Journal of Photochemistry, 3 (1974) 247 - 248

Short Communication

Solvent effect on eximer emission from pyrene

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(Received May 21, 1974)

Although extensive experimental [1] and theoretical [2] work has been done on eximer fluorescence, the nature of intermolecular interaction in these complexes is incompletely understood. Most of the existing theories

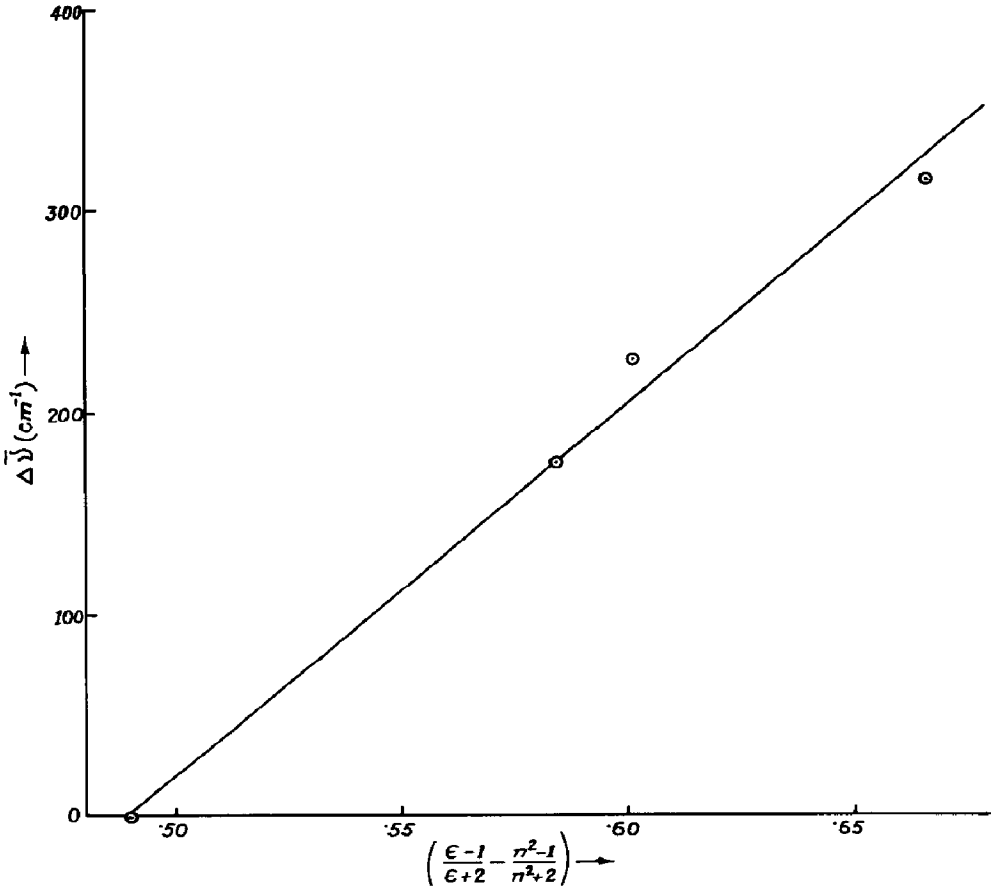

Fig. 1. Shift in eximer emission with dielectric constant.

make the eximers non-polar. Since the ground states of the hydrocarbons are definitely non-polar, there should be a characteristic shift in the emission spectra with high dielectric solvents if the eximer be polar [3]. It has further been shown that if the excited state be more polar than the ground state then a linear relationship should exist between $\Delta\tilde{\nu}$ $(=\tilde{\nu} - \tilde{\nu}_0)$ and $[(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)]$, where ϵ and n are the dielectric constant and refractive index respectively of the solvent and $\tilde{\nu}$ and $\tilde{\nu}_0$, the emission peak in solution and in vacuum. With this object in view the eximer emission spectra of pyrene were measured in media of dielectric constants ranging from 2.2 to 35.0, the $\tilde{\nu}$ value in medium of $\epsilon = 2.2$ being taken as the gas phase value. As our instrument could measure the wavelength shift with an accuracy of 60 cm^{-1}, the shift was practically zero in medium $\epsilon = 12.0$ The plot of $\Delta\tilde{\nu}$ *vs.* $[(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)]$ (Fig. 1) was found to be linear. Using the reaction field concept of Onsagar, the slope of the curve could be equated to μ_e^2/a^3 where a is Onsager's cavity radius, calculated from the molar volume of the solute, and μ_e is the dipole moment of the eximer. μ_e calculated by this method was found to be 2.46 D. If we assume that the eximers are stabilized by admixture of charge transfer state with exciton state, *i.e.*,

$$\psi = a\,AA^* + b(A^+ - A^-)$$

then the estimated dipole moment suggests that the eximers have 84% exciton and 16% charge transfer character.

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