DELOCALIZED ELECTRONIC EXCITATIONS OF PENTACENE DIMERS IN A p-TERPHENYL HOST: PICOSECOND PHOTON ECHO EXPERIMENTS

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Photon echo experiments are performed on delocalized electronic excitations of optical dimer states The delocalized dimer states are found to have very long coherence times, close to the coherent limit The dimer dephasing is qualitatively similar to dephasing of pentacene monomers.

1. Introduction

The concept of a delocalized electronic state implies the existence of long-term quantum-mechanical phase relationships among the component basis states If these phase relationships are lost rapidly on the time scale of an experimental observable, the state is incoherent, i.e. it will not exhibit phase-dependent properties. For example, the transport of electronic excitations among dye molecules in solution can be described in terms of a master equation [1]. It is unnecessary to consider the relative phases of excitations on different molecules. In contrast, the propagation of a coherent exciton wave packet depends on changing regions of constructive and destructive interference. Therefore, it involves in detail the phases of excitations on different molecules. The phase relationships giving rise to a coherent delocalized electronic state can be lost via dynamical interactions of the system with its environment.

The shapes and widths of homogeneous optical absorption lines provide information on the basic dynamical processes affecting electronic excitations. However, inhomogeneous broadening can frequently mask the homogeneous line. In addition, the homogeneous line shape does not distinguish T_2^* (pure dephasing) from T_1 (lifetime) processes. Application of optical coherence experiments, such as photon echo [2–4] and

stimulated photon echo [4], can be used to remove the effects of inhomogeneous broadening and distinguish T_1 processes, such as spectral diffusion, from T_2^* processes.

Until recently picosecond optical coherence experiments on large molecules have examined the states of isolated molecules in dilute mixed crystals [3,4] However, in recent experiments we have investigated delocalized optical excitations of pentacene dimers in concentrated pentacene in p-terphenyl crystals. In this crystal, some of the many possible types of near-neighbor dimers have large spectral shifts from the monome $S_0 \rightarrow S_1$ origin This is due to dipole—dipole interactions which delocalize the excitation over the molecular pair. Differences in van der Waals interactions (crystal shift) of an isolated molecule and the molecular pair can also contribute to the spectral shifts. The dipole interaction between the pentacenes comprising the dimer splits the S_1 state into a doublet. Consider the states of the system in a site representation $|00\rangle$, both molecules are unexcited, $|10\rangle$ and $|01\rangle$, respectively, the first and second molecule is excited, and $|11\rangle$, both molecules are excited For a pair of identical molecules, the eigenstates of the system including the dipolar interactions are

$$|00\rangle, \quad |+\rangle = 2^{-1/2}(|10\rangle + |01\rangle),$$

$$|-\rangle = 2^{-1/2}(|10\rangle - |01\rangle), \quad |11\rangle \qquad (1)$$

The energies of these states are given by

$$E_{00} = 0, \quad E_{+} = E + \beta - D,$$

$$E_{-} = E - \beta - D, \quad E_{11} = 2E - D_{11} . \qquad (2)$$

E is the monomer excitation energy β is the dipolar intermolecular interaction matrix element which delocalizes the excitation. D accounts for the difference in crystal shift of a singly excited molecular pair and an isolated molecule in the p-terphenyl lattice. D_{11} accounts for the difference in crystal shift of the doubly excited pair The monomer crystal shift is absorbed into E. Some dimers, arising from equivalent pentacenes, are composed of monomers with degenerate electronic states. Eqs. (1) and (2) are exact for these dimers. However, in the p-terphenyl host there are four well-defined site energies for pentacene [5] arising from the four symmetry inequivalent positions in the low-temperature host unit cell [6]. Many of the monomer pairs have $E_{01} \neq E_{10}$. Even in this situation, for some molecular pairs, the dipolar interaction is so great that the excited state is effectively delocalized over the two molecules, and eqs. (1) and (2) are basically correct [7].

In fig. 1 the transmittance spectrum to the red of the pentacene in p-terphenyl origin is shown The sample is so highly concentrated that the monomer peaks are 100% absorbing over a broad spectral region (In a
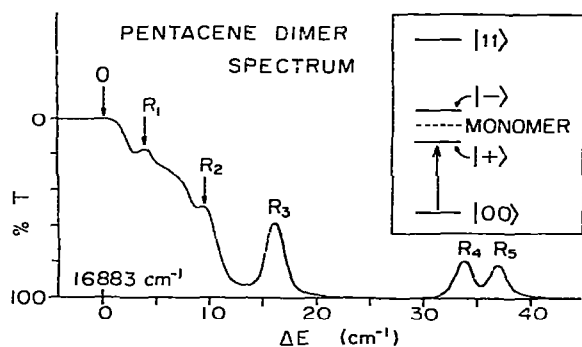
non-saturated monomer spectrum the monomer peaks are ≈ 1 cm^{-1} wide [5].) In this spectrum five peaks are clearly visible to the red of the monomer origin These are labeled R_1-R_5. R_1 and R_2 appear as shoulders on the monomer absorption while R_3, R_4 and R_5 are well resolved.

Conclusive evidence that these peaks are in fact dimers comes from absorption spectra. The integrated absorbances of the R_3-R_5 absorptions at 1.4 K were measured on a series of crystals of varying pentacene concentration. The monomer concentrations of the same crystals were measured by observing a vibrational excitation at room temperature so the absorptions would be thermally broadened and have reasonably low ODs. A log–log plot of these pairs of measurements is given in fig. 2. A line of slope two fits the points well. Thus, the concentrations of R_3-R_5 go as the *square* of the monomer concentration, demonstrating unambiguously that R_3-R_5 are dimer absorptions

The dimer splittings can be calculated approximately using the low-temperature p-terphenyl crystal structure [6] and an atom–atom potential calculation to obtain the orientation of pentacene molecules in each of the four sites in the p-terphenyl lattice [7]. These calculations demonstrate that the majority of the red-

Fig 1 Transmittance spectrum of pentacene dimers, R_1-R_5, in p-terphenyl at 1 4 K. Total pentacene concentration is 2.5 × 10^{-4} mol/mol The monomer origin, O, absorbs 100% due to its high concentration. The scale is the red-shift in wave numbers from the monomer. Inset energy level diagram showing pentacene monomer and the $|+\rangle$, $|-\rangle$ and $|11\rangle$ dimer states The large dipole interaction splits the $|+\rangle$ and $|-\rangle$ states by tens of cm^{-1}. The vertical line represents the laser optical field which couples the ground state to the delocalized state, $|+\rangle$. All other states are far off-resonance and are not affected by the laser.
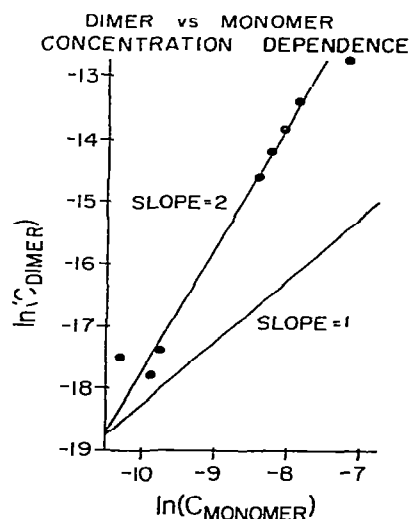

Fig 2 Concentration of R_3 plotted against pentacene monomer concentration for several crystals. A line of slope two fits the log–log plot, indicating that the R_3 concentration goes as the *square* of the monomer concentration. Identical results were obtained for R_4 and R_5. This conclusively demonstrates that R_3-R_5 are dimer absorptions

shifted dimer lines have small splittings of less than
2 cm^{-1}. These will be obscured under the intense monomer peak. Attention must be focused on the red
side of the origin as the intense absorption by the monomer phonon sideband dominates the spectrum to
the blue of the monomer peak For a number of the
crystallographically different dimer pairs, the dipolar
splitting is large enough to produce the observed
R_1–R_5 peaks An exact calculation of the spectrum
is not possible for two reasons. First, the exact orientations of the pentacenes in the lattice are unknown.
Second, the differences between monomer and dimer
van der Waals interactions with the host lattice (D
terms) are unknown Although the spectrum cannot
be calculated exactly, the observed peaks, R_1–R_5, are
entirely consistent with good estimates of the energies
of the red-shifted dimer states.

Fig. 1 shows a simplified energy level diagram of a
monomer and a set of dimer states $|+\rangle$, $|-\rangle$, and $|11\rangle$
The $|+\rangle$ and $|-\rangle$ dimer states are truly delocalized
entities. They have been referred to as "mini excitons"
as they are the smallest, multi-molecule system which
can exhibit delocalization

There have been a number of experiments which
examine spin coherence in triplet dimer systems [8].
However, it can be difficult to relate spin coherence
measurements to the basic question of optical coherence times [9]. By performing photon echo experiments on the dimer states described above, we have
been able to unambiguously measure the optical coherence time associated with a delocalized state

2. Experimental

The fast decay times of large molecules require
high-energy, tunable, picosecond light pulses to perform photon echo experiments These are provided by
a mode-locked, cavity-dumped dye laser synchronously pumped by the frequency-doubled output of a cw
pumped, acousto-optically mode-locked and Q-
switched Nd : YAG laser. This dye laser system provides a very stable source of 30 ps, 20 μJ pulses at a
400 Hz repetition rate [4]. A dye laser single pulse
passes through a network of beam splitters and a motorized optical delay line. This splits the pulse into a
sequence of excitation pulses with appropriate intensities and variable temporal delays for the photon echo

experiments The excitation pulse sequence is then directed to the sample, located in a liquid-helium Dewar.
The generated echo signal leaves the sample and is
temporally, spatially and frequency selected by summing with a single, 80 ps IR pulse. The up-converted
echo signal is then detected. Further details of the experimental procedures appear elsewhere [4].

The dye laser was tuned to the absorption maxima
of the R_3, R_4 and R_5 lines and echo decay curves were
recorded The R_1 and R_2 lines are not sufficiently well
resolved from the monomer peak to obtain unambiguous results. The spectral spread of the dye laser and
the Rabi frequency, ω_1, are sufficiently small to ensure that only the selected line was excited in a given
experiment (see fig 1). Thus, the ground state was
coupled to a single delocalized dimer state without interference from the monomer excited state or other
dimer states, including the doubly excited $|11\rangle$ state.
These other states are not in resonance with the laser

The lifetimes of the dimer lines R_3, R_4 and R_5
were obtained by selectively exciting each line and
measuring its fluorescence decay time using a fast photomultiplier tube (rise time <2 ns) and a computer-interfaced Tektronix R-7912 transient digitizer The
pentacene in p-terphenyl crystals were immersed in
liquid helium and the sample temperature controlled
by the rate of pumping on the liquid helium. The temperature was measured with a calibrated digital manometer.

3. Results

Table 1 gives the results of the photon echo decay
(T_2) and fluorescence decay (T_1) measurements on
the three dimer lines R_3, R_4 and R_5. Included in table
1 is the pure dephasing time, T_2^*, obtained from

$$1/T_2 = 1/2T_1 + 1/T_2^* .$$ (3)

The lifetime of the pentacene monomer in p-terphenyl
is 24.5 ns. The lifetimes of the three distinct delocalized dimer states are all somewhat faster than this and
differ somewhat among themselves This is not unreasonable since both the radiative and non-radiative
rates of decay to the ground state for a delocalized
dimer can be different from the monomer rates. The
transition dipole of a dimer state is the appropriate
vector sum of the transition dipoles of the constituent

Table 1

The photon echo decay time T_2, fluorescence decay time T_1, pure dephasing time T_2^* and red-shift of the dimer absorption from th the pentacene origin Δ of the three dimer lines R_3, R_4 and R_5.

Dimer site	λ (A)	Δ (cm^{-1})	T_2 (ns)	T_1 (ns)	T_2^* (ns)
R_3	5927 2	16	21	19 5	46
R_4	5933 5	34	22	16 5	67
R_5	5934 6	37	11 5	15 5	19

monomers. The electronic excitation—phonon coupling for a delocalized dimer state also differs from that of a monomer state. This can affect the rate of vibrational relaxation to the ground state.

The values of T_2 obtained from the photon echo decay measurements are all significantly smaller than $2T_1$, the decay time which arises from the excited state lifetimes, but all have $T_2 > 10$ ns. The corresponding homogeneous linewidths, $1/\pi T_2$, are more than a thousand times narrower than the spectroscopically observed dimer widths, showing that the absorption line shapes arise from inhomogeneous broadening and do not reveal information about the dimer dynamics. *The important fact uncovered by the optical coherence experiments is that the delocalized dimer state optical coherence time is very long.* These dimer "mini excitons" are close to the coherent limit $(T_2 = 2T_1)$ [‡].

The splitting between the $|+\rangle$ and $|-\rangle$ states of each of the dimers that give rise to the R_3–R_5 absorptions (tens of cm^{-1}) is large relative to $kT (\approx 1$ cm^{-1}). Thus, phonon scattering between the $|+\rangle$ and $|-\rangle$ states of a dimer cannot occur since only the lower-energy state is excited and there is vastly insufficient thermal energy available for the scattering process. Since $T_2 \neq 2T_1$, the additional dephasing must arise from a pure dephasing process characterized by T_2^* This decay results from phonon modulation of the dimer state energy, causing the transition correlation function to decay. All of the echo experiments gave exponential curves (lorentzian homogeneous line shape) indicating that the correlation function decays rapidly compared to T_2 [10]. In fig. 3 a temperature-dependent study is

shown. T_2^* is observed to be temperature independent for all three dimer lines examined.

Pentacene dimer dephasing is qualitatively similar to monomer dephasing. Both monomer and dimer dephasing are temperature independent at low temperature and, in the zero-concentration limit, $T_2 \neq 2T_1$. These similarities suggest that the same dephasing mech anism is operant for monomers and dimers. At present, no detailed explanation exists for the observed dephasing rates. However, our experiments on pentacene in the hosts p-terphenyl, naphthalene, and benzoic acid show a positive correlation between the strength of the phonon sideband relative to the zero-phonon line and the low-temperature, low-concentration, pure dephasing rate. This suggests that linear phonon coupling could be the source of the pure dephas-
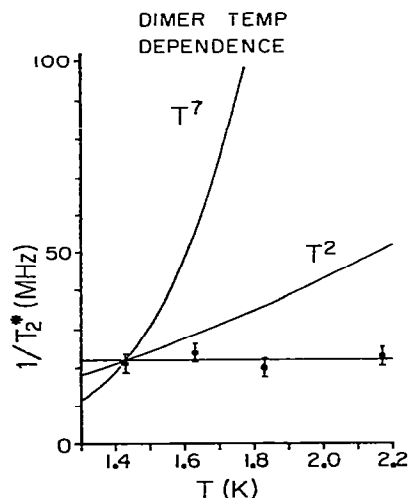

Fig. 3 Temperature dependence of dephasing time, T_2^*, of R_3 pentacene dimers. The behavior of R_4 and R_5 is identical. A T^7 temperature dependence would result from quadratic coupling to harmonic phonons. A quadratic temperature dependence is shown for comparison.

[‡] Strictly speaking, the dimer coherence time is the scattering time between the delocalized states. If the scattering rate, K, is zero, $T_2 = 2T_1$ *in the absence of pure dephasing.* If there is a pure dephasing process, and $K = 0$, $T_2 \neq 2T_1$. Therefore the coherence time is equal to or longer than T_2

ing. We are currently investigating this and other possibilities theoretically

We have demonstrated directly that delocalized optical excitations of dimer states can have extremely long coherence times. In addition, the echo measurements reveal a very interesting and possibly important feature. Geometrically different dimers can have substantially different pure dephasing rates, T_2^*. R_3 has a value of ≈ 50 ns, while R_4 gives ≈ 70 ns and R_5 gives ≈ 20 ns. If this arises due to the coupling of the delocalized dimer state to phonons, there must be a sizeable dependence on the details of the dimer geometry That is, the dimer electronic excitation—phonon coupling is spatially anisotropic This could have implications for our understanding of coherence in exciton bands of pure crystals. Since the exciton band dispersion is based on pair-wise interactions, the rate of loss of exciton coherence could also be spatially anisotropic. In an extreme situation, coherent exciton propagation could effectively be limited in spatial direction, not because the energy dispersion is anisotropic, but because the rate of exciton coherence loss is anisotropic

Acknowledgement

References

[1] C R Gochanour, H C Andersen and M D Fayer, J Chem Phys 70 (1979) 4254

[2] I D Abella, N A Kurnit and S R Hartmann, Phys Rev 141 (1966) 391

[3] D A Wiersma, Advan Chem Phys. (1980), to be published

[4] D E Cooper, R W. Olson and M D Fayer, J Chem Phys 72 (1980) 2332.

[5] R W Olson and M D Fayer, J Phys. Chem 84 (1980) 2001

[6] J L Badour, Y Delugeard and H Cailleau, Acta Cryst B32 (1976) 150

[7] R.W Olson, F G Patterson, H W H Lee, J L Skinner, H C Andersen and M D Fayer, J Chem Phys, to be published

[8] B J Botter, A J. van Strien and J Schmidt, Chem Phys Letters 49 (1977) 39,
D.M Burland and A H Zewail, Advan Chem Phys 40 (1979) 369.

[9] R D Wieting and M D Fayer, J. Chem Phys 73 (1980) 744

[10] A G Redfield, Advan Mag Reson. 1 (1965) 1