EXCITON MIGRATION WITH END DETECTORS: CALCULATION OF TIME-DEPENDENT LUMINESCENCE *

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We present explicit plots of the time dependence of the detector luminescence intensity in surface quenching observations. They are obtained with the aid of numerical inversion methods applied to exact consequences of a master-equation theory of exciton migration. The existing disparity in reported values of the singlet diffusion constant in aromatic hydrocarbon crystals is one of the main issues addressed. It is shown how the theory can be used to extract the exciton diffusion constant without prior knowledge of the (detector) trapping rates, by combining information obtained from steady-state (yield) and time-resolved experiments.

1. Introduction

One of the most direct experimental methods of probing into the phenomenon of energy transfer via Frenkel exciton motion in molecular crystals consists of end-to-end migration observations of the kind pioneered by Simpson [1]. The basic idea is to illuminate one end of the crystal thereby creating excitons in the vicinity of that end, and to detect them at the *other* end by monitoring the luminescence from a coating of detector (or guest) molecules placed there. More recent experiments of this kind have been performed by Gallus and Wolf [2], Kurik [3], and Tomura and Takahashi [4], related but different observations have been made by Mulder [5] and Haarer and Castro [6], and a review in the singlet exciton context has been given by Powell and Soos [7].

We have recently carried out a series of theoretical investigations into this particular observational technique for exciton dynamics. A theory based on master equations has been developed and used to provide a possible explanation of the reported orders-of-magnitude disparity in values of the singlet diffusion constant [8]. New experiments have been suggested [9] which would allow the resolution of the disparity problem and, more generally, would provide values of the diffusion constant on the basis of observations of the dependence of the detector yield on the wavelength of excitation. Most of the observations carried out so far for this (end-detector) experimental arrangement are time independent. In this paper we present explicit calculations of time-dependent observables and demonstrate how time-resolved experiments could be used to complement the earlier experiments and also to resolve the questions that continue to exist concerning the value of the diffusion constant.

The object of our analysis is the time dependence of the intensity of luminescence from the detector coating. As excitons travel to the detector, the luminescence intensity rises from zero, and eventually decays as a result of radiative decay. The shape of the curve is obviously dependent on the rate at which excitons move within the host crystal. It is also dependent on the trapping (and detrapping) rates at which excitons are fed into (and return from) the detector. The perfect-absorber assumption which is at the basis of traditional analyses [1–4] of the steady-state experiments of this kind, neglect the dependence of luminescence observables on the trapping and detrapping rates; they are assumed to be infinite and zero respectively.

We follow the theoretical development of Kenkre and Wong [8] which starts with the master equation

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for the probability $P_m(t)$ that the exciton is at the mth state:

$$dP_1/dt + P_1/\tau_H = F(P_2 - P_1)\,, \tag{1a}$$

$$dP_m/dt + P_m/\tau_H = F(P_{m+1} + P_{m-1} - 2P_m)\,,$$

$$N - 1 \geqslant m \geqslant 2\,, \tag{1b}$$

$$dP_N/dt + P_N/\tau_H = FP_{N-1} + fP_G - (F + \mathcal{F})P_N\,, \tag{1c}$$

$$dP_G/dt + P_G/\tau_G = \mathcal{F}P_N - fP_G\,. \tag{1d}$$

The assumption of a one-dimensional system in these equations corresponds to the experimental situation since the relevant motion is in a single dimension. This assumption is not essential to the analysis and may be relaxed easily, if necessary.

Here F is the intersite transfer rate in the host, $\mathcal{F}$ is the host-to-detector rate, f the detector-to-host (detrapping) rate, P_G denotes the detector excitation probability and τ_H and τ_G are the host and detector radiative lifetimes respectively. We point out that the model explicitly includes the trapping and detrapping rates with no a priori assumptions as to their values. Eqs. (1) are solved by Kenkre and Wong in ref. [8] to produce the following expression for the detector excitation probability $n_G(t)$:

$$\tilde{n}_G(\epsilon) = \mathcal{F}[\epsilon + f + 1/\tau_G + (\epsilon + 1/\tau_G)\mathcal{F}$$

$$\times \tilde{\psi}_{NN}(\epsilon + 1/\tau_H)]^{-1}\left(\sum_{n=1}^{N} P_n(0)\,\tilde{\psi}_{Nn}(\epsilon + 1/\tau_H)\right)\,. \tag{2}$$

In (2) and subsequently, tildes denote Laplace transforms with ϵ as the Laplace variable, and the propagators $\psi_{m,n}(t)$ are the solutions of (1) for $P_m(t)$ without the detector or radiative decay, and for the initial conditions $P_l(0) = \delta_{l,n}$. These propagators ψ are given by the analysis of Lakatos-Lindenberg et al. [10]:

$$\tilde{\psi}_{mn}(\epsilon) = F^{-1}\cosh[\tfrac{1}{2}\xi(2N - |m+n-1| - |m-n|)]$$

$$\times \cosh[\tfrac{1}{2}\xi(|m+n-1| - |m-n|)]/\sinh\xi\,\sinh(N\xi)\,, \tag{3}$$

where ξ is defined through

$$\cosh\xi = 1 + \epsilon/2F\,. \tag{4}$$

For the sake of simplicity we shall restrict the following analysis to the specific initial condition corresponding to spatially uniform initial illumination. Such would be the case, for example, for relatively thin samples. This allows a simplification of (2) since the sum appearing in the rhs of that expression becomes:

$$\sum_{n=1}^{N} P_n(0)\,\tilde{\psi}_{Nn}(\epsilon + 1/\tau_H) = N^{-1}\sum_{n=1}^{N}\tilde{\psi}_{Nn}(\epsilon + 1/\tau_H)$$

$$= [N(\epsilon + 1/\tau_H)]^{-1} \tag{5}$$

and the corresponding expression for the observable $n_G(t)$ becomes

$$\tilde{n}_G(\epsilon) = \frac{\mathcal{F}/N\epsilon'}{\epsilon + f + 1/\tau_G + (\epsilon + 1/\tau_G)\,\mathcal{F}\tilde{\psi}_{NN}(\epsilon')}\,, \tag{6}$$

with $\epsilon' = \epsilon + 1/\tau_H$ and

$$\tilde{\psi}_{NN}(\epsilon) = F^{-1}\cosh(\tfrac{1}{2}\xi)$$

$$\times \cosh[\tfrac{1}{2}\xi(2N-1)]/\sinh\xi\,\sinh(N\xi)\,. \tag{7}$$

We use these results below with the simplification $\tau_H = \tau_G = \tau$. It is made only for simplicity and may easily be relaxed.

2. Time-dependent luminescence

While (7) was used earlier [8,9] directly for the analysis of quantum yields, an explicit inversion of the Laplace transform is required if one is interested in examining the effects of the trapping parameters on the time dependence of $n_G(t)$. We have carried out such an inversion numerically using the Stehfest algorithm [11] for a wide range of the parameter values. To facilitate comparison with ref. [8] we present in fig. 1 three time-dependent curves as calculated numerically from (6) corresponding to the three cases considered in that reference. They all correspond to a measured yield value of $\phi_G = 0.316$ and a crystal $\frac{1}{2}$ μm thick with a lattice constant of 5 Å, i.e. with 1000 sites along the line between the detector end and the illuminated end. The diffusion constants for the three curves vary, however, by an order of magnitude. The curve labeled (c) in fig. 1 corresponds to the perfect absorber assumption, i.e. the limit $\mathcal{F}/F \to \infty$. It is seen to be measurably different from the other two curves, (a) and (b) which were produced with finite values for the ratio $\mathcal{F}/F$: 5 and 12 respectively.

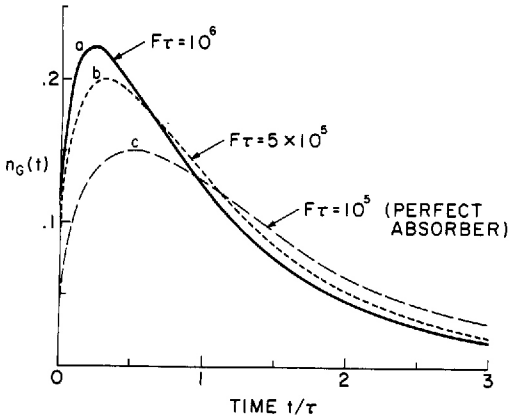

Fig. 1. Time-dependent detector luminescence intensity as a function of time, plotted in units of the radiative lifetime. The three curves correspond to three values of F (10^6, 5×10^5, 10^5), equivalently to three values of the diffusion constant (1, 0.5, and 0.1 cm^2/s) respectively for a lattice constant of 5 Å. The values of the trapping rate are different for the three curves and adjusted so that the steady state yield ϕ_G equals 0.316 in all of them.

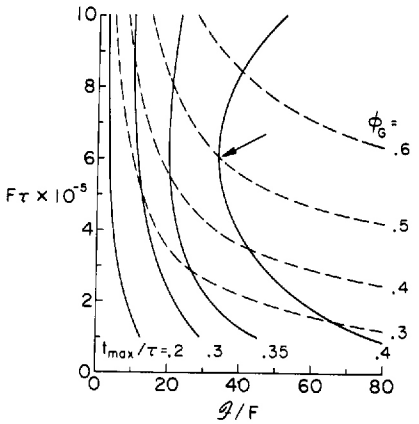

Fig. 2. Two families of curves presented to allow the extraction of the motion rate F (or equivalently the diffusion constant) without prior knowledge of the trapping parameter $\mathcal{F}/F$. Each of the dotted curves corresponds to a fixed value of the steady state detector yield ϕ_G and each of the solid curves to a fixed value of t_{max}/τ. the time at which the detector luminescence intensity peaks, measured in units of the radiative lifetime.

In particular, we note that, although the trapping rate is infinite for curve (c), the initial rise tends to be slower since the motion in the host crystal is substantially reduced in comparison with the other two cases. This slower motion allows the exciton population around the detector to become depleted more easily and hence reduces the trapping efficiency. This noticeable change in the rise time of the detector luminescence with variations in the diffusion constants suggests a means for extracting this information from time-resolved experiments. This point is dealt with in section 3. At long times the curves appear to decay at the same rate, which is expected to be that of the radiative decay, although the values of each are different, reflecting the area-conserving property that the curves must have in order to produce the same quantum yield.

3. Determination of the diffusion constant and trapping parameters

A conclusion drawn in ref. [8] was that the steady-state yield experiments of the kind being discussed here cannot provide us with a value of the diffusion constant unless the trapping rate $\mathcal{F}$ is known. This need for additional information (about $\mathcal{F}$) was bypassed in ref. [9] in the suggested experiments on the effects of the variation of penetration length. We see here another way of bypassing the need for such a priori information. We show in fig. 2 how time-resolved experiments can be combined with steady state (yield) experiments to determine the diffusion constant *and the trapping parameters as well.* In fig. 2 we have plotted two families of curves which were produced in the following way. In ref. [8] expressions are presented for ϕ_G as a function of F and $\mathcal{F}$. Conversely, fixing a value of ϕ_G yields a functional relationship between F and $\mathcal{F}$ which can be determined either graphically or analytically from the expressions in that paper. This relationship, or equivalently that between $F\tau$ and $\mathcal{F}/F$, is presented in the dashed curves of fig. 2. In a completely analogous fashion, the peak of the detector luminescence intensity, which we denote by t_{max}, can be plotted for various values of the motion rate F, as a function of the trapping parameter $\mathcal{F}/F$. This information, obtained from expression (6) and the numerical inversion routine, can then be used to produce, for a fixed value of t_{max}, a new functional relation between $F\tau$ and $\mathcal{F}/F$. That relation is represented in the solid lines of fig. 2. Needless to say, the plots depend on the value of the detrapping rate (detector-to-host) f. For simplicity, we have exhibited above the results for a single fixed value of this rate, corresponding to $f\tau = 10^4$ as in ref. [8]. It is straight-

forward to modify the analysis for other situations, e.g. when the relationship of f to $\mathcal{F}$ is known through detailed balance considerations.

The intersection of the two families of curves obtained in this fashion allows us to determine both the diffusion constant *and* the trapping parameter. As an example, consider the case of a hypothetical system in which the measured yield value is reported to be 0.5 and for which the time-resolved detector luminescence peaks at 0.4 times the radiative lifetime. From the intersection of the two corresponding curves of fig. 2 (see the arrow) one determines the motion rate F (as read horizontally from the point of intersection) to be $6 \times 10^5/\tau$ and the trapping parameter $\mathcal{F}/F$ (as read vertically) to be 34.

4. Remarks

This paper is one in a series [8,9] directed at exciton migration observations with end detectors (surface quenching). In all these papers, the model used assumes that the excitons move incoherently on a discrete lattice with nearest-neighbor transfer rates F, and that trapping and detrapping of the excitons occur at one end of the crystal with rates $\mathcal{F}$ and f respectively. The basic theory was given in the first paper of the series, with a primary focus on the time-independent observable ϕ_G (detector yield). In this paper we have used that analysis as a starting point to examine the *time dependence* of the luminescence intensity of the detector molecule. Although the general case is quite straightforward to analyse, we have, for simplicity, considered only the case of uniform initial host illumination here. We have presented results of the numerical inversion of expressions [8] for the Laplace transform of the detector excitation probability. These results demonstrate the usefulness of time-resolved data in determining microscopic information about the system. Moreover, we have presented in section 3 a simplified demonstration of how a determination of the diffusion constant *and* trapping parameters can be made based on a combination of steady-state (yield) and time-resolved (detector luminescence peak) information.

The question of coherence effects is interesting, has been briefly discussed in the present context earlier [8], and we postpone a detailed discussion to a future publication. The possibility of long-range transfer, especially to and from the detector molecules, and particularly for singlets, also deserves serious consideration. However, we feel that the model, although simplified due to the restriction to short-range transfer rates and incoherent motion, captures the essential qualitative aspects of the problem.

In conclusion, our analysis points clearly to the advantages to be gained by the performance of time-resolved surface quenching experiments. Although many observations with end detectors have been carried out, time-resolved techniques have seldom been used in them. We suggest that such experiments be performed.

Note added in proof

We have just become aware of the experimental work of Heisel et al. [12] on time-resolved surface quenching. That work deals with metal detectors widely believed to be near-perfect absorbers and the experiment belongs to the category of those in refs. [5,6] rather than those in refs. [1–4] which are quite different. In principle, our analysis in the present paper can be applied to the observations of Heisel et al. [12] but it is primarily directed at the kind of experiments in refs. [1–4].

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