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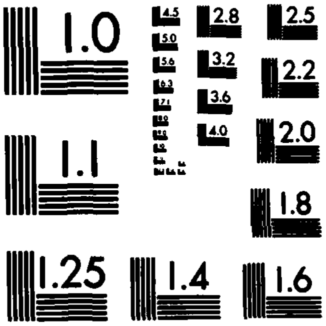
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ENERGY TRANSFER MECHANISM SWITCHING IN DISORDERED SOLIDS

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ABSTRACT

The excitation decay of the long wavelength portion of the inhomogeneously broadened 0,0 band of the $T_1 \leftarrow S_0$ transition due to triplet-triplet energy transfer in 1-bromo-4-chloronaphthalene (orientationally disordered solid) at 4.2 K is analyzed in terms of one-dimensional exchange and 3-dimensional dipole-dipole mechanisms. The fit to a dipole-dipole mechanism is observed at long decay times and very long excitation wavelength (i.e., very low acceptor concentrations). As the excitation wavelength decreases (i.e., as the acceptor concentration increases), the one-dimensional exchange mechanism, which describes only the early portion of the decay at the longest wavelength, begins to dominate in describing the full decay range.

I. INTRODUCTION

Disordered solids have a number of properties not possessed by crystalline solids. For example, excitation energies of the different molecules in the disordered solid have a larger spread in excitation energy than in crystalline solids, resulting in a larger inhomogeneous linewidth for the former (100 cm^{-1} as compared to 1 cm^{-1} at 4.2 K). Furthermore, in disordered solids, the distance between molecules than can exchange excitation energy is not constant leading to an energy diffusion constant which changes in time[1] after a pulsed excitation of the donor in the system. Since the different energy transfer interactions may be of different dimensionality and are expected to be most effective at different ranges of donor-acceptor separation, i.e. at different time scales after the donor excitation, it is possible that by selecting the proper disordered solid, a switch in the excitation transfer mechanism from a shorter range and less isotropic interaction to a long range and more isotropic interaction might be observed by analyzing the temporal dependence of an excited donor population at a certain acceptor concentration.(2) Such a behavior is not expected for crystalline materials.

Two different types of energy transfer studies have been carried out. The usual one is that in which the donor and acceptor are two different chemical species. In the second one, using lasers, a set of molecules or ions within the inhomogeneous profile ($\Delta\nu_{inh}$) can be excited, thus acting as the donors. Some of the species of the same chemical remaining unexcited can act as the acceptors. If $kT > \Delta\nu_{inh}$, then all the unexcited species are indeed acceptors and the energy transfer process occurs to species of higher or lower frequency than the donor by phonon assisted processes,[3] e.g. Eu^{3+} in phosphate glasses.[4] If, however, $kT \ll \Delta\nu_{inh}$, only those species with absorption frequencies equal or lower than those excited with the laser are potential acceptors, e.g. the transfer in orientationally disordered 1-bromo, 4-chloronaphthalene[5] (BCN) at 4.2K.

In BCN, the naphthalene skeletal of the different BCN molecules are stacked along a one dimensional array[6], similar to the 1,4-dibromonaphthalene crystal for coupling.(7) The disorder, however, arises from the relative orientation of the chlorine and bromine atoms in the solid. The disorder changes the inhomogeneous line width at 4.2 K from 1 cm^{-1} for 1,4-dibromonaphthalene to over 80 cm^{-1} in BCN.(8) Steady state excitation of the singlet manifold of this system results in phosphorescence(8) with a 20 cm^{-1} half width appearing at the long wavelength edge of the 0,0 band of the T_1-S_0 absorption.(8) Time resolved spectral diffusion results at 4.2 K following excitation in the 0,0 band of the T_1-S_0 transition of the BCN solid have recently been published.(5) These studies(5) showed that the rate of the triplet energy transfer increased as the wavelength of the laser (the donor absorption) decreases. As the laser excites molecules of higher triplet energy within the inhomogeneous linewidth, the mole fraction of molecules within the BCN solid to which the excitation can be transferred increases. This leads to an increase in the transfer rate.

The BCN system seems to be the appropriate solid for these studies. At 4.2 K pulsed laser excitation produces a set of donors of a certain energy. The emission intensity from these molecules, after correcting for first order decay, monitors the population of the donor decay due to the energy transfer process to molecules having equal or lower T_1-S_0 transition energy. Analysis of this decay in terms of available theoretical expressions for different transfer mechanisms could examine the possibility of energy transfer mechanism switching. Such a possibility has previously been discussed.

The results show that at low acceptor concentrations (i.e., when exciting at the very long wavelength edge of the 0,0 band), the decay curve could not be fitted to a single mechanism. It could however be fitted to a one-dimensional electron exchange expression(9) at short times and a 3-dimensional dipole-dipole expression(10,11) at long times. The range of the fit of the exchange mechanism increases and that for dipole-dipole decreases as the excitation wavelength decreases (i.e., as the acceptor concentration increases). These results are explained as follows: At low acceptor concentrations the probability of finding a BCN molecule with triplet energy equal or less than the donor energy and which is located nearby on the linear chain for electron exchange coupling is very small. This freezes the short range exchange mechanism and allows for the long range 3-dimensional dipole-dipole mechanism to take over. Of course, as the excitation wavelength decreases and the acceptor concentration increases, the probability of finding a nearby BCN molecule which satisfies the energy conservation condition during the transfer process also increases, leading to the dominance of the exchange mechanism.

II. EXPERIMENTAL

The 1-bromo, 4-chloronaphthalene was supplied to us by Professor P. Prasad. It was extensively zone refined. Crystals were grown from the melt in a Bridgmann furnace. Samples were immersed in liquid helium at 4.2 ^{o}K. A Quanta-Ray Nd:YAG pumped PDL-1 pulsed dye laser with a spectral width of ~0.3 cm^{-1} and a pulse width of 6 nsec was used as the T_1-S_0 excitation source at ~0.5 mjoule/pulse. Front surface excitation was used throughout. The emission was dispersed with a 1-m Jarrell-Ash monochromator with a 2 cm^{-1} slit width. The monochromator was carefully tuned to the donor 0,0 -321 cm^{-1} vibronic band so as to follow the donor phosphorescence. A gated phototube[12] was used in order to reject the intense scattered laser light. The first 8 μsec of signal following the laser pulse was rejected due to interference from switching the focus electrode. The signal was fed into a Biomation 805 waveform recorder. The digitized signal was averaged by a homebuilt signal averaging computer and analyzed on a PDP 11/45 computer.

III. RESULTS AND DISCUSSION

The physical quantity of interest in these experiments is the donor excitation probability after correcting for the population loss due to unimolecular decay processes, P(t), and is given by $(I(t)/I_0)\ \exp(t/t_0)$, where I(t) is the phosphorescence intensity at time t, I_0 is the intensity at $t = 0$. and τ_0 is the first order lifetime of the $T_1 \leftrightarrow S_0$ transition. I_0 was determined by extrapolating a logI vs t fit to the first 10 to 50 μsec of signal to $t = 0$. We estimate I_0 determined in this manner to be accurate to ± 20%. τ_0 was determined by fitting the decay at long wavelength and time, where the unimolecular decay dominates, to the first order decay law and found to be 20 msec.

A. Fit of Donor Excitation Decay to One-Dimensional Exchange Mechanism

It is generally accepted that triplet-triplet energy transfer between organic molecules occurs via an electron exchange mechanism. Though the nature of the exchange interaction is of short range, even trap-to-trap migration of triplet excitations over an order of ten intervening host molecules in mixed organic crystals has been interpreted in terms of exchange or superexchange.(13) For a single donor-accepter pair, the energy transfer rate W(R), where R is the position of the acceptor relative to the donor position, can be written for the exchange coupling as:(14)

$$W(R) = 1/\tau \exp[\alpha(d-R)] \qquad (1)$$

where d is the nearest neighbor distance, τ is the transfer time at the nearest neighbor distance and α is a measure of the dependence of the transfer rate on distance. For superexchange(13)

$$W(r) = 1/\tau \exp[n \ln(\beta/\Delta E)] \qquad (2)$$

where τ is the nearest neighbor transfer time via direct exchange, β is the near neighbor energy transfer matrix, ΔE is the energy difference between host and guest bands and is $\gg\beta$, and n is the number of host molecules over which guest-guest transfer occurs.

The theory of the time dependence of the donor luminescence for direct energy transfer via exchange to randomly distributed acceptors has been worked out for all dimensions.(9) Triplet-triplet exchange interactions in 1-4-dihalonaphthalenes have been shown to be highly anisotropic, with the dominant interaction along the direction almost perpendicular to the plane leading to a one-dimensional character for the exchange interaction.(6) For one-dimensional exchange, Blumen(9) finds that the time dependence of the donor excitation probability, P(t), after subtracting out the first order decay, can be described by:

$$\ln P(t) = -(\alpha d)^{-1} C_a \left(\ln\left(\frac{t}{\tau} e^{\alpha d}\right) + 0.57722\right) \qquad (3)$$

where C_a is the mole fraction of sites occupied by acceptor molecules. For superexchange interactions, equation (3) describes the decay with $-\ln(B/\Delta E)$ substituted for αd.(15)

Figure 1 shows the fit at early times to equation (3) for several excitation frequencies (ν_{exc}) on the low energy side of the 0,0 absorption band of the $T_1 \leftarrow S_0$ transition. We plot log P vs log t. On this choice of scales, the decay should be linear for transfer to randomly distributed acceptors by the exchange mechanism with a slope of $-C_a/\alpha d$. Table 1 gives the value of P for each excitation wavelength at which the observed decay curve starts to deviate from the fit. It is clear from these numbers that although the fit is poor at long excitation wavelengths (4947-4945Å) (low acceptor concentrations), the fit describes almost the entire decay at the lowest excitation wavelength used (4939Å) (i.e., higher acceptor concentrations). At shorter than 4939Å, the expected exchange mechanism must then be the sole transfer mechanism in this crystal.

B. Fit to a Dipole-Dipole Mechanism

Could the deviation from the fit to an exchange mechanism at long times and excitation wavelengths (low acceptor concentrations) be a result of competition with the long range dipole-dipole mechanism? In order to test this possibility, we examine the fit of the long time of the decay to theoretical expressions derived for dipolar three dimensional transfer in disordered systems.

For a single donor-acceptor pair, the energy transfer rate for multipolar interactions can be written as:(14)

$$W(R) = 1/\tau(d/R)^{S} \qquad (4)$$

where S = 6, 8, 10 for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. The time dependence of donor excitation probability for transfer to randomly distributed acceptors by multipolar interactions has been worked out in three dimensions(10) and later generalized to all dimensions.(11) For dipole-dipole transfer in three dimensions, neglecting back transfer, the decay of the donor can be described by:(11)

$$\ln(P(t)) = -4/3\pi\Gamma(1/2)C_a(t/\tau)^{1/2} \qquad (5)$$

where Γ is the gamma function.

The fit of the long-time donor decay to equation (5) is shown in Figure 2 where we plot log (P) vs $t^{1/2}$. It is interesting to observe that the fit covered a larger portion of the decay for long excitation wavelength (low acceptor concentrations). Table 1 shows this clearly. It gives the maximum value of P at which the observed decay data begins to deviate for the dipole-dipole equation for the different excitation wavelengths used. P_{max} is highest for longer wavelengths of excitation (lowest acceptor concentrations).

The above results shown in Figures 1 and 2 as well as in Table 1 can be summarized as follows: At short times of decay, the exchange mechanism seems to fit the data. This fit continues for longer times as the acceptor concentration increases (i.e. donor excitation wavelength decreases). Three dimensional dipolar mechanism might be involved at very low acceptor concentrations at longer decay times. If this is true, the above data demonstrate for the first time that a switch of the transfer mechanism is taking place during the energy transfer for low acceptor concentrations. At short times, donor molecules lose their energy to nearby molecules with triplet energies equal or lower than their own. As time goes on, the probability of finding this type of molecule decreases and the long-range three-dimensional dipole-dipole mechanism takes over. As the excitation energy increases, i.e., the acceptor concentration increases, the probability of finding molecules with equal or lower energy at close distances becomes nonvanishing even at long decay times and the exchange mechanism becomes dominant, as expected for triplet-triplet energy migration in crystalline solids. As support for possible competition between two mechanisms at low acceptor concentrations, Table I shows that the value of P at which the exchange mechanism begins to fail in describing the decay data (taken from Figure 1) is similar to that at which the dipole-dipole mechanism begins to describe the transfer decay process at long times (taken from Figure 2). Detailed concentration dependence of the transfer in both mechanisms is now under examination and will be published soon.

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REFERENCES

1) S. W. Haan and R. Zwanzig, J. Chem. Phys. 68, 1879 (1978).

2) J. Klafter and R. Silbey, J. Chem. Phys. 72, 849 (1980).

3) T. Holstein, S. K. Lyo and R. Orbach, Phys. Rev. Lett. 36, 891 (1976).

4) a. P. Avouris, A. Campion and M. A. El-Sayed, Chem. Phys. Lett. 50, 9 (1977).
   b. J. R. Morgan and M. A. El-Sayed, J. Phys. Chem. 85, 3566 (1981).

5) P. N. Prasad, J. R. Morgan and M. A. El-Sayed, J. Phys. Chem. 85, 3569 (1981).

6) J. C. Bellows, E. D. Stevens and P. N. Prasad, Acta Crystallogr. 1334, 3256 (1978).

7) R. M. Hochstrasser and J. D. Whiteman, J. Chem. Phys. 56, 5945 (1972).

8) J. C. Bellows and P. N. Prasad, J. Phys. Chem. 86, 328 (1982).

9) A. Blumen, J. Chem. Phys. 72, 2632 (1980).

10) M. Inokuti and F. Hirayama, J. Chem. Phys. 43, 1978 (1965).

11) A. Blumen and J. Manz, J. Chem. Phys. 71, 4694 (1979).

12) W. D. Hopewell, Thesis, University of California, Los Angeles, 1980.

13) G. G. Nieman and G. W. Robinson, J. Chem. Phys. 37, 2150 (1962).

14) D. L. Dexter, J. Chem. Phys. 21, 830 (1953).

15) A. Blumen and R. Silbey, J. Chem. Phys. 70, 3707 (1979).

Table 1. A comparison of the value of the excitation probability (P) for which the one-dimensional exchange fit ends and the three-dimensional dipolar mechanism begins for different excitation wavelengths.

Excitation Wavelength	Value of P* at end of 1-D EXCHANGE FIT	Value of P* at start of 3-D DIPOLAR FIT
4947	0.55	0.66
4946	0.56	0.62
4945	0.49	0.57
4944	0.28	0.34
4943	0.28	0.24
4942	0.19	0.17
4941	0.08	0.10
4940	0.015	
4939	0.015	

*These values are obtained from one set of data. A least squares fit was made with a value for

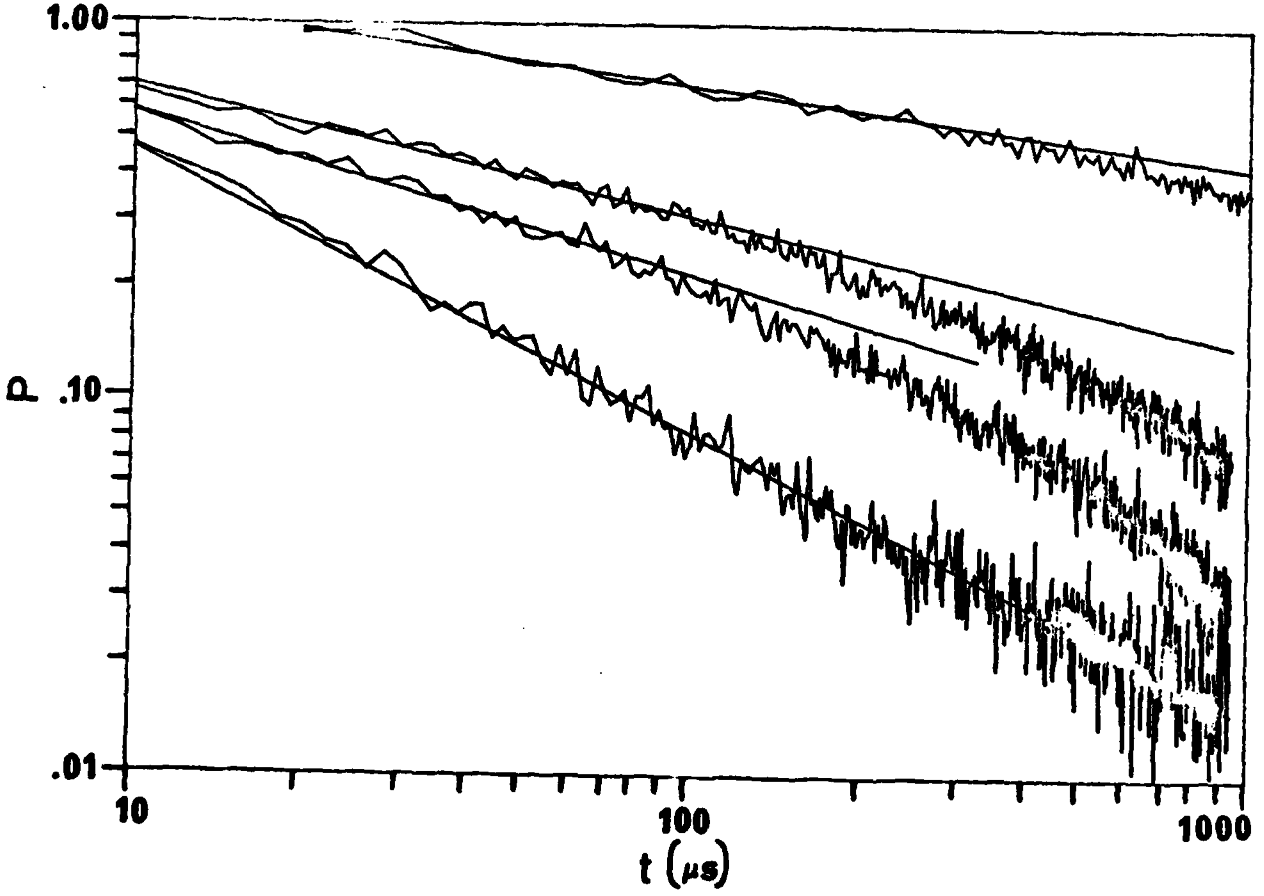
$$\chi^2 \text{ of } 10^{-3} - 10^{-4}$$

These values are the point where the data begin to deviate from the fitted line and should be good to ± 10-20%.

FIGURE CAPTIONS

Fig. 1 The fit of the early portion of the decay of the triplet excitation due to triplet-triplet energy transfer to an exchange mechanism for different excitation wavelengths (4947 Å, 4943 Å, 4942 Å, and 4940 Å from top to bottom, respectively) within the 0,0 band of the $T_1 \leftarrow S_0$ transition in 1-bromo, 4-chloronaphthalene at 4.2 K. The range of the fit increases as the excitation wavelength decreases, i.e., as the acceptor concentration increases.

Fig. 2 The fit of the long time portion of the decay of the triplet excitation of the 0,0 band of the $T_1 \leftarrow S_0$ transition of 1-bromo, 4-chloronaphthalene at 4.2 K due to triplet-triplet energy transfer to a three-dimensional dipolar mechanism for the excitation wavelengths given in Fig. 1. The range of the fit is better at longer excitation wavelengths, i.e., at low acceptor concentrations.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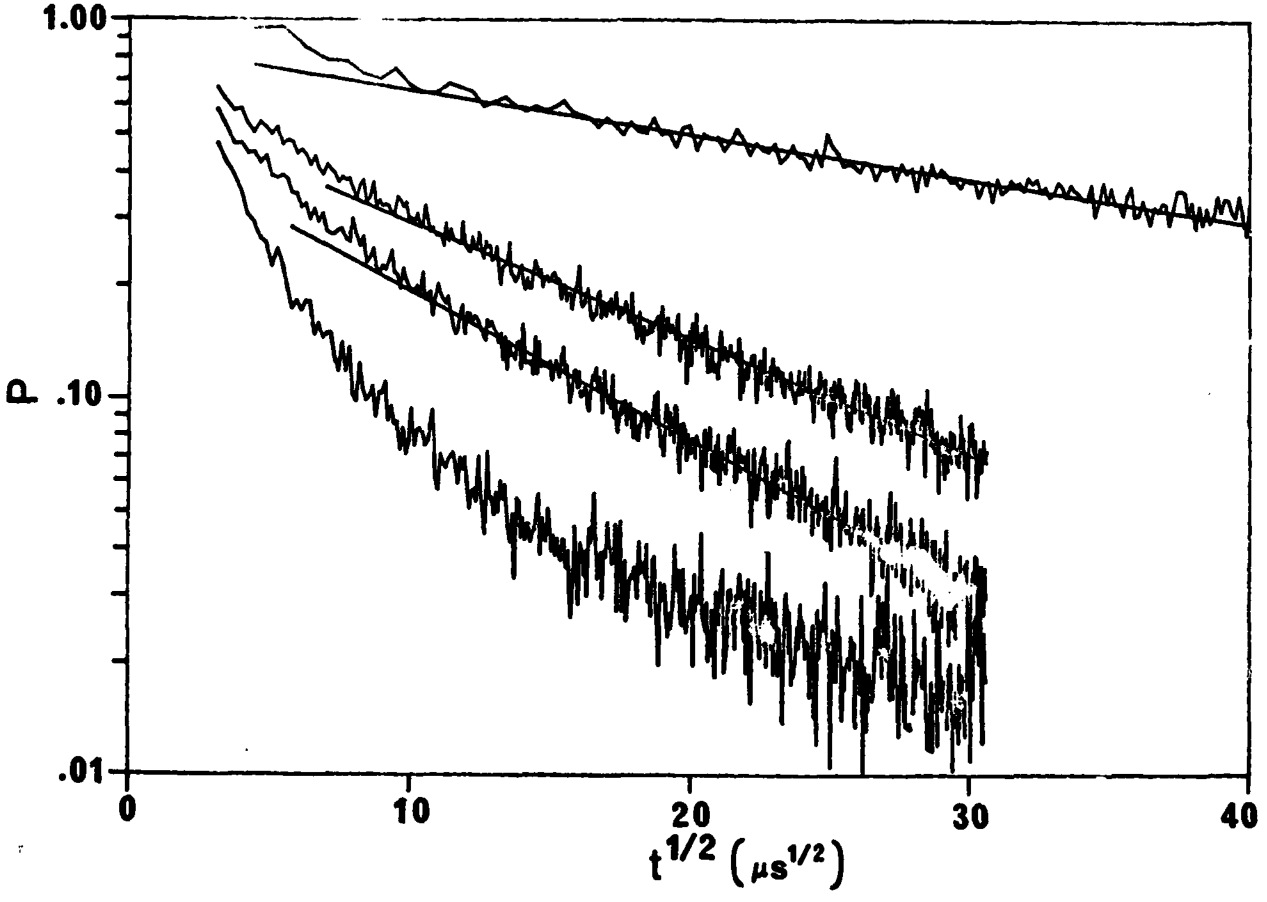
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