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Fluorescence Lifetime of Pyrene in Different Solvents

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As has been reported in a previous paper,[1] the forbidden components in the vibrational structures of the absorption and fluorescence spectra of aromatic hydrocarbons are markedly enhanced in very polar solvents. These intensity enhancements have been shown to be well correlated with the dielectric property of the solvent. It is known that the radiative lifetime of the fluorescence can be estimated using the theoretical relation[2-4] from the integral of the corresponding absorption spectrum. Experimentally it is determined from the observed fluorescence lifetime and quantum yield.[2] It is supposed that the intensity enhancements by solvents may be accompanied by a decrease in the radiative lifetime. Under these circumstances, it is of interest to study the applicability of the relation

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[1] A. Nakajima, This Bulletin, **44**, 3272 (1971).

[2] J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970).

[3] S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 79 (1962).

[4] J. B. Birks, *Proc. Roy. Soc., Ser. A*, **275**, 135 (1963).

Table 1. Fluorescence lifetimes (τ) of pyrene in three solvents

Excitation Concentration	Air-gap discharge 9.7×10^{-6} M	Ruby laser 9.7×10^{-6} M	Ruby laser 1.07×10^{-4} M
	τ (ns)		
Cyclohexane	408± 5	338± 9	369±11
1,2-Dichloroethane	202± 3	170±12	187± 4
Dimethyl sulfoxide	275±11	233± 8	238± 6

and the change in the radiative rate.

In this work, the fluorescence lifetimes were measured at various vibronic bands in three representative solvents, and the radiative rate constants calculated from the observed lifetimes and quantum yields were compared with those estimated from the integrated absorption spectra. In addition, on the basis of the constancy of the fluorescence lifetimes over the vibronic band system, it was confirmed that there was no appreciable specific interaction between the solute and solvent molecules.

Experimental

The fluorescence lifetimes were measured by excitation with the frequency-doubled light pulses from a Q-switched ruby laser (a duration of ~20 ns, 3472 Å) and with the UV light pulses from an air-gap discharge (a duration of ~10 ns). An about 2% mesh filter was used for attenuation of the strong exciting laser light. The fluorescence emission was detected with a Hamamatsu TV R-446 photomultiplier through a Hitachi G-3 grating monochromator. The slit width of the monochromator was less than 3 mμ for the laser excitation and 10 to 30 mμ for the discharge excitation. The fluorescence decay curves were displayed on an Iwasaki SS-112 synchroscope and photographed. The lifetimes were estimated from the photographs, the analyses of which gave most part of errors of about 10 ns.

The fluorescence spectra were measured with a Hitachi MPF-2A spectrofluorometer. The absolute quantum yields of pyrene fluorescence in various solvents were calculated assuming the value of 0.65[5] in a degassed cyclohexane solution from the relative yields, which were evaluated from the areas under the corrected fluorescence spectra.

The concentrations of the solutions were 9.7×10^{-6} and 1.07×10^{-4} M. The solutions used were thoroughly deaerated by the usual method of freeze-pump-thaw cycles.

Pyrene was purified by recrystallization, zone-refining, and vacuum sublimation. Super-special grade cyclohexane, G. R. grade 1,2-dichloroethane, and spectroscopic grade dimethyl sulfoxide were used without further purification. The purities of pyrene and these solvents were checked by measuring the fluorescence and excitation spectra.

Results and Discussion

Since there are two kinds of components, solvent-sensitive and insensitive, in the vibronic band system, the possibility can be considered that the fluorescence decay times might be different between these components in various solvents. Thus, the lifetimes of pyrene fluorescence were measured at several vibrational band peaks in three solvents of different polarities. Table 1 gives the fluorescence lifetimes averaged over the vibronic band system with the maximum deviations. As seen from Table 1, the lifetimes measured by the laser excitation were appreciably shorter than those measured by the discharge excitation. This phenomenon may be much related to the bimolecular decay process due to the interaction between the excited molecules found by excitation at a high photon density.[6,7] In fact, a slight deviation from the single exponential curve could be observed in the initial time region. In cyclohexane and 1,2-dichloroethane by the laser excitation, the lifetimes in 1.07×10^{-4} M solutions are about 10% longer than those in 9.7×10^{-6} M solutions. This may be caused by the dissociation of excimers formed in a small amount due to the low viscosity of these solvents and the somewhat high concentration of the solutions. Weak excimer emission was actually observed in 1.07×10^{-4} M cyclohexane solutions.

In view of the considerable errors in the decay time analysis, the lifetimes given in Table 1 should be regarded as taking almost the same values in the whole region of the fluorescence spectrum in each solvent. If the solvent-enhanced bands are assumed to arise from some species such as a specifically solvated solute molecule or more unlikely, a complex formed between the solute and solvent molecules, the lifetimes observed at the solvent-sensitive bands might differ from those observed at the solvent-insensitive bands. However, the constant lifetimes obtained over the whole vibronic band system indicate the participation of a single species responsible for both these bands, in accord with the conclusions derived from the fluorescence spectra by excitation at different wavelengths and the excitation spectra by monitoring at various vibrational bands.

Since the intensities of the forbidden bands change in various solvents, the corresponding changes in the radiative rate can be expected. In general, the radiative rate constant, k_0, can be calculated from the observed fluorescence lifetime, τ, and the quantum yield, η, by the following relation:[2)]

$$k_0=\eta/\tau\,. \tag{1}$$

On the other hand, k_0 can also be estimated from the absorption spectrum of the first electronic transition by the well-known equation:[2–4)]

$$k_0=2.88\times10^{-9}n^2\bar{\nu}_0{}^2\int\varepsilon\mathrm{d}\bar{\nu}\,, \tag{2}$$

where ε is the molar extinction coefficient and n is the

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6) H. Masuhara and N. Mataga, *Chem. Phys. Lett.*, **7**, 417 (1970).

7) T. Kobayashi, K. Yoshihara, and S. Nagakura, *Mol. Phys.*, **21**, 573 (1971).

Table 2. Radiative rate constants (k_0) estimated by Eqs. (1) and (2)

Solvent	k_0 (s^{-1})	
	(1)	(2)
Cyclohexane	1.6×10^6	1.9×10^6
1,2-Dichloroethane	1.8×10^6	2.1×10^6
Dimethyl sulfoxide	2.0×10^6	2.6×10^6

refractive index of the solvent. $\bar{\nu}_0$ was taken to be the wave number of the 0–0 band. This simplified formula[2] was used in view of the accuracy of the present results.

In Table 2, the values of the radiative rate constants evaluated by Eqs. (1) and (2) are given. In spite of the large errors inherent to the evaluations, the agreement between the values obtained by these two different methods is good. Though the applicability of Eq. (2) to weak or forbidden transitions may be questionable,[3] it can be well employed for an order estimation, including the cases of enhancements by solvents.

As seen from Table 2, the k_0 values increase appreciably on going from cyclohexane to dimethyl sulfoxide, corresponding to the enhancements of the forbidden bands with the increase in the solvent polarity. In a highly polar solvent, the contribution of the forbidden components to the vibronic band system can be comparable to that of the vibronically allowed components, indicating that the intermolecular perturbation by solvent can become as important as the intramolecular perturbation due to vibronic coupling.