

PERCOLATIVE VERSUS HOMOGENEOUS ENERGY TRANSPORT KINETICS:
TIME-RESOLVED DONOR AND ACCEPTOR FLUORESCENCE
OF ISOTOPIC MIXED NAPHTHALENE CRYSTALS*

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Received 11 January 1982

Time-resolved spectral studies of the singlet exciton transport threshold in doped naphthalene-perdeuterionaphthalene mixed crystals are presented. While a homogeneous kinetic model adequately explains many of the results, some strong deviations from its predictions are found. These are attributed to clusterization effects

1. Introduction

The characteristics of electronic energy transport (exciton migration) in isotopic binary mixed molecular crystals have recently attracted considerable attention. In these systems, energy transport is restricted to one of the isotopic components (the *guest*), the higher-lying energy levels of the other component (the *host*) being thermally inaccessible. Several studies [1-3] have shown that the extent of migration depends strongly upon the guest concentration, increasing sharply over a narrow "critical" range. This phenomenon has been interpreted according to models based upon Anderson localization [4], percolation theory [1,2,5], and lifetime-limited diffusion [4,6]. For the case of singlet exciton transport in naphthalene-perdeuterionaphthalene mixed crystals, it is generally agreed [1,4,6] that an Anderson transition is not involved, and that the existence of a threshold for migration can be explained by a kinetic scheme emphasizing the limited exciton lifetime and the short range of the intermolecular interactions which enable energy transfer, however, the extent to which the local concentration fluctuations emphasized by the percolation models contribute to the characteristics of the transport has not been determined. We present here time-resolved studies of singlet exciton transport in this system which we believe provide some insights into this problem.

As in previous studies [1-3], the extent of energy

migration in the mixed crystal is determined with the aid of a third component (sensor), which is present in low concentrations. The energy states of the sensor lie well below those of the guest, so that energy transfer from guest to sensor is irreversible. The relative number of excitons trapped by the sensor, which we denote as P , serves as a convenient parameter for describing the extent of energy transfer. The appropriate length scale for migration is determined by the ratio of sensor concentration to guest concentration, in the present work, this ratio is held at 0.001, so that we are concerned with multistep transport processes, which are nevertheless fairly short ranged (10-100 lattice sites). This relatively high sensor concentration ensures that trapping by unknown impurities or structural defects will be negligible compared to the trapping by the sensor. Thus, the only possible channels for guest exciton decay are intramolecular relaxation, governed by the natural lifetime of the guest, and energy transfer to the sensor. A third possibility, exciton-exciton annihilation, has been shown to be unimportant under our experimental conditions [7]. Experimental studies of the time evolution of the guest and sensor populations thus provide direct information about the energy transport processes.

In constructing a description of such processes, one may consider two limiting cases, one in which local guest concentration fluctuations are unimportant, and one in which they are dominant. We refer to these as the "homogeneous" and "local supertransfer" limits, respectively. In the first case, one can define a macroscopic rate of energy transport, with a corresponding

* Supported by NSF Grant No. DMR 800679.

rate constant K_{ct} . The time evolution of the populations is then given by the familiar [6,8] rate equations

$$dN_g/dt = \tau_g^{-1}N_g - K_{ct}N_g + F(t), \quad (1)$$

$$dN_s/dt = K_{ct}N_g + \tau_s^{-1}N_s, \quad (2)$$

where N_g and N_s are the populations of guest and sensor, and τ_g and τ_s are their natural lifetimes. $F(t)$ is a source term for creation of guest excitons: in the experiments it is equated with the excitation pulse shape. The natural lifetime of a species is identified with its lifetime when present as a very dilute guest in the host crystal, so that the effects of all decay channels except energy transfer are included. If $F(t)$ is non-zero only for a period short compared to the natural lifetimes, one can infer from this description that shortly after excitation, the populations are given by

$$N_g(t) \propto \exp[-(\tau_g^{-1} + K_{ct})t], \quad (3)$$

$$N_s(t) \propto \exp(-\tau_s^{-1}t) - \exp[-(\tau_g^{-1} + K_{ct})t] \quad (4)$$

and that the time-averaged trapping ratio is given by

$$P = K_{ct}/(K_{ct} + \tau_g^{-1}). \quad (5)$$

At long times, $N_s(t)$ will asymptotically approach an exponential decay governed by the smaller of τ_s^{-1} and $(K_{ct} + \tau_g^{-1})$. Furthermore, the risetime of the sensor population will be finite, although it may be obscured by the source term.

In this scheme, all of the concentration dependence of the energy transport is incorporated in a concentration-dependent K_{ct} . The observed threshold behavior of P thus implies that K_{ct} varies strongly with concentration. Blumen and Silbey [6] have shown that such a behavior follows naturally from the short range of the intermolecular interactions in this system.

In the local supertransfer limit, exciton migration is limited by local concentration fluctuations. Within isolated clusters of guest sites, the excitons move sufficiently quickly to be trapped at any accessible sensors within a period much shorter than all experimental timescales. Thus excitons created in clusters containing sensors give rise only to the observed sensor emission, so that only those excitons created in clusters containing no sensors contribute to the observed guest emission. It follows that both guest and sensor populations will be seen to decay with their natural lifetimes. In these circumstances, the time decays contain little information.

The intermediate case presents major theoretical difficulties. Although considerable progress has been made in the theory of dispersive exciton transport [9], these studies are not easily applied to our multidimensional, highly concentrated systems. Moreover, our experimental data is insufficiently precise in the short- and long-time limits to be compared with the theoretical asymptotic behavior. In our discussion we therefore refer our data only to the simple limiting cases. By measuring the time evolution of the guest and sensor emissions, we can determine whether either limit is approximately attained, and come to conclusions about the nature of the transport threshold.

2. Experimental

The mixed crystals were prepared from zone-refined, potassium fused naphthalenes and sublimed 2-methylnaphthalene according to previously described techniques [10]. The relative sensor (2-methylnaphthalene) concentration ranged from 0.00063 to 0.00130. No additional impurities were identified in low-temperature absorption and emission spectra of the starting materials.

Single crystals were cleaved along the *ab* plane, mounted in a strain-free cage and immersed in superfluid helium (1.7 K). A frequency-doubled Molelectron DL400 dye laser, pumped by a Molelectron UV1000 nitrogen laser, was used to excite the samples at a wavelength of 3125 Å (in the upper vibronic manifold). The spectrally-resolved emissions from the naphthalene- \mathcal{H}_g 0-512 vibronic transition and the 2-methylnaphthalene 0-0 transition were detected by an EMI 9781R photomultiplier tube, and signal-averaged time decays were obtained with a pre-triggered PAR 162/165 boxcar averager. Analog data was recorded on chart paper, converted to digital and stored on magnetic disc by a DEC PDP-11/03 microcomputer. The overall time resolution was ≈ 5 ns.

3. Results and discussion

The natural decays of naphthalene and 2-methylnaphthalene were obtained from crystals of naphthalene- \mathcal{d}_8 containing 0.1% of the species; the decay of dilute 2-methylnaphthalene in naphthalene- \mathcal{H}_g was also

measured and found to be the same as in naphthalene- d_8 . The measured lifetimes for guest and sensor were 127 ± 3 ns and 51 ± 3 ns, respectively. These results are in agreement with previous work by this group [10], but are significantly larger than the values obtained by others [11]. Although we have not accounted for this discrepancy, we point out that only relative values are important for our work, which is in this sense self-consistent.

The guest decays were found to be, within experimental error, exponential over the entire range of concentrations studied. We were thus able to obtain the trapping ratio P both from the decay constants and by numerically integrating the guest decays:

$$P = 1 - \int_0^{\infty} N_g(t) dt / \int_0^{\infty} N_g^0(t) dt. \quad (6)$$

where $N_g^0(t)$ is the natural decay, defined as the decay in the absence of trapping. In this procedure, which is valid for exponential decays convoluted with the same source function, the area under each decay curve is normalized to the maximum of the curve, and then the ratio indicated taken. Fig. 1 shows that the results obtained from the lifetimes and from the integrations agree well.

Although the guest decays are consistent with the homogeneous model, in the lower portion of the threshold (40–50%) they are not very sensitive to the de-

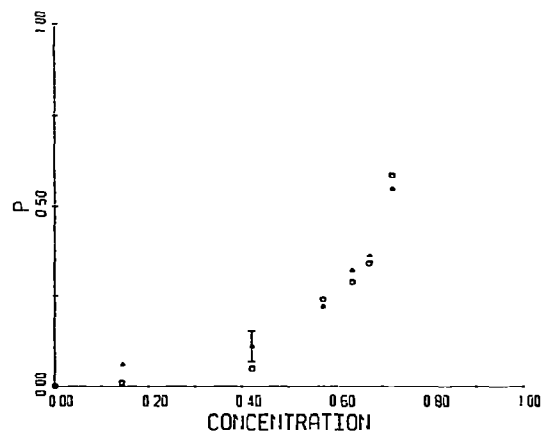


Fig. 1 Trapping ratio P for various guest concentrations. Triangles: derived by integrating decay curves [eq. (6)]. Circles: derived from measured rate constants [eq. (5)].

tails of the transport, since the measured lifetime is close to the natural lifetime so that the relative error of the results is rather large. In this "subcritical" region, the sensor decays provide the more useful information, because nearly all of the sensor emission is a result of energy transfer from the guest. (This is true even though relatively few guest excitons are being trapped. The sensor fluorescence from a 14% guest crystal is barely noticeable, whereas that from a 35% crystal is easily measured.)

Fig. 2a shows a typical sensor decay for a subcritical sample, together with the predictions of the limiting

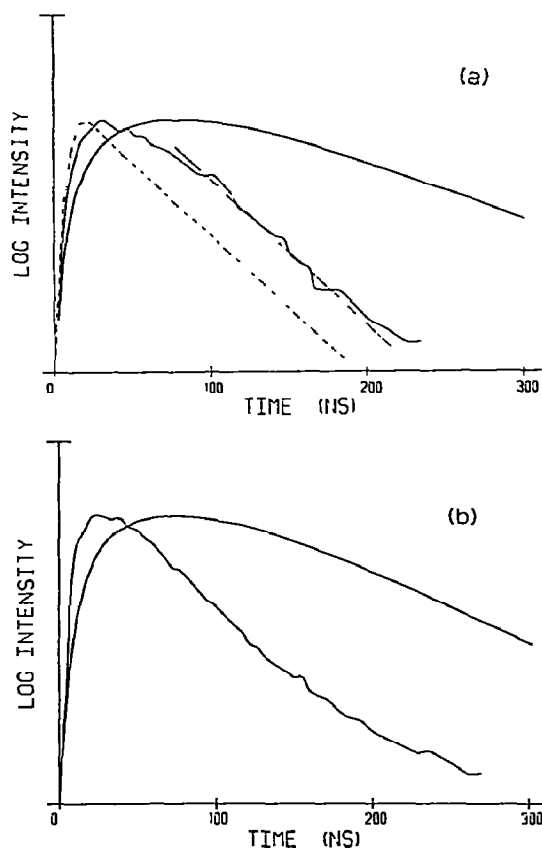


Fig. 2. Calculated and observed sensor decays for crystals containing (a) 0.42 and (b) 0.57 mole fraction of guest. Light curve: experimental. Heavy curve: homogeneous case. Dashed curve: local supertransfer case. A copy of the lower portion of the last curve is superposed (long dashes) on the experimental curve to show the agreement of the asymptotic slopes.

cases described above. The homogeneous curve is obtained from the solutions to the rate equations (including the source term, determined from the measured laser pulse shape), using a value of K_{et} obtained from the guest decay in the same sample. The local supertransfer curve is merely the convolution of the natural sensor decay with the source term. The strong deviation from homogeneity is evident: the asymptotic lifetime is identical with that of the natural decay, and the risetime is very short. One must conclude that the rate of transfer to the sensor is faster than the sensor decay rate. In the homogeneous limit this would imply an *observed* guest lifetime of less than 51 ns, when in fact it is quite close to the natural value (121 ns in this sample). The observed behavior is similar to that predicted for the local supertransfer limit.

At higher concentrations, within the critical region, the sensor decays show a complicated behavior, as can be seen in fig. 2b. The asymptotic slope is quickly established, but at later times the decay rate actually begins to decrease, so that the logarithmic plot becomes concave upwards. The simple biexponential decay laws can never produce such a result. With increasing concentration, this long-time tail becomes more prominent, until at 72% the "fast" component has nearly disappeared. We tentatively ascribe the tail to a homogeneous component in the decay, so that the observed emission contains contributions from both short-range and long-range transport events. Unfortunately, the information contained at long times is quite unreliable, because of low S/N and possible contributions from delayed fluorescence, so that our statements must remain qualitative.

Finally, we comment upon the relationship between the present work and earlier time-domain research published by this group. This is the first investigation of the time behavior within the critical region. The earlier work of Ahlgren et al. [10] was actually limited to the subcritical region (contrary to a statement made in that reference), within which their conclusions are correct. The work of Argyrakis and Kopelman [12] was confined to guest concentrations above the threshold and to very lower sensor concentrations. Their study actually complements this one, in that the effects of partially coherent transport, neglected here, are considered. Such considerations are necessary when the length scale for transport is large, as is guaranteed by the low sensor concentrations and high guest concentrations used by Argyrakis and Kopelman.

4. Conclusion

A kinetic model which assumes the applicability of the homogeneous limit, such as that presented by Blumen and Silbey [6], is capable of explaining the existence and qualitative features of the critical energy transport threshold in this system. However, in a subcritical concentration regime, in which extensive energy transport first begins to occur, such a treatment is invalid. The observed behavior in this regime is fairly close to a limit in which energy transfer to the sensor is extremely rapid, but only occurs during a short portion of the guest exciton lifetime. Such a limit is expected to hold when the extent of migration is controlled by the local topology of the guest quasilattice, rather than by the exciton lifetime. This should be the case near the static site percolation threshold [13]. At higher concentrations, it appears that these fluctuation effects become less important, and the homogeneous limit eventually becomes applicable. Our system thus provides an example of a smooth transition from heterogeneous to homogeneous, i.e. percolative to diffusive trapping kinetics [14].

Acknowledgement

We wish to thank Mr. Stuart Gentry for supplying crystals and steady-state fluorescence spectra.

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