Exciton percolation and exciton coherence

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Molecular exciton coherence has been of much interest recently, but the correct interpretation of current experimental methods is under some dispute. We propose here a new method of measuring exciton coherence, which may also become an independent source of information on exciton-phonon coupling and scattering in molecular crystals. Our method is based on exciton percolation experiments in isotopic mixed crystals. The coherence time (or length) appears as a parameter used to fit the percolation probability, measured for ternary mixed crystals that are very dilute in supertrap concentrations. We note here that previous measurements of the lower supertrap concentrations require more refined analytical procedures, which will be described elsewhere. The experimental percolation probability is given by

\[ P = I_a / (I_b + \alpha I_a) \]

where \( I_a \) is the integrated intensity of the 0-0 fluorescence line (including all isotopic species and their sidebands) of betamethylnapthalene (BMN), the supertrap; \( I_b \) is the integrated intensity of the vibronic 0-510 fluorescence line (including all isotopic species and their phonon sidebands) of naphthalene (C16H10), the trap; and \( \alpha \) is given by the ratio (supertrap over trap) of the radiative yields and host−exciton trapping efficiencies (relative cross sections). We use here \( \alpha = 1.9 \). The total guest concentration is \( C_g = C_{10} + C_{10} = C_{10} \), because \( C_{10} \approx 2 \times 10^{-5} \) throughout. The host is C16H10. The optically single crystals (ab faces) are illuminated by broad-band excitation at 2 K.

The theoretical expression for the exciton percola-
The parameter $x$ is independent of the coherency lengths in the MIN-HS in the literature. At low concentration, the quantities taken from Roshen, Monberg and Kopelman (unpublished, see also Refs. 9-11) at large particle sizes. We also define the coherency $I = T_c/k_B T$ and use Gaussian distributions of $I$, with a standard deviation $\sigma$ (i.e., $0.3$). The time $I \leq 1$ gives the limit of completely incoherent exciton motion (hopping). We also assume that random exciton scattering occurs either after time $T_c$ (Gaussian distributed) or when the exciton hits a host (C$_{10}$D$_4$) site. In our computer simulations$^{9,10}$ we generate a binary random lattice of $500 \times 500$ sites and find $n_m$ as a function of $I$, for $I < I < 250$ (note that larger $I$ parameters are inconsistent with the size of our simulated lattice$^{11}$). From $n_m(C_r)$ we calculate $P(C_r)$ for $C_r = 1.5 \times 10^{-6}$ mole fraction (see Fig. 1) and other values. We also calculated $P$ for a variety of $\tau/T_j$ values.$^{10,11}$ We thus get $P(C_r)$ for a variety of $I$ values (as well as $C_r$ and $\tau/T_j$).$^{11}$ Some of these results are given in Fig. 1.

The coherence time derived above should be mostly due to exciton–phonon scattering because effects due to impurity and/or imperfection scattering should be negligible in systems where $10\%-40\%$ of the sites are already built-in scatterers ("host"). We thus assume that our scattering time $T_c$ represents the exciton–phonon scattering time. On the other hand, ordinary spectroscopic linebroadening measurements only give upper limits to the exciton–phonon (homogeneous) linebroadening because of the always possible contributions from inhomogeneous linebroadening, owing to lattice imperfections. However, we note that the narrowest linewidths measured for this system$^{5,18}$ on carefully prepared samples, have been about $1$ cm$^{-1}$ (but may have been limited by instrumental resolution).$^{19}$ Thus, there appears to be good agreement between the lower limit to the first singlet exciton coherence time derived from spectral linewidths and that derived from the exciton percolation method.$^{20}$ While work is still in progress on more definitive values of $Z$, $d$, and $I$, the basic approach seems to be valid.$^{21}$ We note that while our work seems to be more in line with the view of shorter coherence lengths and times$^{4,16}$ rather than very long ones,$^{5,22}$ our specific results given here relate to a system with a different molecule, crystal topology, and excited state multiplicity (i.e., compared with the triplet exciton state of tetrachlorobenzene$^{22}$).

In summary, we demonstrated here a technique, aimed at coherence data of excitons in molecular solids, which is based on time independent (CW) measurements.

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**FIG. 1.** Experimental and theoretical percolation probability $P$ vs guest concentration $C_g$. The theoretical curves are derived from Eq. (2) (the second term contributes little$^{9-11}$ at the given $Z$ and has been omitted), with $G = 250000 C_r, C_r = \gamma C_g = 1.5 \times 10^{-6}$, $Z = 250000 C_r, P_m(C_r)$ of the square lattice was taken from Hoshen, Monberg and Kopelman (unpublished, see also Ref. 10$^1$). $I = (\text{total number of steps})/T_j = 200000$, and the parameters $I$ (coherence) and $\sigma$ (std. deviation) are indicated. The experimental points are derived via Eq. (1) with$^{11}$ $\alpha = 1.9$ and $I_m(C_r)$ and $I_m(C_r)$ from the $2 \text{K}$ fluorescence of betamethylnaphthalene (supertrap) and naphthalene-n$_h$ (trap), respectively. The $I_m(C_r)$ is the mode fraction of naphthalene-n$_h$ in the C$_{10}$D$_4$/C$_{10}$D$_4$: EMN mixed crystal. The computational statistical fluctuations are visible. The experimental uncertainties are mainly in the value of $C_r$ (compare Refs. 8-11). At low $C_r$ the experimental points are an expression of the "dark current," which is irrelevant to exciton transport.$^{11}$

For $C_r < C_c$ only the second term of Eq. (2) contributes, and it is independent of the coherency $I$. See the text for details on the parameters of the considered system.

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In summary, we demonstrated here a technique, aimed at coherence data of excitons in molecular solids, which is based on time independent (CW) measurements.
A photochemical study of rotational state dependence by laser excitation of formaldehyde \( \left( ^1A_2 \right) \). I. Coriolis and singlet–triplet perturbation

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Studies of radiationless transitions from single vibronic levels (SVL) in "isolated" small polyatomic molecules can provide invaluable understanding of primary photochemical processes, but they cannot be complete without information about the role played by the rotational eigenstates as has been well recognized in high resolution molecular electronic spectroscopy. Studies of radiationless transitions and photodecomposition from the SVL's of formaldehyde in its first excited singlet state \( \left( ^1A_2 \right) \) have been reported. Recently we have been able to extend our studies to include selective excitation of rotational states in a given SVL by tunable dye laser, and we wish to report here some of the most interesting results.

Formaldehyde is ideally suited for such a study since a small portion of the results obtained for the rovibrionic contour of the \( \Delta v = 3 \) transition \( \nu_0'' = 0; \nu_0' = 0 \), where congestion is minimum at the blue end, is shown in Fig. 1, since there are 900 lines in a 320 cm\(^{-1} \) span. In the pressure ranges employed,