Investigations of the Reversible Energy Transfer in Concentrated Dye Solutions

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In the system rhodamine 6G (donor)/rhodamine B (acceptor) the reverse energy transfer considerably increases the donor fluorescence quantum yield, particularly in the high concentration region. These experimental results confirm a theoretical model with no adjustable parameters.

1. Introduction

The phenomenon of quenching and sensitisation of fluorescence (FL) by non-radiative electronic excitation energy transfer (NET) between donor (D) and acceptor (A) molecules statistically distributed in an isotropic condensed medium was dealt with in a number of papers [1]. In these the transfer from A* to D was neglected, an assumption which is justified when the energy gap \( \Delta E \) between the \( S_i \) levels of D and A is large enough \((\Delta E > 500 \text{ cm}^{-1})\) [2]. However, in systems with closely located \( S_i \) levels of D and A showing partial overlap of the acceptor fluorescence and donor absorption spectra, consideration of the reverse non-radiative energy transfer (RNET) may be found indispensable. This process will influence the FL quantum yield as well as other luminescent characteristics of the system. As far as we know the influence of the RNET on the luminescence of solutions has not been studied experimentally so far. However, investigations of donor-acceptor systems with closely located \( S_i \) levels seem to be important especially in relation to the NET process occurring between chlorophyll forms [3] as well as between fractions of luminescent molecules in inhomogeneously broadened systems [4].

As shown in [5] and preceding papers, the energy transfer from D to A and its reverse process is determined by the four overlap integrals \( I_{xy} \), where \( x, y = A, D \), combined with the two quantum-yields \( \eta_{D,x} \) or by the four corresponding characteristic concentrations \( C_{0,xy} \) (9) and the two concentrations \( C_x \).

These 6 determining parameters can be transformed, introducing the reduced concentrations \( \gamma_D, \gamma_A \), \( \gamma'_D, \gamma'_A \), \( \gamma \) and \( \gamma' \), to six new parameters:

\[
\begin{align*}
\gamma &= \gamma_D + \gamma_A = \frac{\pi^{1/2}}{2} \left( \frac{C_D}{C_{0,DD}} + \frac{C_A}{C_{0,DA}} \right) ; \quad \gamma = \gamma_D, \\
\gamma' &= \gamma'_A + \gamma'_D = \frac{\pi^{1/2}}{2} \left( \frac{C_A}{C_{0,AA}} + \frac{C_D}{C_{0,AD}} \right) ; \quad \gamma' = \gamma'_A.
\end{align*}
\]

With these parameters (or the combinations \( \tilde{\gamma}; \tilde{\gamma}' \)) the quantum yield of the D-fluorescence \( \eta_x^D \) relative to \( \eta_{0,D} \) without acceptor molecules can be written as

\[
\frac{\eta_x^D}{\eta_{0,D}} = \frac{1 - f(\gamma)}{1 - x f(\gamma)} \frac{1}{1 - B} = \frac{\eta_D}{\eta_{0,D}} \frac{1}{1 - B},
\]

where

\[
B = \frac{\eta_{DA} \eta_{AD}}{\eta_{AA} \eta_{DD}} = \frac{(1 - x) f(\gamma)}{1 - x f(\gamma)} \frac{(1 - x') f(\gamma')}{1 - x' f(\gamma')},
\]

\[
f(\gamma) = \frac{\pi^{1/2} \gamma \exp(\gamma^2)}{\sqrt{\pi}} [1 - \text{erf}(\gamma)].
\]

The factor \( \eta_{0,D}/\eta_{0,D} \) should be the relative quantum yield without the reverse transfer process.

As can be seen from (1) and (2), \( x \) and \( \gamma' \) can be expressed by \( \gamma_D \) and \( \gamma_A \):

\[
\gamma' = \gamma'_A (1 + b \gamma_D/\gamma_A) x' = 1/(1 + b \gamma_D/\gamma_A)
\]

with the two combinations of the characteristic concentrations

\[
\begin{align*}
b &= \frac{C_{0,AA} - C_{0,DD}}{C_{0,AD} - C_{0,DA}}, \\
d &= \frac{C_{0,DA} - C_{0,AA} - C_{0,AD}}{C_{0,AD} - C_{0,DA}}.
\end{align*}
\]

Thus, taking the characteristic concentrations \( C_{0,xy} \) (or the combinations \( b \) and \( d \)) as given constants (spec-

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troskopically determinable), the quantities $B$ or $\eta_0^*\eta_{0D}$ prove to be functions of the two reduced concentrations $\gamma_{D}$, and $\gamma_{A}$ as variables.

On the basis of a numerical analysis of (3) it was shown [5] that the influence of the RNET process on the donor quantum yield $\eta_0^*$ is expected to be most important for systems with large $\gamma_{D} / \gamma_{A}$ ratio and high donor concentration. This makes the experimental investigation of the RNET process difficult because of ground state dimer formation in concentrated dye solutions. Strong overlapping of the absorption and fluorescence bands of D and A leads to reabsorption, and secondary fluorescence produces an additional difficulty in determining the true FL quantum yield of the donor. This work reports the experimental results for the donor fluorescence quantum yield in mixed systems of D and A molecules with closely located singlet levels $S_1$.

2. Experimental

The object of the investigation was rhodamine 6G (Rh 6G, donor) and rhodamine B (Rh B, acceptor) in glycerol-ethanol solutions. Rh 6G (BDH) and Rh B (Schuchardt) were additionally purified by multiple crystallisation from ethyl alcohol and evaporation in vacuum. Anhydrous glycerol (Fluka AG) and spectro grade ethanol without further purification were used as solvents. Some of the data for the system investigated are listed in Table 1.

A series of solutions of different donor concentrations and a fixed acceptor concentration $C_A = 5 \cdot 10^{-4}$ M was prepared. The sample cell thickness $d$ was small enough to ensure the relation $2.3 \varepsilon_{D}^{\text{max}} C_D d < 0.1$, where $\varepsilon_{D}^{\text{max}}$ is the maximum value of the donor extinction coefficient. The effect of reabsorption and secondary fluorescence on the yield $\eta_D$ may be neglected under these conditions [7].

The FL spectra as well as the FL quantum yield were measured at a frontal excitation and observation perpendicular to the surface of the cell. The fluorescence was excited with a halogen lamp light of $(500 \pm 8)$ nm wavelength selected by means of a “Zeiss Jena” SPM-2 monochromator. The exciting beam was focussed onto the sample forming an angle of 15° with the observation direction perpendicular to the surface of the cell. The fluorescence was viewed through a Russian DSF 12 double grating monochromator and detected by a P12FQS52A photomultiplier.

The fluorescence spectra were corrected for the spectral sensitivity of the photomultiplier and also for the anisotropy of the spatial distribution of the observed emission according to the Shinitzky’s method [8]. Because of strong overlap of the absorption and fluorescence bands the fluorescence quantum yields of the donor $\eta_D$ and the acceptor $\eta_A^*$ were calculated from the relations

\[
\eta_D(\lambda_{ex}) = [g_D + (1 - g_D) \eta_{AD} \eta_0^*], \quad (7a)
\]

\[
\eta_A = [(1 - g_D) + g_D \eta_{AD}] \eta_A^*, \quad (7b)
\]

where $\eta_{AD}$ and $\eta_{AD}$ are transfer efficiencies defined in (4) and $g_D = \varepsilon_D C_D(\varepsilon_D C_D + \varepsilon_A C_A)$. $\varepsilon_D$ and $\varepsilon_A$ are the extinction coefficients of D and A at the exciting light wavelength $\lambda_{ex}$, respectively. The second term in (7a) [(7b)] represents the contribution to $\eta_D(\eta_A)$ of molecules A [D] excited directly by light absorption. The yields $\bar{\eta}_D$ and $\bar{\eta}_A$ were evaluated to ensure the best fitting of the function $f(\lambda) = \bar{\eta}_D f_D(\lambda) + \bar{\eta}_A f_A(\lambda)$ to the spectrum $\Phi(\lambda) = F(\lambda) [E(\lambda_{ex}) \cdot C(\lambda)]$, where $f_D(\lambda)$ and $f_A(\lambda)$ denote the respective fluorescence spectra, $F(\lambda)$ is the actually measured fluorescence spectrum of the system, $C(\lambda)$ the spectral sensitivity of the experimental device and $E(\lambda_{ex})$ the optical density of the sample.

The calculations consisted in finding values of $\bar{\eta}_D$ and $\bar{\eta}_A$ for which the deviation

\[
\delta = \sum_{i=1}^{n} [\Phi(\lambda_i) - (\bar{\eta}_D f_D(\lambda_i) + \bar{\eta}_A f_A(\lambda_i))]^2
\]

reaches its minimum.

Table 1. Data of rhodamine 6G plus rhodamine B in solutions.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$n$</th>
<th>$T$</th>
<th>$\eta'$</th>
<th>$\lambda_{ex}$</th>
<th>$\eta_{0D}$</th>
<th>$\tau_{rot}$</th>
<th>$\lambda^2(\gamma_{min})$</th>
<th>$\lambda^2(\gamma_{max})$</th>
<th>$D_D$</th>
<th>$10^{-9}$ cm$^2$</th>
<th>$r_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol + 10% Ethanol + trace HCl</td>
<td>1.4653</td>
<td>295</td>
<td>0.57</td>
<td>500 ± 8</td>
<td>0.95</td>
<td>0.6</td>
<td>3.78</td>
<td>125</td>
<td>0.4804</td>
<td>0.4761</td>
<td>5.13</td>
</tr>
</tbody>
</table>

* from ref. [22].
3. Results and Discussion

The electronic absorption spectra of rhodamine 6G in glycerol-ethanol solutions were measured at wavelengths from 450 to 600 nm and concentrations from $10^{-4}$ to $2 \cdot 10^{-2}$ M. They remain unchanged with rise in concentration up to $5 \cdot 10^{-3}$ M. It was also stated that for $C_D < 5 \cdot 10^{-3}$ M ($C_A = 0$) the donor FL quantum yield $\eta_D$ remains constant. The same is true for the mean FL decay time $[9]$. Thus the presence of the ground state donor dimer in this $C_D$ region can be neglected. For $C_D > 5 \cdot 10^{-3}$ M a slight deformation of spectra appears, being the evidence of dimer formation in the solution.

Figure 1 shows the electronic absorption and fluorescence spectra of rhodamine 6G (Rh 6G) and rhodamine B (Rh B) in glycerol–ethanol solution. The overlap of the acceptor (Rh B) fluorescence and donor (Rh 6G) absorption spectra, which makes the reverse energy transfer from $A^*$ to D possible, should be emphasized.

Table 2 contains values of the parameters required for the comparison of (3) with the experimental data. They were obtained from independent measurements. The critical concentrations $C_{0,xy}$ were determined from the overlapping integrals $I_{xy}$ [10]:

$$C_{0,xy} = 4.23 \cdot 10^{-10} n^2 \langle \langle x^2 \rangle \rangle \eta_0 I_{xy}^{1/2}, \ x, y = D, A,$$

(9)

where $n$ is the refractive index of the medium, $x$ the orientation factor for the donor and acceptor transition moments and $\eta_0$, the absolute FL quantum yield. The critical concentrations $C_{0,xy}$ as well as the critical distances $R_{0,xy} = (3/4 \pi C_{0,xy})^{1/3}$ were calculated for $\langle \langle x^2 \rangle \rangle = 0.476$ assuming D and A to be statistically distributed fixed dipoles [11, 12]. On Fig. 2 the experimental values of $\eta_D^*/\eta_0$ are compared to theoretical curves calculated from (3) taking into account both donor-donor energy transfer and the RNET process. Curve 1 corresponds to the case when the RNET process is taken into account ($I_{AD} > 0, B > 0$) and curve 6 to the case when it is neglected ($I_{AD} = 0, B = 0$). The experimental points are well fitted to curve 1 while their deviation from curve 6 is large, particularly in the range of high concentrations. The yield $\eta_D^*/\eta_0$ does not decrease with the rise in $\gamma_D$ but shows a significant tendency to increase. It should be emphasized that curve 1 was calculated with no adjustable parameters.

![Image](image-url)

Fig. 1. Electronic absorption and fluorescence spectra of rhodamine 6G and rhodamine B in glycerol-ethanol solutions.

![Image](image-url)

Fig. 2. The rhodamine 6G (donor) fluorescence quantum yield at a fixed concentration $\gamma_A$ of rhodamine B (acceptor) versus reduced concentration $\gamma_D$. Curves 1–6 were computed for different values of $I_{AD}$ and the same values of the other parameters listed in Table 1. $\gamma_D$ – experimental points, $I_{AD}$ in $10^{-13}$ M$^{-1}$ cm$^3$.

### Table 2. Values of energy transfer parameters for the system investigated.

<table>
<thead>
<tr>
<th>System</th>
<th>Rh 6G + Rh B in glycerol-ethanol solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_0$ [Å]</td>
<td>48.92</td>
</tr>
<tr>
<td>$C_0$ [$\times 10^{-3}$ M]</td>
<td>3.387</td>
</tr>
<tr>
<td>$f$ [$10^{-13}$ M$^{-1}$ cm$^3$]</td>
<td>1.512</td>
</tr>
<tr>
<td>$\eta_D^*$/$\eta_0$</td>
<td>0.2735</td>
</tr>
<tr>
<td>$\gamma_D$</td>
<td>0.01</td>
</tr>
<tr>
<td>$\gamma_A$</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Curves 2–5 were calculated for the same values of the parameters as curve 1 but for the smaller \( I_{AD} \) values which can be expected at lower temperatures for the investigated systems. They show a single minimum shifted towards higher concentrations for smaller \( I_{AD} \). This kind of relation between \( \eta_0^D \) and \( \gamma_D \) originates from two competing processes: energy migration in the set of donors increasing with \( \gamma_D \) and leading to decrease in \( \eta_0^D \) and, on the other hand, rise in the rate constant for the reverse transfer from \( A^* \) to \( D \) leading to increase in \( \eta_0^D \). The latter process dominates for the highest concentrations when each molecule \( A \) is surrounded mainly by \( D \) molecules and the transfer from \( A^* \) to \( D \) can efficiently compete with other ways of deactivation of \( A^* \), that is \( \sum_k k_{AD} \approx k_{AF} + k_{AA} \), where \( k_{AF} \) and \( k_{AA} \) are rate constants for the acceptor FL emission and internal conversion, respectively.

According to Shipman [13] similar conditions are found in photosystems of green plants where the excited trap can depopulate via excitation detrapping to the chlorophylls. It was shown there that the detrapping process is important and should not be neglected.

The influence of the reverse transfer from acceptors (traps) on the donor quantum yield has been recently considered by Yelutin and Isakova [14]. The analysis of the obtained results permitted the authors to draw a conclusion about the nonmonotonic dependence of the \( \eta_0^D \) yield on \( \gamma_D \) concentration.

The trapping of the excitation energy by rhodamine 6G dimers was not accounted for in (3). However, it is known that in the high concentration region the donor-donor transfer can lead to effective excitation trapping even in systems with low values of the dimerization constant [15, 16].

In order to estimate the contribution of Rh 6G dimers, as the centers competing with the acceptors, to the excitation energy trapping we have calculated the ratio of the mean rate constants

\[
k_{DD}/k_{DA} \approx (C^*/C_A)^2 \cdot (C_{DA}/C_{DD})^2
\]

for a few high values of the concentration \( C_D \). The corresponding concentrations \( C^* \) have been calculated for the equilibrium constant \( K = 1 \, \text{M}^{-1} \) obtained for a similar system on the basis of concentration-dependent variations of the emission anisotropy and the quantum yield [17]. The critical concentrations \( C_{DD} \) and \( C_{DA} \) for Rh 6G in four different solvents, in which the absorption spectra depend heavily on the concentration have been reported in [17]. Values of \( p = C_{DD}/C_{DD}^* \) for particular systems differed at most by 18% from the mean value \( p = 1.35 \) calculated for these systems. If \( C_{DD}/C_{DD}^* \) for our glycerol-ethanol solutions is taken equal to this mean value then we obtain \( C_{DD} = 2.26 \cdot 10^{-3} \, \text{M} \) and \( C_{DA}/C_{DD}^* = 0.242 \). Table 3 contains values of \( C^*/C_A \) and \( k_{DD}/k_{DA} \) calculated for a few concentrations \( C_D \). The concentration of dimers is close to the acceptor concentration for the three highest concentrations \( C_D \). However, the values of \( k_{DD}/k_{DA} \) show that the contribution of dimers to the excitation energy trapping is small compared to that of the acceptors.

The orientation factor \( x \) has been treated [18, 19] in the regime intermediate between fast rotating molecules (\( \langle x^2 \rangle_d = 2/3, \langle y_D \rangle \rangle and resting molecules (\( \langle x^2 \rangle_a = 0.476 \)). As shown in [18], \( x^2 \) is a function of the parameter \( \alpha = \gamma_D/\gamma_{DA} \) and the concentration \( \gamma \) and can be calculated from the expression

\[
\langle x^2(\gamma) \rangle = \langle x^2 \rangle_d \frac{\varphi(\gamma)}{\varphi(\gamma) + a} + \langle x^2 \rangle_a \frac{a}{\varphi(\gamma) + a}, \tag{10}
\]

where

\[
\varphi(\gamma) = 1 + \gamma - (1.5 + \gamma^2)f + x f(f + \gamma^2 - 0.5) - x^2 f. \tag{11}
\]

\( \tau_{OD} \) is the FL decay time for \( C_A = 0 \) and \( f \equiv f(\gamma) \) is defined in (5). The rotation time \( \tau_r = 125 \, \text{ns} \) was calculated from the Stokes-Einstein relation [20] for the viscosity \( n^* \) and temperature \( T \) of the solvent listed in Table 1 and the Rh 6G molecule radius \( r = 0.6 \, \text{nm} \) [21]. Accepting \( \tau_{OD} = 3.78 \, \text{ns} \) [22] we obtain from (10) \( \langle x^2(\gamma_{min}) \rangle = 0.4804, \langle y_{min} \rangle = \gamma_{min} \). Thus the maximum deviation of \( \langle x^2(\gamma > \gamma_{min}) \rangle \) from the earlier assumed value of 0.476 does not exceed 0.9% and can be neglected.

We have also neglected the physical bulk diffusion of \( D \) and \( A \) since the mean diffusion length satisfies the relation \( \langle r_D^2 \rangle^{1/2} = 1.03 \, \text{Å} \approx R_{DA} \).

An equimolar system of Rh 6G and Rh B in glycerol-ethanol solutions was also studied by Bauer.

### Table 3. Contribution of Rh 6G dimer of energy trapping.

<table>
<thead>
<tr>
<th>( C_D ) \cdot 10^{-2} , \text{M}</th>
<th>( C^*/C_A )</th>
<th>( k_{DD}/k_{DA} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.03</td>
<td>0.0004</td>
</tr>
<tr>
<td>0.60</td>
<td>0.08</td>
<td>0.0025</td>
</tr>
<tr>
<td>1.00</td>
<td>0.19</td>
<td>0.0156</td>
</tr>
<tr>
<td>1.26</td>
<td>0.30</td>
<td>0.0385</td>
</tr>
<tr>
<td>1.58</td>
<td>0.47</td>
<td>0.0930</td>
</tr>
<tr>
<td>2.00</td>
<td>0.74</td>
<td>0.2316</td>
</tr>
</tbody>
</table>
and Cherek [9]. However, the RNET process was not observed since it is clearly visible for high concentrations and large $\gamma_D/\gamma_A$ ratios only [5].

Expression (3) was obtained under the assumption of no statistical correlation between configurations surrounding the excited donor molecule before and after the hopping act. This is true when the excitation transfer is due to a hopping mechanism and the critical distances satisfy the inequality $R_{0,DD} \geq R_{0,DA}$ [23, 24]. However, as shown in [25] the values of $\eta_D/\eta_{0,D}$ obtained from (3) (for $B = 0$) with correlations left out of account are very close to those obtained from the simulation in the whole range of concentrations $\gamma$, ($\gamma \leq 10$). In the latter case the correlations were taken into account in a natural way. It follows therefrom that there is no need to consider correlations in the above calculations of the quantum yield.

In this paper we have shown experimentally that the RNET process has an important influence on the yield $\eta^{\text{RNET}}_{\text{D}}$ in the range of high concentration $\gamma_D$. This influence depends strongly on the value of the overlap integral $I_{AD}$ (see Fig. 2), and this suggests that the RNET efficiency may remarkably depend on temperature.

Further experiments on the temperature dependence of the RNET in donor-acceptor systems are in progress.

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