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Vasudev M. Kenkre

Paul Ernest Parris

Missouri University of Science and Technology, parris@mst.edu

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Exciton trapping and sensitized luminescence: A generalized theory for all trap concentrations

V. M. Kenkre and P. E. Parris

Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

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The generalized-master-equation theory of sensitized luminescence in molecular crystals is extended to cover arbitrary guest concentrations by making use of a recently introduced formalism. Central to the formalism is a quantity termed the ν function, which is an ensemble average of the sum of host propagators over guest-influenced host sites. A variety of experimentally relevant sensitized luminescence observables, such as the host (and guest) luminescence intensity, the quantum yields, and the energy-transfer rates are simply related to the ν function. It is shown how the latter can be calculated for exciton motion possessing an arbitrary degree of coherence, dimensionality, and other transport characteristics, and for guest-molecule placement represented by any given pair correlation function. Specific cases are treated and results, some exact and others approximate, are presented for experimental observables.

I. INTRODUCTION

This paper addresses the dependence of exciton-trapping phenomena, specifically of sensitized luminescence observables, on the concentration of guest (or trap, detector, or acceptor) molecules. The system under study is a molecular crystal such as anthracene, and the guest molecules could be, for instance, those for tetracene. The relevant experiments consist of shining light on the crystal selectively so as to excite only the host, e.g., anthracene (or only the guest, e.g., tetracene). The intensity of light emitted by the host and/or the guest is the basic observable. Motion characteristics of excitons propagating through the host, for instance their transport coherence and the magnitude of their diffusion constant, and generally the phenomenon of energy transfer are the target of these investigations.

There has been much renewal of interest in this field both on the part of experimentalists¹⁻¹⁰ and theorists.¹¹⁻¹⁸ The approach of the present paper is that of generalized master equations,¹⁸⁻²¹ and the primary new ingredient in the paper is the analysis of many traps, i.e., the extension of the theory¹⁸ to

the intermediate- and high-concentration regime.

The organization of this paper is as follows. In Sec. II we give a brief summary of the basic formalism based on the ν function introduced recently^{20,21} by one of the present authors. In that section we also show the simple connection that the ν function has with experimental observables such as the host and guest yields and the host and guest luminescence intensities. The meaning of the ν function is elucidated in physical terms in Sec. III, by studying it at short and long times and by exhibiting its direct relations to the surviving number of excitons at large times as well as to the trap pair-correlation function and the host propagators for all times. On the basis of the latter relation, several exact results for the ν function are obtained in Sec. IV, along the resulting yields and luminescence intensities. The discussion and the plots presented in this section examine and compare the case of random traps to that of periodic traps. A simple prescription for approximate calculations is discussed in Sec. V, an explicit demonstration of the combined effect of coherence and non-negligible guest concentration is given in Sec. VI, and concluding remarks form Sec. VII.

II. THE BASIC FORMALISM

The exciton-trapping problem has been analyzed by a number of authors¹¹⁻¹⁸ with the help of a variety of techniques. We use the approach and notation of Kenkre and Wong.¹⁸ If $P_m(t)$ denotes the probability that the m th site in the host crystal is occupied at time t , then the generalized master equation (GME) augmented by decay and trapping terms is

$$\frac{dP_m(t)}{dt} + \frac{P_m(t)}{\tau_H} = \int_0^t dt' \sum_n [W_{mn}(t-t')P_n(t') - W_{nm}(t-t')P_m(t')] - c \sum_r \delta_{m,r} P_r(t). \quad (2.1)$$

Equation (2.1), whose Markoffian case appears in Refs. 11–17, represents the simplest trapping model. More elaborate trapping models and detailed explanations may be found elsewhere.^{18,20} The decay-time constant is τ_H in the host crystal, W 's are memory functions describing exciton motion within the host crystal, and c is the rate at which the trap molecules are fed by the trap-influenced host sites r . The primed summation covers only those sites r . The words trap and guest are used interchangeably throughout this paper. Using the Montroll defect technique,²² one may write the "solution" of (2.1) as

$$\tilde{P}_m(\epsilon) = \tilde{\eta}_m(\epsilon') - c \sum_r' \tilde{\psi}_{m-r}(\epsilon') \tilde{P}_r(\epsilon). \quad (2.2)$$

Here $\psi_m(t)$ is the propagator for (2.1) without the decay and trapping terms, i.e., the solution of (2.1) for $c=1/\tau_H=0$ and for the initial condition $P_n(0)=\delta_{n,0}$, where $\eta_m(t)$ is the corresponding solution for the actual initial condition $P_n(0)$, i.e.,

$$\eta_m(t) = \sum_n \psi_{m-n}(t) P_n(0), \quad (2.3)$$

where ϵ is the Laplace variable, tildes denote Laplace transforms, and $\epsilon' = \epsilon + (1/\tau_H)$. Explicit expressions for the propagators may be found in a larger number of earlier publications, e.g., Ref. 20.

Exact solution of (2.2) is straightforward for the single-trap case. One obtains,¹⁸ for instance, the host excitation probability n_H as

$$\begin{aligned} \tilde{n}_H(\epsilon) &= \sum_m \tilde{P}_m(\epsilon) \\ &= \frac{1}{\epsilon'} \left[1 - \frac{c \tilde{\eta}_r(\epsilon')}{1 + c \tilde{\psi}_0(\epsilon')} \right]. \end{aligned} \quad (2.4)$$

For the particular case of uniform initial host illumination, one has

$$\eta_r(t) = \frac{1}{N}, \quad (2.5)$$

where N is the total number of host sites in the crystal. The host quantum yield ϕ_H may then be written¹⁸ as

$$\begin{aligned} \phi_H &= \frac{1}{\tau_H} \int_0^\infty dt n_H(t) \\ &= 1 - \frac{\rho}{\frac{1}{c\tau_H} + \frac{1}{\tau_H} \tilde{\psi}_0 \left[\frac{1}{\tau_H} \right]}, \end{aligned} \quad (2.6)$$

where $\rho = 1/N$. In any realistic system N is so large that $1/N$ effectively vanishes giving $\phi_H = 1$. Surely this is a result of treating a *single* trap in an infinitely large host. For low trap concentrations (2.6) may,

however, still be used¹⁸ as an approximation with the understanding that $\rho = N'/N$, where N' is the number of trap-influenced host sites. Provided that $N' \rightarrow \infty$ and $N \rightarrow \infty$ with ρ finite, (2.6) gives a usable result for low concentrations. To understand how high concentrations could invalidate such results, consider that the capture rate c is large enough to eliminate the term $1/c\tau_H$ in (2.6). Since the value of $(1/\tau_H)\tilde{\psi}_0(1/\tau_H)$ is dictated by motion and decay but is independent of the trap concentration ρ , it will be smaller than ρ for sufficiently large values of ρ . A negative yield ϕ_H will then be obtained from (2.6).

In most of the aromatic hydrocarbon crystals, solubility restrictions limit the trap concentration ρ to values as small as 10^{-4} . One might therefore argue that a low-concentration analysis¹⁸ is adequate for those systems. Such an argument is indeed valid in the context of steady-state observables such as the yields, which were the aim of the investigation of Ref. 18. However, when *time-dependent* observables such as the luminescence intensities [see, e.g., (2.4)] are calculated, there is always the concern that the above low-concentration approximation might run into difficulties at sufficiently *large times*. The ν -function approach^{20,21} removes these shortcomings.

Summation of (2.2), in one case over all the host sites and in the other only over the trap-influenced host sites, gives

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} \left[1 - c \sum_s' \tilde{P}_s(\epsilon) \right], \quad (2.7)$$

$$\sum_s' \tilde{P}_s(\epsilon) = \sum_s' \tilde{\eta}_s(\epsilon') - c \sum_r' \tilde{\nu}_r(\epsilon') \tilde{P}_r(\epsilon), \quad (2.8)$$

$$\nu_r = \sum_s' \psi_{s-r}. \quad (2.9)$$

It is clear from (2.7) that all that is required for obtaining observables such as $n_H(t)$ is $\sum_s' P_s(t)$, the total probability that the trap-influenced host region is excited. This probability cannot be extracted from (2.8) directly. To make such an extraction possible, Kenkre^{20,21} made the assumption that $\nu_r(t)$ defined in (2.9) and appearing in (2.8) is independent of the label r . Equation (2.8) now reduces immediately to

$$\sum_s' \tilde{P}_s(\epsilon) = \frac{\sum_s' \tilde{\eta}_s(\epsilon')}{1 + c \tilde{\nu}(\epsilon')}, \quad (2.10)$$

and we have

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} \left[1 - \frac{c \sum_s' \tilde{\eta}_s(\epsilon')}{1 + c \tilde{\nu}(\epsilon')} \right]. \quad (2.11)$$

Comparison of (2.10) and (2.11) to the respective single-trap expressions¹⁸ shows that this analysis re-

sults merely in $\tilde{\psi}_0(\epsilon)$ being replaced by $\tilde{\nu}(\epsilon)$ in the expressions for observables derived earlier¹⁸ for the low-concentration case.

Thus the ν -function approach consists of tackling the multitrapping system by focusing attention on $\sum'_s P_s$ rather than on the individual probabilities P_m and of making the assumption that the propagator sum $\sum'_r \psi_{r-s}$ connecting a given site s to other sites r , all within the set of the trap-influenced host sites, may be taken to be independent of the site s . We believe this assumption, which can be shown to be exact in some situations and which generally involves a configuration average, is reasonable for many systems of interest. The rest of this paper explores the consequences of this assumption.

The primary experimentally accessible observables are the host and guest luminescence intensities which are, respectively, proportional to the host and guest excitation probabilities $n_H(t)$ and $n_G(t)$. Equation (2.11) gives $n_H(t)$ for arbitrary initial conditions and reduces to

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} \left[1 - \frac{c\rho}{\epsilon' + c\epsilon'\tilde{\nu}(\epsilon')} \right] \quad (2.12)$$

for initially uniform host illumination. To obtain (2.12) we have utilized the obvious result valid for this initial condition:

$$\sum'_s \tilde{\eta}_s(\epsilon') = \left[\sum'_s \frac{1}{\epsilon'} \right] \frac{1}{N} = \frac{\rho}{\epsilon'}. \quad (2.13)$$

If detrapping is neglected for simplicity,

$$\frac{dn_G(t)}{dt} + \frac{n_G(t)}{\tau_G} = c \sum'_r P_r(t) \quad (2.14)$$

describes the time evolution of the guest luminescence intensity. Taking Laplace transforms and making use of (2.10), we find that

$$\tilde{n}_G(\epsilon) = \left[\frac{\sum'_r \tilde{\eta}_r(\epsilon')}{\frac{1}{c} + \tilde{\nu}(\epsilon')} \right] \left[\frac{1}{\epsilon' + \frac{1}{\tau_G} - \frac{1}{\tau_H}} \right], \quad (2.15)$$

where we have assumed the guest molecules to be initially unpopulated. For a delocalized initial host population, (2.15) may be reexpressed as

$$\tilde{n}_G(\epsilon) = \left[\frac{\rho}{\frac{\epsilon'}{c} + \epsilon'\tilde{\nu}(\epsilon')} \right] \left[\frac{1}{\epsilon' + \frac{1}{\tau_G} - \frac{1}{\tau_H}} \right]. \quad (2.16)$$

To deemphasize unimportant proportionality con-

stants, the host and guest excitation probabilities n_H and n_G will be called the host and guest luminescence intensities in the rest of the paper. They are given by (2.12) and (2.16) and may be used to extract other observables immediately. Thus the host yield ϕ_H , defined in (2.6), is now

$$\phi_H = 1 - \frac{\rho}{\frac{1}{c\tau_H} + \frac{1}{\tau_H} \tilde{\nu} \left[\frac{1}{\tau_H} \right]}, \quad (2.17)$$

and the guest yield ϕ_G , in the absence of nonradiative decay processes, is

$$\phi_G = 1 - \phi_H = \frac{\rho}{\frac{1}{c\tau_H} + \frac{1}{\tau_H} \tilde{\nu} \left[\frac{1}{\tau_H} \right]}. \quad (2.18)$$

While expressions (2.17) and (2.18) apply to delocalized initial conditions, it is straightforward to write more general ones for arbitrary conditions. The energy-transfer rate $k(t)$, traditionally defined² through

$$\frac{dn_H(t)}{dt} + \frac{n_H(t)}{\tau_H} = -k(t)n_H(t), \quad (2.19)$$

may be obtained from (2.11) or (2.12) through Laplace inversion and through the use of

$$k(t) = - \left[\frac{d}{dt} [\ln n_H(t)] - \frac{1}{\tau_H} \right]. \quad (2.20)$$

The energy-transfer memory $k_m(t)$ has been defined through

$$\frac{dn_H(t)}{dt} + \frac{n_H(t)}{\tau_H} = - \int_0^t dt' k_m(t-t') n_H(t'), \quad (2.21)$$

and has been argued by Huber¹³ as well as by us²⁰ to be the more useful quantity in sensitized luminescence phenomena. An expression for it in terms of the ν function follows²⁰ from (2.21) and (2.12):

$$\tilde{k}_m(\epsilon) = \frac{\rho\epsilon'}{\frac{\epsilon'}{c} + [\epsilon'\tilde{\nu}(\epsilon') - \rho]}. \quad (2.22)$$

To obtain k_m valid for arbitrary initial conditions corresponding to (2.11), one merely replaces ρ by $\epsilon' \sum'_r \tilde{\eta}_r(\epsilon')$ in (2.22). Finally, we show the expression for the steady-state energy-transfer rate k_s used by Wolf¹ and others and defined as being proportional to the "flux" ratio:

$$k_s = \frac{1}{\tau_H} \frac{\phi_G}{\phi_H}. \quad (2.23)$$

Kenkre has shown²⁰ that this traditional energy-

transfer rate k_s is merely the Markoffian limit ($\epsilon' \rightarrow 1/\tau_H$) of the energy-transfer memory k_m . Therefore,

$$k_s = \frac{1}{\tau_H} \left[\frac{\rho}{\frac{1}{c\tau_H} + \left[\frac{1}{\tau_H} \tilde{\nu} \left[\frac{1}{\tau_H} \right] - \rho \right]} \right] \quad (2.24)$$

for delocalized initial conditions.

Equations such as (2.15)–(2.18), (2.22), and (2.24) show explicitly how knowledge of ν leads directly to knowledge of the various experimental observables viz. the luminescence intensities, the yields, and the energy-transfer memories and rates.

III. MEANING OF THE ν FUNCTION

In this section we explore the physical significance of the ν function, which we have shown above to be connected in a straightforward way to the observables. The definition (2.9) shows that $\nu(t)$ is the total probability (in the trapless and decayless host) that the trap-influenced host region is occupied at time t given that it was occupied at time 0. It is thus a natural extension of the self-propagator ψ_0 to the multitraps case. At $t=0$, $\nu(t)$ is clearly equal to $\psi_0(0)$ and is thus 1. As time progresses, $\psi_0(t)$ in the summation (2.9) decays but $\psi_{r \neq s}(t)$'s for $r \neq s$ become nonzero. As $t \rightarrow \infty$, all the $\psi_{r \neq s}$'s become equal to one another and to $1/N$. It is clear from (2.9) that the ν function is thus initially 1 but becomes eventually equal to the trap concentration ρ , i.e., to N'/N . This is a consequence of the fact that the summation in (2.9) contains N' terms.

The low-concentration analysis approximates ν by ψ_0 in the Laplace domain. The above remarks show that $\psi_0(t)$ is similar to $\nu(t)$ at short times but quite different at large times. This difference becomes particularly important in realistic systems, where one may take the above-mentioned limit $N' \rightarrow \infty, N \rightarrow \infty$, their ratio ρ remaining finite. Then

$$\lim_{t \rightarrow \infty} \psi_0(t) = \lim_{\epsilon \rightarrow 0} \epsilon \tilde{\psi}(\epsilon) = \frac{1}{N} \quad (3.1)$$

shows that $\psi_0(t)$ decays to zero for infinite systems while

$$\lim_{t \rightarrow \infty} \nu(t) = \lim_{\epsilon \rightarrow 0} \epsilon \tilde{\nu}(\epsilon) = \rho \quad (3.2)$$

shows that $\nu(t)$ decays to the trap concentration ρ , i.e., to a finite value. Figure 1 exhibits this comparative behavior of ν and the self-propagator ψ_0 .

A direct physical meaning may be associated with $\nu(t)$ for large times. Thus letting $\tau_H \rightarrow \infty$ for simplicity, the expression (2.12) for the host luminescence intensity gives

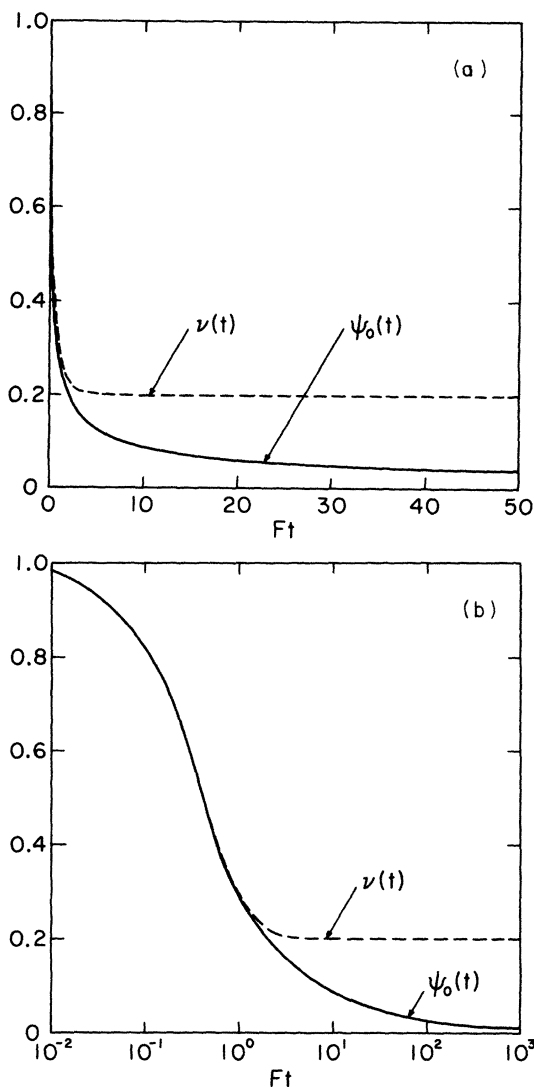


FIG. 1. ν function and the self-propagator ψ_0 plotted as a function of the dimensionless time Ft for an infinite linear chain wherein the exciton moves incoherently via nearest-neighbor rates F . The traps are placed periodically and their concentration is 0.2; the time scales in Figs. 1(a) and 1(b) are linear and logarithmic, respectively. Note that ν and ψ_0 are identical at short times and that the latter eventually decays to zero while the former tends to $\rho=0.2$.

$$\lim_{\epsilon \rightarrow 0} \epsilon \tilde{n}_H(\epsilon) = \lim_{\epsilon \rightarrow 0} \left[1 - \frac{\rho}{\epsilon \tilde{\nu}(\epsilon)} \right]. \quad (3.3)$$

At large times one therefore has

$$\nu(t) \approx \rho [1 - n_H(t)]^{-1}. \quad (3.4)$$

Thus an intimate connection exists in the time domain between the observable $n_H(t)$ and the ν function.

The third manner of extracting the physical significance of ν proceeds by rewriting (2.9) as

$$\begin{aligned} \nu_r(t) &= \sum'_s \sum_m \psi_{m-r}(t) \delta_{m,s} \\ &= \sum'_s \sum_m \psi_m(t) \delta_{m,s-r}, \end{aligned} \quad (3.5)$$

the m summation being unrestricted, i.e., over all host sites. Since the r -independent ν is obtained from ν_r through an ensemble average, we may write

$$\nu(t) = \langle \nu_r(t) \rangle = \sum_m \psi_m(t) p_m, \quad (3.6)$$

$$p_m = \left\langle \sum'_s \delta_{m,s-r} \right\rangle. \quad (3.7)$$

Equation (3.6) shows that the ν function is a sum over all host sites of the host propagators ψ_m and the quantities p_m . From (3.7) we see that p_m is the probability that the m th host site is trap influenced, given that the 0th host site is trap influenced. Thus p_m is essentially the guest pair correlation function.

Equation (3.6) is a rather useful result. The nature of trap-trap interactions leads to the nature of their placement within the host, i.e., to specific forms of their pair correlation function. The nature of exciton dynamics in the pure host decides the form of the host propagators. These two in turn determine the ν function in a straightforward way through (3.6).

IV. EXACT CALCULATIONS

The last of the three results presented in Sec. III, specifically (3.6), provides us with an explicit prescription to calculate ν from the trap pair correlation function. The latter may be obtained directly from experiment through scattering observations. It may also be calculated under model assumptions. In this section we present exact calculations for (i) periodic trap placement and (ii) random trap placement. These would correspond to the existence of very strong repulsive interactions among traps and of no interactions, respectively. We shall call the latter the uncorrelated and the former the fully anticorrelated case, and reserve the term fully correlated to describe clusters which would form in the presence of strong attractive interactions (which we do not treat in this section). The terminology is obviously related to ferromagnetism and antiferromagnetism.

A. Periodic traps

The results we present are valid for systems of arbitrary number of dimensions. However, to emphasize the simplicity of the argument involved, we

restrict the demonstration to a one-dimensional system and thereby avoid the slight clutter that vector notation would introduce. If the trap-influenced host sites form a superlattice, p_m equals 1 whenever m equals $nN/N' = n/\rho$, i.e., an integer n divided by the concentration ρ :

$$p_m = \sum_n \delta_{m,n/\rho} \quad (4.1)$$

Substitution of (4.1) in (3.6) leads to

$$\nu = \sum_n \psi_{n/\rho}. \quad (4.2)$$

In (4.1) and (4.2) n takes the values $0, 1, 2, \dots, N'-1$. Notice that although (4.2) has been derived from (4.1) and (3.6), i.e., from a result that has employed the assumption of the r independence of ν_r [see (2.9)], (4.2) is actually exact. If we calculate (2.9) for periodic traps we find that ν_r has no dependence on r at all. Thus no configuration averaging is necessary to obtain (4.2) in this case. We define the discrete Fourier transform ψ^k through

$$\psi^k = \sum_m \psi_m e^{ik \cdot m}, \quad (4.3)$$

where the m summation is over all host sites. The inverse transform

$$\psi_m = \frac{1}{N} \sum_k \psi^k e^{-ik \cdot m} \quad (4.4)$$

when used in (4.2) gives

$$\nu = \frac{1}{N} \sum_n \sum_k \psi^k e^{-ik \cdot n/\rho}. \quad (4.5)$$

Since k in (4.5) takes on values $2\pi l/N$ where l is an integer, and since $\rho = N'/N$, (4.5) reduces to

$$\nu = \left[\frac{N'}{N} \right] \sum'_k \psi^k. \quad (4.6)$$

The prime on the k summation in (4.6) indicates that k does not take on all the values $2\pi l/N$ as in (4.5) but only the restricted values $2\pi l/N'$. In going from (4.5) to (4.6), use has been made of the relation

$$\sum_n e^{-ik \cdot n} = N' \delta_{k, 2\pi l/N'}. \quad (4.7)$$

Note that, just as in (4.1), (4.2), and (4.5), n takes on values $0, 1, 2, \dots, (N'-1)$ in (4.7).

An inspection of (4.6) shows that its right-hand side is exactly of the form of that of (4.4) with $m=0$, with n replaced by N/N' , and with a restricted k summation. Indeed it follows immediately that ν equals the *self-propagator* ψ_0 for the smaller (periodic) lattice of $1/\rho$ sites:

$$\nu = \psi_0^{1/\rho}. \quad (4.8)$$

The superscript $1/\rho$ emphasizes the size of the lattice to which ψ_0 corresponds. This is a highly convenient result since it means that all trapping calculations in the actual periodic lattice require no more than the self-propagator in the smaller lattice. The convenience is particularly apparent at high concentrations ρ since large propagator summations such as in (2.9) are replaced by small summations as in (4.4). Consider, for instance, the one-dimensional infinite host chain over which the exciton moves through nearest-neighbor incoherent rates F , every $(1/\rho)$ th host site being trap influenced. An exact computation of (2.9) is possible^{20,21} through the evaluation of a geometric series in the Laplace domain:

$$\epsilon \tilde{\nu}_r(\epsilon) = \epsilon \tilde{\nu}(\epsilon) = \frac{\tanh(\xi/2)}{\tanh(\xi/2\rho)}, \quad (4.9)$$

where ξ is defined through

$$\cosh \xi = 1 + \frac{\epsilon}{2F}. \quad (4.10)$$

It is easy to show explicitly how, through a standard formula²³ for $\coth(\xi/2\rho)$, (4.9) can be converted into an expression for ν as a sum of $1/\rho$ terms (appropriate to a self-propagator in a lattice of $1/\rho$ sites). The exercise is, however, not particularly illuminating and will therefore be omitted. Notice, however, the particular case of (4.9) for the situation when every other site is trap influenced. The value of ρ is $\frac{1}{2}$. Either by substituting this value in (4.9) or more directly from (4.8), we get

$$\nu(t) = \psi_0^{(2)} = \frac{1}{2}(1 + e^{-4Ft}). \quad (4.11)$$

All trapping observables in this chain with periodic traps with concentration $\rho = \frac{1}{2}$ are thus immediately obtained from the trivially simple two-site self-propagator (4.11), although the number of traps is infinite and the individual host propagators are modified Bessel functions $e^{-2Ft} I_m(2Ft)$.

As stated above, the result (4.8) is by no means restricted to one dimension. For a system of arbitrary dimensions, m , k , etc. in (4.3)–(4.8) are vectors of the appropriate dimensions in the direct and reciprocal lattices, respectively, a symbol such as $k \cdot m$ denotes a dot product, and the ν function equals the self-propagator ψ_0 for a periodic lattice consisting entirely of a unit cell of the trap superlattice.

B. Random traps

In the absence of any trap-trap interaction, the trap-influenced host sites are located completely randomly. The quantity p_m , which represents the conditional probability of finding a trap-influenced host site at m given that there is one at site 0, is ob-

viously a constant for $m \neq 0$ for this random case. The constant equals $(N' - 1)/(N - 1)$ and is indistinguishable from $\rho \equiv N'/N$ in the limit of large N' and N . In such a case

$$p_m = \delta_{m,0} + \rho(1 - \delta_{m,0}). \quad (4.12)$$

Substitution of (4.12) in (3.6) gives

$$\nu = \psi_0 + (1 - \psi_0)\rho = \rho + (1 - \rho)\psi_0. \quad (4.13)$$

Both the expressions given above, (4.13) for the random case and (4.8) for the periodic one, allow one to recover known results in extreme limits. Thus for the single-trap case the “smaller” lattice whose self-propagator equals ν from (4.8) is the actual host lattice itself and thus $\nu = \psi_0$. In (4.13), ρ , which is actually $(N' - 1)/(N - 1)$ as explained above, equals 0 for the single-trap case and (4.13) too shows that ν reduces to ψ_0 . When ρ equals 1, i.e., when every host site feeds a trap, (4.13) and (4.8) both show that $\nu(t) = 1$ and that the host-excitation probability $n_H(t)$ decays as a single exponential $e^{-t(c + 1/\tau_H)}$, as it obviously should.

Periodic traps have been analyzed by a number of authors^{13–17,21} recently. It has been argued that they can represent random traps reasonably well, provided exciton motion is not too coherent.¹⁵ It is therefore instructive to compare observables in the periodic and random cases.²⁴ A respective substitution of (4.9), and (4.13) with $\psi_m(t) = e^{-2Ft} I_m(2Ft)$, in the various expressions for luminescence observables given in Sec. II followed by a Laplace-inversion produces the results in Figs. 2–6. In Figs. 2 and 3, the guest yield ϕ_G and the steady-state energy-transfer rate k_s are, respectively, plotted versus the trap concentration ρ for the single-trap, the periodic-trap and the random-trap cases. In Figs. 4 and 5 the host and guest luminescence intensities are plotted as functions of time for several values of ρ , to bring out the comparison between the periodic and random cases. All these figures are constructed for one-dimensional systems. This has been done for simplicity. However, to emphasize that our methods are applicable without modification to systems of arbitrary dimensions we have provided Fig. 6 which shows the guest yield versus the trap concentration for a two-dimensional square lattice (with nearest-neighbor incoherent rates F). If necessary, we can construct such plots for arbitrary lattice structures as well as arbitrary dimensionality.

V. CALCULATIONS VIA AN APPROXIMATION PROCEDURE

The exact expressions presented in Sec. IV for the luminescence intensities n_H and n_G , although readily usable through numerical Laplace-inversion rou-

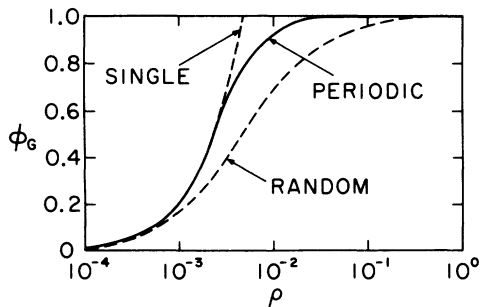


FIG. 2. Guest yield ϕ_G plotted as a function of the trap concentration ρ (logarithmic scale) for the single-trap ($\nu = \psi_0$), the periodic-trap ($\nu = \psi_0^{1/\rho}$), and the random-trap [$\nu = \rho + (1 - \rho)\psi_0$] theories. The values of $F\tau_H$ (motion) and $c\tau_H$ (capture) are 10^4 and 10^5 , respectively, and $\tau_G = 2\tau_H$.

tines, suffer the drawback that they do not easily allow one to examine the analytical behavior of the observables in the time domain. In this section we therefore present expressions obtained via an approximation procedure by making a simple choice for the function $\nu(t)$, which allow analytical inversions of the quantities of interest to be carried out. Our choice for $\nu(t)$ is guided by the property, stated in Sec. III and illustrated in Fig. 1, that $\nu(t)$ starts at the value 1 at time zero and decays at long times to the value ρ . The simplest function with this feature is given by the form

$$\nu(t) = \rho + (1 - \rho)e^{-\Gamma t}. \quad (5.1)$$

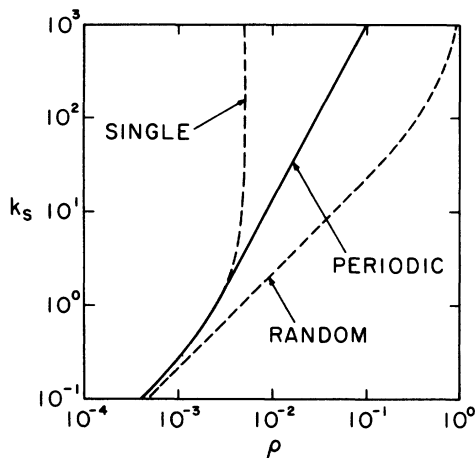


FIG. 3. Steady-state energy-transfer rate k_s , defined in (2.23), plotted as a function of the trap concentration ρ (logarithmic scale) for the single-trap, the periodic-trap, and the random-trap theories. Parameter values are as in Fig. 2. Note the approximate linear dependence on ρ in the random case and the approximate bilinear dependence in the periodic case in the middle of the ρ region displayed.

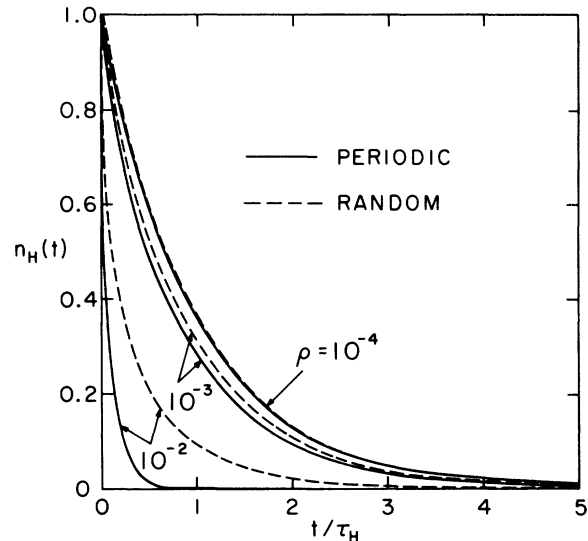


FIG. 4. Host luminescence intensity $n_H(t)$ plotted as a function of the dimensionless time t/τ_H for several trap concentrations ρ (as labeled) for the periodic-trap and random-trap cases. The two curves are essentially coincident for $\rho = 10^{-4}$. Values of $F\tau_H$, $c\tau_H$, and τ_G/τ_H are as in Fig. 2.

Comparison with (4.13) shows that this will be a good approximation for systems with randomly placed traps whenever ψ_0 , the self-propagator for the trap-free crystal, can be approximated by an ex-

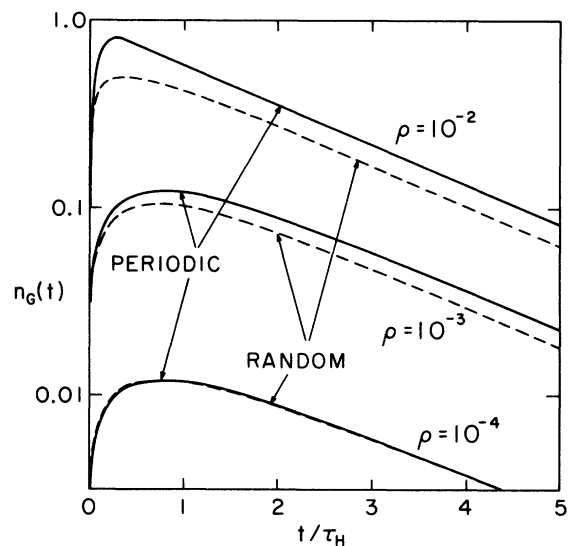


FIG. 5. Guest luminescence intensity $n_G(t)$ plotted as a function of the dimensionless time t/τ_H for the same values of the trap concentration ρ as in Fig. 4. The other parameter values are also as in Fig. 4. The luminescence intensity is plotted logarithmically. The curves for the periodic and the random cases are coincident for $\rho = 10^{-4}$ as in Fig. 4.

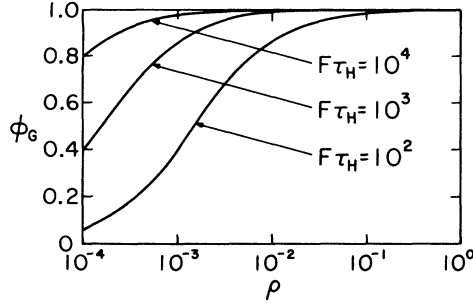


FIG. 6. Guest yield ϕ_G plotted as a function of the trap concentration ρ for the random-trap case in a two-dimensional square lattice with nearest-neighbor transfer rates F , for $c\tau_H = 10^5$, $\tau_G = 2\tau_H$, and three values of $F\tau_H$ as labeled.

potential, the constant Γ being a measure of the rate of motion. In addition, Eq. (4.11) shows that, for a concentration of $\frac{1}{2}$, (5.1) becomes exact in the limiting case of fully anticorrelated (periodic) traps in a one-dimensional crystal. Thus it may be a useful approximation in systems with a relatively large number of traps. For any concentration, however, the choice (5.1) for $\nu(t)$ possesses the correct long- and short-time limits and is of a simple enough form to allow one to carry out a complete analytical inversion of the time-dependent observables. It is therefore a useful tool for examining the general features of the concentration dependence of the experimental observables. It also provides an interesting comparison to the numerical inversions presented in the last section in which more complicated propagators were used to construct the ν function.

$$n_H(t) = e^{-[(1/\tau_H) + \Theta]t} \left[\cosh(\Omega t) + \left[\frac{\Theta\delta + \Omega^2}{\Gamma\Omega} \right] \sinh(\Omega t) \right], \quad (5.7)$$

$$n_G(t) = e^{-t/\tau_G} \left\{ 1 - e^{-\Theta t} \left[\cosh(\Omega t) + \left[\frac{\Theta'\delta + \Omega^2}{\Gamma\Omega} \right] \sinh(\Omega t) \right] \right\}, \quad (5.8)$$

where we have defined

$$\begin{aligned} \Theta &= \frac{\Gamma + c}{2}, \quad \delta = \frac{\Gamma - c}{2}, \\ \Theta' &= \Theta + \left[\frac{1}{\tau_H} - \frac{1}{\tau_G} \right], \quad \Omega = (\Theta^2 - \Gamma c \rho)^{1/2}. \end{aligned} \quad (5.9)$$

In Figs. 7–10 are plotted the results of expressions (5.3), (5.4), (5.7), and (5.8) for various values of the system parameters, in a fashion analogous to that presented for the exact results of Sec. IV. Note the similarity of the general features of the concentration dependence of these quantities to their counter-

To use Eq. (5.1) we insert its Laplace transform, given by

$$\tilde{\nu}(\epsilon) = \frac{\rho}{\epsilon} + \frac{1-\rho}{\epsilon + \Gamma}, \quad (5.2)$$

into the expressions derived in Sec. II for the various observables such as ϕ_G , ϕ_H , k_S , $n_H(t)$, and $n_G(t)$. Substitution of (5.2) in (2.17) immediately gives an expression for the guest quantum yield

$$\phi_G = \rho / \left[\frac{1}{c\tau_H} + \frac{1 + \Gamma\tau_H\rho}{1 + \Gamma\tau_H} \right]. \quad (5.3)$$

The host yield ϕ_H is equal to $1 - \phi_G$. The energy-transfer rate k_s is

$$k_S = \frac{1}{\tau_H} \rho / \left[\frac{1}{c\tau_H} + \frac{1-\rho}{1 + \Gamma\tau_H} \right]. \quad (5.4)$$

For the time-dependent observables we substitute (5.2) into (2.12) and (2.16). We obtain the following expressions for the host and detector luminescence intensities:

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon'} \left[1 - \frac{c\rho(\epsilon' + \Gamma)}{\epsilon'^2 + (c + \Gamma)\epsilon' + c\Gamma\rho} \right], \quad (5.5)$$

$$\tilde{n}_G(\epsilon) = \frac{c\rho(\epsilon' + \Gamma)}{[\epsilon'^2 + (c + \Gamma)\epsilon' + c\Gamma\rho] \left[\epsilon + \frac{1}{\tau_G} \right]}. \quad (5.6)$$

The inversion of these quantities is straightforward. We find

parts in Figs. 2–5 when appropriate values for the motion parameter $\Gamma\tau_H$ are used. In Fig. 7 we present plots of the guest yield versus trap concentration as expressed by (6.3) for three values of the motion parameter $\Gamma\tau_H$: 10^4 , 10^3 , 10^2 , and with the trapping parameter $c\tau_H$ equal to 10^4 . At low concentrations the curves are linearly dependent upon the trap concentration ρ . The initial slope of the curves is calculated to be

$$c\tau_H(1 + \Gamma\tau_H)/1 + \Gamma\tau_H + c\tau_H.$$

At higher concentrations the curves approach the value attained at $\rho = 1$, i.e., $c\tau_H/(1 + c\tau_H)$. As the

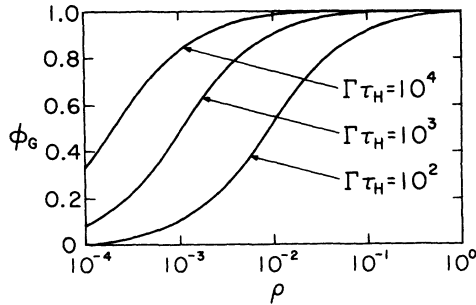


FIG. 7. Guest yield plotted as a function of the trap concentration in the exponential approximation of (5.1) for $\Gamma\tau_H = 10^4, 10^3,$ and 10^2 .

trapping rate becomes very large with respect to the radiative lifetime this value approaches 1, reflecting the fact that all host sites are trap influenced when $\rho = 1$: Any initial excitation is instantaneously trapped in the limit $c\tau_H \rightarrow \infty$. In Fig. 8 a plot of the energy-transfer rate (5.4) is presented as a function of the trap concentration for several values of the motion parameter $\Gamma\tau_H$ as in Fig. 7. This figure should be compared with Fig. 3 of Sec. IV. In Figs. 9 and 10 we present the time-dependent observables $n_H(t)$ and $n_G(t)$ for three values of the trap concentration ρ : $10^{-2}, 10^{-3}, 10^{-4}$, corresponding to similar plots in Figs. 4 and 5. For the curves in these two figures we have taken $\Gamma\tau_H = 10^3, c\tau_H = 10^4,$ and $\tau_G = 2\tau_H$.

The exponential approximation presented above is useful in making rapid analytical investigations of the trapping process and in gaining an intuitive understanding of the dependence of the sensitized luminescence observables on the trap concentration, the motion rate and the capture rate. The results of

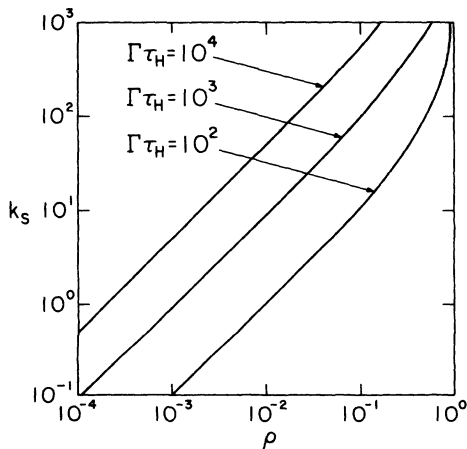


FIG. 8. Steady-state energy-transfer rate in the exponential approximation of (5.1) plotted as a function of ρ . Values of $\Gamma\tau_H$ are as in Fig. 7.

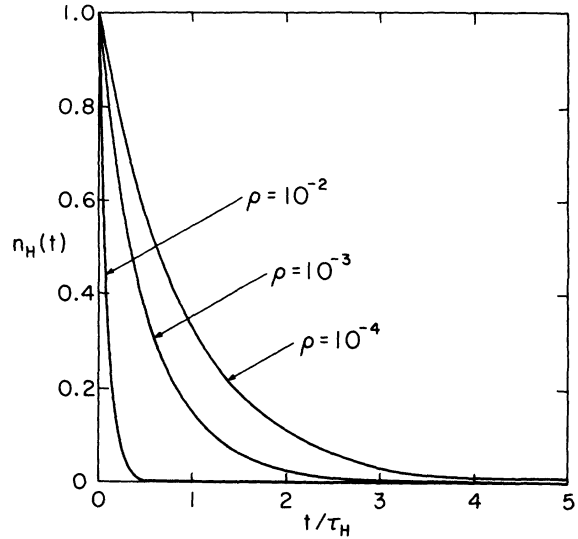


FIG. 9. Host luminescence intensity in the exponential approximation of (5.1) for several values of ρ to correspond to those in Fig. 4. The values of $\Gamma\tau_H$ and $c\tau_H$ are 10^3 and 10^4 , respectively.

this approximation procedure are closely related to those of a simple three-state model of trapping introduced recently by Kenkre²⁰ to examine the question of time-dependent versus time-independent energy-transfer rates and to remove some obvious inconsistencies in the usual two-state model (often termed the exciton-hopping model). The three-state

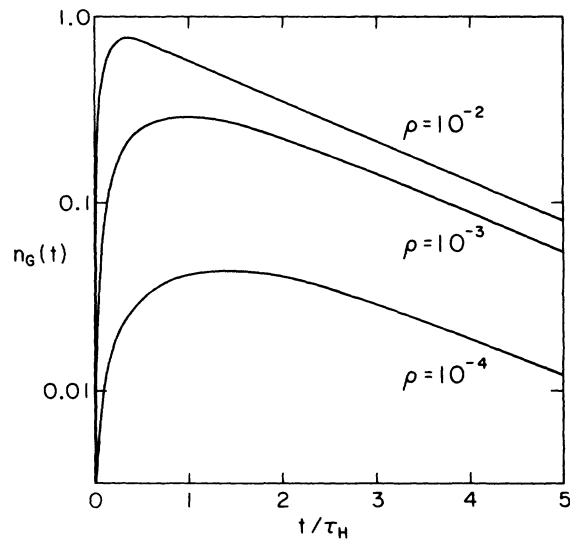


FIG. 10. Guest luminescence intensity in the exponential approximation of (5.1) for several values of ρ to correspond to those in Fig. 5. Parameter values are as in Fig. 9.

model²⁰ is based on the following equations:

$$\frac{dn_H^d}{dt} + \frac{n_H^d}{\tau_H} = M(n_H^n - n_H^d), \quad (5.10)$$

$$\frac{dn_H^n}{dt} + \frac{n_H^n}{\tau_H} = M(n_H^d - n_H^n) - Cn_H^n, \quad (5.11)$$

$$\frac{dn_G}{dt} + \frac{n_G}{\tau_G} = Cn_H^n, \quad (5.12)$$

where n_G is, as before, the guest-excitation probability, but now n_H^d and n_H^n represent the excitation probabilities of regions of the host crystal, which are, respectively, distance from and near the trapping center. The rate M describes exciton motion between these two host regions and the capture rate C accounts for the transfer of excitation into the traps from the host sites near them. The exact solution of (5.10)–(5.12) is straightforward. The resulting expressions for the host luminescence intensity $n_H \equiv n_H^n + n_H^d$ and the guest luminescence intensity n_G become identical to the results (5.7) and (5.8) of the exponential approximation to the ν function, with the correspondence $2M = \Gamma$, $[n_H^n(0)/n_H(0)] = \rho = \frac{1}{2}$, and $C = c$. The meaning of this correspondence should be obvious. Indeed, the essential equivalence of the exponential approximation and the three-state model can be understood easily in terms of the result (4.11) of Sec. IV. The three-state model envisages the host as a two-state system, with the trapping occurring from one of those two states. For a two-site host with one trap, however, we know that $\nu(t)$, which equals just the self-propagator $\psi_0(t)$, is equal to the exponential expression as in (4.11). The results of the three-state model must therefore coincide with those of the exponential approximation for the initial condition considered.

VI. EFFECT OF COHERENCE

The form of the expressions (2.11)–(2.24) clearly shows that the analysis in the present paper provides

$$\begin{aligned} \tilde{\psi}_0(\epsilon) = & \frac{\alpha}{[(\epsilon^2 + 2\epsilon\alpha)(\epsilon^2 + 2\epsilon\alpha + 16V^2)]^{1/2}} + \frac{2/\pi}{[(\epsilon + \alpha)^2 + 16V^2]^{1/2}} \mathcal{X}(k) \\ & + \frac{\alpha^2}{[(\epsilon + \alpha)^2 + 16V^2]^{1/2}} \frac{2/\pi}{(\epsilon^2 + 2\epsilon\alpha + 16V^2)^{1/2}} \Pi(a_1^2, k), \end{aligned} \quad (6.3)$$

where $a_1^2 = 16V^2(\epsilon^2 + 2\epsilon\alpha + 16V^2)^{-1}$ and $k = 4V[(\epsilon + \alpha)^2 + 16V^2]^{-1/2}$, and $\mathcal{X}(k)$ and $\Pi(a_1^2, k)$ are the elliptical integrals of the first and third kinds, respectively. As in Ref. 18, the motion is one-dimensional with nearest-neighbor interaction matrix elements V and randomizing bath parameter

a theory of exciton trapping which may be used to study systems with arbitrary values of the trap concentration *and* arbitrary degree of transport coherence. Thus for random placement of traps the guest yield is given by

$$\phi_G = \frac{\rho}{\frac{1}{c\tau_H} + \left[\rho + (1-\rho) \frac{1}{\tau_H} \tilde{\psi}_0 \left(\frac{1}{\tau_H} \right) \right]}, \quad (6.1)$$

$$\frac{1}{\tau_H} \tilde{\psi}_0 \left(\frac{1}{\tau_H} \right) = \int dk \left[\frac{1}{1 + \tau_H \tilde{\mathcal{A}}^k \left(\frac{1}{\tau_H} \right)} \right]. \quad (6.2)$$

The integration in (6.2) is over the Brillouin zone in k space and the result is valid for arbitrary number of dimensions and lattice structure. The degree of coherence enters into these calculations through the memories \mathcal{A} . If in the time domain the memories decay rapidly with respect to the radiative lifetime, the results for the yield are indistinguishable from those for incoherent motion. As has been explained in detail elsewhere,²⁰ the radiative lifetime serves as the coherence probe time in yield experiments. The yield result (6.1), the corresponding luminescence expressions, and similar results for trap placements other than the random one considered in (6.1), constitute the generalization of the theory of Kenkre and Wong.¹⁸ That theory had been constructed specifically to address arbitrary degree of coherence. Its restriction to small concentrations is removed by the present analysis. In Fig. 11 we present plots of the guest yield versus the (in)coherence parameter (α/V) for several values of the concentration ρ . They correspond to (6.1) with a propagator $\tilde{\psi}_0(\epsilon)$ given by

α . The degree of coherence is measured by the value of V/α , which is also the ratio of the lattice constant to the mean free path of the exciton. The relevant evolution equation for the matrix elements ρ_{mn} of the density matrix in the absence of decay and traps is^{18,20}

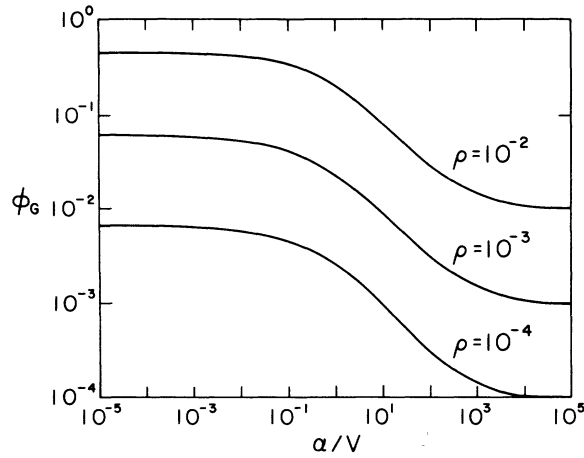


FIG. 11. Guest yield plotted as a function of the (in)coherence parameter α/V , i.e., the ratio of the mean free path to the lattice constant, for several values of the trap concentration. Parameter values correspond to Fig. 1 of Ref. 18.

$$\frac{d\rho_{mn}}{dt} = -iV(\rho_{m+1,n} + \rho_{m-1,n} - \rho_{m,n+1} - \rho_{m,n-1}) - \alpha(1 - \delta_{m,n})\rho_{mn}, \quad (6.4)$$

and the memory functions are known²⁰ to be

$$W_{mn}(t) = 2V^2 e^{-\alpha t} [J_{m-n+1}^2 + J_{m-n-1}^2 + 2J_{m-n-1}J_{m-n+1} - 2J_{m-n}^2 - J_{m-n}(J_{m-n+2} + J_{m-n-2})], \quad (6.5)$$

the J 's being Bessel functions of argument $2Vt$.

In Fig. 12 we have plotted the guest luminescence intensity as a function of time for the extreme limits of coherent ($\alpha=0$) and incoherent ($\alpha \rightarrow \infty$, $V \rightarrow \infty$, $2V^2/\alpha = F$) motion. The former corresponds to the propagator

$$\psi_0(t) = J_0^2(2Vt) \quad (6.6)$$

and the latter to

$$\psi_0(t) = e^{-2Ft} I_0(2Ft). \quad (6.7)$$

We have taken $F = 1.1 \times 10^{12} \text{ sec}^{-1}$, which corresponds to a diffusion constant of $2.8 \times 10^{-3} \text{ cm}^2/\text{sec}$ for a lattice constant of 5 \AA and $\tau_G = 2\tau_H = 32 \times 10^{-9} \text{ sec}$. These values are appropriate²⁵ to singlet-exciton motion in anthracene and to tetracene being the guest. We have also taken $V = 1.1 \times 10^{13} \text{ sec}^{-1}$ in keeping with the fact that the exciton bandwidth in these aromatic hydrocarbons is several hundred cm^{-1} . While there is not much qualitative difference in the shapes of the

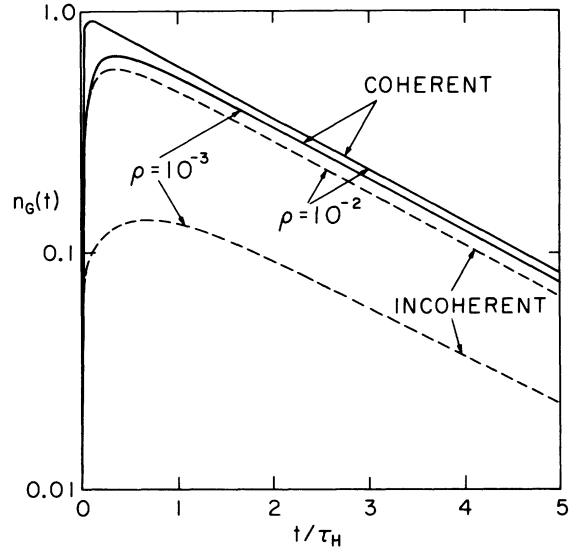


FIG. 12. Guest luminescence intensity plotted as a function of time for two values of the trap concentration to show the explicit effect of transport coherence. The extreme limits of completely coherent motion and completely incoherent motion are shown. The parameter values are $V\tau_H = 1.8 \times 10^5$, $F\tau_H = 1.8 \times 10^4$, $c\tau_H = 10^5$, and $\tau_G = 2\tau_H$.

coherent and the incoherent curves for the above parameter values, it is clear that for this system trapping is *much* more effective in the case of coherent motion. We would like to mention in passing that oscillations in $n_G(t)$ have appeared in some of our studies of very coherent motion at low trap concentrations. However, we believe that subtle issues which are not entirely understood at the moment remain in the limit of very coherent trapping. We are working on their clarification and hope to report on them in a future publication.

VII. DISCUSSION

Studies of exciton dynamics in general, and trapping and sensitized luminescence in particular, have witnessed intense activity in recent times, both on the theoretical and the experimental front. We believe, however, that a criticism made by Powell and Soos² in their review several years ago, that the dialogue between theory and experiment has been rather poor in this field, continues to be applicable even today. One of the purposes of the present paper is to make a positive contribution in this regard. We have therefore refrained from making memory functions, transition rates, asymptotic dependence, surviving fractions, or number of sites visited the prime target of the investigations in this paper. In-

stead we have presented calculations of quantities which are directly accessible through experiment, viz., the quantum yield and the time-dependent luminescence intensities of the host and the traps, and of the derived quantity, the energy-transfer rate, which for many years has served as a familiar and useful construct in the interpretation of experiment. We have given general formulas to calculate these direct observables from the microscopic dynamics. We have also presented plots of those observables versus trap concentration and time so that comparison to experiment could be made in a straightforward way. For the sake of simplicity we have treated one-dimensional crystals with nearest-neighbor incoherent motion in most of the plots, specifically, in Figs. 1–5. But Figs. 11 and 12 pertain to motion with various degrees of coherence, Fig. 6 to two-dimensional motion as is expected in many aromatic hydrocarbon crystals, and Figs. 7–10 to an analysis which, while it is approximate, is independent of the dimensionality of the crystal. Furthermore, we are able to prepare such explicit plots of the experimental observables for motion of arbitrary dimensionality and degree of coherence. In preparing the plots we have used in most cases parameter values (bandwidth, lattice constants, diffusion coefficient) which are known or believe to hold in aromatic hydrocarbon crystals such as anthracene. In other cases we have chosen those values which would elucidate the point under discussion in the best possible way. Although we have taken the radiative lifetime to be the total lifetime in all cases, it is straightforward to change the analysis for systems in which this assumption is not valid. The resulting expressions for yields and intensities are obtained from those given in this paper by merely multiplying the latter by the ratio of the radiative lifetime to the total lifetime, e.g., τ_H^0/τ_H .

The central result of the work reported here is the following explicit prescription. The pair correlation function p_m is to be obtained from knowledge of the placement of traps within the host. The propagators ψ_m are to be obtained from knowledge of exciton motion within the pure (undoped) host. The ν function is to be calculated from the p_m and ψ_m through (3.6). Finally, the experimental luminescence observables, i.e., the intensities, the yields, and even the energy-transfer rate, are to be extracted directly from (2.12), (2.16)–(2.18), (2.22), and (2.24). The calculation of the propagators ψ_m is related to extensive past work done on pure host crystals, involves objects such as generalized master equations, memory functions, and transition rates, and has been reported in detail in the past.²⁰ The trap pair correlation function p_m may be obtained from scattering experiments or through static calculations

from the partition function as is done in the theory of liquids or of alloys. The trap-trap interactions obviously decide the form of p_m . The analysis in Sec. IV has treated the extreme limits of total anticorrelation and of no correlation. Intermediate cases involving clustering tendencies may also be treated within our formalism. To see this explicitly let us assume that the trap pair correlation function is changed as a result of the trap-trap interactions from the form given in (4.12) to one which results in

$$\nu = \rho + (1 - \rho)\psi_0 + c_1\rho(1 - \rho). \quad (7.1)$$

Equation (7.1) reduces to the uncorrelated case (4.13) for $c_1 = 0$ and generally results in yield curves which exhibit the effect of trap correlation explicitly. The extent of the trap-trap interactions is represented by c_1 . We have plotted the guest yield versus trap concentration in Fig. 13(a) and the corresponding ν functions in Fig. 13(b) for several values of c_1 . Dependence of yield on trap-trap interactions has, to our knowledge, never been discussed before either in an experimental or a theoretical context. We have also used the simple picture provided by plots such as those in Fig. 13 to explore the effects of phase tran-

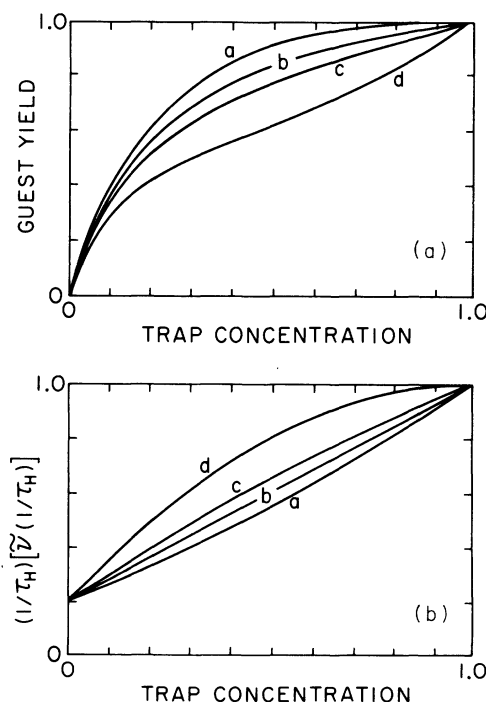


FIG. 13. Guest quantum yield (13a) and the ν function (13b) plotted vs the trap concentration ρ for several values of c_1 ($-0.2, 0, 0.2,$ and 0.8 for $a, b, c,$ and $d,$ respectively) showing the effect of trap-trap attraction or repulsion on luminescence observables. The relevant equation is (7.1) and parameter values are arbitrary: $(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = 0.2$.

sitions (among traps) on the luminescence observables.

The present theory is built on a single basic assumption: that ν_r of (2.9) is independent of r , i.e., that the sum of pure host propagators from one trap-influenced host site to all other trap-influenced host sites changes negligibly on changing the starting site. The range of the validity of the theory is determined by the range of the validity of this assumption. It is therefore important to understand when the assumption does and does not break down. The r independence of ν_r , and therefore the theory, happens to be *exact* in three cases. The first is that of a single trap. The second is that of two traps. The third is that of periodically arranged traps. For a single trap ν_r equals ψ_0 itself and is therefore "independent of r ." For two traps ν_r is again independent of r no matter what the relative location of traps, because the propagators summed to get ν_r are the self-propagator and the single relative propagator. The invariance (translational periodicity) of the periodic-trap arrangement results in the exact r independence of ν_r in the periodic case. We stress that our theory is exact for this latter case *no matter what* the trap concentration is. In this regard our theory is superior to several other approximation procedures that have been reported in the literature, whose validity always decreases with increasing concentration.

The other assumptions of our theory are the use of the generalized master equation for exciton transport in the pure host and the use of the simple sink model. The former has an extremely wide range of

validity, has been discussed extensively (see, e.g., Ref. 20), and will not be elaborated upon here. The sink model, which describes trapping through a simple addition of a capture term as in (2.1) has been used here because it is the simplest trapping model imaginable. Extensions of the theory to include detrapping within this model or to cover the totally different substitutional model are straightforward. A discussion of these extensions has been given in Ref. 18 in the context of low concentrations.

We have used analytical inversions of Laplace transforms in the context of our exponential approximation procedure in Sec. V but have had to use numerical inversion techniques²⁶ in the exact results of Sec. IV. We emphasize that, even in the latter case, the only numerical work appears in the inversions, the work in obtaining all expressions for the yields and those for the intensities in the Laplace domain being totally analytical.

Much further work is being done on this theory. The directions include application to existing observations such as those in Refs. 1–10 and extraction of microscopic memories and rates from them, further development of the ν -function theory to remove its mean-field character, and investigation of the relations the ν -function formalism bears to other multiple-trap theories existing in the literature.^{13–17}

ACKNOWLEDGMENTS

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Phenomena, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1979); J. Stat. Phys. 13, 17 (1975), and references therein; E. W. Montroll, *Energetics in Metallurgical Phenomena* (Gordon and Breach, New York, 1967), Vol. 3.

²³I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products*, 4th ed. (Academic, New York, 1965), p. 33.

²⁴In studying the comparison we give between the periodic and random cases, it should not be forgotten that our

random case is not identical to that treated by Scher and Wu in Ref. 15 or by Movagher *et al.* in Ref. 14. Being derived from an overall pair correlation function, our random result has only a mean-field character.

²⁵M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Oxford University Press, New York, 1982), pp. 58,122.

²⁶H. Stehfest, Commun. ACM 13, 47 (1970); 13, 624 (1970).