QUENCHING OF MERCURY-SENSITIZED FLUORESCENCE IN THALLIUM BY COLLISIONS WITH N_2 MOLECULES*,**

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The behaviour of the sensitized fluorescent spectrum of thallium, produced by irradiating Hg-Tl-N_2 mixtures with Hg 2537 Å resonance radiation, was studied in relation to N_2 pressure. The thallium atoms in the vapor-gas mixture become excited by collisional transfer from Hg 6^3P_1 atoms, and also from Hg 6^3P_0 atoms which are formed in $Hg(6^3P_1)+N_2$ collisions. The spontaneous decay of the collisionally populated S, P and D thallium states gives rise to the fluorescent spectrum, and their radiationless decay (quenching) caused by collisions with N_2 molecules manifests itself in a decrease of the fluorescent intensities as N_2 pressure is increased. An analysis of the variation of the fluorescent intensities with N_2 pressure yielded quenching cross sections of 110 Å^2, 10.2 Å^2 and 40.0 Å^2 for the $8^2S_{1/2}$, $7^2S_{1/2}$ and $6^2D_{5/2}$ states, respectively. The cross sections appear to exhibit resonance properties with respect to upward vibrational transitions in N_2.

1. Introduction

When a mixture of mercury and thallium vapors is irradiated with Hg 2537 Å resonance radiation, the resulting fluorescence includes, in addition to the mercury resonance fluorescence, several spectral components arising from the decay of various thallium states. These components which are indicated in Fig. 1, belong to the series $nS \rightarrow 6P$ and $nD \rightarrow 6P$, and their appearance in the fluorescent light is due to inelastic collisions during which excitation energy is transferred from excited mercury to ground state thallium atoms. It has been shown [1] that, at low vapor densities, the efficiency of such excitation transfer depends radically on the magnitude of the energy defect ΔE between the primarily excited Hg 6^3P_1 state and the appropriate S or D thallium state which becomes excited as the result of a binary collision. The excitation transfer cross sections which vary with ΔE lie on a resonance curve which spans four orders of magnitude over a ΔE range of almost 1.6 eV [2]. When the cross sections are determined at low mercury and thallium

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vapor pressures, only $Hg(6^3P_1)$ and ground-state thallium atoms participate in the collisional processes and contributions from $Hg(6^3P_0)$ metastable atoms, Hg_2 molecules and HgTl "excimers" can be ruled out because of their negligible concentration. However, it was deemed worthwhile to investigate also the collisional excitation energy transfer to

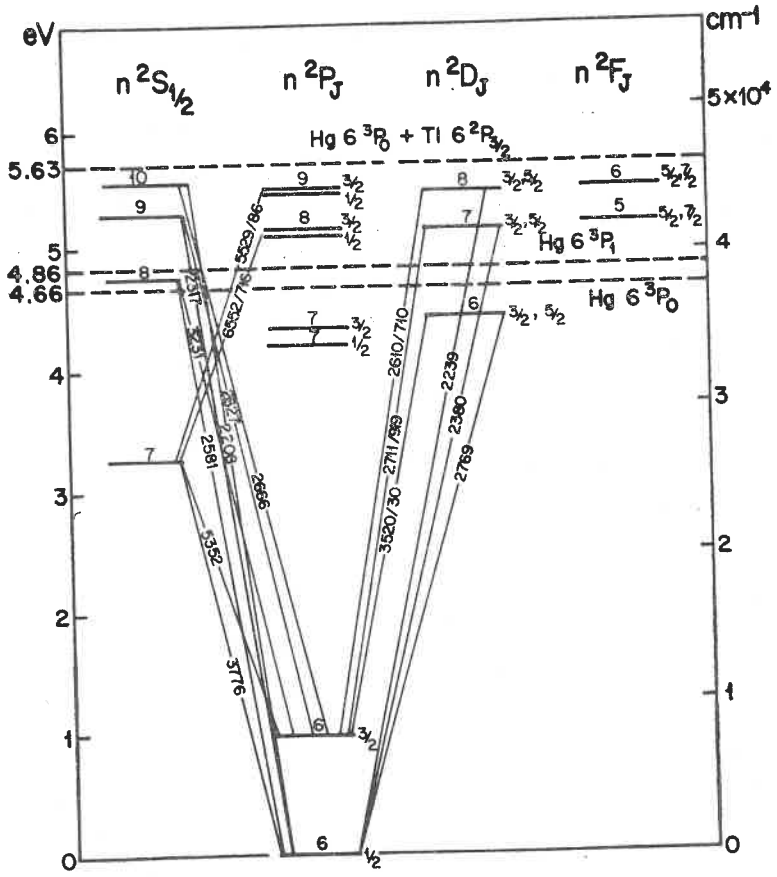

Fig. 1. The Hg and Tl energy levels involved in the sensitized fluorescence of thallium in the presence of N_2. The energy of $Hg(6^3P_0)$ relative to $Tl(6^2P_{3/2})$ is also indicated

thallium atoms from the metastable Hg 6^3P_0 state which has a very long lifetime and from which, therefore, excitation transfer should proceed with greater efficiency than from the relatively short-lived 6^3P_1 state. The efficient population of excited thallium states by collisions with $Hg(6^3P_0)$ atoms is of considerable interest, in view of recent studies [3] which indicate the possibility of a high-ower Hg–Tl laser operating in the spectral region 4500–6500 Å.

Although the direct optical excitation of the Hg 6^3P_0 state is forbidden by selection rules, a significant concentration of 6^3P_0 atoms may be produced indirectly through inelastic collisions between $Hg(6^3P_1)$ atoms and N_2 molecules [4, 5]. Nitrogen molecules

have been shown to be very much more effective in inducing energy transfer to the metastable state than other diatomic molecules, probably because the downward transition in mercury is accompanied by an upward transition from the ground vibrational state to the $v = 1$ state in nitrogen. Another distinct advantage of using nitrogen for the production of $Hg(6^3P_0)$ atoms arises from the fact that collisions with N_2 molecules induce exclusively $6^3P_1 - 6^3P_0$ transfer, without quenching the 6^3P_1 or 6^3P_0 atoms to the ground state [5].

When a mixture of mercury and thallium vapors with nitrogen is irradiated with Hg 2537 Å resonance radiation, various radiative and collisional processes ensue, the most likely of which are represented by the following equations:

$$Hg\,(6^1S_0) + h\nu \rightarrow Hg\,(6^3P_1) \tag{1}$$

$$Hg\,(6^3P_1) \rightarrow Hg\,(6^1S_0) + h\nu \tag{2}$$

$$Hg\,(6^3P_1) + Tl\,(6^2P_{1/2}) \rightarrow Hg\,(6^1S_0) + Tl^* \tag{3}$$

$$Hg\,(6^3P_1) + Tl\,(6^2P_{3/2}) \rightarrow Hg\,(6^1S_0) + Tl^* \tag{4}$$

$$Hg\,(6^3P_1) + N_2(v = 0) \rightarrow Hg\,(6^3P_0) + N_2(v = 1) \tag{5}$$

$$Hg\,(6^3P_0) + Tl\,(6^2P_{1/2}) \rightarrow Hg\,(6^1S_0) + Tl^* \tag{6}$$

$$Hg\,(6^3P_0) + Tl\,(6^2P_{3/2}) \rightarrow Hg\,(6^1S_0) + Tl^* \tag{7}$$

$$Tl^* \rightarrow Tl\,(6^2P_{1/2,3/2}) + h\nu' \tag{8}$$

$$Tl^* + N_2(v = 0) \rightarrow Tl^{\dagger} + N_2(v = n) \tag{9}$$

Equations (1) and (2) represent the optical excitation of the mercury atom and its decay resulting in the emission of resonance fluorescence, (3) indicates the collisional excitation transfer from $Hg(6^3P_1)$ atoms to various close-lying states in thallium, (5) represents the production of Hg (6^3P_0) metastable atoms, (6) represents excitation transfer from Hg 6^3P_0 to various states in thallium, (8) describes radiative decay of excited thallium, and (9) radiationless decay (quenching) to lower states, induced by collisions with N_2 molecules. The processes represented by Eqs. (4) and (7) are of secondary significance because of the low density of $6^2P_{3/2}$ thallium atoms which tend to be quenched by collisions with the cell walls and with N_2 molecules [1]. Equations (1)–(9) make no provision for the formation of Hg_2 or HgTl "excimers", which is unlikely to take place at the low mercury and thallium densities that were employed [3, 6]. As may be seen, the addition of N_2 to the Hg–Tl vapor mixture ought to cause an increase in the population of the S and D thallium states, attributable to the emergence of a second channel for excitation transfer, involving the $Hg(6^3P_0)$ atoms. Its effectiveness would largely depend on the energy defect ΔE between the particular thallium state and Hg 6^3P_0. On the other hand, the competing quenching process represented by (9), should diminish the population of the various thallium states, bearing in mind that N_2 molecules are known to quench the Tl $7^2S_{1/2}$ resonance state with considerable efficiency [7, 8].

Under these conditions it is virtually impossible to obtain actual excitation transfer cross sections from Hg 6^3P_0 to the various thallium states because the density of the Hg(6^3P_0) atoms must be known for their calculation and the determination of this density at low vapor pressures is difficult. Also, in allowing for the presence of the two channels for excitation transfer, a large error would be introduced into the cross section. Nevertheless, if one investigates how the sensitized fluorescence of thallium behaves in relation to nitrogen density, one can follow quite well the course of the various processes and identify the most significant among them. Similar investigations of the mercury-thallium system were carried out by other authors [9, 10] who, however, worked at metal vapor and buffer gas pressures much higher than those employed in this investigation. It should be stressed that the quenching of the various thallium states is also of considerable interest. Quenching of the higher-lying states would be rather difficult to study using direct optical excitation, but if the 3-component system is in dynamic equilibrium such that the densities of the Hg 6^3P_1, Hg 6^3P_0 and Tl $6^2P_{1/2}$ states remain constant, it then becomes possible to obtain the quenching cross sections by following the variation of the intensities of the various sensitized fluorescent components in relation to nitrogen pressure. The determination and study of these cross sections are the main object of this investigation.

2. Experimental

The apparatus used in this investigation has been described previously [1, 11, 12]. An r. f. electrodeless discharge lamp containing mercury vapor and about 0.8 — 1.1 torr of argon, generated Hg 2537 Å resonance radiation which had a narrow line width and was relatively free from self-reversal. The emitted light was rendered monochromatic by means of an interference filter which transmitted 10% of the Hg 2537 Å radiation with a spectral purity better than 0.1%, and was brought to focus within the fluorescence cell, in the corner between the entrance and observation windows, where it excited fluorescence in the vapor mixture; the optical path of the exciting and fluorescent light in the vapor did not exceed 1 mm. The fluorescence was observed at right angles to the direction of excitation and was focused onto the entrance slit of a 0.5 m grating spectrometer equipped with a Jarrell-Ash grating ruled at 1180 grooves/mm, and with a calibrated EMR 514N–03–14–03900 photomultiplier which had an "extended" S–20 sensitivity. The photomultiplier was cooled to liquid nitrogen temperature at which the dark current was about 5×10^{-13} A; its signal was amplified with a Keithley model 417 electrometer and was recorded with a strip-chart recorder.

The fluorescence cell [1] was mounted in a constant-temperature oven and was fitted with two side-arms, one of which contained metallic thallium and the other contained mercury, sealed in a reservoir to prevent the uncontrolled migration of mercury vapor into the cell. The cell was connected to the vacuum and gas-filling system by a 50 cm capillary; nitrogen pressure was measured with an accuracy of about ± 0.02 mm Hg by means of a silicon oil manometer. All gas pressures were corrected for thermal transpiration.

At the beginning of each experimental run, the r. f. lamp was stabilized so as to produce a constant intensity of the mercury resonance radiation, which was continuously monitored.

During a particular run the Hg–Tl mixture in the cell was excited with the Hg 2537 Å radiation while the temperature of the thallium side-arm was kept constant in the range 430°C—500°C which was sufficient to produce a thallium density of about 10^{+12}—10^{+11} cm^{-3}. The density of mercury in the mixture was kept constant at about 10^{+11} cm^{-3} [1]. The relative intensities I_0 of the thallium fluorescent components were first determined in the absence of N_2. Controlled quantities of N_2 were then admitted to the cell and, at each pressure, we measured the intensities I of the sensitized fluorescent components. To reduce the time required to reach equilibrium, the N_2 pressure was always increased (rather than decreased) between successive sequences of measurements. This procedure was carried out several times over a range of N_2 pressures extending from 0.1 torr to about 8 torr, which corresponds to an N_2 density range $10^{15} - 10^{16}$ cm^{-3}. Several runs, using three different cells each with new or repolished windows and fresh charges of thallium and mercury [1], were performed to establish the reproducibility of the results.

3. *Results and discussion*

Figure 2 shows plots of the experimentally determined ratios of sensitized fluorescent intensities I/I_0 in relation to nitrogen density, for the components at 3231 Å, 3520 Å, 5352 Å and 3776 Å, which arise from the decays $8^2S_{1/2} \rightarrow 6^2P_{3/2}$, $6^2D_{5/2} \rightarrow 6^2P_{3/2}$,

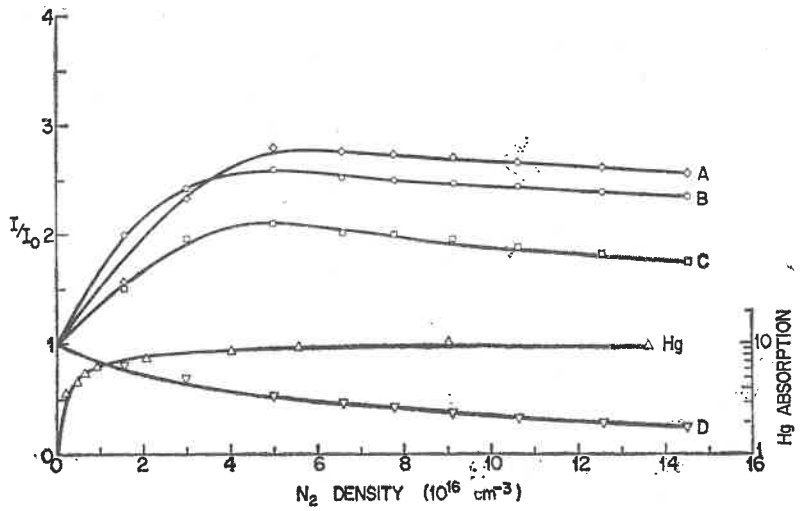

Fig. 2. Plots of I/I_0 against N_2 density for the components in the sensitized fluorescent spectrum of thallium. *A* — 3776 Å; B — 5352 Å; C — 3520 Å; D — 3231 Å. The relative density of Hg 6^3P_0 atoms is also shown

$7^2S_{1/2} \rightarrow 6^2P_{3/2}$ and $7^2S_{1/2} \rightarrow 6^2P_{1/2}$, respectively. Also shown is the Hg 4047 Å ($6^3P_0 \rightarrow 7^3S_1$) absorption curve obtained by Gatzke [13], which indicates the dependence of the Hg(6^3P_0) density on N_2 density, at a mercury vapor pressure similar to that employed in this experiment. Since both the Hg and Tl atomic densities were constant, as was the temperature of the fluorescence cell, the variations of I/I_0 with N_2 density provide direct

information about the relative changes in the populations of the particular thallium states, that are caused both directly and indirectly by inelastic collisions with N_2 molecules. The effectiveness of excitation transfer from Hg 6^3P_0 to the various thallium states, depends on the concentration of the Hg(6^3P_0) atoms and thus on the density of N_2 molecules, as well as on the magnitude of the resonance defect ΔE between the particular thallium state and Hg 6^3P_0. Thus, if for a particular thallium state ΔE is small, the ratio I/I_0 should show a tendency to increase with increasing N_2 density. The competing quenching process represented by (9), which causes radiationless transitions from the excited states to the ground state directly or indirectly in a series of cascade transitions, would make the ratio I/I_0 decrease with increasing N_2 density.

The shapes of the curves in Fig. 2 reflect the relative effectiveness of the excitation transfer and quenching processes as they affect specific thallium states. For example, the $6^2D_{5/2}$ state lies 0.40 eV below Hg 6^3P_1 but anly 0.18 eV below Hg 6^3P_0, and one would expect energy transfer from the latter state to take place with a 5-fold larger cross section than from Hg 6^3P_1 [1, 11]. Consequently, the population of the Tl $6^2D_{5/2}$ state and the associated fluorescent intensity would be expected to increase with the density of the Hg (6^3P_0) atoms which, as may be seen in Fig. 2, reaches a plateau at an N_2 density of $3–5\times10^{16}$ cm^{-3} [12]. At N_2 densities above the "saturation" level, the quenching effects predominate and the I/I_0 ratio decreases accordingly. The situation is rather different in the case of the Tl ($8^2S_{1/2}$) atoms which decay to the $6^2P_{3/2}$ state emitting 3231 Å fluorescence. The $8^2S_{1/2}$ state lies 0.08 eV below Hg 6^3P_1 and 0.14 eV above Hg 6^3P_0, and a simple estimate [11] suggests that collisions with Hg (6^3P_0) atoms can contribute not more than 10% to the total population of the $8^2S_{1/2}$ state. It is not surprising that the addition of nitrogen to the system results in the immediate decrease in the intensity of the 3231 Å component. The shape of the corresponding curve in Fig. 2 also provides some insight into the role of the Tl ($6^2P_{3/2}$) atoms in the excitation transfer process. If the Tl $6^2P_{3/2}$ state were populated to any significant extent, there would be the possibility of exciting thallium states up to an energy level of 5.83 eV, by collisions of Tl ($6^2P_{3/2}$) and Hg (6^3P_0) atoms. This would produce populations of Tl $9^2S_{1/2}$, $9^2P_{1/2,\,3/2}$, $8^2P_{1/2,\,3/2}$ and $8^2D_{5/2,\,3/2}$ states which, in turn, would populate the $8^2S_{1/2}$ state through cascade transitions. The relative populations of all these thallium states would depend on N_2 density and such dependence should be reflected by an initial increase in the I/I_0 ratio for Tl $8^2S_{1/2}$, reaching a maximum at an N_2 density in the vicinity of 5×10^{16} cm^{-3}. The absence of such a maximum suggests that the population density of the Tl $6^2P_{3/2}$ state is negligible at the low Hg, Tl and N_2 densities.

The curves indicating the effect of N_2 on the population of the Tl $7^2S_{1/2}$ state (which can be monitored by observation of the 3776 Å or 5352 Å fluorescence), are similar in appearance to the curve appropriate to the $6^2D_{5/2}$ state. The somewhat more pronounced effect on the $7^2S_{1/2}$ state is most likely due to the fact that this state, unlike $6^2D_{5/2}$, may be populated by cascade transitions from $7^2P_{1/2,\,3/2}$ as well as by direct transfer from Hg 6^3P_1 and Hg 6^3P_0. The $6^2D_{5/2}$ state, on the other hand, has radiative and collisional decay channels to the 7^2P states, in addition to the decay to the $6^2P_{3/2}$ state which manifests itself in the emission of the 3520 Å fluorescence. The 7^2P state can also be populated by

collisional transfer from Hg atoms, but the $7^2P \rightarrow 7^2S$ decays give rise to infrared emission which lies outside the sensitivity range of the spectrometer.

The quenching cross sections Q for the various thallium states were obtained from the data shown in Fig. 2 and were used in conjunction with the Stern-Volmer [14] relation which may be written:

$$I^0/I = 1+\tau N v_r Q \tag{11}$$

where I^0 is the relative intensity of the fluorescent component at a fixed N_2 density, above which the quenching process becomes dominant, I is the intensity at N_2 density N, τ is

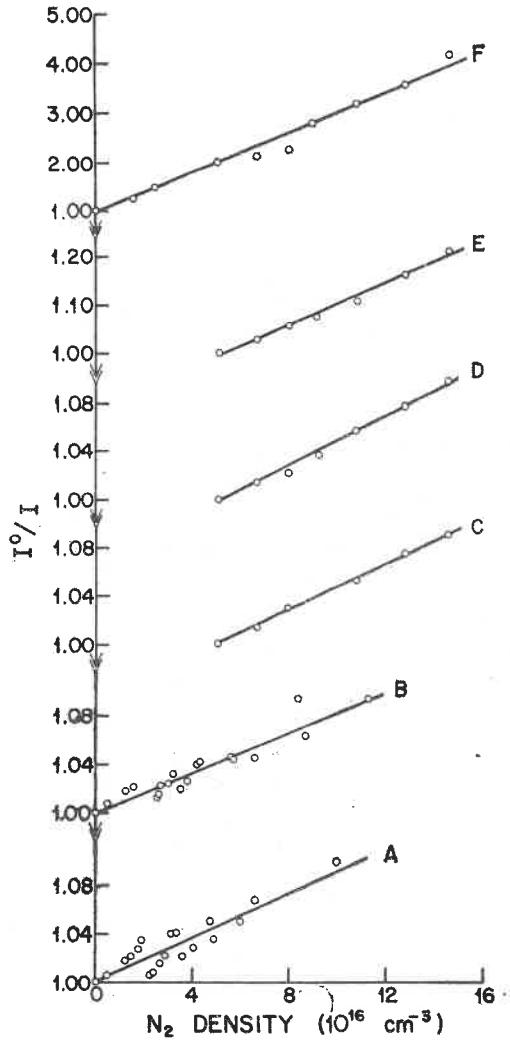

Fig. 3. Stern–Volmer plots of I^0/I against N_2 density. Resonance fluorescence in Tl–N_2 mixtures: A — 5352 Å; B — 3776 Å. Sensitized fluorescence in Tl–Hg–N_2 mixtures: C — 5352 Å; D — 3776 Å; E — 3520 Å; F — 3231 Å

the average lifetime of the appropriate thallium state [15], and v_r is the average relative speed of the colliding partners (Tl−N_2). Except for the $8^2S_{1/2}$ state, for which the whole range of experimental measurements was employed, the cross sections were determined from data obtained at N_2 densities above 5×10^{16} cm^{-3}. Fig. 3 shows plots of I^0/I against N_2 density for the various sensitized fluorescent components, whose slopes yield the quenching cross sections Q which are compared in Table I with values reported by other investigators. It may be seen that the Stern-Volmer relation is obeyed quite well and the plots are indeed linear as expected.

TABLE I

Cross sections for quenching of thallium states by collisions with N_2 molecules

Observed fluorescence		Description of quenched states			Cross sections Q (Å^2)	
Transition	λ (Å)	Tl* state	τ [15] (10^{-9} s)	ΔE[Tl* −Hg(6^3P_0)] (eV)	This investigation (±20%)	Other reports
$8^2S_{1/2}\rightarrow 6^2P_{3/2}$	3231	$8^2S_{1/2}$	22.4	+0.12	110	
$7^2S_{1/2}\rightarrow 6^2P_{3/2}$	5352	$7^2S_{1/2}$	11	−1.38	10.2	
$7^2S_{1/2}\rightarrow 6^2P_{3/2}$	5352	$7^2S_{1/2}$	11	n.a [a]	10.3	20.1[7]; 10[8]
$7^2S_{1/2}\rightarrow 6^2P_{1/2}$	3776	$7^2S_{1/2}$	11	−1.38	11.1	
$7^2S_{1/2}\rightarrow 6^2P_{1/2}$	3776	$7^2S_{1/2}$	11	n.a [a]	11.4	20.1[7]; 10[8]
$6^2D_{5/2}\rightarrow 6^2P_{3/2}$	3520	$6^2D_{5/2}$	5.1	−0.20	40	

[a] values obtained from resonance fluorescence experiment.

In order to verify the accuracy of the quenching cross sections obtained from sensitized fluorescent intensity measurements, an auxiliary experiment was carried out with a Tl-N_2 mixture, in which the Tl $7^2S_{1/2}$ state was excited with Tl 3776 Å resonance radiation emitted from a filtered Osram spectral lamp, and the intensities of Tl 3776 Å and Tl 5352 Å resonance fluorescent components were monitored in relation to N_2 density. The results of this experiment are also shown in Fig. 3 and the resulting cross sections, listed in Table I, are in good agreement with those obtained using the method of sensitized fluorescence and with values reported by Prileshayeva [8]; it is difficult to effect a meaningful comparison with the much larger cross sections obtained by Jenkins [7] who carried out his measurements in flames, at a temperature of 1400 K, rather than in a fluorescence cell. No quenching cross sections for states higher than $7^2S_{1/2}$ have been previously reported in the literature.

It may be seen in Table I that the quenching cross sections for the $6^2D_{5/2}$ state are four times larger, and those for the $8^2S_{1/2}$ state ten times larger, than the value for the $7^2S_{1/2}$ state. This disparity may well be caused by a resonant energy transfer from the excited thallium atom into specific vibrational states of the N_2 molecule, as indicated by Eq. (9), with the magnitude of the cross section depending on the closeness of the resonance. In Table II we show the various possible radiationless transitions in thallium, that could result from quenching collisions, together with the most probable corresponding vibra-

TABLE II

Resonance properties of the quenching cross sections in the Tl–N_2 system

Quenching transitions in Tl	Vibrational transitions in N_2	$\Delta E'$ (eV)	Quenching cross section Q (Å^2)
$8^2S_{1/2} \rightarrow 7^2P_{1/2}$	$v = 0 \rightarrow v = 2$	+0.01	110
$7^2S_{1/2} \rightarrow 6^2P_{1/2}$	$v = 0 \rightarrow v = 12$	+0.06	10.7 [a]
$6^2D_{5/2} \rightarrow 6^2P_{3/2}$	$v = 0 \rightarrow v = 13$	+0.04	40

[a] average value.

tional excitations in N_2, $\Delta E'$ being the resonance defect between the two processes (the energies of the N_2 vibrational states were taken from Gilmore [16]). It seems that a quenching transition $8^2S_{1/2} \rightarrow 7^2P_{1/2}$ exhibits the closest resonance with the $v = 0 \rightarrow v = 2$ excitation, followed by the resonance of the $6^2D_{5/2} \rightarrow 6^2P_{3/2}$ transition with the $v = 0 \rightarrow v = 13$ excitation. The resonant behaviour is depicted in Fig. 4 which shows a plot of

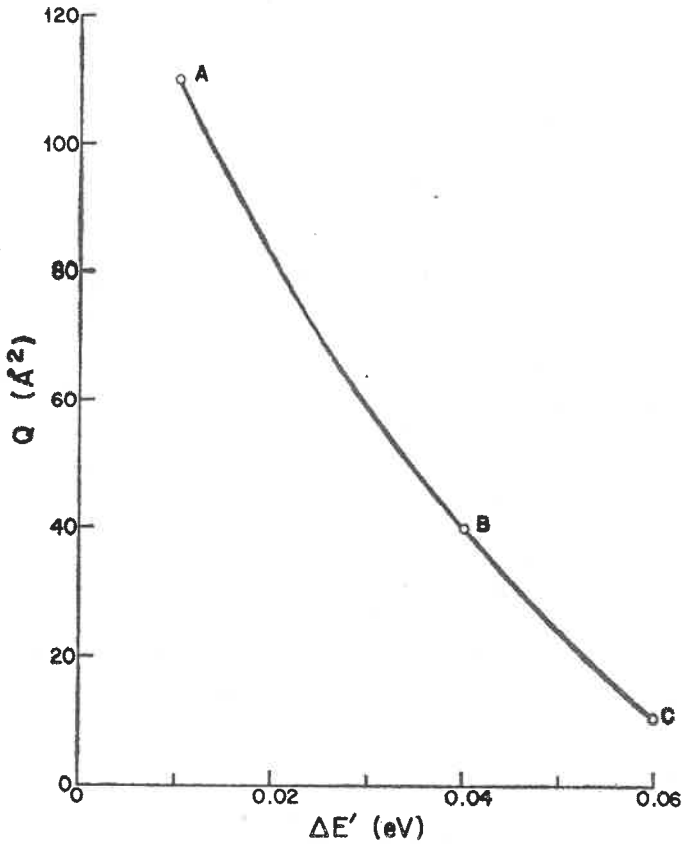

Fig. 4. Plots of quenching cross sections against $\Delta E'$, the defect between the energies of the downward radiationless transitions in thallium and of the accompanying upward vibrational transitions in N_2. A — $8^2S_{1/2}$; B — $6^2D_{5/2}$; C — $7^2S_{1/2}$ (see Table II)

the quenching cross section against $\Delta E'$. Although the number of quenched states is too small to provide adequate evidence for the presence of a resonance effect in quenching, such an effect has been indicated in previous studies of quenching in sodium by N_2 [12, 17], mercury by N_2 [5] and mercury by CO [18]. On the whole, the resonance effect has not been found to be very strong, possibly because of the influence of the rotational structure of the vibrational states, which tends to detract from the sharpness of the resonance.

A final comment should be made about the applicability of the experimental approach employed in this investigation, to the determination of quenching cross sections. It has recently been suggested [19, 20] that cross sections for quenching of states that are populated by collisional transfer, are subject to serious error arising from collisional cascade effects; that the effect of increasing N_2 pressure is to populate the particular state by collisional transfer from higher states, as well as depopulate or quench it by transfer to lower states; that, consequently, cross sections determined in a sensitized fluorescence experiment will be grossly underestimated. It appears, nevertheless, that the quenching cross sections for the Tl $(7^2S_{1/2})$ state, obtained from the subsidiary experiment involving resonance fluorescence (with the Tl $(7^2S_{1/2})$ atoms excited optically from the ground state), are in very good agreement with values obtained from the sensitized fluorescence experiments. This result which upholds the validity of our method, is consistent with similar observations reported for the Hg–Na–N_2 system [12].

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