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COHERENT AND INCOHERENT EXCITON TRANSPORT, EXTENDED AND LOCALISED
TRIPLET STATES IN MIXED NAPHTHALENE CRYSTALS

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Résumé : En nous référant à la dépendance en température du transport d'excitations dans les états triplet de pièges de naphthalène-H₈ dans le naphthalène-D₈, nous proposons qu'en-dessous de 5K le transport est surtout cohérent et qu'il dépend de l'étendue des états propres des pièges. Nous esquissons un modèle où le couplage exciton-phonon et des calculs numériques importants d'états propres sont employés afin de rendre compte du piégeage donneur-accepteur.

Abstract: Starting from the temperature dependence of triplet exciton transport in the trap states of naphthalene-H₈ in naphthalene-D₈, we argue that below 5K, transport is predominantly coherent, being dependent on the extension of the trap eigenstates. A model of donor to acceptor trapping, including exciton-phonon coupling and large scale numerical calculations of the eigenstates is proposed.

This work addresses the interpretation of experiments on exciton transport in the triplet states of naphthalene-H₈ donor molecules and 2-methylnaphthalene acceptors in a naphthalene-D₈ host crystal at temperatures below 10K. Exciton transport following excitation of the randomly distributed donors may be measured by the yield of acceptor phosphorescence, or by the total yield of delayed fluorescence (*partial* yields of each species reflect *singlet* state dynamics) due to fusion of the triplet excitons, cf. Fig. 1.

In order to test delocalisation quantitatively, we are considering the form of trapping from extended donor states and acceptors, and actual numerical values are derived from exact donor eigenstates of model crystals of a few thousand sites.

I. TRAPPING BETWEEN DONORS AND ACCEPTORS.

We consider the electronic Hamiltonian

$$H = \sum_m E_m B_m^+ B_m + 1/2 \sum_{mn} V_{mn} (B_m^+ B_n + B_n^+ B_m)$$

where E_m is the energy of site m and V_{mn} is the exchange coupling between sites m and n , mn limited to nearest neighbours in the (a,b) plane for the triplet state of naphthalene [9]. The donor and the acceptor lie respectively 100 cm⁻¹ and 240 cm⁻¹ below the host band, while $V_{mn} \sim 1$ cm⁻¹. The site energies and the couplings have a spread of values around these figures, inhomogeneous broadening due to faults inevitable in any real crystal. This broadening tends to limit the spatial extension of the eigenstates of H , until the "average" coupling at higher concentrations overwhelms it: If B , the bandwidth determined by the couplings, verifies $B < \delta$, states are localised. As the concentration rises B increases due to stronger coupling. When $B \sim \delta$, there appear *delocalised* states in the middle of the band. Between these extremes, there is a distribution of *extended* states i.e. states with a strong, distinguishable centre or "nucleus" and a tail whose decay depends on δ and the concentration. An upper limit on the broadening, δ , has been set by high resolution

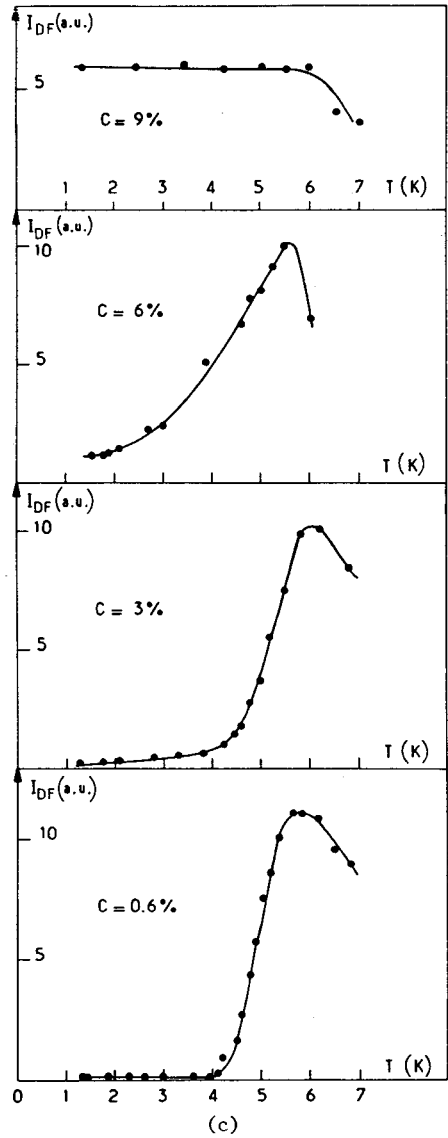
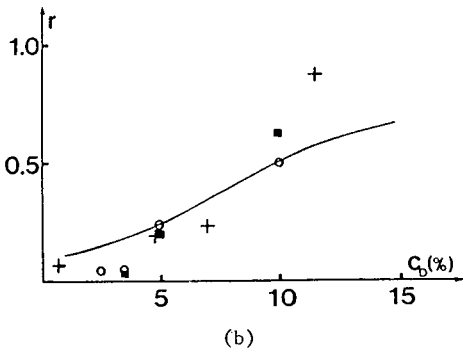
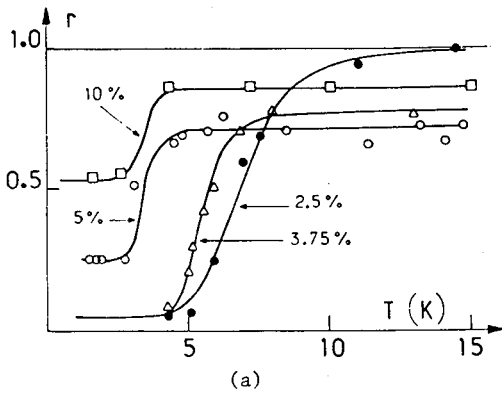


Figure 1
 a) Yield of acceptor phosphorescence ($c_a = 10^{-3}$) vs. temperature after selective excitation of the donors.
 b) Yield vs. donor concentration at $T = 1.6$ K; + ref. 1; ■, o ref. 2; continuous curve calculated below.
 c) Total yield of delayed fluorescence vs. temperature ref. 3.
 Note the temperature and concentration thresholds, and the absence of temperature dependence below ca. 5K.

spectroscopy at $\delta \sim 10^{-3} \text{ cm}^{-1} / 10/$ but it should be remembered that this may be due to the envelope of many microscopic domains where local broadening is much smaller. Introducing the donor and acceptor eigenstates, $|D\rangle, |A\rangle$ we have

$$H = \sum_D E_D B_D^+ B_D + \sum_A E_A B_A^+ B_A, \quad B_D^+ = \sum_m c_{Dm} B_m^+, \quad B_A^+ = \sum_m c_{Am} B_m^+$$

where E_D, E_A and c_{Dm}, c_{Am} the energies and site projections may be determined by diagonalisation of H . Trapping between D and A states is introduced by the exciton-phonon coupling, of the form:

$$H' = \sum_{m,q} F_1(m,q) B_m^+ B_m (b_q^+ + b_{-q}^-) + \sum_{m,q,q'} F_2(m,q,q') B_m^+ B_m (b_q^+ + b_{-q}^-) (b_{q'}^+ + b_{-q'}^-),$$

where F_1 and F_2 are the linear and the quadratic terms of the local exciton-phonon coupling $/11/$. The energy gap between donor and acceptor levels corresponds to the emission of two optical phonons, with a maximum contribution, (determined by the density of phonon states $/12/$) from small wavevector modes, q, q' . Replacing B_m^+ by the eigenstates of H , we obtain via the density matrix and the Golden Rule, for the one site two phonons process for example,

$$\Gamma_{A \leftarrow D} = \sum_{q,q'} \sum_{m,n} \bar{c}_{Dm} c_{Am} \bar{c}_{Dn} c_{An} \exp(i(q+q')(r_n - r_m)) |F(q,q')|^2 \cdot x$$

$$\delta(E_D - E_A - (E_q + E_{q'}))$$

($F_2(m,q,q') = \exp(-i(q+q')r_m) F_2(q,q')$), where F_2 is at first approximation independent of $m, /11/$).

Trapping thus depends on the overlap of the donor and the acceptor states on all sites. A similar expression for donor-donor relaxation or "hopping" between eigenstates may be deduced, but will be neglected here, since we are interested in the consequences of assuming it goes to zero at low temperatures $/8/$. As a first approach, interference terms in Γ_{AD} are neglected, leading to the simple form:

While most interpretations of the fixed low temperature results have assumed hopping transport between traps in mixed molecular crystals $/1,4,5/$, Klafter and Jortner $/6/$ have suggested that the "threshold" of acceptor emission, cf. Fig. 1b, could be due to an Anderson transition from localised to extended states in the donor band. Now phonon assisted incoherent hopping rates between nearly resonant donors depend on the temperature $/7,8/$, whereas there is in fact very little temperature dependence of the emissions of these crystals below $T=5K$. The sharp rise in transport phenomena has been attributed to scattering on two optical phonons, between nearly resonant donor states $/8/$. It is, moreover, absent at the higher donor concentrations, where delocalisation could be expected to be greater.

$$\Gamma_{AD} = \Gamma_0 \sum_m |c_{Dm}|^2 |c_{Am}|^2.$$

II. DONOR EIGENSTATES.

Random distributions of donor molecules at several mean donor concentrations are generated in model crystals of from 40×40 to 80×80 sites. The donor site energies are allowed to fluctuate in a range $\pm \delta/2$, to simulate the presence of inhomogeneous broadening, at values $10^{-6} \text{ cm}^{-1} < \delta < 5 \cdot 10^{-3} \text{ cm}^{-1}$. Other values in the Hamiltonian are $V = 1.2 \text{ cm}^{-1}$ inequivalent neighbours, $V = 0.5 \text{ cm}^{-1}$ equivalent neighbours along the b axis, $V = 0$ otherwise and $E_A - E_D = 100 \text{ cm}^{-1}$. The eigenvalues and eigenvectors are extracted by Ritz iteration $/13/$ with iterative refinement $/14/$ to separate the nearly degenerate eigenvectors in each cycle. Projections fall into two classes: (a) A "nucleus" of large projections on a cluster of contiguous donors e.g. monomers, dimers, trimers, ... and (b) A tail of overlap on other clusters, plus of course smaller projections on the host sites. The donor tail is plotted in Fig. 2 as a function of the radial distance from the nucleus, for several middle of the band states. These are the most extended states, as Fig. 2c shows. In Fig. 2 we observe that the tail decays very approximately exponentially and that it is more ex-

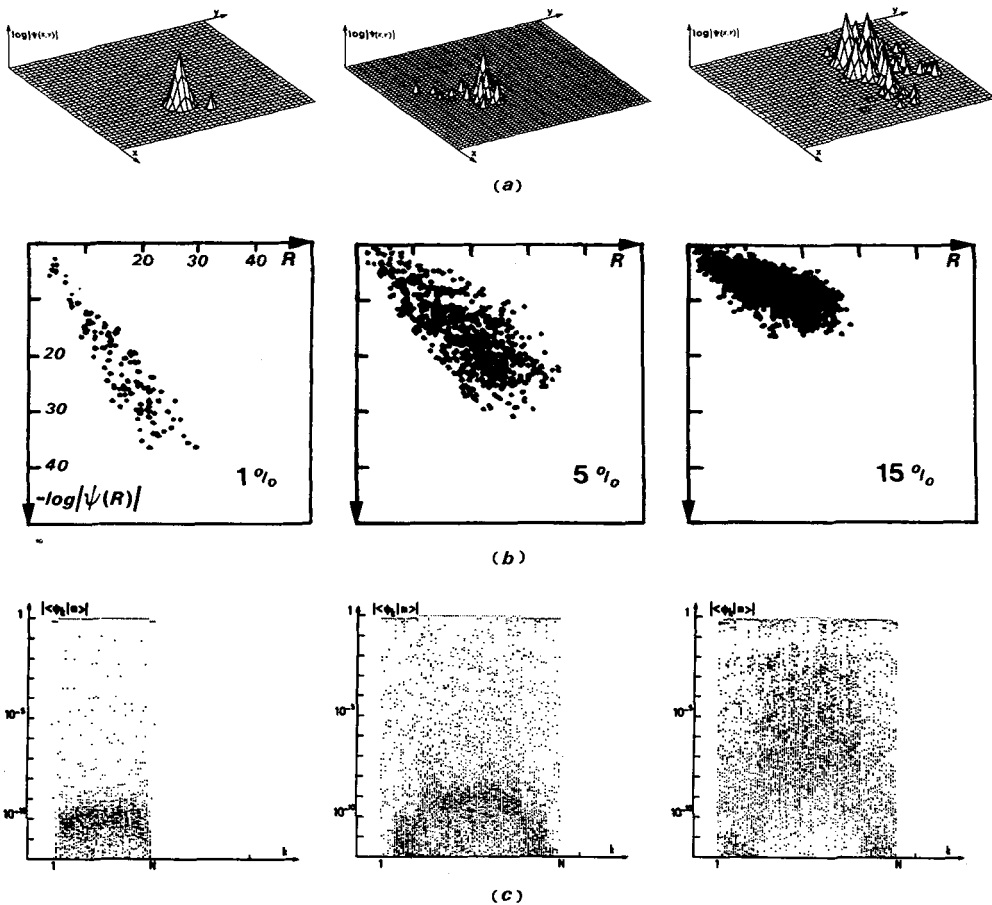


Figure 2 a) Example of three eigenstates with inhomogeneous broadening $5 \cdot 10^{-3} \text{ cm}^{-1}$, showing all sites where the projection exceeds 10^{-5} . Logarithmic vertical scale.
 b) Radial decline of five eigenstates in the middle of the donor band with the same broadening.
 c) Distribution of the site projections as a function of the number of the eigenstate, at the same broadening.

tended at higher concentrations. The change in the tail occurs in the concentration range where transport properties vary rapidly, $c \lesssim 20\%$. Eigenstates are also calculated for the same crystals, using the renormalised or "super-exchange" Hamiltonian where host sites are replaced by an effective tunneling interaction between donors. This yields projections on the donor sites only, which are compared with the values of the complete eigenvalue problem. Both the ordering of the states and the values obtained are inaccurate, which is interesting since the naphthalene triplet state is generally considered to be a deep trap limit. The change in the tail of the wavefunction found here is not inconsistent with the small change in the delocalisation index $L = \sum_m |c_{Dm}|^4$ over the same concentration range/15/ since L is sensitive to the nucleus, which expands only on nearest neighbour percolation, long after the threshold in transport properties.

III. PRELIMINARY YIELD OF ACCEPTOR PHOSPHORESCENCE.

As a first step we replace the acceptor states by Dirac functions so that the trapping rate may be further simplified to

$$\Gamma = \Gamma_0 |c_{DA}|^2$$

Donor states are calculated without the acceptors, but since $E_H - E_D \sim E_D - E_A$, the projection c_{DA} on any host site is about what it would be if it were replaced by an acceptor. Trapping requires that $\Gamma \gtrsim 1/\tau_0$ so that $|c_{DA}| \gtrsim (\Gamma_0 \tau_0)^{-1/2} = \epsilon_0$ where τ_0 , is the intrinsic lifetime. Thus the average yield of trapping from state $|D\rangle$ depends on the number of host sites with projections over ϵ_0 , $N(\epsilon_0, D)$. The average yield of acceptor emission, $r = I_A / (I_A + I_D)$, is then found from

$$r = 1 - 1/N_D \sum_D (1 - c_A)^{N(\epsilon_0, D)}$$

where $(1 - c_A)^{N(\epsilon_0, D)}$ is just the probability D that no possible acceptor site emerges above the level ϵ_0 (sea-level in Fig. 2a). Γ_0 is varied until agreement with the experimental values of Fig. 1b. The diagram shows some calculated points for $\delta = 5 \cdot 10^{-3} \text{ cm}^{-1}$ with $\Gamma_0 = 10^{25} \text{ s}^{-1}$. This value corresponds of course to a ridiculous nearest neighbour rate. However, current work indicates strong interference effects in the trapping rate at short distances. We should simply like to point out that :
 1) This corresponds to coupling between donor tails and acceptors about 2 sites away.
 2) Dephasing in the triplet state is rather slow so the dynamics is sensitive to very small perturbations. If we set the homogeneous width at 10^{-6} cm^{-1} /6/, electronic coherence effects may be expected between donor sites separated by 4 lattice lengths. Interestingly enough, this is the interaction radius required to account for transport in hopping percolation models. The point to be made is that percolation underlies both the coherent and the incoherent pictures, so that we must refer to temperature dependence in order to determine which model is more appropriate at a given temperature.

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