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

Part II: Effects due to He, Ne and Ar

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The broadening and shift of the 535.0 nm thallium line resulting from the photodissociation of thallium iodide perturbed by helium, neon and argon were investigated at low densities using a photoelectric Fabry-Perot interferometer. The Doppler and collision broadening components of the line profiles have been determined. Linear variations of both the Lorentzian half-width and the shift of the line with the perturbing gas density were found and interpreted in terms of Van der Waals and Lennard-Jones potentials.

1. Introduction

This paper reports measurements of the shape, width and shift of the 535.0 nm fluorescence line of thallium resulting from the photodissociation of thallium iodide molecules perturbed by helium, neon and argon. The broadening and shift of this line due to collisions with noble gas atoms have been studied by Cheron at al. [1]. Their experiment was carried out on the fluorescence light emitted from a natural thallium vapour mixed with a noble gas and with a grating spectrograph, so that rather high foreign gas pressures (500–1500 Torr at temperature 743 K) could be used. In this pressure region, however, some objections to the applicability of the impact theory of line broadening [2, 3] may be raised since significant deviations of experimental line profiles from the Lorentzian profiles were found by Cheron et al. [1].

In the present work, high-resolution spectroscopy techniques were used to measure the profiles of the 535.0 nm Tl line at low pressures of foreign gas (He, Ne, Ar), where the impact theory is valid. The main interest of this work was to establish the magnitudes of the collision broadening and shift parameters for the low pressure region and to compare them with the high pressure data of Cheron et al. as well as with the predictions of the impact theory.

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2. Experimental

The experimental arrangement and the line profile analysis were identical with those used in our previous investigations of the broadening and shift of the 535.0 nm Tl line by krypton and xenon [4] and by molecular hydrogen [5, 6] and deuterium [7]. The atomic fluorescence of thalium was excited by the photodissociation of thallium iodide molecules due to the irradiation of the TlI vapour with ultraviolet light of an r.f. electrodeless mercury discharge lamp. The line profiles were analysed using a grating spectrograph and a Fabry-Perot etalon with 1.204 cm spacer and dielectric coatings. The etalon which was pressure scanned [8, 9] resolved the hyperfine structure into two components, separated by the $7s\ ^2S_{1/2}$ Tl level interval of 0.42 cm^{-1}. The intensity distribution was monitored using a photomultiplier in the photon counting mode. The numerical methods of the analysis of line profiles were described in our previous work [4–7]. A low pressure r.f. electrodeless thallium discharge lamp was used as the reference source in the line shift measurements. All measurements were performed at the temperature 733 K for various densities of the perturbing gas up to about 4×10^{18} cm^{-3} (this corresponds to foreign gas pressures up to 100 Torr at temperature 273 K).

3. Results and Interpretation

For all densities of the perturbing gas used in the present experiment we have found that the non-

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instrumental component of the measured shape of the 535.0 nm Tl line emitted due to the photodissociation of TlI can be fitted well to a Voigt profile, i.e. the convolution of the Lorentzian and Gaussian profiles. The half-widths of the Lorentzian and Gaussian components of the Voigt profile were determined using a method proposed by Ballik [10] combined with a least squares method.

3.1. Doppler Broadening Parameters

Figure 1 shows the plot of the Gaussian half-width γ_D of the 535.0 nm Tl line emitted from the thallium iodide cell at the temperature 733 K against the density of perturbing gas. The Gaussian width is practically independent of the density. The average values γ_D of Gaussian half-width at 733 K were found to be 0.0507 cm^{-1} for TlI + He, 0.0500 cm^{-1} for TlI + Ne and 0.0479 cm^{-1} for TlI + Ar. We should note that the Gaussian half-width γ_d corresponding to the usual Doppler broadening resulting from thermal motion of Tl atoms at 733 K is equal to 0.020 cm^{-1}. The difference $\Delta\gamma_D = \gamma_D - \gamma_d$ (0.031 cm^{-1} for TlI + He, 0.030 cm^{-1} for TlI + Ne and 0.028 cm^{-1} for TlI + Ar) can thus be used to estimate the additional Doppler broadening arising from the recoil of the excited $Tl(7^2S_{1/2})$ atom after photodissociation of the TlI molecule. As was shown by Zare and Herschbach [11] in the general case the Doppler shape of fluorescence lines emitted by a fragment atom excited due to the photodissociation of the parent molecule may differ significantly from the Gaussian profile. However, in the case of excitation by unpolarized light the Zare and Herschbach theory predicts profiles which resemble very much to the Gaussian profiles as they are found in the present work.

We should emphasize that at very low pertubing gas densities the Gaussian half-widths γ_D are always greater than the average value $\bar{\gamma}_D$. For the TlI cell with no perturbing gas we found at 733 K the same value $\gamma_D = 0.0573$ cm^{-1} as in our previous measurements [3—7]. This value is 12% greater than the average value $\bar{\gamma}_D$ for TlI + He, 13% greater than $\bar{\gamma}_D$ for TlI + Ne, 16% greater than $\bar{\gamma}_D$ for TlI + Ar, 26% greater than $\bar{\gamma}_D$ for TlI + Kr and 26% greater than $\bar{\gamma}_D$ for TlI + Xe.

3.2. Lorentzian Broadening and Shift Parameters

In Fig. 2 the Lorentzian half-widths γ_L of the 535.0 nm Tl line emitted from the thallium iodide cell are plotted against the density of perturbing

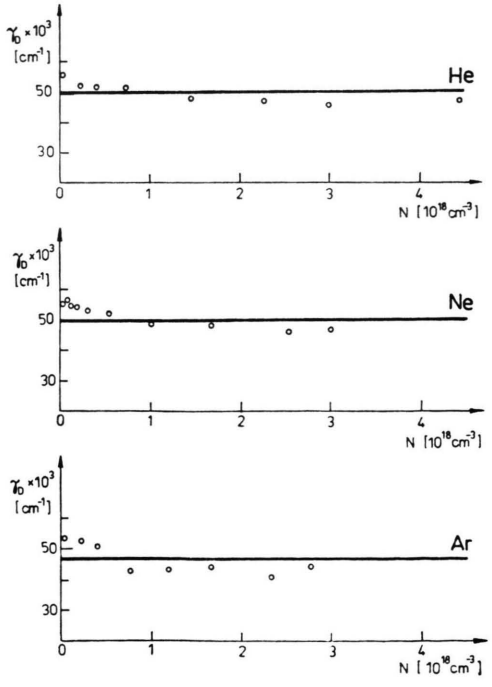

Fig. 1. Plots of the Gaussian half-width γ_D of the 535.0 nm Tl line against the density of perturbing gas.

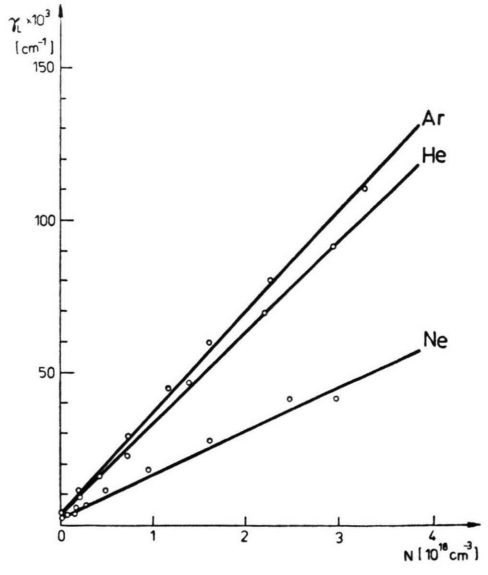

Fig. 2. Plots of the Lorentzian half-width γ_L of the 535.0 nm Tl line against the density of perturbing gas.

gas. As can be seen for all perturbing gases the Lorentzian half-widths depend linearly on the density according to the relation

$$\gamma_L = \gamma_0 + \gamma_1 + \beta N, \quad (1)$$

where N is the perturber density and β is the pressure broadening coefficient related to the interaction between the radiating Tl-atom and the perturbing atom. In Eq. (1) γ_0 is the sum of the natural width of the line and the residual Lorentzian half-width of the instrumental function. γ_1 denotes the Lorentzian half-width of the 535.0 nm line due to the interaction between the radiating Tl-atom and the TlI molecule.

Measurements performed on TlI cells with no perturbing gas have confirmed our previous results [4] for the asymptotic value of the sum $\gamma_0+\gamma_1$. For the temperature 733 K we found the value 0.0022 cm^{-1}. Using a least squares method the values β of the pressure broadening coefficient were determined from the slopes of the straight lines shown in Figure 2. These experimental values of β are listed in Table 1, where they are compared with the results of β determined by Cheron et al. [1]. It must be remembered that the experiment of Cheron et al. was carried out at perturbing gas densities one order of magnitude higher ($0.5-2.0 \times 10^{19}$ cm^{-3}) than those ($0-4 \times 10^{18}$ cm^{-3}) used in the present investigation.

Figure 3 shows the plot of the shift Δ of the 535.0 nm Tl line emitted from the TlI cell against the number density of the perturbing gas. For all perturbing gases the shift is linear over the density range measured according to the relation:

$$\Delta = \Delta_0 + \delta N, \quad (2)$$

where δ denotes the pressure shift coefficient corresponding to the interaction of the radiating Tl atom with the perturbing atom. In Eq. (2) the

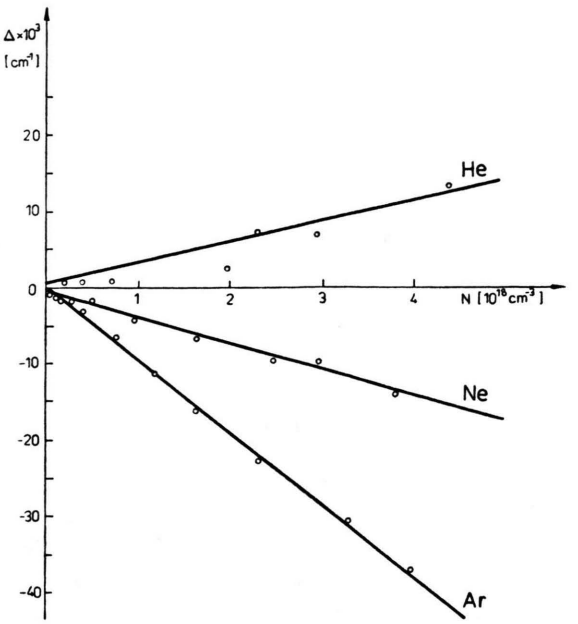

Fig. 3. Plots of the shift Δ of the 535.0 nm Tl line against the density of perturbing gas.

quantity Δ_0 comprises the residual shift due to the interaction between the radiating Tl atom and the TlI molecule, the shift of the line in the reference source and that resulting from the numerical data analysis. In our experimental conditions we found $\Delta_0 = -0.0017$ cm^{-1} at the temperature 733 K.

As can be seen in Fig. 3 neon and argon produce a red shift (minus sign) of the 535.0 nm Tl line. On the other hand, a shift towards the blue (plus sign) is observed when helium is used as the perturbing gas.

The values δ of the pressure shift coefficient determined from the slopes of the straight lines shown in Fig. 3 are listed in Table 2, where they are compared with the experimental values obtained by Cheron et al. [1] in their studies at perturbing gas

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

Perturber	Experiment		Theory					
	this work	Cheron et al. [1]	Lennard-Jones			van der Waals		
			coul	H–F	D–H–F	coul	H–F	D–H–F
He	3.05 (0.03)	3.38 (0.22)	2.90	3.68	3.30	2.13	2.45	2.25
Ne	1.45 (0.02)	1.49 (0.15)	1.52	2.07	1.72	1.75	1.98	1.82
Ar	3.36 (0.09)	3.12 (0.22)	2.00	1.99	1.84	2.58	2.90	2.67

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

Perturber	Experiment		Theory					
	this work	Cheron et al. [1]	Lennard-Jones			van der Waals		
			coul	H–F	D–H–F	coul	H–F	D–H–F
He	+ 0.30 (0.03)	+ 0.24 (0.06)	+ 0.20	+ 0.32	+ 0.27	− 0.77	− 0.89	− 0.82
Ne	− 0.34 (0.02)	− 0.32 (0.07)	− 0.14	− 0.07	− 0.08	− 0.64	− 0.72	− 0.68
Ar	− 0.98 (0.01)	− 1.00 (0.07)	− 1.10	− 1.04	− 0.99	− 0.94	− 1.06	− 0.97

densities one order of magnitude higher than those used in the present measurements.

3.3. *Interatomic Potential Parameters*

In order to interpret our experimental values of β and δ for the 535.0 nm Tl line perturbed by Ar, Ne and He we have applied the procedure identical with that used in our previous work [4] on the broadening and shift caused by Kr and Xe. Firstly, we have determined the values σ_b and σ_s of the effective cross sections for the broadening and shift of the 535.0 nm Tl line by Ar, Ne and He. To this end we have applied the impact theory of pressure broadening according to which the coefficients β and δ (in angular frequency units) can be written in the form [2, 3]

$$\beta = 2\bar{v}\sigma_b, \tag{3}$$

$$\delta = \pm\bar{v}\sigma_s, \tag{4}$$

where $\bar{v}$ is the mean relative velocity of colliding atoms.

The values σ_b and σ_s determined from the straight lines shown in Figs. 2 and 3 are equal to:

$$\sigma_b = 4.64 \times 10^{-14}\ \text{cm}^2 \quad \text{and}$$
$$\sigma_s = 0.27 \times 10^{-14}\ \text{cm}^2$$

for Tl + Ar ($\bar{v} = 6.81 \times 10^4$ cm s^{-1}),

$$\sigma_b = 1.48 \times 10^{-14}\ \text{cm}^2 \quad \text{and}$$
$$\sigma_s = 0.69 \times 10^{-14}\ \text{cm}^2$$

for Tl + Ne ($\bar{v} = 9.19 \times 10^4$ cm s^{-1}) and

$$\sigma_b = 1.45 \times 10^{-14}\ \text{cm}^2,$$
$$\sigma_s = 0.29 \times 10^{-14}\ \text{cm}^2$$

for Tl + He ($\bar{v} = 1.98 \times 10^5$ cm s^{-1}).

As in the case of collision effects caused by Kr and Xe [4], we have used an empirical (6—12) Lennard-Jones potential to approximate the interaction energy $V(R)$ between the perturbing atom and the Tl atom (R the interatomic distance):

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

The constants C_6 and C_{12} have been calculated using three methods which were thoroughly discussed in our previous paper [4]. The first method consists in the application of a simple Coulomb approximation introduced by Unsöld [12]. In the remaining methods either non-relativistic Hartree-Fock (H-F) wave functions evaluated from the computer program given by Froese-Fischer [13] or multiconfiguration relativistic Dirac-Hartree-Fock (D-H-F) wave functions evaluated from the program given by Desclaux [14] have been applied. Using these methods the values of the Lennard-Jones potential parameters have been calculated from analytic formulae given by Unsöld [12] for C_6 and by Hindmarsh et al. [15] for C_{12}. These theoretical values of C_6 and C_{12} for Tl + He, Tl + Ne and Tl + Ar are listed in Table 3. This Table contains also the values of the van der Waals constant C_6 for the Tl atom in the $7^2\,S_{1/2}$ state calculated by Wu et al. [16] from a formula [18] more general than that given by Unsöld.

The values of the repulsive constant C_{12} termed as "coul" in Table 3 were obtained from the formula proposed by Hindmarsh et al. [15] using the Coulomb approximation of the Bates-Damgaard type [17] (cf. Eq. (15) in [4]).

We have then used the values of the C_6 and C_{12} constants computed in this way to calculate the pressure broadening and shift coefficients β and δ, respectively. The calculations were performed using expressions derived by Hindmarsh et al. [15] on the basis of the classical impact theory (cf. Eqs. (6) and (7) in [4]). The calculated values of β and δ are listed in Tables 1 and 2, where they are compared with our experimental values as well as with the results of the experiment by Cheron et al. [1] car-

Perturber	Tl-state	C_6			Ref. [16]	C_{12}		
		coul	H–F	D–H–F		coul	H–F	D–H–F
He	$6^2P_{3/2}$	0.145	0.236	0.25	—	0.003	0.03	0.038
	$7^2S_{1/2}$	0.8	1.12	0.969	0.735	2.52	8.69	4.823
Ne	$6^2P_{3/2}$	0.264	0.432	0.461	—	0.006	0.05	0.061
	$7^2S_{1/2}$	1.46	2.072	1.785	1.429	3.52	11.74	6.617
Ar	$6^2P_{3/2}$	1.09	1.784	1.886	—	0.025	0.19	0.208
	$7^2S_{1/2}$	6.07	8.478	7.313	5.867	8.57	26.31	15.390

Table 3. The Lennard-Jones potential parameters for Tl + He, Tl + Ne and Tl + Ar. (C_6 in units 10^{-31} cm^6 rad/s, C_{12} in units 10^{-74} cm^{12} rad/s).

ried out at perturbing gas densities one order of magnitude higher than those used in our work. In both Tables the columns termed as "van der Waals" represent the theoretical values of β and δ obtained from the impact theory for the purely attractive van der Waals potential, i.e. when $C_{12}=0$.

Table 4 contains the comparison of the theoretical and experimental values of the ratio δ/β of the pressure shift to the pressure broadening coefficients. We should mention that in Tables 1—4 the columns termed as "coul" correspond to the Coulomb approximation applied in the calculations of the C_6 and C_{12} force constants.

3.4. Discussion

The first conclusion which can be drawn from the comparisons shown in Tables 1 and 2 is that for Tl + Ar and Tl + Ne the purely attractive van der Waals potential leads to quite a good agreement of the calculated values of β and δ for the 535.0 nm Tl line with the measured ones. Moreover, as can be seen from Table 4 the experimental values of the ratio δ/β are for Tl + Ar and Tl + Ne in better agreement with the theoretical value $\delta/\beta=-0.36$ resulting from the impact theory for the van der Waals potential than with those resulting from the Lennard-Jones potential. We should also mention that our experimental results of β and δ for Tl + Ar agree well with theoretical values of Wu et al. [16]

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

Perturber	Experiment		Theory		
	this work	Cheron et al. [1]	Lennard-Jones		
			coul	H–F	D–H–F
He	+ 0.099	+ 0.071	+ 0.068	+ 0.086	+ 0.082
Ne	− 0.234	− 0.21	− 0.089	− 0.033	− 0.047
Ar	− 0.291	− 0.31	− 0.55	− 0.522	− 0.537

calculated for the van der Waals potential. In their calculations the C_6 constant was computed using a method proposed by Proctor and Stwalley [18]. On the other hand, however, for the 535.0 nm Tl line perturbed by He the calculations based on the assumption of the van der Waals potential yield values for the shift which are in qualitative disagreement with experiment: a blue shift is observed while a red one results from theory. As can be seen from Tables 1, 2 and 4 the Lennard-Jones potential yields values of β and δ for the 535.0 nm Tl line, perturbed by He, which are in reasonable agreement with experimental values. We should emphasize that in this case the Coulomb approximation as well as those based on the Hartree-Fock and Dirac-Hartree-Fock wave functions yield results for the coefficients β and δ which agree reasonably with experiments. Let us note, however, that for Tl + Ne the theoretical values of the pressure shift coefficient δ and the ratio δ/β calculated from the Lennard-Jones potential on the basis of the Coulomb approximation are in much better agreement with experiment than those resulting from calculations based on the Hartree-Fock and Dirac-Hartree-Fock wave functions. On the other hand, however, as we have emphasized above for Tl + Ne and Tl + Ar the van der Waals potential yields much better results than the Lennard-Jones potential. Thus we can conclude that in this case the Lennard-Jones potential may not deal adequately with the Tl-Ne and Tl-Ar interaction. Further more accurate studies on interaction potentials for Tl-noble gas system are thus necessary to explain the experimental data for the collision effects on the 535.0 nm thallium line.

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[1] B. Cheron, R. Scheps, and A. Gallagher, Phys. A **15**, 651 (1977).
[2] F. Schuller and W. Behmenburg, Phys. Rep. **12** C, 274 (1974).
[3] J. Szudy and W. E. Baylis, J. Quant. Spectr. Radiat. Transfer **15**, 641 (1975).
[4] E. Lisicki, A. Bielski, and J. Szudy, Z. Naturforsch. **35a**, 1249 (1980).
[5] E. Lisicki, J. Szudy, and J. Wolnikowski, Acta Phys. Polon. A **56**, 557 (1979).
[6] E. Lisicki, Z. Naturforsch. **35a**, 773 (1980).
[7] E. Lisicki, J. Szudy, and J. Wolnikowski, Acta Phys. Polon. A **58**, 105 (1980).
[8] A. Bielski, S. A. Kandela, J. Wolnikowski, and Z. Turlo, Acta Phys. Polon. A **42**, 295 (1972).
[9] A. Bielski, W. Dokurno, E. Lisicki, and Z. Turlo, Optica Applicata **11**, 151 (1981).
[10] E. A. Ballik, Appl. Opt. **5**, 170 (1966).
[11] R. N. Zare and D. R. Herschbach, Proc. IEEE **51**, 173 (1973).
[12] A. Unsöld, Physik der Sternatmosphären, Springer-Verlag, Berlin 1955.
[13] C. Froese-Fischer, Compt. Phys. Comm. **4**, 107 (1972).
[14] J. P. Desclaux, Compt. Comm. **9**, 31 (1975).
[15] W. R. Hindmarsh, A. D. Petford, and G. Smith, Proc. Roy. Soc. London A **297**, 296 (1967).
[16] C. Y. Wu, W. C. Stwalley, and T. R. Proctor, J. Chem. Phys. **61**, 4238 (1978).
[17] D. R. Bates and A. Damgaard, Phil. Trans. **242**, 101 (1949).
[18] T. R. Proctor and W. C. Stwalley, J. Chem. Phys. **66**, 2063 (1977).