Effect of excitation migration on the decay of excited states via electron transfer to acceptors

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Abstract Simulation of fluorescence quenching due to electron transfer from a photoexcited donor to an acceptor, in a rigid matrix has been performed. The model assumes competition between processes of the electron transfer and the resonant excitation energy transfer among donors. Electron and energy transfers are described in terms of the Marcus and the Förster theories, respectively. Dependence of the fluorescence quenching on the donor concentration and on the parameters of the Marcus and Förster equations has been investigated at a fixed acceptor concentration. Fluorescence decay curves calculated for various concentrations of donors have been compared with experimental decays.

Key words electron transfer • energy migration • simulation • fluorescence decay • polymer matrix

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Introduction

Ohta *et al.* [8, 9] have studied the external electric field effect on electron transfer (ET) between excited N-ethylcarbazole (ECZ*) as an electron donor and dimethylterephthalate (DMTP) as an electron acceptor, which were doped in a poly-methylmethacrylate (PMMA) film at room temperature. They measured the ECZ* fluorescence decay at various strengths F of the applied field and for various concentrations of ECZ and DMTP. They found that at weak fields the variation in the steady-state fluorescence intensity of ECZ* induced by the field is proportional to F^2 and to the concentration of acceptors c_A. These relations have been reproduced recently by the theoretical model [5], which assumes that the external field causes a modification of the free energy change ΔG of the ET reaction. Based on this modification it appears possible to correlate successfully the experimentally observed field induced reduction (or, for other donor-acceptor systems, enhancement) of the donor fluorescence with the enhanced (or reduced) ET rate [4]. The model concerns, however, the case of constant donor concentration c_D and does not explain why the experimentally observed reduction in ECZ* fluorescence intensity due to the electric field becomes larger as the ECZ concentration is increased [9]. Theoretical attempts to explain this observation are based on the assumption that the donor excitation can migrate among donors before it is finally quenched by the randomly distributed quenchers. The migration of excitation does not shorten its lifetime, but only enhances the excitation encounter with quenchers, which eventually leads to faster quenching with increasing donor concentration. Two analytical models describe the effect of excitation migration on

the fluorescence quenching kinetics; one of them adopts a diffusion mechanism for the excitation migration [1] and the other assumes the energy hopping mechanism [2, 4]. Application of these models is, however, limited to the systems with relatively high (the former model) or low (the latter model) donor concentrations. In the present paper, we introduce a new theoretical approach, which seems to be correct throughout the entire donor concentration range employed. Our approach produces the fluorescence quenching kinetics in a donor*-acceptor system in a rigid matrix via direct computer simulation of two competing processes: the ET and the excitation migration by resonant energy transfer. We express the ET and the energy transfer rate constants by the Marcus and Förster equations, respectively, and check how the donor fluorescence decay rate depends on the parameters of these equations and on the concentration c_D. Finally, we compare the fluorescence decay profiles calculated for various c_D with the experimental decays measured for the ECZ*-DMTP system in the PMMA film.

Model

Let us consider m donors (D) randomly distributed in a box of volume V and one acceptor (A) situated at the center of the box. The position of A is chosen as the origin and the position of i-th donor is denoted by the vector r_i. D and A molecules do not move during each simulation run, and the concentration (number density) of donors is equal to $c_D = m/V$. Suppose that at time $t = 0$ a donor is excited. The excitation energy can hop among donors with the rate constant given by the Förster equation

$$(1) \qquad u\left(R_{ij}\right) = \frac{1}{\tau_0}\left(\frac{R_0}{R_{ij}}\right)^6$$

where $R_{ij} = |r_i - r_j|$ is the relative separation of i-th and j-th D molecules, τ_0 is the D^* fluorescence lifetime in the absence of acceptors, and R_0 is the Förster radius [3]. The excitation of D is quenched either by electron transfer to A or by other processes, which are independent of the presence of electron acceptors (natural decay). Deactivation due to the latter mechanism can be described by the rate constant $k_0 = 1/\tau_0$ (cf. equation (16) below). The rate constant k of the ET to A is described by the Marcus equation

$$(2) \qquad k(r) = \frac{2\pi}{\hbar}\frac{J^2(r)}{\sqrt{4\pi\lambda(r)k_BT}}\exp\left\{-\frac{[\Delta G(r)+\lambda(r)]^2}{4\lambda(r)k_BT}\right\}$$

where the Gibbs free energy change ΔG depends on the donor-acceptor distance r through

$$(3) \qquad \Delta G(r) = \Delta G_0 - \frac{e^2}{\varepsilon_S r}$$

ΔG_0 is the standard free energy change and ε_s is the static dielectric constant of the solvent. Other parameters

in equation (2) are as follows:

$$(4) \qquad \lambda(r) = \lambda_i + \lambda_s(r)$$

where λ_i stands for the average vibrational reorganization energy of the D-A system, λ_s is the solvent reorganization energy, expressed in terms of the dielectric continuum model as

$$(5) \qquad \lambda_s(r) = \frac{e^2}{2}\left(\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_s}\right)\left(\frac{1}{d}+\frac{1}{a}-\frac{2}{r}\right)$$

and J is the transfer integral [7]

$$(6) \qquad J^2(r) = J_0^2\exp\{-\beta[r-(d+a)]\}$$

ε_{op} is the optical dielectric constant of the solvent, d and a are the radii of the D and A molecules, respectively, J_0 is the transfer integral at the encounter distance $(d + a)$, and β stands for the attenuation constant.

Let $W_j(t,r_i)$ be the pair survival probability of the excitation initially located at i-th D, in the presence of a single A. We consider various configurations of m donors randomly distributed in the box. The subscript j denotes j-th configuration. If the excitation is produced at any D with equal probability, then the averaged pair survival probability for j-th distribution of D is given by

$$(7) \qquad W_j(t) = \frac{1}{m}\sum_{i=1}^{m}W_j\left(t,r_i\right)$$

Next, we average $W_j(t)$ over L different configurations of m donors

$$(8) \qquad W(t) = \frac{1}{L}\sum_{j=1}^{L}\frac{1}{m}\sum_{i=1}^{m}W_j\left(t,r_i\right)$$

The survival probability $W(t)$ in the presence of n acceptors randomly distributed in the volume V is given as

$$(9) \qquad P_n(t) = \left[\frac{1}{L}\sum_{j=1}^{L}\frac{1}{m}\sum_{i=1}^{m}W_j\left(t,r_i\right)\right]^n$$

Finally, assuming the Poisson distribution with the mean $\mu = c_A V$ for the number of acceptors in the volume V, we perform the averaging of $P_n(t)$ over this distribution and obtain the macroscopic expression for the excitation survival probability

$$(10) \qquad P_{ET}(t) = \sum_{n=0}^{\infty}\frac{\mu^n}{n!}e^{-\mu}P_n(t)$$

$$= \exp\left\{-\frac{c_A}{c_D}\frac{1}{L}\sum_{j=1}^{L}\sum_{i=1}^{m}\left[1-W_j\left(t,r_i\right)\right]\right\}$$

Expression $1 - W_j(t,r_i)$ in eq. (10) can be considered as a fraction of i-th D excitation that decays before time t. The sum over m donors in j-th configuration

(11)
$$N_j(t) = \sum_{i=1}^{m} \left[1 - W_j\left(t, r_i\right)\right]$$

gives the number $N_j(t)$ of excitations that decay before time t by ET to an acceptor when the donors in j-th configuration are excited. The quantity $N_j(t)$ can be calculated from the following set of the rate equations for the population of excitations $p_i(t)$, $i \in [1,m]$, at i-th D molecule,

(12)
$$\frac{dp_i(t)}{dt} = -\sum_{i \neq j}^{m} u\left(R_{ij}\right) p_i(t)$$
$$+ \sum_{i \neq j}^{m} u\left(R_{ij}\right) p_j(t) - k\left(r_i\right) p_i(t)$$

where u and k are the rate constants given by eqs. (1) and (2), respectively. The initial conditions are given by

(13)
$$p_i(t = 0) = 1 \quad \text{for all } i$$

In terms of $p_i(t)$ the quantity $N_j(t), j \in [1,m]$ is expressed as

(14)
$$N_j(t) = \sum_{i=1}^{m} \left[1 - p_i(t)\right]$$

The average survival probability $P_{ET}(t)$ can be rewritten now as

(15)
$$P_{ET}(t) = \exp\left[-\frac{c_A}{c_D} \frac{1}{L} \sum_{j=1}^{L} N_j(t) \right]$$

with $N_j(t)$ given by eq. (14).

Equation (15) takes into account the decay of excitations which is caused only by the ET from D^* to A. To get the excitation survival probability that can be verifiable experimentally, we should include into (15) the expression

(16)
$$P_{Nat}(t) = \exp(-k_0 \cdot t)$$

which is connected with the natural decay of the donor excitation. Thus, the final formula for the excitation survival probability is as follows

(17)
$$P(t) = \exp\left[-\frac{c_A}{c_D} \frac{1}{L} \sum_{j=1}^{L} N_j(t) - k_0 t \right]$$

Results and discussion

We take the volume V as a cubic box with the side-length $b = (m/c_D)^{1/3}$. The value of m for each concentration c_D is different and chosen to preserve an approximately constant value of V ($\sim 65^3\ \text{Å}^3$) in all calculations performed. The coordinates of donors in the box are generated using the random number generator and the applied procedure assures that the distance between

any pair of donors and between any D and A are greater than 6 Å, i.e., greater than the sum of radii of the two molecules.

For a given configuration of m donors, we solve the set (12) of ordinary differential equations for $p_i(t)$ with initial conditions (13) by using the Bader and Deuflhard modification of the Bulirsh and Stoer method with the Richardson extrapolation [10]. This method is especially efficient in the case of a set of stiff differential equations. While calculating the distances R_{ij} between D molecules in the right-hand sides of eqs. (12), we apply the periodic boundary conditions to mimic the bulk system. The calculations were performed for $c_A = 1$ mol% and $c_D = 2$, 5, and 10 mol% (concentrations are expressed in the molar ratio to the monomer unit of PMMA). The values of the other parameters (i.e., $T = 298$ K, $\varepsilon_s = 3.6$, $\varepsilon_{op} = 2.33$, $a = d = 3$ Å, $\lambda_i = 0.3$ eV, $R_0 = 17$ Å, $k_0 = 8 \times 10^7\ \text{s}^{-1}$) are the same as in Refs. [4, 5]. The obtained functions $p_i(t)$ allow us to calculate the time evolution of $N_j(t)$ by using eq. (14). Next, we generate a new (k-th) configuration of m donors in the same box and repeat the calculation to obtain the new function $N_k(t)$. The same procedure is repeated up to L times. Having the functions $N_j(t)$ for $j \in [1,L]$, we evaluate the excitation survival probability given by eq. (15) or, when including the natural decay of excitation, by eq. (17). To perform the calculations we prepared the program in ANSI C, compiled it under GCC and run mostly on IBM PC with Pentium 4, 1.7 GHz and Windows XP O/S. The computation time was dependent on the values of c_D and L considered and in the case of $L = 100$ was equal to 26 or 515 s for $c_D = 2$ or 10 mol%, respectively.

Figure 1 shows $P(t)$ as a function of time calculated for $c_D = 2$ mol% and averaged over L configurations of donors. The full lines illustrate the individual decay curves obtained for three different single configurations of $m = 36$ donors ($L = 1$). The survival probability averaged over 10 configurations differs considerably from those averaged over a larger number of configurations. Small differences between the curves for $L = 100$
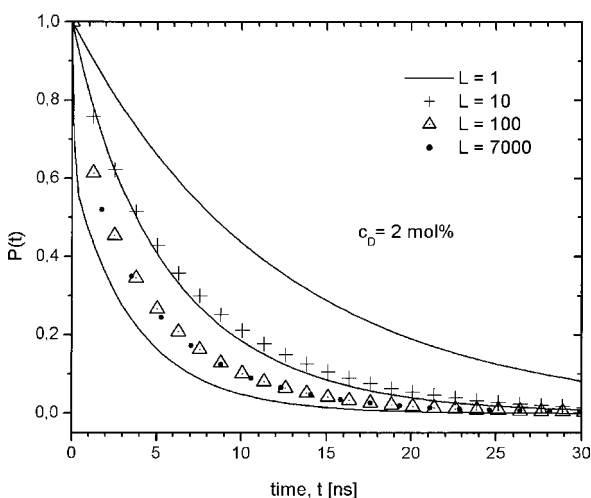

Fig. 1. Time dependence of the survival probability of the excitation $P(t)$ given by eq. (17) and averaged over $L = 10$, 100, and 7000 different configurations of $m = 38$ donors in the volume V. Full lines show the decay curves for three different single configurations of m donors ($L = 1$); $J_0 = 3.6 \times 10^{-3}$ eV, $\beta = 1.0\ \text{Å}^{-1}$, $\Delta G_0 = 0$.

and $L = 7000$ prove that the statistical error of the latter result is negligible. The higher c_D the lower scatter of individual decays – this effect can be expected as the increase of the number of D molecules in the volume V (up to 90 or 165 for c_D equal to 5 or 10 mol%, respectively) results in narrowing of the donor-donor distance distribution. Although the statistical error decreases with increasing c_D we perform averaging over $L = 7000$ configurations for all c_D considered.

Figure 2 gives an insight into the sensitivity of the simulated survival probabilities $P_{ET}(t)$ to the values of the Marcus equation parameters: ΔG_0, J_0, and β. The lower panel of the figure shows that the dependence of $P_{ET}(t)$ on β is negligible within the range of $\beta = 0.9$–1.1 Å^{-1}. The parameter J_0 exerts a significant influence on the decay rate of the donor excitation (middle panel). The increase of J_0 accelerates the excitation decay. The upper panel shows the dependence of $P_{ET}(t)$ on the standard free energy change. The fastest decay is obtained for $\Delta G_0 = -0.3$ eV and this curve lies beneath the line for the zero standard free energy change. Further decrease of ΔG_0 results in slowing down the decay rate of the excitation survival probability. The dependence of $P_{ET}(t)$ on ΔG_0 reflects the dependence of the ET rate constant on ΔG_0, as well as the relative magnitude of $k(r)$ to $u(R)$. Let consider the value of the ET rate constant $k(r_{nn})$ at the average distance from an acceptor to the nearest-neighbor donor, r_{nn} [6]. The
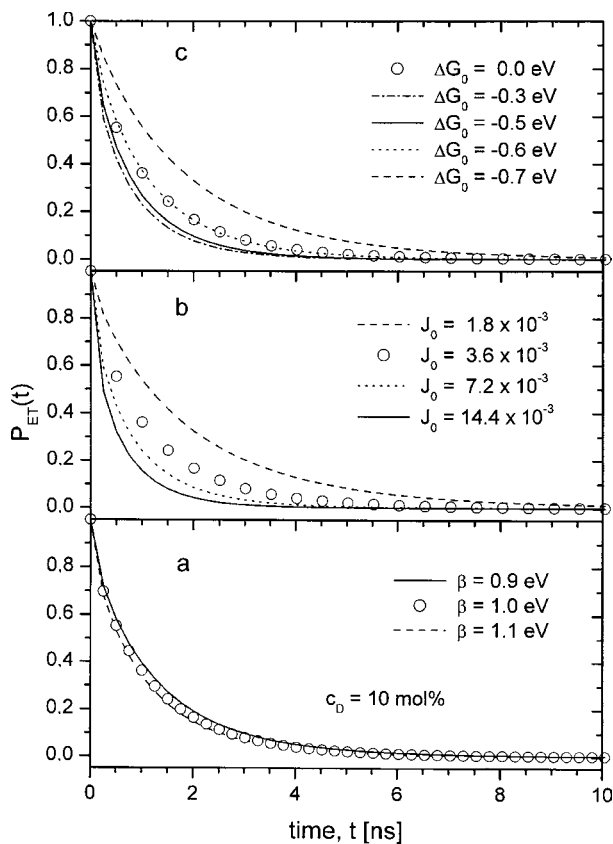
Fig. 2. Dependence of $P_{ET}(t)$, given by eq. (15), on the parameters of the ET rate constant. In each panel the decay curves are calculated by varying the value of β, or J_0, or ΔG_0. The values of the other two parameters used are as follows: (a) $\Delta G_0 = 0$, $J_0 = 3.6 \times 10^{-3}$ eV; (b) $\Delta G_0 = 0$, $\beta = 1.0$ Å^{-1}; (c) $\beta = 1.0$ Å^{-1}, $J_0 = 3.6 \times 10^{-3}$ eV.
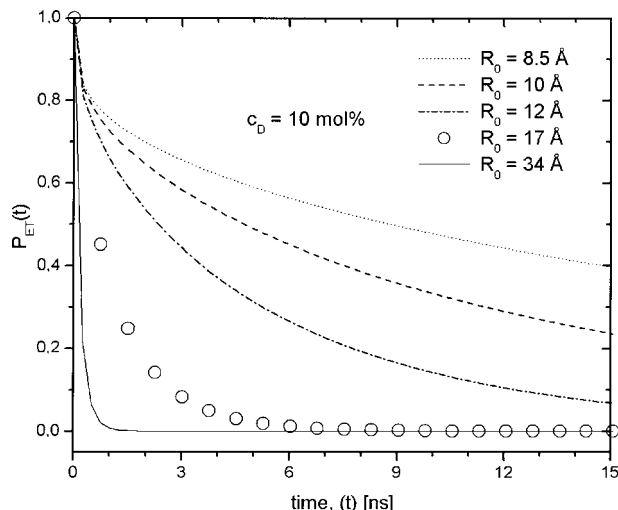
**Fig. 3.** Dependence of $P_{ET}(t)$ on the value of the Förster radius R_0; $J_0 = 3.6 \times 10^{-3}$ eV, $\beta = 1.0$ Å^{-1}, $\Delta G_0 = 0$.

value of r_{nn} depends on the concentration of donors, and is equal to 8.2 Å for $c_D = 10$ mol%. The value of $k(r_{nn})$ is 1.05×10^{10} s^{-1} at the zero free energy change (quite close to $k(r_{nn}) = 7.12 \times 10^9$ s^{-1} at $\Delta G_0 = -0.6$ eV), increases to 2.74×10^{10} s^{-1} at $\Delta G_0 = -0.3$ eV, and drops down to 2.73×10^9 s^{-1} at $\Delta G_0 = -0.7$ eV. The average donor-donor distance at $c_D = 10$ mol% is $R_{av} = 11.9$ Å, and the energy migration rate constant at this distance is equal to 6.8×10^8 s^{-1}. Hence, the ratio $k(r_{nn})/u(R_{av})$ decreases from 40 to only 4 when ΔG_0 changes from -0.3 to -0.7 eV. This explains a relatively slow decay of $P_{ET}(t)$ calculated with $\Delta G_0 = -0.7$ eV and the fastest decay of $P_{ET}(t)$ for small negative values of the standard free energy change.

Figure 3 presents the dependence of $P_{ET}(t)$ on the value of the Förster radius R_0. The increase of R_0 by a factor of 4 accelerates the excitation energy migration among donors by a factor of 4^6. For $R_0 = 8.5$ Å the value of $u(R_{av})$ is 1.04×10^3 times lower than $k(r_{nn})$, and, therefore, the energy transfer process is not effective for the kinetics of the fluorescence decay. On the contrary, $u(R_{av})$ with $R_0 = 34$ Å is ~4 times higher than $k(r_{nn})$ and all the excitations are very efficiently transferred into the vicinity of the electron acceptors and immediately quenched via ET reactions. This figure proves that the excitation migration can indeed considerably influence the fluorescence quenching process.

In Fig. 4, we compare the excitation survival probability $P(t)$, calculated for $c_D = 2$, 5, and 10 mol%, to the respective experimental decays of the ECZ* fluorescence [9]. Simulations were performed for reasonable values of the parameters: $\Delta G_0 = 0$ eV, $J_0 = 3.6 \times 10^{-3}$ eV, $\beta = 1.0$ Å^{-1}, and $R_0 = 17$ Å. The values of β and R_0 are taken to some extent arbitrily, but the values of ΔG_0 and J_0 have been roughly optimized in order to reproduce the experimental profiles presented in the figure.

Conclusions

The present paper introduces a simulation model which includes the competition between two processes, the
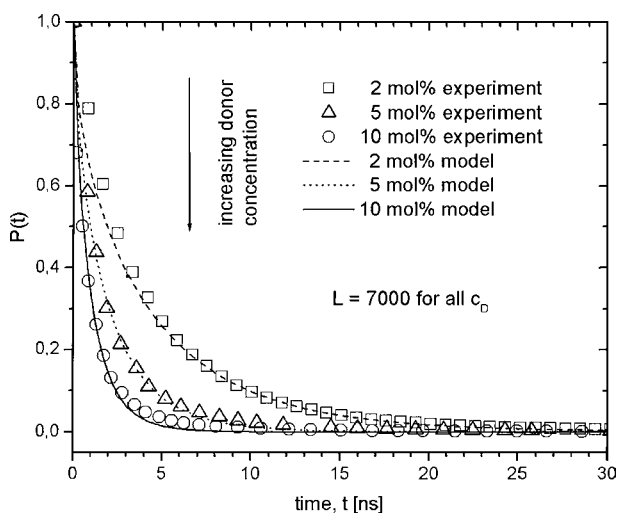
Fig. 4. $P(t)$ averaged over $L = 7000$ different configurations of m donors with concentrations $c_D = 2, 5$ and 10 mol% (lines), and compared with the respective experimental fluorescence decay curves (open symbols).

electron and the excitation-energy transfers, in a rigid matrix with randomly distributed donor and acceptor molecules. The calculations performed for the mixture of ECZ and DMTP in the PMMA film show that the model is able to reproduce correctly the kinetics of the ECZ* fluorescence quenching within a wide range of the donor concentration. The model can be easily modified to simulate the kinetics of donor fluorescence quenching for the system, which is placed in an external electric field **F**. Similarly as in Ref. [5], we can assume that the applied electric field influences the rate of the ET through a modification of the free energy change and calculate the excitation survival probability $P(t,F)$ in the presence of the field **F** employing eq. (2) of Ref. [5] for the ET rate constant $k(\mathbf{r},\mathbf{F})$. These simulations allow us to determine the effect of the field **F** on the donor fluorescence quenching (cf. eqs. (15) and (16) of Ref. [5]) and, when performed for various values of c_D, the dependence of the field effect on the concentration of donors in the considered matrix. Such calculations are in progress in our laboratory.

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