Momentum-space theory of exciton transport. II. Sensitized luminescence calculations for specific trapping models

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On the basis of a recently developed formalism utilizing exciton transport equations in momentum space, experimentally relevant sensitized luminescence quantities are calculated for specific models of exciton capture by traps in molecular crystals. The quantities studied are host and trap luminescence (fluorescence or phosphorescence), quantum yield, and energy-transfer rate. Exact expressions are obtained and the behavior valid for long times is examined. The effect of variation in the initial condition involved in photon absorption is studied. While most of the calculations are based on the assumption that the temperatures are low enough to allow the neglect of detrapping, a brief description of detrapping effects is also given. The analysis is also applicable to situations other than those involving excitons or luminescence and generally describes the kinetics of a capture process occurring simultaneously with scattering in a band characteristic of motion in a crystal, without reference to the detailed nature of the moving quasiparticles.

I. INTRODUCTION

Electronic excitations, produced in the molecules of a molecular crystal as a result of light absorption, generally travel within the crystal on account of dipole-dipole or other intermolecular interactions. The dynamics of such exciton transport may be studied experimentally by the methods of sensitized luminescence, which consist of monitoring the light emission from guest molecules introduced into the crystal. If light absorption by guest molecules is prevented by the choice of a suitable frequency range, the guest luminescence will directly reflect the transport characteristics of the exciton as it moves from the various host sites to the traps (i.e., the guest sites). Both sensitized fluorescence[1,2] and sensitized phosphorescence[3] have thus been studied experimentally for many years. The problem presented to the theorist is of intrinsic interest as it consists of transport on a defective lattice. The trapping molecules constitute the defects in an otherwise translationally periodic structure provided by the host crystal.

Most theoretical analyses of this and related situations have used transport equations in real space. Various random walk techniques,[4–5] master equation methods,[6–10] memory-function approaches,[10,11] and other ways of attack,[12–15] have been used. On the other hand, wishing to exploit the translational periodicity of the host crystal from the very beginning, and in the light of the current feeling[3,16] that exciton motion is coherent in at least some of the experimentally studied systems, one of us recently developed[17] a theoretical formalism for exciton transport based on a Boltzmann-like equation in momentum space. We shall refer to that paper as I. In this paper we shall use that formalism for analyzing specific models for trapping. It has been stressed by earlier authors[2] that the mechanism of trapping has received less attention from theorists than it deserves and that the idea of exciton capture on the first visit to the trap can be quite unrealistic. While the situation we consider in this paper is no doubt also highly idealized, we shall specifically focus on the trapping interaction, exploit explicitly the crystal periodicity by using k-space equations, and obtain exact expressions for the relevant observables. These are: host and trap luminescence, energy transfer rate, and the quantum yield.

The paper is set out as follows: A very brief description of the basic formalism constructed in I is given in Sec. II along with a general exact expression for the host luminescence (fluorescence or phosphorescence). Explicit calculations are carried out in Sec. III for short-range trapping models. The Laplace transform of the host luminescence is obtained exactly, thus reducing the problem to quadratures and making possible an exact calculation of the quantum yield. For two specific models, luminescence expressions in the time domain are given. Section IV constitutes the asymptotic analysis (valid for long times) of the luminescence expressions and of the energy transfer rate. The effect of variation in the initial condition involved in exciton creation is briefly studied in Sec. V, the consequences of not neglecting detrapping rates are explored in Sec. VI, and conclusions form the content of Sec. VII.

II. GENERAL EXPRESSIONS FOR HOST LUMINESCENCE AND RELATED QUANTITIES

The basic transport equation[17] of our analysis in this paper,

$$\frac{df_k}{dt}+\frac{1}{\tau}f_k+\alpha_k f_k=\sum_{k'}[Q_{kk'}f_{k'}(t)-Q_{k'k}f_k(t)]\ , \quad (2.1)$$

describes the probability $f_k(t)$ that the kth state in the band of the host crystal is excited at a time t, the quantities α_k and $Q_{kk'}$ being, respectively, the trapping rate from the kth state of the host to the trap, and the scattering rate from the k' to the k state in the host band, which arises from exciton-phonon or exciton-impurity interactions. The radiative lifetime is denoted by τ and we have suppressed its k dependence for simplicity.

Equation (2.1) would be identical to the usual linearized Boltzmann equation used routinely for electron transport in metals and semiconductors if one were to put $\alpha_k+1/\tau=0$. Note also that a large part (if not all) of the subsequent analysis is applicable for the transport of other quasiparticles moving and being scattered within a band and being simultaneously captured by traps.

Equation (2.1) results from a consideration of the phase space of the system depicted in Fig. 1. Two coupled equations[17] describing the evolution of $f_k(t)$ and $f_\theta(t)$, where the latter denotes the probability that the exciton is captured by the trap, reduce to Eq. (2.1) above and a separate equation for $f_\theta(t)$, under the assumption of temperatures low enough to justify the neglect of detrapping rates. The general program consists then of solving Eq. (2.1) and calculating from $f_k(t)$ relevant quantities such as the host or trap luminescence, the quantum yield, and the energy-transfer rate. As in all realistic transport problems, exact solution of Eq. (2.1) with nontrivial $Q_{kk'}$ is almost always out of the question. One therefore uses the standard relaxation-time assumption, albeit in a generalized form.[17] It has the form

$$\sum_{k'}Q_{kk'}f_{k'}(t)\simeq\left(\sum_{k'}Q_{k'k}\right)f_k^{\rm th}\sum_{k'}f_{k'}(t)$$

$$\equiv\Gamma_k f_k^{\rm th}F(t)\ . \quad (2.2)$$

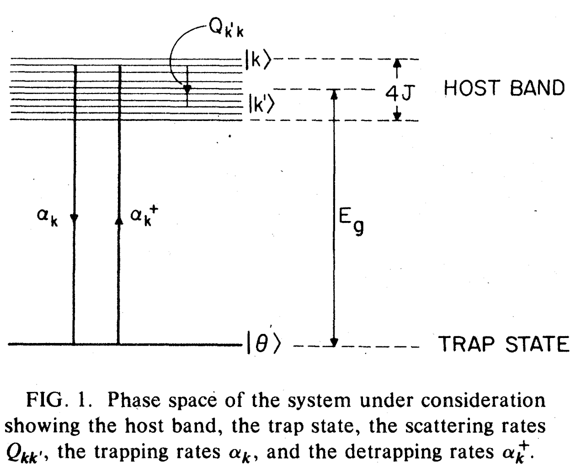

FIG. 1. Phase space of the system under consideration showing the host band, the trap state, the scattering rates $Q_{kk'}$, the trapping rates α_k, and the detrapping rates α_k^+.

Here $1/\Gamma_k$ is the usual relaxation time obtained from $Q_{kk'}$ through standard prescriptions,[18] $f_k^{\rm th}$ is the thermal distribution that $f_k(t)$ would attain from Eq. (2.1) at long times if there were no traps, and $F(t)\equiv\sum_k f_k(t)$ is the host excitation probability or the host luminescence that we seek. The extended[17] relaxation-time assumption (2.2) when used in Eq. (2.1) gives for the Laplace transform of $F(t)$,

$$\tilde F(\epsilon)=\left[1-\sum_k\left(\epsilon+\frac{1}{\tau}+\alpha_k+\Gamma_k\right)^{-1}\Gamma_k f_k^{\rm th}\right]^{-1}$$

$$\times\left[\sum_k\left(\epsilon+\frac{1}{\tau}+\alpha_k+\Gamma_k\right)^{-1}f_k(0)\right]\ , \quad (2.3)$$

or, more simply,

$$\tilde F(\epsilon)=\left[1-(\Gamma/N)\sum_k\left(\epsilon+\frac{1}{\tau}+\Gamma+\alpha_k\right)^{-1}\right]^{-1}$$

$$\times\left[\sum_k\left(\epsilon+\frac{1}{\tau}+\Gamma+\alpha_k\right)^{-1}f_k(0)\right] \quad (2.4)$$

wherein the k dependence of Γ_k has been dropped and the thermal distribution $f_k^{\rm th}$ has been written as $(1/N)$, where N is the number of k states in the band. This reduction from Eq. (2.3) to Eq. (2.4) is exact under the constant scattering rate condition (i.e., if $Q_{kk'}$ are independent of k and k') and corresponds to high temperatures with respect to the ratio of the bandwidth and the Boltzmann constant. More generally Γ may be interpreted as an average relaxation time.

Equation (2.4) has been obtained in I, where details and a discussion of the validity of Eq. (2.1) and of the approximations used may be found. It, or its more general form (2.3), will constitute the basis of the analysis in this paper. Several model expressions for α_k will be written down in Secs. III–VI and $\tilde F(\epsilon)$ calculated from them. The four experimentally relevant quantities of interest in this paper, viz., the host luminescence $F(t)$, the quantum yield ϕ, the trap luminescence $f_\theta(t)$ and the energy transfer rate $k(t)$ will then be obtained, respectively, by Laplace-inverting Eq. (2.4) and through

$$\phi=(1/\tau)\int_0^\infty dt\,F(t)\ , \quad (2.5)$$

$$k(t)=-\frac{1}{F(t)}\frac{dF(t)}{dt}-\frac{1}{\tau}\ , \quad (2.6)$$

$$\frac{df_\theta(t)}{dt}+\frac{f_\theta(t)}{\tau_\theta}=-\left(\frac{dF(t)}{dt}+\frac{F(t)}{\tau}\right)\ . \quad (2.7)$$

III. MODEL CALCULATIONS FOR SHORT-RANGE TRAPPING

A. Model and general results

For a linear chain of host molecules with a single trap introduced interstitially or substitutionally, straightforward considerations[19] of the golden rule allow one to calculate the trapping rate as

$$\alpha_k = \text{const} \times |\langle k|V|\theta\rangle|^2 = \text{const}\left(\sum_{m,n} V_m V_n^* e^{ik(m-n)}\right)^2 . \qquad (3.1)$$

The constant in Eq. (3.1) contains all temperature dependences and density-of-states factors but the entire k dependence, which is of primary concern in the present paper, is displayed explicitly in Eq. (3.1). The host-trap interaction V has matrix element V_m between the localized host state $|m\rangle$ (Wannier state) and the trap state $|\theta\rangle$, and the factors e^{ikm} arise from the expansion of Wannier states in terms of Bloch states in the crystal.

If the trap state interacts with a single localized host state, i.e., if trapping occurs from a single site, V_m is nonzero for only a single value of m, and Eq. (3.1) gives a constant trapping rate over the band. If, however, the host-trap interaction is of very short range but of nearest-neighbor character, Eq. (3.1) leads to

$$\alpha_k = (V_0 + 2V_1 \cos k)^2/\gamma , \qquad (3.2)$$

where γ is the constant factor which will generally depend on the temperature and on exciton-bath interaction parameters. Expression (3.2) for the trapping rate, which will be used in this section and Sec. III B, is of direct physical interest and it has been derived and discussed earlier.[19] It is to be substituted in Eq. (2.4). A procedure for calculating the host and guest luminescence and the energy transfer from arbitrary α_k's has been given in I. It uses a certain averaging approximation which replaces the summation over k's by a term containing a single average α. In this paper, however, Eq. (2.4) will be evaluated *exactly* in the limit of a large crystal. The k summation is thus converted into an integral

$$\lim_{N\to\infty} \frac{1}{N} \sum_k \frac{1}{\epsilon + 1/\tau + \Gamma + (V_0 + 2V_1\cos k)^2/\gamma} = \frac{1}{2\pi} \int dk \frac{1}{\epsilon + 1/\tau + \Gamma + (V_0+2V_1\cos k)^2/\gamma} \equiv \tilde{S}(\epsilon) . \qquad (3.3)$$

Examination of Eq. (2.4) shows that another quantity of importance for finite as well as infinite crystals is

$$\tilde{I}(\epsilon) = \sum_k \frac{f_k(0)}{\epsilon + 1/\tau + \Gamma + \alpha_k} . \qquad (3.4)$$

Its effects for various initial conditions $f_k(0)$ will be studied in Sec. V. In terms of $\tilde{I}(\epsilon)$ and of $\tilde{S}(\epsilon)$ the general expression for $\tilde{F}(\epsilon)$ is

$$\tilde{F}(\epsilon) = \tilde{I}(\epsilon) \frac{1}{1 - \Gamma \tilde{S}(\epsilon)} . \qquad (3.5)$$

In this section we shall use $\tilde{I}(\epsilon) = (\epsilon + 1/\tau + \Gamma + \alpha_0)^{-1}$, which arises from $f_k(0) = \delta_{k,0}$. This result is relevant to optical absorption, and corresponds to many experimental situations. We evaluate $\tilde{S}(\epsilon)$ explicitly from Eq. (3.3) by splitting the integrand through partial fractions and integrating over the unit circle. The result, when substituted in Eq. (3.4) gives

$$\tilde{F}(\epsilon) = \frac{1}{\epsilon + 1/\tau + \Gamma + \alpha_0} \left\{ 1 \pm \frac{\Gamma/2}{\epsilon + 1/\tau + \Gamma} \left[\left(1 - \frac{V_0^2 - 4V_1^2}{(\epsilon + 1/\tau + \Gamma)\gamma} + \frac{2iV_0}{[(\epsilon + 1/\tau + \Gamma)\gamma]^{1/2}} \right)^{-1/2} + \left(1 - \frac{V_0^2 - 4V_1^2}{(\epsilon + 1/\tau + \Gamma)\gamma} - \frac{2iV_0}{[(\epsilon + 1/\tau + \Gamma)\gamma]^{1/2}} \right)^{-1/2} \right] \right\}^{-1} , \qquad (3.6)$$

where the (+) or (−) sign is to be chosen depending on whether the magnitude of the quantity x given by

$$x = \frac{1}{2V_1} \left[-V_0 + i \left[\left(\epsilon + \frac{1}{\tau} + \Gamma \right) \gamma \right]^{1/2} + \left(\left\{ -V_0 + i \left[\left(\epsilon + \frac{1}{\tau} + \Gamma \right) \gamma \right]^{1/2} \right\}^2 - 4V_1^2 \right)^{1/2} \right]$$

is larger or smaller than 1, respectively.

Equation (3.6) constitutes the exact expression for the host excitation probability brought to quadratures. The evaluation of the Bromwich integral is, however, nontrivial and exact expressions in the time domain will therefore be obtained below only for the limits $V_0 >> V_1$ and $V_0=0$. It is possible however to deduce from Eq. (3.6) certain general results which hold for arbitrary values of V_0 and V_1:

(i) Since the quantum yield ϕ given by Eq. (2.5) may be rewritten

$$\phi=\frac{1}{\tau}\left[\lim_{\epsilon\to 0}\tilde{F}(\epsilon)\right] , \quad (3.7)$$

the exact expression for ϕ is obtained directly from Eq. (3.6) without inverting the transform. The condition on the magnitude of the quantity x given above then becomes a simple relation among the magnitudes of V_0, V_1, Γ, and τ.

(ii) If we note from Eq. (3.2) that the trapping rate α_k at $k=0$ equals $(V_0+2V_1)^2/\gamma$ we find by letting $\Gamma\to 0$ in Eq. (3.6) that, for this situation signifying little scattering or very coherent exciton transport,

$$F(t)=e^{-t/\tau}e^{-t(V_0+2V_1)^2/\gamma}=e^{-t(1/\tau+\alpha_0)} . \quad (3.8)$$

Equation (3.8) shows that, as expected, the capture of the excitation by the trap occurs essentially from the initially occupied state.

(iii) For the opposite case $\Gamma\to\infty$ representing strong scattering one can show from Eq. (3.6) that

$$F(t)=e^{-t/\tau}e^{-t(V_0^2+2V_1^2)/\gamma}=e^{-t(1/\tau+\alpha)} . \quad (3.9)$$

The significance of Eq. (3.9) and of the quantity α becomes clear when one observes that the latter is the average of α_k [see Eq. (3.2)] over the band. Note that the band averages of $\cos^2 k$ and $\cos k$ are, respectively, $\frac{1}{2}$ and 0. The result (3.9) is indeed expected on physical grounds. Strong scattering mixes the excitation over the band quickly and the capture process then occurs with an average rate.

(iv) Finally, the limit $V_1\to 0$ of Eq. (3.6) gives

$$F(t)=e^{-t/\tau}e^{-tV_0^2/\gamma} . \quad (3.10)$$

For $V_1=0$ the trapping rate is k independent, the energy-transfer rate $k(t)$ is therefore time independent, and $F(t)$ is exponential. There is no dependence on the scattering strength as is expected from the fact that α_k does not vary over the band.

B. Exact results for $F(t)$

We have mentioned above that an exact inversion of the Laplace transform in Eq. (3.6) can be performed only in limiting cases. The case $V_0 >> V_1$ is of obvious physical interest. The trapping range of the model we are considering is small by assumption. Furthermore, we may assume it to be so small that $V_0 >> V_1$ applies. Here V_0 would represent the interaction of the trap state with the host Wannier state localized on the site nearest to the trap site. We then neglect quantities such as $(V_1/V_0)^2$ and approximate α_k in Eq. (3.2) by $(V_0^2+4V_0V_1\cos k)/\gamma$. This reduces Eq. (3.6) to

$$\tilde{F}(\epsilon)=\frac{1}{\epsilon+1/\tau+\Gamma+(V_0^2+4V_0V_1)/\gamma}\left(1+\frac{\Gamma}{[(\epsilon+1/\tau+\Gamma+V_0^2/\gamma)^2-(4V_0V_1/\gamma)^2]^{1/2}-\Gamma}\right) . \quad (3.11)$$

To invert Eq. (3.11) we utilize the relation[20]

$$g(t)=f(t)+a\int_0^t ds\frac{s}{(t^2-s^2)^{1/2}}f(s)I_1[(t^2-s^2)^{1/2}] , \quad (3.12)$$

where $g(t)$ is the Laplace inverse transform of $\tilde{f}[(\epsilon^2-a^2)^{1/2}]$ and $I_1(s)$ is the modified Bessel function. Along with the use of standard shift and scale theorems of Laplace-transform theory, Eqs. (3.12) and (3.11) result in

$$F(t)=e^{-t/\tau}\left(\frac{\Gamma e^{-\alpha t}+\Delta e^{-(\Gamma+\alpha_0)t}}{\Gamma+\Delta}+\int_0^t ds\int_0^s du\, e^{-(\Gamma+\alpha_0)(t-s)-(\Gamma+\alpha)(s-u)}h(s,u)\right) . \quad (3.13)$$

Here

$$h(s,u)=\Gamma\Delta e^{-\alpha u}u(s^2-u^2)^{-1/2}I_1[\Delta(s^2-u^2)^{1/2}]$$

and $\Delta=\alpha_0-\alpha$. The quantities α_0 and α are the $k=0$ value of the trapping rate α_k and the band average value of α_k, respectively. Thus the respective values are $(V_0^2+4V_0V_1)/\gamma$ and V_0^2/γ.

Equation (3.13) for the probability of host excitation embodies a striking result. The first term on its right-hand side exactly equals the $F(t)$ calculated in I through an averaging approximation. The host luminescence and the energy-transfer rate corresponding to this term have been plotted in I. Thus the exact analysis in this paper merely adds the term containing $h(s,u)$ to the result of I. However, as we shall see in Sec. III C, the new term results in a power-law dependence of the energy-transfer rate at long times which is very different from the result in I. The correction term is seen to be proportional to $\Gamma\Delta$. The averaging approximation introduced in I is thus particularly applicable for $\Gamma\to 0$ which represents coherent exciton motion and for $\Delta\to 0$ which represents weak variation of the trapping rate α_k over the band. It is straightforward to take Γ within the integral and show that in the incoherent limit too $(\Gamma\to\infty)$, the correction terms vanishes. Another interesting result that the model calculation in the present paper yields is that the band average of α_k to be used in the computation of the average α in the expressions of I [or of Eq. (3.13)] is an *arithmetic* rather than a *harmonic* average. This question has been discussed in I.

The averaging approximation introduced in I uses the replacement $\sum_k e^{-\alpha_k t}=e^{-\alpha t}$ and thus leads to an $F(t)$ that is the sum of two exponentials. Highly nonexponential luminescence decay curves have been reported[2,21] in some experiments. Generally the correction term in Eq. (3.13) is indeed able to give rise to such departure from exponential behavior.

In addition to the case $V_0 >> V_1$ discussed above, $V_0=0$ is also of interest. This situation may be applicable when the trap is introduced substitutionally and there is no single neighboring host site which can feed the trap more efficiently than others. We then have $\alpha_k=(4V_1^2\cos^2 k)/\gamma$. With only slight differences the calculation proceeds as above and yields

$$F(t)=e^{-t/\tau}\left[\frac{\Gamma e^{-\alpha t}+\alpha_0 e^{-(\Gamma+\alpha_0)t}}{\Gamma+\alpha_0}+\int_0^t ds\int_0^s du\, e^{-(\Gamma+\alpha_0)(t-s)-(\Gamma+\alpha)(s-u)}h'(s,u)\right], \tag{3.14}$$

where

$$h'(s,u)=\Gamma\alpha e^{-\alpha u}u(s^2-u^2)^{-1/2}I_1[\alpha(s^2-u^2)^{1/2}] . \tag{3.15}$$

Note that except for the factor $e^{-\alpha u}$, the replacement $\Delta\to\alpha$ in $h(s,u)$ gives $h'(s,u)$. Once again the first term on the right-hand side is seen to reproduce the average result of Ref. 17, while the second constitutes the correction.

C. Exact expression for the quantum yield

The quantum yield ϕ, defined as the ratio of the number of photons emitted by the host to that introduced into it through absorption, is given by Eq. (2.5). Since simple expressions for $\tilde{F}(\epsilon)$ are always obtainable from our analysis, we can directly compute the quantum yield even when simple time-domain expressions for $F(t)$ cannot be found. This is a consequence of Eq. (2.5) and is given in Eq. (3.7).

When Eq. (3.7) is substituted in Eq. (3.11), one obtains

$$\phi=\left[\frac{\Gamma+(V_0/\gamma)(V_0-4V_1)}{\Gamma+(V_0/\gamma)(V_0+4V_1)}\right]^{1/2}\times\left[\left\{\left[1+\left[\Gamma+\frac{V_0^2}{\gamma}\right]\tau\right]^2-\left[\frac{4V_0V_1\tau}{\gamma}\right]^2\right\}^{1/2}-\Gamma\tau\right]^{-1} \tag{3.16}$$

which applies to the case $V_0 >> V_1$. Similarly Eq. (3.14) gives along with Eq. (3.7)

$$\phi=\left[\frac{1+\Gamma\tau}{1+\Gamma\tau+4V_1^2\tau/\gamma}\right]^{1/2}\times(\{(1+\Gamma\tau)(1+\Gamma\tau+4V_1^2\tau/\gamma)\}^{1/2}-\Gamma\tau)^{-1} \tag{3.17}$$

for the case $V_0=0$. One may easily obtain the coherent and incoherent limits of Eq. (3.16) or Eq. (3.17)

$$\lim_{\Gamma\to 0}\phi=\frac{1}{1+\alpha_0\tau}, \tag{3.18}$$

$$\lim_{\Gamma\to\infty}\phi=\frac{1}{1+\alpha\tau} . \tag{3.19}$$

These correspond to Eqs. (3.8) and (3.9), respectively. As expected, the quantum yield decreases from 1 to 0 with an increase in the trapping rate, and changes from the value in Eq. (3.18) to that in Eq. (3.19) with an increase in the scattering strength. To exhibit this behavior the expression in Eq. (3.16) is plotted versus $\alpha_0\tau$ and $\Gamma\tau$, respectively, in Figs. 2(a) and 2(b). For the sake of comparison with Eqs. (3.16) and (3.17) we display here the quantum yield approximation given by the averaging approximation in I or equivalently from the first term in Eq. (3.13) or Eq. (3.14)

$$\phi=\frac{1}{1+\alpha_0\tau}\left[\frac{1+\dfrac{\Gamma\tau}{1+\alpha\tau}}{1+\dfrac{\Gamma\tau}{1+\alpha_0\tau}}\right]=\frac{1}{1+\alpha\tau}\left[\frac{1+\dfrac{\alpha\tau}{1+\Gamma\tau}}{1+\dfrac{\alpha_0\tau}{1+\Gamma\tau}}\right]. \tag{3.20}$$

The limits of Eq. (3.20) are obvious.

One may also recover other limiting results from Eq. (3.16) such as

$$\phi=\frac{1}{1+(V_0^2\tau/\gamma)}, \tag{3.21}$$

for the simple case $V_1=0$. The observed temperature dependence of the quantum yield may be interpreted in terms of the above results after microscopic expressions for γ and Γ explicitly involving their temperature dependence are available. It is expected that in view of the narrowness of exciton bands the temperature dependence of γ and Γ will be more readily reflected in the observations than the temperature variation that would be introduced by using for our analysis the specific f_k^{th} instead of its simplified form $1/N$.

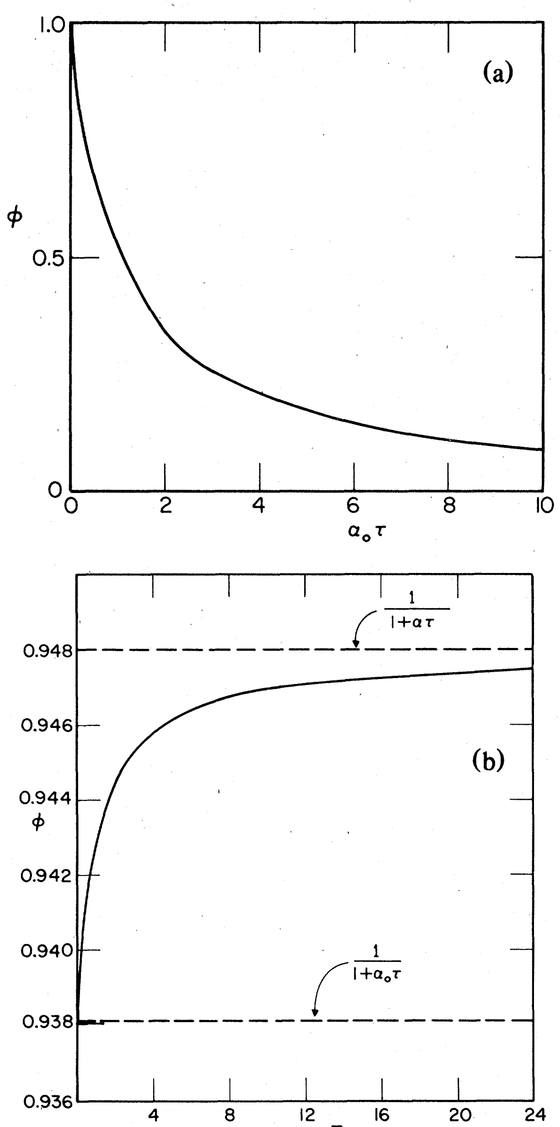

FIG. 2. (a) Dependence of the quantum yield ϕ on the strength of the trapping interaction in the short-range trapping case as given in Eq. (3.16). The abscissa is $\alpha_0\tau=(V_0^2+4V_0V_1)\tau/\gamma$ and arbitrary parameters $V_0/V_1=20$, $\Gamma\tau=1$ have been used. (b) Dependence of the quantum yield ϕ on the strength of the scattering for the short-range trapping model as given in Eq. (3.16). The abscissa is $\Gamma\tau$ and arbitrary parameters $V_0/V_1=20$, $V_0^2\tau/\gamma=0.055$ have been used. Note the limits $\phi=1/(1+\alpha_0\tau)$ and $\phi=1/(1+\alpha\tau)$ for very small and very large scattering strengths, respectively.

IV. LONG-TIME ANALYSIS: $F(t)$ AND THE ENERGY-TRANSFER RATE $k(t)$

The time-domain expressions (3.13) and (3.14) given in Sec. III are exact but involve convolutions. Thus, although numerical computation from them may be easily performed, their qualitative behavior is not transparent. We shall therefore explore their asymptotic behavior at long times. We examine the case $V_0 >> V_1$ in detail.

The definition

$$s=\frac{\gamma(\epsilon+1/\tau+\Gamma)+V_0^2}{4V_0V_1}\ , \tag{4.1}$$

transforms Eq. (3.11) into

$$\tilde{F}(s)=\frac{\gamma}{4V_0V_1}\frac{1}{s+1}\left[\frac{1}{1-(\Gamma\gamma/4V_0V_1)(s^2-1)^{-1/2}}\right]\ , \tag{4.2}$$

which shows a pole at $s=-1$, two poles at

$$s=\pm s_p\equiv\pm[1+(\gamma\Gamma/4V_0V_1)^2]^{1/2}\ ,$$

and two branch points at $s=\pm 1$. Standard asymptotic analysis[22] shows that the long-time behavior, which is dominated by the singularities lying farthest to the right on the complex s plane, is given by the inverse transform of the limits of Eq. (4.2) as s tends to s_p, i.e., of

$$\tilde{F}(s)=\frac{\gamma}{4V_0V_1s_p}\left[\frac{s_p-1}{s_p+1}\right]^{1/2}\frac{1}{s-s_p}-\frac{1}{\sqrt{2}\Gamma}(s-1)^{1/2}\ . \tag{4.3}$$

In Eq. (4.3) we have considered contributions from $s=1$ as well as $s=s_p$. Standard procedures of Laplace inversion then lead to the long-time expression

$$F(t)=\left[\frac{A}{t^{3/2}}e^{-Bt}+Ce^{-Dt}\right]e^{-t/\tau}\ , \tag{4.4}$$

where

$$A=\frac{1}{2\sqrt{2}\Gamma}\frac{1}{\sqrt{\pi}}\frac{1}{(4V_0V_1/\gamma)^{1/2}}\ , \tag{4.5a}$$

$$B=\Gamma+(V_0^2+4V_0V_1)/\gamma\ , \tag{4.5b}$$

$$C=\left[1+\left(\frac{\Gamma\gamma}{4V_0V_1}\right)^2\right]^{-1/2}\left\{\frac{\left[1+\left(\frac{\Gamma\gamma}{4V_0V_1}\right)^2\right]^{1/2}-1}{\left[1+\left(\frac{\Gamma\gamma}{4V_0V_1}\right)^2\right]^{1/2}+1}\right\}^{1/2}\ , \tag{4.5c}$$

$$D=\Gamma+\frac{V_0^2}{\gamma}-\left[\left(\frac{4V_0V_1}{\gamma}\right)^2+\Gamma\right]^{1/2} . \tag{4.5d}$$

Equation (4.4) makes clear the nonexponential nature of the host excitation probability. The $t^{-3/2}$ factor however makes negligible contribution at extremely large times because C is larger than D. At such times exponential behavior sets in.

The well-known energy-transfer rate $k(t)$ (Ref. 23) defined through Eq. (2.6) may be computed for our model from the asymptotic expression (4.4)

$$k(t)=\frac{(3/2t+B)At^{-3/2}e^{-Bt}+DCe^{-Dt}}{At^{-3/2}e^{-Bt}+Ce^{-Dt}} . \tag{4.6}$$

The above long-time expression for the energy-transfer rate contains a power-law dependence on time. This dependence is, however, very different from the usual[2] $t^{-1/2}$ result. Although the $t^{-1/2}$ behavior has been often discussed in the literature and used in fitting observations, doubts have been continually raised concerning its applicability. For instance Refs. 2 and 21 support the $t^{-1/2}$ behavior whereas it is strongly argued against in Refs. 24–26.

V. EFFECT OF INITIAL CONDITIONS INVOLVED IN PHOTON ABSORPTION

The above calculations have been performed from the general expression in Eq. (3.5) under the assumption that $f_k(0)=\delta_{k0}$. Although optical absorption is expected to result in this initial condition as a consequence of selection rules, experiments with higher-frequency photons have also been carried out.[2] We therefore study the effect of a more general form for $f_k(0)$, viz., a Gaussian of arbitrary width $\pi\sqrt{2}/b$

$$f_k(0)=\frac{b}{(\pi)^{3/2}\,\mathrm{erf}(b)}e^{-b^2(k/\pi)^2} . \tag{5.1}$$

The error function in Eq. (5.1) ensures the normalization $\int_{-\pi}^{\pi}dk\, f_k(0)=1$ and Eq. (5.1) reduces to the completely localized limit $f_k(0)=\delta_{k0}$ for $b\to\infty$ and to the completely delocalized limit $f_k(0)=\frac{1}{2}\pi$ for $b\to 0$.[27]

We shall now substitue Eq. (5.1) in Eq. (3.4) and evaluate Eq. (3.5) for the two cases $V_0 >> V_1$ and $V_0=0$. In the former case the observables depend only weakly on b, the width of the initial excitation. This is expected since the trapping rate varies only slightly over the band in this case. The situation $V_0=0$ is more interesting and is analyzed below. We Fourier decompose $f_k(0)$ as

$$f_k(0)=\sum_{-\infty}^{\infty}a_n(0)e^{ikn} , \tag{5.2}$$

which yields from Eq. (5.1)

$$a_n(0)=\frac{1}{\pi}e^{-n^2\pi^2/b^2}\frac{\mathrm{Re\,erf}[b/2+i(n\pi/b)]}{\mathrm{erf}(b)} , \tag{5.3}$$

where Re denotes the real part of the function.

Substitution of Eq. (5.3) in Eq. (3.4) gives

$$\tilde I(\epsilon)=\frac{\gamma}{2V_1^2}\sum_{-\infty}^{\infty}(-1)^n e^{-n^2\pi^2/b^2}\frac{\mathrm{Re\,erf}\left(\frac{1}{2}b+in\pi/b\right)}{\mathrm{erf}(b)}\int_0^{\infty}dt\exp\left[-\left(\frac{\epsilon+1/\tau+\Gamma+2V_1^2/\gamma}{2V_1^2/\gamma}\right)t\right]I_n(t) , \tag{5.4}$$

where I_n is the modified Bessel function of order n. It is worth observing that the inverse transform of Eq. (5.4) equals the host excitation probability for the purely coherent case $\Gamma=0$. Expressions for finite Γ are obtained from Eq. (3.5).

Equation (5.4) may be inverted exactly to give

$$I(t)=e^{-t/\tau}\sum_{-\infty}^{\infty}(-1)^n e^{-n^2\pi^2/b^2}\frac{\mathrm{Re\,erf}\left(\frac{1}{2}b+in\pi/b\right)}{\mathrm{erf}(b)}e^{-(\Gamma+2V_1^2/\gamma)t}I_n\left(\frac{2V_1^2}{\gamma}t\right) . \tag{5.5}$$

The exact expression for the host excitation probability is then given by

$$F(t)=\sum_{n=0}^{\infty}A_nW_n(t) , \tag{5.6a}$$

$$A_n=e^{-n^2\pi^2/b^2}\frac{\mathrm{Re\,erf}\left(\frac{1}{2}b+in\pi/b\right)}{\mathrm{erf}(b)} , \tag{5.6b}$$

$$W_0(t)=e^{-t/\tau}\left[e^{-(2V_1^2/\gamma)t}+e^{-(\Gamma+2(V_1^2/\gamma))t}\int_0^{2(V_1^2/\gamma)t}du\, I_1(u)e^{(\Gamma^2t^2-u^2)^{1/2}}\right] , \tag{5.6c}$$

$$W_n(t)=\frac{2n}{t}\int_0^t dt'\, e^{-[\Gamma+(2V_1^2/\gamma)]t'} I_n\left[\frac{2V_1^2}{\gamma}t'\right] W_0(t-t') \qquad (n\geq 1) \ . \tag{5.6d}$$

If the excitation is narrow in k space one need consider only the first few terms in Eq. (5.2) and therefore in Eq. (5.6a). In the extreme limit $f_k(0)=\delta_{k,0}$ only $a_0(0)$ survive with the result

$$F(t)=W_0(t)=e^{-t/\tau}\left[e^{-2(V_1^2/\gamma)t}+e^{-[\Gamma+2(V_1^2/\gamma)]t}\int_0^{2(V_1^2/\gamma)t} du\, I_1(u)\, e^{(\Gamma^2 t^2-u^2)^{1/2}}\right] \ . \tag{5.7}$$

The opposite limit of a completely delocalized (in k space) initial condition is represented by $f_k(0)=\frac{1}{2}\pi$ and gives

$$F(t)=\left[e^{-(2V_1^2/\gamma)t}+2\Gamma\frac{2V_1^2}{\gamma}e^{-[\Gamma+2(V_1^2/\gamma)]t}\int_0^t du\, e^{\Gamma u}\frac{u}{(t^2-u^2)^{1/2}}I_1\left[\frac{2V_1^2}{\gamma}(t^2-u^2)^{1/2}\right]\right]e^{-t/\tau} \ . \tag{5.8}$$

We have already mentioned that Eq. (5.5) equals $F(t)$ for *arbitrary* width of the excitation in the coherent case $\Gamma=0$. In the extreme incoherent limit we obtain

$$F(t)\simeq e^{-t/\tau}\left[\left[1-\frac{4V_1^2}{\gamma\Gamma}e^{-\pi^2/b}\frac{\mathrm{Re\,erf}\left[\frac{1}{2}b+i\pi/b\right]}{\mathrm{erf}(b)}\right]e^{-2(V_1^2/\gamma)t}-\frac{4V_1^2}{\gamma\Gamma}\frac{\mathrm{Re\,erf}\left[\frac{1}{2}b+i\pi/b\right]}{\mathrm{erf}(b)}e^{-\Gamma t}\right] \tag{5.9}$$

from (3.5).

The trap luminescence and the energy-transfer rate may be calculated in a straightforward way, at least in principle, from the above expressions for $F(t)$. While this is also true of the quantum yield we shall exhibit here the ratio of the value of this quantity for $b=0$ to that for $b\to\infty$:

$$\frac{\lim_{b\to 0}\phi}{\lim_{b\to\infty}\phi}=\left[1+\frac{\alpha_0}{1/\tau+\Gamma}\right]^{1/2} \ . \tag{5.10}$$

Here $\alpha_0=4V_1^2/\gamma$ as mentioned in Sec. III.

Equation (5.10) shows that there can be substantial variation in the values of observables with changes in the width of the initial excitation. We also see that this variation will be larger for more coherent transport, for larger radiative life-times and for larger trapping rates. All these consequences agree with physical expectation. For completeness we give the value of the ratio in Eq. (5.10) for the case $V_0>>V_1$

$$\frac{\lim_{b\to 0}\phi}{\lim_{b\to\infty}\phi}=\left[1+\frac{2(\alpha_0-\alpha)}{1/\tau+\Gamma+\alpha_0}\right]^{1/2} , \tag{5.11}$$

then $\alpha_0=(V_0^2+4V_0V_1)/\gamma$ and $\alpha=V_0^2/\gamma$ as stated earlier. Equation (5.11) shows that there is a much weaker dependence of ϕ on b in this case as stated at the beginning of this section.

VI. EFFECT OF DETRAPPING INTO THE HOST BAND

In Secs. I–V the temperature has been assumed to be low enough to allow detrapping to be neglected. In this section we shall relax this restriction. The point of departure now is Eqs. (1) and (2) of I

$$\frac{df_k}{dt}+\left[\frac{1}{\tau}+\alpha_k\right]f_k=\alpha_k^+ f_\theta+\sum_{k'}(Q_{kk'}f_{k'}-Q_{k'k}f_k) \ , \tag{6.1}$$

$$\frac{df_\theta}{dt}+\left[\frac{1}{\tau_\theta}+\sum_k \alpha_k^+\right]f_\theta=\sum_{k'}\alpha_{k'}f_{k'} \ . \tag{6.2}$$

Here α_k^+ are the detrapping rates related to the trapping rates α_k (termed α_k^- in I) through Boltzmann factors required by detailed balance.

Substitution of Eq. (2.7) into Eq. (6.1), the use of the relaxation-time approximation made to derive Eq. (2.3), and a summation over k give

$$\tilde F(\epsilon)=\left[\sum_k\frac{f_k(0)}{D_k}+\frac{1}{\epsilon+1/\tau_\theta}\sum_k\frac{\alpha_k^+}{D_k}\right]\left[1-\sum_k\frac{\Gamma_k f_k^{\mathrm{th}}}{D_k}+\frac{\epsilon+1/\tau}{\epsilon+1/\tau_\theta}\sum_k\frac{\alpha_k^+}{D_k}\right]^{-1} \tag{6.3}$$

where we have abbreviated $\epsilon+1/\tau+\alpha_k+\Gamma_k$ by D_k. For very low temperatures α_k^+ may be set equal to zero in Eq. (6.3) reducing the equation to the previous result (3.5). The detailed balance expression for α_k^+ to be substituted in Eq. (6.3) is obviously

$$\alpha_k^+ = \alpha_k e^{-\beta(E_g + 2J\cos k)} , \tag{6.4}$$

where $\beta = 1/k_B T$, E_g is the energy of the trap state measured below the center of the host band, and $4J$ is the host bandwidth (see Fig. 1). The main new quantity in Eq. (6.3) is $\sum_k (\alpha_k^+/D_k)$. It has been calculated in the Appendix in the limit $N \to \infty$, which has been used in the model expressions in this paper. From Eq. (A7) we see that

$$\lim_{N\to\infty} \sum_k \frac{\alpha_k^+}{D_k} = 2\pi e^{-\beta E_g} \left[I_0(2J\beta) - \frac{\gamma(\epsilon + 1/\tau + \Gamma)}{4V_0V_1} \sum_{-\infty}^{\infty} I_n(2J\beta) \int_0^\infty dt \exp\left[-t \frac{\gamma(\epsilon + 1/\tau + \Gamma) + V_0^2}{4V_0V_1} \right] I_n(t) \right] . \tag{6.5}$$

This result applies specifically to the case $V_0 >> V_1$ which is the only one we shall study in this section.

Equation (6.5), after Eq. (6.3) is substituted in it, contains all the effects of detrapping, in particular the dependence of various quantities on the temperature. Observe that the thermal distribution f_k^{th} in Eq. (6.3) equals $e^{-2J\beta\cos k}/NI_0(2J\beta)$. We shall now study the situation $2J << k_B T$ which has been assumed in reducing Eq. (2.3) to Eq. (2.4) and in the model calculations presented in Secs. I–V. We then have the simple relation

$$\alpha_k^+ = \alpha_k e^{-\beta E_g} , \tag{6.6}$$

instead of Eq. (6.4) and

$$\lim_{N\to\infty} \sum_k \frac{\alpha_k^+}{D_k} = 2\pi e^{-\beta E_g} \left[1 - \frac{\epsilon + \frac{1}{\tau} + \Gamma}{\left[\left(\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma} \right)^2 - \left(\frac{4V_0V_1}{\gamma} \right)^2 \right]^{1/2}} \right] , \tag{6.7}$$

instead of Eq. (6.5). For the initial condition $f_k(0) = \delta_{k,0}$ (e.g., optical absorption), the Laplace transform of the host fluorescence is given by

$$\tilde{F}(\epsilon) = \left[\frac{1}{\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma}} + \frac{1}{\epsilon + \frac{1}{\tau_\theta}} 2\pi e^{-\beta E_g} \left[1 - \frac{\epsilon + \frac{1}{\tau} + \Gamma}{\left[\left(\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma} \right)^2 - \left(\frac{4V_0V_1}{\gamma} \right)^2 \right]^{1/2}} \right] \right]$$

$$\times \left[1 - \frac{\Gamma}{\left[\left(\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma} \right)^2 - \left(\frac{4V_0V_1}{\gamma} \right)^2 \right]^{1/2}} + \frac{\epsilon + \frac{1}{\tau}}{\epsilon + \frac{1}{\tau_\theta}} 2\pi e^{-\beta E_g} \left[1 - \frac{\epsilon + \frac{1}{\tau} + \Gamma}{\left[\left(\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma} \right)^2 - \left(\frac{4V_0V_1}{\gamma} \right)^2 \right]^{1/2}} \right] \right]^{-1} \tag{6.8}$$

Needless to say Eq. (6.8) reduces to the previously obtained result (3.11) when the temperature is so low that $e^{-\beta E_g}$ may be replaced by zero. In the intermediate temperature range Eq. (6.8) gives correction factors:

$$\tilde{F}(\epsilon) = \frac{\left(\epsilon + \frac{1}{\tau} + \Gamma + \alpha_0 \right)^{-1}}{1 - \Gamma \left[\left(\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma} \right)^2 - \left(\frac{4V_0V_1}{\gamma} \right)^2 \right]^{-1/2}} + \frac{2\pi e^{-\beta E_g}}{\epsilon + 1/\tau_\theta} \left[1 - \frac{\epsilon + \frac{1}{\tau}}{1 - \Gamma \left[\left(\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma} \right)^2 - \left(\frac{4V_0V_1}{\gamma} \right)^2 \right]^{-1/2}} \right]$$

$$\times \left[1 - \frac{\left(\epsilon + \frac{1}{\tau} \right) \left(\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma} \right)^{-1}}{1 - \Gamma \left[\left(\epsilon + \frac{1}{\tau} + \Gamma + \frac{V_0^2}{\gamma} \right)^2 - \left(\frac{4V_0V_1}{\gamma} \right)^2 \right]^{-1/2}} \right] . \tag{6.9}$$

Note that the first term on the right-hand side of Eq. (6.9) is the right-hand side of Eq. (3.11). If we further consider in Eq. (6.9) the incoherent limit $\Gamma \to \infty$ we obtain

$$\tilde{F}(\epsilon)=\frac{1}{\epsilon+1/\tau+V_0^2/\gamma}+2\pi e^{-\beta E_g}\frac{1}{\epsilon+1/\tau_\theta}\left[\frac{V_0^2}{\gamma(\epsilon+1/\tau)+V_0^2}\right]^2 , \tag{6.10}$$

which is inverted to give

$$F(t)=e^{-t(1/\tau+V_0^2/\gamma)}+2\pi e^{-\beta E_g}\left[\frac{\dfrac{V_0^2}{\gamma}}{\dfrac{1}{\tau_\theta}-\dfrac{1}{\tau}-\dfrac{V_0^2}{\gamma}}\right]^2\left[e^{-t/\tau_\theta}+\left\{\left[\frac{1}{\tau_\theta}-\left(\frac{1}{\tau}+\frac{V_0^2}{\gamma}\right)\right]t-1\right\}e^{-t(1/\tau+V_0^2/\gamma)}\right] . \tag{6.11}$$

Consider now the limit of high temperatures. If $k_BT >> E$, the factor $e^{-\beta E_g}=1$, the detrapping rates α_k^+ equal the trapping rates α_k and Eq. (6.8) reduces to

$$\tilde{F}(\epsilon)=\left[\frac{1}{\epsilon+\dfrac{1}{\tau}+\Gamma+\dfrac{V_0^2}{\gamma}}+\frac{1}{\epsilon+\dfrac{1}{\tau_\theta}}\left(1-\frac{\epsilon+\dfrac{1}{\tau}+\Gamma}{\left[\left(\epsilon+\dfrac{1}{\tau}+\Gamma+\dfrac{V_0^2}{\gamma}\right)^2-\left(\dfrac{4V_0V_1}{\gamma}\right)^2\right]^{1/2}}\right)\right]$$

$$\times\left[1-\frac{\Gamma}{\left[\left(\epsilon+\dfrac{1}{\tau}+\Gamma+\dfrac{V_0^2}{\gamma}\right)^2-\left(\dfrac{4V_0V_1}{\gamma}\right)^2\right]^{1/2}}+\frac{\epsilon+\dfrac{1}{\tau}}{\epsilon+\dfrac{1}{\tau_\theta}}\left(1-\frac{\epsilon+\dfrac{1}{\tau}+\Gamma}{\left[\left(\epsilon+\dfrac{1}{\tau}+\Gamma+\dfrac{V_0^2}{\gamma}\right)^2-\left(\dfrac{4V_0V_1}{\gamma}\right)^2\right]^{1/2}}\right)\right]^{-1} . \tag{6.12}$$

The result (6.12) may be used directly by attempting to invert it, indirectly through the prescription (2.5) to obtain the quantum yield, or by studying it in limiting cases. Thus for the incoherent limit $\Gamma \to \infty$,

$$\tilde{F}(\epsilon)=\frac{\epsilon+\dfrac{1}{\tau_\theta}+\dfrac{V_0^2}{\gamma}}{\epsilon^2+\left(\dfrac{1}{\tau_\theta}+\dfrac{1}{\tau}+\dfrac{2V_0^2}{\gamma}\right)\epsilon+\dfrac{V_0^2}{\gamma}\left(\dfrac{1}{\tau_\theta}+\dfrac{1}{\tau}\right)+\dfrac{1}{\tau_\theta}\dfrac{1}{\tau}} , \tag{6.13}$$

which gives, in the time domain,

$$F(t)=\frac{C'-A'}{C'-B'}e^{-C't}-\frac{B'-A'}{C'-B'}e^{-B't} , \tag{6.14a}$$

where

$$A'=\frac{1}{\tau_\theta}+\frac{V_0^2}{\gamma} , \tag{6.14b}$$

$$B'=\frac{1}{2}\left\{\left(\frac{1}{\tau_\theta}+\frac{1}{\tau}+\frac{2V_0^2}{\gamma}\right)+\left[\left(\frac{1}{\tau_\theta}-\frac{1}{\tau}\right)^2+\left(\frac{2V_0^2}{\gamma}\right)^2\right]^{1/2}\right\} , \tag{6.14c}$$

$$C'=\frac{1}{2}\left\{\left(\frac{1}{\tau_\theta}+\frac{1}{\tau}+\frac{2V_0^2}{\gamma}\right)-\left[\left(\frac{1}{\tau_\theta}-\frac{1}{\tau}\right)^2+\left(\frac{2V_0^2}{\gamma}\right)^2\right]^{1/2}\right\} , \tag{6.14d}$$

The quantum yield ϕ corresponding to this case is

$$\phi=\frac{\dfrac{1}{\tau_\theta}+\dfrac{V_0^2}{\gamma}}{\dfrac{1}{\tau_\theta}\dfrac{1}{\tau}+\dfrac{V_0^2}{\gamma}\left(\dfrac{1}{\tau}+\dfrac{1}{\tau_\theta}\right)} . \tag{6.15}$$

Since $1/\tau$ and $1/\tau_\theta$ occur symmetrically in Eq. (6.14a) one will have the same time dependence of $F(t)$ whether $\tau > \tau_\theta$ or $\tau < \tau_\theta$. This is expected because the detrapping rates in the high-temperature limit are so strong that the origin of light emission can only be distinguished from the frequencies and not from the form of $F(t)$. Particularly when $1/\tau=1/\tau_\theta$, one obtains from Eq. (6.14a)

$$F(t)=\tfrac{1}{2}(1+e^{-(2V_0^2/\gamma)t})e^{-t/\tau} . \tag{6.16}$$

VII. CONCLUDING REMARKS

If theoretical studies of transport are divided into a class containing investigations of the basic interactions responsible for motion, and another containing the examination of the consequences of various transport equations into which those interactions are fed as inputs, the theory presented in this paper (as well as in I) belongs to the second class. The relevant studies of the first class are those of Förster,[28] Dexter,[29] and others.[30] As in Refs. 4–10 we are interested here in the kinetic problem.

Some of the results obtained in this paper are expected intuitively but others are surprising. In the former category belong most of the equations obtained and the quantum yield curves shown in Figs. 2(a) and 2(b). Among the surprises are the following: (i) No $t^{-1/2}$ dependence of the energy-transfer rate emerges from the analysis. (ii) The averaging prescription which had been put forward in I merely as an approximate procedure turns out to have a well-defined range of validity. (iii) The present k-space formalism is unable to reproduce, even in principle, certain results expected on the basis of intuition grounded in real-space considerations.

Equation (4.6) shows that there is no $t^{-1/2}$ dependence in the energy-transfer rate $k(t)$. It is important to point out that the $t^{-1/2}$ dependence is by no means an established experimental observation. A study of Figs. 3 and 4 of Ref. 2 for instance, will make it clear that, while a t-dependent energy transfer rate appears fairly well established, the scatter in the data would allow various other forms for the time dependence. This observation holds for other data too.[21] The absence of the $t^{-1/2}$ dependence of $k(t)$ should not be considered as a consequence of using a momentum-space description rather than a real-space one. In fact, we have been unable to obtain that dependence even from real-space *discrete* master equations. The Smoluchowski or Chandrasekhar derivations[31] that are often quoted as forming the theoretical basis of the $t^{-1/2}$ dependence use *continuum* equations and boundary conditions which may not describe the usual experimental situation in sensitized luminescence. It may well be that the correct dependence is $t^{-1/2}$ despite these considerations. In that case, the k-space analysis reported in this paper would be clearly seen to be inapplicable.

The averaging approximation introduced in I replaced a sum of exponentials with exponents α_k by a single exponent. Whether this single exponent should be an arithmetic average, a harmonic average, or obtained in some different way altogether, was not clear until the exact results reported here were obtained. We now see [Eqs. (3.13) and (3.14)] that the arithmetic averaging prescription $\alpha=(1/N)\sum_k \alpha_k$ applies and that the approximation procedure in I is valid for small Δ's and extreme Γ's. The question of how the single average exponent representing a sum of exponentials may be computed from the individual exponents is of importance in various transport problems. The unresolved issue of resistance versus conductance formulas,[32] and the Callaway versus Ziman limits in thermal conductivity[33] are examples. Our present analysis by no means settles this issue but makes an unexpected contribution.

On the basis of real-space considerations one would believe that, if the strength of the trapping interaction is increased while the host-host interaction (responsible for the motion of the exciton through the crystal) is held fixed, the energy transfer from host to trap would increase. This is borne out by the present formalism as it results in increased α_k's. On the other hand, one would also normally expect an increase in the efficiency of energy transfer if the *host-host* interaction is increased keeping the trapping interaction fixed. This expectation is based on the fact that the exciton would then move faster and thus arrive more quickly within the influence of traps. However the present formalism shows no effect whatsoever of changes in the host-host interaction. The reason is that this interaction affects only the bandwidth $4J$ and the bandwidth never appears in a Boltzmann equation. This presents an interesting problem in the relation of k-space to real-space transport equations, which will be discussed in greater detail elsewhere. It will suffice to state here that the role of the bandwidth (i.e., of host-host interactions) in momentum space is to make the *off-diagonal* elements of the density matrix oscillate in time and that it will therefore never affect analyses such as the present one, based on closed equations for the *diagonal* elements of the density matrix. It can be shown that the presence of traps generally destroys the closed character of the Boltzmann equation and connects the diagonal elements to the off-diagonal ones. The present formalism can be shown to be valid in the limit of large host-host interactions. The general situation can be analyzed in terms of k-space (or real-space) equations containing the full density matrix.[34]

The assumptions underlying the analysis in this paper are: (i) Transport equations for the diagonal elements of the density matrix in k space may be written in closed form (i.e., without including off-diagonal terms) even in the presence of traps. (ii) The radiative liftime τ_k is independent of k. (iii) The relaxation-time approximation is applicable. (iv) The temperature T, the host bandwidth $4J$, and the trap depth E_g have such values that $E_g > k_B T > 4J$. (v) The trapping interaction is short ranged and may be described completely by transition rates from host k states to the trap state.

Assumptions (i) and (ii) are both valid only in limiting cases. Of these (i) has been discussed above.

The radiative lifetime τ_k is actually strongly dependent on k at least for those situations in which there are no exciton-bath interactions. On the other hand assumption (ii) is perfectly valid if the exciton is looked upon as a nondecaying particle during its transport and radiative decay is later appended to the transport analysis through a lifetime. Such a point of view certainly constitutes an approximation. However, it is basic not only to the analysis presented in this paper but to almost all existing exciton transport theories.[4–14] The relaxation time approximation (iii) is necessary here from a practical standpoint for the same reasons as in other transport considerations: the complexity of the transition rates $Q_{kk'}$. It is doubtful that exact incorporation of realistic Q's will ever be possible analytically. The approximation (iv) has been relaxed in Sec. VI and therefore will not be commented upon here. Finally, we have performed calculations on the effects of long-range trapping on the luminescence quantities and plan to report them elsewhere.

As we have stated in the abstract, the present analysis may also be applied, without essential modification, to other quasiparticles that are scattered within a band and simultaneously captured by traps.[35] If their lifetime is infinite, as in the case of electrons, we merely put $\tau\rightarrow\infty$ in our analysis. Quantities such as the quantum yield then cease to exist but the host excitation probability and the trap excitation probability continue to be relevant.

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APPENDIX

In deriving Eq. (6.5), one needs to examine the consequences of the $N\rightarrow\infty$ limit on various quantities in Eqs. (6.1) and (6.2). For the sake of completeness we rewrite Eq. (6.1) and its continuous correspondence below

$$\frac{df_k}{dt}+\left(\frac{1}{\tau}+\alpha_k\right)f_k=\alpha_k^+f_\theta+\sum_{k'}(Q_{kk'}f_{k'}-Q_{k'k}f_k) \tag{A1}$$

and

$$\frac{df_k'}{dt}+\left(\frac{1}{\tau}+\alpha_k'\right)f_k'=\alpha_k'^+f_\theta'+\int dk'(Q_{kk'}'f_{k'}'-Q_{k'k}'f_k) \ . \tag{A2}$$

We have used primes to denote the quantities in the continuum limit here but have dropped them in the text of this paper. To obtain the correct transformation, one has to note that f_k, f_θ, and f_θ' are probabilities whereas f_k' is a probability density and that one requires, for normalization

$$\sum_k f_k=\int dk\, f_k' \ . \tag{A3}$$

Equation (A3) immediately implies that to make the transition from Eq. (A1) to Eq. (A2), f_k should be replaced by $(2\pi/N)f_k'$ in Eq. (A1). On the other hand, $f_\theta'=f_\theta$. It then follows that $\alpha_k'=\alpha_k$, $\alpha_k^+=(2\pi/N)\alpha_k'^+$ and $Q_{kk'}=(2\pi/N)Q_{kk'}'$. With all these Eq. (6.3) becomes

$$\tilde{F}(\epsilon)=\frac{\int dk\,[f_k(0)/D_k]+(\epsilon+1/\tau_\theta)^{-1}\int dk\,(\alpha_k^+/D_k)}{1-\int dk\,(\Gamma_k f_k^{\text{th}}/D_k)+(\epsilon+1/\tau)(\epsilon+1/\tau_\theta)^{-1}\int dk\,(\alpha_k^+/D_k)} \tag{A4}$$

as expected.

Restricting the analysis to the case $V_0>>V_1$ and using Eq. (6.4), the expression $\int dk\,(\alpha_k^+/D_k)$ can be rewritten

$$\int dk\,\frac{\alpha_k^+}{D_k}=2\pi e^{-\beta E_g}\left[\int\frac{dk}{2\pi}e^{-2J\beta\cos k}-\frac{\epsilon+\frac{1}{\tau}+\Gamma}{\left(\frac{4V_0V_1}{\gamma}\right)}\int_0^\infty dt\,\exp\left(-\frac{\epsilon+\frac{1}{\tau}+\Gamma+\left(\frac{V_0^2}{\gamma}\right)}{\left(\frac{4V_0V_1}{\gamma}\right)}\right)\int\frac{dk}{2\pi}e^{-(t+2J\beta\cos k)}\right] \ . \tag{A5}$$

Using the following integral representation and some properties of the modified Bessel function, e.g.,

$$I_0(x+y)=\sum_{n=-\infty}^{\infty} I_n(x)I_{-n}(y) \;, \tag{A6}$$

one obtains

$$\int dk\,\frac{\alpha_k^+}{D_k}=2\pi e^{-\beta E_g}\left\{ I_0(2J\beta)-\frac{\epsilon+\Gamma+\frac{1}{\tau}}{\left[\frac{4V_0V_1}{\gamma}\right]}\sum_{-\infty}^{\infty} I_n(2J\beta)\int_0^\infty dt\,\exp\left[-\frac{\epsilon+\frac{1}{\tau}+\Gamma+\left[\frac{V_0^2}{\gamma}\right]}{\left[\frac{4V_0V_1}{\gamma}\right]}t\right] I_n(t)\right\} . \tag{A7}$$

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