Pressure Effects of Neon and Argon on the 535 nm Thallium Line*

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Experimental studies of collisional broadening and shift of the 535 nm thallium line perturbed by neon and argon were performed using a pressure-scanned Fabry-Perot interferometer. The 535 nm line was excited by irradiation of the thallium vapour with the resonance thallium line (377.68 nm). The present results are compared with previous experimental data obtained by different methods as well as with theoretical ones.

1. Introduction

This paper describes experimental studies of the collisional broadening and shift of the 535 nm line of thallium perturbed by neon and argon. The pressure effects of noble gases on this line were studied by Cheron et al. [1] who performed line shape measurements on the fluorescence light emitted from a mixture of natural thallium vapour and noble gas at rather high density ((6.5—19.5) x 10^18 cm^-3). They determined the width and shift parameters corresponding to the Lorentzian profile of this line. The Lorentzian distribution is a typical feature of the impact theory of pressure broadening and it is usually valid at low densities. However, in the density range used in the experiments described in [1] the applicability of the impact theory becomes questionable. For this reason, we recently performed in this laboratory a series [2,3] of experiments on the collisional broadening and shift of the 535 nm TI line by foreign gases at much lower densities than those used by Cheron et al. [1]. In this density region the impact theory is fully applicable. On the other hand, however, in experiments described in [2,3] the atomic fluorescence of thallium was excited by the photodissociation of thallium iodide (TII) molecules. This technique of excitation may introduce a certain error to the Lorentzian width and shift parameters determined from the total line profile measured by means of a Fabry-Perot interferometer. This error is connected with the fact that the atomic fluorescence line emitted by a fragment atom excited due to the photodissociation of the parent molecule exhibits an additional Doppler broadening arising from the recoil of the excited atom after the dissociation. The resultant Doppler shape of the atomic fluorescence line may differ significantly from the Gaussian distribution corresponding to the usual thermal Doppler broadening [4] and this makes the accurate interpretation of the measured values of the line shape parameters very difficult.

For this reason it is desirable to have further measurements for low pressures performed under conditions allowing for a precise determination of pressure broadening and shift coefficients. In the present work, in order to avoid possible errors connected with the non-Gaussian distribution of the Doppler broadening as in our earlier experiments performed by means of the photodissociation technique, the 535 nm line was excited by the irradiation of the thallium vapour with the resonance thallium line (377.68 nm). High-resolution spectroscopy techniques were used to measure the profiles of the 535 nm fluorescence line emitted by thallium vapour mixed with a perturbing gas (neon and argon).

2. Experimental

The fluorescence 535 nm TI line (see Fig. 1) was analysed by means of a grating spectrograph with a...
Fig. 1. Schematic diagram of the lowest energy levels of neutral thallium.

Fabry-Perot interferometer using photoelectric detection [5]. The 535 nm line was emitted from a fluorescence cell 3.4 cm long and 2.8 cm in diameter. The intensity distribution was monitored using a photomultiplier in a photon counting mode. The pressure-scanned Fabry-Perot interferometer was used with plates coated with a dielectric layer, and spacers of 1.204 cm and 0.845 cm were applied. Two low pressure r.f. electrodeless thallium discharge lamps were used: one served as the reference source in the line shift measurements and the second one with a 377.68 nm filter was applied to excite the green fluorescence at 535 nm of thallium vapour in the cell. The fluorescence quartz cell with thallium vapour was mounted in an Al-block oven which was operated at a temperature of 793 K with a stability of ± 2 K over several hours. The temperature of the fluorescence cell was measured with a thermocouple which was placed in contact with this cell. All measurements were performed at a temperature of 793 K for various densities of neon and argon in the region between $9.5 \times 10^{16}$ cm$^{-3}$ and $7.0 \times 10^{17}$ cm$^{-3}$.

3. Analysis of the Profiles

Natural thallium consists of two isotopes: 29.46% of $^{203}$Tl and 70.54% of $^{205}$Tl. The wave numbers and relative intensities of the various hyperfine-structure components of the 535 nm Tl line are shown in Figure 2. These wave numbers are based on hyperfine splittings and isotope shifts of thallium obtained by Odintsov [6]. Under our experimental conditions only two hyperfine-structure components are seen. A typical interferogram of the 535 nm line obtained in the present work for the spacer of 0.845 cm is shown in Figure 3. The hyperfine-structure components are resolved. Both the maxima correspond to the groups $B_n$, $C_n$, $b_n$, $c_n$, and $A_n$, and $a_n$, respectively, of hfs components in the interferogram of $n$-th order. Let us note that in Figs. 2 and 3 the origin of the wave number scale is shifted to the center of gravity of the 535 nm line.

In most cases we used the Fabry-Perot interferometer with the spacer of 1.204 cm. For this spacer the free spectral range of 0.415 cm$^{-1}$ is approximately equal to the hyperfine-structure splitting of the 535 nm line. A typical interferogram is shown in Figure 4. It must be emphasized, however, that this interferogram does not correspond to the profile of an isolated line because the components $C_n$, $B_n$, $c_n$, $b_n$, and $A_{n+1}$, $a_{n+1}$ of the interferograms of orders $n$ and $(n + 1)$ respectively, overlap with one another. Since the separation between the hfs components $C_n$ and $A_{n+1}$, $c_n$ and $a_{n+1}$ is small we can include in our numerical analysis of line profiles four components: $C_n + A_{n+1}$, $B_n$, $c_n + a_{n+1}$, $b_n$. In previous work done in this laboratory [2, 7] the numerical analysis was per-
formed using a more simplified method in which only two components were taken into account.

In our analysis we have assumed that the pressure broadening and shift of all components of the line is the same. We have also assumed that the intensity distribution in a broadened line resulting from both Doppler and pressure broadening can be described by the Voigt profile, with the Lorentzian full half-width $\gamma_L$ and shift $\Delta$ proportional to the number density of perturbers $N$, and with the density independent Gaussian half-width $\gamma_D$ corresponding to the Doppler temperature of a gas. The measured line profile $I(v)$ is the convolution of the Voigt profile and the instrumental profile of the Fabry-Perot interferometer. Following Ballik [8] this convolution can be written in the form

$$I(v) = A \sum_{k=1}^{p} \eta_k \left\{ \frac{1}{2} + \sum_{m=-\infty}^{\infty} (R e^{-L})^m \exp(-0.25 D^2 m^2) \right\} \cos \left( \frac{2\pi}{\Delta v_i} m (v - v_k - d_k - \Delta) \right),$$  

where $p$ is the number of line components, $v_k$ is the wave number of the strongest component, $\eta_k$ denotes the relative intensity of the $k$-th component of a line and $d_k$ is its shift relative to the strongest component. $A$ is a normalizing factor independent of the wave number $v$. In (1) $R$ is the reflection coefficient of the etalon plates and $\Delta v_i$ denotes the free spectral range of the interferometer. The dimensionless parameters $L$ and $D$ are connected with the Lorentzian and Gaussian half-width $\gamma_L$ and $\gamma_D$ by the formulae

$$L = \frac{\pi}{A v_i} \gamma_L \tag{2}$$

and

$$D = \frac{\pi}{A v_i} \frac{1}{\ln 2} \gamma_D. \tag{3}$$

The experimental values of the Lorentzian and Gaussian half-width $\gamma_L$ and $\gamma_D$ as well as the pressure shift $\Delta$ of the 535 nm Ti line reported in this work were determined by a least-squares fit of measured profiles to (1) using an algorithm given by Marquardt [9].

It should be noted that (1) was originally derived by Ballik [8] for an ideal Fabry-Perot interferometer for which the instrumental function is given by an Airy profile. Its width depends on the reflection coefficient $R$ of the etalon plates only. In such a case $\gamma_D$ can be identified with the Doppler half-width $\gamma_D$ resulting from the thermal motion of emitting atoms with the Maxwellian distribution of velocities. It is given by [10]

$$\gamma_D = 2 \frac{v_0}{c} \sqrt{\frac{2k_B}{M}} \ln 2, \tag{4}$$

where $v_0$ is the unperturbed wave number of a line, $M$ is the mass of the emitting atom, $T$ is the temperature and $k_B$ the Boltzmann constant.

We should emphasize, however, that in the case of a real Fabry-Perot interferometer the Airy-type profile appears to be a rather poor approximation to the instrumental function. This is caused by various imperfections of the interferometer, mainly those due to the deviation of the surfaces of the etalon plates from an ideal plane, as well as those due to slight inclinations of the two surfaces. These imperfections lead to the decrease of the total finesse of the real interferometer in comparison with its “ideal” value which is determined by the reflection coefficient of the etalon plates only. This effect gives rise to an additional instrumental broadening [11].

Its contribution to the instrumental profile of the real Fabry-Perot interferometer can be approximated by a Gaussian profile with the half-width $\gamma_G^{(a)}$. In such an approximation Ballik’s formula (1) can also be used in the analysis of line profiles by means of real interferometers. In this case, however, $\gamma_G$ plays...
the role of an effective Gaussian half-width which is connected with $\gamma_G^{(a)}$ and the Doppler-half-width $\gamma_D$ by the formula

$$\gamma^* = \sqrt{\gamma_D^2 + (\gamma_G^{(a)})^2}. \quad (5)$$

The half-widths $\gamma_G^{(a)}$ of the Gaussian component of the instrumental profile of the Fabry-Perot interferometer used in this work were estimated as 0.013 cm$^{-1}$ and 0.020 cm$^{-1}$ for the spacers of 1.204 cm and 0.845 cm respectively.

In the present work the numerical analysis of interferograms was performed by taking into account the full hyperfine structure of the 535 nm line emitted by natural thallium which consists of six components ($p = 6$ in (1)).

In previous experiments in this laboratory [2, 3, 7] a simplified analysis was carried out for two components ($p = 2$) only. We therefore made a test in order to establish how the parameters $\gamma_L$ and $\gamma^*$ depend on the number $p$ of components used in the numerical analysis. The results of this test-analysis are listed in Table 1 for $p = 2, 4$ and 6. This analysis shows that the Gaussian half-widths $\gamma^*$ obtained from the two-component approximation are significantly greater than those resulting from the four- or six-component analysis. It is interesting to note that the Lorentzian half-widths $\gamma_L$ obtained in the two-component approximation are only slightly smaller than those resulting from the analysis in which the full hyperfine structure is taken into account.

Special attention in the present work was focused on the influence of reabsorption on the measured line profiles. We have found that under our experimental conditions the effects caused by reabsorption may be neglected.

Table 1. The Lorentzian $\gamma_L$ and the effective Gaussian $\gamma^*$ half-widths of the 535 nm TI line perturbed by Ne and Ar determined for three values $p$ of hfs components used in the numerical analysis (spacer of 1.204 cm).

<table>
<thead>
<tr>
<th>The number $p$ of hfs components</th>
<th>Interferogram I</th>
<th>Interferogram II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_L$</td>
<td>$\gamma^*$</td>
<td>$\gamma_L$</td>
</tr>
<tr>
<td>$10^{-3}$ cm$^{-1}$</td>
<td>$10^{-3}$ cm$^{-1}$</td>
<td>$10^{-3}$ cm$^{-1}$</td>
</tr>
<tr>
<td>6</td>
<td>11.70</td>
<td>3.06</td>
</tr>
<tr>
<td>4</td>
<td>11.94</td>
<td>3.12</td>
</tr>
<tr>
<td>2</td>
<td>10.63</td>
<td>2.24</td>
</tr>
</tbody>
</table>

4. Results and Interpretation

As can be seen (see Fig. 5) $\gamma^*$ is practically independent of the perturbing gas density. The average values of $\gamma^*$ at a temperature of 793 K with the spacer of 1.204 cm were found to be 0.030 cm$^{-1}$ for TI + Ne and 0.042 cm$^{-1}$ for TI + Ar. The Doppler half-width $\gamma_D$ calculated from (4) for 793 K is equal to 0.026 cm$^{-1}$. In the case of TI + Ne the discrepancy between $\gamma_G^{(a)}$ and $\gamma_D$ can also be explained on the grounds of (5) as a result of the contribution of the Gaussian component of the instrumental profile. For TI + Ar, however, the average value of $\gamma^*$ is slightly higher than that resulting from (5).

Figure 6 shows the Lorentzian half-width $\gamma_L$ of the 535 nm TI line plotted against the number density of perturbers. As can be seen, the Lorentzian half-width of this line depends linearly on the density in accordance with the impact theory of pressure broadening. The straight line in Fig. 6 is determined by least-squares fitting. The linear dependence of the Lorentzian half-width $\gamma_L$ on the number density of perturbers $N$ can be written as

$$\gamma_L = \gamma_0 + \beta N. \quad (6)$$

where $\beta$ is the pressure broadening coefficient related to the interaction between the radiating TI-atom and the perturbing atom. In (6) $\gamma_0$ is the sum of the natural width of the line and the residual Lorentzian half-width of the instrumental function.
Experimental values of $\beta$ are listed in Table 2, where they are compared with the results determined by Cheron et al. [1] and by Lisicki et al. [2]. It must be remembered, however, that Cheron's experiment was carried out at perturbing gas densities two orders of magnitude higher (($0.6-2.0) \times 10^{19} \text{cm}^{-3}$) than those (($0.1-7.0) \times 10^{17} \text{cm}^{-3}$) used in the present investigation. On the other hand, the data of Lisicki et al. were obtained from experiments on the 535 nm thallium line resulting from the photodissociation of thallium iodide.

Figure 7 shows the plot of the shift $\Delta$ of the 535 nm TI line against the number density of perturbers. For both neon and argon the shift is linear over the density range measured according to the relation

$$\Delta = \Delta_0 + \delta N,$$

(7)

where $\delta$ denotes the pressure shift coefficient corresponding to the interaction of the radiating TI atom with the perturbing atom. In (7) the quantity $\Delta_0$ comprises the shift of the line in the reference source and that resulting from the numerical data analysis. As can be seen in Fig. 7 neon and argon produce a red shift (minus sign) of the 535 nm TI line.

The values $\delta$ of the pressure shift coefficient determined from the slopes of the straight lines shown in Fig. 7 are listed in Table 3, where they are

![Graph](image_url)
compared with the experimental values obtained by Cheron et al. [1] and Lisicki et al. [2].

The theoretical values of $\beta$ and $\delta$ for the 535 nm Tl line were calculated in our previous paper [2] for the Lennard-Jones and Van der Waals potentials. The constants $C_6$ and $C_{12}$ of the Lennard-Jones function have been calculated using three methods. The first method (coul) consists of the application of a simple Coulomb approximation introduced by Unsöld [10]. In the remaining two methods either non-relativistic Hartree-Fock (H-F) wave functions or multiconfiguration relativistic Dirac-Hartree-Fock (D-H-F) wave functions have been applied. The values of $\beta$ and $\delta$ obtained from the Lindholm-Foley impact theory for these values of $C_6$ and $C_{12}$ are listed in Tables 2 and 3. It should be noted that our measured values of $\beta$ and $\delta$ for Tl + Ar are in reasonable agreement with theoretical values of Wu et al. [12] (calculated for the Van der Waals potentials using the $C_6$ constant computed by Proctor and Stwalley [13]), as well as with those computed by Czuchaj et al. [14].

5. Conclusion

The comparison of experimental results determined in the present work (Tables 2 and 3) with those obtained in earlier investigations shows that our values of $\beta$ and $\delta$ are smaller than both the width and shift parameters obtained by Cheron et al. [1] in their high-pressure emission study, and the values by Lisicki et al. [2] from the photodissociation experiment performed on thallium iodide vapour. However, the discrepancies between these three sets of experimental data obtained by means of different experimental techniques are not large. Special attention in the present study was focused on the problem of accuracy in determining the width of the Gaussian component of the profile. We have found that in the case of the spectral line with a complex hyperfine structure a very careful numerical analysis of the Fabry-Perot interferograms is necessary to obtain reliable results for the Gaussian width. In particular it turned out that the Gaussian width is much more sensitive to the finesse of the Fabry-Perot etalon than the width of the Lorentzian component of the total profile. The results of the present work corroborate the conclusion given in [2] that for Tl + Ar and Tl + Ne the purely attractive Van der Waals potentials lead to reasonable agreement of the theoretical values of $\beta$ and $\delta$ for the 535 nm line with the measured ones.

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