Site-Dependent Vibronic Line Widths and Relaxation in the Mixed Molecular Crystal Pentacene in p-Terphenyl

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The different line widths and shapes observed in absorption spectra of the first vibronic transition of the four sites of pentacene in p-terphenyl are examined. A model involving vibrationally induced line narrowing and lattice coupling is suggested to explain the differences. The importance of local environment in vibrational relaxation is discussed.

Introduction

Intramolecular vibrational relaxation is an area of substantial interest for molecules in gas, liquid, and solid phases.[1] In all phases the density of final states and the nature of the interactions with the final states are important in determining relaxation and dephasing rates. In solid-state systems, coupling to lattice phonons, either directly or via intervening intramolecular vibrations, can affect the relaxation and dephasing processes. Here we present an example in which pentacene molecules in different sites of a p-terphenyl host lattice, hence experiencing the same bulk phonon environment, exhibit substantially different vibrational dephasing properties. This demonstrates that subtle details of the local environment must be considered to obtain a clear understanding of vibrational dephasing.

Pentacene in the low temperature p-terphenyl lattice exhibits four distinct sites.[3] These sites result from the p-terphenyl phase transition at ~190 K in which p-terphenyl ring rocking freezes out.[4] The final ring distribution causes the low temperature unit cell to contain four conformationally different p-terphenyl molecules.[4] Each pentacene molecule presumably replaces one p-terphenyl

molecule in the lattice, yielding four conformationally different pentacene environments. Since these crystals are grown well above the phase transition temperature, pentacenes populate the four sites equally.

Each of the four $S_0 \rightarrow S_1$ origin transitions is Gaussian, characteristic of inhomogeneously broadened lines. The first vibronic transition of each site might be expected to exhibit a line shape which is the convolution of the inhomogeneous Gaussian width of the origin and a vibrational-lifetime-broadened Lorentzian. Although the three lower energy sites' vibronic lines are of about the same width, only one exhibits the expected shape, while one is a pure Gaussian and one is a pure Lorentzian. The first vibronic transition of the fourth (highest energy) site differs strikingly from the others. It is Lorentzian in shape, much narrower than the other sites' vibronic transitions, and considerably narrower than its origin. We wish to report and discuss these four vibronic transitions and propose a static and a dynamic model to explain the observed behaviors.

Experimental Section

Absorption spectra were recorded at 1.4 K by using a xenon arc lamp, a $^3/_4$-m monochromator (slits set for 0.1-Å resolution), and a 1P28 phototube. Numerical convolution

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TABLE I

	O_1	O_2	O_3	O_4
electronic energy,[a] cm^{-1}	16883.0 ± 0.2	16886.8 ± 0.2	17006.1 ± 0.2	17064.6 ± 0.2
fwhm,[b] GHz	41	39	38	37
optical density (max)[c]	0.42	0.39	0.42	0.42
lifetime, ns	24.1 ± 0.5	24.5 ± 0.5	9.5 ± 0.5	8.7 ± 0.5

[a] Deviations are 95% confidence limits ($\pm 1.96\sigma/n^{1/2}$) where n = 19, 20, 21, and 23 for O_1–O_4, respectively. [b] The full-width at half-maximum varies slightly from sample to sample, but the four sites are always uniform. [c] Crystal concentration is 3×10^{-6} mol/mol.

TABLE II

	V_1	V_2	V_3	V_4
vibronic energy,[a] cm^{-1}	17149.4 ± 0.4	17155.0 ± 0.5	17272.4 ± 0.4	17334.6 ± 0.1
vibrational energy,[a] V_n–O_n, cm^{-1}	266.4 ± 0.5	268.2 ± 0.6	266.3 ± 0.5	270.0 ± 0.2
fwhm,[b] GHz	115	110	100	34
optical density (max)[c]	0.25	0.26	0.25	0.24
qualitative line shape	Gaussian	Lorentzian	Voight	Lorentzian
estimated vibrational lifetime, ps	[d]	2	3	5

[a] Deviations are 95% confidence limits ($\pm 1.96\sigma/n^{1/2}$) where n = 10, 10, 15, and 16 for V_1–V_4, respectively. [b] The full-width at half-maximum varies slightly from sample to sample, but the similarity of V_1–V_3 and disparity of V_4 are always maintained. [c] Crystal concentration is 2×10^{-5} mol/mol. [d] Gaussian line shape precludes lifetime estimate.
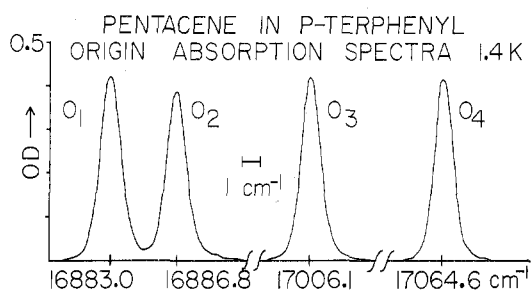

Figure 1. Typical pentacene in *p*-terphenyl absorption spectra at 1.4 K of the four $S_0 \rightarrow S_1$ origins, O_1–O_4. Note that they are virtually identical in shape, width, and height. Crystal concentration is 3×10^{-6} mol/mol.

calculations show that the line shapes were not distorted by the monochromator slit function.

Crystals of pentacene in zone-refined *p*-terphenyl were grown from the melt by using standard Bridgeman techniques. Optically clear and nondistorted regions of the sample crystals were mounted over 600-μm pinholes. Some variation in absorption line widths occurs for different samples. The lack of correlation between line width and concentration indicates that sample cutting and handling procedures probably cause the variations. The experiments, performed on many samples over a wide concentration range, are reproducible. The results discussed below are representative.

The line shape fittings were performed by using digitized absorption data. It must be emphasized that small amounts of noise, uncertainties in baseline location, and problems in defining a "best" fit lead to some variation in fitting results. These factors make the fitting procedure semiquantitative but do not affect the general results presented here.

Results and Discussion

Typical absorption spectra of the $S_0 \rightarrow S_1$ origin of each site, O_1–O_4, are shown in Figure 1. Associated parameters appear in Table I. The homogeneous line widths, measured by optical coherence experiments,[5] are >1000 times narrower than the observed absorption line widths. Thus, the Gaussian absorption lines truly indicate the inhomogeneous broadening of the purely electronic transition.

Typical absorption spectra of the first vibronic transition of each site, V_1–V_4, are shown in Figure 2. Associated parameters appear in Table II. The inhomogeneous widths of the origins of the lines shown in Figure 2 were
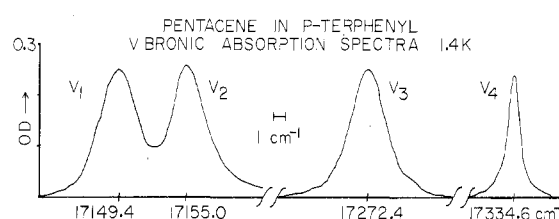

Figure 2. Typical pentacene in *p*-terphenyl absorption spectra at 1.4 K of the four first vibronic transitions, V_1–V_4. Crystal concentration is 2×10^{-5} mol/mol. Origin width associated with these four lines is 58 GHz (~ 2 cm^{-1}). Note that V_1–V_3 are all much wider than the origin width. V_4 is of distinctly different shape and much narrower than V_1–V_3 and the origin.
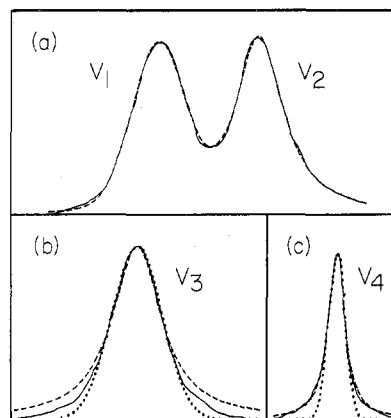

Figure 3. Pentacene in *p*-terphenyl first vibronic transitions (solid lines) as in Figure 2. V_1 and V_2 are shown fit to a Gaussian and a Lorentzian, respectively (dashed line). V_3 and V_4 appear with Gaussian (dotted) and Lorentzian (dashed) fits. Note that V_1 and V_3 have substantial Gaussian (inhomogeneous) character while V_2 and V_4 are pure Lorentzians.

58 GHz. The most striking feature of the four vibronic lines is that V_4 is substantially narrower than V_1–V_3 and is almost half the width of its origin, O_4.

Vibrational relaxation is expected to occur on the picosecond timescale,[2] resulting in a considerably broadened homogeneous line (T_1 process). If the homogeneous line width becomes significant relative to the inhomogeneous broadening, the line shape becomes a Voight profile, a convolution of the Lorentzian homogeneous line with the Gaussian inhomogeneous broadening.[6] The net result would be a vibronic line broadened by the addition of Lorentzian character. Only V_3 behaves in this manner.
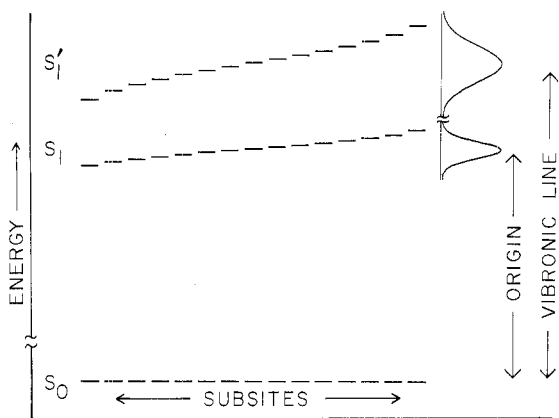
Figure 4. Schematic illustrating the inhomogeneous broadening of an electronic origin and a vibronic transition. The lower stair steps represent the variation in electronic transition energy with position in the inhomogeneous line. Variations in vibrational potential surfaces caused by the electronic inhomogeneity result in slightly different vibrational transition energies across the inhomogeneous line (illustrated as smoothly varying for clarity). Thus, the vibronic transition (upper stair steps) exhibits both electronic and vibrational inhomogeneities. S_0 is illustrated as constant energy for clarity.

Detailed examination of V_1 and V_2 shows that V_1 is Gaussian and V_2 is Lorentzian (see Figure 3a). This has been observed previously.[5b] Simultaneous Voight profile fits indicate that the width of any Lorentzian (Gaussian) underlying $V_1(V_2)$ is at most $\sim 10\%$ of the full line width. It must be emphasized that a Gaussian (Lorentzian) convolved with a much narrower Lorentzian (Gaussian) is essentially indistinguishable in shape from the original pure Gaussian (Lorentzian). Thus, within the error of the fit, V_1 is a pure Gaussian of about twice the width of O_1. Similarly, V_2 is a pure Lorentzian with none of the inhomogeneous (Gaussian) broadening seen in O_2.

The increased inhomogeneous broadening of V_1 can be explained in terms of a straightforward static model. Site-specific differences in *p*-terphenyl conformations around the pentacenes cause the $S_0 \rightarrow S_1$ energy differences of the four sites. Within any one site, some small amount of additional, local disorder results in the narrow, ~ 2 cm^{-1}, inhomogeneous origin broadening. These various local environments will be called subsites. The different subsite environments cause the pentacenes to have slightly different electron distributions which, within the confines of the Born–Oppenheimer approximation, results in a distribution of potential energy hypersurfaces for nuclear motion. Because subsites possess unique vibrational potential surfaces, they are expected to have slightly different vibrational energy level structures. Vibronic transitions, then, should exhibit not only the inhomogeneous broadening of the origin but also an inhomogeneous energy distribution due to subsite-dependent variations in vibrational energy. This is illustrated schematically in Figure 4. Thus, this model predicts that, in general, vibronic transitions will have different inhomogeneous widths than their corresponding electronic origins.

The V_3 absorption line shape is intermediate between Gaussian and Lorentzian, as shown in Figure 3b. A Voight profile fit indicates V_3 is a ~ 70-GHz Gaussian convolved with a ~ 50-GHz Lorentzian. Although some additional inhomogeneous broadening probably has occurred due to the static mechanism suggested above, the Gaussian width approximately equals that of the O_3 origin. Thus, V_3 corresponds approximately to the situation in which the inhomogeneous broadening of the electronic origin is convolved with a lifetime broadened homogeneous Lorentzian. If the Lorentzian width is due entirely to lifetime

processes, the V_3 lifetime is ~ 3 ps. This compares favorably with the 2 ± 1 ps value obtained by Wiersma in a picosecond laser experiment.[2]

The V_4 line, which is ~ 34 GHz wide, is within experimental uncertainty described by a pure Lorentzian as shown in Figure 3c. The inhomogeneous broadening (Gaussian character) in V_4 is negligible compared to the 58 GHz exhibited by O_4. *As with V_2, the inescapable conclusion is that the inhomogeneous broadening has disappeared.*

One simple explanation of this phenomenon, using the static model presented above, would be that the subsite-dependent vibrational inhomogeneity exactly cancels the inhomogeneous broadening of the origin for both V_2 and V_4. This would be an extremely unlikely coincidence.

Another possible explanation is based upon a dynamic model involving vibrationally induced line narrowing. Kubo[7] has described the spectral effect of random modulation of an ensemble of two-level systems over a Gaussian distribution of energies. If the transition correlation function decays exponentially with decay constant γ and the width of the Gaussian energy distribution is Δ, then, in the slow modulation limit ($\gamma/\Delta \ll 1$), the observed spectrum exhibits the Gaussian shape of the inhomogeneous energy distribution. In the fast modulation limit ($\gamma/\Delta \gg 1$), the line is motionally narrowed and becomes Lorentzian with a homogeneous linewidth of

$$\frac{1}{\pi T_2'} = \Delta^2 \gamma^{-1} \qquad (1)$$

To this must be added the line width due to lifetime processes. Thus, the total homogeneous line width would be

$$\frac{1}{\pi T_2} = \frac{1}{\pi T_2'} + \frac{1}{2\pi T_1} \qquad (2)$$

where T_1 is the lifetime of the two-level system.

We *postulate* that, for the V_4 vibronic transition, the internal 270-cm^{-1} vibrational motion of the pentacene molecule couples to the local lattice environment allowing sampling of the various subsite energies. Then the rate of frequency fluctuations is the vibrational frequency, $\gamma = 270$ cm^{-1}, and the fluctuations occur over an energy distribution corresponding to the inhomogeneous line width, i.e., $\Delta \approx 2$ cm^{-1}. Thus, $\gamma/\Delta \gg 1$ and the Gaussian inhomogeneous width is motionally narrowed. It becomes Lorentzian in shape with a width of $\sim 10^{-2}$ cm^{-1}.

With the extensive motional narrowing of the inhomogeneous line, the dominant contribution to the observed V_4 line width is due to the vibrational lifetime, T_1, as in eq 2. Thus, this model predicts a Lorentzian line shape and the V_4 Lorentzian width corresponds to a vibrational lifetime of ~ 5 ps.

Since V_2 is also Lorentzian, we postulate that it too is undergoing motional narrowing. The same considerations used for V_4 imply that the V_2 width is also due to the lifetime. The observed Lorentzian width yields a lifetime estimate of 2 ps.

The questions arise of why only V_2 and V_4 exhibit vibrational motional narrowing of the inhomogeneous line and what is the mechanism of this narrowing. We propose that the answer lies in a detailed comparison of the V_1–V_4 vibrational frequencies and the *p*-terphenyl host vibrational frequencies.

Low temperature infrared and Raman spectra of *p*-terphenyl have been recorded.[8] The infrared spectrum contains modes at 134 and 135 cm^{-1}. These are exactly half the energies of the pentacene vibrations in sites two and four, respectively (see Table II). Thus the V_2 and V_4

vibrations are degenerate with two-quantum excitations of host lattice modes while V_1 and V_3 are not. Coupling between the pentacene vibration and the two-quantum-excited lattice modes would be expected to be very weak ($\ll 1$ cm^{-1}) but could become significant when they are degenerate. Therefore the vibration excited on pentacene in sites two and four is not a pure intramolecular pentacene vibration. Due to the weak coupling to lattice modes, *a superposition of pentacene and p-terphenyl vibrational states is excited.* The nature of the 134- and 135-cm^{-1} lattice modes is unknown. However, it is suggestive that the phase transition associated with the freezing out of the p-terphenyl ring rocking occurs at $\sim$190 K, i.e., $\sim$132 cm^{-1}. If the inhomogeneous distribution is due to a slight variation of angular orientation of p-terphenyl rings about the pentacenes, then excitation of V_2 and V_4 could set these rings in motion and provide a mechanism for motional averaging of the V_2 and V_4 inhomogeneous lines.

Thus, degeneracy of V_2 and V_4 with lattice modes provides a mechanism for vibrational motional narrowing of the inhomogeneous character in V_2 and V_4 while permitting V_1 and V_3 to retain their inhomogeneous line widths. Clearly, a more detailed understanding of the source of the inhomogeneous broadening as well as greater knowledge of the specific site geometries and the nature of the pentacene and p-terphenyl vibrations would materially add to our understanding of this phenomenon.

Regardless of whether the above model is correct, the fact remains that the V_2 and V_4 lines are fundamentally different from V_1 and V_3, although all involve the same vibration of the same molecule in the same bulk phonon bath. The differences in the local environments of sites two and four change the vibrational energy of the molecule only slightly, yet have a major effect on the vibrational coupling to the environment. Even subtle differences in local environment can have major effects on vibrational relaxation and dephasing. When examining vibrational dephasing of a molecule in several host lattices, great care must be exercised in explaining observed differences. In noncrystalline solutions there are not four discrete sites but a very large distribution of local environments. Our results indicate that uniformity of properties throughout this distribution is by no means guaranteed. Thus, understanding of vibrational dephasing in solution may require detailed examination of the role of local environments on the relaxation process.

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