Shift of the TlI 535.0 nm line by hydrogen *

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Z. Naturforsch. **35 a**, 773 – 774 (1980);
received March 28, 1980

The shift by hydrogen of the 535.0 nm Tl line resulting from photodissociation of thallium iodide was investigated at low densities. A linear variation of the shift with the hydrogen density was found with a shift coefficient of $-(0.443 \pm 0.012) \times 10^{-20}$ cm^{-1}/(molecules cm^{-3}).

In a recent paper [1] experimental results on the Doppler and collision broadening of the 535.0 nm ($7\,^2S_{1/2} - 6\,^2P_{3/2}$) thallium line resulting from atomic fluorescence accompanying the photodissociation of thallium iodide molecules perturbed by molecular hydrogen were reported. These measurements have shown that studies of collision broadening of spectral lines associated with the atomic fluorescence of thallium iodide vapour mixed with a foreign gas can provide information about interactions between the excited Tl atoms and the perturbing gas molecules.

The present paper describes an extension of these studies to measurements of the collision shift of the 535.0 nm Tl line emitted due to the photodissociation of TlI molecules perturbed by H_2.

The main interest of this work is to establish the magnitude of the collision shift coefficient at low hydrogen densities, i. e. in the linear region where two-body interactions predominate.

The photodissociation of TlI was excited by irradiation of a mixture of the thallium iodide vapour and hydrogen with the ultraviolet light emitted from a radio-frequency mercury discharge lamp. The collision shift measurements were carried out at a cell temperature of 733 K and at hydrogen densities from 0 to 3.5×10^{18} cm^{-3}, which corresponds to hydrogen pressures from 0 to 110 Torr at room temperature.

The 535.0 nm line was analysed using a grating spectrograph with a photoelectric Fabry-Perot interferometer of the type described by Bielski et al. [2] Measurements were performed on natural thallium which consists of 70.45% ^{205}Tl and 29.46% ^{203}Tl. The two hyperfine-structure components determined by the splitting of the $7\,^2S_{1/2}$ level were completely resolved while the splitting due to the hyperfine-structure of $6\,^2P_{3/2}$ was not resolved by our Fabry-Perot etalon with 1.204 cm spacer and dielectric coatings. The method of analysis of the profiles was the same as that in [1].

The shift of the centre of the 535.0 nm fluorescence line emitted from the TlI-cell relative to the 535.0 nm emission line produced in a low pressure r. f. electrodeless discharge thallium lamp was measured as a function of the hydrogen density.

The thallium lamp used in these measurements consisted of a fused silica tube 5 cm long and 1.5 cm in diameter which contained pure thallium. The tube was placed in the coil of r. f. oscillator operating at 100 Mc/s. The power used by the r. f. thallium lamp was 100 Watts.

Figure 1 shows the measured values of the shift δ of the 535.0 nm Tl line as a function of the hydrogen density N (in molecules/cm^3). The shift is towards the red and is seen to be a closely linear function of the hydrogen density. The least-squares slope of the straight line in Figure 1 is

$$\delta/N = -(0.443 \pm 0.012) \times 10^{-20}\ \text{cm}^{-1}/\text{molecule cm}^{-3}.$$

This linear dependence agrees with the prediction of the impact theory of pressure effects on spectral lines [3, 4] according to which

$$\delta = \pm N \bar{v}\, b_s\,, \tag{1}$$

where b_s denotes the effective cross section for the pressure shift of the line and $\bar{v}$ is the mean relative velocity. Using the value of δ/N determined in the present measurements and $\bar{v} = 2.8 \times 10^5$ cm/s one gets $b_s = 2.99\ 10^{-15}$ cm^2. Let us note that an effective cross section $b_b = 1.24 \times 10^{-14}$ cm^2 for the impact broadening of the 535.0 nm Tl line by hydrogen was found in [1].

In order to compare the experimental values of δ with theory the difference of interaction potentials $\Delta V(R)$ in the upper ($7\,^2S_{1/2}$) and lower ($6\,^2P_{3/2}$) level of a Tl-atom situated at a distance R from a H_2-molecule was assumed to be of the Van der Waals type: $\Delta V(R) = -\hbar\, C_6\, R^{-6}$, where C_6 is the Van der Waals parameter.

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* This work was carried on under the Research Project MR.I.5.

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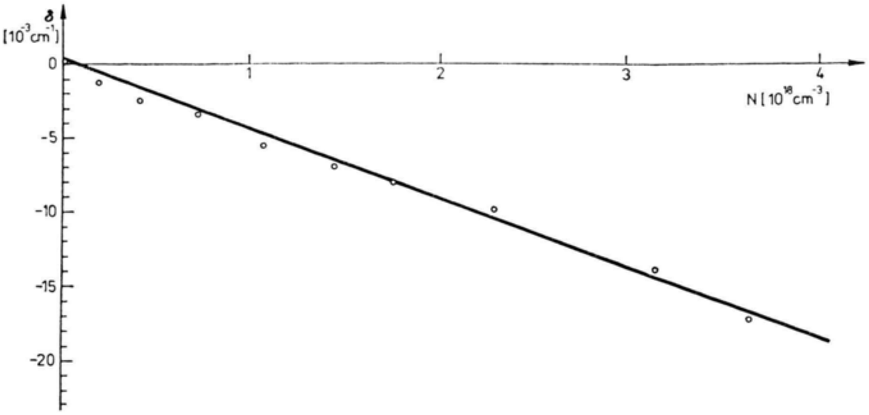

Fig. 1. Plot of the shift of the 535.0 nm Tl line against the density of hydrogen.

According to the impact theory [4] the line shift (in angular frequency units) is then given by

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

In the previous work [1] the method of Unsöld [5] was applied to calculate the theoretical value of the Van der Waals parameter for Tl(535.0 nm) + H_2 and gave $C_6 = 3.9 \times 10^{-32}$ cm^6 s^{-1}. Substituting this value for $\bar{v} = 2.8 \times 10^5$ cm/s into (2) we get for the collision shift coefficient the value $\delta/N = -1.34 \times 10^{-20}$ cm^{-1}/molecules cm^{-3}, which is about three times greater than the experimental value. Thus we can see that for Tl + H_2 the Van der Waals potential gives qualitative but not quantitative agreement with experiment.

Arepetition of the measurements of the widths of the Gaussian γ_g and Lorentzian γ_l components of the profile of the Tl 535.0 nm line gave the same results as those reported previously [1]. It is interesting to note that the value $\gamma_l/N = (3.7 \pm 0.1) \times 10^{-20}$ cm^{-1}/molecules cm^{-3} of the pressure coefficient for the 535.0 nm Tl line perturbed by H_2 [1] agrees very well with the theoretical value $\gamma_l/N = 3.69 \times 10^{-20}$ cm^{-1}/molecules cm^{-3} calculated from the impact theory for a Van der Waals potential with $C_6 = 3.9 \times 10^{-32}$ cm^6 s^{-1}.

On the other hand, as we have seen, the agreement between the experimental value of the collision shift coefficient δ/N and the theoretical value calculated for the Van der Waals potential is rather poor.

Let us also mention that the experimental value δ/γ_l of the ratio of the line shift to the Lorentzian hilf-width determined in the present work is $\delta/\gamma_l = -0.119$ while the value $\delta/\gamma_l = -0.362$ results from the Lindholm-Foley impact theory for the Van der Waals potential (cf. [6]). We thus conclude that the Van der Waals potential is inadequate to interpret quantitatively the line shift data for Tl(535.0 nm) + H_2. This is due to the fact that the shift is much more sensitive to the details of both the upper and lower state interaction potentials than the half-width of the line (cf. [6]).

In order to improve the theoretical predictions for the shift more realistic interaction potentials such as the Lennard-Jones type potential should be used [7].

Unfortunately for Tl + H_2 the parameters describing the repulsion branches of the Lennard-Jones potential in the lower and upper state are not known. Further studies on the interaction potentials for Tl + H_2 are thus necessary to explain the experimental data for the shift.

The author is indebted to Dr. J. Szudy for many helpful sugestions.

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