Collision Broadening and Shift of the 535.0 nm Tl Line Accompanying the Photodissociation of Thallium Iodide Perturbed by Noble Gases

Part I: Effects due to Kr and Xe.

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The shape and shift of the 535.0 nm thallium line resulting from the photodissociation of thallium iodide perturbed by krypton and xenon were investigated at low densities. The Doppler and collision broadening components of the line shape have been determined. The linear dependence of both the Lorentzian half-width and the shift on the perturbing gas density was found and interpreted in terms of Van der Waals and Lennard-Jones potentials.

1. Introduction

In recent papers [1—3] studies of pressure effects on the 535.0 nm Tl fluorescence line resulting from the photodissociation of thallium iodide molecules perturbed by hydrogen and deuterium were reported and the values of the effective cross sections for the impact shift and broadening of this line were determined from the Lorentzian component of the line profile. In the present paper we describe an extension of these studies on the same Tl line to mixtures of thallium iodide vapours and heavy noble gases (Kr and Xe) used as the perturbing gases.

The only experimental study of the pressure shift and broadening of the 535.0 nm thallium line by these noble gases was that of Cheron et al. [4]. Their experiment was performed on fluorescence light emitted from a natural thallium vapour mixed with a noble gas at rather high pressure (500—1500 Torr at temperature 743 K). In this pressure range the impact approximation of the line shape theory becomes questionable [5—7] and this makes it very difficult the interpretation of the measured values of the half-width and shift of the line. Such a conclusion can be drawn directly from experimental results of Cheron et al. [4], who have found that the Lorentzian distribution fits the measured profile in the very close vicinity of the core of the line only.

The purpose of the present work was to measure the shift and the broadening of the 535.0 nm Tl line perturbed by krypton and xenon at much lower pressures than those used in experiments of Cheron et al. [4]: from 0 to 250 Torr at temperature 733 K. In this pressure region two body interactions predominate so that the impact approximation of the line shape theory is fully applicable.

In the present work the photodissociation of TlI molecules was used to excite the atomic fluorescence in thallium ($7^2S_{1/2} - 6^2P_{3/2}$) in the same way as in our previous work [1—3]. We found this technique of excitation of thallium fluorescence line 535.0 nm very useful for profile measurements at low pressures of the perturbing gas. The profiles were measured using a Fabry-Perot etalon and a very careful analysis of these profiles was carried out to determine the reliable values of the shift and width parameters connected with both the collision and Doppler effects on the 535.0 nm Tl line.

2. Experimental

The experimental procedure used in the present work is similar to previously described measurements of the pressure effects on the 535.0 nm Tl line perturbed by H_2 and D_2, so we give only a brief description here.

A cell containing thallium iodide vapour up to 100 Torr of noble gas at room temperature was mounted in an electric oven, whose temperature could be maintained in the region from 300 to 750 K with a stability of ± 2 K over several hours. The cell was 3.4 cm long and 2.8 cm in diameter and was illuminated by the ultraviolet light of an r.f.

electrodeless mercury discharge tube. Both the r.f. Hg tube and the TlI fluorescence cell were made from a quartz with high transparency in the 200 nm region. The shortwave length limit of the absorption band of the TlI molecule that produces the thallium $(7^2S_{1/2} - 6^2P_{3/2})$ fluorescence due to the photo-dissociation of TlI lies at 208 nm [8].

The following mercury lines can excite this type of photodissociation of TlI: 194.2, 197.2 and 200.2 nm. The sufficient absorption of the ultra-violet light in the fluorescence cell is obtained if the density of TlI vapour is of the order of 10^{17} cm^{-3} which corresponds to the temperature range from 650 to 775 K.

The thallium fluorescence light emitted from the TlI cell was observed at the right angle to the direc-tion of excitation and was analysed by means of a pressure scanned Fabry-Perot interferometer (spacer 1.204 cm, free spectral range 0.415 cm^{-1}) using a photoelectric detection as described in the paper by Bielski et al. [9]. The Fabry-Perot etalon plates were coated with a dielectric layer with reflection coefficient 0.95. Our Fabry-Perot spectrometer has recently been modified to permit simultaneous measurement of the profile and shift of the line [10]. The auxiliary dispersion in this spectrometer is provided by a grating spectrograph (600 lines/mm). In the measurements of the pressure shift of the centre of the 535.0 nm Tl fluorescence line an r.f. electrodeless discharge thallium lamp was used as the reference source.

3. Analysis of Line Profile

The analysis of Fabry-Perot interferograms was essentially the same as in our previous works [1—3]. Our measurements were performed for natural thallium (29.46% of ^{203}Tl and 70.54% of ^{205}Tl). Although for each isotope the 535.0 nm line is split into three hyperfine structure components only two of them are resolved in usual experimental condi-tions. To obtain the reliable line shift and broaden-ing parameters the resultant profile of overlapping components was separated into that corresponding to an isolated line by means of a computer using an algorithm proposed recently [12]. This separation procedure was performed assuming that the profile of a particular hyperfine-structure component is the same.

The instrumental profile of our Fabry-Perot interferometer at 535.0 nm was found to be well described by an Airy profile [13]. Using both an analytic method due to Ballik [13] and a least square method we have confirmed our previous result [1—3] that the non-instrumental component of the profile of the 535.0 nm Tl line resulting from the photodissociation of TlI molecules can be fitted very well to Voigt profile which is a convolution of the Lorentzian and Gaussian distribution. In all cases studied in the present work the deviations of the real profile from the Voigt profile were less than 10%. The largest deviations (about 10%) were found for pure TlI cell (with no perturbing gas) and they decreased with the increase of the perturbing gas density. To determine the half-width of the Lo-rentzian and Gaussian components of the Voigt profile we have applied a procedure described by Ballik [13] combined with a least squares method.

4. Results and Interpretation

4.1. Doppler Broadening parameters

The Gaussian half-width γ_D of the 535.0 nm Tl line is plotted versus density of perturbing gas in Figure 1. As can be seen the Gaussian width is practically independent of the density. The average values of γ_D for the temperature 733 K of the TlI cell were found to be 0.042 cm^{-1} for TlI + Kr and 0.043 cm^{-1} for TlI + Xe. Let us note that the Gaus-sian half-width γ_d corresponding to the usual Doppler broadening resulting from the thermal motion of Tl atoms at 733 K is equal to $\gamma_d = 0.020$ cm^{-1}. Thus the difference $\Delta\gamma_D = \gamma_D - \gamma_d$ (0.022 cm^{-1} for TlI + Kr and 0.023 cm^{-1} for TlI + Xe) can be regarded as some measure of the additional Doppler broadening arising from the recoil of the excited Tl$(7^2S_{1/2})$ atom after photo-dissociation of TlI molecule. We should empha-size that in general case the resultant Doppler line shape of fluorescence emitted by an excited frag-ment atom due to the photodissociation of the parent molecule may differ significantly from the Gaussian profile. Zare and Herschbach [14] have derived a general Doppler line shape to be expected for atomic fluorescence excited by both polarized and unpolarized ultraviolet light. Because some parameters of TlI potential curves are not known we cannot compare by now our results with the results to be expected from Zare and Herschbach's

theory. Calculations for Tl 535.0 nm line based on this theory are planned in our laboratory. We should mention, however, that in the case of excitation by unpolarized light the Zare and Herschbach profiles resemble very much the Gaussian profile as it is found in the present experiment.

Let us note, as it can be seen from Fig. 1, for very low perturbing gas densities the Gaussian half-width γ_D of the resultant Doppler profile is somewhat greater than the average value. In particular, for the TlI cell with no perturbing gas we found the average value of $\gamma_D = 0.0573$ cm^{-1} which is 32% greater than the average value for TlI + Kr and 33% greater than average value for TlI + Xe.

These results are understood because the largest departures of the total line shape from the Voigt profile were found for the fluorescence cell with no perturbing gas.

4.2. Lorentzian Broadening and Shift Parameters

Figure 2 shows the plot of the Lorentzian half-width γ_D of the 535.0 nm Tl line emitted from the Tl cell against the density of perturbing gas. Both
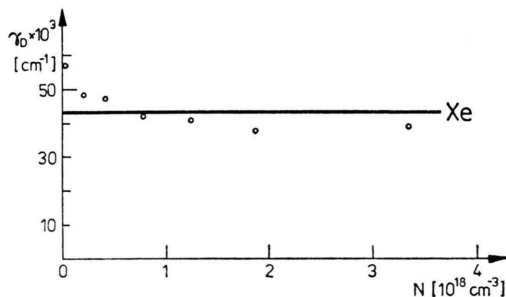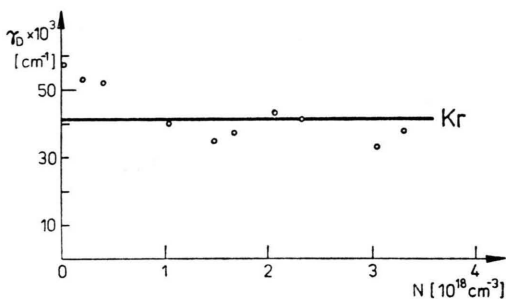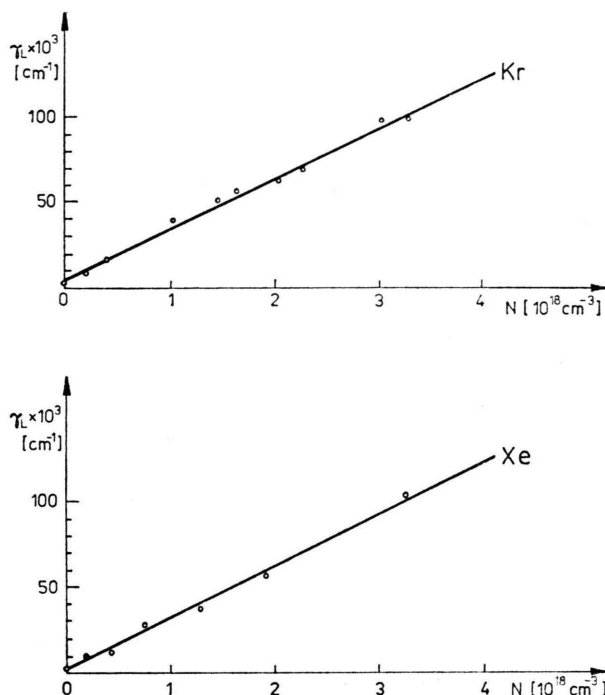

Fig. 2. Plots of the Lorentzian half-width γ_L of the 535.0 nm Tl line against the density of perturbing gas.

for Kr and Xe we found a linear variation of the Lorentzian half-width with perturbing gas density over the whole of the pressure range investigated according to the relation

$$\gamma_L = \gamma_0 + \gamma_1 + \beta N. \qquad (1)$$

Here N is the density number of foreign gas and β is the pressure broadening coefficient corresponding to the interaction of the emitting Tl-atom with foreign gas atom. In Eq. (1) γ_0 is the asymptotic value which is the sum of the natural width of the line and the residual Lorentzian half-width of the instrumental profile. γ_1 is the Lorentzian half-width of the 535.0 nm line due to the interaction of the Tl-atom with TlI molecule.

The sum $\gamma_0 + \gamma_1$ is the Lorentzian half-width of the 535.0 nm line emitted from the TlI cell with no perturbing gas. We found the value $\gamma_0 + \gamma_1 = 0.0022$ cm^{-1} at temperature 733 K.

The values β were determined from the slope of straight lines shown in Fig. 2 using a least squares method. In the case of broadening by Kr we found $\beta = (2.96 \pm 0.03) \times 10^{-20}$ cm^{-1}/atom cm^{-3}. Cheron et al. have obtained for the same case a value $\beta =$

Fig. 1. Plots of the Gaussian half-width γ_D of the 535.0 nm Tl line against the density of perturbing gas.

$(2.68 \pm 0.15) \times 10^{-20}$ cm^{-1}/atom cm^{-3} from measurements of profiles emitted from thallium fluorescence cell (not TlI). It should be noted, however, that their experiment was performed at perturbing gas densities one order of magnitude higher ($0.5 - 2 \times 10^{19}$ cm^{-3}) than those ($0 - 4 \times 10^{18}$ cm^{-3}) used in the present work.

In the case of broadening by Xe we found $\beta = (3.05 \pm 0.03) \times 10^{-20}$ cm^{-1}/atom cm^{-3} while the value determined by Cheron et al. [4] is $\beta = (2.68 \pm 0.07) \times 10^{20}$ cm^{-1}/atom cm^{-3}.

The plot of the shift $\varDelta$ of the 535.0 nm Tl line against the perturbing gas density is shown in Figure 3. Both for Kr and Xe the shift is directed towards the red (minus sign) and is linear over the perturbing gas density range measured according to the relation:

$$\varDelta = \varDelta_0 + \delta N, \qquad (2)$$

where δ is the pressure shift coefficient related to the interaction between Tl atom and the foreign gas (Kr or Xe) atoms. The value $\varDelta_0$ represents the residual shift due to the interaction between Tl

Fig. 3. Plots of the shift Δ of the 535.0 nm Tl line against the density of perturbing gas.

atom and TlI molecule, the shift of the line in the reference source and the numerical data analysis. In our case at temperature 733 K we found $\varDelta_0 = -0.0017$ cm^{-1}.

The values of the coefficient δ determined from the slopes of the straight lines shown in Figure 3 are $\delta = (-0.947 \pm 0.03) \times 10^{-20}$ cm^{-1}/atom cm^{-3} for the shift by Kr and $\delta = (-0.977 \pm 0.03) \times 10^{-20}$ cm^{-1}/atom cm^{-3} for the shift by Xe. These values are in satisfactory agreement with the values $\delta = (-0.929 \pm 0.074) \times 10^{-20}$ cm^{-1}/atom cm^{-3} for Tl-Kr and $\delta = (-1.04 \pm 0.074) \times 10^{-20}$ cm^{-1}/atom cm^{-3} for Tl-Xe determined by Cheron et al. [4] from thallium measurements at perturbing gas densities one order of magnitude higher than those used in the present work.

4.3. Interaction potentials

According to the impact theory of pressure broadened line profiles (cf. [5, 6]) the pressure broadening and shift coefficients β and δ defined in Eqs. (1) and (2) are given by:

$$\beta = 2 \bar{v} \sigma_{\mathrm{b}}, \qquad (3)$$

$$\delta = \bar{v} \sigma_{\mathrm{s}}, \qquad (4)$$

where $\bar{v}$ is the mean relative velocity and σ_{b} (or σ_{s}) denote the effective cross section for the impact broadening (or shift) of the line.

The values σ_{b} and σ_{s} determined from the slopes of straight lines shown in Figures 2 and 3 are equal to $\sigma_{\mathrm{b}} = 5.45 \times 10^{-14}$ cm^2 and $\sigma_{\mathrm{s}} = 3.48 \times 10^{-14}$ cm^2 for Tl + Kr ($\bar{v} = 5.1 \times 10^4$ cm s^{-1}) and $\sigma_{\mathrm{b}} = 6.52 \times 10^{-14}$ cm^2, $\sigma_{\mathrm{s}} = 4.17 \times 10^{-14}$ cm^2 for Tl + Xe ($\bar{v} = 4.4 \times 10^4$ cm s^{-1}).

Since accurate interaction potentials for the thallium-noble gas systems are not available we have attempted to interpret our results in terms of the classical impact theory assuming an empirical $(6 - 12)$ Lennard-Jones function to describe the interaction potential $V(R)$ between the perturbing atom situated at the distance R from the radiating atom:

$$V(R) = \hbar C_{12} R^{-12} - \hbar C_6 R^{-6} \qquad (5)$$

where C_6 and C_{12} are the constants.

According to Hindmarsh et al. [15] for this potential the pressure broadening and shift coefficient are given by

$$\beta = 8 \pi \left(\frac{3 \pi}{8} \right)^{2/5} \bar{v}^{3/5} |\varDelta C_6|^{2/5} B(\xi), \qquad (6)$$
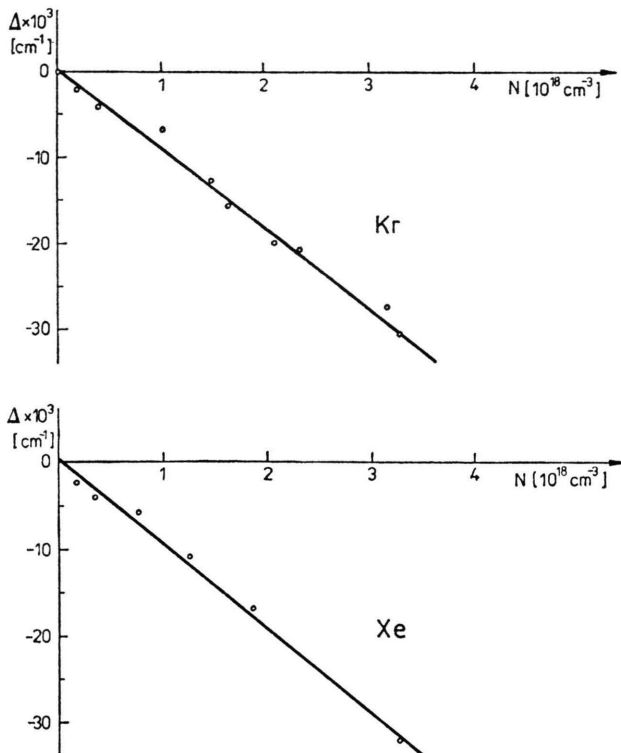
$$\delta = 2\pi \left(\frac{3\pi}{8}\right)^{2/5} \bar{v}^{3/5} |\Delta C_6|^{2/5} S(\xi), \qquad (7)$$

where

$$\xi = 0.536\, \bar{v}^{6/5} \Delta C_{12} |\Delta C_6|^{-11/5}. \qquad (8)$$

ΔC_6 and ΔC_{12} denote the differences of potential parameters C_6 and C_{12} for the upper and lower levels of the radiating atom.

The functions $B(\xi)$ and $S(\xi)$ are given by the following integrals:

$$B(\xi) = \int_0^\infty x \sin^2 \tfrac{1}{2} (\xi x^{-11} - x^{-5})\, dx, \qquad (9)$$

$$S(\xi) = \int_0^\infty x \sin (\xi x^{-11} - x^5)\, dx. \qquad (10)$$

In the limit of purely Van der Waals interactions, i.e. when repulsion is neglected ($\Delta C_{12} = 0$, $\xi = 0$), these broadening and shift integrals reduce to constant quantities $B(0) = 0.301$ and $S(0) = -0.438$. In this case Eqs. (6) and (7) become identical to the well-known Lindholm-Foley expressions (cf. [16])

$$\beta = 8.08\, \bar{v}^{3/5} |\Delta C_6|^{2/5}, \qquad (11)$$

$$\delta = -2.94\, \bar{v}^{3/5} |\Delta C_6|^{2/5}. \qquad (12)$$

The Van der Waals constant C_6 can be computed using the formula given by Unsöld [17]:

$$C_6 = \sigma \hbar^{-1} e^2 \langle r^2 \rangle, \qquad (13)$$

where e is the elementary charge, and σ is the polarizability of the perturbing atom. Here $\langle r^2 \rangle$ is the quantum-mechanical average value of r^2 for the given level of the radiating atom.

In many papers one estimates $\langle r^2 \rangle$ using the Coulomb approximation [17]:

$$\langle r^2 \rangle = \tfrac{1}{2} a_0^2 (n^*)^2 \cdot [5(n^*)^2 + 1 - 3l(l+1)], \qquad (14)$$

where n^* is the effective quantum number, a_0 is the Bohr radius and l is the orbital quantum number. Using the values of n^* for Tl given by Kuhn [18]

and the theoretical values of σ for Kr and Xe reported by Dalgarno and Kingston [19] we have calculated the C_6 constants for the 535.0 nm Tl line perturbed by Kr and Xe. These constants are listed in Table 1 in the column denoted by coul.

We have also performed more accurate calculations of C_6 constants for Tl + noble gas system using both a non-relativistic Hartree-Fock (H-F) wave functions evaluated from the computer program given by Froese-Fischer [20] and a multiconfiguration relativistic Dirac-Hartree-Fock (D-H-F) wave functions evaluated from the program given by Desclaux [21].

Using these programs the $\langle r^2 \rangle$ values in Eq. (13) were computed. The Hartree-Fock and Dirac-Hartree-Fock values of Van der Waals constants for Tl (535.0 nm) line perturbed by Kr and Xe are listed in Table 1. As can be seen the H-F as well as the D-H-F values of C_6 are greater than those obtained from the Coulomb approximation.

It should be emphasized that both H-F and D-H-F values listed in Table 1 are obtained from the Unsöld formula (Equation (13)). Proctor and Stwalley [22] have recently developed a more general method applicable for the S-states of the radiating atom. Using this method Wu et al. [23] have calculated the C_6 constants for the interaction of the Tl atom in the $7^2S_{1/2}$ state with heavy noble gas atoms. Their results are listed in Table 1.

The repulsive potential parameter C_{12} of the Lennard-Jones function (Eq. (5)) can be roughly estimated using a formula proposed by Hindmarsh et al. [15]:

$$C_{12} = q \hbar^{-1} R_{AB}^{12} \qquad (15)$$

where $q = (0.9 \pm 0.3) \times 10^{-16}$ erg. $R_{AB} = r_A + r_B$.

Here r_A denotes the so-called "Hindmarsh radius", i.e. the distance from the nucleus of the radiating atom A in the given state at which the unperturbed radial charge density has the value 0.012 atomic units.

Per-turber	Tl-state	C_6				C_{12}		
		coul	H-F	D-H-F	Ref. [23]	coul	H-F	D-H-F
Kr	$6^2P_{3/2}$	1.66	2.71	2.87	—	0.04	0.29	0.32
	$7^2S_{1/2}$	9.18	12.91	11.12	8.83	11.75	34.21	20.81
Xe	$6^2P_{3/2}$	2.70	4.39	4.64	—	0.08	0.51	0.59
	$7^2S_{1/2}$	14.96	20.87	17.99	14.14	18.01	51.89	31.28

Table 1. The Lennard-Jones potential parameters for Tl + Kr and Tl + Xe. (C_6 in units 10^{-31} cm^6/rad s, C_{12} in units 10^{-74} cm^{12}/rad s).

Table 2. Experimental and theoretical values of the pressure broadening coefficient β (in units 10^{-20} cm^{-1}/atom cm^{-3}). Numbers in parantheses are standard deviations of the least-square-fit.

Perturber	Experiment		Theory					
	this work	Cheron et al. [4]	Lennard-Jones			van der Waals		
			coul	H-F	D-H-F	coul	H-F	D-H-F
Kr	2.96 (0.03)	2.68 (0.15)	2.79	2.75	2.57	2.56	2.88	2.65
Xe	3.05 (0.03)	2.68 (0.07)	2.73	3.42	3.11	2.85	3.20	2.94

r_B is the corresponding Hindmarsh radius for the ground state perturbing atom. To estimate C_{12} from Eq. (12) we have computed the radii r_A for Tl in the states $7^2 S_{1/2}$ and $6^2 P_{3/2}$ using the non-relativistic Hartree-Fock (H-F) [20] as well as the multiconfiguration relativistic Dirac-Hartree-Fock (D-H-F) method [21]. The values of the Hindmarsh radius r_B for the ground state Kr and Xe atoms were calculated in Ref. [24]. The C_{12} constants obtained in this way are listed in Table 1. The "Coulomb" C_{12} values listed in Table 1 were obtained using the Bates-Daamgard wavefunction [25] to calculate r_A.

Using these theoretical values of C_6 and C_{12} constants we have calculated from Eqs. (6) and (7) the values of the pressure broadening and shift coefficients β and δ. The theoretical values of β and δ are listed in Tables 2 and 3, where they are compared with experimental values determined in the present investigation. Table 4 contains the theoretical and experimental values of the ratio δ/β. In Tables 1—4 the columns termed as "coul" correspond to C_6 constants calculated from Eq. (12) and C_{12} constants calculated from Eq. (13) with r_A computed from the Bates-Daamgard wave functions.

4. 4. Discussion

The comparison of the measured and theoretical values of β and δ (Tables 2 and 3) shows that the

Table 4. Experimental and theoretical values of the ratio δ/β.

Per-turber	Experiment		Theory		
	this work	Cheron et al. [4]	Lennard-Jones		
			coul	H-F	D-H-F
Kr	− 0.32	− 0.35	− 0.39	− 0.48	− 0.47
Xe	− 0.32	− 0.39	− 0.37	− 0.32	− 0.32

classical impact theory can adequately deal with the broadening and shift of the Tl 535.0 nm line by Kr and Xe. As can be seen from Tables 2 and 3 both the van der Waals and the Lennard-Jones potential yield the values of β and δ which are in reasonable agreement with experimental results. We can thus conclude that the purely attractive van der Waals potential is sufficient to describe the broadening and shift of the Tl 535.0 nm line by Kr and Xe. Another conclusion which can be drawn from Tables 2 and 3 is that the Lennard-Jones potential changes but a little theoretical results for β and δ. However, no essential improvement of theoretical results is obtained for the Lennard-Jones potential in comparison to those obtained for the van der Waals potential. We should also note that the Coulomb, Hartree-Fock and Dirac-Hartree-Fock approximations yield the results which are in reasonable agreement with experiment. No decisive conclusion about which of these approximations is the best one can be drawn from the present work.

Table 3. Experimental and theoretical values of the pressure shift coefficient δ (in units 10^{-2} cm^{-1}/atom cm^{-3}). Numbers in parantheses are standard deviation of the least-square-fit.

Perturber	Experiment		Theory					
	this work	Cheron et al. [4]	Lennard-Jones			van der Waals		
			coul	H-F	D-H-F	coul	H-F	D-H-F
Kr	− 0.95 (0.03)	− 0.93 (0.07)	− 1.08	− 1.33	− 1.21	− 0.93	− 1.05	− 0.97
Xe	− 0.98 (0.03)	− 1.04 (0.07)	− 1.02	− 1.09	− 0.99	− 1.04	− 1.17	− 1.07

It should be noted, that our experimental results agree well with the theoretical values of Wu et al. [23] calculated for the van der Waals potential with C_6 constant obtained using a method proposed by Proctor and Stwalley [22]. Calculations reported by Wu et al. [23] seem to indicate that the contribution of the higher order attractive forces (R^{-8} and R^{-10}) should not be ignored. However, calculation for the Lennard-Jones potential performed in the present work show that effects due to the repulsion parts of potential curves may be even more important than those due to higher order terms in the purely attractive potential.

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