Influence of O_2 on the 535.0 nm Thallium Line

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The effect of molecular oxygen on the broadening and shift of the 535.0 nm Tl line resulting from the photodissociation of thallium iodide vapour was studied at low densities of O_2. The broadening and shift coefficients were determined.

As a sequel to previous papers [1 – 3] this note reports results of measurements of the Doppler- and pressure-broadened profiles of the green thallium fluorescence line 535.0 nm ($7s\,{}^2S_{1/2} - 6p\,{}^2P^0_{3/2}$) accompanying the photodissociation of TlI molecules in thallium iodide vapour mixed with oxygen used as perturbing gas.

The experimental and numerical procedures used to study the half-widths of the Lorentzian and Gaussian components of the 535.0 nm Tl line have been described in detail in references [1 – 3]. An r.f. electrodeless mercury discharge lamp was used to excite the photodissociation of the TlI vapour in a fluorescence cell kept at temperature of 733 K. The measurements were performed for thallium iodide-oxygen mixtures at the constant TlI density and at different densities of O_2 up to $2 \times 10^{18}\,cm^{-3}$ which corresponds to pressures of O_2 below 50 Torr at room temperature. Intensity distributions in the broadened line were measured using a grating spectrograph and a pressure scanned Fabry-Perot etalon with 1.204 cm spacer and dielectric coating of mirrors. A low pressure r.f. electrodeless thallium discharge lamp operating at 100 MHz was applied as the reference source in the line shift determination.

Similarly as in our previous work [1 – 3] we have found that the resultant shape of the 535.0 nm Tl line emitted due to the photodissociation of TlI can be fitted well enough to a Voigt profile which is the convolution of the Lorentzian and Gaussian profiles. To determine the magnitudes of the half-widths γ_D and γ_L of the Gaussian and Lorentzian components of the total line shape, respectively, a procedure given by Ballik [4] combined with a least squares method was used.

Figure 1 shows the plots of the Gaussian and Lorentzian half-widths as well as the shift Δ of the maximum of the 535.0 nm Tl line against the oxygen density. We should emphasize that the Gaussian half-width γ_D of the 535.0 nm Tl line emitted from the TlI-O_2 mixture is practically constant over the whole density range. Its average value $\bar{\gamma}_D$ is equal to $0.055\,cm^{-1}$. This value is close to the values $\bar{\gamma}_D = 0.055\,cm^{-1}$ for TlI + H_2 [1], $\bar{\gamma}_D = 0.0512\,cm^{-1}$ for TlI + D_2 [2] and $\bar{\gamma}_D = 0.051\,cm^{-1}$ for TlI + N_2 [3]. The Gaussian half-width γ_d corresponding to the usual Doppler broadening due to the thermal motion of Tl atoms with the Maxwellian velocity distribution at 733 K is equal to $0.020\,cm^{-1}$. Thus the additional Doppler broadening arising from the recoil of the excited Tl $7\,{}^2S_{1/2}$ atom after the photodissociation of TlI [5] can be estimated from the difference $\gamma_D - \gamma_d$ to be $0.035\,cm^{-1}$.

As can be seen from Fig 1 both the Lorentzian half-width γ_L and the shift Δ of the 535.0 nm Tl line depend linearly on the oxygen density. The least-squares slopes of straight lines shown in

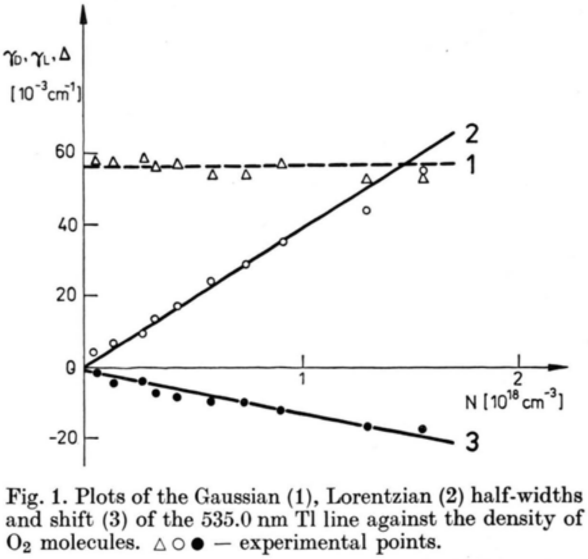

Fig. 1. Plots of the Gaussian (1), Lorentzian (2) half-widths and shift (3) of the 535.0 nm Tl line against the density of O_2 molecules. △ ○ ● – experimental points.

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Fig. 1 are

$$\gamma_L/N = (8.02 \pm 0.25) \times 10^{-20}\ \text{cm}^{-1}/\text{molecule cm}^{-3}$$

for the broadening by O_2 and

$$\Delta/N = -(2.53 \pm 0.23) \times 10^{-20}\ \text{cm}^{-1}/\text{molecule cm}^{-3}$$

for the shift which is towards the longer waves (minus sign).

Let us emphasize that the linear variation of both the Lorentzian half-width and the shift with the oxygen density agrees well with the predictions of the impact theory of line broadening [6]. Because the interaction potentials for the $TlI + O_2$ system are not known we cannot compare our experimental data with theory. Let us note, however, that the red shift observed in the present work indicates that the essential contribution to the pressure effects on the 535.0 nm line is due to the long range attractive part of the Tl-O_2 interaction potential. We should also mention that the experimental value of the ratio of the shift to the Lorentzian half-width (Δ/γ_L) found in the present work which is equal to $\Delta/\gamma_L = -0.316$ is in reasonable agreement with the theoretical value of -0.362 for a purely attractive Van der Waals potential [6]. We can thus conclude that for $Tl(7\,^2S_{1/2}) - O_2$ the long-range Van der Waals interaction is dominant and in the first approximation the repulsion effects can be neglected.

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