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Time Resolved Energy Migration in an Energetically Disordered Molecular Crystal†

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Time resolved emission spectroscopy is used to monitor triplet exciton migration in *p*-dichlorobenzene-*p*-dibromobenzene mixed crystals. The migration efficiency is varied by adjusting the concentration and the temperature (2–12°K). Long range migration is found even though the static energy disorder parameter W is much larger than the exciton band width B. Because of exciton tunneling, the range of the transfer is only limited by the maximum lifetime of an exciton. These results illustrate the importance of at least six key parameters in determining the efficiency of long range exciton migration; B, W, the range of transfer, the temperature, the exciton lifetime and the topology of the excitation exchange interactions through its effect on the long range connectedness of the system.

I. INTRODUCTION

Soon after the pioneering work by Frenkel[1] and Peierls[2] on excitation energy migration in molecular solids, Frank and Teller[3] considered its parallel to the energy harvesting mechanism in photosynthesis; this application continues to be one motivation for the study of energy migration in solids. Subsequently Halford *et al.*[4] and Broude *et al.*[5] demonstrated how the effects of intermolecular interactions were revealed by the fine structure in the infrared and electronic spectra respectively. Following the development[6] of exciton theory relating the observed fine structure to specific molecule-molecule interactions, a large body of work led to refinements in the theory and to detailed measurements of intermolecular interactions (i.e. excitation exchange, electron-phonon coupling, dispersion etc.) in molecular crystals. From recent reviews[7] it can be seen that Broude and his coworkers made significant contributions to this

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development. The knowledge of excitation exchange interactions has provided a basis for the detailed interpretation of the energy migration studies begun by Nieman and Robinson.[8] Their suggestion that isotopic mixed molecular crystals be used to study electronic energy migration led to a large body of research and a reasonably clear picture of the energy migration mechanism at low temperatures (2–4°K). As these findings became available, they were used to continually refine our understanding of the efficiency of the energy migration processes involved in photosynthesis.[9] While there are significant differences between the photosynthetic system and the isotopic mixed crystal model, the effects of these differences are thought to be quantitative in nature and, to a degree, predictable. However, it has recently been suggested[10] that static[11] electronic energy disorder can have a major qualitative effect on the energy migration efficiency even for isotopic mixed crystals where it is often ignored. The primary purpose of this work is to probe the significance of the energy disorder parameter.

Nieman and Robinson[8] observed electronic energy transfer from one isotopic energy trap to another [e.g. from $C_6H_3D_3$ (donor) to C_6H_6 (acceptor) molecules in a C_6D_6 host crystal where the more protonated species have the lower excitation energies.] Increasing the donor (trap) concentration increases the efficiency of energy transfer to the acceptor (supertrap) and transfer is monitored via changes in the donor/acceptor emission intensity ratio. This approach has been used in our laboratory to study the effects of donor-acceptor energy differences, exciton-phonon coupling, exciton tunneling and led to the suggestion that static energy disorder could have a significant effect on donor-donor energy migration.[12] Others[13] have also found this to be a fruitful approach for studying excitation exchange processes in molecular crystals. If the acceptor concentration is kept at a low value, donor-acceptor transfer proceeds via many donor-donor transfer steps and mimics long range energy migration in pure crystals. In this case, one observes a dramatic increase in the extent of excitation energy migration when the donor concentration exceeds a certain threshold value.[14–16] The position of the threshold has been interpreted in terms of the range and topology of the excitation exchange interactions using percolation theory to describe the connectedness of the donors as a function concentration.[14–15]

Following the work by Anderson and Mott[17] on electron conduction band states, it has been shown[11] that energy disorder can result in the localization of all exciton levels in the limit where the spread in the excited state energy disorder W is 4–10 times greater than B, where B is the exciton band width. Furthermore it was proposed that "Anderson localized" states would be much less efficient conduits for energy migration and that the observed threshold could be due to an abrupt localization of the exciton wavefunctions —an Anderson–Mott transition.

There are however several problems that must be addressed before interpreting an observed threshold as being due to an Anderson–Mott transition. First, focusing on the total band width in a crystal where the excitation exchange interactions are *non-isotropic* can be misleading due to the importance of cluster states within the band. Consider, for example, a hypothetical molecular crystal wherein all of the nearest neighbor excitation exchange interactions are equal. By isotopic dilution (e.g. adding C_6D_6 to a C_6H_6 crystal) one can reduce the half-width of a given excited state exciton band in a manner that will be related to concentration. Assume that at 90% isotopic dilution (10% protonated species) B has been reduced to the order of W and such that further dilution results in an Anderson–Mott transition to all localized exciton states. Now, consider the effect of increasing one translationally equivalent pair of the nearest neighbor interactions until they are an order of magnitude *larger* than in the above case. This will significantly increase the total bandwidth, formally forestalling the onset of an Anderson–Mott transition. Nevertheless, a little thought will reveal that, at low temperatures where $B > KT$, increasing B in this manner will *decrease* rather than increase the energy migration efficiency. The larger interactions will generate states at the edges of the exciton band. At low temperatures, the states at the bottom of the band must carry the excitation energy. Because of the large anisotropy in the interactions, these states are essentially linear crystal type states which are very easily broken up or localized by the isotopic dilution itself. (Conduction in a wire can be stopped by cutting it at one point while, in a two or three dimensional network, many "cuts" are needed to isolate one point from another.) Thus, even in the $W < B$ limit, the range of the energy migration in a pseudolinear crystal will be severely limited in other than nearly pure crystals. It is for this reason that Kopelman *et al.*[14] have chosen to focus on those chains or clusters of molecules thought to be actually responsible for the energy migration in a specific isotopic mixed crystal rather than to use the *total* band width as a measure of the long range coupling of states. By using percolation theory to predict the probability for the existence of such clusters, they have been able to provide an alternative explanation for the dramatic effect of concentration on the energy transfer efficiency, without considering the effects of static energy disorder W.

The states associated with a specific cluster of donors can themselves be subject to severe, dynamic[11] energy disorder. For instance, for triplet excitons, the donors are primarily coupled via weak, non-nearest neighbor interactions. In this case, the occasional nearest neighbor link will result in a resonance splitting much larger than the half-width of the cluster exciton band. Efficient trapping (localization) of the excitation energy into these pseudolocalized, "dimer" states has been observed by Smith *et al.*[16] This type of energy disorder will affect the migration efficiency in much the same manner as static energy disorder. For these reasons, it is not obvious how to apply Anderson–Mott theory to isotopic mixed molecular crystal results.

Even neglecting the above complications, there is another basic problem with the assertion that exciton migration *efficiency* should be significantly perturbed when the exciton band is subject to an Anderson–Mott type transition. Above the transition limit ($B \gg W$) at least some of the exciton states are delocalized, i.e. have nearly equal amplitude throughout the crystal. Below the transition limit ($B \ll W$) all exciton states are said to be localized, i.e. have a maximum amplitude at some specific location in the crystal and lesser amplitude elsewhere. Nevertheless, because of superexchange interactions involving the host states, such states are only pseudolocalized and will still have some amplitude *throughout* the *entire* crystal. From this one can see that, even below the Anderson–Mott transition, and given sufficient time, excitation initiated at any site in the crystal can migrate to any other energetically accessible site in the crystal via coupling through these pseudolocalized states. Localization does not necessarily block energy migration. Furthermore, the effects of an Anderson–Mott transition will only have an *abrupt* effect on the transfer efficiency if the last states to become localized are themselves involved in the migration dynamics in a rate determining manner. This will obviously depend upon the sample temperature and the range (distance) of the excitation migration being probed in a given experiment. From these considerations, one can see that an experiment must be carefully designed if it is to reveal the effects of an Anderson–Mott transition.

One objective of this paper is to report the observation of a threshold for excitation energy migration in the limit where $W \gg B$, i.e. well below the Anderson–Mott transition. The energy migration is monitored via time resolved emission spectroscopy obtained as a function of temperature and concentration. The spectra are recorded using a gated SIT image tube in the focal plane of a monochromator. This allows us to obtain time slices of the entire spectral region of interest, generating data more accurately and much more rapidly than by other techniques. The availability of such time resolved spectral data should be very useful in the evaluation of the kinetic theories of energy migration presently being developed.[18]

Triplet excitons in the *p*-dichlorobenzene/*p*-dibromobenzene DCB/DBB mixed crystal system were chosen for study for several reasons. The system is known[19] to form solid solutions at nearly all concentration ratios. The pure and mixed crystal spectra have been studied extensively with the following pertinent findings. The DCB triplet state is 50 cm^{-1} below that of DBB in the mixed crystal.[20] The pure crystal triplet exciton band widths are known to be less than 0.5 cm^{-1}.[21] The static energy disorder W, as measured by the spectral linewidths,[22] is of the order of 10 to 100 cm^{-1} depending upon the DCB/DBB concentration ratio[23] and preliminary data suggest the existence of two energy migration thresholds, at 10% and 99.5% respectively.[23] The lower concentration threshold will be the subject of this paper.

II. EXPERIMENTAL RESULTS

Mixed crystals were prepared from zone refined, *p*-dichlorobenzene and *p*-dibromobenzene, using greaseless vacuum techniques. The crystals were grown in quartz cells using a standard Bridgman-type furnace as described previously.[24]

For temperatures between 1.8°K and 5°K, the spectra were taken with the samples immersed in liquid helium. At higher temperatures, the samples were placed in a cryostat which provided a constant flow of cooled helium gas. The temperature was measured either via the helium vapor pressure and/or with a calibrated doped germanium resistor. The samples were excited into high vibrational levels of the triplet state with a defocused nitrogen laser. Front surface emission spectra were recorded with a P.A.R. 1254 S.I.T. detector head (with UV scintillator) mounted on a 2 m. Jarrell Ash Monochromator. The 1200 line grating was blazed at 7500 Å. About 50 Å were dispersed across the 12.5 × 12.5 mm target located at the focal plane of the monochromator. The experiments were performed with the aid of a computer (LSI-11 CPU) and a P.A.R. 1216 detector controller for scanning control and data acquisition.

Time resolved spectra were obtained by gating the detector on with a high voltage pulse. The gating acts effectively as a shutter, with time windows between 40 ns and 1 ms. In this experiment, intensities were too weak to be measured for pulse widths < 0.1 msec.

The effects of concentration on the spectrum which were reported earlier[23] are reestablished for the 5% to 10% concentration range as seen in Figure 1. As the DCB concentration is increased, emission from the DCB monomer (peak M) decreases while the emission from the rest of the spectrum, which is due to aggregate species (dimers, trimers, etc.) and DCB molecules in other special sites, increases. Above 10% DCB, their relative intensities change such that emission from the statistically improbable species becomes much more intense than that from the more probable monomer species. This was the basis for the suggestion[23] of energy migration occuring even in this case where $W \gg B$.

We knew[25] that, with extensive zone refining, a DCB/DBB mixture could be partially separated. To determine whether a concentration gradient had been developed in our crystals during their growth, we sampled the spectrum of the 9% crystal as a function of the vertical growth axis. This is a straightforward application of an OMA when used in conjunction with a sigmatic

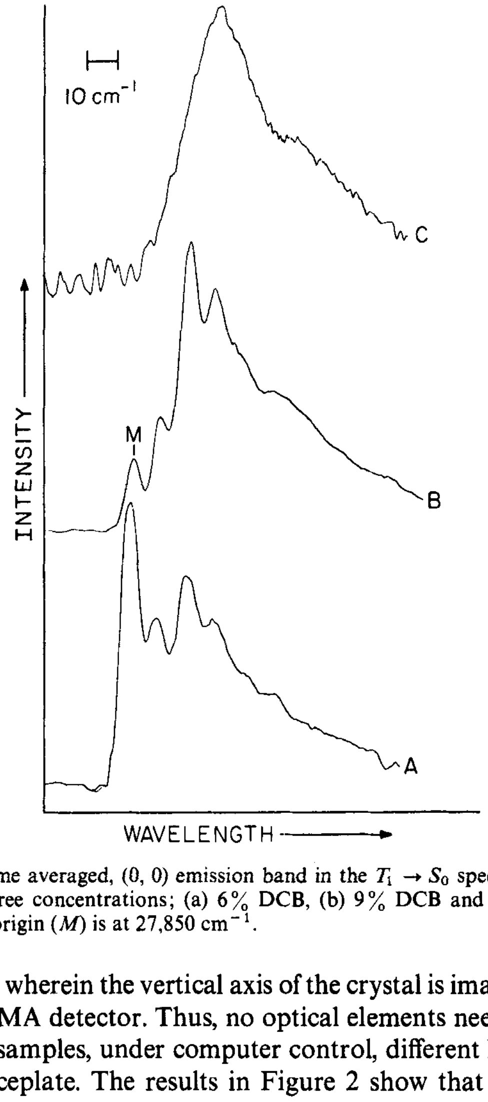

FIGURE 1 The time averaged, (0, 0) emission band in the $T_1 \rightarrow S_0$ spectrum of DCB/DBB mixed crystals at three concentrations; (a) 6% DCB, (b) 9% DCB and (c) 14% DCB. The monomer emission origin (M) is at 27,850 cm^{-1}.

monochromator wherein the vertical axis of the crystal is imaged on the vertical axis of the OMA detector. Thus, no optical elements need to be adjusted and one merely samples, under computer control, different horizontal strips on the OMA faceplate. The results in Figure 2 show that a concentration gradient does exist as illustrated by the different emission lineshapes. The spectra indicate that the gradient may be as much as 4%. Thus, the spectra in Figure 1 represent an average over a range of concentrations whose mean may not be equal to that of the bulk, although the spectra were taken from the central portion of the crystal.

Even with these uncertainties in mind, it is clear from Figures 1 and 2 that there exists a sharp change in the relative monomer emission at about 10% DCB. It must now be determined whether this is due to an energy migration

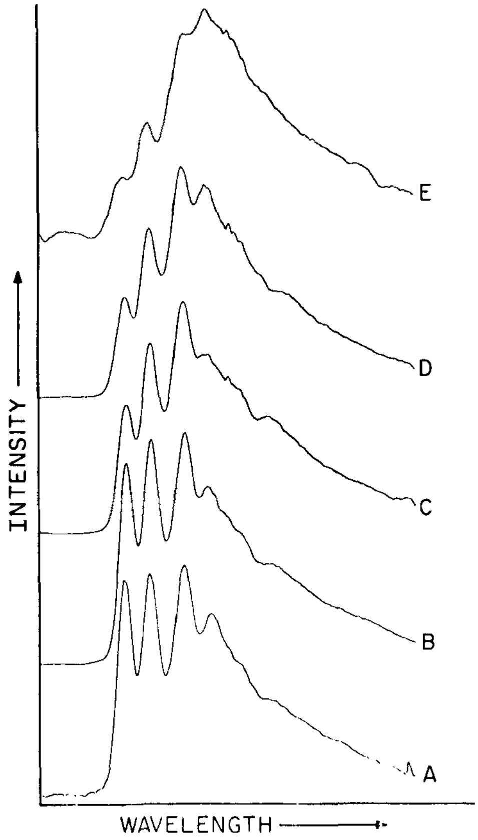

FIGURE 2 The time averaged, (0, 0) emission band in the $T_1 \rightarrow S_0$ spectrum of a 9% DCB in DBB mixed crystal at 2°K as a function of distance along the vertical axis of the crystal. The spectra labeled A through E come from adjacent, 0.25 mm high strips starting near the bottom A and ending near the top E of the crystal.

threshold or to some other effect. For instance, it is conceivable that there is an abrupt change in the crystal growth habit strongly favoring DCB aggregation at this concentration. The energy migration hypothesis would be strongly supported if the low concentration sample could be made to give the "high concentration spectrum" by increasing the temperature. The increased temperature should enhance the migration efficiency in an energy disordered crystal. Figure 3 shows the temperature dependence of the emission from the 6% DCB sample, confirming the energy migration interpretation of the threshold.

For further confirmation, we obtained the spectrum of the 6% DCB sample as a function of time at 8°K. In Figures 4 and 5 it can be seen that the monomer

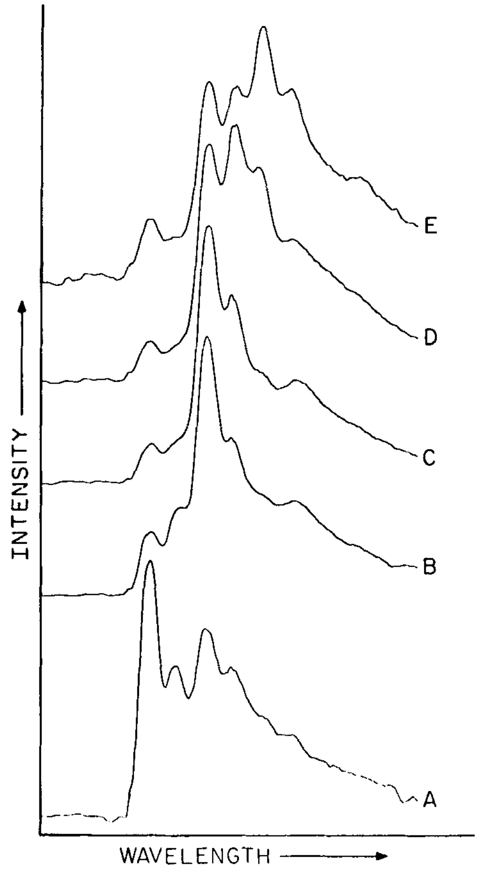

FIGURE 3 The time averaged, (0, 0) emission band in the $T_1 \rightarrow S_0$ spectrum of a 6% DCB in DBB mixed crystal at the following temperatures: (a) 4.2°K, (b) 7°K, (c) 8°K, (d) 9°K, and (e) 11°K.

emission is relatively intense at short times and is degraded at the expense of aggregate emission at long times. Thus, under these conditions, the energy migration timescale is of the order of the emission lifetime ($\sim$5 msec).

To illustrate the effects of temperature and to determine the energy migration timescale under other conditions, the time resolved spectra were also obtained for all three samples at 2°K. In the 6% crystal, the monomer emission was always the most intense component. In contrast, at 14% DCB the migration was essentially complete in 0.1 msec. We were unable to detect any monomer emission during the first 0.3 msec and only a small red shift of the broad aggregate emission could be seen at longer times. The time evolution of the emission from the 9% crystal at 2°K is shown in Figure 6.

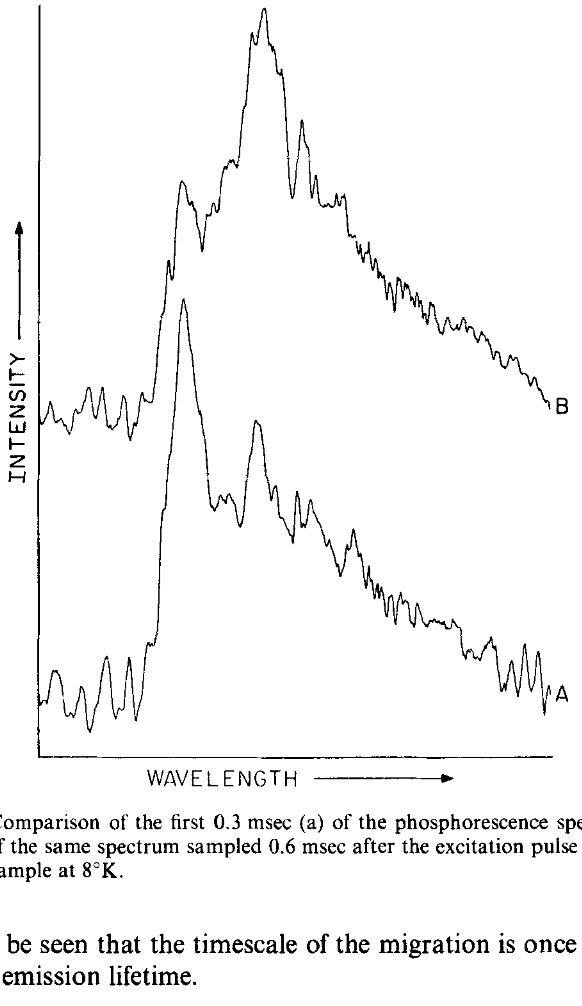

FIGURE 4 Comparison of the first 0.3 msec (a) of the phosphorescence spectrum to a 0.3 msec portion of the same spectrum sampled 0.6 msec after the excitation pulse (b) using a 6% DCB in DBB sample at 8°K.

There it can be seen that the timescale of the migration is once again of the order of the emission lifetime.

III. DISCUSSION

The results reported above reveal a triplet excitation energy migration threshold at 10% DCB in a DCB/DBB mixed crystal at 2°K. These results show that even extensive energy disorder $W \gg B$ does not preclude long-range exciton energy migration. One might ask whether the disorder in the DCB/DBB system is really Anderson-type because it is due to differences in guest-host, static interactions and will therefore depend explicitly upon guest concentration. While this may be a matter of definition resulting in no significant difference, it should be emphasized that the same type of disorder exists

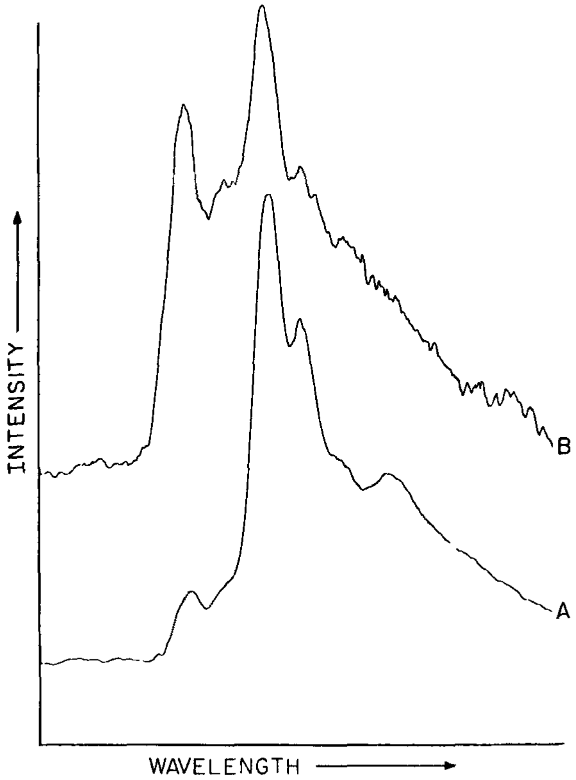

FIGURE 5 Comparison of the time averaged (a) phosphorescence spectrum to that obtained during the first 1 msec after excitation (b) using a 6% DCB in DBB sample at 8°K.

to a lesser degree in isotopic mixed crystals.[26] Before comparing these results to the predictions of Anderson–Mott theories, one must also establish that the disorder is short range compared to the migration distances. All the available experimental data indicate that the DCB/DBB crystal is a uniform, amalgamated solid.[19] Because the energy disorder results from (1) formation of the mixture which is random and (2) dispersion forces which are short range, one can assume that the disorder itself is random and short range. Thus, the DCB/DBB results provide direct evidence that energy disorder does not *block* triplet excitation energy migration.

The range (distance) of the migration appears to be quite similar to that found for triplet excitons in isotopic mixed phenazine crystals.[6] The onset for efficient monomer to aggregate transfer is found to occur at about 6% phenazine in a deuterated phenazine host crystal. This is true even though the triplet exciton band width is more than an order of magnitude *smaller*

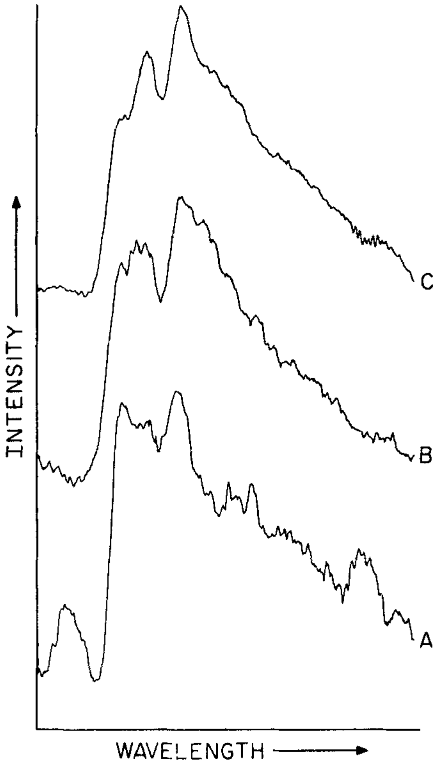

FIGURE 6 The time evolution of the (0, 0) emission band in the $T_1 \rightarrow S_0$ spectrum of a 9% DCB in DBB mixed crystal at 2°K. The spectra represent 0.5 msec time slices taken 0(*A*), 1(*B*), and 5(*C*) sec after the excitation pulse. They should be compared to Figure 1b which shows the time averaged spectrum taken under the same conditions.

and the energy disorder is more than an order of magnitude *larger* in the DCB/DBB system. The only property which the two systems appears to have in common is their triplet lifetimes which are of the same magnitude. In light of the DCB/DBB results, there is no a priori reason to attribute the threshold observed in phenazine to an Anderson–Mott transition. Smith, *et al.* have independently been lead to the same conclusion by their more recent findings.[16b]

The observation of nearly equal concentration thresholds for energy migration in the DCB/DBB and phenazine systems dramatically illustrates the necessity for considering all important parameters in the interpretation of an observed threshold. Considering only the *band widths*, *energy disorder*, *range of transfer*, *temperature* and *lifetimes*, one would have predicted the DCB/DBB threshold to occur at *much* higher concentrations than that for phenazine crystals. Their similarity suggests the existence of at least one more critical parameter which enhances the migration efficiency in DCB/DBB relative to phenazine. As pointed out in the introduction, a pseudolinear excitation migration topology will be very inefficient in a mixed crystal if $B > KT$. The migration efficiency will generally increase as the topology is made more isotropic. In the language of percolation theory, the onset of long range connectedness of donor sites will move to lower donor concentrations as the number of directly coupled sites increases and becomes more isotropic.[14,15] In the phenazine crystal, one pair of translationally equivalent interactions is an order of magnitude larger than all others and is greater than KT at the temperature of the observed threshold. This can project out special (pseudo-linear) clusters of sites upon which energy must migrate in this system, reducing the efficiency at a given concentration. A more isotropic transfer topology in the DCB/DBB system might explain in part the otherwise surprising similarity of the migration efficiency in these two systems.

The effect of the exciton lifetime in limiting the extent of energy migration is graphically illustrated by these results. At every concentration studied, there is evidence that, given more time, a larger fraction of the excitation finds its way into the lower energy sites. In the 14% DCB crystal for example the excitation is rapidly (<0.1 msec) dumped into a large variety of presumably dilute, low energy sites, resulting in a broad ($\sim 60\ \text{cm}^{-1}$) nearly structureless peak. However, 10 msec later energy has funneled into lower energy sites and this peak has shifted $10\ \text{cm}^{-1}$ to the red. Given sufficient time, all the emission would evidently come from those sites with energy levels within KT of the lowest energy levels. This observation supports our assertion that exciton super exchange interactions couple all donor sites and allow for long range exciton tunneling in a mixed crystal of this type.

Another way of looking at these results is to say that whenever one has a way of varying the energy transfer rate (the time required to get from an average donor to and average acceptor) an abrupt change in the efficiency will occur when this rate passes through the natural exciton decay rate. The steepness of the transition will depend upon how rapidly the transfer rate varies with the parameter (donor concentration, acceptor concentration, temperature, etc.) being used to adjust the rate and upon the fraction of populated donor sites coupled in going through the transition. Obviously even a fairly simplistic theory could be parameterized to agree with a given experimental result. Thus, finding such agreement with a given theory (dynamic percolation, Anderson–Mott transition, dynamic calculation, etc.) does not justify its underlying assumptions. Clearly, Anderson–Mott transition theory cannot explain these new results. However, the steep temperature dependence of the results are also inconsistent with any theory which ignores energy disorder. What seems to be needed in this case is a full dynamical calculation which explicitly includes the energy disorder and the effects of exciton phonon coupling which allow for the exchange of energy between nonresonant states.

In summary, these new results have clarified our understanding of excitation energy migration in disordered molecular crystals as follows.

1) They demonstrate long range energy migration among pseudo-localized states in an energy disordered crystal.

2) The explicit relationship between the exciton lifetime (or more generally, the time available for transfer) and the position of an observed migration threshold has been illustrated.

3) In combination with previous studies, these results demonstrate the existence of at least six key parameters in determining the efficiency of long range energy migration: namely, the exciton *band width*, the magnitude of the *energy disorder*, the *range* (distance) of transfer, the *temperature* via exciton-phonon coupling, the exciton *lifetime* and the *topology* of the excitation exchange interactions through its effect on the long range connectedness of the system.

Obviously, there will be limiting cases wherein some of these key parameters do not play an important role in the migration dynamics. However, this fact must be explicitly established for a given system before it can be used to probe the effects of the remaining parameters. Based upon these findings and those most recently reported by Kopelman *et al.*[14] and Smith *et al.*,[16] there seems to be no example of an exciton migration threshold which can be safely attributed to an Anderson–Mott transition.

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