

# Structural and Vibrational Characterization of Tetracene as a Function of Pressure

The multi-billion dollar electronic and optical device industry is always searching for inexpensive and adaptable materials for use in a wide variety of applications such as display screens for communications, entertainment and computers. Semiconducting organic molecules are currently under intense investigation in this regard as it is possible to precisely tune their properties through synthetic modification and to easily control self-assembly. However, for the full promise of organic semiconductors to be realized, a thorough understanding of the physical properties that control electronic charge transport and photonic behavior is required.

Tetracene, an aromatic molecule consisting of 4 fused benzene rings, adopts a layered, herringbone structure in the solid state (Fig. 1). When a layer of tetracene is incorporated as the functional component of a field effect transistor, the edge-on-face molecular orientation within the  $ab$ -plane of the crystal evidently provides sufficient  $\pi$ -electron cloud overlap between adjacent molecules to enable conduction of charge carriers. Conduction measurements have been performed on tetracene as a function of pressure between ambient and 620 MPa at room temperature [1]. The results indicate a linear increase in conductance between ambient pressure up to  $\approx 300$  MPa and a sharp quenching of conduction as the pressure is increased above 300 MPa. In order to ascertain the physical underpinnings of this observation (which yield insight into the conduction mechanism), neutron powder diffraction and inelastic neutron scattering measurement techniques have been employed to characterize the pressure-dependent structural and vibrational behavior of tetracene up to approximately 360 MPa at 298 K.

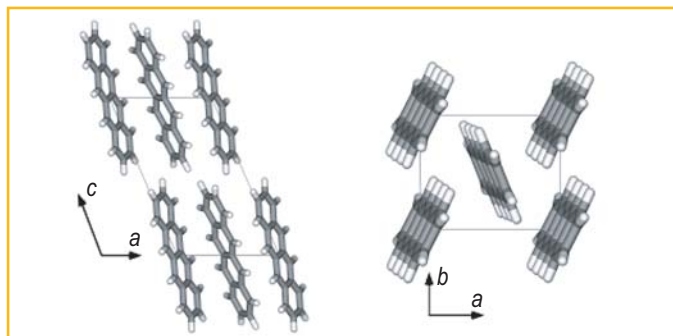


Fig. 1. The crystal structure of tetracene.

The diffraction data were collected at NCNR's High Resolution Neutron Powder Diffractometer at BT-1 using the Cu(311) monochromator and neutron wavelength of 1.54 Å. The six unit-cell parameters were extracted by fitting the powder diffraction patterns using the graphical user interface EXPGUI to the General Structure Analysis System (GSAS) program assuming the known solid tetracene structure [2, 3].

These unit cell parameters are shown as a function of pressure in Fig. 2. As the pressure is increased, each side of the unit cell contracts, resulting in a material with a higher electron density. It is likely that the increase in electron density accounts for the observed increase in conduction in tetracene at pressures up to 300 MPa. However, apparent from the unit cell angle parameters alpha and gamma is a modification of the crystalline structure between 210 MPa and 280 MPa. The change in trend of the unit cell angle parameter is likely due to a strain-induced phase transition that is believed to result in the relative rotation of adjacent tetracene molecules within the herringbone layer [4]. It is thought that this structural modification is of sufficient magnitude to disrupt the continuous  $\pi$ -electron cloud overlap in the low-pressure phase of tetracene to the extent that it is no longer able to conduct charge carriers.

In order to ascertain the role of molecular vibrations on the conduction behavior of tetracene as a function of pressure, inelastic neutron scattering (INS) spectra were collected using the NCNR Filter Analyzer Spectrometer at BT-4. The INS spectra at ambient, 218 MPa, and 359 MPa pressures are shown in Fig. 3. In addition to the experimental data, a theoretical spectrum was constructed from the results of an *ab initio* density functional theory (for an individual molecule) employing the B3LYP functional and 6-31-G\* basis set. The spectral peaks in the experimental data at 27, 41, and 47 meV are affected relatively strongly by the application of pressure (indicated by their shifts to higher energy), whereas the peaks at 34 and 59 meV are moderately shifted and the peaks at 37, 56 and 68 meV display almost no shift with increasing pressure.

Trajectories defining the atomic displacement of the tetracene molecule for each calculated vibrational mode observed in the experimental data are schematically depicted in Fig. 4. The vibrational modes of tetracene can

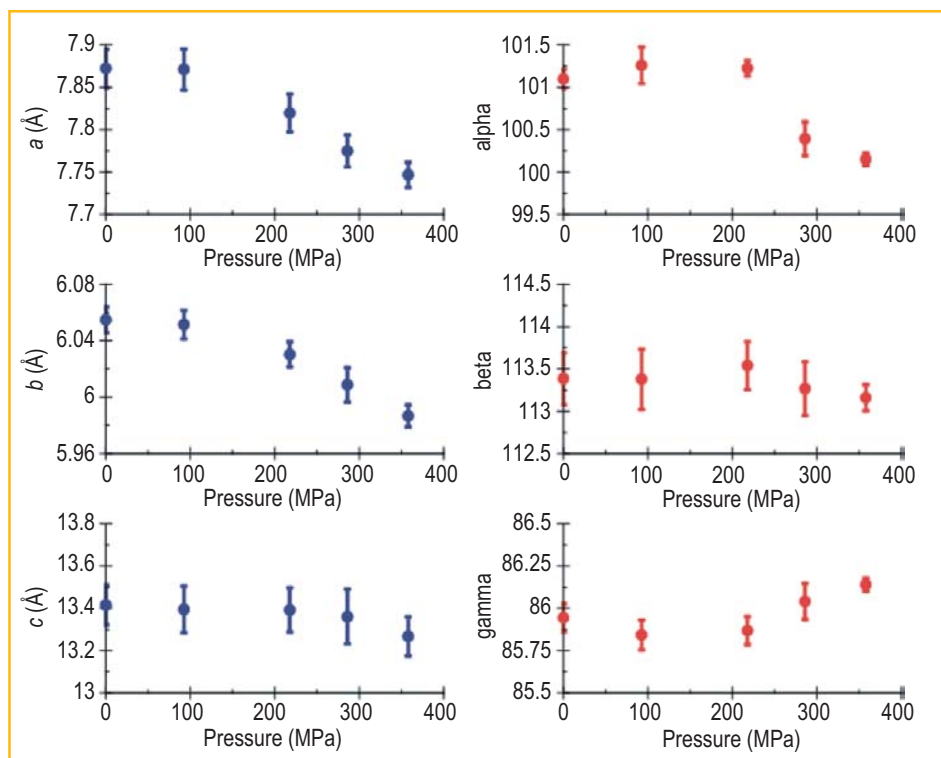


Fig. 2. The unit cell parameters of tetracene as a function of pressure at 298 K determined by fitting the neutron powder diffraction data with EXPGUI and GSAS.

be divided into two types of motions, occurring either within or perpendicular to the  $ab$  crystal plane. Comparison of the vibrational trajectories with the peak shifts observed in the INS data indicates that vibrational modes occurring within the  $ab$  crystal plane are affected by the application of pressure and those perpendicular remain unaffected. Because the vibrational modes do not indicate

a discrete change in behavior upon transition to the high pressure structural phase, it appears that the phase transition does not affect the dynamic behavior of the molecules within the resolution and pressure range of these experiments.

In summary, we have utilized neutron scattering to investigate the physical properties of tetracene as a function of pressure. The conduction mechanism appears to be more strongly dependent on the structural arrangement of molecules within the crystal lattice, most likely associated with changes in  $\pi$ -electron cloud overlap, than on the vibrational behavior of the molecules. Further studies on a series of molecules will indicate whether this observation is generic to all organic semiconductors or unique to tetracene.

## References

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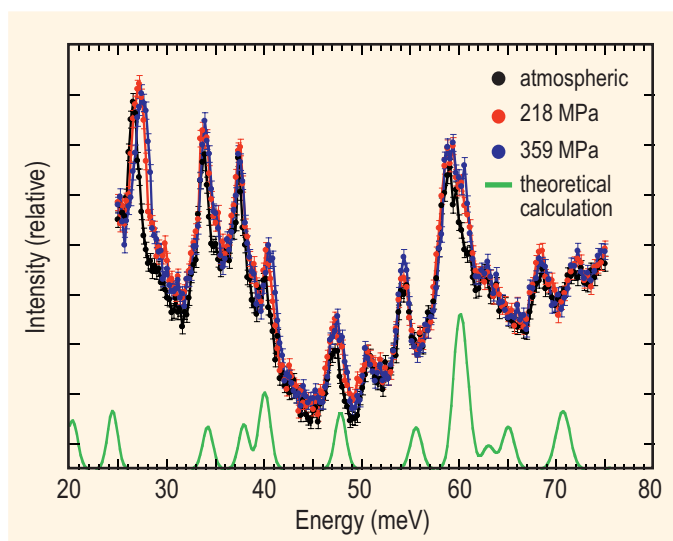


Fig. 3. Inelastic neutron scattering spectra of tetracene at 298 K at pressure and the theoretically calculated spectrum of a tetracene molecule.

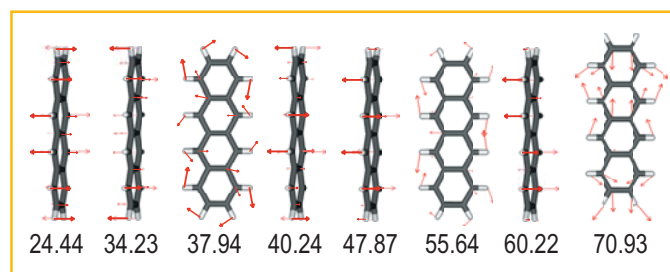


Fig. 4. Schematic representation of the atomic trajectories of the theoretically calculated vibrational modes of tetracene between 20 meV and 75 meV.

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