

\* Present address : Physics Department, Ravi-shanker University, Raipur, Raipur (M.P.).

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### ISOTOPE SOLVENT EFFECT ON TRIPLET STATE OF XANTHENE DYES\* IN H<sub>2</sub>SO<sub>4</sub> AND D<sub>2</sub>SO<sub>4</sub> SOLUTIONS

OBSERVATIONS have been made and reported on the enhancement of phosphorescence to fluorescence emission yields, and the triplet state decay time for deuterated as compared to perprotonated hydrocarbons<sup>1-3</sup>. Similar increase has been observed in both lifetime and intensity of emission in rare-earth and uranyl ions<sup>4-6</sup>. Pant and Pant have observed the enhancement of phosphorescence decay time and ratio of phosphorescence to fluorescence emission yield of sodium fluorescein in solutions by substituting the perprotonated solvents by deuterated solvents<sup>7</sup>. Similar effect has also been observed by the authors for xanthene dyes in H<sub>3</sub>BO<sub>3</sub> and D<sub>3</sub>BO<sub>3</sub> glasses<sup>8</sup>. All these observations have been explained on the basis of theories on radiationless transitions<sup>9-11</sup>.

In the present communication deuterium solvent effect is studied for xanthene dyes using concentration  $\approx 5 \times 10^{-5}$  M in H<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>SO<sub>4</sub> as solvent. It is observed that both triplet decay time and the ratio of phosphorescence to fluorescence emission yield increase in solvent D<sub>2</sub>SO<sub>4</sub> as compared to H<sub>2</sub>SO<sub>4</sub> for dyes mentioned above. The phosphorescence to fluorescence emission yields and triplet state decay time for these dyes in H<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>SO<sub>4</sub> at 80° K are given in Table I. Within the experimental errors of 10% the two values ( $\Phi_p/\Phi_f$  and  $\tau_{pd}/\tau_{ph}$ )<sup>†</sup> are the same for each dye.

The kinetics<sup>9</sup> of radiative and nonradiative processes yields the following :<sup>12</sup>

$$\Phi_f = \frac{k_f}{k_f + k_{qf} + K_{is}}$$

$$\Phi_p = \frac{k_{is} \cdot k_p}{(k_f + k_{qf} + k_{is})(k_p + k_{qp})}$$

and

$$\Phi_p/\Phi_f = \frac{k_p \cdot k_{is}}{k_f (k_p + k_{qp})}$$

where  $k_f$  = intrinsic fluorescence rate constant

$k_{qf}$  = fluorescence quenching rate

$k_{is}$  = intersystem crossing from singlet to triplet state

$k_p$  = intrinsic phosphorescence decay rate

$k_{qp}$  = phosphorescence quenching rate.

The increase in the lifetime and the ratio of phosphorescence to fluorescence emission yield of xanthene dyes in D<sub>2</sub>SO<sub>4</sub> suggests that the vibrational modes of the solvent are involved to some extent in determining the decay rate for triplet to ground state transition. From this it is concluded that the solvent plays an important role in causing the radiationless decay. According to Robinson and Frosch<sup>9</sup>, the radiationless transition probability depends on the Franck-Condon overlap factor between the zero point vibrational wavefunction of the upper state and the isoenergetic vibrational wavefunction of the lower state. The CH and OH vibrational modes of system (solvent plus molecules) are important in determining the magnitude of this overlap. Since CD and OD vibrational modes require higher quantum numbers to be isoenergetic, the overlap integral is expected to be smaller, which results in a diminution in nonradiative processes from triplet to ground state.

In the present study the deuteration of the solvent (D<sub>2</sub>SO<sub>4</sub>) produces a change in the vibrational modes of the solvent which is responsible for decreasing the magnitude of the overlap factor and

TABLE I

Triplet state decay time and the ratio of phosphorescence to fluorescence emission for xanthene dyes in H<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>SO<sub>4</sub> at 80° K

Dyes	Triplet state decay time $\tau$ in			Ratio of phosphorescence to fluorescence emission $\Phi_p/\Phi_f$ in		
	H <sub>2</sub> SO <sub>4</sub> (1)	D <sub>2</sub> SO <sub>4</sub> (2)	2/1	H <sub>2</sub> SO <sub>4</sub> (3)	D <sub>2</sub> SO <sub>4</sub> (4)	4/3
Dichloro (K) fluorescein	280 msec	480 msec	1.53	2.3	3.0	1.56
Dibromo (R) fluorescein	6 ms	9 ms	1.50	2.9	4.4	1.51
Diiodo (R) dimethyl (R) fluorescein	350 $\mu$ sec	540 $\mu$ sec	1.54	3.8	5.9	1.55

hence increase in the phosphorescence lifetime and the ratio of  $\Phi_p/\Phi_f$  for dyes.

Physical Laboratory,  
D.S.B. Government College,  
Naini Tal, July 10, 1972.

D. D. PANT,\*  
K. C. PANT.  
N. B. JOSHI.

\* Dichloro (R) fluorescein. Dibromo (R) fluorescein and Diiodo (R) dimethyl (R) fluorescein.

†  $\tau_{pi}$ —triplet state decay time in  $D_2SO_4$

$\tau_{ph}$ —triplet state decay time in  $H_2SO_4$

\*\* Present address: Director of Education, U.P., Lucknow.

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### X-RAY DETERMINATION OF MEAN AMPLITUDE OF VIBRATION AND DEBYE TEMPERATURE OF LEAD SULPHIDE

LONSDALE<sup>1</sup> quotes a value of 190° K for the Debye temperature of lead sulphide, estimated from specific heat data in the  $T^3$  region. Recently, Anderson<sup>2</sup> obtained a value of 230° K for the Debye temperature from room temperature elastic constants. We report here the results of an X-ray determination of the Debye temperature and mean amplitude of vibration at room temperature for lead sulphide.

Lead sulphide was prepared by passing hydrogen sulphide in an aqueous solution of Analar grade lead nitrate. The precipitated lead sulphide was repeatedly washed with distilled water to remove any unprecipitated lead nitrate. The precipitate was in the form of a very fine powder suitable for diffractometric work.

Diffractograms were obtained with a Siemens diffractometer using Mo radiation and a krypton-

filled halogen-quenched G.M. counter. The linear response of the diffractometer was checked by a preliminary experiment with a set of standard Al foils. A  $2\theta$  scan was adopted.

Integrated intensities of ten reflections were repeatedly and independently measured and were corrected for thermal diffuse scattering according to the Chipman-Paskin procedure<sup>3</sup>. Theoretical intensities were calculated according to the relation:

$$I_o = \text{constant (L.P.) } j F^2$$

where L.P. is the Lorentz-polarization factor,  $j$  the multiplicity factor and  $F$  the structure factor. It may be mentioned that for a flat sample and for the geometry of the diffractometer, the absorption correction is the same for all reflections and is therefore lumped with the constant. Lead sulphide has the sodium chloride structure. As such, the structure factor is given by:

$$F = 4(f_{ph} + f_s) \text{ for even reflections}$$

$$F = 4(f_{ph} - f_s) \text{ for odd reflections}$$

where the  $f$ 's are the atomic scattering factors. Since there is some doubt<sup>4</sup> about the nature of the bonding in lead sulphide, the intensities were calculated using atomic scattering factors corresponding to (a) neutral atoms and (b) doubly charged ions. As recommended by Cromer<sup>5</sup>, Dirac-Slater atomic scattering factors given by Cromer and Waber<sup>6</sup> were used for Pb and for  $Pb^{++}$  and those given in the *International Tables for Crystallography* (1962) for  $S^{--}$ . The atomic scattering factors for neutral sulphur also were taken from Cromer and Waber<sup>6</sup>. All these atomic scattering factors were corrected for anomalous dispersion<sup>7</sup>.

The values of  $\log I_o/I_c$  were plotted against  $\sin^2 \theta/\lambda^2$ . These plots are shown in Fig. 1. There are slight differences in the values of  $I_o/I_c$  corresponding to the two sets of atomic scattering factors. However, the slopes of the two plots agree within limits of experimental errors. The slope, which equals twice the Debye factor  $B$ , was determined by a least squares procedure. The r.m.s. amplitude of vibration was evaluated from  $B$  by using the relation:

$$B = (8\pi^2/3)u^2$$

The Debye temperature ( $\theta$ ) was evaluated from  $B$  by the use of the Tables of Integral Functions compiled by Benson and Gill<sup>8</sup>. The results are summarised in Table I. The present X-ray study leads to an average value of  $150 \pm 6^\circ$  K for the Debye temperature of lead sulphide and to a value of 0.22 Å for the mean amplitude of vibration. These values pertain to the room temperature,