## E-X Band System of the Copper lodide Molecule

THE coarse spectrum of copper iodide in the visible region was investigated by Mulliken<sup>1</sup> in 1925 and Ritschl<sup>2</sup> in 1927. Ritschl recorded five extensive band systems in absorption, all degraded to red in the region 3750–5500 Å. From a study of their vibrational analysis he concluded that all systems have a common lower state which is the ground state of the molecule. This communication reports the results of the rotational analysis of the E-X bands of <sup>63</sup>Cu<sup>127</sup>I.

The molecule was excited in an electrodeless discharge tube by a 2,450 Mc/s 'Raytheon' microwave oscillator and the rotational structure was photographed in the second order of a 10 m concave grating spectrograph<sup>3</sup> (dispersion 0.33 Å/mm). The overlapping structure duto the less abundant species  $^{65}$ Cu<sup>127</sup>I has been avoided by adjusting the time of exposures. Exposures of 1.5 h duration on 'Kodak II-O' plates were found to be suitable for recording the structure of the main bands. The iron are spectrum was used as the comparison spectrum. The probable error of the measurements is estimated to be  $0.04 \text{ cm}^{-1}$ .

The seven bands (4,0), (3,0), (2,0), (1,0), (1,1), (0,1) and (0,2) which were found suitable for measurement have been analysed. Each of these bands shows the existence of only two branches P and R. The J numbering was fixed in the usual way by comparing the combination differences and the various rotational constants were determined by the graphical procedures described by Herzberg<sup>4</sup>. Results are given in Tables 1 and 2.

|   |                           | Table 1. Ro  | TATIONAL CO  | NSTANTS          |   |
|---|---------------------------|--|--|------------------|---|
| Band  |                           | Bv' (cm-1)   | Bv'' (cm <sup>-1</sup> )   |                  | γ <sub>0</sub> (cm <sup>-1</sup> )  |
| 4,0<br>3,0<br>2,0<br>1,0<br>1,1<br>0,1<br>0,2 |                           | 0.0642<br>0.0645<br>0.0649<br>0.0652<br>0.0652<br>0.0656<br>0.0656 | 0.0732<br>0.0732<br>0.0732<br>0.0732<br>0.0732<br>0.0730<br>0.0730<br>0.0730 |                  | 24,882.06<br>24,660.62<br>24,436.90<br>24,211.30<br>23,948.00<br>23,720.50<br>23,458.37 |
|   |                           | Table 2. MoL   | ECULAR CONS  | FANTS            |   |
| State   | Be<br>(cm <sup>-1</sup> ) | <i>De</i><br>(cm <sup>-1</sup> )                                   | (cm <sup>-1</sup> )  | 7.e<br>(Å)       | $I_e \times 10^{-40}$ (g cm <sup>2</sup> )  |
| $E \\ X$                                      | 0.0660                    | $2 \cdot 2 \times 10^{-8}$<br>$1 \cdot 6 \times 10^{-8}$           | 0.0004<br>0.0003   | $2.463 \\ 2.334$ | $423.64 \\ 380.41$  |

From the fact that a single P and a single R branch are observed, it is concluded that the bands arise from a transition of the type  ${}^{1}\Sigma - {}^{1}\Sigma$ . A recent rotational analysis of the analogous E-X system of copper chloride by Rao, Asundi and Brody<sup>5</sup> lends support to this assignment. Rotational analyses of the other band systems are in progress.

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## Effect of Temperature on the Triplet-Triplet Annihilation Rate in Anthracene Crystals

Jortner, Rice, Katz and Choi have recently shown that triplet-triplet annihilation leading to delayed fluorescence in crystalline anthracene can be adequately described in terms of a random walk diffusion model when the effects of charge transfer interactions are included<sup>1</sup>. This model is valid if the scattering of the triplet excitation wave by lattice phonons is so strong that the mean free path of the triplet exciton is of the same order of magnitude as the crystal lattice spacing. On the basis of the random walk model the triplet-triplet interaction rate constant ( $\gamma$ ) is given by

$$\gamma = 8\pi DR \tag{1}$$

where D is the triplet excitation diffusion constant and R is the triplet-triplet interaction distance, taken to be  $10^{-7}$  cm for crystalline anthracene<sup>2</sup>. The value of  $\gamma$  calculated by Jortner et al. for anthracene is  $4 \times 10^{-11}$ /cm<sup>3</sup>/sec, and is in good agreement with the experimental values<sup>2</sup> which range from  $1 \times 10^{-11}$  to  $5 \times 10^{-11}/\text{cm}^3/\text{sec.}$  (Moore and Munro<sup>3</sup> have recently reported  $\gamma$  = 2.1  $\times$  10<sup>-11</sup>/cm<sup>3</sup>/ sec for a carefully purified anthracene crystal.) The value of D calculated using equation (1) is  $30 \times 10^{-6}/\text{cm}^2/\text{sec}$ which shows quite good agreement with the value of  $6 \times 10^{-6}$ /cm<sup>2</sup>/sec obtained by King and Voltz<sup>2</sup>. (In calculating the value of D, Jortner et al.1 assume a pure anthracene crystal; King and Voltz<sup>2</sup>, however, analysed the slow scintillation component obtained from anthracene They suggest that the crystals of commercial grade. ionizing radiation may perturb the crystal lattice, thus giving a value of D which may be different from diffusion in the perfect lattice.)

The diffusion length (L) of a triplet exciton is given by<sup>1</sup>

$$L = (2D T_0)^{\frac{1}{2}} \tag{2}$$

where  $T_0 = 10^{-2}$  sec is the approximate value of the lifetime of the anthracene triplet<sup>4</sup>. This gives  $L = 3.5 \times 10^{-4}$ cm which is in quite good agreement with the experimental value of  $10 \pm 5 \times 10^{-4}$  cm reported by Avakian and Merrifield<sup>5</sup>.

Jortner et al.<sup>1</sup> have also considered the effect of temperature on the triplet diffusion constant (D) and the bimolecular annihilation rate constant  $(\gamma)$  as predicted by the strong scattering model. Considering the effect of thermal expansion of anthracene crystals, Jortner et al. expect the diffusion constant to increase by about 20–50 per cent on cooling the crystal from 300° K to 77° K. They suggest that investigations of the temperature dependence of the triplet-triplet annihilation process will provide an important test of the applicability of their theory<sup>1</sup>.

In the present work the triplet-triplet annihilation rate constant ( $\gamma$ ) has been determined as a function of temperature for a pure anthracene crystal 4 mm thick. For times short compared with the triplet lifetime ( $T_0$ ) the fluorescence signal (F) is given by<sup>3</sup>

$$F = \frac{1}{2}A\gamma \left[N_0/(1+\gamma N_0 t)\right]^2$$
(3)

where A is an instrumental factor and  $N_0$  is the initial density of triplet states. From a plot of  $F^{-1/2}$  against t the ratio of the slope/intercept gives the quantity  $\gamma N_0$ . For excitation times  $(t_x)$  short compared with the triplet lifetime the initial density of triplet states is

$$N_0 \doteq Q_T t_x \in I_0 \tag{4}$$

 $Q_T$  is the triplet quantum yield, equal to unity minus the prompt fluorescence quantum yield<sup>6</sup>. This gives  $Q_T = 0.35$  for thick anthracene crystals<sup>7</sup>.  $\varepsilon$  is the absorption coefficient of the light and  $I_0$  is the exciting light intensity measured using a thermopile.  $N_0$ , and hence  $\gamma$ , can therefore be determined<sup>3</sup>.

Moore and Munro have used this technique to determine  $\gamma$  for several crystalline anthracene samples using exciting radiation at 434 nm to produce volume excitation of the crystals. The average value of  $\gamma$  obtained from four commercial grade crystals was  $1.4 \times 10^{-11}/\text{cm}^3/\text{sec}$ , this value being correct to within an order of magnitude<sup>3</sup>.

Decay curves were obtained at various temperatures for a pure anthracene crystal using 434 nm exciting radiation, and the linear plots of  $F^{-\frac{1}{2}}$  against t obtained at each temperature are shown in Fig. 1.  $I_0$  and  $t_x$  are