidth production by adiabatic pumping, Harris and Sokolov also discussed how the coherence caused the electric field to be frequency modulated [46]. This frequency modulated field could then be compressed by the dispersion
of the medium to create single cycle pulses with envelopes of 0.72 fs duration.

Experimentally the group timed the Raman orders and measured sub-2 fs pulses. In their first experimental work they dispersed just 5 orders in a prism and timed the orders by retro-reflecting them back through the prism [47]. In each beam line glass plates are rotated to correct the phase delay of each field. They performed a correlation measurement using ionization as the nonlinearity and confirmed that the pulses were less than 2 fs. They improved the phase matching apparatus by using a 4-prism delay line with a liquid crystal phase modulator at the center so that each line could be accurately phased [3]. In this arrangement they used 7 lines spanning the spectrum from 1.56 µm to 410 nm and generated 1.6 fs.

Katsuragawa and colleagues used a simple compression set-up comprised of a pair of chirped mirrors with a small movable mirror to generate a stable train of sub-20 fs pulses, with a repetition rate of 10.6 THz. A dual-wavelength, injection locked Ti:sapphire laser adiabatically modulated the rotational Raman transition in liquid nitrogen [48]. The optical axis at the output of the compressor remained fixed as the number of passes of the chirped mirrors was varied by translating the mirror. My varying the compressor, they were able to measure the spectral chirp imposed on the modulated field.

VII. TRANSIENT REGIME

Losev and Lutsenko followed the steady state theory derived by Shen and Bloembergen [19] and numerically solved the equations to determine the maximum bandwidth that could be obtained through multi-frequency Raman generation [49]. For the case of two pumps with equal intensity and a dispersion free Raman medium, they found that a total bandwidth equal to the pump frequency could be theoretically realized. The authors also investigated the role of phase matching on achieving the maximum bandwidth. They calculated the spectrum as a function of the normalized detuning, γ, given by: \( \gamma = \frac{\Delta k}{gI_0(0)} \), where \( \Delta k = 2k_0 - k_1 - k_{-1} \) is the wave-vector mismatch, \( I_0 \) is the total input intensity and \( g \) is the steady state gain coefficient. As expected, the broadest spectrum occurs for \( \gamma = 0 \), with the spectrum shifted to the anti-Stokes side because of the higher gain with increasing frequency. As \( \gamma \) increases the spectrum narrows and becomes more pronounced on the Stokes side. The authors also studied the process experimentally but were not able to have the Stokes signal at the same intensity as the pump laser. They used a hydrogen Raman cell to generate the Stokes radiation and then focused both the pump and Stokes into a second cell. As they increased the intensity of the two pumps the generated spectrum broadened and the anti-Stokes bandwidth grew faster than the Stokes side in agreement with the theory. The maximum energy that they used was 28.1 mJ for the pump at a wavelength of 532 nm and 0.64 mJ for the Stokes with the pump duration of 7 ns. The number of experimental orders did not increase as the Raman growth rate \( B = gI_0(0)z \) as the theory predicted.

More recently in 2007, Losev worked with the group of Takahashi, Kato and Matsumoto and carried out a similar experiment but improved both the ratio of the two pump
energies, increased the pump frequency which increases the Raman gain and contained the Raman medium, $D_2$, in a hollow fiber to eliminate diffraction effects [50]. They first pumped a Raman cell with a KrF excimer laser operating at 248 nm with circular polarization to excite the rotational transition and generated Stokes radiation at 249.1 nm. As this wavelength falls within the gain region of the KrF amplifier both the pump and the Stokes field could be amplified together before being focused into the hollow fiber. 5 mJ of total pump power was focused into the 30 cm long, 124 μm diameter hollow fiber. 34 rotational Raman lines were generated that had power of at least 10% of the output pump pulse. When the $D_2$ pressure was increased to 60 kPa, a spectrum extending from 220 to 600 nm was achieved. The lines were a combination of vibrational and rotational lines.

Carman and coworkers [51] as well as Akhmanov et al. [52] derived the classical theory of SRS in the transient regime where the pulse duration is equal to or shorter than the collisional dephasing time of the Raman transition. It was found that rather than depending on the pump intensity, the transient gain was given by the energy flux and was only weakly dependent on the pulse profile. The Raman power gain in the transient regime is inversely proportional to the dephasing time. May and Sibbett confirmed this theoretical prediction by experimentally investigating transient SRS in hydrogen and methane [53]. As predicted, they found that more AS orders were achieved in the methane which had the much shorter dephasing time. Hickman and Bischel then generalized their multi-wave theory to include phase mismatch between the orders due to dispersion, which becomes important in the transient regime [54]. Their work showed that for low Stokes input energy, the anti-Stokes gain is a minimum for perfect phase matching, which matches the steady state result. However with high power Stokes input signal, where pump depletion occurs, the maximum anti-Stokes gain occurs for perfect phase matching. McDonald and co-workers theoretically modeled multi-frequency Raman generation for transient stimulated rotation Raman scattering in H$_2$ gas with two pumps having equal intensity [55]. They calculated the maximum generated bandwidth for different pulse durations as a function of dispersion. The amplitude of the grating is increased for short pulses because of the increase in intensity but this increase is balanced by the increased demand on phase matching. They found that the maximum bandwidth occurred for pulse durations equal to the dephasing time or longer. As in the earlier work of Losev and Lutsenko, the anti-Stokes orders dominate when the pulse duration is on the order of or greater than the dephasing time and there is perfect phase matching. The total bandwidth is maximized with a small positive dispersion because this causes an increase in the number of Stokes lines. On the other hand, with short pulses the maximum bandwidth occurs for perfect phase matching.

Losev and Lutsenko followed up this transient theory and found that a larger bandwidth can be generated in the highly transient regime [9]. Where their steady state calculations showed a maximum bandwidth equal to the pump frequency, in the transient regime they found conditions that allowed a bandwidth of 1.4 times the pump frequency. The number of Raman orders scales as the ratio of pulse duration to dephasing time. This theory then points to using a Raman medium with a short dephasing time so that you can maximize the generated spectrum with a short pulse, which will produce the most intense pulses in the shortest pulse train.
Losev collaborated with my group to test this idea using a solid Raman media of KGD(WO$_4$)$_2$ (KGW) that has a short dephasing time of 1.6 ps and a high Raman gain of $\sim 4$ cm/GW [56]. The high Raman gain was necessary because of the increased dispersion in a solid. The Raman gain length needs to be shorter than the coherence length. The experiment used two pulses having duration of 150 fs and intensities of $2 \times 10^{12}$ W/cm$^2$ in the crystal. At these intensities a large number of Raman orders should have been generated but less than 10 were observed. In fact, with the pulse duration at 150 fs only a few orders were observed over a continuum spectrum. The experiment highlighted that with short pulses the Raman gain is competing with SPM. In order to detect the Raman lines, the pulse duration was increased to 2 ps and so matched the dephasing time, but the intensity was then also reduced by a factor of 10. Most of the Raman lines were Stokes rather than AS indicating that the dispersion was playing a large role. We compared the Raman generating with single pulse pumping where only a single Stokes and AS were generated. The following year, Inasaka’s group studied MRG in KGW [57]. They used single pulse excitation with three different pulse durations of 200 ps, 20 ps and 200 fs. They got the most orders for the 20 ps pulses, which were again predominantly on the Stokes side. These experiments in KGW both showed that the high Raman gain was not sufficient to beat the phase mismatch due to dispersion for either single frequency or two frequency collinear pumping.

Sali and co-workers investigated multi-frequency Raman generation in the transient regime in both H$_2$ and methane in a hollow fiber [58, 59]. They measured the generated spectra for varying gas pressure from 300 mbar to 3 bar. A hollow fiber was used to ensure a long interaction length. The two pulses were from an amplified Ti:sapphire laser at 800 nm and an OPA that could be tuned from 450 to 800 nm. The Stokes pulse from the Ti:sapphire laser had energy of 500 $\mu$J and the duration was 70 fs, the pump pulse had an energy of just 60 $\mu$J and a pulse duration of 250 fs. The powers of the pump pulses and the gas pressure of the Raman media are both significantly smaller than the previous single pump pulse experiments. With just the single pulse at 800 nm present, no MRG was observed confirming that the MRG process is significantly enhanced with two pumps. In H$_2$, up to 5 AS orders were generated with energy greater than 10% of the strongest line at a pressure of 0.9 bar. In methane up to 7 AS orders were generated at the optimum pressure of 1.6 bar. Even with both inputs present there was a significant amount of continuum present because of SPM of the strong pumps. To avoid SPM, the short 800 nm pulses were then stretched to 400 fs, and keeping the energy the same as the previous experiment they were able to generate the same number of Raman lines and greatly reduce the continuum background.

Losev collaborated with my group to study transient MRG in Sulphur Hexafluorine, SF$_6$ gas contained in a hollow fiber [60]. The Raman transition in SF$_6$ is much smaller than hydrogen or methane. We used two 300 fs pulses from a two-color Ti:sapphire laser system, with a total maximum energy of 6 mJ equally split between the two pumps. We measured the MRG spectrum as a function of pump energy and found that the MRG spectrum increased with energy until a continuum formed under the orders. At higher pump energies, only the continuum spectrum grew. We observed 6 generated Stokes orders and 17 AS orders covering the spectral range of 200 to 700 THz. The AS spectrum in
SF$_6$ is not as wide as what was observed in hydrogen or methane indicating that the phase mismatch from dispersion limits the bandwidth, not the number of orders. This is also seen in the rotational Raman MRG studies where many more orders are generated but over a similar bandwidth.

Turner and Strickland [61] used a smaller diameter hollow fiber of 129 $\mu$m. As will be discussed later in this paper, increased MRG bandwidth had previously been shown in the impulsive regime using the smaller diameter [62]. The geometry-dependent negative GVD of the small diameter fiber can compensate for the positive material GVD of the gas. By balancing the two GVD components the phase matching conditions for MRG can be improved. For these experiments, we stretched the pulses to 600 fs by linearly chirping the pulses and measured the MRG spectrum as a function of pressure. As the dispersion was minimized by reducing the pressure, more orders were generated until a continuum formed under the AS orders, but not under the more intense pump lines and red shifted shoulders appeared on the AS orders. We then studied the MRG spectrum as a function of delay between the two linearly chirped pump pulses [63]. By varying the delay, the instantaneous frequency separation is varied. We could then tune through the Raman transition by varying the time delay. We noted that the frequency separation of the red shifted shoulders varied with time delay, but the separation did not match the separation of the pump frequencies. The appearance of the shoulders is still not understood.

As has been previously discussed the timescale for transient regime in the HC-PCF is 10 to 30 ns. Transient MRG has been carried out with nanosecond pulses from a microchip laser in HC-PCF [64]. The 1064 nm pump pulse was split with 10 $\mu$J of pump energy used to efficiently generate a Stokes beam in a hydrogen filled hollow photonic bandgap fiber. The Stokes field was combined with the remaining 90 $\mu$J of pump radiation and launched into a Kagome HF-PCF filled with hydrogen. The Kagome fiber can support a much wider spectrum. 4 AS orders and 5 Stokes orders were generated covering the wavelength range from 800 to 1600 nm. Coherence between the orders was demonstrated by observing the sum-frequency of different Raman components.

A similar experiment was carried out in a photonic crystal fiber (PCF) [65]. The Stokes seed at 1117 nm was a cw signal provided by a diode pump Yb doped fiber. When just the 1064 nm radiation from the pulsed microchip laser is launched into the PCF, 2 Stokes and 4 AS orders are observed. The spectral width of each order is quite large indicating small coherence between the orders. When the narrow band cw Stokes field is added, more Raman lines are observed from the 6th Stokes to the 6th AS and each of the lines has a narrow spectral bandwidth.

VIII. IMPULSIVE REGIME

Kinsler and New developed a single field theory, which was felt to be more appropriate as the pulses get shorter [66]. In this theory the coupling constants oscillate at the Raman frequency and impose the sideband modulation on the propagating field. This single electric field can then no longer have a slowly varying envelope and the authors used a general-
ized few cycle envelope approximation. This theory can then handle broader overlapping spectrum and so could be beneficial in the impulsive regime.

Korn, Duhr and Nazarkin experimentally studied SRS in the impulsive regime [67]. They pumped SF$_6$ that has a Raman vibrational period of 43 fs with a 40 fs pulse at a wavelength 400 nm, from a frequency doubled Ti:sapphire laser system. The Raman shift is now less than the bandwidth and so a spectrum of discrete orders is not possible. Rather, they observed a broadening of the pump spectrum on the blue side, corresponding to a number of AS orders.

Nazarkin and co-workers [10] generated a discrete multi-order Raman spectrum by scattering a longer pulse from an impulsively excited molecular vibration in SF$_6$ contained in a hollow fiber. They excited the molecular oscillation with 30 fs pulses from a Ti:sapphire laser system with 500 μJ of energy. Some of the fundamental radiation was frequency doubled in a BBO crystal to be an injection pulse that would be modulated by the molecular oscillation. The frequency of the probe pulse is shifted from the pump so the modulation frequencies are not obscured by the pump radiation. For the probe to generate discrete Raman orders the spectral bandwidth needs to be less than the Raman spectral shift. By tuning the angle of the BBO crystal, the bandwidth could be reduced and produce a longer blue pulse duration of 200 fs. The blue pulse was delayed by ~100 fs from the infrared pulse. The sideband generation is investigated as a function of pressure. At first, the MRG spectral width scaled linearly with pressure. The spectrum was symmetric about the pump achieving up to the third Stokes and anti-Stokes orders. At higher pressures, the injection frequency was almost fully converted into side band energy. The authors confirmed that the modulation went away when the pump spectral bandwidth was reduced to below the transition frequency.

Wittman, Nazarkin and Korn, later demonstrated that the spectrally modulated blue field could be compressed to a train of ultrashort pulses [68]. They used chirped mirrors that provided a negative GVD of ~−300 fs$^2$. A small variable positive material GVD was introduced by a pair of fused silica wedges. With either a positive or negative net GVD of ~100 fs$^2$, a pulse train of 16 fs pulses separated by the vibrational period of 43 fs was measured using a self-diffraction correlation technique. The peaks of the pulses in the positive GVD case fell exactly in the space between the peaks in the negative GVD case. This clearly showed that the blue probe field had been frequency modulated with sinusoidal character allowing compression with either sign of GVD. Nazarkin and co-workers improved on their earlier MRG results by using a hollow fiber of smaller, 126 μm, diameter [62]. With the GVD minimized they were able to achieve 15 orders symmetrically about the 400 nm input.

Zhavoronkov and Korn also generated single 3.8 fs pulses from impulsive molecular modulation in SF$_6$ [12]. Rather than reducing the spectral bandwidth of the probe pulse they compressed it to 15 fs which is well below the vibrational period. In this way, the probe spectrum experiences a continuous broadening from MRG that gives single pulses rather than a pulse train. This continuous spectral broadening is different than broadening from SPM, which follows the intensity and cannot be easily compressed. The pump pulse experiences SPM, and so a delayed lower power, frequency doubled probe is used. The
pressure of the gas was set to have the pump and probe wavelength phase matched so that the delay remained constant with propagation. The frequency modulation imposed from the impulsive scattering as already demonstrated is sinusoidal and so can be easily compressed with linear GVD supplied by chirped mirrors. The author’s showed that the modulation phase changed with delay between the probe and pump pulses and that they had optimum compression resulting in a duration of 3.8 fs for a delay of 242 fs.

Bustard, Sussman and Walmsley demonstrated that the coherence produced by impulsive pumping could be amplified by pumping with a long pulse from a second laser [69]. A linearly polarized beam of 55 fs pulses was split to both impulsively excite the rotational Raman transition in hydrogen and also be a probe pulse. A circularly polarized, frequency doubled, Q-switched Nd:YAG laser was used to pump the coherence. The energy of the first Stokes was measured as a function of pump energy with and without the short seed pulse. More Stokes energy was generated with a seed pulse present. The enhancement saturated at a seed energy of 12 μJ, which would suggest that at this energy the impulsively excited coherence exceeds the spontaneous Raman scattering rate.

IX. ANGLE TUNING IN CRYSTAL MEDIA

For gaseous Raman media, the Raman orders were collinear with the pumps. This was achieved in the adiabatic regime, by the refractive index being controlled by the Raman process itself so that all the orders were phase matched in the forward direction. In the transient and impulsive regimes, the collinear propagation was guided by using hollow fibers. For these cases then, the hollow fiber had to also compensate for the material dispersion so that the orders could be phase matched in the forward direction. The collinear arrangements were chosen so that all the orders could be easily superimposed to give the ultrashort pulses. Crystals have much higher Raman gain but are very dispersive making collinear propagation not possible. The orders tend to phase match by radiating at different angles. In the early SRS experiments with single pumps, the Raman orders radiated at cones with angles given by phase matching. In more recent MRG experiments, it was realized that by crossing two beams at the phase matching angle would cause the higher orders to radiate in single directions, each at their own phase matching angle. The disadvantage of this technique is that the generated Raman orders will have to be both spatially and temporally overlapped.

In 1997, Hakuta and co-workers studied SRS in solid hydrogen placed in a 2 cm long cavity [70]. They observed two Stokes and two anti-stokes orders for pump energy above a threshold of 70 μJ, with 532 nm pulses with duration of 10 ns. They observed that there was AS radiation emitted collinearly with the pump and Stokes showing that the Raman gain was sufficient to overcome the large phase mismatch due to material dispersion. When the Raman cavity is tilted such that the Stokes radiation is no longer collinear with the pump, than the AS line is emitted on the opposite side of the pump for tilt angles of 0 to 45 mrad.

Shon and colleagues numerically modeled adiabatic MRG in solid hydrogen for a tilt angle between the two driving fields [71]. The two driving pulses were long in order to
adiabatically drive the Raman coherence. They studied the sideband generation of a short probe pulse that is input at an angle to the generated Raman coherence. The calculated the generated MRG spectrum as a function of propagation distance and different input angles. They found that they could either optimize the arrangement to have a broad MRG signal or have the energy efficiently driven into a single higher order.

Takashashi, Mano and Yagi [72] experimentally studied impulsive MRG in a 1 mm thick SrTiO$_3$ crystal. The two pumps were from the same 130 fs Ti:sapphire laser system. The laser pulse was split into two pulses and recombined in the crystal at a crossing angle of 1 to 5° between them. Threshold behaviour was observed where a large number of Raman orders were generated when the two beams had intensities greater than 5 GW/cm$^2$. The higher orders are phase matched by radiating at higher angles from the input Stokes beam. The frequency separation of the lower orders is 340 cm$^{-1}$ and the higher orders are at 230 cm$^{-1}$. It was also noted that the slope of the curve of output angle versus frequency also changed when the frequency changed, corresponding to different phase matching conditions. The two different frequencies correspond to two different phonon modes of the crystal.

Matsuki, Inoue and Hanamura carried out a similar experiment in the crystal KNbO$_3$, but used the 150 fs signal and idler pulses of an OPA so that the two pumps could have a peak frequency separation that was set to a phonon mode [73]. The two input frequencies were separated by 613 cm$^{-1}$ corresponding to the frequency of the phonon mode of the crystal. The beams crossed at an angle of 4.5°. The crystal was angle tuned such that the inputs were frequency doubled in the crystal. Several Raman orders were scattered at frequency separations of 613 cm$^{-1}$ from the 2$\omega_1$ and the 2$\omega_2$ frequencies, each radiating at an angle given by phase matching.

Zhi and Sokolov were able to generate up to 20 AS orders and 2 Stokes orders by using a similar approach in lead tungstate [74]. They varied the crossing angle and noted that not only does the MRG efficiency change as you go through the phase matching angle of 4°, but that at angles smaller or larger, the frequency spacing of the orders changes even though the two pump frequencies were held fixed at the Raman separation of 930 cm$^{-1}$. They also held the angle fixed and changed the frequency separation and noted that the strongest signal occurred at the resonant frequency, but multiple orders occurred even at other frequencies. At other frequencies, the orders are double peaked one at the Raman frequency and one given the four wave mixing signal of the two peak input frequencnes. This works shows the importance of phase matching on side band generation. The resonant nature of the Raman process demonstrates that the Raman signal should be much stronger than the non-resonant 4-wave mixing signal if phase matching can be ignored.

Liu, Zhang and Kobayashi used a similar arrangement with a BBO crystal, but one of the input pulses was frequency broadened in a hollow fiber filled with krypton gas so that the one pump had a wavelength span from 660 to 900 nm [75]. Similar to Zhi’s and Sokolov’s work they showed that if the crossing angle was smaller than the resonant angle the frequency spacing of the orders was closer together and that as the angle increased the frequency spacing increased. Looking at the dependence of output angle as a function of frequency they noted that the slope was 843 cm$^{-1}$/degree for any of the crossing angles showing that the angular dependence is wavelength dependent and not order dependent.
confirming the importance of phase matching.

Zhi and Sokolov generated a broad MRG spectrum by using two linearly chirped pulses [76]. Both pulses were derived from a single, 35 fs pulse that could impulsively drive the Raman transition. However, this spectrally broad pulse was linearly chirped to durations varying between 100 fs and 2 ps and then split into two pulses with equal energy. The instantaneous frequency separation of the two pulses can then be tuned through the Raman resonance, by varying the delay between the two pulses. In this way, the Raman transition is driven in the transient regime and it may be optimum to have the stretched duration match the Raman coherence time. They were able to generate up to 40 AS orders of the 325 cm\(^{-1}\) Raman order. The highest order is radiated at an angle of 80° to the pump beam. It is not surprising that this Raman order can be driven by a pump pulse, having a bandwidth of 460 cm\(^{-1}\) FWHM. However, they were also able to drive the 903 cm\(^{-1}\) Raman order, by chirping the pulses with the rate of 620 cm\(^{-1}\) ps\(^{-1}\) and separating the pulses by 1.43 ps. The Raman coherence was then driven at intensities well below the peak intensity. 19 AS orders were observed. Along with the Raman orders, there were also orders appearing that the authors assume come from the non-resonant 4-wave mixing process. Zhi, Wang and Sokolov used a similar arrangement and achieved broadband coherent radiation in diamond [77]. They observed that the frequency spacing of the orders was more dependent on the phase matching than the Raman resonance. If the crossing angle of the pumps was less than the phase matching angle, the frequency spacing was again less than the Raman frequency and as the angle was tuned through resonance the frequency increased beyond the Raman transition.

The disadvantage of generating the broad spectrum through angled phase matching is that the orders must be recombined both spatially and temporally. Matsubara and colleagues solved this problem by using a pulse compressor comprised of two spherical mirrors and a single prism [78]. The arrangement is depicted in Fig. 2. A KTaO\(_3\) crystal was pumped by \(\sim\) 200 fs pulses from the signal and idler of an OPA. The Raman spectrum consisted of 6 spectrally broad orders, separated by 692 cm\(^{-1}\). The Raman orders were reflected by a 100 mm focal length, spherical mirror. The spherical mirror imaged the plane of the crystal onto the prism, so that all the beams were focused together onto the prism. The diffracted beam from the prism was collimated with a 500 mm focal length spherical mirror and directed to a SPIDER [79] for pulse characterization. They measured a pulse duration of 13 fs where the transform limited duration of the generated spectrum would be 9.8 fs.

Zhi and co-workers used a similar arrangement but added a combination of glass plates in the different beam lines and a programmable pulse shaper after the prism to better control the phases of Raman lines [80]. They focused the first 5 AS lines generated in diamond onto the prism. They pre-compensated the delays by adding different amounts of glass in each beam line. The programmable pulse shaper was placed in the recombined beam to adjust the phase between the orders. They verified that they could achieve flat spectral phase across the five orders. The phase was measured by a technique developed by the Katsuragawa group [81], which is based on the SPIDER technique [79]. They combine the generated Raman spectrum with the two pump beams in a nonlinear crystal to produce
FIG. 2: Experimental setup for ultrashort pulse generation using multiple RN-CARS signals. Figure reproduced with permission from ref. 75 © 2009 OSA

a sum-frequency spectrum. The resulting spectrum is then the addition of two overlapping spectra from the second harmonic of the nth order and from the sum-frequency of the n − 1 and n + 1 orders. The interference in the spectrum then gives the spectral phase in the same way as the SPIDER.

X. PHASE STABLE, ULTRASHORT PULSE GENERATION

An excellent review of the field of ultra-short pulse formation created from Raman excitation has been written by Baker and colleagues [82]. I have already described many of the experiments to generate ultra-short pulse that have been carried out in each of the temporal regimes. I want to conclude this review with two recent achievements to generate phase stable trains of ultra-short pulses. In the first Suzuki, Hirai and Katsuragawa have generated a frequency comb with carrier envelope offset (CEO) control [84]. Their experimental arrangement is shown in Fig. 3. The key is that the two pump frequencies are integer multiples of the Raman transition frequency. Because of that a third pulse made from the frequency doubled Stokes line is then also a multiple of the Raman frequency. In this way the third input exactly matches the line generated by MRG. By adding the third input, a very broad frequency comb was generated. In addition to these conditions, the two driving frequencies are generated in a single laser cavity and so they are both integer multiples of the cavity free spectral range (FSR). Therefore with this arrangement the pump frequency is \( \Omega_0 = i \times \text{FSR} \), and the Stokes frequency is \( \Omega_{−1} = k \times \text{FSR} \), the Raman transition frequency would be given by \( \Omega_r = (k − i) \times \text{FSR} \) and the Raman components have frequency \( \Omega_n = i \times \text{FSR} + n \times (k − i) \times \text{FSR} \), where \( i, k \) and \( n \) are all integers. The CEO frequency of the Raman frequency comb is restricted to integer multiples of the cavity.
FSR. By setting the pump frequency to also be a multiple of $\Omega_r$, makes the CEO frequency zero.

FIG. 3: Generation of octave-spanning Raman comb with control of carrier-envelope-offset frequency. (a) Experimental setup and scheme for Raman comb generation. (b) $\Omega_0$, $\Omega_{-1}$, and $2\Omega_{-1}$ are located at equidistant frequency markers whose spacing is the FSR of the dual-frequency injection-locked Ti:sapphire laser. The expected parametric Raman spectrum is shown, when $\Omega_0$ and $\Omega_{-1}$ are set so as to satisfy the zero-CEO frequency condition. Figure reproduced with permission from ref. 80 © 2008 APS

The second approach to CEO phase stabilized frequency comb is MRG that looks like harmonic generation [83]. The Stokes frequency matches the AC Stark shifted vibrational Raman transition frequency of 4155.235 cm$^{-1}$ in hydrogen. To obtain this Stokes frequency, the Kung group difference frequency mixed the transform limited pulses from a dye laser and a Ti:sapphire laser. The pump frequency is then achieved by frequency doubling the Stokes field. The two frequencies are then input to the hydrogen Raman cell. As the lowest possible frequency generated frequency is one of the inputs, only AS orders can be generated. The Raman orders occur at the harmonic frequencies of the input Stokes field. They used a similar phase measurement technique described in [81] but because the orders are harmonic orders of the Stokes, now any order $\omega_k$ can be used to heterodyne with the sum frequency of two other order $\omega_i$ and $\omega_j$, where $k = i + j$. The authors showed that CEP control of a Raman comb is possible with nanosecond long pumps.
XI. CONCLUSIONS

Broadband MRG spectra have now been generated in all three temporal regions and pulse durations down to 1.6 fs have been achieved. Single pulses with 3.8 fs have been measured and stable pulse trains with CEO control have been achieved. With the new methods of phase controlling the broad spectrum MRG should soon be able to produce high intensity, single to sub-femtosecond pulses in the visible to UV ranges that should open up new possibilities in pump-probe spectroscopy or Coulomb explosion spectroscopy.

References

Review

Atomic and Molecular Photoelectron Holography in Strong Laser Fields

Xue-Bin Bian¹,²,* and André D. Bandrauk²

¹State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, People’s Republic of China
²Laboratoire de chimie théorique, Faculté des Sciences, Université de Sherbrooke, Québec, J1K2R1, Canada

(Received August 29, 2013)

Recent progress in photoelectron holography with atoms and molecules in strong laser fields is reviewed. From a semi-classical model, four kinds of holography patterns are predicted, which include two forward rescattering interference patterns and two backward rescattering patterns involving subcycle interference of electron dynamics. One of the forward rescattering patterns has been experimentally demonstrated with mid-infrared free-electron lasers. The other three interference patterns are obtained from numerical simulations by solving the time-dependent Schrödinger equations for symmetric and nonsymmetric molecular ions in ultrashort intense lasers. It is shown that photoelectron holography is a new tool for attosecond-resolved imaging of molecular structure.

DOI: 10.6122/CJP.52.569 PACS numbers: 32.80.Wr, 33.60.+q, 61.05.jp

I. INTRODUCTION

The holographic method was first invented by Gabor [1] for improving the resolution limit of electron microscopy. The central idea is to use a reference wave to interfere with the signal wave to record both the amplitude and the phase information. The method is widely used in optics as the development of lasers. Photoelectron holography has been studied recently in new areas of research. It has been applied to image the crystal structure of solid surfaces [2]. Photoelectron holography in above-threshold ionization (ATI) from strong laser-atom and molecule interaction with elliptical and linear laser field has also been investigated [3–5]. In the process, part of free electrons after ionization directly arrive at a detector, while some of the free electrons are rescattered by the atomic or molecular cores, and then they reach the detector. We call the former as reference electrons and the latter as signal electrons, which contain detailed information on atomic and molecular structure. Photoelectron holography in ATI is unique and different from optical holography. The reference and signal photoelectrons produced by the strong laser field come from the same object, but with different transverse momentum. The reference and signal electrons with the same final momentum in the detector interfere with each other, thus recording

*Electronic address: xuebin.bian@wipm.ac.cn
both the phase and amplitude information of different trajectories. Photoelectrons with
different final momentum correspond to different birth (ionization) times in the laser field,
which can be determined approximately by a semiclassical model [4, 6, 7]. As a result, this
kind of photoelectron holography is dynamic, and can be resolved on attosecond (1 as =
10^{-18} s) time scale, the scale of the electronic motion in matter [4, 7, 8]. The energy of the
rescattered electron can reach up to 10 U_p [6], where U_p = I/4m\omega^2 is the ponderomotive
energy at intensity I and frequency \omega. The corresponding electron de Broglie wavelength
\lambda_e = 2\pi/p can be controlled and made comparable to or even smaller than molecular
internuclear distances R, with Ångström (10^{-10} m) spatial resolution [9].

Since the reference and signal electrons register new information about the initial
state and even atomic and molecular cores by laser-induced electron diffraction, LIED [10],
photoelectron holography can be used as a new tool for dynamic imaging [10–12]. Photo-
electron holography is a 4-D movie, recording the motion of electrons in molecules on their
own attosecond time scale.

II. STRONG-FIELD MODEL FOR PHOTOELECTRON HOLOGRAPHY

In this section, we present photoelectron holography patterns in linearly polarized
laser field obtained by a semiclassical model. The recollision model is described in the
strong-field approximation (SFA) [6, 13, 14]. The following assumptions [7] form the basis
of the model:

1. The phase changes during electron tunnel ionization and rescattering process are
   neglected. Multiple rescattering of the signal electron by the atomic and molecular
   cores is not considered.

2. Once the electrons are ionized, their motions are dominated by the laser field. The
   Coulomb force is neglected, the basis of the SFA model.

3. The initial velocity of the photoelectrons is zero after tunnelling ionization along the
   laser polarization direction. In the perpendicular direction, the initial velocity of
   the reference electrons is not zero, and is conserved. In this classical model, these
   electrons will not return to the cores due to their displacement in the perpendicular
direction. For the signal electrons, their initial velocity in the perpendicular direction
   is zero. After ionization, when the laser field changes its phase (direction), some of the
   electrons will be driven back to the core and elastically rescattered to any direction.

4. We assume the free electrons are born at a distance z_0 = I_p/E_0 from the core by
tunnelling ionization [15], where I_p is the ionization potential, E_0 is the amplitude
of the laser field. This corresponds to ionization at the outer turning point of the
potential barrier created by the Coulomb and static electric field E_0.

Assuming that the laser field is polarized along the z direction and the electric field is
expressed by E(t) = E_0 cos(\omega t + \varphi), where \omega is the carrier frequency and \varphi is the phase
where the electron is ionized, the velocity and the displacement of the free electron can be written from Newton’s equations of motion \( \dot{z} = -E(t) \) (in atomic units: \( e = \hbar = m = 1 \)) as:

\[
\dot{z} = v(t, \phi) = \int_0^t -E(t')dt' = -\frac{E_0}{\omega} [\sin(\omega t + \phi) - \sin(\phi)],
\]

(1)

\[
z(t, \phi) = \int_0^t v(t')dt' = \frac{E_0}{\omega^2} [\cos(\omega t + \phi) - \cos(\phi) + \omega \sin(\phi)t] - z_0.
\]

(2)

In this classical model, the signal electron is driven back to the parent core after a travel time \( t_c \) in the laser field, \( z(t_c, \phi) = 0 \). The relation between \( t_c \) and \( \phi \) can be obtained from Eq. (1) and (2),

\[
\cos(\omega t_c + \varphi) - \cos(\varphi) + \omega \sin(\varphi)t_c = \gamma^2/2,
\]

(3)

where \( \gamma = \frac{\omega}{E_0} \sqrt{2T_p} \) is the Keldysh parameter, the ratio of the bound electron energy to the free “dressed” or ponderomotive electron energy.

When the signal electron returns to the core, we assume it is elastically rescattered by the core at an angle \( \theta_c \). Then the velocity in the perpendicular direction is constant:

\[
v_\perp = v(t_c, \phi) \sin(\theta_c).
\]

The velocity along the laser polarization direction is:

\[
v_\parallel = \int_{t_c}^t E(t')dt' = -\frac{E_0}{\omega} [\sin(\omega t + \phi) - \sin(\omega t_c + \phi)] + v(t_c, \phi) \cos(\theta_c).
\]

(4)

The total zero area condition, \( \int E(t)dt = 0 \), implies that the vector potential \( A(t) \) is zero at the beginning and end of the pulse. From this condition, the measured final momentum by the detectors is:

\[
P_\parallel = \frac{E_0}{\omega} \sin(\omega t_c + \phi) + v(t_c, \phi) \cos(\theta_c).
\]

(5)

For the reference electrons, after setting their final momentum, the same as the signal electrons, one can calculate their ionization phase \( \phi' \) and traveling time \( t' \). The phase difference between these two trajectories, reference and signal, is obtained as:

\[
\Delta \Phi = \int_{t_c}^t \frac{v^2(t', \phi)}{2} dt' - \int_0^{t'} \frac{v'^2(t', \phi')}{2} dt' - \frac{v'^2}{2} t' I_p (\phi - \phi').
\]

(6)

In Figure 1, we show the typical interference patterns for signal and reference electrons ionized from different laser field quarter cycles. Fig. 1 (a) and (b) corresponds to total forward rescattering, while Fig. 1 (c) and (d) represents total backward rescattering. The interference dynamics are clearly occurring on subcycle time scale.

In ATI experiments, many interference patterns including temporal and spatial interference [16] will appear, such as ATI rings in a relatively long laser pulse [4, 7], time double-slit interference in phase-stabilized ultra short laser pulses [7, 17, 18]. How can
we separate the holography from the final spectra? To reduce the ATI rings and time double-slit interference patterns, one can change the length of the laser pulse to a medium length to observe clear holography patterns. In our numerical simulations, the total pulse duration between five and ten optical cycles is found to be optimal. To further disentangle the forward and backward rescattering holography patterns, one can choose atoms and molecules with relatively small and large rescattering cross sections to suppress or enhance the scattering probability.

III. PHOTOELECTRON HOLOGRAPHY WITH ATOMS IN STRONG LASER FIELD

As shown in Fig. 2, time-resolved atomic photoelectron holography was experimentally observed by Huismans et al. using a 7 μm free-electron laser (FEL) [4, 19]. This long wavelength FEL is favorable for the forward rescattering holography as illustrated in Fig. 1 (a). Due to the long period of this low-frequency laser field, the ionized electronic wave packets are widely spread when they are driven back to the core. As a result, the rescattering cross sections are relatively small, and the angular distributed forward rescattering holography pattern in Fig. 1 (a) calculated by SFA for Xe atom is clearly observed.

FIG. 1: Sketch of the interference trajectories from different subcycles in photoelectron holography. A represents the signal electron, B stands for the reference electron. The laser intensity is \( I = 7.1 \times 10^{11} \text{ W/cm}^2 \), and the wavelength is 7 μm. The ionization potential corresponds to the metastable 6s of Xe. Adapted from Ref. [7], copyright APS.
As described by our model in Section II, the Coulomb potential is neglected due to the dominant effect of the laser field. Taking into account Coulomb effects [4, 20], the experimental results and the results by solving the corresponding time-dependent Schrödinger equations (TDSE) agree well with the results by SFA, thus confirming the validity of SFA. The wide spreading of the wave packets is not helpful for observing the second forward rescattering holography pattern predicted by SFA as illustrated in Fig. 1 (b). The overlap of the two trajectories, reference and signal, is relatively small, as their amplitudes are not comparable.

The distribution of the reference electrons is essentially determined by the initial state of the system [7]. The photoelectron hologram will therefore image the initial wave function. It has been illustrated theoretically by using the degenerate 3s, 3p and 3d states of the H as examples of an initial state, respectively [7]. The shape of the original orbital is imprinted in the photoelectron holography. It has also been experimentally confirmed that the shape and orientation of an initial Rydberg state leaves its own fingerprint on the final angular distribution of photoelectron spectra [21]. Thus photoelectron holography can provide an important new tool to extract useful orbital information by ultrafast strong-field processes.

In the SFA model described in Section II, multiple scattering of the signal electrons was neglected. Low-energy features in the spectra can reflect multiple rescattering of photoelectrons in laser fields [22–24]. The interference structure between unrescattered photoelectrons perpendicular to the laser polarization direction has also been confirmed experimentally and theoretically [25]. Such photoelectron spectra encode novel information of ultrafast processes in LIED.

The forward rescattering holographic patterns depend generally strongly on the laser wavelength $\lambda$ and intensity $I$. It has been shown that the condition $U_p/h\omega \gg 1$ is crucial for the holographic interference [26], i.e., high ponderomotive energy much larger than photon
energy. Although forward rescattering photoelectron holography has been clearly illustrated by using long-wavelength FELs [4], the backward rescattering photoelectron holography has not been identified yet experimentally.

IV. PHOTOELECTRON HOLOGRAPHY WITH MOLECULAR IONS IN STRONG LASER FIELD

To observe the backward rescattering holography, the scattering cross section must be relatively large as in molecules. In this section, we review the backward rescattering holography studied by using molecules with more scattering centres than atoms [8]. The wavelength of the laser field should be short to produce short recollision times, which are generally 2/3 of a laser cycle [7, 13, 14]. Short laser pulses also reduce the spread of the wavepackets. In addition, to reduce the dissociation effect of molecules in the ATI process, short-wavelength and short-pulse lasers in the near fs regime allow investigating the ultrafast process under Born-Oppenheimer approximation (BOA), corresponding to frozen nuclei. Coulomb focusing effect on the ionized electrons will also increase the relative scattering cross section [27]. Photoelectron holography from molecules should provide a useful tool for imaging molecular structure due to the above effects. We use symmetric H$_2^+$ [8] and asymmetric HeH$^+$ [28] molecular ions as examples to illustrate the motion of electrons in molecules measured by photoelectron holography.

In the simulations, the wavelength of the laser field used is $\lambda = 532$ nm (1 optical cycle is around 1.8 fs), the laser intensity is $I = 1.5 \times 10^{15}$ W/cm$^2$. The total pulse duration is $T = 5$ cycles with polarization along the $z$ axis. The vector potential of the pulse is given by $A(t) = \frac{E_0}{\omega} \sin^2(\frac{\pi t}{T}) \cos(\omega t)$, thus ensuring total zero area for $E(t) = -\frac{\partial A(t)}{\partial t}$. The vibrational period of H$_2^+$ is around 15 fs. The total duration of the laser pulse is around 9 fs. The dominant ionization time of photoelectron occurs around two cycles near the peak intensity of the pulse. Furthermore the recollision time $t_c$ is around 1 fs, thus making the fixed-nuclei approximation in the numerical simulations valid. We set the internuclear distance at equilibrium $R = 2$ a.u. The photoelectron angular momentum distribution of H$_2^+$ is illustrated in Fig. 3 with both parallel ($z$) and perpendicular ($x$) orientations. With momentum $|P_z| < 1$ a.u., the backward rescattering holographic interference pattern in Fig. 1 (c) predicted by SFA agrees with the results by TDSE qualitatively. The shape and the number of the stripes agree. The density of stripes becomes sparse as $|P_z|$ increases. This interference pattern remains with different orientations. With $|P_z| > 1$ a.u., clear interference structure can be found with parallel ($z$) orientation. The density of the stripes becomes dense as $|P_z|$ increases, and their shape also quantitatively agrees with the SFA model in Fig. 1 (d). We attribute the observation of the weak holography to the Coulomb focusing effect. It is natural that it becomes defocusing effect when the orientation of the molecule is perpendicular. As a result, no clear interference structure appears in Fig. 3 (b) with $|P_z| > 1$ a.u.

The parallel laser-molecule orientation is optimal to identify the backward rescattering holography predicted in Fig. 1 (d). However, the signal is weak in Fig. 3 (a) and perfect
FIG. 3: Photoelectron angular momentum distribution of $\text{H}_2^+$ in a strong laser field of intensity $I = 1.5 \times 10^{15}$ W/cm$^2$, and wavelength 532 nm. The polarization of the laser field is along the $z$ axis. In (a), the molecular axis is along the $z$ direction. In (b), the molecular axis is along the $x$ axis. The color is plotted on the logarithmic scale. Adapted from Ref. [8], copyright APS

orientation control is generally difficult in experiments. The positive aspect is that the holographic pattern in Fig. 1 (c) is not sensitive to the orientation of the molecules in our simulations. The laser parameters used in our calculations are experimentally accessible currently. Hopefully “backward rescattering” holography may be experimentally developed and confirmed in the future.

Is it possible to observe the four kinds of holography patterns at the same time? To achieve this, we study the photoelectron holography from the asymmetric molecular ion $\text{HeH}^2+$ [28]. When the laser field polarization is along the molecular $z$ axis, the ionization rate from $+z$ and $-z$ is quite different [29]. The former may be two orders higher than the latter due to enhanced ionization via enhanced excitation [30] and the lower $I_p$ of the H atom. We may therefore neglect the ionization from the $-z$ direction. Consequently, the forward rescattering and the backward rescattering of photoelectron will not overlap, which allows us to study the forward and backward holography simultaneously. The internuclear distance of $\text{HeH}^2+$ is fixed at $R = 4$ a.u. The laser field is the same as that used for studying $\text{H}_2^+$. The photoelectron angular momentum distribution of $\text{HeH}^2+$ is illustrated in Fig. 4 with both parallel and perpendicular orientations. For parallel orientation, with $P_z > 0$, the backward rescattering patterns shown in Fig. 1 (c) and (d) from the SFA model, can be clearly identified in Fig. 4. The patterns are similar to the results with $\text{H}_2^+$ presented in Fig. 3. Due to the larger ionization potential and nuclear charge, the interference patterns are distorted, but still distinguishable. For $P_z < 0$, the pattern corresponds to forward rescattering holography. The angular stripes agree with the SFA model illustrated in Fig. 1 (a). The radial rings agree with the SFA model in Fig. 1 (b). The space between
the rings increases as $|P_z|$ increases, agreeing with the SFA model. When we change the laser field polarization direction to be perpendicular to the molecular axis of HeH$^2+$, the momentum distribution of the photoelectrons changes dramatically. This corresponds to forward rescattering holography, similar to the holography patterns shown in Fig. 2. This is attributed to the Coulomb defocusing effect with larger internuclear distance $R$, where the scattering cross section is relatively small.

FIG. 4: Photoelectron angular momentum distribution of HeH$^2+$ in strong laser field. The laser parameters are the same as in Fig. 3. The molecular axis is along the $z$ direction. In (a), the polarization of the laser field is parallel to the molecular axis. In (b), the molecular axis is perpendicular to the laser polarization. The color is plotted on the logarithmic scale.

V. DISCUSSION AND CONCLUSIONS

In summary, four kinds of photoelectron holography patterns are predicted by an SFA model. These represent subcycle electron dynamics. The first kind of forward rescattering holography has been identified experimentally using low-frequency FELs. The other three kinds of holography patterns are simulated by solving TDSE for symmetric H$_2^+$ and non-symmetric HeH$^2+$ molecular ions in strong short-wavelength lasers. The simulations show that Coulomb focusing effects are crucial for observing backward rescattering interference patterns in ATI. Photoelectron holography encodes rich information on the structure of initial electron states of an electronic system as well as ultrafast processes induced by the laser field. It can provide an attosecond-resolved tool for dynamic imaging of electronic and molecular structure due to subcycle recollision times of ionized electrons. The laser parameters used are accessible experimentally currently due to advances in laser technology.
The present review should stimulate experimental study of photoelectron holography as a new tool in molecular structure research.

Acknowledgements

We thank Y. Huismans, O. Smirnova, K. J. Yuan, and M. J. J. Vrakking for valuable discussions. We thank the RQCHP and Compute Canada for access to massively parallel computer clusters and the CIPI (Canadian Institute for Photonic Innovations) for financial support in its ultrafast science program.

References

Review


John Heslar,1,* Dmitry A. Telnov,2,† and Shih-I Chu ‡1,3,§

1Center for Quantum Science and Engineering, Department of Physics, National Taiwan University, Taipei 10617, Taiwan
2Department of Physics, St. Petersburg State University, St. Petersburg 198504, Russia
3Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, USA

(Received August 29, 2013)

We present a brief account of several recent ab initio nonperturbative studies of very-high-order nonlinear optical processes of diatomic molecular systems in intense ultrashort laser fields with arbitrary molecular orientation. We discuss some recent development of the self-interaction-free time-dependent density functional theoretical (TDDFT) methods with correct long-range asymptotic behavior. The time-dependent Kohn-Sham equations are accurately and efficiently treated by means of the time-dependent generalized pseudospectral (TDGPS) methods in space and time. The procedures are applied to the comprehensive investigation of the multiphoton ionization (MPI) and high-order harmonic generation (HHG) processes of homonuclear (H₂, N₂, and F₂) and heteronuclear (CO, BF, and HF) diatomic molecules in the presence of intense ultrashort laser pulses. Novel high-order nonlinear optical behavior including the electron correlation, multi-orbital effects, orientation-dependence, wavelet time-frequency spectra, and the interfacing of electronic structure with multiphoton dynamics, etc., are presented and discussed in details.

DOI: 10.6122/CJP.52.578 PACS numbers: 33.80.Rv, 42.65.Ky, 31.15.E-, 31.15.A-

I. INTRODUCTION

The study of attosecond physics in intense ultrashort laser fields is a forefront subject of much current significance in ultrafast science and technology. Attosecond pulses can be produced by means of high harmonic generation (HHG) of atoms in intense laser fields [1–7] and the time profile of the attosecond pulses can be controlled by tuning the carrier envelope phase [8]. Recent progress of attosecond physics includes control of electron wave packets [9], probing of nuclear dynamics [10] and electronic dynamics [11], attosecond time-resolved spectroscopy [12], tomographic imaging of molecular orbitals [13], etc. One of the most novel features in an attosecond time scale is the real time observation of the motion of
electrons in atoms and molecules [14]. The generation of ever shorter attosecond pulses has continued to attract much interest and has become one of the most active research directions in attosecond metrology today. In this connection, we note that ultrahigh harmonics, up to orders greater than 5,000, have been recently realized experimentally [15].

A major role for theory in attosecond ultrafast science is to elucidate novel ways to investigate and to control electronic and other processes in matter on attosecond time scales. Strong-field multiphoton dynamics is central to many extreme nonlinear optical processes such as high-order harmonic generation (HHG), multiphoton ionization (MPI), above-threshold ionization (ATI), and attosecond pulse generation, etc. Fully ab initio nonperturbative treatment of many-electron quantum systems in strong fields in full dimensionality is a formidable task beyond the capability of current computational technology for the number of electrons \( N > 2 \). Even for the two-electron systems \( (N = 2) \) with 6 spatial dimensions, accurate solution of the time-dependent Schrödinger equation (TDSE) is still a challenging and hot topic in atomic, molecular, and optical (AMO) physics today.

Due to the complexity of the time-dependent dynamics of many-electron quantum systems in intense laser pulses, most of our understanding of the strong-field multiphoton dynamics is based on approximate models, such as Keldysh-Faisal-Reiss (KFR) model [16–18], Ammosov-Delone-Krainov (ADK) model [19, 20], strong-field approximation (SFA), and single-active-electron (SAE) model [21], etc. The SAE method has been successfully used for explaining several important aspects of HHG and ATI phenomena of rare gas atoms in linearly polarized laser fields in weak to medium-strong laser fields [21, 22]. However, the SAE and other approximate models can fail completely to explain experimental observations in strong fields.

There is currently a great demand and grand challenge to develop accurate theoretical formulations and precision computational methods for reliable nonperturbative treatment of ultrafast strong-field AMO physics, taking into account the electron structure and electron correlations. In this article, we focus on some of the recent developments and applications of the self-interaction-free time-dependent density functional theory (TDDFT) for the ab initio nonperturbative treatment of MPI and HHG processes in intense ultrashort laser fields.

The density functional theory (DFT), based on the fundamental work of Hohenberg and Kohn [23] and Kohn and Sham [24], has been widely used for the calculation of ground-state electronic structure of many-electron atoms, molecules, and solids in recent decades. DFT is a many-body theory in terms of the electron density \( \rho(r) \). It provides a powerful alternative to ab initio wave function approach since the electron density \( \rho(r) \) possesses only three spatial dimensions no matter how large the system is. DFT proves accurate and computationally much less expensive than usual ab initio wave function methods and this accounts for its great success. However, the universal exchange-correlation (xc) energy functional form, which is a functional of the total electron density and the central ingredient of DFT, is not known exactly, and thus approximate xc energy functionals must be used. Due to the existence of the spurious self-interaction energy in the commonly used local spin density approximation (LSDA) [25] or the more refined generalized gradient approximation (GGA) [25–29] the corresponding xc potentials either decay exponentially and/or do not
have the correct long-range Coulombic (−1/r) behavior. As such, the excited-state and ionization potential properties of conventional DFT calculations are not as reliable as those of the ground state. For example, the ionization potentials calculated by the LSDA or GGA energy functionals are typically 30 to 50% too low. It is clear that for proper TDDFT description of atomic and molecular dynamics, including multiphoton excitation, ionization, dissociation, and HHG processes, etc., the deficiency of self-interaction energy and long-range potential in the conventional steady-state DFT must be addressed first.

To advance the field in this direction, we have previously presented a self-interaction-free DFT for accurate treatment of excited states, autoionizing resonances, and ionization potentials of atoms [30, 31]. The method is based on the extension of the optimized effective potential (OEP) formalism [32, 33], the Krieger-Li-Iafrate (KLI) semi-analytical solution [34, 35] of the OEP, and the implementation of an explicit self-interaction-correction (SIC) term [31]. The OEP formalism is a rigorous many-body theory which takes as a starting point a given expression for the total energy $E[\Psi_1 \Psi_2 \Psi_3 ... \Psi_N]$ for an N-electron system as a functional of a set of single-particle orbitals. Then the variationally best local effective potential is determined in such a way that when it is inserted in a stationary single-particle Schrödinger equation, it yields a set of N-eigenfunctions (corresponding to the N lowest energies) that minimize $E[\Psi_1 \Psi_2 \Psi_3 ... \Psi_N]$. In practice, the full OEP scheme is computationally rather formidable but the KLI semianalytical approach [34, 35] to the solution of OEP makes the computational scheme feasible. However, the KLI method [34–36] still requires the use of the nonlocal Hartree-Fock (HF) energy functionals in the construction of OEP. As shown in our previous work [31], the proposed OEP/KLI-SIC procedure uses only orbital-independent single-particle local potentials and is thus computationally more efficient than the KLI method [34, 35] but maintains similar accuracy. Further, the OEP so constructed is self-interaction-free and has the correct long-range (−1/r) potential [31]. The binding energies of the highest occupied spin-orbitals also provide an excellent approximation to the ionization potentials of atoms (to within 1-5% of the experimental values) [37]. Furthermore, the OEP/KLI-SIC procedure also allows accurate description of the photoabsorption of autoionizing resonances within DFT for the first time [31] in good agreement with experimental data [38, 39]. Then the OEP/KLI-SIC procedure is further extended to the relativistic domain [40]. The theory is applied to the calculation of ground-state properties of atoms with $Z = 2$ to 106 [40]. It is found that the ionization potentials (obtained from the highest occupied orbital energies) determined by the present relativistic OEP/KLI-SIC method [40] agree well with the experimental data [41] to within a few percent across the periodic table. To our knowledge this is the first DFT atomic-structure calculation that has achieved such a quantitative accuracy. These initial studies indicate that DFT with OEP/SIC can now be refined to the level that is capable of providing quantitative prediction of both static and dynamical properties of many-electron atomic systems.

To study the multiphoton processes of atomic systems in strong fields, we have developed a self-interaction-free time-dependent density functional theory (TDDFT) by extending the static OEP/KLI-SIC approach to the time domain [42], taking into account the proper long-range potential behavior. Similar to the static case [31], our TD-OEP/KLI-
SIC method [42] uses only local potential in the construction of (orbital-independent) OEP and is thus computationally more efficient. To solve the TD-OEP/KLI-SIC equations, we extend the time-dependent generalized pseudospectral (TDGPS) method [43] for nonuniform and optimal spatial grid discretization, allowing accurate and efficient solution of the time-dependent wave functions of many-electron atomic systems. The TD-OEP/KLI-SIC method has been applied successfully to the study of MPI/HHG processes of He [42] and heavier rare gas atoms [44] in intense laser pulses, as well as for the recent exploration of the frequency comb structure and coherence of rare gas atoms in the vuv-xuv regimes via HHG [45].

More recently, we have extended the self-interaction-free TDDFT to the diatomic molecular systems [30, 46, 47]. For the diatomic molecular systems, we used the prolate spheroidal coordinates, and a generalized pseudospectral (GPS) procedure is developed for nonuniform and optimal spatial discretization of the two-center Hamiltonian systems. High-precision molecular electronic structure information can be obtained by the use of only a modest number of grid points. Further extension of the TDDFT approach to the accurate study of MPI processes of triatomic molecular systems (CO$_2$ and H$_2$O) have been recently carried out by means of the time-dependent Voronoi-cell finite difference (VFD) method [48, 49].

This paper is organized as follows. In Sec. II, we describe the TDDFT approaches for the treatment of multiphoton processes in diatomic molecules. In Sec. III, we present the results for MPI and HHG studies of oriented H$_2$ molecules. In Sec. IV, we analyze multiple orbital contributions to the MPI and HHG processes of homonuclear and heteronuclear diatomic molecules in intense ultrashort laser fields. We identify the patterns of constructive and destructive interference in the high-order harmonics for F$_2$, N$_2$, CO, BF, and HF diatomic molecules. In Sec. V, we study orientation-dependent MPI and HHG of N$_2$ and F$_2$ molecules. We also investigate the high-order harmonic generation of aligned CO molecules. Section VI contains concluding remarks. Atomic units are used throughout the paper unless specified explicitly.

II. TDDFT APPROACH WITH PROPER LONG-RANGE POTENTIAL FOR THE TREATMENT OF MULTIPHOTON PROCESSES OF DIATOMIC MOLECULES

In this section, we extend the time-dependent density functional theory (TDDFT) for the nonperturbative treatment of multiphoton processes of diatomic molecular systems in the presence of intense ultrashort laser pulses. Consider the solution of the time-dependent Kohn-Sham (TDKS) equations. In the spin-polarized theory, the spin-orbitals $\psi_{n\sigma}(r,t)$ corresponding to different spin projections $\sigma$ satisfy the equations with different effective potentials $v_{\text{eff},\sigma}(r,t)$:

$$i \frac{\partial}{\partial t} \psi_{n\sigma}(r,t) = \left[ -\frac{1}{2} \nabla^2 + v_{\text{eff},\sigma}(r,t) \right] \psi_{n\sigma}(r,t), \quad n = 1, 2, ..., N_\sigma,$$

(1)
where \( N_\sigma (= N_\uparrow \text{ or } N_\downarrow) \) is the total number of electrons for a given spin \( \sigma \). The total number of electrons in the system is \( N = \sum_\sigma N_\sigma \). Within the single determinant approximation, the total \( N \)-electron wave function of the Kohn-Sham non-interacting system can be expressed as follows:

\[
\Psi(t) = \frac{1}{\sqrt{N!}} \det[\psi_1 \cdot \psi_2 \cdot \ldots \cdot \psi_N].
\] (2)

The electron spin-orbital densities \( \rho_{i\sigma}(\mathbf{r},t) \) are determined by the occupied single-electron Kohn-Sham spin orbitals:

\[
\rho_{i\sigma}(\mathbf{r},t) = |\psi_{i\sigma}(\mathbf{r},t)|^2.
\] (3)

Then the spin densities \( \rho_\sigma(\mathbf{r},t) \) \([= \rho_\uparrow(\mathbf{r},t) \text{ or } \rho_\downarrow(\mathbf{r},t)]\) are calculated as

\[
\rho_\sigma(\mathbf{r},t) = \sum_{i=1}^{N_\sigma} \rho_{i\sigma}(\mathbf{r},t),
\] (4)

and the total electron density is a sum of the spin densities:

\[
\rho(\mathbf{r},t) = \sum_\sigma \rho_\sigma(\mathbf{r},t).
\] (5)

The time-dependent effective potential \( v_{\text{eff},\sigma}(\mathbf{r},t) \) is a functional of both electron spin densities \( \rho_\uparrow(\mathbf{r},t) \) and \( \rho_\downarrow(\mathbf{r},t) \). The potential \( v_{\text{eff},\sigma}(\mathbf{r},t) \) can be written in the general form

\[
v_{\text{eff},\sigma}(\mathbf{r},t) = v_n(\mathbf{r}) + v_H(\mathbf{r},t) + v_{xc,\sigma}(\mathbf{r},t) + v_{\text{ext}}(\mathbf{r},t)
\] (6)

where \( v_n(\mathbf{r}) \) is the electron interaction with the nuclei,

\[
v_n(\mathbf{r}) = -\frac{Z_1}{|\mathbf{R}_1 - \mathbf{r}|} - \frac{Z_2}{|\mathbf{R}_2 - \mathbf{r}|}
\] (7)

with \( Z_1 \) and \( Z_2 \) being the charges of the nuclei, and \( \mathbf{R}_1 \) and \( \mathbf{R}_2 \) being the positions of the nuclei (which are assumed to be fixed at their equilibrium positions); \( v_H(\mathbf{r},t) \) is the Hartree potential due to electron-electron Coulomb interaction,

\[
v_H(\mathbf{r},t) = \int d^3 r' \frac{\rho(\mathbf{r}',t)}{|\mathbf{r} - \mathbf{r}'|}.
\] (8)

The potential \( v_{\text{ext}}(\mathbf{r},t) \) in Eq. (6) describes the interaction with the laser field. Using the dipole approximation and the length gauge, it can be expressed as follows:

\[
v_{\text{ext}}(\mathbf{r},t) = (\mathbf{F}(t) \cdot \mathbf{r}).
\] (9)

Here \( \mathbf{F}(t) \) is the electric field strength of the laser field, and the linear polarization is assumed. For the laser pulses with the sine-squared envelope, one has:

\[
\mathbf{F}(t) = F_0 \sin^2 \frac{\pi t}{T} \sin \omega_0 t
\] (10)
where $T$ and $\omega_0$ denote the pulse duration and the carrier frequency, respectively; $F_0$ is the peak field strength.

The wave functions and operators are discretized with the help of the generalized pseudospectral (GPS) method in prolate spheroidal coordinates [46, 50–52]. The prolate spheroidal coordinates $\xi$, $\eta$, and $\varphi$ are related to the Cartesian coordinates $x$, $y$, and $z$ as follows [53]:

$$
\begin{align*}
x &= a\sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \varphi, \\
y &= a\sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \varphi, \\
z &= a\xi \eta \quad (1 \leq \xi < \infty, -1 \leq \eta \leq 1).
\end{align*}
$$

In Eq. (11), we assume that the molecular axis is directed along the $z$ axis, and the nuclei are located on this axis at the positions $-a$ and $a$, so the internuclear separation $R = 2a$. For the unperturbed molecule, the projection $m$ of the angular momentum onto the molecular axis is conserved, and the exact spin orbitals have factors \((\xi^2 - 1)^{|m|/2}(1 - \eta^2)^{|m|/2}\) which are non-analytical at nuclei for odd $|m|$. Straightforward numerical differentiation of such functions could result in significant loss of accuracy. Therefore different forms of the kinetic energy operators have been suggested for even and odd $m$ [50, 54]. However, for the molecules in the linearly polarized laser field with arbitrary orientations of the molecular axis, the projection of the electron angular momentum onto the molecular axis is not conserved anymore. In this case, we apply a full 3D discretization with respect to the coordinates $\xi$, $\eta$, and $\varphi$. For $\xi$ and $\eta$, we use the GPS discretization with non-uniform distribution of the grid points; for $\varphi$, the Fourier grid (FG) method [55] with uniform spacing of the grid points is more appropriate. To take care of the possible singularities at the nuclei, we use special mapping transformations of the coordinates $\xi$ and $\eta$ [56] which make the wave functions analytic at the nuclei for both even and odd projections of the angular momentum. The discretized kinetic energy operator takes the form of the matrix $T_{ijjk;iljj'}$:

$$
T_{ijjk;iljj'} = \frac{1}{2a^2} \left[ \frac{T^{(n)}_{ij} \delta_{jj'} + T^{(n)}_{jj} \delta_{i'i'}}{\sqrt{(\xi_i^2 - \eta_j^2)(\xi_i^2 - \eta_j^2)}} \delta_{kk'} + \frac{T^{(\varphi)}_{kk'} \delta_{ii'} \delta_{jj'}}{(\xi_i^2 - 1)(1 - \eta_j^2)} \right]
$$

where the partial matrices $T^{(n)}_{ii'}$, $T^{(n)}_{jj}$, and $T^{(\varphi)}_{kk'}$ related to the coordinates $\xi$, $\eta$, and $\varphi$, respectively, have quite simple expressions [56]. The GPS method allows to achieve a high precision when using only a moderate number of grid points. For example, in the calculations of the unperturbed bound state energies of the hydrogen molecular ion, we used the kinetic energy matrices with only 72 grid points for $\xi$ and 24 grid points for $\eta$ (the $\varphi$ angle is irrelevant in this case) and obtained the energies of the first several bound states very high accuracy; the computation time did not exceed a few minutes [57]. Table I shows the first 12 fully converged eigen-energies with 28 accurate digits.

The time-dependent Kohn-Sham equations (1) for two-center diatomic molecular systems are expressed in terms of prolate spheroidal coordinates and solved accurately and efficiently by means of the time-dependent generalized pseudospectral (TDGPS) method.
TABLE I: High-precision bound state energies of H_{2}^{+} at internuclear separation 2 a.u.

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (a. u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1σ_{g}</td>
<td>-1.1026342144946461508968945</td>
</tr>
<tr>
<td>1σ_{u}</td>
<td>-0.6675343922023829303619702115</td>
</tr>
<tr>
<td>1π_{u}</td>
<td>-0.4287718198958564363139600911</td>
</tr>
<tr>
<td>2σ_{g}</td>
<td>-0.3608648753395038450386997512</td>
</tr>
<tr>
<td>2σ_{u}</td>
<td>-0.2554131650864845614172502361</td>
</tr>
<tr>
<td>3σ_{g}</td>
<td>-0.2357776288255547907092435479</td>
</tr>
<tr>
<td>1π_{g}</td>
<td>-0.2266996266436576389675221554</td>
</tr>
<tr>
<td>1δ_{g}</td>
<td>-0.2127326818107631498576063244</td>
</tr>
<tr>
<td>2π_{u}</td>
<td>-0.2008648299115413183937711539</td>
</tr>
<tr>
<td>4σ_{g}</td>
<td>-0.1776810451262412913662883797</td>
</tr>
<tr>
<td>3σ_{u}</td>
<td>-0.137312924277157836485227973</td>
</tr>
<tr>
<td>5σ_{g}</td>
<td>-0.1307918776321809748361441234</td>
</tr>
</tbody>
</table>

[46, 50, 51, 58]. The procedure consists of the following two steps: First a generalized pseudospectral (GPS) method is developed for nonuniform and optimal spatial discretization of the two-center Hamiltonian systems. Second, the TDKS equations are propagated in space and time by means of the split-operator method in the energy representation with spectral expansion of the propagator matrices. We employ the following split-operator, second-order short-time propagation formula:

\[
\psi_{n\sigma}(\mathbf{r}, t + \Delta t) = \exp \left( -\frac{i}{2} \Delta t \hat{H}_0 \right) \exp \left( -i \Delta t V(\mathbf{r}, t + \frac{1}{2} \Delta t) \right) \times \exp \left( -\frac{i}{2} \Delta t \hat{H}_0 \right) \psi_{n\sigma}(\mathbf{r}, t) + O((\Delta t)^3). \tag{13}
\]

Here \(\Delta t\) is the time propagation step, \(\hat{H}_0\) is the unperturbed electronic Hamiltonian which includes the kinetic energy and the the effective potential before the laser field switched on,

\[
\hat{H}_0 = -\frac{1}{2} \nabla^2 + v_{\text{eff},\sigma}(\mathbf{r}, 0). \tag{14}
\]

The potential \(V(\mathbf{r}, t)\) describes the interaction with the laser field and can be expressed as follows:

\[
V(\mathbf{r}, t) = v_{\text{eff},\sigma}(\mathbf{r}, t) - v_{\text{eff},\sigma}(\mathbf{r}, 0). \tag{15}
\]
It contains the direct interaction with the field \( v_{\text{ext}}(r,t) \) (9) as well as terms due to the variation of the density. For the field polarized under the angle \( \gamma \) with respect to the molecular axis, the direct interaction can be expressed as follows, using the prolate spheroidal coordinates:

\[
v_{\text{ext}}(\xi, \eta, \varphi, t) = aF(t) \left( \xi \eta \cos \gamma + \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \varphi \sin \gamma \right).
\]

Note that Eq. (13) is different from the conventional split-operator techniques [59, 60], where \( \hat{H}_0 \) is usually chosen to be the kinetic energy operator and \( \hat{V} \) the remaining Hamiltonian depending on the spatial coordinates only. The use of the energy-representation in Eq. (13) allows the explicit elimination of the undesirable fast-oscillating high-energy components and speeds up considerably the time propagation [43, 46, 58]. For the given \( \Delta t \), the propagator matrix \( \exp \left( -\frac{i}{2} \Delta t \hat{H}_0 \right) \) is time-independent and constructed only once from the spectral expansion of the unperturbed Hamiltonian \( \hat{H}_0 \) before the propagation process starts. The matrix \( \exp \left( -i \Delta t V(r, t + \frac{1}{2} \Delta t) \right) \) is time-dependent and must be calculated at each time step. However, for interaction with the laser field in the length gauge, this matrix is diagonal (as any multiplication by the function of the coordinates in the GPS and FG methods), and its calculation is not time-consuming.

### III. MULTIPHOTON IONIZATION AND HIGH-ORDER HARMONIC GENERATION OF ORIENTED \( \text{H}_2 \) MOLECULES

The exact form of the exchange-correlation (xc) potential \( v_{\text{xc},\sigma}(r, t) \) is unknown. However, high-quality approximations to the xc potential are becoming available. When these potentials, determined by time-independent ground-state DFT, are used along with TDDFT in the electronic structure calculations, both inner shell and excited states can be calculated rather accurately [61]. In the time-dependent calculations, we adopt the commonly used adiabatic approximation, where the xc potential is calculated with the time-dependent density. The adiabatic approximation had recently many successful applications to atomic and molecular processes in intense external fields [30, 61]. Previously we have developed a self-interaction-free TDDFT approach for the treatment of MPI and HHG of \( \text{H}_2 \) diatomic molecules [46] by means of the TD-OEP/KLI-SIC formalism. The resulting equations are structurally similar to the time-dependent Hartree-Fock equations, but include the many-body effects through an orbital independent single-particle local time-dependent xc potential. A numerical time-propagation technique is introduced for accurate and efficient solution of the TDDFT/OEP-SIC equations for two-center diatomic molecular systems. This procedure involves the use of a generalized pseudospectral method for nonuniform optimal grid discretization of the Hamiltonian in prolate spheroidal coordinates and a split-operator scheme in the energy representation for the time development of the electron orbital wave functions. High-precision time-dependent wave functions can be obtained by this procedure with the use of only a modest number of spatial grid points. Particular attention is paid to the exploration of the spectral and temporal structures of HHG by means of the wavelet...
time-frequency analysis. The results reveal striking details of the spectral and temporal fine structures of HHG, providing new insights regarding the detailed HHG mechanisms in different energy regimes.

For our more recent study of the MPI and HHG processes of H\(_2\) molecules, we use the LB94 (van Leeuwen – Baerends) xc potential [62]:

\[
v_{xc,\sigma}^{LB94}(r, t) = v_{xc,\sigma}^{LSDA}(r, t) + v_{c,\sigma}^{LSDA}(r, t) - \beta x_\sigma^2(r, t)\rho_\sigma^{1/3}(r, t)
\]

\[
\frac{1}{1 + 3\beta x_\sigma(r, t) \ln\{x_\sigma(r, t) + [x_\sigma^2(r, t) + 1]^{1/2}\}}.
\]

The LB94 potential contains a parameter \(\beta\), which has been adjusted in time-independent DFT calculations of atomic and molecular systems and has the value \(\beta = 0.05\) [62]. The first two terms in Eq. (17), \(v_{xc,\sigma}^{LSDA}\) and \(v_{c,\sigma}^{LSDA}\) are the exchange and correlation potentials within the local spin density approximation (LSDA). The last term in Eq. (17) is the gradient correction with \(x_\sigma(r) = |\nabla \rho_\sigma(r)|/\rho_\sigma^{4/3}(r)\), which ensures the proper long-range asymptotic behavior \(v_{xc,\sigma}^{LB94} \to -1/r\) as \(r \to \infty\). The correct long-range asymptotic behavior of the LB94 potential allows to reproduce the orbital energy of H\(_2\) with high accuracy (15.3 eV, that is within 1% of the exact ionization energy of 15.426 eV [63]; the internuclear separation is set to the experimental value of 1.4 a.u. [63].)

We have performed calculations of MPI probabilities and HHG spectra of H\(_2\) molecules for the parallel and perpendicular orientations with respect to the polarization of

FIG. 1: MPI probabilities of H\(_2\) molecule for the parallel and perpendicular orientation as a function of the peak intensity of the laser field.
FIG. 2: HHG spectra of H₂ molecule for the parallel and perpendicular orientation at the peak intensity of the laser field $2 \times 10^{14}$ W/cm².

The laser field. The carrier wavelength is 780 nm, the laser pulse has a sine-squared envelope with 24 optical cycles (full width at half maximum is 31 fs). The intensity-dependent MPI probabilities are shown in Fig. 1. As one can see, the results for the parallel and perpendicular orientations do not differ much and become closer as the peak intensity of the laser field increases. A weak orientation dependence of the MPI probability can be explained by the properties of the electron density distribution in the unperturbed H₂ molecule which possesses only a weak anisotropy. The latter is due to the short internuclear distance, $\sigma_g$ symmetry of the electronic orbital, and moderate ionization potential which makes the density distribution spread over larger space domain.

In Figs. 2 and 3, we show the spectral density of the harmonic radiation energy at the peak intensities of the laser field $2 \times 10^{14}$ W/cm² and $3 \times 10^{14}$ W/cm². Again, the HHG spectra corresponding to the parallel and perpendicular orientation look similar. One can notice, however, a minimum in the vicinity of the 35th harmonic which is present for the parallel orientation only. The existence of this minimum can be attributed to destructive two-center interference [64] during the recombination stage of the HHG process [65]. Destructive interference is possible at the parallel orientation for some kinetic energy of the recombining electron, depending on the internuclear separation [64], while at the perpendicular orientation the contributions from the two centers in H₂ to the harmonic signal always interfere constructively.
IV. MULTIPHOTON IONIZATION AND HIGH-ORDER HARMONIC GENERATION OF HETERONUCLEAR AND HOMONUCLEAR DIATOMIC MOLECULES IN INTENSE ULTRASHORT LASER FIELDS: AN ALL-ELECTRON TDDFT STUDY

IV-1. Multiphoton Ionization of Heteronuclear and Homonuclear Diatomic Molecular Systems

In this section, we present all-electron TDDFT calculations of the MPI of N\textsubscript{2} and CO diatomic molecules [47]. The ground-state electronic configurations is 1\sigma\textsubscript{g}\textsuperscript{2}1\sigma\textsubscript{u}\textsuperscript{2}2\sigma\textsubscript{g}\textsuperscript{2}2\sigma\textsubscript{u}\textsuperscript{2}1\pi\textsubscript{u}\textsuperscript{4}3\sigma\textsubscript{g}\textsuperscript{2} for N\textsubscript{2} and 1\sigma\textsuperscript{2}2\sigma\textsuperscript{2}3\sigma\textsuperscript{2}4\sigma\textsuperscript{2}1\pi\textsubscript{u}\textsuperscript{4}5\sigma\textsuperscript{2} for CO, respectively. N\textsubscript{2} and CO are isoelectronic molecules, both having 14 electrons and triple bonds. Since the CO molecule has unequal nuclear charges, its ground electronic state possesses a permanent dipole moment, calculated here to be 0.149 Debye. The corresponding experimental value is 0.112 Debye [66]. Furthermore, there is no concept of gerade and ungerade orbitals for CO (or any other heteronuclear diatomic molecule) since the inversion symmetry of the potential is broken. For the studies of the diatomic molecules, we utilize the modified van Leeuwen – Baerends
TABLE II: Comparison of the field-free molecular orbital energy levels of CO and N₂, calculated with the LBα potential, and the experimental ionization potentials (in a.u.).

<table>
<thead>
<tr>
<th>Orbital</th>
<th>CO</th>
<th>Expt. [69]</th>
<th>LBα</th>
</tr>
</thead>
<tbody>
<tr>
<td>1σ</td>
<td>19.9367</td>
<td>19.6142</td>
<td></td>
</tr>
<tr>
<td>2σ</td>
<td>10.8742</td>
<td>10.6556</td>
<td></td>
</tr>
<tr>
<td>3σ</td>
<td>1.3964</td>
<td>1.2549</td>
<td></td>
</tr>
<tr>
<td>4σ</td>
<td>0.7239</td>
<td>0.7071</td>
<td></td>
</tr>
<tr>
<td>1π</td>
<td>0.6247</td>
<td>0.6276</td>
<td></td>
</tr>
<tr>
<td>5σ</td>
<td>0.5144</td>
<td>0.5086</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Orbital</th>
<th>N₂</th>
<th>Expt. [70–72]</th>
<th>LBα</th>
</tr>
</thead>
<tbody>
<tr>
<td>1σ₉</td>
<td>15.0492</td>
<td>14.7962</td>
<td></td>
</tr>
<tr>
<td>1σₜ</td>
<td>15.0492</td>
<td>14.7950</td>
<td></td>
</tr>
<tr>
<td>2σ₉</td>
<td>1.3708</td>
<td>1.2162</td>
<td></td>
</tr>
<tr>
<td>2σₜ</td>
<td>0.6883</td>
<td>0.6786</td>
<td></td>
</tr>
<tr>
<td>1πₜ</td>
<td>0.6233</td>
<td>0.6199</td>
<td></td>
</tr>
<tr>
<td>3σ₉</td>
<td>0.5726</td>
<td>0.5682</td>
<td></td>
</tr>
</tbody>
</table>

xc potential, LBα [67]:

\[
v_{\text{LBα},\sigma}(\mathbf{r}, t) = \alpha v_{\text{LSDA},\sigma}(\mathbf{r}, t) + v_{\text{LSDA},\sigma}(\mathbf{r}, t) - \frac{\beta x_\sigma^2(r,t)\rho_\sigma^{1/3}(r,t)}{1 + 3\beta x_\sigma(r,t) \ln \{x_\sigma(r,t) + [x_\sigma^2(r,t) + 1]^{1/2}\}}.
\]

The LBα potential contains two parameters, α and β, which have been adjusted in time-independent DFT calculations of several molecular systems and have the values α = 1.19 and β = 0.01 [67]. The first two terms in Eq. (18), \(v_{\text{LSDA},\sigma}^{\text{LSDA}}\) and \(v_{\text{LSDA},\sigma}^{\text{LSDA}}\) are the exchange and correlation potentials within the local spin density approximation (LSDA). The last term in Eq. (18) is the gradient correction with \(x_\sigma(r) = |\nabla \rho_\sigma(r)|/\rho_\sigma^{4/3}(r)\), which ensures the proper long-range asymptotic behavior \(v_{\text{LBα},\sigma}^{\text{LBα}} \to -1/r\) as \(r \to \infty\). The potential (18) has proved to be reliable in molecular TDDFT studies [47, 68]. The correct long-range asymptotic behavior of the LBα potential is crucial in photoionization problems since it allows to reproduce accurate MO energies, and the proper treatment of the molecular continuum. Table II lists the MO energies calculated with the LBα potential, using 50 grid points in ξ and 30 grid points in η. The agreement of the calculated valence MO energies with the experimental data is well within 0.01 a.u.

Once the time-dependent wave functions and the time-dependent electron densities are obtained, we can calculate the time-dependent (multiphoton) ionization probability of an individual spin-orbital according to

\[
P_{i,\sigma} = 1 - N_{i,\sigma}(t)
\]

where

\[
N_{i,\sigma}(t) = \langle \psi_{i,\sigma}(t) | \psi_{i,\sigma}(t) \rangle
\]
FIG. 4: The time-dependent population of electrons in different spin orbitals of CO and N$_2$ in 800 nm, sin$^2$ pulse laser field, with 20 optical cycles in pulse duration. N$_2$ molecule (a) $5 \times 10^{13}$ W/cm$^2$, (b) $1 \times 10^{14}$ W/cm$^2$, CO molecule (c) $5 \times 10^{13}$ W/cm$^2$, (d) $1 \times 10^{14}$ W/cm$^2$.

is the time-dependent population (survival probability) of the $i\sigma$-th spin-orbital.

Figure 4 presents the time-dependent (multiphoton) ionization probability of individual spin orbital, as defined in Eq. (19). The slope of the decay of the electron population in time determines the ionization rate. The laser (electric) field is assumed to be parallel to the internuclear axis, and the internuclear distance for the CO ($R_e = 2.132$ a$_0$) and N$_2$ ($R_e = 2.072$ a$_0$) molecules is fixed at its equilibrium distance $R_e$. Results for two laser intensities ($5 \times 10^{13}$ W/cm$^2$ and $1 \times 10^{14}$ W/cm$^2$) and a wavelength of 800 nm, 20-optical-cycle laser pulse are shown for CO and N$_2$. The orbital structure and ionization potentials of the two molecules under consideration are close to each other. That is why one can expect similar behavior in the laser field with the same wavelength and intensity. The multiphoton ionization in the laser field is dominated by HOMO, that is $3\sigma_g$ in N$_2$ and $5\sigma$ in CO. As one can see from Figs. 4(a) and 4(c), at lower intensity $5 \times 10^{13}$ W/cm$^2$, the HOMO survival probabilities of N$_2$ and CO are close to each other. However, at higher intensities, the difference becomes more pronounced, at the intensity $1 \times 10^{14}$ W/cm$^2$, the ionization probability of CO is much larger than that of N$_2$ (Figs. 4(b) and 4(d)). The explanation of the phenomenon can be as follows. In intense low-frequency laser fields, the multiphoton ionization occurs mainly in the tunneling regime. In this picture, the ionization takes place
in the DC field with slowly varying amplitude from zero to its peak value. The width of the potential barrier depends on the field strength; the stronger the field, the narrower the barrier. Thus the ionization occurs mainly at the peak values of the field strength. The probability of the tunneling ionization is very sensitive with respect to the HOMO energy. However, in the external field this energy is changed due to the Stark shift. The nitrogen molecule is symmetric with respect to inversion, that is why the Stark shift in the DC field is quadratic in the field strength and its value is quite small. On the contrary, the carbon monoxide molecule has a permanent dipole moment, and the DC Stark shift is linear in the field strength; at the peak values of the field, the HOMO energy can differ significantly from its unperturbed value. We have performed the self-consistent DFT calculations of N\textsubscript{2} and CO in the DC electric field parallel to the molecular axis to see how large the Stark shift can change the ionization potential of the molecule. On Table III we show the HOMO energies computed at the field strength 0.7549 \times 10^{-2} \text{ a.u.} which corresponds to the intensity 2 \times 10^{12} \text{ W/cm}^2. As one can see, even in the field as weak as 2 \times 10^{12} \text{ W/cm}^2, the shift of the HOMO energy in CO molecule is large. The shift depends on the direction of the external field with respect to the position of the carbon and oxygen nuclei. In one direction the energy level becomes higher, and in the other direction it becomes lower than the unperturbed level. Decrease of the binding energy will result in the enhanced ionization. In intense low-frequency laser fields, this effect can be responsible for the enhancement of ionization of CO molecule as compared with N\textsubscript{2}.

**IV-2. High-Order Harmonic Generation of Heteronuclear and Homonuclear Diatomic Molecules in Intense Laser Fields**

After the time-dependent single electron wave functions \{\psi_{i\sigma}\} are obtained, the total electron density \(\rho(r, t)\) can be determined. The time-dependent induced dipole moment can now be calculated as

\[
d(t) = \int d^3 r \, z \rho(r, t) = \sum_{i\sigma} d_{i\sigma}(t),
\]

where

\[
d_{i\sigma}(t) = n_{i\sigma} \langle \psi_{i\sigma}(r, t) | z | \psi_{i\sigma}(r, t) \rangle,
\]

**TABLE III: HOMO energies of N\textsubscript{2} and CO molecules in DC electric field (positive field direction is from C to O).**

<table>
<thead>
<tr>
<th>Electric field (a.u.)</th>
<th>N\textsubscript{2} HOMO energy (a.u.)</th>
<th>CO HOMO energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.5682</td>
<td>-0.5086</td>
</tr>
<tr>
<td>0.7549 \times 10^{-2}</td>
<td>-0.5681</td>
<td>-0.5149</td>
</tr>
<tr>
<td>-0.7549 \times 10^{-2}</td>
<td>-0.5681</td>
<td>-0.5026</td>
</tr>
</tbody>
</table>
is the induced dipole moment of the $i\sigma$-th spin orbital, and $n_{i\sigma}$ is its electron occupation number. The power spectrum of the HHG is then acquired by taking the Fourier transform of the total time-dependent induced dipole moment $d(t)$:

$$S(\omega) = \frac{4\omega^4}{3c^3} \left| \frac{1}{t_f - t_i} \int_{t_i}^{t_f} d(t)e^{-i\omega t} dt \right|^2.$$ (23)

Here $c$ is the speed of light, and $S(\omega)$ has the meaning of the energy emitted per unit time at the particular photon frequency $\omega$. In figures 5–6 we present the HHG power spectra (Eq. (23)) for the laser field intensities $5 \times 10^{13}$ W/cm$^2$, and $1 \times 10^{14}$ W/cm$^2$. An important difference between the N$_2$ and CO spectra is that the latter contain even as well as odd harmonics. Generation of even harmonics is forbidden in systems with inversion symmetry, such as atoms and homonuclear diatomic molecules. This selection rule does not apply to the heteronuclear molecules with no inversion center (CO). From Figs. 5–6, one can see that in general HHG is more efficient in CO than in N$_2$. However, for higher harmonics (17 and above) the N$_2$ spectra become dominant at the same laser intensity. As the laser intensity increases, the maximum in the power spectra is shifted towards higher harmonics.

To investigate the detailed spectral and temporal structure of HHG for homonuclear and heteronuclear systems, we perform the time-frequency analysis by means of the wavelet transform of the total induced dipole moment $d(t)$ [46, 73],

$$d_\omega(t) = \int d(t) \sqrt{\frac{\omega}{\tau}} e^{i\omega(t-t_0)} e^{-(\omega(t-t_0))^2/2\tau^2} dt.$$ (24)
The parameter $\tau = 15$ is chosen to perform the wavelet transformation in the following study.

The peak emission times, $t_e$, represent the instance when the maxima of the dipole time profile occur, and semiclassically are interpreted as the electron-ion recollision times [73]. For the case of the $N_2$ molecule, the time profiles of the 19th to 25th harmonic orders are shown in Fig. 7(a). There are two emissions occurring at each optical cycle, and the most prominent bursts take place at the center of the laser field envelope. The time profiles of the superimposed harmonics are rather uniform among themselves implicating that the harmonics are partially synchronized. More importantly for the CO molecule, a distinct feature possibly characteristic of all heteronuclear diatomic systems is observed in Fig. 7(b) for the harmonic orders 22th to 26th. The number of dominant emissions per optical cycle is now limited to only one. This finding is in contrast with results normally obtained in the HHG for atoms and homogeneous molecules in which two bursts per optical cycle are observed. The spectral profiles are as uniform as those obtained for $N_2$, though the CO harmonics appear to be more synchronized than those of $N_2$. In this research, we present a detailed comparison of the very high-order nonlinear optical response of the homonuclear $N_2$ and heteronuclear CO diatomic molecules in intense ultrashort laser fields by means of a TDDFT with correct asymptotic long-range ($-1/r$) potential to ensure individual spin-orbital has the proper ionization potential. We consider only the case that the molecular axis is aligned with the laser beam direction. This is justified based on the recent experimental development of the laser molecular alignment techniques [74–77]. We found that although CO has only a very small permanent dipole moment, qualitatively different nonlinear optical responses are predicted for CO and $N_2$. First, the MPI rate
FIG. 7: Time profiles for (a) N\textsubscript{2} and (b) CO. Laser intensity used is $5 \times 10^{13}$ W/cm\textsuperscript{2}, wavelength used is 800 nm, with 20 optical cycles in pulse duration.

for the heteronuclear diatomic CO molecules is larger than that for the N\textsubscript{2} homonuclear diatomic molecules. Second, while the laser excitation of the N\textsubscript{2} molecules can generate only odd harmonics, both even and odd harmonics can be produced for the CO case. In this connection, we note that the even-order harmonics were also predicted in an earlier study of the HHG of a one-dimensional model HD with unequal nuclear mass [78]. In this model, even-order harmonics can be produced only by means of the breakdown of the Born-Oppenheimer approximation. However, in our \textit{ab initio} 3D study of CO with unequal nuclear mass and charge, even-order harmonics can still be produced when the internuclear separation is fixed. Third, from our wavelet time-frequency analysis, we found that there are two dominant rescattering (and harmonic emission) events within each optical cycle for the N\textsubscript{2} molecules, while there is only one dominant rescattering event for the CO molecules.

IV-3. HHG Spectra of Homonuclear and Heteronuclear Diatomic Molecules: Exploration of Multiple Orbital Contributions

In this section, we explore the nonlinear response of individual molecular orbitals (MO) to the laser field and their dynamic role in formation of the HHG spectra of multi-electron heteronuclear and homonuclear diatomic molecules [79]. We analyze the effect of asymmetry of the heteronuclear molecules on their HHG spectra, a subject of largely unexplored area of intense field molecular physics. In contrast with the homonuclear molecules which generate only odd harmonics of the laser frequency, oriented heteronuclear molecules
can produce even harmonics as well [47]. We identify the patterns of constructive and destructive interference of the orbital contributions to the total HHG spectrum. In the high-energy part of the HHG spectrum, the interference of contributions from different MO is mostly constructive for the heteronuclear molecules and destructive for the homonuclear molecules. We present an all-electron nonperturbative investigation of the HHG mechanisms taking into account the detailed electronic structure and the responses of individual electrons and using N\(_2\), F\(_2\), CO, BF, and HF as examples (N\(_2\), CO, and BF are isoelectronic molecules with 14 electrons). The ground state electronic configuration of N\(_2\) and F\(_2\) (homonuclear molecules) is 1\(\sigma_g^21\sigma_u^22\sigma_g^22\sigma_u^21\pi_u^43\sigma_g^2\) and 1\(\sigma_g^21\sigma_u^22\sigma_g^22\sigma_u^23\sigma_g^21\pi_u^41\pi_g^4\), respectively. The heteronuclear molecules CO and BF have the ground state electronic configuration of 1\(\sigma^22\sigma^23\sigma^24\sigma^21\pi^4\)\(5\sigma^2\) and for the HF molecule its ground state configuration appears as 1\(\sigma^22\sigma^23\sigma^21\pi^4\). Table IV lists the MO energies calculated with the LB\(\alpha\) potential, using 50 grid points in \(\xi\) and 30 grid points in \(\eta\). The agreement of the calculated valence MO energies with the experimental data is well within 0.01 a.u.

For the CO molecule, the HOMO (5\(\sigma\)) is dominant for the whole HHG spectrum (Fig. 8); other orbitals contribute much less. The distinct harmonic peaks are seen up to the order 30. In CO, the 5\(\sigma\) (HOMO) permanent dipole is 1.57 a.u. which is much larger than that of the other orbitals. The density for the 5\(\sigma\) (and 2\(\sigma\)) is mostly localized on the carbon atom. For all other orbitals the density is localized on the oxygen atom. Looking at the time-dependent orbital dipoles for the CO molecule (Fig. 9), we can see that all other orbitals that are localized on the oxygen atom are in phase and 5\(\sigma\) (carbon) is out of phase in time.

The N\(_2\) molecule has dipole amplitudes that follow the trend:

\[
d_{2\sigma_g} < d_{1\pi_u} < d_{\text{total}} < d_{3\sigma_g} < d_{2\sigma_u}.
\]  

(25)

The orbital dipole moments 2\(\sigma_g\), 1\(\pi_u\), and 2\(\sigma_u\) are oscillating with the same sign (in phase) of the total dipole, the 3\(\sigma_g\) has opposite sign (out of phase). So when we look at the two orbital dipole amplitudes 2\(\sigma_u\) and 3\(\sigma_g\) with similar intensities, they oscillate in time with different sign, canceling each other out (Fig. 10), leading to a smaller total dipole.

The behavior of the HHG spectrum (Fig. 11) for N\(_2\) is quite different than that of a heteronuclear diatomic molecule. The HOMO (3\(\sigma_g\)) is dominant in the middle part of the spectrum (again up to the order 31). However, starting the 33th harmonic, the 2\(\sigma_u\) orbital has a comparable contribution which interferes destructively with that of 3\(\sigma_g\). Thus the result of interference is much lower than both of the single orbital spectra. Then this two-orbital spectrum becomes comparable in magnitude with the 2\(\sigma_g\)-only HHG. Again, the destructive contributions takes place, and the result is much lower than any of the single orbital contributions. In summary, we can say that the long HHG spectrum of N\(_2\) is a collective multielectron effect. Destructive interference between 2\(\sigma_u\) and 3\(\sigma_g\) orbital contributions makes the resulting total HHG spectrum lower in amplitude with distinct harmonic peaks up to the order 49. Note that single orbital HHG do not have distinct peaks, just a smooth background, so the peaks in the high harmonic part of the total HHG spectra are the pure multielectron interference effect.

In contrast to the N\(_2\) molecule, the full destructive interference is not possible in CO.
TABLE IV: Comparison of the field-free molecular orbital energy levels of $F_2$, BF, CO, $N_2$ and HF, calculated with the LB$\alpha$ potential, and the experimental ionization potentials (in a.u.).

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$F_2$</th>
<th>$BF$</th>
<th>$CO$</th>
<th>$N_2$</th>
<th>$HF$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1\sigma_g$</td>
<td>$1\sigma_u$</td>
<td>$2\sigma_g$</td>
<td>$2\sigma_u$</td>
<td>$3\sigma_g$</td>
</tr>
<tr>
<td>Expt. [80]</td>
<td>25.601</td>
<td>25.609</td>
<td>1.534</td>
<td>1.377</td>
<td>0.775</td>
</tr>
<tr>
<td>$LB\alpha$</td>
<td>25.1531</td>
<td>25.1531</td>
<td>1.4508</td>
<td>1.2252</td>
<td>0.7907</td>
</tr>
<tr>
<td>Expt. [81, 82]</td>
<td>0.4085</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$LB\alpha$</td>
<td>25.1669</td>
<td>7.1745</td>
<td>1.414</td>
<td>0.7763</td>
<td>0.6970</td>
</tr>
<tr>
<td>Expt. [69]</td>
<td>19.9367</td>
<td>10.8742</td>
<td>1.3964</td>
<td>0.7239</td>
<td>0.6247</td>
</tr>
<tr>
<td>$LB\alpha$</td>
<td>19.6142</td>
<td>10.6556</td>
<td>1.2549</td>
<td>0.7071</td>
<td>0.6276</td>
</tr>
<tr>
<td>Expt. [83–85]</td>
<td>15.0492</td>
<td>15.0492</td>
<td>1.3708</td>
<td>0.6883</td>
<td>0.6233</td>
</tr>
<tr>
<td>$LB\alpha$</td>
<td>14.7962</td>
<td>14.7950</td>
<td>1.2162</td>
<td>0.6786</td>
<td>0.6199</td>
</tr>
<tr>
<td>Expt. [86]</td>
<td>25.5132</td>
<td>1.4545</td>
<td>0.7284</td>
<td>0.5898</td>
<td></td>
</tr>
<tr>
<td>$LB\alpha$</td>
<td>25.0786</td>
<td>1.3074</td>
<td>0.7070</td>
<td>0.5741</td>
<td></td>
</tr>
</tbody>
</table>

because of the broken g-u symmetry. The induced dipole moment of the HOMO $5\sigma$ is so large that no other orbital can make a comparable contribution. To prove this point about heteronuclear and homonuclear diatomic molecules, we look at $F_2$, BF, and the heteronuclear molecule that has the greatest dipole moment, HF. Here, we can see if these molecules exhibit similar properties of CO and $N_2$. We see the same characteristics in $F_2$, as we can see in $N_2$. The orbital dipole moments of $2\sigma_u$ and $1\pi_g$ are oscillating out of phase, from other orbitals, including the total. So when we look at the two orbital dipole amplitudes $1\pi_u$ and $1\pi_g$, they oscillate in time with different sign, canceling each other out (Fig. 12), leading to a smaller total dipole. The behavior of the HHG spectrum of $F_2$ is similar to that of $N_2$. If we look at Fig. 13, the $1\pi_u$ and $1\pi_g$ orbitals dominate the HHG spectrum, and it has much greater intensity than that of the total HHG. In this Fig. 13, we see there is destructive interference between the contributions from the $1\pi_u$ and $1\pi_g$
FIG. 8: Total (a) and orbital (b) harmonic power spectra of the CO molecule in the $\sin^2$ laser pulse with a peak intensity of $I_0 = 1 \times 10^{14}$ W/cm$^2$. The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles.

FIG. 9: Time-dependent orbital (a, 5$\sigma$; b, 4$\sigma$; c, 1$\pi$) and total (d) dipole moments of the CO molecule in the $\sin^2$ laser pulse with a peak intensity of $I_0 = 1 \times 10^{14}$ W/cm$^2$. The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles. All dipoles are in a.u.

orbitals, we explained this previously with their dipole moments being out of phase with one another. Since these two orbitals (1$\pi_u$ and 1$\pi_g$) have the greatest amplitude of the induced dipole, they will have the greatest contributions to the power spectrum.

Previously, we only looked at the CO molecule for the heteronuclear diatomic system,
FIG. 10: Time-dependent orbital and total dipole moments of the N₂ molecule in the sin² laser pulse with a peak intensity of \( I_0 = 1 \times 10^{14} \) W/cm². The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles. All dipoles are in a.u.

FIG. 11: Total and orbital harmonic power spectra of the N₂ molecule in the sin² laser pulse with a peak intensity of \( I_0 = 1 \times 10^{14} \) W/cm². The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles.

and saw where the HOMO dominates the HHG spectrum and dipole moment. Now we examine two other heteronuclear molecules (BF and HF), and see if their characteristics resemble that of the CO molecule. To understand the HHG spectrum, again we look at the orbital dipole moment of BF. Fig. 14 shows that the 5σ orbital (like that of CO, since they
FIG. 12: Time-dependent orbital and total dipole moments of the F$_2$ molecule in the sin$^2$ laser pulse with a peak intensity of $I_0 = 1 \times 10^{14}$ W/cm$^2$. The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles. All dipoles are in a.u.

FIG. 13: Total (a) and orbital (b) harmonic power spectra of the F$_2$ molecule in the sin$^2$ laser pulse with a peak intensity of $I_0 = 1 \times 10^{14}$ W/cm$^2$. The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles.

are isoelectronic) has the greatest dipole moment. This is understandable, since most of the electronic density resides on the fluorine atom. The fluorine atom is more electronegative than that of the boron atom, so it will have the greater electron density. As previously seen in the CO molecule, BF has the same physical characteristics of its orbital HHG spectrum. Fig. 15 shows that HOMO (5σ) has the greatest contribution to the total HHG.
FIG. 14: Time-dependent orbital and total dipole moments of the BF molecule in the \( \sin^2 \) laser pulse with a peak intensity of \( I_0 = 1 \times 10^{14} \text{ W/cm}^2 \). The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles. All dipoles are in a.u.

FIG. 15: Total (a) and orbital (b) harmonic power spectra of the BF molecule in the \( \sin^2 \) laser pulse with a peak intensity of \( I_0 = 1 \times 10^{14} \text{ W/cm}^2 \). The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles.

Now we will study the heteronuclear molecule that has the greatest permanent dipole moment, and look at the physical characteristics of hydrogen fluoride. HF has a permanent dipole moment of 1.820 Debye, where most of the electron density resides on the fluorine atom. For HF molecule, the HOMO is the 1\( \pi \) orbital, and it has the greatest negative value of the orbital dipole moment (see Fig. 16). However, when we look at the orbital
FIG. 16: Time-dependent orbital and total dipole moments of the HF molecule in the $\sin^2$ laser pulse with a peak intensity of $I_0 = 1 \times 10^{14}$ W/cm$^2$. The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles. All dipoles are in a.u.

FIG. 17: Total (a) and orbital (b) harmonic power spectra of the HF molecule in the $\sin^2$ laser pulse with a peak intensity of $I_0 = 1 \times 10^{14}$ W/cm$^2$. The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles.

HHG spectrum (Fig. 17), we see the greatest orbital contribution to the HHG spectrum was from $3\sigma$, not the HOMO orbital ($1\pi$). Since the field is linearly polarized to the $z$ axis and the $1\pi$ orbital is perpendicular to the $z$ axis, the induced dipole moment is aligned not with the $1\pi$ orbital but with the $3\sigma$ orbital. We see between harmonic order peaks (even and odd), the $1\pi$ orbital has greater intensity than that of the $3\sigma$ orbital. At peak values
(even and odd harmonic orders) the $3\pi$ orbital has almost the same intensity as that of the total HHG spectrum. We conclude that HF follows the same orbital characteristics of other heteronuclear molecules studied (CO and BF).

Our analysis of the HHG spectra for the parallel orientation of the molecular axis with respect to the polarization of the laser field reveals that homonuclear molecules have destructive interference between the orbital contributions to the total harmonic signal. This happens because the induced dipole moments of different orbitals oscillate in time with opposite phases, so their contributions are canceled out in the total dipole moment. Therefore a close look at the induced dipole moment of the homonuclear diatomic molecules can give predictions of what orbital contributions will interfere destructively in the total HHG spectrum. The destructive interference in the HHG spectrum accounts for the unexpected observation that some of the individual orbitals harmonic power spectra have greater intensity than that of the total HHG. The HHG process by the heteronuclear diatomic molecules has a quite different characteristic. First, heteronuclear molecules can generate even and odd harmonics since they lack the inversion symmetry. Second, for all the studied heteronuclear molecules, the HOMO contribution to the total HHG spectrum is by far dominant, and the total harmonic signal has almost the same intensity as that produced by HOMO only. The interference between the different orbitals in the total HHG spectrum is mostly constructive. The same features are observed in the time-dependent induced dipole moments, with the HOMO dipole moment having the largest oscillation magnitude.

V. ORIENTATION-DEPENDENT MULTIPHOTON IONIZATION AND HIGH-ORDER HARMONIC GENERATION OF DIATOMIC MOLECULES

V-1. AN ALL-ELECTRON TDDFT APPROACH FOR N$_2$ AND F$_2$ MOLECULES

In our calculations of multiphoton processes in N$_2$ and F$_2$ [56, 87], we used the laser wavelength 800 nm ($\omega_0 = 0.056954$ a.u.) and the sine-squared envelope with 20 optical cycles. The propagation procedure based on Eq. (13) is applied sequentially starting at $t = 0$ and ending at $t = T$. As a result, the spin orbitals $\psi_{n\sigma}(\xi, \eta, \varphi, t)$ are obtained on a uniform time grid within the interval $[0, T]$. The space domain is finite with the linear dimension restricted by the end point $R_b$. We choose $R_b = 40$ a.u.; the corresponding space volume contains all relevant physics for the laser field parameters used in the calculations. Between 20 a.u. and 40 a.u. we apply an absorber which smoothly brings down the wave function for each spin orbital without spurious reflections. Absorbed parts of the wave packet localized beyond 20 a.u. describe unbound states populated during the ionization process. Because of the absorber, the normalization integrals of the wave functions $\psi_{n\sigma}(r, t)$ decrease in time. Calculated after the pulse, they give the survival probabilities $P_{n\sigma}^{(s)}$ for each spin orbital:

$$P_{n\sigma}^{(s)} = \int d^3r |\psi_{n\sigma}(r, T)|^2.$$  \hspace{1cm} (26)
Then one can define the spin orbital ionization probabilities $P_{n\sigma}^{(i)}$ as
\[ P_{n\sigma}^{(i)} = 1 - P_{n\sigma}^{(s)}. \]  
(27)

We note that the quantities $P_{n\sigma}^{(s)}$ represent the survival probabilities for the electron occupying the unperturbed $\psi_{n\sigma}(r, t = 0)$ spin orbital before the laser pulse. Accordingly, the quantity $P_{n\sigma}^{(i)}$ represents the ionization probability for the electron originally occupying the unperturbed $\psi_{n\sigma}(r, t = 0)$ spin orbital.

The total survival probability $P^{(s)}$ can be calculated as a product of the spin orbital survival probabilities:
\[ P^{(s)} = \prod_{n\sigma} P_{n\sigma}^{(s)} = \prod_{n\sigma} \left( 1 - P_{n\sigma}^{(i)} \right), \]  
(28)

and the total ionization probability can be written as
\[ P^{(i)} = 1 - P^{(s)} = 1 - \prod_{n\sigma} \left( 1 - P_{n\sigma}^{(i)} \right). \]  
(29)

The total ionization probability as defined by Eq. (29) reduces to the sum of the spin orbital probabilities only in the limit of the weak laser field (small $P_{n\sigma}^{(i)}$). In the calculations, we used the experimental values of the equilibrium internuclear separations for the diatomic molecules [63] (2.074 a.u. for $N_2$ and 2.668 a.u. for $F_2$). In Table V, we summarize the energies for the spin orbitals that have a significant contribution to MPI and HHG and the

**TABLE V:** Absolute values of spin orbital energies of $N_2$, $F_2$, and Ar. (A) DFT calculations [56] (eV). (B) Experimental ionization energies (eV).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Spin-orbital</th>
<th>A</th>
<th>B</th>
<th>(Ref.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>$2\sigma_u$</td>
<td>18.5</td>
<td>18.7</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td>$1\pi_u$</td>
<td>16.9</td>
<td>17.2</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td>$3\sigma_g$</td>
<td>15.5</td>
<td>15.6</td>
<td>[88]</td>
</tr>
<tr>
<td>$F_2$</td>
<td>$3\sigma_g$</td>
<td>21.9</td>
<td>21.0</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>$1\pi_u$</td>
<td>19.2</td>
<td>19.0</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>$1\pi_g$ (HOMO)</td>
<td>16.0</td>
<td>15.7</td>
<td>[89]</td>
</tr>
<tr>
<td>Ar</td>
<td>$3s$</td>
<td>29.0</td>
<td>29.3</td>
<td>[90]</td>
</tr>
<tr>
<td></td>
<td>$3p$</td>
<td>15.3</td>
<td>15.8</td>
<td>[90]</td>
</tr>
</tbody>
</table>
corresponding experimental vertical ionization energies. Also presented are the data for the companion Ar atom which has an ionization potential close to that of N₂ and F₂ and is expected to manifest close ionization probabilities as well. The agreement between the calculated and experimental values is fairly good for all three systems indicating a good quality of the LBα exchange-correlation potential.

V-1-1. Multiphoton ionization

We present the orientation-dependent MPI probabilities for N₂ molecule at the peak intensity $2 \times 10^{14}$ W/cm² (Fig. 18). The orientation dependence of the total MPI probability is in a good accord with the experimental observations [91, 92] for this molecule and reflects the symmetry of its HOMO: the maximum corresponds to the parallel orientation.

![Fig. 18: MPI probabilities of N₂ molecule and Ar atom for the peak intensity $2 \times 10^{14}$ W/cm² in polar (panel A) and Cartesian (panel B) coordinates: (a) total probability for N₂, (b) $3\sigma_g$ (HOMO) probability for N₂, (c) $1\pi_u$ (HOMO−1) probability for N₂, (d) $2\sigma_u$ probability for N₂, (e) total probability for Ar, (f) $3p_0$ probability for Ar.](image)

However, multielectron effects are quite important for N₂, particularly at intermediate orientation angles. In the angle range around 30°, the orbital probability of HOMO−1 (1π_u) is larger than that of HOMO (3σ_g). Despite the orbital probabilities have local minima and maxima, the total probability shows monotonous dependence on the orientation angle. With increasing the peak intensity of the laser field, the orientation angle distribution of the total ionization probability becomes more isotropic. For comparison, we show also the ionization probability of the Ar atom. As one can see from Fig. 18, the absolute values of the ionization probabilities of N₂ and Ar are close to each other. However, the inner shell contributions are less important for Ar: the total probability is dominated by the highest-occupied (3p) shell contribution. An analysis of the spin orbital energies (Table V) can help to understand the relative importance of MPI from the inner shells in N₂ compared to that in Ar. The smaller the ionization potential of the electronic shell, the easier
it can be ionized. That is why HOMO is generally expected to give the main contribution to the MPI probability. However, in N₂ the ionization potential of HOMO−1 is quite close to that of HOMO (the difference between the calculated values is 1.4 eV), and in the strong enough laser field both shells show comparable ionization probabilities (a possible resonance between HOMO and HOMO−1 in the 800 nm laser field also favors that; see discussion of HHG in Sec.V-1-2 below). At the same time, the gap between the 3p and 3s spin orbital energies in Ar is much larger (our calculation gives the value 13.7 eV), and the 3p contribution to the MPI probability remains dominant for all three laser intensities.

For F₂, the total ionization probability appears smaller than that of N₂ (and Ar) at the same laser intensity $2 \times 10^{14}$ W/cm² (Fig. 19). The ratio of the MPI probabilities of Ar and F₂ (at 40°) is approximately equal to 4.2. The pattern for the orientation dependence of MPI in F₂ resembles that experimentally observed in O₂ [91] since both molecules have the HOMO of the same symmetry ($1\pi_g$), and the HOMO contribution is dominant at this intensity. The maximum in the orientation angle distribution of the total MPI probability points at 40°. The HOMO−1 contribution is less important than that in N₂, and this is well explained by the larger gap between the HOMO and HOMO−1 energies (3.2 eV).

**V-1-2. High-order harmonic generation**

For non-monochromatic fields, the spectral density of the radiation energy emitted for all the time is given by the following expression [93]:

$$ S(\omega) = \frac{2\omega^4}{3\pi c^3} |\tilde{D}(\omega)|^2. $$

(30)
FIG. 20: Energy emitted in harmonic radiation by N$_2$ molecule for the peak intensity $2\times10^{14}$ W/cm$^2$: left (blue) bar, orientation angle $\gamma = 0^\circ$; middle (green) bar, orientation angle $\gamma = 40^\circ$; right (red) bar, orientation angle $\gamma = 90^\circ$.

Here $\omega$ is the frequency of radiation, $c$ is the velocity of light, and $\tilde{D}(\omega)$ is a Fourier transform of the time-dependent dipole moment:

$$\tilde{D}(\omega) = \int_{-\infty}^{\infty} dt D(t) \exp(i\omega t).$$  (31)

The dipole moment is evaluated as an expectation value of the electron radius-vector with the time-dependent total electron density $\rho(r, t)$:

$$D(t) = \int d^3r \rho(r, t).$$  (32)

The total energy $\mathcal{E}$ emitted in the harmonic radiation can be calculated by integration of $S(\omega)$:

$$\mathcal{E} = \int_0^{\infty} d\omega S(\omega).$$  (33)

For a long enough laser pulse, the radiation energy spectrum (30) contains peaks corresponding to odd harmonics of the carrier frequency $\omega_0$. We define the energy $\mathcal{E}(N_h)$ emitted in the $N_h$th harmonic ($N_h$ is an odd integer number) as follows:

$$\mathcal{E}(N_h) = \int_{(N_h-1)\omega_0}^{(N_h+1)\omega_0} d\omega S(\omega).$$  (34)
In Figs. 20 and 21 we present the HHG data for N$_2$ and F$_2$ molecules, respectively, at the peak intensity $2 \times 10^{14}$ W/cm$^2$. The cutoff position in the HHG spectrum for this intensity is expected at the harmonic order 35, in fair agreement with the computed data. To show the orientation dependence of the HHG spectra, we choose three values of the orientation angle $\gamma$: 0°, 40°, and 90° which represent the limiting cases of the parallel and perpendicular orientation as well as the intermediate angle case. For all three orientations, the HHG signal from N$_2$ is about an order of magnitude stronger than that from F$_2$; this observation is consistent with the MPI results of Sec.V-1-1: at this intensity, the MPI signal from F$_2$ is 4 to 10 times weaker than that from N$_2$, depending on the orientation. The orientation dependence of HHG also resembles that of MPI: HHG is more intense for the orientations where MPI reaches its maximum. It is clearly seen for F$_2$ where the radiation energy at 40° exceeds that at other orientations for almost every harmonic. For N$_2$, the HHG signal at 0° is dominant in the low-order part of the spectrum whereas in the central part a stronger signal is observed at 40°. One can also see that the emission of the harmonic radiation at the perpendicular orientation ($\gamma = 90°$) is suppressed for both N$_2$ and F$_2$ in the low-order and central parts of the HHG spectra. The maximum in the harmonic energy distribution at 90° is shifted to higher orders. This result is in a good accord with the recent experimental measurements on N$_2$ [94]. Also, we would like to comment on the minimum seen in the HHG spectrum of N$_2$ (Fig. 20) at the parallel orientation near the
25th harmonic order (photon energy \(\sim 39\) eV). This minimum has been observed in the same photon energy region in a recent experimental work [95]; it appears independent of intensity and wavelength of the laser field. We take an in depth look at the multielectron effect on the HHG minimum for aligned CO molecules in the next section.

**V-2. High-Order Harmonic Generation of Aligned CO Molecules**

![Harmonic order vs. Spectral density of harmonics energy](image)

**FIG. 22:** Total harmonic power spectra of the CO molecule in the \(\sin^2\) laser pulse with a peak intensity of \(I_0 = 3 \times 10^{14}\) W/cm\(^2\). The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles: orientation angle \(\gamma = 90^\circ\).

In this section, we study the effects of correlated multielectron responses on HHG of aligned CO molecules in intense 800 nm laser pulses. Considering aligned rather than oriented heteronuclear molecules has a closer relation to the experimental situation where the aligning field creates equal numbers of molecules with opposite orientations. The average permanent dipole moment of a macroscopic sample of aligned molecules vanishes, and only odd harmonics can be generated, in contrast to oriented heteronuclear molecules where generation of even harmonics is possible. On the microscopic level, the HHG spectrum of a sample of aligned molecules can be modeled as a coherent average of the signals from two oriented molecules with opposite orientations. We have found that the high-energy part of the HHG spectrum of aligned CO molecules exhibits a strong dependence on the alignment angle between the molecular axis and the polarization direction of the laser field with the sharp minimum at the perpendicular alignment. An analysis of the HHG spectra at the perpendicular alignment revealed also two minima, one of them corresponding to the photon energy in the range 37 eV to 45 eV, and another one in the range 63 eV to 69 eV. Positions of both minima only slightly depend on the peak intensity of the laser field.
We have computed the alignment-dependent HHG spectra for CO at a range of peak intensities, $3 \times 10^{14}$ W/cm$^2$ to $5 \times 10^{14}$ W/cm$^2$. (Figs. 22–25). For the laser intensity of $3 \times 10^{14}$ W/cm$^2$, one can see a minimum at the 27th harmonic order (Fig. 22). For higher laser intensities and the same alignment angle $90^\circ$, the minimum is still present but shifted to higher harmonic orders (photon energies). To explore the nature of this minimum, we analyze the individual orbital HHG spectra and their contributions to the total HHG spectrum. In Fig. 23, one can see that the $5\sigma$, $1\pi$ and $4\sigma$ orbital spectra all have minima at the 27th harmonic. This observation suggests that the minimum has a kinematic nature, such as related to the two-center interference, and does not depend on the specific electronic structure. On the other hand, multielectron structure effects are clearly seen in the other part of the HHG spectrum, in the vicinity of the 11th harmonic where the orbital contributions are enhanced due to the resonance between the $4\sigma$ and $1\pi$ orbitals. However, since these orbitals are occupied, no real transitions can occur between them, that is why these two orbital contributions interfere destructively, and the total HHG spectrum does not exhibit the resonance enhancement. One can also see from Fig. 23 that the multielectron effects are very important in the central and high-energy parts of the HHG spectrum where the $1\pi$ orbital makes comparable and even greater contribution than that of the $5\sigma$ orbital (HOMO). In our previous work, we showed that the multielectron effects are responsible for enhanced HHG at some orientations of the molecular axis. Even strongly bound electrons may have a significant influence on the HHG process [56, 79].

At the laser intensity of $4 \times 10^{14}$ W/cm$^2$, the minimum in the HHG spectrum is blue shifted to the 29th harmonic order (Fig. 24). We note that in another theoretical work [96] where only the HOMO contribution to the HHG spectrum of the CO molecule was considered, the minimum at the laser intensity of $4 \times 10^{14}$ W/cm$^2$ was detected in the vicinity of the harmonic order 50. In Fig. 25, we show alignment angle dependence of the minimum and cutoff region in the HHG spectrum at the higher laser intensity of $5 \times 10^{14}$ W/cm$^2$. Besides the minimum at the 29th harmonic ($\sim 45$ eV), we can also see another minimum at the 44th order (69 eV) which is more distinct at the alignment angle $90^\circ$ and becomes less pronounced at other angles ($80^\circ$ and $85^\circ$, respectively). Also, the cutoff region of the spectrum exhibits a sharp dependence on the alignment angle, decreasing more rapidly at $90^\circ$.

Finally, we would like to comment on the shift of the minimum in the HHG spectrum as a function of the laser intensity. As one can see in Figs. (22–25), the minimum is shifted to higher harmonic orders as the laser intensity increases. This phenomenon was also recently discovered for CO$_2$ molecules [97]. This shift is due to the time interval between ionization and recombination steps of the HHG process. Therefore, this shift should depend linearly on the laser intensity.

VI. CONCLUSION

In this paper, we have presented self-interaction-free TDDFT approaches recently developed for accurate and efficient treatment of the high-order multiphoton dynamics
FIG. 23: Total (black dotted line) and orbital (5σ (black line), 1π (red line), and 4σ (blue dashed line)) harmonic power spectra of the CO molecule in the \( \sin^2 \) laser pulse with a peak intensity of \( I_0 = 3 \times 10^{14} \text{ W/cm}^2 \). The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles: orientation angle \( \gamma = 90^\circ \).

of many-electron quantum molecular systems in the presence of intense ultrashort laser fields. They allow the construction of orbital-independent single-particle local exchange-correlation potential which possesses the correct \((-1/r)\) long-range asymptotic behavior. With the asymptotically correct potential, the energy of the highest occupied spin-orbital provides a good approximation to the ionization potential. The generalized pseudospectral
FIG. 24: Total harmonic power spectra of the CO molecule in the $\sin^2$ laser pulse with a peak intensity of $I_0 = 4 \times 10^{14}$ W/cm$^2$. The laser pulse has a wavelength of 800 nm and a time duration of 20 optical cycles: orientation angle $\gamma = 90^\circ$.

(GPS) technique allows the construction of non-uniform and optimal spatial grids, denser mesh nearby each nucleus and sparser mesh at longer range, leading to high-precision solution of both electronic structure and time-dependent quantum dynamics with the use of only a modest number of spatial grid points. The TDDFT formalism along with the use of the time-dependent GPS numerical technique provides a powerful new nonperturbative time-dependent approach for exploration of the electron correlation and multiple orbitals effects on strong field multiphoton processes.

Like the steady-state case, the exact form of time-dependent xc energy functional is unknown. Most of the strong-field calculations so far (including those discussed in this chapter) have used the adiabatic approximation, neglecting the memory-effect terms in the xc potential. As shown by the recent study [98], the adiabatic approximation is well justified in the case of medium-strong low-frequency laser fields. However, its validity in very strong fields still remains to be investigated. More rigorous nonadiabatic treatment of the time-dependent xc energy functional can be facilitated if some information regarding the electron density for $N$-electron systems can be determined by means of the fully ab initio wavefunction approach. But this task is not feasible at the current time for $N > 2$. Since the exact time-dependent xc energy functional form is supposed to be universal and independent of $N$, the information of the strong-field behavior of the simplest but nontrivial two-electron systems will be very valuable for the future construction of time-dependent xc energy functional.

Applicability of the modern TDDFT approaches for the treatment of multiple elec-
tron ionization processes is another problem related to the quality of time-dependent xc energy functionals. Most of approximate xc functionals lack the important property of the exact functional, the discontinuity of its derivative with respect to the number of particles $N$, when $N$ passes through integer values [99]. Several attempts to apply TDDFT with such approximate functionals for calculations of nonsequential double ionization were un-
successful [100, 101]. Recently it was shown [102] that the derivative discontinuity is crucial for correct description of double ionization. The TD-OEP/KLI-SIC xc potential possesses an integer discontinuity with respect to the spin particle number $N_\sigma$ which improves description of the ionization process. However, we have found [103] that such a discontinuity of the TD-KLI-SIC potential is not sufficient to reproduce characteristic features of double ionization. However, when an integer discontinuity is enforced with respect to the total particle number $N$, the famous “knee” structure, experimentally observed in double ionization of He atoms, can be reproduced in TDDFT calculations [104].

At this time, the TDDFT is the primary approach available for the nonperturbative treatment of time-dependent processes of many-electron quantum systems in strong fields. Further extension of the self-interaction-free TDDFT approaches to larger molecular systems will be valuable and can lead to significant advancement in the understanding of strong-field chemical physics and atomic and molecular physics in the future. Work in this direction is under progress.

Acknowledgments

This work was partially supported by National Science Council of Taiwan and National Taiwan University (Grant No. 102R104021 and 102R891401). D.A.T. acknowledges the partial support of St. Petersburg State University (Grant No. 11.38.654.2013).

References


Phys. 54, 2651 (1971).
Review

Nonadiabatically Coupled π-Electron Rotation and Molecular Vibration in Aromatic Molecules Excited by Polarized UV/Vis Laser Pulses

Manabu Kanno,¹ Yukari Ono,¹ Hirohiko Kono,¹ and Yuichi Fujimura¹,²

¹Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
²Department of Applied Chemistry, Institute of Molecular Science and Center for Interdisciplinary Molecular Science, National Chiao-Tung University, Hsin-Chu 300, Taiwan

(Received September 20, 2013)

We review our theoretical studies on laser-driven ultrafast π-electron rotation (ring current) and vibronically coupled molecular vibrations in aromatic molecules with quasi-degenerate excited states. The main focus of discussion is on the role of laser polarization in controlling the coherent vibronic dynamics. We first present general formulations of the coherent electronic wave packet and expectation value of electronic angular momentum for arbitrary laser polarization within a frozen-nuclei model. We show that the relative quantum phase of the superposed quasi-degenerate states, which determines the oscillating behavior of angular momentum, can be manipulated by the ellipticity and orientation of the incident laser. The controllability of π-electron rotation is demonstrated by electronic wave packet simulations for a model molecule. The results of nuclear wave packet simulations on effective potential energy surfaces of the molecule have revealed that the angular momentum is gradually reduced by nonadiabatic transitions. The amplitude of induced molecular vibration depends significantly on the direction of linear polarization vectors but is insensitive to the helicity of circular polarization. The characteristic feature in vibrational amplitudes is attributed to the interference between nuclear wave packets that acquire different quantum phases in nonadiabatic transition. This feature offers a new strategy for laser control of molecular vibrations through the wave packet interference in nonadiabatic transition.

DOI: 10.6122/CJP.52.617 PACS numbers: 31.50.Gh, 33.15.Bh, 82.50.Hp, 82.53.-k

I. INTRODUCTION

Continuous technological advances in optical pulse generation have been vigorously promoting applications of attosecond/several-femtosecond lasers in molecular physics, chemistry, nanoscience, etc [1]. Such ultrashort lasers instantaneously change the electronic state of molecular systems. In recent years, control and observation of ultrafast dynamics in polyatomic molecules such as valence-electron motion and molecular vibration have been attempted by means of ultrashort laser pulses. For instance, from both experimental and theoretical aspects, time-resolved photoelectron angular distribution has been utilized to monitor the ultrafast dynamics through conical intersections, e.g., in the nonadiabatic transition in nitrogen dioxide NO₂ [2], in the photodissociation of carbon disulfide CS₂ [3], and in the internal conversions of aromatic hydrocarbons [4–7]. Each of the parameters that characterize a laser pulse plays a decisive role in the excitation of molecules; the light
intensity of the pulse affects the number of molecules excited and the central frequency specifies the average energy absorbed by the molecules. The bandwidth of the incident laser is inversely proportional to the pulse duration. Among the parameters, laser polarization is attracting more and more attention as a key controlling factor of molecular motion. So far, intense polarized light pulses have been extensively employed for the alignment [8–13] and orientation [8, 11, 14–17] of molecules by manipulating their rotational states. The nonadiabatic alignment technique [12, 18], which achieves the field-free periodic alignment of linear [19–21] or nonlinear [22, 23] molecules due to their rotational revival after pulse irradiation (from several tens of femtoseconds to picoseconds), has been used in the prestige for high harmonic generation [24–26] and molecular orbital (MO) tomography [27–29].

The present state of the application of polarized lights is entering into the next stage, namely, control of vibronic dynamics in polyatomic molecules with the polarization of shorter attosecond/several-femtosecond laser fields. For C_{60} fullerene, which is a large three-dimensional π-conjugated system, Hertel et al. have experimentally revealed that the patterns of multiphoton ionization and subsequent fragmentation caused by an intense femtosecond near-infrared laser depend significantly on optical ellipticity [30]. They have attributed the ellipticity dependence of the ion yield to that of the two-photon absorption process to a doorway excited state of C_{60} followed by efficient multielectron dynamics.

As for theoretical work, electronic and nuclear probability density currents or fluxes in molecules triggered by polarized femtosecond lasers have been actively investigated [31–36]. Among them, we refer to the quantum simulation by Barth et al. of laser-driven electron ring currents in Mg porphyrin, which is a planar two-dimensional π-conjugated system, i.e., an aromatic molecule [31]. The results of the simulation performed under a frozen-nuclei condition indicated that π electrons of the molecule can be rotated along its aromatic ring by applying a circularly polarized ultraviolet (UV) laser pulse. The circular motion of π electrons around the ring is associated with the angular momentum along the molecular axis perpendicular to the ring plane. Mg porphyrin has a pair of doubly degenerate π-electronic excited states, which are the eigenstates of the electronic angular momentum with opposite signs, owing to its high molecular symmetry. On irradiation the spin angular momentum of a photon is transferred to π electrons to produce one of the eigenstates selectively, and therefore the rotation direction of π electrons is predetermined by the helicity of circular polarization. Rodriguez and Mukamel have predicted that ring currents in Mg porphyrin can be probed by circular dichroism spectroscopy [37].

Laser-induced electron dynamics in ring-shaped systems such as aromatic molecules have been reported by other authors as well [38–41]. Nobusada and Yabana have calculated electric currents and an inverse Faraday effect in cyclic Na_{10} and benzene exposed to circularly polarized laser pulses by solving the time-dependent Kohn-Sham equation in real space and real time [40]. Ulusoy and Nest have shown by optimal control simulations that the aromaticity of benzene can be switched off by exciting it to nonaromatic target states [41].

In contrast to the work by Barth et al., we have demonstrated that transient rotation of π electrons in an ansa (planar-chiral) aromatic molecule can be induced along its aromatic ring by a linearly polarized UV laser pulse [42, 43]. Lowering the molecular
symmetry breaks the degeneracy of relevant excited states. In this case, the origin of directional ring current is not photon helicity but the asymmetry of the molecule. Ultrashort laser pulses can create a coherent superposition of optically-allowed quasi-degenerate excited states. The relative quantum phase of the superposed quasi-degenerate states can be controlled by the polarization direction of the incident laser with respect to the spatial configuration of the molecule. When the nonstationary electronic state is so prepared, $\pi$ electrons travel in an intended direction, clockwise or counterclockwise, around the ring. Moreover, as an extension to nonadiabatic vibrational dynamics coupled to the laser-driven $\pi$-electron rotation, we have also performed nuclear wavepacket (WP) simulations including nonadiabatic interactions between quasi-degenerate excited states [44]. To the best of our knowledge, Ref. [44] is the first report on electron rotation dynamics perturbed by molecular vibrations. The amplitudes of vibronically coupled molecular vibrations in the quasi-degenerate states dramatically vary depending on the initial rotation direction of $\pi$ electrons, which is determined by the linear polarization direction. We have explained this in both intuitive [45] and analytical [46, 47] ways as an interference effect between nuclear WPs ramified by nonadiabatic transition. This finding suggests that the information on attosecond $\pi$-electron dynamics can be obtained by spectroscopic detection of femtosecond molecular vibrations. Recently, we have further extended our investigation to nonadiabatic dynamics of aromatic molecules with quasi-degenerate excited states for arbitrary laser polarization including linear, circular, and elliptical ones [48]. The initial relative phase between the quasi-degenerate states is subject not only to the orientation of the applied laser but also to its ellipticity. It is therefore possible to create a desired superposition of the quasi-degenerate states, that is, to control $\pi$-electron rotation and vibrational amplitudes by tuning these laser parameters properly.

This article is intended to review the series of our studies on laser-driven ultrafast $\pi$-electron rotation and associated nonadiabatic couplings with molecular vibrations in aromatic molecules that have quasi-degenerate $\pi$-electronic excited states. We provide theoretical and numerical analyses in molecular optical response based on the time-dependent Schrödinger equation (TDSE) explicitly taking into account laser polarization. In Section II, we describe the concept of electronic angular momentum for aromatic molecules in terms of MO theory so as to introduce approximate angular momentum eigenstates in a quasi-degenerate system. In Section III, first, the optical excitation process of aromatic molecules is theoretically analyzed within a frozen-nuclei model to clarify the laser-polarization dependence of the relative quantum phase of the superposed quasi-degenerate states. Next, we present the numerical results of electronic WP simulations for a model system with a six-membered ring. The comparison between the excitations by linearly and circularly polarized UV laser pulses exemplifies the laser-polarization effects on $\pi$-electron rotation. In Section IV, we report the numerical results of nuclear WP simulations on effective potential energy surfaces (PESs) of the same molecule. It is shown that noticeable polarization-dependent nonadiabatic effects are found in both electronic angular momentum and vibrational amplitudes. We also discuss the laser control of the interference between the nuclear WPs of quasi-degenerate states that is caused by nonadiabatic transition. Finally, Section V concludes this article.
II. BASIC IDEA OF LASER-DRIVEN π-ELECTRON ROTATION IN AROMATIC MOLECULES

To begin with, we present the basic idea of generating ultrafast π-electron rotation in aromatic molecules by polarized lights. Because in general angular momentum serves as a measure of circular motions of a particle, introducing the concept of angular momentum eigenstates of π electrons is essential to quantify their rotation along an aromatic ring. In this section, we briefly summarize the mechanism of optically induced π-electron rotation from a viewpoint of the relationship between angular momentum eigenstates and molecular symmetry.

II-1. Angular Momentum Eigenstates: Complex and Real Orbitals

The system under consideration is an aromatic molecule of $D_{Nh}$ symmetry and its $C_N$ axis is chosen as the $z$ axis. According to MO theory, complex MOs \{|$\pi_m$}\} of the molecule are given as linear combinations of atomic orbitals (LCAO-MOs) in the form [49]

$$ |\pi_m\rangle = \frac{1}{N^{1/2}} \sum_{j=1}^{N} \exp \left( i m \frac{2j \pi}{N} \right) |p_{zj}\rangle = \frac{1}{N^{1/2}} \sum_{j=1}^{N} \exp (im\phi_j) |p_{zj}\rangle, $$

where $\phi_j \equiv 2j\pi/N$ and $|p_{zj}\rangle$ denote the azimuthal angle and $p_z$ orbital at the $j$th atom in the aromatic ring, respectively. The range of the integer $m$ depends on whether $N$ is odd or even: When $N$ is an odd number, $m$ reads $-(N - 1)/2, \ldots, 0, \ldots (N - 1)/2$ (for even $N$, $-N/2 + 1, \ldots, 0, \ldots, N/2$). The energy levels of \{|$\pi_m$\}\} are well known as a Frost circle [50]: $|\pi_0\rangle$ is the lowest MO and, for the other values of $m$, $|\pi_m\rangle$ and $|\pi_{-m}\rangle$ are degenerate. For odd $N$, $|\pi_{\pm(N-1)/2}\rangle$ are the highest MOs; for even $N$, the nondegenerate $|\pi_{N/2}\rangle$ is the highest. When a molecular polygon is approximated with a complete cylindrical ring, the molecule belongs to the $D_{\infty h}$ point group and the $z$ component of electronic angular momentum is quantized in units of the Dirac constant $\hbar$. In Eq. (1), the expansion coefficients $N^{-1/2} \exp (im\phi_j)$ have the same mathematical form as the eigenfunctions of the angular momentum operator $\hat{L}_z = -i\hbar \partial / \partial \phi$, $(2\pi)^{-1/2} \exp (im\phi)$, except for the normalization constant. Hence, the complex MO $|\pi_m\rangle$ can be regarded as an angular momentum eigenstate and its eigenvalue of $\hat{L}_z$ is $m\hbar$ for degenerate MOs or zero for nondegenerate ones.

Here, we define real MOs $|\pi_{mx}\rangle$ and $|\pi_{my}\rangle$ ($m > 0$) as linear combinations of the complex degenerate ones $|\pi_m\rangle$ and $|\pi_{-m}\rangle$:

$$ |\pi_{mx}\rangle \equiv 2^{-1/2} \left( |\pi_{+m}\rangle + |\pi_{-m}\rangle \right), $$

$$ |\pi_{my}\rangle \equiv -2^{-1/2} i \left( |\pi_{+m}\rangle - |\pi_{-m}\rangle \right). $$

(2a)

(2b)
From these definitions, the real MOs can be expanded in terms of \(|p_{zj}\rangle\) as

\[
|\pi_{mx}\rangle = \left(\frac{2}{N}\right)^{1/2} \sum_{j=1}^{N} \cos(m\phi_j) |p_{zj}\rangle,
\]

\[
|\pi_{my}\rangle = \left(\frac{2}{N}\right)^{1/2} \sum_{j=1}^{N} \sin(m\phi_j) |p_{zj}\rangle.
\]

From Eqs. (2a) and (2b), we immediately obtain

\[
|\pi_{\pm m}\rangle = 2^{-1/2} \left(|\pi_{mx}\rangle \pm i |\pi_{my}\rangle\right).
\]

Recalling that complex AOs \(|2p_{+1}\rangle\) and \(|2p_{-1}\rangle\) are angular momentum eigenstates of an electron in a hydrogen atom, the relation in Eq. (4) is similar to that between the complex AOs and real ones \(|2p_x\rangle\) and \(|2p_y\rangle\) with the real azimuthal functions \(\pi^{-1/2} \cos \phi\) and \(\pi^{-1/2} \sin \phi\), respectively.

II-2. Angular Momentum Eigenstates: Perspective of Molecular Symmetry

On the basis of the concept of angular momentum eigenstates, we next explain the mechanism of \(\pi\)-electron rotation in Mg porphyrin interacting with a circularly polarized laser pulse [31] as an example. The symmetry of Mg porphyrin at its equilibrium geometry is \(D_{4h}\) and its highest occupied and lowest unoccupied MOs (HOMO and LUMO) are nondegenerate \(a_{1u}\) and doubly degenerate \(e_g\) orbitals, respectively [51, 52]. The degenerate LUMOs are one-electron angular momentum eigenstates with \(m = \pm 1\). As for multielectron states constructed from MOs, there exist doubly degenerate \(^1E_u\) excited states, which mainly consists of single excitations from nondegenerate MOs such as the HOMO to the LUMOs. The doubly degenerate \(^1E_u\) states are viewed as the eigenstates of the total angular momentum operator \(L_{z}\) of the multielectron system with the quantum number \(M = \pm 1\). We use the notations \(|^1E_{u\pm}\rangle\) for the \(^1E_u\) state with \(M = \pm 1\). As in the case of MOs, the multielectron angular momentum eigenstates \(|^1E_{u\pm}\rangle\) can be expressed in terms of real excited states \(|^1E_{ux}\rangle\) and \(|^1E_{uy}\rangle\):

\[
|^1E_{u\pm}\rangle = 2^{-1/2} \left(|^1E_{ux}\rangle \pm i |^1E_{uy}\rangle\right).
\]

When a circularly polarized laser pulse propagates along the \(C_4\) axis of Mg porphyrin, either \(|^1E_{u+}\rangle\) or \(|^1E_{u-}\rangle\) is selected by the spin angular momentum of a photon and \(\pi\) electrons start to rotate clockwise or counterclockwise depending on the selected state. This is the origin of the unique correspondence between the rotation direction of \(\pi\) electrons and that of the polarization plane of a circularly polarized laser pulse. In this way, one finds it impossible to circulate \(\pi\) electrons in Mg porphyrin by a linearly polarized laser pulse, which has no spin angular momentum.

Here, let us suppose that the molecular symmetry is lowered, e.g., by introducing functional groups and/or replacing some carbon atoms in the aromatic ring with heteroatoms. For this molecule, no two-dimensional irreducible representation \(E\) is allowed
to exist and, accordingly, relevant MOs or multielectron states are not fully degenerate but quasi-degenerate. We denote the lower and higher of the quasi-degenerate excited states by $|L\rangle$ and $|H\rangle$, respectively. There exists no excited state that is an exact eigenstate of $\hat{L}_z$ in such a system. Then, how can $\pi$-electron rotation be induced in an aromatic molecule with lower symmetry? Ultrashort laser pulses can prepare a coherent superposition of the optically-allowed quasi-degenerate states. The approximate angular momentum eigenstates can be defined in analogy to Eq. (5) as

$$|\pm\rangle \equiv 2^{-1/2} (|L\rangle \pm i|H\rangle),$$

where

$$\left\langle \pm | \hat{L}_z| \pm \right\rangle \simeq \pm \hbar.$$  

After a laser pulse prepares either $|+\rangle$ or $|-\rangle$, it subsequently evolves in time as a coherent nonstationary state because of the nonzero energy gap between the quasi-degenerate states:

$$e^{-i\hat{H}_0 t/\hbar}|\pm\rangle = 2^{-1/2} \left( e^{-i\omega_L t} |L\rangle \pm ie^{-i\omega_H t} |H\rangle \right) = e^{-i\omega_L t} 2^{-1/2} \left( |L\rangle \pm ie^{-i2\Delta\omega t} |H\rangle \right),$$

where $\hat{H}_0$ is the field-free electronic Hamiltonian and $\omega_L$ ($\omega_H$) is the angular frequency of $|L\rangle$ ($|H\rangle$). The energy gap is given by $2\hbar\Delta\omega \equiv \hbar(\omega_H - \omega_L)$. From Eq. (8), the approximate angular momentum eigenstates $|+\rangle$ or $|-\rangle$ can be transiently created within the period of the electronic state change, $T \equiv \pi/\Delta\omega$, except for the global phase factor $e^{-i\omega_L t}$. Therefore, transient rotation of $\pi$ electrons along an aromatic ring can be achieved by selective generation of an approximate angular momentum eigenstate. The strategy for producing predominantly either $|+\rangle$ or $|-\rangle$ by a polarized laser field will be discussed in Section III.

### III. LASER-POLARIZATION EFFECTS ON $\pi$-ELECTRON ROTATION

In this section, the role of laser polarization in an optical excitation of aromatic molecules with quasi-degenerate excited states is analyzed by using a three-level model. All nuclear degrees of freedom are ignored. We construct a theoretical model explicitly taking into account the polarization of an incident laser and show that the resultant superposition of the quasi-degenerate states is determined by the ellipticity and orientation of the polarization ellipse with respect to the molecule. The results of numerical electronic WP simulations in a six-membered ring molecule based on ab initio MO methods are also presented.

#### III-1. Three-Level Model Analysis

In this study, a laser field is treated classically and its spatial dependence is neglected under the dipole approximation. The time-dependent electronic Hamiltonian with a molecule-laser interaction in the length gauge is

$$\hat{H}(t) = \hat{H}_0 - \hat{\mu} \cdot \varepsilon(t),$$

where

$$\langle \pm | L_z | \pm \rangle \simeq \pm \hbar.$$
where $\hat{\mu}$ is the electric dipole moment operator and $\varepsilon(t)$ is a laser field. The TDSE for an electronic WP is

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle$$  \hfill (10)

with

$$|\Psi(0)\rangle = |G\rangle$$  \hfill (11)

as the initial condition, where $|G\rangle$ is the electronic ground state. To analytically solve the TDSE (10), we adopt the so-called V-type three-level model [53(a)], in which the electronic WP is expanded in terms of the minimum set, i.e., the ground and quasi-degenerate excited states:

$$|\Psi(t)\rangle = c_G(t) |G\rangle + c_L(t) e^{-i\omega_L t} |L\rangle + c_H(t) e^{-i\omega_H t} |H\rangle,$$  \hfill (12)

where the angular frequency of $|G\rangle$, $\omega_G$, is set to be zero. The optically-allowed quasi-degenerate states $|L\rangle$ and $|H\rangle$ are independently coupled to $|G\rangle$, that is, $\langle L | \hat{\mu} | H \rangle$ = $\langle H | \hat{\mu} | L \rangle$ = 0; the other off-diagonal matrix elements of $\hat{\mu}$ are real. For simplicity, all the diagonal elements of $\hat{\mu}$ are assumed to be zero, which implies the presence of the inversion center in the molecule. When Eq. (12) is inserted into Eq. (10), the equation of motion for the expansion coefficient vector

$$C(t) \equiv \begin{pmatrix} c_G(t) \\ c_L(t) \\ c_H(t) \end{pmatrix}$$  \hfill (13)

is derived as

$$\frac{dC(t)}{dt} = i \begin{pmatrix} 0 & g_L(t) & g_H(t) \\ g_L(t)^* & 0 & 0 \\ g_H(t)^* & 0 & 0 \end{pmatrix} C(t),$$  \hfill (14)

where

$$g_n(t) \equiv \frac{\langle G | \hat{\mu} | n \rangle \cdot \varepsilon(t)}{\hbar} e^{-i\omega_nt} \ (n = L \ and \ H).$$  \hfill (15)

From Eq. (11), at the initial time $t = 0$, $C(t)$ satisfies

$$C(0) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$  \hfill (16)

For convenience, we use the notations $\mu_n \equiv \langle G | \hat{\mu} | n \rangle = \langle n | \hat{\mu} | G \rangle$. As defined in Section II-1, the $z$ axis is perpendicular to the ring plane, which coincides with the $xy$ plane. Both $\mu_L$ and $\mu_H$ lie in the $xy$ plane [Fig. 1(a)] for $\pi\pi^*$ transitions corresponding to the excitations to
FIG. 1: (a) Spatial configurations of transition moments \( \mathbf{\mu}_L \) and \( \mathbf{\mu}_H \) and (b) orientation of the polarization ellipse. An aromatic molecule is represented by a hexagon. Both \( \mathbf{\mu}_L \) and \( \mathbf{\mu}_H \) lie in the ring plane defined as the \( xy \) plane; in a degenerate system, the \( x \) and \( y \) axes can be parallel to the directions of the transition moments. \( \chi_H - \chi_L \) denotes the angle between \( \mathbf{\mu}_L \) and \( \mathbf{\mu}_H \). The laser field propagates in the \( z \) direction and oscillates in the \( xy \) plane. The orientation angle of the major axis of the polarization ellipse with respect to the \( x \) axis is represented by \( \delta \). The minor-to-major axial ratio is \(|\tan(\pi/4 - \beta)|\).

The quasi-degenerate states. Hence, the transition electric dipole moments can be expanded as

\[
\mathbf{\mu}_n = \mu_{nx}\mathbf{e}_x + \mu_{ny}\mathbf{e}_y \quad (n = L \text{ and } H),
\]  

where \( \mathbf{e}_x \) and \( \mathbf{e}_y \) are the unit vectors in the \( x \) and \( y \) directions, respectively.

The laser field is supposed to propagate in the \( z \) direction and thus \( \mathbf{\varepsilon}(t) \) oscillates in the \( xy \) plane. The mathematical form of \( \mathbf{\varepsilon}(t) \) is given by

\[
\mathbf{\varepsilon}(t) = \frac{\mathbf{\varepsilon}_p}{2} f(t) \left[ e^{-i(\omega t + \varphi)} \mathbf{e} + e^{i(\omega t + \varphi)} \mathbf{e}^* \right],
\]  

where \( \mathbf{\varepsilon}_p \) is the peak field strength, \( \omega \) is the central frequency, \( \varphi \) is the optical phase, and \( \mathbf{e} \) is the complex polarization unit vector. The time-dependent envelope function \( f(t) \) varies between zero and unity for \([0, t_d]\) with \( t_d \) being the pulse duration; otherwise \( f(t) = 0 \). The central frequency \( \omega \) is set to be resonant with the average energy of the quasi-degenerate states:

\[
\omega = \omega_L + \Delta \omega = \omega_H - \Delta \omega.
\]

The complex polarization unit vector \( \mathbf{e} \) is expressed for an arbitrary polarization as

\[
\mathbf{e} = e^{-i\delta} (\cos \beta) \mathbf{e}_{+1} + e^{i\delta} (\sin \beta) \mathbf{e}_{-1},
\]

where \( \mathbf{e}_{+1} \) and \( \mathbf{e}_{-1} \) are the spherical unit vectors corresponding to positive and negative helicities (spins), respectively, defined in this article as

\[
\mathbf{e}_{\pm 1} = 2^{-\frac{11}{2}} \left( \mathbf{e}_x \pm i \mathbf{e}_y \right).
\]
In some references the spherical unit vectors are accompanied by the signs \( \mp \) before \( 2^{-1/2} \) but in this article the definitions in Eq. (21) are adopted. Following the convention in optics, we refer to \( e_{+1} \) (\( e_{-1} \)) as left (right) circular polarization. In Eq. (20), \( \delta \) represents the orientation angle of the major axis of the polarization ellipse with respect to the \( x \) axis and \( \beta \) is called the ellipticity angle in this article [Fig. 1(b)]. The range of \( \beta \) is \([0, \pi/2]\) and the minor-to-major axial ratio of the polarization ellipse is equal to \( |\tan(\pi/4 - \beta)| \); for example, \( \beta = 0, \pi/4, \) and \( \pi/2 \) designate left circular, linear, and right circular polarizations, respectively. Substituting Eq. (18) into Eq. (15) yields

\[
g_L(t) = \frac{f(t)}{2} \left\{ \Omega_L e^{-i[(2\omega - \Delta\omega)t + \varphi]} + \Omega_L^* e^{i(\Delta\omega t + \varphi)} \right\},
\]

\[
g_H(t) = \frac{f(t)}{2} \left\{ \Omega_H e^{-i[(2\omega + \Delta\omega)t + \varphi]} + \Omega_H^* e^{i(\Delta\omega t - \varphi)} \right\},
\]

where

\[
\Omega_n \equiv \frac{\varepsilon_p}{\hbar} \mu_n \cdot e \quad (n = L \text{ and } H)
\]

are the complex Rabi frequencies. Note that the Rabi frequencies are dependent on the polarization of the laser field, that is, on \( \beta \) and \( \delta \). Here, we resort to the rotating-wave approximation (RWA) [53(b)], in which the contribution of the rapidly oscillating exponentials, i.e., the first terms in Eqs. (22a) and (22b) to the time evolution of \( C(t) \) is averaged out and removed (since \( \omega \gg \Delta\omega \)). Under the RWA, Eq. (14) is rewritten as

\[
\frac{dC(t)}{dt} = i \frac{f(t)}{2} \begin{pmatrix}
0 & \Omega_L e^{i(\Delta\omega t + \varphi)} & \Omega_H^* e^{-i(\Delta\omega t - \varphi)} \\
\Omega_L e^{-i(\Delta\omega t + \varphi)} & 0 & 0 \\
\Omega_H e^{i(\Delta\omega t - \varphi)} & 0 & 0
\end{pmatrix} C(t).
\]

Even for a molecule without the inversion center, which has nonzero permanent electric dipoles, the diagonal terms in the equation of motion for \( C(t) \) vanish in the RWA and thereby Eq. (24) is obtained.

For the purpose of efficiently producing an approximate angular momentum eigenstate \( |+\rangle \) or \(|-\rangle \) defined by Eq. (6), the quasi-degenerate states \( |L\rangle \) and \( |H\rangle \) need to be populated equally. The laser field is therefore assumed to satisfy \( |\Omega_L| = |\Omega_H| \) or, at least, \( |\Omega_L| \approx |\Omega_H| \). This leads to the orthogonality

\[
(e^{i\theta} \mu_L - \mu_H) \cdot e = 0,
\]

where \( \theta \) is the relative phase between \( \Omega_L \) and \( \Omega_H \), that is,

\[
\theta \equiv \arg \left( \frac{\Omega_H}{\Omega_L} \right).
\]

When Eq. (20) is inserted into Eq. (25), the ellipticity angle \( \beta \) and orientation angle \( \delta \) are related to the relative phase \( \theta \) by

\[
e^{i2\delta} \tan \beta = -\frac{(e^{i\theta} \mu_L - \mu_H) \cdot e_{+1}}{(e^{i\theta} \mu_L - \mu_H) \cdot e_{-1}}.
\]
Hence, the values of $\beta$ and $\delta$ that meet the condition $|\Omega_L| = |\Omega_H|$ are determined by the absolute value and argument of the right-hand side of Eq. (27), respectively. To further simplify Eq. (24), we introduce an alternative pair of superposition states

$$|S_\pm\rangle \equiv \frac{1}{\Omega} (|\Omega_L\rangle \pm |\Omega_H\rangle) = \frac{\Omega_L}{\Omega} (|L\rangle \pm e^{i\theta} |H\rangle),$$

where

$$\Omega \equiv \left(|\Omega_L|^2 + |\Omega_H|^2\right)^{1/2} = 2^{1/2} |\Omega_L| = 2^{1/2} |\Omega_H|.$$  \hspace{1cm} (29)

The superposition states in Eq. (28) are obviously normalized and the overlap between them is

$$\langle S_+ | S_- \rangle = \frac{|\Omega_L|^2 - |\Omega_H|^2}{\Omega^2} = 0,$$

which proves their orthogonality. Using these superposition states, the electronic WP can be expanded as

$$|\Psi(t)\rangle = c_G(t) |G\rangle + e^{-i(\omega t + \varphi)} \left[c_+(t) |S_+\rangle + c_-(t) |S_-\rangle\right],$$

where

$$c_{\pm}(t) \equiv \frac{1}{\Omega} \left[\Omega_L^* e^{i(\Delta \omega t + \varphi)} c_L(t) \pm \Omega_H^* e^{-i(\Delta \omega t - \varphi)} c_H(t)\right].$$

Then, the time evolution of the new coefficient vector

$$\mathbf{D}(t) \equiv \begin{pmatrix} c_G(t) \\ c_+(t) \\ c_-(t) \end{pmatrix}$$

obeys

$$\frac{d\mathbf{D}(t)}{dt} = i \frac{1}{2} \begin{pmatrix} 0 & \bar{\Omega} f(t) & 0 \\ \bar{\Omega} f(t) & 0 & 0 \\ 0 & 0 & 2\Delta \omega \end{pmatrix} \mathbf{D}(t)$$

with the initial condition

$$\mathbf{D}(0) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$
III-2. Degenerate Case

Before proceeding to the solution of Eq. (34) for a quasi-degenerate system, let us consider the degenerate case of $\Delta \omega = 0$. In this case, Eq. (34) becomes extremely simple:

$$\frac{d\mathbf{D}(t)}{dt} = i \frac{\Omega}{2} \mathbf{f}(t) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \mathbf{D}(t).$$  \hspace{1cm} (36)

This clearly indicates that the system can be treated in practice as a two-level one consisting of $|G\rangle$ and $|S_+\rangle$. After integrating Eq. (36), one obtains

$$\mathbf{D}(t) = \begin{pmatrix} \cos \left[ \frac{\Omega}{2} F(t) \right] \\ i \sin \left[ \frac{\Omega}{2} F(t) \right] \\ 0 \end{pmatrix},$$  \hspace{1cm} (37)

where

$$F(t) \equiv \int_0^t dt' f(t').$$  \hspace{1cm} (38)

From Eq. (37), the system can be completely transferred from $|G\rangle$ to $|S_+\rangle$ by the so-called $\pi$ pulse \[53(c)\], which fulfills $\bar{\Omega} F(t_d) = \pi$. When Eq. (37) is inserted into Eq. (31), the electronic WP can be written down as

$$|\Psi(t)\rangle = \cos \left[ \frac{\Omega}{2} F(t) \right] |G\rangle + i \frac{\Omega_L}{\Omega} \sin \left[ \frac{\Omega}{2} F(t) \right] e^{-i(\omega t + \varphi)} \left( |L\rangle + e^{i\theta} |H\rangle \right).$$  \hspace{1cm} (39)

The relative quantum phase between the degenerate excited states $|L\rangle$ and $|H\rangle$ coincides with that between the Rabi frequencies $\Omega_L$ and $\Omega_H$, i.e., $\theta$. Note that the relative quantum phase $\theta$ is independent of time and controllable by the ellipticity angle $\beta$ and orientation angle $\delta$. This implies that a desired superposition of the degenerate states can be created by tuning the polarization of an incident light properly. The populations of the exact angular momentum eigenstates $|+\rangle$ and $|-\rangle$, $P_{\pm}(t) \equiv |\langle \pm |\Psi(t)\rangle|^2$, are derived as

$$P_{\pm}(t) = \frac{1}{2} \sin^2 \left[ \frac{\Omega}{2} F(t) \right] (1 \pm \sin \theta)$$  \hspace{1cm} (40)

and the expectation value of electronic angular momentum, $L_z(t) \equiv \langle \Psi(t) | \hat{L}_z | \Psi(t) \rangle$, is given by

$$L_z(t) = \hbar [P_+(t) - P_-(t)] = \hbar \sin^2 \left[ \frac{\Omega}{2} F(t) \right] \sin \theta.$$  \hspace{1cm} (41)

The sign of $L_z(t)$ (in other words, the rotation direction of $\pi$ electrons) is determined by the relative quantum phase $\theta$ and remains unchanged throughout the time evolution: $\pi$ electrons flow in a sole direction even after a laser pulse is turned off at $t = t_d$. 
Let us revert to Eq. (27), which links the relative quantum phase $\theta$ with the ellipticity angle $\beta$ and orientation angle $\delta$. For aromatic molecules with degenerate states, there are special relationships between the transition moments $\mathbf{\mu}_L$ and $\mathbf{\mu}_H$: They have the same magnitude and are perpendicular to each other, that is, $||\mathbf{\mu}_L|| = ||\mathbf{\mu}_H||$ and $\mathbf{\mu}_L \cdot \mathbf{\mu}_H = 0$. The $x$ and $y$ axes can thus be chosen to be parallel to $\mathbf{\mu}_L$ and $\mathbf{\mu}_H$, respectively, so that $\mu_{Lx} = \mu_{Hy} \neq 0$ and $\mu_{Ly} = \mu_{Hx} = 0$; in the case of Mg porphyrin, this holds when $|L \rangle = |1E_{ux}\rangle$ and $|H \rangle = |1E_{uy}\rangle$. Consequently, for a degenerate system, Eq. (27) is simplified as

$$e^{i2\delta} \tan \beta = -\frac{e^{i\theta} - i}{e^{i\theta} + i} = e^{i\pi/2} \tan \left[ \frac{1}{2} \left( \frac{\pi}{2} - \theta \right) \right],$$

which involves neither transition moments nor spherical unit vectors and is purely imaginary. Given a value of $\beta$, there exist two solutions of Eq. (42):

$$\delta = \pm \frac{\pi}{4} \text{ and } \theta = \frac{\pi}{2} \mp 2\beta.$$  

(43)

The major axis of the polarization ellipse with $\delta = \pi/4$ bisects the angle between $\mathbf{\mu}_L$ and $\mathbf{\mu}_H$ and is perpendicular to that with $\delta = -\pi/4$. In both cases, the final angular momentum $L_z(t_d)$ for the $\pi$-pulse excitation is $\hbar \sin \theta = \hbar \cos 2\beta$. In the case of circular polarization in which $\beta = 0$ or $\pi/2$, the value of $\delta$ is indeterminate from Eq. (42) or (43); in fact, it can be chosen arbitrarily as will be mentioned later.

We present illustrative examples. The case of linear polarization ($\beta = \pi/4$) is taken as the first one; Eq. (20) is then rewritten as

$$\mathbf{e} = (\cos \delta) \mathbf{e}_x + (\sin \delta) \mathbf{e}_y$$

(44)

and $\delta$ determines the polarization direction. The Rabi frequencies $\Omega_L$ and $\Omega_H$ are thus real-valued and their relative phase $\theta$ takes either zero or $\pi$ ($e^{i\theta} = \pm 1$). Hereafter, the linear polarization vectors for $\theta = 0$ and $\pi$ are denoted by $\mathbf{e}_{in}$ and $\mathbf{e}_{out}$, respectively. From Eq. (43), the values of $\delta$ for the two polarization vectors are $\delta_{in} = \pi/4$ and $\delta_{out} = -\pi/4$. As in Eq. (39), a linearly polarized laser pulse with the polarization vector $\mathbf{e}_{in}$ ($\mathbf{e}_{out}$) produces an in-phase (out-of-phase) superposition $|L\rangle + |H\rangle$ ($|L\rangle - |H\rangle$), which is an equal mixture of the exact angular momentum eigenstates $|+\rangle$ and $|\rangle$. This leads to $P_+(t) = P_-(t)$ and hence $L_z(t) = 0$ for all $t$. π-Electron rotation cannot be induced in a degenerate system by a linearly polarized laser pulse.

Next, for circular polarization, $\beta = 0$ ($\pi/2$) reads

$$\mathbf{e} = e^{-i\delta} \mathbf{e}_{+1} + e^{i\delta} \mathbf{e}_{-1}.$$  

(45)

When Eq. (45) is inserted into Eq. (18), the orientation angle $\delta$ is indistinguishable from the optical phase $\varphi$. Therefore, for circular polarization, $\delta$ acts as an additional optical phase and can be set to any value because Eq. (39) shows that the optical phase $\varphi$ does not affect the superposition of the degenerate states. From the definition of $\theta$ in Eq. (26), we have

$$\theta = \pm (\chi_H - \chi_L) \text{ for } \mathbf{e}_{\pm 1},$$  

(46)
where $\chi_{H} - \chi_{L}$ is the angle between $\mu_{L}$ and $\mu_{H}$, that is,

$$\tan \chi_{n} = \frac{\mu_{ny}}{\mu_{nx}} \quad (n = L \text{ and } H). \quad (47)$$

Accordingly, $\theta = \pm \pi/2$ ($e^{i\theta} = \pm i$) in a degenerate system. The superposition states $|S_{\pm}\rangle$ are equivalent to the exact angular momentum eigenstates $|\pm\rangle$ ($|\mp\rangle$) for left (right) circular polarization, while the population is transferred only to $|S_{+}\rangle$ as in Eq. (37). $\pi$ Electrons of the molecule circulate along its ring in the direction inherent to the eigenstate generated.

The above consequences for linear and circular polarizations are consistent with the discussion on laser-driven $\pi$-electron rotation in Mg porphyrin in Section II-2. The phase factor $e^{i\theta}$ yielded by elliptical polarization is neither real nor purely imaginary regardless of whether $\delta = \pm \pi/4$. As seen in Eqs. (40) and (41), the resultant behavior of $\pi$ electrons is intermediate between those for linear and circular polarizations: The rotation direction of $\pi$ electrons is subject to the more populated of $|+\rangle$ or $|-\rangle$, while the magnitude of $L_z(t_d)$ is less than $\hbar$ even for the $\pi$-pulse excitation.

### III-3. Quasi-Degenerate Case

Now, we turn to the quasi-degenerate case of $\Delta \omega \simeq 0$. Because it is impossible to analytically integrate Eq. (34) with an arbitrary envelope function $f(t)$, we restrict $f(t)$ to a rectangular form: $f(t) = 1$ for $[0, t_d]$ and otherwise zero. Then, Eq. (34) becomes solvable: During irradiation,

$$\frac{dD(t)}{dt} = \frac{i}{2} \begin{pmatrix} 0 & \bar{\Omega} & 0 \\ \bar{\Omega} & 0 & 2\Delta \omega \\ 0 & 2\Delta \omega & 0 \end{pmatrix} D(t), \quad (48)$$

of which the solution is

$$D(t) = \begin{pmatrix} \left(\frac{\bar{\Omega}}{\Omega} \right)^2 \cos \left(\frac{\Omega}{2} t \right) + \left(\frac{2\Delta \omega}{\bar{\Omega}} \right)^2 \\ i\frac{\bar{\Omega}}{\Omega} \sin \left(\frac{\Omega}{2} t \right) \\ -\frac{\Omega(2\Delta \omega)}{\bar{\Omega}} \left[1 - \cos \left(\frac{\Omega}{2} t \right) \right] \end{pmatrix}. \quad (49)$$

The generalized Rabi frequency

$$\Omega \equiv \left[\bar{\Omega}^2 + (2\Delta \omega)^2 \right]^{1/2} \quad (50)$$

is the root-mean-square of the Rabi frequencies and the detuning frequency $2\Delta \omega$. One can readily confirm that Eq. (49) for $\Delta \omega = 0$ is identical to Eq. (37) for $f(t) = 1$. The pulse area of a laser field for a quasi-degenerate system is defined as $\Omega F(t_d)$, which is equal to $\Omega t_d$ in the rectangular-envelope case. The ground state $|G\rangle$ can be fully emptied if the rectangular-envelope pulse satisfies $2\Delta \omega \leq \bar{\Omega}$ with a pulse area of $2\arccos \left[-\left(2\Delta \omega/\bar{\Omega} \right)^2 \right]$; this laser field is named the full-excitation pulse. The pulse area of the full-excitation pulse
is larger than that of the \( \pi \) pulse, that is, 
\[
2 \arccos \left[ - \frac{2(\Delta \omega/\Omega)}{\Omega} \right] > \pi \text{ (but not larger than } 2\pi) .
\]
Finally, we acquire the coherent electronic WP in a quasi-degenerate system:

\[
|\Psi(t)\rangle = \left[ \left( \frac{\tilde{\Omega}}{\Omega} \right)^2 \cos \left( \frac{\Omega}{2} t \right) + \left( \frac{2\Delta \omega}{\Omega} \right)^2 \right] |G\rangle + i \frac{\Omega_L}{\Omega} \alpha(t) e^{-i(\omega t + \varphi)} \left\{ |L\rangle + e^{i(\theta - \vartheta(t))} |H\rangle \right\},
\]

(51)

where

\[
\alpha(t) \equiv 2 \sin \left( \frac{\Omega}{4} t \right) \bar{\alpha}(t) \text{ and } \vartheta(t) \equiv 2 \arg \bar{\alpha}(t)
\]

(52)

with

\[
\bar{\alpha}(t) \equiv \cos \left( \frac{\Omega}{4} t \right) + i \frac{2\Delta \omega}{\Omega} \sin \left( \frac{\Omega}{4} t \right)
\]

(53)

The relative quantum phase between the quasi-degenerate excited states \(|L\rangle\) and \(|H\rangle\) is given by \(\theta - \vartheta(t)\) and its temporal behavior is the main point of this model analysis. Using \(\alpha(t)\) in Eq. (52), the populations \(P_{\pm}(t)\) are expressed as

\[
P_{\pm}(t) = \frac{1}{2} \left( \frac{\tilde{\Omega}}{\Omega} \right)^2 |\alpha(t)|^2 \left\{ 1 \pm \sin [\theta - \vartheta(t)] \right\}
\]

(54)

and the angular-momentum expectation value \(L_z(t)\) is

\[
L_z(t) = \Lambda [P_+(t) - P_-(t)] = \Lambda \left( \frac{\tilde{\Omega}}{\Omega} \right)^2 |\alpha(t)|^2 \sin [\theta - \vartheta(t)],
\]

(55)

where

\[
\Lambda \equiv \left\langle + |L_z| + \right\rangle = - \left\langle - |L_z| - \right\rangle.
\]

(56)

In distinction from Eq. (41), the rotation direction of \(\pi\) electrons can be reversed during irradiation owing to the presence of the time-dependent phase \(\vartheta(t)\) in Eq. (55).

For aromatic molecules with quasi-degenerate states, Eqs. (42) and (43) do not strictly hold because in general lowering the molecular symmetry leads to \(\|\mu_L\| \neq \|\mu_H\|\) and \(\mu_L \cdot \mu_H \neq 0\). In this case, the linear polarization vectors \(e_{in}(\theta = 0)\) and \(e_{out}(\theta = \pi)\) can be derived by substituting Eq. (44) into Eq. (25):

\[
\delta_{in, out} = \arctan \left( \frac{-\mu_{Lx} + \mu_{Hx}}{\mu_{Ly} \mp \mu_{Hy}} \right).
\]

(57)

It is straightforward to find a pair of \(\beta\) and \(\delta\) for the other values of \(\theta\) from Eq. (27) with the transition moments specified. Circular polarizations do not exactly satisfy Eq. (27), i.e., the condition \(|\Omega_L| = |\Omega_H|\) unless the magnitudes of \(\mu_L\) and \(\mu_H\) happen to be equal.
(\||\mu_L|| = ||\mu_H||). On the assumption that the energy gap between |L⟩ and |H⟩ is small (Δω ≃ 0), the transition moments approximately fulfill ||\mu_L|| ≃ ||\mu_H|| and/or \mu_L \cdot \mu_H ≃ 0 and accordingly the relationship among β, δ, and θ should be close to that in the degenerate case. For example, if ||\mu_L|| ≃ ||\mu_H||, e_{in} and e_{out} whose polarization directions are defined by Eq. (57) should be almost perpendicular to each other. If also \mu_L \cdot \mu_H ≃ 0, we have 

\[ ±Ω_L ≃ ±Ω_H (θ ≃ ±π/2) \] for e_{±1}.

The time-dependent part of the relative quantum phase, i.e., \vartheta(t) follows

\[ \tan \left[ \frac{\vartheta(t)}{2} \right] = \frac{2Δω}{Ω} \tan \left( \frac{Ω}{4t} \right) \]

from Eqs. (52) and (53). Hence, \vartheta(t) changes temporally as 0 → π/2 → π → 3π/2 → 2π → ... with the progression of time, 0 → TR − γ → TR → TR + γ → 2TR → ..., where TR ≡ 2π/Ω is the period of the (generalized) Rabi oscillations and γ ≡ 4 \arctan(2Δω/Ω)/Ω. Because 2Δω ≤ Ω, TR is not larger than the period T of the field-free electronic state change and γ ≤ TR/2. The relative quantum phase grows from its initial value θ in the negative direction by \vartheta(t); if the full-excitation pulse is employed, \vartheta(t_d) ≤ π from the inequality TR/2 < 2 \arccos \left[ \frac{−(2Δω/Ω)^2}{2} \right] /Ω ≤ TR. The populations \(P_\pm(t)\) and the expectation value \(L_z(t)\) vary in time according to the relative quantum phase \(θ − \vartheta(t)\) as shown in Eqs. (54) and (55), respectively.

After the end of a laser pulse at \(t = t_d\), the electronic WP propagates freely. In a similar fashion to Eq. (8), the relative quantum phase in the free propagation is \(θ − \vartheta(t_d) − 2Δω(t − t_d)\) and thereby the coherent superposition of the quasi-degenerate states oscillates with the period T. Eventually, the populations \(P_\pm(t)\) and the expectation value \(L_z(t)\) for \(t > t_d\) are also the oscillating functions of \(t\) in the form

\[ P_\pm(t) = \frac{1}{2} \left( \frac{Ω}{Ω} \right)^2 |α(t_d)|^2 \{1 ± \sin[θ − \vartheta(t_d) − 2Δω(t − t_d)]\} \]

and

\[ L_z(t) = \Lambda \left( \frac{Ω}{Ω} \right)^2 |α(t_d)|^2 \sin[θ − \vartheta(t_d) − 2Δω(t − t_d)], \]

respectively. The approximate angular momentum eigenstates |+⟩ and |−⟩ are alternately generated as predicted in Section II-2 and therefore the rotation direction of π electrons switches between clockwise and counterclockwise. This is a notable difference from the degenerate case, in which the rotation direction is fixed and the angular-momentum expectation value \(L_z(t)\) is constant after the applied pulse fully decays.

We have formulated the coherent electronic WP |Ψ(t)⟩ and the angular-momentum expectation value \(L_z(t)\) of aromatic molecules with quasi-degenerate excited states irradiated by a laser pulse of arbitrary polarization. It should be emphasized that, despite the subsequent oscillating behavior, the initial relative phase of the superposed quasi-degenerate states or the initial rotation direction of π electrons depends on the relative phase between
the Rabi frequencies, $\theta$, which is defined by Eq. (26) and can be manipulated by the ellipticity angle $\beta$ and orientation angle $\delta$ of the incident laser. Generation of polarization-shaped femtosecond UV laser pulses has become experimentally realizable [54, 55]. The efficient scheme for production of circularly polarized attosecond extreme UV laser pulses has been theoretically proposed [56]. In Section III-4, comparison will be made between this theoretical analysis in the rectangular-envelope case and numerical electronic WP simulations for pulse excitation with smooth rise and decay.

III-4. Numerical Demonstration for a Six-Membered Ring Molecule

We present the numerical results of electronic WP simulations for an aromatic molecule with a six-membered ring, 2,5-dichloropyrazine (DCP), of which the molecular formula is illustrated in Fig. 2(a). All ab initio electronic structure computations in this article were performed with the 6-31G* Gaussian basis set [57] by using the quantum chemistry program MOLPRO [58]. The geometry of DCP was optimized in the ground state at the level of the second-order Møller-Plesset perturbation theory (MP2) [57] and the optimized geometry was of $C_{2h}$ symmetry. Then, to evaluate the excited-state properties at this geometry, the single-point ground- and excited-state calculation was executed at the state-averaged complete-active-space self-consistent field (CASSCF) [57] level of theory with ten active electrons and eight active (four $a_u$ and four $b_g$) orbitals [abbreviated as CASSCF(10,8)]. At the optimized geometry in the ground state $|G\rangle = |1^1A_g\rangle$, DCP has a pair of optically-allowed quasi-degenerate excited states, $|L\rangle = |3^1B_u\rangle$ and $|H\rangle = |4^1B_u\rangle$, with the energy gap $2\hbar \Delta \omega = 0.44$ eV (Table I). As presented in Table I, the magnitudes of the transition electric dipole moments between the ground and two excited states, $\mu_L$ and $\mu_H$, are 1.66$ea_0$ and 1.58$ea_0$, respectively, where $e$ is the elementary charge and $a_0$ is the Bohr radius; these values ensure $||\mu_L|| \simeq ||\mu_H||$. The directions of $\mu_L$ and $\mu_H$ are depicted in Fig. 2(b). The angle between them is $\chi_H - \chi_L = 0.35\pi$, which is smaller than $\pi/2$ in the degenerate case. The approximate angular momentum eigenstates $|+\rangle$ and $|-\rangle$ in DCP are superpositions of $|L\rangle$ and $|H\rangle$ as in Eq. (6), where $\Lambda = 0.98\hbar$. $\pi$ Electrons with positive (negative) angular momentum travel counterclockwise (clockwise) around the ring in Fig. 2(a).

To elucidate the effects of laser polarization on $\pi$-electron rotation, we compare the results of electronic WP simulations for linear ($\beta = \pi/4$) and circular ($\beta = 0$ and $\pi/2$) polarizations. The orientation angles $\delta$ of the linear polarization vectors $e_{in}$ and $e_{out}$ were evaluated from Eq. (57) [Fig. 2(b)]; the two polarization vectors are almost perpendicular with an angle of $0.48\pi$ as expected from $||\mu_L|| \simeq ||\mu_H||$. For circular polarizations ($e_{+1}$ and $e_{-1}$), we set $\delta = 0$. The excitations by a laser pulse $\varepsilon(t)$ with the four different polarization vectors are termed $e_{in}$, $e_{out}$, $e_{+1}$, and $e_{-1}$ excitations. Instead of the rectangular function adopted in the model analysis in Section III-3, we here assumed a $\sin^2$ envelope:

$$f(t) = \sin^2 \left( \frac{\pi t}{t_d} \right) \text{ for } [0, t_d]$$

(61)

and otherwise zero. The central frequency $\omega$ was determined from Eq. (19) with the energies in Table I: $\omega = 9.62$ eV/$\hbar$ (corresponding to the wavelength of 129 nm). The other common
FIG. 2: (a) Molecular formula of DCP. (b) Directions of transition moments $\boldsymbol{\mu}_L$ and $\boldsymbol{\mu}_H$ at the ground-state optimized geometry of DCP as well as those of linear polarization vectors $\mathbf{e}_{\text{in}}$ and $\mathbf{e}_{\text{out}}$ whose orientation angles are defined by Eq. (51). The angle between $\boldsymbol{\mu}_L$ and $\boldsymbol{\mu}_H$ is $0.35\pi$ and that between $\mathbf{e}_{\text{in}}$ and $\mathbf{e}_{\text{out}}$ is $0.48\pi$.

TABLE I: Properties of optically-allowed $\pi$-electronic excited states of DCP. The excited states whose transition energies from the ground state $|G\rangle = |1^1A_g\rangle$ are less than 10.0 eV are listed. The magnitudes of the transition moments between $|G\rangle$ and the respective excited states are also presented. The \textit{ab initio} geometry optimization for $|G\rangle$ and succeeding single-point calculation were carried out at the MP2/6-31G* and CASSCF(10,8)/6-31G* levels of theory, respectively.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>Transition energy (eV)</th>
<th>Magnitude of transition moment ($e\alpha_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>4^1B_u\rangle$</td>
<td>9.84</td>
</tr>
<tr>
<td>$</td>
<td>3^1B_u\rangle$</td>
<td>9.40</td>
</tr>
<tr>
<td>$</td>
<td>2^1B_u\rangle$</td>
<td>8.04</td>
</tr>
<tr>
<td>$</td>
<td>1^1B_u\rangle$</td>
<td>4.78</td>
</tr>
</tbody>
</table>

laser parameters for the four types of excitations were $t_d = 7.26$ fs and $\varphi = 0$. In analogy to the full-excitation pulse in the rectangular-envelope case, the peak field strength $\varepsilon_p$ was set so that the pulse area $\Omega F(t_d)$, which is equal to $\Omega t_d/2$ for a $\sin^2$ envelope, was $2\arccos \left[-\left(2\Delta\omega/\tilde{\Omega}\right)^2\right]$ with $2\Delta\omega \leq \tilde{\Omega}$. The Rabi frequencies to meet this requirement for $t_d = 7.26$ fs were $\tilde{\Omega} = 0.62$ eV/$\hbar$ and $\Omega = 0.76$ eV/$\hbar$. The values of $\varepsilon_p$ determined from the Rabi frequencies for $\mathbf{e}_{\text{in}}$, $\mathbf{e}_{\text{out}}$, $\mathbf{e}_{+1}$, and $\mathbf{e}_{-1}$ excitations were 5.99, 9.80, 7.22, and 7.22.
the peak positions of a spontaneous e-ring currents should continue flowing (oscillating) even after the end of a laser pulse until ionization on excitations, we numerically solved Eqs. (14) and (15) without the RWA by the Runge-Kutta method. The time step for the numerical integration was 0.0024 fs (2.4 as).

Figure 3 shows the expectation value of electronic angular momentum $L_z(t)$ for the four types of excitations as a function of time. In the course of the interaction with the laser pulse $\gamma(t)$, the timing of the initial increase in the magnitude of $L_z(t)$ and its sign (i.e., the phase in the oscillation of angular momentum) evidently depend on the type of excitation. In Fig. 3(a), the temporal behaviors of $L_z(t)$ for $e_{in}$ and $e_{out}$ excitations are identical except for opposite signs: For $e_{in}$ ($e_{out}$) excitation, $\pi$ electrons start to rotate clockwise (counterclockwise), while in both cases the amplitude of $L_z(t)$ reaches almost $\hbar$ at $t = 5.4$ fs, which is designated by the vertical broken line in Fig. 3(a). This agrees with the difference in the initial relative phase $\theta$ by $\pi$ between the two linear polarization vectors predicted in the model analysis. Compared to $e_{in}$ and $e_{out}$ excitations, the magnitudes of $L_z(t)$ for circular polarizations in Fig. 3(b) grow earlier. In addition, a peak of angular momentum for $e_{+1}$ ($e_{-1}$) excitation indicated by the vertical broken lines in Fig. 3(b) appears 1.6 fs later (1.0 fs earlier) than those at $t = 5.4$ fs in Fig. 3(a). Although there is a small difference between the time intervals 1.6 and 1.0 fs due to the relatively slow rise of the $\sin^2$ envelope, the peak positions of $L_z(t)$ in Fig. 3(b), which oscillate with different phases from those for linear polarizations, are fairly consistent with $\theta = \pm (\chi_H - \chi_L) = \pm 0.35\pi$ for $e_{\pm 1}$. These agreement with the model analysis manifest the controllability of the initial relative phase of the superposed quasi-degenerate states by laser polarization. As in Eq. (55), the magnitude of $L_z(t)$ turns to decrease or even the rotation direction of $\pi$ electrons flips before the laser pulse ceases at $t = t_d = 7.26$ fs. Finally, the total population in the quasi-degenerate states reaches 0.995 and thus the amplitude of $L_z(t)$ achieves 0.97$\hbar$ for all the four types of excitations. This indicates that a smoothly rising and decaying pulse with a pulse area of $2 \arccos \left[ -\frac{2\Delta \omega}{\bar{\Omega}} \right]^2$ can excite almost all the population in $|G\rangle$ as does the full-excitation pulse in the rectangular-envelope case. After irradiation, the angular momentum oscillates with the period of $T = \pi/\Delta \omega = 9.4$ fs as in Eq. (60).

High-intensity UV lights such as used for the simulations in Fig. 3 may induce two-photon excitations to higher excited states or ionizations but the contribution of these additional processes is not large [42, 45, 47]. The use of weaker laser pulses does not affect the conclusions of this article, although less population is transferred to the quasi-degenerate excited states.

IV. LASER-POLARIZATION EFFECTS ON NONADIABATICALLY COUPLED VIBRONIC DYNAMICS

In Section III, we theoretically and numerically examined the effects of laser polarization on $\pi$-electron rotation under the frozen-nuclei condition. Without nuclear motions, ring currents should continue flowing (oscillating) even after the end of a laser pulse until a spontaneous emission relaxes the molecule. However, nonadiabatic couplings with molec-
FIG. 3: Expectation value of the electronic angular momentum $L_z(t)$ in DCP irradiated by (a) linearly and (b) circularly polarized UV laser pulses calculated from electronic WP simulations at the optimized geometry of $|G\rangle$. In panel (a), the expectation values for $e_{in}$ and $e_{out}$ excitations are denoted by the solid and dotted lines, respectively. The peaks at $t = 5.4$ fs are indicated by the vertical broken line. In panel (b), the expectation values for $e_{+1}$ and $e_{-1}$ excitations are denoted by the solid and dotted lines, respectively. The peaks at $t = 4.5$ and 7.0 fs are indicated by the vertical broken lines. The laser pulses fully decay at $t = 7.26$ fs.

It should also be clarified how the polarization of the applied laser influences vibrational motions of the molecule through $\pi$-electron rotation. In this section, we report the results of nuclear WP simulations on effective PESs with respect to selected vibrational modes of the same molecule DCP. The molecule is assumed to be preoriented, e.g., by the nonadiabatic optical alignment technique [12, 18].
IV-1. Effective Potential Energy Surfaces

To select the effective vibrational degrees of freedom for nuclear WP simulations, the geometry of DCP was optimized in the quasi-degenerate excited states |L⟩ and |H⟩ at the CASSCF(10,8) level of theory. The optimized geometries of both |L⟩ and |H⟩ also belong to the C₂ᵥ point group. Hence, the displacements from the optimized geometry of |G⟩ to that of |L⟩ and |H⟩ are totally symmetric. Furthermore, vibrational modes that nonadiabatically couple two ¹B₁u states |L⟩ and |H⟩ are totally symmetric A₉ modes as well. For these reasons, we consider two types of A₉ normal modes with large potential displacements and nonadiabatic coupling matrix element between |L⟩ and |H⟩, namely, breathing and distortion modes of which the vibrational vectors are illustrated in Fig. 4. The harmonic wave numbers of the breathing and distortion modes in |G⟩ are 1160 and 1570 cm⁻¹, respectively. Nonadiabatic couplings between the ground and two excited states were neglected because |L⟩ and |H⟩ lie far above |G⟩ and there is no potential crossing between them near the Franck-Condon region. The two-dimensional adiabatic PESs of |L⟩ and |H⟩ with respect to the normal coordinates of the breathing and distortion modes were calculated at the CASSCF(10,8) level of theory (Fig. 5). There exists an avoided crossing (not a conical intersection) between the PESs, although whether it is an avoided crossing or a conical intersection does not influence the qualitative discussion below. At the crossing point, the two PESs are separated by about 190 cm⁻¹. We performed a calculation at the level of the second-order CAS perturbation theory (CASPT2) [57] and confirmed that the position of the avoided crossing remains unchanged when dynamical electron correlation is taken into account, while the PESs are lowered by ∼3 eV.

FIG. 4: Effective vibrational modes of DCP. Normal mode vectors of the breathing and distortion-modes are represented by arrows.
IV-2. Propagation of Nuclear Wave Packets

We describe the method of real-time nuclear WP propagation for nonadiabatically coupled vibronic dynamics. The initial nuclear WP is set to be the wave function of the vibrational ground state \((v_b, v_d) = (0, 0)\) in \(|G\rangle\), where \(v_b\) and \(v_d\) designate the vibrational quantum numbers of the breathing and distortion modes, respectively. The system is then electronically excited by a laser pulse \(\varepsilon(t)\) of the form in Eq. (18). If the state vector of the system is expanded in terms of the three adiabatic states \(|n\rangle; n = G, L, \text{ and } H\}, the time evolution of the expansion coefficients \(\psi_n(Q,t)\), where \(Q\) is the mass-weighted nuclear position or vibrational mode vector, can be obtained, in principle, from the following equations of motion [59]:

\[
\frac{i\hbar}{\partial t} \psi_n(Q,t) = \left[ -\frac{\hbar^2}{2} \nabla^2 + V_n(Q) \right] \psi_n(Q,t) + \sum_{n'} [G_{nn'}(Q) - \mu_{nn'}(Q) \cdot \varepsilon(t)] \psi_{n'}(Q,t),
\]

where \(\nabla\) is the nabla with respect to \(Q\). \(V_n(Q)\) are the adiabatic potentials and \(G_{nn'}(Q)\) are the nonadiabatic terms defined as

\[
G_{nn'}(Q) \equiv -\frac{\hbar^2}{2} \left( \langle n|\nabla^2 n'\rangle + 2 \langle n|\nabla n'\rangle \cdot \nabla \right).
\]

Nevertheless, in practice, it is difficult to evaluate the nonadiabatic terms \(G_{nn'}(Q)\). An alternative approach is needed to include the effects of nonadiabatic couplings on nuclear WP propagation.

To avoid the above-mentioned problem inherent in the adiabatic representation, we take advantage of the diabatic one. Rigorous construction of the adiabatic-diabatic unitary
transformation matrix requires the derivative coupling matrix \( \langle n | \nabla n' \rangle \) [60, 61], which is, as noted above, difficult to compute. Instead, we utilize the quasi-diabatization scheme proposed by Simah et al. [62] that is based on an analysis of configuration interaction vectors; it has been implemented by the original authors in MOLPRO. We expanded the state vector of the system in terms of the three diabatic states \( \{ | n^D \rangle \} \), each of which is a linear combination of the adiabatic states \( |G \rangle, |L \rangle, \) and \( |H \rangle \). The diabatic WPs \( \psi^D_n (Q,t) \) (expansion coefficients for \( | n^D \rangle \)) can be propagated by solving the coupled equations [59]

\[
i\hbar \frac{\partial}{\partial t} \psi^D_n (Q,t) = -\frac{\hbar^2}{2} \nabla^2 \psi^D_n (Q,t) + \sum_{n'} \left[ V^D_{nn'} (Q) - \mu^D_{nn'} (Q) \cdot \varepsilon (t) \right] \psi^D_{n'} (Q,t), \tag{64}
\]

where \( V^D_{nn'} (Q) \) are the diabatic potentials \( (n = n') \) and couplings \( (n \neq n') \) and \( \mu^D_{nn'} (Q) \) are the transition moments between the two diabatic states. The coupled equations can be integrated numerically with the split-operator method for a multisurface Hamiltonian [63]. The resultant diabatic WPs \( \psi^D_n (Q,t) \) are converted to adiabatic WPs \( \psi_n (Q,t) \).

The split-operator integration of Eq. (64) was executed with the aid of the fast Fourier transform algorithm. For each of the two modes, the domain \([-1.60 \text{ u}^{1/2} \text{a}_0, 1.55 \text{ u}^{1/2} \text{a}_0]\) with \( \text{u} \) being the unified atomic mass unit was divided into 64 grid points at intervals of 0.05 \( \text{u}^{1/2} \text{a}_0 \) so as to represent nuclear WPs. The time step for the WP propagation was 0.0024 fs (2.4 as).

IV-3. Nonadiabatic Population Transfer

Figure 6 shows the temporal change in the populations of the quasi-degenerate states \( |L \rangle \) and \( |H \rangle \) for \( e_{in}, e_{out}, e_{+1}, \) and \( e_{-1} \) excitations. The laser pulses for the four types of excitations were the same as used for the frozen-nuclei simulations in Fig. 3. The populations on the two adiabatic PESs are defined as

\[
P_n (t) \equiv \int dQ | \psi_n (Q,t) |^2 \quad (n = L \text{ and } H).	ag{65}
\]

In all the four cases, a significant amount of the population is transferred to the quasi-degenerate states and divided almost equally between them at \( t < 4 \text{ fs} \). When the laser pulse vanishes at \( t = t_d = 7.26 \text{ fs} \), the total population in the quasi-degenerate states, \( P_L (t_d) + P_H (t_d) \), reaches 0.84, 0.93, 0.89, and 0.91 for \( e_{in}, e_{out}, e_{+1}, \) and \( e_{-1} \) excitations, respectively. The polarization-dependent reductions in \( P_L (t_d) + P_H (t_d) \) from those under the frozen-nuclei condition (0.995) are ascribed to the coordinate dependence of \( \mu_L (Q) \) and \( \mu_H (Q) \) in the Franck-Condon region because the laser pulses were designed with the transition moments at the optimized geometry of \( |G \rangle \) as described in Section III-4.

The subsequent behaviors of \( P_L (t) \) and \( P_H (t) \) are entirely different among the four types of excitations. For \( e_{in} \) excitation [Fig. 6(a)], a small fraction of the population shifts from \( |L \rangle \) to \( |H \rangle \) by \( t \sim 10 \text{ fs} \) and then a downward population transfer takes place around \( t \sim 10-14 \text{ fs} \) by nonadiabatic transition. In the case of \( e_{out} \) [Fig. 6(b)], a considerable amount of the population is transferred from \( |H \rangle \) to \( |L \rangle \) and consequently \( P_L (t) \) is more than seven-times larger than \( P_H (t) \) at \( t \sim 10 \text{ fs} \). Afterwards, the direction of population
transfer is reversed periodically with the rather small portion of the population transferred. In contrast, the nonadiabatic transition for \( e_{+1} \) excitation persists much longer [Fig. 6(c)]: A part of the population is continuously exchanged between the quasi-degenerate states and thus electronic relaxation is completed after \( t = 30 \) fs. In the remaining case, i.e., \( e_{-1} \) excitation [Fig. 6(d)], the behaviors of \( P_L(t) \) and \( P_H(t) \) are more or less intermediate between those for \( e_{in} \) and \( e_{out} \) excitations: A substantial population transfer from \( |H\rangle \) to \( |L\rangle \) is observed around \( t \sim 8–13 \) fs. These distinct patterns in the evolutions of \( P_L(t) \) and \( P_H(t) \) will be explained in Section IV-6. The results in Fig. 6 indicate that the polarization of the applied laser exerts a profound influence on the nonadiabatic transition between the quasi-degenerate states, which occurs mainly after irradiation.

IV-4. Electronic Angular Momentum and Vibrational Spectrum

The expectation value of electronic angular momentum \( L_z(t) \) for the four types of excitations are plotted as a function of time in Fig. 7. For both linear and circular polarizations, the behavior of \( L_z(t) \) is similar to that in Fig. 3 while \( P_L(t) \approx P_H(t) \) \((t < 4 \) fs\) except...
FIG. 7: Expectation value of the electronic angular momentum $L_z(t)$ in DCP irradiated by (a) linearly and (b) circularly polarized UV laser pulses calculated from nuclear WP simulations. In panel (a), the expectation values for $e_{\text{in}}$ and $e_{\text{out}}$ excitations are denoted by the solid and dotted lines, respectively; in panel (b), those for $e_{+1}$ and $e_{-1}$ excitations are denoted by the solid and dotted lines, respectively. The laser pulses fully decay at $t = 7.26$ fs.

for its smaller amplitude due to the less efficiency of excitation and the coordinate dependence of $\Lambda(Q)$ defined by Eq. (56). Then, the amplitude of $L_z(t)$ is reduced gradually, which is a characteristic feature absent in the frozen-nuclei model. The reduction in the angular momentum is attributed to two factors: decrease of the overlap between the WPs moving on the relevant two adiabatic PESs, which is observed even within the Born-Oppenheimer approximation (BOA) [64], and electronic relaxation due to nonadiabatic couplings shown in Fig. 6, which is the major factor. The angular-momentum expectation value $L_z(t)$ can
be expressed using the WPs $\psi_L(Q, t)$ and $\psi_H(Q, t)$ as

$$L_z(t) = 2 \int dQ \text{Im}[\psi_L^*(Q, t) \psi_H(Q, t)] \Lambda(Q).\quad (66)$$

Both of the two factors cause the loss of a superposition of $|L\rangle$ and $|H\rangle$, that is, $\psi_L^*(Q, t) \psi_H(Q, t) \to 0$. The oscillatory curves of $L_z(t)$ for $e_{in}$ and $e_{+1}$ excitations can be approximated by a sinusoidal exponential decay. The lifetime of the decay is $\sim 6$ fs for $e_{in}$ and $\sim 18$ fs for $e_{+1}$, of which difference originates from the different rates of nonadiabatic transition in Figs. 6(a) and 6(c). On the other hand, the amplitudes of $L_z(t)$ for $e_{out}$ and $e_{-1}$ excitations do not undergo a monotonic decrease but make a small transient recovery (around $t \sim 14$–20 fs for $e_{out}$ and $t \sim 18$–24 fs for $e_{-1}$). This recovery arises from the regeneration of the superposition of $|L\rangle$ and $|H\rangle$ due to the upward population transfer in the respective time ranges in Figs. 6(b) and 6(d). A little difference in the oscillation period among the four types of excitations stems from the fact that the energy difference between the two adiabatic PESs in the regions where the WPs run depends on the type of excitation. It turned out from the results in Fig. 7 that $\pi$-electron rotation controlled by the polarization of a laser pulse is attenuated on the timescale of several tens of femtoseconds by nonadiabatic couplings.

Figure 8 depicts the expectation value of the normal coordinates $Q(t) \equiv \langle \Psi(t) | \hat{Q} | \Psi(t) \rangle$ with $\hat{Q}$ being the operator of $Q$. In Fig. 8(a), the behaviors of $Q(t)$ triggered by linearly polarized laser pulses are remarkably dependent on the polarization direction: The vibrational amplitude for $e_{out}$ excitation is more than two-times larger than that for $e_{in}$ excitation. Contrary to this, in Fig. 8(b), the vibration of DCP differs only slightly between circular polarizations $e_{+1}$ and $e_{-1}$, and the trajectories of $Q(t)$ are located between those for linear ones. These findings are reinforced by vibrational spectral analysis. The frequency spectrum of the WP on the lower PES, $\psi_L(Q, t)$, after the nonadiabatic transition from $|H\rangle$ to $|L\rangle$ is given by the Fourier transform of its autocorrelation function \[65]:

$$\sigma_L(\omega) \equiv \text{Re} \int_{t_i}^{t_f} dt e^{i(\omega-1/\tau)(t-t_i)} \int dQ \psi^*_L(Q, t_i) \psi_L(Q, t).\quad (67)$$

The parameter $\tau$ was introduced to smooth the spectra and set at 39.6 fs, which is longer than the vibrational periods of the breathing and distortion modes (28.8 and 21.2 fs). The values of $t_i$ for $e_{in}$ and $e_{out}$, $e_{+1}$, and $e_{-1}$ excitations were 14.0, 10.0, 34.0, and 13.0 fs, respectively, and $t_f - t_i = 99.1$ fs for all of them. The zero of $\omega$ was chosen to be the minimum of the lower PES.

Figure 9 displays the frequency spectra for the four types of excitations. For $e_{in}$ excitation, the maximum value of $\sigma_L(\omega)$ is located at $\tilde{\nu} \sim 1400$ cm$^{-1}$ and another peak appears at $\tilde{\nu} \sim 2500$ cm$^{-1}$ in Fig. 9(a); for $e_{out}$ excitation, the strongest peak of $\sigma_L(\omega)$ is found at $\tilde{\nu} \sim 2500$ cm$^{-1}$ and besides a couple of strong peaks are exhibited at $\tilde{\nu} > 3000$ cm$^{-1}$. The wave numbers of 1400, 2500, and 3000 cm$^{-1}$ are almost identical to those of the lowest three vibrational states $(v_b, v_d) = (0, 0), (1, 0)$, and (0, 1) in $|G\rangle$ owing to the
analogy between $|G\rangle$ and $|L\rangle$ in the PES around its minimum. The frequency spectra for linear polarizations in Fig. 9(a) support that at $t > t_i$, $\psi_L (Q, t)$ is mainly composed of low (high) vibrational quantum states for $e_{in}$ ($e_{out}$) excitation. In marked distinction from linear polarizations, the spectral features for circular ones in Fig. 9(b) are very similar to each other: The primary peaks of $\sigma_L (\omega)$ for $e_{+1}$ and $e_{-1}$ excitations are both at $\tilde{\nu} \sim 1400$ cm$^{-1}$, while the intensities of the other peaks are a little stronger for the latter. This obviously indicates that $\psi_L (Q, t)$ contains the same frequency components for left and right circular polarizations after the nonadiabatic transition.

The striking difference in the vibrational amplitude between $e_{in}$ and $e_{out}$ excitations suggests that ultrafast $\pi$-electron dynamics in aromatic molecules such as DCP for linear polarizations can be distinguished experimentally by vibrational spectroscopy in the frequency domain without time-resolved measurements. This idea may be utilized for rapid identification of molecular chirality since the rotation direction of $\pi$ electrons basically differs between enantiomers according to their alignments with respect to the linear polarization direction.

**IV-5. Comparison to the Born-Oppenheimer Approximation**

We also carried out nuclear WP simulations under the BOA by solving Eq. (62) without the nonadiabatic terms $G_{nn'} (Q)$. The procedure of numerical integration was the same as described in Section IV-2. In this approximation, the nonadiabatic coupling between the quasi-degenerate states was completely neglected and thereby the WPs simply propagated on the individual PESs. As seen in Fig. 10, the phase in the oscillation of angular momentum is dependent on laser polarization in this case as well. However, other features
FIG. 9: The frequency spectra of $\psi_L(Q, t)$, $\sigma_L(\omega)$, defined by Eq. (67) for DCP irradiated by (a) linearly and (b) circularly polarized UV laser pulses. In panel (a), the spectra for $e_{in}$ and $e_{out}$ excitations are denoted by the solid and dotted lines, respectively; in panel (b), those for $e_{+1}$ and $e_{-1}$ excitations are denoted by the solid and dotted lines, respectively. In each case, the values of $\sigma_L(\omega)$ were scaled so that the maximum value is unity.

in Figs. 7 and 8 which are deemed to be caused by nonadiabatic couplings disappear under the BOA as expected: The amplitude of $L_z(t)$ does not decay exponentially but exhibits periodic reduction and recovery in turn owing to the temporal change in the WP overlap. The trajectory of $Q(t)$ in Fig. 11 hardly depends on the type of excitation and the vibrational amplitude is larger than that for $e_{in}$ excitation in Fig. 8(a) but smaller than those for circular polarizations in Fig. 8(b). These facts corroborate that the laser-polarization effects on nonadiabatic transition indeed give birth to the polarization-dependent behaviors in $\pi$-electron rotation and molecular vibration such as the decay of angular momentum with different lifetimes.

IV-6. Wave Packet Interference

Figures 12 and 13 illustrate the propagations of the WPs on the relevant two adiabatic PESs to take a close look at the laser-polarization effects on nonadiabatic transition. For both linear and circular polarizations, the probability densities $|\psi_L(Q, t)|^2$ and $|\psi_H(Q, t)|^2$ created in the two excited states at $t \sim 5$ fs resemble that of the initial WP $|\psi_G(Q, 0)|^2$, and then the WPs start to move along the gradient of each PES. Yet, when the WPs approach the avoided crossing, the nonadiabatic nature of vibronic dynamics in this system emerges differently for the four types of excitations. For $e_{in}$ excitation, the WP on the higher PES is diminished by nonadiabatic transition at $t \sim 12$ fs and the contour map of $|\psi_L(Q, t)|^2$ clearly displays the node originating from the interference which is represented by the broken line in Fig. 12(a); thereafter, the WPs on the two adiabatic PESs are deformed largely. In contrast, the WPs for $e_{out}$ excitation in Fig. 12(b) maintain a Gaussian-like form even after the nonadiabatic transition which is already in progress at $t \sim 8$ fs.

For circular polarizations, the WPs on the two PESs behave as expected from the
FIG. 10: Expectation value of the electronic angular momentum $L_z(t)$ in DCP irradiated by (a) linearly and (b) circularly polarized UV laser pulses calculated from nuclear WP simulations under the BOA. In panel (a), the expectation values for $e_{in}$ and $e_{out}$ excitations are denoted by the solid and dotted lines, respectively; in panel (b), those for $e_{+1}$ and $e_{-1}$ excitations are denoted by the solid and dotted lines, respectively. The laser pulses fully decay at $t = 7.26$ fs.

The laser-polarization effects on the populations $P_L(t)$ and $P_H(t)$, expectation values $L_z(t)$ and $Q(t)$, and WPs $\psi_L(Q,t)$ and $\psi_H(Q,t)$ can be interpreted in terms of interferences between the WP existing on the original PES and that created by nonadiabatic couplings. First, we take the case of $e_{out}$ excitation. As mentioned in the model analysis in Section III,
FIG. 11: Expectation value of the normal coordinates $Q(t)$ of the breathing and distortion modes in DCP irradiated by (a) linearly and (b) circularly polarized UV laser pulses under the BOA. In panel (a), the expectation values for $e_{\text{in}}$ and $e_{\text{out}}$ excitations are denoted by the solid and dotted lines, respectively; in panel (b), those for $e_{+1}$ and $e_{-1}$ excitations are denoted by the solid and dotted lines, respectively. The laser pulses fully decay at $t = 7.26$ fs.

A linearly polarized laser pulse with $e_{\text{out}}$ achieves $\theta = \pi$; in other words, it initially produces a linear combination of $\psi_L(Q, t)$ and $\psi_H(Q, t)$ out of phase in aromatic molecules. Then, their relative quantum phase evolves during irradiation [by $-\vartheta(t)$ in the cases of rectangular-envelope pulses as in Eq. (51)] and also gains a dynamical phase associated with the shape of each PES as the WPs propagate. In nonadiabatic transition, an additional phase shift is further imposed on the WP created by nonadiabatic couplings, which interferes with that on the other PES. We do not quantify the additional phase in DCP, but the downward population transfer around $t \sim 5–10$ fs in Fig. 6(b) implies opposite interferences on the two PESs: The WPs are almost in phase after the nonadiabatic transition from $|H\rangle$ to $|L\rangle$ and interfere constructively on the lower PES, while those after the transition from $|L\rangle$ to $|H\rangle$ are out of phase with destructive interference on the higher PES. The constructive interference on the lower PES works particularly on high vibrational quantum states in $\psi_L(Q, t)$, yielding the strong peaks of $\sigma_L(\omega)$ at $\tilde{\nu} \sim 2500$ cm$^{-1}$ and $\tilde{\nu} > 3000$ cm$^{-1}$ in Fig. 9(a). The direction of the population transfer flips as the relative quantum phase develops as in Fig. 6(b).

Next, for $e_{\text{in}}$ excitation in which the two initially prepared WPs are in phase ($\theta = 0$), the interference effects are reversed from those for $e_{\text{out}}$ excitation: For DCP, the interference is destructive on the lower PES but constructive on the higher one around $t \sim 5–10$ fs. The amount of the WP created by the nonadiabatic transition from $|L\rangle$ to $|H\rangle$, which interferes with $\psi_H(Q, t)$, is less than that for the transition from $|H\rangle$ to $|L\rangle$, which interferes with $\psi_L(Q, t)$; this is the reason why the resultant upward population transfer around $t \sim 5–10$ fs in Fig. 6(a) is small. The WPs on the two PESs then reach the avoided crossing and the reverse population transfer takes place around $t \sim 10–14$ fs. The interference enhances low
the avoided crossing is designated by a circle. | for (a) region on the lower PES as seen in Fig. 12(a).

destructive interferences on the lower and higher PESs, respectively. Consequently, the vibrational quan-

tu

646

NONADIABATICALLY COUPLED π-ELECTRON ... VOL. 52

FIG. 12: Propagation of the adiabatic WPs on the two-dimensional adiabatic PESs of |L⟩ and |H⟩ for (a) e_{in} and (b) e_{out} excitations. The origin of the PESs is the optimized geometry of |G⟩ and the avoided crossing is designated by a circle. The bold contours represent the probability densities |ψ_L(Q, t)|^2 and |ψ_H(Q, t)|^2. The arrows indicate the motion of the center of the WPs. In panel (a), the node in ψ_L(Q, 12.3 fs) is represented by the broken line.

vibrational quantum states in ψ_L(Q, t), increasing the probability density in a low-energy region on the lower PES as seen in Fig. 12(a).

In the cases of circular polarizations, ψ_L(Q, t) and ψ_H(Q, t) are initially neither in phase nor out of phase because θ = ±(χ_H − χ_L) for e_{±1}; for DCP, θ = ±0.35π. Hence, no fully constructive or destructive interference occurs on either PES at t ≈ 5–10 fs, resulting in the vibrational amplitudes in Fig. 8(b) which are intermediate between those for linear polarizations in Fig. 8(a). As the relative quantum phase between the WPs evolves in the negative direction, for e_{−1} excitation with θ = −0.35π, it takes more time than for e_{out} with θ = π but less time than for e_{in} with θ = 0 to experience constructive and destructive interferences on the lower and higher PESs, respectively. Consequently, the downward population transfer for e_{−1} excitation appears at t ≈ 8–13 fs in Fig. 6(d). For e_{+1} excitation with θ = 0.35π, the WPs pass through the avoided crossing before matching the requirement of interference for population transfer and thus the nonadiabatic transition is unfinished until they come closer again to the avoided crossing at t ≈ 30 fs as in Fig. 6(c).
FIG. 13: Propagation of the adiabatic WPs on the two-dimensional adiabatic PESs of $|L\rangle$ and $|H\rangle$ for (a) $e_{+1}$ and (b) $e_{-1}$ excitations. The origin of the PESs is the optimized geometry of $|G\rangle$ and the avoided crossing is designated by a circle. The bold contours represent the probability densities $|\psi_L(Q,t)|^2$ and $|\psi_H(Q,t)|^2$. The arrows indicate the motion of the center of the WPs.

The nuclear WP simulations in this section demonstrated that the initial relative phase $\theta$ between the WPs of the quasi-degenerate excited states, which is determined by the ellipticity angle $\beta$ and orientation angle $\delta$ of the incident light, governs not only electron ring currents but also the subsequent molecular vibration through nonadiabatic couplings. What is more, we can also manipulate the time-dependent phase due to irradiation, namely, $\vartheta(t)$ by tuning the other laser parameters such as the peak field strength $\varepsilon_p$ and pulse duration $t_d$. This suggests that by applying a laser pulse of arbitrary polarization, in principle, it is possible to produce a superposition of the quasi-degenerate states with an arbitrary relative phase. Ultimately, the interference between nuclear WPs in nonadiabatic transition can be controlled as desired by means of attosecond/several-femtosecond laser pulses, leading to sophisticated control of molecular vibrations.
V. CONCLUSIONS

We have reviewed our recent studies on the nonadiabatically coupled vibronic dynamics of aromatic molecules with quasi-degenerate $\pi$-electronic states excited by an ultrashort UV laser pulse of arbitrary polarization. First, the concept of electronic angular momentum eigenstates in aromatic molecules was introduced to quantify laser-driven $\pi$-electron rotation (ring current) in reference to MO theory. Next, for the purpose of analyzing the role of laser polarization in the optical excitation process, we employed the V-type three-level model under the frozen-nuclei condition and derived general formulations of the coherent electronic WP and angular-momentum expectation value in both degenerate and quasi-degenerate systems. The initial relative phase between the quasi-degenerate excited states, $\theta$, is determined by the ellipticity angle $\beta$ and orientation angle $\delta$ of an applied laser field, and the relation among the three variables was provided in Eq. (27). The time-dependent part of the relative quantum phase, $\vartheta(t)$, is adjustable by the laser pulse as well. A desired superposition of the quasi-degenerate states can therefore be created by applying ultrashort laser pulses. The angular-momentum expectation value follows the temporal behavior in the relative quantum phase as shown in Eq. (55) and oscillates after irradiation with the period corresponding to the energy gap between the quasi-degenerate states. The numerical results of electronic WP simulations for a model system of DCP confirmed the controllability of the phase in the oscillation of angular momentum.

Nuclear WP simulations were also carried out on effective PESs of DCP. By nonadiabatic couplings with molecular vibrations, the angular momentum of $\pi$ electrons decays on the timescale of several tens of femtoseconds. The comparison in the expectation values of vibrational coordinates between the linear and circular polarization cases revealed an interesting finding: The amplitude of the molecular vibration coupled to $\pi$-electron rotation is prominently dependent on the orientation of linear polarization vectors, while it is almost the same for left and right circular polarizations. This characteristic dependence of vibrational amplitudes on laser polarization is ascribed to the interference effects in nonadiabatic transition dictated by the relative quantum phase between the WPs. These results suggest the potential application of attosecond/several-femtosecond polarized laser pulses as a promising tool to control molecular vibrations through the WP interference in nonadiabatic transition.

In this article, we focused on ultrafast $\pi$-electron rotation and vibronically coupled molecular vibrations induced by a single-color laser. If a two-color laser is employed, another controlling factor of coherent vibronic dynamics is the relative optical phase between different frequency components [43, 45]. Very recently, the scheme for optical generation of $\pi$-electron rotation has been extended to a nonplanar system [66, 67]. We expect that the knowledge obtained for aromatic molecules serves as a basis for studying more complicated polarization-dependent dynamics in larger systems, e.g., intense-field fragmentation of $C_{60}$ [30]. Control of nonadiabatic vibrational/fragmentation dynamics induced by multiphoton electronic excitation is a worthwhile subject for future research.
Acknowledgements

This work was supported in part by JSPS Research Grants (No. 23550003, No. 23750003, and No. 24245001).

References


I. INTRODUCTION

Innovative progress of ultrashort laser technology in the last three decades has enabled to generate intense laser fields whose electric field strength is comparable to or even exceeds that of the Coulomb binding field within atoms and molecules [1]. Exposed to such intense laser fields, polyatomic molecules have been found to exhibit a variety of characteristic dy-
namical processes such as field alignment [2], molecular orientation [3], stabilization [4], enhanced ionization [5, 6], and dissociation [7]. In particular, fragmentation of multi-charged polyatomic molecules in intense laser fields [1, 8–15], in which molecules undergo rapid bond breaking by “Coulomb explosion” due to intra-molecular Coulombic repulsive forces between the positively charged constituents in the highly charged parent ion, is one of such fundamental dynamical processes. Since the Coulomb explosion occurs very rapidly, the resultant fragmented ions would carry valuable information on instantaneous geometrical structure of the parent molecule just before the Coulomb explosion, providing direct access to the investigation on the structural deformation of molecules induced by laser irradiation [16, 17]. Thus, fragmentation of polyatomic molecules via Coulomb explosion has been an attractive research field in the last decade both experimentally and theoretically [18].

A recently developed experimental method called coincidence momentum imaging (CMI) [16], which allows the determination of the full momentum vectors of all the fragmented ions ejected from a single parent molecular ion in an ultrashort intense laser field, provides the possibility to snapshot the molecular structure just before Coulomb explosion in intense laser fields. The CMI method employs a multi-hit position sensitive detector (PSD), which offers two major advantages over the previous momentum imaging methods such as the mass-resolved momentum imaging [19, 20] and the covariance mapping [10]. First, all the fragment ions originating from a single parent ion are identified in coincidence so that the charge number of the parent ions as well as its dissociation pathways can be specified definitively. Second, the three-dimensional (3D) momentum vectors of respective fragment ions are determined in the laboratory frame for every single event of the Coulomb explosion. For example, for hydrocarbon molecules, it was reported by using CMI method that di- and tri-atomic hydrogen molecular ions can be ejected from alcohol molecules in an intense, short-pulse laser field [21, 22], which revealed that the fragmentation of hydrocarbon molecules via Coulomb explosion is generally accompanied by remarkably fast hydrogen and/or proton migration from one site to another within a molecule.

Due to the large mobility of hydrogen atom or proton, ultrafast intra-molecular processes of hydrogen migration can lead to large-scale deformation of molecular skeletal structure and rearrangement of chemical bonds, and thus often determine the main reaction routes of fragmentation by suppressing other competing processes [23]. Especially fragmentation of hydrocarbon molecules may result in new fragment species that could not be realized from the initial geometry of molecules by direct bond breaking, which makes hydrogen migration one of the most important molecular rearrangement processes in various chemical reactions [24, 25] as well as in strong laser field phenomena [13, 26, 27].

So far, a series of intensive studies of laser-induced hydrocarbon molecular fragmentation via Coulomb explosion has been investigated by the CMI method, which aimed to explore more details about the ultrafast dynamics of molecules and to control the molecular bond-breaking and bond-creation behaviors in chemical reactions induced by intense laser fields. Indeed, impressive study progress in the fragmentation of hydrocarbon molecules induced by intense laser fields has been made by using the CMI method, which includes different species of hydrocarbon molecules such as alkanes (e.g. acetonitrile [26, 28]), alkenes including olefin (e.g. ethylene [29], allene [27, 30, 31]) and diolefins (e.g. 1,3-
butadiene [29, 32–35]), alkynes (e.g. acetylene [36, 37] and methyl acetylene [38, 39]), alcohol (e.g. methanol [22, 40–44] and ethanol [29]) and aromatic hydrocarbon such as benzene [45]. Identification of the fragmentation channels from two-body [26, 28, 30, 38, 40, 43, 44, 46], three-body [27, 34, 36, 41, 44], four-body [37], even complete Coulomb explosion process [34] has been successfully realized. Furthermore, based on the correlations of the fragment momentum vectors determined by the CMI method, identification of the fragmentation of a specific channel occurring in a sequential or a concerted manner can also be realized [35, 41].

By using the CMI method, the fragmentation of hydrocarbon molecules accompanied with the hydrogen atom (or proton) migration has been studied as well [28], which revealed that, taking the triply charged 1,3-butadiene for example, not only one proton but two protons can migrate in intense laser fields [34]. It was also shown that the intense laser field can induce two distinctively different stages of the hydrogen migration in hydrocarbon molecules, that is the hydrogen migration occurring within the laser pulse and the post-pulse hydrogen migration process [47]. In addition, the competition between the hydrogen-atom migration and the Coulomb explosion during the fragmentation in intense laser fields was studied [48, 49]. It is worth of stressing that isomerization of acetylene to vinylidene has been extensively studied as a prototype of hydrogen migration in intense laser fields by different methods [23, 46, 50–53].

Since one of the major goals in modern photochemistry is to control photo-induced chemical reactions by designing light pulses, the effects of parameters of ultrashort laser pulses such as intensity [35], pulse duration [54], polarization state [35] and wavelength [54] on the fragmentation of hydrocarbon molecules in intense laser fields have also been investigated. Control of hydrocarbon molecular fragmentation channels on sub-fs time scale via optical waveform controlled laser field was realized [55]. Recently, the effects of laser parameters on ultrafast hydrogen migration in the fragmentation of methanol have been systematically studied as well [56], in order to show the feasibility for controlling chemical bond formation as well as chemical bond breaking by controlling the motion of hydrogen atoms (or protons) within a hydrocarbon molecule.

Therefore, the purpose of this article is to review recent progress in the study of fragmentation of hydrocarbon molecules induced by intense laser fields using the CMI method, which can provide definite information on the ultrafast fragmentation dynamics of molecules. The article is organized as following: In Section II we will briefly introduce the CMI method, which shows itself as a versatile tool for investigating ultrafast molecular reaction dynamics. Section III we will give an overview of the recent achievements in the study of fragmentation of hydrocarbon molecules via Coulomb explosion CMI method. In Section IV real-time visualizing ultrafast fragmentation dynamics of hydrocarbon molecules by the pump-probe Coulomb explosion CMI method will be presented. In Section V a short summary is given.
II. COINCIDENCE MOMENTUM IMAGING

The CMI method has been growing in popularity and sophistication over the last 20 years [57–66], and was first introduced for studying the decomposition processes of molecules in intense laser fields in 2001 [16]. In the CMI method, all the fragment ions produced from a single parent molecular ion are detected in coincidence using a PSD, allowing a secure assignment of the fragmentation pathways. In addition, the momentum vectors of the respective fragment ions ejected by a single Coulomb explosion event are determined in the laboratory frame, from which detailed information on the geometrical structure of a parent ion at the instance of the Coulomb explosion can be obtained. It has been demonstrated in the previous studies that the CMI method is an ideal approach to investigate, at a single molecular level, the fragmentation dynamical processes of polyatomic molecules including the ultrafast hydrogen migration dynamics in an intense laser field.

A typical CMI apparatus is shown in Fig. 1 [16]. Intense laser fields in laser-molecule interaction region were generated by focusing ultrashort femtosecond laser pulses (e.g. from a femtosecond Ti: Sapphire Chirped Pulse Amplification (CPA) laser system) onto the crossing point of a sample molecular beam at right angles in an ultrahigh vacuum chamber (up to $10^{-11}$ mbar). The density of the molecular beam was controlled so that the number of ionized molecules per laser pulse becomes less than one unity. The laser polarization direction was set to be parallel to the detector plane.

![Diagram](image)

FIG. 1: A typical CMI experimental apparatus (Adapted from [16]).

The laser produced ions or electrons in the intersection area can be extracted by a three-electrode electrostatic lens to a Position Sensitive Detector (PSD) with delay-line anodes [61]. The three-electrode electrostatic lens is composed of three equally spaced ($d = 15$ mm) parallel plate electrodes, which are defined as repeller, accelerator and ground electrodes. The electrodes are 0.2-mm-thick stainless steel plates with a 70 mm diameter. The repeller electrodes contain a small hole $\sim 1–2$ mm, which passes through the on-axis
molecular beam, and the accelerator and ground electrodes are with a 20-mm diameter hole in the velocity mapping configuration to avoid the blurring effect on the ion images, which could occur when mesh grids are employed. Ions produced by the laser excitation are first pushed away by the repeller plate, and then accelerated after passing the accelerator plate toward the open ground electrode. And then the ions enter a time-of-flight (TOF) tube between the ground electrodes and the detector, which is a vacuum enclosure, free of electrical fields, and usually referred to “field free drift region”. The voltages applied to the repeller and the accelerator plates can be adjusted to achieve optimized conditions of the ion images.

After passing through the TOF tube, the charged particles are detected by a position-sensitive microchannel plate (MCP) detector with delay-line-anode readouts, which can realize acquisition of the signals from the hardware modules and recording of data event-by-event to PCs for further online/offline data analysis. The delay-line anode also benefits in many aspects, such as allowing the detection for much higher rates in MHz, achieving high position and time resolution and extending the capability to handle multiple hits in nanosecond time intervals. The signals on each end of the anodes generated from the respective fragment ions generated by an event of the Coulomb explosion of a single parent molecule are amplified and discriminated, and then processed to a time-to-digital converter, based on which the \((x, y)\) positions on the PSD and the time of flight, \(T\), of the respective ions can be obtained. The position resolution of the MCP delay-line detector can be less than 0.1 mm, and the MCP multi-hit dead time is about 10-20 ns. Therefore the MCP detector with delay-line-anode can provide high resolution of three-dimensional imaging and timing information for charged particles detection at high rates with multi-hit capability.

The 3D momentum vector, \(p = (p_x, p_y, p_z)\), of a single fragmented ion at its birth can be retrieved by its recorded position \((x, y)\) on the detector plane and its time-of-flight, \(T\) [16]. The two momentum components, \(p_x\) and \(p_y\), along the \(x\)- and \(y\)-axes in the laboratory frame (see Fig. 1) are expressed as

\[
p_x = m \Delta x / T, \tag{1}
\]

\[
p_y = m \Delta y / T, \tag{2}
\]

with \(m\) being the mass of the ion, and \((\Delta x, \Delta y)\) the displacements of the fragment ion from the position where the ion with \(p_x = p_y = 0\) would hit. The momentum component \(p_z\) along the \(z\)-axis is expressed as

\[
p_z = \{\alpha q \cdot (U_{rep} - U_{acc})/d\} \cdot (T_0 - T) \tag{3}
\]

where \(q\) is the charge of the ion, \(T_0\) is the arrival time of fragment ion with \(p_z = 0\), and \(U_{rep}\) and \(U_{acc}\) are the electric potentials at the repeller and accelerator plate electrodes, respectively. The correction factor \(\alpha\) is introduced for compensating a weak inhomogeneity of the electric field in the repeller and accelerator region.

The spectrometer in the CMI technique can also be used to project ions and electrons onto oppositely positioned detectors equipped at the two ends of the spectrometer, as shown in Fig. 2.
Here we will briefly give the forms of the 3D momentum vector, \( p = (p_x, p_y, p_z) \), for both ions and electrons recorded by the CMI technique with a uniform electrostatic field and a uniform magnetic field applied to the spectrometer [62–64]. Supposing the Cartesian lab-coordinate system is defined as following: the direction of the cold gas jet is along the \( x \) axis, the direction of the laser beam propagation is along the \( y \) axis and the electrostatic field direction is along the \( z \) axis.

The initial three momentum components of the \( i \)th ion from a single parent molecular ion, \( p^i = (p^i_x, p^i_y, p^i_z) \), in the laboratory frame can be expressed as
\[
p^i_x = m_i \Delta x / T, \tag{4}
\]
\[
p^i_y = m_i \Delta y / T, \tag{5}
\]
\[
p^i_z = m_i l_a / T - (1/2)q_i E_s T, \tag{6}
\]
where \( m_i \) and \( q_i \) are the mass and the charge of the ion from a single parent molecule respectively, and \( \Delta x, \Delta y \) are the displacements of the fragment ion from the position where the ion with \( p_x = p_y = 0 \) would hit, \( T \) is the time-of-flight of the ion from the reaction volume to the detector, \( l_a \) is the travelling distance of the ion in the \( z \)-axis direction, and \( E_s \) is the magnitude of the uniform electrostatic field of the spectrometer.

The initial three momentum components of electron, \( p^e = (p^e_x, p^e_y, p^e_z) \), in the laboratory frame can be expressed as
\[
p^e_x = \{eB/(2 \sin(\alpha/2))\} \{-x \cdot \cos(\alpha/2) + y \cdot \sin(\alpha/2)\}, \tag{7}
\]

FIG. 2: A typical CMI apparatus for photon-electron and photon-ion detection.
\[ p_y^e = \left\{ eB/(2\sin(\alpha/2)) \right\}\{x \cdot \sin(\alpha/2) + y \cdot \cos(\alpha/2)\}, \tag{8} \]
\[ p_z^e = m_e l_a / T - (1/2)eE_s T, \tag{9} \]
where \( m_e \) and \( e \) are the mass and the charge of the electron respectively, and \( B \) is the magnitude of the uniform magnetic field. \( \alpha \) depends on the ratio of the time-of-flight to the electron orbital period \( T \) with the following relation

\[ \alpha = \text{mod} \left( T, T_0 \right) \times 360^\circ, \tag{10} \]
where \( T_0 = 2\pi m_e/eB \). For details of expressions of the full momentum vectors for both ions and electrons in the CMI technique, the readers are referred to Ref. [60].

III. FRAGMENTATION OF HYDROCARBON MOLECULES IN INTENSE LASER FIELDS STUDIED BY CMI

Fragmentation reactions of polyatomic molecules are essential building blocks of chemistry. Earlier investigations on fragmentation of triatomic molecules such as CO\(_2\) [19] and CS\(_2\) [20] in intense laser fields have unveiled the large deformation of their skeletal structure along both the bending and the stretching coordinates. Since the CMI technique was successfully applied to strong field physics and chemistry for studying the decomposition processes of molecules [16], intensive studies of fragmentation dynamical processes of hydrocarbon molecules have been carried out, which pushes forwards a lot on current understanding of strong field laser-induced molecular dynamics. In this section, we will give an overview of the recent (after the year 2000) achievements in the study of fragmentation dynamics of different hydrocarbon molecules by the Coulomb explosion CMI method, which includes the identification of the fragmentation channels, molecular structural deformation, the ejection of di- and tri-hydrogen molecular ions, the ultrafast hydrogen migration dynamics, the sequential versus concerted fragmentation dynamics, and control of molecular fragmentation dynamics via laser pulse parameters and intra-molecular hydrogen migration process. The reason why hydrocarbon molecules were paid much attention is due to ultrafast hydrogen migration which may proceed when hydrocarbon molecules are exposed to intense laser fields and makes the full characterization of fragmentation dynamics complicated. It would be very meaningful to get a more detailed insight into the fascinating ultrafast hydrogen migration phenomena that may contribute to controlling laser-induced chemical bond breaking and formation in photo-chemistry.

III-1. Identification of molecular fragmentation channels

By using the CMI method as introduced previously, the position and the time of flight of each detected charged particle can be measured, based on which the 3D momentum vector of the particle can be deduced. To identify a specific fragmentation channel of a molecule from the multi-body Coulomb explosion, the momentum of electrons can be
neglected because the momentum imposed on an emitted electron is more than two orders of magnitude smaller than that of the fragment ions. Therefore, according to the momentum conservation conditions in all three spatial dimensions, a particular fragmentation channel of molecules decomposed from one particular charge state of interest can be uniquely identified by selecting only sets of fragment ions whose sum-momentum \( P_s = p_i^s \) fulfills \(|P_s| = 0\), where \( p_i^s \) (\( s = x, y, z \) in the laboratory frame) denotes the momentum of the \( i \)th fragment ion produced from a single parent ion along the \( s \)-axis. As a result false coincidence events originating from more than two parent ions in the interaction region were excluded based on the momentum vectors of all the fragment ions from a single parent ion detected in coincidence.

By using the CMI method, two-body Coulomb explosions of acetylene \([46]\), acetonitrile (CH\(_3\)CN) and deuterated acetonitrile (CD\(_3\)CN) \([26, 28]\), methanol (CH\(_3\)OH) \([22, 40, 42, 44]\) and its isotopomers (CD\(_3\)OH, CH\(_3\)OD) \([40, 42, 43]\), allene \([30]\), 1,3-butadiene \([32]\), methylacetylene (CH\(_3\)CCH) and its isotopomer methyl-d\(_3\)-acetylene (CD\(_3\)CCH) \([38]\) in intense laser field have been investigated and the corresponding two-body Coulomb explosion fragmentation channels have been identified. Three-body Coulomb explosion fragmentations of methanol-d\(_2\) (CH\(_3\)OD\(_3^+\)) \([41]\), acetylene \([36, 37]\), methanol \([44]\), allene \([27, 31]\), 1,3-butadiene \([33, 35]\), acetylene \([36]\), methylacetylene (CH\(_3\)CCH) and its isotopomer methyl-d\(_3\)-acetylene (CD\(_3\)CCH) \([39]\) in intense laser field have also been identified. Four-body Coulomb explosion fragmentation channels of acetylene \([37]\) and even complete Coulomb explosion of highly charged 1,3-butadiene (CH\(_2\)CHCHCH\(_2\)) \([34, 67]\) and methane (CH\(_4\)) molecules \([67]\) in intense laser fields have been identified as well. In the later study of complete Coulomb explosion of molecule, it was very interesting that the energetic protons could be ejected from a concerted Coulomb explosion from unexpectedly high charge states of polyatomic hydrocarbon molecules induced by intense laser fields \([34]\). The observations were explained by the enhanced ionization taking place at many C-H bonds simultaneously. The occurrence of enhanced ionization of hydrocarbon molecules was also observed in dissociative double ionization of formic acid by intense 100 fs laser pulses at 800 nm using ion–ion coincidence momentum spectroscopy \([68]\).

III-2. Molecular structural deformation

With the identification of the fragmentation channels of a molecule, the fragmentation dynamics with interest can be discussed based on the momentum correlations of the involved fragment ions as they provide a deeper understanding on the molecular structural deformation. In early measurement using the CMI technique, the molecular geometrical structure of CS\(_2^+\) just before the Coulomb explosion of CS\(_2^+\) \(\rightarrow\) S\(^+\) + C\(^+\) + S\(^+\), was constructed straightforwardly from the momentum correlations of the three fragment ions, which exhibited that the C-S bond length and the S-C-S bond angle vary rapidly in the laser fields, revealing the skeletal structural deformation of CS\(_2\) (see Fig. 3) \([16]\). Subsequent investigation of structural deformation of hydrocarbon molecules induced by intense laser fields was carried out by the CMI method.

In the investigation of the two-body Coulomb explosions of acetonitrile, CH\(_3\)CN\(^{2+}\) \(\rightarrow\) CH\(_{3-n}^+\) + H\(_n\)CN\(^+\) \((n = 0–2)\), and of deuterated acetonitrile, CD\(_3\)CN\(^{2+}\) \(\rightarrow\) CD\(_{3-n}^+\) + D\(_n\)CN\(^+\)
FIG. 3: The reconstructed geometrical structure of CS$_2^{3+}$ just before the three-body Coulomb explosion of CS$_2^{3+} \rightarrow S^+ + C^+ + S^+$ (Adapted from [16]).

$(n = 0–2)$, in intense laser fields (0.15 PW/cm$^2$, 70 fs) by the CMI method [26, 28], it was found that the doubly charged parent molecules undergo the substantial structural deformation in intense laser fields along the C–C–N bending coordinate prior to the two body explosion. The two-body Coulomb explosion of allene (CH$_2$CCH$_2$) induced by an ultrashort ($\sim$ 40 fs) intense laser field by the CMI method [30] reported that structural deformation of the C-C-C skeleton was expected to occur by the migration of the hydrogen atom in C$_3$H$_4$ based on the fragmentation channels of C$_3$H$_2^{4+} \rightarrow$ CH$^+ +$ C$_2$H$_3^{+}$ and C$_3$H$_2^{4+} \rightarrow$ CH$_3^+ +$ C$_2$H$^+$. However, by the two-body Coulomb explosion, it is difficult to obtain the information on how large the structural deformation proceeds.

The three-body Coulomb explosion of hydrocarbon molecules was also used to study the structural deformation by using the triple-ion CMI method [27, 33]. From the momentum correlation maps, the geometrical structures of triply charged allene [27] and 1,3-butadiene [33] were shown. In particular, it was recently revealed that the molecular structural deformation to non-planar geometry can be identified by the time-resolved four-body Coulomb explosion CMI, highly charged deuterated acetylene (C$_2$D$_2^{4+}$) [37].

III-3. Ejection of di- and tri-atomic hydrogen molecular ions

The ejection of hydrogen molecular ions, H$_2^+$ and H$_3^+$ is a noteworthy dynamical process in the fragmentation of hydrocarbon molecules in intense laser fields because it may reflect the ultrafast intramolecular dynamics of hydrogen atoms in hydrocarbon molecules. By using the CMI method, formation of H$^+$, H$_2^+$ and H$_3^+$ was confirmed from the ion ejection
through two-body coulomb explosions of \( \text{CH}_3\text{OH}^{2+} \rightarrow \text{H}^+_n + \text{COH}^+_4-n \) \( (n = 1\text{–}3) \) of doubly charged methanol [22], and the lifetimes of the corresponding precursor ions \( \text{CH}_3\text{OH}^{2+} \) are estimated to be 70–290 fs for the \( \text{H}^+ \) ejection, 110–550 fs for the \( \text{H}_2^+ \) ejection, and a much longer value than 1.4 ps for the \( \text{H}_3^+ \) ejection.

The ejection of hydrogen molecular ions from two-body Coulomb explosion processes of methanol (\( \text{CH}_3\text{OH} \)) and its isotopomers (\( \text{CD}_3\text{OH} \) and \( \text{CH}_3\text{OD} \)) was also systematically studied by using the CMI method in order to clarify ultrafast dynamics of hydrogen atoms in hydrocarbon molecules in intense laser field [42]. In this study, the ejection hydrogen molecular ions through the fragmentation channels of \( \text{CH}_3\text{OH}^{2+} \rightarrow \text{H}^+_m + \text{CH}_{(3-m)}\text{OH}^+ \) \( (m = 2, 3) \), \( \text{CD}_3\text{OH}^{2+} \rightarrow \text{D}^+_m + \text{CD}_{(3-m)}\text{OH}^+ \) \( (m = 2, 3) \) and \( \text{CH}_3\text{OD}^{2+} \rightarrow \text{H}^+_m + \text{CH}_{(3-m)}\text{OD}^+ \) \( (m = 2, 3) \) were identified. In addition, the ejections of H/D exchanged hydrogen molecular ions (\( \text{HD}^+, \text{HD}_2^+ \) and \( \text{H}_2\text{D}^+ \)) were observed, and the timescales for the H/D exchanging processes were also estimated from the extent of anisotropy in the ejection directions [42]. Formation of \( \text{H}^+, \text{H}_2^+ \) and \( \text{H}_3^+ \) through two-body Coulomb explosion of other hydrocarbon molecules such as allene has also been identified, as shown in Fig. 4.

**FIG. 4:**Observed two-dimensional coincidence momentum maps of (a) \( \text{H}^+ \), (b) \( \text{H}_2^+ \), and (c) \( \text{H}_3^+ \) produced through the two-body Coulomb explosion processes of \( \text{C}_3\text{H}_4^{4+} \). (Adapted from [30].)

Furthermore, ejections of \( \text{H}^+ \) and \( \text{H}_2^+ \) ions from three-body fragmentation channels of triply charged methanol and methanol-d through \( \text{CH}_3\text{OH}^{3+} \rightarrow \text{H}^+ + \text{H}_2^+ + \text{COH}^+ \) and \( \text{CH}_3\text{OD}^{3+} \rightarrow \text{H}^+ + \text{H}_2^+ + \text{COD}^+ \) induced by an ultrashort intense laser field was investigated [41], in which it was identified for the first time that there are two types of sequential pathways: one is a pathway in which \( \text{H}^+ \) is ejected first and the other is a pathway in which \( \text{H}_2^+ \) is ejected first.

### III-4. Ultrafast hydrogen migration

The hydrogen migration process, in which hydrogen atom(s) or proton(s) migrates from one site to another within a molecule, can lead to large-scale deformation of molecular skeletal structure and chemical bond rearrangement, and thus may result in reaction channels that could not be realized when reactions start from the initial molecular geometries [26]. Investigations of fragmentation of polyatomic molecules in intense laser fields by the CMI method have revealed the existence of ultrafast hydrogen migration in a series of hydrocarbon molecules [52, 73].
Two-body Coulomb explosion of acetonitrile (CH$_3$CN) and deuterated acetonitrile (CD$_3$CN), in intense laser fields (0.15 PW/cm$^2$, 70 fs) was reported in 2004 by the CMI method, in order to clarify the hydrogen migration process occurring simultaneously with the abrupt C-C bond breaking [26, 28]. Three different explosion pathways for the respective species, i.e., CH$_3$CN$^{2+} \rightarrow$ CH$_3^+ + H_n$CN$^+$ ($n = 0$–2) and CD$_3$CN$^{2+} \rightarrow$ CD$_3^+ + D_n$CN$^+$ ($n = 0$–2), were securely identified, and the migration of hydrogen atom (or proton) from CH$_3$ moiety to the CN moiety was readily identified by detecting HCN$^+$ or H$_2$CN$^+$ fragments because all the three hydrogen atoms belong initially to the terminal carbon atom. It was found that the fragment anisotropy becomes more isotropic as $n$ increases from 0 to 2, showing that the rate of the Coulomb explosion becomes comparable with or even longer than the rotational period of the parent molecule as the migration of hydrogen atoms from the methyl group to the nitrile group proceeds.

To give a deeper understanding of the hydrogen migration, the dissociation pathways with hydrogen/deuterium migration or hydrogen/deuterium exchange have been investigated [38–40]. It was shown on methanol (CH$_3$OH, CD$_3$OH, CH$_3$OD) that hydrogen/deuterium migration or hydrogen/deuterium exchange prior to the C-O bond breaking in an intense laser field (0.2 PW/cm$^2$, 60 fs) was securely confirmed by the CMI method [40]. From the anisotropic angular distributions and the relative yields of the fragment ions, it was revealed that the hydrogen migration process was terminated within the period of an intense ultrashort laser pulse. A comparison of the results obtained from CH$_3$OH and those from its isotopomers showed that the hydrogen migration was decelerated by the isotope substitution. By studying the two-body Coulomb explosion of methanol by the CMI method, pulse duration effect on the hydrogen migration has also been explored. In comparison of hydrogen migration pathway and non-hydrogen migration pathway of methanol with the C-O bond breaking obtained with the pulse durations [43], it was shown that when the pulse duration becomes longer, the major ionization mechanism for both the direct and the migration pathways changes from the nonsequential ionization to the sequential ionization and the hydrogen migration occurs more efficiently.

The two-body and three-body break-up channels involving association and migration of hydrogen atoms during the fragmentation of methanol dication were also investigated via the CMI technique to further study how the hydrogen atom migrates during a sequential breakup fragmentation channel [44]. Three-body associative break-ups were found to occur sequentially, triggered by the loss of one hydrogen atom, followed by separation of charges. Based on the fragment momentum distributions it was proposed that hydrogen atom migration was induced in the first stage of the sequential breakup.

The isomerization between acetylene (HCCH) and vinylidene (H$_2$CC) via hydrogen migration has been extensively studied as a prototype of hydrogen migration [8, 14–22, 36, 46]. The angle between the momenta of C$^+$ and H$^+$ fragments exhibited a sharp distribution peaked at a small angle ($\sim 20^\circ$) when ultrashort ($\sim 9$ fs) laser pulses was applied, showing that the hydrogen atom remained near the original carbon site in the acetylene configuration. However a significantly broad distribution extending to larger momentum angles ($\sim 120^\circ$) was observed when the pulse duration was increased to 35 fs, indicating that the ultrafast isomerization to vinylidene was induced in the longer laser
pulse.

Ultrafast hydrogen migration in allene (CH$_2$=C=CH$_2$) in intense laser fields was also investigated by the CMI method [27, 30, 31]. Two types of two-body Coulomb explosion pathways, C$_3$H$_7^{2+} \rightarrow$ CH$_3^+ +$ C$_2$H$_4^{m-}$ (m = 1–3) and C$_3$H$_7^{2+} \rightarrow$ C$_3$H$_5^{-n} +$ H$_n^+$ (n = 1–3), were securely identified. The formation of CH$_3^+$, C$_2$H$_3^+$, and H$_3^+$ showed that the chemical bond rearrangement associated with the ultrafast hydrogen migration occurs and that the extent of the hydrogen migration determines either one of the two initially identical C=C chemical bonds was broken [30]. By the combination of the momentum correlation maps and the geometrical structure of triply charged allene reconstructed from the observed momentum vectors of fragment ions, the migrating proton covering the entire range of an allene molecule was visualized, as shown in Fig. 5 [27]. The extent of hydrogen migration was also found to play a decisive role in breaking selectively one of the two initially equivalent C–C chemical bonds that become inequivalent in the course of the hydrogen migration. Moreover it was further shown that the decomposition of highly charged allene ion via three-body Coulomb explosion proceeds in a stepwise manner as well as in a concerted manner, and the time scale of the hydrogen migration within allene was estimated to be $\sim$ 20 fs [31].

The existence of ultrafast hydrogen atom migration was also found in 1,3-butadiene (H$_2$C=CH-CH=CH$_2$) in intense laser fields using the CMI method [32, 33]. In the two-body dissociation processes of doubly charged 1,3-butadiene, the existence of the two dissociation pathways, C$_4$H$_8^{2+} \rightarrow$ CH$_3^+ +$ C$_3$H$_3^+$ and C$_4$H$_8^{2+} \rightarrow$ C$_2$H$_2^+ +$ C$_2$H$_4^+$, can be regarded as evidences of the chemical bond rearrangement processes associated with hydrogen migration in the intense laser field. It was found that the hydrogen atom bonded originally to one of the two central carbon atoms migrates preferentially to its neighboring terminal carbon atom site [32, 33]. The spatial distribution maps of a migrating proton reconstructed for the two three-body Coulomb explosion pathways, C$_4$H$_6^{3+} \rightarrow$ H$^+$ + CH$_3^+ +$ C$_3$H$_3^+$ and C$_4$H$_6^{3+} \rightarrow$ H$^+$ + C$_2$H$^+$ + C$_2$H$_4^+$, revealed that two protons migrate within a 1,3-butadiene molecule, prior to the three-body decomposition [33]. Two-proton migration process was also found in the two-body decomposition processes of methylacetylene (CH$_3$CCH) and its isotopomer methyl-d$_3$-acetylene (CD$_3$CCH) in intense laser fields (790 nm, 40 fs, 5.0 $\times$ 10$^{13}$ W cm$^{-2}$). It was revealed from the analysis of the CMI data that the migration of two deuterons as well as the exchange between a proton and a deuteron occurs prior to the two-body decomposition of a doubly charged parent molecule [38].

Hydrogen and deuteron migration processes were further investigated in the three-body Coulomb explosion processes of triply charged ions of methylacetylene (CH$_3$-C≡C-H) and its isotopomer, methyl-d$_3$-acetylene (CD$_3$-C≡C-H), induced by an ultrashort intense laser field (790 nm, $\sim$ 40 fs, 5.0 $\times$ 10$^{13}$ W cm$^{-2}$), from the observed momentum vectors of all the three fragment ions for each decomposition pathway and the proton and deuteron distributions constructed in the coordinate space [39]. It was shown that the hydrogen migration proceeds more efficiently from the methyl group than from the methane group. In addition to the decomposition pathways accompanying the migration of one H (or D) atom, the decomposition pathways accompanying the migration of two light atoms (H/D exchange and 2D migration) were identified. Furthermore, the decomposition pathways ascribable to
III-5. Sequential versus concerted fragmentation dynamics

Using the CMI method, it was possible to elucidate how the Coulomb explosion actually proceeds, whether in a concerted manner or in a sequential manner. The first investigation using CMI technique to explore this issue was successfully carried out for CS$_2^{3+}$ in intense laser fields [17] where the formation of a sequential explosion of CS$_2^{3+}$ prior to the complete three-body fragmentation was unveiled. Similar investigations were subsequently carried out on hydrocarbon molecules.

The three-body Coulomb explosion of triply charged methanol-d (CH$_3$OD$^{3+}$) through CH$_3$OD$^{3+}$ → H$^+$ + H$_2^+$ + COD$^+$ induced by a laser field of $\sim 2 \times 10^{14}$ W/cm$^2$ was investigated by the CMI method [41], in which it was identified that the explosion proceeds in a stepwise manner with two types of sequential pathways: one is the pathway in which H$^+$ is ejected first, and the other is the pathway in which H$_2^+$ is ejected first. It was revealed from
the CMI data that when $H^+$ is ejected first the broad distribution of $H^+$ ejection direction indicates that the torque is efficiently imposed on $\text{CH}_2\text{OD}^{2+}$ for the rotational excitation, and/or the lifetime of $\text{CH}_2\text{OD}^{2+}$ is longer than the rotational period of $\text{CH}_2\text{OD}^{2+}$; however when the $H_2^+$ is ejected first the narrow distribution of $H_2^+$ ejection angle suggested not large enough torque on $\text{CHOD}^{2+}$ at the first-step decomposition for the efficient rotational excitation of the $\text{CHOD}^{2+}$. The narrow distribution was also considered to come from the shorter lifetime of $\text{CHOD}^{2+}$.

Three-body associative break-ups of methanol dication were found to occur sequentially, triggered by the loss of one hydrogen atom, followed by separation of charges [44].

The analysis of the fragment momentum correlations in the fragmentation of deuterated benzene ($C_6D_6$) in ultrashort intense laser fields (9 fs, $1 \times 10^{15}$ W/cm$^2$) by the CMI method revealed that all the observed three-body explosion processes proceed sequentially via the formation of molecular dications $C_mD_n^{2+}$, with $(m,n) = (6,5), (5,5), (5,4), (4,4), (4,3),$ and (3,3) as precursors, which further dissociate into pairs of monocations [45].

The three-body Coulomb explosion of allene ($\text{CH}_2=\text{C}=\text{CH}_2$) induced by ultrafast intense laser fields was also analyzed to investigate the fragmentation dynamics by the Coulomb explosion CMI method [31]. On the basis of the kinetic energy distributions of the fragment ions produced through the two three-body Coulomb explosion pathways, $\text{C}_3\text{H}_4^{3+} \rightarrow \text{H}^+ + \text{CH}^+ + \text{C}_2\text{H}_2^{+}$ and $\text{C}_3\text{H}_4^{3+} \rightarrow \text{H}^+ + \text{C}_2\text{H}^+ + \text{CH}_2^+$, as well as the proton maps of both pathways, it was shown that the decomposition proceeds in a stepwise manner as well as in a concerted manner. Whether the proton ejection proceeds concerted or sequentially was also studied for triply charged 1,3-butadiene molecules through examining the three-body fragmentation of $\text{C}_4\text{H}_6^{3+}$ [35].

Field ionization and Coulomb explosion of very highly charged hydrocarbon molecules, methane ($\text{CH}_4$) and 1,3-butadiene ($\text{C}_4\text{H}_6$), driven by intense laser pulses were studied in a combined theoretical framework and the experimental CMI method [67]. It was demonstrated that the high degree of ionization leads to the complete Coulomb explosion of the molecules, and the Coulomb explosion in the studied molecular systems is a sudden, all-at-once fragmentation where the ionization step is followed by a simultaneous ejection of the charged fragments. In this case protons are ejected simultaneously in a concerted process.

III-6. Control of molecular fragmentation dynamics

Controlling of chemical reaction dynamics of hydrocarbon molecules with different methods, such as chirped intense laser fields [69], the pulse width and wavelength [54], the intensity [35] and polarization state of the laser pulse [35], the shaped intense few-cycle laser pulses [55, 70–72] and so forth, have been carried out. Recently the effect of hydrogen migration on fragmentation of hydrocarbon molecules has also been investigated. The hydrogen migration process can lead to large-scale deformation of molecular skeletal structure and chemical bond rearrangement, and thus may open new reaction pathways that could not be realized when reactions start from the initial molecular geometries [47, 52, 73]. Here we will only focus on recent works of controlling fragmentation dynamics of hydrocarbon molecules studied by using the CMI method.
Using the CMI method, the effect of the pulse duration of intense laser fields on hydrogen migration dynamics in methanol was examined, where two-body Coulomb explosion channels with the C-O bond breaking of methanol induced by ultrashort intense laser fields whose pulse durations are $\Delta t = 7$ and 21 fs respectively, were investigated [43]. When $\Delta t = 7$ fs, the angular distribution of recoil vectors of the fragment ions for the hydrogen migration pathway of $\text{CH}_3\text{OH}^{2+} \rightarrow \text{CH}_2^+ + \text{H}_2\text{O}^+$, in which one hydrogen migrates from the carbon site to the oxygen site prior to the C–O bond breaking, exhibits a peak deflected from the laser polarization direction by $30^\circ$–$45^\circ$. When the laser pulse duration was stretched to $\Delta t = 21$ fs, the angular distributions for the migration pathways exhibit a broad peak along the laser polarization direction which is probably due to the dynamical alignment and/or the change in the double ionization mechanism; that is, from the non-sequential double ionization to the sequential double ionization. It was also shown that the stretch of the laser pulse duration from 7 fs to 21 fs does not influence the momentum distribution, suggesting that $\Delta t = 21$ fs is not long enough for the C-O bond distance to be elongated so that the enhanced ionization proceeds. However when a pulse with pulse duration of $\Delta t = 60$ fs [40] was used, it is found that the $\Delta t = 60$ fs pulse is sufficiently long for the C-O bond distance to become stretched so that the major ionization mechanism changes to the enhanced ionization. Therefore changing the pulse duration may lead to the ionization process occurring in different mechanism, thus makes it possible to control the ejection directions and the momentum distributions of the fragment ions produced through the hydrogen migration pathway.

The effect of laser parameters (intensity, duration, and polarization) of ultrashort laser pulses (795 nm, 40–100 fs, and $0.15$–$1.5 \times 10^{15}$ W/cm$^2$) on the ultrafast hydrogen migration in methanol was systematically investigated using the Coulomb explosion CMI technique. It was reported that the ratio of the ion yield $\gamma$ obtained for the migration pathway $\text{CH}_3\text{OH}^{2+} \rightarrow \text{CH}_2^+ + \text{OH}_2^+$ with respect to the sum of the yields obtained for the
migration pathway and for the nonmigration pathway $\text{CH}_3\text{OH}^{2+} \rightarrow \text{CH}_3^{+} + \text{OH}^{+}$ exhibits a small but clear dependence on laser pulse properties. It was found that the yield ratio becomes larger by a factor of $\sim 20\%$ when the laser pulse duration increases from 40 to 100 fs, as can be seen in Fig. 6(a) [56]. However the ratio becomes smaller by $\sim 17\%$ when the laser intensity increases from $0.15 \times 10^{15}$ to $1.5 \times 10^{15}$ W/cm$^2$ (see Fig. 6(b)). It was also found that the ratio of the hydrogen migration is enhanced by 10–18% in a circularly polarized laser field as compared to that in a linearly polarized laser field with the same laser peak intensity, as shown in Fig. 6(c).

The dependence of the fragmentation dynamics of 1,3-butadiene on the intensity and polarization state of the laser pulse was also investigated by the CMI technique [35]. It was found that both the relative probability of fragmenting via a certain path and the probability of hydrogen migration prior to the Coulomb explosion depend on the two varied laser pulse parameters, intensity and polarization, as can be seen in Fig. 7.

![Graph showing fragment number distribution](image)

**FIG. 7:** (a) Event numbers of the two dominant paths of channels (A)–(C) normalized to the sum of events for all three channels as a function of pulse intensity and laser polarization state, i.e. channel (A): $\text{H}^+ + \text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_4^+$, full red; channel (B): $\text{H}^+ + \text{CH}_3^+ + \text{C}_3\text{H}_3^+$, dashed green; channel (C): $\text{H}^+ + \text{CH}_3^+ + \text{C}_4\text{H}_4^+$, dotted blue. (b) Ratio of bond breaking events of doubly charged 1,3-butadiene involving hydrogen-atom migration normalized to the number of counts where the same bond is broken without hydrogen-atom migration as a function of pulse intensity and laser polarization state. The columns denoted with *centre bond* correspond to the ratio of events in the two fragmentation channels: $\text{C}_4\text{H}_6^{2+} \rightarrow \text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_4^+$ and $\text{C}_4\text{H}_6^{2+} \rightarrow \text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_4^+$ respectively, the columns denoted with *terminal bond* correspond to the two fragmentation channels: $\text{C}_4\text{H}_6^{2+} \rightarrow \text{CH}_3^+ + \text{C}_3\text{H}_3^+$ and $\text{C}_4\text{H}_6^{2+} \rightarrow \text{CH}_2^+ + \text{C}_3\text{H}_3^+$ respectively (Adapted from [35]).

Control over various fragmentation reactions of a series of hydrocarbon molecules (acetylene, ethylene, 1,3-butadiene) by the optical waveform-controlled intense few-cycle laser pulses was also demonstrated experimentally by using the CMI method [55]. A strong carrier-envelope phase (CEP) dependence on the fragmentation yields obtained from different fragmentation channels of all the three hydrocarbon molecules was found, as can be seen in Figs. 8(a)–(c). The intensity dependence on the ion yield was also demonstrated, as seen Figs. 8(d)–(f). It was proposed that the responsible mechanism behind is inelastic ionization.
from inner-valence molecular orbits by recolliding electron wave packets, whose recollision energy in few-cycle ionizing laser pulses strongly depends on the optical waveform. This work demonstrated an efficient and selective way of predetermining fragmentation reaction in hydrocarbon molecules on sub-femtosecond time scales.

**FIG. 8:** (a)–(c) Measured fragmentation and ionization yields, normalized to 1 at their respective maxima, as a function of CEP for different fragmentation channels of acetylene (a), ethylene (b), and 1,3-butadiene (c), measured at the laser intensities indicated in the panels. The various fragmentation reactions are $\text{C}_2\text{H}_2^+ \rightarrow \text{CH}^+ + \text{CH}^+$ (red dots) and $\text{C}_2\text{H}_2^+ \rightarrow \text{H}^+ + \text{C}_2\text{H}^+$ (blue squares) for acetylene in (a); $\text{C}_2\text{H}_4^+ \rightarrow \text{CH}_2^+ + \text{CH}_2^+$ (red dots), $\text{C}_2\text{H}_4^+ \rightarrow \text{H}^+ + \text{C}_2\text{H}_3^+$ (blue squares), and $\text{C}_2\text{H}_4^+ \rightarrow \text{C}_2\text{H}_2^+ + \text{H}_2^+$ (green triangles) for ethylene in (b); $\text{C}_4\text{H}_6^+ \rightarrow \text{C}_2\text{H}_3^+ + \text{C}_2\text{H}_3^+$ (red dots) and $\text{C}_4\text{H}_6^+ \rightarrow \text{CH}_3^+ + \text{C}_3\text{H}_3^+$ (blue squares) for 1,3-butadiene in (c). The ionization yields of the singly and doubly charged molecular ions are denoted by black dots and gray squares, respectively. (d), (e) Fragmentation yields over the CEP of the same channels as in (a) and (b) (same color and point styles apply), but measured for a slightly higher intensity (as indicated). (f) Measured intensity dependence of the yield of the fragmentation channel $\text{C}_4\text{H}_6^+ \rightarrow \text{CH}_3^+ + \text{C}_3\text{H}_3^+$ over CEP. The intensities are indicated in the figure (Adapted from [55]).
IV. REAL-TIME VISUALIZING ULTRAFAST DYNAMICS OF HYDROCARBON MOLECULES BY PUMP-PROBE COULOMB EXPLOSION CMI METHODS

So far tracing/visualizing the ultrafast dynamics such as hydrogen migration during molecular fragmentation processes in real time has become one of the most attractive challenges in ultrafast molecular science. Investigations on this subject have been carried out by the pump-probe Coulomb explosion CMI methods for hydrocarbon molecules [47, 52].

It was demonstrated in 2007 that the visualization of ultrafast hydrogen migration in deuterated acetylene dication (C$_2$D$_2^{2+}$) was achieved in real time by employing the pump-probe Coulomb explosion imaging with sub-10-fs intense laser pulses (9 fs, 0.13 PW/cm$^2$, 800 nm) [52]. The pump laser pulses were used to doubly ionize the deuterated acetylene as well as to trigger the hydrogen migration. The probe laser pulses with a time delay $\Delta t$ relative to the pump pulses were then applied to ionize C$_2$D$_2^{2+}$ to C$_2$D$_3^{2+}$ and to probe the structural change of C$_2$D$_2^{2+}$. The instantaneous location of the migrating deuterium atom between the two carbon sites, DCCD$_2^{2+} \leftrightarrow$ D$_2$CC$_2^{2+}$, was identified from the momenta of fragment ions in the three-body Coulomb explosion process through C$_2$D$_2^{2+} \rightarrow$ D$^+$ + C$^+$ + CD$^+$. It was shown from the temporal evolution of the momenta of the fragment ions produced from this three-body Coulomb explosion that the migration proceeds in a recurrent manner: the deuterium atom first shifts from one carbon site to the other in a short time scale ($\sim$ 40 fs) and then migrates back to the original carbon site by 280 fs, as can be seen in Fig. 9, in competition with the molecular dissociation.

Using the pump-probe CMI method, hydrogen migration in methanol induced by an intense laser field (0.2 PW/cm$^2$) was also investigated in real time [47]. Singly charged molecular ions, (CH$_3$· · · OH)$^+$ and (CH$_2$· · · OH$_2$)$^+$, which was prepared by the pump pulses are further ionized by the probe pulse into doubly charged molecular ions, CH$_3$$^+$$\cdot$ · · · OH$^+$ and CH$_2$$^+$$\cdot$ · · · OH$_2$$^+$, leading to the two-body Coulomb explosion, respectively. One fragmentation channel produces CH$_3$$^+$ and OH$^+$ without hydrogen migration, and the other generates CH$_2$$^+$ and OH$_2$$^+$ through a hydrogen atom migration.

The yields of the two Coulomb explosion channels of CH$_3$OH$_2^{2+}$ $\rightarrow$ CH$_3$$^+$ + OH$^+$ and CH$_3$OH$_2^{2+}$ $\rightarrow$ CH$_2$$^+$ + OH$_2$$^+$, and the obtained sum of the kinetic energy released from a pair of the fragment ions, $E_{\text{kin}}$, as functions of the relative delay $\Delta t$ between the pump and probe pulses are shown in Figs. 10(a) and (b). It was observed that the peak position of the kinetic energy distributions for the lower strip with $E_{\text{kin}} \leq 3.8$ eV in both pathways shifts toward lower energies when $\Delta t$ increases. The time-dependent lower strips in Figs. 10(a) and (b) reflect the temporal evolution of a dissociating wave packet of (CH$_3$· · · OH)$^+$ and that of (CH$_2$· · · OH$_2$)$^+$, respectively. Thus the distance between CH$_3$$^+$ and OH$^+$ through the nonmigration pathway, and that between CH$_2$$^+$ and OH$_2$$^+$ through the migration pathway from the two-body Coulomb explosion processes, can be estimated as a function of the delay time, as can be seen in Figs. 10(a) and (b). The yield ratios of the nonmigrated and migrated species $\eta_{\text{non mig}}$ and $\eta_{\text{mig}}$ for the lower strips shown in Figs. 10(a) and 10(b) exhibit clear temporal change: as the time delay increases, $\eta_{\text{non mig}}$ decreases, but $\eta_{\text{mig}}$ increases, showing that the hydrogen migration proceeds even after molecules interact with the intense laser field. The time constant for this post-laser pulse hydrogen migration
was evaluated to be $\sim 150$ fs. In addition, the ejection of the fragment ions through the migration pathway shown in the upper strip with $E_{\text{kin}} > 3.8$ eV indicates the existence of the hydrogen migration occurring with the laser pulse. Thus, this work revealed that the intense laser fields can induce two distinctively different hydrogen migration processes, that is, ultrafast hydrogen migration occurring within the intense laser field and slower post laser pulse hydrogen migration.

The visualization of ultrafast isomerization of deuterated acetylene dication ($\text{C}_2\text{D}_2^{2+}$) was also demonstrated by time-resolved Coulomb explosion imaging with sub-10 fs intense laser pulses (9 fs, 0.13 PW/cm$^2$, 800 nm). The Coulomb explosion imaging monitoring the three-body explosion process, $\text{C}_2\text{D}_2^{3+} \rightarrow \text{D}^+ + \text{C}^+ + \text{CD}^+$, as a function of the delay between the pump and probe pulses revealed that the migration of a deuterium atom proceeds in a recurrent manner: one of the deuterium atoms first shifts from one carbon site to the other in a short timescale ($\sim 90$ fs), and then migrates back to the original carbon site by 280 fs, in competition with the molecular dissociation. Correlated motions of the two deuterium atoms associated with the hydrogen migration and structural deformation to non-planar geometry were also identified by the time-resolved four-body Coulomb explosion imaging, $\text{C}_2\text{D}_2^{4+} \rightarrow \text{D}^+ + \text{C}^+ + \text{C}^+ + \text{D}^+$ [37].
V. SUMMARY

In this article, we reviewed the fragmentation of hydrocarbon molecules in intense laser fields studied by the CMI method. Since in the hydrocarbon molecules, the dynamics of hydrogen atoms (or protons) takes place on a timescale that is in between the one of the sub-femtosecond motion of electrons and the one of the other moieties, which due to their much bigger mass are by at least an order of magnitude slower, leading to a much more complicated reactions when hydrocarbon molecules are exposed to intense laser fields. The CMI method has been proved to be a powerful tool for characterizing the fragmentation dynamics of chemical reaction of molecules at a single molecule level. Using the Coulomb explosion CMI method, various types of fragmentation processes associated with the hydrogen migration processes in hydrocarbon molecules in intense laser fields were identified, and it was found that hydrogen atom or proton plays an important role in the chemical bond formation and breaking reaction. By introducing recent achievements in the study of fragmentation of hydrocarbon molecules by using Coulomb explosion CMI method, as well as real-time visualizing ultrafast fragmentation dynamics of hydrocarbon molecules by the pump-probe Coulomb explosion CMI method, we expect that this article could provide a more detailed insight into chemical reactions of hydrocarbons in intense laser field as well as new prospects for efficient coherent reaction control with tailored laser pulses.
Acknowledgement

This work is financially supported by National Natural Science Foundation of China (Grant Nos. 11074098, 61235003 and 61308030), the Open Fund of the State Key Laboratory of High Field Laser Physics (SIOM), the Fundamental Research Funds of Jilin University, and JSPS short-term fellowship program.

References

Cumulative Author Index
(for Volume 52)

Abaab, M. (1) 272
Bandraud, Andre D. (1) 569
Becker, Andreas (1) 404
Belgacem, J. B. (1) 272
Bian, Xue-Bin (1) 569
Busuladzic, Mustafa (1) 389

Chaabouni, F. (1) 272
Chen, Chiang-Mei (1) 111
Chen, Jing (1) 366, (1) 389
Chen, YongJu (1) 389
Cheng, Ya (1) 366
Chu, Shih-I (1) 578
Chu, Wei (1) 366
Chu, Wei-Chun (1) 301
Clough, Benjamin (1) 416
Corkum, P. B. (1) 537

Dai, Jianming (1) 416
Dai, Jun (1) 320
Dai, Yujie (1) 205
Dharmadhikari, Aditya K. (1) 431
Dharmadhikari, Jayashree A(1) 431
Dlimi, S. (1) 251
Dota, Krithika (1) 431
Duan, Wei-Long (1) 224

Ebrahimzadeh, Majid (1) 233
El kaouachi, A. (1) 251
Errai, M. (1) 251
Eto, Shuzo (1) 440
Fan, Ze-Bin (1) 224
Fang, Q. O. (1) 286
Feng, Yuanyuan (1) 90
Fujii, Takashi (1) 440

Fujimura, Yuichi (1) 617
Ghaffary, Tooraj (1) 233
Ghaforyan, Hossein (1) 233
Gigure, M. (1) 537
Goto, Naohiko (1) 440
Han, Mi-Kyung (1) 239
Hao, XiaoLei (1) 389
Hao, Z. Q. (1) 519
Hasovic, Elvedin (1) 389
He, G. (1) 286
Heslar, John (1) 578
Hotta, Eiki (1) 440
Hu, Chin-Kun (1) 1
Hu, ZiLong (1) 389
Itoh, Ayaka (1) 504
Jahromi, Zahra Sokout (1) 233
Jaro’n-Becker, Agnieszka (1) 404
Jawad, Abdul (1) 101
Jin, Z. (1) 519
Johnson, Allan S. (1) 329
Kanno, Manabu (1) 617
Kawashima, Yukio (1) 126
Kharin, V. Yu. (1) 340
Kii, Toshiteru (1) 163
Kim, HeeJin (1) 239
Kim, Sung-Jin (1) 239
Kono, Hirohiko (1) 617
Kripal, Ram (1) 262
Kubota, Shingo (1) 215
Kurosawa, Shigeru (1) 215
<table>
<thead>
<tr>
<th>Author Name</th>
<th>Volume(s)</th>
<th>Page(s)</th>
<th>Author Name</th>
<th>Volume(s)</th>
<th>Page(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lai, XuanYang</td>
<td>(1)</td>
<td>389</td>
<td>Oishi, Yuji</td>
<td>(1)</td>
<td>440</td>
</tr>
<tr>
<td>Lassonde, P.</td>
<td>(1)</td>
<td>537</td>
<td>Ono, Yukari</td>
<td>(1)</td>
<td>617</td>
</tr>
<tr>
<td>Lee, Wooyoung</td>
<td>(1)</td>
<td>239</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Legare, F.</td>
<td>(1)</td>
<td>537</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leng, Yuxin</td>
<td>(1)</td>
<td>524</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li, Guihua</td>
<td>(1)</td>
<td>366</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li, Hongyu</td>
<td>(1)</td>
<td>524</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li, M.</td>
<td>(1)</td>
<td>286</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li, Ruxin</td>
<td>(1)</td>
<td>320, (1) 662</td>
<td>Qiao, Ying</td>
<td>(1)</td>
<td>77</td>
</tr>
<tr>
<td>Liang, C.-T.</td>
<td>(1)</td>
<td>251</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liang, Xiaoyan</td>
<td>(1)</td>
<td>524</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limouny, L.</td>
<td>(1)</td>
<td>251</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lin, J. Q.</td>
<td>(1)</td>
<td>519</td>
<td>Rajput, Debangana Rajput</td>
<td>(1)</td>
<td>185</td>
</tr>
<tr>
<td>Liu, Candong</td>
<td>(1)</td>
<td>320</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liu, Jiangsheng</td>
<td>(1)</td>
<td>524</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liu, Jian-Liang</td>
<td>(1)</td>
<td>111</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liu, Weiwei</td>
<td>(1)</td>
<td>465</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liu, Xiao Dong</td>
<td>(1)</td>
<td>77</td>
<td>Sharma, Vineet Kumar</td>
<td>(1)</td>
<td>185</td>
</tr>
<tr>
<td>Liu, XiaoJun</td>
<td>(1)</td>
<td>389</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liu, Y. M.</td>
<td>(1)</td>
<td>286</td>
<td>Shrivastava, V.</td>
<td>(1)</td>
<td>192</td>
</tr>
<tr>
<td>Lu, Haiyang</td>
<td>(1)</td>
<td>524</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lu, Xiaoming</td>
<td>(1)</td>
<td>524</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lv, Q. R.</td>
<td>(1)</td>
<td>286</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ma, Xiao San</td>
<td>(1)</td>
<td>77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Massaouti, M.</td>
<td>(1)</td>
<td>490</td>
<td>Sugiyama, Kiyohiro</td>
<td>(1)</td>
<td>440</td>
</tr>
<tr>
<td>Mathur, Deepak</td>
<td>(1)</td>
<td>431</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Miki, Megumu</td>
<td>(1)</td>
<td>440</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milosevic, Dejan B.</td>
<td>(1)</td>
<td>389</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mishra, Nidhish Kumar</td>
<td>(1)</td>
<td>185</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morishita, Toru</td>
<td>(1)</td>
<td>301</td>
<td>Tachikawa, Masanori</td>
<td>(1)</td>
<td>126</td>
</tr>
<tr>
<td>Nakajima, Takashi</td>
<td>(1)</td>
<td>163</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nakashima, Nobuaki</td>
<td>(1)</td>
<td>504</td>
<td>Tikhonova, O. V.</td>
<td>(1)</td>
<td>340</td>
</tr>
<tr>
<td>Narjis, A.</td>
<td>(1)</td>
<td>251</td>
<td>Toh, Sing Poh</td>
<td>(1)</td>
<td>153</td>
</tr>
<tr>
<td>Nemoto, Koshichi</td>
<td>(1)</td>
<td>440</td>
<td>Trallero-Herrero, C.</td>
<td>(1)</td>
<td>537</td>
</tr>
<tr>
<td>Nester, James M.</td>
<td>(1)</td>
<td>111</td>
<td>Tzortzakis, S.</td>
<td>(1)</td>
<td>490</td>
</tr>
<tr>
<td>Ni, Guoquan</td>
<td>(1)</td>
<td>524</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni, Hongcheng</td>
<td>(1)</td>
<td>404</td>
<td>Villeneuve, D. M.</td>
<td>(1)</td>
<td>329, (1) 537</td>
</tr>
<tr>
<td>Ni, Jielei</td>
<td>(1)</td>
<td>366</td>
<td>Volkova, E. A.</td>
<td>(1)</td>
<td>340</td>
</tr>
<tr>
<td>Ohgaki, Hideaki</td>
<td>(1)</td>
<td>163</td>
<td>Wang, An Min</td>
<td>(1)</td>
<td>77</td>
</tr>
<tr>
<td>Name</td>
<td>Pages</td>
<td>Name</td>
<td>Pages</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>--------</td>
<td>--------------------</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang, De-hua</td>
<td>(1) 138</td>
<td>Yang, Bosi</td>
<td>(1) 652</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang, Xiaolong</td>
<td>(1) 163</td>
<td>Yao, Jinping</td>
<td>(1) 366</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang, Xuehui</td>
<td>(1) 205</td>
<td>Yatshuhashi, Tomoyuki</td>
<td>(1) 504</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang, Cheng</td>
<td>(1) 524</td>
<td>Yi, Houhui</td>
<td>(1) 174</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang, ChuanLiang</td>
<td>(1) 389</td>
<td>Yoshimoto, Minoru</td>
<td>(1) 215</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang, Wentao</td>
<td>(1) 524</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wu, Liang</td>
<td>(1) 90</td>
<td>Zen, Heishun</td>
<td>(1) 163</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wu, M. Z.</td>
<td>(1) 286</td>
<td>Zeng, Bin</td>
<td>(1) 366</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zeng, Zhinan</td>
<td>(1) 320, (1) 366</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xia, Changquan</td>
<td>(1) 524</td>
<td>Zhang, Chaojin</td>
<td>(1) 366</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xu, Huailiang</td>
<td>(1) 652</td>
<td>Zhang, Li</td>
<td>(1) 652</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xu, Yi</td>
<td>(1) 524</td>
<td>Zhang, X. H.</td>
<td>(1) 519</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xu, Zhizhan</td>
<td>(1) 320, (1) 366</td>
<td>Zhang, X.-C</td>
<td>(1) 416</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1) 524</td>
<td>Zhidkov, Alexei</td>
<td>(1) 440</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zhou, Lei</td>
<td>(1) 90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yamada, Kenta</td>
<td>(1) 126</td>
<td>Zhou, Zili</td>
<td>(1) 524</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yamanaka, Ken-ichi</td>
<td>(1) 504</td>
<td>Zhu, Shiqun</td>
<td>(1) 90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yamanouchi, Kaoru</td>
<td>(1) 652</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>