# Generalized models for spectral transfer in disordered systems

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We analyze the early-time development of the spectral transfer of optical excitation in inhomogeneously broadened systems. Previous models for the decay of the narrow-band fluorescence are generalized to include systems with asymmetric energy-dependent transfer rates. It is assumed that the energy splittings of the ions are uncorrelated. An analogous model for the early-time development of the background fluorescence is outlined. Detailed results are presented for spectral transfer over a Gaussian line shape assuming a dipole-dipole mechanism with rates that are inversely proportional to the square of the energy mismatch. Comparison is made with the treatment of Holstein *et al*.

## I. INTRODUCTION

The development of the techniques of time-resolved fluorescence line narrowing has facilitated the study of the time dependence of the spectral transfer of optical excitation in inhomogeneously broadened systems. By fitting the measured decay curves it has been possible to obtain information about the range and energy dependence of the microscopic transfer rates.[1] Theories for the time development of the spectral transfer have been discussed in a number of recent papers.[2-5] Most of the work in Refs. 2–5 has been based on the coupled rate equations

$$\frac{dP_n(t)}{dt} = -\sum_{n'} W_{nn'} P_n(t) + \sum_{n'} W_{n'n} P_{n'}(t), \qquad (1)$$

where $P_n(t)$ is the probability that ion $n$ is excited at time $t$ and $W_{nn'}$ is the transfer rate from ion $n$ to ion $n'$. It is assumed that the transfer rates are both symmetric, i.e., $W_{nn'} = W_{n'n}$, and independent of the energy mismatch between the excited states of the two ions. As long as the ions excited at $t = 0$ have near-neighbor configurations which are representative of the configurations for all of the ions then in the single-excitation limit the ratio of the narrow-band fluorescence to the total fluorescence across the inhomogeneous line is expressed as the configurational average of the solution to (1) with the initial conditions $P_n(0) = \delta_{n0}$. In Ref. 2 it was shown that this average, $\langle P_0(t) \rangle_c$, which is the probability that an ion excited at time 0 is still excited at time $t$, and hence characterizes the decay of the narrow-band fluorescence, can be written as the Laplace transform of the distribution of eigenvalues of the associated relaxation matrix whose elements are given by

$$\Gamma_{nn'} = \delta_{nn'} \sum_{n''} W_{nn''} - (1 - \delta_{nn'}) W_{n'n}. \qquad (2)$$

Most of the time-resolved fluorescence-line-narrowing experiments have been done on systems

which have a lattice of sites occupied at random by a fraction $c$ of optically active ions. Since the calculation of the eigenvalue spectrum of the relaxation matrix for a random system is a complicated problem it is important to develop simple approximations to $\langle P_0(t) \rangle_c$ which can be used in the analysis of the data. Three such approximations were introduced in Ref. 2. They took the form

$$\langle P_0(t) \rangle_c = \prod_l \{ 1 + c[e^{-W_{0l}t} f(W_{0l}t) - 1] \}, \qquad (3)$$

where the index $l$ now refers to sites. The function $f(W_{0l}t)$ is given by

$$f(W_{0l}t) = 1 \quad \text{(model 1)}, \qquad (4)$$

$$f(W_{0l}t) = \cosh(W_{0l}t) \quad \text{(model 2)}, \qquad (5)$$

$$f(W_{0l}t) = 1 + \tfrac{1}{2}(W_{0l}t)^2 \quad \text{(model 3)}. \qquad (6)$$

Equations (3)–(6) represent various versions of the "pair approximation." The repeated exchange of excitation by pairs of ions which is incorporated into model 2 will of course only be important when the two ions are close together. If ions 0 and $l$ are widely separated transfer to a third ion closer to $l$ will be more important than backtransfer to ion 0. However when ions 0 and $l$ are widely separated $W_{0l}$ is so small that the three-ion process has a negligible effect on $\langle P_0(t) \rangle_c$.

The accuracy of the models has been assessed in Ref. 3. It was concluded that at low concentrations, $c < 0.2$, model 2 is a reasonable approximation for $1 \gtrsim \langle P_0(t) \rangle_c \gtrsim 0.05$ whereas at high concentrations, $c > 0.5$, model 3 is to be preferred. In the intermediate range $0.2 \lesssim c \lesssim 0.5$, neither model 2 nor model 3 work particularly well. In no case is model 1, which neglects backtransfer altogether (an thus is equivalent to an expression first obtained by Inokuti and Hirayama[6]), the preferred approximation.

In this paper, we generalize models 2 and 3 so as to make them applicable to systems which have

asymmetric, energy- (mismatch) dependent transfer rates. In addition, we develop analogous approximations for the time development of the background fluorescence from ions which were not excited at $t=0$. In the latter study we make contact with the recent work of Holstein et al.[7] which is based on the integral equation of Montegi and Shionoya.[8] Our results for $\langle P_0(t) \rangle_c$ are given in Sec. II. The evolution of the background fluorescence is discussed in Sec. III. In Sec. IV, we report the results of numerical calculations for a system which has a Gaussian line shape and a dipole-dipole transfer rate which is inversely proportional to the square of the energy mismatch.

To our knowledge, there are as yet no systems which have been studied using time-resolved fluorescence-line-narrowing techniques where the dominant transfer processes are energy dependent. However with the growing interest in spectral transfer it seems likely that such systems will be found.

## II. GENERALIZED MODELS FOR $\langle P_0(t) \rangle_c$

The extension of Eq. (3) to systems where the transfer rates are symmetric but depend on the energy mismatch between the ions as well as on their relative separation is straightforward provided it can be assumed that the excited-state energies of the various ions are uncorrelated. By this we mean that in an arbitrarily chosen region of the crystal containing $N$ ions if $\mathcal{P}(E_1, \ldots, E_N)$ $dE_1 \cdots dE_N$ is the probability that ion 1 has an energy level between $E_1$ and $E_1 + dE_1$, etc., then we have

$$\mathcal{P}(E_1, \ldots, E_N) = \prod_{i=1}^{N} p(E_i). \tag{7}$$

It should emphasized that Eq. (7) represents the extreme limit of microscopic strain broadening. Provided (7) is valid, then each of the factors in (3) can be averaged separately and we obtain the result

$$\langle P_0(t) \rangle_c = \prod_l \int dE_l \, p(E_l)\{1 + c[e^{-W_{0l}(\Delta E_{0l})t}$$
$$\times f\,(W_{0l}(\Delta E_{0l})t) - 1]\}. \tag{8}$$

Here $\Delta E_{0l} = E_0 - E_l$, where $E_0$ is the energy of the ions excited at $t=0$. Note that since we have assumed the same distribution for all of the sites $p(E)$ is to be identified with the inhomogeneous line shape.

The case of asymmetric transfer is slightly more complicated. Such a situation will occur whenever the inhomogeneous linewidth is much less than $k_B T$ since $W_{0l}$ and $W_{l0}$ are related by the detailed balance condition

$$e^{-E_0/k_B T} W_{0l} = e^{-E_l/k_B T} W_{l0}. \tag{9}$$

A reasonable approximation to $\langle P_0(t) \rangle_c$ can be obtained by considering the mutual exchange of excitation by an isolated pair of ions at sites 0 and $l$. The corresponding rate equations are

$$\frac{dg_0^l}{dt} = -W_{0l}g_0^l + W_{l0}g_l^l, \tag{10a}$$

$$\frac{dg_l^l}{dt} = -W_{l0}g_l^l + W_{0l}g_0^l. \tag{10b}$$

The solution to (9a) and (9b) with initial conditions $g_0^l(0) = 1$, $g_l^l(0) = 0$ is given by

$$g_l^l(t) = 1 - g_0^l(t), \tag{11}$$

$$g_0^l(t) = \frac{e^{-W_{0l}t}}{W_{l0} + W_{0l}}(W_{l0}e^{W_{0l}t} + W_{0l}e^{-W_{l0}t}). \tag{12}$$

As in the derivation of (3) and (8) we approximate $\langle P_0(t) \rangle_c$ by a product of pair terms for the form $[1 - c + cg_0^l(t)]$. Our final result is

$$\langle P_0(t) \rangle_c = \prod_l \int dE_l \, p(E_l) \left[ 1 + c \left( \frac{e^{-W_{0l}t}}{W_{0l} + W_{l0}}(W_{l0}e^{W_{0l}t} \right.\right.$$
$$\left.\left. + W_{0l}e^{-W_{l0}t}) - 1 \right) \right], \tag{13}$$

where it is understood that $W_{0l}$ and $W_{l0}$ are functions of $\Delta E_{0l}$.

In the limit $W_{0l} = 0$, all $l$, there is no transfer from the initially excited sites so that $\langle P_0(t) \rangle_c = 1$. In the opposite case, $W_{l0} = 0$, there is no backtransfer and $\langle P_0(t) \rangle_c$ takes the form

$$\langle P_0(t) \rangle_c = \prod_l \int dE_l \, p(E_l)[1 + c(e^{-W_{0l}t} - 1)], \tag{14}$$

which is essentially the result of Inokuti and Harayama.[6] Finally, when $W_{l0} = W_{0l}$ Eq. (13) reduces to an appropriately averaged model 2.

We are unable to put precise limits on the accuracy of the approximations. However from our analysis of the symmetric, energy-independent transfer problem[3] we expect (13) to be a reasonable approximation at low concentrations ($c < 0.2$) over the interval $1 \geq \langle P_0(t) \rangle_c \geq 0.05$. At higher concentrations an approximation equivalent to model 3 is obtained by expanding the factor in parentheses. We have

$$\langle P_0(t) \rangle_c = \prod_l \int dE_l \, p(E_l)$$
$$\times \{1 + c[e^{-W_{0l}t}(1 + \tfrac{1}{2}W_{0l}W_{l0}t^2) - 1]\}, \tag{15}$$

which should be fairly accurate out to $\langle P_0(t) \rangle_c \approx 0.05$ for $c > 0.5$.

Equations (13) and (15) are the extensions of models 2 and 3, respectively, to the general case

of asymmetric, energy-dependent transfer rates. When the microscopic transfer rates are dependent on the energy mismatch, the background fluorescence will have a time dependence which reflects both the inhomogeneous line shape and the variation in transfer rates across the line. This aspect of the problem is discussed in the following section.

### III. BACKGROUND FLUORESCENCE

In this section, we outline an approximate theory for the background fluorescence coming from ions which were not excited at $t=0$. The theory is applicable to the early-time behavior in dilute systems and has approximately the same range of applicability as Eq. (13). We write the intensity of the background fluorescence at frequency $E/\hbar$, $I_B(E, E_0, t)$, in the form

$$I_B(E, E_0, t) = \gamma_L E N_0 e^{-\gamma_L t} f(E, E_0, t). \tag{16}$$

Here $\gamma_L$ is the radiative lifetime of the upper state (we assume the only decay mode involves fluorescence to the ground state) and $N_0$ is the number of ions initially excited by the laser pulse at frequency $E_0/\hbar$. The dimensionless function $f(E, E_0, t)$ is

independent of these parameters and depends implicitly on the fraction of occupied sites, the inhomogeneous line shape, and the microscopic transfer rates.

A simple approximation for $f(E, E_0, t)$ is suggested by writing Eq. (13) in the form

$$\langle P_0(t)\rangle_c = \exp[-cU(t)], \tag{17}$$

which is valid as long as $c \ll 1$. Here we have

$$U(t) = \sum_l \int dE_l \, p(E_l)[1 - g_0^l(t)], \tag{18}$$

where $g_0^l(t)$ is given by Eq. (12). For times such that $cU(t) < 0.5$ we can approximate $\langle P_0(t)\rangle_c$ by $1 - cU(t)$. Since apart from radiative losses the number of excited ions remains constant, we identify $N_0 cU(t)$ with the number of excited ions at time $t$ which were not excited at $t=0$. Also, we see that the number of excited ions with energy levels between $E$ and $E + dE$ is proportional to the integrand in (18). Thus, we can obtain an approximate expression for $f(E, E_0, t)$ by multiplying the integrand by an appropriate time-dependent normalization factor. In this way we obtain the expression

$$f(E, E_0, t) = (1 - e^{-cU(t)})U(t)^{-1} p(E) \sum_l \left( 1 - \frac{e^{-W_{0l}(\Delta E)t}}{W_{0l}(\Delta E) + W_{l0}(\Delta E)} [W_{l0}(\Delta E) e^{W_{0l}(\Delta E)t} + W_{0l}(\Delta E) e^{-W_{l0}(\Delta E)t}] \right), \tag{19}$$

where $\Delta E = E_0 - E$. Our approximation conserves the number of excited ions in the sense

$$\int dE f(E, E_0, t) = 1 - \exp[-cU(t)]$$
$$= 1 - \langle P_0(t)\rangle_c, \tag{20}$$

and is expected to be reasonably accurate out to times such that $\langle P_0(t)\rangle_c \approx 0.05$, i.e., $cU(t) \approx 3$.

Equation (19) simplifies considerably when the transition rates are symmetric. In this case, we have

$$f(E, E_0, t) = (1 - e^{-cU(t)})U(t)^{-1}$$
$$\times p(E) \sum_l e^{-W_{0l}(\Delta E)t} \sinh[W_{0l}(\Delta E)t]. \tag{21}$$

In situations where $W_{0l}(\Delta E)$ depends on the separation between site 0 and site $l$ through an equation of the form

$$W_{0l}(\Delta E) = (R_{\min}/r_{0l})^s w(\Delta E), \tag{22}$$

where $R_{\min}$ is the nearest-neighbor distance, the sum in (21) becomes a function of the variable $wt$, i.e.,

$$\sum_l e^{-W_{0l}t} \sinh(W_{0l}t) = C_s(wt), \tag{23}$$

where

$$C_s(x) = \sum_l \exp[-(R_{\min}/r_{0l})^s x] \sinh[(R_{\min}/r_{0l})^s x]. \tag{24}$$

For $x \ll 1$, $C_s(x)$ varies linearly with $x$. To obtain an asymptotic ($x \gg 1$) expression for $C_s$ we convert the sum to an integral obtaining the result[2]

$$C_s(x) = \tfrac{4}{3}\pi \rho R^3_{\min} 2^{3/s-1} \Gamma(1 - 3/s) x^{3/s}, \tag{25}$$

where $\rho$ is the number of lattice sites per unit volume and $\Gamma(x)$ denotes the gamma function.

In Sec. IV we apply the equations developed here to the case of a fcc lattice with dipole-dipole ($r^{-6}$) transfer rates which vary inversely as the square of the energy mismatch.

### IV. NUMERICAL RESULTS

In this section, we report the results of numerical calculations of the time development of the background fluorescence in a fcc lattice with dipole-dipole ($r^{-6}$) transfer. We assume a Gaussian

line shape[6]

$$p(E) = \pi^{-1/2} e^{-E^2}, \tag{26}$$

and a transfer rate which varies inversely as the square of the energy mismatch[9]

$$W_{0I} = (R_{min}/r_{0I})^6 (\Delta E^2 + \gamma^2)^{-1}. \tag{27}$$

We take $\gamma = 0.1$ and measure time in units of the reciprocal of the nearest-neighbor transfer rate for $\Delta E = 1$.

From Eq. (21), we see that $f(E, E_0, t)$ can be written in the form

$$f(E, E_0, t) = (1 - e^{-cU(t)}) U(t)^{-1} p(E) C_6 (t(\Delta E^2 + 0.1^2)^{-1}), \tag{28}$$

with $p(E)$ given by Eq. (26) and $C_6$ by Eq. (24). In Fig. 1, we plot $C_6(x)$ vs $x$. It is seen that $C_6(x)$ is a linear function of $x$ for $0 \leqslant x \lesssim 0.2$. Beyond 0.2 there is a crossover to the asymptotic form given by Eq. (25), $C_6(x) = \frac{4}{3}\pi^{3/2} x^{1/2}$.

In Figs. 2–4 we plot the product $p(E)C_6(t(\Delta E^2 + 0.1^2)^{-1})$ vs $E$ at different values of the time for $E_0 = 0$, 1, and 2, respectively. The values of $t$ and the corresponding values of $U(t)$, Eq. (18), are given in the captions. We emphasize that these curves characterize the initial development of the fluorescence and are appropriate only when $cU(t) \lesssim 3$. Moreover the values of $U(t)$ are sensitive to the value of $\gamma$ in Eq. (27). In the case of Fig. 2 ($E_0 = 0$) the spectrum is dominated by transfer to ions with energies near the center of the line. The corresponding profile is more sharply peaked than $p(E)$. When $E_0 = 1$ (Fig. 3) the background comes up more slowly. There is also a pronounced asymmetry in the profile reflecting the competition between the rapid transfer associated with small



FIG. 2. $p(E)C_6(t[(E - E_0)^2 + 0.1^2]^{-1})$ vs $E$ for $E_0 = 0$. (a) $t = 1$, $U(t) = 22$; (b) $t = 10$, $U(t) = 70$; (c) $t = 100$, $U(t) = 216$.



FIG. 1. $C_6(x)$ vs $x$ for a fcc lattice. The straight line indicates the linear behavior at small $x$. The broken curve is Eq. (25).
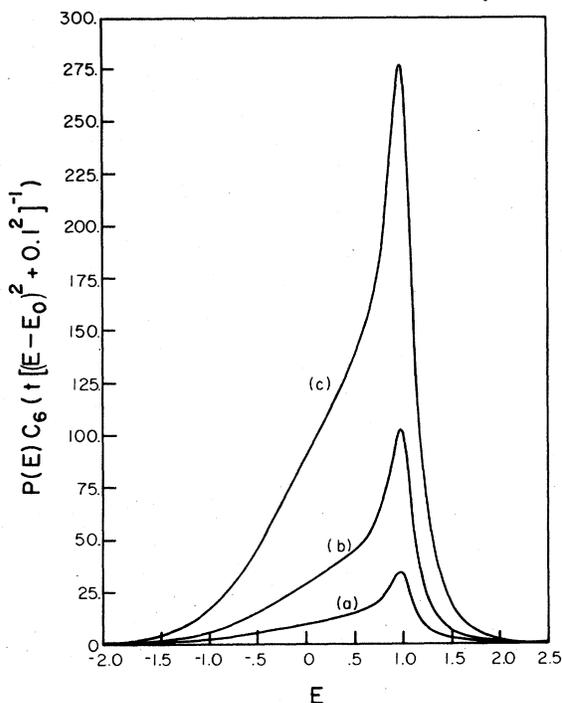


FIG. 3. $p(E)C_6(t[(E - E_0)^2 + 0.1^2]^{-1})$ vs $E$ for $E_0 = 1$. (a) $t = 5$, $U(t) = 28$; (b) $t = 50$, $U(t) = 87$; (c) $t = 500$, $U(t) = 261$.
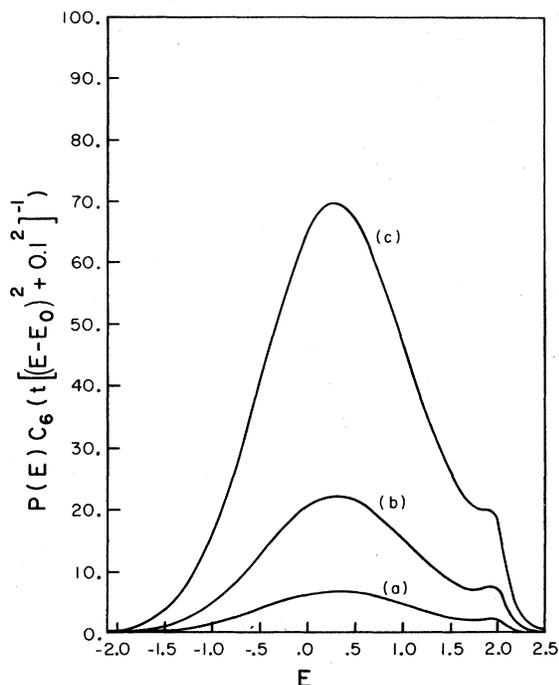
FIG. 4. $p(E)C_6(t[(E-E_0)^2+0.1^2]^{-1})$ vs $E$ for $E_0=2$. (a) $t=10$, $U(t)=14$; (b) $t=100$, $U(t)=45$; (c) $t=1000$, $U(t)=140$.

values of $(\Delta E)^2$ and the peaking of $p(E)$ at $E=0$. In the case where $E_0=2$ (Fig. 4) the line-shape factor dominates so that the profile approximates $p(E)$. However there is still some structure near $E=2$ arising from transfers between quasidegenerate ions. Although not obvious from the figure the peak in the curve shifts slightly toward the origin with increasing values of the time.

The results displayed in Figs. 2–4 are qualitatively similar to the intensity profiles characterizing the initial development of the fluorescence that were given in Ref. 7. As noted in the Introduction the calculations outlined in Ref. 7 were based on the integral equation of Montegi and Shionoya.[8] However as emphasized in Ref. 5 in the derivation of the Motegi-Shionoya equation the various microscopic transfer rates are replaced by an average transfer rate, $\overline{W}(E-E')$, which depends on the concentration and the energy mismatch. From Eq. (22) it is evident that the microscopic transfer rates are functions of the relative separation between the ions. The dependence on separation leads to a distribution in transfer rates. By using an average transfer rate, one is neglecting significant fluctuation effects. The importance of fluctuations can be seen in the time development of $\langle P_0(t)\rangle_c$ in the case where there is no backtransfer. Provided Eq. (7) is applicable Eq. (14) gives the exact

result when $W_{l0}=0$. When the approximation of an average transfer rate is made the corresponding expression for $\langle P_0(t)\rangle_c$ takes the form where

$$\langle P_0(t)\rangle_c=e^{-\overline{W}t}, \tag{29}$$

$$\overline{W}= \int dE' \; p(E')\overline{W}(E_0-E'),$$

$$=c\sum_l \int dE_l \; p(E_l)W_{0l}(\Delta E_{0l}). \tag{30}$$

The approximate expression has the same initial slope as the exact expression but differs significantly at finite times. This is evident in the case where $W_{0l}$ is independent of $\Delta E_{0l}$. In this limit, we have the exact result

$$\langle P_0(t)\rangle_c=\prod_l \left[1+c(e^{-W_{0l}t}-1)\right], \tag{31}$$

whereas (29) becomes

$$\langle P_0(t)\rangle_c=\exp\left(-c\sum_l W_{0l}t\right), \tag{32}$$

which agrees with (31) only when $c=1$. On the basis of this analysis, we conclude that since it neglects fluctuations in the transfer rates the Montegi-Shionoya approach is incapable of providing a quantitative characterization of the early-time development of the fluorescence. In contrast, the theory outlined in this paper does take into account those fluctuations which are most important at early times. Examination of the relevant equations, (13) and (19), shows that the use of an average transfer rate is appropriate only at very short times (i.e., on the order of the reciprocal of the nearest-neighbor transfer rate) where $\langle P_0(t)\rangle_c$ and $f(E,E_0,t)$ are linear functions of $t$.

## V. SUMMARY

In this paper, we have extended the analysis of spectral transfer that was begun in Ref. 2 to the general case of energy-dependent, asymmetric transfer rates. Approximate theories are presented for the early-time development of the narrow-band and background fluorescence which are applicable as long as the energy levels of the various ions are uncorrelated in the sense of Eq. (7).

## ACKNOWLEDGMENT

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