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 (qM).

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 qM by comparing the areas under the FS of a standard (quinine sulphate) and 0.09 mole/l A in D. To evaluate qM 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.](image_url)
Table 1. Experimental excimer and molecular properties of \( A \) at 293 K. Concentrations are given in molalities \( M \). Last column: Data from [9].

<table>
<thead>
<tr>
<th>Property</th>
<th>( K ) ( [M^{-1}] )</th>
<th>( c_h ) ( [M] )</th>
<th>( q_M )</th>
<th>( K_e ) ( [M^{-1}] )</th>
<th>( c_e )</th>
<th>( q_E )</th>
<th>( k_{FE}/k_{FM} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.06 ± 0.01</td>
<td>3.6 ± 0.4</td>
<td>0.36 ± 0.04</td>
<td>0.16 ± 0.02</td>
<td>0.59 ± 0.03</td>
<td>0.07 ± 0.01</td>
<td>2.0 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td></td>
<td>0.12</td>
<td>0.29</td>
<td>0.04 ± 0.01</td>
<td>0.16</td>
<td>0.39 ± 0.04</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( k_{FE}/k_{IM} )</th>
<th>( k_{FE} ) ( [s^{-1}] )</th>
<th>( k_{FM} ) ( [s^{-1}] )</th>
<th>( k_{ME} ) ( [s^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.9 ± 0.3</td>
<td>2.3 ± 0.3</td>
<td>3.1 ± 0.3</td>
<td>2.0 ± 0.2</td>
</tr>
</tbody>
</table>

is obtained by subtraction of the spectrum \( M \) from the total spectrum of neat \( A \) (see [7]). Having the areas \( \phi \) under the spectra, we obtained the relative \( E/M \) fluorescence yield \( K = (\phi_E/\phi_M) c^{-1} \), 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 \( \tilde{\nu}_M = 33.5 \cdot 10^3 \text{ cm}^{-1} \)) 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 \( \tilde{\nu}_E = 28.5 \cdot 10^3 \text{ cm}^{-1} \)). Then the rate parameters of excimerization \( k_{EM} \) and dissociation \( k_{ME} \) fulfill the condition \( k_{EM} \geq k_E, k_M \), where \( k_E, k_M \) are the deactivation rate parameters of the \( E \) and \( M \) states, respectively. Thus the equilibrium constant of excimerization \( K_e = k_{EM}/k_{ME} \) is obtained by subtraction of the spectrum \( M \) from the total spectrum of neat \( A \) (see [7]). Having the areas \( f \) under the spectra, we obtained the relative \( E/M \) fluorescence yield \( K = (\phi_E/\phi_M) c^{-1} \), where \( c \) is the concentration of \( A \) in \( D \) (Table 1).

The quantum efficiency of \( E \) fluorescence \( q_E \) was determined from the relation \( \phi = \phi_M + \phi_E = m q_M + c q_E \).

The ratios of the \( E/M \) radiative \((k_{FE}/k_{FM})\) and deactivation \((k_E/k_M)\) rate parameters are given by \( k_{FE}/k_{FM} = K/K_c \) and \( k_E/k_M = c_h K_e \), respectively. The values of \( e, q_E, k_E/k_M \) and \( k_{FE}/k_{FM} \) are presented in Table 1.

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Using the data of \( \tau_M \) and \( \tau_{FM} \) (\( \tau_M \) is the decay time and \( \tau_{FM} \) the natural lifetime) according to [6] we calculated \( k_{EM} = 1/\tau_M = 1.2 \cdot 10^8 \text{ s}^{-1} \), \( k_{FM} = 1/\tau_{FM} = 3.7 \cdot 10^7 \text{ s}^{-1} \) and \( k_{IM} = k_{IM} - k_{FM} \). Having the \( k_{FM} \), \( k_{EM} \) and \( k_{IM} \) we estimated the values of \( k_{FE}, k_E \), and \( k_{IF} \) (Table 2).

The values of \( k_{EM} \) and \( k_{ME} \) were calculated from the relations \( K_e = k_{EM}/k_{ME} \) and \( c_h = k_M(k_{EM}+k_{ME})/k_{EM} \) (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 \( k_{FE}/k_{FM} \) 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.

Acknowledgement

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