Theory of exciton migration experiments with imperfectly absorbing end detectors

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Experiments wherein excitons created at one end of a crystal through illumination are detected at the other end through capture and subsequent radiative emission by a detector layer have been often used to determine the diffusion constant of excitons. However, reported values span several orders of magnitude for similar or even identical systems. A theory of exciton migration which addresses this issue is constructed on the basis of an exact model calculation. It results in a possible explanation of the experimental situation in terms of the observation that the detectors are not perfect absorbers of excitons. We also indicate the effect of transport coherence on these experiments.

I. INTRODUCTION

The values of the diffusion constant of singlet excitons in aromatic crystals at room temperatures reported by experimentalists in the last thirty years span several orders of magnitude.[1] The systems on which the experiments were performed are very similar, and in some cases identical. Evidently this is a very unsatisfactory state of affairs and it is imperative that attempts be made to understand the source of the enormous disparity. This paper contains such an attempt based on what we believe to be a careful first-principles theoretical analysis of exciton kinematics.

We introduce the basic experimental situation and its usual[2] analysis below, state our model and give its exact solution in Sec. II, obtain the results of the earlier analysis[2] in Sec. III as a limit of our result, explain the novel features of our theory including a discussion of how it could explain the disparity in the value of the diffusion constant in Sec. IV, and summarize our findings in Sec. V.

Simpson[2] was the first among a group of experimentalists who deduced the diffusion length and hence the diffusion constant of excitons in aromatic crystals on the basis of what we shall call direct migration observations. The experiment consisted of illuminating one side of the crystal by light and detecting the excitons thus created with the help of a coating of guest molecules placed at the other side. Simpson used anthracene as host and naphthacene for the detector coating. The latter emits with a characteristic frequency different from that of the anthracene host molecules. A study of the quantum yield led to values of the diffusion constant. Simpson's analysis was based on the steady-state solution of the usual continuum diffusion equation satisfied by the exciton population $n(x,t)$, i.e.,

$$\frac{\partial n(x,t)}{\partial t} = -\frac{n}{\tau_H} + D\frac{\partial^2 n}{\partial x^2} + kIe^{-kx}, \tag{1.1}$$

where I is the incident photon intensity, τ_H is the radiative lifetime of the exciton, D is the diffusion constant, and k is the absorption coefficient. By imposing the obvious boundary condition that no transport of excitons occurs across the illuminated surface and an assumption that the detector is a perfect absorber for excitons, he obtained the following expression for the exciton flux S which is defined as $-D\partial n/\partial x\big|_{x=L}$ (where L is the length of the sample):

$$S = I\frac{k^2 l_D^2}{k^2 l_D^2 - 1}\left[\operatorname{sech}\left(\frac{L}{l_D}\right) - e^{-kL}\left(1 + \frac{\tanh(L/l_D)}{kl_D}\right)\right], \tag{1.2}$$

where $l_D \equiv \sqrt{D\tau_H}$. By performing an appropriate subtraction of the background signal due to the direct transmission of light from the experimental flux, and by fitting (1.2) to the S thus obtained, the diffusion length l_D was found to be 460 Å at room temperature. Here the value of kl_D was treated as a parameter in the process of fitting. From its value obtained from the best fit and from k taken from other independent measurements, l_D was determined. As τ_H was well known, the diffusion constant was evaluated.

The experiment was repeated by Kurik[3] for the same system but at two different temperatures (300 and 77 K). The same analysis was performed. The results l_D (300 K) = 1300 Å and l_D (77 K) = 900 Å were stated to be consistent with those of Simpson and any discernible discrepancies were attributed to the use of a thinner host crystal which, it was assumed, avoided reabsorption. The change of the diffusion length l_D with respect to the temperature variation is generally believed to be due to the temperature dependence of the overlap integral which, in principle, determines the Förster-Dexter transfer rate and hence the

diffusion constant.

On the basis of their observation of the existence of a temperature-dependent probability of energy transfer from host to trap per unit concentration of trap for different types of guest molecules in the same host crystal, Tomura and Takahashi[4] have suggested that the specific detector used by Simpson[2] and Kurik[3] may not have been a *perfect* absorber. Therefore, any estimation of the diffusion length based on this perfect-absorber hypothesis would inevitably *underestimate* the diffusion length. This idea is supported by their drift-time measurement in which the relative time shift between the exciting light pulse and the emission pulse from the guest molecules was measured. By employing perylene as a detector, which is believed to be a better absorber than naphthalene, they actually obtained a value for the diffusion length ($l_D = 3800$ Å) which is much larger than the one obtained by Simpson ($l_D = 460$ Å).

The analysis that we give in the next section has, as its natural consequence, the above-mentioned feature, viz., the dependence of the value of D on the nature of the detector used in the experiment. It therefore contains a natural possible explanation of the disparity in the reported values of D.

II. MODEL AND SOLUTION FOR THE QUANTUM YIELD

The experimental setup suggests that we consider a one-dimensional crystal with N lattice sites, a guest site being appended to it at one of its ends. If the length of the crystal used (the distance between the illuminated side and the detector side) is L and a is the intersite distance, then $N = L/a$. The assumption of a one-dimensional crystal is hardly a restriction and corresponds to the experimental situation since the relevant motion is in a single dimension.

We first assume the dynamics to be incoherent, i.e., to be described by a Master equation for the probabilities. This assumption will allow us to make contact with Simpson's expression (1.2). In Sec. III we shall mention how to generalize the analysis to treat coherent motion of the exciton.

The transport equation for the probability $P'_m(t)$ that the exciton is at the mth site, is thus

$$\frac{dP'_1}{dt} = -\frac{1}{\tau_H} P'_1 + F(P'_2 - P'_1), \tag{2.1a}$$

$$\frac{dP'_m}{dt} = -\frac{1}{\tau_H} P'_m + F(P'_{m+1} + P'_{m-1} - 2P'_m) \quad (N-1 \geq m \geq 2), \tag{2.1b}$$

$$\frac{dP'_N}{dt} = -\frac{1}{\tau_H} P'_N + FP'_{N-1} + fP'_G - (F + \mathfrak{F})P'_N, \tag{2.1c}$$

$$\frac{dP'_G}{dt} = -\frac{1}{\tau_G} P'_G + \mathfrak{F} P'_N - fP'_G \tag{2.1d}$$

where the label G denotes the detector or guest, F is the intersite transfer rate in the host crystal taken to be nearest-neighbor character for simplicity, $\mathfrak{F}$ is the host-to-detector rate, and f is the detector-to-host rate. We specifically allow $\mathfrak{F} \neq F$ and $\tau_H \neq \tau_G$. Introducing quantities $x(t) \equiv x'(t)e^{t/\tau_H}$, (2.1) becomes

$$\frac{dP_1}{dt} = F(P_2 - P_1), \tag{2.2a}$$

$$\frac{dP_m}{dt} = F(P_{m+1} + P_{m-1} - 2P_m) \quad (N-1 \geq m \geq 2), \tag{2.2b}$$

$$\frac{dP_N}{dt} = F(P_{N-1} - P_N) + fP_G - \mathfrak{F} P_N, \tag{2.2c}$$

$$\frac{dP_G}{dt} = \mathfrak{F} P_N - \left(f + \frac{1}{\tau_G} - \frac{1}{\tau_H}\right) P_G. \tag{2.2d}$$

From (2.2d) one has, with ϵ as the Laplace variable and tildes denoting Laplace transforms, a relation between the detector probability and P_N:

$$\tilde{P}_G(\epsilon) = \frac{\mathfrak{F}}{\epsilon + f + (1/\tau_G - 1/\tau_H)} \tilde{P}_N. \tag{2.3}$$

Using (2.3) and (2.2c) we obtain

$$\frac{dP_1}{dt} = F(P_2 - P_1), \tag{2.4a}$$

$$\frac{dP_m}{dt} = F(P_{m+1} + P_{m-1} - 2P_m) \quad (N-1 \geq m \geq 2), \tag{2.4b}$$

$$\frac{dP_N}{dt} = F(P_{N-1} - P_N) + \mathfrak{F} f \int_0^t dt' e^{-(f+1/\tau_G - 1/\tau_H)(t-t')} \times P_N(t') - \mathfrak{F} P_N(t). \tag{2.4c}$$

We have eliminated the detector probability exactly in going from (2.3) to (2.4). The latter is immediately solved as

$$\tilde{P}_m(\epsilon) = \sum_{n=1}^{N} \tilde{\psi}_{mn} P_n(0) - \mathfrak{F} \tilde{\psi}_{mN} \frac{\epsilon + (1/\tau_G - 1/\tau_H)}{\epsilon + f + (1/\tau_G - 1/\tau_H)} \tilde{P}_N, \tag{2.5}$$

where $\psi_{mn}(t)$ is the propagator for the nonradiative open chain, i.e., the solution for $P_m(t)$ for the system without the detector and without radiative decay and for the initial condition $P_l(0) = \delta_{l,n}$. Equation (2.5) leads to

$$\tilde{P}_N = \frac{1}{1+\dfrac{\epsilon+(1/\tau_G-1/\tau_H)}{\epsilon+f+(1/\tau_G-1/\tau_H)}\,\mathfrak{F}\tilde{\psi}_{NN}}\sum_{n=1}^{N}\tilde{\psi}_{Nn}P_n(0) \tag{2.6}$$

for the probability of occupation of the end site of the host in the presence of the detector and of radiative decay. With (2.3) we then have

$$\tilde{P}_G = \frac{\mathfrak{F}}{\epsilon+f+(1/\tau_G-1/\tau_H)+[\epsilon+(1/\tau_G-1/\tau_H)]\mathfrak{F}\tilde{\psi}_{NN}}\sum_{n=1}^{N}\tilde{\psi}_{Nn}P_n(0)\,. \tag{2.7}$$

The inverse Laplace transform of (2.7) gives, when multiplied by e^{-t/τ_H}, the probability that the detector is excited. The probability that the host is excited is given similarly by multiplying by e^{-t/τ_H}, the inverse transform of $\tilde{n}_H(\epsilon)\equiv\sum_m\tilde{P}_m(\epsilon)$, i.e., of

$$\tilde{n}_H(\epsilon) = \frac{1}{\epsilon} - \frac{\epsilon+1/\tau_G-1/\tau_H}{\epsilon}\,\frac{\mathfrak{F}}{\epsilon+f+(1/\tau_G-1/\tau_H)+[\epsilon+(1/\tau_G-1/\tau_H)]\mathfrak{F}\tilde{\psi}_{NN}}\sum_{n=1}^{N}\tilde{\psi}_{Nn}P_n(0)\,. \tag{2.8}$$

Finally, the most easily accessible experimental quantity, viz., the quantum yield, is obtained directly, without Laplace inverse transformations from (2.7) and (2.8). Thus the guest quantum yield, defined as the ratio of the number of excitons that emerges radiatively from the detector to that put into the host through initial illumination, is

$$\phi_G = \int_0^\infty dt\,\frac{1}{\tau_G}P'_G(t) = \int_0^\infty dt\,\frac{1}{\tau_G}P_G(t)e^{-t/\tau_H} = \left(\frac{\mathfrak{F}}{1+f\tau_G+\mathfrak{F}\tilde{\psi}_{NN}(1/\tau_H)}\right)\sum_{n=1}^{N}\tilde{\psi}_{Nn}\left(\frac{1}{\tau_H}\right)P_n(0)\,. \tag{2.9}$$

The first equality in (2.9) comes from (2.1d), the second from the transformation that allows the passage from (2.1) and (2.2), and the third from the recognition of the expression as a Laplace transform and from (2.7). A similar equation may be written for the similarly defined host quantum yield ϕ_H. It is easy to verify that

$$\phi_H = \int_0^\infty dt\,\frac{1}{\tau_H}n'_H(t) = 1-\phi_G\,. \tag{2.10}$$

III. EXPLICIT EXPRESSIONS AND THE CONTINUUM LIMIT

To evaluate the observables such as (2.9) we require the initial condition $P_n(0)$ and the propagators $\psi_{mn}(t)$. The latter are found in the analysis of Lakatos-Lindenberg *et al.*[5] With the definition of ξ',

$$\cosh\xi' = 1+\frac{\epsilon}{2F}\,, \tag{3.1}$$

they are given by

$$\tilde{\psi}_{mn}(\epsilon) = \frac{1}{F}\,\frac{\{\cosh[(\xi'/2)(2N-|m+n-1|-|m-n|)]\}\{\cosh[(\xi/2)(|m+n-1|-|m-n|)]\}}{(\sinh\xi')(\sinh N\xi')}\,. \tag{3.2}$$

The initial condition relevant to the experiment is

$$P_m(0) = \frac{e^{-\kappa(m-1)}}{\sum_{m=1}^{N}e^{-\kappa(m-1)}} = \left(\frac{1-e^{-\kappa}}{1-e^{-\kappa N}}\right)e^{-\kappa(m-1)}\,, \tag{3.3}$$

where κ is a discrete version of the absorption coefficient k in Simpson's analysis. We have evaluated ϕ_G of (2.9) in terms of (3.2) and (3.3) in the Appendix. We obtain

$$\phi_G = \frac{\dfrac{\mathfrak{F}}{F}\,\dfrac{\cosh(\xi/2)}{(\sinh\xi)(\sinh N\xi)}}{1+f\tau_G+\dfrac{\mathfrak{F}}{F}\,\dfrac{(\cosh\xi/2)\{\cosh[(\xi/2)(2N-1)]\}}{(\sinh\xi)(\sinh N\xi)}}\left(\frac{1}{2}\,\frac{1-e^{-\kappa}}{1-e^{-\kappa N}}\right)\left(\frac{e^{\xi/2}(1-e^{-N(\kappa-\xi)})}{1-e^{-(\kappa-\xi)}}+\frac{e^{-\xi/2}(1-e^{-N(\kappa+\xi)})}{1-e^{-(\kappa+\xi)}}\right). \tag{3.4}$$

Equation (3.4) is one of the primary results of this paper. Notice that it involves ξ rather than the quantity ξ' defined in (3.1). The former is obtained by replacing ϵ by $1/\tau_H$ in (3.1).

The exact result (3.4) for the observable ϕ_G is obviously more accurate than expressions obtained by approximating the host crystal by a continuum and using an equation such as (1.1) for describing

exciton motion. However, to make contact with traditionally used expressions,[2-4] the continuum limit of (3.4) must be taken. This limiting procedure is straightforward: we let the lattice constant a tend to zero and define the following quantities:

$$\lim_{a\to 0} Fa^2 = D\,, \tag{3.5a}$$

$$\lim_{a\to 0} \mathfrak{F}a = \mathfrak{D}\,. \tag{3.5b}$$

$$\lim_{a\to 0} \kappa/a = k\,, \tag{3.5c}$$

$$\lim_{a\to 0} P_n(0)/a = p(x,0)\,, \tag{3.5d}$$

$$\lim_{a\to 0} Na = L\,. \tag{3.5e}$$

Note that κ tends to zero, N and $\mathfrak{F}$ tend to infinity as fast as $1/a$, but F tends to infinity as $1/a^2$. We now have

$$p(x,0) = \frac{k}{1-e^{-kL}}\, e^{-kx} \tag{3.6}$$

from (3.5) and (3.3). Equation (3.1) and the definition of ξ show that, since $F\to\infty$, we may replace $\cosh\xi$ by $[1+(\xi^2/2)]$ which gives

$$\xi = (F\tau_H)^{-1/2}\,. \tag{3.7}$$

We also can replace $\sinh\xi$ by ξ and finally obtain, as the continuum limit of (3.4),

$$\phi_G = \frac{1}{\dfrac{1+f\tau_G}{\mathfrak{D}\tau_H} + \dfrac{1}{l_D\tanh(L/l_D)}} \times\left(\frac{k}{1-e^{-kL}}\,\frac{1}{l_D}\,\frac{1}{\sinh(L/l_D)}\,\frac{l_D^2}{k^2-l_D^2} \times\left\{k - e^{-kL}\left[k\cosh\left(\frac{L}{l_D}\right)+\frac{1}{l_D}\sinh\left(\frac{L}{l_D}\right)\right]\right\}\right). \tag{3.8}$$

Note here that L is the length of the crystal, l_D is the usual diffusion length $\sqrt{D\tau_H}$, and $\mathfrak{D}$ is a trapping parameter of the dimensions of cm/sec^{-1}. The fact that of the three rates f, $\mathfrak{F}$, and F, the detrapping rate f remains finite, the trapping rate $\mathfrak{F}$ goes to infinity as $1/a$, and the motion rate F goes to infinity as $1/a^2$, should not be surprising. The rate f describes loss of excitons from the entire detector, the rate $\mathfrak{F}$ describes such a loss from $(1/N)$ of the host crystal, and the rate F controls a second derivative in space.

Our continuum result (3.8) is not identical to earlier results[2-4] because we have not assumed that f is zero and $\mathfrak{D}$ is infinite. If we make those restrictive assumptions or equivalently assume that $(1+f\tau_G)\ll\mathfrak{D}\tau_H$, the recovery of (1.2) from (3.8) is immediate:

$$\phi_G(\mathfrak{D}\to\infty) = \frac{k^2l_D^2}{k^2l_D^2-1}\left[\operatorname{sech}\left(\frac{L}{l_D}\right) - e^{-kL}\left(1+\frac{\tanh(L/l_D)}{kl_D}\right)\right] \times\frac{1}{1-e^{-kL}}\,. \tag{3.9}$$

Equation (3.9) is nothing other than (1.2). For the factor $(1-e^{-kL})^{-1}$ in (3.9) arises from the normalization and corresponds to I in (1.2) and the flux S and the yield ϕ_G are essentially identical to each other. With the help of (3.9) we can write (3.8) as

$$\phi_G = \left[1+\left(\frac{1+f\tau_G}{\mathfrak{D}\tau_H}\right)l_D\tanh\left(\frac{L}{l_D}\right)\right]^{-1}\phi_G(\mathfrak{D}\to\infty)\,. \tag{3.10}$$

IV. POSSIBLE EXPLANATION OF SPREAD IN OBSERVED VALUES OF D

In Eq. (3.12) we have a possible explanation of the large spread in the reported values of the diffusion constant. The assumption that the detector is a perfect absorber which underlies the previous analysis,[2] corresponds to approximating the right-hand side of (3.10) by that of (3.11) through the neglect of $(1+f\tau_G/\mathfrak{D}\tau_H)$. It might be valid in some situations to put the detrapping rate f equal to zero on the grounds of detailed balance and a sizable energy difference between the host and detector states. However, a vanishing f does *not* mean that we have a perfect absorber. It is $\mathfrak{F}\tau_H\to\infty$ that makes the detector a perfect absorber. It will be seen that such an assumption always results in an *underestimation* of the diffusion length l_D or of the diffusion constant D, and that a variation in $\mathfrak{F}$ (or equivalently in $\mathfrak{D}$) corresponding to the use of different detectors, could lead to considerable variation in the reported value of F, D, or l_D. We shall now clarify both these points further.

We return to the exact result (3.4) and reexpress it in the form

$$\phi_G = (\mathfrak{s})\{\operatorname{sech}[\xi(N-1/2)]\}\left(\frac{(\mathfrak{F}/F)}{(\mathfrak{F}/F)+c}\right), \tag{4.1}$$

where c is given by

$$c = \left(\frac{1+f\tau_G}{\sqrt{F\tau}}\right)\left(\frac{\sinh(N\xi)}{\cosh[\xi(N-1/2)]}\right). \tag{4.2}$$

and $\mathfrak{s}$ is the product of the last two factors in (3.4). This $\mathfrak{s}$ describes the initial population of excitons determined by the value of the dimensionless absorption coefficient κ. If the latter is taken to be zero, signifying spatially uniform initial illumination which would hold in a relatively thin sample, one has

$$\lim_{\kappa\to 0}\mathfrak{s} = (1/N)(\sqrt{F\tau})\,[\sinh(N\xi)]\,. \tag{4.3}$$

The opposite limit, which describes excitons

placed completely at one end of the sample, gives

$$\lim_{\kappa\to\infty} \mathcal{G} = \cosh(\xi/2). \tag{4.4}$$

For simplicity, let us consider uniform initial illumination. With (4.3) in (4.1) we then have

$$\phi_G = \phi_G^s \left(\frac{(\mathfrak{F}/F)}{(\mathfrak{F}/F)+c} \right), \tag{4.5}$$

where c is as in (4.2) and the value ϕ_G^s at which ϕ_G saturates for large values of $(\mathfrak{F}/F)$ is given by

$$\phi_G^s = \left(\frac{\sqrt{F\tau}}{N} \right) \left(\frac{\sinh(N\xi)}{\cosh[\xi(N-1/2)]} \right)$$
$$= (1/N) \left[\frac{F\tau}{1+f\tau_G} \right] c \tag{4.6}$$

Equation (4.5) shows that whereas ϕ_G^s would be the yield for a perfect absorber, the actual yield ϕ_G would be smaller for a finite $(\mathfrak{F}/F)$. Conversely, for a given observed value of the yield, the assumption $\mathfrak{F}/F \to \infty$, implicit in the earlier interpretations, results in a lower deduced value for the diffusion constant D, or equivalently, for the transfer rate F. In Fig. 1 we have plotted the yield ϕ_G as a function of $(\mathfrak{F}/F)$, the ratio of the trapping rate to the motion rate, for three different values of F. In units of $1/\tau_H$, the reciprocal of the host radiative lifetime, they are 10^6, 5×10^5, and 10^5, respectively. For $\tau_H = 10^{-8}$ sec and for a lattice distance of $a = 10$ Å, these F's correspond to the range 1 to 10^{-1} cm^2/sec for the diffusion constant. The figure also shows a hypothetical observed detector yield. The previous analysis[2-4] would be based on $\phi_G^s = 0.316$, the asymptotic value of ϕ_G, and would therefore result in the conclusion that the diffusion constant is 0.1 cm^2/sec. However, it is possible that the actual trapping rate $\mathfrak{F}$, far from being infinite, is of the order of F, say $5F$. The true diffusion constant could thus be 1 cm^2/sec rather than 0.1 cm^2/sec. The previous analysis[2-4] would thus indeed result in an underestimated value of the diffusion constant. Also, various detectors would correspond to various points on the $(\mathfrak{F}/F)$ axis in the figure. A disparity in reported values of D would thus result. While we have not yet made estimates of this effect for real crystals because values of $\mathfrak{F}$ are not easily available, the curves in Fig. 1 could correspond to Simpson's experiments. Thus N, the number of sites, has been taken to be 1000 to reflect the fact that the samples used in Ref. 2 were about one micron thick. Also it is to be noted that our present calculation contains the essential feature that *large* changes in the concluded F can occur as a result of the assumption that $\mathfrak{F}/F \to \infty$.

It is instructive to obtain the direct dependence of the interpreted value of the diffusion constant

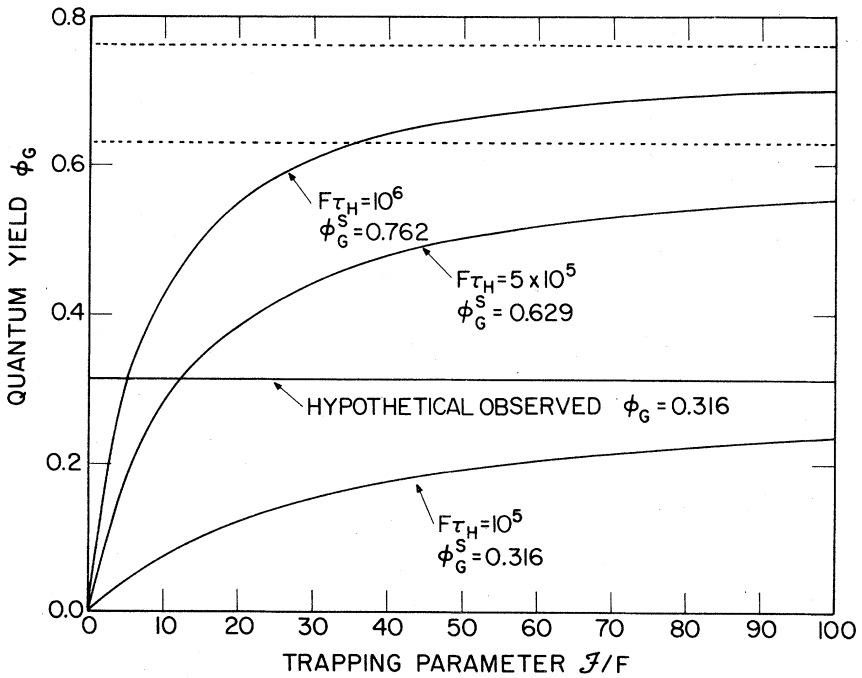

FIG. 1. Quantum yield ϕ_G plotted as a function of the trapping parameter $(\mathfrak{F}/F)$ for three values (10^6, 5×10^5, and 10^5) of $F\tau_H$. Each curve thus corresponds to a given value of the diffusion constant: 1, 0.5, and 0.01 cm^2/sec, respectively. The dotted lines represent the value of ϕ_G for perfect absorbers $(\mathfrak{F}/F \to \infty)$. The solid straight line shows a hypothetical observed $\phi_G = 0.316$. The value of $f\tau_G$ is 10^4. The plots correspond to Eqs. (4.5) and (4.6).

on the trapping rate $\mathfrak{F}$ from (4.5). For simplicity, let us consider $F\tau_H \gg 1$ so that ξ is small enough to approximate $[(\sinh N\xi)/\cosh\xi(N-1/2)]$ by $N\xi$. Equations (4.5) and (4.6) then give

$$\frac{1}{\sqrt{F\tau_H}} = -(1+f\tau_G)\frac{1}{\mathfrak{F}\tau_H} + \frac{1}{N\phi_G}. \tag{4.7}$$

This equation displays a relation between $(1/\sqrt{F\tau_H})$ which equals $(a/\sqrt{D\tau_H})$, the ratio of the lattice distance to the diffusion length, and the reciprocal trapping parameter $(1/\mathfrak{F}\tau_H)$. A plot of (4.7) results in a straight line with intercept $1/N\phi_G$. The intercept corresponds to the earlier interpretations involving $\mathfrak{F}\to\infty$. The slope of the line is proportional to $(1+f\tau_G)$. Whether the dependence of the deduced value of D on the trapping parameter $\mathfrak{F}\tau$ will be significant is thus decided by the detrapping parameter $f\tau_G$. Its value could be very large (e.g., 10^4 as in Fig. 1) even for cases wherein detailed balance and a sizable energy difference between host and detector states makes $f \ll F$ or $f \ll \mathfrak{F}$. Equation (4.7) has an interesting interpretation. Multiplying it by N we see that $1/\phi_G$ equals the sum of two ratios of the length of the sample: one to the diffusion length, and the other to the effective trapping quantity $(\mathfrak{F}a\tau_H/1+f\tau_G)$.

For the sake of completeness we now examine an unrelated effect on these experiments, viz., that of transport coherence. It is possible to show that an approximate description of exciton transport in these systems for a low but nonzero degree of coherence is given by replacing the quantity F by $F\alpha(\epsilon+\alpha)^{-1}$ in the expressions for the Laplace transform of the propagator $\tilde{\psi}_{mn}(\epsilon)$ of (3.2) and all the further consequent expressions. Thus we now have

$$\tilde{\psi}_{mn}(\epsilon) = \left(\frac{\epsilon+\alpha}{\alpha}\right)\frac{\{\cosh[(\xi'/2)(2N-|m+n-1|-|m-n|)]\}\{\cosh[(\xi'/2)(|m+n-1|-|m-n|)]\}}{F[\sinh(\xi')][\sinh(N\xi')]}. \tag{4.8}$$

As a simple example of the consequence of (4.8), note that the diffusion length $l_D = \sqrt{D\tau_H}$ should be replaced by $[D\tau_H(\alpha\tau_H)(1+\alpha\tau_H)^{-1}]^{1/2}$. For complete incoherence $\alpha\to\infty$ and the previous results are recovered. This discussion is equivalent to the replacement of terms such as $FP(t)$ in (2.1) by memory function terms such as $F\alpha\int_0^\infty dt' e^{-\alpha(t-t')} \times P(t')$. The limit $\alpha\to\infty$ makes the memory functions delta functions in time. This prescription is *not* valid for high degrees of coherence because simple exponential memories would lead to negative probabilities[6] for sufficiently low α. The discussion in this paragraph is meant to be no more than an indication of how transport coherence would affect the diffusion constant, and is quantitatively usable only for a low degree of coherence.

V. SUMMARY

We have constructed a theory of exciton transport for direct migration experiments of the kind pioneered by Simpson.[2] Our assumption is that the transport can be described by (2.1). Physically we envisage the excitons moving in the discrete space provided by the lattice sides of the host through transfer rates F, decaying radiatively through a rate $1/\tau_H$, and being captured by the detector at one end through rates $\mathfrak{F}$. A detrapping rate f is also included and it brings in the radiative lifetime τ_G of the detector into the calculated expressions. We calculate the quantum yield of the detector defined through (2.9): our result is (3.4).

Our expression (3.4) or (4.1) for the detector yield and its particular case (4.5) are free of the usually-made approximation wherein the discrete crystal is replaced by a continuum. In interpreting experiment, (3.4) should be used directly. It contains the quantities F, f, $\mathfrak{F}$, $1/\tau_H$, $1/\tau_G$, and κ. It is impossible to determine F, or equivalently the diffusion constant $D = Fa^2$ from these experiments unless the trapping rate $\mathfrak{F}$ is known *a priori*. Yet earlier analyses have attempted precisely such a determination. Their implicit assumption is that $\mathfrak{F}\tau_H \to \infty$. As was pointed out, for instance, by Tomura and Takahashi,[4] this perfect-absorber assumption is definitely suspect. We have shown that it leads to an *underestimation* of F or of the diffusion constant. We have also shown, specifically in Sec. IV and Fig. 1, how values reported for the diffusion constant could arise from the perfect-absorber assumption. It is planned to apply this theory to the reported observations[1-4] in a future publication.

We have shown that (3.8), the continuum limit of our result (3.4), reduces to the Simpson result (1.2) under the perfect-absorber approximation. Thus, if the latter is to be dropped but the continuum approximation is to be made, (3.8) is the result that should be used. We have also indicated how partially coherent exciton transport should be handled.

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APPENDIX

From (3.2) one obtains

$$\tilde{\psi}_{Nn}(\epsilon) = \frac{1}{F}\frac{[\cosh(\xi'/2)\{\cosh[(\xi'/2)(2n-1)]\}}{(\sinh\xi')(\sinh N\xi')} \tag{A1a}$$

and

$$\tilde{\psi}_{NN}(\epsilon) = \frac{1}{F}\frac{[\cosh\xi'/2]\{\cosh[(\xi'/2)(2N-1)]\}}{(\sinh\xi')(\sinh N\xi')} \tag{A1b}$$

as particular cases. Expressing the hyperbolic cosine in terms of exponentials and summing the geometric series, one finds

$$\sum_{n=1}^{N}\cosh[\xi'(n-1/2)]e^{-kn} = \frac{e^{-k}}{2}\left(\frac{e^{\xi'/2}(1-e^{-N(k-\xi')})}{1-e^{-(k-\xi')}} + \frac{e^{-\xi'/2}(1-e^{-N(k+\xi')})}{1-e^{-(k+\xi')}}\right). \tag{A1c}$$

Finally, the substitution of (A1b) and (A1c) in (2.9) leads in a straightforward manner to the exact expression (3.4) for ϕ_G given in the text.

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