DETERMINATION OF THE EXCITON DIFFUSION CONSTANT FROM VARIATION OF QUANTUM YIELD WITH PENETRATION LENGTH

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A master equation analysis of Frenkel exciton motion in molecular crystals shows how the exciton diffusion constant may be experimentally determined from end-to-end migration observations, without prior information of trapping interactions at the detection surface. Experiments are suggested, and theoretically predicted curves are provided.

1. Introduction

One of the experimental ways of deducing the diffusion constant of excitons in molecular crystals is based on observations of the quantum yield (or exciton flux) in situations wherein excitons are created at one end of the crystal through illumination and detected at the other end where they are captured by a detector layer. Such experiments were performed by Simpson [1], Kurik [2], Takahashi and Tomura [3] and Gallus and Wolf [4].

A theory of these experiments was recently constructed by Kenkre and Wong [5] on the basis of a master equation to describe exciton transport. General expressions, which can take into account the discrete nature of the lattice, and which reduce to diffusion equation results used earlier by Simpson [1] and others, were given and a possible explanation of the large spread [1–4] in interpreted values of the diffusion constant (involving several orders of magnitude) was advanced. The explanation was based on the idea [3,6] that the detector layers are not perfect absorbers. The idea of imperfect absorption was first suggested by Tomura and Takahashi [3] and discussed by Powell and Soos [6]. However it appears that the resulting spread had been expected to be not too large. It was shown in ref. [5] that the spread can indeed be quite large. In the continuum treatment used earlier two parameters appear and their ratio determines the amount of reflection from the detector surface. In our discrete treatment [5], however, three parameters are important: F, the motion rate in the host crystal, $\mathcal{F}$, the rate of trapping by the detector, and f, the rate of detrapping from the detector. It can be shown that the observed detector yield ϕ_G can be a *highly sensitive* function of $\mathcal{F}/F$. The sensitivity depends on the value of $1 + f\tau_G$ where τ_G is the lifetime of the detector. The larger the value of $1 + f\tau_G$ the larger is the sensitivity. The primary point of the analysis in ref. [5] was that $f\tau_G \gg 1$ is quite compatible with $\mathcal{F}/F$ not being unduly large and that *considerable* underestimation of the diffusion constant can result.

It would appear, therefore, that the extraction of F, the diffusion constant, from these experiments necessitates prior knowledge of the trapping and detrapping rates. A procedure which involves the determination of these rates from spectra through a Förster–Dexter prescription [7,8], is under way and its results will be reported elsewhere [9]. One can conclude, however, that there are at least two simple ways of extending the experimental observations, which do *not* require information about $\mathcal{F}$ and f for the extraction of the diffusion constant. The theory of one of these consists of predictions [10], not of the yield but of the time dependence of the intensity of the detector (or host) luminescence and will not be discussed here. The other way concerns the variation of the yield with the penetration length or, what is the same, its variation with the wavelength of excitation. This latter method is the subject of this paper.

2. Analytic expressions

The analysis will be based on the following equations [5] obeyed by $P_m(t)$, the probabilities of occupation of site m counted from the illuminated end (where $m = 1$), by an exciton at time t:

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

$$N - 1 \geqslant m \geqslant 2, \quad (1)$$

$$dP_1/dt + P_1/\tau_H = F(P_2 - P_1), \quad (2)$$

$$dP_N/dt + P_N/\tau_H = F(P_{N-1} - P_N) + fP_G - \mathcal{F}P_N, \quad (3)$$

$$dP_G/dt + P_G/\tau_G = \mathcal{F}P_N - fP_G. \quad (4)$$

As stated above, F is the motion rate which is taken to be nearest neighbour for simplicity and which is related to the diffusion constant D through $D = Fa^2$, a being the lattice distance. We ignore factors of order unity which may need to be multiplied by Fa^2 to give D. The radiative lifetime (for simplicity, taken equal to the total lifetime) of the host is τ_H and that of the detector is τ_G. The probability of occupation of the guest or detector molecule at the end opposite to the illuminated one is P_G. The number of host molecules along the line between the illuminated and the detector end is N.

The observed quantity is the detector yield ϕ_G defined as the ratio of the number of excitons put into the host through illumination to the number radiatively put out by the detector. With the initial condition $\Sigma_{m=1}^{N} P_m(0) = 1$

$$\phi_G = \int_0^\infty [P_G(t)/\tau_G]\, dt. \quad (5)$$

The explicit evaluation of the yield ϕ_G in (5) in terms of (1)–(4) has been carried out in ref. [5]. With the initial condition

$$P_m(0) = e^{-\kappa(m-1)}\left[\sum_{m=1}^{N} e^{-\kappa(m-1)}\right]^{-1}, \quad (6)$$

where κ is the discrete version of the absorption coefficient, the yield is [5]

$$\phi_G = \phi_G^s \frac{\mathcal{F}/F}{\mathcal{F}/F + c}, \quad (7)$$

$$\phi_G^s = \operatorname{sech}[\xi(N - \tfrac{1}{2})]\, \mathcal{I}(\kappa), \quad (8)$$

$$\mathcal{I}(\kappa) = \frac{1}{2}\frac{1 - e^{-\kappa}}{1 - e^{-\kappa N}}\left[\frac{e^{\xi/2}(1 - e^{-N(\kappa-\xi)})}{1 - e^{-(\kappa-\xi)}} + \frac{e^{-\xi/2}(1 - e^{-N(\kappa+\xi)})}{1 - e^{-(\kappa+\xi)}}\right]. \quad (9)$$

Eq. (7) shows that the yield is a function of the ratio $\mathcal{F}/F$ and saturates at large values of $\mathcal{F}/F$. The saturated value corresponds to earlier analyses [1] which did not take into account, the fact that $\mathcal{F}/F$ is not infinite. One also sees explicitly that the variation of the interpreted value of F due to this source is by no means restricted to a small range: the sensitivity depends on the magnitude of c:

$$c = \frac{1 + f\tau_G}{(F\tau_H)^{1/2}} \sinh(N\xi) \operatorname{sech}[\xi(N - \tfrac{1}{2})]. \quad (10)$$

The quantity ξ appearing in (7)–(10) is given by

$$\cosh \xi = 1 + 1/2F\tau_H. \quad (11)$$

3. Proposed experiment

The proposal in this paper is based on a noteworthy feature of (7) and (8) above: The effect on ϕ_G of the initial variation of the exciton density or probability which can be brought about by varying κ [see (6)], appears solely in the term $\mathcal{I}(\kappa)$. And this term, while dependent on F, is independent of detector quantities $\mathcal{F}$ or f. What is proposed therefore is observation of the variation of the quantum yield ϕ_G with changes in the wavelength of excitation expressed as changes in the penetration length l_p. This length is written in terms of κ and the lattice distance a as

$$l_p = a/\kappa, \quad (12)$$

since it is the reciprocal of the absorption coefficient k, which equals κ/a.

Fig. 1 shows the ratio of yields ϕ_G for extreme values of the penetration length l_p, plotted as a function of the exciton motion rate (or the diffusion constant). Specifically the ordinate in fig. 1 is $\lim_{\kappa\to\infty}\phi_G/\lim_{\kappa\to 0}\phi_G$ and the abscissa is $F\tau_H$ on a logarithmic scale. The sample length L has been taken to be 0.5 μm and the lattice distance a to be 5 Å. Fig. 1 shows

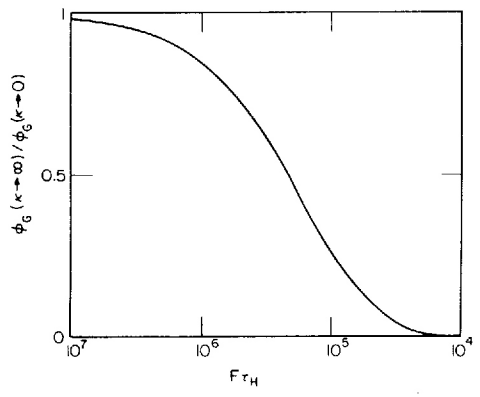

Fig. 1. The detector yield ratio from (13) plotted as a function of $F\tau_H$, showing the sensitivity (insensitivity) of the yield to variations in the penetration length for low (high) values of the diffusion constant. Sample length L = 5000 Å, and lattice distance a = 5 Å.

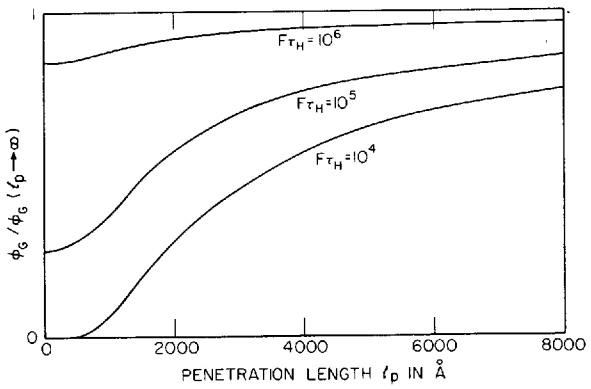

Fig. 2. The detector yield plotted as a function of the penetration length for three values of $F\tau_H$ as shown. The yield is normalized to its limiting value for uniform illumination. Sample length L = 5000 Å and lattice distance a = 5 Å.

that there is little variation of ϕ_G^s with l_p if the diffusion constant is large enough. Thus for a diffusion constant of 2.5 cm^2/s which corresponds in the present case to $F\tau_H = 10^7$, the values of ϕ_G for extreme l_p values bear a ratio of 0.98. However for a diffusion constant of 2.5×10^{-2} cm^2/s, which corresponds to $F\tau_H = 10^5$, the ratio is 0.27. And for a diffusion constant of 2.5×10^{-3} cm^2/s equivalently $F\tau_H = 10^4$, the ratio is less than 10^{-3}. In other words, observation of the yield as a function of l_p can show a variation over a factor of 1000 for $D \approx 2 \times 10^{-3}$ cm^2/s but only a factor of 1 for $D \approx 2$ cm^2/s. Little observed variation is therefore indicative of a high value of D, and considerable variation represents slow exciton transport.

Fig. 2 shows these predicted variations explicitly: ϕ_G normalized with respect to its value for the case of uniform illumination across the length of the sample ($l_p \to \infty$) is plotted as a function of l_p. The three curves correspond to the values of the diffusion constant or of $F\tau_H$ as shown. The curve for $F\tau_H = 10^4$ tends on the left ($l_p \to 0$) to extremely small values, which in fig. 2 appear to be zero. Whereas fig. 1 has been shown primarily to explain the essential idea in the proposed experiment, plots such as those in fig. 2 will provide the practical means to deduce the value of F or D when the experiments are carried out.

The expression plotted in fig. 2 is obtained directly from (8) and (9) and their limiting form as $\kappa \to 0$.

Those results as well as the limiting form of (9) for $\kappa \to \infty$ are used in fig. 1. Specifically, the yield ratio plotted in fig. 1 is

$$\lim_{\kappa\to\infty} \phi_G / \lim_{\kappa\to 0} \phi_G = \frac{N}{\sinh(N\xi)} \frac{\cosh(\xi/2)}{(F\tau_H)^{1/2}}, \tag{13}$$

the separate limits being

$$\lim_{\kappa\to\infty} \phi_G^s = \cosh(\xi/2)\,\mathrm{sech}[\xi(N-\tfrac{1}{2})], \tag{14}$$

$$\lim_{\kappa\to 0} \phi_G^s = \frac{\sinh(N\xi)}{N} \frac{(F\tau_H)^{1/2}}{\cosh[\xi(N-\tfrac{1}{2})]}. \tag{15}$$

It is to be emphasized that prior knowledge of the trapping rate and the detrapping rate is not required to deduce the exciton diffusion constant from this proposed experiment. The use of the expressions for the saturated value ϕ_G^s (rather than ϕ_G) in (14) and (15) does *not* mean that it is assumed that $\mathcal{F}/F \to \infty$. Eqs. (7) and (10) show that ϕ_G and ϕ_G^s differ by a factor which, while it depends on $\mathcal{F}$ and f, is completely independent of l_p. That factor therefore disappears from the expressions for the ratios used in the discussion and in the plots.

The proposed experiment should not be confused with observations of Mulder [11], and Haarer and Castro [12]. They do involve measurements of ϕ_G as a function of l_p. However the physics involved is quite different because the illuminated end is the same as the detection end in those experiments. Thus, in those

observations, the yield ϕ_G decreases with an increase in the penetration length, whereas it will clearly increase in our proposed experiment. It is straightforward to repeat the analysis of ref. [5] for the case of the observations of refs. [11,12]. The resulting expression, however, differs from that used in refs. [11,12] only in a trivial way and clearly reduces to the latter in the continuum limit.

It is hoped that the experiment suggested in this paper will be carried out and that definitive values of the singlet diffusion constant in aromatic hydrocarbon crystals will be established.

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