

Influence of the Reversible Energy Transfer on the Donor Fluorescence Quantum Yield in Donor-Acceptor Systems*

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In mixed systems of donor and acceptor molecules having closely located S_1 levels a reversible nonradiative energy transfer should occur. It influences remarkably the dependence of the donor quantum yield η_D on the acceptor concentration in the range of high acceptor concentrations of systems with high donor-to-acceptor reduced concentration ratios.

1. Introduction

Nonradiative electronic excitation energy transfer (NET) from donor (D) to acceptor (A) molecules in mixed dye systems was dealt with in a number of papers [1]. In the investigations of the singlet-singlet NET, reversible nonradiative energy transfer (RNET) from A to D has not been taken into account so far. Such a procedure, according to Rozman [2], should be permissible if the energy difference $E_{0D} - E_{0A}$ of pure electronic transition in D and A exceeds 500 cm^{-1} . However, in a system with closely located S_1 levels of D and A, showing partial overlap of the acceptor fluorescence and the donor absorption spectra a consideration of the reverse energy transfer may be found indispensable, in particular in systems of high donor concentrations. It influences the fluorescence quantum yield as well as the decay time and the energy transfer efficiency, depending on the D and A concentrations and the excitation light wavelength.

Systems of D and A molecules with closely located S_1 levels, between which the NET process may take place, are chlorophyll forms [3], ionic forms of dye molecules [4, 5], and also subgroups of luminescent molecules in the case of heterogeneous broadening of their energy levels [6, 7]. In the present paper, a theoretical analysis of the influence of the RNET on the donor FL quantum yield in mixed systems of the D and A molecules is given.

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2. Donor Quantum Yield in the Presence of RNET

For the long-range energy transfer resulting from the dipole-dipole interaction in systems in which the material diffusion of the D and A molecules need not be taken into account, the concentration changes in the donor fluorescence quantum yield can be described by the relation [8, 9]:

$$\eta_D = \eta_{0D} (1 - f(\gamma)) / (1 - \alpha_0 \alpha f(\gamma)) \quad (1)$$

using the abbreviations

$$f(\gamma) = \pi^{1/2} \gamma \exp(\gamma) [1 - \text{erf}(\gamma)], \quad (2)$$

$$\gamma = \gamma_D + \gamma_A = \frac{1}{2} \pi^{1/2} (C_D/C_{0DD} + C_A/C_{0DA}) \\ = (y + 1) \gamma_A, \quad (3)$$

$$y = \gamma_D/\gamma_A; \quad \alpha = \gamma_D/\gamma = y/(y + 1). \quad (4)$$

C_D and C_A are the concentrations of the D and A molecules, C_{0DD} and C_{0DA} denote the critical concentrations for the NET process from D^* to D and from D^* to A, respectively; η_{0D} is the donor quantum yield when $C_A \rightarrow 0$, α_0 is the probability of a loss-free transfer between the donors (we further suppose $\alpha_0 = 1$).

An analogous expression holds for the acceptor FL quantum yield:

$$\eta_A = \eta_{0A} \frac{1 - f(\gamma')}{1 - \alpha' f(\gamma')} \quad (5)$$

with the abbreviations

$$\gamma' = \gamma'_A + \gamma'_D = \frac{1}{2} \pi^{1/2} (C_A/C_{0AA} + C_D/C_{0AD}) \\ = (y' + 1) \gamma'_A, \quad (6)$$

$$y' = \gamma'_D/\gamma'_A; \quad \alpha' = \gamma'_A/\gamma' = (y' + 1)^{-1}. \quad (7)$$

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η_{0A} is the acceptor quantum yield at $C_A \rightarrow 0$, C_{0AA} and C_{0AD} are critical concentrations for the energy transfer from A^* to A and from A^* to D , respectively.

The critical concentrations C_{0xy} ($x \wedge y \in \{D, A\}$) can be obtained from the relation [10]:

$$C_{0xy} = 4.23 \times 10^{-10} n^2 \bar{v}_{xy}^2 \cdot (\eta_{0x} \bar{k}^2 I_{xy})^{-1/2} (\text{mol} \cdot \text{dm}^{-3}), \quad (8)$$

where

$$I_{xy} = \int_0^\infty f_x(v) \varepsilon_y(v) dv \quad (9)$$

is the overlap integral of the x molecule FL spectral distribution $f_x(v)$, expressed in number of quanta and normalized to unity ($\int f_x(v) dv = 1$), and the y molecule absorption spectrum $\varepsilon_y(v)$, n is the refractive index of the medium, v – the wave-number, \bar{v}_{xy} – the mean value of v in the region of the spectral overlap of $f_x(v)$ and $\varepsilon_y(v)$, k^2 – the orientation factor.

Expression (1) was obtained [8] under the assumption that the NET from D^* to A proceeds as a sequence of elementary onestep processes $D^* + D \rightarrow D + D^*$, terminating with the process $D^* + A \rightarrow D + A^*$, and that the reverse transfer is negligible. However, if $\eta_{0A} > 0$ and $I_{AD} > 0$, then the RNET is possible. Energy transfer between the D and A molecules is assumed to proceed repeatedly in both directions. After the first reverse energy transfer, the donor FL quantum yield is

$$\eta_D^{(1)} = \eta_D + B \eta_D,$$

and after the n -th step

$$\eta_D^{(n)} = \eta_D (1 + B + \dots + B^n), \quad (11)$$

$$B = \eta_{DA} \cdot \eta_{AD}, \quad (12)$$

where η_{DA} and η_{AD} are the transfer efficiencies from D to A and from A to D molecules, respectively. In view of $B < 1$ we obtain the following relations for the donor FL quantum yield $\eta_D^* = \lim_{n \rightarrow \infty} \eta_D^{(n)}$, and for the transfer efficiency $\eta_{DA}^* = \lim_{n \rightarrow \infty} \eta_{DA}^{(n)}$:

$$\eta_D^* = \eta_D / (1 - B), \quad (13)$$

$$\eta_{DA}^* = \eta_{DA} \cdot (1 - \eta_{AD}) / (1 - B) \quad (14)$$

with

$$\eta_D^* / \eta_{0D} + \eta_{DA}^* = 1.$$

Expressions (13) and (14) imply that the donor quantum yield η_D^* is higher, and the transfer effi-

ciency η_{DA}^* lower than the respective quantities η_D and η_{DA} , when there is no reverse transfer. Formulae (13) and (14) correspond to the case in which only molecules D are excited by the light absorption. If also molecules A absorb a fraction of the excitation beam, which occurs in particular in systems with closely located S_1 levels, then (13) should be replaced by the relation

$$\eta_D' = g_D \frac{\eta_D^*}{\eta_{0D}} + (1 - g_D) \eta_{AD} \frac{\eta_D^*}{\eta_{0D}}, \quad (15)$$

where $g_D = \varepsilon_D C_D / (\varepsilon_D C_D + \varepsilon_A C_A)$. ε_D and ε_A are the extinction coefficients of D and A , respectively, for the exciting light wavelength. The second term in (15) represents the contribution to η_D' of molecules A excited directly by the light absorption.

Taking (1), (5), (13) and (14) into consideration, and assuming $\eta_D / \eta_{0D} + \eta_{DA} = 1$ and $\eta_A / \eta_{0A} + \eta_{AD} = 1$, we obtain

$$\frac{\eta_D^*}{\eta_{0D}} = \frac{1 - f(\gamma)}{1 - \alpha f(\gamma)} \cdot \frac{1}{1 - B}, \quad (16)$$

$$B = \frac{(1 - \alpha) f(\gamma)}{1 - \alpha f(\gamma)} \cdot \frac{(1 - \alpha') f(\gamma')}{1 - \alpha' f(\gamma')}. \quad (17)$$

The quantities γ , γ' , α and α' in (16) are described by the concentrations C_D and C_A and by the critical concentrations C_{0xy} ($x \wedge y \in \{D, A\}$). The determination of C_{0xy} requires the knowledge of the absolute yields η_{0D} and η_{0A} and of the four overlap integrals I_{xy} . When $\eta_{0A} = 0$ or $I_{AD} = 0$, a reversible transfer of energy does not occur. In such a case, $\alpha' = 1$ [cf. (6) to (8)] and (16) becomes (1).

To have a significant RNET process apart from satisfying the conditions $I_{AD} > 0$ and $\eta_{0A} > 0$, a sufficiently high concentration C_D (cf. curves a, a' and b, b' on Fig. 1A) is necessary. Thus there may exist donor dimer molecules which play the role of acceptors and lead to concentration quenching of fluorescence (CQF) [1, 11].

Equation (16) was obtained for two-component systems and may be useful to describe the yield of donor fluorescence only in that range of C_D and C_A concentrations in which the CQF phenomenon does not occur.

3. Numerical Results and Final Remarks

Equation (16) can be represented as a function of the one parameter γ_A alone, taking a fixed value for

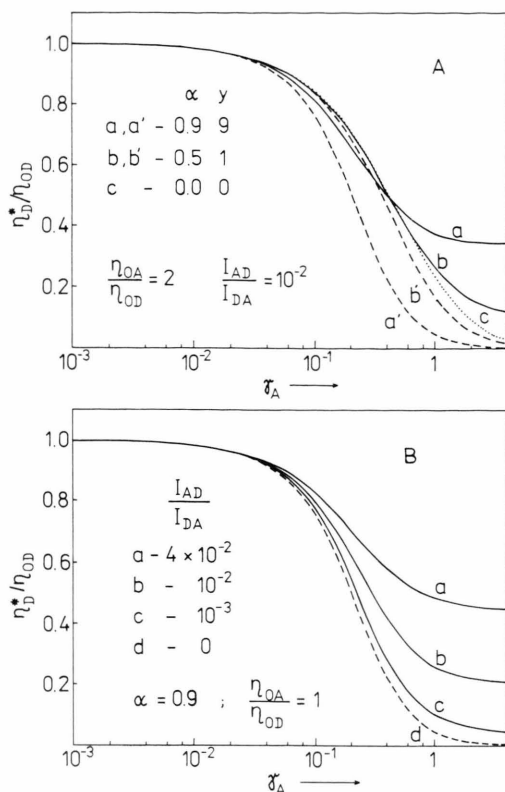


Fig. 1. Donor FL quantum yield as a function of the acceptor reduced concentration $\gamma_A = \frac{1}{2} \pi^{1/2} C_A / C_{0DA}$, calculated from expression (16); solid curves: with energy migration ($\alpha > 0$) and RNET ($B > 0$) being taken into account; dashed curves: $\alpha > 0$, $B = 0$; dotted curve: the Förster curve, $\alpha = 0$, $B = 0$.

y (and x) in (4). Then, for a given donator-acceptor system (with given values of the C_{0xy} or of the overlap integrals I_{xy} , quantum yields η_{0x} and mirror frequencies $\bar{\nu}_{xy}$) the values

$$y' = \frac{C_D}{C_A} \frac{C_{0AA}}{C_{0AD}} = y \cdot \frac{C_{0AA}}{C_{0AD}} \cdot \frac{C_{0DD}}{C_{0DA}} \quad \text{and} \quad \alpha'$$

are known fixed values too, and γ and γ' depend on γ_A through the relations

$$\frac{\gamma'}{\gamma} = \frac{C_{0DA}}{C_{0AA}} \cdot \frac{1 + y'}{1 + y}; \quad \gamma = (1 + y) \gamma_A.$$

For a hypothetical donator-acceptor system with the special assumptions of the overlap integrals, the quantum yields and mirror frequencies:

$$I_{DD} = I_{AA} = 0.5 I_{DA}; \quad I_{AD} = 10^{-2} I_{DA}; \\ \eta_{0A}/\eta_{0D} = 2 \quad \text{and} \quad (\bar{\nu}_{AA} \bar{\nu}_{DD})/(\bar{\nu}_{AD} \bar{\nu}_{DA}) = 1$$

we have calculated η_D^*/η_{0D} as function of γ_A for three different α values. The results are represented in Fig. 1A in comparison to the results neglecting the RNET process ($B = 0$) and moreover neglecting the transfer between donors ($\alpha = 0$) (Förster et al. [12], [13]).

The effect of RNET on the donor fluorescence quantum yields is considerable at high concentrations in systems with high $y = \gamma_D/\gamma_A$ values. Under such conditions each molecule A has in its vicinity mainly D molecules. Therefore the NET from A* to D may be predominant as compared to other ways of deactivation of the A* molecule

$$\left(\sum_D k_{AD} > k_{AF} + k_{Aq} \right).$$

The effectiveness of the RNET process should essentially depend on the values of the overlap integral ratio I_{AD}/I_{DA} and quantum yield ratio η_{0A}/η_{0D} .

Figure 1B represents analog curves, all with the same fixed α value (or y), but for different ratios I_{AD}/I_{DA} , i.e. different donator-acceptor systems. As expected, for systems with higher values of I_{AD}/I_{DA} the RNET process is more significant. The same concerns systems with higher values of η_{0A}/η_{0D} (see (8)).

As mentioned above, the application of (16) is limited to systems in which concentration quenching is absent. That may be a difficulty in the experimental verification of (16). The comparison of the curves a and a' in Fig. 1A shows, however, that a certain influence of the RNET process may be expected in the range $\gamma_A \lesssim 0.2$ or equivalently $\gamma_D \lesssim 2$. Numerous dyes are known, such as Na-fluoresceine, rhodamine 6G, rhodamine B, in which polar organic solvents do not show CQF (η_D yield remains constant) in the range $\gamma_D \lesssim 2$ [14–16], and therefore may be utilized as donors.

But at higher γ_A concentrations concentration quenching in the set of donor molecules also takes place. If, however, we are able to determine the concentration of quenchers (playing the role of additional acceptors) then measurements of $\eta_D^*(\gamma_A)$ seem to be possible. Then we will have a three-component system in which the NET process can take place not only from D* to A but from D* to dimers D₂ as well, while the RNET process occurs from A* to D and from A* to D₂. The respective expressions for quantum yields of the i -th compo-

nent and quantum yields of energy transfer from i -th to the k -th component

$$(i \in \{D, A\}, k \in \{D, A, D_{\text{D}}\})$$

are known (17).

Moreover (16) was obtained under the assumption that the donor FL quantum yield η_D upon light excitation as well as that due to the RNET process is the same. However, D molecules excited as a result of the RNET acquire energies $E < E_{0D}$ since the overlap of the acceptor fluorescence and donor absorption spectra occurs in the anti-Stokes region of the donor. Therefore, if one assumes [18–20] that the donor FL quantum yield, when excited within the anti-Stokes region, is lower than that for the Stokes excitation ($\eta'_{0D} < \eta_{0D}$), then, instead of (16)

one obtains the relation

$$\frac{\eta_D^*}{\eta_{0D}} = \frac{1-f(\gamma)}{1-\alpha f(\gamma)} + \frac{\eta'_{0D}}{\eta_{0D}} \frac{1-f(\gamma)}{1-\alpha f(\gamma)} \cdot \frac{B}{1-B} \quad (21)$$

which predicts lower values for the quantum yield than does (16).

An additional difficulty in measuring the $\eta_D^*(\gamma_A)$ yield may be due to strong overlapping of donor fluorescence and acceptor absorption bands, leading to reabsorption and secondary fluorescence. These effects may be eliminated by employing sufficiently thin layers of the luminophore [21] or by taking into account, on the basis of theory, the influence of these effects on the luminescent properties of solutions [22, 23].

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