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ARTICLES

Dipole−Dipole Electronic Energy Transfer. Fluorescence Decay Functions for Arbitrary Distributions of Donors and Acceptors. II. Systems with Spherical Symmetry

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Many interesting systems of nanometer dimensions form spherically symmetric domains, either by design or through spontaneous self-assembly. The technique of direct nonradiative resonance energy transfer (DET) can be used to characterize the morphology of such structures on a nanometer scale. One needs to label the domain of interest with appropriate donor and acceptor dye moieties. One measures the fluorescence decay of the donors ($I_D(t)$) in the presence of acceptors. The underlying geometry and physics of the system dictate how the dyes distribute themselves along the radial axis R of the system, according to concentration profiles ($C_D(R)$, and $C_A(R)$) which need not be uniform. Because DET is sensitive to the distribution of dye interdistances, $I_D(t)$ contains information about the underlying morphology. In this work we obtain an analytic expression relating $I_D(t)$ to the donor/acceptor concentration profiles. This extends our previous contribution for systems with a plane of symmetry. The expression developed is general and capable of handling geometries in both extended and/or restricted spaces. It does not require a specific spatial locus for the donors nor does it require prior calculation of the pair-distribution function of the donor−acceptor distances. The development also provides one with an analytic expression for the evaluation of the interdistance distribution functions.

Introduction

The morphological characterization of nanoscale structures is an area of activity fueled by recent advances in materials science, nanochemistry, and the invention of various novel microscopies. While the microscopy techniques have generated impressive images of surface nanodomains, one normally obtains information only about the geometry of structures larger than ca. 10 nm. For a complete characterization of the morphology of a nanodomain, one would like to have information not only about the size and shape of the domain but also about its composition and how the various components making up the system distribute themselves across space. That is, one would like to determine the concentration profiles of each of the components across the system. Where sufficient phase contrast can be established, X-ray and neutron scattering provide techniques for determining concentration profiles. For organic materials, neutron scattering is more generally useful because one can in principle label any component with the deuterium atoms needed for contrast. The task of synthesizing material with deuterium-labeled components is not always so simple, and other methods which require different labeling schemes would be welcome.

The technique of direct nonradiative electronic (Förster[1]) energy transfer (DET) between donors (D) and acceptors (A) is also a powerful method for the measurement of distances on the nanometer scale, particularly for biological[2] and organic systems.[3] In this approach, one labels specific sites of interest, on a large molecule or in a specific domain, with two dyes that will serve as D and A, respectively. One measures the increase in the rate of the donor fluorescence decay, from an inherent value of ($1/\tau_D$) in the absence of A to a rate of ($w + (1/\tau_D)$) in the presence of A. The measured rate of DET is then related to the distance r separating the centers of the transition dipoles of D and A by the Förster relation

$$w(r) = \frac{\frac{3}{2}\kappa^2}{\tau_D}(R_o/r)^6 \tag{1}$$

where R_o (the Förster radius) is a constant that can be calculated from the spectroscopic properties of the D/A pair and normally has a value in the range of 2−7 nm. The factor $3\kappa^2/2$ is related to the orientation of the transition moments of D* and A. For the case of rapidly reorienting dipoles, the orientationally averaged value of this factor is exactly equal to unity. For most other situations lacking strong orientational correlations, this term takes a value within ca. 10% of unity.[4] In this work we shall assume a value of unity for this factor.

According to eq 1, if all D/A pairs are separated by the same distance r, as in the case of dyes attached to sites on a large rigid molecular framework, where experiments are carried out at sufficient dilution such that no intermolecular DET is possible, the donor decay profile will be exponential with a decay rate faster than that of the unquenched decay. Most systems, however, have a distribution of D/A distances. Subsequent to pulsed excitation, the observed fluorescence decay function $I_D(t)$ is no longer a simple exponential. $I_D(t)$ now displays a faster decay in the early time region (DET between closely spaced

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pairs) followed by slower decay at longer times (DET between more distant pairs).

Two factors affect the distribution of the interdistances: the shape and size of the space in which the D and A are distributed and the variation of the concentration of D and A over the nanodomain in the system. Early treatments of DET kinetics treated systems with uniform D and A distributions over extended space in three and two dimensions. When the D and A groups are distributed over domains which are finite in size, i.e., with at least one dimension on the order of R_o, edge effects become important. Here one has to take into account the consequences of the restricted geometry. Initial steps in this direction were taken by Fayer and co-workers for D−D energy migration[5] and Klafter, Blumen, and others for direct D−A energy transfer.[6] In the Klafter−Blumen (KB) formulation, the expression for evaluating $I_D(t)$ is given by

$$I_D(t,\vec{r}_o) = \exp\{-t/\tau_D\}\varphi(t,\vec{r}_o) \tag{2}$$

$$\varphi(t,\vec{r}_o) = \exp\{-p\int_V[1 - \exp\{-tw\}]\rho(r)\,dV\} \tag{3}$$

Here, $\varphi(t,\vec{r}_o)$ is the survival probability of the excited donor due to all DET-related processes; $w(r)$ is the rate of DET given by eq 1; $\rho(r)$ is a "site density function" proportional to the probability distribution of finding a donor−acceptor pair separated by r; p (the probability of occupation of a site) is a constant proportional to the acceptor concentration. The integration is carried over the volume of the microdomain. To make use of the KB expression, one needs to make a prior calculation of $\rho(r)$ by considering the geometry of the system. The notation $\vec{r}_o$ in eq 3 is used to emphasize the fact that the KB formulation is restricted in application to conditions where all donors are situated in equivalent environments; i.e., when each D is in a translationally invariant locus $\vec{r}_o$ and sees the same distribution of A's around it. For example, this applies to the situation of D and A covering the surface of a sphere, but it would not apply to the same sphere when the D's are moved to the inside. In this case, a D near the surface sees a different distribution of A's than one closer to the center.

Recently we were able to extend the KB formalism to situations lacking translational invariance.[7] While this work laid the foundations of the new methodology, its application was limited to systems where the concentration profiles have a plane of symmetry. Concentration profiles describing the distribution of the D/A labels in systems of spherical symmetry are also important, because in a large number of cases, the various coexisting phases making up the system tend to minimize surface energy by forming spherical shapes. Examples abound in block copolymer morphology,[8] latex films,[9] and colloidal systems such as micelles[10] and core-shell latex particles.[11] In this work we wish to extend our formalism to situations where the concentration profiles $C_D(R)$ and $C_A(R)$ are functions describable along the radial axis R of a spherical system.

The Model

We follow a line of development similar to that of our earlier report.[7a] Let the position of any point in the sample be specified by the radial axis R, measuring distance to the center of symmetry. The observable donor fluorescence intensity $I_D(t)$ will be a sum of the elemental intensities $\delta I_D(R,t)$ emanating from thin onion-skin-like shells of thickness dR. $\delta I_D(R,t)$ is proportional to the number of donors initially excited in the shell and also to the product $\exp\{-t/\tau_D\}\varphi(R,t)$. Here $\varphi(R,t)$ is the local donor survival probability due to all DET-related processes. The number of donors initially excited in the shell is in turn proportional to the local concentration of ground-state donors, $C_D(R)$, and we can write

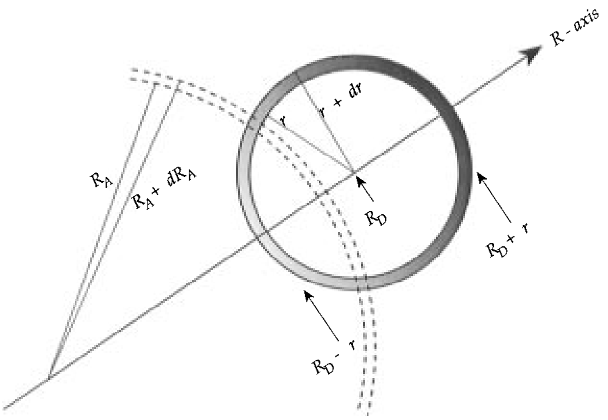

Figure 1. Schematic representation of a nonuniform distribution of acceptors (graduated shading) surrounding an excited donor positioned at a distance R_D from the center of symmetry *O*. The figure shows only the acceptors contained within a spherical shell of radius r and thickness dr. The shell spans an R domain of $|R_D - r|$ to $(R_D + r)$. The acceptor concentration is uniform within the ring formed by taking a scooplike slice of the shaded shell, here cut between the two surfaces at R_A and $R_A + dR_A$.

$$I_D(t) = \exp\{-t/\tau_D\}\int C_D(R)\,\varphi(R,t)R^2\,dR \tag{4}$$

The integration is carried over the radial thickness of the sample. In eq 4, $C_D(R)$ can have any convenient unit of concentration, and for simplicity of notation, we omit the use of all proportionality constants. The problem of evaluating $I_D(t)$ is now reduced to one of finding the local DET-related survival probability $\varphi(R,t)$, which takes the form of a KB-type equation (eq 3). The latter assertion is valid because the KB expression holds true for systems in which all the donor loci are equivalent. Because of the symmetry of the concentration profiles, this is the case for the donors within the R to $R + dR$ shell. In light of our previous arguments,[7] in the KB eq 3, we can replace the term $p\rho$(r) by C_A and write

$$\varphi(R,t) = \exp\{-\int_V[1 - \exp\{-tw\}]C_A(R)\,dV\} \tag{5}$$

where the differential $C_A(R)$ dV is now interpreted as equal to the mean number of acceptor molecules existing in a spherical shell of thickness dr and radius r, surrounding an excited donor molecule located in a spherical shell of the sample, between R and $R + dR$.

We can calculate C_A dV by the following procedure. In Figure 1 we depict an excited donor positioned at R_D and surrounded by a spherical shell of radius r. The graduated shading represents some arbitrary variation of $C_A(R)$ within the shell. We need to evaluate the mean number of acceptors within the shaded shell. Considering the spherical symmetry, we note that C_A is a constant within any thin scooplike cut taken out of the shaded shell, say between R_A and $R_A + dR_A$. The resulting section, when viewed in the radial R direction, resembles a concave ring of volume dv_{ring}. Therefore

$$C_A\,dV = \int_{|R_D - r|}^{(R_D + r)} C_A(R_A)\,dv_{\text{ring}} \tag{6}$$

Figure 1 shows that the integration limits span the R domain of the shaded shell. The lower limit must be in the form of an absolute value because, for radii, only positive values are allowed. In Appendix A we utilize geometrical considerations to show

$$\mathrm{d}v_{\mathrm{ring}} = \frac{2\pi r}{R_{\mathrm{D}}} R_{\mathrm{A}}\, \mathrm{d}R_{\mathrm{A}}\, \mathrm{d}r \qquad (7)$$

Substituting this result in eq 6 we obtain

$$C_{\mathrm{A}}\, \mathrm{d}V = \frac{2\pi r\, \mathrm{d}r}{R_{\mathrm{D}}} \int_{|R_{\mathrm{D}} - r|}^{(R_{\mathrm{D}} + r)} \mathrm{d}R_{\mathrm{A}}\, R_{\mathrm{A}} C_{\mathrm{A}}(R_{\mathrm{A}}) \qquad (8)$$

Equation 8, when substituted in eq 5, completes the formal solution of the problem.

At this point, we find it useful to define a new function that simplifies notation, will have physical significance, and juxtaposes the present formulation with the earlier works of Förster, Klafter, and Blumen.[1,6] We define a new number-density function $\langle C_{\mathrm{A}} \rangle$, obtained by dividing the total number of acceptors in the shaded shell of Figure 1 by the volume element of that shell.

$$\langle C_{\mathrm{A}}(R_{\mathrm{D}},r) \rangle \equiv \frac{C_{\mathrm{A}}\, \mathrm{d}V}{4\pi r^2\, \mathrm{d}r} = \frac{1}{2rR_{\mathrm{D}}} \int_{|R_{\mathrm{D}} - r|}^{(R_{\mathrm{D}} + r)} \mathrm{d}R_{\mathrm{A}}\, R_{\mathrm{A}} C_{\mathrm{A}}(R_{\mathrm{A}}) \qquad (9)$$

$\langle C_{\mathrm{A}}(R_{\mathrm{D}},r) \rangle$ can be interpreted as the directionally-averaged concentration of acceptors that a donor sees at a distance r around itself. Using Figure 1, this can be visualized if we homogenize the graded shading through the whole available volume of the shell. By using eqs 4, 5, and 9, while dropping the subscripts for R, the final result is simplified to

$$I_{\mathrm{D}}(t) = \exp\{-t/\tau_{\mathrm{D}}\} \int_0^{\infty} \mathrm{d}R\, R^2 C_{\mathrm{D}}(R)\, \varphi(R,t) \qquad (10a)$$

$$\varphi(R,t) = \exp\{-g(R,t)\} \qquad (10b)$$

$$g(R,t) = 4\pi \int_0^{\infty} \mathrm{d}r\, r^2 \langle C_{\mathrm{A}}(R,r) \rangle \left[1 - \exp\left\{-\frac{t}{\tau_{\mathrm{D}}}(R_{\mathrm{o}}/r)^6\right\}\right] \qquad (10c)$$

$$\langle C_{\mathrm{A}}(R,r) \rangle = \frac{1}{2rR} \int_{|R - r|}^{(R + r)} \mathrm{d}R'\, R' C_{\mathrm{A}}(R') \qquad (10d)$$

A discussion about the use of eqs 10 is in order. First, the expressions are exact and describe DET in all systems of spherical symmetry. The only assumption involved is that pertaining to the orientation factor, where we have somewhat arbitrarily set the factor $3\kappa^2/2$ in eq 1 to unity. Next, while $C_{\mathrm{D}}(R)$ can have any unit of concentration, $C_{\mathrm{A}}(R)$ must have units expressed as number density. Third, from the definition given in eq 9, it follows that $4\pi r^2 \langle C_{\mathrm{A}}(R,r) \rangle$ is proportional to the probability distribution of finding an acceptor at a distance r from a D positioned at R. For the special cases where all the donor loci are equivalent, $\langle C_{\mathrm{A}}(R,r) \rangle$ becomes proportional to the site density function $\rho(r)$ first formulated by Klafter and Blumen in eq 3.[6] Consequently, an interesting feature of the present formalism is that one is now provided with an analytic relationship (c.f. eq 10d) for calculating the pair-distribution functions.

In eqs 10a,c we have set the limits of integration from zero to infinity for the convenience of dealing with continuously extended concentration profiles. No particular difficulty is caused here, because if one deals with restricted geometries or samples of finite size, then $C(R)$ will be associated with appropriate truncating functions that will restrict the domain of integration. We shall see some examples of truncation in the applications section described below. The lower limit of integration implicitly allows for the possibility of D−A pairs with $r = 0$. Some workers correct for this by taking $r = \sigma$ as the lower limit, where σ is the sum of the D + A van der Waals radii, typically 0.3−1.0 nm. By taking $\sigma = 0$ we gain analytical simplicity and the error introduced for analyzing experimental fluorescence decay data is negligible, because the very high rate of DET ensures that no significant emission is detectable from such closely spaced pairs. These closely space pairs will quench excited donors, and their presence contributes to the quantum efficiency of energy transfer. Under these circumstances, the quantitative importance of these pairs can be assessed by comparing the DET quantum yield measured by steady state spectroscopy with that calculated by integrating the donor decay profile.

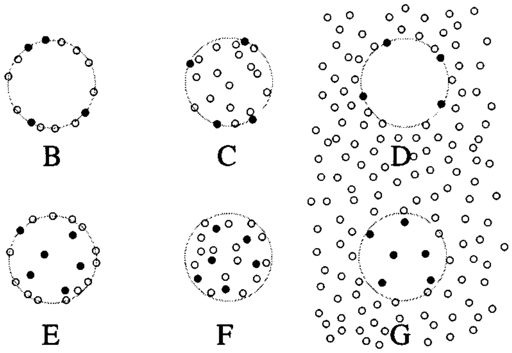

Figure 2. Depiction of the various random but uniform distributions of donors (●) and acceptors (○) pertaining to cases B−G of the text. In situations B−D, all donors have translationally invariant positions. In situations D and G the acceptors occupy all space outside of the spheres.

For the purpose of numerical evaluation of eq 10, it is useful to note that a decay experiment is usually followed for $0 < t < 6\tau_{\mathrm{D}}$. During this time window, the function $r^2\,(1 - \exp(-tw))$ is sharply peaked, with a maximum near $r \approx R_{\mathrm{o}}$, a feature which is almost independent of the time t. Depending on the degree of numerical accuracy desired, one need not carry the integration over r to more than several times R_{o}.

Application to Specific Systems

In this section we consider various modes of DET in the restricted space of a sphere of radius R_{s}. We expect that in real systems one deals with concentration profiles that most likely are spatially extended and nonuniform. In such cases one needs a pertinent physical theory to describe the concentration profiles. The nonuniform concentration profiles can occur as a result of the natural tendency of the system for microphase separation (equilibrium systems) or because one has arrested the interdiffusion of initially separated donors and acceptors. At present we are actively applying the new methodology to the analysis of data from both types of these systems.[9d,e]

In this work, we will consider uniform and sharply discontinuous concentration profiles to show the simplicity and power of the present formulation for the derivation of the $I_{\mathrm{D}}(t)$ profile. The extension of these examples to unbounded spaces with nonuniform profiles will be straightforward. That is, once $\langle C_{\mathrm{A}}(R,r) \rangle$ is calculated from eq 10d, the desired solution is formally available.

In Figure 2 we depict the various spherically symmetric donor/acceptor distributions that we shall be considering here. Only the case of an infinitely extended isotropic mixture (Case A) is not shown. The first four cases we treat were worked out by others, the first by Förster[1] and the next three by Klafter and Blumen.[6] These examples involve situations where all donors have equivalent loci; i.e., each donor sees the same distribution of acceptors. The other cases we consider are for situations involving nonequivalent donor positions and to our knowledge have not been dealt with before.

A. Donors in an Isotropic Three-Dimensional Medium of Acceptors. Here the acceptors uniformly fill all 3-D space with a uniform concentration C_A, all having equivalent loci. The resulting expression for $I_D(t)$, also known as the Förster expression, is independent of how the donors occupy space. C_A is a constant, and from eq 10d we find $\langle C_A(R,r)\rangle = C_A$. Equation 10c yields the exponent function, and we obtain[12]

$$I_D(t) = \exp\{-t/\tau_D\}\exp\{-g_{3\text{-}D}(t)\} \tag{11a}$$

$$g_{3\text{-}D}(t) = 2\gamma_3(t/\tau_D)^{1/2};\quad \gamma_3 = {}^2\!/_3\pi^{3/2}C_AR_o^3;\quad {}^2\!/_3\pi^{3/2} = 3.712\,22 \tag{11b}$$

B. Surface-to-Surface DET. Here both donors and acceptors are distributed over the surface of a sphere of radius R_s, each with uniform surface densities C_D and C_A (cf. Figure 2b). All donors have equivalent loci. The concentration profiles are given by δ functions.

$$C_D(R) = C_D\delta(R-R_s) \tag{12}$$

$$C_A(R') = C_A\delta(R'-R_s) \tag{13}$$

When applied to eq 10a, eq 12 dictates that R can only equal R_s. Next, we find $\langle C_A(R_s,r)\rangle$ by evaluating $\int_{|R_s-r|}^{(R_s+r)} \mathrm{d}R'\, R'\delta(R'-R_s)$. The latter has a nonzero value only if R_s lies in the domain of integration. Since the upper limit is clearly higher than R_s, to be in the proper range, we must have $|R_s - r| \le R_s$. That is, $0 < r < 2R_s$, yielding

$$\langle C_A(R,r)\rangle = \frac{C_A}{2r} \qquad 0 < r < 2R_s \tag{14}$$

Now the substitution of eq 14 in eq 10c yields[12]

$$I_D(t) = \exp\{-t/\tau_D\}\exp\{-g(t)\} \tag{15a}$$

$$\begin{aligned} g(t) &= 2\pi C_A\int_0^{2R_s}\mathrm{d}r\, r\left[1-\exp\left\{-\frac{t}{\tau_D}(R_o/r)^6\right\}\right] \\ &= g_{2\text{-}D}(t)\mathbf{[}1 + 0.0231(R_o/R_s)^4(t/\tau_D)^{2/3} - 7.21\times10^{-5}(R_o/R_s)^{10}(t/\tau_D)^{5/3} + \ldots\mathbf{]} \end{aligned} \tag{15b}$$

$$g_{2\text{-}D}(t) = 2\gamma_2(t/\tau_D)^{1/3};\quad \gamma_2 = \frac{\pi}{2}\Gamma({}^2\!/_3)C_AR_o^2;\quad \frac{\pi}{2}\Gamma({}^2\!/_3) = 2.127\,05 \tag{15c}$$

where the function $g_{2\text{-}D}(t)$ corresponds to the exponent function for DET on an infinitely-extended two-dimensional flatland, originally derived by Hauser et al.[13] Equation 15b shows that for values of $(R_s/R_o) \ge 1$, the higher order terms are negligible and DET on the surface of a sphere is practically identical to DET on a two-dimensional flat surface.

C. Surface-to-Inside DET. Here the donors are on the surface of a sphere and acceptors uniformly distributed on the inside of it (cf. Figure 2c). Again, all donors have equivalent loci, and C_D is represented by eq 12, while

$$C_A(R') = C_AH(R_s-R') \qquad 0 < R' < R_s \tag{16}$$

H defines a Heaviside truncating step function, such that $H(x)$ has either a value of unity (for $x > 0$) or a value of zero (for $x < 0$). Equation 12 implies that $R = R_s$. To find $\langle C_A(R_s,r)\rangle$, we substitute eq 16 into eq 10d and note that the upper limit of integration cannot be higher than R_s. Also, as long as $r < 2R_s$, we deal with a lower limit that remains within the range allowed by eq 16. These observations are expressed by

$$\langle C_A(R_s,r)\rangle = \frac{C_A}{2rR_s}\int_{|R_s-r|}^{R_s}\mathrm{d}R'\,R' = \frac{C_A}{2}\left(1-\frac{r}{2R_s}\right);\qquad 0 \le r \le 2R_s \tag{17}$$

Observe that in eq 17, as well as eq 14, the quantity $4\pi r^2\langle C_A(R_s,r)\rangle$ is proportional to the corresponding pair-distribution function $(\rho(r))$ of distances between D's and A's. These functions were previously derived by KB and other workers through the application of various procedures.[6,14] The substitution of eqs 12 and 17 in eq 10 yields

$$\begin{aligned} g(t) &= 2\pi C_A\int_0^{2R_s}\mathrm{d}r\, r^2\left(1-\frac{r}{2R_s}\right)\left[1-\exp\left\{-\frac{t}{\tau_D}(R_o/r)^6\right\}\right] \\ &= {}^1\!/_2 g_{3\text{-}D}(t)\mathbf{[}1 + 0.566\,785(R_o/R_s)(t/\tau_D)^{1/6} - 0.035\,262(R_o/R_s)^3(t/\tau_D)^{1/2} + \ldots\mathbf{]} \end{aligned} \tag{18a}$$

$$I_D(t) \approx \exp\{-t/\tau_D\}\exp\{-{}^1\!/_2 g_{3\text{-}D}(t)\} \qquad \text{only if } \frac{R_o}{R_s} \gg 1 \tag{18b}$$

where $g_{3\text{-}D}(t)$ was defined in eq 11b for the simplest possible case, i.e., that of DET in an isotropic three-dimensional medium. The asymptotic form of eq 18a shows that the higher order terms cannot be neglected, and only when the ratio (R_s/R_o) is much larger than unity is the approximation in eq 18b justified.

D. Surface-to-Outside DET (Complementary to Surface-to-Inside DET). Here the donors cover the surface of the sphere while acceptors uniformly fill the outer space of the sphere (cf. Figure 2d). We can evaluate the appropriate expressions by noting an interesting property of DET systems which we call complementary. Observe that DET-related survival probabilities to various parts of space are independent and multiplicative (cf. eq 10). If we divide all space arbitrarily to complementary parts I and II, we can write

$$\varphi_{\text{all space}} = \varphi_{3\text{-}D}(t) = \varphi_{I}(R,t)\,\varphi_{II}(R,t) \tag{19}$$

$$g_{\text{all space}} = g_{3\text{-}D}(t) = g_{I}(R,t) + g_{II}(R,t) \tag{20}$$

where $g_{3\text{-}D}(t)$ is the exponent function corresponding to DET in 3-D isotropic space (the Förster expression, eq 11b). It follows that $g(t)$ for the geometry of this section can be found as the difference of $g_{3\text{-}D}(t)$ and that given by eq 18a of section C.

$$g(t) = {}^1\!/_2 g_{3\text{-}D}(t)\mathbf{[}1 - 0.566\,785(R_o/R_s)(t/\tau_D)^{1/6} + 0.035\,262(R_o/R_s)^3(t/\tau_D)^{1/2}\ldots\mathbf{]} \tag{21}$$

E. Inside-to-Surface DET. This is the same geometry as that of section C except that the D's and A's have exchanged positions (cf. Figure 2E). DET is, however, not symmetrical to the exchange of the donor/acceptor positions. This is the first example we consider where not all donor locations are equivalent and the interdistance distribution function of donor–acceptor pairs becomes dependent on the donor position. The use of the KB eq 3 is no longer justified. For this case, the acceptor profile is the same as that of case B (eq 13), while

$$C_D(R) = C_DH(R_s-R) \tag{22}$$

Substituting eq 13 in eq 10d shows that we need to evaluate $\int_{|R-r|}^{(R+r)}\mathrm{d}R'\,R'\delta(R'-R_s)$ which has a nonzero value only if the peak of the δ function lies in the domain of integration. This means that both conditions $|R - r| < R_s$ and $(R + r) > R_s$ should be satisfied simultaneously. By inspection, the restrictions can be expressed as $(R_s - R) \le r \le (R_s + R)$, leading to

$$\langle C_A(R,r)\rangle = \frac{C_A R_s}{2rR} \qquad (R_s - R) \le r \le (R_s + R) \quad (23)$$

$$I_D(t) = \exp\{-t/\tau_D\}\int_0^{R_s} dR\, R^2 \exp\{-g(R,t)\} \quad (24a)$$

$$g(R,t) = \frac{2\pi C_A R_s}{R}\int_{(R_s - R)}^{(R_s + R)} dr\, r\left[1 - \exp\left\{-\frac{t}{\tau_D}(R_o/r)^6\right\}\right] \quad (24b)$$

which, for the purpose of numerical evaluation, can be expressed in terms of incomplete γ functions. It should be mentioned that experimental models of inside-to-surface DET for which $(R_s/R_o) \gg 2$ would not be very illuminating for experimental studies because the observable donor fluorescence signal will be dominated from core portions of the sample unaffected by energy transfer.

F. Inside-to-Inside DET. Here both donors and acceptors are uniformly distributed inside of the sphere (cf. Figure 2f). Again, not all donor loci are equivalent. In this case, $C_D(R) = C_D H(R_s - R)$, and $C_A(R) = C_A H(R_s - R)$. We find (Appendix B)

$$\begin{aligned}\langle C_A(R,r)\rangle &= C_A && 0 \le r \le (R_s + R) \quad (25)\\ &= \frac{C_A}{4rR}(R_s^2 - (R - r)^2) && (R_s - R) \le r \le (R_s + R)\\ &= 0 && \text{elsewhere}\end{aligned}$$

Substitution in eq 10c yields

$$I_D(t) = \exp\{-t/\tau_D\}\int_0^{R_s} dR\, R^2 \exp\{-g(R,t)\} \quad (26a)$$

$$g(R,t) = 4\pi C_A\int_0^{(R_s - R)} dr\, r^2\left[1 - \exp\left\{-\frac{t}{\tau_D}(R_o/r)^6\right\}\right] + \frac{\pi C_A}{R}\int_{(R_s - R)}^{(R_s + R)} dr\, r(R_s^2 - (R - r)^2)\left[1 - \exp\left\{-\frac{t}{\tau_D}(R_o/r)^6\right\}\right] \quad (26b)$$

The expression for eq 26b looks cumbersome to handle. However, for the purpose of data fitting, it can be expressed in terms of incomplete γ functions that are amenable to facile numerical integration.[15]

From the past literature we are aware of a single report where an attempt was made to fit experimental energy transfer data from micellar solutions to the inside-to-inside DET model.[16] In order to derive $I_D(t)$ for this case, the authors assume an approach equivalent to that of KB, which implicitly presumes equivalent loci for all donors and requires input of the function for the donor−acceptor distance distribution of random points in a sphere. This function has been obtained by various methods as[14,17]

$$\rho(r) = 3x^2(1 - (x/2))^2(1 + (x/4)); \quad x = (r/R_s) \quad (27)$$

The substitution of a distance-distribution function such as eq 27 in the KB eq 2 is justifiable only if the geometry of the system implies that all the loci $\vec{r}_o$ of the excited donors are equivalent. This is certainly true when the donors are all on the surface of the sphere (cf. Figure 2c). However, when the donors are on the inside of the sphere, not all loci are equivalent. For example, equally separated pairs on the outer periphery of the sphere are more probable than those near the core. The use of KB eq 2 is then not justifiable, and eq 26 must be used instead.

G. Inside-to-Outside DET (Complementary to Inside-to-Inside DET). Here the donors are on the inside and the acceptors on the outside of the sphere (cf. Figure 2g). The geometry here is complementary to that depicted in Figure 2f. Using arguments similar to those leading to eq 19, we obtain

$$I_D(t) = \exp\{-t/\tau_D\}\exp\{-g_{3\text{-D}}(t)\}\int_0^{R_s} dR\, R^2 \exp\{-g(R,t)\} \quad (28)$$

where $g_{3\text{-D}}(t)$ is the exponent function of the Förster expression (eq 11) and $g(R,t)$ is that given in eq 26b.

Conclusion

We have obtained a theoretical expression (eqs 10) for the fluorescence decay of excited chromophores ($I_D(t)$) in the presence of acceptors, under conditions where the donor/acceptor concentration profiles are nonuniform but have spherical symmetry. The expression developed is general and capable of handling geometries in both extended and/or restricted spaces. It does not require a specific spatial locus for the donors nor does it require prior calculation of the pair-distribution function of the donor−acceptor distances. The method enables one to evaluate $I_D(t)$ from a knowledge of the donor and acceptor concentration profiles. It reduces to known expressions in the case of DET in infinite media and allows simplified asymptotic solutions or facile numerical analysis for systems with more complicated concentration profiles. When desired, the present methodology would also provide one with an analytic expression for the evaluation of pair distribution functions (cf. eq 10d).

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Appendix A

The volume element of the ring-shaped object (dv_{ring}) can be calculated as follows. Consider the interpenetration volume (v) of two spheres of radii R_A and r, respectively. The ring is obtained through the differential growth of the radii by dR_A and dr, respectively. To calculate v, we refer to Figure 1 and divide the interpenetration volume across the plane of intersection into $v = v_1 + v_2$, obtaining the segments of two spheres of heights h_1 and h_2, with corresponding radii R_A and r, respectively. From the geometry of the figure, we can write

$$h_1 + h_2 = R_A - (R_D - r) \quad (A1)$$

$$r^2 - (r - h_2)^2 = R_A^2 - (R_D - r + h_2)^2 \quad (A2)$$

The above can be solved to obtain

$$h_1 = \frac{r^2 - (R_D - R_A)^2}{2R_D} \quad (A3)$$

$$h_2 = \frac{R_A^2 - (R_D - r)^2}{2R_D} \quad (A4)$$

The volume of each segment v_i is given by

$$v_i = \frac{\pi}{3} h_i^2\,(3r_i - h_i) \qquad \text{(A5)}$$

In this way we can write an expression for $v = v_1 + v_2$ and solve for the differential as

$$\mathrm{d}v_{\mathrm{ring}} = \left(\frac{\partial^2 v}{\partial r\,\partial R_{\mathrm{A}}}\right) \mathrm{d}r\,\mathrm{d}R_{\mathrm{A}} = \frac{2\pi r}{R_{\mathrm{D}}} R_{\mathrm{A}}\,\mathrm{d}R_{\mathrm{A}}\,\mathrm{d}r \qquad \text{(A6)}$$

Appendix B

We need to evaluate

$$\langle C_{\mathrm{A}}(R,r)\rangle = \frac{C_{\mathrm{A}}}{2rR}\int_{|R-r|}^{(R+r)} \mathrm{d}R'\,R' H(R_{\mathrm{s}} - R') \qquad \text{(B1)}$$

The Heaviside function sets the R' values in the range of $0 \le R' \le R_{\mathrm{s}}$. Therefore

$$\text{if} \quad |R - r| \ge R_{\mathrm{s}}, \qquad \text{then } \langle C_{\mathrm{A}}\rangle = 0$$

$$\text{if} \quad |R - r| \le R_{\mathrm{s}} \text{ and } (R + r) \ge R_{\mathrm{s}}, \text{ then } \langle C_{\mathrm{A}}\rangle = \frac{C_{\mathrm{A}}}{2rR} \times \int_{|R-r|}^{R_{\mathrm{s}}} \mathrm{d}R'\,R'$$

$$\text{if} \quad (R + r) \le R_{\mathrm{s}}, \qquad \text{then } \langle C_{\mathrm{A}}\rangle = \frac{C_{\mathrm{A}}}{2rR} \times \int_{|R-r|}^{(R+r)} \mathrm{d}R'\,R'$$

The integrals are easily worked out. The restrictions are expressed as follows: $|R - r| \ge R_{\mathrm{s}}$ implies $r \ge (R_{\mathrm{s}} + R)$; $|R - r| \le R_{\mathrm{s}}$ implies $r \le (R_{\mathrm{s}} + R)$, leading to eq 25 of the text.

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(12) In dealing with DET problems one frequently encounters integrals of the type

$$g(t) = \int_0^\infty [1 - \exp[-tw(r)]]\, r^m\, \mathrm{d}r = \frac{\Gamma[(5-m)/6]}{(m+1)} R_{\mathrm{o}}^{(m+1)} (t/\tau_{\mathrm{D}}^{\circ})^{(m+1)/6}$$

where m is a whole number, $-1 < m < 5$, and the Euler Γ numbers can be tabulated as $\Gamma[1/6] = 5.5663$; $\Gamma[2/6] = 2.6789$; $\Gamma[3/6] = \pi^{1/2} = 1.7724$; $\Gamma[4/6] = 1.3541$; $\Gamma[5/6] = 1.1288$.

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