

## SPATIAL PROFILE OF THE STEADY-STATE EXCITON DISTRIBUTION IN DOPED MOLECULAR CRYSTALS\*

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We present calculations of the steady-state spatial distribution of excitons created continuously by illumination and depleted continuously by radiative decay in a doped molecular crystal, e.g. tetracene-doped anthracene. The calculation is exact for low guest concentrations and allows explicit description of the hole in the exciton distribution that surrounds a trapping site.

### 1. Introduction

If Frenkel excitons, created by illumination in a molecular crystal such as anthracene, and travelling within that host crystal as a result of inter-site interactions, arrive within the trapping influence of guest molecules such as tetracene placed in the host crystal through doping, the excitons could be captured by the guest. This phenomenon is the basis of sensitized luminescence studies of exciton motion in molecular crystals [1–8]. We consider here the situation where in a steady state is achieved in the crystal as a result of continuous creation of excitons through illumination and their continuous depletion via radiative decay. It is clear that in the steady state the exciton distribution in the host crystal will exhibit a non-uniform profile with dips at the location of the guest molecules. We present a calculation of this profile and suggest how it may be probed experimentally.

We describe the exciton through  $P_m(t)$ , the probability that it occupies the site  $m$  in the crystal at time  $t$ . This  $P_m(t)$  obeys the generalized master equation (GME) whose memory functions  $\mathcal{W}_{mn}(t)$  describe

transport with arbitrary degree of coherence. The details of the GME may be found elsewhere [9–11]. If we envisage the capture process as causing decay of  $P_m(t)$ , at rate  $c$ , from host sites  $r$  which are influenced by the guest molecules, the starting equation may be written as

$$\begin{aligned} dP_m(t)/dt + P_m(t)/\tau = & \int_0^t dt' \sum_n [\mathcal{W}_{mn}(t-t')P_n(t')] \\ & - \mathcal{W}_{nm}(t-t')P_m(t')] - c \sum_r' \delta_{m,r} P_r(t) + S(t). \end{aligned} \quad (1)$$

The prime on the summation in the second last term signifies that the summation covers only the guest-influenced host sites, and the second term in the left-hand side of (1) describes radiative decay from the host. Detrapping from the guest is neglected for simplicity. The last term in (1) describes the source term which (via illumination) creates the excitons.

### 2. Solution for small guest concentration

If  $\psi_{m-n}(t)$  is the propagator, i.e. the solution  $P_m(t)$  of (1) for the case  $\tau = \infty$ ,  $c = 0$ ,  $S(t) = 0$  and  $P_r(0) =$

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$\delta_{r,n}$  (we have already used the translational periodicity of the undoped host crystal to write the propagator as a single-indexed quantity), it is straightforward to write (1) as

$$\tilde{P}_m(\epsilon) = \sum_n \tilde{\psi}_{m-n}(\epsilon') P_n(0) - c \sum_r \tilde{\psi}_{m-r}(\epsilon') \tilde{P}_r(\epsilon) + \tilde{S}(\epsilon)/\epsilon' . \tag{2}$$

Here tildes denote Laplace transforms,  $\epsilon$  is the Laplace variable and  $\epsilon' = \epsilon + 1/\tau$ .

We shall restrict our analysis to low guest concentrations and therefore consider a single trap-influenced host site at  $r$ . Then the defect technique [12] allows us to solve (2) explicitly. For the initial condition that there are *no excitons* in the host crystal we have  $P_n(0) = 0$ . Writing  $m = r$  and solving for  $\tilde{P}_r(\epsilon)$  explicitly we have

$$\tilde{P}_m(\epsilon) = \left[ 1 - \frac{c \tilde{\psi}_{m-r}(\epsilon')}{1 + c \tilde{\psi}_0(\epsilon')} \right] \frac{\tilde{S}(\epsilon)}{\epsilon'} . \tag{3}$$

If we take a source function which is constant in time, i.e. if we illuminate the crystal continuously,  $S(t) = S\theta(t)$  where  $\theta(t)$  is a step function, and (3) gives

$$\epsilon(\epsilon + 1/\tau)\tilde{P}_m(\epsilon) = S \left[ 1 - \frac{\tilde{\psi}_{m-r}(\epsilon + 1/\tau)}{1/c + \tilde{\psi}_0(\epsilon + 1/\tau)} \right] . \tag{4}$$

We analyze the steady state. We therefore have  $dP_m(t)/dt = 0$ . From standard Laplace theorems [13] we then have

$$\lim_{\epsilon \rightarrow 0} \epsilon^2 \tilde{P}_m(\epsilon) = 0 , \tag{5}$$

$$\lim_{\epsilon \rightarrow 0} \epsilon \tilde{P}_m(\epsilon) = P_m(\infty) , \tag{6}$$

where  $P_m(\infty)$  is the steady-state value of  $P_m(t)$ . Taking the limit  $\epsilon \rightarrow 0$  of (4) and using (5) and (6), we get our primary result:

$$P_m(\infty) = S\tau \left[ 1 - \frac{\tilde{\psi}_{m-r}(1/\tau)}{1/c - \tilde{\psi}_0(1/\tau)} \right] . \tag{7}$$

### 3. Evaluation of the profile for a one-dimensional crystal

If we consider nearest-neighbour incoherent motion with rates  $F$ , i.e. if in (1) we use

$$\mathcal{W}_{mn}(t) = F\delta(t)(\delta_{m,n+1} + \delta_{m,n-1}) , \tag{8}$$

the propagator  $\psi_m(t)$  is given by [10]

$$\psi_m(t) = I_m(2Ft)e^{-2Ft} , \tag{9}$$

where  $I$  is the modified Bessel function. Thus, putting  $r = 0$  in (7) without loss of generality (that is, calling the trap site the zeroth site), we get

$$P_m(\infty) = S\tau \left[ 1 - \frac{\{[(1+2F\tau) - (1+4F\tau)^{1/2}]/2F\tau\}^m}{1 + (1+4F\tau)^{1/2}/c} \right] . \tag{10}$$

For the above one-dimensional crystal we have therefore (10) as the explicit profile. The distance dependence is a power law. For the case that the capture rate is large with respect to the "motion rate"  $1/\tilde{\psi}_0(1/\tau)$ , we may neglect  $1/c$  in (10) and obtain the simple expression

$$p_m(\infty) = 1 - x^m . \tag{11}$$

Here  $p_m(\infty)$  is the scaled probability or exciton density, the ratio of  $P_m(\infty)$  to  $S\tau$ , and  $x$  is given by

$$x = (1/2F\tau)[1 + 2F\tau - (1 + 4F\tau)^{1/2}] . \tag{12}$$

We see that the profile is pinned to the value zero at the trap-influenced host site. This is because  $c \rightarrow \infty$  has been assumed above and the exciton from that site is forced therefore to disappear into the trap. More generally it will be pinned to a finite value as is clear from (10). We see that as  $F\tau$  gets larger,  $x$  gets larger.

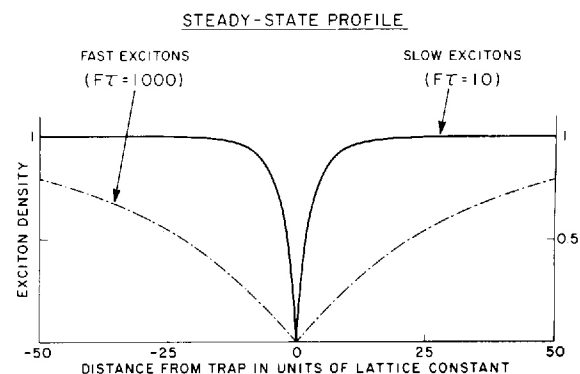


Fig. 1. The steady-state exciton profile around a trapping site: plotted is  $p_m(\infty)$  from eq. (11). Parameter values are arbitrary:  $F\tau = 10$  and  $F\tau = 1000$ . Here  $F$  is the rate at which the exciton hops from a site to its neighbour;  $F$  gives the diffusion constant when multiplied by the square of the lattice constant.  $\tau$  is the radiative lifetime.

Thus, the faster the exciton motion (relative to radiative decay), the larger the "radius" of the hole in the profile formed around the trapping site. If we define  $R$ , the radius of this hole, as the distance from the trap for which  $p_m(\infty)$  equals  $\frac{1}{2} p_0(\infty)$  we have

$$R = a \ln(\frac{1}{2}) / \ln x \quad (13)$$

and a similar expression from the more general (10) where  $a$  is the lattice constant. We have plotted (11) in fig. 1 for two different values of  $F\tau$ .

#### 4. Remarks

It is fortunate that one can obtain exact usable expressions such as (7) and (10) without having to Laplace-invert rather hefty expressions. Such a state of affairs occurs in our yield calculations and it is remarkable (but not surprising) that it occurs also in these calculations of the steady-state spatial profiles. It is not surprising because we are here dealing with time-independent quantities. When time-dependent observables, such as the luminescence intensities in a picosecond experiment [3], are required, it is necessary to use numerical inversion techniques [14].

There are two experimental methods of probing these profiles that we suggest. The first would consist of diffraction. After illuminating the crystal by a steady-state beam of light, neutron diffraction could perhaps be used if the excitons are triplets. The diffraction signal would be compared to one in the absence of the triplets and the difference would yield information about the profile. In turn, as is clear from (7), information on exciton motion would be deduced from the profile. Notice that it would be possible to study a variety of effects including that of coherence and to disentangle the capture rate  $c$  from the motion quantities such as  $F$  or  $\psi$ . We see, for instance, that changing  $c$  would not affect the  $m$  dependence of  $P_m(\infty)$  but changing  $F$  certainly would. Detailed studies of this kind along with realistic profiles in 3-d lattices will be presented in a future publication. Here we mention the second experimental method of measuring (7). This method would not actually probe the profile but the overall effect from the crystal. After the steady state is reached we may study *absorption* of light. Wherever  $p_m(\infty)$  is close to 1 there will be little absorption and wherever it is far

from 1 there will be much absorption. The total absorption will thus be proportional to

$$\sum_m [1 - (1/S\tau)P_m(\infty)] = \frac{\tau}{1/c + \tilde{\psi}_0(1/\tau)}. \quad (14)$$

This is the "area over the curve" corresponding to the exciton profile. We observe that the right-hand side of (14) is essentially the guest yield in a pulsed experiment. It can be shown that such a connection between this kind of absorption experiment and the other yield experiment is universal. These matters will be elaborated upon elsewhere. Measurements would thus allow us to deduce information about the motion and/or capture processes.

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