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Effect of chromophore diffusion on electronic excitation transfer in micellar systems

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Abstract

An analytical theory and Monte Carlo simulations are used to study electronic excitation transport (EET) among chromophores diffusing on the surface of spherical micelles. The effect of molecular diffusion on the experimental observables is analyzed for two limiting cases, donor–trap (DT) and donor–donor (DD) EET. Analytical expressions are given for the time-dependent ensemble averaged survival probability of the excited donor $\langle P(t) \rangle$ in the DT case. Diffusion is found to have a pronounced effect on the excitation transfer kinetics except when chromophores have long Förster transfer distances R_0 and short fluorescence lifetimes. © 1997 Elsevier Science B.V.

1. Introduction

Measurement of electronic excitation transport (EET) among chromophores has become widely used to probe structure and dynamics of various microheterogeneous environments in which these chromophores are embedded. The strong dependence of the transfer probability on separation and relative orientation of the two chromophores makes EET a particularly useful tool to investigate structural details of micelles, vesicles and other systems of nanometer scale size. In order to extract quantitative parameters from decay curves obtained in time-resolved fluorescence or fluorescence depolarization experiments, a theoretical model for the experimental observables is needed. A quantitatively correct theory for EET in micellar systems is fairly complex, but many aspects of the modeling process are by now well understood [1–6] and some of the theories have also been tested against experimental results [7–13]. The recent developments in reaction kinetics in micelles have also been summarized in excellent review articles [14,15].

In order to develop a theory of EET among chromophores in micelles, a number of simplifications are usually introduced. Among others these involve the micelle shape, monodispersity, chromophore distribution statistics, chromophore location, validity of the dipole–dipole mechanism and orientational effects. An additional assumption is that the positions of the chromophores are fixed. This is usually justified by the argument that the inside of a micelle is very viscous and that therefore diffusion is negligible on the time scale of the fluorescence experiments. It is difficult to define the concept of microviscosity unambiguously because the chemical potential varies inside a micelle [16,17]. The attempt to obtain lateral diffusion constants via the Debye–Stokes–Einstein equation for a microheterogeneous system seems therefore questionable. Nevertheless, diffusion constants for molecules diffusing in micelles have been obtained in different ways, i.e. from

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reaction kinetics of excimer formation, from fluorescence quenching or NMR spin echo experiments [9,18–20]. These and other sources [21] reported diffusion constants on the order of 0.5–50 $\text{Å}^2/\text{ns}$. Therefore, we must assume that the chromophores can move significantly during the lifetime of excited donor molecules, especially if the fluorescence lifetime is long. However, EET experimental studies found reasonably good agreement between the simplified static theories and the experiments [7,11]. Deviations were attributed to effects due to occupation statistics and attractive interactions among the chromophores and not to diffusion [9,12,13]. Although, the effect of diffusion on EET is well established for isotropic liquid solutions [22], no study for EET in micelles has to our knowledge included the possibility for lateral chromophore diffusion. The goal of this Letter is to include diffusion in the EET theory for micelles and study its effect on the experimental observables.

In the next two sections we develop an analytical theory of DT EET which accounts for chromophore diffusion on the surface of a spherical micelle. In section we will describe the numerical methods used to solve the expressions obtained in section. In addition, Monte Carlo simulations are presented, which validate the analytical DT theory and provide results for the DD EET problem. In section we will compare the results of the analytic theory and the Monte Carlo simulations and discuss the effect of diffusion on experimental observables.

2. The model

Excitation transfer among chromophores on the surface of micelles is a complex phenomenon. To successfully model it, a series of simplifications and assumptions have to be introduced. The restricted geometry system modeled here is one where excitation transfer occurs among non-interacting chromophores lying on the surface of monodisperse spherical micelles of radius R. Depending on the types of chromophores present, we will consider two limiting cases. The first is the DT case, where one donor is surrounded by several acceptors. EET occurs from the donor to one of the traps. No back transfer to the donor is allowed. The concentration of the donor is chosen sufficiently low so there is only one donor per micelle, thus preventing EET among donors. The second case is the DD case, where only one kind of chromophore is present. The excitation can be transferred many times between the donors before deactivation through fluorescence occurs. From here on we will refer to the excited donor, as donor and to the chromophores capable of accepting the excitation upon EET, as acceptors, regardless of whether they are donors or traps. The chromophores in our model are curved disks with a curvature matching that of the micelle (see Fig. 1). Without loss of generality, the sphere can always be rotated to place the initially excited donor at the north pole. The choice of this coordinate frame allows us to characterize the distance between donor and acceptor by one polar angle θ only. The chromophores are allowed to diffuse on the surface of the micelle, characterized by their relative diffusion constant, $D = D_D + D_A$, where D_D and D_A are the lateral diffusion constants of the donor and acceptor, respectively. The micelle concentration is chosen to be low, so that excitation transfer between different micelles can be excluded [3,13,5].

The present model is not meant to describe all possible situations but represents a reasonable model case for which the effect of diffusion on the energy

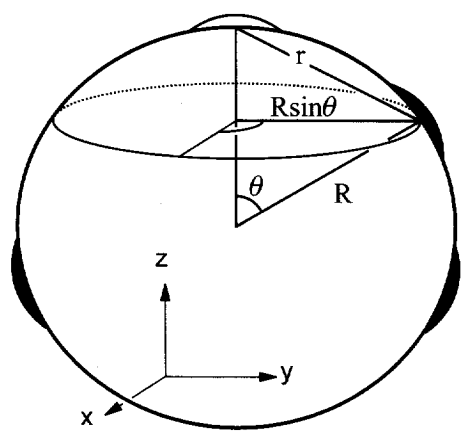

Fig. 1. Schematic representation of the spherical micelle system. The donor and acceptors are modeled as curved disks on the surface of the sphere, with a radius of curvature matching that of the micelle. The donor is shown as a unfilled disk, while the acceptors are represented by the filled disks. The relevant excitation transfer distance is the through-sphere distance r, which is related to the angular distance θ by $r = 2R\sin(\theta/2)$.

transfer observables can be studied conveniently. It is noteworthy that we constrained the chromophores to be placed on the surface of a sphere. As the volume fraction close to the surface is much larger than the one close to the core, the probability that the chromophores lie close to the surface is large. This condition is generally satisfied for chromophores which are the head groups of surfactants themselves. Furthermore, it has been shown that the chemical potential $\mu(d)$ varies with the distance d from the center of the micelle [16,17] making it necessary to model diffusion in the presence of a potential. Due to a different chemical environment in the core and peripheral regions in the micelle, it can also be expected that the diffusion constant D is dependent on d. These problems are avoided in the present model, as the chemical potential $\mu(d)$ and the diffusion tensor $D(d)$ are taken to be constant over the surface of the sphere.

3. Theory

In this section we will develop the equations for the observables of the donor–trap EET case according to the model outlined in the previous section. The theoretical quantity of interest is the ensemble averaged survival probability $\langle P(t)\rangle$, which is the probability that a donor excited by a δ-pulse of light at $t=0$ is still excited at some later time t. $\langle P(t)\rangle$ is experimentally measured as the decay of fluorescence intensity with time. The underlying mathematics of the excitation transfer problem at hand are closely related to the problem of forward electron transfer on micelle surfaces which has very recently been reported [23]. However, because we do not have to describe a process analogous to back electron transfer here, the derivation can be simplified in that the additional step involving the adjoint of the Green's function can be skipped. We start with the following diffusion equation describing the state of the initially excited donor for the special case of a single acceptor. It can be expressed in terms of a Green's function as follows [24,25],

$$\frac{\partial}{\partial t}G(\theta,t|\theta_0)=\left[D\nabla_\theta^2-w(\theta)\right]G(\theta,t|\theta_0) \qquad (1)$$

where $G(\theta,t|\theta_0)$ represents the probability density of the donor being excited at time t, when donor and acceptor are separated by θ given that they were separated by an angle θ_0 at $t=0$. The intrinsic self-decay term has been factored out of $G(\theta,t|\theta_0)$. To compare $G(\theta,t|\theta_0)$ to experimental data, it must be multiplied by $\exp(-t/\tau)$ to account for the lifetime decay term. ∇_θ^2 is the component of the Laplacian describing motion tangential to the surface of the micelle and it is defined as

$$\nabla_\theta^2=\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin(\theta)\frac{\partial}{\partial\theta}\right] \qquad (2)$$

Examination of Fig. 1 shows that the donor–acceptor distance is completely characterized by a single angle, θ, given the radius of the micelle R, and thus, only the polar component of the Laplacian is needed to describe the Brownian motion in the system. The donor and acceptor molecules undergo diffusive motion characterized by their corresponding diffusion constants D_D and D_A. It is convenient to describe the position of the acceptor in a reference frame whose origin coincides at any instant with the center of mass of the donor. In this reference frame the acceptor undergoes diffusive motion relative to a stationary donor characterized by the diffusion constant $D=D_D+D_A$ [24,26,27]. Although this expression is exact for the two particle situation, a coordinate transformation of this type is not exact for the general many-body problem. It has been shown, however, that $D=D_D+D_A$ is an excellent approximation [27].

The second term in Eq. (1), $\omega(\theta)$, is the Förster transfer rate for excitation transfer which arises from transition dipole – transition dipole interactions. This is an approximation to the true transfer rate, especially at distances close to contact, where higher order multipole and exchange terms might contribute. $\omega(\theta)\ G(\theta,t|\theta_0)$ acts as a sink term in the diffusion equation and the EET rate $\omega(\theta)$ is conveniently expressed as a function depending only on the through sphere separation $r=2R\sin(\theta/2)$ between the donor and acceptor. $\omega(r)$ is

$$\omega(r)=\frac{3}{2}\kappa^2\frac{1}{\tau}\left(\frac{R_0^{DT}}{r}\right)^6 \qquad (3)$$

where τ is the measured excited state lifetime in the absence of acceptors, κ^2 is the orientational factor and R_0^{DT} the critical Förster transfer distance for donor–trap excitation transport [28]. Eq. (3) is valid in the dynamic limit with $\langle \kappa^2 \rangle = 2/3$, i.e. for rapidly reorienting chromophores, assuming an isotropic angular distribution of the transition dipoles [29,30,6,12]. In the other limit, i.e. the static case, the survival probability itself has to be averaged over all possible molecular orientations. It is not possible to use a simple scaling technique [7,3,13] to describe the resulting lower EET efficiency in static finite volume systems as has been pointed out in the recent literature [6,12]. It is also possible that molecular reorientation happens on the same timescale as EET [29] and translational diffusion. Such a case is difficult to treat analytically and Monte Carlo simulations would have to be used to obtain a solution. For certain chromophores which are surfactants themselves, the molecular axis might be restricted to a cone about the surface normal and the assumption of an isotropic angular distribution of the transition dipoles might not be fulfilled. However, Riehl [31] demonstrated that the difference between the EET observables for a situation where the direction of the transition dipole is restricted to be parallel to the surface normal and the isotropic case which we assume here is rather small. Because we are interested in the influence of translational diffusion on EET, which will not depend on the angular factor, we will restrict our discussion to the dynamic regime for simplicity.

Eq. (1) must be solved under the following initial and boundary conditions:

$$G(\theta,t=0|\theta_0) = \frac{\delta(\theta-\theta_0)}{2\pi R^2 \sin(\theta_0)} \tag{4}$$

$$2\pi R^2 \sin(\theta_c) D \frac{\partial}{\partial\theta} G(\theta,t|\theta_0)\Big|_{\theta=\theta_c} = 0 \tag{5}$$

Eq. (4) defines the initial distribution density (at $t=0$) of the acceptor. Eq. (5) is a reflecting boundary condition expressed by Fick's first law. It states that the particle flux through a circular band at separation θ_c is zero, where θ_c is the angular donor–acceptor separation at contact. The use of a reflective boundary condition rather than a partially reflective one allows us to model the transfer probability at contact through the transfer rate (Eq. 3) rather than through some arbitrary boundary condition.

We define the two-particle survival probability density $S(\theta,t)$ by a weighted integral of $G(\theta,t|\theta_0)$ over all the initial positions of the acceptor θ_0.

$$S(\theta,t) = \int_0^\pi G(\theta,t|\theta_0) \frac{\sin\theta_0}{2} \mathrm{d}\theta_0 \tag{6}$$

a similar integration on both sides of Eq. (1) leads to

$$\frac{\partial}{\partial t} S(\theta,t) = \left[D\nabla_\theta^2 - \omega(\theta) \right] S(\theta,t) \tag{7}$$

The initial condition for Eq. (7) is derived from Eq. (4) and the definition of $S(\theta,t)$ in Eq. (6).

$$S(\theta,t=0) = \int_0^\pi \frac{\delta(\theta-\theta_0)}{2\pi R^2 \sin\theta_0} \frac{\sin\theta_0}{2} \mathrm{d}\theta_0 = \frac{1}{4\pi R^2} \tag{8}$$

The reflecting boundary condition, i.e. Eq. (5) transforms to

$$2\pi R^2 \sin(\theta_c) D \frac{\partial}{\partial\theta} S(\theta,t)\Big|_{\theta=\theta_c} = 0 \tag{9}$$

Let us now consider the general case in which one donor is surrounded by several acceptors positioned at the angular positions $\theta_1 \cdots \theta_N$. The survival probability density $P(\theta_1 \cdots \theta_N,t)$ can be expressed as a product of independent two-particle probability densities because energy transfer from the donor to one acceptor does not depend on the presence of other acceptors [32].

$$P(\theta_1 \cdots \theta_N,t) = \prod_{i=1}^N S(\theta_i,t) \tag{10}$$

Differentiation of Eq. (10) with respect to t gives

$$\frac{1}{P(\theta_1 \cdots \theta_N,t)} \frac{\partial P(\theta_1 \cdots \theta_N,t)}{\partial t} = \sum_{i=1}^N \frac{1}{S(\theta_i,t)} \frac{\partial S(\theta_i,t)}{\partial t} \tag{11}$$

which can be further transformed by using Eqs. (7) and (11) to

$$\frac{\partial P(\theta_1 \cdots \theta_N,t)}{\partial t} = \sum_{i=1}^N \left(D\nabla_{\theta_i}^2 - \omega(\theta_i) \right) P(\theta_1 \cdots \theta_N,t) \tag{12}$$

To obtain the ensemble average of the survival probability $\langle P(t)\rangle$ we need to integrate the probability density over all positions of θ [33,34], as follows

$$\langle P(t)\rangle = \int_{\theta_c}^{\pi} \cdots \int_{\theta_c}^{\pi} P(\theta_1) \cdots \theta_N, t) \cdot 2\pi R^2 \sin(\theta_1) \cdots 2\pi R^2 \sin(\theta_N) \cdot d\theta_1 \cdots d\theta_N \quad (13)$$

Substitution of $P(\theta_1 \cdots \theta_N, t)$ by the expression from Eq. (10) gives

$$\langle P(t)\rangle = \int_{\theta_c}^{\pi} \cdots \int_{\theta_c}^{\pi} \prod_{i=1}^{N} S(\theta_i, t) 2\pi R^2 \sin(\theta_i) d\theta_i \quad (14)$$

and because all the acceptors are equivalent

$$\langle P(t)\rangle = \left[\int_{\theta_c}^{\pi} S(\theta, t) 2\pi R^2 \sin(\theta) d\theta \right]^N \quad (15)$$

Eq. (7) for $S(\theta,t)$ cannot be solved analytically, and numerical calculation of $S(\theta,t)$ must be followed by numerical integration as indicated in Eq. (15) to give $\langle P(t)\rangle$.

4. Numerical methods and Monte Carlo simulations

To solve for $S(\theta,t)$ in Eq. (7) we used the Crank–Nicholson algorithm and a finite differencing scheme suggested by Agmon and Hopfield [35]. $\langle P(t)\rangle$ was then calculated from Eq. (15) via numerical integration using a Gauss quadrature algorithm. Step sizes of 0.005 ns in time and 0.002 rad in space for θ gave converged results.

We also conducted Monte Carlo simulations to verify the above analytical theory for the DT case and to obtain results for the mathematically more challenging DD case. The same physical model and boundary conditions as described in sections and were used. In brief, a random configuration of N acceptors and one donor (placed at the north pole of the sphere) was generated appropriately [5]. All N acceptors were then allowed to undergo Brownian motion, with each acceptor stepping a distance of $\sqrt{4D\Delta t}$, where Δt is the size of the time step used in the simulation. This distance is the average distance for Brownian motion on an infinite plane during a time Δt which is, for small time steps, a good approximation to describe diffusion on the surface of a sphere. The choice of 0.01 ns for Δt proved to be a good compromise between accuracy and efficiency of the simulation. Steps causing particles to overlap were rejected thus including effects due to excluded volume and implementing a reflective boundary at the same time. For congruity to the analytical model only donor–acceptor excluded volume was modeled in the MC simulations. Inclusion of acceptor–acceptor excluded volume had a negligible effect on $\langle P(t)\rangle$ for the low number of chromophores we considered. After each time step the probability of excitation transfer from the donor to each acceptor was calculated as $(1 - \exp(\omega(\theta_i)\Delta t))$, where θ_i is the angular distance from the donor to the i-th acceptor. A pseudo random number then determined whether excitation transport occurred during this time step or not. If not, the simulation continued with another diffusion step as mentioned above. If EET occurred in a DT simulation, $\langle P(t)\rangle$ was updated and the entire simulation was repeated many times to allow for a sufficient sampling of the configuration space (in general 10^5 times). In the DD case the excitation was transferred to the appropriate molecule (while still keeping track of the originally excited donor) and a coordinate transformation was used to rotate the sphere ensuring that the now excited donor is placed at the north pole. The simulation was then allowed to continue up to a maximum time t_{max} $(= 3\tau)$ before updating $\langle P_1(t)\rangle$, the probability that the initially excited donor (i.e. the 1 subscript) is excited at a later time. $\langle P_1(t)\rangle$ is updated with a histogram of ones and zeros which indicate for each time step if the initially excited donor is excited.

5. Results and discussion

In the DT case we obtained the donor excited state population $\langle P(t)\rangle$ in two independent ways, namely from a numerical solution of an analytical expression and from Monte Carlo simulations. Fig. 2 shows a comparison of decay curves obtained in these ways. The points represented by circles were obtained from the Monte Carlo simulation, and they are in very close agreement to those obtained by the

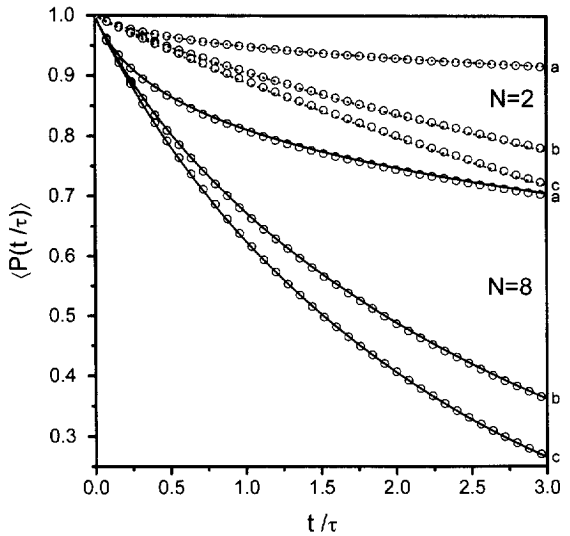

Fig. 2. Comparison of the analytical theory (lines) with the Monte Carlo simulation (circles) for a donor–trap case ($R = 37$ Å, $R_0 = 12.4$ Å). The dotted curves are obtained for the case of one donor and two acceptors ($N = 2$), while the solid curves result from a calculation for one donor and eight acceptors ($N = 8$). A diffusion constant of 0 Å^2/ns was chosen for the a curves, 5 Å^2/ns for the b curves and 15 Å^2/ns for the c curves.

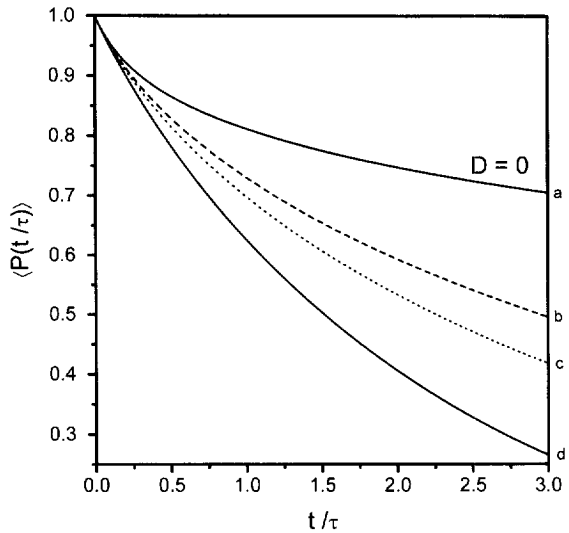

Fig. 3. Effect of different chromophore lifetimes τ on $\langle P(t)\rangle$ determined by the analytical theory for a donor–trap case ($R = 37$ Å, $R_0 = 12.4$ Å, one donor and 8 acceptors). Curve a is obtained in the limit of no diffusion for $\tau = 5$, 10 and 50 ns (curve independent of τ because the time is scaled by τ). Curves b–d are obtained with a diffusion constant $D = 15$ Å^2/ns and $\tau = 5$ ns (curve b), $\tau = 15$ ns (curve c) and $\tau = 50$ ns (curve d).

analytical theory (the small deviations are within the expected statistical error). This adds to our confidence that the analytical theory is correct within the model assumed and that our simulations are working correctly.

Analysis of decay curves as represented in Fig. 2 shows that even slow diffusion can have a large accelerating effect on the excitation transfer observables, especially if the Förster transfer distance is small and the fluorescence lifetime is long ($R_0 = 12.4$ Å, $\tau = 50$ ns. These are the parameters of naphthalene if a naphthalene-like molecule is also the acceptor). We limit the observation time frame to three fluorescence lifetimes τ because most of the excited states have decayed by then. For a diffusion constant D of 5 or 15 Å^2/ns, values often suggested for diffusion in micelles [9,18–21], a $> 50\%$ increase in the transfer probability compared to the static case is found after about one lifetime. The effect of diffusion on $\langle P(t)\rangle$ increases with the number of acceptors as the curves for two and eight acceptors in Fig. 2 indicate. For a very high number of chromophores, however, EET becomes so fast compared to diffu-

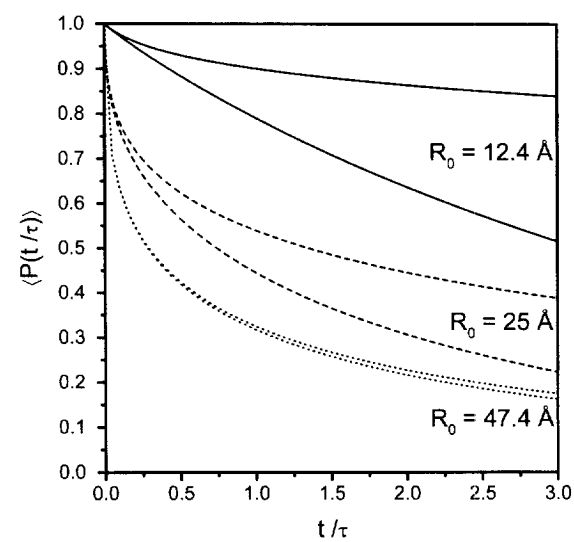

Fig. 4. Effect of different Förster transfer distances R_0 on $\langle P(t)\rangle$ determined by the analytical theory for a donor–trap case ($R = 37$ Å, $\tau = 10$ ns, one donor and 4 acceptors). R_0 was set to 12.4 Å for the two solid curves, 25 Å for the two dashed curves and to 47.4 Å for the dotted curves. The upper curve of the curve pairs was obtained in the limit of no diffusion while the lower curve includes diffusion ($D = 15$ Å^2/ns).

sion that the rate of diffusion becomes less important.

Several experimental studies have found that a diffusion free theory was capable of fitting their experimental data, and therefore they concluded that diffusion need not to be considered [7,9,12,13]. The parameters used to obtain the curves in Fig. 2 were chosen because they show how much diffusion can change the picture under the right circumstances. In particular, the lifetime $\tau = 50$ ns is quite long. All of the chromophores chosen in the experimental studies had significantly shorter lifetimes, thereby shortening the distance traveled by the chromophores undergoing Brownian motion. Fig. 3 shows the effect of shorter lifetimes on $\langle P(t)\rangle$ while keeping the transfer distance constant ($R_0 = 12.4$ Å). However, a significant effect remains even with a lifetime as short as 5 ns (curve *b*). The fact that the simple diffusion-free theory fits the experimental data, can therefore not be explained solely by the short fluorescence lifetimes of the used chromophores.

In Fig. 4 we investigate the effect of different Förster transfer distances R_0 on $\langle P(t)\rangle$ while keeping τ and D constant ($\tau = 10$ ns, $D = 15$ Å^2/ns). As the R_0 increases the differences between the curves with and without diffusion become small. As R_0 gets larger than R, the micelle radius, EET is possible to almost all locations on the micelle and diffusion ceases to have an important effect on $\langle P(t)\rangle$. This is clearly an effect due to the finite size of the system. The fact that diffusion-free theories were successfully applied to fit experimental observables of EET in micellar systems can therefore be attributed to the fact that chromophores with a large Förster transfer distance and a short lifetime were used. However, in general, the neglect of diffusion can lead to substantial errors in the interpretation of experimental results.

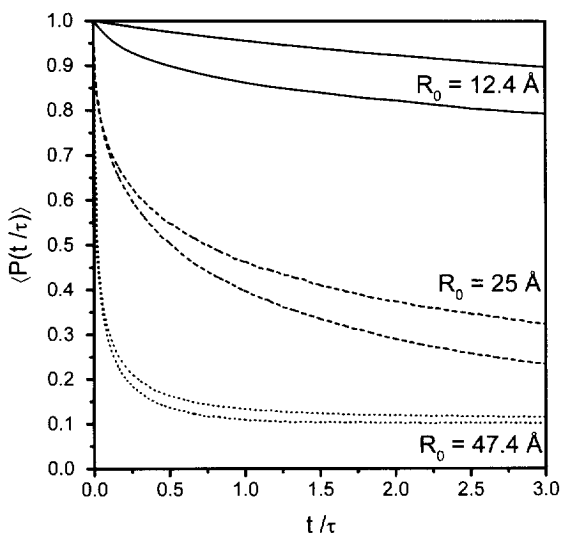

Fig. 5. Effect of different Förster transfer distances R_0 on $\langle P_1(t)\rangle$ determined by Monte Carlo simulations for a donor–donor case ($R = 37$ Å, $\tau = 10$ ns, one donor and 8 acceptors). R_0 was set to 12.4 Å for the two solid curves, 25 Å for the two dashed curves and to 47.4 Å for the dotted curves. The upper curve of the curve pairs was obtained in the limit of no diffusion while the lower curve includes diffusion ($D = 15$ Å^2/ns).

The previous results were obtained for donor–trap EET. Similar considerations apply for donor–donor EET. Fig. 5 shows the results of donor–donor EET Monte Carlo simulations for three different transfer distances. The results display behavior that is similar to the DT case (compare to Fig. 4). However, the magnitude of the changes between the curves modeled with and without diffusion is smaller than in the DT case. This is most likely due to the possibility of back-EET in the DD system.

6. Conclusions

It has been found that inclusion of diffusion is necessary to obtain an accurate description of EET observables in spherical micellar systems. Only in the limit that the Förster transfer distance R_0 becomes large, comparable or greater than the micelle size, can a theory that excludes diffusion be safely used. Some experiments have fallen in this limit, which accounts for the success of the theory without diffusion in describing those systems [7–13]. However, for chromophores with short transfer distances and long fluorescence lifetimes, a correct treatment of diffusion becomes necessary to describe either DT or DD EET.

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