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New Odd Levels of Pr I with Low Angular Momentum

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Ten new odd levels, of praseodymium I (Pr I), having angular momentum less than 3.5, have been discovered through Fourier transform spectroscopy and presented in this paper. The discovered levels not only explain previously known lines, but also explain some new lines of Pr I. All the new levels together explain fifty-six atomic lines. Previously known classifications of two of the lines of Pr are incorrect, new classifications of these lines have been suggested.

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I. INTRODUCTION

Praseodymium (Pr) is an element belonging to the lanthanide group. Praseodymium is very rich in spectral lines as well as in hyperfine levels. The recently recorded Fourier transform (FT) spectra at Germany revealed more than 20000 spectral lines of Pr. The hyperfine structure of neutral and ionic Pr has been studied in great detail; some important and recent works have been given in Refs. [1–25]. The work of Ginibre [11–14], on the hyperfine structure studies is remarkable. Although she classified a huge number of spectral lines of Pr, thousands of spectral lines were left unclassified, due to unknown levels of Pr I and Pr II. Our group at Graz, in collaboration with the group at Hamburg, has been studying the hyperfine structure (hfs) of Pr using laser induced fluorescence (LIF) spectroscopy since 2005, and has studied thoroughly the hyperfine structures of Pr [20–25]. But still many lines (in the FT spectrum) in the far-infrared and green region of the electromagnetic spectrum are unclassified, indicating a further need to study the hyperfine structure of Pr. The unavailability of lasers in the UV and far-infrared region limited the study of the hfs of Pr by laser induced fluorescence spectroscopy.

II. HYPERFINE STRUCTURE

The hyperfine structure is explained in terms of properties of the nucleus other than its charge. It acts as fingerprints in identifying atoms and molecules.

Usually we deal with the two lowest orders of interaction: (i) the magnetic dipole

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interaction and (ii) the electric quadrupole interaction.

The interaction of a nuclear magnetic moment with the average magnetic field $\vec{B}$ produced by the electron is considered as a small perturbation to the energy of the atoms. The interaction Hamiltonian leads to an energy given by

$$E_\mu = \left(\frac{A}{2}\right)[F(F+1) - I(I+1) - J(J+1)]. \tag{1}$$

The interaction of the average gradient of the electric field produced by the electron at the place of the nucleus and the nuclear quadrupole moment gives rise to an electric hyperfine structure. Unlike the magnetic dipole interaction which splits hyperfine levels, the quadrupole interaction causes only a shift in the energy of hyperfine levels. The shift in energy is given by

$$E_Q = \left(\frac{B}{4}\right)\left[\frac{\frac{3}{2}C(C+1) - 2I(I+1)J(J+1))}{(IJ(2I-1)(2J-1))}\right]. \tag{2}$$

The transitions between two hyperfine levels follow the selection rules $\Delta F = 0, \pm 1$ and $\Delta J = 0, \pm 1$. Each allowed transition represents a component of the hyperfine structure pattern of a spectral line. The frequency of a component is given by

$$\nu = \nu_c + E_\mu(F_o, J_o, I) + E_Q(F_o, J_o, I) - E_\mu(F_u, J_u, I) - E_Q(F_u, J_u, I). \tag{3}$$

ν_c is the energy difference between fine structure levels, 'o' and 'u' represents upper and lower levels, respectively. The relative intensity of each individual hyperfine component is given by [16]

$$I(F_o \to F_u) = \frac{(2F_o+1)(2F_u+1)}{2I+1}\left\{\begin{matrix} J_o & F_o & I \\ F_u & J_u & 2 \end{matrix}\right\}^2, \tag{4}$$

where $\left\{\begin{matrix} J_o & F_o & I \\ F_u & J_u & 2 \end{matrix}\right\}$ is the 6J symbol.

III. THE FOURIER TRANSFORM SPECTRA OF PR

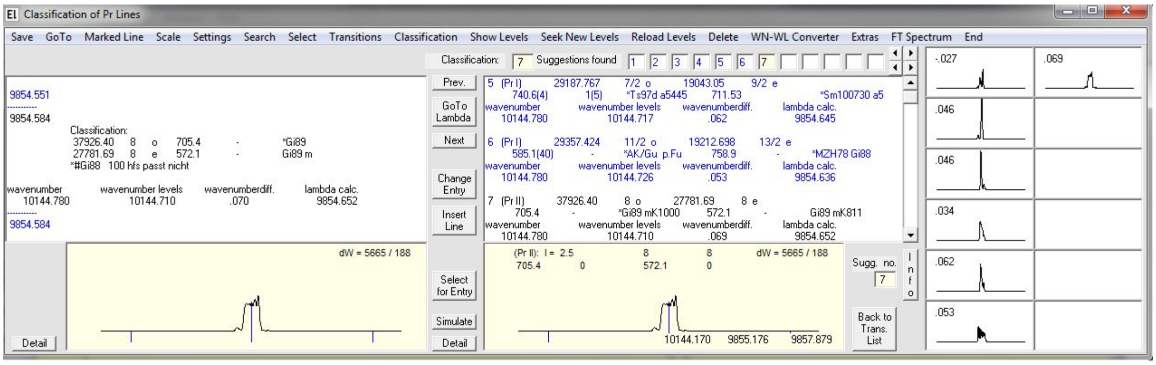
The investigation of the hyperfine structure of praseodymium was carried out by its Fourier transform spectrum. The FT spectra of Pr have more than 20000 spectral lines. The signal to noise ratio of the hfs of most of the lines is good enough to be fitted. The FT spectra were recorded at the Institute of Quantum Optics at the Leibniz University in Hannover with a high resolution FT-IR spectrometer (Bruker IFS 120 HR) (further details can be found in Ref. [20]).

Two special computer programs were also used for the investigation of the hyperfine structures.

III-1. The classification program

The classification program, which classifies spectral lines by means of their hyperfine structure, was written by L. Windholz (Institute of Experimental Physics, Graz, Austria) [27]. This program can be used for any element. The program can simultaneously be used for atomic or ionic lines or both. This program uses three data files, (i) a level file for atoms, which contains all known levels of atomic states, (ii) a level file for ions, which contains all known levels of the first ionic state of the atoms, and (iii) the wavelength file, which contains all known lines, whether classified or unclassified. This program has the ability to deal with a large number of spectral lines and levels.

Fig. 1 shows a screenshot of the classification program. It shows the classification of the line 9854.584 Å. The middle window displays all possible suggestions for classification of the line. The right side window shows the hyperfine structure of each of these suggestions. The suggestion for the line is generated by the difference of energies of odd and upper levels from the level file of atoms and ions. One of the suggestions is the actual explanation if both levels are known. This suggestion is selected and stored in the left window. If no suggestion matches with the hf structure in FT, this is an indication that at least one of the levels is unknown. In this case the left side window remains empty.



```
9854.551
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9854.584
          Classification:
           37926.40    8    o    705.4          -            *Gi89
           27781.69    8    e    572.1          -            Gi89 m
          *#Gi88  100 hfs passt nicht

wavenumber          wavenumber levels     wavenumberdiff.      lambda calc.
   10144.780             10144.710             .070              9854.652
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9854.584

                                                       dW = 5665 / 188
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Classification:  7  Suggestions found  1  2  3  4  5  6  7

5  (Pr I)      29187.767     7/2  o      19043.05      9/2  e
       740.6(4)        1(5)       *Ts97d a5445      711.53              *Sm100730 a5
wavenumber          wavenumber levels     wavenumberdiff.      lambda calc.
   10144.780             10144.717              .062              9854.645

6  (Pr I)      29357.424     11/2  o     19212.698     13/2  e
       585.1(40)        -         *AK/Gu  p.Fu      758.9        -       *MZH78 Gi88
wavenumber          wavenumber levels     wavenumberdiff.      lambda calc.
   10144.780             10144.726              .053              9854.636

7  (Pr II)     37926.40      8  o       27781.69       8  e
       705.4            -         *Gi89 mK1000      572.1        -        Gi89 mK811
wavenumber          wavenumber levels     wavenumberdiff.      lambda calc.
   10144.780             10144.710              .069              9854.652

   (Pr II):  I =  2.5           8             8          dW = 5665 / 188
    705.4          0           572.1          0

                                   10144.170     9855.176     9857.879
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FIG. 1: A screenshot of the classification program showing the Ginibre classification [13] of the line 9845.584 Å.

If the line is classified, the left side of the window shows the center of gravity wavelength of the spectral line, the wave numbers, the angular momenta, the hyperfine constants of the upper and lower levels, and remarks against each level. The remarks usually display the name/s of the person or group who discovered the level.

III-2. Fitter program

The hyperfine structures are an intensity distribution function of the frequency. To evaluate the hyperfine constants and center of gravity of a laser spectroscopically recorded line or of a line extracted from the FT spectra the fitter program, especially designed for this purpose, is used. This program was designed in Hamburg, Germany [28]. In order to evaluate the physical information contained in the recorded hyperfine structure, a mathematical model of the intensity distribution is computed which best fits an already recorded intensity distribution 'I'. The position of each individual component is calculated by Equation (3) and the intensity of each component is introduced theoretically by Equation (4).

The mathematical model contains the physical boundary conditions as parameters. The model is developed by the variation of these parameters gradually according to the method of least square errors or Gauss-Newton procedures. The error function is the squared error sum of the difference of the measured intensity at a given frequency point and the calculated intensity at the corresponding position. The error function can be expanded using a Taylor series, and a number of nonlinear, inhomogeneous equations are obtained. The number of such equations are exactly equal to the number of parameters in the fit. The solution of these equations is obtained in such a way that the deviation from the measured intensity becomes less and less, and the solution also gives a new set of parameters. These new parameters are used as starting values for the next iteration, and this procedure is repeated until an abort criterion is reached.

IV. RESULT AND DISCUSSION

New odd levels of Pr I with low angular momentum were found through the Fourier transform spectrum of Pr. Shamim *et al.* [21] has also found new Pr I levels with low angular momentum using laser induced fluorescence (LIF) spectroscopy through the investigation of spectral lines in the range 4200 Å to 7500 Å. The unavailability of a laser beyond 7500 Å disallowed them to continue their studies beyond 7500 Å through LIF spectroscopy. In this paper we targeted this region and studied it through the FT spectrum of Pr. Here one can realize the advantage of the FT spectrum over other methods for the investigation of spectral lines, provided these lines have enough intensity so that the hyperfine structure could be fitted.

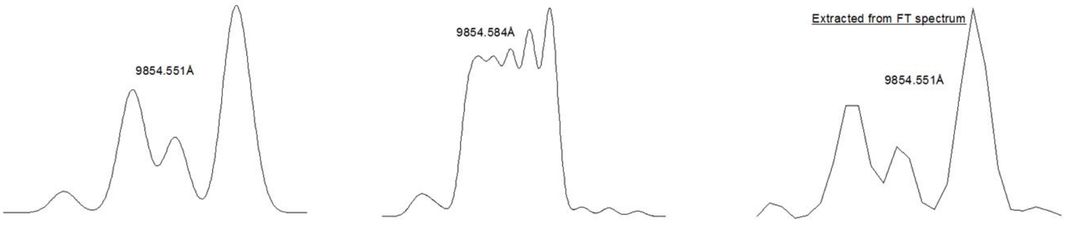
The theoretical hyperfine structure of the classification of the line 9854.584 Å suggested by Ginibre [13] does not match with the corresponding hfs in the Fourier transform spectrum of Pr (see Fig. 2). This leads us to work on this line, and, by fitting the hyperfine structure (extracted from the FT spectrum), we were successful in finding an unknown level that explains not only this line but also seven other lines of Pr (see Table III).

TABLE I: The new classification of lines 9522.721 Å and 9854.551 Å

Wavelength	Upper level			Lower Level			Remarks
Å	J	Parity	Energy/cm^{-1}	J	Parity	Energy/cm^{-1}	
9522.740	4.5	even	29384.440	4.5	odd	18886.070	Ginibre classification [13]
9522.721	1.5	odd	22409.678	1.5	even	11911.350	this work
9854.584	8	odd	37926.400	8	even	27781.690	Ginibre classification [13]
9854.551	1.5	odd	22409.678	0.5	even	12264.864	this work

TABLE II: New odd levels with low angular momentum

Energy $\pm 0.10/\mathrm{cm}^{-1}$	J_o	A_o/MHz
22409.670	1.5	1012(9)
22595.375	2.5	340(5)
23755.490	2.5	201(2)
24063.650	2.5	622(5)
24137.503	1.5	1038(10)
24761.845	1.5	2091(10)
24865.030	2.5	1182(3)
25121.220	2.5	887(5)
25505.495	0.5	1000(20)
25571.030	1.5	−12(6)



(a) (b) (c)

FIG. 2: (a) Theoretical hf structure of the line 9854.551 Å, drawn from the hyperfine structure found in this study, (ii) Theoretical hf structure of the line 9854.584 Å, drawn from the hyperfine structure of the levels of the classification suggested by Ginibre [13], (iii) the hf structure of Pr extracted from the FT spectrum.

The best fit of the line 9854.584 Å was obtained by the Fitter program. The best fit shows that the spectral line is a transition from an upper level with $J = 3/2$ and $A = 1011$ to a lower level with $J = 1/2$ and $A = 1534$. The center of gravity of the spectral line was determined as 10144.814 cm^{-1}. Fig. 3 shows the best fit of the hf structure.

The odd level 12264.864 cm^{-1} has $J = 1/2$ and $A = 1534$. Assuming it as the lower level of the transition, the center of gravity wavenumber was added in to its energy. The energy of the new even upper level was found to be 22409.678 cm^{-1}. The transition list of the upper level was generated. It was found that one of the lines (6264.771Å) of the new level blends with another line (6264.696Å) of Pr. The blend structure was fitted by keeping fixed the hyperfine constants of the levels. The best fit is shown in Fig. 4. It is apparent from the best fit that the line 6264.771 belongs to the new level and this confirms its existence. The new level classifies all together 8 lines of Pr. Some of the lines have

TABLE III: Spectral lines of Pr I explained by new levels

Wavelength	Upper level				Lower levels				Remarks
±0.100	Energy ±0.10	J	Parity	A	Energy ±0.10	J	Parity	A	& Ref.
Angstrom	cm^{-1}			MHz	cm^{-1}			MHz	col. 9
5228.883	25571.03	1.5	o	-12(6)	6451.808	2.5	e	1191(2)	* [16]
5459.969	24761.85	1.5	o	2091(10)	6451.808	2.5	e	1191(2)	* [16]
6078.750	24063.65	2.5	o	622(5)	7617.44	3.5	e	868v	* [16]
6238.795	24761.85	1.5	o	2091(10)	8737.556	2.5	e	1149(5)	* [29]
6264.771	22409.67	1.5	o	1012(9)	6451.808	2.5	e	1191(2)	* [16]
6350.513	23755.5	2.5	o	201(2)	8013.089	3.5	e	165v	** [23]
6523.002	24063.65	2.5	o	622(5)	8737.556	2.5	e	1149(5)	** [29]
6855.743	22595.39	2.5	o	340(5)	8013.089	3.5	e	165v	** [23]
6871.503	25505.49	0.5	o	1000(20)	10956.65	0.5	e	560(10)	* [29]
6935.939	24063.65	2.5	o	622(5)	9649.97	1.5	e	1554.9v	** [29]
7550.429	25505.49	0.5	o	1000(20)	12264.86	0.5	e	1534	* [29]
7562.950	24865.03	2.5	o	1182(3)	11646.31	2.5	e	317(10)	* [29]
7575.832	24865.03	2.5	o	1182(3)	11668.79	3.5	e	805.5v	* [29]
7665.941	25505.49	0.5	o	1000(20)	12464.37	1.5	e	712(4)	* [29]
7692.711	24865.03	2.5	o	1182(3)	11869.29	3.5	e	210(1)	** [29]
7755.437	22595.38	2.5	o	340(5)	9704.744	3.5	e	779.1(6)	* [29]
7835.019	22409.67	1.5	o	1012(9)	9649.97	1.5	e	1554.9v	* [29]
7886.016	22595.38	2.5	o	340(5)	9918.19	3.5	e	1057.4(5)	* [16]
7904.344	23755.5	2.5	o	201(2)	11107.7	2.5	e	658(2)	* [23]
7973.718	25571.03	1.5	o	-12(6)	13033.28	1.5	e	905(4)	* [23]
8030.244	25505.49	0.5	o	1000(20)	13056	0.5	e	-330(2)	* [29]
8034.237	25571.03	1.5	o	-12(6)	13127.72	2.5	e	156(1)	** [29]
8061.870	24865.03	2.5	o	1182(3)	12464.37	1.5	e	712(4)	* [29]
8085.314	25571.03	1.5	o	-12(6)	13206.33	1.5	e	256	* [29]
8139.045	23755.5	2.5	o	201(2)	11472.41	3.5	e	272.9v	* [29]
8255.935	23755.5	2.5	o	201(2)	11646.31	2.5	e	317(10)	* [29]
8400.450	25571.03	1.5	o	-12(6)	13670.18	2.5	e	18v	** [29]

continued . . .

Wavelength	Upper level				Lower levels				Remarks
±0.100	Energy ±0.10	J	Parity	A	Energy ±0.10	J	Parity	A	& Ref.
Angstrom	cm^{-1}			MHz	cm^{-1}			MHz	col. 9
8420.413	24137.52	1.5	o	1038(10)	12264.86	0.5	e	1534	* [29]
8540.267	23755.5	2.5	o	201(2)	12049.47	3.5	e	871(2)	* [29]
8632.760	22409.67	1.5	o	1012(9)	10829.07	2.5	e	979.7	* [29]
8700.448	24137.52	1.5	o	1038(10)	12647	2.5	e	891.8	* [23]
8702.587	22595.38	2.5	o	340(5)	11107.7	2.5	e	658(2)	** [23]
8741.630	24137.52	1.5	o	1038(10)	12701.12	1.5	e	833(3)	* [29]
8830.602	22595.38	2.5	o	340(5)	11274.24	3.5	e	285.6(6)	* [23]
8845.583	22409.67	1.5	o	1012(9)	11107.7	2.5	e	658(2)	** [23]
8899.408	22595.38	2.5	o	340(5)	11361.76	1.5	e	53.8	* [29]
8987.935	22595.38	2.5	o	340(5)	11472.41	3.5	e	272.9v	* [29]
9003.111	24137.52	1.5	o	1038(10)	13033.28	1.5	e	905(4)	* [23]
9021.552	24137.52	1.5	o	1038(10)	13056	0.5	e	-330(2)	* [29]
9043.717	23755.5	2.5	o	201(2)	12701.12	1.5	e	833(3)	* [29]
9179.224	25571.03	1.5	o	−12(6)	14679.85	0.5	e	-1239v	* [29]
9215.389	23755.5	2.5	o	201(2)	12907.06	2.5	e	1336(4)	* [23]
9288.231	22409.67	1.5	o	1012(9)	11646.31	2.5	e	317(10)	* [29]
9291.113	24865.03	2.5	o	1182(3)	14104.96	1.5	e	653	* [23]
9323.870	23755.5	2.5	o	201(2)	13033.28	1.5	e	905(4)	* [23]
9342.165	25121.19	2.5	o	887(5)	14420	1.5	e	780	* [29]
9352.404	24137.52	1.5	o	1038(10)	13448.02	2.5	e	825(1)	** [23]
9417.424	24063.65	2.5	o	622(5)	13448.02	2.5	e	825(1)	** [23]
9480.762	22409.67	1.5	o	1012(9)	11864.89	0.5	e	654.5v	** [29]
9522.721	22409.67	1.5	o	1012(9)	11911.35	1.5	e	920v	*** [29]
9578.860	25505.49	0.5	o	1000(20)	15068.73	1.5	e	-238.7v	** [29]
9668.762	23755.5	2.5	o	201(2)	13415.74	3.5	e	797	* [23]
9679.442	24063.65	2.5	o	622(5)	13735.3	2.5	e	775(3)	* [29]
9704.879	23755.5	2.5	o	201(2)	13454.22	3.5	e	432(5)	* [29]
9720.092	25121.19	2.5	o	887(5)	14836.07	2.5	e	1340(3)	* [29]
9854.559	22409.67	1.5	o	1012(9)	12264.86	0.5	e	1534	*** [29]

* newline, **Previously known but unclassified line, *** new classification

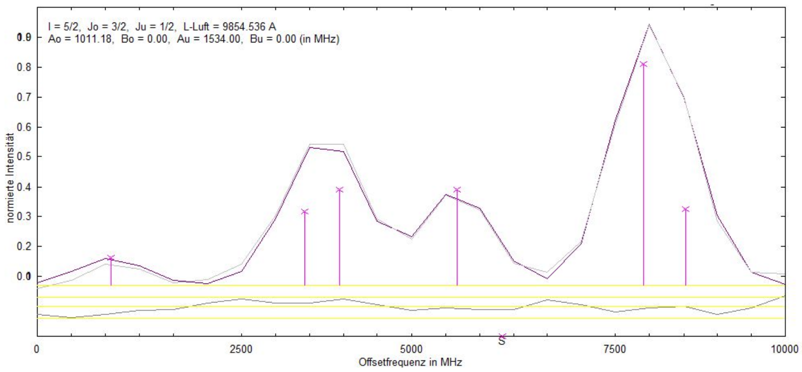


FIG. 3: The best fit of the line 9854.551 Å.

relatively good SNR. These lines were fitted and an average value of the hf constant A was determined.

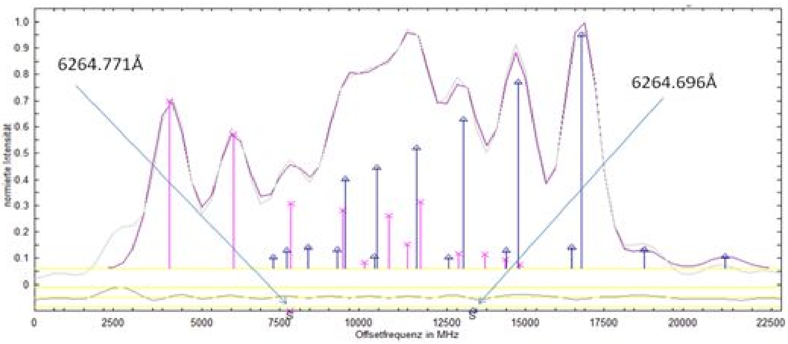


FIG. 4: The best fit of the blend situation of 6264.771 Å (a spectral line of new level 22409.678 cm^{-1}) and 6264.696 Å.

We suggest a new classification of the already classified spectral lines 9854.584 Å and 9522.740 Å. The center of gravity wavenumbers are also modified by the new classifications. The line 9854.584 was classified as an ionic line of Pr II, here we suggest it is an atomic line of Pr I. Table I gives the new classification of both the lines.

The other levels given in Table II have been found in the similar manner by fitting one of their lines given in Table III. The procedure is similar to the one explained above for the new level 22409.678 cm^{-1}.

V. CONCLUSIONS

The hyperfine structure of the praseodymium spectral lines (unclassified), was investigated through the FT spectrum. Ten new odd levels with lower angular momenta were discovered. The new levels found in this work explain fifty-six lines; thirteen of them were known but unclassified, two of them were classified but the hyperfine structure suggests that the classification was not correct. New classifications for these lines have been suggested. Forty-one lines explained by new levels are new lines of Pr I and are reported for the first time. This work is one further step towards the complete knowledge of the hyperfine structure of praseodymium.

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References

[1] H. E. White, Phys. Rev. **34**, 1397 (1929). doi: 10.1103/PhysRev.34.1397
[2] H. Ma *et al.*, J. Phys. B: At. Mol. Opt. Phys. **32** 1345 (1999). doi: 10.1088/0953-4075/32/5/023
[3] B. Furmann, D. Stefanska, E. Stachowska, J. Ruczkowski, and J. Dembczynski, Eur. Phys. J. D **17**(3), 275 (2001). doi: 10.1007/s100530170001
[4] R. M. MacFarlane, D. P. Burum, and R. M. Shelby, Phys. Rev. Lett. **49**(9), 636 (1982). doi: 10.1103/PhysRevLett.49.636
[5] M. Li *et al.*, Hyperfine Interact. **128**(4), 417 (2000). doi: 10.1023/A:1012660321742
[6] K. Murakawa, J. Phys. Soc. Japan **15**, 2306 (1960). doi: 10.1143/JPSJ.15.2306
[7] B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961). doi: 10.1103/PhysRev.122.1802
[8] B. Furmann, D. Stefanska, J. Dembczynski, and E. Stachowska, Phys. Scr. **72**, 300 (2005). doi: 10.1238/Physica.Regular.072a00300
[9] A. Y. Cabezas, Phys. Rev. **126**, 1004 (1962). doi: 10.1103/PhysRev.126.1004
[10] B. Furmann, A. Krzykowski, D. Stefanska, and J. Dembczynski, Phys. Scr. **74**, 658 (2006). doi: 10.1088/0031-8949/74/6/010
[11] A. Ginibre, Phys. Scr. **23**, 260 (1981). doi: 10.1088/0031-8949/23/3/008
[12] A. Ginibre, Phys. Scr. **39**, 694 (1989). doi: 10.1088/0031-8949/39/6/005
[13] A. Ginibre, PhD Thesis, Université de Paris-Sud, Centre d'Orsay Paris (1988) (unpublished).
[14] A. Ginibre, Phys. Scr. **39**, 710 (1989). doi: 10.1088/0031-8949/39/6/006
[15] W. J. Childs and L. S. Goodman, Phys. Rev. A **24**, 1342 (1981). doi: 10.1103/PhysRevA.24.1342
[16] T. Kuwamoto *et al.*, J. Phys. Soc. Japan **65**, 3180 (1996). doi: 10.1143/JPSJ.65.3180
[17] B. Furmann, G. Szawiola A. Jarosz, A. Krzykowski, D. Stefanska, and J. Dembczynski, Hyperfine Interact. **196**(1-3), 61 (2010). doi: 10.1007/s10751-009-0152-0
[18] A. Krzykowski, B. Furmann, D. Stefanska, A. Jarosz, and A. Kajoch, Opt. Commun. **140**, 216 (1997). doi: 10.1016/S0030-4018(97)00165-X
[19] J. Ruczkowski, E. Stachowska, E. Elantkowska, G. H. Guthöhrlein, and J. Dembczyński, J. Phys. Scr. **68**, 133 (2003). doi: 10.1238/Physica.Regular.068a00133
[20] B. Gamper *et al.*, J. Phys. B **44**, 45003 (2011).

[21] K. Shamim, I. Siddiqui, and L. Windholz, Eur. Phys. J. D **64**, 20250 (2011).

[22] T. Syed *et al.*, Phys. Scr. **84**, 65303 (2011).

[23] Z. Uddin *et al.*, Adv. Opt. Sc. **2012**, 639126 (2012).

[24] Z. Uddin *et al.*, J. Phys. B: At. Mol. Opt. Phys. **45**, 205001 (2012).
doi: 10.1088/0953-4075/45/20/205001

[25] Z. Uddin *et al.*, J. Phys. Sc. & App. **2(4)**, 88 (2012).

[26] K. Marinova, Z. Blaszczak, and B. Markov, *Proceedings of the 6th International Workshop on Application of Lasers in Atomic Nuclei Research* (LASER 2004 , Poznan, Poland, (2004).

[27] L. Windholz, and G. H. Guthöhrlein, Phys. Scr. **T105**, 55 (2003).
doi: 10.1238/Physica.Topical.105a00055

[28] Program package “Fitter”, developed by G. H. Guthöhrlein, Helmut-Schmidt-Universität, Universität der Bundeswehr, Hamburg, Germany (1998) (unpublished).

[29] Helmut-Schmidt-Universität, Universität der Bundeswehr Hamburg, Laboratorium für Experimentalphysik, unpublished material taken from several diploma theses (supervisor G. H. Guthöhrlein).