Short Communication

State of polarization of monomer and eximer emission from pyrene

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The phenomenon of eximer fluorescence has been studied extensively since Förster and Kasper [1] discovered the concentration dependent association of the electronically excited pyrene molecule with another pyrene molecule in its ground state. It has also been suggested [2] that a sandwich configuration of the two molecules is a necessary condition for the observation of eximer fluorescence. This model automatically suggests that the eximer fluorescence should be polarized at right angles to the monomer fluorescence, which is polarized in the plane of the pyrene molecule. This point may be settled by the measurement of depolarization factor, ρ, of the monomer and eximer fluorescence in a rigid glass medium. According to Perrin–Joblonski [3] theory if the angle between the absorption and emission oscillators be β, then the depolarization factor ρ for unpolarized exciting light is given by:

$$\frac{I_\| - I_\perp}{I_\| + I_\perp} = \rho = (3 \cos^2 \beta - 1)/(7 - \cos^2 \beta)$$
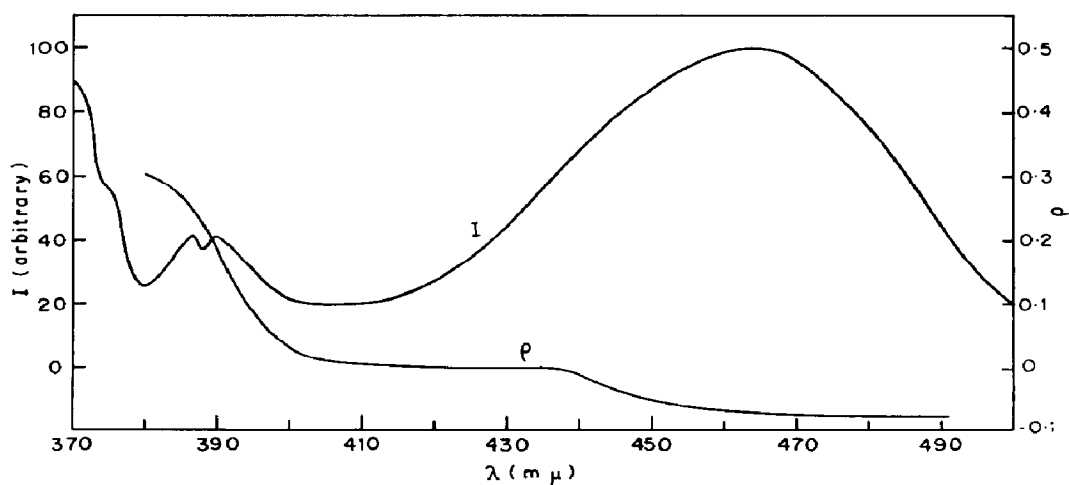

Fig. 1.

Since the π electronic absorption is polarized in the plane of the pyrene molecule, we conclude that ρ should vary between $+1/3$ and $-1/7$ for monomer and eximer emission. Measurement of ρ has been made over the monomer and eximer emission band of 10^{-2} M solution of pyrene in 22% polystyrene in benzene (the system was practically solid glass). The results are given graphically in Fig. 1. It may be observed that ρ passes from a positive to a negative value while going from the monomer to the eximer emission band and the extreme values of ρ lie very close to the theoretical values. This definitely supports the accepted configuration of the eximer.

1 T. Förster and K. Kasper, Z. Electrochem., 59 (1955) 977.
2 J. Ferguson, J. Chem. Phys., 28 (1958) 765; B. Stevens, Spectrochim. Acta, 18 (1962) 439.
3 F. Perrin, Ann. Phys., 17 (1932) 283.