EXCITATION TRANSPORT AND DYNAMICS IN SOLID STATE SYSTEMS[*]

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Recently we have been involved in experimental and theoretical investiga-
tions of electronic excited state transport and excitation dynamics in a
variety of condensed phase systems. Pure crystals, mixed crystals and amor-
phous materials such as polymer blends containing chromophores are being
studied. Picosecond transient grating methods,[1,2,3] picosecond photon echo
and other optical coherence experiments[4,5,6] and time resolved fluorescence
measurements[7,8,9,10] are being used in the experimental studies. We are
employing statistical mechanics to investigate excitation transport and trapping
in mixed crystal[11] and solution[12] systems, photon echo observables associ-
ated with impurity band states of mixed crystals[13] and delocalized dimer
states,[14] and excitation transport in finite volume systems[15] such as
isolated polymer coils containing chromophores in polymer blends.[16].

The application of the picosecond transient grating technique to the inves-
tigation of exciton migration works in the following manner.[1] A picosecond
time scale pulse of light is split in two. The paths of the resulting pulses
are arranged to have a known angle between them and to intersect simultaneously
in the sample. Interference between the two coherently related pulses creates
an optical fringe pattern in the sample such that the intensity of light varies
sinusoidally in the beam overlap region. The interference fringe spacing is
determined by the angle between the beams and by the wavelength of the light.

When the frequency of the exciting light coincides with an absorption band
of the sample molecular crystal, excitations are produced. These excitations
will have the same spatial distribution as the sinusoidal optical interference
pattern, i.e. there will be a continuous oscillatory variation in the concentra-
tion of excited states. After a suitable time delay, a probe pulse is directed
into the sample along a third path. The probe pulse will exxperience an inhomo-
geneous optical medium, resulting from alternating regions of high and low
concentrations of excited states which have different complex indices of

refraction.[3] Thus, the probe pulse encounters a *diffraction grating* which causes itto diffract into one or more orders. The diffracted pulse leaves the sample along a unique direction.

Consider the effect of mobile excitations on the diffracted signal. Migration will move excitons from areas of high exciton concentration, grating peaks, to areas of low concentration, grating nulls. Thus, the exciton motion will fill in the grating nulls and deplete the peaks. Destruction of the grating pattern by spatial redistribution of the excitations will lead to a decrease in the intensity of the diffracted probe pulse as the probe delay time is increased. Thus the time dependence of the grating signal is directly determined by the rate of exciton transport and by the exciton lifetime.

We have performed experiments which demonstrate that the transient grating method is a tool capable of providing in depth information on exciton transport. Exciton transport along the anthracene $\vec{a}$ crystallographic direction was measured at 20 °K, 10 °K and 1.8 °K.[1] On the distance scale of the experiments, transport was observed to be diffusive (exponential decays),[1] and the diffusion constants are 0.8 ± 0.2 cm^2/sec, 1.3 ± 0.4 cm^2/sec, and 10 ± 2 cm^2/sec at 20 °K, 10 °K and 1.8 °K, respectively.

Although the temperature dependence is preliminary, it is interesting to speculate on its nature. Hopping transport is mildly temperature activated. Then strictly incoherent transport appears to be inconsistent with the observed increase in diffusion constant with decreasing temperature. Although the transient grating decays are exponential, indicating diffusive transport on the 1 µ distance scale of the experiment, coherent transport could none-the-less be responsible for the observed temperature dependence. If at temperature T the exciton has an ensemble average coherence length $\langle\ell(T)\rangle$, which is long relative to a lattice spacing, but short relative to the experimental fringe spacing, d, (1 µ), then the observed decays will be exponential. The exciton ensemble will appear to be executing a random walk with an average step size $\langle\ell(T)\rangle$. As the temperature decreases, the exciton-phonon scattering rate decreases and $\langle\ell(T)\rangle$ increases. For a random walk with step size ℓ, the diffusion constant is proportional to ℓ^2. Therefore, an increase in D is expected as the temperature decreases for quasi-coherent transport. If the excitons are in fact quasi-coherent with a coherence length $\langle\ell(T)\rangle$, then for $\langle\ell(T)\rangle \gtrsim d/2$ the coherence should manifest itself directly in the functional form of the decays.[1] Fringe spacings of ~ 1000 Å are practical, and will be employed in future experiments.

Electronic excitation of interacting molecules can result in a state which is delocalized, i.e., at a given instant of time, there is finite probability of finding the excitation on more than one molecule. Molecular dimers are the

smallest systems in which delocalization can occur. As in any system which can show delocalization, dimer electronic excitations will be delocalized if the strengths of the intermolecular interactions are large relative to the magnitudes of the fluctuations in site energies and intermolecular coupling matrix elements.

We have performed a detailed experimental and theoretical examination of the temperature-dependent optical dephasing of delocalized tetracene and pentacene dimer states, and tetracene and pentacene monomers in p-terphenyl host crystals.[4,5,6,14] The relative orientations of the molecules in the dimer pairs are similar to the orientation of host molecules in the pure crystal. Thus there are a variety of possible dimer pairs having various intermolecular interactions. The experiments demonstrate that at the lowest experimental temperature (1.4 °K), the coherence is limited only by the excited state lifetime.

A comparison of picosecond photon echo experiments on tetracene and pentacene dimers in the same host crystal permits an unambiguous determination of the mechanism responsible for the temperature-dependent optical dephasing of the delocalized excited states of these dimer systems. In contrast to isotopically mixed crystal dimers, e.g., h_8-naphthalene dimers in d_8-naphthalene host crystals or h_2-tetrachlorobenzene dimers in d_2-tetrachlorobenzene host crystals, these chemical impurity dimers do not have as their principle dephasing mechanism scattering between the delocalized dimer states. Rather, these chemical impurity dimers dephase because of phonon excitation of local phonon (librational) modes of the dimers.

There are a variety of interesting systems in which chromophores are contained in a volume sufficiently small that energy transport properties are significantly affected by the limited size of the system.[7,8,15,16] Such finite volume systems include isolated polymer coils containing chromophores, small aggregates of coils in polymer blends, micelles containing dye molecules, and photosynthetic units.

Constraining chromophores to a finite volume increases the theoretical complexity of the excitation transport problem.[15] For an infinite volume system, the ensemble averaged Green function solution to the master equation (high temperature limit) is independent of the initial position of the excitation.[10] This property allows a very accurate approximation to be obtained by nonperturbative techniques.[11,12,13] In contrast, a chromophore near the surface of a finite sphere of randomly distributed chromophores experiences a very different local distribution of chromophores than a chromophore near the center. Therefore, an additional average over the excitation starting point must be performed. The finite volume theory must also be able to handle finite numbers of

particles. These differences from the infinite volume problem make the nonper-
turbative theoretical techniques inapplicable to finite volume systems. Instead
a density expansion with a Padé approximant is used. These theoretical results
have been shown to be accurate.[15]

As an example of excitation transfer in a finite volume system, picosecond
fluorescence mixing experiments on octadecyl rhodamine B (ODRB) in triton X-100
micelles have been performed.[7] The ODRB is insoluble in water and is totally
associated with the micelles. ODRB in micelles forms a clustered energy trans-
port system. By clustering the dye molecules in a small volume, the transport
efficiency is greatly increased over a solution with the same dye concentration
but with the molecules randomly distributed throughout the solution. Very rapid
energy transport is observed and agreement with theory is very good. The
experiments provide an accurate determination of the micelle size.

The finite volume excitation transport theory and experiment have also been
applied to isolated polymer coils and small aggregates of coils, for polymers
that contain chromophores.[8,16] Due to the strong distance dependence of the
transfer rate, the dynamics of excitation transport in a finite volume are
intimately related to the average inter-chromophore separation, and hence the
overall size of the chromophore distribution. Excitation transport observables
serve as a tool for examining the spatial configuration of polymer coils[8] just
as these observables allowed the determination of the Triton micelle size. Of
particular interest is how coil sizes change in various polymer blends. We have
examined[8] various copolymers of methyl methacrylate and vinyl naphthalene in
polymethyl methacrylate and polyethyl methacrylate. Several different hosts
molecular weights were studied. The theoretical treatment based on a finite
volume excitation transport theory which incorporates polymer statistics,
accurately describes the time dependence of fluorescence depolarization follow-
ing picosecond excitation of the naphthalene chromophores. Information on the
copolymer coil size and phase separation in the blend is obtained from the
experiments.

REFERENCES

1) Todd S. Rose, Roberto Righini, and M. D. Fayer, Chem. Phys. Lett. 106
   (1984) 13.

2) M. D. Fayer, Ann. Rev. Phys. Chem. 33 (1982) 63.

3) Keith A. Nelson, R. Casalegno, R. J. Dwayne Miller, and M. D. Fayer,
   J. Chem. Phys. 77 (1982) 1144.

4) F. G. Patterson, William L. Wilson, H. W. H. Lee, and M. D. Fayer, Chem. Phys. Lett (1984) in press.

5) F. G. Patterson, H. W. H. Lee, William L. Wilson, and M. D. Fayer, Chem. Phys. 84 (1983) 51.

6) H. W. H. Lee, F. G. Patterson, R. W. Olson, D. A. Wiersma, and M. D. Fayer, Chem. Phys. Lett. 90 (1982) 172.

7) M. D. Ediger, R. P. Domingue, and M. D. Fayer, J. Chem. Phys. 80 (1984) 1246.

8) M. D. Ediger, K. Peterson, R. P. Domingue, and M. D. Fayer, Macromolecules, (1984) in preparation.

9) R. J. Dwayne Miller, Marc Pierre, and M. D. Fayer, J. Chem. Phys. 78 (1983) 5138.

10) C. R. Gochanour and M. D. Fayer, J. Chem. Phys. 85 (1981) 1989.

11) Roger F. Loring, Hans C. Andersen, and M. D. Fayer, J. Chem. Phys. 80 (1984) 5731; Roger F. Loring, Hans C. Andersen, and M. D. Fayer, Chem. Phys. 85 (1984) 149.

12) C. R. Gochanour, Hans C. Andersen, and M. D. Fayer, J. Chem. Phys. 70 (1979) 4254; Roger F. Loring, Hans C. Andersen, and M. D. Fayer, J. Chem. Phys. 76 (1982) 2015.

13) Roger L. Loring, Hans C. Andersen, and M. D. Fayer, J. Chem. Phys. (1984) in press.

14) H. W. H. Lee and M. D. Fayer, J. Chem. Phys. (1984) in preparation.

15) M. D. Ediger and M. D. Fayer, J. Chem. Phys. 78 (1983) 2518.

16) M. D. Ediger and M. D. Fayer, Macromolecules 16 (1983) 1839.