

**VARIABLE RANGE CLUSTER MODEL OF EXCITON MIGRATION:
DIMENSIONALITY AND CRITICAL EXPONENTS FOR
NAPHTHALENE***

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Relative luminescence intensities for randomly substituted ternary systems with two major components and a minor one (sensor), for four triplet and one singlet exciton systems, identify the maximal effective exciton interaction distance for each system. The critical exponents β and γ show an effective 2-dimensional exciton topology and are consistent with dynamic exciton percolation.

Crystal luminescence is an excellent tool for studying non-radiative processes such as excitonic energy transfer. Of these processes, the nature of exciton hopping or tunneling, especially in regard to guest–guest (“impurity”–“impurity”) transport [1–3] is of much interest. Some relevant parameters accessible by this technique are the exciton interactions, the exciton–phonon coupling, the locally heterogeneous structure of the medium and the excitation lifetime. To avoid the oversimplifications and pitfalls involved in one-dimensional cases as well as the complexities of three-dimensional ones we study the quasi-two-dimensional system of naphthalene. The latter is anisotropic enough to give essentially two-dimensional exciton migration for both the first triplet and the first singlet excitations [4–9]. We compare our experimental results to a theoretical exciton cluster model, based on variable range connectivity and percolation [10]. We assume the extended exciton interactions to exhibit a sharp cut-off at some range due to either the kinetics of exciton transfer and/or phonon activation (“dynamic percolation” [11]) or due to the nature of the lattice eigenstates (localized vs. extended, as in “static percolation” [9] or “Anderson localization” [12]).

We first establish the “universal” nature of the relevant cluster distribution functions in two-dimensional systems. Fig. 1 shows the “percolation probability” (the probability of a guest site to be part of a macroscopically extended cluster)

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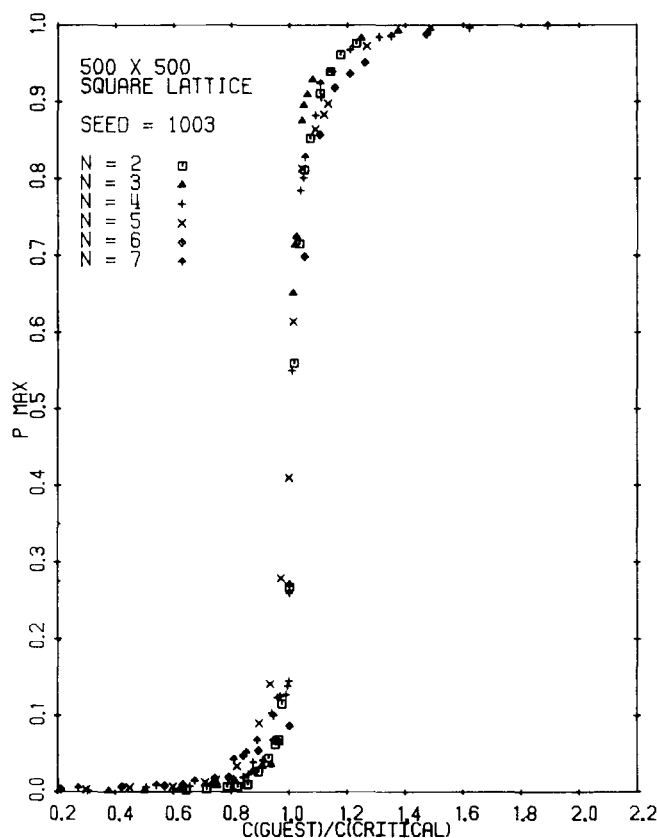


Fig. 1. The probability of the largest cluster P_{\max} (giving, above $C/C_c = 1$, the percolation probability \bar{P}_∞) vs. the scaled guest concentration C/C_c for a square lattice with a cluster defining bond varying from $n = 2$ (any combination of two nearest neighbor spacings) to $n = 7$ (any combination of seven nearest neighbor spacings). These are derived from a Monte Carlo simulation on a 500×500 random binary lattice. Here $C = G/250,000$. This illustration is based on a single configuration ("seed"). For C_c values, see ref. 10.

for a reduced concentration scale (i.e., normalized by the critical concentration for the given interaction topology). We see that the "universality" is valid over a wide range of interactions. Fig. 2 demonstrates the same for the mean finite cluster size (i.e., the average size of a microscopic guest cluster, normalized by the total number of guest sites).

Fig. 3 shows some of the experimental energy transfer results. Specifically we plot the luminescence-monitored probability of a guest exciton reaching a sensor, as a function of guest concentration. We note that the guest ($C_{10}H_8$) differs from the host ($C_{10}D_8$) only by isotopic substitution and, likewise, the sensor site differs only by minor chemical or isotopic substitution. Thus, we had no major problem in accounting for relative quantum yields, trapping efficiencies and Franck–Condon factors and also could rely on perfectly random site substitution with no major lattice distortions.

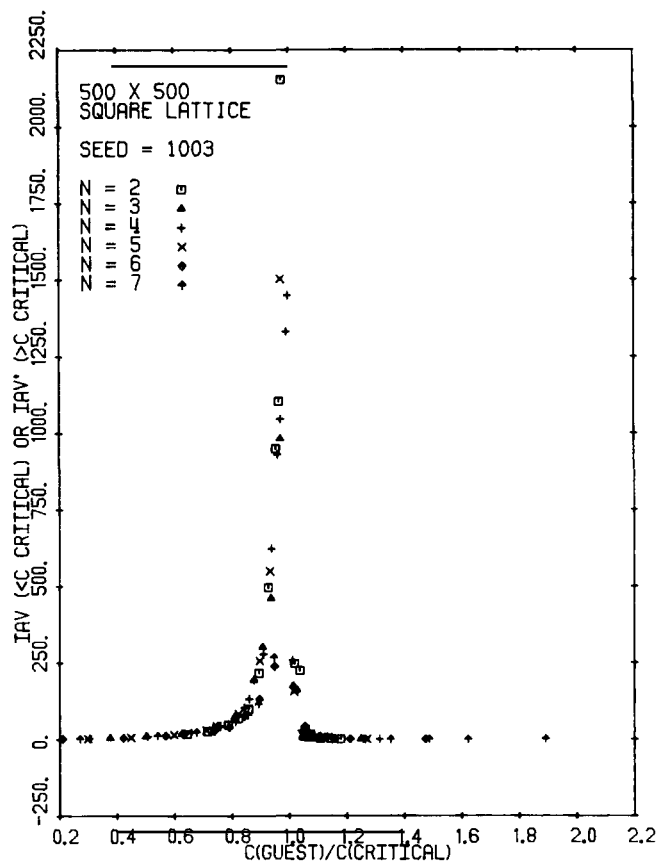


Fig. 2. The mean finite cluster size I_{AV} vs. the scaled guest concentration C/C_c . (I_{AV} is the same as I_{AV} (eq. 3), except that the largest cluster contribution is omitted from the summation.) The derivation is based on the same Monte Carlo simulations described in the previous figure caption. We do not give I_{AV} above $C/C_c = 1$, because there it becomes "infinite", but the finite quantity I'_{AV} .

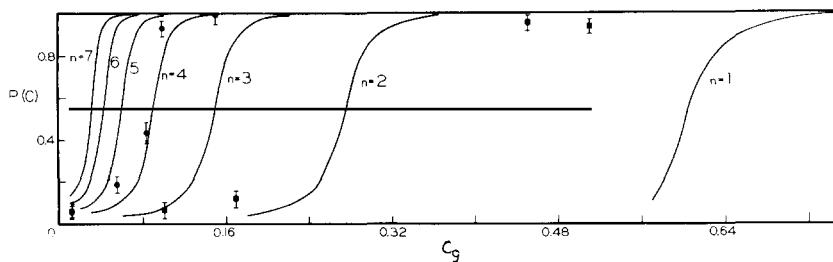


Fig. 3. Calculated and experimental exciton percolation for the system $C_{10}H_8/C_{10}D_8$. The triplet data (circles) are at 1.8 K while the singlet data (squares) are at 8 K to ensure dynamic percolation [13]. The sensor is beta-methylnaphthalene, at a concentration of about 10^{-3} throughout [13]. We use the expression $P(C) = I_s/I_{total}$ where I_s is the sensor luminescence and I_{total} is the normalized [13] total emission (sensor plus $C_{10}H_8$). The theoretical $P(C)$ is plotted according to eq. 1, based on cluster distributions derived from Monte Carlo simulations explained in the caption of fig. 1.

In a binary lattice with a random distribution of G exciton carrier sites (concentration C), a small fraction S (of G) acts as sensor sites. The probability of exciton registration by sensors is [11]

$$P(C, S) = 1 - G^{-1} \sum_m i_m m \lambda^m, \quad \lambda \equiv (1 - m/G)^{SG/m}, \quad (1)$$

where m is the cluster size and i_m its frequency*. For finite clusters in a

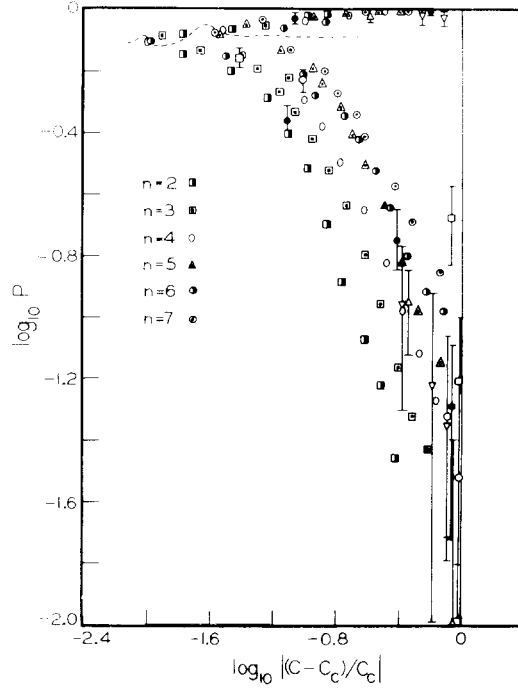


Fig. 4. Scaled calculated and experimental two-dimensional variable-range exciton percolation. The calculated points are derived from a Monte Carlo simulation on a 500×500 square lattice with a cluster defining bond varying from $n = 2$ (any combination of two nearest neighbor spacings) to $n = 7$ (any combination of seven nearest neighbor spacings) [8, 10] i.e., with effective coordination numbers [10] from 12 to 112. The resulting cluster distributions $i_m(C)$ are used in eq. 1 with $SG = 125$, to give $P(C)$ for each n . The critical concentrations are 0.29, 0.16, 0.10, 0.07, 0.0475, 0.037, for $n = 2$ to 7, respectively. The experimental points are given for four triplet exciton systems [8, 11] (see also fig. 3), $C_{10}H_8/C_{10}D_8$ (solid circles), $\beta D_1 C_{10}H_7/C_{10}D_8$ (triangles), $\alpha D_1 C_{10}H_7/C_{10}D_8$ (squares), $\alpha D_2 C_{10}H_6/C_{10}H_8$ (open circles) and for the singlet exciton system (fig. 3), $C_{10}H_8/C_{10}D_8$ (inverted triangles). The respective experimental [11] n values are 4.3, 4.4, 5.6, 5.8 and 2.0 and the corresponding C_c values are 0.091, 0.088, 0.0565, 0.052 and 0.29 (see fig. 3). We note that the triplet values come from 1.8 K measurements, while those of the singlet come [13] from a temperature of 8 K, to assure phonon assisted tunneling [11]. The dashed line separates the region below C_c (bottom) from that above C_c (top). The large error bars for the experimental values stem mainly from the experimental variation in the sensor concentration [8, 9] from the nominal value of 5×10^{-4} for S used for the calculated points. The spread with n , for the calculated points, is due to the use of a constant $SG (= 125)$, rather than a constant S . This choice was influenced by the experimental constraints.

* Alternatively one can define $\lambda \approx 1 - S$.

macroscopic crystal $\lambda \equiv e^{-S}$, giving the general result

$$\lim_{S \rightarrow 0} P(C, S) = \bar{P}_\alpha(C), \quad (2)$$

where $\bar{P}_\alpha(C)$ is the site percolation probability (fig. 1). Also, below the critical percolation concentration C_c ,

$$P(C, S) \equiv SI_{AV}(C), \quad I_{AV} \equiv G^{-1} \sum_m i_m m^2, \quad (3)$$

where I_{AV} is the mean cluster size (fig. 2). Thus, one expects the exciton percolation function $P(C, S)$ to exhibit the critical exponent β above C_c and γ somewhat below C_c . Monte Carlo simulations (figs. 3, 4) of eq. (1) for a square lattice confirm the expected behavior over a range of nearest neighbor bondlengths ($n = 2$ to $n = 7$) giving $\beta \approx 0.14$ and $\gamma \approx 2.3$. Experimental data on four distinct naphthalene triplet systems and one singlet system (figs. 3, 4) are consistent with the cluster model of exciton percolation. While they exclude an isotropic 3-dim. exciton migration topology, they strongly support a 2-dim. one, in agreement with spectroscopic and ESR data on the exciton interactions [4–7].

The excellent agreement between theory and experiment (without the use of any “fudge factors”) supports our percolation (cluster) model. It does not, however, prove or disprove Anderson localization [12] or the dynamic (kinetic) nature of the interaction cut-off [11]. It is only on the basis of independent information [11] that we get a picture of dynamic percolation controlled by phonon-assisted hopping. Specifically, time evolution experiments show a definite *rise-time* in the phosphorescence of the sensor just *below* the critical guest concentration. This, however, is absent in samples including only host and sensor (but no guest) molecules, as well as in samples with very low guest concentrations [14].

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Note added in proof: Based on new data (H. Port, private communication) the homogeneous linewidth of triplet naphthalene is $\Gamma \approx 0.01 \text{ cm}^{-1}$, while the inhomogeneous linewidth is smaller. Thus the local inhomogeneity w has to be less than Γ , rendering an Anderson localization unlikely. Also $w \ll kT$, leading one to expect a redelocalization of any Anderson localized exciton. On the other hand, having $\Gamma \gg J(C_c)$, where J is the long-range superexchange interaction for the triplet excitons (at $n \geq 4$), indicates a simple hopping model. With a hopping time of $t_h \approx \hbar\Gamma/J^2$ one satisfies, for all triplet systems, the dynamic percolation criterion, $t_h(C_c) \approx \tau S$, where τ is the lifetime.