

Monte Carlo Simulation of Electronic Excitation Migration and Trapping in Disordered Two-Component Systems. A Comparison with Analytical Theories

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Z. Naturforsch. **44a**, 257–261 (1989); received February 3, 1989

Monte Carlo simulations of quantum yield and anisotropy of fluorescence in two-component systems have been conducted with various donor and acceptor concentrations and Förster radii ratios R_0^{DA}/R_0^{DD} . The influence of excitation migration and trapping on the fluorescence of the viscous solution has been considered. The results of the simulations have shown that steady-state fluorescence of a two-component system depends on the R_0^{DA}/R_0^{DD} ratio as predicted in LAF theory.

1. Introduction

The last few years have seen considerable progress in the theory of electronic excitation transport in infinite disordered systems [1, 2]. Incoherent transport of excitation, taking place due to the resonant dipole-dipole interaction between luminescent molecules, plays an important role in natural and synthetic systems [3]. An exact theoretical description of excitation transport in donor and acceptor solutions is possible only in the extreme case of lack of excitation migration between donors [4]. Excitation migration does, however, have a significant effect on fluorescence of two-component systems [5–12]. Most recent theories give a satisfactory description of excitation transport, although they contain distinct approximations, because consideration of migration requires the solution of a many-body problem.

According to the theory of Loring, Andersen and Fayer (LAF) [9], as opposed to other theories [5, 7, 11], the kinetics of excitation transport depends on the Förster radii ratio R_0^{DA}/R_0^{DD} (R_0^{DD} and R_0^{DA} are the Förster radii for donor-donor and donor-acceptor excitation transfer, respectively). No experiments have, so far, been conducted which would directly show this. The selection of a system for such an experiment is not easy. Also, the need to carry out precise measurements of quantum yield, anisotropy or decay of fluorescence in high concentration solutions make this experiment

the more difficult. Moreover, in concentrated dye solutions additional pathways of fluorescence quenching may occur, which complicate the theoretical understanding of observations. That is why the investigation of this effect has been undertaken using Monte Carlo simulation. This work describes the method of simulation and presents its results.

2. Method of Simulation

So far the Monte Carlo method has been used to investigate mainly the kinetics of excitation transport in one-component systems [13–16]. Systems in which donor pairs, apart from each other less than the critical distance, are excitation acceptors have also been simulated [17, 18]. Disordered two-component systems have been subject of a few attempts [19].

The simulation described here has been conducted in a similar fashion to the one presented by Knoester and Van Himbergen [17]. In a cubic box N donors and M acceptors have been randomly arranged without taking into account the excluded volume. The quantum yield and anisotropy of donor fluorescence have been calculated for every configuration of molecules and averaged through an ensemble of configurations, as in [17] (see appendix).

This computational scheme is independent of analytical LAF theory. In the LAF theory the primary Master equation is solved in thermodynamical limit by diagrammatic expansion with so-called two- or three-body approximation [9]. In our simulation the same Master equation was solved numerically with-

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out other approximations, but for a limited number of molecules.

The finite size of the set of molecules is the source of errors in the present method of simulation. However, an increase of the number of molecules might cause substantial numerical errors arising from matrix inversion. The application of periodic boundary conditions and the averaging of calculated values through the set of simulated molecule configurations allows for good results in the case of a finite number of molecules [17].

The simulation has been conducted for a wide range of total reduced donor and acceptor concentration

$$\gamma = \frac{\sqrt{\pi}}{2} (c_D + c_A),$$

where $c_D = \frac{4}{3} \pi (R_0^{DD})^3 \varrho_D$, $c_A = \frac{4}{3} \pi (R_0^{DA})^3 \varrho_A$ and ϱ_D , ϱ_A are the number densities for donor and acceptor, respectively. Depending on the share of donors ($\kappa = c_D/(c_D + c_A)$), N was assumed to be 112 or 144. The value of M was established from the equation

$$M = N \left(\frac{1}{\kappa} - 1 \right) (R_0^{DA}/R_0^{DD})^{-3}.$$

At least 200 molecule configurations have been simulated, so that the standard deviations of calculated η/η_0 and r/r_0 did not exceed 2%.

3. Discussion of Results

Figures 1 and 2 show the theoretical dependence of quantum yield and anisotropy of donor fluorescence, obtained using the analytical formulae of LAF (see appendix), on the reduced concentration γ and the ratio κ for different R_0^{DA}/R_0^{DD} ratios. The dependence of both steady-state quantities on the R_0^{DA}/R_0^{DD} ratio is not prominent, becoming evident only in the case of high concentrations.

The results of simulations, carried out for $\kappa = 0.7$ (maximum effect) and $\kappa = 0.9$ (low trapping – high migration) with the R_0^{DA}/R_0^{DD} ratio equal to 0.5, 1 and 2, are presented in Figs. 3 and 4, along with the corresponding theoretical relationships following from LAF. The influence of the R_0^{DA}/R_0^{DD} ratio on the simulation results is evident and in agreement with the theoretical predictions. On this basis one may deduce that a precise analysis of results of steady-state measurements of quantum yield and anisotropy of fluores-

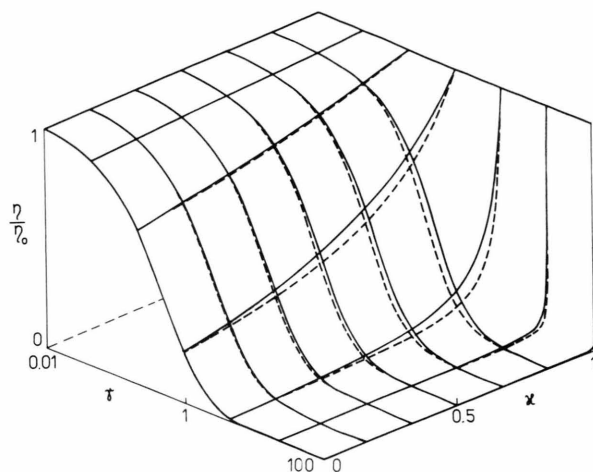


Fig. 1. Fluorescence quantum yield of a two-component system for $R_0^{DA}/R_0^{DD} = 0.5$ (dashed lines) and $= 2$ (solid lines), calculated according to LAF theory. The definitions of reduced concentration γ and the ratio κ are given in the text.

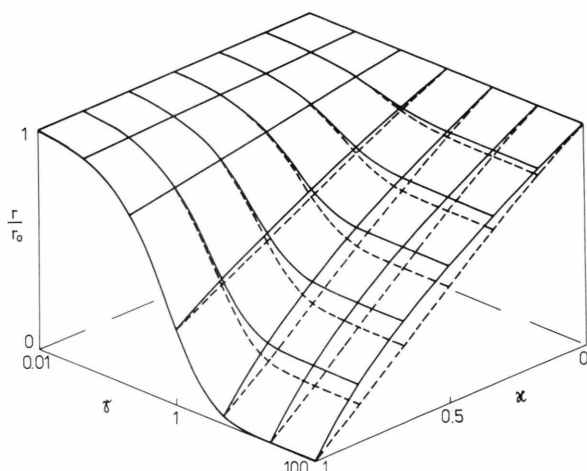


Fig. 2. Fluorescence anisotropy of a two-component system for $R_0^{DA}/R_0^{DD} = 0.5$ (solid lines – opposite to Fig. 1) and $= 2$ (dashed lines) calculated according to LAF theory.

cence, as well as measurements of fluorescence decays, in solutions containing excitation acceptors (traps), requires consideration of the influence of the ratio of excitation transfer strength from donor to donor and from donor to acceptor.

The agreement of the simulation results with theoretical predictions is surprising in view of the approximate nature of the LAF theory. The accuracy of this approximation is difficult to determine, since calcula-

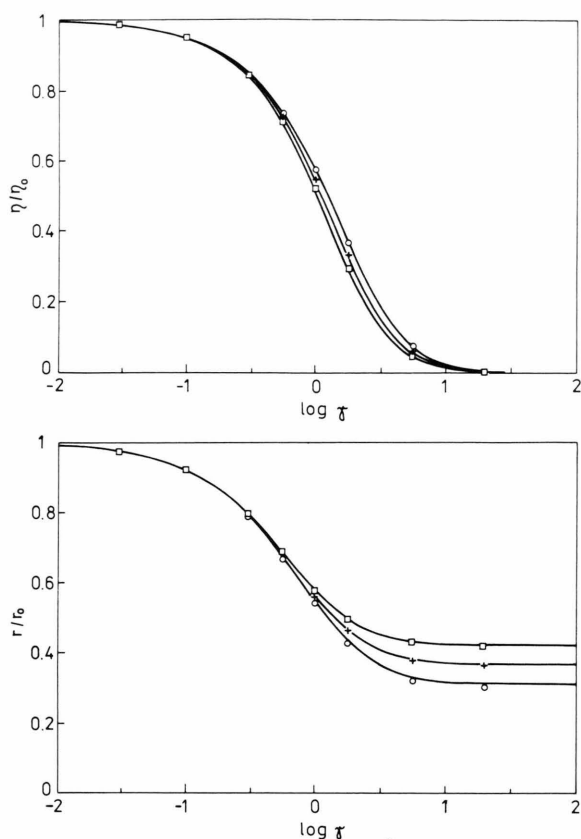


Fig. 3. Simulation results of quantum yield (a) and anisotropy (b) of fluorescence for $\zeta = 0.7$ and $R_0^{DA}/R_0^{DD} = 0.5$ (\square), $= 1$ ($+$) and $= 2$ (\circ). Solid lines represent equivalent theoretical relations according to LAF.

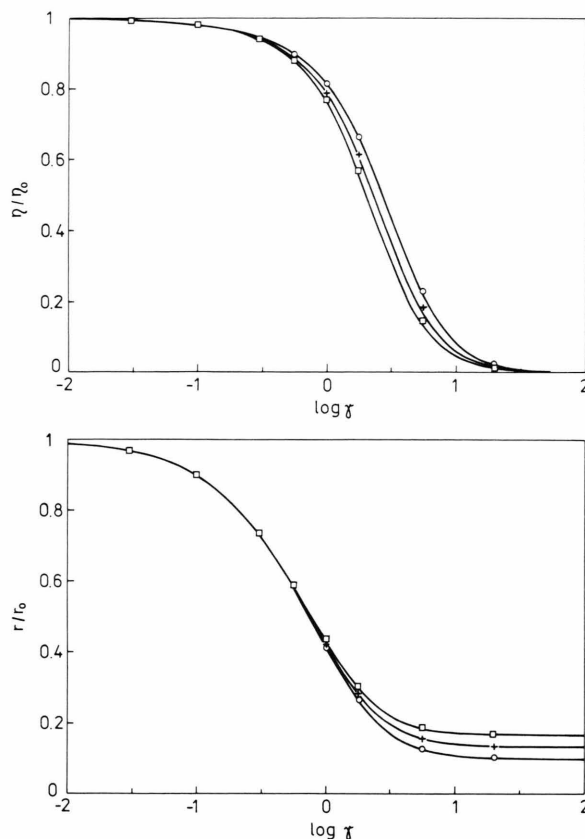


Fig. 4. As in Fig. 3, but for $\zeta = 0.9$.

tions beyond the three-body result have not been hitherto carried out. In our opinion the Monte Carlo data allow to conclude that four-body and higher-order contributions to the diagrammatic expansion developed by Fayer and coworkers [1] are negligible small.

The dependence of the excitation transport on the R_0^{DA}/R_0^{DD} ratio is not predicted in the two-body approximation of LAF theory. This relation appears in the three-body contributions to the diagrammatic expansion, which consider the interactions between two donors and one acceptor. In this way the LAF theory takes into account not only the topological correlations between donor configurations over which excitation migrates, but also the correlations between acceptor surroundings. Therefore the LAF theory may be applied to systems having any value of the R_0^{DA}/R_0^{DD} ratio.

It must be noted that in the range of small and medium concentrations, where the dependence of the fluorescence on the R_0^{DA}/R_0^{DD} ratio is minimal (see Figs. 1 and 2), the theories of Bojarski et al. [5, 7] and Burshtein [11], which do not take this effect into consideration, give values which are in good agreement with the simulation results (see Figure 5). Moreover, these theories prove to be true in the whole range of studied concentrations for selected values of R_0^{DA}/R_0^{DD} : Bojarski's theory for $R_0^{DA}/R_0^{DD} \lesssim 0.5$ and Burshtein's theory for $R_0^{DA}/R_0^{DD} \approx 1$.

The difference between these theories lies in the omission [5, 7] and partial consideration [11] of the influence of correlations between donor configurations over which excitation migrates on quantum yield of donor fluorescence. In both theories, correlations between configurations of acceptors surround-

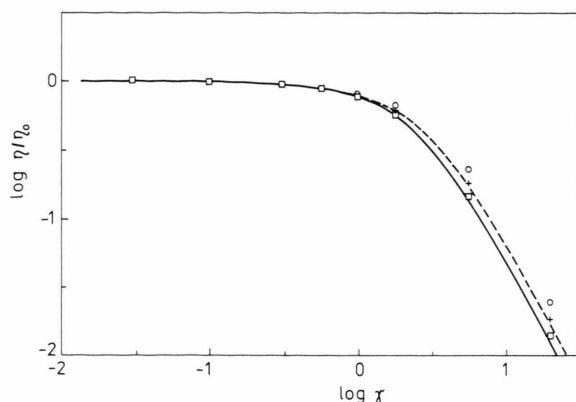


Fig. 5. Quantum yield of a two-component system for $\alpha = 0.9$ calculated according to Bojarski's theory [5, 7] (solid line), Burshtein's theory [11] (dashed line) and obtained from simulation. Points marked as in Figure 3.

ing donors involved in the excitation migration are not taken into account, because the models consider only the interaction between pairs of molecules. The feasibility of incorporating correlations better in these theories is attractive, but this is a difficult theoretical problem beyond the scope of the present paper.

4. Conclusions

The performed Monte Carlo simulation excitation migration and trapping in a disordered system of donors and acceptors has shown that the fluorescence properties of such a system depend not only on the reduced concentrations of donors and acceptors, but also on the ratio of excitation transfer strengths from donor to donor and donor to acceptor. The dependence is not prominent, but in our view this will be essential in some biological and artificial systems with special configurations of dye molecules.

The LAF theory yields good prediction of the dependence of fluorescence on the R_0^{DA}/R_0^{DD} ratio. However, one should mention that this theory exhibits incorrect long-time behaviour [20]. Furthermore, with respect to the rotational motion of molecules, the LAF theory is restricted to the two limiting cases of transfer rate averaging over all orientations of molecules. First, where the molecular orientations are fixed on the time scale of the fluorescence decay, and second, where the molecules exhibit all relative orientations in a time much shorter than one excitation

transfer step. Moreover, in high concentrated dye solutions molecular aggregates may occur, on which an excitation can be additionally trapped. In the LAF theory this pathway of excitation relaxation is not taken into consideration. Therefore, further studies on the excitation transport phenomenon are required before a fully consistent picture is available.

Appendix

For every configuration of molecules the quantum yield of donor fluorescence η was calculated from the equation [17]

$$\eta = \frac{\eta_0}{N} \sum_{k=1}^N \sum_{l=1}^N [(\mathbf{I} + \tau \mathbf{W})^{-1}]_{kl}, \quad (1)$$

in which η_0 and τ are the quantum yield and the lifetime of an isolated donor, \mathbf{I} is the identity matrix, and \mathbf{W} is the relaxation matrix. The fluorescence anisotropy r was obtained from the relation [17]

$$r = r_0 \left\{ \sum_{k=1}^N [(\mathbf{I} + \tau \mathbf{W})^{-1}]_{kk} \right\} \left\{ \sum_{k=1}^N \sum_{l=1}^N [(\mathbf{I} + \tau \mathbf{W})^{-1}]_{kl} \right\}^{-1}, \quad (2)$$

where r_0 is the anisotropy of isolated donor fluorescence.

The elements of the relaxation matrix \mathbf{W} are described as

$$[\mathbf{W}]_{kl} = \delta_{kl} \left(\sum_{i=1}^N w_{ki} + \sum_{i=1}^M v_{ki} \right) - w_{lk}, \quad (3)$$

where the orientation averaged Förster rates are given by the expressions

$$w_{kl} = \frac{1}{\tau} \left(\frac{R_0^{DD}}{r_{kl}} \right)^6, \quad v_{kl} = \frac{1}{\tau} \left(\frac{R_0^{DA}}{r_{kl}} \right)^6. \quad (4)$$

r_{kl} is the distance between the k -th and l -th molecule.

The three-body LAF approximation [9] gives the expressions for quantum yield and anisotropy of steady-state fluorescence of a two-component system in the form

$$\frac{r}{r_0} = 1 - \frac{\pi}{2\sqrt{2}} c_D x + \{0.1887 c_D^2 + [0.3832 - \alpha(R_0^{DA}/R_0^{DD})] c_D c_A\} x^2, \quad (5a)$$

$$\frac{\eta}{\eta_0} = x^2 \left(\frac{r}{r_0} \right)^{-1}, \quad (5b)$$

where

$$x = \frac{\sqrt{p^2 + q} - p}{q}; \quad p = \frac{\pi}{4} \left(\frac{c_D}{\sqrt{2}} + c_A \right),$$

$$q = 1 - 0.1887 c_D^2 - 0.3371 c_A^2$$

$$- [0.13716 - \alpha(R_0^{DA}/R_0^{DD}) + \beta(R_0^{DA}/R_0^{DD})] c_D c_A.$$

The values of the functions $\alpha(R_0^{DA}/R_0^{DD})$ and $\beta(R_0^{DA}/R_0^{DD})$ have been calculated numerically by LAF and tabulated [9]. Selected values of these functions are presented in Table 1.

R_0^{DA}/R_0^{DD}	$\alpha(R_0^{DA}/R_0^{DD})$	$\beta(R_0^{DA}/R_0^{DD})$
0.5	0.079409	0.15703
1.0	0.23911	0.5299
2.0	0.3354	0.87595

Table 1.
Selected values
of the functions
 $\alpha(R_0^{DA}/R_0^{DD})$ and
 $\beta(R_0^{DA}/R_0^{DD})$
from [9].

Acknowledgement

This work was carried out under the Research Project CPBP 01.06.

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