Theory on the Raman Intensities of Diatomic Molecules

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A very simple formula for calculating the derived polarizabilities of diatomic molecules is derived from the Kramers-Heisenberg dispersion equation. The derived polarizabilities of H_2, N_2, O_2, CO and NO are calculated and compared with the values deduced from the Raman spectra of these molecules. Calculated and experimental values agree within a factor of three except the case of H_2, in which there is significant vibronic coupling neglected in the theory.

THERE are two ways of predicting theoretically the absolute intensities in the Raman scattering process. An obvious way is to calculate the polarizability of a molecule with internulear distances as parameters, and then it is possible to evaluate the derived polarizabilities (differentials of polarizability with respect to normal coordinates) of various normal modes.[1] To carry out this type of calculation, the precise wavefunction of the molecule as a function of all nuclear coordinates has to be solved first, which is by no means an easy task.

The alternative way is to use Kramers and Heisenbergs' dispersion theory[2] in which scattering is considered as a second order interaction between matter and radiation. Here polarizability as well as derived polarizabilities of a molecule can be calculated from data derived from the electronic spectrum of the molecule. This method is not only simpler in actual computation, but also shows the close relationship between Raman spectroscopy and ordinary electronic spectroscopy[3] and gives us much deeper insight into the scattering processes. We shall use this approach to discuss the absolute Raman intensities in a number of diatomic molecules.

THEORY

Kramers and Heisenberg related the polarizability of a molecule to the energies and transition moments of the allowed excited states in this molecule:

$$(oj/\alpha_{\rho\sigma}/oi) = \sum_{n,k} [(oj/\mathbf{M}^\rho/nk)(nk/\mathbf{M}^\sigma/oi)(E_{nk} - E_{oi} - \hbar w)^{-1} + (oj/\mathbf{M}^\sigma/nk)(nk/\mathbf{M}^\rho/oi)(E_{nk} - E_{oj} + \hbar w)^{-1}] \tag{1}$$

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(3) C. H. Ting, Spectrochim. Acta 24A, 1177 (1968).

in which $/oi)$, $/nk)$ and $/oj)$ are the initial, intermediate and final states in the scattering process, respectively; the energies of them are E_{oi}, E_{nk} and E_{oj}; M^{ρ} and M^{σ} are transition moment operators in the directions of ρ and σ axes, respectively; and $\hbar w$ is the energy of incident photons. Letters i, j and k denote vibrational quantum numbers while o and n denote the electronic quantum numbers. For simplicity, only the first term in equation (1) will be considered in this work.

All quantities in equation (1) are physical observables; i. e., the energies of various states and their transition moments. In principle equation (1) can be rigorously used to calculate the polarizability of a molecule, if its electronic spectrum is known. However, it is very difficult to carry out the double summation shown in equation (1) and get a closed, analytical expression for polarizability. Nevertheless, by introducing a few appropriate approximations, we can perform the summation over k, the vibrational quantum number, with ease. Since there are relatively few strongly allowed electronic states which dominate the scattering processes, summing over n is relatively simpler and can be done even without a closed formula.

To sum over k alone, it is necessary to separate the vibrational wavefunctions from the electronic wavefunction. Employing the Born-Oppenheimer approximation,[4] the Schrodinger equation of a molecular system

$$\mathbf{H}/nk) = E_{nk}/nk) \qquad (2)$$

can be written as follows:

$$\mathbf{H}/nk) = (\mathbf{H}_e + \mathbf{H}_n)/n)/k) = (E_n + \mathbf{H}_n)/n)/k) = (E_n + E_k)/nk) \qquad (3)$$

in which $\mathbf{H}_e$ is the electronic Hamiltonian, and $\mathbf{H}_n$ is the nuclear Hamiltonian in the nth excited state; E_n is the zero-point energy of the nth excited state and E_k is the vibrational energy of the kth vibrational level in the nth excited state. $E_n + E_k = E_{nk}$. The electronic wave function $/n)$ depends upon the nuclear coordinates as parameters. Since $/k)$ is an eigenfunction of $\mathbf{H}_n$ with eigenvalue E_k the summation over k in equation (1) can be eliminated as follows: [5]

$$
\begin{aligned}
(oj/a_{\rho o}/oi) &= \sum_{n, k} (oj/\mathbf{M}^{\rho}/nk)(nk/\mathbf{M}^{\sigma}/oi)(E_k + E_n - E_{oi} - \hbar w)^{-1} \\
&= (j/\{\sum_n (o/\mathbf{M}^{\rho}/n)[\sum_k (\mathbf{H}_n + E_n - E_{oi} - \hbar w)^{-1}/k)(k/](n/\mathbf{M}^{\sigma}/o)\}/i) \\
&= (j/[\sum_n (o/\mathbf{M}^{\rho}/n)(\mathbf{H}_n + E_n - E_{oi} - \hbar w)^{-1}(n/\mathbf{M}^{\sigma}/o)]/i) \qquad (4)
\end{aligned}
$$

If it is further assumed that the transition moment matrix elements are independent of the nuclear displacements from their equilibrium positions or that

（4） M. Born, R Oppenheimer, Ann. Physik 84. 457 (1927).

(5) K. Poiker, E. D. Trifonov, Soveit Phys. Solid State **8,** 1621 (1967).

the vibronic coupling interaction is neglected, the contribution to molecular polarizability operator from an allowed electronic state n is

$$a_{\rho\sigma}^n = M_n^\rho M_n^\sigma (\mathbf{H}_n + E_n - E_{oi} - \hbar w)^{-1} = M_n^\rho M_n^\sigma G_n \qquad (5)$$

where $M_n^\rho = (o/\mathbf{M}^\rho/n)$ is a constant. The dependence of $a_{\rho\sigma}^n$ on nuclear coordinates is due to the fact that the operator $\mathbf{H}_n$ depends on the normal coordinates in the ground state of the molecule, and it is not diagonal in the basis of vibrational wavefunctions in the ground state.

In the cases of diatomic molecules, the vibrational Hamiltonian operator in the ground state is

$$\mathbf{H}_0 = -\frac{\hbar^2}{2\mu} \frac{d^2}{dq^2} + \tfrac{1}{2} kq^2 \qquad (6)$$

in which q is the internuclear distance and μ is the reduced mass. The vibrational Hamiltonian in the excited states is slightly complicated because the equilibrium internuclear distance and the force constant are different from those in those in the ground state. Expressing the excited state Hamiltonian in terms of the normal coordinate q in the ground state, we have

$$\mathbf{H}_n \frac{d^2}{2\mu} + \frac{^2}{dq^2} \qquad \tfrac{1}{2} k_n (\mathbf{q} + q_n)^2 \qquad (7)$$

$$= \mathbf{H}_0 + \tfrac{1}{2} k_n q_n^2 + k_n q_n \mathbf{q} + \tfrac{1}{2} (k_n - k)\mathbf{q}^2 = A_n + B_n \mathbf{q} + C_n \mathbf{q}^2 \qquad (8)$$

in which k_n is the force constant and q_n is the equilibrium position of the nth excited state. It should be noted that the operator A,, is now diagonal in the basis of ground state vibrational wavefunctions; i. e., $(j/\mathbf{A}_n/i) = a_n^i \delta_{ij}$. Let a,, be the mean eigenvalue of $\mathbf{A},$,

$$\text{a}, = \tfrac{1}{2} (j/\mathbf{A}_n/j) + \tfrac{1}{2} (i/\mathbf{A}_n/i) = \tfrac{1}{2}(a_n^j + a_n^i) \qquad (9)$$

and the polarizability operator shown in equation 5 can be expanded into a power series of $(\mathbf{H}_n - a_n)$:

$$a_{\rho\sigma}^n = M_n^\rho M_n^\sigma (\mathbf{H}_n - a_n + a_n + E_n - E_{oi} - \hbar w)^{-1}$$
$$= M_n^\rho M_n^\sigma (\mathbf{H}_n - a_n + E_n')^{-1}$$
$$= M_n^\rho M_n^\sigma \sum_{N=0}^\infty (a_n - \mathbf{H}_n)^{-N} (E_n')^{-N-1} \qquad (10)$$

Since $E_n' = a_n + E_n - E_{oi} - \hbar w$ and is generally much larger than the expectation value of (H,-a,), the power series shown in equation 10 is rapidly converging. Only a few leading terms are needed to represent $a_{\rho\sigma}^n$ accurately. To calculate Raman intensities of the fundamental tones, only the terms with $N \leqslant 1$ are necessary.

$$a_{\rho\sigma}^n = M_n^{\rho} M_n^{\sigma} / E_n' [1 + (a_n - H_n)/E_n' + \cdots] \tag{11}$$

$$= M_n^{\rho} M_n^{\sigma} / E_n' [1 - (k_n q_n / E_n') q + \cdots] \tag{12}$$

In the above equation $M_n^{\rho} M_n^{\sigma} / E_n'$ is the contribution to the molecular polarizability from the nth excited state because E_n' is the vertical transition energy, and the term $(k_n q_n / E_n')$ gives the ratio of thee derived polarizability to the molecular polarizability contributed by the nth excited state. With the knowledge of the energies, oscillator strengths, vibrational force constants and displacements of equilibrium nuclear distance of all allowed excited states, in principle we are able to calculate the contributions from all excited states to the polarizability and derived polarizability. In practice, however, this kind of calculation is very difficult because not all these data needed are accurately measured. In order to calculate the derived polarizabilities of diatomic molecules and compare them with those computed from the intensities of Raman lines, we shall adopt the following procedure of approximation.

The procedure of calculation is first to select a representative excited state in a molecule, and calculate the ratio of the derived polarizability of to the polarizability, $k_n q_n / E_n'$, in this state assuming $\hbar w = 0$. To obtain the derived polarizability of this molecule, this ratio is multiplied by the observed stationary molecular polarizability a_0.[6] The representive derived polarizability can thus be compared with the experimental derived polarizability da/dq.[7] Because the representative excited state is not the only one contributing to the Raman scattering, and sometimes not even the most intense one, large errors are expected. However, as we shall immediately see, the results are quite good.

RESULTS AND DISCUSSION

The derived polarizabilities of H_2, N_2, O_2, CO, and NO and the relevant data in the calculation are tabulated in Table I, and they are compared with the derived polarizabilities compiled by Murphy, Holzer and Bernstein.[8] Except O_2, the molecules have more than one very intense excited states. In each molecule we select two most intense excited states as representatives, and calculate their representative derived polarizabilities according to the procedure outlined previously.

As shown in Table I, our calculation is the worst in the case of hydrogen, in which the calculated derived polarizability is only about a tenth of the observed value. The reason of this failure is the adoption of Franck-Condon approximation,

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Table I. Representative derived polarizabilities of diatomic molecules

Molecule	Repr. Exc. State	En (E_n^*) (cm^{-1})	Vib. Freq. (cm^{-1})	q_n (Å)	$k_n q_n/E_n$ $(10cm^{-1})$	α_0 $(10^{-24}cm^3)$	$d\alpha/dq$ $(10^{-17}cm^2)$ Calc.	$d\alpha/dq$ $(10^{-17}cm^2)$ Obsv.	Reference
H_2	$B^1\Sigma_u^+$	90,196	1,357	0.551	1.56	0.79	1.32	12.3	11
	$C^1\pi_u$	99,080	2,443	0.291	2.63	0.79	2.07	12.3	11
N_2	$p'^1\Sigma_u^+$	104,328	2,217	0.026	2.56	1.76	4.50	17.5	11,12
	$b'^1\Sigma_u^+$	103,679	752	0.356	4.10	1.76	7.20	17.5	13,20
O_2	$B^3\Sigma_u^-$	49,363	700	0.397	9.50	1.60	15.2	14.6	15.16
CO	$A^1\pi$	64,747	1,516	0.107	7.64	1.95	14.6	15.0	11
	$C^1\Sigma^+$	91,920	2,133	0.003	0.31	1.95	0.50	15.0	11,14
NO	$C^2\Sigma^+$	52,253	2.347	0.076	19.6	1.72	33.6		17,18
	$D^2\Sigma^+$	53,172	2,327	0.096	22.2	1.72	38.5		11,19

which assumes that the electronic transition moment of an excited state is a constant independent of the vibrational wavefunctions involved or of the nuclear coordinate. According to Hesser, Brooks and Lawrence[9] the transition moment of the Lyman band and the internuclear distance have the following relationship:

$$M(\text{Lyman}) = \text{Const} \ (-1 + 1.82q) \tag{13}$$

in which q is the internuclear distance in the units of Å. This kind of strong vibronic coupling also contributes significantly to Raman intensity, and its contribution to the derived polarizability of H_2 is calculated to be about $2.5 \times 10^{-16} cm^2$ which is twice the observed value.

In N_2 the most intense transition from the ground state is to the p' state.[11,12] However, the contribution of this excited state to Raman scattering is less than that of the next most intense excited state b'[13] because the equilibrium distance of P' state is very close to that of the ground state. In either case, the calculated derived polarizability is two to three times smaller than the observed value. This is about the accuracy expected for our calculations with so many approximations introduced.

The seemingly excellent agreement in the case of O_2 is rather fortuitous because the Schumann-Runge band in oxygen is not the most intense band, but these stronger bands are not resolvable and data needed for our calculation are not available.

The strongest absorption band of CO is due to C state,[" "*"] but the calculated derived polarizability with this representative state is extremely small because

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(10) C. H. Ting, unpublished work.
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(13) R. E. Huffman, Y. Tanaka, J. Chem. Phys. 39. 910 (1963).
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its q_n is only 0.003 A. Using the next strongest excited state A,[11] the derived polarizability is calculated to be $1.46 \times 10^{-16} cm^2$ which agrees very well with the observed $1.50 \times 10^{-16} cm^2$.

All other diatomic molecules can be treated this way, but for the less stable molecules accurate measurements on their Raman intensities are still to be carried out. As an example, the derived polarizability of NO is calculated and listed also in Table I. Because of the low-lying and also intense excited states in this molecule, its Raman intensity is expected to be much larger than all other molecules discussed. This prediction should be checked experimentally. The halogen molecules, F_2, Cl_2 and Br_2, and their hydrides can not be treated by this method to calculate their Raman intensities because their absorption spectra are broad and structureless. Their vibrational frequencies and bond lengths in the excited states cannot be determined accurately.

In conclusion, we see that this method is capable of predicting the correct order of magnitude for the derived polarizabilities. Though the numerical agreements are not completely satisfactory, the theory clearly relates the scattering processes with the more fundamental process of electronic transitions in a molecule. From this point of view we can have a much better insight into the Raman spectroscopy.

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