PHYSICAL REVIEW B VOLUME 23, NUMBER 8 15 APRIL 1981

Effect of transport coherence on trapping: Quantum-yield calculations for excitons in molecular crystals

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(Received 27 October 1980)

On the basis of a general transport formalism and two models of the trapping interaction, a description of Frenkel exciton transport in molecular crystals doped with traps is given in terms of an exact calculation. The analysis is directed particularly at the coherence question. The observables calculated are the quantum yields (explicitly) and the time-dependent luminescence intensities (to quadratures). It is shown that the neglect of coherence in interpretations of yield experiments leads to an underestimation of the exciton diffusion constant, and a prescription for evaluating the extent of coherence from bulk quenching observations is suggested.

I. INTRODUCTION

Although much formal work has been recently done in theoretical investigations of exciton coherence in molecular aggregates[1,2] it has been rightly felt[3] that more calculations addressed directly to observable quantities are required. We present here such calculations in two physically reasonable models, for a specific observable in sensitized luminescence, viz., quantum yield, with attention on a particular phenomenon, viz., exciton capture by traps. The basis of our calculations is a general formalism[4,5] which is able to analyze, in a *unified* way, coherent and incoherent motion of the exciton. The system we address is a molecular crystal in which guest molecules (i.e., traps) are introduced interstitially or substitutionally. The output of our theory consists of explicit simple expressions for the quantum yield and quadrature expressions for the time-dependent luminescence. These expressions clearly show the effects of coherence of exciton motion in the host crystal. Our analysis is applicable to sensitized fluorescence situations[3,6] as also to sensitized phosphorescence[7] observations.

The present analysis differs from our previous theory[8] of these processes in that it is a real-space treatment. It thus complements the momentum-space treatment of Ref. 8. It is close in spirit to earlier work by Pearlstein *et al.*[9] and recent work by Huber.[10] The experiments we are interested in here create excitons in the bulk of the host crystal through illumination, an appropriate frequency range being chosen to ensure that only the host (or guest) is excited. The excitons decay radiatively and also move within the host. If they arrive within the sphere of influence of the traps they may be captured. If they are captured, they later decay radiatively in a different frequency range. The monitored luminescence intensities (of the host and the guest) thus contain information about the motion of the exciton through the host.

Our theoretical analysis must therefore be based on a formalism to describe the motion of the excitons and on assumptions concerning the trapping of the excitons. For the former we employ here the generalized master equation[5] and for the latter, two trapping models that we shall describe below. We ignore exciton annihilation[11] and nonradiative processes and concentrate our attention entirely on trapping.

The paper is set out as follows. In Sec. II we give the transport description and introduce the trapping models. In Sec. III we give general expressions for the experimental observables in terms of the exciton propagator. In Sec. IV we introduce a specific generalized master equation, calculate the propagator and consequently the observables, and explore various limits including the extreme coherent and incoherent ones. In Sec. V we present a discussion. The Appendix presents details of the calculation of the propagator.

II. DESCRIPTION OF TRANSPORT AND TRAPPING MODELS

In a trapless crystal noninteracting excitons may be taken to move in accordance with the equation

$$\frac{dP_m(t)}{dt} + \frac{P_m(t)}{\tau_H} = \int_0^t dt' \sum_n [\mathfrak{w}_{mn}(t-t')P_n(t') - \mathfrak{w}_{nm}(t-t')P_m(t')] \quad (2.1)$$

for the probability $P_m(t)$ that an exciton occupies site m at time t, τ_H being the radiative decay time in the host. The memory functions $\mathfrak{w}_{mn}(t)$ contain the dynamics of the system. The extremes of completely coherent and completely incoherent motion as well as motion with an intermediate

degree of coherence may all be described by (2.1) and correspond to different forms of $\mathcal{W}_{mn}(t)$. The latter can be obtained[5,12,13] from the microscopic Hamiltonian. It has been shown[14] that (2.1) is valid for completely delocalized as well as completely localized initial conditions. The former are applicable to the experiments of interest here since the k-selection rule does place the excitons initially more or less uniformly in the host crystal. To introduce the host-trap interaction, terms describing exciton capture must be appended to (2.1). We shall present two different models of this interaction below.

A. The sink model

In the simpler version of this model we assume that exciton probability decays to the traps at a constant rate γ whenever the exciton occupies a host site influenced by the trap. This model, which should work best for the case of interstitially placed guest molecules, is represented by

$$\frac{dP_m}{dt}+\frac{P_m}{\tau_H}=\sum_n(\mathcal{W}_{mn}*P_n-\mathcal{W}_{nm}*P_m)-\sum_r{}'\delta_{m,r}\gamma P_m\ , \tag{2.2}$$

wherein (and henceforth) asterisks (*) denote convolutions as in (2.1), the primed summation extends only over the sites r influenced by traps and the unprimed summation covers all the host sites.

Let us consider the simple case of a guest molecule which traps excitons from the single host site r. Equation (2.2) may then be solved exactly with the help of the well known defect technique[15] if the solution of (2.2) without the trapping terms is known. The details are straightforward[11,15] and will not be given here. The result, expressed in terms of Laplace transforms, is

$$\tilde{P}_m(\epsilon)=\tilde{\eta}_m(\epsilon')-\gamma\left(\frac{\tilde{\psi}_{m-r}(\epsilon')\tilde{\eta}_r(\epsilon')}{1+\gamma\tilde{\psi}_0(\epsilon')}\right)\ , \tag{2.3}$$

where $\epsilon'=\epsilon+(1/\tau_H)$, where $\tilde{\psi}_m(\epsilon)$ is the solution of (2.2) for $\tau_H=\infty$ and $\gamma=0$ and for the initial condition $P_m(0)=\delta_{m,0}$, translational invariance of the $\mathcal{W}$'s appropriate to motion in a crystal being assumed, and where $\eta_m(t)$ is the solution of the homogeneous equation, given by

$$\eta_m(t)=\sum_n\psi_{m-n}(t)P_n(0)\ . \tag{2.4}$$

In (2.3) and throughout the paper, tildes denote Laplace transforms and ϵ is the Laplace variable. Summing (2.3) over m we obtain the probability $n_H(t)$ that the host is excited:

$$\tilde{n}_H(\epsilon)=\frac{1}{\epsilon'}\left(1-\frac{\gamma\tilde{\eta}_r(\epsilon')}{1+\gamma\tilde{\psi}_0(\epsilon')}\right)\ . \tag{2.5}$$

In deriving (2.5) we have used the obvious result

$$\sum_n\tilde{\psi}_{m-n}(\epsilon)=\frac{1}{\epsilon} \tag{2.6}$$

which represents the fact that in the absence of $1/\tau_H$ and of γ the probability is conserved.

If we allow detrapping, the sink model takes on a slightly less simple appearance. What multiplies the δ_{mr} in the last term of (2.2) is now $(\gamma P_m-\gamma' P_\theta)$ where γ' is the detrapping rate from the trap to the host site which it influences, and P_θ is the probability that the trap is occupied. The latter has, for its evolution,

$$\frac{dP_\theta}{dt}+\frac{P_\theta}{\tau_G}=(\gamma P_r-\gamma' P_\theta)\ , \tag{2.7}$$

where τ_G is the radiative lifetime in the trap or guest. Note that while for the sake of simplicity we have assumed that a guest site communicates with only one host site and with no other guest site, it is straightforward to generalize the treatment.

Eliminating the P_θ in the new version of (2.2) by using the solution of (2.7) one can see that for the case of initially unexcited traps all expressions in the Laplace domain for this version of the model are obtained from those in the $\gamma'=0$ version by substituting γ by $\gamma[\epsilon+(1/\tau_G)][\epsilon+(1/\tau_G)+\gamma']^{-1}$. Equation (2.5), with and without this modification, will be used in Sec. III below to derive expressions for the experimental observables.

B. The substitutional trap model

An entirely different trapping model suggests itself if our system has, as it normally does, substitutionally placed guest molecules. The index m now runs over the guest as well as the host sites, the former being denoted by r. There is no decay of probability our of the totality of sites m through trapping. The latter is represented by transfer of the excitons to the sites r. There is no γ but the memory functions $\mathcal{W}_{mn}(t)$ are generally modified whenever either m or n is a trap site. For simplicity we shall further assume that the memories (or rates) from host sites to traps (denoting trapping) are unmodified but that those from the traps to the host sites (denoting detrapping) are reduced in strength by the detailed balance factor $\exp(-\beta\Delta)$ where $\beta=1/k_BT$, with k_B the Boltzmann constant and T the temperature, and Δ is the amount by which the trap energy is less than the host energy. Thus

$$\frac{dP_m}{dt}+\frac{P_m}{\tau_H}=\sum_n\left(\mathcal{W}_{mn}*P_n-\mathcal{W}_{nm}*P_m\right)$$
$$-\delta_{m,r}\left[\left(\frac{1}{\tau_G}-\frac{1}{\tau_H}\right)+(e^{-\beta\Delta}-1)\sum_n\mathcal{W}_{nr}*\right]P_r$$
$$+(e^{-\beta\Delta}-1)\mathcal{W}_{mr}*P_r\ . \qquad (2.8)$$

The application of the defect technique[15] to (2.8) also leads to an exact solution. However, unlike the case of (2.3), we shall present the details because (2.8) is an unusual case of a problem with an extended defect region which is exactly soluble. We first have

$$\tilde{P}_m(\epsilon)=\tilde{\eta}_m(\epsilon')-\tilde{\psi}_{m-r}(\epsilon')\tilde{P}_r(\epsilon)$$
$$\times\left[\left(\frac{1}{\tau_G}-\frac{1}{\tau_H}\right)+(e^{-\beta\Delta}-1)\sum_n\mathcal{W}_{nr}(\epsilon')\right]$$
$$+(e^{-\beta\Delta}-1)\sum_n\tilde{\psi}_{m-n}(\epsilon')\tilde{\mathcal{W}}_{nr}(\epsilon')\tilde{P}_r(\epsilon)\ , \qquad (2.9)$$

where $\epsilon'=\epsilon+1/\tau_H$ as in (2.3). The special case $m=r$ of (2.9) gives

$$\tilde{P}_r(\epsilon)=\tilde{\eta}_r(\epsilon')\Big\{1+\left(\frac{1}{\tau_G}-\frac{1}{\tau_H}\right)\tilde{\psi}_0(\epsilon')+(1-e^{-\beta\Delta})$$
$$\times\Big[\sum_n\tilde{\psi}_{r-n}(\epsilon')\mathcal{W}_{nr}(\epsilon')$$
$$-\tilde{\psi}_0(\epsilon')\Big(\sum_n\mathcal{W}_{nr}(\epsilon')\Big)\Big]\Big\}^{-1}\ . \qquad (2.10)$$

The evaluation of the right-hand side of (2.10) requires the evaluation of the expression $\Sigma_n\tilde{\psi}_{r-n}\tilde{\mathcal{W}}_{nr}-\tilde{\psi}_0\Sigma_s\tilde{\mathcal{W}}_{sr}$. We first rewrite $\mathcal{W}$'s in terms of $\mathfrak{a}$'s through

$$\mathfrak{a}_{mn}=-\mathcal{W}_{mn}\quad m\neq n\ , \qquad (2.11a)$$

$$\mathfrak{a}_{mm}=\sum_n\mathcal{W}_{nm}\ , \qquad (2.11b)$$

and use discrete Fourier transforms suggested by the crystal translational invariance. Thus with $\psi^k=\Sigma_m\psi_m e^{ikm}$, etc.,

$$\sum_n\tilde{\psi}_{r-n}(\epsilon)\tilde{\mathcal{W}}_{nr}(\epsilon)-\tilde{\psi}_0(\epsilon)\sum_n\tilde{\mathcal{W}}_{nr}(\epsilon)$$
$$=-\int dk\ \tilde{\mathfrak{a}}^k(\epsilon)[\epsilon+\tilde{\mathfrak{a}}^k(\epsilon)]^{-1} \qquad (2.12)$$

where we have used the result[13] $\tilde{\psi}^k(\epsilon)=[(\epsilon+\tilde{\mathfrak{a}}^k)(2\pi)]^{-1}$ describing the fact that ψ's are solutions of the homogeneous part (2.2) for a localized initial condition. But the right-hand side of (2.12) simplifies immediately to $\epsilon\tilde{\psi}_0(\epsilon)-1$. This result may also be obtained directly from the left-hand side of (2.12) by switching site indices through the use of translational invariance and recognizing from (2.1) that it is just the Laplace transform of $[d\psi_0(t)/dt]$. Equation (2.10) now simplifies to

$$\tilde{P}_r(\epsilon)=\tilde{\eta}_r(\epsilon')\Big\{e^{-\beta\Delta}+\tilde{\psi}_0(\epsilon')\Big[\epsilon'(1-e^{-\beta\Delta})$$
$$+\left(\frac{1}{\tau_G}-\frac{1}{\tau_H}\right)\Big]\Big\}^{-1}\ . \qquad (2.13)$$

For this model, $n_G(t)$, the probability that the guest is excited is given precisely by the Laplace inverse of (2.13) since $P_r(t)$ and $n_G(t)$ are identical. Expressions for the experimental observables will be deduced below from (2.13).

III. GENERAL EXPRESSIONS FOR EXPERIMENTAL OBSERVABLES

The observables are the host and guest luminescence and the host and guest yield. Unlike the latter, the former are time-dependent quantities. Called more specifically the differential photon count rates, they are given, respectively, by

$$\mathcal{J}_H(t)=\frac{1}{\tau_H}n_H(t) \qquad (3.1a)$$

$$\mathcal{J}_G(t)=\frac{1}{\tau_G}n_G(t) \qquad (3.1b)$$

and in principle from the Laplace inversion of expressions such as (2.5) and (2.13). While we have thus reduced the problem of their determination to quadratures (requiring only a Laplace inversion), completely explicit algebraic expressions are available for the quantum yields, which are also more easily accessible experimentally.

The host (and guest) quantum yield, defined, respectively, as the ratio of the number of excitons that come out radiatively from the host (and the guest) to the number initially put into the host through illumination, is given by

$$\phi_H=\frac{1}{\tau_H}\int_0^\infty dt\ n_H(t)=\frac{1}{\tau_H}\tilde{n}_H(0) \qquad (3.2)$$

$$\phi_G=\frac{1}{\tau_G}\int_0^\infty dt\ n_G(t)=\frac{1}{\tau_G}\tilde{n}_G(0)=1-\phi_H \qquad (3.3)$$

and it should be immediately clear that Laplace inversions are not necessary for their evaluation.

Equations (3.2) and (3.3) give us general expressions for the quantum yields ϕ_H and ϕ_G. As these add up to 1 we shall only give expressions for ϕ_G below. In the case of the sink model, we have

$$\phi_G=\left(\frac{\gamma^{\text{eff}}\tau_H}{1+\gamma^{\text{eff}}\tau_H[(1/\tau_H)\psi_0(1/\tau_H)]}\right)\left[\frac{1}{\tau_H}\tilde{\eta}_r\left(\frac{1}{\tau_H}\right)\right]\ , \qquad (3.4)$$

and in the case of the substitutional trap model we obtain, after simplification, the remarkably similar form

$$\phi_G = \left(\frac{(\tau_H/\tau_G)e^{\beta\Delta}}{1+[(\tau_H/\tau_G)e^{\beta\Delta}-1][(1/\tau_H)\tilde{\psi}_0(1/\tau_H)]}\right) \times \left[\frac{1}{\tau_H}\tilde{\eta}_r\left(\frac{1}{\tau_H}\right)\right] . \quad (3.5)$$

We have displayed (3.4) and (3.5) in a manner which will make their similarities and differences immediately apparent. The quantity $\gamma^{\text{eff}}\tau_H$, which equals $\gamma\tau_H$ in the absence of detrapping but is generally given by

$$\gamma^{\text{eff}}\tau_H = \gamma\tau_H(1+\gamma'\tau_G)^{-1} , \quad (3.6)$$

is the trapping parameter of the sink model. Its counterpart in the substitutional trap model is $(\tau_H/\tau_G)e^{\beta\Delta}$. At low temperatures, such that $(\tau_H/\tau_G)e^{\beta\Delta} \gg 1$, the correspondence between (3.4) and (3.5) is perfect. At higher temperatures however we see that while $\gamma^{\text{eff}}\tau_H$ appears both in the numerator and the denominator in (3.4), $(\tau_H/\tau_G)e^{\beta\Delta}-1$ appears in the denominator of (3.5).

The analogy between the results for the two models may be appreciated further if we write in (3.6), the detrapping rate γ' as related to the trapping rate through detailed balance, i.e., $\gamma' = \gamma e^{-\beta\Delta}$. Then, if $\gamma'\tau_G \gg 1$, (3.6) shows that the sink-model parameter $\gamma^{\text{eff}}\tau_H$ *exactly* equals the substitutional trap-model parameter $(\tau_H/\tau_G)e^{\beta\Delta}$.

It should be noted that in (3.4) and (3.5) the motion characteristics are entirely (and only) placed in the quatities $(1/\tau_H)\tilde{\psi}_0(1/\tau_H)$ and $(1/\tau_H)\tilde{\eta}_r(1/\tau_H)$. The latter controls the initial (illumination) condition. For experimentally relevant host excitation the delocalized condition $P_m(0) = 1/N$, where N is the number of sites in the crystal, applies rather well as a result of the k-selection rule. We then obtain from (2.4), (3.4), and (3.5),

$$\phi_G = \rho\left(\frac{\gamma^{\text{eff}}\tau_H}{1+(\gamma^{\text{eff}}\tau_H)[(1/\tau_H)\tilde{\psi}_0(1/\tau_H)]}\right) \quad (3.7)$$

for the sink model, and

$$\phi_G = \rho\left(\frac{(\tau_H/\tau_G)e^{\beta\Delta}}{1+[(\tau_H/\tau_G)e^{\beta\Delta}-1][(1/\tau_H)\tilde{\psi}_0(1/\tau_H)]}\right) \quad (3.8)$$

for the substitutional model. Here $\rho = 1/N$. We have shown elsewhere that while the above results have been obtained for the system with a single trap site, they apply for a system with a low concentration of traps with the replacement of $(1/N)$ by the trap concentration. Thus, henceforth ρ will mean the trap concentration.

For initial excitation of the *trap* rather than the host, $\tilde{\eta}_r(1/\tau_H)$ is replaced by $\tilde{\psi}_0(1/\tau_H)$ in (3.5). In the case of the sink model one has to return to (2.7) because (3.4) explicitly assumes the traps to be initially unexcited. In this paper we shall analyze further only the initial host excitation case.

We emphasize that (3.7) and (3.8) as well as (3.4) and (3.5) are general results, *independent* of the nature of exciton motion within the host. Given the trapping description of Sec. II, the applicability of the generalized master equation, which is always ensured[14] for sufficiently localized *or* delocalized initial conditions, is all that is necessary for the validity of these results. The entire information about exciton transport, including the extent of its coherence, is present in $\tilde{\psi}_0(1/\tau_H)$ for the yields, and generally in $\tilde{\psi}_0(\epsilon)$ for the luminescence intensities. In the next section we evaluate these $\tilde{\psi}_0$'s for a specific model describing unified coherent and incoherent motion.

IV. UNIFIED COHERENT AND INCOHERENT MOTION

Consider a model for the exciton motion wherein the crystal has N sites, obeys periodic boundary conditions, and wherein the motion is described by the density matrix equation

$$\frac{d\rho_{mn}(t)}{dt} = -i\sum_s (J_{ms}\rho_{sn} - J_{ns}\rho_{sm}) - (1-\delta_{m,n})\alpha\rho_{mn} . \quad (4.1)$$

This simple equation describes motion of an arbitrary degree of coherence quite naturally and has appeared in many contexts, within exciton physics[16] as well as outside it. The matrix elements J_{ms} describe coherent flow from site s to site m, and α describes a randomizing rate arising, for instance, from exciton-phonon interactions. The J_{ms}'s satisfy translational invariance. The exact memory functions $w_{mn}(t)$ corresponding to (4.1) have been evaluated by Kenkre.[13,17] Their Laplace transform is [see Eq. (3.14) of Ref. 13]

$$\tilde{w}_{mn}(\epsilon) = -\sum_k \left(e^{-ik(m-n)} \Big/ \sum_q [\epsilon+\alpha+i(J^{k+q}-J^k)]^{-1}\right) . \quad (4.2)$$

If the site labels m, n and the crystal momentum labels k, q, which are both generally vector labels are now taken to be scalars, i.e., if the crystal is assumed to be one dimensional, if it is taken to be infinite in extent, and if the matrix elements J are assumed nearest neighbor in character, (4.2) can be eval-

uated[13,17] as

$$\mathcal{W}_{mn}(t) = 2J^2 e^{-\alpha t}(J^2_{m-n+1} + J^2_{m-n-1} + 2J_{m-n+1}J_{m-n-1} - 2J^2_{m-n} - J_{m-n}J_{m-n+2} - J_{m-n}J_{m-n-2}) \tag{4.3}$$

wherein the J's appearing in the parentheses are Bessel functions of argument $2Jt$.

Equation (4.3), which reduces to the completely coherent limit [given by putting $\alpha = 0$ in (4.1)] and the completely incoherent limit denoted by

$$\mathcal{W}_{mn}(t) = (2J^2/\alpha)\,\delta(t)\,(\delta_{m,n+1} + \delta_{m,n-1}) \tag{4.4}$$

for extreme values of (J/α) (see Ref. 13 for details), will provide the unified transport description in the rest of the paper. Our starting point is thus (2.2) and (2.8) with (4.3) for the memory functions.

The key quantity for sensitized luminescence calculations is the propagator $\tilde{\psi}_0(\epsilon)$. It has been given by Kenkre[13] in the integral form

$$\tilde{\psi}_0(\epsilon) = (1/2\pi)\int_0^{2\pi} d\theta\{[(\epsilon+\alpha)^2 + 16J^2\sin^2(\theta/2)]^{1/2} - \alpha\}^{-1}. \tag{4.5}$$

We now evaluate it explicitly as

$$\tilde{\psi}_0(\epsilon) = \frac{\alpha}{[(\epsilon^2+2\epsilon\alpha)(\epsilon^2+2\epsilon\alpha+16J^2)]^{1/2}} + \frac{(2/\pi)}{[(\epsilon+\alpha)^2+16J^2]^{1/2}}\,\mathcal{K}(k)$$
$$+ \frac{\alpha^2}{[(\epsilon+\alpha)^2+16J^2]^{1/2}}\,\frac{(2/\pi)}{(\epsilon^2+2\epsilon\alpha+16J^2)^{1/2}}\,\Pi(a^2,k), \tag{4.6}$$

where $a^2 = 16J^2(\epsilon^2 + 2\alpha\epsilon + 16J^2)^{-1}$ and $k = 4J[(\epsilon + \alpha)^2 + 16J^2]^{-1}$ and $\mathcal{K}(k)$ and $\Pi(a^2,k)$ are elliptical integrals of the first and third kinds, respectively, defined through

$$\mathcal{K}(k) = \int_0^1 \frac{dx}{(1-x^2)^{1/2}}\left(\frac{1}{(1-k^2x^2)^{1/2}}\right) \tag{4.7a}$$

$$\Pi(a^2,k) = \int_0^1 \frac{dx}{(1-x^2)^{1/2}}\left(\frac{1}{(1-k^2x^2)^{1/2}}\right)\left(\frac{1}{1-a^2x^2}\right). \tag{4.7b}$$

The evaluation of (4.5) in the form (4.6), carried out in detail elsewhere,[18] has been briefly sketched in the Appendix.

The conjunction of (4.6) with (3.4) and (3.5) in general, and (3.7) and (3.8) in particular, provides an exact calculation of the luminescence observables, particularly quantum yields, for arbitrary degrees of coherence. In Fig. 1 we have plotted the propagator, specifically the quantity $(1/\tau_H)\tilde{\psi}_0(1/\tau_H)$ as a function of the (in) coherence parameter (α/J). The significance of that quantity is that its *reciprocal* is a rate describing the exciton motion and equals the guest yield ϕ_G (per concentration ρ) for the case when the trapping rate $\gamma^{\text{eff}}\tau_H$[or $e^{\beta\Delta}(\tau_H/\tau_G)$] is much larger than this motion rate. Each one of the curves in Fig. 1 corresponds to a fixed $J\tau_H$. This figure is thus useful in deducing quantitatively the extent of coherence from yield observations if J is known, for instance, from band calculations or splittings in optical spectra. Note that all curves rise to the value one on the right for sufficiently large values of α/J. This may not be directly apparent from the figure. We also notice from Fig. 1 that for a given J the greater the amount of coherence, the greater the transfer to the traps. In Fig. 2 we have plotted the quantum yield ϕ_G (per concentration ρ) and for each one of the curves have held (J^2/α) constant. Since the latter is proportional to the diffusion constant, we see that the neglect of coherence which corresponds to the limit $(\alpha/J)\to\infty$ in Fig. 2 always leads to an *underestimation* of the diffusion constant.

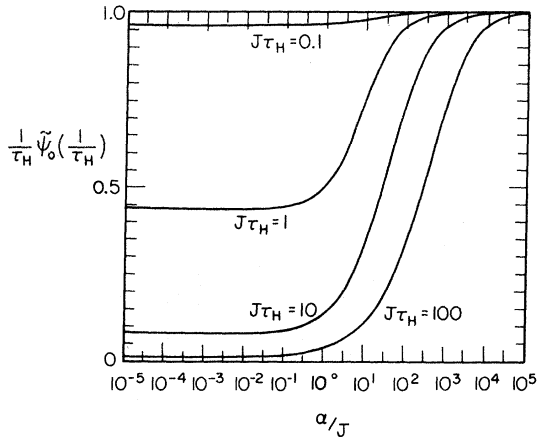

FIG. 1. Effect of coherence on the guest quantum yield. The dimensionless "inverse motion rate" $(1/\tau_H)\tilde{\psi}_0(1/\tau_H)$ which when small with respect to the trapping rate equals the reciprocal of the guest yield per guest concentration is plotted versus the (in) coherence parameter (α/J) for several values of $J\tau_H$ as shown.

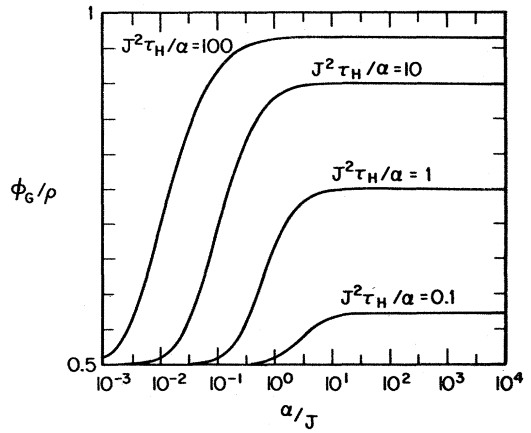

FIG. 2. Effect of coherence on yield and underestimation of the diffusion constant. The guest yield ϕ_G per guest concentration for an arbitrary trapping parameter $\gamma\tau_H=1$ plotted versus the (in) coherence parameter (α/J) for several values of $(J^2/\alpha)\tau_H$ as shown.

We now analyze the exact propagator (4.6) in various limits. We shall use the following results:

$$\lim_{k\to 0} \mathcal{K}(k) = (\pi/2)[1+(k^2/4)], \tag{4.8a}$$

$$\lim_{k\to 1} \mathcal{K}(k) = \ln[4(1-k^2)^{-1/2}], \tag{4.8b}$$

$$\lim_{k\to 0;a^2\to 0} \Pi(a^2,k) = (\pi/2)[1+(k^2/4)+(a^2/2)], \tag{4.8c}$$

$$\lim_{k\to 0} \Pi(a^2,k) = (\pi/2)[1+(k^2/2a^2)](1-a^2)^{1/2}, \tag{4.8d}$$

$$\lim_{k\to 1;a^2\to 1} \Pi(a^2,k) = (\pi/4)(1-k^2a^2)(1-a^2)^{-1/2}(1-k^2)^{-3/2}. \tag{4.8e}$$

The extreme incoherent case corresponds to the case (4.4) of (4.3), modified Bessel functions appear in the propagator in the time domain and the expression

$$(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = (1+4F\tau_H)^{-1/2} \tag{4.9}$$

is obtained. The recovery of (4.9) from (4.6) is immediate. The second term in (4.6) tends to zero and the use of (4.8d) leads to (4.9) with the identification of $2J^2/\alpha$ as the transfer rate F.

The extreme coherent limit corresponding to the transport equation

$$\frac{dC_m}{dt} = -iJ(C_{m+1}+C_{m-1}) \tag{4.10}$$

for the *amplitudes* C_m, has the propagator $J_m^2(2Jt)$ (for probabilities) and leads to

$$(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = \frac{(2/\pi)}{(1+16J^2\tau_H^2)^{1/2}}\mathcal{K}\left(\frac{4J\tau_H}{(1+16J^2\tau_H^2)^{1/2}}\right). \tag{4.11}$$

The recovery of (4.11) from the general expression (4.6) is also immediate since in the limit $\alpha\to 0$, the first and third terms in (4.6) merely drop out.

In both the coherent and incoherent cases above, one may further ask whether the motion is very fast or very slow with respect to the radiative decay. In the coherent case these limits correspond, respectively, to $F\tau_H \gg 1$ and $F\tau_H \ll 1$ and lead from (4.9), to

$$(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = 1/(2\sqrt{F\tau_H}) \tag{4.12a}$$

$$(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = 1-2F\tau_H. \tag{4.12b}$$

In the coherent case they are represented by $J\tau_H \gg 1$ and $J\tau_H \ll 1$ and lead from (4.11), (4.8a), and (4.8b) to

$$(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = [(2/\pi)(1+16J^2\tau_H^2)^{-1/2}] \times \ln[4(1+16J^2\tau_H^2)^{1/2}] \tag{4.13a}$$

$$(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = (1+16J^2\tau_H^2)^{-1/2}. \tag{4.13b}$$

Notice that although we could have simplified the right side of (4.13b) to $1-8J^2\tau_H^2$, we have retained the original form to emphasize its remarkable similarity to the general incoherent case (4.9). Other limiting cases are shown for the sake of completeness and the event that the corresponding values of $J\tau$ and $\alpha\tau$ become relevant for future experiments:

Case (a): for $1 \ll \alpha\tau_H \ll J\tau_H$;

$$(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = [(3/8\sqrt{2})(\sqrt{\alpha\tau_H})/J\tau_H] + (1/2\pi)(1/J\tau_H)\ln 16J\tau_H/\alpha\tau_H \tag{4.14a}$$

which further reduces to $(3/8\sqrt{2})(\sqrt{\alpha\tau_H})/J\tau_H$ for extremely large values of $J\tau_H$.

Case (b): for $\alpha\tau_H \ll 1 \ll J\tau_H$,

$$\frac{1}{\tau_H}\tilde{\psi}_0(1/\tau_H) = (1/4\pi J\tau_H)\ln(16J\tau_H). \tag{4.14b}$$

Case (c): for $1 < J\tau_H < J^2\tau_H^2 < \alpha\tau_H$,

$$\frac{1}{\tau_H}\tilde{\psi}_0(1/\tau_H) = 1-\left(\frac{4J^2}{\alpha}\right)\tau_H \tag{4.14c}$$

which should be compared with (4.12b).

Case (d): for $1 < J\tau_H < \alpha\tau_H < J^2\tau_H^2$,

$$(1/\tau_H)\tilde{\psi}_0(1/\tau_H) = (1/2\sqrt{2})(\sqrt{\alpha\tau_H}/J\tau_H). \tag{4.14d}$$

V. DISCUSSION

As stated in the Introduction, this paper addresses a specific observable in sensitized luminescence which is generally affected by the nature of exciton motion in molecular crystals. This observable is the (host or guest) quantum yield.

In terms of our theory it is given by (3.3)–(3.5) under general conditions and by (3.7) and (3.8) under spatially homogeneous initial illumination of the host. These expressions, and indeed our entire analysis, are valid for trap concentrations that are not too large and this is explicitly clear in the linear dependence on the concentration shown in (3.7) and (3.8).

The trapping process has been described in our theory through the use of two different models which we have called the "sink model" and the "substitutional trap model." In the former the key trapping quantity is the trapping rate γ or more generally the effective trapping rate γ^{eff}, whereas in the latter it is the energy difference Δ. It is remarkable that the two models result in almost identical expressions for the observable yields.

In both models the effect of exciton motion is manifest only in, and entirely in, the propagator $\tilde{\psi}_0(1/\tau_H)$. This quantity is actually the Laplace transform of the probability of occupation of an initially wholly occupied site of the trapless crystal, evaluated by equating the Laplace variable to the reciprocal of the radiative lifetime of the host. It equals the effective energy-transfer rate under the conditions of infinitely fast trapping. Stated differently, $(1/\tau_H)\tilde{\psi}_0(1/\tau_H)$ equals the reciprocal of the guest yield per concentration under the limit that $\tilde{\psi}_0(1/\tau_H)$ is small with respect to the trapping rate.

It is worth observing that almost no restriction is placed on the motion of the exciton in arriving at these results. It may be coherent or incoherent, one, two, or three dimensional, characteristic of this or that lattice structure. The generalized master equation that the analysis assumes is valid under an extremely large class of conditions.[14] In future publications propagators particular to various lattice structures and coherence conditions will be used in the analysis of experimental data such as those in Refs. 3, 6, and 7. Here we have illustrated our theory by the unified description of coherent and incoherent motion in one dimension given in Sec. IV. Equation (4.6) for the propagator when substituted in (3.3)–(3.8) gives the yields for an arbitrary degree of coherence, (4.9) and (4.11) representing the respective incoherent and coherent limits. Figure 1 brings out the effect of coherence graphically and Fig. 2 establishes the important result that the neglect of coherence in interpreting data leads to an underestimation of the diffusion constant of excitons. Similarly it can be shown that assuming the trapping rate to be infinite which underlies the use[3] of the Chandrasekhar-Smoluchowski[19] theory in the present problem also leads to an *underestimation* of the diffusion constant.

In addition to the application of this theory to quantum yield experiments and of the expressions derived for the differential photon count rates to the time-dependent experiments, there are several theoretical problems that remain to be tackled along the lines of this paper. They are (i) clarification of the relation of this approach to that of Huber,[10] including in particular the simultaneous analysis of coherence and randomness,[20] (ii) clarification of the relation of this approach to our k-space approach[8] and the construction of a unified k-space and real-space formalism as was done for dimers by Rahman *et al.*[21] in the context of fluorescence depolarization, and (iii) analysis of the temperature dependence of the observables on the basis of microscopic calculations of transfer rates F and trapping rates γ, perhaps as in the analysis of Fayer and Harris[7] or of Craig and Dissado.[22]

In closing we point out that this is one in a series of papers devoted to the elucidation of how *observable* coherence effects may be analyzed in terms of generalized master equations. The others in this series have treated effects of exciton coherence on annihilation,[11] and transient grating observations.[23]

ACKNOWLEDGMENTS

One of us (V.M.K.) thanks Professor H. Haken and Professor P. Reineker for their hospitality, respectively, in the University of Stuttgart and the University of Ulm, and acknowledges the award of a visiting professorship by the Deutsches Forschungsgemeinschaft. He also thanks Professor D. Schmid for helpful conservations. This work was supported in part by the National Science Foundation Grant No. DMR7919539.

APPENDIX: EVALUATION OF THE PROPAGATOR

The denominator of (3.4) can be rationalized, i.e.,

$$\tilde{\psi}_0(\epsilon) = \int_0^{2\pi} \frac{dk}{2\pi}\left(\frac{\alpha}{\epsilon^2 + 2\epsilon\alpha + 16J^2\sin^2(k/2)}\right) + \int_0^{2\pi} \frac{dk}{2\pi}\left(\frac{[(\epsilon+\alpha)^2 + 16J^2\sin^2(k/2)]^{1/2}}{\epsilon^2 + 2\epsilon\alpha + 16J^2\sin^2(k/2)}\right). \tag{A1}$$

The first term is just $\alpha[(\epsilon^2 + 2\epsilon\alpha)(\epsilon^2 + 2\epsilon\alpha + 16J^2)]^{-1/2}$ if one makes use of the identity

$$\int \frac{dx}{2\pi}\,\frac{1}{C + D\cos x} = \frac{1}{(C^2 - D^2)^{1/2}} \text{ for } C^2 > D^2.$$

To evaluate the second term on the right-hand

side, one makes a sequence of change of variables to obtain the following expression:

$$\frac{1}{4J}\,\frac{2}{\pi}\int_0^{\pi/2} dk\,\frac{(A^2-\cos^2 k)^{1/2}}{B^2-\cos^2 k}\,, \tag{A2a}$$

where

$$A^2 \equiv \frac{(\epsilon+\alpha)^2+16J^2}{16J^2} > \frac{\epsilon^2+2\alpha\epsilon+16J^2}{16J^2} \equiv B^2 > 1\,. \tag{A2b}$$

After another change of variables, viz., $x=\cos k$, (A2a) becomes

$$\frac{1}{4J}\,\frac{2}{\pi}\left((A^2-B^2)\int_0^1 \frac{dx}{(1-x^2)^{1/2}}\,\frac{1}{(A^2-x^2)^{1/2}}\,\frac{1}{B^2-x^2} + \int_0^1 \frac{dx}{(1-x^2)^{1/2}}\,\frac{1}{(A^2-x^2)^{1/2}}\right). \tag{A3}$$

The second term is $k\,\mathcal{K}(k)$ if one defines $k\equiv 1/A$ and uses the definition of (k), the complete elliptic integral of the first kind. The first term is

$$\frac{4J\alpha^2}{[(\epsilon+\alpha)^2+16J^2]^{1/2}}\,\frac{1}{\epsilon^2+2\epsilon\alpha+16J^2} \times \Pi\left(\frac{16J^2}{\epsilon^2+2\epsilon\alpha+16J^2}, \frac{4J}{[(\epsilon+\alpha)^2+16J^2]^{1/2}}\right) \tag{A4}$$

where $\Pi(a^2,k)$ is the complete elliptic integral of the third kind. Putting the above results together, one finally obtains the desired expression (3.5) in the text.

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