

THEORY OF THE ENERGY TRANSFER RATE IN SENSITIZED FLUORESCENCE IN MOLECULAR CRYSTALS

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Received 22 May 1978

Based on a Boltzmann-like equation in reciprocal space, a theory is developed to describe sensitized fluorescence in molecular crystals. Fluorescence (or phosphorescence) curves describing light emission from the host crystal as well from the guest traps are obtained in terms of parameters pertaining to the host exciton band. An expression for the energy transfer rate is derived and shown to be time dependent and to have the qualitative features of the experimental rate.

1. Introduction

A typical experiment in the study of sensitized fluorescence in molecular aggregates consists of pulse excitation of the host, such as an anthracene crystal, followed by observation of the time dependence of the emission (fluorescence) from the host as well as from guest molecules, such as tetracene, introduced into the host. Such studies have been reviewed, for instance, by Wolf [1] and by Powell and Soos [2]. A key quantity in these studies is the “energy transfer rate” governing the transfer of excitation from the host to the guest. This rate, denoted usually by $k(t)$ but in this paper by $E(t)$, is found experimentally to be time dependent in contrast to the prediction of the standard diffusion theory. Much theoretical work has been done [2] on the problem of deriving this time dependence from exciton transport equations. However the equations used in the literature have pertained almost always to real space. If the molecular aggregate under consideration is a crystal (as is often the case) translational periodicity should suggest analysis in terms of bands and allied concepts in k -space (reciprocal space), particularly in the light of the current feeling [3,4] that exciton transport

in some crystals is rather coherent. We begin such an analysis in this paper.

The transport equation that serves as our point of departure is suggested by the phase space of the system, as depicted for instance in fig. 4 of ref. [1] or fig. 2 of ref. [3]. Denoting by f_k and f_θ , the probability of occupation by the exciton of the state k of the host and of the trap (guest molecules) respectively, we write

$$\begin{aligned} df_k/dt + (1/\tau + \alpha_k^-)f_k \\ = \alpha_k^+ f_\theta + \sum_{k'} (Q_{kk'} f_{k'} - Q_{k'k} f_k) \end{aligned} \quad (1)$$

$$df_\theta/dt + \left(1/\tau_\theta + \sum_{k'} \alpha_{k'}^+\right) f_\theta = \sum_{k'} \alpha_{k'}^- f_{k'}. \quad (2)$$

Here τ 's denote radiative lifetimes and we have suppressed any k -dependence of τ_k , the trapping rate from and the detrapping rate to the state k of the host are denoted respectively by α_k^- and α_k^+ , and $Q_{kk'}$ are the transition rates from k' to k arising from scattering mechanisms in the host band. Direct trap-to-trap transfer, which would be negligible for small trap concentrations, has been excluded for simplicity. To be applicable for large trap concentrations, our theory must therefore be modified, at least in detail.

In the absence of traps and of radiative decay [1] reduces to the Boltzmann equation [5] which is

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completely analogous to the one used [6,7], with wide success, in electron transport in metals and semiconductors. This analogy should lend support for such a starting point. An elucidation of how to arrive directly at that equation from the microscopic Liouville–von Neumann equation, as well as a demonstration of the relation of the transition rates $Q_{kk'}$ to quantities appearing in real-space transport equations will be reported elsewhere. Here we are interested only in arriving from (1) and (2) at expressions for the energy transfer rate $E(t)$. This rate appears in equations [2] for the probabilities of excitation of the guest and the host, which are respectively $f_\theta(t)$ and $F(t) \approx \sum_k f_k(t)$:

$$dF(t)/dt + [1/\tau + E(t)]F(t) = 0, \quad (3)$$

$$df_\theta(t)/dt + f_\theta(t)/\tau_\theta = E(t)F(t). \quad (4)$$

Note, for instance, that eq. (3) is identical to eq. (1) of ref. [2] with the correspondence $F = n_s$, $\tau = 1/\beta_s$, $E(t) = k(t)$, provided the initial excitation pulse is sufficiently short-lived. We shall now derive (3) and explicit expressions for $E(t)$ from our k space transport equations.

2. Investigation in the absence of detrapping

The detrapping rates α_k^+ are smaller than the trapping rates α_k^- by Boltzmann factors involving the ratio of the energy difference between the k -state and the trap state to the product $k_B T$, where k_B is the Boltzmann constant and T the temperature. We shall consider temperatures which are sufficiently low to justify the neglect of the detrapping rates in eqs. (1) and (2). Then (1) reduces to

$$df_k/dt + (1/\tau + \alpha_k^-)f_k = \sum_{k'} (Q_{kk'}f_{k'} - Q_{k'k}f_k). \quad (5)$$

Denoting Laplace-transforms by tildes and the Laplace-variable by ϵ , we get from (5):

$$\begin{aligned} \tilde{f}_k(\epsilon) &= \frac{f_k(0)}{\epsilon + (1/\tau) + \alpha_k^- + \sum_{k'} Q_{k'k}} \\ &+ \frac{\sum_{k'} Q_{kk'} \tilde{f}_{k'}(\epsilon)}{\epsilon + (1/\tau) + \alpha_k^- + \sum_{k'} Q_{k'k}}. \end{aligned} \quad (6)$$

Detailed expressions for $Q_{kk'}$ can be taken from re-

cent investigations concerning exciton scattering mechanisms, such as those of Burland et al. [8]. Exact solution of (6) with such realistic expressions is however not possible analytically. If we make the approximation that the scattering rates are independent of k and k' , i.e. $Q_{kk'} = \Gamma/N$, where N is the number of k states in the band, summation of (6) over k gives

$$\begin{aligned} \tilde{F}(\epsilon) &= \sum_k \tilde{f}_k(\epsilon) = \left[1 - \frac{\Gamma}{N} \sum_k \frac{1}{\epsilon + (1/\tau) + \alpha_k^- + \Gamma} \right]^{-1} \\ &\times \sum_k \frac{f_k(0)}{\epsilon + (1/\tau) + \alpha_k^- + \Gamma}. \end{aligned} \quad (7)$$

Analytic inversion of this Laplace-transform is practical either for a very small number of k states, which would correspond to a very small host crystal (containing only a few molecules), or for an infinitely large host crystal, as the summations in eq. (7) would then be replaced by integrals. Here, however, we shall make neither of these extreme size assumptions. Instead we make the further approximation

$$(1/N) \sum_k e^{-t\alpha_k^-} \approx e^{-t\alpha}, \quad (8)$$

which is essentially in the nature of the single relaxation-time assumption in transport theory. It allows the replacement of the summation in the first factor on the rhs of eq. (7) by a single term. Using eq. (8) and observing that light excitation produces $f_k(0) = \delta_{k,0}$ as a result of selection rules, we find for $F(t)$, the probability that the host is excited,

$$F(t) = \frac{e^{-t/\tau}}{\Gamma + \Delta} [\Gamma e^{-t\alpha} + \Delta e^{-t(\alpha_0^- + \Gamma)}], \quad (9)$$

where Δ is the difference ($\alpha_0^- - \alpha$) between the $k = 0$ trapping rate and an average trapping rate over the band. By making the above assumption $f_k(0) = \delta_{k,0}$ we exclude situations relevant to some of the experiments done in this field [2], which involve X-ray or deep ultraviolet excitation. The analysis of those situations will be reported elsewhere in the context of the applications of our theory to specific experiments.

The main quantity of interest is $E(t)$ and it has been derived from (9) in the next section. We first also obtain $f_\theta(t)$ the probability of excitation of the trap. From eq. (2) its Laplace-transform is shown to obey

$$\tilde{f}_\theta(\epsilon) = \left[\frac{1}{\epsilon + (1/\tau_\theta)} \right] \left[\frac{\alpha_0^-}{\epsilon + (1/\tau) + \alpha_0^- + \Gamma} + \tilde{F}(\epsilon) \frac{\Gamma}{N} \sum_k \left(\frac{\alpha_k^-}{\epsilon + (1/\tau) + \alpha_k^- + \Gamma} \right) \right]. \quad (10)$$

A separate averaging approximation is not necessary for the k summation in (10). Using the time-derivative of (8) above we get

$$\tilde{f}_\theta(\epsilon) = [\epsilon + (1/\tau_\theta)]^{-1} [\epsilon + (1/\tau) + \alpha_0^- + \Gamma]^{-1} \times \left[\alpha_0^- + \frac{\Gamma\alpha}{\epsilon + (1/\tau) + \alpha} \right], \quad (11)$$

which is inverted to give

$$f_\theta(t) = A_1 e^{-t/\tau_\theta} - e^{-t/\tau} [A_2 e^{-t(\alpha_0^- + \Gamma)} + A_3 e^{-t\alpha}], \quad (12)$$

where

$$A_1 = [\alpha(\alpha_0^- + \Gamma - \delta) - \Delta\delta][(\alpha - \delta)(\alpha_0^- + \Gamma - \delta)]^{-1}, \quad (13)$$

$$A_2 = \Delta(\alpha_0^- + \Gamma)[(\Delta + \Gamma)(\alpha_0^- + \Gamma - \delta)]^{-1}, \quad (14)$$

$$A_3 = \Gamma\alpha[(\Delta + \Gamma)(\alpha - \delta)]^{-1}. \quad (15)$$

Here δ is the difference $1/\tau_\theta - 1/\tau$ between the reciprocals of the guest and host lifetimes. In the particular case of tetracene and anthracene ($\tau_\theta = 1.3 \times 10^{-8}$ s and $\tau = 2.7 \times 10^{-8}$ s), δ roughly equals $1/\tau$. Note that for $\delta = 0$ one gets from eqs. (12)–(15) and (9) the expected result that $f_\theta(t)$ merely equals the product of $[1 - F(t)]$ and the decay factor $\exp(-t/\tau)$.

3. The energy transfer rate

Eq. (9) immediately results in (3) wherein the energy transfer rate $E(t)$ is given by

$$E(t) = \frac{\Gamma\alpha e^{-t\alpha} + \Delta(\alpha_0^- + \Gamma)e^{-t(\alpha_0^- + \Gamma)}}{\Gamma e^{-t\alpha} + \Delta e^{-t(\alpha_0^- + \Gamma)}}. \quad (16)$$

It is clear from (16) that energy transfer from the host to the trap occurs initially with the $k = 0$ trapping rate, since $E(0) = \alpha_0^-$, and that at long times it occurs with the average rate α since the latter is the limit of $E(t)$ at $t \rightarrow \infty$. In the highly incoherent limit, which corresponds to standard diffusion theory in

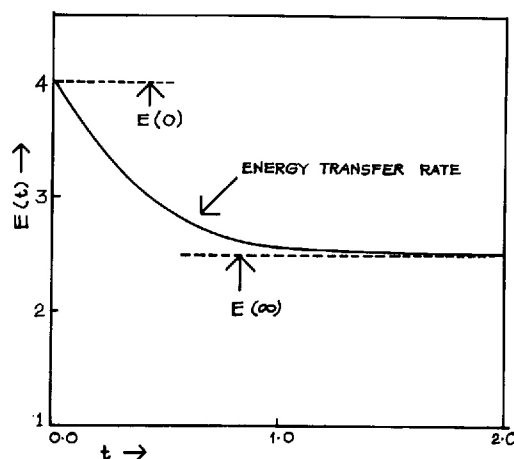


Fig. 1. Time-dependent energy transfer rate $E(t)$ as given by eq. (16). Parameter values are arbitrary. $\tau_\theta = 1$, $\tau = 2$, $\alpha_0^- = 4$, $\alpha = 2.5$, $\Gamma = 1.5$.

real space, the lifetime of the k states is very small and thus Γ is very large. Eq. (16) shows that in this limit $E(t) = \alpha$ and describes the rapid motion among the band states that the exciton performs before transferring itself to the trap. The usual result for this limit is thus recovered from (16). In the highly coherent limit, $\Gamma \rightarrow 0$, and again $E(t)$ sheds its time dependence but equals α_0^- in this case. This corresponds to the exciton being scattered only slowly and therefore transferring itself to the trap primarily from the $k = 0$ state. Finally, a constant $E(t)$ also obtains for $\Delta = 0$, i.e. if the trapping rate does not vary over the band. This last result is obviously independent of the strength of the scattering Γ .

We have plotted the energy transfer rate as a function of time in fig. 1 for arbitrary values of the parameters. Note the qualitative resemblance of the curve to the experimental curves as given in figs. 3 and 4 of ref. [2]. The corresponding curves for the host and guest fluorescence are plotted in fig. 2 from eqs. (9) and (12) and should be compared to experimental curves such as those in fig. 2 of ref. [2] or fig. 7 of ref. [3].

4. Discussion of the assumptions

Three assumptions have been made in the foregoing analysis starting from (1) and (2). These are: the

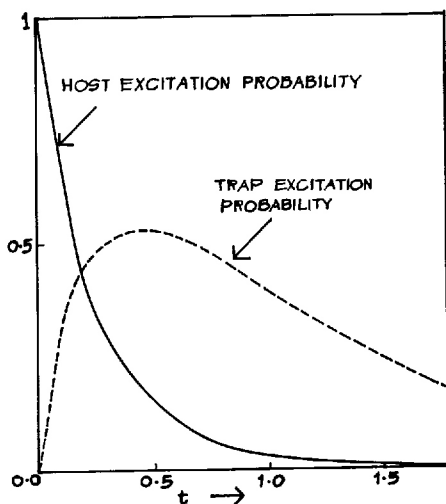


Fig. 2. Host and trap fluorescence (or phosphorescence) curves as given by eqs. (9) and (12). The ordinate is the probability that the host (or trap) is excited. Parameter values are arbitrary and correspond to fig. 1.

neglect of detrapping rates in (1) which allows the reduction of (1) to (5), the constant scattering rate assumption $Q_{kk'} = (\Gamma/N)$, and the averaging approximation stated in (8). To complete the third assumption a prescription to compute the average rate α from the individual α_k^- must be given. We point out two such prescriptions described by the following two equations

$$\alpha = (1/N) \sum_k \alpha_k^-, \quad (17)$$

$$1/\alpha = (1/N) \sum_k (1/\alpha_k^-). \quad (18)$$

It is trivially verified that (17) is consistent with the equality of the initial (at $t = 0$) derivatives of the two sides of eqs. (8) whereas (18) is consistent with the equality of their time-integrals (from $t = 0$ to $t = \infty$). The meaning of these prescriptions can be made clearer as follows. It is possible to demonstrate that the lhs of eq. (8), which we shall term $Z(t)$, obeys

$$dZ(t)/dt + \int_0^t dt' Y(t-t')Z(t') = 0. \quad (19)$$

The approximation (8) corresponds to the replacement of the "memory function" $Y(t)$ by a constant times a δ -function in time. Eqs. (17) and (18) can then be shown to correspond to the replacement of

the Laplace-transform of $Y(t)$ by its value at $\epsilon = \infty$ and at $\epsilon = 0$, respectively. They thus respectively constitute, in some sense, a short-time and long-time approximation. One might argue that they should therefore be used in the respective limits of large and small Γ in relation to the quantities $\alpha_k^- + (1/\tau)$.

The assumption of constant scattering rates is consistent with high temperatures. For, in the absence of $(1/\tau)$ and of the α_k^- 's, it would lead to an equal population for any two k -states in the band for long times, and this can only happen for $T \rightarrow \infty$. However, it should not be considered to contradict the low-temperature assumption made above to justify the neglect of the detrapping rates. The latter assumption requires $k_B T$ to be small with respect to the energy difference between the host band and the trap state, whereas the former assumption is consistent with $k_B T$ being larger than the bandwidth. It is often possible to satisfy both these requirements simultaneously because the bandwidth is often much smaller than the band-to-trap energy difference.

Nevertheless, it would be desirable to improve upon the constant $Q_{kk'}$ approximation. This can be done within the framework of the relaxation-time assumption well-known in transport theory [6,7] in a form modified [9] to account for the presence of true decay terms. In the absence of the latter that assumption would consist of the replacement of the rhs of eq. (5) by $\Gamma_k [f_k^{\text{th}} - f_k(t)]$, where $(1/\Gamma_k)$ is the relaxation time and f_k^{th} is the constant thermal distribution [6,7]. However, this procedure, if used in (5), i.e. in the presence of the sink terms appearing on its left side, leads to the absurd result that $f_k(t)$ tends at $t \rightarrow \infty$ to a nonzero constant, whereas (5) obviously shows it tending to zero. A valid relaxation-time procedure for this case consists of the definition $\Gamma_k = \sum_{k'} Q_{k'k}$ and of the replacement [9]

$$\sum_{k'} Q_{kk'} f_{k'}(t) \approx f_k^{\text{th}} \Gamma_k \left[\sum_{k'} f_{k'}(t) \right]. \quad (20)$$

It is trivial to check that the prescription (20) reduces to the one given earlier in the limit of high temperatures and that it is generally consistent with the relaxation-time assumption. A k -summation of (6) after substitution in it of (20) is then seen to retrieve (9) and other results derived above provided an average over the relaxation times Γ_k is carried out in addition to that over the trapping rates α_k^- . Specifically one

assumes

$$\sum_k f_k^{\text{th}} \Gamma_k e^{-t(\alpha_k^- + \Gamma_k)} \approx \Gamma e^{-t(\alpha + \Gamma)}, \quad (21)$$

in place of (8). Here Γ is an average over Γ_k 's and note that (21) implies a *thermal* averaging procedure wherein f_k^{th} replaces $(1/N)$ in prescriptions (17) or (18).

It is also possible to refrain from making averaging approximations such as (8) or (21) and to attempt calculation of their left-sides in terms of known forms for Γ_k and α_k^- . Systematic approximation schemes have been developed for such an activity and will be reported elsewhere.

5. Concluding remarks

The main features of this paper are: a Boltzmann equation approach to sensitized fluorescence, i.e. one based on k -space transport equations, and the reproduction of the host and guest fluorescence curves and of the energy transfer rate which possess the qualitative features of the experimentally observed quantities. The time-dependent nature of the energy transfer rate is an immediate consequence of this theory. The observed decrease rather than increase in the transfer rate, with the passage of time, obviously represents that the trapping rate is largest at $k = 0$, which is the initially occupied point in the host band. While no microscopic derivation of the trapping rate has been given in this paper we have recently deduced [10] the k -dependence of α_k^- on the basis of microscopics and it indeed shows a maximum at $k = 0$. Such microscopic analysis of the trapping and detrapping rates, solution of the transport equations in the presence of detrapping, and going beyond the relaxation-time assumption, are some of the theoretical problems that are to be completed in this area. In applying the results of this paper to actual experimental systems the parameters α , α_0^- , Γ , $(1/\tau)$ and $(1/\tau_\theta)$ must be evaluated. The latter two are well-known for all systems of interest and for singlets are of the order of 10^8 s^{-1} . The value of Γ is generally expected to be of the order of 10^{12} s^{-1} but in systems in which scattering is thought to be rather infrequent [4], Γ would be as low as 10^7 s^{-1} . While microscopic estimation of the α 's would be possible

only after microscopic theories of the α 's are complete, the experimental determination of α_0^- and α is straightforward as they are respectively proportional to the initial and the final values of the experimental $E(t)$ curve.

Coherence of exciton transport has been studied very actively in recent times by experimentalists and theorists. As some of the experiments [3,4] employed are analogous to sensitized fluorescence observations, the theory developed in this paper may be immediately applied to interpret those experiments. Earlier interpretations have used theoretical analysis in real space and conflicts in them have not yet been resolved [11]. In the language of this paper coherence investigations would consist of the extraction of Γ from the observed phosphorescence curves [3,4]. Large or small Γ in relation to the bandwidth of the exciton would then represent incoherent or coherent transport respectively.

Finally, a remark concerning quantitative comparison of this theory with experiment is in order. The exponential nature of the curves in our figures is a consequence of the simplifying approximations made in section 2 to illustrate our theory. The power law behaviour in the time-dependence of those curves may be obtained from the original expressions in our theory. Thus our recent result [10], that the k -variation of the rate α_k^- is trigonometric for a reasonable model (specifically the rate goes as $(A + B \cos k)^2$) allows an exact evaluation of the lhs of eq. (8) for large systems. The averaging approximation (8) is then unnecessary, Bessel functions rather than exponentials appear, and asymptotic analysis may then be used to get power-law behaviour which appears to be compatible with the experimental curves in ref. [2]. However, it is not clear that the experimental situation at the moment is itself without doubt and these calculations will not therefore be presented here.

Acknowledgement

I thank Professor J.S. Murty and Dr. M.J. Patni for many conversations on this and allied topics, Dr. R. Ramani for assistance in computation, and Professor R.P. Singh for his invitation to and hospitality at the Indian Institute of Technology, Bombay.

This article is dedicated to Professor Max Dresden on the occasion of his sixtieth birthday.

Note added in proof

While the initial condition $f_k(0) = \delta_{k,0}$ relevant to optical absorption has been used explicitly in this paper, situations, such as those involving X-rays, which do not satisfy it may also be analyzed in a straightforward manner within the averaging approximation scheme developed above. The results embodied in eqs. (9), (12)–(16) then still apply with only one modification: α_0^- is to be interpreted not as the rate at $k = 0$ but as an average rate over the region of k -space which is initially excited.

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