EFFECTS OF DEUTERIUM PRESSURE ON THE WIDTH AND SHIFT OF ATOMIC FLUORESCENCE OF THALLIUM IODIDE*

By E. Lisicki, J. Szudy and J. Wolnikowski

Institute of Physics, Nicholas Copernicus University, Toruń**

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Profiles of the 535 nm thallium line resulting from photodissociation of thallium iodide vapour mixed with deuterium have been measured for various gas densities using a photoelectric Fabry-Perot interferometer. The Doppler and collision broadening components of profiles have been determined and the linear variation of both the width and shift of the Lorentzian profile with the deuterium density has been found. Values of the cross sections for the impact broadening and shift of the 535 nm Tl line perturbed by D_2 were determined and interpreted in terms of van der Waals and Lennard-Jones potentials.

1. Introduction

Studies of the collision broadening and shift of spectral lines can provide information about interaction involving excited atomic states. In a recent paper [1] results of fluorescence measurements of the Doppler- and collision-broadened line profiles of the thallium green line 535 nm ($7^2S_{1/2}-6^2P_{3/2}$) perturbed by hydrogen were reported and the value of the van der Waals constant for the Tl-H_2 long range interaction was determined from the Lorentzian half-width of this line. These measurements were carried out using the thallium atomic fluorescence resulting from the optical dissociation of thallium iodide vapour mixed with hydrogen. In the present investigation, the same technique of excitation of the atomic fluorescence was used to study the Doppler and collision broadening and shift of the 535 nm Tl line perturbed by deuterium. The profiles of this line have been measured using high resolution spectroscopy methods for various temperatures and pressures of deuterium. A very careful analysis of line profiles has been performed to determine reliable values of the widths of the Gaussian and Lorentzian line profile components which yield information on the Doppler effect as well as the interaction between excited Tl-atoms and D_2-molecules. The half-width of the Lorentzian component and its shift have been measured as a function of deuterium density and the effective cross sections for the impact broadening and shift of the 535 nm line perturbed by D_2 have been determined.

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** Address: Instytut Fizyki, Uniwersytet M. Kopernika, Grudziądzka 5, 87-100 Toruń, Poland.

2. Experimental details

The apparatus used in the present investigation was similar to that described previously [1]. Light was collected from the fluorescence cell containing thallium iodide vapour mixed with deuterium. The thallium iodide salt was distilled into an evacuated quartz tube which was then filled with deuterium and mounted in an electric oven, which could be maintained at any temperature between 300 and 750 K with stability of ± 2 K over several hours. The temperature of the heated thallium iodide salt was measured with a thermocouple placed in a contact with the fluorescence cell, which was 3.4 cm long and 2.8 cm in diameter.

The atomic fluorescence of thallium was excited by irradiating the TlI-cell with the ultraviolet light of an r.f. electrodeless mercury discharge lamp. Previous experiments have shown that the photodissociation of thallium iodide molecules can produce the excited thallium atoms in the $7^2S_{1/2}$ level if the TlI-salt is illuminated by the ultraviolet radiation in the region of 200 nm [2–4]. Temperatures of 650 to 775 K provide sufficient vapour pressure of the TlI-salt so the profiles of the atomic thallium fluorescence line 535 nm ($7^2S_{1/2}-6^2P_{3/2}$) can be measured.

In our work high resolution was obtained with a Fabry-Perot interferometer and a grating spectrograph using a photoelectric detection as described by Bielski et al. [5]. The plates of the Fabry-Perot etalon were coated with dielectric layer and the 1.204 cm spacer (free spectral range 415 mK) was used. Some modifications of our Fabry-Perot spectrometer have recently been made, which also permitted measurements of the shift of the line.

3. Analysis of line profiles

Measurements reported in this paper were performed for the natural thallium which consists of two isotopes: 70.54% of ^{205}Tl and 29.46% of ^{203}Tl. For each isotope the 535 nm line is split into three hyperfine-structure components but only two of them are resolved in usual experimental conditions [6]. In order to obtain the reliable line broadening and shift parameters the resultant profile of overlapping components must be separated into that corresponding to an isolated line. The separation procedure used in this work was identical to that described in our previous paper [1] for Tl + H_2, where also the positions and relative intensities of various hyperfine-structure components of the 535 nm Tl line were thouroughly discussed. We have verified that the instrumental function of our Fabry-Perot etalon is well approximated by an Airy profile [7]. New tests have been made in the present work to establish the influence of TlI-molecules on the shape of the 535 nm thallium line. Experiments performed on pure thallium iodide vapour (with no deuterium) for different temperatures in the range from 600 to 775 K have confirmed our previous result [1] that in this case the broadening effects caused by TlI-molecules are much smaller than the Doppler broadening and can be neglected.

We should emphasize, however, that in case of spectral lines resulting from the photodissociation of molecules apart from the usual Doppler broadening corresponding to the

thermal motion the additional Doppler broadening may arise due to the additional kinetic energy of photodissociation products ("recoil effect"). In the case of the Maxwellian distribution of velocities the thermal motion leads to a Gaussian profile of the line. The Doppler shape caused by the recoil effect due to the additional kinetic energy of excited atoms is not, in general case, the Gaussian shape. In the previous work [1] we have found, however, that the resultant Doppler profile of the 535 nm Tl line, which is a superposition of the one corresponding to the Maxwellian distribution of velocities with that arising from the additional kinetic energy of photodissociation products, can be, with good approximation, described by the Gaussian profile, but with the half-width γ_G significantly greater than the usual Doppler half-width, γ_D corresponding to the temperature of the fluorescence cell. This result was also confirmed in the present work for Tl + D_2. We have found that for all densities of deuterium used in the present investigation the resultant profile of the 535 nm Tl line is well described by the Voigt profile, which is the convolution of the Lorentzian and Gaussian distributions. The deviations of the measured profile from the Voigt profile for TlI + D_2 were always less than 10%. We have also found that these deviations decrease with the increase in the deuterium density. The half-widths of the Lorentzian and Gaussian components of the Voigt profile of the 535 nm Tl line were determined using both a least squares method and a method proposed by Ballik [7].

4. Results

Fig. 1 shows the plot of the half-width γ_G of the Gaussian component of the profile of the 535 nm Tl line against the density of deuterium. It can be seen that the Gaussian half-width of this line is approximately constant over entire deuterium density range. The average value of γ_G determined from our experimental values for the TlI-cell temperature

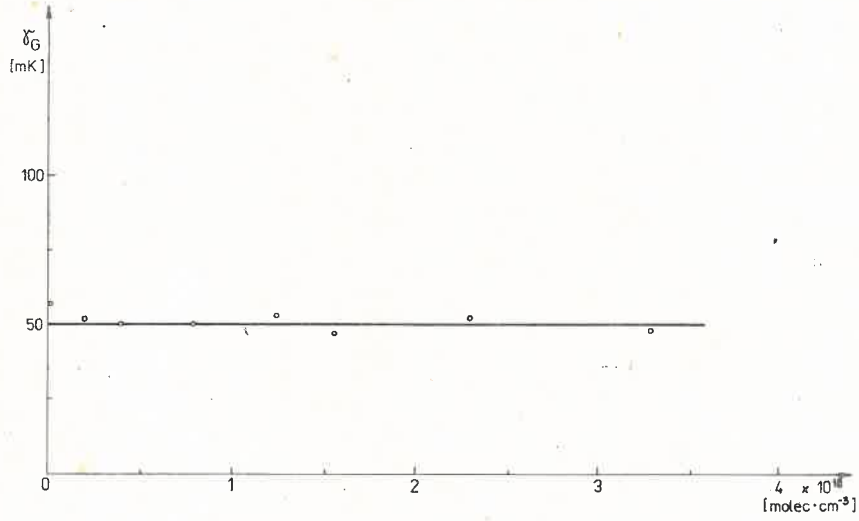

Fig. 1. The plot of the Gaussian width of the 535 nm Tl line resulting from the photodissociation of TlI at the cell temperature of 733 K against the density of deuterium; o — experimental points

of 733 K was found to be 51.2 mK, while the usual Doppler half-width γ_D, corresponding to this temperature, is 20 mK. Thus the additional Doppler broadening of the 535 nm Tl line emitted due to the photodissociation of TlI-molecules in the presence of deuterium is about 31.2 mK. It should be noted that this value is close to that (30 mK) determined previously for TlI + H_2 [1].

Fig. 2 shows the plot of the half-width γ_L of the Lorentzian component of the 535 nm Tl line profile against the density number N of deuterium. Within the experimental uncer-

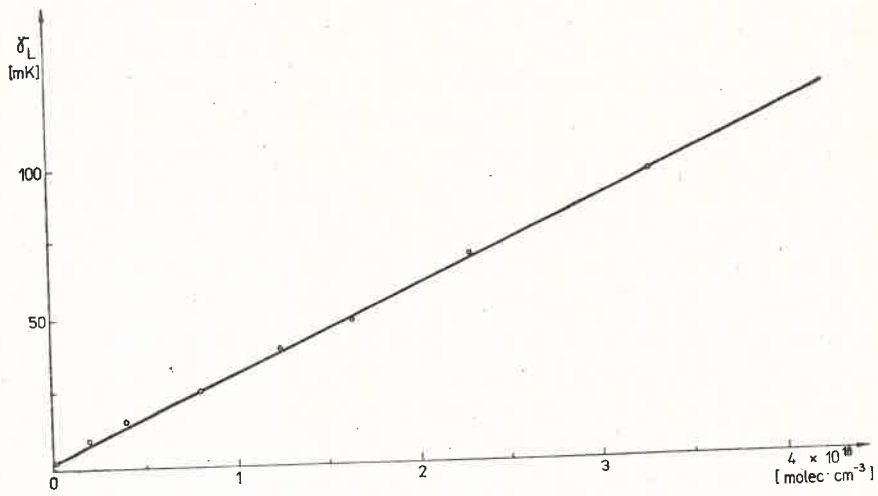

Fig. 2. The plot of the Lorentzian width of the 535 nm Tl line against the density of deuterium; o — experimental points

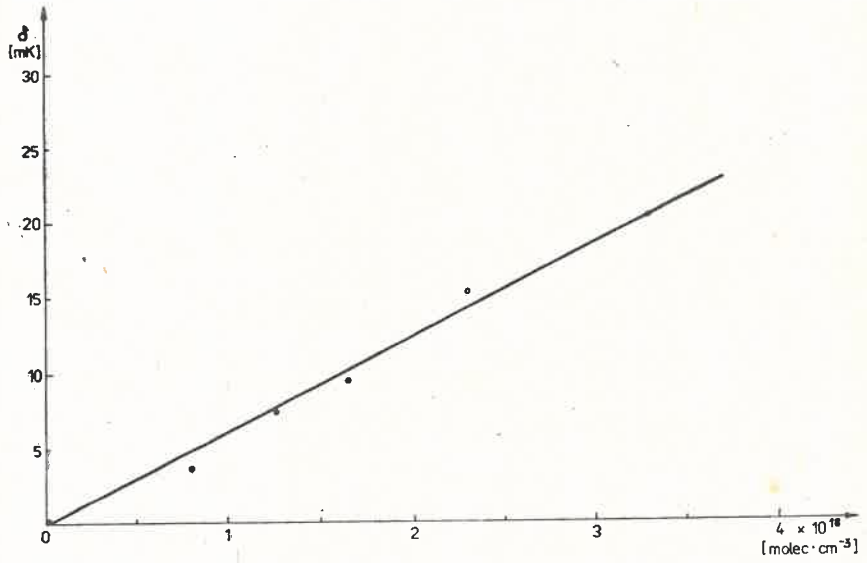

Fig. 3. The plot of the shift of the 535 nm Tl line against the density of deuterium; o — experimental points

tainty, the Lorentzian half-width of this line varies linearly with D_2 density. The slope of the straight line in Fig. 2 determined by least-square fitting was found to be $\gamma_L/N = (2.84 \pm 0.04) \times 10^{-20}$ cm^{-1}/molecule cm^{-3}.

The shift δ of the centre of the 535 nm fluorescence line emitted from the TlI-cell relative to the 535 nm emission line produced in a low pressure r.f. electrodeless discharge thallium lamp was measured as a function of the deuterium density. The thallium lamp used in our measurements of the shift consisted of a fused silica tube 5 cm long and 1.5 cm in diameter containing pure thallium. The tube was placed in the coil of an r.f. oscillator operating at 100 Mc/s. The r.f. power used by the thallium lamp was about 100 watts.

Fig. 3 shows a plot of the shift of the 535 nm line, which is towards the red and is seen to be closely linear with the deuterium density. The least-squares slope of the straight line in Fig. 3 yields the value $\delta/N = -(0.64 \pm 0.03) \times 10^{-20}$ cm^{-1}/molecule cm^{-3}.

4. Interpretation of the results

The linear dependence of both the Lorentzian width and shift of the 535 nm Tl line on the deuterium density which is seen in Fig. 2 and 3 agrees with the predictions of the impact theory [8–10], according to which γ_L and δ are given by (in angular frequency units)

$$\gamma_L = 2N\bar{v}\sigma_b, \tag{1}$$

$$\delta = \pm N\bar{v}\sigma_s. \tag{2}$$

Here σ_b and σ_s denote the effective cross sections for the impact broadening and shift of the line, respectively, and $\bar{v}$ is the mean relative velocity [8]. Using the values of the slopes γ_L/N and δ/N determined in the present work for $\bar{v} = 1.98 \times 10^5$ cm/s we obtain for these cross sections the values $\sigma_b = 1.35 \times 10^{-14}$ cm^2 and $\sigma_s = 0.609 \times 10^{-14}$ cm^2. It is interesting to note that our experimental value of the cross section σ_b for the impact broadening of the 535 nm line by D_2 is very close to the value 1.4×10^{-14} cm^2 of the cross section for the impact broadening of the same line by H_2 [1].

In order to calculate the theoretical values of the half-width and shift of the 535 nm Tl line perturbed by D_2 we have assumed that the difference of interaction potentials $\Delta V(R)$ in the upper and lower state of the Tl-atom, situated at the distance R from the D_2-molecule is given by the van der Waals potentials: $\Delta V(R) = -hC_6R^{-6}$. Here h is the Planck constant and C_6 is the van der Waals parameter for the line. According to the impact Lindholm-Foley theory [9, 10] γ_L and δ are then given by

$$\gamma_L = 8.08 C_6^{2/5} \bar{v}^{3/5} N, \tag{3}$$

$$\delta = -2.94 C_6^{2/5} \bar{v}^{3/5} N. \tag{4}$$

The van der Waals parameter C_6 can be approximately calculated from the formula given by Unsöld [10]:

$$C_6 = \frac{\alpha e^2}{h} [\langle r^2 \rangle_u - \langle r^2 \rangle_l], \tag{5}$$

where α is the polarizability of the perturbing molecule, e is the elementary charge and $\langle r^2\rangle_u$(or $\langle r^2\rangle_l$) denotes the expectation value of r^2 for the upper or lower level of the radiating atom, respectively.

Using the Coulomb approximation we have

$$\langle r^2\rangle = \tfrac{1}{2}\, a_0^2 (n^*)^2 [5(n^*)^2 + 1 - 3l(l+1)], \tag{6}$$

where a_0 is the Bohr radius, n^* is the effective quantum number and l is the orbital quantum number. For deuterium the theoretical polarizability is $\alpha = 0.794 \times 10^{-24}$ cm^3 [12]. Using the values of n^* for Tl given by Kuhn [13] we find for the average value of the C_6 constant for the 535 nm Tl line perturbed by D_2 the value $C_6 = 2.3 \times 10^{-32}$ cm^6 s^{-1}. Substituting this value into Eq. (3) and (4) we obtain for the collision broadening and shift coefficients the values: $\gamma_L/N = 3.0 \times 10^{-20}$ cm^{-1}/molecule cm^{-3} and $\delta/N = -1.1 \times 10^{-20}$ cm^{-1}/molecule cm^{-3}. Hence we conclude that in the case of purely attractive van der Waals potential theoretical values of both the shift and half-width of the 535 nm Tl line perturbed by D_2 are greater than the experimental values determined in the present work. These discrepancies are probably caused by the effects due to the repulsion between Tl-atom and D_2-molecule, which are not taken into account in the van der Waals potential. Since the repulsion energies for Tl+D_2 cannot be, as yet, calculated theoretically we can only make some estimations using model potentials such as those given by the Lennard-Jones (12–6) function:

$$\Delta V(R) = hC_{12}R^{-12} - hC_6R^{-6}, \tag{7}$$

where C_{12} is the constant describing the repulsion branch of the potential difference curve.

Hindmarsh et al. [14] have shown that for this type of the Lennard-Jones potential the Lindholm-Foley expressions for the half-width and shift of the line are given by

$$\gamma_L = 8\pi \left(\frac{3\pi}{8}\right)^{2/5} \bar{v}^{3/5} N (2\pi C_6)^{2/5} B(\xi), \tag{8}$$

$$\delta = 2\pi \left(\frac{3\pi}{8}\right)^{2/5} \bar{v}^{3/5} N (2\pi C_6)^{2/5} S(\xi), \tag{9}$$

where

$$B(\xi) = \int_0^\infty x \sin^2 \tfrac{1}{2}(\xi x^{-11} - x^{-5})\, dx, \tag{10}$$

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

and

$$\xi = \frac{63\pi}{256} \left(\frac{8}{3\pi}\right)^{11/5} \left(\frac{\bar{v}}{2\pi}\right)^{6/5} C_{12} |C_6|^{-11/5}. \tag{12}$$

The broadening and shift functions $B(\xi)$ and $S(\xi)$ have been tabulated in the paper by Hindmarsh et al. [14]. These authors have also shown that when repulsion is neglected, i.e. for $C_{12} = 0$ and $\xi = 0$, Eqs. (8) and (9) become identical to Eqs. (3) and (4) of the van der Waals approximation.

For the Tl+D_2 interaction the parameter C_{12} in the Lennard-Jones potential cannot be calculated exactly. Following the method proposed by Hindmarsh et al. [14] we have determined the value of this parameter from the experimental value of the ratio δ/γ_L. According to Eqs. (8) and (9) this ratio is given by

$$\frac{\delta}{\gamma_L} = \frac{1}{4}\frac{S(\xi)}{B(\xi)}. \tag{13}$$

Using the experimental value $\delta/\gamma_L = -0.225$ determined in the present work we have deduced the value $\xi \simeq 0.85$. Substituting for C_6 the theoretical value 2.3×10^{-32} cm^6 s^{-1} we have found the value $C_{12} = 1.6 \times 10^{-75}$ cm^{12} s^{-1}. This value has the same order of magnitude as C_{12} parameters describing the repulsive branches of potential curves in the alkali atom-noble gas atom systems [14].

5. Summary

A careful analysis of the shape of the 535 nm Tl fluorescence line resulting from photodissociation of thallium iodide molecules perturbed by deuterium molecules has been made and both the Doppler and collision broadening components of the line shape have been determined. It was found that the Doppler component can be fitted to a Gaussian profile but with the width differing significantly from the usual Doppler width corresponding to the fluorescence cell temperature. The additional Doppler broadening of the 535 nm Tl line resulting from the photodissociation of TlI mixed with D_2 has been determined. The Lorentzian half-width and shift of the 535 nm Tl line have been found to be linearly dependent on the deuterium density. The values of the cross sections for the impact broadening and shift of the 535 nm Tl line perturbed by D_2 have been determined. We have shown that a purely attractive van der Waals potential permits the qualitative explanation of pressure effects caused by D_2 on the 535 nm Tl line. However, for the quantitative interpretation of the width and shift of this line the inclusion of the repulsive part of the interaction potential was shown to be necessary.

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