

EXCITON PERCOLATION KINETICS AND EXCITON COHERENCY: ${}^1B_{2u}$ NAPHTHALENE *

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The time evolution of the fluorescence from a naphthalene "guest" and a betamethylnaphthalene "sensor" in a $C_{10}D_8$ "host" was measured at 1.8 and 4.2 K. A rigorous heterogeneous kinetic model is used to fit the data, based on quasi-coherent exciton motion, giving a mean-free-path of $\approx 10^2$ lattice spacings for pure naphthalene.

Molecular exciton coherence is of much interest [1–5], but the interpretation of experimental measurements is somewhat uncertain [6]. We demonstrated that fluorescence measurements on ternary crystals (host, guest and sensor) can contribute to this problem [7]. These cw measurements have shown that the lowest singlet exciton of naphthalene is "quasi-coherent" at 2 K, that is, its mean free path is one or more orders of magnitude above one lattice spacing. We report here time-resolved measurements, which offer more direct, reliable and precise information. In addition, they yield quantitative results on the perennial problem of trapping efficiency (sensor cross section) and also enable us to formulate a simple, rigorous and satisfactory model of exciton migration in both pure and isotopic mixed crystals. At the same time, this is an example for a newly developed rigorous approach to heterogeneous kinetics, based on a Monte Carlo method. We are able to circumvent the problems due to the effects of defects and impurities in real (neat) crystals, by essentially "saturating" this effect. This saturation is achieved through an introduction into the sample of large, controlled, amounts of isotopically substituted molecules, which act as exciton scatterers, as well as controlled amounts of sensors that have high trapping efficiencies and quantum yields.

Experimentally we used zone refined naphthalene (Materials Ltd., 99.999%) and $C_{10}D_8$ from Merck.

Sharp and Dohme (99% D) which contains a small amount ($\approx 10^{-4}$ mole fraction) of perdeuterobeta-methylnaphthalene ("sensor"). Our analytical methods for determining the sensor concentration are described elsewhere [8]. The excitation source was a Molelectron 1000 N_2 laser pumped dye laser, the latter using rhodamine 640 (made by "Exciton"). The doubled laser radiation (3–4 ns fwhh) was focused on the crystal and the intensity reduced until no non-linear effects could be observed. Also, scanning the exciting light over regions including both host and guest absorption did not affect the results (however, excitation below the guest level resulted in little fluorescence). The details of the optical train, cryostat, etc. are given elsewhere [8]. The spectrally resolved time-evolution data were obtained with a PAR model 162 box car integrator with a 350 ps sampling head. The computer processing of the data is also described elsewhere [8].

We define a *coherency parameter* $l = \tau_c / t_j$, where τ_c is a mean correlation (memory) time and t_j is a one-step hopping time [9]. We also interpret this quantity l as a *dimensionless mean free path*, where the length of the actual mean free path is divided by the nearest neighbor distance (center-to-center), which in naphthalene is $|(a+b)/2|$. We also use a *gaussian distribution* with an sd ("standard deviation") for the values of l . Obviously $l \leq 1$ gives the case of simple random walk or simple stochastic motion, which is our "completely incoherent" limit for exciton transport. In our computer simulations we assume that random exciton scattering occurs either after time τ_c (gaussianly dis-

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tributed) or when the exciton "hits" a host ($C_{10}D_8$) site, whichever occurs first [9]. In these simulations we generate binary random lattices of $500 \times 500 = 250000$ sites and calculate ϵ (see below) as a function of l and the number of steps \bar{l} , for $1 \leq l \leq 250$ (note that larger l parameters are inconsistent with the size of the simulated lattice [8,9]).

The usual kinetic formalism for binary crystals can also be written down for our ternary lattice:

$$dN/dt = -N/\tau_N - k(t)N, \quad (1)$$

$$dB/dt = -B/\tau_B + k(t)N, \quad (2)$$

where $N = N(t)$ is the fraction of guest (naphthalene) excitons, $B = B(t)$ the fraction of sensor (betamethylnaphthalene) excitons, and τ_N and τ_B the respective time constants (inverse natural decay rate constants). Our approach is only novel in the way $k(t)$ is determined for the ternary (or binary) lattice. The probability of a guest exciton being trapped by a sensor, with relative (to guest) concentration S and trapping efficiency γ , after time t , is

$$P(t) = \bar{P}_\infty \{1 - \exp[-n_m(t)\gamma S]\} + SI'_{AV}. \quad (3)$$

Here $\bar{P}_\infty = \bar{P}_\infty(C)$ is the site percolation probability [10], which is a steep function of the guest concentration C (vanishing below the critical guest site concentration C_c and approaching unity well above C_c), $n_m(t) = n_m(t, C)$ is the number of distinct sites visited, after time t , and depends also on the "coherency parameter" l , and $I'_{AV}(C)$ is the average size of the finite clusters [10]. All above three quantities (\bar{P}_∞ , n_m and I'_{AV}) are derived by Monte Carlo simulations on binary lattices and depend also on the interaction topology (bond order). The only quantity related to the ternary system is $P(t) = P(t, C, l, \gamma, S)$. Using the percolation efficiency [11]

$$\epsilon(t, C, l) = n_m/\bar{l} = m_m t_j/t, \quad (4)$$

where t_j is the "jump time" and \bar{l} the number of steps after time t , one gets

$$P(t, C, l, \gamma, S) = \bar{P}_\infty [1 - \exp(-a\epsilon t)] + SI'_{AV}, \quad (5)$$

where

$$a = \gamma S/t_j. \quad (6)$$

One can show [8] that, rigorously, the exciton transfer "rate constant" $k(t)$ is given by:

$$k(t) = (\partial P/\partial t)(1 - P)^{-1}, \quad (7)$$

giving a precise but complex expression [8] for $k(t)$. For $C \geq 0.7$, i.e. well above C_c , where $\bar{P}_\infty \rightarrow 1$ and $I'_{AV} \rightarrow 0$, one gets [8] the simple expression:

$$k(t) = a(\epsilon + t \partial \epsilon/\partial t). \quad (8)$$

Once the percolation efficiency $\epsilon(t, C, l)$ has been derived numerically for the given topology, C , l and t , one can calculate $k(t)$. Now $k(t)$ can be substituted into the rate equations, (1) and (2), and the latter solved numerically. As our excitation (at $t = 0$) is *not* a Dirac δ function, we actually convolute our theoretical predictions of $N(t)$ and $B(t)$ by the experimentally measured laser excitation function [8].

Based on [7-10] $t_j = 0.5$ ps and an effective $\gamma = 1$ we have $a = 1000 S$ (ns) $^{-1}$. Some typical results are given in figs. 1 and 2. We see that the incoherent case ($l = 1$) is incompatible with our data, while a "quasi-coherent" description, based on $l = 100$, agrees with the experimental curve within the precision of the data. We note though that for our concentrations ($C \geq 0.7$), the results for $l \geq 10^3$ also fit the data, because high coherency values will not alter the actual particle motion, as long as $(1 - C)^{-1}$ is of the order of l or smaller. This means that scattering by the host often suffices to make the mean free path *in the binary lattice* short compared to l . Thus additional experiments are necessary, at low values of $(1 - C)$, to further pinpoint the "coherency". However, the fact that we found little change in the time evolution from 1.8 to 4.2 K indicates to us that even at the higher temperature $l \geq 100$, implying that l is even higher at 1.8 K. These results are consistent with the only other reliable indication of coherence we know of for this system, namely the linewidth measurements [12]. The measured upper limit to the homogeneous broadening, 0.2 cm^{-1} in the 2 K neat crystal, is consistent with our results, if one uses the common crude picture [13] according to which l would be given by the ratio of the exciton bandwidth [14] (150 cm^{-1}) to that of the homogeneous linewidth.

We note that our experimental results agree qualitatively with the results on doped naphthalene crystals (but with 0% $C_{10}D_8$) of Powell and Soos [15] and of Braun et al. [16]. However, our interpretation is not based on a diffusion constant. We do not believe that such a constant can be defined for our substitutional

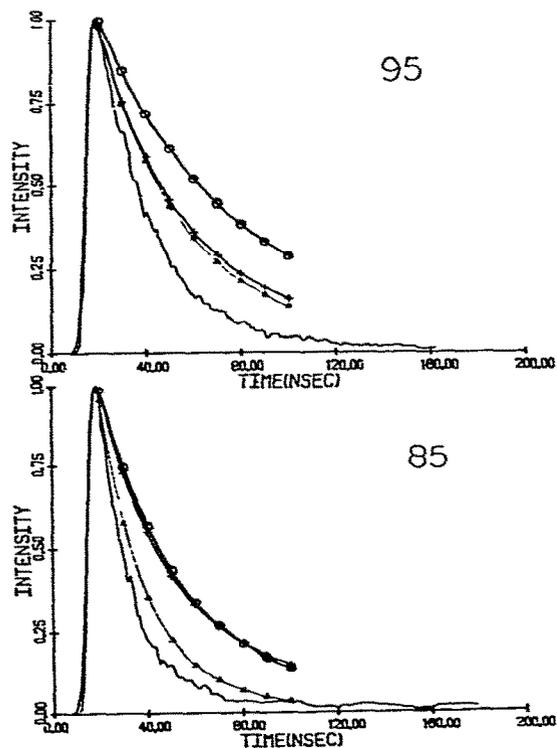


Fig. 1. Time evolution study of the ternary crystal naphthalene-perdeuteronaphthalene-perdeuterobetamethylnaphthalene. The emission monitored is of the naphthalene 0- 5^{10} vibronic band at 2 K. The intensity is normalized to units at the maximum. The mole fractions of naphthalene are 0.95 (top) and 0.85 (bottom), those of betamethylnaphthalene- d_{10} are 1.7×10^{-5} (top) and 5.1×10^{-5} (bottom). The uncertainties are about 20% (y-axis). The theoretical curves (convoluted with the laser excitation line) are calculated for the 4-nearest-neighbor case [7-10] with coherency values of $l = 1$ (circles), 10 (triangles, $sd = 3$), and 100 (crosses, $sd = 30$). Here nominal values were used for the lifetimes (naphthalene 100 ns, sensor 35 ns) and the sensor trapping efficiency was set to unity. Reducing the latter by about a factor of two improves significantly [8] the fits for $l = 100$ (but not for $l = 1$).

random system of $C_{10}H_8/C_{10}D_8$ (where the concept of diffusion has to be generalized to that of percolation). Furthermore, we doubt that it is even justified for the case of a pure naphthalene crystal, due to the short lifetime of the singlet state, combined with the effectively two-dimensional nature of the exciton transport. As we discuss this important point in detail

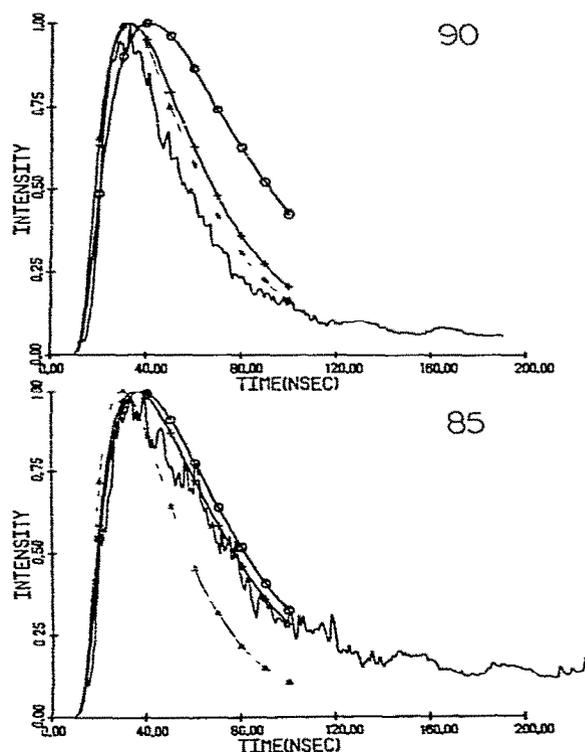


Fig. 2. Time evolution study of the ternary crystal naphthalene-perdeuteronaphthalene-perdeuterobetamethylnaphthalene. The emission monitored is the 0-0 line of betamethylnaphthalene- d_{10} . The mole fractions of naphthalene are 0.90 (top) and 0.85 (bottom) and those of betamethylnaphthalene are 3.4×10^{-5} (top) and 5.1×10^{-5} (bottom). All else is the same as in fig. 1, except for reduced signal/noise

elsewhere, we just emphasize here that our treatment is based on random walk simulations containing a relatively small number of steps.

In conclusion we notice that our observed guest exciton decay is far from exponential, and that we have fitted a large amount of data points with a single "coherency" parameter. The large value of this parameter, compared to unity, indicates that, at these temperatures, the exciton transport in both pure and mixed crystals is far from being simply stochastic. Our quasicohherent (or "quasistochastic") model gives a good description of our observed heterogeneous exciton kinetics, within the general framework of dynamic percolation [17].

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