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BROADENING AND SHIFT OF OPTICAL LINES OF ARGON INVOLVING QUASI-RYDBERG STATES

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The extended Omont–Ueda–Kaulakys treatment of collisional effects on quasi-Rydberg states, which takes into account the perturbation of the lower state, is applied to Ar*–He, Ar*–Ne and Ar*–Ar systems. The pressure broadening and shift coefficients of spectral lines of argon involving the $3p^5ns$ ($n = 6$–9) and $3p^5nd$ ($n = 4$–8) states are determined and compared with those resulting from the experiment.

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1. Introduction

Pressure effects on optical lines originating from highly excited levels of alkali-metal and noble-gas atoms perturbed by ground-state atoms continue to be the subject of numerous investigations [1–10]. Recent theoretical calculations of collisional widths and shifts of such spectral lines have been performed using a theory developed by Omont [11], Kaulakys [12] and Ueda [13] (hereafter referred to as OKU) which is based on the famous Fermi model [14] of Rydberg atom–normal atom interaction. According to Fermi, for sufficiently large values of the principal quantum number n, there are two factors responsible for the collisional broadening and shift of corresponding spectral lines. The first factor is the scattering of the radiating atom electron (treated as the quasi-free "Rydberg" electron) on the perturbing atom and the second factor is the effect of polarization of the perturbing atom due to the ionic core of the radiating atom. Assuming that the perturbers move along classical paths (straight lines), Omont [11], Kaulakys [12] and Ueda [13] have adapted the Fermi model to calculate the width and shift parameters in the framework of the impact theory of pressure broadening which yields the line shape in the form of a Lorentzian distribution with half-width γ and shift Δ linearly dependent on the number density N of the perturbing atoms. In the OKU treatment, the width and shift parameters are given by simple analytic formulae expressed in terms of the electron scattering length L of the perturbing atom as

well as its polarizability α and the effective quantum number n^* of the radiating atom. An essential assumption in the OKU treatment is that the broadening and shift are entirely determined by the perturbation of the upper state of the radiating atom so that the perturbation of the lower state can be ignored. This assumption restricts the applicability of the OKU theory to optical lines of "true" Rydberg atoms, i.e. those corresponding to the transitions between highly excited Rydberg states characterized by very high values n^* of the effective quantum number and the low-lying states.

Collisional effects on spectral lines originating from excited states corresponding to the intermediate region of n^*-values, i.e. the so-called "quasi-Rydberg" states lying between the resonance and true Rydberg states, are also of considerable interest but not many of them have been studied in detail. Such effects have been the subject of recent experimental study from this laboratory on the $2p^5ns$–$2p^53p$ (n = 5–7) transitions in neon perturbed either by He or Ne [8] as well as on the $3p^5np$–$3p^54s$, $3p^5ns$–$3p^54p$ and $3p^5nd$–$3p^54p$ (n = 4–9) transitions in argon perturbed by He or by Ne or by Ar [10, 15–21]. Results of this study indicate that in some cases they can be qualitatively explained on the basis of the OKU treatment.

It was found, however, that in general case the OKU treatment fails for the intermediate region states, first of all in case of perturbation of both the neon and argon spectral lines involving d-states.

In a recent paper, Trawiński and Bielski [22] have shown that one of the reasons of the failure of the OKU model for the intermediate n^*-region is the neglect of perturbation of the lower state in the radiating atom. Starting from the general formula of the impact theory for the width and shift they have extended the OKU treatment by taking into account the perturbation of the lower state as well as the anisotropy of the optical electron–perturber interaction.

The main advantage of the extended OKU treatment is that it is free of the shortcomings of the conventional OKU treatment such as those connected with some discontinuities at the borders between various n^*-intervals. In order to test the applicability of the extended OKU treatment for the description of collisional effects for the intermediate n^*-region, Trawiński and Bielski [22] have used this treatment to calculate the broadening and shift coefficients of many spectral lines of neon corresponding to the $2p^5nd$–$2p^53p$ (n = 3–7), $2p^5ns$–$2p^53p$ (n = 5–7) transitions perturbed by He and Ne for which the experimental values of the width and shift are known with a great experimental accuracy. It was found that although the agreement with experiment was not satisfactory in all cases, the extended OKU model reproduces well the general features of the n^*-dependence of the broadening coefficients both for Ne*–Ne and Ne*–He.

The purpose of the present paper is to apply the extended OKU model to calculations of the width and shift coefficients of the argon spectral lines corresponding to the $3p^5ns$–$3p^54p$ (n = 6–9) and $3p^5nd$–$3p^54p$ (n = 4–8) transitions in the Ar-atom perturbed by the He-, Ne- and Ar-ground state atoms. All these lines correspond to the intermediate n^*-region and were the subject of very precise interferometric line profile analysis done in this laboratory in recent years [10, 15–21].

2. Theoretical background

Extensive experimental studies of profiles of many spectral lines of argon emitted from a low-pressure glow discharge in pure argon as well as in argon–helium or argon–neon mixtures have shown that the collisional component of the total profile may be fitted well to the Lorentzian profile

$$I(\omega) = \frac{N\beta}{2\pi} \frac{1}{(\omega - \omega_0 - N\delta)^2 + \left(\frac{N\beta}{2}\right)^2}. \tag{1}$$

Here $\beta = \gamma/N$ is the pressure broadening coefficient which characterizes the total Lorentzian half-width γ, and $\delta = \Delta/N$ is the pressure shift coefficient which determines the shift Δ of the maximum of the line with respect to the unperturbed frequency ω_0.

According to the classical phase-shift theory the thermally-averaged broadening (β) and shift (δ) coefficients can be calculated from the formulae

$$\beta = 4\pi \int_0^\infty \mathrm{d}v f(v) v \int_0^\infty \rho \{1 - \cos[\eta_v(\rho) - \tilde{\eta}_v(\rho)]\} \mathrm{d}\rho \tag{2}$$

and

$$\delta = 2\pi \int_0^\infty \mathrm{d}v f(v) v \int_0^\infty \rho \sin[\eta_v(\rho) - \tilde{\eta}_v(\rho)] \mathrm{d}\rho, \tag{3}$$

where $f(v)$ is the Maxwellian distribution of velocities. In these expressions $\eta_v(\rho)$ and $\tilde{\eta}_v(\rho)$ denote the phase shifts in the upper and lower state of the radiating atom, respectively, caused by a single collision occurring at impact parameter ρ and relative velocity v. Assuming that the perturber follows a straight-line trajectory, $\eta_v(\rho)$ can be written as

$$\eta_v(\rho) = \frac{2}{v\hbar} \int_\rho^\infty \frac{RV(R)}{\sqrt{R^2 - \rho^2}} \mathrm{d}R, \tag{4}$$

where $V(R)$ is the interaction potential describing the interaction between the perturber and the radiating atom in its upper state. For the lower state the phase-shift $\tilde{\eta}_v(\rho)$ can be calculated from the formula identical to Eq. (4) with the replacement of $V(R)$ by $\tilde{V}(R)$.

In the conventional OKU treatment the phase shifts $\tilde{\eta}_v(\rho)$ caused by the perturbation of the lower state in the radiating atom are ignored and the integrals in Eqs. (2) and (3) are evaluated using an approximation due to Anderson [23]. In a recent paper Trawiński and Bielski [22] have extended the OKU model in such a way that both the phase-shifts $\eta_v(\rho)$ and $\tilde{\eta}_v(\rho)$ for the upper and lower state are taken into account. Moreover, in their treatment (to be referred to as extended OKU treatment) the Anderson approximation is not applied and the integrals over the impact parameters ρ are evaluated numerically without any simplifying assumptions.

Following Fermi [14] and Omont [11] the radius $r_B = (n^*)^2$ of the Bohr orbit of an optical quasi-Rydberg electron can be used as a parameter which determines the border between two regions of the radiator–perturber interaction. In the first region ($0 < \rho < r_B$) which corresponds to a case of a perturber flights "inside"

the Bohr orbit, the interaction potential may be approximated as a sum of the Fermi potential V_F describing the optical electron–perturber interaction and the polarization potential V_P for the ionic core–perturber interaction. The phase shift $\eta_v(\rho)$ (and $\tilde{\eta}_v(\rho)$) is then the sum [12, 13]:

$$\eta_v(\rho) = \eta_F(\rho, v) + \eta_P(\rho, v), \tag{5}$$

where

$$\eta_F(\rho, v) = \frac{L}{2v(n^*)^3\sqrt{\rho}} \tag{6}$$

is the phase shift corresponding to the Fermi potential, and

$$\eta_P(\rho, v) = -\frac{\pi\alpha}{4v\rho^3} \tag{7}$$

is the phase shift caused by the polarization interaction. In the second region ($\rho > r_B$) corresponding to a case of a perturber flights outside the Bohr orbit the ionic core is screened by the optical electron so that the polarization interaction may be neglected. Following Kaulakys [12] and Ueda [13] for $r_B < \rho < 2r_B$ the phase shift $\eta_v(\rho)$ (or $\tilde{\eta}_v(\rho)$) is assumed to be pure Fermi shift: $\eta_v(\rho) = \eta_F(\rho, v)$.

For $\rho > 2r_B = 2(n^*)^2$ the perturbers are moving far enough from the radiating atom for both the electron scattering and polarization effects to be omitted. In this region the emitter and perturber can be treated as two spacially separated neutral particles. Kaulakys [12] and Ueda [13] have assumed the interaction between them in the form of a simple van der Waals ($-C_6R^{-6}$) potential which yields for the phase shift a formula

$$\eta(\rho) \approx \eta_{vdW}(\rho) = \frac{15\pi\alpha(n^*)^4}{16v\rho^5}. \tag{8}$$

In the extended OKU treatment the interaction between the perturber and the radiating atom for $\rho > 2(n^*)^2$ was approximated by the empirical Lennard–Jones (12-6) potential $V(R) = C_{12}R^{-12} - C_6R^{-6}$. The phase shift $\eta_{LJ}(\rho)$ is then

$$\eta_{LJ}(\rho) = \frac{63\pi C_{12}}{256\hbar v\rho^{11}} - \eta_{vdW}(\rho). \tag{9}$$

With these approximative formulae for the upper- ($\eta_v(\rho)$) and lower-state ($\tilde{\eta}_v(\rho)$) phase shifts the broadening and shift coefficients can be computed from Eqs. (2) and (3) provided the integrals over impact parameters ρ and relative velocities v are evaluated numerically. Details of these calculations are described in a recent paper by Trawiński and Bielski [22] who have also taken into account the effects due to anisotropy of the Fermi potential in the framework of a method proposed by Hermann et al. [6].

3. Broadening and shift in the argon spectrum

Since 1985 systematic experimental studies on the low pressure broadening and shift of the argon quasi-Rydberg spectral lines have been performed in this laboratory using high resolution spectroscopy techniques [15–21]. In the recent paper [10] results of these experiments for 17 spectral lines of argon involving quasi-Rydberg states belonging to the $3p^5np$ (with $n = 4$–6), $3p^5ns$ (with $n = 6$–9)

and $3p^5nd$ (n = 4–8) configurations were summarized and interpreted within the framework of the conventional OKU treatment. It was found that in pure argon and in the Ar–He mixture the experimental data are in qualitative agreement with those calculated from the OKU model. Contrary to that, for Ar–Ne mixture the theoretical broadening and shift coefficients calculated on the basis of the OKU treatment do not agree with experiment. One cause of this disagreement seemed to be the neglect of the lower state perturbation in the OKU model. In order to verify such an interpretation in the course of the present work we performed new calculations of β- and δ-coefficients on the basis of the extended OKU model. In our calculations the thermal averaging over Maxwellian distribution and integration over impact parameters in Eqs. (2)–(3) were done numerically in the same way as in recent study by Trawiński and Bielski [22] for the neon spectral lines. The van der Waals constants C_6 for Ar*–Ar, Ar*–Ne and Ar*–He interactions were computed using the Coulomb approximation due to Unsöld [24] while the C_{12} constants describing the repulsive branches of the potential curves were calculated on the basis of a semi-empirical method put forward by Hindmarsh et al. [25]. The values of the polarizability α and the electron-scattering length L for He, Ne and Ar used in the present calculations were the same as those applied in the previous study [10] based on the conventional OKU treatment.

In Fig. 1 the theoretical values of the pressure broadening coefficient of the argon spectral lines perturbed by He computed from the extended OKU treatment are plotted against the effective quantum numbers n^* and compared with experimental values. β^s and β^d are the thermally-averaged pressure broadening coefficients calculated from Eqs. (2)–(3) for spectral lines originating from the ns and nd states, respectively. β_K are the pressure broadening coefficients calculated from the Kaulakys [12] version of the conventional OKU treatment. As is seen, the broadening coefficients calculated from the extended OKU treatment are in satisfactory agreement with experiment both for spectral lines originating from the s-states and for those originating from d-states. Note that for the lines involving d-states the theoretical values calculated from the extended OKU model are in better agreement with experiment than those resulting from the conventional OKU model.

Figure 2 shows the comparison of the experimental pressure shift coefficients for Ar-lines perturbed by He with those calculated in the present work in the framework of the extended OKU treatment. Figure 2 also shows comparison with pressure shift coefficients calculated in the previous work [10] from the conventional OKU theory. It should be emphasized that in the Ar*–He case the Kaulakys [12] version of the OKU theory predicts no shift up to $n^* = 4.7$. Note that both the conventional and the extended OKU treatment yield the blue shift ($\delta > 0$) for Ar*–He as found in experiment for all spectral lines under investigation.

In Fig. 3 the theoretical values of β of the Ar lines perturbed by Ne calculated in the present work from the extended OKU treatment are compared with those calculated previously [10] from the conventional OKU treatment as well as with experiment. It is seen that except one spectral line corresponding to $n^* = 5.85$ the experimental values of β are in better agreement with theoretical values calculated

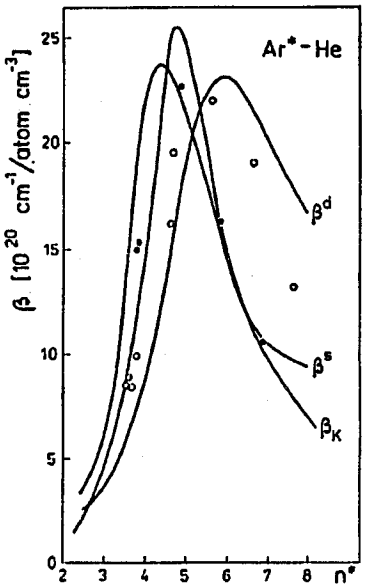

Fig. 1

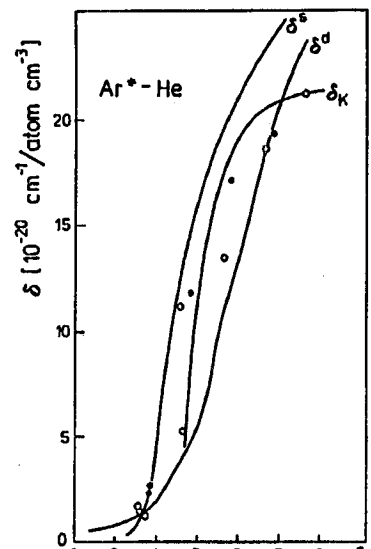

Fig. 2

Fig. 1. Plots of the β-coefficients determined for 14 argon spectral lines perturbed by helium corresponding to the transitions between levels of the following configurations: $3p^5 4p$–$3p^5 ns$ (n = 6–9) and $3p^5 4p$–$3p^5 nd$ (n = 4–8) as a function of effective quantum number n^* of the upper state. Curves β^s and β^d are the theoretical broadening coefficients calculated from Eqs. (2) and (3), for spectral lines emitted from ns (•) and nd (o) states, respectively. The β_K curve represents the pressure broadening coefficients calculated from the Kaulakys [12] version of the conventional OKU treatment.

Fig. 2. Plots of the δ-coefficients determined for argon spectral lines perturbed by helium as a function of effective quantum number n^* of the upper state.

from the extended OKU model than those resulting from the conventional OKU model.

The comparison of the calculated and experimental values of the pressure shift coefficient for Ar*–Ne is presented in Fig. 4. As was already emphasized in our previous paper [10] the case of broadening and shift induced by Ne-atoms must be treated with extreme caution. This is due to the fact that both the theoretical and experimental values of the electron-scattering length L for neon reported in various papers differ markedly from each other. The theoretical values of β and δ shown in Figs. 3 and 4 were calculated for $L = 0.2$. It is important to note that all known values of L (both theoretical and experimental) for Ne are positive although rather small which in case of the Fermi potential leads to the blue shift ($\delta > 0$) for Ar*–Ne. Nevertheless, for two spectral lines involving $4d$-states with $n^* = 3.57$ and $n^* = 3.68$ the red shift is observed in experiment [17] which corresponds to negative although very small values of the shift coefficient ($\delta < 0$). As is seen from Fig. 4 neither the conventional nor the extended OKU treatment can explain these

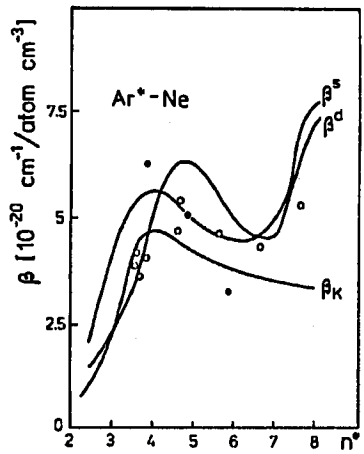

Fig. 3

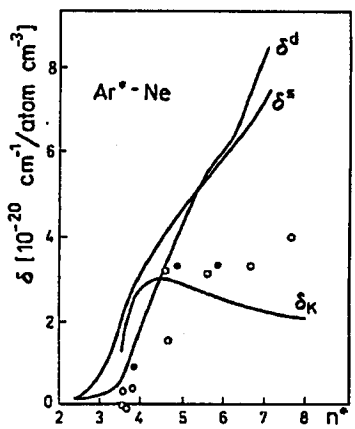

Fig. 4

Fig. 3. Plots of the β-coefficients determined for argon spectral lines perturbed by neon as a function of effective quantum number n^* of the upper state.
Fig. 4. Plots of the δ-coefficients determined for argon spectral lines perturbed by neon as a function of effective quantum number n^* of the upper state.

experimental findings. It is also seen from Fig. 4 that for larger values of n^* the theoretical values of δ resulting from the extended OKU model are too large while those calculated from the conventional OKU theory are too small. This clearly indicates that the Lennard-Jones potential assumed to describe the interaction between excited argon atom and the ground state neon atom for $\rho > 2(n^*)^2$ fails. First of all, the comparison shown in Fig. 4 demonstrates that the real repulsion energy between ground-state Ne-atoms and the excited Ar*-atoms for $n^* \geq 5$ is much weaker than that predicted by the Lennard-Jones potential.

Figure 5 shows the comparison of the theoretical values of the pressure broadening coefficient calculated in this work from both the extended and the conventional OKU model for Ar*–Ar with experiment.

The shift coefficients for Ar*–Ar are shown in Fig. 6, where the theoretical δ-coefficients calculated from the extended and conventional OKU treatment are compared with experiment. In Fig. 6 we have also shown the theoretical values of pressure shift coefficients δ_v^s calculated from the extended OKU treatment assuming that for $\rho > 2(n^*)^2$ the interaction potential between excited (Ar*) and ground-state Ar-atoms is of the pure van der Waals form $-C_6 r^{-6}$, i.e. when the phase shifts are given by Eq. (8).

As is seen from Fig. 6 in the Ar*–Ar case the extended OKU model with the Lennard-Jones potential fails as it gives rise to the blue shift for some values of n^* contrary to experimental data which are all red-shifted. The conventional OKU model although for two spectral lines with $n^* = 6.63$ ($\lambda = 522.1$ nm, $3p^5 7d$–$3p^5 4p$) and $n^* = 6.85$ ($\lambda = 539.4$ nm, $3p^5 9s$–$3p^5 4p$) gives good agreement with experiment is unrealistic for smaller n^* as it does predict no shift for $n^* \leq 6.4$. On the other hand, however, good agreement between experimental values of the shift coefficient

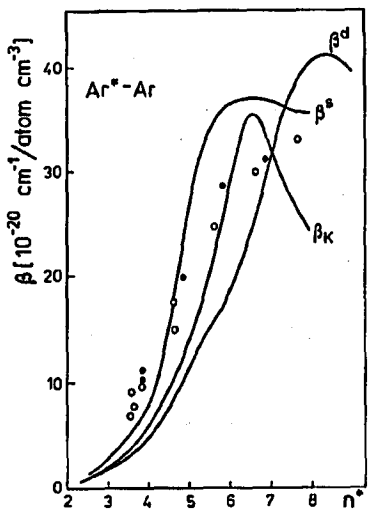

Fig. 5

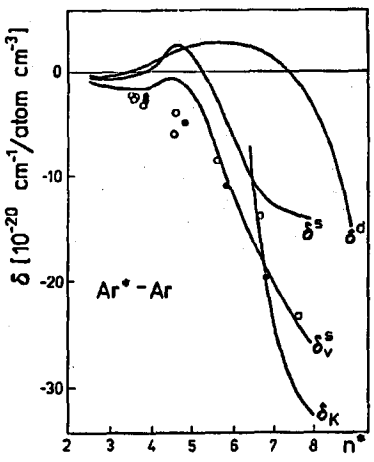

Fig. 6

Fig. 5. Plots of the β-coefficients determined for argon spectral lines perturbed by argon as a function of effective quantum number n^* of the upper state.
Fig. 6. Plots of the δ-coefficients determined for argon spectral lines perturbed by argon as a function of effective quantum number n^* of the upper state. Curve δ_v^s represents the theoretical shift coefficients calculated from the extended OKU treatment with the assumption of the pure van der Waals potential.

and those calculated from the extended OKU model is obtained assuming the pure van der Waals potential for $\rho > 2(n^*)^2$, i.e. when the repulsion parts of the potential curves are neglected.

4. Concluding remarks

In the course of the present study the calculations of the pressure broadening and shift coefficients for spectral lines emitted from low excited and quasi-Rydberg argon states have been performed on the basis of the extended OKU treatment. It was shown that the extended OKU treatment reproduces the general features of the n^*-dependence of the pressure broadening (β) coefficient for Ar*–He, Ar*–Ne and Ar*–Ar systems. We should emphasize that in the case of Ar*–He system our theoretical shift coefficients for argon spectral lines are in reasonable agreement with experiment. For Ar*–Ne and Ar*–Ar systems the discrepancies between theoretical and experimental shift data may be caused by the fact that we have used the Lennard–Jones potential to describe the interaction involving excited Ar*-atoms. Results obtained in this work indicate that the Lennard–Jones potential may be inadequate for Ar*–Ne and Ar*–Ar interactions. To our knowledge, however, for the interactions involving the excited states of Ar-atoms studied in the present work the interaction potentials more realistic than those of the Lennard–Jones type have not been found yet. We can thus conclude that in order to explain all

experimental data on pressure broadening and shift of the argon spectral lines involving quasi-Rydberg states the realistic theoretical potentials should first be found.

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References

[1] D.C. Thompson, E. Kammermayer, B.P. Stoicheff, E. Weinberg, *Phys. Rev. A* **36**, 2134 (1987).

[2] M. Borstel, G. Hermann, G. Lasnitschka, *Z. Phys. D* **9**, 15 (1988).

[3] K.D. Heber, P.J. West, E. Mattias, *Phys. Rev. A* **37**, 1438 (1988).

[4] J.Q. Sun, P.J. West, *J. Phys. B* **23**, 4119 (1980).

[5] J.Q. Sun, E. Mathias, K.D. Heber, P.J. West, J. Güdde, *Phys. Rev. A* **43**, 5956 (1991).

[6] G. Hermann, B. Kaulakys, G. Lasnitschka, G. Mahr, A. Scharmann, *J. Phys. B* **25**, L407 (1992).

[7] A. Bielski, S. Brym, J. Szudy, R.S. Trawiński, J. Wolnikowski, *J. Phys. B* **24**, 4909 (1991).

[8] A. Bielski, J. Szudy, R.S. Trawiński, J. Wolnikowski, *Acta Phys. Pol. A* **81**, 369 (1992).

[9] R.S. Trawiński, A. Bielski, R. Ciuryło, J. Szudy, *Ann. Phys. (Germany)* **2**, 1 (1993).

[10] J. Wolnikowski, A. Bielski, R.S. Trawiński, J. Szudy, *Phys. Scr.* **47**, 186 (1993).

[11] A. Omont, *J. Phys. (Paris)* **38**, 1343 (1977).

[12] B. Kaulakys, *J. Phys. B* **17**, 4485 (1984).

[13] K. Ueda, *J. Quant. Spectrosc. Radiat. Transfer* **33**, 77 (1985).

[14] E. Fermi, *Nuovo Cimento* **11**, 157 (1934).

[15] A. Bielski, J. Wawrzyński, J. Wolnikowski, *Acta Phys. Pol. A* **67**, 621 (1985).

[16] J. Wolnikowski, A. Bielski, J. Szudy, *Acta Phys. Pol. A* **69**, 361 (1986).

[17] J. Wawrzyński, J. Wolnikowski, *Phys. Scr.* **33**, 113 (1986).

[18] J. Wolnikowski, J. Wawrzyński, A. Bielski, J. Szudy, *Phys. Scr.* **35**, 153 (1987).

[19] J. Wolnikowski, *Phys. Scr.* **42**, 220 (1990).

[20] A. Bielski, J. Pośpieszny, J. Szudy, R.S. Trawiński, J. Wolnikowski, *J. Phys. B, At. Mol. Opt. Phys.* **23**, 2003 (1990).

[21] A. Bielski, R.S. Trawiński, J. Wolnikowski, J. Szudy, *Phys. Scr.* **44**, 141 (1991).

[22] R.S. Trawiński, A. Bielski, *J. Phys. B, At. Mol. Opt. Phys.* **26**, 4789 (1993).

[23] P.W. Anderson, *Phys. Rev.* **76**, 647 (1949).

[24] A. Unsöld, *Physik der Sternatmosphären*, Springer-Verlag, Berlin 1955.

[25] W.R. Hindmarsh, A.D. Petford, G. Smith, *Proc. R. Soc. A* **297**, 296 (1967).