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CRITICAL EXCITON ANNIHILATION: DIFFUSION, PERCOLATION OR ANDERSON TRANSITION?*

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Guest-Guest Triplet-Triplet annihilation in highly purified mixed crystals of naphthalene (guest)-naphthalene-d_8(host) was studied at 1.8 K via spectrally and time-resolved phosphorescence and delayed-fluorescence. We find significant deviations from current diffusion theories and homogeneous kinetics but consistency with local heterogeneities (clusterization) and dynamic exciton percolation, as well as with long-range annihilation (via superexchange). There is negative evidence for an Anderson transition.

The transport of excitations in disordered media has several interesting aspects: 1) Potentiai observation of an Anderson-Mott transition [1]. 2) Tests of current theories on diffusion in disordered media [2-4]. 3) Search for the effects of local heterogeneities ("clusters") and their relation with critical phenomena [5]. 4) Simple, reproducible, systems for studying the principles of heterogeneous kinetics and interface reactions. 5) The possibility of obtaining biomimetic systems. 6) The study of energy upconversion via long-range annihilation (exciton fusion).

The steady-state excitation (Xe lamp) of highly purified isotopic mixed naphthalene crystals ($C_{10}H_8$ in $C_{10}D_8$ at 1.8 K) is shuttered-off and spectrally resolved phosphorescence (0-0) and delayed fluorescence (0"-512")decays are monitored as a function of time, light intensity guest ($C_{10}H_8$) concentration etc. Crystals with 0.1 % mole guest show no delayed fluorescence (time resolution ≈ 1 ms) and just normal triplet decay curves (τ = 2.7 s). All host homofusion, heterofusion, prompt fluorescence, radiative trapping, intersystem crossing etc. are over within 1 ms and no guest homofusion takes place. However, guest-guest homofusion (triplet-triplet annihilation) is the phenomenon studied at higher guest concentrations. The negligible importance of any third channel of decay (i.e. supertrapping by impurities or X-traps) was demonstrated both spectroscopically and kinetically (Fig. 1). The absolute and relative delayed fluorescence (DF) and phosphorescence (P) rates were studied as a function of light (3 orders of magnitude) and time. An explicit example of a DF decay curve is given in Fig. 1.

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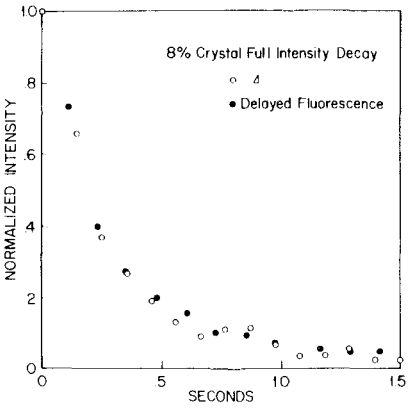

Fig. 1: Sample Delayed Fluorescence and "differential" Phosphorescence under identical conditions (Δ = measured phosph. decay rate minus "natural" one).

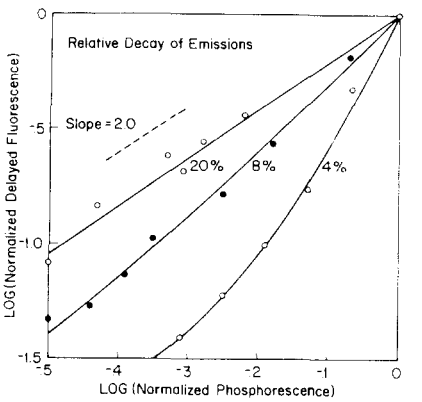

Fig. 2: Test of $(DF) \propto P^2$. For each curve DF and P are at identical decay, time points and initial excitation.

Similar curves have been obtained for different light intensities and guest concentrations (4-20 %), with a constant (±10 %) ratio of $\Delta/(DF)$. The "differential" phosphorescence decay rates Δ (Fig. 1) would be the ones observed in the limit of zero "natural" decay rate rather than the real one ($0.37\ s^{-1}$) obtained from the low guest concentration samples (0.1 %). Fig. 2 shows the relative DF and P rates at various points in time for given samples. Upon extrapolation of DF (Δ) and P to t = 0 one obtains in Fig. 3 the effective steady-state annihilation probability as a function of guest concentration and excitation rate.

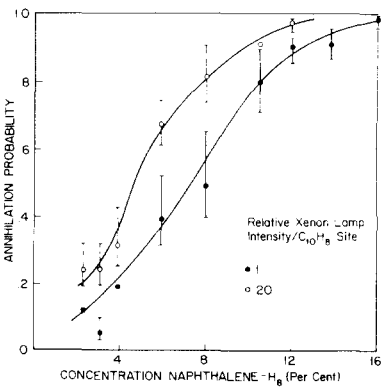

Fig. 3:

Guest Concentration Dependence of Annihilation, at constant excitation per guest site (probability from phosphorescence and "differential" phosphorescence decays extrapolated to t = 0).

The quasicritical behavior of Fig. 3 is interesting but similar to previous energy transport work measured via supertrapping [5]. However, the most striking result is found in Fig. 2 for the samples at and below the "critical" guest concentration (C_c). While for the 20 % guest sample (Fig. 2) one gets $(DF) \propto P^2$, as has been standard in previous triplet-annihilation work [5,6], for the 4 % sample the result in the high exciton density range is clearly $(DF) \propto P^X$ where $X > 2$. We note that P is linear with the exciton density (in the guest) due to the monomolecular nature of the "natural decay", and, similarly, DF has usually been expected to be quadratic with exciton density due to the bimolecular nature of the annihilation process [5,6].

In the limit of long times ($t \to \infty$), or for steady-state conditions, one gets from current theories of diffusion in disordered media essentially the same answer as from diffusion theories in homogeneous lattices, namely $X = 2$. On the other hand, the clusterization ("percolation") approach allows for both $X = 2$ and $X > 2$, depending on specific conditions, as has recently been demonstrated with the aid of Monte-Carlo calculations [7].

The dependence of C_c (the "critical guest concentration", where $(DF) \cong P$) on excitation intensity (Fig. 3) and on time cannot easily be reconciled with an Anderson transition [1]. This is especially true in view of the further shifts in C_c observed [5] in supertrapping experiments on the same systems ($C_{10}H_8/C_{10}D_8$). The experiments are also consistent with long-range annihilation (via superexchange [8,9]).

In conclusion, the annihilation experiments are not well described by current theories of diffusion in heterogeneous media. Our system can be considered as a model for heterogeneous kinetics. As both excitation transfer and annihilation processes are most probably limited to the ab crystal plane [5], this is actually a model system for interfacial reactions in synthetic and biological systems. We further believe that cluster-type exciton annihilation may be important for the study of photosynthetic systems.

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