Theory of donor fluorescence in the diffusion limit

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(Received 14 April 1980)

Time dependence of fluorescence from donors is studied in the diffusion limit when there is a large number of donors in the sphere of influence of an acceptor. The average t-matrix approximation is used to derive the Laplace transform of the normalized intensity in this limit. The time dependence of the decay of the fluorescence is compared with experimental data on $Pr_{0.95}F_3:Nd^{3+}_{0.05}$ and also with the results of the diffusion model of Yokota and Tanimoto.

I. INTRODUCTION

In a recent paper[1] the time dependence of the donor fluorescence from inhomogeneously broadened levels has been studied in considerable detail. A random distribution of acceptor ions acting as traps for the excitation is assumed. The starting point is, as in some of the past work,[2-5] a set of coupled linear equations for the probability $P_n(t)$ that ion n is excited at time t, all other ions being in the ground state. If X_{on} is the rate of transfer of excitation from a donor at n to a trap at o, and $W_{nn'}$ the rate of donor-donor transfer, the dynamics of the system of optically excited ions is described by

$$\frac{dP_n(t)}{dt} = -\left(\gamma_R + X_n + \sum_{n''} W_{nn''}\right) P_n(t) + \sum_{n'} W_{n'n} P_{n'}(t) . \tag{1}$$

The quantity of interest is the normalized fluorescence intensity $F(t)$, which is essentially the sum over the P_n's. The radiative part $\exp(-\gamma_R t)$ is factored out to give

$$F(t) = e^{-\gamma_R t} f(t) , \tag{2}$$

where $f(t)$ is obtained from Eq. (1) after setting $\gamma_R = 0$ and averaging over all trap configurations. For simplicity we suppress the notation $\langle \cdots \rangle_c$ indicating a configurational average.

As has been pointed out in Ref. 1, the exact calculation of $f(t)$, generally a formidable problem, is possible for all values of trap concentration c_A either if there is no donor-donor transfer or if the donor-donor transfer is very rapid. For the regime intermediate between these limits the average-t-matrix approximation[1] (ATA) has proved to be a very useful technique as long as $c_A \ll 1$. The Laplace transform $\hat{f}(s)$ of $f(t)$ is

$$\hat{f}(s) = \left(s + c_A \sum_{l,l'} t_{ll'}(s)\right)^{-1} . \tag{3}$$

The elements $t_{ll'}(s)$ of the t matrix associated with a single impurity at site o and donors at sites l and l' are obtained as a solution to the equation

$$t_{ll'}(s) = X_{ol}\delta_{ll'} - \sum_{l''} X_{ol} g_{ll''}(s) t_{l''l'}(s) . \tag{4}$$

When the donor array has translational symmetry the elements $g_{ll'}(s)$ are given by

$$g_{ll'}(s) = \frac{1}{N_D} \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}_l - \vec{r}_{l'})} g(\vec{k}, s) , \tag{5}$$

where

$$g(\vec{k}, s) = \left(s + \sum_{n'} W_{nn'}\{1 - \cos[\vec{k}\cdot(\vec{r}_n - \vec{r}_{n'})]\}\right)^{-1} . \tag{6}$$

The ATA has been successfully used in Ref. 6 to analyze the fluorescence of donor arrays which form simple cubic, face-centered-cubic, and body-centered-cubic lattices. Nearest-neighbor transfers between donors and between donors and acceptors was assumed throughout the analysis.

To construct a theory not restricted to nearest-neighbor transfers we must take into account the fact that the nature of the transfer depends crucially on the number of donors in the sphere of influence of an acceptor. When the number of donors in the sphere of influence of an acceptor is large, the diffusion model of Yokota and Tanimoto[7] is applicable. On the other hand, if the number of donors in the sphere of influence is small, the hopping model introduced by Burshtein[8] is appropriate. It is our aim in this paper to analyze the former situation in the light of the ATA.

II. RESULTS

In this section we develop a theory appropriate for the case of a large number of donors in the sphere of influence of an acceptor. We relax the restriction of nearest-neighbor transfer and consider the continuum limit of Eq. (3). The counterpart of Eqs. (3) and (4) in the continuum approximation are, respectively,

$$f(s) = \left(s + n_A \int d\vec{r}\, d\vec{r}'\, t(\vec{r}, \vec{r}'; s)\right)^{-1} \tag{7}$$

and

$$t(\vec{r},\vec{r}';s)=v(r)\delta(\vec{r}-\vec{r}') - \int d\vec{r}''\, v(r)g(\vec{r},\vec{r}'',s)t(\vec{r}'',r',s)\,, \quad (8)$$

where n_A is the concentration of acceptors and $v(r)$ is the donor-acceptor transfer rate at a separation r. Motivated by the technique used in Ref. 5 to handle Eq. (4) we define a quantity $T(\vec{r},s)$ as follows:

$$T(\vec{r},s)=\int d\vec{r}'\, t(\vec{r},\vec{r}';s)\,. \quad (9)$$

Using Eqs. (8) and (9) we then obtain

$$T(\vec{r},s)=v(r)-\int d\vec{r}'\, v(r)g(\vec{r},\vec{r}',s)T(\vec{r}',s)\,, \quad (10)$$

where

$$g(\vec{r},\vec{r}',s)=\frac{1}{(2\pi)^3}\int d\vec{k}\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}g(\vec{k},s)\,, \quad (11)$$

with

$$g(\vec{k},s)=(s+Dk^2)^{-1}\,. \quad (12)$$

The constant D can be identified as the diffusion constant appearing in an equation of the form

$$D\nabla^2\tilde{g}(\vec{r},\vec{r}')-\frac{\partial}{\partial t}\tilde{g}(\vec{r},\vec{r}')=-\delta(\vec{r}-\vec{r}')\,. \quad (13)$$

Here $\tilde{g}(\vec{r},\vec{r}')$ is the inverse Laplace transform of $g(\vec{r},\vec{r}',s)$. For a set of donors forming a lattice D is obtained from the small-k expansion of Eq. (6):

$$D=\tfrac{1}{6}\sum_{n'} W_{nn'}(\vec{r}_n-\vec{r}_{n'})^2\,, \quad (14)$$

assuming cubic symmetry. In general, the exact value of D for a disordered system is unknown. Often it can be inferred from comparison with experiment. This will be discussed later.

Next, we cast the integral equation

$$T(\vec{r},s)=v(r)-v(r)\int d\vec{r}'\, d\vec{k}\frac{e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}}{s+Dk^2}T(\vec{r}',s) \quad (15)$$

into a form free of any angular dependence. We introduce the expansion

$$T(\vec{r},s)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} h_{lm}(r,s)Y_{lm}(\Omega)\,, \quad (16)$$

where the Y_{lm}'s are spherical harmonics associated with direction of $\vec{r}$. The unknown coefficients $h_{lm}(r,s)$ will be the solution of a new one-dimensional integral equation discussed below. We expand $\exp(i\vec{k}\cdot\vec{r})$ and $\exp(-i\vec{k}\cdot\vec{r}')$ in spherical harmonics to give

$$e^{i\vec{k}\cdot\vec{r}}=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} 4\pi i^l j_l(kr)Y^*_{lm}(\Omega_k)Y_{lm}(\Omega)\,, \quad (17)$$

etc., where the j_l's are spherical Bessel functions. The solid angle Ω_k refers to $\vec{k}$. The orthogonality relation

$$\int d\Omega_k Y^*_{lm}(\Omega)Y_{l'm'}(\Omega)=\delta_{ll'}\delta_{mm'} \quad (18)$$

can be used to perform the Ω_k, Ω', and Ω integrations to give

$$h_{lm}(r,s)=v(r)\int Y_{lm}(\Omega)d\Omega-\frac{(4\pi)^2}{(2\pi)^3}v(r)\int dr'\frac{dk}{s+Dk^2}r'^2k^2j_l(kr)j_l(kr')h_{lm}(r',s)\,. \quad (19)$$

Also, since

$$\int d\Omega\, Y_{lm}(\Omega)=\sqrt{4\pi}\,\delta_{l,0}\delta_{m,0}\,, \quad (20)$$

we obtain, using Eq. (16),

$$\int d\vec{r}\, T(\vec{r},s)=\sqrt{4\pi}\int dr\, r^2h_{00}(r,s)\,. \quad (21)$$

This last result may be used in Eq. (7).

Equation (21) suggests that it will suffice to focus attention only on $h_{00}(r,s)$ from now on. From Eq. (19) we get, on defining $h=h_{00}$,

$$h(r,s)=\sqrt{4\pi}\,v(r)-v(r)(4\pi)^2\frac{1}{(2\pi)^3}\int_0^{\infty}dr'r'^2\int_0^{\infty}dk\,k^2\frac{j_0(kr)j_0(kr')}{s+Dk^2}h(r',s)\,. \quad (22)$$

The k integration is easily performed, giving

$$h(r,s)=\sqrt{4\pi}\,v(r)-v(r)\frac{1}{2\sqrt{sD}}\int dr'(e^{-\kappa|r-r'|}-e^{-\kappa(r+r')})\left(\frac{r'}{r}\right)h(r',s)\,, \quad (23)$$

where

$$\kappa=\sqrt{(s/D)}\,.$$

It is known from the analysis of Yokota and Tanimoto[7] that for large t, or equivalently, for small s, $\hat{f}(s)$ is given by

$$\hat{f}(s)=(s+4\pi D n_A a_s)^{-1}\,. \tag{24}$$

Here a_s is the scattering length in a potential $v(r)$ of a particle of mass $(2D)^{-1}$.[1,2] We now make the connection between the diffusion model and our results as follows:

$$a_s=\frac{1}{4\pi D}\sqrt{4\pi}\int_0^\infty dr\, h(r,s=0)r^2\,, \tag{25}$$

where $h(r,s=0)$ satisfies the integral equation

$$h(r,s=0)=\sqrt{4\pi}\,v(r)-v(r)\left(\frac{1}{2D}\right)\int_0^\infty dr'(r+r'-|r-r'|)\left(\frac{r'}{r}\right)h(r',s=0)\,. \tag{26}$$

Equation (26) can be used as a check on the theory for a variety of transfer rates $v(r)$, once the integral equation for $h(r,s=0)$ is solved.

III. NUMERICAL SOLUTION

The technique used for solving the integral equations (23) and (26) is one that is closely related to the evaluation of integrals using quadrature formulas.[9] We consider the integral

$$\int_0^\infty G(r)\,dr$$

and replace it by an approximate representation as follows[10]:

$$\int_0^\infty G(r)\,dr=\sum_{i=1}^n w_i e^{r_i}G(r_i)\,, \tag{27}$$

where the r_i's are the n zeros of the nth-order Laguerre polynomial. The w_i are weight factors (also called Christoffel numbers) given by

$$w_j=\frac{1}{L_n'(r_j)}\int_0^\infty e^{-r}\frac{L_n(r)}{r-r_j}dr\,. \tag{28}$$

L_n' is the first derivative of $L_n(r)$. The r_j's and w_j's are tabulated in Ref. 10. Using Eq. (27) with Eq. (26), $h(r,s)$ is obtained as a solution to the matrix equation

$$H=(I+M)^{-1}V\,, \tag{29}$$

where H and V are column matrices:

$$H_i=h(r_i)\,,\qquad 1\le i\le n\,.$$
$$V_i=\sqrt{4\pi}\,v(r_i)\,,$$

M is an $n\times n$ matrix whose elements are

$$M_{ij}=\frac{1}{2(sD)^{1/2}}v(r_i)(e^{-\kappa|r_i-r_j|}-e^{-\kappa(r_i+r_j)})\times(r_j/r_i)e^{r_j}w_j\,. \tag{30}$$

I is the $n\times n$ unit matrix. The matrix operation in Eq. (29) provides H_k's which may be used as shown below:

$$\int_0^\infty dr\; r^2h(r,s)\simeq\sum_{k=1}^n e^{r_k}w_k r_k^2 H_k\,. \tag{31}$$

Equation (31) combined with Eq. (21) determines the Laplace transform $\hat{f}(s)$ described by Eq. 7 for all values of s. The normalized fluorescent intensity $f(t)$ is obtained by numerically inverting Eq. (7).[11]

IV. DISCUSSION

We have computed a_s for an exponential transfer rate $v(r)=V_0e^{-r/R}$ using Eqs. (25) and (26). The exact result is[12]

$$a_s=R\left[\ln\left(\frac{V_0R^2}{D}\right)+1.1544+2\frac{K_0[2(V_0R^2/D)^{1/2}]}{I_0[2(V_0R^2/D)^{1/2}]}\right], \tag{32}$$

where K_0 and I_0 are modified Bessel functions. As shown in Fig. 1 the agreement of the theory with the exact result is excellent over the full range of the parameter $D/(V_0R^2)$ including the Born approximation limit of

$$a_s\to 2R^3V_0/D,\quad D/(V_0R^2)\to\infty\,.$$

Finally, the theory has been compared with experimental data on the transfer of electronic en-

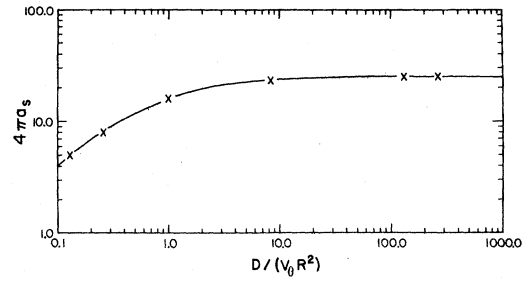

FIG. 1. $4\pi a_s$ vs $D/(V_0R^2)$ for the exponential transfer rate $V_0\exp(-r/R)$. a_s is measured in units of R^3V_0/D. Solid curve is the analytic result, Eq. (32). $\times$ denotes the numerical results obtained using methods outlined in Sec. III. The numerical results here and in Fig. 2 were obtained using a 15 point quadratures.

ergy from Pr to Nd in $Pr_{1-x}F_3:Nd_x^{3+}$.[13] Following Ref. 13 we assume a temperature-independent donor-acceptor transfer rate of α/r^6 with $\alpha = 5.4 \times 10^{-38}$ cm^6 s^{-1}. Since the transfer rate $v(r)$ can not go to infinity as $r \to 0$, a more reasonable choice is

$$v(r) = 1/r^6, \quad r \geq r_c$$
$$v(r) = 0, \quad r < r_c \tag{33}$$

where r_c is chosen such that

$$\sum_n \frac{1}{r_{0n}^6} = 4\pi n_L \int_{r_c}^{\infty} r^{-4} dr = \frac{4n_L}{3r_c^3}, \tag{34}$$

n_L being the number of Pr sites per unit volume. Our estimate of r_c, 3.1 Å for PrF_3, is the same as that used by Hegarty *et al.*[13] As discussed in Ref. 13 the coupling strength β of the donor-donor transfer rate β/r^6 satisfies $\beta \ll \alpha$ at the temperatures involved (12.5 K) so that the criterion of applicability of the diffusion model is met. The measured time development of the integrated donor fluorescence from the $^3P_0$ level of Pr is shown in Fig. 2 along with our theoretical "best fit."[14] The latter was obtained by assuming α and r_c to have the values given above and then adjusting the diffusion constant to maximize agreement over the entire range of observation. In this way we obtain the value $D = 14.0 \times 10^{-9}$ cm^2 s^{-1} for $T = 12.5$ K. This value is to be compared with the value $D = 8.5 \times 10^{-9}$ cm^2 s^{-1} inferred by fitting the asymptotic slope of $\ln[1/f(t)]$, Λ, to the equation[7]

$$\Lambda = 8.55 n_A \alpha^{1/4} D^{3/4}. \tag{35}$$

The difference in the two values of the diffusion constant is attributed to the fact that Eq. (35) applies to a transfer rate which varies as r^{-6} $0 \leq r \leq \infty$, in contrast to the more realistic behavior which we assumed in our calculation [cf. Eq. (33)]. With the transfer rate cut off at r_c we obtain the limiting slope $\Lambda = 6.5 n_A \alpha^{1/4} D^{3/4}$.

It is also interesting to compare our results for $f(t)$ with the following approximate formula of Yokota and Tanimoto[7]

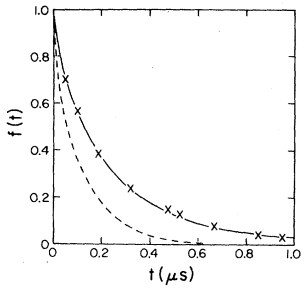

FIG. 2. $f(t)$ vs t for Pr in $Pr_{0.95}F_3:Nd_{0.05}^{3+}$ at 12.5 K. Solid line is theory with $D = 12.3 \times 10^{-9}$ cm^2 s^{-1}; $\times$ experiment. Broken curve Yokota-Tanimoto approximate formula with $D = 12.3 \times 10^{-9}$ cm^2 s^{-1}.

$$f(t) = \exp\left[-\frac{4\pi^{3/2}}{3} n_A (\alpha t)^{1/2} \times \left(\frac{1 + 10.87x + 15.50x^2}{1 + 8.743x}\right)^{3/4}\right], \tag{36}$$

where $x = D\alpha^{-1/3} t^{2/3}$. Our theory is developed in the Laplace-transform space whereas the result of Yokota and Tanimoto is obtained by solving the problem in the time domain. The prediction $f(t)$ from the Yokota-Tanimoto expression with $D = 14.0 \times 10^{-9}$ cm^2 s^{-1} is shown in Fig. 2. The agreement improves if we use $D = 3.0 \times 10^{-9}$ cm^2 s^{-1} for the extrapolation.

V. SUMMARY

In summary, the ATA is found to provide a good description of the time dependence of donor fluorescence in the diffusion limit when there is a large number of donors in the sphere of influence of the acceptor. We find excellent agreement between our numerical results for the scattering length and the exact values obtained analytically. Lastly, the ATA enables us to compute the donor fluorescence at all times provided the strength α of the DA transfer and the diffusion constant are known. Alternatively, if α is known, an estimate of D can be obtained by fitting the observed decay curves.

ACKNOWLEDGMENT

This research was supported by the NSF under Grant Nos. DMR-7904154 and DMR-7920070.

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