Triplet exciton percolation and superexchange: Naphthalene C_{10}H_{8}-C_{10}D_{8}

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The concept of exciton percolation has already been utilized to account for the transition from discrete to continuous crystal energy levels and the concomitant transition in the optical absorption spectrum. However, the traditional physical application of the percolation concept involves a transition concerning a dynamical property, like the onset of water flow in the soil or of electron conduction in amorphous semiconductors or in solutions. Here we demonstrate that (1) dynamical exciton percolation does occur (i.e., a transition from an exciton insulator to an exciton conductor), that (2) it is very useful for the investigation of energy transfer in molecular aggregates, and that (3) it is a critical test of our current knowledge of exciton exchange and superexchange.

The ternary system naphthalene-d_8/naphthalene-h_8/betamethylnaphthalene (BMN) was selected because of a number of theoretical and experimental advantages. Highly purified C_{10}H_8/C_{10}D_8 mixed crystals, doped with about 10^-3 mole fraction of BMN, were excited at about 1.8 K by an appropriately filtered xenon lamp and monitored at 1 cm^-1 resolution with photon counting (interphased with an IBM 360/67 computer, enabling calibration, smoothing, and differential integration on a Graphics terminal). For each C_{10}H_8 concentration, we plot (Fig. 1) the intensity fraction of the BMN phosphorescence (0-0), the rest of the intensity being due to naphthalene-h_8 (the naphthalene-d_8 phosphorescence is quenched throughout). This BMN intensity fraction is a measure of the exciton free flow (see below).

Figure 1 shows that the critical concentration is 0.095 mole fraction C_{10}H_8. This is far below the theoretical site percolation concentration, based on nearest neighbor interactions: We know that the lowest triplet exciton interactions in naphthalene are extremely short ranged and essentially two-dimensional (limited to the ab plane); the crystal structure yields a square lattice topology for this ab plane and for a square lattice the site percolation concentration (nearest neighbor) is 0.59. The apparent contradiction is easily overcome if one considers exciton superexchange. With only nearest neighbor interactions one still gets effective long-range interactions (in the ab plane), enabling the C_{10}H_8 exciton to "jump over" (or rather tunnel through) a number of C_{10}D_8 sites (trap-to-trap migration restricted to the ab plane only). The largest necessary jump ("tunnel length") for C_A = 0, 10 is seen from Fig. 2 to cover about 5 sites. One can say that the "dynamic" radius of the corresponding conglomerate is 5 units of nearest neighbor spacings (5 x 5.11 Å = 25.55 Å), and the conglomerate is disk-shaped. We note that with a nearest neighbor interaction of 1.25 cm^-1 one gets for a five sites-removed superexchange pairwise interaction about 10^-8 cm^-1 (3 x 10^2 Hz), giving a time constant of about 5 x 10^-4 sec. With a lifetime of 2.6 sec this gives a transfer constant of 5 x 10^3 (such conglomerates). The fact that most of the tunnel lengths are much shorter makes the exciton percolation quite feasible. On the other hand, a single 6-site tunneling may require 1%...
The minority sites are often separated by five nearest neighbor spacings. We thank P. Argyrakis for producing this representation.

of an exciton lifetime and a 7-site tunneling about a lifetime. Such lengths are common in an 0.09 mole fraction random lattice. We thus expect the dynamic percolation concentration to be about 0.095 mole fraction, in excellent agreement with the experimental value. However, we believe this agreement to be somewhat for¬
tuitous, in view of the relative crudeness of the model

development of this representation.

Finally, exciton percolation might play an important role in many chemically mixed molecular aggregates, both synthetic and natural, an example of the latter being the photosynthetic units ("photosystems") containing a mixture of two dyes at high concentration together with a low concentration "supertrap." It also opens up various possibilities for exciton-conduction "switching," some of which are presently under study.

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