# ENERGY TRANSFER FOR SYSTEMS POSSESSING LONG-RANGE RATES OF CAPTURE

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The authors' recent theory of exciton trapping and sensitized luminescence is extended to cover long-range capture processes. Expressions are given for the energy transfer rate $k_s$ and the quantum yield $\varphi_G$, which show the interplay of exciton migration with the strength and range of the capture process.

## 1. Introduction

Sensitized luminescence experiments [1–5] are the primary source of information regarding exciton transport characteristics in organic solids. In a series of recent papers, however, the present authors [6,7] and others [8,9] have argued that serious questions involving the interpretation of exciton trapping data have yet to be entirely resolved. Indeed, such questions have led to the practical consequence that reported values of the exciton diffusion constant, for as well-studied a system as singlet excitons in anthracene, vary by two to three orders of magnitude. Part of the problem, as we have pointed out, is the use of the so-called Smoluchowski prescription $k = 4\pi\rho RD/\mathcal{V}$ for the energy transfer rate, in which $\rho$ is the mole–mole trap concentration, $R$ is a capture radius, $\mathcal{V}$ is the unit cell volume, and $D$ is the exciton diffusion constant. While the use of this expression for the average rate of transfer $k_s$ is, in fact, justified under the conditions for which it was derived, viz., three-dimensional isotropic diffusion, and perfectly absorbing spherical traps of radius $R$, it is not entirely clear how relevant the Smoluchowski rate is for molecular crystals, which are known to possess high degrees of anisotropy, and where little information is generally available regarding either the strength or the range of the interaction responsible for exciton capture.

In a previous publication [6] we have presented a theory of exciton trapping based upon the generalized master equation, that models the capture event as a short-range (e.g. nearest-neighbor) process. In that theory, which allows the treatment of arbitrary degrees of exciton transport coherence, the presence of traps in the crystal causes excitation transfer from neighboring host sites to the trap molecules at a capture rate $c$. One of us [10] has shown how the theory presented in ref. [6] gives the Smoluchowski result in the appropriate limit of incoherent transport in three dimensions with $c \to \infty$, provided that one identifies the capture radius $R$ with the lattice constant, as would be suggested by the model. More generally, however, the theory predicts, in the limit of perfectly absorbing traps, an expression of the form [8,9]

$$k_s = \rho\lambda^3\mathcal{M}/\mathcal{V}, \tag{1}$$

where $\lambda$ is a length on the order of a lattice constant and the quantity $\mathcal{M}$ is a motion rate, defined for low concentrations through the relation

$$\mathcal{M}^{-1} \equiv \int_0^\infty \mathrm{d}t \, \exp(-t/\tau_H)\, \psi_0(t). \tag{2}$$

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Here, $\tau_H$ is the radiative lifetime of the host molecules, and the quantity $\psi_0(t)$ is, in the trap-free crystal, the time-dependent probability for the exciton to be found at the site at which it was initially created. It contains, therefore, information about the manner and rate at which excitation migrates through the unperturbed crystal. When the rate associated with the capture process is not infinite, i.e. for traps of finite strength, one obtain a correct expression from (1) by replacing the constant $\mathcal{W}$ by the quantity $(1/c + 1/\mathcal{W})^{-1}$, which reduces to (1) in the limit $c \to \infty$. This latter form has been used recently [8,9] to address issues concerning the amount of information regarding exciton transport actually obtained in the sensitized luminescence data of several systems.

The theory of ref. [6], although capable of treating arbitrary types of exciton motion (i.e. degrees of transport coherence) and finite capture strengths, does not allow the investigation of changes in the energy transfer rate with changes in the capture radius, i.e. with the *range* of the capture event. It is the range dependence of the trapping process we wish to examine in this Letter. To that end, we consider a specific model in which the trapping rate is uniform, but finite, throughout some radius $R$ surrounding the trap. We then calculate, in a manner analogous to the calculations presented in ref. [6] and for low trap concentrations, the guest quantum yield $\varphi_G$, i.e. that fraction of excitation that becomes trapped during the lifetime of the exciton, and the steady-state energy transfer rate $k_s$, i.e. the average rate at which trapping occurs following initial excitation.

As in ref. [6], the starting point for our analysis is the following generalized master equation for the probabilities $P_m(t)$ of finding the $m$th site in the crystal excited at time $t$:

$$\partial P_m(t)/\partial t + P_m(t)/\tau_H = \int_0^\infty \mathrm{d}\tau \sum_n [\mathcal{W}_{mn}(t-\tau)P_n(\tau) - \mathcal{W}_{nm}(t-\tau)P_m(\tau)] - c \sum_s{}' \delta_{ms} P_m(t). \qquad (3)$$

The memory functions [10] $\mathcal{W}_{mn}(t)$ appearing in (3) contain dynamical information regarding exciton transport and depend on $m$ and $n$ through their difference $|m - n|$ only, due to the translational invariance of the host crystal. The primed summation over the index $s$ includes only those sites in the crystal located within the capture range $R$ of a trap. For notational simplicity, we first outline the calculation for a one-dimensional system and then subsequently indicate the manner in which the results thus obtained become modified for higher dimensions. Consider, therefore, a single trap of capture radius $R = ra$ located at the origin of a one-dimensional chain. We will assume $r$ to be an integer; $a$ is the lattice spacing. Introducing Laplace transforms, we first rewrite (3) in the form [6]

$$P_m(\epsilon) = \eta_m(\epsilon') - c \sum_{s=-r}^{r} \psi_{ms}(\epsilon') P_s(\epsilon), \qquad (4)$$

in which $\epsilon = \epsilon' - 1/\tau_H$ is the Laplace variable; $\psi_{ms}(t)$ is the perfect crystal propagator, i.e. the solution to (3) with $c = 1/\tau_H = 0$, obeying the initial condition $\psi_{ms}(0) = \delta_{ms}$. Again, due to translational invariance, these propagators, like the memory functions, may be expressed as a function of the difference $|m - s|$ only; we therefore write then with a single subscript, $\psi_{ms} = \psi_{m-s}$. The quantity $\eta_m(t)$ is the homogeneous solution for the initial conditions of experimental relevance: $\eta_m(t) = \Sigma_n \psi_{m-n}(t) P_n(0)$. The $2r + 1$ equations that result from (4) with $m = 0, \pm 1, \cdots, \pm r$ constitute a closed set of algebraic equations that may be straightforwardly solved when $r$ is sufficiently small. This becomes increasingly difficult, however, as the range of the capture process increases. We seek therefore an approximation scheme that will allow us to decouple eqs. (4). We proceed as follows: Summing (4) over the trap-influenced host sites we obtain

$$\sum_{s=-r}^{r} P_s(\epsilon) = \sum_{s=-r}^{r} \eta_s(\epsilon') - c \sum_{s=-r}^{r} \xi_s(\epsilon') P_s(\epsilon); \qquad (5)$$

in which we have defined, for $s = 0, \pm 1, \cdots, \pm r$, the quantity $\xi_s(t) \equiv \Sigma_q \psi_{s-q}(t)$, the sum over $q$ running from $-r$ to $r$. Now, as in ref. [6], we make an approximation to the second sum on the right-hand side of (5) and assume that we may replace the quantity $\xi_s$ by its average over $s$, i.e. over the sites within range of the trap. This immediately allows us to obtain an expression for the quantity appearing on the left-hand side of (5), which is just the probability for the trap-influenced host region to be excited:

$$\sum_{s=-r}^{r} P_s(\epsilon) = [1 + c\xi(\epsilon')]^{-1} \sum_{s=-r}^{r} \eta_s(\epsilon'), \qquad (6)$$

where $\xi \equiv (2r + 1)^{-1} \Sigma_s \xi_s$ is the aforementioned

average. Following ref. [6], we thus obtain a low concentration expression for the excited trap probability $n_G(t)$, valid for the initial condition $P_m(0) = 1/N$, where $N$ is the number of host sites in the crystal,

$$n_G(\epsilon) = \frac{\rho(2r+1)}{\epsilon'(\epsilon + 1/\tau_G)[1/c + \xi(\epsilon')]} . \quad (7)$$

The factor of $\rho(2r+1)/\epsilon'$ appearing in (7) comes from the homogeneous solution corresponding to the initial conditions we have considered. We mention in passing, that there are times when it may be more convenient to rewrite (7) in the form

$$n_G(\epsilon) = \frac{\rho}{\epsilon'(\epsilon + 1/\tau_G)[1/C + (2r+1)^{-1}\,\xi(\epsilon')]} , \quad (8)$$

in which we have introduced a renormalized capture strength $C \equiv c/(2r+1)$. By rescaling the capture strength in this way it is possible to examine the effects of capture *range* independently of capture *strength*. There are, in other words, two different ways in which one might compare systems with different capture range. One can keep the rate for a single trap–host pair constant and just increase the number of host sites within range of the trap, i.e. keep $c$ fixed and let $C$ vary with $R$; alternatively, one can require that the total capture rate be the same for the two systems in the absence of exciton transport. The total capture rate for each is the capture rate from one host site to a neighboring trap multiplied by the number of host sites within range of the trap. To make the total rate the same we just scale the capture rates by the volume of the trapping region, or, equivalently, keep $C$ fixed while changing $R$.

From the guest probability (7) we immediately obtain the guest quantum yield $\varphi_G$, since [10]

$$\varphi_G \equiv (1/\tau_G)\int_0^\infty \mathrm{d}t\, n_G(t) = (1/\tau_G)\, n_G(\epsilon = 0) . \quad (9)$$

Hence,

$$\varphi_G = \frac{\rho}{1/(2r+1)c\tau_H + (2r+1)^{-1}(1/\tau_H)\,\xi(1/\tau_H)} . \quad (10)$$

At low concentrations the average rate of transfer $k_s$ will just be the trapped fraction $\varphi_G$ divided by the excitation lifetime $\tau_H$, and hence is trivially obtainable from (10). It should be pointed out that the analysis presented here, as well as that in ref. [6], is valid for times immediately following excitation and gives an adequate description of the decay of the host population $n_H(t)$ out to times such that $n_H(0) \geqslant n_H(t) \geqslant 0.01 n_H(0)$, which is typically the time regime accessible experimentally. The analysis breaks down at extremely long times where, for diffusive motion, the host decay in $d$ dimensions is known [11] to decay with the asymptotic law $n_H(t) \sim \exp(-at^{d/(d+2)})$. This does not present a problem for the present analysis for two reasons. The first is the fact that numerical work [12] has shown that the time $\tau_a$ at which the asymptotic regime typically begins is excessively long compared to times on the order of $k_s^{-1}$ which are of experimental interest: in two dimensions, e.g., $n_H(\tau_a)/n_H(0) \leqslant 10^{-13}$. Moreover, the natural exciton lifetime $\tau_H$ provides an additional cutoff that prevents the asymptotic regime from ever being reached. The average energy transfer rate, the exciton lifetime, and the asymptotic scale, for systems of experimental interest, therefore, satisfy $k_s^{-1} \ll \tau_a, \tau_H \ll \tau_a$, and for this regime the expressions derived here are appropriate. We have, therefore, with the aforementioned comments in mind, obtained expressions for the quantities of interest in terms of the capture strength, the capture range, and the details of exciton motion. In section 2 we discuss some consequences of these results.

## 2. Discussion

As they stand, the results (7)–(10) are applicable to arbitrary types of exciton motion for sufficiently low concentrations of trapping impurities. To make the results more useful, however, we clearly have to investigate the nature of the quantity $\xi(\epsilon)$ appearing in those expressions. To this end, and also to facilitate comparison to more standard treatments, we now restrict ourselves to a discussion of incoherent transfer, in which the generalized master equation (3) reduces to a normal Pauli master equation with delta-function kernels. Consider first the standard limit, viz., that of infinitely fast capture and diffusive transport. In this limit $c \to \infty$, the factor $1/c\tau_H$ goes to zero and the expression for $k_s$ reduced to $\rho(2r+1)/\xi(1/\tau_H)$. While this would appear to resemble the Smoluchowski result, with $\xi(1/\tau_H)$ replacing the motion rate $\mathcal{M}$ obtained earlier, it must be pointed out that the apparently linear dependence on capture range is merely a result of our performing a one-dimensional calculation.

Indeed, to modify (7)–(10) for higher dimensions we must replace the $r$-dependent factor $2r + 1$ by the number of sites within range of a trap, which will go like $(R/a)^d$ in $d$ dimensions. To examine the $R$ dependence of $k_s$, therefore, we must determine the $R$ dependence of $\xi(t)$. From its definition following (6) and (5), it will be seen that this quantity represents the average probability, at time $t$, for the exciton to be found in a region of the pure host crystal the precise size and shape of the trapping region, if it has unit probability of being there at $t = 0$. Moreover, it is the Laplace transform of this quantity that is required in the analysis of the energy transfer rate. For incoherent transport a good estimate of the $R$ dependence of this function may be obtained by considering solutions to the diffusion equation. For example, in $d$ dimensions $\xi(t)$ will behave like the probability for finding a diffusing exciton inside a $d$-sphere of radius $R$, given that it was inside the sphere (e.g. at the origin) at $t = 0$, i.e.

$$\xi(\epsilon) \approx \int \mathrm{d}\Omega \int_0^R \rho^d \, \mathrm{d}\rho \int_0^\infty \mathrm{d}t \times \left( \frac{\exp(-\epsilon t) \exp(-\rho^2/4Dt)}{(2\pi Dt)^{d/2}} \right) . \quad (11)$$

Thus, for the three-dimensional case we find upon performing the integrals,

$$\xi(\epsilon) = (8/\epsilon^2)^{1/2} \left[ 1 - (1 - \alpha R) \exp(-\alpha R) \right] , \quad (12)$$

where $\alpha \equiv (\epsilon/D)^{1/2}$. We are interested in values of the trapping radius which, while large compared to the lattice spacing, are certainly short compared to the distance traveled by the exciton in its lifetime, viz., the diffusion length $L_D = (D\tau_H)^{1/2}$. Thus when (11) is evaluated at $\epsilon = 1/\tau_H$, as is required for the energy transfer rate, the quantity $\alpha R$ appearing in (12) will equal $R/L_D$, which we have assumed to be small. We may therefore expand the exponential and find to lowest order in $R/L_D$ that $\xi(1/\tau_H) \sim R^2/D$. When this is combined with the factor of $R^3$ discussed above we recover the result $k_s \sim \rho\lambda RD/\mathcal{V}$ as found in the standard treatments ($\lambda$ is now a pure numerical constant $\approx 1$). When the capture rate is not infinite, however, the dependence of $k_s$ on $R$ is more complicated, i.e. $k_s = (\rho\lambda RD/\mathcal{V}) \left[ 1 + \lambda D/(cR^2) \right]^{-1}$. Thus, it is when $R \gg (D/c)^{1/2}$, i.e. when the trapping radius is much larger than the distance over which the particle diffuses during the time required for a capture event to take place, that the Smoluchowski result is recovered. We may take this as a definition of "motion-limited" energy transfer. In the opposite limit, i.e. when $R \ll (D/c)^{1/2}$, the energy transfer rate behaves like $\rho c R^3/\mathcal{V}$ which is just the capture rate $c$ times the fraction of host sites that are within the sphere of influence of a trap. It therefore represents "capture-limited" energy transfer.

For dimensions greater than or equal to 3, a calculation along the lines of that given above is possible and one finds that the lowest order (in $R/L_D$) contribution to the integral (11) is independent of $\tau_H$ and leads to

$$k_s = (\lambda\rho R^{d-2} D/\mathcal{V}) \left[ 1 + \lambda D/(cR^2) \right]^{-1} , \quad d \geq 3 , \quad (13)$$

where $\lambda = \lambda(d)$ is a constant related to the volume of the unit sphere in $d$ dimensions, and $\mathcal{V} = a^d$. Note that for dimensions larger than or equal to 3, the region defining motion-limited energy transfer is given by the same relationship, viz., $R \gg (D/c)^{1/2}$. This will not be the case for dimensions less than 3 as we shall see below. In the motion-limited regime the trapping rate becomes, from (13), $k_s = \lambda\rho R^{d-2} D/\mathcal{V}$, while in the opposite limit we obtain $k_s = c\rho R^d/\mathcal{V}$.

For one and two dimensions greater care must be taken in determining the limiting behavior of $k_s$ for small $R/L_D$ since in this case the integrals in (11) diverge as $R/L_D \to 0$. In fact, we do not strictly want to take this limit completely since in order for $R/L_D \to 0$ we must have $\tau_H \to \infty$. This however would violate the previously mentioned inequalities $k_s^{-1}, \tau_H \ll \tau_a$. This is neither a conceptual nor a practical problem, however, since in the first case the known [11] long-time asymptotic behavior of $n_H(t)$ provides a cutoff which makes the average rate of transfer finite and well defined even in the limit $\tau_H \to \infty$, and in the second case we may still obtain an asymptotic expression for $k_s$, valid in the limit $R/L_D \ll 1$, in the regime where the aforementioned inequalities are also satisfied, but now the energy transfer rate will depend, even to lowest order, explicitly on $\tau_H$. The analysis is straightforward, and we find to lowest order in $R/L_D$ that in one dimension $\xi(1/\tau_H) \sim RL_D/\lambda D$ so that

$$k_s = (\rho\lambda D/L_D a)(1 + \lambda D/cRL_D)^{-1} , \quad d = 1 . \quad (14)$$

Notice now that in one dimension the motion-limited regime is defined by the requirement that $Dc^{-1} \ll RL_D$, i.e. that the distance traveled by an exciton

during the time required for a capture event to take place is small compared to the geometric mean of the trapping radius and the diffusion length. In this limit the energy transfer rate becomes equal to the leading factor in (14), which, it will be noted, is independent of $R$. This is not altogether suprising since in this limit the exciton cannot penetrate very far into the sphere of influence of a trap before capture takes place. Thus the actual size of the region is unimportant (provided it is large enough) because the exciton samples only the ends of the linear region in which trapping can occur. In the opposite limit $Dc^{-1} \gg RL_D$, (14) reduces to $\rho cR/a$ which has the same meaning as the corresponding limit in three (or more) dimensions, viz. the capture rate for one site multiplied by the number of sites within the capture radius.

In two dimensions we find from consideration of the integral (11) that, to lowest order in $R/L_D$, $\xi(1/\tau) \sim (R^2/D)\ln(L_D/R)$; hence

$$k_s = \frac{\rho\lambda D[a^2 \ln(L_D/R)]^{-1}}{1 + D[cR^2 \ln(L_D/R)]^{-1}}, \quad d = 2, \qquad (15)$$

which, as with the one-dimensional case, depends upon $\tau_H$. The motion-limited regime is defined in two dimensions by the requirement that $D[R^2 \ln(L_D/R)]^{-1} \ll c$, in which case one obtains $k_s = \rho\lambda D[a^2 \ln(L_D/R)]^{-1}$; and the capture-limited regime by the opposite inequality, whence one obtains $k_s = c\lambda\rho R^2/a^2$.

## 3. Summary

We have obtained expressions for the average rate of energy transfer in systems containing traps which are capable of long-range capture. For incoherently migrating excitons we have obtained the leading range dependence of the energy transfer rate and shown how it varies with dimensionality and with the strength of the capture process. These expressions help to elucidate the precise criteria for the existence of diffusion-limited and capture-limited energy transfer, and indicate how these criteria depend upon dimensionality. For the most part, these results have been obtained through consideration of solutions to the diffusion equation and are, therefore, primarily relevant to incoherent transport. Obtaining similar results for situations where the transport may be coherent over large distances is a considerably more complicated proposition, and one which we will present in a future publication. In principle one proceeds as in the incoherent case by evaluating the probability for an exciton to be found in a volume the size of the trapping region, following an initial placement of the exciton in that region. The process of taking the continuum limit of a microscopically coherent, lattice transport equation, however, is considerably more subtle than that required for the incoherent case. One is, it turns out, effectively, forced to retain the lattice structure, making the evaluation of $\xi(t)$ more difficult. One would expect, however, that considerable differences would arise in the coherent case, since the $R$ dependence of $\xi(t)$ depends critically on the *time* dependence of the underlying dynamics, in particular on the manner in which the exciton leaves or remains in the trapping volume. The dynamical processes underlying coherent transport are known [10] to exhibit markedly different time dependences than those giving rise to incoherent transport and it is expected that these will have a marked effect on the results we have derived above.

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