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On Argon-Induced Pressure Shifts of ^{198}Hg Spectral Lines Associated with Quasi-Rydberg Transitions

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The extended Omont–Kaulakys–Ueda treatment of collisional effects on quasi-Rydberg states, in which the perturbation of the lower state is taken into account, is applied to mercury–argon system. The pressure shift coefficients of 6*p*–*n*s and 6*p*–*n*d spectral lines are calculated and compared with available experimental data.

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1. Introduction

In a recent paper Veza et al. [1] reported results of their measurements of argon-pressure-induced shifts of twenty ^{198}Hg emission lines corresponding to the transitions between the $6p-ns$ ($n = 7$, 8) and $6p-nd$ ($n = 6$, 7) states. Some of these lines are recommended and used as wavelength standards in plasma spectroscopy. Electrodeless discharge lamps containing ^{198}Hg vapour and argon at low pressure are at present an important tool for wavelength calibration in spectroscopy laboratories [2, 3]. For this reason an accurate knowledge of the pressure effects produced by argon on the ^{198}Hg emission lines is of considerable practical interest. On the other hand, the knowledge of these effects, in particular the pressure-induced shifts and widths, is significant for fundamental study of interatomic interactions. Veza et al. [1] interpreted their results on the basis of the Lindholm–Foley impact theory [4, 5] assuming the interaction between Hg and Ar atoms to have the form of a van der Waals or Lennard–Jones potential and found a reasonable agreement with experimental values. They finally concluded, however, that a better representation for the interaction potentials of excited mercury atoms with argon could be potentials which are a superposition of the polarization

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potential and the Fermi potential. Such potentials were applied long time ago in calculations of collisional widths and shifts using a theory developed by Omont [6], Kaulakys [7] and Ueda [8] (hereafter referred to as OKU) which is based on the famous Fermi model [9] of Rydberg atom–normal atom interaction. In order to verify the conclusion expressed in Ref. [1] in the present work we have applied the treatments based on the Fermi model to calculate the argon-induced shifts of the $6p{-}ns$ ($n = 7, 8$) and $6p{-}nd$ ($n = 6, 7$) ^{198}Hg lines. It should be emphasized, however, that in the OKU theory the perturbation of the lower state is ignored so that its applicability is limited to the "true" Rydberg spectral lines with upper states corresponding to very large effective quantum numbers n^*. To account for the shift and broadening of spectral lines originating from excited states corresponding to the intermediate values of n^* the OKU treatment has been extended in Ref. [10] by inclusion of the perturbation of the lower state as well as the anisotropy [11] of the electron-perturber interaction. The main advantage of such an extended OKU approach (hereafter referred to as ExOKU) is that it is free of the shortcomings of the conventional OKU theory such as those connected with some discontinuities at the borders between various n^*-intervals.

The ExOKU model was successfully applied in calculations of the pressure width and shift of several 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 [10] as well as argon spectral lines corresponding to the $3p^5np{-}3p^54s$, $3p^5ns{-}3p^54p$ and $3p^5nd{-}3p^54p$ (n = 4–9) transitions perturbed by He, Ne, and Ar [12]. All the above lines which correspond to the intermediate n^* region were the subject of the precise interferometric line profile analysis done in our laboratory in recent years [10, 12] and references therein). As the result the experimental values of pressure broadening and shift coefficients were determined with a great accuracy. It was found that although the agreement between experimental and calculated pressure broadening and shift coefficients was not satisfactory in all cases, the ExOKU model reproduced well the overall feature of the n^*-dependence of the broadening and shift coefficients.

Bielski et al. [13] have used the ExOKU treatment to interpret the broadening and shift of thallium lines corresponding to the transitions from the ground $6P_{\frac{1}{2}}$ state to $nP_{\frac{1}{2}}$ and $nP_{\frac{3}{2}}$ quasi-Rydberg (n = 9–14) states of thallium perturbed by rare-gas atoms measured by Hermann et al. [14]. It was shown that the broadening and shift coefficients calculated on the basis of ExOKU model were in a better agreement with experimental values than those calculated from the Kaulakys [7] version of the conventional OKU treatment. It was seen especially for the line shifts where the conventional model is unrealistic for small and intermediate n^* as it predicts no shift in this region.

The main goal of the present paper is to apply the ExOKU treatment to interpret the experimental results of pressure shift in the mercury spectrum reported by Veza et al. [1] in the framework of the ExOKU treatment. As in Ref. [13] we

calculated the pressure shift coefficients δ assuming the argon-induced phase shifts for Hg spectral lines in the form of a sum of the phase shift due to Fermi and that due to polarization potential. For large impact parameters both the polarization and the Fermi potential were omitted and the phase shift was assumed to be identical with that for the van der Waals potential. All the mathematical formulae used in the present calculations are given in detail in Ref. [13].

2. Pressure shift in the mercury spectrum

In our calculations of the pressure shift (δ) coefficients for ^{198}Hg $6p-ns$ and $6p-nd$ transitions perturbed by Ar we used the same value of argon polarizability $\alpha = 11.08$ a.u. and van der Waals C_6 force constants as those used by Veza et al. [1]. For the argon scattering length we used the value $L = -1.459$ a.u. reported by Petrovic et al. [15]. In order to complete the available set of pressure shift data in our analysis we have also added two earlier values of the pressure shift coefficients determined by Kaufman [16] for the 257.7 nm ($6p\,^3P_1-9s\,^3S_1$) and 292.6 nm ($6p\,^3P_2-9s\,^3S_1$) ^{198}Hg lines perturbed by Ar. The values of n^* of the mercury spectral lines analyzed in this paper cover the range from 2.9 to 4.3. Figure 1 shows the overall feature of the pressure shift coefficient (δ) for the ^{198}Hg $6p-ns$ lines calculated from the Lindholm–Foley treatment assuming the van der Waals potential, Kaulakys [7] model and ExOKU treatment [10] as a function of n^*. As it can be seen Kaulakys model is unrealistic in this case as it predicts no shift ($\delta = 0$) for $n^* \leq 7.3$. The ExOKU model covers the whole range of n^* and for small n^*-values it converges to "pure" van der Waals treatment, which in fact is naturally incorporated in the ExOKU model [10].

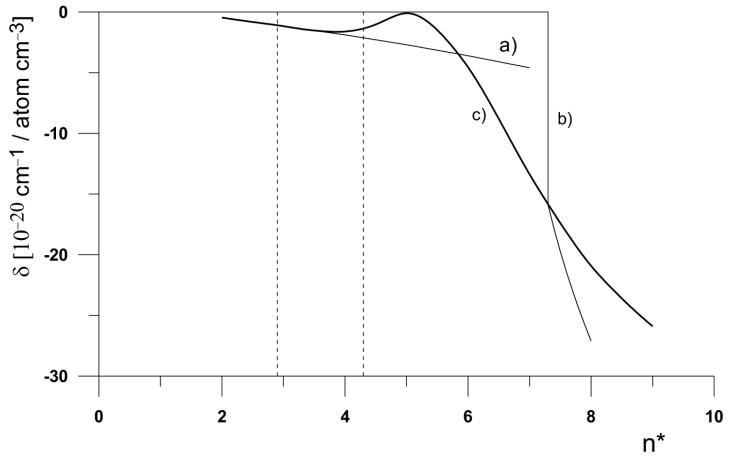

Fig. 1. The pressure shift coefficient δ of ^{198}Hg–Ar $6p\ ^1P_1-ns$ lines as a function of effective quantum number n^* calculated for: a) van der Waals potential, b) Kaulakys model, c) ExOKU treatment. Vertical dash-lines show the n^* region of spectral lines studied experimentally in [1, 16].

In Figs. 2 and 3 we present the calculated values of the pressure shift coefficients for $6p-ns$ and $6p-nd$ transitions, respectively, compared with experimental values of Veza et al. [1]. Following [1] the error bars of the experimental δ-values are given for a 95% level of confidence.

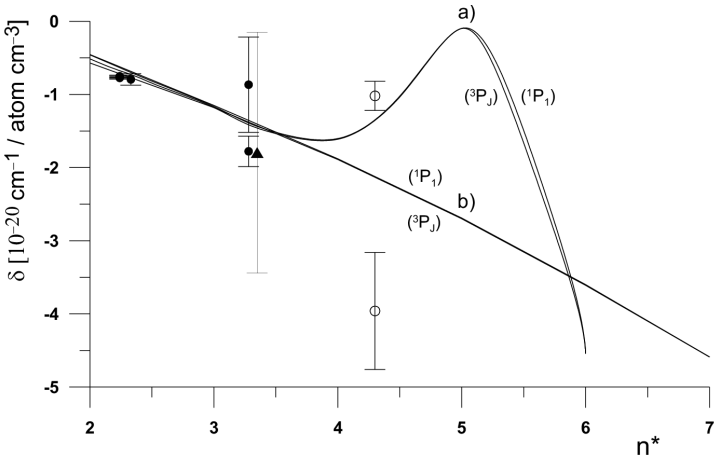

Fig. 2. Experimental values of the pressure shift coefficients, δ of argon perturbed ^{198}Hg lines: $6p\ ^1P_1-ns$ full (full circles), and $6p\ ^3P_J-ns$ (full triangles) of Veza et al. [1] and Kaufman [16] (open circles) versus the theoretical predictions from the ExOKU (a) and van der Waals (b) treatments. The error bars of the experimental δ-values are given for a 95% level of confidence.

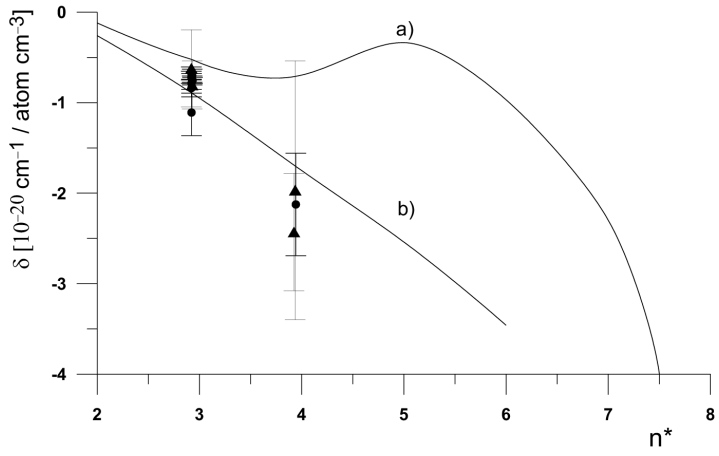

Fig. 3. Comparison of theoretical and experimental values of the pressure shift coefficients, δ of ^{198}Hg: $6p\ ^1P_1-nd$ (circles), and $6p\ ^3P_J-nd$ (triangles) lines perturbed by Ar. Other notations as in Fig. 2. Plots of theoretical values for $^1P_1$ and ^3P_J states are not distinguishable in the scale of this figure.

In our calculations we have taken into account the perturbation of the lower $6p$ level and distinguished the transitions with lower levels belonging to the $6p\ ^3P_J$ triplet (with average $n^* = 1.61$) and the $6p\,^1P_1$ singlet (with $n^* = 1.91$).

In addition in Figs. 2 and 3 we also presented the values of δ coefficients calculated for "pure" van der Waals potential.

As can be seen from Fig. 2, for the spectral lines of mercury belonging to the $6p{-}ns$ (n = 7–8) transitions we have found a relatively good agreement between experimental and calculated values of pressure shift coefficients both for the van der Waals and ExOKU treatment, however for the 292.6 nm ($6p\ ^3P_2{-}9s\,^3S_1$) line measured by Kaufman [16] with relatively good accuracy the better agreement is with ExOKU model.

For the $6p{-}nd$ transitions presented in Fig. 3 ExOKU model gives a poorer agreement between measured and calculated δ-values than pure van der Waals treatment. This corroborates our earlier results obtained for neon [10] and argon [12] spectral lines where for the lines originating from the s-states we got a better agreement between measured and calculated values of pressure broadening and shift coefficients than for those originating from the d-states. Although the limited range of experimental data for Hg–Ar does not allow one to draw definitive conclusions about the supremacy of one of two competing theoretical models, the results plotted in Figs. 1, 2, and 3 may be used as a basis for future tests of theoretical predictions at higher n^*.

3. Concluding remarks

In the present study, calculations of the pressure shift coefficients of mercury $6p{-}ns$ and $6p{-}nd$ spectral lines have been performed on the basis of the ExOKU treatment. It is shown that this simple model reproduces the general features of the n^*-dependence of the pressure shift coefficient for the Hg–Ar system. The calculated values are in reasonable (or even good) agreement with experiment. Finally, we agree with the conclusion of Veza et al. [1] that for a better understanding of the pressure effects on Hg–Ar system there is an urgent need for additional experiments involving higher excited states of mercury.

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