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Time-resolved Emission Spectra of 2-Acetylanthracene/Methanol/Hexane System. Evidence for the Photoassociation of a 1 : 2 Hydrogen Bonded Complex

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Synopsis. The deconvolved time-resolved emission spectra of 2-acetylanthracene in hexane containing 0.1 mol dm^{-3} of methanol revealed a considerable time-dependent spectral shift associated with the photoassociation of the hydrogen-bonded complex which includes two methanol molecules.

The photodynamics of solvent-solute interaction have been extensively investigated. It is of particular interest that the fluorescence spectra of aromatic compounds, such as heterocycles, amines, and ketones, in nonpolar solvents are significantly perturbed by the addition of small amounts of polar solvents (<1% by volume).[1-8] This fluorescence perturbation is due to a specific solvent-solute interaction giving rise to a hydrogen-bonded (H-bonded) complex and/or an exciplex. Acylanthracenes are suitable for the purpose of this investigation, because their fluorescence characteristics (intensity, lifetime, and emission maximum) are very sensitive to the addition of alcohols to the nonpolar solutions.[9,10] This communication describes the time-resolved emission spectra (TRES) of 2-acetylanthracene (**2A**) in hexane containing 0.1 mol dm^{-3} of methanol at 20 °C under an air atmosphere. The results obtained are in excellent consistence with a photostationary study which indicated that at least two methanol molecules participate in the complex formation in the excited singlet state.[10b]

Experimental

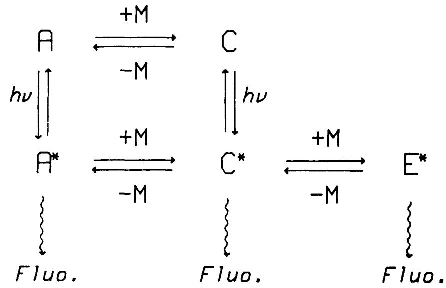
2A was the same as that used previously.[10] The hexane and methanol were Spectro- and GR-grade reagents, respectively. To a 3 cm^3 hexane solution of **2A** (3×10^{-5} mol dm^{-3}) was added 1.4×10^{-2} cm^3 of methanol. The nanosecond decay curves and corrected steady-state fluorescence spectra were obtained similarly to those described previously.[11] The fluorescence decay curves collected at every 5 nm from $\lambda=400$ to 520 nm were subjected to deconvolution analysis by an iterative nonlinear least squares method.[11] The decay function, $i(\lambda, t)$, was chosen to be a sum of three exponential terms,

$$i(\lambda,t)=\sum_{j}^{3}C_j(\lambda)\cdot\exp\{-t/\tau_j(\lambda)\}$$

where $C_j(\lambda)$ and $\tau_j(\lambda)$ were treated as free parameters. This decay function gave a good fit between the observed and simulated decay curves at every wavelength and the three decay times were found to be 11±1.6, 4.9±0.1, and 2.1±0.9 ns. The value of $C(\lambda)$ associated with the shortest decay time was negative at wavelengths above 490 nm and at the red end, $i(\lambda, t)$ showed a typical rise and decay, indicating that a large portion of the long wavelength emission results from an excited-state reaction. The deconvolved TRES were constructed by multiplying $i(\lambda, t)/\sum_{j}^{3}C_j(\lambda)\tau_j(\lambda)$ by the corrected total fluorescence spectrum at the corresponding wavelength.[12,13]

Results and Discussion

Figure 1 shows the deconvolved TRES obtained at four delay times. These spectra are normalized at the maximum intensity. Time-dependent spectral shifts are clearly evident, whereas little spectral shift could be detected by convolved spectroscopy.[10b] The TRES in Fig. 1 can be compared with the spectra of the fluorescence origins which have been assigned to the system concerned, as shown in the following reaction scheme;[10b]



where M, A, C, and E are methanol, an uncomplexed **2A**, a 1 : 1, and a 1 : 2 complex respectively. Figure 2 shows the normalized steady-state fluorescence spectra of C and E obtained from the photostationary study, together with that of A, which is assumed to be the same as in pure hexane.

The spectrum at 24.3 ns shown in Fig. 1 has a remarkable resemblance to spectrum E shown in Fig. 2. In fact, this component spectrum is dominant even at 6—7 ns delay times. On the other hand, the TRES at shorter delay times can not be matched identically with

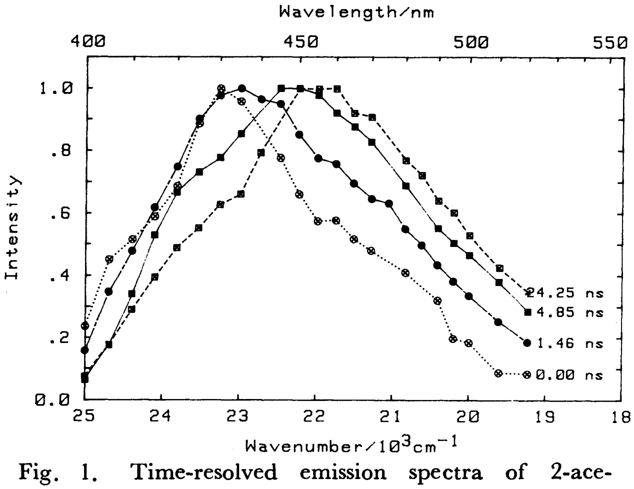


Fig. 1. Time-resolved emission spectra of 2-acetylanthracene in hexane containing 0.1 mol dm^{-3} of methanol at 20 °C. Normalized at the maximum intensity.

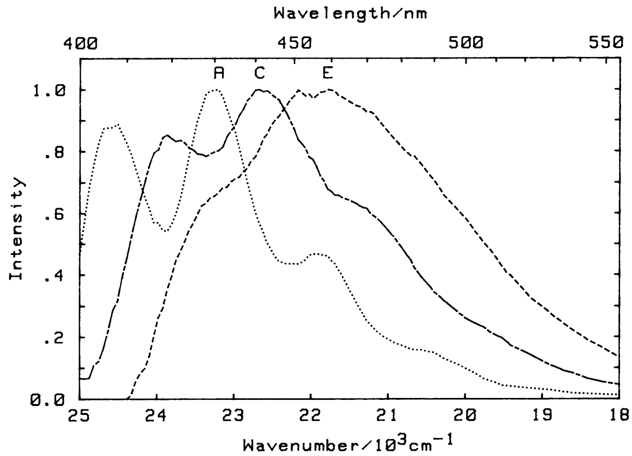


Fig. 2. Fluorescence spectra of three component origins involved in a 2-acetylanthracene/methanol/hexane system; A) an uncomplexed, C) a 1 : 1 complex, and E) a 1 : 2 complex. Normalized at the maximum intensity.

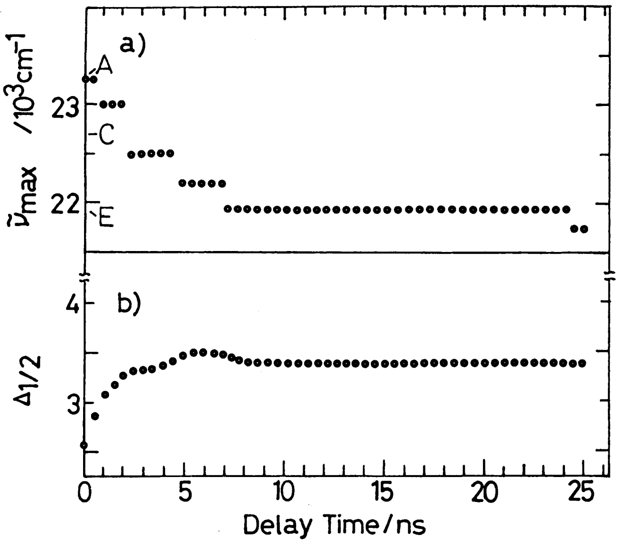


Fig. 3. Time-dependent changes in a) emission maxima ($\tilde{\nu}_{max}$) and b) half bandwidths ($\Delta_{1/2}$) of the TRES observed.

the individual component spectrum, but they can be simulated by superimposing the spectra from selected component sources with a variety of their contributions which depend on the delay time. Indeed, the TRES at 4.85 and 1.46 ns are approximately identical with the spectrum of C plus E (the relative fluorescence intensity of E to C, $F_{E/C}\simeq 1$) and of A plus C ($F_{C/A}\simeq 3.5$), respectively. It can be safely said that the contribution from E* is negligible for the TRES at delay times <2 ns. The spectrum at t_0 itself contains a considerable contribution from C* as well as from A* ($F_{C/A}\simeq 2$). This may result from the static formation of C prior to the pulse excitation.[14] About 1.7 times increase in the relative contribution from C* at 1.46 ns suggests that the dynamic formation of this component is important in this time region. It is also probable that at the longer delay times, the formation of E* prevails at the expense of C*.

The emission maxima, $\tilde{\nu}_{max}(t)$, and half bandwidths, $\Delta_{1/2}(t)$, of the observed TRES are shown in Figs. 3a and 3b, respectively. The emission maxima of the three components (A, C, and E) are also shown in Fig. 3a. From this figure, it is clear that the spectral relaxation of the TRES is substantially complete in 10 ns with the relaxed $\tilde{\nu}_{max}$ reaching the energy level of E. As is shown in Fig. 3b, $\Delta_{1/2}(t)$ first increases rapidly, then more slowly to a maximum value; later it decreases to a plateau value corresponding to the half bandwidth of the spectrum of E (*ca.* 3900 cm^{-1}), This variance of $\Delta_{1/2}(t)$ occurs just in the time period at which the spectral relaxation is occuring. These facts indicate that the observed TRES reflect the photodynamics of the specific H-bond interaction.

In conclusion, the excellent agreement between the photostationary and photodynamic studies strongly supports the validity of the reaction scheme postulated, which describes a step-wise photoassociation of the H-bonded complexes. It appears likely that the photoassociation of C occurs during the first 2 ns, followed by the formation of E. Finally, it should be mentioned that little effect on the fluorescence of **2A** could be detected when the methanol was replaced by acetonitrile. This confirms that H-bonding is responsible for the interaction. In pure methanol, the photostationary fluorescence of **2A** showed a large red-shift due to the combination of the specific H-bonding and nonspecific solvent relaxation.[10] However, the latter effect may be negligible for the present system and if any, the ultra fast relaxation of the surrounding solvent ($\approx 10^{-11}$ s) could not be associated with the TRES observed in the ns domain.

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14) From absorption measurements, the static formation of C amounts to *ca.* 20% (*i.e.*, [C]/[A]$\simeq$0.27) under the experimental conditions, indicating that the fluorescence efficiency of C is about 7 times greater than that of A. This fluorescence enhancement is the result of the inhibition of the intersystem crossing due to the displacement of the singlet energy level.[10,11]