Influence of SF_6 on the Broadening and Shift of the 535.0 nm Thallium Line *

E. Lisicki, R. Bobkowski, J. Szudy, and J. Wolnikowski
Institute of Physics, Nicholas Copernicus University, Toruń, Poland

Z. Naturforsch. **38 a,** 838 – 840 (1983); received March 4, 1983

The pressure broadening and shift of the 535.0 nm Tl line resulting from the photodissociation of thallium iodide mixed with sulfur hexafluoride were studied at low densities using a Fabry-Perot interferometer. A linear variation of both the width and shift of the line with the SF_6 density was found and the cross sections for the broadening and shift were determined.

1. Introduction

In recent papers [1 – 3], studies of the Doppler and pressure broadening of the atomic fluorescence of thallium iodide perturbed by rare gas atoms and some non-polar molecules such as H_2, D_2, N_2, O_2 as well as CO_2 were reported. In these studies the values of the effective cross sections for the collision shift and broadening of the 535.0 nm ($7^2S_{1/2}-6^2P_{3/2}$) atomic thallium fluorescence line resulting from the photodissociation of thallium iodide molecules were determined from the Lorentzian component of the line profile.

The present paper describes an extension of these investigations to measurements of collision effects on the same Tl line accompanying the photodissociation of TlI perturbed by sulfur hexafluoride (SF_6). This research is stimulated, in part, by recent work on collisions between Rydberg atoms and SF_6 molecules which has shown that the cross sections for the excitation transfer between various fine structure levels were smaller than those observed when polar molecules have been used as perturbing gas but close to those caused by rare gas atoms [4, 5]. Such results were not unexpected since SF_6 has no permanent dipole moment and its mass and polarizability are comparable to those of the xenon atom. We have therefore thought it useful to study the broadening and shift effects on atomic thallium fluorescence produced by SF_6 in order to compare them with those due to rare gas atoms, especially due to xenon.

2. Experimental

The experimental procedure and the line shape analysis used in the present work were identical to those described in our previous papers on the pressure broadening and shift of the 535.0 nm Tl line accompanying the photodissociation of thallium iodide [1 – 3]. The light was collected from the fluorescence cell containing TlI vapour with SF_6. The photodissociation of TlI was excited by irradiation of the TlI-SF_6 mixture with the ultraviolet light emitted from a radio-frequency mercury discharge lamp. The fluorescence cell was 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 was measured with a thermocouple placed in a contact with the fluorescence cell. Measurements reported in the present paper were carried out at the temperature of 733 K and at densities of sulfur hexafluoride up to $9 \times 10^{17}\ \mathrm{cm}^{-3}$ which corresponds to a pressure of SF_6 up to 16 Torr at room temperature.

Line profiles were analysed using a grating spectrograph and a pressure scanned Fabry-Perot etalon with 1.204 cm spacer and dielectric coating [6]. Our studies were performed on natural thallium which consists of 70.54% ^{205}Tl and 29.46% ^{203}Tl. The two hyperfine-structure components determined by the splitting of the $7^2S_{1/2}$ level of Tl were resolved while the splitting due to the hyperfine-structure of $6^2P_{3/2}$ Tl level was not resolved by our interferometer. The methods of numerical analysis of the resultant profiles of overlapping line components were the same as in previous works [1 – 3]. In measurements of the collision shift of the centre of the 535.0 nm Tl line a low pressure r.f. electrodeless discharge thallium lamp was used as a reference source.

---

* Work supported by the Committee of Spectroscopy of the Polish Academy of Sciences.

Reprint requests to Dr. E. Lisicki, Institute of Physics, Nicholas Copernicus University Toruń, Grudziadzka 5, 87-100 Toruń/Poland.

0340-4811 / 83 / 0800-0838 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

3. Results and Discussion

A very careful numerical analysis has shown that the resultant shape of the 535.0 nm Tl line emitted due to the photodissociation of TlI can be sufficiently well approximated by the Voigt profile, which is the convolution of the Lorentzian and Gaussian profiles. The half-widths γ_L and γ_D of the Lorentzian and Gaussian components of the resultant profile, respectively, were determined using both a procedure given by Ballik [7] and a least squares method.

The results of our measurements are shown in Fig. 1, where the Gaussian and Lorentzian half-width, γ_D and γ_L, of the 535.0 nm Tl line as well as the shift Δ of this line are plotted against the sulfur hexafluoride density. It is seen that the Gaussian half-width is practically constant over the entire range of the SF_6 density. The mean value $\bar{\gamma}_D$ of the Gaussian half-width is equal to 0.052 cm^{-1} which is significantly greater than the Gaussian half-width $\gamma_d = 0.020$ cm^{-1} corresponding to the usual Doppler broadening resulting from the thermal motion of Tl atoms with the Maxwellian velocity distribution at the temperature 733 K. The difference between $\bar{\gamma}_D$ and γ_d is due to the additional Doppler broadening arising from the recoil of the excited Tl $(7^2S_{1/2})$ atom after the photodissociation of TlI. It should be noted that the average Doppler width of the 535.0 nm Tl line perturbed by SF_6 at 733 K is close to the values found for this line perturbed by rare gas atoms and such non-polar molecules as H_2, D_2, N_2, O_2 and CO_2 at the same temperature [1–3].

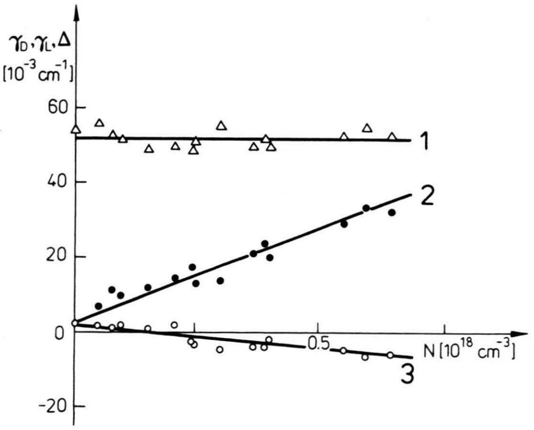

Fig. 1. Plots of the Gaussian (1), Lorentzian (2) half-widths and the shift (3) of the 535.0 nm Tl line against the density of sulfur hexafluoride. △ ● ○ – experimental points.

As it is seen from Fig. 1 the Lorentzian (full) half-width γ_L of the 535.0 nm Tl line depends linearly on the density N of sulfur hexafluoride according to the relation:

$$\gamma_L = \gamma_0 + \beta N\,, \tag{1}$$

where γ_0 is the asymptotic value of the Lorentzian half-width for the fluorescence cell with no perturbing gas and β is the pressure broadening coefficient. Using the least-squares analysis we found for Tl + SF_6 the value $\beta = (5.12 \pm 0.47) \times 10^{-20}$ cm^{-1}/molecule cm^{-3}. Let us note that in the case of the same line perturbed by Xe the measured value of the pressure broadening coefficient was found to be $\beta = (3.05 \pm 0.03) \times 10^{-20}$ cm^{-1}/atom cm^{-3} [2].

Figure 1 shows that the shift Δ of the 535.0 nm Tl line is a linear function of the sulfur hexafluoride density:

$$\Delta = \Delta_0 + \delta N\,, \tag{2}$$

where Δ_0 is the asymptotic shift for the TlI fluorescence cell without perturbing gas and δ is the pressure shift coefficient. From the least-squares analysis we found for Tl + SF_6 the value of the coefficient to be $\delta = (-1.59 \pm 0.30) \times 10^{-20}$ cm^{-1}/molecule cm^{-3}. For the same line perturbed by Xe we have determined previously the value

$$\delta = (-0.977 \pm 0.03) \times 10^{-20}\,cm^{-1}/\text{molecule}\ cm^{-3}$$

[2]. Let us note that the shift is towards the red like in the case of perturbation by atoms of comparable polarizability (Xe, Kr).

The red shift of the 535.0 nm Tl line perturbed by SF_6 is indicative of an attractive long-range potential for Tl + SF_6. The experimental value of the ratio of the shift to the Lorentzian half-width determined in the present work is equal to $\Delta/\gamma_L = -0.311$. This value does not differ much from the theoretical value of this ratio $\Delta/\gamma_L = -0.362$ calculated on the assumption that the interaction energy for Tl + SF_6 is given by the pure Van der Waals interaction [8].

Since our experimental values of the Lorentzian half-width γ_L and shift Δ are closely linear function of the SF_6-density we can determine the cross-sections σ_b and σ_s for the pressure broadening and shift of the 535.0 nm Tl line, respectively, using the impact approximation [8], according to which

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

and

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

Here $\bar{v}$ is the mean relative velocity of the colliding atom and molecule. Using the values β and δ determined in the present investigation for $\bar{v} = 6.4 \times 10^4$ cm/s we found the values $\sigma_b = 7.5 \times 10^{-14}$ cm^2 for the cross-section for the broadening and $\sigma_s = 4.6 \times 10^{-14}$ cm^2 for the cross-section for the shift of the 535.0 nm Tl line. These values of cross-sections are greater than those determined in our previous experiments on Tl perturbed by rare gas atoms, hydrogen, deuterium, oxygen, nitrogen and carbon dioxide. The reasonable agreement between our experimental data and theoretical values obtained for a Van der Waals interaction shows that in the first approximation the broadening and shift of the 535.0 nm Tl line by SF_6 are mainly due to purely adiabatic effects caused by the long range attractive forces between Tl-atom and SF_6-molecule. However, there is a number of factors whose role should first be clarified before the final conclusions on the effects of the SF_6 pressure on the atomic fluorescence of TlI are drawn.

First of all, the quenching of the thallium $7^2S_{1/2}$ state by SF_6 should be determined in order to estimate the influence of inelastic collisions on the 535.0 nm line. Secondly, reactive collisions between SF_6 and the products of the photodissociation of thallium iodide which are possible may cause additional broadening effects superimposed on that resulting from the Tl-SF_6 interaction. To clarify this problem studies of the pressure effects caused by SF_6 on the fluorescence radiation emitted from the pure thallium vapour should be performed.

[1] E. Lisicki, J. Szudy, and J. Wolnikowski, Acta Phys. Polon. **A56,** 557 (1979); **A58,** 105 (1980).

[2] E. Lisicki, A. Bielski, and J. Szudy, Z. Naturforsch. **35a,** 1249 (1980); **37a,** 93 (1982); **37a,** 1094 (1982).

[3] E. Lisicki, A. Bielski, R. S. Dygdala, and J. Szudy, Acta Phys. Polon. **A61,** 421 (1982).

[4] F. G. Kellert, C. Higgs, K. A. Smith, G. H. Hildebrandt, F. B. Dunning, and R. F. Stebbings, J. Chem. Phys. **72,** 6312 (1980).

[5] F. B. Dunning and R. F. Stebbings, in: Rydberg Atoms, eds. R. F. Stebbings and F. B. Dunning, Cambridge University Press, Cambridge 1982.

[6] A. Bielski, W. Dokurno, E. Lisicki, and Z. Turlo, Opt. Appl. **11,** 151 (1981).

[7] E. A. Ballik, Appl. Opt. **5,** 170 (1966).

[8] I. I. Sobelman, Introduction to the Theory of Atomic Spectra, Pergamon Press, Oxford 1972.