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THE PRESSURE AND DOPPLER LINE BROADENING OF ATOMIC FLUORESCENCE OF THALLIUM IODIDE PERTURBED BY HYDROGEN*

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

Institute of Physics, Nicholas Copernicus University, Toruń**

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The influence of hydrogen on the shape of the 535 nm thallium line resulting from the photodissociation of thallium iodide has been studied using a photoelectric Fabry–Perot interferometer. The Doppler and pressure broadening components of the line shape have been determined. The linear dependence of the Lorentzian width on the hydrogen pressure was found. The value of the effective cross section for the impact broadening for Tl (535 nm) $+H_2$ was determined and interpreted in terms of the Van der Waals potential.

1. *Introduction*

In this paper we report the results of measurements of the Doppler- and collision-broadened line profiles of the thallium spectral line 535 nm ($7^2S_{1/2}-6^2P_{3/2}$) resulting from atomic fluorescence of thallium iodide which accompanies the photodissociation of the TlI molecules in the vapour state with hydrogen used as the perturbing gas. Many earlier studies of the influence of foreign gases on the atomic fluorescence resulting from photodissociation of molecules dealt with quenching effects [1–3]. Dudkin et al. [4] as the first have investigated the dependence of line-width of such an atomic fluorescence on the foreign gas pressure. In their work, however, only the total half-width of the line has been measured and no separation of the resultant line profile into those corresponding to the Doppler and pressure effects has been made. Therefore, their results must be treated as qualitative.

In the present investigation the main attention has been paid to the methods of analysis of measured profiles of the 535 nm line in order to obtain reliable values of line-widths caused by collisions of the Tl-atom with the H_2-molecule as well as widths due to the Doppler effect. The Lorentzian half-width of this line has been measured as a function of hydrogen density, and the effective cross section for the impact broadening has been determined.

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

2. *Experimental*

In this work light emitted from the fluorescence cell due to the photodissociation of TlI-molecules was analysed by means of a grating spectrograph with a Fabry–Perot interferometer using a photoelectric detection as described in the paper by Bielski et al. [5]. The Fabry–Perot etalon plates were coated with a dielectric layer and the 12.04 mm spacer was used in the line profile measurements of the 535 nm Tl-line. Additional measurements for this line were also carried out using the 3.16 mm spacer in order to get information about the pressure dependence of line profiles for various hyperfine-structure components.

The thallium iodide supplied by B.D.H. Laboratory Chemicals Division, England was distilled into a quartz cell which was then filled with hydrogen. The TlI-cell was mounted in an oven which could be maintained at any temperature between 300 and 750 K with a stability of ±2 K over several hours. The temperature of the heated TlI-salt was measured with a thermocouple which was placed in contact with the cell. The cells were 3.4 cm long and 2.8 cm in diameter.

In order to excite the photodissociation of TlI-molecules the cell was irradiated with ultraviolet light emitted by a radio-frequency electrodeless mercury discharge lamp. This lamp is a tube made of quartz with high transparency in the 200 nm region. High transparency in this region is necessary because the shortwavelength limit of the absorption band of the TlI-molecule corresponding to the photodissociation of TlI and the production of Tl-atoms in the excited $7^2S_{1/2}$ state lies at 208 nm [4]. To obtain the sufficient absorption of the ultraviolet light in the TlI-cell the density of the TlI-molecules should be of the order of 10^{17} cm^{-3} which corresponds to a temperature of 730 K.

3. *Analysis of the profiles*

Natural thallium consists of two isotopes: 29.46% of ^{203}Tl and 70.54% of ^{205}Tl. For each isotope the 535 nm line is subject to the hyperfine splitting shown in Fig. 1. According to Jackson [6], the isotope shift for thallium is approximately 60 mK. The

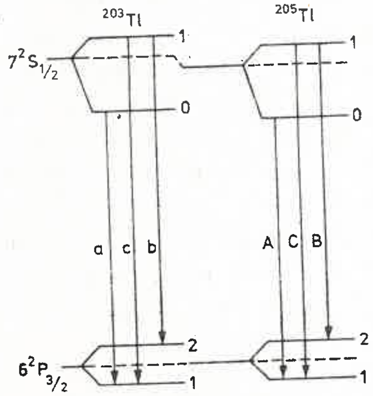

Fig. 1. Hyperfine splitting of the $7^2S_{1/2}$–$6^2P_{3/2}$ line in two isotopes of thallium

positions and relative intensities of various hyperfine-structure components of the 535 nm Tl line are shown in Fig. 2. In this figure the capital letters A, B and C denote the hyperfine-structure components for ^{205}Tl, while a, b and c denote those for ^{203}Tl. Under usual experimental conditions the components B and C or b and c are not resolved due to the Doppler effect so that only two hyperfine-structure components are seen for the 535 nm line. The mean hyperfine splitting of this line is 420 mK [6].

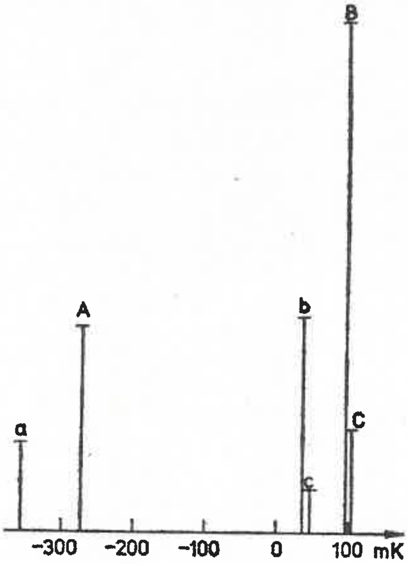

Fig. 2. Positions and relative intensities of the hyperfine-structure components of the 535 nm Tl line. The letters A, B and C denote the $F' = 0$—$F'' = 1$, $F' = 1$—$F'' = 2$ and $F' = 1$—$F'' = 1$ components, respectively for ^{205}Tl while a, b and c denote those for ^{203}Tl

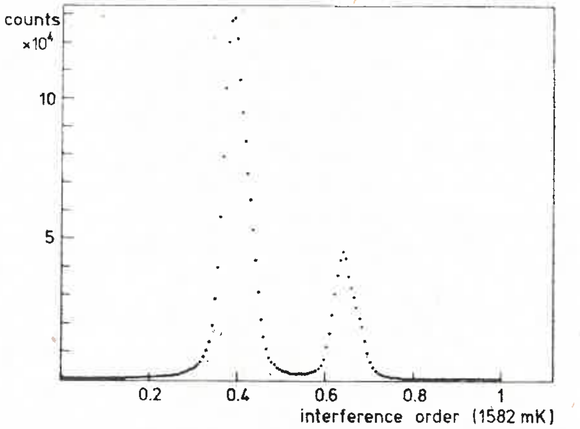

Fig. 3. The Fabry–Perot interferogram of the 535 nm Tl line for the Tl-fluorescence cell with no hydrogen for the 3.16 mm spacer

When the line is not broadened by the perturbing gas, the hyperfine-structure components are perfectly resolved by our Fabry–Perot interferometer of the type described elsewhere [5]. Fig. 3 shows an example of the interferogram of the 535 nm Tl line for the 3.16 mm spacer of the Fabry–Perot etalon obtained for the TlI-cell at 730 K with no perturbing gas. As can be seen from Fig. 3 for the 3.16 mm spacer there are two maxima in the profile within the one interference order: the higher maximum corresponds to the group of hyperfine-structure components B, C, b, c of two thallium isotopes and the lower one corresponds to the A and a components.

For the 12.04 mm spacer the free spectral range is 415 mK and is close to the mean hyperfine splitting in Tl. In this case the line profile with a single maximum is obtained as shown in Fig. 4. It must be emphasized, however, that the single maximum in Fig. 4 does not correspond to the shape of an isolated line because of overlapping of various hyperfine-structure components. In order to obtain the reliable line broadening parameters the separation of overlapping components leading to the shape of the isolated line must be performed. In the present work the separation was made by means of a computer using an algorithm proposed recently [7], which is applicable in cases of two isotopes with a two-component hyperfine structure each. The only assumption made in the separation procedure is that the shape of a particular hyperfine-structure component is the same.

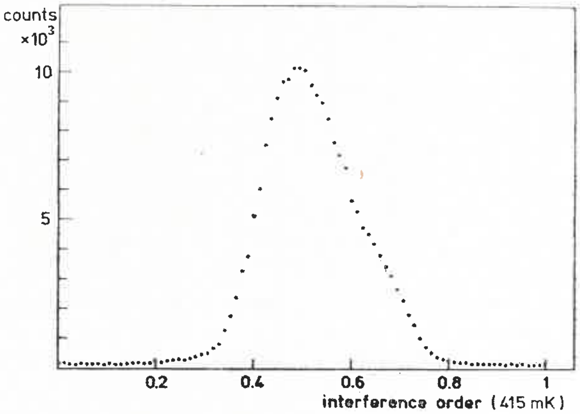

Fig. 4. The Fabry-Perot interferogram of the 535 nm Tl line for the Tl-cell with no hydrogen for the 12.04 mm spacer

For the TlI-fluorescence cell with no perturbing gas the 535 nm Tl line can be broadened by the Doppler effect and collisions of the excited Tl-atoms with the TlI-molecules. We have found, however, that the broadening caused by TlI-molecules is much smaller than Doppler broadening. This result was confirmed by line shape measurements at different temperatures. It turned out that the variation of temperature in the region from 650 to 775 K does not change the shape of the 535 nm line significantly. On the other hand, in that temperature region the concentration of TlI vapour changes significantly. Thus we conclude that for the fluorescence cell with no perturbing gas the Doppler effect is the most essential factor causing the line broadening.

In the case of atomic fluorescence resulting from the photodissociation of molecules apart from the usual Doppler broadening caused by the thermal motion additional Doppler broadening may arise due to the additional kinetic energy of photodissociation products (*recoil effect*). This additional broadening occurs if the excitation photon energy is greater than the minimal energy required for the dissociation of a molecule with simultaneous excitation of an atom.

Thermal motion with a Maxwellian distribution of velocities gives rise to the Gaussian shape of the line. On the other hand, the Doppler shape caused by the additional kinetic energy of the excited atoms resulting from the photodissociation is not Gaussian and can be described by a rectangular function provided the exciting light is strictly monochromatic. In our experiment the photodissociation of TlI-molecules is caused by the following mercury lines: 194.2, 197.2 and 200.2 nm which are emitted from the discharge tube. Therefore, in our study the exciting light is not monochromatic and the *recoil effect*-component of the Doppler profile may differ from the pure rectangular distribution.

The resultant Doppler profile which is a superposition of that corresponding to the Maxwellian distribution of velocities with that corresponding to the recoil effect due to photodissociation is not, in general, the Gaussian profile. We have found, however, that in spite of the above restrictions the resultant Doppler profile of the 535 nm Tl line may be described by a profile of the Gaussian type but with the half-width γ_G significantly greater than the usual Doppler half-with γ_D corresponding to the temperature of the TlI-fluorescence cell. The resultant Gaussian half-width γ_G may then be written as

$$\gamma_G = \gamma_D + \gamma_R, \tag{1}$$

where γ_R is the additional Doppler width caused by the recoil of atoms after photodissociation.

With the temperature of the TlI-fluorescence cell 730 K with no perturbing gas a least square fit of the Gaussian profile to the measured one gave $\gamma_G = 52$ mK while the usual Doppler half-width for this temperature is $\gamma_D = 20$ mK. Thus additional Doppler broadening is equal to about 32 mK.

When the TlI-cell is filled with hydrogen the profile of the 535 nm Tl line will be markedly modified because of pressure broadening due to collisions between excited Tl-atoms and the perturbing H_2-molecules. The pressure broadening measurements were carried out over the region of hydrogen densities from 0 to 4.8×10^{18} cm^{-3} at the cell temperature 730 K. This corresponds to the hydrogen pressure region from 0 to 150 Torr at room temperature. After separation of hyperfine-structure components each profile of the 535 nm Tl line corresponding to a given pressure of H_2 was compared to a Voigt profile. We have found that for all pressures of H_2 used in the present work the shape of the 535 nm Tl line fits the Voigt profile sufficiently well. The deviations of the experimental shape from the Voigt profile were found to be less than 8.6% for the fluorescence cell wtih no hydrogen. It turned out that these deviations decrease with an increase in hydrogen pressure. In particular, for the highest pressure of H_2 used in the present work (150 Torr at room temperature) they were less than 2.2%.

The half-widths of the Gaussian and Lorentzian components of the Voigt profile were determined by the computer using both a least square method and a method due to Ballik [8]. We have also made an additional test of the correctness of our analysis of the profiles using a third method which is based on the direct comparison of the experimental profile to the Voigt profile after the elimination of the overlapping of interference orders by equating the widths and heights of these two profiles as well as their integrals over the period.

The instrumental function of our Fabry–Perot interferometer was verified to be well described by an Airy profile [8]. The convolution of the Airy profile with the Voigt profile was computed using expressions derived by Ballik [8].

4. *Results and discussion*

The values of the half-widths γ_G of the Gaussian component of the 535 nm Tl line determined by us are shown in Fig. 5, where they are plotted on the hydrogen density. As can be seen the Gaussian half-width of this line is approximately independent of the density of hydrogen. The average value of γ_G was found to be 55 mK.

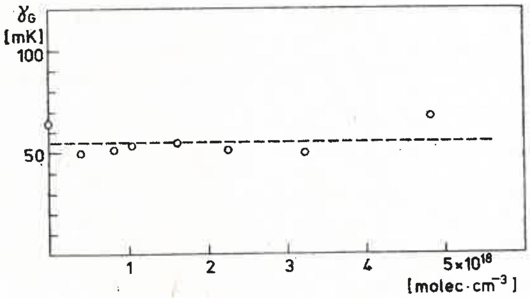

Fig. 5. The variation of the Gaussian half-width of the 535 nm Tl line with hydrogen density

The half-width $\gamma_G^{(i)}$ of the Gaussian component of the instrumental function of the Fabry–Perot interferometer used in our work may change in the range of 1/100 to 1/50 of the interference order and it depends on the accuracy of the adjustment of the interferometer. For the 12.04 mm spacer $\gamma_G^{(i)}$ was estimated to be in the range from 4 to 8 mK. The usual Doppler half-width γ_D corresponding to the gas kinetic temperature of the cell 730 K is about 20 mK. Hence we conclude that when the photodissociation of the TlI-molecules is excited by the ultraviolet light of the mercury r.f. discharge lamp the additional Doppler half-width γ_R of the 535 nm Tl line is about 30 mK. This value is in reasonable agreement with the estimations of Dudkin et al. [4], who used a similar type of excitation.

Fig. 6 shows the half-widths γ_L of the Lorentzian component of the 535 nm Tl line plotted against the density of hydrogen. As can be seen the Lorentzian half-width of this line depends linearly on the density of the perturbing gas in accordance with the impact theory of pressure broadening. The straight line in Fig. 6 is determined by least-square fitting. The broadening constant obtained from the slope was found to be $(3.7 \pm 0.1) \times 10^{-20}$ cm^{-1}/molecules per cm^3.

In the impact approximation the Lorentzian half-width is given by

$$\gamma_L = \frac{1}{\pi}\,\bar{v}N\sigma, \tag{2}$$

where N is the perturber density, $\bar{v}$ is the mean relative velocity and σ denotes the effective cross section for the impact broadening (cf. e.g. [9]). Using the value of the slope γ_L/N determined in the present work for $\bar{v} = 2.5\times10^5$ cm s^{-1} we obtain for this cross section the value $\sigma = 1.4\times10^{-14}$ cm^2. This value is in good agreement with the value $\sigma = 1\times10^{-14}$ cm^2 estimated by Dudkin et al. [4] on the basis of a semi-quantitative analysis of the line shape. It is interesting to note that although in the study of Dudkin et al. [4] no separation of the line shape into the Gaussian and Lorentzian profiles was made their estimation of the cross section σ appears to be close to that determined by us from a more elaborate line shape analysis.

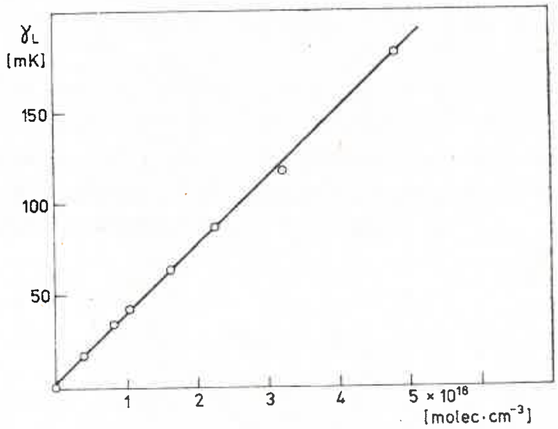

Fig. 6. The variation of the Lorentzian half-width of the 535 nm Tl line with hydrogen density

It is well known [4, 13] that hydrogen shows no quenching action on the resonance fluorescence of thallium. Hence we can conclude that the essential contribution to the pressure broadening of the 535 nm line comes from elastic collisions of the excited Tl-atoms with H_2-molecules. Therefore, we can interpret our experimental results using an adiabatic impact theory in which non-elastic collisions are neglected [9–10].

If we assume 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 perturbing H_2-molecule is given by the Van der Waals potentials: $\Delta V(R) = -hC_6R^{-6}$ (h is the Planck constant and C_6 is the force constant for the line) then in the classical limit Eq. (2) becomes identical to the Lindholm–Foley expression [9]:

$$\gamma_L = 2.71\bar{v}^{3/5}N(C_6)^{2/5}. \tag{3}$$

Using the experimental value of the slope γ_L/N determined in the present work we obtain for the Van der Waals constant C_6 for the 535 nm Tl line broadened by H_2 the value $C_6 = 2.7\times10^{-32}$ cm^6 s^{-1}.

The theoretical value of C_6 for the Tl-H_2 interaction can be estimated using the approximate formula given by Unsöld [14]:

$$C_6 = \frac{\alpha e^2}{h}\left[\langle r^2\rangle_u - \langle r^2\rangle_l\right], \tag{4}$$

where e is the elementary charge, and α is the polarizability of the perturbing molecule. Here $\langle r^2\rangle_u$ and $\langle r^2\rangle_l$ denote the expectation values of r^2 for the upper and lower states of the radiating atom, respectively. In the Coulomb approximation $\langle r^2\rangle$ is [14]:

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

where n^* is the effective quantum number, l is the orbital quantum number and a_0 is the Bohr radius. Using the theoretical value $\alpha = 0.8045\times10^{-24}$ cm^3 for the polarizability of hydrogen reported by Kołos and Wolniewicz [11] and the values of n^* for Tl given by Kuhn [12] we obtain for the average Van der Waals constant C_6 for the $7^2S_{1/2}$–$6^2P_{3/2}$ transition the value $C_6 = 3.9\times10^{-32}$ cm^6 s^{-1} which is in reasonable agreement with our experimental value.

5. *Summary*

We have demonstrated that studies of the line shapes associated with the atomic fluorescence of thallium iodide vapour mixed with a foreign gas can provide information about interactions between the excited thallium atoms and the foreign gas molecules. An accurate analysis of the shape of the 535 nm Tl line has been made and both the Doppler and pressure broadening components of the profiles have been determined. The Doppler component was found to be well described by the Gaussian profile but with the half-width differing significantly from the usual Doppler width corresponding to the cell temperature. The additional Doppler broadening of the 535 nm Tl line caused by an excess of kinetic energy of excited Tl-atoms resulting from photodissociation of TlI-molecules has been determined. The pressure broadening component of the line profile was shown to be described by the Lorentzian profile with the half-width depending linearly on the hydrogen pressure. We have shown that the dependence of the Lorentzian half-width on the hydrogen pressure can be quantitatively interpreted in terms of a Van der Waals potential with the impact line broadening theory.

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