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Radiative lifetimes of 7d, 8d $^1D_2$ excited states of Hg I

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Abstract. Radiative lifetimes of $7d, 8d\ ^1D_2$ excited states of Hg I are measured using pulsed two-photon excitation from the ground $[Xe]5d^{10}6s^2\ ^1S_0$ mercury state, detecting the decay of the laser-induced fluorescence. The results are compared with theoretical values, obtained by means of a Hartree-Fock single configuration method, taking into account electron configuration interaction. The radiative lifetime value dependence on the effective principal quantum number for the $nd\ ^1D_2$ series is analyzed and compared with the quantum defect dependence.

PACS. 32.70.Cs Oscillator strengths, lifetimes, transition moments

1 Introduction

Radiative lifetimes of excited mercury states and transition probabilities within the mercury level scheme are important for the investigation of different types of light sources in which mercury is used. Values of radiative lifetimes of Hg I singlet states $[Xe]5d^{10}6snl\ ^1L$ can be found in several papers. A short review of the literature shows, however, that most of them treat low lying excited states of Hg I while high lying excited singlet states have been investigated only occasionally. Experimental radiative lifetimes of $ns\ ^1S_0$ states (n = 7–10) are published in references [1–5], but the values obtained by electron excitation of the investigated states [1] are considerably higher than those obtained by selective excitation [3,5] as well as those measured using electron-photon and photon-photon coincidence methods [2,4]. For the $8s\ ^1S_0$ excited state, data derived by laser excitation [3] and electron-photon coincidence [2] experiments are in a good agreement, while a value obtained in a two-photon laser excitation experiment [5] is about 30% smaller. Several papers in the literature report on experimental determinations of the radiative lifetime of the resonance $6p\ ^1P_1$ state but only one experimental value for an upper lying member of this series, the state $10\ ^1P_1$ [2], is available. Data for radiative lifetimes of the $nd\ ^1D_2$ states (n = 6–9) are available; the investigations were performed using different experimental methods [1–10]. The results obtained by different authors agree well for the 6 and $7d\ ^1D_2$ states, but the values for the $8d\ ^1D_2$ state, obtained by the electron excitation method [1] and the two-photon excitation method [5] differ considerably.

There exist only few theoretical calculations of radiative constants for the Hg I spectrum, which mainly concern low lying electron configurations.

Along with experimental values Chantepie *et al.* [9] obtained theoretical data for the $6s7d\ ^{1,3}D$ excited states using the Bates-Damgaard approximation. In these calculations the $6s7p–5d^96s^26p(6p')$ electron configuration interaction was also taken into account. Relativistic configuration interaction Hartree-Fock (HF) calculations including core polarization in the perturbed Hamiltonian (CIRHF + CP) for $6s6p$ and $6s^2$ electron configurations and a number of relevant perturbing configurations was used in reference [11]. The obtained $6s6p\ ^{1,3}P–6s^2\ ^1S_0$ transition probabilities are in good agreement with experimental data.

Using a relativistic pseudopotential method [12] the radiative lifetimes of $6, 7p\ ^{1,3}P$ and $6, 7d\ ^{1,3}D$, as well as of $ns\ ^{1,3}S$ (n = 7, 8, 9) states were calculated.

A single-configuration interaction approximation was employed in the calculation of the $6s6d–6s6p$ transition probabilities, which are in good agreement with experimental data [13]. In reference [3] theoretical single-configuration intermediate coupling branching ratios for transitions from $6s7s$, $6s8s$, $6s6d$, $6s7d$ excited states are reported. The results agree well with experimental data. A single configuration approximation was used for the calculation of $6p–n\ ^3S$ ($n \leq 11$) oscillator strengths in reference [14]. In reference [15] model potential configuration interaction calculations of $6s^2–6s6p$ oscillator strengths were performed. In these calculations the core polarization and penetration by the valence electron were taken into account.

There are no experimental and theoretical data available for radiative constants of excited states belonging to the other singlet spectral series ($6snl\ ^1F,\ ^1G$).

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The aim of this work is to investigate experimentally the radiative lifetimes of $7,8d\ ^1\mathrm{D}_2$ excited states and to clarify the discrepancies one can find in the mentioned papers, as well as to obtain theoretical data for radiative lifetimes of $nd\ ^{1,3}\mathrm{D}$ ($n \leq 9$) states.

2 Experiment

In the present experiment, we employed laser induced fluorescence detection after pulsed laser excitation using the same experimental set-up as in our previous work [16]. The investigated states were excited by two-photon absorption from the mercury $[\mathrm{Xe}]5d^{10}6s^2\ ^1\mathrm{S}_0$ ground state. The excitation was realized in a quartz cell with a side arm container in which a natural isotope mixture was placed. The cell and the container had independent heating systems. While during the experiment the cell temperature was kept constant, the arm temperature was varied in the interval 286−324 K by means of a semiconductor element, which was used either as a refrigerator or heater. The side arm temperature was maintained with an accuracy of 1 K.

The exciting laser light was generated by a tunable laser system: a Nd:YAG-laser (Spectra Physics, Quanta Ray GCR 170) was pumping a dye laser (Radiant Dyes DL midi E). Coumarin 307 dissolved in Isopropanol was used to obtain UV radiation in the spectral region 240–260 nm after frequency doubling. During the experiments the output power was kept constant within 10% by a computer controlled autotracking system. The excitation UV laser pulses had the following parameters: a spectral width of 0.1 Å; duration ≈ 10 ns; repetition rate 10 Hz and pulse energy up to 2 mJ. In the excitation region the laser beam had a diameter of 2 mm. The registration of the two-photon resonances was carried out in the way used in our previous work [16]. We have observed two-photon resonances of $nd\ ^1\mathrm{D}_2$ states for principal quantum numbers up to $n = 11$, but the signals for states with $n \geq 9$ had insufficient intensity for lifetime measurements in an appropriate region of mercury atom concentrations. The radiative lifetimes of $7,8d\ ^1\mathrm{D}_2$ states were measured using the spectral lines 3906.37 Å ($7d\ ^1\mathrm{D}_2$–$6p\ ^1\mathrm{P}_1$) and 3704.17 Å ($8d\ ^1\mathrm{D}_2$–$6p\ ^1\mathrm{P}_1$) (see Fig. 1) [17,18].

These spectral lines were selected by a grating monochromator and the time-dependence of their intensity was detected by a photomultiplier (Hamamatsu R-955). The decay curves were recorded by a digital oscilloscope (LeCroy 9360), averaging the signal of 1000 excitation pulses, and then stored in a computer. The obtained decay curves were checked for being influenced by laboratory stray magnetic fields.

3 Results and discussion

The radiative lifetimes of Hg I $7,8d\ ^1\mathrm{D}_2$ states obtained in the present work are presented in Table 1 and compared with results of other authors. The values were derived after extrapolation of the data measured at different mercury atom concentrations to zero concentration. The number density of mercury atoms was varied in the interval $2.3 \times 10^{13}-7\times10^{14}$ cm^{-3} [19]. More then 40 points were used in the extrapolation. In the process of decay curve treatment the first 20 ns of the initial part were discarded, in order to prevent any influence of the excitation laser pulse. The errors of the decay curve parameters, obtained at different atom concentrations were less than 1%. The error of the values, obtained after extrapolation, which are presented in Table 1, corresponds to twice the standard deviation.

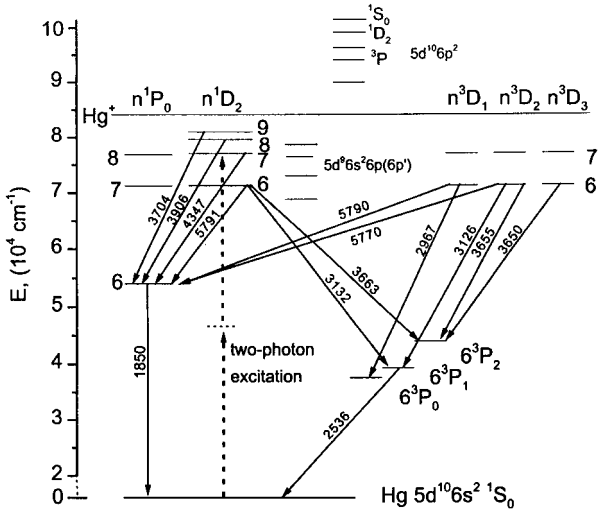

Fig. 1. Partial Grotrian diagram of Hg I excited states.

A delayed coincidence method with nonselective electron excitation was used in reference [1]. The spectral lines emitted from the $nd\ ^1\mathrm{D}_2$ states ($nd\ ^1\mathrm{D}_2$–$6p\ ^1\mathrm{P}_1$), which were used in this paper for radiative lifetime measurements were not resolved from the intercombination spectral lines from the $nd\ ^3\mathrm{D}$ states ($n\ ^3\mathrm{D}_{1,2}-6p\ ^1\mathrm{P}_1$). The higher the $n\ ^1\mathrm{D}_2$ state is, the more this problem becomes serious. Therefore the radiative lifetimes obtained in that paper have smaller values for higher lying states than our and other author results, obtained by employing selective excitation. The same problem raised in reference [3], where selective laser excitation of the $7d\ ^1\mathrm{D}_2$ state from the $6p\ ^3\mathrm{P}_1$ state was realized. The interference filter, which was used in [3] did not resolve the investigated spectral line 4347 Å ($7d\ ^1\mathrm{D}_2-6p\ ^1\mathrm{P}_1$) from the 4358 Å ($7s\ ^3\mathrm{S}_1-6p\ ^3\mathrm{P}_1$) spectral line. The $7s^3\mathrm{S}_1$ state was populated in this case from the $7d^1\mathrm{D}_2$ state *via* a spin-forbidden transition to $7p\ ^3\mathrm{P}$. When the UV-line 2655 Å ($7d\ ^1\mathrm{D}-6p\ ^3\mathrm{P}_1$) was used, it again was not totally resolved from the intercombination spectral line 2536 Å ($6p\ ^3\mathrm{P}_1-6s\ ^1\mathrm{S}_0$). That is the reason why, as the authors have emphasized in their paper [3], the radiative lifetime value of the $7d\ ^1\mathrm{D}_2$ excited state obtained is smaller than the other experimental values.

Our value for the $7d\ ^1\mathrm{D}_2$ state agrees well with data obtained by electron-photon coincidence [2] technique and the delayed coincidence experiment with electron excitation [1], as well as with the Hanle experiment [9] and is close to the values obtained by two-photon excitation [5, 8]. For the $8d\ ^1\mathrm{D}_2$ state our result agree well with the

Table 1. Experimental data for radiative lifetimes of $nd\ ^1D_2$ states of Hg I (in ns).

State	This	Comparison/reference number								
	experiment	[1]	[2]	[3]	[5]	[6]	[7]	[8]	[9]	[10]
$6d\ ^1D_2$					10.9(30)	10.5(3)	14(2)	10.6(3)		10.5(10)
$7d\ ^1D_2$	38.3(11)	37.7(8)	38.5(0.8)	34.9(17)	40(1)			37(1)	38.5(5)	
$8d\ ^1D_2$	122(6)	91.1(25)			126(7)					
$9d\ ^1D_2$		139(5)								

[1] Delayed coincidence method electron excitation, [2] delayed coincidence method, photon electron coincidence, [3] delayed coincidence method laser excitation, [5] laser induced fluorescence detection two photon excitation, [6] delayed coincidence method; electron laser excitation, [7] beam foil method, [8] laser induced fluorescence detection two photon excitation, [9] Hanle method, [10] Hanle method.

value obtained by two-photon excitation in reference [5]. The possible reason for the disagreement with the value obtained in [1] for the $8d\ ^1D_2$ state has already been discussed.

4 Theory

In the present work the Cowan code [20] was used to calculate the radiative lifetimes of the $6snd\ ^{1,3}D$ ($n = 6$–9) states of Hg I. The single-configuration HF method produces the one electron orbitals, which allow to obtain the needed radial integrals. Configuration interaction between even parity electron configurations ($6s^2$; $6sns$ ($n \leq 12$); $6snd$ ($n \leq 10$); $6p^2$) and odd parity configurations ($6snp$ ($n \leq 11$); $6snf$ ($n \leq 8$); $5d^9 6s^2 6p(6p')$) was taken into account.

It should be mentioned that in the mercury spectrum the singlet $6snd\ ^1D$ states are located below the triplet $6s6d\ ^3D$ states, *i.e.* these states have inverted relative positions. A possible reason for this arrangement of states could be spin-other-orbit interaction [21]. However, the formulae accounting for spin-other-orbit interaction in the single-configuration approximation [22] do not produce the inverted position of the $6snd\ ^{1,3}D$ states, despite of the sign of the exchange integral G. When the configuration interaction with $6p^2$ configuration is taken into account, the relative positions of the $6snd\ ^{1,3}D$ states coincide with the experimental one's.

The configuration interaction (CI) integrals (R) for all electron configurations were fixed at 0.85 of their HF values. The exchange integrals G, spin-orbit integrals ζ as well as the averaged energies $E_{\rm av}$ of the relevant configurations were let to vary in the process of fitting the state energies. For energy fitting, we used experimental values of the excited state energies [18]. For the states of the configuration $6p^2$ we used the energies from [23] (and references therein).

Taking into account a larger number of electron configurations, both odd and even parity, did not lead to substantial changes in the obtained data. The main CI occurs with $6p^2$ and $6p'$ configurations. When all CI integrals of the considered even configurations were let variable the radiative lifetime values for $nd\ ^3D$ (but not for $6d\ ^3D_1$) practically coincided with experimental data, but at the same time the radiative lifetime data for singlet $nd\ ^1D$ became approximately half the experimental values.

Table 2. Theoretically obtained radiative lifetimes of $nd\ ^{1,3}D$ states of Hg I (in ns).

State	Theory			Experiment
	This work	[12]	[9]	
$6d\ ^1D_2$	8	17		10.6
$^3D_1$	4	6.9		7.2
$^3D_2$	7	7.0		9.2
$^3D_3$	8	7.9		7.8
$7d\ ^1D_2$	37	50		38.3
$^3D_1$	11	16	10.4	12.4
$^3D_2$	16	17	16.9	17.0
$^3D_3$	20	18	19.9	18.2
$8d\ ^1D_2$	82			122
$^3D_1$	24			
$^3D_2$	31			35.8
$^3D_3$	38			
$9d\ ^1D_2$	144			139
$^3D_1$	47			
$^3D_2$	59			55.0
$^3D_3$	73			

[9] Bates-Damgaard method, CI with $6p^2$ electron configuration, [12] relativistic pseudopotential method.

Relativistic effects were accounted for the way the Cowan code provides. Breit's approach for relativistic effects (which is included as an option in the code) was also tried and produced similar results.

The fitted values of the radial integrals produced mixing coefficients between triplet and singlet states of any one of the relevant electron configurations close to the corresponding values [3] calculated from Landé factors, radiative lifetime data and level energy fitting in a single configuration approximation.

Our results are presented in Table 2 and are compared with other theoretical and with experimental data. The values for the $6, 7d\ ^{1,3}D$ states given are obtained from experiments where selective laser excitation was employed [3,5,8]. For $7d\ ^3D$ states these values are also close

to the ones obtained in a experiment employing the Hanle method [9]. For $7,8d\ ^1D_2$ and $7,8,9d\ ^3D_2$ our experimental data are used (this work and Ref. [16]). Our theoretical data are also compared with other author's theoretical results. It should be mentioned that for triplet $nd\ ^3D$ states theoretical values increase with the total angular momentum J. This behaviour is not observed in any of the experimental works. Our theoretical data agree well with data of [9,12] (except for $6,7\ ^1D_2$; $6,7\ ^3D_1$ for which our data are smaller) and agree well with most of the experimental data. A discrepancy is observed for $6d\ ^1D_2$, $8d\ ^1D_2$, $6d\ ^3D_{1,2}$.

The difference between experimental and present theoretical results may have the following reasons:

- core polarization is not taken into account in the Cowan code, but effects strongly low lying states $6p\ ^{1,3}P$ and $6d\ ^{1,3}D$;
- the disagreement of 30–35% for the $8d\ ^1D_2$ state is due to an overestimation of the $8d\ ^1D_2$–$7p$ transitions, which could be a result of improper account for the $7p$–$6p'$ configuration interaction. We could not properly fit all relevant parameters related with the $6p'$ configuration since there are no experimental data available for energies for some of the theoretically predicted states, belonging to this configuration. Therefore, CI integrals between $6snp$ and $6p'$ states can be different from their proper values.

The data obtained in the present work and by other authors allow to treat the dependency of the radiative lifetimes of the $nd\ ^1D_2$ states on the effective principal quantum number: $\tau = \tau(n^*)$, where $n^* = n - \mu$; n is the principal quantum number; μ is the quantum defect. For unperturbed series, the dependency should follow the law

$$\tau = Cn^{*\alpha}$$

where C and α are constants characteristic for each spectral series.

For nonperturbed spectral series the $\tau = \tau(n^*)$ dependence (in double logarithmic scale), presented in Figure 2, therefore should follow a straight line: $\ln\tau = \alpha \ln n^* + \ln C$. For hydrogen-like spectral series, α should have a value close to 3. In Figure 2, the value for the $6d\ ^1D_2$ state is taken from the two-photon excitation experiment [5], the only one available value for the $9d\ ^1D_2$ state is taken from reference [1].

For principal quantum numbers $n = 6,7,8$, the predicted dependence is in fact observed, but with $\alpha = 4.65$. It can be seen that the dependence deviates from the straight line for the $9d\ ^1D_2$ state, in contradiction to reference [1] where a linear dependence of the $nd\ ^1D_2$ series including the $9d\ ^1D_2$ state is proposed. At the first glance this seems to be caused by the fact that the radiative lifetime of the $9d\ ^1D_2$ state given in reference [1] may be considerably smaller than the real one. As mentioned above, the influence of the unresolved spectral lines from the triplet $nd\ ^3D$ states increases with increasing principal quantum number of the investigated $nd\ ^1D_2$ state. Otherwise, if we suppose that the proposed $\tau(n^*)$ dependence

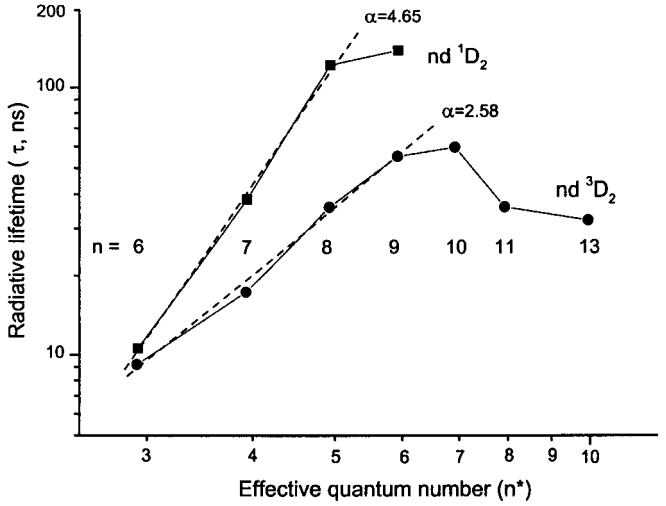

Fig. 2. Radiative lifetime dependences on effective principal quantum $\tau(n^*)$ for $nd\ ^{1,3}D_2$ excited states.

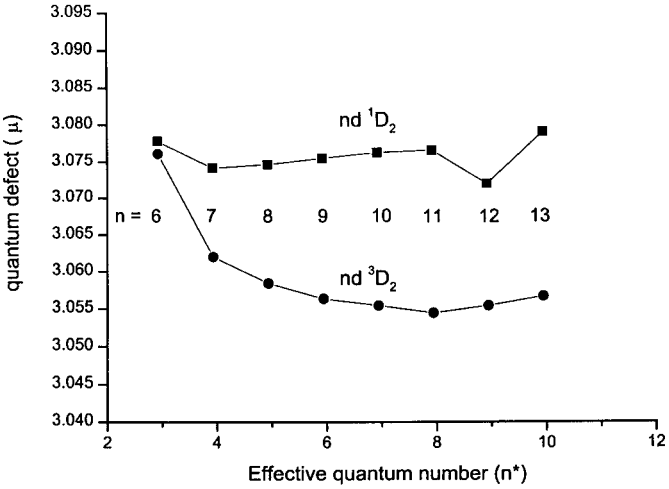

Fig. 3. Quantum defect dependences on effective principal quantum $\mu(n^*)$ for $nd\ ^{1,3}D_2$ excited states of Hg I.

is fulfilled for the $9d\ ^1D_2$ state, the corresponding value would be approximately 300 ns, which is considerably and surprisingly higher than the value obtained in [1]. Thus, really for the $9d\ ^1D_2$ state a deviation from linear dependence occurs.

In Figure 2 also the $\tau(n^*)$ dependence for $nd\ ^3D_2$ states is presented for comparison. Here one gets $\alpha = 2.58$ for the first four states ($n = 6$ to 9). For this spectral series a deviation from linear dependence is observed for $n \geq 10$ [16]. This behaviour supports the appearance of a deviation also for the $nd\ ^1D_2$ series.

On the other hand, for an unperturbed series the quantum defect μ is constant and independent from n^*. Therefore it is of interest to compare its behaviour with that of $\tau(n^*)$. The $\mu(n^*)$ dependence for the $nd\ ^1D_2$ and the $nd\ ^3D_2$ series is shown in Figure 3. The energies of the excited states given in reference [18] are used for the calculation of μ. But no considerable deviation from a smooth behavior of $\mu(n^*)$ is observed in the region of the investigated

states ($n = 8, 9, 10$). So the $\mu(n^*)$ dependence does in fact not support the observed behaviour of $\tau(n^*)$. It seems, that the perturbations in the lifetimes are not caused by perturbing (eventually unknown) levels, since such levels should influence also $\mu(n^*)$.

Conclusion

Radiative lifetimes of $7, 8d$ $^1D_2$ excited states of Hg I have been measured using two-photon excitation from the ground Hg I state and laser induced fluorescence detection. The theoretical calculation of radiative lifetimes of nd ^{1,3}D states was performed using relativistic HF single-configuration approximation, taking into account electron configuration interaction. The theoretical data agree relatively well with experimental values. The radiative lifetime τ depends on n^* like $\tau = Cn^{*\alpha}$, with α close to 3, for the nd ^{1}D ($n = 6, 7, 8$) states and nd ^{3}D ($n = 6, 7, 8, 9$), and therefore corresponds to a smooth behaviour of $\mu = \mu(n^*)$. But for the $9d$ $^1D_2$ and the nd $^3D_2$ ($n = 10, 11, 13$) states significant deviations from this potential law are found (Fig. 2), which are not mirrored in the $\mu = \mu(n^*)$ behaviour. Strong perturbations of the $\mu = \mu(n^*)$ dependence can be found for main quantum numbers $n \geq 15$.

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References

1. A.L. Osherovich, E.N. Borisov, M.L. Burshtein, Ya.F. Verolainen, Opt. Spectrosc. **39**, 820 (1975).
2. G.C. King, A. Adams, D. Cvejanović, J. Phys. B: At. Mol. Phys. **8**, 365 (1975).
3. E.C. Benck, J.E. Lawler, J.T. Dakin, J. Opt. Soc. Am. B **6**, 11 (1988).
4. K.M. Mohamed, J. Quant. Spectr. Radiat. Transfer **30**, 225 (1983).
5. F.H.M. Faisal, R. Wallenstein, R. Teets, J. Phys. B: At. Mol. Phys. **13**, 2027 (1980).
6. E.N. Borisov, A.L. Osherovich, V.N. Yakovlev, Opt. Spectrosc. **47**, 193 (1979).
7. E.H. Pinnington, W. Ansbacher, J.A. Kernahan, T. Ahmad, Z.Q. Ge, Can. J. Phys. **66**, 960 (1988).
8. M. Darrach, R.J. Niefer, J.B. Atkinson, L. Krause, J. Quant. Spectr. Radiat. Transfer **36**, 483 (1986).
9. M. Chantepie, B. Lanieple, I. Landais, Opt. Commun. **18**, 354 (1976).
10. P.Y. LeCluse, J. Phys. France **28**, 671 (1967).
11. J. Migdalek, A. Bojara, J. Phys. B: At. Mol. Phys. **21**, 2221 (1988); *ibid.* **20**, L1 (1987).
12. P. Hafner, W.H.E. Schwarz, J. Phys. B: At. Mol. Phys. **11,** 2975 (1975).
13. P. Jean, M. Martin, J.-P. Barrat, J.-L. Cojan, C. R. Acad. Sc. Paris B **264**, 1709 (1967).
14. P.F. Grousdev, Opt. Spectrosc. **22,** 89 (1967).
15. M. Mohan, A. Hiblert, J. Phys. B: A. Mol. Phys. **20**, 907 (1987).
16. K. Blagoev, K. Iskra, L. Windholz, Phys. Scripta **60**, 32 (1999).
17. A.N. Zaidel, V.K. Prokofiev, C.M. Raiskii, V.A. Slavnii, E.Ya. Shraider, *Tables of Spectral Lines* (Nauka, 1977).
18. Ch.E. Moor, *Atomic Energy Levels* (Circular of the NBS, 467, Washington, 1958), Vol. 3.
19. T.B. Douglas, A.F. Ball, D.C. Grinnings, J. Resear. NBS **46,** 334 (1951).
20. R.D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkely, 1981); a modification for use on PC was prepared by A.E. Kramida, Yu.V. Ralchenko, private communication.
21. R. Anderson, E. Lee, C. Lin, Phys. Rev. **157**, 31 (1967).
22. E.U. Condon, G.H. Shortley, *The Theory of Atomic Spectra* (Cambridge at the University press, 1967).
23. Z. Cai, D. Beck, W. Perger, Phys. Rev. A **43,** 4660 (1991).