Effect of Acceptor Concentration upon Donor Fluorescence Decay and Quantum Yield *

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Z. Naturforsch. 35 a, 1030–1035 (1980); received June 27, 1980

The fluorescence decay times $\tau/\tau_0$ and quantum yields $\eta/\eta_0$ of rhodamine 6G (donor) in their dependence on the concentration of malachite green (acceptor) in ethanol were measured for the donor to acceptor concentration ratios $\gamma_D/\gamma_A = 3.48$ and 0.35. At fixed $\gamma_A$, the values of $\tau/\tau_0$ and $\eta/\eta_0$ are markedly lower for the systems with higher $\gamma_D/\gamma_A$.

The experimental results are compared with the theory of a multistep excitation energy transfer from donor to acceptor. Good agreement between theory and experiment was found for the critical distances $R_{OD} = 60.7 \AA$ and $R_{OA} = 69.3 \AA$ calculated from spectroscopic data. In the case of $\gamma_D/\gamma_A = 0.35$, the experimental results can also be properly described using the Förster-Galanin theory, whereas for the system with $\gamma_D/\gamma_A = 3.48$ the multistep energy transfer plays a significant role.

1. Introduction

The concentration effects in luminescent systems consisting of the donor (D) and acceptor (A) molecules, randomly distributed in space, afford valuable information on the nonradiative electronic excitation energy transfer (NEEET) from D* to A [1, 2]. In particular, this concerns the dependence of the donor photo-luminescence (PL) decay times $\tau$ on the concentration $C_A$ of the acceptor molecules. For a proper interpretation of the experimental results, it is indispensable to know the relation between $\tau$ and $C_A$. If the reduced acceptor concentration exceeds considerably that of the donor, i.e., when

$$\gamma_A > \gamma_D,$$  

and if NEEET occurs as the result of the dipole-dipole interaction, this relation is given by [3]

$$\frac{\tau}{\tau_0} = \frac{1 + \gamma_A^2 - (1.5 + \gamma_A^2) f(\gamma_A)}{1 - f(\gamma_A)},$$  

where

$$f(\gamma_A) = 2 \gamma_A \exp(\gamma_A^2) \text{erfc}(\gamma_A), \quad \gamma_A = \sqrt{\frac{\gamma_D}{\gamma_{OA}}},$$  

$\tau_0$ is the PL decay time for $C_A \to 0$, $C_{OA}$ the critical concentration and $\text{erfc}(\gamma_A)$ the complementary error function. In (2) the NEEET occurring in one step only from $D*$ to A is taken into account. However, if

$$\gamma_D \gg \gamma_A,$$  

then NEEET can occur by successive single-step process in the same manner as the concentration quenching by nonluminescent dimers [1, 4]. For a multistep NEEET process, the following equation for the PL decay time has been obtained recently [5]:

$$\frac{\tau}{\tau_0} = \frac{1 + \gamma_A^2 - (1.5 + \gamma_A^2) f(\gamma_A)}{1 - f(\gamma_A)} \left[1 - \frac{2 - \gamma_A}{\gamma} \frac{f(\gamma) + \gamma^2 - 0.5}{1 - f(\gamma)}\right],$$  

where

$$\gamma = \gamma_D + \gamma_A = \sqrt{\frac{\gamma_D \gamma_{OA}}{\gamma_D + \gamma_A}}, \quad \alpha = \frac{\gamma_D}{\gamma}.$$

$c_0$ is the probability that no degradation of the excitation energy occurs during the transfer between the donor molecules, and $f(\gamma)$ has the same meaning as in (2).

For $\gamma_D \ll \gamma_A$, $\alpha \to 0$ and expression (5) becomes (2), whereas for $\gamma_D \gg \gamma_A$ (\(\alpha \to 1\)) the values of $\tau/\tau_0$ calculated from (5) and (2) differ considerably.

The present paper aims at the experimental verification of expression (5) [6].
Donor fluorescence decay times \( \tau/\tau_0 \) and quantum yields \( \eta/\eta_0 \) versus the acceptor concentration are given for \( C_D/C_A \) ratios equal to 5 and 0.5.

2. Experimental

Two series of alcohol solutions of rhodamine 6G (donor) and malachite green (acceptor) were prepared with values of \( C_D/C_A \) equal to 5 (system I) and 0.5 (system II). 99.8% ethyl alcohol, with 6% \( \text{CH}_3\text{COOH} \) added, was used as a solvent without further purification. Rhodamine 6G (\( \text{C}_{26}\text{H}_{27}\text{O}_3\text{N}_2\text{C}_1 \), m.w. = 450.98) and malachite green (\( \text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_4 \), m.w. = 418.53) were purified by repeated crystallization from ethyl alcohol under vacuum. The mean fluorescence decay times were measured on a phase fluorometer described elsewhere [8]. For the frontal excitation we used the wavelength 510 \( \pm 8 \) nm. In view of the very low absolute yield of malachite green in liquid solutions \( \eta_0 \approx 10^{-4} \) [9] one needs an OG-5 cutoff filter (\( \lambda > 548 \) nm) only for the observation of the rhodamin 6G-fluorescence. The quantum yield, \( \eta/\eta_0 \), was measured in the spectral range of \((560 \pm 3)\)nm using a method proposed by Förster [10], on a device described previously [11]. Fluorescence spectra were corrected for the spectral sensitivity of photomultiplier and reabsorption according to [12].

Reabsorption and secondary fluorescence have to be taken into account.

True values for \( \tau \) were calculated from the relation [13]

\[
\tau = \tau' (1 - \kappa),
\]

where \( \tau' \) is the measured PL decay time, \( \kappa \) the ratio of the primary to the secondary fluorescence. Values of \( \kappa \) for individual concentrations were computed on an Odra 1204 digital computer, basing on the theory presented in references [14, 15]. The computations for \( \eta \) and \( \tau \) were carried out separately due to different observation conditions. A VSU2-P spectrophotometer was used to measure the absorption spectra. All measurements were carried out at 293 K.

3. Experimental Results and Discussion

Some data concerning the absorption \( (\varepsilon_D) \) and fluorescence \( (\varepsilon_D) \) spectra of rhodamine 6G (donor) and the absorption spectrum \( (\varepsilon_A) \) of malachite green (acceptor) in ethanol are given in Table 1. In the concentration range of \( C_D < 10^{-2} \) M/l and \( C_A < 10^{-2} \) M/l, the \( \varepsilon_D \) and \( \varepsilon_A \) spectra remained unchanged, the spectra of mixed solutions of rhodamine and malachite green were found to be additive. Thus we assume that the substances occur as monomers and do not form complexes. Considerable spectral overlaps of \( \varepsilon_D \) with \( \varepsilon_A \) and \( \varepsilon_D \) with \( \varepsilon_D \) (high values of overlap integrals — compare Table 1) facilitate the NEEET both from \( D^* \) to \( A \) and from \( D^* \) to \( D \).

Table 2 summarizes the measured \( \tau' \) values, true \( \tau \) values determined from (7), as well as the values of the correction factor \( \kappa \). For both systems the changes in \( \tau' \) and \( \tau \) have similar character, i.e. the \( \tau' \) values increase at first and then decrease with increasing \( C_A \). The values of \( \tau \), however, remain constant over a certain range of concentrations and then rapidly drop.

Absolute PL yields \( \eta(c) = \eta_0 \cdot \eta(c)/\eta_0 \) of rhodamine 6G- necessary to calculate \( \kappa \), were obtained by the measurements of relative PL yield, \( \eta(c)/\eta_0 \)

### Table 1. Data characterizing the photoluminescence of ethanolic solutions of rhodamine 6G and malachite green.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( n' )</th>
<th>( \lambda [\text{nm}] )</th>
<th>( \varepsilon_D )</th>
<th>( \varepsilon_A )</th>
<th>( f_D )</th>
<th>( f_A )</th>
<th>( \eta_0 )</th>
<th>( \tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>poise</td>
<td>poise</td>
<td>poise</td>
<td>poise</td>
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<td>poise</td>
<td>poise</td>
<td>poise</td>
<td>poise</td>
</tr>
<tr>
<td>1.36</td>
<td>0.01</td>
<td>530</td>
<td>622</td>
<td>555</td>
<td>1.05</td>
<td>0.93</td>
<td>0.9</td>
<td>4.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( I_{DD} )</th>
<th>( I_{DA} )</th>
<th>( C_D )</th>
<th>( C_A )</th>
<th>( R_D )</th>
<th>( R_A )</th>
<th>( \langle \chi^2 \rangle )</th>
<th>( \langle \tau^2 \rangle^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-13} \cdot \text{cm}^3/\text{M} )</td>
<td>( 10^{-3} \cdot \text{M/l} )</td>
<td>( [\text{Å}] )</td>
<td>( [\text{Å}] )</td>
<td>( \langle \chi^2 \rangle )</td>
<td>( \langle \tau^2 \rangle^{1/2} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.63</td>
<td>3.25</td>
<td>2.54</td>
<td>1.77</td>
<td>53.8</td>
<td>60.7</td>
<td>0.995</td>
<td>0.667</td>
</tr>
</tbody>
</table>

a mean diffusion length from Ref. [20].
Table 2. Values of the measured fluorescence decay times ($\tau'$) and those corrected for secondary effects ($\tau$), and the values of the factor $x$ for individual acceptor concentrations.

<table>
<thead>
<tr>
<th>$C_D/C_A = 5$</th>
<th></th>
<th>$C_D/C_A = 0.5$</th>
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</thead>
<tbody>
<tr>
<td>$C_A$</td>
<td>$\tau'$</td>
<td>$x$</td>
</tr>
<tr>
<td>[M/l]</td>
<td>[ns]</td>
<td></td>
</tr>
<tr>
<td>2 $\cdot 10^{-6}$</td>
<td>4.2 ± 0.1</td>
<td>0.026</td>
</tr>
<tr>
<td>3.6</td>
<td>4.4 ± 0.2</td>
<td>0.043</td>
</tr>
<tr>
<td>6.4</td>
<td>4.7 ± 0.1</td>
<td>0.069</td>
</tr>
<tr>
<td>1.1 $\cdot 10^{-5}$</td>
<td>5.0 ± 0.1</td>
<td>0.114</td>
</tr>
<tr>
<td>2.0</td>
<td>5.2 ± 0.1</td>
<td>0.145</td>
</tr>
<tr>
<td>3.6</td>
<td>5.4 ± 0.1</td>
<td>0.198</td>
</tr>
<tr>
<td>6.4</td>
<td>5.8 ± 0.1</td>
<td>0.236</td>
</tr>
<tr>
<td>1.1 $\cdot 10^{-4}$</td>
<td>5.8 ± 0.1</td>
<td>0.254</td>
</tr>
<tr>
<td>2</td>
<td>5.2 ± 0.2</td>
<td>0.248</td>
</tr>
<tr>
<td>3.6</td>
<td>4.2 ± 0.1</td>
<td>0.192</td>
</tr>
<tr>
<td>6.4</td>
<td>3.2 ± 0.1</td>
<td>0.086</td>
</tr>
<tr>
<td>1.1 $\cdot 10^{-2}$</td>
<td>1.8 ± 0.2</td>
<td>0.086</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0 ± 0.2</td>
<td>0.038</td>
</tr>
</tbody>
</table>

where $n$ is the refractive index of the environment and $I_{DA}$ is the spectral overlap given by

$$I_{DA} = \int_{0}^{\infty} f_0(\tilde{v}) \sigma_A(\tilde{v}) d\tilde{v} / \tilde{v}^4. \quad (9)$$

$f_0(\tilde{v})$ is the normalized donor fluorescence intensity at wavenumber $\tilde{v}$, and $\sigma_A(\tilde{v})$ is the acceptor molar decadic extinction coefficient at $\tilde{v}$. $\langle \chi^2 \rangle$ in (8) represents an orientation factor of the transition dipole moments of the interacting D* and A molecules. Calculating the critical concentrations $C_{OD}$ and $C_{OA}$ we assumed $\langle \chi^2 \rangle = 2/3$ in the whole concentration range. Values of $C_{OD}$ and $C_{OA}$, and of the corresponding critical distances $R_{OD}$ and $R_{OA}$ are given in Table 1. As known [16], $\langle \chi^2 \rangle = 2/3$ corresponds to the case of sufficiently fast Brownian rotational motions of the molecules, i.e. when the rotation time $\tau_r \ll \tau_1$, where

$$\tau_1 = [\sum_{D} k_{D*D} + \sum_{A} k_{D*A} + k_F + k_q]^{-1}$$

is the localization time of the excitation energy. For a statistical distribution of immobile rigid molecular dipoles, however, a value of $\langle \chi^2 \rangle = 0.476$ [17, 18] is valid. Since the localization time $\tau_1$ depends on the concentration of the D and A molecules, $\langle \chi^2 \rangle$ should depend upon concentration also. Thus, the assumption of $\langle \chi^2 \rangle = 2/3$ and for liquid systems (when $\sim \tau_r \ll \tau_1$) is approximate only.

Let us consider the effect of this simplification upon the values of $\gamma_D$ and $\gamma_A$. For any concentra-
tion \( \langle x^2 \rangle \) can be calculated from the relation [19]
\[
\langle x^2(\gamma) \rangle = \langle x^2 \rangle_0 \frac{F(\gamma)}{F(\gamma) + a} + \langle x \rangle^2 \frac{a}{F(\gamma) + a},
\]
where \( a = \tau_a / \tau_1 \), \( F(\gamma) \) the same as in (2), with \( \gamma \) being the argument instead of \( \gamma_A \). Function \( F(\gamma) \) was obtained using an approximate formula for \( \gamma \). Assuming \( a = 0.076 \) for rhodamine 6G in ethanol (\( \tau_r = 320 \text{ ps} \) and \( \tau_0 = 4200 \text{ ps} \) from Ref. [20]), we calculated \( \langle x^2 \rangle \) as a function of \( \gamma \). The results are shown in Figure 2. Solid curves were obtained from (11) for \( a = \gamma_D / \gamma_A = 0.26 \) (curve 2), and \( a = 0.75 \) (curve 1), dottet curve — from (10). Differences in \( \langle x^2 \rangle \) calculated from (9) and (11) are small and are completely eliminated for \( a \rightarrow 0 \) (compare (2) and (12)). Given the values of \( \langle x^2(\gamma) \rangle \) and assuming
\[
\frac{\langle x^2(\gamma) \rangle}{\langle x^2 \rangle_0} = \left( \frac{\gamma_D}{\gamma_A} \right) = \left( \frac{\gamma}{\gamma_A} \right) \frac{1}{\sqrt{2/3}},
\]
one can calculate the corrected concentrations \( \gamma_A^\prime \) (compare (6) and (8)) from
\[
\gamma_A^\prime = \gamma_A \left( \frac{\gamma^2(\gamma)}{\gamma^2(\gamma_A)} \right)^{1/2}. (13)
\]
Figure 3 gives the comparison between the true decay times \( \tau \), summarized in columns 4 and 8 of Table 2, and those obtained from (5). Empty circles and triangles correspond to \( \gamma_A \) calculated for \( \langle x^2 \rangle = 2/3 \), black circles and triangles to those obtained from (13). As is seen from the figure, the differences \( \gamma_A - \gamma_A^\prime \) are small. Nevertheless, for the highest concentration in the case of system II, \( \gamma_A \) exceeds \( \gamma_A^\prime \) already by about 10%. A more significant effect may be expected for higher reduced concentrations \( \gamma = \gamma_D + \gamma_A \) and for greater \( a \) (compare Figure 2). \( \tau_0 \) was set equal to 4.3 ns, the mean value over several \( \tau \) in the range of the lowest concentrations. It is very close to a value of 4.2 ns obtained recently by Porter and Tredwell [20].

Theoretical curves 1 and 2 were calculated from (5) for \( \gamma_D / \gamma_A = 3.48 \) (\( C_D / C_A = 5 \)) and \( \gamma_D / \gamma_A = 0.35 \) (\( C_D / C_A = 0.5 \)), respectively. We note that at moderate and high \( \gamma_A \), the PL decay times \( \tau / \tau_0 \) are significantly lower in system I. In addition, a good fit of the experimental results to expression (5) can be noted. We would like to emphasize this fact as all quantities needed for the comparison between experiment and theory were determined by independent measurements.

Figures 4a and 4b show the quantum yields \( \eta \) for systems I (\( C_D / C_A = 5 \)) and II (\( C_D / C_A = 0.5 \)). Black circles denote experimental points, corrected for reabsorption and secondary fluorescence, curve 1 points computed from the relation [21]
\[
\frac{\eta}{\eta_0} = \frac{1 - f(\gamma)}{1 - a_0 \alpha f(\gamma)}, (14)
\]
with \( a_0 , \alpha \) and \( f(\gamma) \) as in (5). For \( \gamma_D \ll \gamma_A \), \( \alpha \rightarrow 0 \) and expression (14) becomes the well known Förster formula [10]
\[
\eta / \eta_0 = 1 - f(\gamma_A). (15)
\]
As is seen from the figures, the experimental points fit well the theoretical curves. In the case of system II, also equation (15) describes properly the experimental results (curve 3). With system I, however, the discrepancies are considerable. Similar results were obtained also in the case of other two-
component systems [22, 23]. For the comparison of $\eta/\eta_0$ and $\tau/\tau_0$ in Figs. 4 a and 4 b, we also gave the results concerning the PL decay times $\tau/\tau_0$ for these systems versus the reduced concentration $\gamma = \gamma_D + \gamma_A$. A marked deviation from proportionality between the decay time and the PL quantum yield can be noted. According to the theory, this deviation is smaller for system I having the higher $\gamma_D/\gamma_A$.

4. Final Comments

The PL decay times $\tau/\tau_0$ of systems with different $\gamma_D/\gamma_A$ show that the energy transfer from the donor to the acceptor molecules is more efficient in systems with higher $\gamma_D/\gamma_A$. The same conclusion may be reached from the quantum yields $\eta/\eta_0$.

The experimental results obtained confirm the validity of formulae (5) and (14), and the necessity for the concentration changes in the decay times and quantum yield for multistep NEEET from the donor to the acceptor molecules, to be taken into account. Due to the considerable value of the mean diffusion length (compare $\langle r^2 \rangle^{1/2}$ and $R_{0D}$ in Table 1) one should expect lower values of $\tau/\tau_0$ and $\eta/\eta_0$ compared with those predicted by the theory developed for rigid solutions. However, the good agreement of the experimental results with the theory permits to believe that NEEET is not influenced significantly by the material diffusion. Also the measurements of the fluorescence decay curves for rhodamine 6G in the presence of malachite green in ethanol, carried out by Porter and Tredwell [20] have shown that the system investigated may be assigned to the Förster-type kinetic behaviour [24].


[6] Similar investigations for one-component systems were carried out recently [7].


