Pressure induced phase transitions in pentacene doped para-terphenyl probed by changes in the impurity absorption spectrum

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The pressure dependence (0–10 kbar) of the low temperature (15 K) absorption spectrum of pentacene impurities in a para-terphenyl host crystal is used to investigate the pressure and/or temperature induced triclinic to monoclinic phase change of the para-terphenyl host crystal. Due to the characteristic absorption spectrum of pentacene in these two crystal phases, the pentacene impurity proves to be a sensitive probe of the structure of the surrounding para-terphenyl matrix.

There has been considerable interest in the structure[1–3] and dynamics[4–10] of pentacene doped para-terphenyl. Furthermore, pressure provides a particularly relevant experimental parameter,[11] given the recent observations of homogeneous spectral line narrowing for impurity absorption bands at high pressures.[10,12] Pentacene crystallographically substitutes into four inequivalent sites in the low temperature–low pressure para-terphenyl crystal lattice, resulting in four electronic origin bands in the absorption spectrum of the dilute mixed crystal (labeled O_1, O_2, O_3, and O_4).[13–15] Furthermore, each of these impurity sites has unique electronic and vibronic dynamics.[6,7] Para-terphenyl has two known solid phases, it has a monoclinic structure above 193 K (space group $P2_1/a$) with two molecules per unit cell in equivalent positions, while below this temperature the ambient pressure crystal structure is triclinic (space group $P\bar{1}$) with four crystallographically inequivalent molecules per unit cell. However, at low temperature (15 K), one obtains the monoclinic crystal phase at pressures above about 6.0 kbar. Since the monoclinic host crystal should yield only one photosite, the pentacene impurity spectrum is a sensitive indicator of the local crystal structure, and we have used it to establish the triclinic and monoclinic phase boundaries of the mixed crystal.

High pressures were generated using gasketed diamond anvil cells of the Merrill–Bassett design[16] with 0.8 mm culets, a 400 μm aperture, and a sample thickness of 0.1 to 0.2 mm. The cell was mounted inside a closed cycle helium cryostat (15–300 K) and the sample pressure was measured by the ruby luminescence method.[17,18] Dilute pentacene doped para-terphenyl was loaded into the gasket aperture of the diamond anvil cell, melted under pressure, and a single crystal was grown from the melt at constant pressure by slow compression of the cell during crystal growth. The low temperature optical absorption spectra have an instrumental resolution of 2 cm^{-1} and were obtained using a zenon arc excitation source, scanned by a SPEX 3/4 meter monochromator, and directed through the cell by fiber optic light guides.

The absorption spectrum of pentacene doped para-terphenyl. At low temperature and at pressures below 5.5 kbar, the pentacene impurity spectrum in para-terphenyl yields the four photosites, O_1, O_2, O_3, and O_4, characteristic of the triclinic para-terphenyl crystal structure, as shown in Fig. 1(a). The absorption frequency of these four origins redshift with increasing pressure, as is typical of many hydrocarbons, yielding site specific pressure shifts of 16.0, 15.0, 14.0, and 15.0 cm^{-1}/kbar, for the O_1–O_4 photosites, respectively. The increased splitting between the O_1 and O_2 bands with pressure (1.0 cm^{-1}/kbar) was not resolved in a previous study.[11]
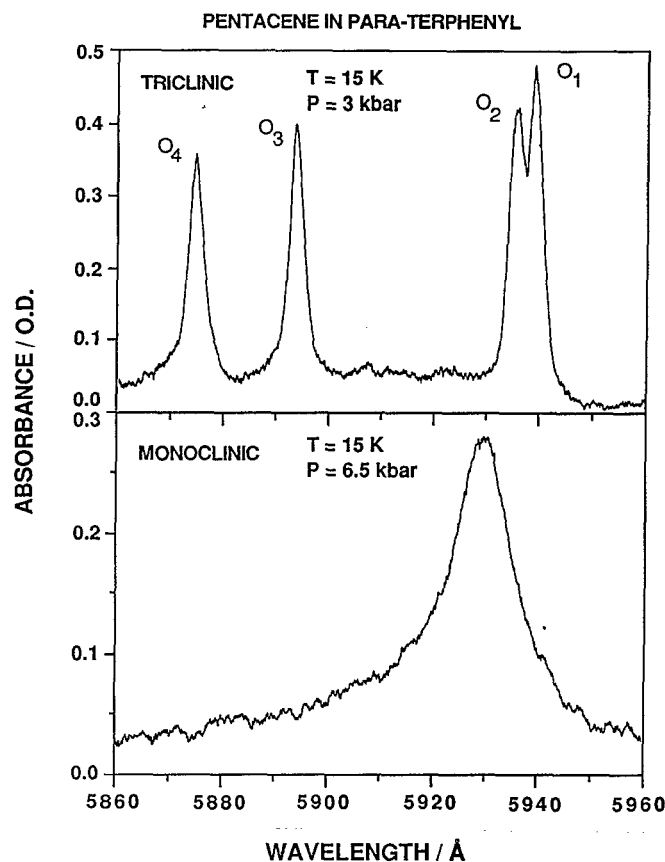

FIG. 1. The effect of pressure on the low temperature absorption spectrum of pentacene doped para-terphenyl. (a) The (15 K) absorption spectrum of pentacene in the triclinic para-terphenyl crystal phase at a pressure of 3.0 kbar. The spectrum is composed of four photosites, labeled O_1, O_2, O_3, and O_4, resulting from the four inequivalent sites in the triclinic crystal phase. (b) In contrast, the low temperature (15 K) absorption spectrum of pentacene in the monoclinic para-terphenyl crystal phase at a pressure of 6.5 kbar yields only one photosite.
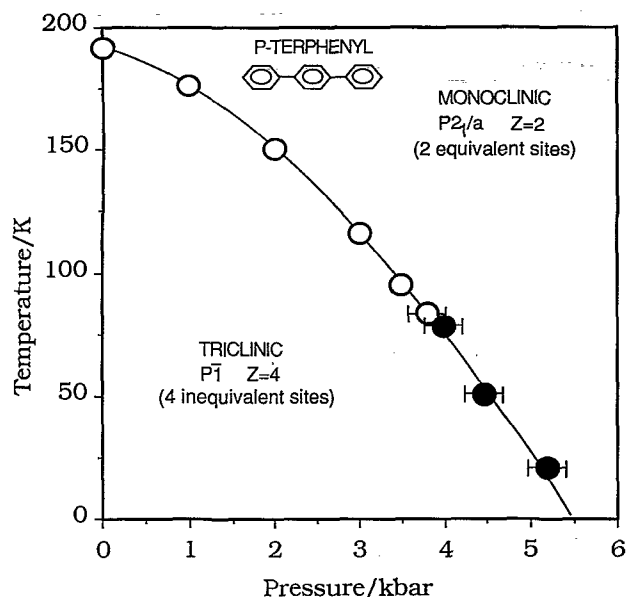
FIG. 2. The pressure–temperature phase diagram for crystalline para-terphenyl. The open circles were taken from the low frequency Raman results of Ref. 3. The solid circles were obtained from changes in the pentacene doped para-terphenyl absorption spectrum, as illustrated in Fig. 1. The solid line represents the triclinic/monoclinic crystal phase boundary.

At high pressures and/or high temperatures the absorption spectrum is characteristic of the monoclinic crystal phase, yielding only one photosite, as shown in Fig. 1(b). The pronounced changes in the pentacene impurity spectrum are used as a sensitive probe of pressure or temperature induced changes in the local crystal structure. However, the high pressure spectra shown in Fig. 1 are considerably broadened by inhomogeneous pressure strain effects and photon echo measurements can be used to obtain the homogeneous linewidth at high pressure.[10]

The para-terphenyl host crystal phase diagram. The triclinic and monoclinic phase boundary of crystalline para-terphenyl, determined from Raman[19] and neutron diffraction[3,20] measurements, are indicated in Fig. 2 by the open circles. Also shown in Fig. 2 is the triclinic/monoclinic phase boundary at low temperature determined from the pentacene impurity absorption spectra obtained in this study (solid circles). At low temperature (15 K), the pentacene absorption spectrum is characteristic of the triclinic

phase up to 5.5 kbar. In addition, changes in the absorption spectra indicate a phase transition temperature of 50 K and 80 K at pressures of 4.5 kbar and 4.0 kbar, respectively. The correspondence between the pentacene impurity absorption spectra and the phase change data from neutron diffraction and Raman studies of pure para-terphenyl indicates that the pentacene impurity does not significantly perturb the host crystal structure. However, at higher pentacene concentrations ($>5\times10^{-6}$ mol/mol) the pentacene impurities may nucleate and stabilize the triclinic phase at higher temperatures and pressures.

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