

LETTERS TO THE EDITOR

The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area. (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 January 1975 for a fuller description of Letters to the Editor.

COMMUNICATIONS

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^{1,2} 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 semiconductors³ or in solutions.⁴ Here we demonstrate that (1) dynamical exciton percolation⁵ 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 transfer⁶ in molecular aggregates, and that (3) it is a critical test of our current knowledge of exciton exchange and superexchange.⁷

The ternary system naphthalene- d_8 /naphthalene- h_8 /betamethylnaphthalene (BMN) was selected because of a number of theoretical and experimental advantages.⁵ Highly purified⁵ $C_{10}H_8/C_{10}D_8$ mixed crystals, doped with about 10^{-3} mole fraction of BMN, were excited at about 1.8°K by an appropriately filtered⁵ 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).⁵ 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 ranged¹ and essentially two-dimensional (limited to the ab plane); the crystal structure⁸ yields a square lattice topology for this ab plane and for a square lattice the site percolation concentration (nearest neighbor) is³ 0.59. The apparent contradiction is easily overcome if one considers exciton superexchange.^{7,9} 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 migration⁹ 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 conglomerate¹ is 5 units of nearest neighbor spacings ($5 \times 5.11 \text{ \AA} = 25.55 \text{ \AA}$), and the conglomerate is disk-shaped. We note that with a nearest neighbor interaction¹⁰ of 1.25 cm^{-1} one gets for a five-sites-removed superexchange pairwise interaction⁵ about 10^{-8} cm^{-1} ($3 \times 10^2 \text{ Hz}$), giving a *time constant*¹¹ of about $5 \times 10^{-4} \text{ sec}$. With a lifetime¹² of 2.6 sec this gives a *transfer constant*¹¹ of 5×10^3 (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%

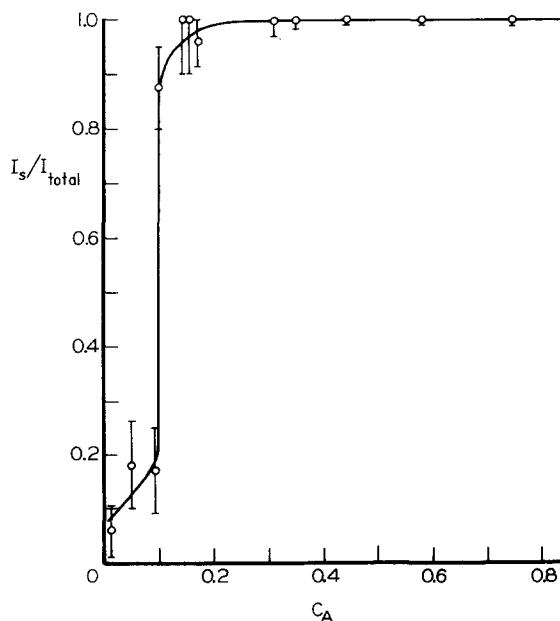


FIG. 1. Exciton transfer in naphthalene- h_8 /naphthalene- d_8 mixed crystals. The $C_{10}H_8$ concentration is C_A , I_S is the super-trap (BMN) intensity, while $I_{total} = I_S + I_A$, I_A being the $C_{10}H_8$ intensity.

⊗: ⊗ = 16:144 (10.0%)

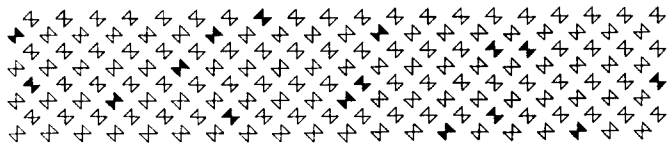


FIG. 2. A binary random square lattice based on a "Monte Carlo" calculation, with 10% black and 90% white "butterflies." Note that this particular domain has an actual ratio of 10:90. It can be seen that the minority sites are often separated by five nearest neighbor spacings. We thank P. Argyrakis for 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.¹³ We thus expect the dynamic percolation concentration to be about 0.095 mole fraction, in excellent agreement with the experimental value.^{14,15} However, we believe this agreement to be somewhat fortuitous, in view of the relative crudeness of the model with regard to the dimensionality and nature of the exciton motion, the super-trapping efficiency, and the specifics of the exciton-phonon interactions. A more detailed report of both the data handling and their interpretation is in progress, as well as a corroborative account on three-component isotopic mixed system studies.⁵

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")¹⁶ 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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⁶See, i.e., H. C. Brenner and C. A. Hutchison, *J. Chem. Phys.* **58**, 1328 (1973), and references therein.

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¹³See Fig. 3 of Ref. 2.

¹⁴We also note that M. Schwörer and H. C. Wolf, *Mol. Cryst.* **3**, 177 (1967), observed a dramatic qualitative change in their 20% C₁₀H₈/C₁₀D₈ sample, compared with a 10% (or lower) sample, involving their ESR spectrum (and the lifetime at 20% got reduced to 0.1 sec).

¹⁵That our result (Fig. 1.) does not reflect a singlet state phenomenon is shown by the latter's percolation⁵ at above 30%.

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Resolution-enhanced Fourier transform ion cyclotron resonance spectroscopy*

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Nuclear magnetic resonance (NMR) and ion cyclotron resonance (ICR) exhibit a number of superficial similarities: coherent motion excited by a radio-frequency oscillator source, with resultant transient or steady-state response monitored by a coherent detector¹; double-resonance² and saturation³ experiments to detect magnetic or kinetic coupling; and the feasibility of obtaining a spectrum by Fourier transformation (FT) of the transient response to a brief excitation^{4,5} rather than by conventional scanning of the steady-state response to a continuous excitation.⁶ However, even for FT-NMR, spec-

tral resolution is still ultimately limited by nuclear magnetic relaxation (spectral line broadening in the usual context) arising from intramolecular magnetic couplings,⁷ so that this contribution to NMR linewidth cannot be reduced by FT methods or by sample dilution. For FT-ICR, on the other hand, ICR linewidth (and thus mass resolution) is determined principally by intermolecular relaxation due to reactive and nonreactive ion-molecule collisions⁸; ICR linewidth may thus be made arbitrarily small by use of an arbitrarily low pressure (sample dilution) and a sufficiently long observation pe-