Excimer Parameters of Anisole

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Fluorescence spectra of anisole at various concentrations and temperatures were measured. Using a standard, the molecular quantum efficiency was obtained. Ours and literature data were analysed to determine the rate parameters and other properties of the anisole excimer-monomer system.

1. Introduction

Knowledge of the excimer (E) parameters of anisole (A) is interesting because A is an effective solvent in liquid scintillators. A-excimers as well as A-monomers can be the excitation energy donors at high concentrations of A in scintillating solutions.

In this paper we determined the UV excited *E* parameters of A. We investigated the concentration change of the fluorescence spectra (FS) of A in 1,4-dioxane (D) and the temperature change of the FS of neat A. Moreover we found the molecular quantum efficiency (q_M).

2. Experimental

A was synthesized according to [1] using phenol as a substrate. The purity of the final product was checked with liquid chromatography.

The solutions of A in 1,4-dioxane (for spectroscopy) were deoxygenated.

The FS, excited at 265 nm, were measured stationary [2] under equal conditions, corrected for the spectral response and normalized to the amount of light absorbed. The effect of fluorescence reabsorption under the given experimental conditions could be neglected [3].

The temperature measurements of the FS were made as in [4].

We determined the q_M by comparing the areas under the FS of a standard (quinine sulphate) and 0.09 mole/l A in D. To evaluate q_M the necessary corrections were made [5, 6].

3. Results and Discussion

Figure 1 shows both the fluorescence spectra of A obtained for four concentrations and the pure molecular (M) and excimer (E) fluorescence bands. M is the spectrum of 0.09 mole/l A in D, and the spectrum E

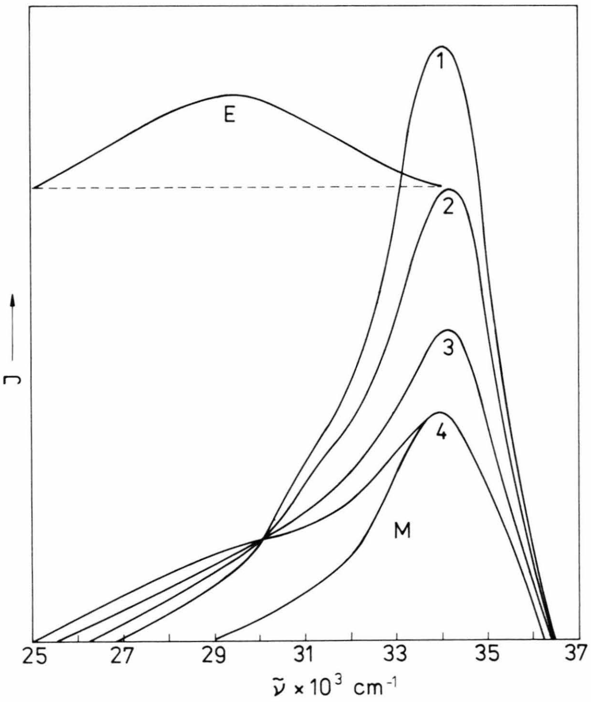

Fig. 1. Fluorescence spectra for four concentrations of anisole in 1,4-dioxane. 1: 2.3, 2: 4.6, 3: 6.9, 4: 9.2 mole/l. E: excimer band, M: monomer band.

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Table 1. Experimental excimer and molecular properties of A at 293 K. Concentrations are given in molalities M. Last column: Data from [9].

K	$[\mathrm{M}^{-1}]$	0.06 ± 0.01	0.12
c_h	[M]	3.6 ± 0.4	–
q_M		0.36 ± 0.04	–
K_e	$[\mathrm{M}^{-1}]$	0.16 ± 0.02	0.29
e		0.59 ± 0.03	–
q_E		0.07 ± 0.01	–
$k_\mathrm{E}/k_\mathrm{M}$		2.0 ± 0.02	0.9
$k_\mathrm{FE}/k_\mathrm{FM}$		0.39 ± 0.04	0.41

Table 2. Excimer parameters of A calculated from experimental and literature [6] data. Last column: Data from [9].

$k_\mathrm{IE}/k_\mathrm{IM}$		2.9 ± 0.3	–
k_IE	$10^8\ [\mathrm{s}^{-1}]$	2.3 ± 0.3	–
k_E	$10^8\ [\mathrm{s}^{-1}]$	2.4 ± 0.3	1.7
k_FE	$10^7\ [\mathrm{s}^{-1}]$	1.4 ± 0.2	–
k_EM	$10^8\ [\mathrm{s}^{-1}\,\mathrm{M}^{-1}]$	3.1 ± 0.3	0.8
k_ME	$10^9\ [\mathrm{s}^{-1}]$	2.0 ± 0.2	0.3

is obtained by subtraction of the spectrum M from the total spectrum of neat A (see [7]). Having the areas ϕ under the spectra, we obtained the relative E/M fluorescence yield $K = (\phi_\mathrm{E}/\phi_\mathrm{M})\, c^{-1}$, where c is the concentration of A in D (Table 1).

The dependence of the intensity of the A molecular fluorescence peak I_M° (at $\tilde{\nu}_\mathrm{M}^\circ = 33.5 \cdot 10^3\ \mathrm{cm}^{-1}$) on c obeys the Stern-Volmer relation. Thus we can determine the half value concentration c_h of A in D (Table 1) [8].

When the temperature is changed (within 263 to 353 K), I_M° depends linearly on I_E° (the intensity of excimer fluorescence peak at $\tilde{\nu}_\mathrm{E}^\circ = 28.5 \cdot 10^3\ \mathrm{cm}^{-1}$). Then the rate parameters of excimerization k_EM and dissociation k_ME fulfill the condition $k_\mathrm{EM}c,\ k_\mathrm{ME} \gg k_\mathrm{E}$, k_M, where k_E, k_M are the deactivation rate parameters of the E and M states, respectively. Thus the equilibrium constant of excimerization $K_\mathrm{e} = k_\mathrm{EM}/k_\mathrm{ME} = 1/c(-\mathrm{d}I_\mathrm{M}^\circ/\mathrm{d}I_\mathrm{E}^\circ)(I_\mathrm{E}^\circ/I_\mathrm{M}^\circ)$, where $(-\mathrm{d}I_\mathrm{M}^\circ/\mathrm{d}I_\mathrm{E}^\circ)$ is the slope of the experimental straight line $I_\mathrm{M}^\circ = 5.8 - 4.6\, I_\mathrm{E}^\circ$ [4]. The value of K_e enables us to calculate the relative fractions of monomers $m = M^*/(M^* + E)$ and excimers $e = E/(M^* + E)$ (M^* and E are the concentrations of excited monomers and excimers) from the relation $e = K_\mathrm{e}c(1 + K_\mathrm{e}c)^{-1}$ and $m = 1 - e$ [5].

The quantum efficiency of E fluorescence q_E was determined from the relation $\phi = \phi_\mathrm{M} + \phi_\mathrm{E} = m q_\mathrm{M} + e q_\mathrm{E}$.

The ratios of the E/M radiative ($k_\mathrm{FE}/k_\mathrm{FM}$) and deactivation ($k_\mathrm{E}/k_\mathrm{M}$) rate parameters are given by $k_\mathrm{FE}/k_\mathrm{FM} = K/K_\mathrm{e}$ and $k_\mathrm{E}/k_\mathrm{M} = c_\mathrm{h} K_\mathrm{e}$, respectively. The values of e, q_E, $k_\mathrm{E}/k_\mathrm{M}$ and $k_\mathrm{FE}/k_\mathrm{FM}$ are presented in Table 1.

The ratio of nonradiative E/M rate parameters equals $k_\mathrm{IE}/k_\mathrm{IM} = k_\mathrm{FE}/k_\mathrm{FM}(q_\mathrm{E} - 1/q_\mathrm{M} - 1)$ (see Table 2).

Using the data of τ_M and τ_FM (τ_M is the decay time and τ_FM the natural lifetime) according to [6] we calculated $k_\mathrm{M} = 1/\tau_\mathrm{M} = 1.2 \cdot 10^8\ \mathrm{s}^{-1}$, $k_\mathrm{FM} = 1/\tau_\mathrm{FM} = 3.7 \cdot 10^7\ \mathrm{s}^{-1}$ and $k_\mathrm{IM} = k_\mathrm{M} - k_\mathrm{FM}$. Having the k_M, k_FM and k_IM we estimated the values of k_FE, k_E, and k_IE (Table 2).

The values of k_EM and k_ME we calculated from the relations $K_\mathrm{e} = k_\mathrm{EM}/k_\mathrm{ME}$ and $c_\mathrm{h} = k_\mathrm{M}(k_\mathrm{E} + k_\mathrm{ME})/k_\mathrm{E}\, k_\mathrm{EM}$ (see Table 2).

We can compare some of our results with those of Joneleit obtained for electron excitation [9] (see Tables 1 and 2). Evidently our $k_\mathrm{FE}/k_\mathrm{FM}$ value agrees with that of Joneleit, but our k_EM and k_ME values differ remarkably from those obtained by Joneleit. They are, however, similar to those for toluene [10].

Our values of k_EM and k_ME will be used to explain the role of excimers as donors in the excitation energy transfer in liquid scintillators.

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