Fluorescence in the presence of traps

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We present a general theory for the time development of the donor fluorescence in the presence of a random distribution of acceptor ions which act as traps for the excitation. The theory is based on a set of coupled rate equations for the donor array. Symmetric transfer rates are assumed which are independent of the energy mismatch between donors. Backtransfer from the traps is neglected. Exact results are obtained in the static and rapid donor-donor transfer limits for all values of the acceptor concentration. An approximate theory based on the average-t-matrix approximation is developed for the regime intermediate between the two limits which is applicable when there is a small concentration of acceptors. We make contact with the stochastic hopping model of Burshtein and the diffusion model of Yokota and Tanimoto in appropriate limits. The range of validity of the two models is established and equations are given for the corresponding phenomenological parameters. The relationship of the calculations to the theory of fluorescence line narrowing is pointed out.

I. INTRODUCTION

One of the oldest problems in the study of the optical properties of solids involves the influence of traps on the time development of the fluorescence from inhomogeneously broadened levels. Such effects are seen in systems where there is an array of "donor" ions which can exchange excitation through various phonon-assisted processes. Embedded in the donor array are "acceptor" ions which act as traps for the excitation. Excitation can be transferred to the traps. However the reverse process in which excitation moves from the acceptors to the donors often has a negligible probability of taking place on the time scales of interest. In a typical experimental study of these effects a small fraction of the donors are excited by the absorption of broad-band radiation. As time passes excitation is transferred among the donors as well as to the acceptors. Aside from radiative decay, in the absence of traps the number of excited donors remains constant. By monitoring the intensity of the donor fluorescence one can determine the fraction of excited donors. Provided the radiative decay rate is known information can be obtained about donor-donor and donor-acceptor transfer rates from an analysis of the decay curves.

Despite the fundamental importance of the phenomenon there has been relatively little theoretical work relating the microscopic transfer processes to the macroscopic fluorescence. Theories for the time development of the fluorescence in the presence of traps are largely phenomenological.[1] As a consequence the connection with the behavior on the microscopic scale is often unclear. The regimes where the theories are applicable are not precisely stated and there is little in the way of microscopic theory for the parameters.

In this paper we outline a microscopic theory for the time development of the donor fluorescence in the presence of traps which has as its starting point the set of coupled rate equations for the donor ions. Although we do not have a complete solution to the problem (except in limiting cases) we do obtain an approximate theory for the fluorescence which is applicable in the limit of low-trap concentration. As a by-product of our work we obtain insight into the limitations of the various phenomenological models as well as approximate expressions for the associated parameters.

The remainder of the paper is divided into four sections. In Sec. II we outline the microscopic model and discuss the exact solutions which are obtained in various limits. Section III is devoted to the development of the approximate microscopic theory. The theory is discussed in Sec. IV, where we compare our work with two widely used phenomenological models: the hopping model introduced by Burshtein[2] and the diffusion model developed by Yokota and Tanimoto.[3] Our findings are summarized in Sec. V. The emphasis in this paper is on theory. Detailed comparisons with experimental studies are left to future publications.

II. MICROSCOPIC MODEL

Our treatment of the dynamics of the donor fluorescence is based on a set of coupled rate equations for the donors. These equations are applicable whenever the transfer is completely incoherent as is the case when it involves phonon-assisted processes between widely separated ions. In the absence of

traps the equations take the form[4]

$$\frac{dP_n(t)}{dt} = -\left(\gamma_R + \sum_{n''} W_{nn''}\right) P_n(t) + \sum_{n'} W_{n'n} P_{n'}(t) \quad , \tag{2.1}$$

where $P_n(t)$ is the probability that the nth donor is excited at time t. The parameter γ_R denotes the radiative decay rate and $W_{nn'}$ is the transfer rate from ion n to ion n'. We assume symmetric transfer rates, $W_{nn'} = W_{n'n}$, which are also independent of the energy mismatch between n and n'. However they do depend on the relative separation between the two ions.[5]

In our model we assume that the transfer of excitation to the traps is a one-way process. The passage of excitation to an acceptor ion represents an absolute loss similar to radiative decay. Because of this we can incorporate the effects of donor-acceptor transfer by including an additional term inside the parentheses on the right-hand side of Eq. (2.1) thus obtaining the expression

$$\frac{dP_n(t)}{dt} = -\left(\gamma_R + X_n + \sum_{n''} W_{nn''}\right) P_n(t) + \sum_{n'} W_{n'n} P_{n'}(t) \quad . \tag{2.2}$$

The donor-acceptor transfer rate, X_n, will depend on the distribution of traps in the vicinity of the nth donor. As a consequence, it will vary from ion to ion in contrast to the radiative decay rate which is assumed to be the same for all donors.

We assume that both the donors and acceptors occupy sites on a lattice. The acceptors and donors are distributed at random such that each site has a probability c_A of being occupied by an acceptor ion and a probability c_D of being occupied by a donor. Thus we have $c_D + c_A \leq 1$ with the equality pertaining to a situation where all sites are occupied either by donors or acceptors. In addition, we make the assumption that there are no isolated donors, that is to say, there are transfer paths connecting all members of the donor array.

Equation (2.2) is appropriate for characterizing a situation where a small fraction of the donors are excited at any given time. Nonlinear effects associated with high levels of excitation do not significantly affect the donor-donor dynamics.[6] However they can influence the donor-acceptor transfer if an appreciable fraction of the acceptors is excited at any given time, since transfer to an excited acceptor will take place at a different rate (if at all) than will transfer to an acceptor ion which is in the ground state.

The property of direct experimental interest is the intensity of the fluorescence from the donors integrated over the inhomogeneous linewidth. It is proportional to the total number of donors in the excited state and hence to the sum $\sum_n P_n(t)$. In the low-excitation limit where the excited ions are widely dispersed we can write the intensity normalized to its initial value in the form

$$F(t) = N_D^{-1} \sum_{n'=1}^{N_D} \sum_{n=1}^{N_D} P_n^{n'}(t) \quad , \tag{2.3}$$

where $P_n^{n'}(t)$ is the solution to Eq. (2.2) with initial condition $P_n(0) = \delta_{nn'}$ and N_D is the number of donors. Equation (2.3) is the average of $\sum_n P_n(t)$ over all solutions with initial conditions corresponding to there being only one donor, n', in the excited state. As such it can equally well be written as a configuration average

$$F(t) = \sum_n \langle P_n^0(t) \rangle_c \quad , \tag{2.4}$$

where the symbol $\langle \cdots \rangle_c$ denotes an average over all configurations of donors and acceptors. It will be convenient to separate the effects due to radiative decay from those associated with donor-acceptor transfer. This can be done by writing

$$F(t) = e^{-\gamma_R t} f(t) \quad , \tag{2.5}$$

where $f(t)$ is calculated from Eq. (2.2) with γ_R set equal to zero.

Although the calculation of $f(t)$ is a problem of great complexity exact solutions for all values of c_A are possible in two limits. The first of these pertains to a situation where there is no transfer between donors. In this limit $f(t)$ is given by a generalization of an equation first derived by Inokuti and Hirayama[4,7]

$$f(t) = \prod_l (1 - c_A + c_A e^{-X_{0l} t}) \quad , \tag{2.6}$$

where the indices 0 and l refer to sites on the lattice and X_{0l} is the transfer rate from a donor on site 0 to an acceptor on site l (or from a donor on site l to an acceptor on site 0).

The other limit applies to a situation where transfer between donors is extremely rapid in comparison with the transfer to traps. We obtain the solution appropriate to this limit directly from the rate equations

$$\sum_{n=1}^{N_D} \frac{d}{dt} P_n(t) = -\sum_{n=1}^{N_D} (\gamma_R + X_n) P_n(t) \quad . \tag{2.7}$$

In the rapid transfer limit all donors have an equal probability of being excited for all times of interest. As a consequence the $P_n(t)$ in Eq. (2.7) are independent of n so that we have

$$N_D \frac{dP}{dt}(t) = -\left(N_D^{-1} \sum_n (\gamma_R + X_n)\right) N_D P(t) \quad , \tag{2.8}$$

from which we obtain the result

$$f(t)=\exp(-\langle X\rangle_c t) \ , \tag{2.9}$$

where $\langle X\rangle_c$ denotes the configuration average of the donor-acceptor transfer rate

$$\langle X\rangle_c = c_A \sum_l X_{0l} \ . \tag{2.10}$$

We see that in neither limit is $f(t)$ an explicit function of the donor-donor transfer rates. However in the case of rapid transfer $f(t)$ decays exponentially in time whereas in the static limit $f(t)$ decays less rapidly, $\ln f(t)$ being a nonlinear function of t.[4,7,8] However despite the qualitative differences in the two limits both Eqs. (2.6) and (2.9) have the same initial slope, $df(0)/dt = -c_A \sum_l X_{0l}$. This is an example of the general result that $df(0)/dt$ is independent of the donor-donor transfer rates, which can be established by computing the derivative directly from Eq. (2.2).

III. INTERMEDIATE REGIME

The complexity of the analysis in the regime intermediate between the static and rapid transfer limits can be traced to the disorder. Were both the donors and acceptors in ordered arrays then an exact solution to Eq. (2.3) could easily be obtained by standard methods. In order to study the effects of disorder it is convenient first to consider systems where the donors form a lattice with the acceptors distributed at random. Generalization of our results to include disorder in the donors as well as in the acceptors is straightforward and will be done later.

As has been noted before, Eqs. (2.1) and (2.2) bear a formal similarity to the equations of motion of the electrons in the tight-binding model of a metal and to the equations of motion for the spins in a Heisenberg ferromagnet. In particular, for imaginary values of t Eq. (2.3) is identical to the linearized equations of motion for the spins in a ferromagnet with exchange integral and anisotropy field proportional to $W_{nn'}$ and $\gamma_R + X_n$, respectively.[4] Because of this similarity we can make use of theoretical techniques developed for disordered alloys and magnets to calculate $f(t)$. An approach particularly well suited to characterizing the effects due to a small number of traps is the average-t-matrix approximation or ATA.[9]

In the Appendix to this paper we calculate the Laplace transform of $f(t)$ in the ATA. Defining the transform by means of the equation

$$\hat{f}(s)=\int_0^\infty dt\, e^{-st} f(t) \ , \tag{3.1}$$

we obtain the result

$$\hat{f}(s)=\left[s + c_A \sum_{l,l'} t_{ll'}(s)\right]^{-1} \ . \tag{3.2}$$

The $t_{ll'}(s)$ denote elements of the t matrix associated with a single impurity at site 0 and l,l' label donor sites in its "sphere of influence." The t matrix is obtained as a solution to the equation

$$t_{ll'}(s) = X_{0l}\delta_{ll'} - \sum_{l''} X_{0l} g_{ll''}(s) t_{l''l'}(s) \ , \tag{3.3}$$

where X_{0l} is the donor-acceptor transfer rate for the lth donor and $g_{ll'}(s)$ is given by

$$g_{ll''}(s) = \frac{1}{N_D} \sum_{\vec{k}} \exp[i\vec{k}\cdot(\vec{r}_l - \vec{r}_{l''})]\, g(\vec{k},s) \ , \tag{3.4}$$

with

$$g(\vec{k},s) = \left[s + \sum_{n'} W_{nn'}\{1-\cos[\vec{k}\cdot(\vec{r}_n - \vec{r}_{n'})]\}\right]^{-1} \ . \tag{3.5}$$

Here the sum on $\vec{k}$ is over the Brillouin zone associated with the donor lattice with ions located at $\vec{r}_l$, $\vec{r}_{l'}$, etc.

There are a number of comments to be made in connection with the ATA. First in our formulation of the ATA $[f(s)]^{-1}$ is obtained exactly only to first order in c_A. Terms which are nonlinear in the acceptor concentration are not taken into account. Second, we obtain the rapid transfer limit discussed in Sec. II by making the Born approximation to the t matrix

$$t_{ll'} \to X_{0l}\delta_{ll'} \ , \tag{3.6}$$

so that

$$\hat{f}(s)=\left[s + c_A \sum_l X_{0l}\right]^{-1} \ , \tag{3.7}$$

which is equivalent to Eq. (2.9). Note that we have made use of the result that X_{0l} depends only on the relative separation of the two ions so that it is also the transfer rate when the donor is at 0 and the acceptor at l.

In the opposite limit, $W_{nn'} \to 0$, we obtain from Eqs. (3.4) and (3.5)

$$g_{ll'}(s) = \delta_{ll'} s^{-1} \ , \tag{3.8}$$

so that the t matrix takes the form

$$t_{ll'}(s) = \frac{\delta_{ll'} X_{0l}}{1 + X_{0l}/s} \ . \tag{3.9}$$

The function $\hat{f}(s)$ is then given by

$$\hat{f}(s) = \left[s + c_A s \sum_l X_{0l}(s + X_{0l})^{-1}\right]^{-1}$$

$$\approx s^{-1} - c_A s^{-1} \sum_l X_{0l}(s + X_{0l})^{-1} \ , \tag{3.10}$$

to first order in c_A. Inverting the transform we find

$$f(t) \approx 1 + c_A \sum_l (e^{-X_{0l}t} - 1) \ , \tag{3.11}$$

which agrees with Eq. (2.6) when the latter is expanded to first order in c_A. Finally, we note that although Eqs. (3.2) and (3.3) were obtained assuming the donor array had translational symmetry the effects of disorder in the donors can be included, in a first approximation, by replacing $g_{ll'}(s)$ with its configurational average $\langle g_{ll'}(s)\rangle_c$.

IV. DISCUSSION

In this section we discuss the results obtained in Sec. III. First of all we note that the behavior of $f(t)$ as $t\to 0$ is determined by the behavior of its transform as $s\to\infty$. In this limit $g_{ll'}(s)\to\delta_{ll'}s^{-1}$ so that $t_{ll'}(s)\to\delta_{ll'}X_{0l}$. As a consequence we have

$$f(t)\sim\exp\left[-c_A\sum_l X_{0l}t\right]$$

$$\approx 1-c_A\sum_l X_{0l}t$$

as $t\to 0$. Thus $df(0)/dt=-c_A\sum_l X_{0l}$ in agreement with the results obtained in Sec. III.

The variation of $f(t)$ as $t\to\infty$ is determined by $\hat{f}(s)$ as $s\to 0$. Provided $g_{ll'}(0)$ is finite we obtain the asymptotic equation

$$f(t)\approx\exp\left[-c_A t\sum_{l,l'} t_{ll'}(0)\right] . \tag{4.1}$$

The exponential decay indicated in Eq. (4.1) will be present in three-dimensional systems as long as $g(\vec{k},s)$ varies as $(Dk^2+s)^{-1}$ for small k, which will be the case if the dynamics of the donors is characterized by a diffusion equation with diffusion constant D in the low-frequency–long-wavelength limit. However in lower dimensional systems exponential behavior is not present even when the dynamics is diffusive since $g_{ll'}(s)\sim s^{-1/2}$ (one dimension) and $g_{ll'}(s)\sim -\ln(s)$ (two dimensions) as $s\to 0$ (see note added in proof).

Since the general solution of the t-matrix equation is a complicated problem it is important to identify simple approximations which can be used in making comparisons between experiment and theory. We will discuss two such approximations. The first of these consists in omitting all off-diagonal elements of the t matrix. When $t_{ll'}(s)$ is set equal to zero for $l\neq l'$ we obtain the result

$$t_{ll}(s)=X_{0l}[1+X_{0l}g_0(s)]^{-1} , \tag{4.2}$$

where $g_0(s)\equiv g_{ll}(s)$ with $g_{ll}(s)$ given by Eq. (3.4).

Using Eq. (4.2) we have

$$\hat{f}(s)=\left[s+c_A\sum_l X_{0l}[1+X_{0l}g_0(s)]^{-1}\right]^{-1} . \tag{4.3}$$

Equation (4.3) reproduces the exact results in the static and rapid transfer limits. However by omitting off-diagonal elements of the t matrix we neglect correlations between different donors in the sphere of influence of the acceptor. The neglect of these correlations will be a reasonable approximation as long as the excitation has a small probability of being transferred between donors in the same sphere of influence. This will be the case if the average number of donors in the sphere of influence is $\lesssim 1$. The criterion for this inequality to be satisfied will be discussed below.

There is a close connection between (4.3) and the hopping model of Burshtein developed in Ref. 2. In this mode $f(t)$ is obtained as the solution to the integral equation

$$f(t)=f_0(t)e^{-t/\tau_0}+\frac{1}{\tau_0}\int_0^t d\tau\, f_0(t-\tau)\,e^{-(t-\tau)/\tau_0}f(\tau) , \tag{4.4}$$

where τ_0 is a phenomenological hopping time. The function $f_0(t)$ is $f(t)$ in the absence of donor-donor transfer and is given by Eq. (2.6).

Equation (4.4) is easily solved for the Laplace transform of $f(t)$. We find

$$\hat{f}(s)=[s+X_B(s)]^{-1} , \tag{4.5}$$

where

$$X_B(s)=\left[\int_0^\infty e^{-(s+\tau_0^{-1})t}f_0(t)\,dt\right]^{-1}-s-\tau_0^{-1} . \tag{4.6}$$

Evaluating $X_B(s)$ to first order in c_A we obtain the result

$$\hat{f}(s)=\left\{s+c_A\sum_l X_{0l}\left[1+X_{0l}\left[s+\frac{1}{\tau_0}\right]^{-1}\right]^{-1}\right\}^{-1} . \tag{4.7}$$

Comparing Eq. (4.7) with Eq. (4.3) we see that Eq. (4.7) is a simplified version of the latter equation in which $g_0(s)$ is approximated by $(s+1/\tau_0)^{-1}$. Provided τ_0 is identified with $g_0(0)$, this approximation reproduces both the large s and small s limits of Eq. (4.3).

In the case of an ordered array of donors the calculation of $g_0(0)$ from Eq. (3.4) is a relatively straightforward problem in numerical analysis. Complications arise when the donor array is disordered. An approximate expression for $\langle g_0(s)\rangle_c$ follows from the observation that $\langle g_0(s)\rangle_c$ [and $g_0(s)$ for the ordered array] is given by

$$\langle g_0(s)\rangle_c=\int_0^\infty dt\, e^{-st}R(t) , \tag{4.8}$$

where $R(t)$ is the conditional probability that an ion excited at $t=0$ is still excited at a later time t.[4] As shown in Ref. 4 this probability is equal to the normalized intensity of the sharp-line fluorescence monitored in a time-resolved fluorescence line-narrowing experiment. Approximations to $R(t)$ were suggested in Ref. 4 and assessed in Ref. 8. These approximations when used in Eq. (4.8) provide a reasonable es-

timate of $\langle g_0(s)\rangle_c$ and hence the parameter τ_0 in the Burshtein model.

The second approximation to the t-matrix equation involves the passage to the continuum limit, which is appropriate whenever there is a large number of donors in the sphere of influence. The continuum analogs of Eqs. (3.2) and (3.3) take the form

$$\hat{f}(s)=\left[s+n_A\int d\vec{r}\,d\vec{r}\,'\,\tilde{t}(\vec{r},\vec{r}\,';s)\right]^{-1} , \tag{4.9}$$

and

$$\tilde{t}(\vec{r},\vec{r}\,';s)=v(r)\delta(\vec{r}-\vec{r}\,')-\int dr''\,v(r)\tilde{g}(\vec{r},\vec{r}\,'';s) \times\tilde{t}(\vec{r}\,'',\vec{r}\,';s) , \tag{4.10}$$

where $v(r)$ is the donor-acceptor transfer rate at a distance r and n_A is the concentration of acceptors. The function $\tilde{g}(\vec{r},\vec{r}\,';s)$ is given by the counterpart of Eq. (3.4),

$$\tilde{g}(\vec{r},\vec{r}\,';s)=\frac{1}{(2\pi)^3}\int d\vec{k}\exp[i\vec{k}\cdot(\vec{r}-\vec{r}\,')]\,\tilde{g}(\vec{k},s) , \tag{4.11}$$

where

$$\tilde{g}(k,s)=(s+Dk^2)^{-1} , \tag{4.12}$$

in which D is identified with the diffusion constant appropriate to the donor array. When the donors form a lattice D is obtained by expanding $g(\vec{k},s)$ [Eq. (3.5)] to order k^2. Assuming cubic symmetry we have[4]

$$D=\tfrac{1}{6}\sum_{n'}W_{nn'}(\vec{r}_n-\vec{r}_{n'})^2 . \tag{4.13}$$

Except for a few special cases the exact value of the diffusion constant of a disordered three-dimensional array is unknown. However in situations where the donor system is dilute, $c_D \ll 1$, and the donor-donor transfer rate varies as β/r^v we have $D\propto\beta n_D^{(v-2)/3}$ on the basis of dimensional arguments, n_D being the concentration of donors. Under these circumstances the result obtained by generalizing the method of Trlifaj[10] to arbitrary v,

$$D=\tfrac{1}{2}(v-5)^{-1}(4\pi n_D/3)^{(v-2)/3}\beta \quad (v>5) , \tag{4.14}$$

is a reasonable approximation.

In the diffusion model of Yokota and Tanimoto[3] when s is small $\hat{f}(s)$ has the form

$$\hat{f}(s)=(s+4\pi Dn_A a_S)^{-1} , \tag{4.15}$$

where a_S is the scattering length associated with a one-particle Schrödinger equation in which the "potential" is equal to the donor-acceptor transfer rate and the "mass" of the particle is $(2D)^{-1}$. We can obtain this result from Eq. (4.9). When $s=0$ the integral of the t matrix in Eq. (4.9) can be identified with $-4\pi D\times$ [zero-energy limit of the scattering amplitude associated with $v(r)$].[11] At low energies the scattering amplitude is approximately $\delta_0(k)/k$ where $\delta_0(k)$ is the $l=0$ phase shift for incident particle "energy" Dk^2. In the limit $k\to 0$ we have $\delta_0(k)/k\approx -a_S$ so that Eq. (4.9) becomes identical to Eq. (4.15).

As was pointed out the approximations leading to Eq. (4.3) are meaningful only when there is a small number of donors in the sphere of influence of the acceptor whereas Eq. (4.9) is valid in the opposite limit. In order to determine the radius of the sphere of influence, R_0, we use the criterion

$$v(R_0)=1/\tau_0 , \tag{4.16}$$

where $v(r)$ is the donor-acceptor transfer rate and $1/\tau_0=g_0(0)$ or $\langle g_0(0)\rangle_c$ as is appropriate. Equation (4.16) has a simple physical interpretation. The radius of the sphere of influence is such that for a donor at R_0 the transfer rate to the acceptor is equal to the donor-donor hopping rate. Thus with R_0 determined by Eq. (4.16) we have

$$n_D R_0^3 \lesssim 1 , \tag{4.17}$$

for Eq. (4.3) to be applicable and

$$n_D R_0^3 \gg 1 , \tag{4.18}$$

for Eq. (4.9) to be appropriate.

As an example of the use of the criteria we consider the case of a dilute array of donors with a donor-acceptor transfer rate equal to α/r^u and a donor-donor transfer rate β/r^v. We obtain τ_0 from Eq. (4.8) using the approximation for $R(t)$ referred to as "model 2" in Ref. 4

$$R(t)=\exp(-A_v t^{3/v}) , \tag{4.19}$$

where

$$A_v=\frac{4\pi}{3}n_D\beta^{3/v}2^{3/v-1}\Gamma\left(1-\frac{3}{v}\right) , \tag{4.20}$$

in which $\Gamma(x)$ denotes the gamma function. Thus from Eqs. (4.19) and (4.20) we obtain the result

$$\langle g_0(0)\rangle_c=\tau_0=\Gamma(v/3+1)A_v^{-v/3} . \tag{4.21}$$

Combining Eq. (4.16) with Eq. (4.21) we conclude that Eq. (4.3) is appropriate when

$$n_D^{1-v/u}(\alpha/\beta)^{3/u}\lesssim 1 , \tag{4.17'}$$

whereas for the diffusion model to apply we must have

$$n_D^{1-v/u}(\alpha/\beta)^{3/u}\gg 1 . \tag{4.18'}$$

Thus if both the donor-donor and donor-acceptor rates vary as the same power of the separation (4.3)

will be applicable when $\alpha \lesssim \beta$.[2] If $v < u$, diluting the donor array will decrease the number of donors in the sphere of influence whereas if $v > u$ the opposite effect occurs. This happens because a decrease in donor concentration reduces the average donor-donor transfer rate as well as the average rate of transfer to acceptors. When $v < u$ the relative decrease in the former will be less than the relative decrease in the latter. As a consequence, the decrease in the effective strength of the donor-acceptor transfer is greater than the decrease in the effective strength of the donor-donor transfer; when $v > u$ the situation is reversed.

Also we note that the criterion for applicability of the diffusion model, Eq. (4.18′), has an alternative interpretation in terms of the ratio of the average donor-acceptor transfer time for ions inside the sphere of influence to the time it takes for the excitation to diffuse across the sphere, R_0^2/D. With the diffusion constant varying as $\beta n_D^{(v-2)/3}$ and the average transfer time as $(\alpha/R_0^u)^{-1}$ we have for the ratio

$$\frac{(\alpha/R_0^u)^{-1}}{R_0^2/D} \approx [n_D^{1-v/u}(\alpha/\beta)^{3/u}]^{-2/3} \quad . \tag{4.22}$$

Thus when the diffusion model is applicable the transfer time is much less than the diffusion time, i.e., the system is close to the static limit.

The question of the magnitude of the diffusion constant relative to the donor-acceptor transfer rate also arises in connection with the calculation of the scattering length. Strictly speaking the transfer rate $v(r)$ cannot go to infinity as $r \to 0$ since there is an upper limit to X_{0l}. Thus instead of $v(r) = \alpha/r^u$, $0 \leq r \leq \infty$ we might have $v(r) = \alpha/r^u$, $r_c \leq r \leq \infty$; $v(r) = \alpha/r_c^u$, $r < r_c$, where r_c is on the order of the minimum donor-acceptor distance. A detailed calculation shows that a_S will be independent of r_c, and hence have the same value as obtained with $r_c = 0$ if

$$(\alpha/r_c^u)/(D/r_c^2) >> 1 \quad . \tag{4.23}$$

With $D \sim \beta n_D^{(v-2)/3}$ Eq. (4.23) is equivalent to

$$\alpha r_D^{v-2}/\beta r_c^{u-2} >> 1 \quad , \tag{4.24}$$

where $(4\pi/3) r_D^3 = n_D^{-1}$. Since $r_D \geq r_c$ Eq. (4.24) will be obeyed if the inequality (4.18′) is satisfied. We conclude from this analysis that if diffusion model is appropriate a_S is the scattering length obtained with $r_c = 0$, e.g.,

$$a_S = (\alpha/D)^{1/(u-2)}(u-2)^{-2/(u-2)}\Gamma(1-1/(u-2)) \times \Gamma(1+1/(u-2))^{-1} \quad , \tag{4.25}$$

for $v(r) = \alpha/r^u$, $0 \leq r \leq \infty$.[12]

V. SUMMARY

The results presented in Secs. II–IV can be summarized as follows. The intensity of the donor fluorescence is proportional to $\exp(-\gamma_R t) f(t)$, γ_R^{-1} being the radiative lifetime of the fluorescing level. The behavior of $f(t)$, which characterizes the loss associated with one-way transfer to traps, is shown schematically in Fig. 1. Curve (a) is obtained from Eq. (2.6). It describes the evolution of the fluorescence in the absence of donor-donor transfer. Curve (b), given by Eqs. (2.9) and (2.10), is $f(t)$ in the rapid transfer limit. Curve (c) shows the behavior of $f(t)$ when the donor-donor transfer rates fall between these limits.[13] The exponential variation of $f(t)$ at long times is characterized by a decay rate equal to

$$c_A \sum_l X_{0l}[1 + X_{0l} g_0(0)]^{-1} \quad ,$$

when the number of donors in the sphere of influence is small [Eq. (4.3) with $s = 0$]. Here $g_0(0)$ is obtained from Eq. (3.4) or (4.21) as is appropriate. In the opposite limit where there is a large number of

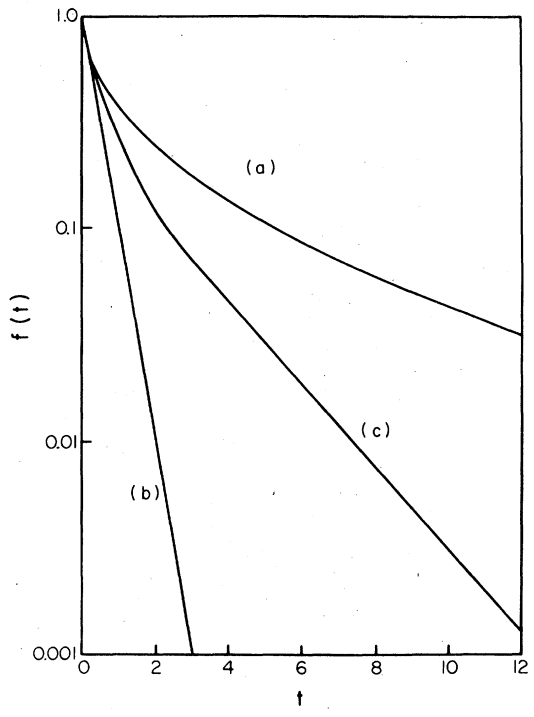

FIG. 1. Schematic semilog plot of $f(t)$ vs t. Curve (a): $f(t)$ in the absence of donor-donor transfer, Eq. (2.6). Curve (b): $f(t)$ in the rapid transfer limit, Eq. (2.9). Curve (c): $f(t)$ in the regime intermediate between the static and rapid transfer limits. All three curves have the same initial slope; (a) is nonexponential at all times, (b) is exponential at all times; (c) becomes exponential as $t \to \infty$.

donors present in the sphere the decay rate is equal to [cf., Eq. (4.15)]

$$4\pi n_A D a_S \ ,$$

where D is given by Eq. (4.13) or (4.14) and a_S is obtained from Eq. (4.25) or the equivalent. The criteria for determining which of the two expressions is appropriate are given in Eqs. (4.17), (4.17'), (4.18), and (4.18'). Note that the decay rates hold only in the limit c_A or $n_A \to 0$, where the ATA is valid.

When there is a small number of donors in the sphere of influence the behavior of $f(t)$ at intermediate times is reasonably well approximated by the solution to Eq. (4.4) as long as τ_0 is identified with $g_0(0)$ or $\langle g_0(0)\rangle_c$.[14] When the diffusion model is appropriate the Padé approximate to $f(t)$ developed in Ref. 3 provides an approximation which interpolates between the short- and long-time limits.

Note added in proof. In one and two dimensions $g_{ll'}(s)$ becomes independent of l-l' in the limit $s \to 0$. As a result it is straightforward to solve the t-matrix equation for the sum $\sum t_{ll'}(s)$. In the one-dimensional case one obtains the expression

$$f(t) = \exp[4(c_A/a)^2 Dt]\,\mathrm{erfc}[2(c_A/a)(Dt)^{1/2}] \ ,$$

in agreement with the random walk analysis of Richards [P. M. Richards (private communication)]. Here a is the lattice constant, D is the diffusion constant and erfc denotes the complementary error function. This equation has the asymptotic limit $f(t) \sim [4\pi(c_A/a)^2 Dt]^{-1/2}$. In two dimensions the corresponding limit is $(4\pi c_A a^{-2} Dt)^{-1}$.

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APPENDIX

In this appendix we outline the steps leading to Eqs. (3.2) and (3.3). According to Eq. (2.3) $f(t)$ can be written

$$f(t) = \exp(\gamma_R t) N_D^{-1} \sum_{n'=1}^{N_D} \sum_{n=1}^{N_D} P_n^{n'}(t) \ . \tag{A1}$$

Equation (A1) can in turn be written as a sum of matrix elements of the operator $\exp[-(\Gamma + X)]$ between states, labelled by the index n, which have only the nth donor in an excited state

$$f(t) = N_D^{-1} \sum_{n,n'} \{\exp[-(\Gamma + X)t]\}_{nn'} \ , \tag{A2}$$

where

$$\Gamma_{nn'} = \delta_{nn'} \sum_{n''} W_{nn''} - (1 - \delta_{nn'}) W_{n'n} \tag{A3}$$

and

$$X_{nn'} = X_n \delta_{nn'} \ . \tag{A4}$$

Taking the transform of Eq. (A2) we obtain the result

$$\hat{f}(s) = N_D^{-1} \sum_{n,n'} G_{nn'}(s) \equiv \sum_{n} \langle G_{n0}(s)\rangle_c \ , \tag{A5}$$

where

$$G(s) = (sI + \Gamma + X)^{-1} \ , \tag{A6}$$

with I being the unit operator.

Since the configurational average of G is translationally invariant we can write it as a Fourier expansion

$$\langle G_{n0}(s)\rangle_c = \frac{1}{N_D} \sum_{\vec{k}} \exp[i\vec{k}\cdot(\vec{r}_n - \vec{r}_0)]\,\langle G(\vec{k},s)\rangle_c \ . \tag{A7}$$

Using Eq. (A7) in Eq. (A5) we obtain the result

$$\hat{f}(s) = \langle G(0,s)\rangle_c \ . \tag{A8}$$

To evaluate $\langle G(0,s)\rangle_c$ we introduce the operator T defined by

$$Tg = XG \ , \tag{A9}$$

where

$$g = (sI + \Gamma)^{-1} \ . \tag{A10}$$

The operator T satisfies the equation

$$T = X - XgT \ , \tag{A11}$$

and can be used to rewrite G in the form

$$G = g - gTg \ . \tag{A12}$$

In the average t-matrix approximation the configurational average of T is given by[9]

$$\langle T\rangle_c = N_A \langle t\rangle_c / (1 + N_A g) \ , \tag{A13}$$

where N_A is the number of acceptors and $\langle t\rangle_c$ is the configurational average of the t matrix associated with a single impurity. Making use of Eq. (A13), (A12), and (A8) along with the equation $\langle G\rangle_c = g - g\langle T\rangle_c g$ we obtain the result

$$\hat{f}(s) = [g(0,s)^{-1} + N_A \langle t(0,s)\rangle_c]^{-1} \ , \tag{A14}$$

where $g(\vec{k},s)$ is given by Eq. (3.5) and $\langle t(\vec{k},s)\rangle_c$ by an equation analogous to the inverse of Eq. (A7). From Eq. (3.5) it is evident that $g(0,s) = s^{-1}$.

In the $\vec{k}=0$ limit we have

$$\langle T(0,s)\rangle_c = \sum_{l'} \langle t_{ll'}(s)\rangle_c = \frac{1}{N_D}\sum_{l,l'} t_{ll'}(s) \quad , \tag{A15}$$

in which $t_{ll'}(s)$ satisfies the analog of Eq. (A11)

$$t_{ll'}(s) = X_{0l}\delta_{ll'} - \sum_{l''} X_{0l} g_{ll''} t_{l''l'}(s) \quad , \tag{A16}$$

where l and l' refer to sites in the neighborhood of the trap located at site 0. Combining these results we obtain the equation

$$\hat{f}(s) = \left(s + c_A \sum_{l,l'} t_{ll'}(s)\right)^{-1} \quad , \tag{A17}$$

where $c_A = N_A/N_D$ is the fraction of sites occupied by acceptors. It should be emphasized that as long as the donor array has translational symmetry the average-t-matrix approximation reproduces the exact result for $\hat{f}(s)^{-1}$ to first order in c_A.

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[11]The scattered amplitude, f_S, of a particle of mass m and energy $k^2/2m$ is related to the t matrix through the integral ($\hbar=1$)

$$f_S = -\frac{m}{2\pi}\int d\vec{r}\, d\vec{r}\,' e^{-i\vec{k}_f\cdot\vec{r}+i\vec{k}_i\cdot\vec{r}'}\, \tilde{t}(\vec{r},\vec{r}\,';-k^2/2m-i\epsilon) \quad ,$$

where $\tilde{t}$ is given by Eq. (4.10) and $\vec{k}_i$ and $\vec{k}_f$ are the incoming and outgoing momenta, respectively, with $|\vec{k}_i| = |\vec{k}_f| = k$ [N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions,* 3rd ed. (Oxford University, New York, 1965), p. 91].

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