

Broadening and Shift of the 535.0 nm Thallium Line by Nitrogen

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The Doppler and collision broadening and shift of the 535.0 nm Tl line resulting from photodissociation of thallium iodide were investigated at low densities of nitrogen. The pressure broadening and shift coefficients were determined.

In previous papers [1–5] results of a detailed study of the effects of various foreign gases such as noble gases, hydrogen, deuterium and carbon dioxide on the thallium fluorescence line 535.0 nm ($7^2S_{1/2} - 6^2P_{3/2}$) were reported. This note describes an extension of these investigations to measurements of the shape, width and shift of the same Tl line perturbed by nitrogen. Reference is made to our earlier papers [1, 5] for experimental details and nomenclature.

The 535.0 nm Tl fluorescence line was excited by the photodissociation of thallium iodide molecules due to the irradiation of the TII vapour with ultraviolet light of an r.f. electrodeless mercury discharge lamp. The measurements were carried out at a fluorescence cell temperature of 733 K and at nitrogen densities up to $3 \times 10^{18} \text{ cm}^{-3}$ which corresponds to a pressure of N_2 up to 100 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, 7]. The shift measurements were performed using a low pressure r.f. electrodeless thallium discharge lamp as the reference source. The r.f. thallium lamp operated at 100 Mc/s.

The methods of line profile analysis were the same as those in our previous works [1–5]. We have found that the resultant profile of the 535.0 nm

Tl line of thallium iodide molecules can be fitted sufficiently well to a Voigt profile which is the convolution of the Lorentzian and Gaussian distribution. Using a procedure first described by Ballik [8], which was combined with a least squares method, the half-widths γ_D and γ_L of the Gaussian and Lorentzian components of the total profile of the 535.0 nm Tl line were determined.

Results of our measurements are shown in Fig. 1, where both the Gaussian and Lorentzian half-widths γ_D and γ_L of the 535.0 nm Tl line are plotted against the density of nitrogen. As can be seen, the Gaussian half-width is practically constant over the entire density range and is equal 0.051 cm^{-1} . This value is much greater than the value $\gamma_d = 0.020 \text{ cm}^{-1}$ of the Gaussian half-width resulting from the usual Doppler broadening due to the thermal motion of Tl atoms with the Maxwellian velocity distribution at 733 K. The difference $\gamma_D - \gamma_d = 0.031 \text{ cm}^{-1}$ can be treated as some measure of the additional Doppler broadening arising from the recoil of the excited Tl ($7^2S_{1/2}$) atom after photodissociation of the TII molecule [9].

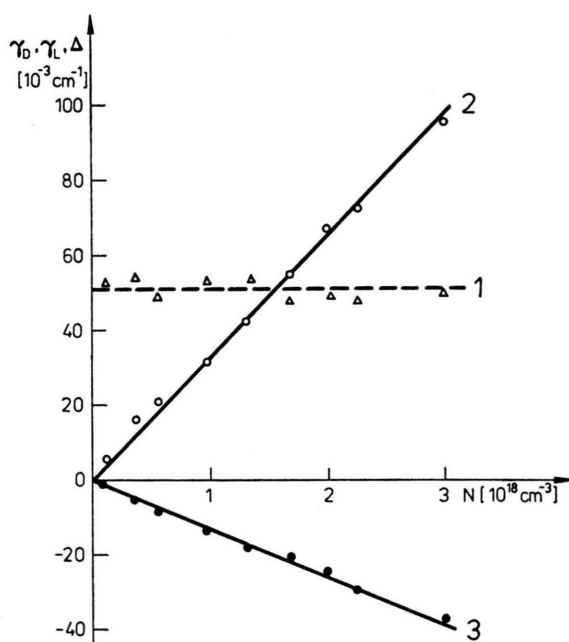


Fig. 1. Plots of the Gaussian (1), Lorentzian (2) half-widths and shift (3) of the 535.0 nm Tl line against the density of N_2 molecules. Δ $\circ$ $\bullet$ — experimental points.

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Figure 1 shows that the Lorentzian half-width γ_L of the 535.0 nm Tl line depends linearly on the nitrogen density N according to the relation $\gamma_L = \gamma_0 + \beta N$, where γ_0 is the asymptotic value of the Lorentzian half-width for the fluorescence cell without nitrogen, and β is the pressure broadening coefficient. Using the least-squares method we found for Tl + N₂: $\beta = (7.55 \pm 0.15) \times 10^{-20} \text{ cm}^{-1}/\text{molecule cm}^{-3}$.

As it is seen from Fig. 1 the shift Δ of the 535.0 nm Tl line, which is towards the red, is a linear function of the nitrogen density: $\Delta = \Delta_0 + \delta N$, where δ is the pressure shift coefficient and Δ_0 is the residual shift for the TII cell with no perturbing gas. The

least-squares analysis yielded the value $\delta = (-3.00 \pm 0.098) \times 10^{-20} \text{ cm}^{-1}/\text{molecule cm}^{-3}$.

The linear dependence of both the Lorentzian half-width and the shift of the line agrees with the predictions of the impact theory of pressure broadening of spectral lines [10]. No quantitative comparison of our experimental results with theory can be made because the interaction potentials for Tl + N₂ are not known. The red shift of the 535.0 nm Tl line caused by the pressure of nitrogen seems to indicate that the essential contribution to the collision effects on this line comes from the long range attractive forces between the Tl-atom and N₂-molecule.

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