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On the anisotropic energy transfer to random acceptors

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We present exact expressions for the ensemble averaged decay of the excitation of a donor molecule, due to the energy transfer via anisotropic dipolar interactions to acceptors distributed randomly on a lattice. We compare in two special cases the approximate, Förstertype expressions, valid for low acceptor concentrations and long times, with the exact results: in the case of a completely random *angular* distribution and in case of a preferential orientation. The connection to the decay law for isotropic interactions [Blumen and Manz, J. Chem. Phys. 71, 4694 (1979)] is also presented. Whereas the approximate expressions show similar qualitative behavior in all cases, their regions of validity (compared to the exact results) differ considerably; the difference is especially large for the decay due to acceptors which are randomly distributed on the lattice but are orientationally ordered.

I. INTRODUCTION

The incoherent direct energy transfer from excited donor molecules to acceptors randomly distributed on a lattice or in a liquid has been a continuous object of study for many years.¹⁻¹² A commonly encountered situation obtains when the concentration of donor molecules is very low; then the donor-donor interactions may be neglected, and each donor excitation decays either intramolecularly or due to direct transfer to acceptors. For microscopic interactions that depend strongly on distance the overall time evolution of the excitation of the donor molecules is given by the decay law for a single donor averaged over all possible configurations of acceptors surrounding it.

In the case that the back transfer from the acceptors to the donors is unimportant the ensemble averaged decay can be expressed in a simple closed form.^{6,9,11-13} This exact expression is valid for all times and concentrations and includes the approximate low concentration results^{1,2,6,14} as special cases. In a previous work (Blumen and Manz, Ref. 12) the exact decay law due to an arbitrary number of *different* types of acceptors simultaneously present in the sample was also derived. Starting from this result we determine in this work the ensemble averaged energy transfer due to anisotropic interactions. The acceptors are assumed to occupy lattice places at random and to have a given probability distribution with regard to orientation. Here particular attention is given to the special cases of completely ordered and of completely random orientations.

Microscopically, anisotropic interactions are rather the rule than the exception. As pointed out by Knox, even in the case of the well-behaved dipolar interaction the angular averaging distorts the energy transfer pattern considerably¹⁵ and the description of the transfer in viscous solutions and in solids should account for the anisotropy. Here we show that angular dependent interactions between oriented molecules are readily incorporated into the exact decay law. Therefore, if the microscopic directional pattern of the energy transfer is known one can easily include it into the formulas giving the macroscopically observable decay.

In many applications the anisotropies of the microscopic interactions and the orientational disorder of the

donor and acceptor molecules are of interest. In biochemical measurements in which the energy transfer acts as "spectroscopic ruler" to determine the distance between fluorophores bound to a substrate¹⁶ the orientational freedom of the active groups is of major importance.¹⁷ The same holds true for the classical problem of fluorescence depolarization^{3,10,18,19} where, due to energy transfer between molecules of different orientations the emitted light from a sample containing a larger concentration of acceptor molecules is less polarized.

In the applications mentioned, the energy transfer is generally dominated by dipolar interactions. Therefore we pay special attention to this type of interaction for which we evaluate the exact decay law numerically and for which we determine explicitly the corresponding approximate forms.

One should note that we use the anisotropic dipolar form as an example and do not imply that it may apply strictly to any particular system. Also our approach is limited by the fact that we assume an incoherent energy transfer to all (even very near) acceptors; this then implicitly assumes that the vibrational relaxation is very fast on the time scale of the transfer. Furthermore, the topics of hot luminescence and of hot transfer are not dealt with.

The subject of this article is restricted to the *direct* energy transfer from an excited donor to acceptors. A related problem is the *indirect* transfer, where the energy migrates over the donor molecules until reaching an acceptor. Several works have suggested approximate expressions which allow the evaluation of parameters of the latter problem from the decay laws pertaining to the direct transfer^{11,20-23}; therefore the equations derived here could turn out to be also of use in the field of the indirect energy transfer.

The paper is structured as follows: In Sec. II we derive the decay law due to the spacial and orientational disorder of the acceptors. There we also obtain from the general equation the expressions for the energy transfer due to dipolar interactions. In Sec. III, using the exact forms, we derive several approximate expressions valid for limiting cases. In Sec. IV we present the numerically evaluated decay laws and determine the regions of validity of the different approxima-

tions. These results are also compared to the behavior of the decay due to isotropic interactions. We end with a summary of results.

II. TIME AND CONCENTRATION DEPENDENT DECAY LAW

An exact expression for the ensemble averaged decay law of the excitation of a donor molecule, surrounded by randomly distributed acceptors is

$$\Psi(p_1, \dots, p_A; t) = \exp(-t/\tau_D) \Phi(p_1, \dots, p_A; t), \quad (2.1)$$

with

$$\Phi(p_1, \dots, p_A; t) = \prod_{i=1}^N \left(\sum_{\alpha=0}^A p_{\alpha} E_{i\alpha}(t) \right) \quad (2.2)$$

[Eq. (2.12) of Ref. 12].

The following assumptions are made in the derivation of this expression:

(i) The energy transfer is not affected by the intramolecular (radiational and radiationless) decay channels whose total rate is τ_D^{-1} ; therefore $\exp(-t/\tau_D)$ factorizes.

(ii) The distribution of acceptors on different sites is uncorrelated. The product extends over N sites (N arbitrary) each of which may be occupied with probability p_{α} by an acceptor molecule of type α ($\alpha = 1, \dots, A$). Also included is the possibility that there are inert non-accepting molecules of type $\alpha = 0$. The probabilities p_{α} are normalized so that

$$p_0 = 1 - \sum_{\alpha=1}^A p_{\alpha}. \quad (2.3)$$

(iii) The donor interacts pairwise with each acceptor surrounding it. We denote by $E_{i\alpha}(t)$ the decay of the donor due to an acceptor of type α at site i . In the absence of back transfer and for time-independent microscopic decay rates $w_{i\alpha}$ one has

$$E_{i\alpha}(t) = \exp(-tw_{i\alpha}). \quad (2.4)$$

Evidently, $E_{i0}(t) = 1$. Therefore, for a particular configuration \mathbf{K} where each site i is occupied by an acceptor of type α_i the decay is given by:

$$\Phi(\mathbf{K}; t) = \prod_{i=1}^N \exp(-tw_{i\alpha_i}) = \prod_{i=1}^N E_{i\alpha_i}(t). \quad (2.5)$$

One verifies readily (as shown in the Appendix of Ref. 12) that the expansion of the product on the right-hand side of Eq. (2.2) term by term results in the ensemble average over the decay laws $\Phi(\mathbf{K}; t)$. In fact, for (2.2) to hold it is only necessary that the time evolution of the donor factorizes according to (2.5), regardless of the specific form of the $E_{i\alpha}(t)$. As an example,

$$\tilde{E}_{i\alpha}(t) = \exp(-tw_{i\alpha}) \cosh(tw_{i\alpha}) = \frac{1}{2} [1 + \exp(-2tw_{i\alpha})] \quad (2.6)$$

is the time evolution of a donor-acceptor pair interacting via $w_{i\alpha}$ both for the direct transfer to and the back transfer from the acceptor α . If one approximates the time evolution of each configuration \mathbf{K} through¹¹

$$\tilde{\Phi}(\mathbf{K}; t) = \prod_{i=1}^N \tilde{E}_{i\alpha_i}(t) \quad (2.7)$$

(pair approximation), the ensemble-averaged decay is again given by Eq. (2.2), with \tilde{E} replacing E ,

$$\tilde{\Phi}(p_1, \dots, p_A; t) = \prod_{i=1}^N \left(\sum_{\alpha=0}^A p_{\alpha} \tilde{E}_{i\alpha}(t) \right). \quad (2.8)$$

Because of Eqs. (2.3) and (2.6), Φ and $\tilde{\Phi}$ are related simply through

$$\tilde{\Phi}(p_1, \dots, p_A; t) = \Phi(\frac{1}{2}p_1, \dots, \frac{1}{2}p_A; 2t). \quad (2.9)$$

As in the case of a single acceptor species,^{11,23,24} one obtains in the pair approximation the time evolution in the presence of back transfer directly from the expressions without back transfer through the transformation

$$t \rightarrow 2t; \quad p_{\alpha} \rightarrow \frac{1}{2}p_{\alpha} \quad (\alpha = 1, \dots, A).$$

Consider now the case that the decay law $E_{i\alpha}(t)$ depends not only on the location i and on the type α of the acceptor, but also on an additional variable Ω ; here Ω denotes the orientation of the acceptor with respect to an external frame of coordinates. By treating the pair (α, Ω) as a new index and observing that Ω is continuous, the extension of Eq. (2.2) is straightforward:

$$\Phi(\mathbf{p}; t) = \prod_{i=1}^N \left(\sum_{\alpha=0}^A \int d\Omega p_{\alpha\Omega} E_{i\alpha\Omega}(t) \right). \quad (2.10)$$

In this expression $p_{\alpha\Omega}$ is the probability density of finding a molecule α in position Ω , and we have used the shorthand notation $\mathbf{p} = (p_{\alpha\Omega})$. For a single acceptor species Eq. (2.10) simplifies to

$$\Phi(p; t) = \prod_{i=1}^N \left(1 - p + p \int d\Omega g(\Omega) E_{i\Omega}(t) \right), \quad (2.11)$$

where $g(\Omega)$ is the probability density of the orientation Ω . A special case of Eq. (2.11) occurs if the acceptors have at each site i a prescribed orientation Ω_i . Then $g(\Omega) = \delta(\Omega - \Omega_i)$ and

$$\Phi(p; t) = \prod_{i=1}^N [1 - p + p E_{i\Omega_i}(t)]. \quad (2.12)$$

In the following we will use Eqs. (2.11) and (2.12) to determine the ensemble averaged decay of the excitation of a donor due to dipolar interactions with the acceptors.

The rate for the incoherent energy transfer due to the dipole-dipole interaction has the following form¹:

$$w = (1/\tau)(d/R)^6 \kappa^2 / \langle \kappa^2 \rangle, \quad (2.13)$$

with

$$\kappa = \mathbf{e}_D \cdot \mathbf{e}_A - 3(\mathbf{e}_D \cdot \mathbf{e}_R)(\mathbf{e}_A \cdot \mathbf{e}_R). \quad (2.14)$$

Here R is the donor-acceptor distance and \mathbf{e}_R is the unit direction vector from the donor to the acceptor. \mathbf{e}_D and \mathbf{e}_A are the unit direction vectors of the transition dipoles of the donor and of the acceptor, respectively. We choose to scale R with respect to a minimal distance d : in a crystal this is the nearest neighbor distance; τ^{-1} is then a typical rate for the transfer to an acceptor in nearest neighbor position. The factor $1/\langle \kappa^2 \rangle$ is introduced for convenience, in order to facilitate the comparison of the final results with those pertaining to the decay due to the isotropic interaction $w = (1/\tau)(d/R)^6$. The

average in $\langle \kappa^2 \rangle$ is to be performed over the prescribed angular distribution.

Choosing the z axis along \mathbf{e}_R and the xz plane such as to include \mathbf{e}_D , κ^2 takes the form⁵

$$\kappa^2 = (\sin\psi \sin\xi \cos\varphi - 2 \cos\psi \cos\xi)^2, \quad (2.15)$$

with $\cos\psi = \mathbf{e}_D \cdot \mathbf{e}_R$, $\cos\xi = \mathbf{e}_A \cdot \mathbf{e}_R$, and φ being the angle of \mathbf{e}_A in the plane xy . Equation (2.15) depends on three angles and is quite cumbersome. A much more elegant expression for κ^2 obtains^{3,7} if one observes that κ is the scalar product of \mathbf{e}_A with the local field vector \mathbf{f} ,

$$\mathbf{f} = \mathbf{e}_D - 3(\mathbf{e}_D \cdot \mathbf{e}_R)\mathbf{e}_R. \quad (2.16)$$

Setting ϑ for the angle between \mathbf{e}_A and \mathbf{f} one has

$$\begin{aligned} \kappa^2 &= \mathbf{f}^2 \cdot \mathbf{e}_D^2 \cos^2\vartheta = [1 - 6(\mathbf{e}_D \cdot \mathbf{e}_R)^2 + 9(\mathbf{e}_D \cdot \mathbf{e}_R)^4] \cos^2\vartheta \\ &= (1 + 3 \cos^2\psi) \cos^2\vartheta. \end{aligned} \quad (2.17)$$

Equation (2.17) depends now only on two variables ψ and ϑ , where ψ is a function of the direction of the transition dipole of the donor and of donor-acceptor position, but does not depend on \mathbf{e}_A .

For a completely random angular distribution, one obtains from (2.17),

$$\langle \kappa^2 \rangle_r = \int_0^1 \int_0^1 dx dy (1 + 3x^2)y^2 = \frac{2}{3}. \quad (2.18a)$$

On the other hand, if all acceptors are parallel to the donor one has from (2.14), $\kappa = 1 - 3 \cos^2\psi$, so that the average for a random distribution of sites or donor directions is

$$\langle \kappa^2 \rangle_n = \int_0^1 dx (1 - 3x^2)^2 = \frac{4}{5}. \quad (2.18b)$$

Similarly, if all acceptors are perpendicular to the donor

$$\langle \kappa^2 \rangle_\perp = \frac{1}{2}(\langle \kappa^2 \rangle_r + \langle \kappa^2 \rangle_n) = \frac{3}{5} \quad (2.18c)$$

We now turn our attention to the exact decay law in the case that each angular direction of \mathbf{e}_D and \mathbf{e}_A is equally probable. Using Eqs. (2.4), (2.13), (2.17), and (2.18a), one obtains for $E_{i\Omega}(t)$ in Eq. (2.11),

$$\begin{aligned} E_{i\Omega}(t) &= \exp \left[-\frac{3t}{2\tau} \left(\frac{d}{R_i} \right)^6 (1 + 3 \cos^2\psi_i) \cos^2\vartheta_i \right] \\ &= \exp[-f_i^2(t) \cos^2\vartheta_i], \end{aligned} \quad (2.19)$$

where we set

$$f_i(t) = (3t/2\tau)^{1/2} (d/R_i)^3 (1 + 3 \cos^2\psi_i)^{1/2}. \quad (2.20)$$

Under our assumption that each angular direction of \mathbf{e}_D is equally probable, the integration in (2.11) is readily performed:

$$\begin{aligned} \int d\Omega g(\Omega) E_{i\Omega}(t) &= \frac{1}{4\pi} \int_0^{2\pi} d\varphi_i \int_0^\pi d\vartheta_i \sin\vartheta_i \\ &\quad \times \exp[-f_i^2(t) \cos^2\vartheta_i] \\ &= \int_0^1 dx \exp[-f_i^2(t)x^2] = \frac{\sqrt{\pi}}{2} \frac{\text{erf}[f_i(t)]}{f_i(t)}, \end{aligned} \quad (2.21)$$

with $\text{erf}(x)$ being the error function [Eq. (7.1.1) of Ref. 25]. Thus the exact decay law for acceptors randomly oriented is

$$\Phi^r(p; t) = \prod_{i=1}^N \left[1 - p \left(1 - \frac{\sqrt{\pi}}{2} \frac{\text{erf}[f_i(t)]}{f_i(t)} \right) \right], \quad (2.22)$$

with $f_i(t)$ given by Eq. (2.20). This expression may be compared to the exact decay law in the presence of isotropic interactions [Eqs. (3.2) and (3.7) of Ref. 12]

$$\Phi(p; t) = \prod_{i=1}^N \left(1 - p \left\{ 1 - \exp \left[-\frac{t}{\tau} \left(\frac{d}{R_i} \right)^6 \right] \right\} \right). \quad (2.23)$$

Let us now consider the case that all acceptors have transition moments oriented parallel to that of the donor molecule. From Eqs. (2.12), (2.13), and (2.18b), one obtains

$$\Phi^n(p; t) = \prod_{i=1}^N \left(1 - p \left\{ 1 - \exp \left[-\frac{5t}{4\tau} \left(\frac{d}{R_i} \right)^6 (1 - 3 \cos^2\psi_i)^2 \right] \right\} \right), \quad (2.24)$$

which is very akin in structure to Eq. (2.23). In Eq. (2.24) only the direction has to be specified since, because of Eq. (2.13), both orientations along the given axis contribute equally.

III. APPROXIMATE EXPRESSIONS FOR THE DECAY LAWS

In this section we derive approximate analytic expressions to the decay laws (2.22) and (2.24). Although they have a restricted range of validity, these forms turn out to be useful for applications since they are easier to evaluate than the exact products, and their dependence on time and concentration is very transparent. In particular we obtain in a straightforward manner Förster-type equations; their regions of validity will be determined in Sec. IV by direct comparison to the numerically computed decay.

Here we follow the approach of Ref. 12, where similar procedures were applied to the problem of the isotropic energy transfer to randomly distributed acceptors. We start by expanding the logarithm of the exact formulas in a series with respect to p (p is the probability that a site is occupied by an acceptor and is thus proportional to the acceptor density in the medium); the Förster-type expressions, whose derivation assumes a very low acceptor concentration are then obtainable from the first term of the expansion.^{8,9}

By taking the logarithm of both sides of Eqs. (2.22) and (2.24) and using the series $\ln(1-x) = -\sum_{k=1}^{\infty} x^k/k$, both decay laws take the form

$$\phi(p; t) = \exp \left(- \sum_{k=1}^{\infty} \frac{p^k S_k(t)}{k} \right). \quad (3.1)$$

In Eq. (3.1), $S_k(t)$ is given through

$$S_k^r(t) = \sum_{i=1}^N \left\{ 1 - \exp \left[-\frac{5t}{4\tau} \left(\frac{d}{R_i} \right)^6 (1 - 3 \cos^2\psi_i)^2 \right] \right\}^k \quad (3.2)$$

for acceptors oriented parallel to the donor molecule, and through

$$S_k^n(t) = \sum_{i=1}^N \left(1 - \frac{\sqrt{\pi}}{2} \frac{\text{erf}[f_i(t)]}{f_i(t)} \right)^k \quad (3.3)$$

for randomly oriented acceptors. In the last expression $f_i(t)$ is given by Eq. (2.20). These equations are exact

since the series (3.1) is absolutely convergent for all $p < 1$.

For simplicity we assume that the donor is located at the origin. We recall that the sums over i extend over all N sites accessible to the acceptors. In applications one is interested in the case that the molecules are imbedded in dense media; if the molecules occupy substitutional sites in a crystal one has to exchange in Eqs. (3.2) and (3.3) the summation from $\sum_{i=1}^N$ to \sum_i' ; the latter symbol denotes a sum over all lattice sites with the exception of the origin.

An approximate way to perform this summation is the continuum approximation, which replaces the sums by integrals. In three dimensions one has the transformation

$$\sum_i' h_i \rightarrow \rho \int d\Omega \int_b^\infty dR R^2 h(R, \Omega), \quad (3.4)$$

where ρ is the density of lattice points in the particular crystal considered; for instance, for the simple cubic lattice $\rho = d^{-3}$; for the fcc lattice $\rho = \sqrt{2}d^{-3}$. Equation (3.4) takes into account the dependence of h on the angular direction Ω , and differs therefore from Eq. (3.8c) of Ref. 12. The integration over Ω has to be performed over all angles; that over R extends from a particular cutoff distance b (of the order of d , the nearest neighbor spacing) to infinity. The cutoff accounts for the exclusion of the origin from the lattice sums \sum_i' .

Let us now evaluate $S_k''(t)$, Eq. (3.2), in the continuum approximation

$$S_k''(t) = 4\pi\rho \int_0^1 dx \int_b^\infty dR R^2 \left\{ 1 - \exp\left[-\frac{5t}{4\tau} \left(\frac{d}{R}\right)^6 (1-3x^2)^2\right] \right\}^k, \quad (3.5)$$

and thus

$$S_k''(t) = \frac{\pi\sqrt{5}}{3} \rho d^3 \left(\frac{t}{\tau}\right)^{1/2} \int_0^1 dx |1-3x^2| \times \int_0^\lambda dy y^{-3/2} (1-e^{-y})^k, \quad (3.6)$$

where

$$\lambda \equiv \frac{5}{4} (t/\tau) (d/b)^6 (1-3x^2)^2.$$

We now consider two limiting cases. For moderately long and long times $t \gg \tau$ one may generally replace λ by infinity. The only exception is $x_0 = 1/\sqrt{3}$, corresponding to the angle $\arccos(1/\sqrt{3}) = 54.74^\circ$. However, because of the subsequent integration over x values around x_0 have very small weight. The extension of the integration over y in Eq. (3.6) to infinity is justified and both integrals are then easily evaluated by noting that

$$\int_0^\infty dy y^{-3/2} (1-e^{-y}) = 2 \int_0^\infty dy y^{-1/2} e^{-y} = 2\Gamma(\frac{1}{2}) = 2\sqrt{\pi} \quad (3.7)$$

and

$$\int_0^1 dx |1-3x^2| = \frac{4}{\sqrt{27}}. \quad (3.8)$$

Making use of the relation [Eq. (3.11) of Ref. 12]

$$(1-e^{-y})^k = \sum_{j=0}^k (-1)^{j-1} \binom{k}{j} (1-e^{-jy}), \quad (3.9)$$

we thus obtain for $S_k''(t)$ in the limit of longer times

$$S_k''(t) = \frac{8}{9} \sqrt{\frac{5}{3}} \pi^{3/2} \left[\sum_{j=1}^k (-1)^{j-1} \binom{k}{j} \sqrt{j} \right] \rho d^3 \left(\frac{t}{\tau}\right)^{1/2}. \quad (3.10)$$

Inserting now Eq. (3.10) into Eq. (3.1) one obtains in the continuum approximation the decay law due to acceptors oriented parallel to the donor, valid for long times.

One should note that even at higher concentrations, where the $S_k''(t)$ terms with $k > 1$ are important, the long time decay behavior is dominated by the \sqrt{t} dependence; this may be compared to the similar occurrence in the isotropic case, Eq. (3.16) of Ref. 12, with $\Delta = 3$, $s = 6$. Restricting ourselves to the case of low acceptor density we retrieve the Förster-type equation⁴

$$\Phi_1^{ic}(p; t) = \exp[-p S_1''(t)] \\ = \exp\left[-\frac{8}{9} \sqrt{\frac{5}{3}} \pi^{3/2} p \rho d^3 (t/\tau)^{1/2}\right]. \quad (3.11)$$

This expression may be compared to the Förster decay¹ due to isotropic three-dimensional dipolar interactions [Eq. (3.15) in Ref. 12]:

$$\Phi_1^{3c}(p; t) = \exp\left[-\frac{4}{3} \pi^{3/2} p \rho d^3 (t/\tau)^{1/2}\right]. \quad (3.12)$$

The difference in the exponent is a factor $\sqrt{20/27}$. For very short times $t \ll \tau$ one has, on the other hand ($\lambda \ll 1$),

$$\int_0^\lambda dy y^{-3/2} (1-e^{-y})^k = \lambda^{k-1/2} / (k - \frac{1}{2}), \quad (3.13)$$

and $S_k''(t)$ is proportional to t^k . Thus $\Phi(p; t)$ depends on the product pt only. Especially one has for $S_1''(t)$:

$$S_1''(t) \approx \frac{4}{3} \pi \rho (d^6/b^3) (t/\tau). \quad (3.14)$$

The decay law for very short times is thus formally identical to the one which obtains due to isotropic interactions Eq. (3.20) of Ref. 12:

$$\Phi_1^{ic}(p; t) \approx \exp\left[-\frac{4}{3} \pi p \rho (d^6/b^3) (t/\tau)\right]. \quad (3.15)$$

Thus one finds for very short times an exponential decay. The identical behavior is, of course, only a consequence of our choice of normalization of the interaction, Eq. (2.13).

For $p = 1$ the decay of $\Phi''(1; t)$ is exponential for all times, Eq. (2.24); in the continuum approximation one has

$$\Phi^{ic}(1; t) = \exp\left(-5\pi\rho d^6 \frac{t}{\tau} \int_b^\infty dR R^{-4} \int_0^1 (1-3x^2)^2 dx\right) \\ = \exp\left(-\frac{4}{3} \pi \rho \frac{d^6}{b^3} \frac{t}{\tau}\right), \quad (3.16)$$

clearly the special case $p = 1$ of Eq. (3.15), valid for all t .

We now turn our attention to the decay law due to randomly oriented and distributed acceptors, and consider the form of $S_k''(t)$, Eq. (3.3), in the continuum approximation

$$S_k''(t) = 4\pi\rho \int_0^1 dx \int_b^\infty dR R^2 \left(1 - \frac{\sqrt{\pi}}{2} \frac{\text{erf}[f(t)]}{f(t)}\right)^k, \quad (3.17)$$

with

$$f(t) = (3t/2\tau)^{1/2} d^3 R^{-3} (1 + 3x^2)^{1/2}. \quad (3.18)$$

Therefore

$$S_k^*(t) = \sqrt{\frac{8}{3}} \pi \rho d^3 \left(\frac{t}{\tau}\right)^{1/2} \int_0^1 dx (1 + 3x^2)^{1/2} \times \int_0^\mu dy y^{-2} \left(1 - \frac{\sqrt{\pi}}{2} \frac{\text{erf}(y)}{y}\right)^k, \quad (3.19)$$

where

$$\mu = (3t/2\tau)^{1/2} (d/b)^3 (1 + 3x^2)^{1/2}. \quad (3.20)$$

For long times we may again extend the integration over y to infinity; then all $S_k^*(t)$ depend only on the square root of t , and the long time behavior of the decay law due to randomly oriented acceptors has the form $\exp[-\varphi(p) \times (t/\tau)^{1/2}]$, with $\varphi(p)$ being a function of p only.

The first integral of Eq. (3.19) is readily determined through the substitution $\sinh(t) = \sqrt{3}x$

$$I \equiv \int_0^1 (1 + 3x^2)^{1/2} dx = \frac{1}{\sqrt{3}} \int_0^{t_0} \cosh^2 t dt \\ = \frac{1}{4\sqrt{3}} \int_0^{t_0} (e^{2t} + e^{-2t} + 2) dt, \quad (3.21)$$

where $t_0 = \text{arcsinh}\sqrt{3}$. Therefore, $\exp(\pm t_0) = 2 \pm \sqrt{3}$ and

$$I = 1 + \ln(2 + \sqrt{3})/2\sqrt{3} = 1.38017. \quad (3.22)$$

Perhaps even more familiar^{3,4,7} is the constant $\frac{1}{2}I = 0.6900865$.

The second integral is also simply evaluated for $k=1$,

$$\int_0^\infty dy y^{-3} \left(y - \frac{\sqrt{\pi}}{2} \text{erf}(y)\right) = \frac{1}{2} \int_0^\infty dy y^{-2} [1 - \exp(-y^2)] \\ = \int_0^\infty dy \exp(-y^2) = \frac{\sqrt{\pi}}{2} \quad (3.23)$$

by integrating twice by parts. Therefore,

$$S_1^*(t) = \pi(\frac{2}{3}\pi)^{1/2} I \rho d^3 (t/\tau)^{1/2}, \quad (3.24)$$

from which one obtains the Förster-type expression, valid for long times and low acceptor concentrations^{3,4,7,10}:

$$\Phi_1^{\text{rc}}(p; t) = \exp[-\pi(\frac{2}{3}\pi)^{1/2} I \rho d^3 (t/\tau)^{1/2}], \quad (3.25)$$

with I given by (3.22). The difference in the exponents of the expressions (3.25) and (3.12) (for isotropic interactions) is a factor $I \cdot \sqrt{\frac{8}{3}} = 0.84518$.^{4,7}

We now turn to the very short time behavior of $S_k^*(t)$, $\mu \ll 1$. Because of the series expansion $\text{erf}(y) \approx (2/\sqrt{\pi}) \times (y - \frac{1}{3}y^3)$, Eq. (7.1.5) in Ref. 25, one obtains

$$S_k^*(t) \approx \frac{4\pi}{3} \frac{\rho d^3}{2k-1} \left(\frac{t}{2\tau}\right)^k \left(\frac{d}{b}\right)^{6k} \int_0^1 dx (1 + 3x^2)^k. \quad (3.26)$$

Thus for $k=1$:

$$\Phi_1^{\text{rc}}(t) = \exp[-\frac{4}{3}\pi \rho d^3 (d^6/b^3)(t/\tau)], \quad (3.27)$$

which is formally again the same short time exponential behavior, Eq. (3.15). For $p=1$ the exact decay law is not exponential for longer times; this is a qualitative difference from the decay due to isotropic interactions or to oriented acceptors. From Eq. (2.22) one has

$$\Phi^{\text{rc}}(1; t) = \prod_i \left\{ \frac{\sqrt{\pi}}{2} \frac{\text{erf}[f_i(t)]}{f_i(t)} \right\}, \quad (3.28)$$

and we obtain, in the continuum approximation,

$$\ln \Phi^{\text{rc}}(1; t) = 4\pi \rho \int_0^1 dx \int_0^\infty dR R^2 \ln \left(\frac{\sqrt{\pi}}{2} \frac{\text{erf}[f(t)]}{f(t)} \right) \\ = \sqrt{\frac{8}{3}} \pi \rho d^3 \left(\frac{t}{\tau}\right)^{1/2} \int_0^1 dx (1 + 3x^2)^{1/2} \int_0^\mu dy y^{-2} \ln \left(\frac{\sqrt{\pi}}{2} \frac{\text{erf}(y)}{y} \right), \quad (3.29)$$

with $f(t)$ and μ given by Eqs. (3.18) and (3.20), respectively. The long time behavior for $p=1$ follows by setting μ to infinity. Defining

$$J \equiv - \int_0^\infty dy y^{-2} \ln \left(\frac{\sqrt{\pi}}{2} \frac{\text{erf}(y)}{y} \right) = 1.475, \quad (3.30)$$

one has

$$\Phi^{\text{rc}}(1; t) = \exp[-\sqrt{\frac{8}{3}} \pi I \rho d^3 (t/\tau)^{1/2}]. \quad (3.31)$$

The long time decay is thus nonexponential and Eq. (3.25) derived for low acceptor concentrations reproduces the correct qualitative long time behavior even for the maximal acceptor concentration $p=1$; for quantitative agreement one has to insert in (3.25) a constant factor $2J/\sqrt{\pi} = 1.66$.

For the short time region one verifies readily that Eq. (3.29) is again well approximated by the expression (3.27), giving an exponential decay. In the next section we will show through evaluation of the exact decay law that for practical purposes this is also the dominant behavior for $p=1$.

IV. NUMERICAL RESULTS AND CONCLUSIONS

In this section we present the results obtained by computing the exact decay laws, Eqs. (2.22)–(2.24), and their approximate expressions, Eqs. (3.11), (3.12), and (3.25), for the face centered cubic (fcc) lattice. We have chosen this particular crystal type since it is fairly common (for instance most rare gas matrices that act as inert hosts crystallize in this form). In all cases the time was varied between $t = \frac{1}{10}\tau$ and $10^6\tau$ and p between 0.002 and 1.

As in Refs. 12 and 24 we prefer to plot $-\ln(-\ln \Phi)$ vs $\ln(t/\tau)$. Apart from the fact that this choice facilitates the comparison of the different results, it also has the advantage of allowing one to show $\Phi(p; t)$ for a large range of time and concentration values and of emphasizing the decay of the donor in the domain 0.9 to 0.01. This region might be more precisely investigated (by means of the radiational decay) than the region under 0.01 (which corresponds to lower intensities). Also, our choice of scales allows the direct comparison to the approximate analytical forms of Sec. III. An exponential decay appears in these scales as a straight line of slope -1 ; to a decay of the form $\exp(-ct^{1/2})$ corresponds to a straight line of slope $-\frac{1}{2}$.

The function $\Phi(p; t)$ due to acceptors oriented parallel to the donor, Eq. (2.24), is plotted in Fig. 1 for the three orientations (1, 0, 0), (1, 1, 0), and (1, 1, 1) and for nine values of p from 0.002 to 1. Superimposed on the

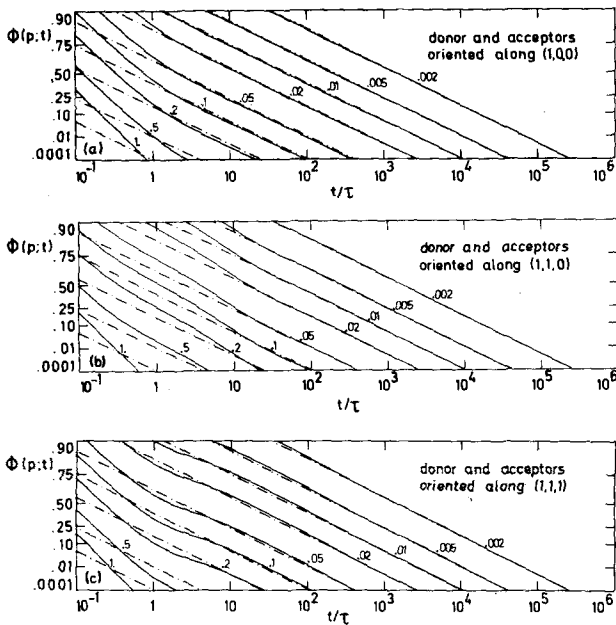


FIG. 1. Time decay of the donor excitation $\Phi(p; t)$ due to the direct energy transfer via anisotropic dipolar interactions to acceptors parallelly oriented to the donor. For the fcc lattice three cases are considered; the molecular orientation is (a) along the (1, 0, 0), (b) along the (1, 1, 0), (c) along the (1, 1, 1) axis. The curves depend parametrically on p ; p is 1, 0, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, and 0.002 from the left below. The full lines are the exact results, whereas the dash-dotted curves are the Förster-type approximation. Note the $-\ln(-\ln\Phi)$ vs $\ln(t/\tau)$ scales.

continuous curves of the exact decay law are the corresponding approximate expressions, Eq. (3.11), which are drawn as dash-dotted lines. As a consequence of our choice of scales the approximate curves are a set of parallel straight lines of slope $-\frac{1}{2}$.

For all three orientations considered one verifies readily by inspection that the long time behavior of the decay law is well described by the approximate Förster-type forms. Also the lower the concentration the better do the approximate expressions reproduce the true decay behavior. As expected, in the short time domain $\Phi(p; t)$ is for all concentrations quasiexponential, as may be inferred from Fig. 1 from the steeper slope (-1) of the decay. Thus the qualitative features of the decay law in the short and long time regimes agree with those of the isotropic decay considered in Ref. 12.

However, there are also marked differences. In order to facilitate the comparison we have plotted in Fig. 2 the curves for the isotropic dipolar law $w = (1/\tau)(d/R)^6$. Again the full line gives the exact decay, Eq. (2.23), whereas the dash-dotted line is Förster's result, Eq. (3.12). In the isotropic case the approximate form holds quite well for times t slightly larger than τ and for values of p up to 0.1, which corresponds to high acceptor concentrations. In the case of anisotropic dipolar interactions between the donor and parallel acceptors Fig. 1 shows that the approximate long time expressions have a more restricted range of validity. The agreement is good only for low values of p (0.01 or less) and for longer times [at least 10τ for the orienta-

tions (1, 0, 0) and (1, 1, 0) or even 100τ for (1, 1, 1)].

The transition from the short time exponential decay law to the $\exp(-ct^{1/2})$ decay valid for longer times is not gradual; similar to the multipolar transfer in lower dimensions, Fig. 1 shows in the transition region a wavy pattern. As we will show in the following, this feature is due to the lattice structure.

Consider first the short time region. From the continuum approximation [Eqs. (3.4) and (3.15)], we obtain the observed exponential decay. However, for a fixed value of the cutoff parameter b , Eq. (3.15) would imply an identical behavior for all cases, regardless of orientation. This is evidently not fulfilled; for very short times the decay is fastest for donor and acceptors oriented along (1, 1, 1) and slowest for the (1, 0, 0) orientation. The reason for this feature can be traced to the acceptor configurations in the neighborhood of the donor:

Starting from the exact form, Eq. (2.24) we obtain for short times

$$\begin{aligned} \phi''(p; t) &\approx \prod_i' \left\{ 1 - p \left[\frac{5t}{4\tau} \left(\frac{d}{R_i} \right)^6 (1 - 3 \cos^2 \psi_i)^2 \right] \right\} \\ &\approx \exp \left[- \frac{5pt}{4\tau} \sum_i' \left(\frac{d}{R_i} \right)^6 (1 - 3 \cos^2 \psi_i)^2 \right]. \end{aligned} \quad (4.1)$$

The initial decay is therefore determined by the value of the sum σ ,

$$\sigma \equiv \sum_i' \left(\frac{d}{R_i} \right)^6 (1 - 3 \cos^2 \psi_i)^2. \quad (4.2)$$

Since the terms in the sum (4.2) depend strongly on the donor-acceptor distance, the main contribution to σ arises from the first few shells surrounding the donor. The total sum (4.2) is 8.62, 12.30, and 13.52 for the (1, 0, 0), the (1, 1, 0), and the (1, 1, 1) directions, respectively. These values may be compared to the contributions of the first two shells of lattice points. In the fcc lattice there are 12 nearest neighbors to the origin at locations $(\pm a, \pm a, 0)$, $(\pm a, 0, \pm a)$, and $(0, \pm a, \pm a)$. Equation (4.2) restricted to this shell is readily evaluated and its contribution σ_1 to σ is 6, 10.5, and 12 for the three orientations ordered as above. By performing also the sum σ_2 over the second shell one obtains the additional values 1.5, 0.375, and 0, again in order.

The σ values for the first few shells of lattice points around the donor allow to understand qualitatively the short time behavior of $\Phi(p, t)$ in Fig. 1. Evidently, the fact that the decay is fastest for the (1, 1, 1) orientation and slowest for (1, 0, 0) is already accounted for by σ_1 ,

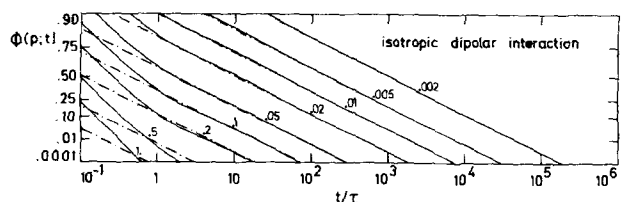


FIG. 2. Time decay of the donor excitation $\Phi(p; t)$ due to the direct energy transfer via isotropic dipolar interactions. The values of the parameter p and the meaning of the full and dash-dotted curves are as in Fig. 1.

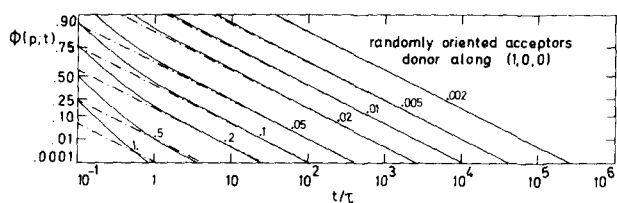


FIG. 3. Time decay of the donor excitation $\Phi^*(p; t)$ due to direct energy transfer via anisotropic dipolar interactions to randomly oriented acceptors. The values of the parameter p and the meaning of the full and dash-dotted curves are as in Fig. 1.

the contribution of the first shell. The contribution of σ_2 has the reverse trend; this explains the slower decay of the (1, 1, 1) curve in the region $\tau < t < 10\tau$ as compared to the other orientations.

Turning now to Eq. (3.15), one reaches quantitative agreement with the computed exact forms by assuming b to be an adjustable constant. Then, by equating (4.1) and (3.15), it follows that

$$b^3 = \frac{16}{15} \pi (\rho d^6 / \sigma) \quad (4.3)$$

and one obtains for the cutoff constant b the values $0.82d$, $0.73d$ and $0.71d$ for the orientations (1, 0, 0), (1, 1, 0), and (1, 1, 1), respectively. One finds therefore the parameter b to be comparable to d , the next-neighbor spacing, as already discussed after Eq. (3.4).

The pattern of the decay laws in Fig. 1 is typically different for the three orientations. Thus, under the assumption that the energy transfer follows the anisotropic dipolar interaction (2.13) also at small distances and that the lattice structure is not strongly distorted by the acceptor molecules, one may even infer from the macroscopically measured decay the orientation of the acceptors in the sample.

We now consider the decay due to randomly oriented acceptors. The exact result, Eq. (2.22), is plotted in Fig. 3 together with the corresponding approximate form, Eq. (3.25). Again the dash-dotted lines denote the approximation. Only the values for the donor pointing along (1, 0, 0) are shown, since the changes in decay due to other donor orientations [especially along (1, 1, 0) and (1, 1, 1)] are so insignificant as to render the drawings almost indistinguishable.

As may be inferred by comparing Figs. 2 and 3, the range of validity of the long time expressions is very similar for the isotropic and for the randomly oriented cases; the approximate formulas reproduce the exact decay for $p < 0.1$ and for $t > \tau$. Also one obtains almost identical values for b when fitting the short time decay to the approximate form (3.27): from the computations one has $b = 0.75d$ for randomly oriented acceptors and $b = 0.74d$ in the isotropic case.

The only qualitative difference between the isotropic decay and the decay due to randomly oriented acceptors is the nonexponential behavior of the latter for $p = 1$. From Fig. 3, however, one deduces that the nonexpo-

ponential regime becomes apparent only for values of $\Phi(p; t)$ below 0.01, i.e., in the less interesting decay region.

By comparing Figs. 1, 2, and 3, we infer that the continuum approximation gets better when the disorder of the system increases. This fact, which is evident in the case of spatial randomness holds also with respect to orientational disorder.

In conclusion, we have shown that even realistic microscopic interactions like the anisotropic dipolar law [Eqs. (2.13) and (2.14)] are amenable to an exact treatment by using the decay formula (2.2). The formula is well suited for numerical evaluation and also allows the derivation of approximate expressions. Depending on the region of interest one has the choice between different approximation schemes; for the long time domain the Förster-type equations are but the first term in a series expansion. As shown above, further terms of this series are readily derived, and their domain of validity is easily determined by comparison to the exact results.

For applications, depending on the precision of the measurements and on the *a priori* knowledge about the system one has then the choice of determining approximate expressions, best suited to the particular experiment, or of using the exact decay law, which contains the maximal information obtainable.

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