Dipole-Dipole Transport of Excitation in Liquid Solutions: Influence of Multi-Stage Energy Transfer on Donor Photoluminescence Yield

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On the basis of expressions obtained earlier, numerical calculations of relative donor quantum yields in the presence of multi-stage dipole-dipole energy transfer and material diffusion are carried out. Transfer rates of the second order obtained from the numerical solution of the diffusion equation with reflecting boundary conditions are used in the calculations. The results reflect the influence of donor and acceptor concentration, magnitude of diffusion coefficients and molecular size effects.

Key words: Molecules – energy transfer – migration – diffusion – quantum yield.

1. Introduction

Non-radiative electron excitation energy transfer between donors D and acceptors A in solution is of theoretical and practical significance. Energy transfer plays a significant role in photosynthesis, convertors of solar energy and dye lasers. The statistics of excitation transfer through dipole-dipole interaction between two types of randomly distributed molecules in a rigid solution has been developed by Förster [1] and Galanin [2]. In their considerations the energy transfer from an excited donor molecule D* to A has been treated as a single-stage process. However, at higher donor concentrations there may appear conditions suitable for excitation energy migration (EEM). Then the transfer from D* to A is a sequence of single-stage processes D* + D → D + D* concluded by a D* + A → D + A*.

The donor fluorescence intensity in the presence of EEM in a donor system has been the subject of many papers [3–14]. The authors conclude that the multi-stage process is a more rapid and efficient than the single-stage process. However, these works are concerned with the donor and acceptor molecules being placed in a rigid solution or a solution with a viscosity high enough for the molecules to remain practically stationary during the average time of life τ_0 of the donor. In this paper we deal with the donor quantum yield in presence of EEM in a solution of any viscosity.

Our considerations shall be based on ref. [15], where the average rate of non-radiative excitation energy transfer in a donor-acceptor system in a liquid solution has been calculated. Moreover, we shall use the results of refs. [12, 16], where general expressions for the donor yield in the presence of EEM have been obtained. The theory of EEM in a donor-acceptor system evolves from two basic models [4, 8]. If there are not too many donors in the vicinity of an acceptor, the excitation may change in one step its acceptor surrounding. This model is called a hopping model. In the opposite case the donor-donor transfer probabilities are correlated and the appropriate model of energy transfer is called a diffusion model. If the energy transfer is caused by dipole-dipole interaction, in the diffusion model the inequality $r_{0DD} \ll r_{0DA}$ has to be satisfied while the hopping model $r_{0DD} \gtrsim r_{0DA}$ holds true [4, 8]. r_{0DD} and r_{0DA} denote the critical distances for donor-donor and donor-acceptor transfer [1, 17], respectively. In this article we restrict ourselves to systems in which the hopping model can be applied. One may assume that the range of application of the hopping model increases with the increase of material diffusion in the system. Diffusion accelerates the change of molecular configuration during the excitation life-time and therefore leads to a quicker change of acceptor surrounding of excitation.

The important fact in EEM-systems is the re-migration of excitation energy to the original centre [18, 19]. In particular, this means that in the theoretical description concerning rigid solutions with dipole-dipole interaction one must divide the donor concentration by a coefficient $\sqrt{2}$, as compared to the

situation when the excitation return is not taken into account. In liquid solutions the magnitude of this effect is difficult to define, but will certainly depend on the viscosity and will be the smaller the greater the diffusion. The increase of translational diffusion decreases the probability of re-migration of the excitation to the primarily excited centre. In this paper the re-migration effects shall not be taken into account. Moreover, in our considerations we shall limit ourselves to cases in which diffusion related collisions of molecules are not connected with activation of any additional means of energy transfer between molecules. This is assumed by considering a reflecting boundary condition when solving the diffusion equation.

2. Theoretical Considerations

It may be concluded from [12, 16] that the relative donor quantum yield in the case of energy transfer from donor to acceptor with participation of EEM is described by the expression

$$\frac{\eta}{\eta_0} = \frac{\int\limits_0^\infty \exp\left[-T - \gamma_D \int\limits_0^T k_{DD}(T')\,dT' - \gamma_A \int\limits_0^T k_{DA}(T')\,dT'\right]dT}{1 - \gamma_D \int\limits_0^\infty k_{DD}(T)\exp\left[-T - \gamma_D \int\limits_0^T k_{DD}(T')\,dT' - \gamma_A \int\limits_0^T k_{DA}(T')\,dT'\right]dT}, \tag{1}$$

where $T = t/\tau_D$, and $k_{DD}(T)$ and $k_{DA}(T)$ are transfer rates for donor-donor and donor-acceptor excitation energy transfer, respectively, averaged over all molecular configurations. Reduced concentrations γ_D of the donor and γ_A of the acceptor are defined as $\gamma_D = (\pi^{1/2}/2)(c_D/c_{0D})$ and $\gamma_A = (\pi^{1/2}/2)(c_A/c_{0A})$, where c_D, c_A are concentrations and c_{0D}, c_{0A} are critical concentrations of the donor and acceptor, respectively.

For molecules having dimensions negligibly small in comparison with the critical distances r_{0DD} and r_{0DA} it is found that

$$k_{DD}(T) = k_{DA}(T) = T^{-1/2}. \tag{2}$$

Expression (2) along with (1) gives [3]

$$\frac{\eta}{\eta_0} = \frac{1 - f(\gamma)}{1 - (\gamma_D/\gamma)f(\gamma)}, \qquad \gamma = \gamma_D + \gamma_A. \tag{3}$$

If the dimensions of molecules are not negligible, then, assuming sphericity, one obtains

$$k_{DD}(T) = T^{-1/2}\,\text{erf}(\varrho_{DD}^{-3}\,T^{1/2}), \tag{4}$$

$$k_{DA}(T) = T^{-1/2}\,\text{erf}(\varrho_{DA}^{-3}\,T^{1/2}), \tag{5}$$

where $\varrho_{DD} = a_{DD}/r_{0DD}$, $\varrho_{DA} = a_{DA}/r_{0DA}$, while a_{DD} and a_{DA} are the distances of closest approach of two donors or donor and acceptor. An account of erf in (4) and (5), η/η_0 can be defined only by numerical calculation.

In the case of simultaneous occurrence of material diffusion and non-radiative dipole-dipole excitation energy transfer the values of $k_{DD}(T)$ and $k_{DA}(T)$ can not be determined analytically. As shown in [15], they may be quite easily determined numerically. Therefore, also in this case the values of η/η_0 may be found only numerically. In this work, a computer program has been developed on the basis of standard numerical methods, enabling the calculation of η/η_0 (1) for any dependence of k_{DD} and k_{DA} on time. Using this program, the quantum yield as a function of donor and acceptor concentration has been calculated for different diffusion coefficients and different molecular sizes. The obtained results shall be discussed in Chapter 3.

3. Calculation Results and Discussion

As one may conclude from [15], the transfer rates $k_{DA}(T)$ or $k_{DD}(T)$ depend on the two parameters $\lambda_{DA} = (D_{DA}\tau_D)^{1/2}/r_{0DA}$ and $\varrho_{DA} = a_{DA}/r_{0DA}$ or $\lambda_{DD} = (D_{DD}\tau_D)^{1/2}/r_{0DD}$ and $\varrho_{DD} = a_{DD}/r_{0DD}$, respectively. Here D_{DA} denotes the sum of diffusion coefficients of donor D_D and acceptor D_A while $D_{DD} = 2D_D$. To simplify the discussion we shall analyse the quantum yield of a system in which $\lambda_{DD} = \lambda_{DA} = \lambda$ and $\varrho_{DD} = \varrho_{DA} = \varrho$. Calculations of η/η_0 have been carried out for three values of λ ($\lambda = 0$, $\lambda = 1$, $\lambda = \infty$) and ϱ ($\varrho = 0$, $\varrho = 0.2$, $\varrho = 0.5$). Variations of transfer rate $k(T) = k_{DD}(T) = k_{DA}(T)$ with time are illustrated in Figure 1. Dashed lines ($\lambda = 0$) correspond to the values of (4) and (5), solid lines ($\lambda = 1$) have been obtained by numerical solution of the diffusion equation, while points ($\lambda = \infty$) represent the rate for the high diffusion limit, when [15] $k(T) = k_0 = 2\pi^{-1/2}\varrho^{-3}$.
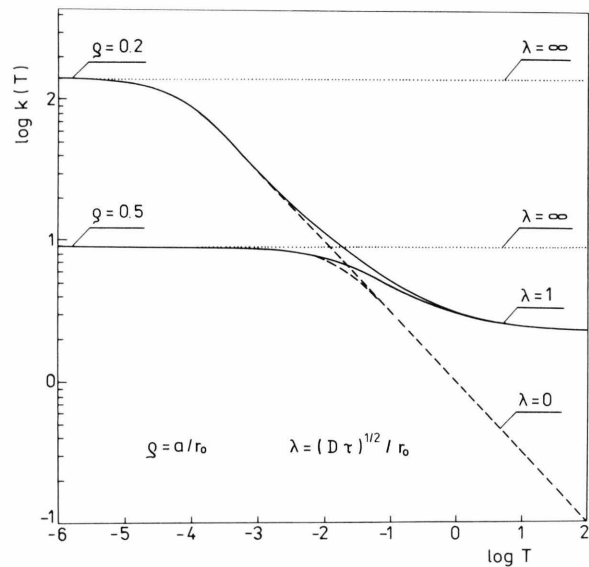
Fig. 1. Variations of excitation transfer rate with time for $\varrho = 0.2$ and $\varrho = 0.5$ and for different values of λ.
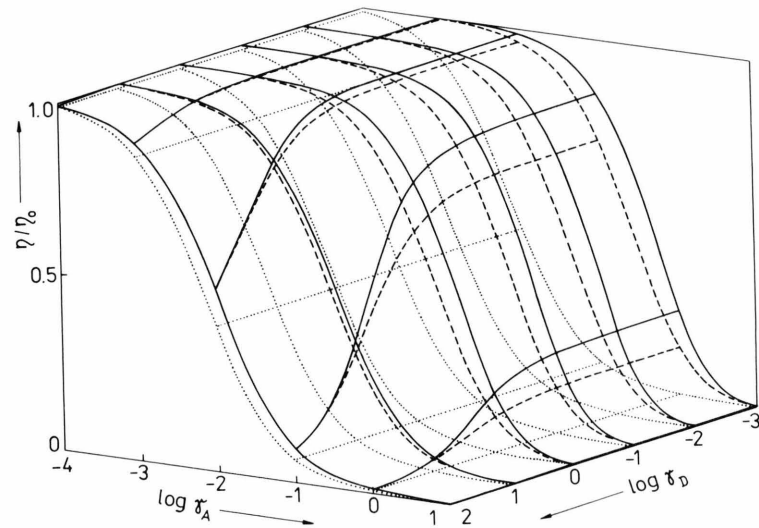

Fig. 2. Relative quantum yield of the donor versus γ_A and γ_D for $\varrho = 0.2$ and for different values of λ. Solid lines: $\lambda = 0$, dashed lines: $\lambda = 1$, points: $\lambda = \infty$.
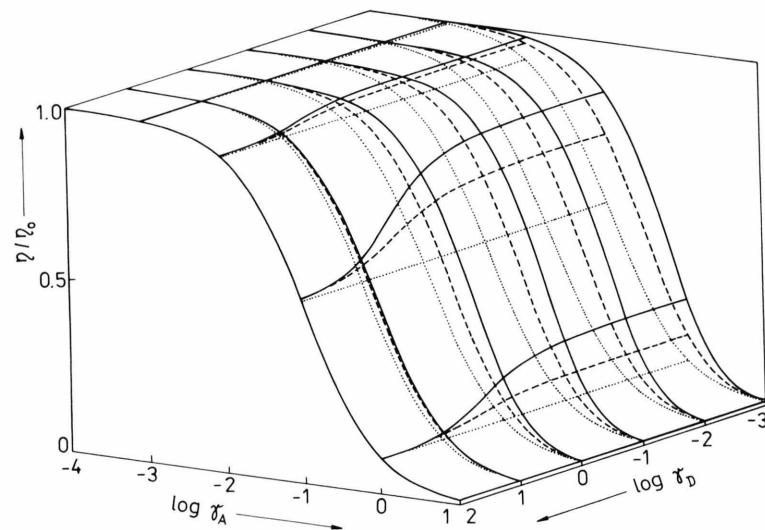

Fig. 3. Relative quantum yield of the donor versus γ_A and γ_D for $\varrho = 0.5$ and for different values of parameter λ. Solid lines: $\lambda = 0$, dashed lines: $\lambda = 1$, dotted lines: $\lambda = \infty$.
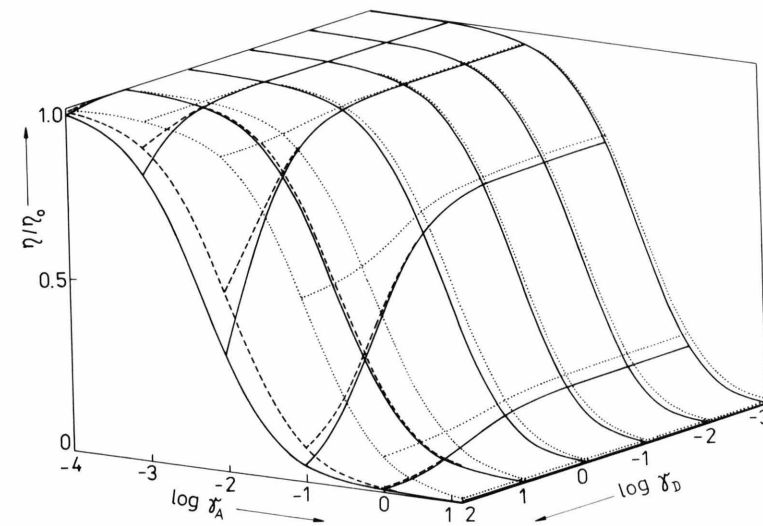

Fig. 4. Influence of molecular size on donor relative quantum yield for $\lambda = 1$. Solid lines: $\varrho = 0$, dashed lines: $\varrho = 0.2$, dotted lines: $\varrho = 0.5$.

The obtained dependence of the relative donor quantum yield on the reduced concentrations γ_D and γ_A is shown in Figs. 2 and 3. One may notice that the influence of material diffusion on the donor photoluminescence yield depends on γ_A as well as γ_D. At small values of γ_D the influence of diffusion on the intensity of energy transfer reaches a maximum for intermediate values of γ_A and is negligibly small for very small as well as very high values of γ_A. This is understandable as for very small γ_A the transfer does practically not take place while for very high γ_A the major number of transfers takes place at very short times, when, as can be observed from Fig. 1, the rates k_{DD} and k_{DA} are constant, independent of diffusion coefficients. At high values of γ_D, the donor yield tends towards the yields obtained in the case of very strong diffusion. Diffusion and migration constitute two competitive processes which endeavour to sustain the uniform spatial distribution of excitation and, thereby, the conditions of most intensive energy transfer to acceptors. In this sense strong diffusion is equivalent to strong migration in the system. Although diffusion, as opposed to migration, causes an increased intensity of collisions of molecules, in the discussed case it has no importance because we have limited our considerations to systems in which collisions of molecules do not activate any additional means of energy transfer.

Figure 4 presents the results obtained with the same computer program, showing the influence of the size of molecules ($\lambda_{DD} = \lambda_{DA} = 1$ is representative for small and intermediate values of λ). Solid curves represent η/η_0 of (1), obtained under the assumption that the extension of molecules is negligibly small ($\varrho_{DD} = \varrho_{DA} = 0$), while dashed and dotted curves have been obtained applying transfer rates taking into consideration the size of the molecules. One may observe that for typical molecules of organic dyes, for which ϱ_{DD} and ϱ_{DA} are not greater than 0.2, consideration of the size of molecules in calculations becomes significant for $\gamma_D > 10$ (dashed curves). Such high concentrations are, however, not usually attainable in real conditions. At higher values of ϱ_{DD} and/or ϱ_{DA} (dotted curves) the significant influence of the finite dimensions of molecules may appear at all values of γ_D, especially at intermediate values of γ_A. The influence is the highest at high values of γ_D, where the restriction of the possibility of molecular centres coming close together limits the intensity of EEM to a great extent. In the case of very strong diffusion ($D_{DD} \to \infty$ and $D_{DA} \to \infty$) or slow reaction ($r_{0DD} \to 0$ and $r_{0DA} \to 0$) the yield η/η_0 becomes independent of donor concentration and tends to $(1 + 2\pi^{-1/2} \varrho_{DA}^{-3} \gamma_A)^{-1}$. Then, especially for small values of ϱ_{DA}, one may expect a strong dependence of the yield on molecular size.

The obtained results allow to ascertain the usefulness of the presented method of calculation of relative donor quantum yield. In the case of small values of diffusion coefficients and small sizes of molecules the obtained quantities are convergent with the results of previous analytical calculations, while for high values of γ_A and/or γ_D the quantities agree with the appropriate boundary values of expression (1) calculated analytically.

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