FIG. 1. A plot of the C_2 fluorescence signal vs $1/I_\nu$. The fluorescence signal has been corrected for efficiency factors.

Boltzmann distribution at 3000 °K at time $t = 0$. A good agreement with the two level model for a partially saturated system is obtained.

It should also be noted that our value of $4.5 \times 10^{15}/$cm^{-3} agrees well with the value found by Bleekrode and Nieuwpoort[5] in a low pressure oxyacetylene flame when their measured number density is scaled to atmospheric

pressure. Experimental details and a discussion of the kinetics and the assumptions made in the treatment of the data will be given elsewhere.[3] An experimental uncertainty of plus or minus a factor of 3 due to uncertainties in the detector and collection efficiencies, the power, and the laser beam waist measurements will be reduced to ~ ± 50% by a more careful calibration of the experimental parameters on an atomic two level system. The applicability of the model can be stringently evaluated best for this type system. Extension of the two level model for systems with intermediate states is underway.[6,7] The application of these techniques for absolute measurement of transient number densities in the reactive zone of a hot atmospheric pressure combustor reported herein represents a significant advance in the application of optical techniques for combustion diagnostics.

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Exciton percolation and exciton coherence*

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(Received 22 November 1976)

Molecular exciton coherence has been of much interest recently,[1-5] but the correct interpretation of current experimental methods is under some dispute.[6] We propose here a new method of measuring exciton coherence, which may also become an independent source for information on exciton–phonon coupling and scattering in molecular crystals. Our method is based on exciton percolation[7-10] 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 concentration.[10] We note here that previously described exciton percolation measurements were performed in the *supertransfer* limit[8-11] (i.e., with much higher supertrap concentrations[7,11]), where the percolation probability (at high guest concentration)[11] is independent of the exciton dynamics and, in particular, does not depend on the coherence time.

The experimental procedures are the same as described before for the supertransfer limit,[11-13] except

that the actual measurement of the lower supertrap concentrations requires more refined analytical procedures, which will be described elsewhere.[14] The experimental percolation probability is given by[11,15]

$$P = I_S/(I_S + \alpha I_t) , \qquad (1)$$

where I_S is the integrated intensity of the 0–0 fluorescence line (including all isotopic species and their sidebands) of betamethylnaphthalene (BMN), the *supertrap*; I_t is the integrated intensity of the vibronic 0–510 fluorescence line (including all isotopic species and their phonon sidebands) of naphthalene ($C_{10}H_8$), the *trap*; and α is given by the *ratio* (supertrap over trap) of the radiative yields and host–exciton trapping efficiencies (relative cross sections).[11] We use here[11] $\alpha = 1.9$. The total *guest* concentration is $C_g = C_t + C_S \cong C_t$, because $C_S \approx 2 \times 10^{-5}$ throughout. The *host* is $C_{10}D_8$. The optically single crystals (ab faces) are illuminated by broad-band excitation[12] at 2 K.

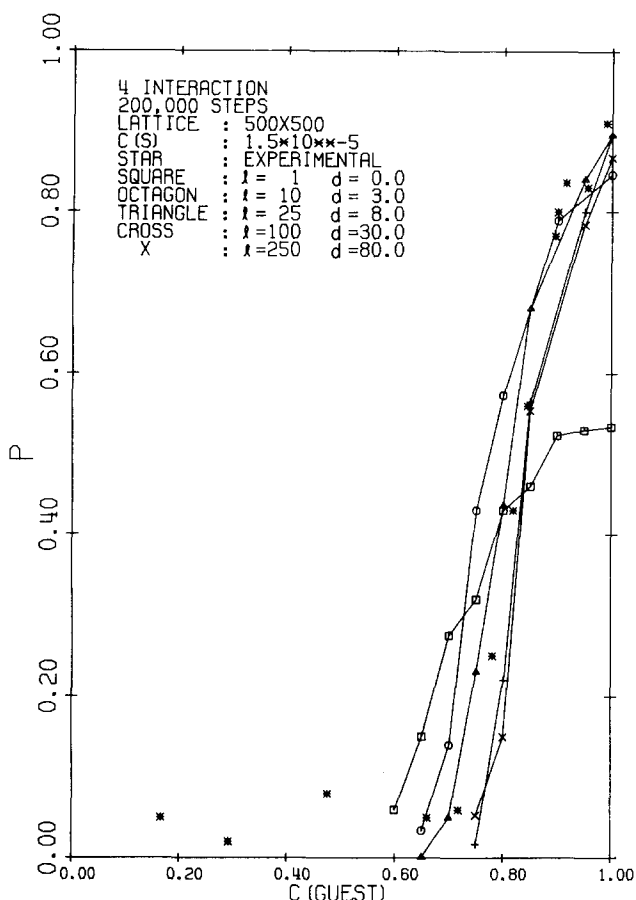The theoretical expression for the exciton percola-

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 $G = 250\,000C_g$; $C_s' = \gamma C_s = 1.5 \times 10^{-5}$; $Z = 250\,000C_s'$; $\bar{P}_\infty(C_g)$ of the square lattice was taken from Hoshen, Monberg and Kopelman (unpublished, see also Ref. 10); t (total number of steps) $= \tau/T_j = 200\,000$; and the parameters l (coherency) and d (std. deviation) as indicated. The experimental points are derived via Eq. (1) with[11] $\alpha = 1.9$ and $I_s(C_g)$ and $I_t(C_g)$ measured (see text) from the 2 K fluorescence of betamethylnaphthalene (supertrap) and naphthalene-h_8 (trap), respectively. $C_g = C_s + C_t \approx C_t$ is the mole fraction of naphthalene-h_8 in the $C_{10}H_8/C_{10}D_8$: BMN mixed crystal. The computational statistical fluctuations are visible. The experimental uncertainties are mainly in the value of C_s' (compare Refs. 8–11). At low C_g the experimental points are an expression of the "dark current," which is irrelevant to exciton transport.[11] For $C_g < C_c$ only the second term of Eq. (2) contributes, and it is independent of the coherency l.

tion probability is[8-10] (note the exclusion of the critical concentration C_C range)

$$P = \bar{P}_\infty[1 - (1 - n_m/G)^Z] + (Z/G)I_{AV}'$$

$$\text{iff } Z \ll G \text{ and } C_g \neq C_c \ ; \tag{2}$$

where $\bar{P}_\infty$ is[16] the probability of a guest site belonging to the largest cluster ("maxicluster"), G is the total number of guest sites, Z the effective[9] number of supertrap sites, I_{AV}' the reduced average cluster size,[16] and n_m the average number of guest sites visited by an exciton generated on the maxicluster,[9,10] if $Z = 0$. While the quantities $\bar{P}_\infty(C_g)$ and $I_{AV}'(C_g)$ depend only on the topology of the exciton interactions,[16] $n_m(C_g)$ depends

on the specifics of the exciton dynamics: the excitation lifetime τ, jumptimes T_j, coherence time T_c, and coherence time distribution.[8,10]

For the naphthalene first singlet exciton system we use[5,10] $\tau \cong 100$ ns and $T_j \cong 0.5$ ps, with an assumption of a nearest-neighbor-only square lattice topology.[10,11] Adding next and next-next nearest neighbor interactions contributes little.[11,17] We also define the coherency $l = T_c/T_j$ and use Gaussian distributions of l, with a standard deviation d (i.e., $0.3l$). Obviously, $l \leq 1$ 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 ($C_{10}D_8$) site. In our computer simulations[10,17] we generate a binary random lattice of $500 \times 500 = 250\,000$ sites and find n_m as a function of l, for $1 \leq l \leq 250$ (note that larger l parameters are inconsistent with the size of our simulated lattice[17]). From $n_m(C_g)$ we calculate $P(C_g)$ for $C_S = 1.5 \times 10^{-5}$ mole fraction (see Fig. 1) and other values. We also calculated P for a variety of τ/T_j values.[10,17] We thus get $P(C_g)$ for a variety of l values (as well as C_S and τ/T_j).[17] Some of these results are given in Fig. 1.

From Fig. 1 we see that our low temperature (2 K) experimental P [Eq. (1)] points fit our theoretical P [Eq. (2)] curves for an l value of about 20 to 100. This gives a coherence time of about 10 to 50 ps. Energy-wise, this is equivalent to a linebroadening of about 0.2 to 1 cm^{-1}. While at this stage we cannot exclude the $l > 100$, we definitely exclude $l \cong 1$.

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,[8,18] 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 here from the exciton percolation method.[20] While work is still in progress on more definitive values of Z, d, and l, 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[1,6] rather than very long ones,[4,22] 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.

Time resolved percolation measurements should significantly improve both precision and reliability. These are now in progress.

*Supported by NSF Grant DMR75-07832 and NIH Grant NS08116-8.

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A photochemical study of rotational state dependence by laser excitation of formaldehyde ($\tilde{A}^1A_2$). 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,[1] 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.[2] Studies of radiationless transitions[3,4] and photodecomposition[5] from the SVL's of formaldehyde in its first excited singlet state ($\tilde{A}^1A_2$) 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 the most interesting results.

Formaldehyde is ideally suited for such a study since an enormous amount of information from the prerequisite high resolution spectroscopy is already available on singlet–triplet perturbation,[6] Coriolis and Fermi perturbations,[7] etc. Accordingly, it was desirable to

obtain three kinds of rotationally resolved spectra at equal spectral resolution: An electronic absorption spectrum (I_a vs λ), a "blue" fluorescence excitation spectrum (I_f vs λ_{ex}) for evaluating relative quantum yield of fluorescence (ϕ_f vs λ_{ex}), and a "red" HNO^* chemiluminescence excitation spectrum (I_c vs λ_{ex}) for evaluating relative quantum yield of the H atom produced from the photochemical decomposition of H_2CO^* (ϕ_H vs λ_{ex}).[5] Frequency of the exciting light from a pulsed dye laser (Chromatix CMX-4) was continuously scanned at a spectral bandwidth of 0.2 cm⁻¹. A boxcar averager with gated integrators was used to record the appropriate signal ratios without delay (for absorption and fluorescence) or with a 2 μsec delay (for chemiluminescence) from the laser pulse (1 μsec and 30 Hz). A small portion of the results obtained for the rovibronic contour of the $2_0^3 4_0^1$ transition ($\nu_2' = 3$; $\nu_4' = 1 - \nu_2'' = 0$; $\nu_4'' = 0$), where congestion is minimum at the blue end, is shown in Fig. 1, since there are ~900 lines in a 320 cm⁻¹ span.[7b] In the pressure ranges employed,