OPTICAL DEPHASING OF MOLECULAR DIMERS IN MIXED CRYSTALS: PICOSECOND PHOTON ECHO EXPERIMENTS

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Picosecond photon echo experiments are used to examine optical dephasing of substitutional dimers and monomers of tetracene and pentacene in *p*-terphenyl host crystals. A comparison of experiments on tetracene and pentacene dimers permits the mechanism responsible for temperature-dependent optical dephasing to be determined. It is shown that excitation of librations rather than scattering between delocalized dimer states is the principal mechanism.

1. Introduction

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 [1]. In pure molecular crystals, delocalization can give rise to exciton band structure [1] and coherent exciton transport [2,3]. 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 [2,3].

In this paper we present a detailed examination of the temperature-dependent optical dephasing of delocalized tetracene and pentacene dimers, and tetracene and pentacene monomers in *p*-terphenyl host crystals. The dimers consist of isolated pairs of guest molecules substitutionally embedded in a host crystalline lattice. 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.

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., naphthalene-h_8 dimers in naphthalene-d_8 host crystals or tetrachlorobenzene-h_2 dimers in tetrachlorobenzene-d_2 host crystals [4], these chemical impurity dimers do *not* have as their principal dephasing mechanism scattering between the delocalized dimer states. Rather, these chemical impurity dimers dephase because of phonon excitation of local phonon (librational) modes of dimers.

2. Experimental procedures

The picosecond photon echo system used to study the pentacene in *p*-terphenyl dimers has been described previously [5,6]. For the tetracene in *p*-terphenyl experiments, a modified version of this system was used. Tunable blue (490 nm region) picosecond pulses were generated by difference mixing a single quadrupled Nd : YAG laser pulse (226 nm, 15 μJ, 40 ps) with a single dye laser pulse (20 μJ, 30 ps) of appropriate wavelength in a 30 mm angle-tuned KDP non-linear crystal. This procedure provides a stable source of 30 ps, 2 μJ tunable blue pulses at a repetition rate of 800 Hz. The experimental arrangement is outlined in fig. 1. A blue single pulse is split into two excitation pulses of appropriate energies and variable

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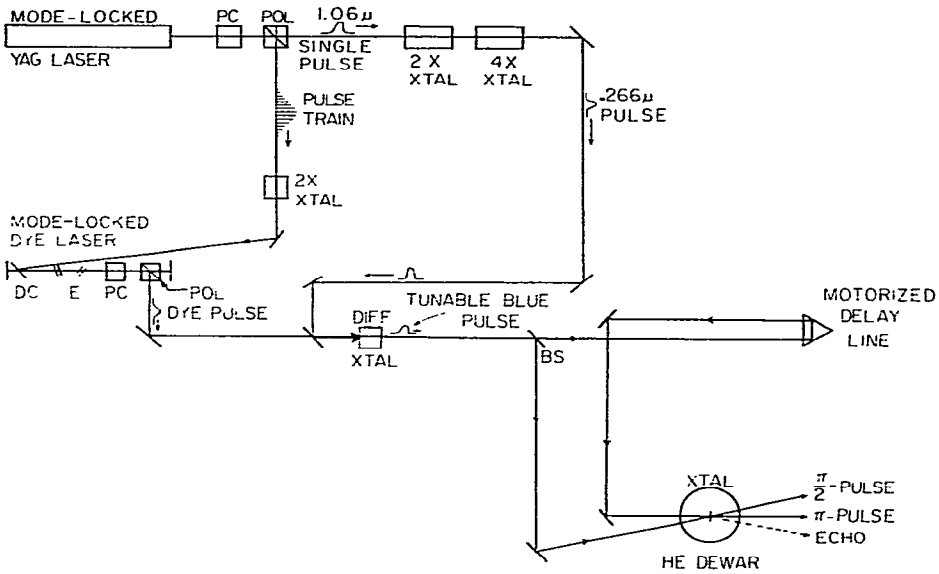

Fig. 1. Photon echo setup used in the tetracene in p-terphenyl experiments. A single 1.06 μm pulse is selected from the acousto-optically mode-locked and Q-switched Nd:YAG laser by a Pockels cell (PC) and calcite cube polarizer (POL). This single pulse is doubled (CD*A crystal) and then quadrupled (KDP crystal) in frequency. The remainder of the Nd : YAG pulse train is doubled and used to pump a cavity-dumped dye laser. The dye laser single pulse is then made temporally and spatially coincident with the quadrupled Nd:YAG pulse in an angle-tuned KDP crystal. This difference mixing process provides a stable source of tunable blue pulses. The single blue pulse is split into two excitation pulses of appropriate energies. One of these pulses is directed into a corner cube on a motorized delay line to provide a variable temporal delay between the pulses. See text for details. BS = beam splitter; E = Fabry–Pérot etalon; DC = flowing dye cell.

temporal delays for the photon echo experiment. Non-collinear excitation geometry (2.75° angle between the two pulses) was employed to spatially isolate the echo signal. Other details involved in detecting the echo signal are as described previously [6].

The samples were mounted on a heating block located in a liquid-helium dewar. Cold helium gas was allowed to flow over the sample. The temperature was varied by controlling the flow of helium gas and the power delivered to the heating block. The temperature was accurately maintained (±0.01 K) by the Scientific Instruments model 3610-B temperature controller which delivered current to the sample block heater, and was measured with a Scientific Instruments model N1G germanium resistance thermometer in thermal contact with the sample (accuracy better than 0.01 K). Details of the sample preparation and the polarized absorption spectrometer are as reported previously [6].

3. Results

Tetracene in the low-temperature p-terphenyl lattice exhibits two distinct sites [7]. Fig. 2a shows a transmission spectrum of a moderately concentrated crystal of tetracene in p-terphenyl. The two $S_0 \rightarrow S_1$ monomer absorption origins, labeled TO_1 and TO_2, have similar splittings and inhomogeneous linewidths as the PO_1 and PO_2 monomer origins of pentacene in p-terphenyl which have been extensively studied [8]. (Transmission spectra of the four pentacene monomers and several pentacene dimers may be found in refs. [5,6].)

At much higher concentrations ($\approx 10^{-3}$ M/M) of tetracene in p-terphenyl, the formation of dimers is expected statistically as found in pentacene in p-terphenyl crystals of similar concentration [5,6]. A transmission spectrum of a high-concentration crystal of tetracene in p-terphenyl in the vicinity of the $S_0 \rightarrow S_1$ absorption origins, TO_1 and TO_2, of tetracene

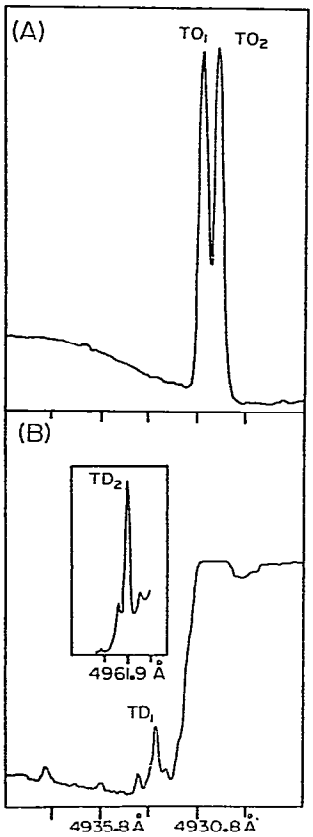

Fig. 2. (a) A tetracene in p-terphenyl transmission spectrum at 1.6 K of the two $S_0 \rightarrow S_1$ monomer origins. TO_1 and TO_2. The two tetracene origins have similar splittings and inhomogeneous linewidths as the PO_1 and PO_2 monomer origins of pentacene in p-terphenyl [8]. The sloping baseline in the spectrum is due to the spectral characteristics of the xenon arc lamp. (b) Transmission spectrum of a high-concentration tetracene in p-terphenyl crystal in the region about the monomer $S_0 \rightarrow S_1$ origins at 1.6 K. The TO_1 and TO_2 monomer origins coalesce into a broad and flat-topped peak because the very high monomer concentration results in zero transmittance. To the red of the broad origin lie several dimer peaks. The inset shows a transmission spectrum of a crystal with an even higher tetracene concentration. At these higher concentrations, several new dimer peaks become clearly visible. The TD_2 dimer is located at 4961.9 Å. (Wavelength scale, 4 Å/division.) A detailed temperature-dependent study was performed on the two well-resolved dimer peaks labeled TD_1 and TD_2 (see text).

monomers is shown in fig. 2b. The TO_1 and TO_2 origins coalesce into a broad and flat-topped peak because the very high monomer concentration results in zero transmittance. To the red of the broad origin lie several dimer peaks. The tetracene dimer splittings and line positions relative to the TO_1, TO_2 tetracene monomers are similar to those found for the pentacene dimers built off of the pentacene PO_1, PO_2 monomers in p-terphenyl [5,6]. However, in tetracene in p-terphenyl there are more dimers split to the red of TO_1 and the largest dimer–TO_1 splitting (128 cm^{-1}) is more than three times that found for pentacene in p-terphenyl (39 cm^{-1}). These differences may be due to the smaller size of the tetracene molecule compared to the pentacene molecule which allows for a greater freedom in the relative positioning of the two molecules which make up the dimers.

Temperature-dependent photon echo measurements were made on tetracene monomers and the two tetracene dimer peaks, labeled TD_1 and TD_2 in fig. 2, and on pentacene monomers and dimers [‡1]. Fig. 3 shows the photon echo decay for the TD_1 dimer at 2.61 K. The data is exponential (see inset), and de-

[‡1] The pentacene dimers labeled PD_1, PD_2, and PD_3 in table 1, were formerly called R_3, R_4 and R_5, respectively, in refs. [5,6].

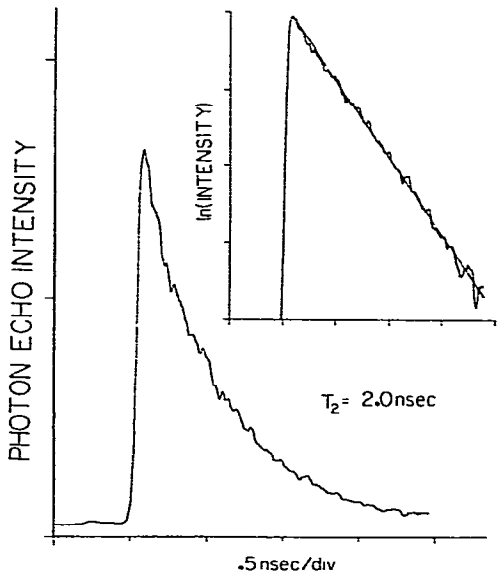

Fig. 3. Photon echo decay for the TD_1 tetracene dimer at 2.61 K. The straight line through the logarithm of the data (see inset) shows that the echo decay is exponential over almost four factors of 1/e in signal intensity. The signal decays as $I_{PE} = I_0\ (-4t/T_2)$ and thus T_2 = 2.0 ns for the data shown in the figure.

cays with a T_2 time constant of 2.0 ns. Two contributions to the photon echo decay constant (T_2) may be defined as follows

$$1/T_2 = 1/2\tau + 1/T_2' \,. \qquad (1)$$

where τ is the excited-state lifetime (decay out of the S_1 state) and T_2' includes any other dephasing processes. For example, modulation of the dimer excited-state energy by phonons is a pure dephasing process, T_2', while phonon scattering between delocalized excited dimer states, is a T_1 process. Both processes would be included in T_2.

For the pentacene in *p*-terphenyl monomers [6] and dimers τ has been measured and is known to be constant over the temperature range of the photon echo measurements. (In general singlet states do not show temperature-dependent lifetimes in this temperature range. In triplet systems temperature-dependent spin–lattice relaxation can cause a temperature-dependent lifetime which will contribute to the temperature dependence of dimer dephasing [9].) This lifetime contribution can be subtracted from the T_2 measured at each temperature and a temperature-dependent plot of T_2' can be made. In the tetracene in *p*-terphenyl system the plots were obtained by assuming that at 1.4 K the system is in the low-temperature limit, and therefore $T_2 = 2\tau$ as has been seen previously for other systems of monomers [6,10,11] and dimers [6]. Since the lifetime contribution to dephasing at these higher temperatures is negligible, even a large error in determining τ has no effect in determining the temperature dependence of T_2'.

A plot of ln T_2' versus $1/T$ for the TD_1 dimer gives a straight line over many orders of magnitude of T_2' (fig. 4). The slope of this line is $\Delta E/k$ and gives an activation energy (ΔE) of 10 cm^{-1} for the TD_1 dimer. Similar plots for the other tetracene and pentacene dimers and monomers were made. These results are summarized in table 1. (The activation energy obtained here for TO_1 (12 cm^{-1}) differs from that reported previously (8 cm^{-1}) [12]. The data compiled in ref. [12] were apparently obtained over too small a temperature range (less than one factor of 1/e change in T_2) to give an accurate determination of the slope.)

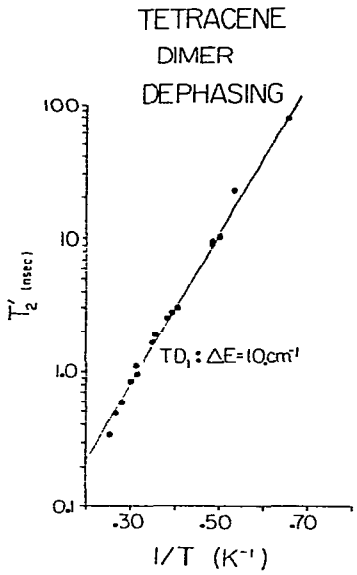

Fig. 4. Temperature dependence of T_2 (the dephasing time excluding the excited-state to ground-state lifetime contribution) of tetracene dimer state TD_1 in *p*-terphenyl. The solid line is the best fit to the data, giving an exponential activation energy, ΔE = 10 cm^{-1}.

4. Discussion

The temperature-dependent optical dephasing of delocalized dimers in *p*-terphenyl host crystal has recently been studied theoretically [13]. In the calculations a canonical transformation partially diagonalized the dimer excitation–phonon coupling terms in the Hamiltonian. Optical Redfield theory was then employed to obtain the temperature dependence of the optical dephasing. Three possible mechanisms are capable of explaining the observed exponentially activated temperature-dependent dephasing: (A) Phonon scattering between delocalized dimer states (a T_1 process), (B) phonon scattering to delocalized librational states (mini-librons) in the dimer ground and excited electronic states (a T_1 process) [‡2], and (C) pure dephasing induced by coupling to optical phonons of

‡2 The definition of this process as a T_1 process is somewhat arbitrary. In our theoretical treatment of the dimer [13] and a previous treatment of the monomer [14,15], the system was taken to include the librational levels, all other phonons being part of the bath. However, in several treatments of the monomer problem [11,14,15] the librational levels were included in the bath. The dephasing librational excitation is then called a T_2^* process. The two approaches are equivalent.

Table 1
Optical dephasing activation energies

	Spectral line	λ(Å) a)	Δ(cm⁻¹) b)	ΔE(cm⁻¹) c)	$T'_{2(\infty)}$(ps) d)
tetracene monomers	TO_2	4929.8	−3.3	11	35
	TO_1	4930.6	0.0	12	18
tetracene dimers	TD_1	4933.0	9.9	10	11
	TD_2	4961.9	128.0	17	6
pentacene monomers	PO_4	5858.5	−181.6	27	5
	PO_3	5878.6	−123.2	30	2
	PO_2	5920.1	−4.0	25	4
	PO_1	5921.5	0.0	27	5
pentacene dimers	PD_1	5928.0	18.5	20	5
	PD_2	5934.0	35.6	23	5
	PD_3	5935.1	38.7	25	8

a) Wavelengths are in air.
b) Δ is the energy separation from TO_1 for the tetracene system and from PO_1 for the pentacene system.
c) ΔE is the optical dephasing (T'_2) activation energy. See text.
d) $T'_{2(\infty)}$ is the optical dephasing (T'_2) pre-exponential factor: $T'_2 = T'_{2(\infty)} \exp(\Delta E/kT)$.

the p- terphenyl host (a T_2 process). Scattering between delocalized dimer states (mechanism A) was eliminated as a possibility in a previous experimental study of pentacene dimers [5] because the exponential activation energy did not correspond to the observed dimer pair splitting as required by theory [13]. However, no conclusive choice could be made between mechanisms B or C based on the pentacene dimer experiments alone.

It has been established that phonon-induced scattering to monomer librations is responsible for the temperature-dependent dephasing of pentacene monomers in naphthalene [15] and benzoic acid [17] host crystals. Pentacene monomers in p-terphenyl are also believed to dephase due to this process, although direct observation of the libration in absorption or emission is lacking in this system. The properties of the guest libration are determined by guest—host interactions but are critically dependent on the nature of the guest. In the case of pentacene monomers in naphthalene this was demonstrated by studying the deuterium isotope (pentacene-d_{10}) shift in frequency of the libration [15]. Thus, this temperature-dependent dephasing arises from properties intrinsic to the guest molecule in addition to the properties of the host lattice. The pentacene monomers have librational energies in a range consistent with the activation energies of the various pentacene dimers.

However, the p-terphenyl crystal has an optical phonon mode observed by Raman spectroscopy at 20.5 cm^{-1} [18]. Coupling of the dimer to an optical phonon band can result in an apparent exponentially activated temperature-dependent dephasing with an apparent activation energy determined by the phonon band position and density of states [13]. The temperature dependence is caused by the thermal occupation of the phonon band which is an intrinsic lattice property independent of the nature of the dilute impurities which form the dimers. The 20.5 cm^{-1} phonon band energy is consistent with the observed (table 1) pentacene dimer activation energies. While pentacene monomers are dephased by the libration mechanism B, dimers have the additional possibility of coupling to optical phonons by the modulation of the intermolecular interaction, mechanism C.

From table 1 it can be seen that the various pentacene dimers have somewhat different activation energies. These are real differences, well outside of experimental error. The libration mechanism can give rise to these differences if it is postulated that each dimer configuration has particular mini-libron splittings and site librational frequencies. The optical phonon mechanism explains the differences by postulating that the various dimer configurations couple selectively to restricted regions of the phonon k-space, regions consistent with the spatial arrangements of the dimers. In general, the phonon dispersion varies as a function of direction in k-space, and since the activation energy

depends on the phonon dispersion, various activation energies could result.

The choice between the libration mechanism (B) and the optical phonon mechanism (C) can be made on the basis of the tetracene dimer photon echo results. If coupling to lattice phonons (in this case coupling to the 20.5 cm^{-1} phonon suggested by the pentacene dimer activation energies) is responsible for dimer optical dephasing, then the activation energies for tetracene and pentacene dimers would be very similar. However, if the libration mechanism is responsible, the activation energies should be significantly different.

The activation energies obtained for the tetracene dimers (10 and 17 cm^{-1}) are very different from those for the pentacene dimers (20,24 and 25 cm^{-1}), although the *p*-terphenyl host is common to both. This rules out a dephasing mechanism due exclusively to bulk properties of the host, such as coupling to the *p*-terphenyl lattice phonons. The differences in activation energies between tetracene and pentacene dimers arise because of the differences in librational frequencies of such physically different guest molecules. Theoretically, uncorrelated scattering to the mini-librons results in a tetra-exponential temperature behaviour with activation energies determined by the librational energies in the dimer ground and excited states and by the mini-libron splittings [13]. However, the temperature dependence appears as a single exponential if the librational energies and splittings in the ground and excited states are comparable and if the librational lifetimes are essentially constant over the temperature range studied [13]. This is evidently the situation for pentacene and tetracene dimers.

Unlike dimers which are only isotopically distinct from the host [4], e.g., naphthalene-h_8 dimers in naphthalene-d_8 host, chemically distinct dimers do not have librational motions which are amalgamated into the host optical phonon bands. Thus dimers made up of molecules such as pentacene and tetracene in a host like *p*-terphenyl exhibit well-defined low-frequency librations. Thermal population of these librations is effective in dephasing the delocalized dimer states. In contrast, isotopic dimers, with amalgamated phonons, do not have these low-frequency local phonons available. This evidently leaves scattering between delocalized states as the dominant dephasing mechanism in isotopic dimers. Thus the temperature-dependent dephasing of chemically distinct dimers is intrinsically different from the dephasing of isotopic dimers.

Finally, it is interesting to note the observation of a peak in the tetracene monomer in *p*-terphenyl phonon sideband 24 cm^{-1} to the blue of the zero-phonon line [7]. This is probably due to a two-quantum transition of the libration responsible for the observed monomer 12 cm^{-1} dephasing activation energy. A similar situation occurs for pentacene monomers in naphthalene [15].

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