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Collisional broadening and shift of Doppler-free two-photon thallium lines perturbed by rare-gas atoms

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Abstract. The extended Omont-Ueda-Kaulakys treatment of collisional effects on quasi-Rydberg states, in which the perturbation of the lower state is taken into account is applied to thallium-rare gas systems. The pressure broadening and shift coefficients of two-photon transitions in thallium involving the $6P_{1/2}$–$n\ P_{1/2,3/2}$ (n = 9–14) states are calculated and compared with experimental data obtained by Hermann *et al.* [Eur. Phys. J. D **1**, 129 (1998)].

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1 Introduction

Pressure effects on optical lines originating from highly excited levels of alkali-metal and rare-gas atoms perturbed by ground-state atoms continue to be the subject of numerous investigations [1–10]. Theoretical calculations of collisional widths and shift of such spectral lines were 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 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 "quasi-Rydberg" states, *i.e.* the excited states corresponding to the intermediate region of n^*-values, 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 that 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 an earlier 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 (hereafter referred to as ExOKU) by taking into account the perturbation of the lower state as well as the anisotropy of the electron-perturber interaction. The main advantage of the ExOKU 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 ExOKU treatment for the

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description of collisional effects for the intermediate n^*-region, Trawiński and Bielski [22] have used it 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 ExOKU model reproduced well the general features of the n^*-dependence of the broadening coefficients both for Ne–Ne and Ne–He. The ExOUK model was also applied in 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 [27]. All these lines correspond to the intermediate n^*-region and were the subject of very precise interferometric line profile analysis done in our laboratory in recent years [10,15–21].

In a recent paper Hermann *et al.* [26] reported results of their broadening and shift measurements of Doppler-free two-photon lines corresponding to the transitions from the ground state 6 $P_{1/2}$ to n $P_{1/2}$ and n $P_{3/2}$ quasi-Rydberg (n = 9–14) states of thallium perturbed by rare-gas atoms.

They interpreted their experimental results on the basis of the Kaulakys version [12] of the OUK treatment in which the perturbation of the 6 $P_{1/2}$ state is neglected. In the present work an alternative interpretation of experimental results of Hermann *et al.* [26] is given using the extended OKU (ExOKU) model. In our interpretation the perturbation of the 6 $P_{1/2}$ state is taken into account assuming the van der Waals potential.

2 Theoretical background

Extensive experimental studies of profiles of many spectral lines have shown that at low pressures of the perturbing gases the collisional component of the total profile may be fitted well to the Lorentzian profile

$$I(\omega) = \frac{N\beta}{2\pi} \frac{1}{(\omega - \omega_0 - N\delta)^2 + (N\beta/2)^2} \cdot \qquad (1)$$

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

$$\frac{\beta}{2} - i\delta = 2\pi \int_0^\infty dv\, f(v) v \times \int_0^\infty d\rho\, \rho \{1 - \exp[i\eta(\rho, v) - i\widetilde{\eta}(\rho, v)]\} \qquad (2)$$

where $f(v)$ is the Maxwellian distribution of velocities. In these expressions $\eta(\rho, v)$ and $\widetilde{\eta}(\rho, v)$ 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 $\eta(\rho, v)$ can be written as

$$\eta(\rho, v) = \frac{2}{v\hbar} \int_\rho^\infty dR\, \frac{RV(R)}{\sqrt{R^2 - \rho^2}} \qquad (3)$$

where $V(R)$ is the interaction potential describing the interaction between the perturber and the radiating atom in its upper state. The lower state phase-shift $\widetilde{\eta}(\rho, v)$ can be calculated from the formula identical to equation (3) with the replacement of $V(R)$ by $\widetilde{V}(R)$. In the conventional OKU treatment the phase shifts $\widetilde{\eta}(\rho, v)$ caused by the perturbation of the lower state in the radiating atom are ignored and the integrals in equation (2) are evaluated using an approximation due to Anderson [23]. On the contrary in the ExOUK treatment both $\eta(\rho, v)$ and $\widetilde{\eta}(\rho, v)$ are taken into account, 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 flights of a perturber "inside" the Bohr orbit the interaction potential may be approximated by the sum of 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 $\eta(\rho, v)$ (or $\widetilde{\eta}(\rho, v)$) is then the sum [12,13]

$$\eta(\rho, v) = \eta_F(\rho, v) + \eta_P(\rho, v), \qquad (4)$$

where

$$\eta_F(\rho, v) = \frac{L}{2v(n^*)^3\sqrt{\rho}} \qquad (5)$$

is the phase-shift corresponding to the Fermi potential, expressed in terms of the electron-perturber scattering length L, and

$$\eta_P(\rho, v) = -\frac{\pi\alpha}{4v\rho^3} \qquad (6)$$

is the phase shift caused by the polarization interaction with α being the dipole polarizability of the perturber.

In the second region ($\rho > r_B$) corresponding to the flights of the perturber 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 $\eta(\rho, v)$ (or $\widetilde{\eta}(\rho, v)$) is assumed to be pure Fermi shift: $\eta(\rho, v) = \eta_F(\rho, v)$.

For $\rho > 2r_B = 2(n^*)^2$ the perturbers are moving far enough from the radiating atom so that both the electron

scattering and polarization effects can be omitted. In this region the emitter and perturber can be treated as two separated neutral particles, and their interaction may be approximated by the van der Waals potential $V_{vdW}(R) = -C_6 R^{-6}$.

3 Broadening and shift in the thallium spectrum

We have used formulae described in Section 2 to calculate the broadening (β) and shift (δ) coefficients for two-photon transitions Tl 6 $P_{1/2}$–n $P_{1/2,\ 3/2}$ (n = 9–14) perturbed by He, Ne, Ar, Kr and Xe studied experimentally by Hermann *et al.* [26]. In our calculations we used the same values of scattering lengths L and polarizabilities α as used by Hermann *et al.* [26]. The van der Waals force constants C_6 were computed using the approximate formula given by Unsöld [24] (see also [25]).

It should be emphasized that equation (2) for β and δ is valid for isotropic potentials only. Hereafter, values of β and δ calculated for isotropic potentials from equations (2–6) will be denoted by $\beta(\alpha, L)$ and $\delta(\alpha, L)$, respectively. In general case, the interaction is essentially anisotropic so that the different potential curves corresponding to various orientations of the angular momenta of the colliding atom with respect to the internuclear axis have to be taken into account. A method of calculation of the broadening and shift coefficients which takes into account the anisotropy of the Fermi potential was proposed by Hermann *et al.* [6]. Collisional broadening (β) and shift (δ) coefficients corresponding to transitions into upper levels with angular momentum $J \geq 1$ are related with the $\beta(\alpha, L)$ and $\delta(\alpha, L)$ coefficients given by equation (2) for the isotropic part of the Fermi potential in the following way. For spectral lines involving $P_{1/2}$ states we have [6,26]

$$\beta(P_{1/2}) = \beta(\alpha, L), \tag{7}$$

$$\delta(P_{1/2}) = \delta(\alpha, L). \tag{8}$$

In Figure 1 the theoretical values of the pressure broadening (β) and shift (δ) coefficients of thallium 6 $P_{1/2}$–n $P_{1/2}$ (n = 9–14) lines perturbed by He, Ne, Ar, Kr and Xe computed from the ExOUK treatment (Eqs. (2, 7, 8)) are plotted against the effective number n^* and compared with experimental values of Hermann *et al.* [26].

The values of the pressure broadening (β) and shift (δ) coefficients calculated from the Kaulakys version of the conventional OUK treatment presented in paper [26] are also plotted in Figure 1.

As can be seen the broadening coefficients (β) calculated from the ExOUK treatment for Tl–He, Tl–Ne and Tl–Xe systems are in better agreement with experiment than those resulting from the conventional OUK model.

For the line shift coefficients (δ) for Tl–Ne system only the Kaulakys model gives rise to a better agreement with experiment than the ExOUK treatment. It should be noted, however, that the ExOUK treatment predicts a red shift ($\delta < 0$) for n^* between 2.0 and 2.5 which agrees with the experimental result obtained for the 6 $P_{1/2}$–7 $P_{1/2}$ [2] transition. We should also note that conventional OUK model is unrealistic for smaller n^* as it predicts no shift for $n^* < 6.2$ for Tl–Ar, $n^* < 8.2$ for Tl–Kr and $n^* < 9.9$ for Tl–Xe system.

For spectral lines associated with $P_{3/2}$ states the broadening $\beta(P_{3/2})$ and shift $\delta(P_{3/2})$ coefficients are given by

$$\beta(P_{3/2}) = \frac{1}{2}\left[\beta\left(\alpha, \frac{1}{2}L\right) + \beta\left(\alpha, \frac{3}{2}L\right)\right], \tag{9}$$

$$\delta(P_{3/2}) = \frac{1}{2}\left[\delta\left(\alpha, \frac{1}{2}L\right) + \delta\left(\alpha, \frac{3}{2}L\right)\right]. \tag{10}$$

In Figure 2 the theoretical values of the pressure broadening (β) and shift (δ) coefficients of thallium 6 $P_{1/2}$–n $P_{3/2}$ (n = 9–14) lines perturbed by He, Ne, Ar, Kr and Xe computed from the ExOUK treatment (Eqs. (2, 9, 10)) are plotted against the effective number n^* and compared with experimental [26] values.

The values of the pressure broadening (β) and shift (δ) coefficients calculated from the Kaulakys version of the conventional OUK treatment presented in paper [26] are also plotted in Figure 2. As it can be seen, also for the $P_{1/2}$–$P_{3/2}$ transitions the broadening coefficients (β) calculated from the ExOUK treatment for Tl–He, Tl–Ne, Tl–Kr and Tl–Xe systems are in better agreement with experiment than those resulting from the conventional OUK model.

For the line shift coefficients (δ) for Tl–Ne system only the Kaulakys model yields a better agreement with experiment than the ExOUK treatment. It should be noted that conventional OUK model is unrealistic for smaller n^* as it predicts no shift for $n^* < 6.2$ for Tl–Ar, $n^* < 8.2$ for Tl–Kr and $n^* < 9.9$ for Tl–Xe system.

4 Concluding remarks

In the course of the present study the calculations of the pressure broadening and shift coefficients for spectral lines of thallium $6P_{1/2}$–n $P_{1/2,\ 3/2}$ (n = 9–14) have been performed on the basis of the ExOKU treatment. It was shown that the ExOKU treatment reproduces the general features of the n^*-dependence of the pressure broadening (β) coefficient for Tl-rare gas systems. For the line shifts caused by heavier (Ar, Kr, Xe) perturbers the theoretical values of the pressure shift coefficients (δ) calculated in the framework of the ExOUK treatment are in reasonable (or even good) agreement with experiment [26], while the conventional OUK treatment predicts no shift for small n^*. We should emphasize that in the case of Tl–Ne system our theoretical shift coefficients are smaller than the experimental ones. Finally, we conclude that in order to explain all experimental data on pressure broadening and shift of the thallium spectral lines involving quasi-Rydberg states the theoretical potentials more realistic than those used in the present work should first be found.

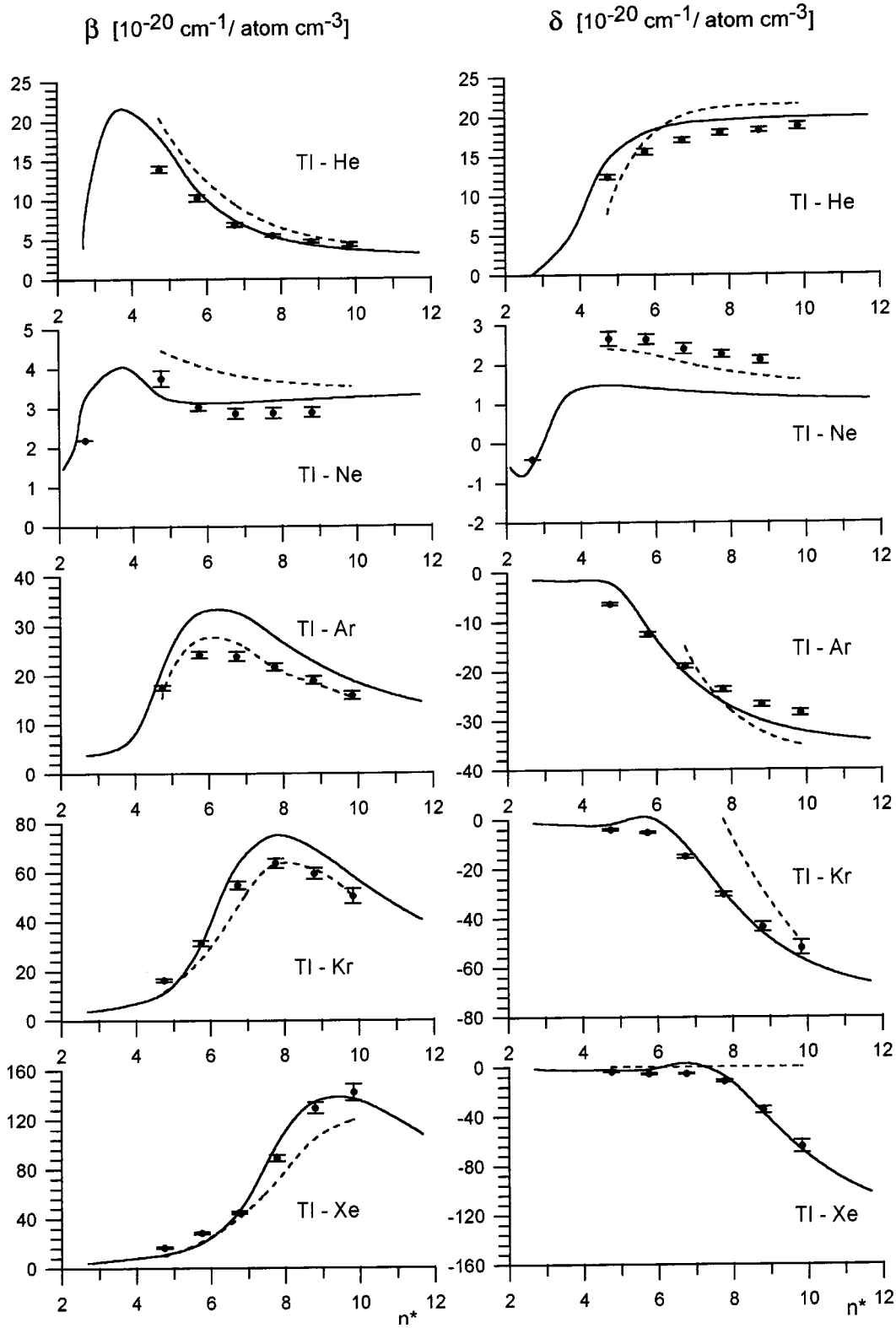

Fig. 1. Comparison of theoretical values of the pressure broadening (β) and shift (δ) coefficients of thallium 6 $P_{1/2}$–n $P_{1/2}$ (n = 9–14) lines perturbed by He, Ne, Ar, Kr and Xe computed from the ExOUK (solid line) and Kaulakys (dashed line) treatments plotted against the effective number n^* with the experimental values of Hermann *et al.* [26].

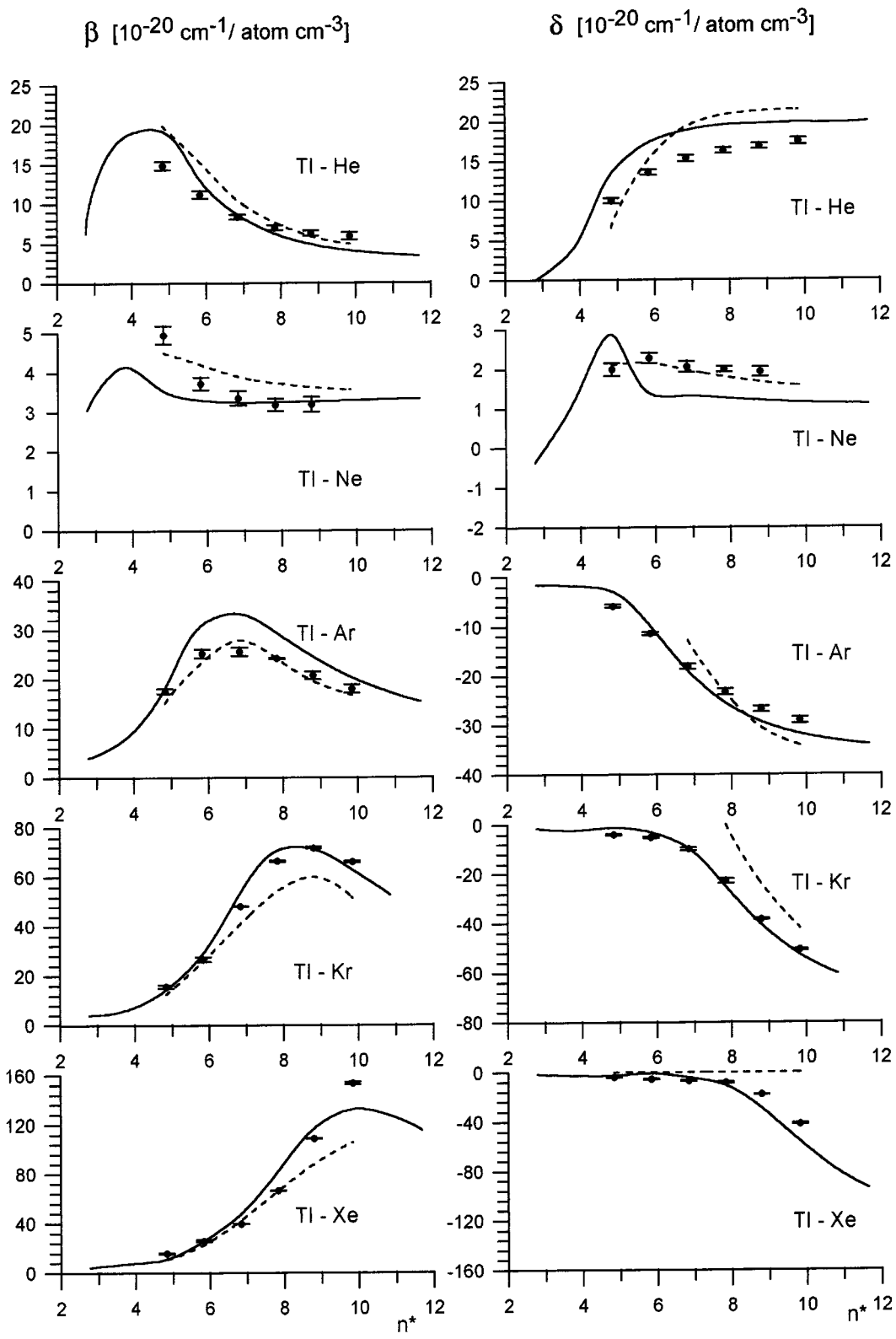

Fig. 2. Same caption as in Figure 1, but for the set of lines 6 $P_{1/2}$–n $P_{3/2}$ ($n = 9$–14).

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