

In an earlier publication⁴ it is mentioned that one requires skill and experience to determine mode angles of a thin film, while observing *m*-lines. But the observation of back scattered *m*-lines as used in our study enables one to locate the angle at which coupling takes place easily and confidently. So, we feel that this technique offers a significant improvement in measurement of mode angles of thin film optical waveguides.

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EXCITED STATE DIPOLE MOMENT OF ACRIDINE ORANGE

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In a previous note, the effect of solvent on the polarization of fluorescence of acridine orange was reported¹. The effect of solvent on excitation and fluorescence spectra of acridine orange has further been investigated to obtain information about the change in dipole moment of the molecule on excitation from the ground state to the next higher singlet state. The excited state dipole moment can be estimated by measuring Stoke's shift in different solvents and making use of the following theoretical relations given by Bakshiev² and Chamma and Viallet³.

Bakshiev's formula is :

$$\begin{aligned} \bar{\nu}_e - \bar{\nu}_f &= \frac{2\Delta\mu^2}{\bar{a}^3 hc} \left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right) \frac{2n^2+1}{n^2+2} \\ &= \frac{2\Delta\mu^2}{\bar{a}^3 hc} F_1(D, n) \end{aligned} \quad (1)$$

where $(\Delta\mu)^2 \approx (\mu_e - \mu_g)^2$. (Kawski *et al.*⁴), μ_e and μ_g are dipole moment in the ground and excited emitting state, '*a*' is the Onsager cavity radius, '*D*' and '*n*' are the solvents, dielectric constants and refractive index.

Chamma and Viallet's³ formula is :

$$\begin{aligned} \frac{\bar{\nu}_e + \bar{\nu}_f}{2} &= \frac{-2(\mu_e^2 - \mu_g^2)}{\bar{a}^3 hc} \left[\frac{2n^2+1}{2(n^2+2)} \left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right) \right. \\ &\quad \left. + \frac{3(n^2-1)}{2(n^2+2)^2} \right] = \frac{-2(\mu_e^2 - \mu_g^2)}{\bar{a}^3 hc} F_2(D, n). \end{aligned} \quad (2)$$

Stoke shift $\bar{\nu}_e - \bar{\nu}_f$ and $\bar{\nu}_e + \bar{\nu}_f/2$ in a series of solvents are plotted according to eqs. (1) and (2), yielding slopes S_1 and S_2 , which then given the value of $\Delta\mu$ as equations (1) and (2) can be used simultaneously.

In the present investigation, the absorption and fluorescence frequency shifts are measured for Acridine Orange in different solvents for a constant concentration $\sim 10^{-6}$ g/cc at temperature 25°C using Aminco Bowman spectrophotofluorometer. Acridine orange used was of spectroscopic grade purity and the solvents used were of AR quality obtained from BDH/EM and were further checked by absorption studies for any possible contamination. The concentration was kept low to minimise reabsorption of the emitted light and the possible changes in the wavelength due to inner filter effect. The entrance and exit slits of the spectrophotofluorometer were adjusted to give a reasonably good signal for detection and also a good resolution. For absorption and emission wavelengths the accuracy of wavelength measured is of the order of ± 2 nm. The effect of scattering and background for each solvent was checked separately using pure solvent in the cuvette and was found to be less than 0.5%. Necessary corrections for the nonuniform spectral emission of xenon lamp and nonlinear response of the photomultiplier tube (IP 21) were applied⁵⁻⁶. The peak absorption and emission wavelengths were located and the results are given in Table I.

Plots of $\bar{\nu}_e - \bar{\nu}_f$ versus F_1 and $\bar{\nu}_e + \bar{\nu}_f/2$ versus F_2 are shown in Figs. 1 and 2. As these plots are linear, they lend support to the Bakshiev's and Chamma, Viallet's theory^{2,3} as given in relations (1) and (2). The slopes of these lines in Fig. (1) and Fig. (2) are $S_1 = 1859.55$ and $S_2 = -1974.34$ respectively (using least square fit method). With these values of S_1 and S_2 and using the equations (1) and (2), the estimated value for the excited state dipole moment of acridine molecule is

$$\mu_e \sim 33\mu_g.$$

The solvent perturbation data given in Table I along with Kasha's test⁷, is helpful in identifying whether the transition is $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$. As the

TABLE I

Solvent	λ_a (nm)	λ_f (nm)	$\bar{\nu}_a$ cm^{-1}	$\bar{\nu}_f$ cm^{-1}	$\bar{\nu}_a - \bar{\nu}_f$ cm^{-1}	$\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ cm^{-1}	$F_1(D, n)$	$F_2(D, n)$
1. Water	484	524	20661	19084	1527	19872.5	0.91	0.68
2. <i>n</i> -butanol	482	514	20747	19455	1292	20101.0	0.77	0.65
3. Methanol	482	518	20747	19305	1442	20026.0	0.85	0.65
4. Iso amyl alcohol	486	518	20576	19305	1271	19940.5	0.73	0.64
5. Formamide	484	525	20661	19078	1583	19854.5	0.89	0.75
6. Acetone	493	522	20408	19157	1256	19782.5	0.79	0.64
7. Acetic anhydride	492	526	20325	19011	1314	19668.0	0.78	0.75
8. Ethanol	480	516	20833	19380	1453	20106.5	0.82	0.66

electron charge distribution of a $\pi \rightarrow \pi^*$ excited state is more extended than that of the ground state, the excited state is more polarizable. Change to a polar from a non-polar media increases the solvent interaction with both states but the corresponding decrease in energy is greater for the excited state resulting in a red shift. On the other hand, a $n \rightarrow \pi^*$ transition gives rise to a blue shift. From Table I it is clear that in the present case as the dipole moment of the solvent increases the $\bar{\nu}_f$ shifts towards red side. This indicates a $\pi \rightarrow \pi^*$ transition and is in conformity with such a transition in other dye molecules.

Present investigations of fluorescence of acridine orange, in addition to the conformation of theoretical

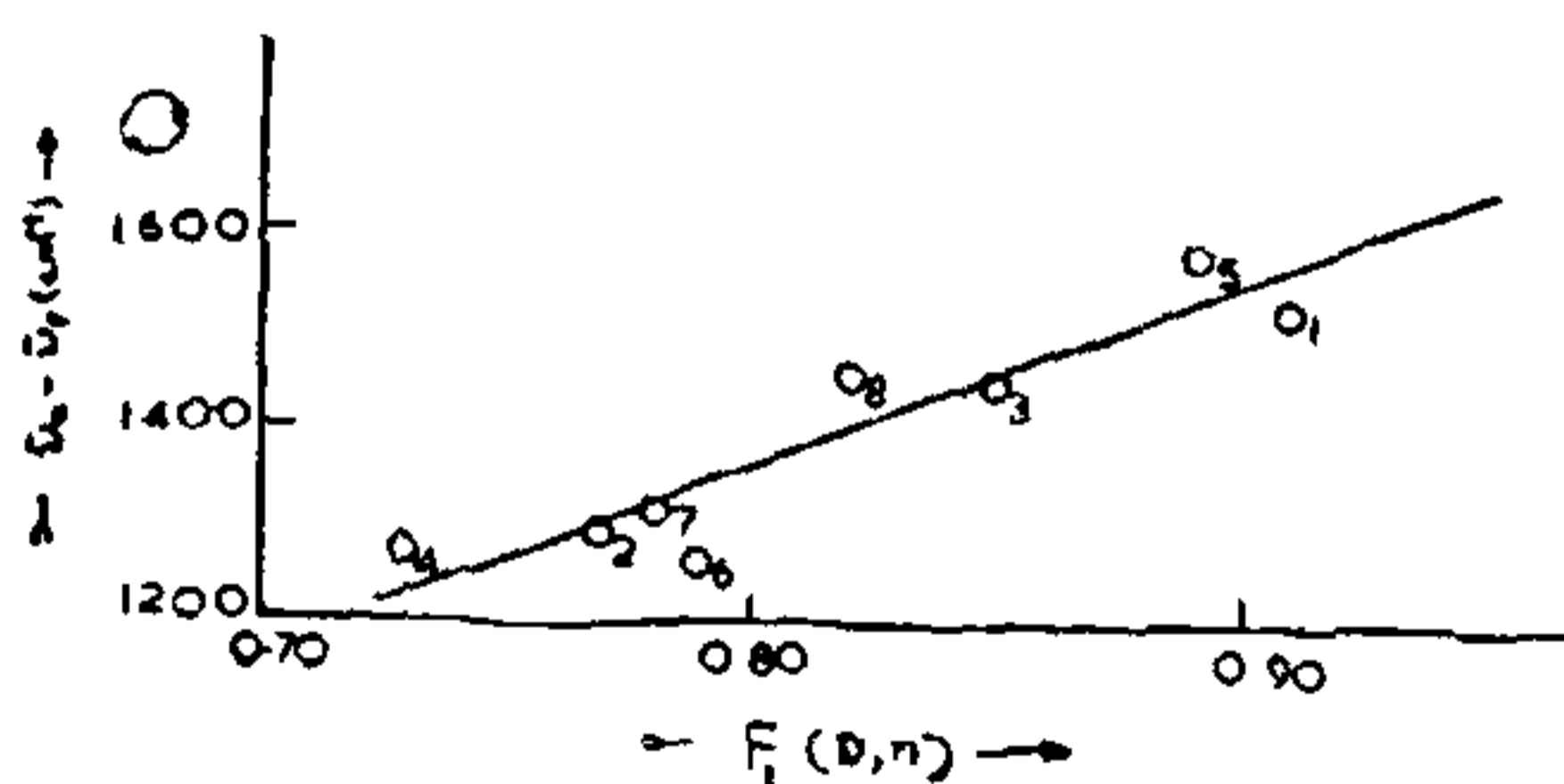


FIG. 1

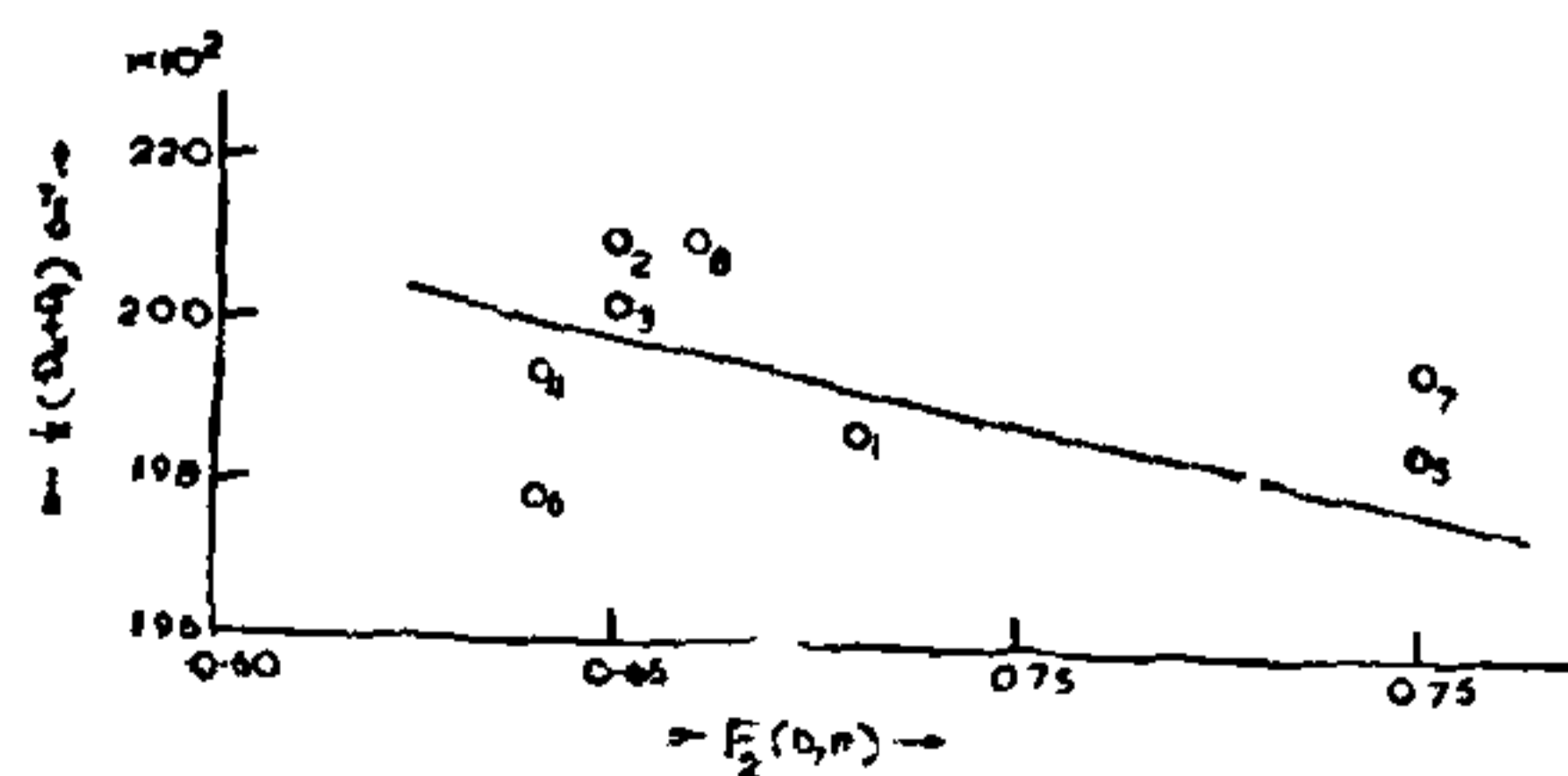


FIG. 2

prediction on solvent effect, leads to the following information :

- (a) The dipole moment of the acridine molecule increases on excitation.
- (b) The excited state dipole moment $\mu_e \sim 33 \mu_D$.
- The absorption and emission in acridine molecule results due to $\pi \rightarrow \pi^*$ transition.

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THE SUPERCONDUCTIVITY OF YRh_4B_4 —AN ENIGMA

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The reentrant behaviour of ErRh_4B_4 type ternary borides has created a considerable interest in these materials and there have been extensive studies of superconductivity and magnetic order in this class of rhodium-boride compounds containing a rare earth element with a localized magnetic moment. Recently