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Inclusion of the Förster-rate orientation factor into the theory of concentration self-quenching by statistical traps

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The incorporation is studied of the orientation factor occurring in the complete Förster rate of incoherent energy transfer, into the theory of concentration self-quenching by statistical pairs of luminescent molecules. Within Burshtein's theory of hopping transport, exact results for the steady state donor fluorescence yield and emission anisotropy are obtained for three-dimensional systems. Two opposite limits to treat the orientations of the molecular transition dipoles within statistical pairs are considered, and it appears that in both cases the fluorescence yield is substantially influenced by inclusion of the orientation factor into the transfer kinetics.

I. INTRODUCTION

Within the field of incoherent transfer of excitation energy the $1/r^6$-Förster rate[1] plays an important role, because of its frequent occurrence in nature. The complete form of this dipole–dipole transfer rate contains the complicated orientation factor κ^2, which introduces additional degrees of freedom and imposes extra difficulties on the theoretical derivation of the fluorescence quantities of interest from the microscopic transfer kinetics.[2–9] Therefore, one mostly, tacitly, preaverages this rate over all orientations, so that an isotropic form for the rate is obtained. Even in this approximation it is difficult to obtain rigorous practical results for the observables in disordered sytems, especially if both migration (between donors) and quenching (due to traps) occurs and (or) if high densities of the interacting molecules are involved. One thus has to fall back on approximate models to solve the transfer kinetics and perform the necessary configurational averages.

In this paper, we consider the fluorescence quantum yield and the emission anisotropy for systems which exhibit fluorescence self-quenching due to statistical trap formation, a phenomenon that may, e.g., occur in solutions of chlorophyll.[10] We recently showed,[11(a),11(b)] by comparison to Monte Carlo calculations, that such a system can be described very well by a suitable application of Burshtein's theory of hopping transport.[12] In these communications, however, only isotropic transfer rates have been considered. Because of the importance of the Förster rate, we now rederive the results of the hopping theory with the complete form of this rate, including the orientation factor. For three-dimensional isotropic systems this can be done in an exact way, and it is shown that substantial corrections to the quantum yield are caused by the orientation factor.

II. THEORY

Before formulating the theory, we first give a brief description of the system and quantities studied. For a more detailed formulation of the problem we refer to Ref. 11(a). We consider a system with a random distribution of luminescent molecules with density ρ, between which incoherent transfer of excitation energy occurs with the Förster rate

$$w_{ij} = \frac{3}{2}\kappa_{ij}^2 \frac{1}{\tau_0}\left[\frac{R_0}{r_{ij}}\right]^6. \tag{2.1}$$

Here r_{ij} is the distance between the molecules i and j involved, τ_0 is the intrinsic radiative lifetime of the excited state of interest, and R_0 determines the strength of the transfer. The orientation factor has the complicated form

$$\tfrac{3}{2}\kappa_{ij}^2 = \tfrac{3}{2}[\mathbf{e}_i\cdot\mathbf{e}_j - 3(\mathbf{e}_i\cdot\mathbf{e}_{ij})(\mathbf{e}_j\cdot\mathbf{e}_{ij})]^2 \tag{2.2}$$

with $\mathbf{e}_i$ and $\mathbf{e}_j$ unit vectors parallel to the transition dipoles of the molecules i and j, and $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$. We assume that the orientations Ω_i of the individual transition dipoles are fixed on the time scale of the transfer phenomena (static limit), and that they are distributed in an isotropic way. Concentration self-quenching is modeled in this system, by supposing that two molecules which are closer to one another than a fixed distance R_s (statistical trap radius) act as perfect traps for excitations, i.e., they can accept an excitation through Eq. (2.1), but they cannot pass it on to other molecules, e.g., because of extremely fast decay channels in the close pair.[13] Molecules that are not in a statistical pair (or even larger cluster) are hereafter called donors.

In a typical steady state experiment,[5] donors are randomly excited by a constant laser beam incident along the y axis and polarized along the z axis of the lab frame. Two interesting observables are the total donor fluorescence yield and the donor emission anisotropy observed along the x axis. The yield is defined by the rate at which excitations are radiated by donors divided by the constant rate of laser induced creation of donor excitations. The (emission) anisotropy is defined by

$$A = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp} \tag{2.3}$$

with $I_\parallel$ and $I_\perp$ the observed intensities of components parallel and perpendicular to the laser beam polarization, respectively.

In Refs. 11(a) and 11(b), we showed that these steady state observables, in the case of an isotropic transfer rate, can be described very well in a semiquantitative way (i) by considering the system as if it contained independently distributed donors and traps with suitable densities, thus neglecting

their common underlying distribution of luminescent molecules and (ii) by applying to this system Burshtein's theory of hopping transport,[12] with the cosh-backtransfer correction, proposed by Huber et al.,[14] built in. In this cosh-hopping model, one derives the following expression for the yield:

$$Q/Q_0 = \frac{\tau^{-1}\widetilde{F}(\tau^{-1})}{1 - \widetilde{\Phi}(\tau^{-1})}, \tag{2.4}$$

where $\tau < \tau_0$ is the total intrinsic lifetime of the molecular excited state and $Q_0 = \tau/\tau_0$ is the yield in very dilute systems. $\widetilde{F}$ and $\widetilde{\Phi}$ are the Laplace transforms of the time-dependent functions

$$F(t) = \left\langle \prod_{d \neq 0} \left[e^{-w_{0d}t} \cosh(w_{0d}t) \right] \prod_p e^{-w_{0p}t} \right\rangle_c \tag{2.5}$$

and

$$\Phi(t) = \left\langle -\frac{d}{dt} \left[\prod_{d \neq 0} \left[e^{-w_{0d}t} \cosh(w_{0d}t) \right] \right] \prod_p e^{-w_{0p}t} \right\rangle_c. \tag{2.6}$$

Here d runs over all donors, except the central excited one, labeled 0, and p over the traps. $\langle \cdots \rangle_c$ stands for the average over all possible configurations of donors and traps, which is an average over the positions and orientations of all molecules. Through omission of the cosh factor, one recovers the no backtransfer (nbt) hopping model.[11(a)] For an isotropic orientational distribution, the anisotropy is given by[11(a)]

$$A/A_0 = 1 - \widetilde{\Phi}(\tau^{-1}), \tag{2.7}$$

where $A_0 = 0.4$ is the anisotropy in very dilute systems. This expression only takes into account contributions of molecules that were excited by the laser beam. It is thus assumed that all memory of the laser polarization is already lost after the first transfer step. This is true for isotropic transfer rates; for the complete Förster rate, however, additional contributions to the anisotropy are to be expected. Since it has been argued, however, that relative corrections due to these contributions do not exceed 3% in pure donor systems,[3,5,15] we do not try to take them into account. Both observables of interest are thus fully determined by $F(t)$ and $\Phi(t)$.

Since donors and traps are considered as independently distributed species, the average in Eqs. (2.5) and (2.6) can be written as

$$\langle \cdots \rangle_c = \langle \langle \cdots \rangle_d \langle \cdots \rangle_p \rangle_0.$$

Here $\langle \cdots \rangle_d$ denotes the average over the configurations of donors surrounding donor 0, and $\langle \cdots \rangle_p$ analogously for traps. Finally, $\langle \cdots \rangle_0$ is the average over the orientation Ω_0 of the central donor. For an isotropic three-dimensional medium with an isotropic orientational distribution, the results of $\langle \cdots \rangle_d$ and $\langle \cdots \rangle_p$ will not depend on Ω_0, so that the average over this orientation is trivial and can be left out. Since this makes it possible to derive exact expressions for F and Φ, we will confine ourselves to this case of general importance. Only the important steps in the calculations will be given, from which the details can be filled in by the reader.

The donor and trap averages are worked out as follows: First they are split into averages over the individual molecules; then the average over the distance to donor 0 is performed in the standard way in which one derives Förster-like decay functions. In the case of isotropic transfer rates this completes the calculations,[11(a)] but for an anisotropic rate, one is left with additional averages involving the orientation factor. To clarify this we give the result for the donor part of Eq. (2.5). The suitable donor density is chosen to be $\rho \exp(-\hat{\rho}v_s)$, where $\hat{\rho} = 4\pi R_0^3 \rho/3$ is the reduced density and $v_s = (R_s/R_0)^3$.[11(a)] The Förster decay now reads

$$F_d(t) = \exp\left[-g\sqrt{\pi/2}\hat{\rho} \, e^{-\hat{\rho}v_s}(t/\tau_0)^{1/2} \right]$$

with g a time-independent factor

$$g = \int \frac{d\Omega_{01}}{4\pi} \int \frac{d\Omega_1}{4\pi} \left[\frac{3}{2}\kappa_{01}^2 \right]^{1/2}, \tag{2.8}$$

which is an average over the orientation Ω_1 of the transition dipole of donor 1, and over the orientation of $\mathbf{r}_{01}$. The fact that inclusion of the orientation factor into the transfer kinetics only changes Förster-like decay by a time-independent factor (g) in the exponential, as shown above, has been reported many times, see, e.g., Refs. 2, 6, 8, and 9, and the numerical value of g is well known to be

$$g = \sqrt{3/2}\left[\frac{1}{2} + \frac{1}{8\sqrt{3}} \log\left[\frac{2\sqrt{3}+3}{2\sqrt{3}-3} \right] \right] \simeq 0.8452. \tag{2.9}$$

The decay due to the donors is thus slowed down by the orientation factor. The traps are treated in the following way. We assume, as in Ref. 11(a), that they predominantly occur in pairs, and we take into account the necessary closeness of such a pair by considering it as one particle. Thus the suitable density of traps is $\rho_t = \frac{1}{2}\rho[1 - \exp(-\hat{\rho}v_s)]$. We now introduce two different ways to incorporate trap orientations. In the first, the pair members are given exactly the same orientations, which finds its physical motivation in a possible alignment of close molecules. This view leads to an effective doubling of the transfer rate (2.1) in case that j is a trap, which amounts to the same procedure as the one followed in Ref. 11(a). Then again, the inclusion of κ^2 is fully described by inferring the same factor g in the exponent of the trap decay. In the second approach, we consider the other limiting case, in which the orientations of the transition dipoles within one pair are completely uncorrelated. Then the transfer rate to a trap has to be altered by replacing in Eq. (2.1) κ_{ij}^2 by $\kappa_{ij}^2 + \kappa_{ij'}^2$ and each trap has to be assigned two orientations. The extra factor in the exponential of the trap part of the decay is now given by

$$\tilde{g} = \frac{1}{\sqrt{2}} \int \frac{d\Omega_{01}}{4\pi} \int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_{1'}}{4\pi} \left[\frac{3}{2}(\kappa_{01}^2 + \kappa_{01'}^2) \right]^{1/2}, \tag{2.10}$$

which, after working out the integrals, yields

$$\tilde{g} = g\frac{2}{3}\left[1 + \frac{1}{\sqrt{2}}\log\tan(3\pi/8) \right] \simeq 0.9146. \tag{2.11}$$

By these and similar methods, F and Φ can be calculated, and, thanks to the time independence of g and $\tilde{g}$, their Laplace transforms, as in Ref. 11(a), can be expressed analytically in the complementary error function. One thus finds

$$Q/Q_0 = \frac{[1 - \sqrt{\pi}\alpha \exp(\alpha^2)\mathrm{erfc}(\alpha)]}{[1 - \sqrt{\pi}\beta \exp(\alpha^2)\mathrm{erfc}(\alpha)]} \qquad (2.12)$$

and

$$A/A_0 = 1 - \sqrt{\pi}\beta \exp(\alpha^2)\mathrm{erfc}(\alpha). \qquad (2.13)$$

These forms hold very generally, even in the nbt-hopping model; only the functional dependence of α and β on the density depends on the precise model. For the six distinct cases, $\alpha(\rho)$ and $\beta(\rho)$ are listed in Table I.

III. DISCUSSION OF RESULTS

The yield and anisotropy were calculated as a function of the density for the different cases listed in Table I, at $Q_0 = 1/3$ and $r_s = 1/5$. These parameters were chosen since they were also used in the Monte Carlo calculations described in Ref. 11(b). In Fig. 1, we present the yield for the two different ways of including κ^2 relative to the yield obtained by neglecting the orientation factor, for the cosh-hopping model. We note the following characteristics: (i) Both ways of incorporating κ^2 decrease the yield, which is easily understood, since both g and $\tilde{g}$ are smaller than 1, so that the average decay of a donor excitation to both donors and traps is always slowed down. Thus the transport of the excitations from the set of donors to the traps is slowed down. (ii) In the case of parallel pair members, the yield is larger than in the case of "uncorrelated" pair members. This, too, is simply understood by realizing that $\tilde{g} > g$: the decay to uncorrelated pairs is faster than to parallel pairs. (iii) The additional contributions generated by inclusion of κ^2 are seen to amount to up to 40% in the parallel case and 20%–30% in the uncorrelated case, so that one must conclude that the orientation factor has an important effect on the yield in high density systems. The three horizontal lines at g^{-2}, $(g\tilde{g})^{-1}$, and $\tilde{g}^{-2}$ mark the behavior of the drawn ratios in the intermediate

$(\hat{\rho}v_s \ll 1, \hat{\rho}Q_0^{1/2} \gg 1)$ and high $(\hat{\rho}v_s \gg 1, \hat{\rho}Q_0^{1/2} \gg 1)$ density regimes, which were introduced in Ref. 11 (b). The fact that the constant ratio g^{-2} holds in the case of parallel pair members over a large density interval, implies that the characteristic slope of log Q–log $\hat{\rho}$ plots, which was discussed in Ref. 11(b), is not affected by the orientation factor.

We do not give graphs for the anisotropy in the different cases, since the discrepancies between the curves are only very small. This can be understood by realizing that the anisotropy is the quotient of the probability that a given excitation is radiated by the donor on which it was created by the laser beam $[\tilde{N}_0(\tau^{-1})]$ and the yield,[11(a)] and that these quantities are both affected in the same sense by incorporating κ^2. We just mention that the anisotropy in the case of uncorrelated pair members is always observed to be larger than the anisotropy in the parallel case, and that this in turn always exceeds the result when the orientation factor is neglected. At high densities (past the minimum of the anisotropy), we do not try to explain this, because the model is not accurate there.[11(b)] At low density $(\hat{\rho} \lesssim 5.0)$ the following explanation may be given. The number of traps is still small in this regime, so that only few excitations reach a trap during their lifetime and the yield is still large ($\gtrsim 0.7$). Then, slowing down the hopping process will not have a large relative influence on the yield, since this quantity is only affected by processes that end on traps. The influence on $\tilde{N}_0(\tau^{-1})$, however, is much more direct, since this quantity involves only one step. Therefore, the anisotropy is increased by including κ^2. It is largest in the case of uncorrelated pair members, since then the final donor-trap step, if present at all, is fastest, thus giving the lowest yield. This effect is very small ($<2\%$ for $\hat{\rho} \gtrsim 5.0$).

The observed effects for the nbt model are, even quantitatively, very similar to the ones mentioned above, as could already be expected from Table I. We will therefore not discuss them in further detail.

TABLE I. The functions $\alpha(\rho)$ and $\beta(\rho)$ for the nbt- and the cosh-hopping models, in the three different cases (i) isotropic rate, (ii) inclusion of κ^2 with parallel pair members, (iii) inclusion of κ^2 with uncorrelated pair members.

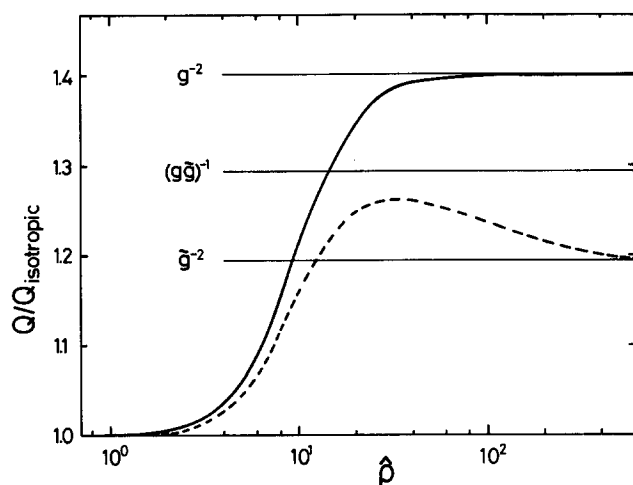|	$\alpha(\rho)$ $a(\rho) \equiv \frac{1}{2}(\pi Q_0)^{1/2}\hat{\rho}$	$\beta(\rho)$ $b(\rho) \equiv \frac{1}{2}(\pi Q_0)^{1/2}\hat{\rho}\, e^{-\hat{\rho}v_s}$
NBT		
Isotropic	$\left[\frac{1}{\sqrt{2}} + \left[1 - \frac{1}{\sqrt{2}}\right]e^{-\hat{\rho}v_s}\right]a(\rho)$	$b(\rho)$
Parallel	$g\left[\frac{1}{\sqrt{2}} + \left[1 - \frac{1}{\sqrt{2}}\right]e^{-\hat{\rho}v_s}\right]a(\rho)$	$gb(\rho)$
Uncorrelated	$g\left[\frac{1}{\sqrt{2}}\frac{\tilde{g}}{g} + \left[1 - \frac{1}{\sqrt{2}}\frac{\tilde{g}}{g}\right]e^{-\hat{\rho}v_s}\right]a(\rho)$	$gb(\rho)$
COSH		
Isotropic	$\frac{1}{\sqrt{2}}a(\rho)$	$\frac{1}{\sqrt{2}}b(\rho)$
Parallel	$g\frac{1}{\sqrt{2}}a(\rho)$	$g\frac{1}{\sqrt{2}}b(\rho)$
Uncorrelated	$g\frac{1}{\sqrt{2}}\left[\frac{\tilde{g}}{g} + \left[1 - \frac{\tilde{g}}{g}\right]e^{-\hat{\rho}v_s}\right]a(\rho)$	$g\frac{1}{\sqrt{2}}b(\rho)$

FIG. 1. Yields obtained upon inclusion of κ^2 into the cosh-hopping model for the two ways of treating the orientations within trap pairs: parallel (—) and uncorrelated (---), relative to the yield for the isotropic Förster rate. $Q_0 = 1/3$ and $r_s = 0.2$.

hopping model for isotropic rates,[11(b)] and of the exact treatment of the orientation factor in the context of the hopping models, the corrections reported here are good measures for the corrections that would be observed in an exact solution. This could be investigated by Monte Carlo simulations as described in Ref. 11(b), but these would now be even more time consuming, because (i) the orientational averages would require a larger number of configurations to be sampled and (ii) extra multiplications would have to be performed for each configuration in order to calculate the orientation factors.

We finally point out that exact analytic results, as given here, are only obtainable in three dimensions. For molecules with positions confined to a surface, even if they have a three-dimensional isotropic orientational distribution, the average over the orientation Ω_0 is not trivial. Therefore, a time-independent g factor can only be defined in a lowest order treatment with respect to time and (or) density.[8] In our opinion, this point has not been fully recognized in several previous studies.[7,9]

IV. SUMMARY AND REMARKS

We incorporate the orientation factor of the Förster rate of energy transfer into the theory of concentration self-quenching by statistical traps. This is done within the framework of Burshtein's hopping models, and for the case of a three-dimensional isotropic system, with an isotropic orientational distribution of the molecular transition dipoles, exact analytic expressions are obtained for the quantum yield and the emission anisotropy. Although, in view of earlier studies, the way in which inclusion of the orientation factor alters the time-dependent quantities is not really surprising, we make the important observation from our calculations, that, in two opposite limits of treating the orientations within one trap pair, substantial corrections (20%–40%) to the quantum yield are generated by this inclusion. Moreover, we believe that, in view of the good performance of the cosh-

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