TIME RESOLVED EXCITON MIGRATION IN MIXED NAPHTHALENE CRYSTALS: TRIPLET AND SINGLET CRITICAL CONCENTRATIONS[*]

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The contrasting temporal characteristics of the triplet and singlet transport (below 4 K) correlate with dynamic and quasistatic percolation, respectively. They do *not* support an Anderson–Mott transition (AMT) for the triplet nor an AMT followed by a kinetic threshold for the singlet critical concentration. The triplet decay-time displays the critical exponent γ.

1. Introduction

The phenomenon of critical concentrations exhibited by energy transport in isotopic mixed molecular crystals [1–3] has attracted much theoretical discussion [2,4–7] touching on some of the fundamentals of solid state theory and appears to have interesting implications for non-molecular crystals like ruby and inorganic glasses [8–10]. Anderson localization [11]. Anderson–Mott transitions [12,13] (AMT) and mobility edges [13], kinetic models, percolation models and combinations thereof have been suggested. Time resolved studies of phosphorescence and fluorescence from the "model system" of naphthalene are presented here and seem to help significantly in reducing the number of acceptable models.

Klafter and Jortner [4] interpreted the *triplet* critical concentration in naphthalene [14] in terms of an AMT mobility edge [12,13]. No explicit time dependence is contained in this model but one expects [15] a drastic reduction in the naphthalene exciton lifetime to occur at the transition, due to supertrapping, but not necessarily below the transition. In a very recent paper [16] Klafter and Jortner pro-

posed that the naphthalene *singlet* [17] exciton transport critical concentration is caused by a kinetic threshold, well above the AMT, due to competition between the diffusion rate and the natural (molecular) excitation decay rate. The expectation is thus for a gradual change in overall naphthalene exciton decay, starting well below the "transition" and continuing above it, with a decay rate *twice* that of the molecular one at the "transition" (branching point). Specifically, they defined a branching factor $f = K_s/(K_s + \tau_0^{-1})$, where K_s is the rate of "supertrapping" (energy transfer) and τ_0 the natural lifetime. At the branching point $f = 0.5$ and thus $K_s = \tau_0^{-1}$ and $K_{tot} = K_s + \tau_0^{-1} = 2\tau_0^{-1}$. Presumably K_s rises monotonically with the naphthalene concentration C. A similar approach has been taken by Blumen and Silbey [5]. However, they applied their diffusion model to the *triplet* rather than the singlet system of naphthalene.

A number of theoretical "percolation" approaches have been suggested [1,2,6,7]. We first consider the supertransfer limit of the Hoshen and Kopelman [6] cluster formalism. Inside a cluster the energy transport is "instantaneous" on the timescale of the experiment. Even inside the "infinite cluster" (formed above the critical percolation concentration) the transport to a supertrap and supertrapping are "instantaneous". Thus an exciton landing on any cluster is instantaneously supertrapped, provided a supertrap

is included in its cluster. If no supertrap is available
(in finite clusters) the exciton lives out its "natural"
lifetime. Thus any *observed* emission of naphthalene
excitons will have the "natural" lifetime, whether
below, at or *above* the *critical concentration*. We call
this limit the "quasistatic" percolation model. It has
been applied before to steady-state experiments on
the singlet system [17], and the results are equivalent
to a completely "static" percolation case, where the
exciton is an extended state of the *entire cluster* (in-
cluding the case of the "infinite" cluster). In the gen-
eral (non-supertransfer) quasi-static percolation case
[1,6] only the excitons in the "infinite" cluster need
a finite time to find the supertrap. This case has been
investigated experimentally by Argyrakis and Kopel-
man [18,19] with the aid of extremely low supertrap
concentrations, and is outside the regime of the pres-
ent discussion. Another variant of the percolation
approach, which is equivalent to a quasistatic ap-
proach where the finite clusters with supertraps are
effectively neglected, was given by Keyes [7] and
by Colson et al. [2]. In all these percolation ap-
proaches it is implied that the exciton *cannot* move
from one cluster to another i.e. the definition of a .
bond is *time-independent*. In the "dynamic percola-
tion" model [1,14,20,21], however, the bond is time-
dependent (as well as exciton interaction dependent).
Thus *the entire cluster topology is time dependent*
or is defined on a "time average" basis. We note that
in the "static" picture, neither a diffusion constant
nor a rate constant can even be defined for excitons
in finite clusters, as the probability of supertrapping
is practically time independent. In the dynamic case,
however, the *bond order* and the *supertrapping prob-
ability increase monotonically with time*. Thus one
can talk about "diffusion" (dynamic percolation) or
supertrapping "rates". Even though, strictly speak-
ing, there may still *not* exist a (time independent)
diffusion constant or rate constant, one can define
"time-averaged" diffusion and rate "constants" (over
a specified time-interval). For a long lifetime it is
reasonable to expect long bonds and a high bond or-
der, i.e. clusters defined by long-range interactions
(direct or indirect), resulting in "long-range percola-
tion". Such a long-range dynamic percolation picture
[20,26] has been adopted for the long-lived triplet
exciton transport experiments [14,20–26].

2. Experimental

The isotopic mixed crystal samples used for the
singlet decay measurements were prepared by mixing
$C_{10}H_8$ (James B. Hinton), $C_{10}D_8$ (Thompson Packard,
99% isotopic purity), and enough betamethylnaph-
thalene (BMN), purified by sublimation, to ensure
saturation [24]. Both $C_{10}H_8$ and $C_{10}D_8$ were puri-
fied by fusion with potassium metal followed by zone
refining (200 passes). Samples were outgassed by
several cycles of melting under helium gas, freezing
and pumping. After sealing the sample in a glass am-
poule and thoroughly mixing the contents, single
crystals were grown using a Bridgman technique.

Crystal samples used for the triplet experiments
were prepared in a similar fashion from potassium
fused, zone refined $C_{10}D_8$ (Merck, Sharp & Dohme,
98% isotopic purity) and a "$C_{10}H_8$/BMN Standard".
The "standard" was made by mixing 5.0 mg zone
refined BMN with 5.00 g potassium fused, zone re-
fined $C_{10}H_8$. This method [23] allowed us to hold
the relative supertrap concentration, S, constant at
10^{-3}. The relative supertrap concentration in this
series of samples did not vary by more than 30% as
compared to more than a factor of five variation in
supertrap concentration in the crystals prepared for
the singlet measurements.

Single crystals were cut along the *ab* (cleavage)
plane, mounted in a sample holder "cage" and im-
mersed in liquid helium. Singlet measurements were
taken by exciting the sample at 3125 Å with the
doubled output pulse of a Molectron DL400 dye la-
ser—Molectron UV1000 nitrogen laser. The decay
of the spectrally resolved $C_{10}H_8$ 0–512 fluorescence
band was detected with an EMI 9785QB phototube.
Signal averaging was performed using a pre-triggered
PAR model 162/164 boxcar averager. Analog data
was digitized and stored on magnetic tape for sub-
sequent processing and plotting. The time resolution
of this apparatus is about 10 ns.

Triplet decay measurements were made by shut-
tering a 1600 W Hanovia xenon lamp (filtered by a
$NiSO_4/CoSO_4$ solution filter) with a Uniblitz pro-
grammable shutter. Spectrally resolved $C_{10}H_8$ 0–0
phosphorescence (at 21208 cm^{-1}) was measured
with an ITT F-4013 phototube mounted in a Prod-
ucts for Research housing (cooled to $-25°C$). Data
was collected with a PAR model 1120 discriminator

and model i110 photon counter using a DEC LSI-11 microcomputer. Specially written software permitted collection of time resolved data in a multi-scaling mode for averaging a number of decay curves. The time resolution was limited by the closing speed of our shutter system to about 4 ms.

3. Results and discussion

Fig. 1 shows "raw" singlet (left) and triplet (right) time evolution data while fig. 2 shows the normalized decay times (τ/τ_0) as a function of reduced concentration (C/C_c) for the low temperature triplet and singlet exciton emissions. Note that $\tau_0 = (128 \pm 2) \times 10^{-9}$ s for the singlet and 2.61 ± 0.02 s for the triplet. A drastic difference is evident: The singlet lifetime is constant, within experimental scatter, throughout the whole range, below, at and above the "critical concentration" [17]; however, the triplet lifetime falls three or more orders of magnitude before reaching the "critical concentration" [23] (and may drop significantly more as it falls below our detection capability). We note that the betamethylnaphthalene

(supertrap) time evolution spectra are completely consistent with the naphthalene ones: They too are independent of C for the singlet [24], but are very sensitive to C, near percolation, in the triplet case [25].

Fig. 2 (insert) shows a "reduced lifetime" versus "reduced concentration" log–log plot for the triplet systems, where the term "reduced" is used in the sense of modern scaling theories (i.e. $T/T_c - 1$ rather than T/T_c). The slope $\gamma = 2.3$ is very significant [26] because it gives (empirically)

$$1 - \tau/\tau_0 = (\tau^{-1} - \tau_0^{-1})/\tau^{-1} \propto |(C - C_c)/C_c|^{-\gamma}. \quad (1)$$

We note that, using the "natural decay constant" $k = \tau_0^{-1}$ as well as $K_{tot} \equiv \tau^{-1}$ and $K_s \equiv K_{tot} - k$, one gets (assuming time independent/and or time averaged quantities) the [1] "percolation probability" $\bar{P}$ (the probability that the excitation has been supertrapped), giving

$$\bar{P} \equiv K_s/K_{tot} \propto |(C - C_c)/C_c|^{-\gamma}. \quad (2)$$

One can show the equivalence between $\bar{P}$ and the steady state percolation probability [23] $P = I_S/I_{tot}$, where I_S and I_{tot} are, respectively, the supertrap and total phosphorescence intensities. It has theoretically
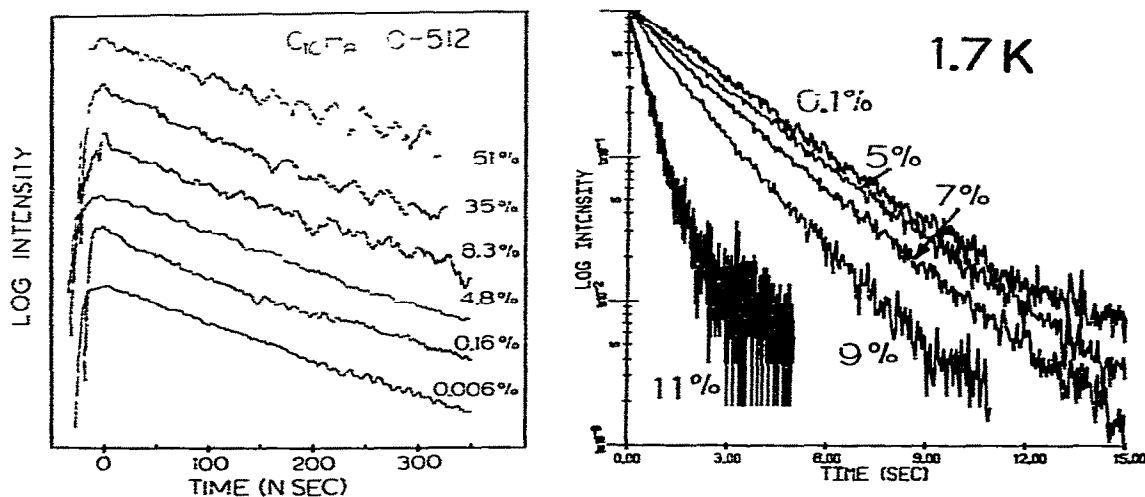

Fig. 1. Log plots of spectrally resolved $C_{10}H_8$ 0–512 singlet (2–4 K) decays (left) and spectrally resolved $C_{10}H_8$ 0–0 triplet decays (right) for several guest concentrations. The singlet decays well below the critical concentration $(C_c = 0.5)$ through slightly above C_c do not vary (within experimental error) from $\tau_0 = (128 \pm 2) \times 10^{-9}$ s. The triplet decays show a significant change as C approaches C_c $(C_c = 0.126$, for these data). Triplet τ_0 measured from low concentration crystals is found to be 2.61 ± 0.02 s.

been shown [22,26] that $P \propto [(C - C_c)/C_c]^{-\gamma}$, well below C_c, provided that S is constant. Thus eqs. (1) and (2) are consistent with percolation theory. The critical exponent γ equals 2.1—2.4, in two dimensions, inclusive of long-range interaction cases [22,26,27]. There is also ample evidence that the triplet energy transport in naphthalene is practically two-dimensional [20,28—30]. We note that K_s may include contributions from exciton—exciton annihilation (excitons as supertraps). We also note that the deviation from linearity, seen in fig. 2 (insert) near the critical concentration, is expected, and in the right direction. It follows the deviation observed for P simulations [22] and P measurements [22]. It should also be noted that all the singlet points would fall on fig. 2 (insert) at "minus infinity".

The figs. 1 and 2 singlet results disagree with the Klafter—Jortner "kinetic threshold" model for the singlet excitation. The figs. 1 and 2 triplet results are also not predictable from their AMT model for the triplet. However, the singlet temporal decay behaviour is fully consistent with the "quasistatic" percolation model [1,14]. Also, the triplet temporal decay behaviour is fully consistent with a "dynamic per-

colation" model [1,20] but also with the Blumen—Silbey kinetic model [5]. However, the fig. 2 (insert) scaling and critical exponent is not quantitatively predictable from the latter model while it has been predicted from the dynamic percolation model [22]. Even if the Klafter—Jortner model is generalized to include a phonon-assisted hopping below the AMT (which, however, should "erode" the critical concentration [16]), we do not see how this could account for the scaling nature and critical exponent behaviour, unless the AMT is completely eroded and the phonon-assisted hopping occurs according to a dynamic percolation model.

4. Conclusion

The naphthalene low temperature triplet and singlet exciton transport near the critical concentrations supports the percolation models (dynamic and static, respectively). Neither an AMT nor a diffusion (kinetic) model account for the time-resolved measurements on the singlet system (i.e. no C-dependence of the decay-time). Also, among the existing models, only the dynamic percolation model predicts the scaling behaviour and critical exponent revealed by the triplet decay times.

Acknowledgement

Fig. 2. Ratio of experimental $C_{10}H_8$ lifetime divided by lifetime at low concentration (τ_0) for singlet (circles, 2—4 K), and triplet (triangles = 4.2 K, squares = 1.7 K). Critical concentrations were determined from steady-state experiments [23,24]. Decay times for the non-exponential triplet data were determined from $t \lesssim 1$ s, where the data were close to exponential. Insert: Log—log plot shows scaling of triplet time-resolved data. The slope of 2.3 was added for comparison with predicted critical exponent, $\gamma = 2.3$. A deviation from this slope of 2.3 is expected as C approaches C_c.

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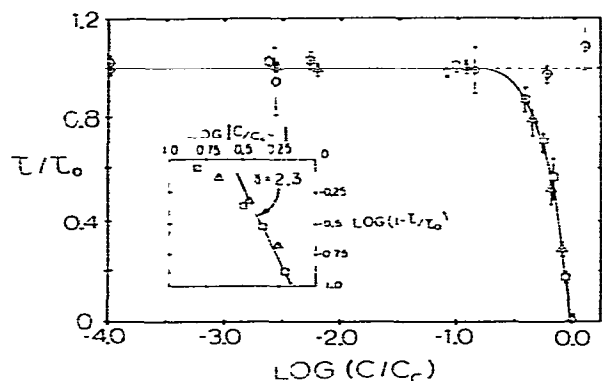[6] J. Hoshen and R. Kopelman, J. Chem. Phys. 65 (1976) 2817

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