



Raman spectroscopic studies on *p*-terphenyl under high pressure



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ABSTRACT

High-pressure Raman scattering studies are performed on *p*-terphenyl up to 5 GPa. The Raman activities of different symmetric molecules were analyzed by means of group theory methods. A phase transition was detected at 1.3 GPa from changes in the slope on plots of frequency versus pressure. The diminishing of internal modes indicated that the molecule symmetry transformed from C_2 to D_{2h} . This is an effective method for detecting planar molecular structure of *p*-terphenyl by ring–ring stretching vibration mode, which can provide a new spectroscopic evidence of planar conjugated polyphenyl molecular conformation.

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1. Introduction

In the search for low-cost, easy-to-process materials for light-emitting devices [1] and as laser dyes [2–5], *para*-terphenyl have attracted considerable attention due to its unique electro-optical properties [6] and structure characteristics [7,8]. Numbers of reports on *para*-terphenyl aggregates have been presented in the papers of Schatschneider et al., Zhou et al. and Era et al. [9–12]. Using hydrostatic pressure and X-ray powder diffraction methods, Puschnig et al. investigated the crystal structure transition of *p*-terphenyl and discussed the intermolecular distance influence on the optical response of the material [13]. Based on the X-ray diffraction values of previous research [14], Murugan and Yashonath suggests that *p*-terphenyl transforms to an ordered phase at about 1.4 GPa. The date reported by Baudour reveals that low-temperature crystal structure is triclinic with space group $P\bar{1}$ ($Z=4$). At higher temperature ($T>193$ K), the crystal undergoes an order–disorder phase transition to a monoclinic crystal phase $P2_1/a$ ($Z=2$). Temperature-induced order–disorder phase transition is a common character for conjugated polyphenyl material [15]. Infrared spectroscopy and theoretical simulation have been used to investigate *p*-terphenyl, it transits from triclinic to monoclinic at 0.6 GPa [10]. The previous investigations provide important theoretical and experimental information about *p*-terphenyl [16–18], but more detail structure should be known.

Temperature and pressure are two fundamental thermodynamic parameters that change the intermolecular distances and tune the structure of conjugated molecules without changing the chemical composition [9,19]. The material under extreme conditions may give us a comprehensive understanding of the molecular conformation change thereby acquire the structure–property correlation [14,20,21]. Some polycyclic aromatics are not planar at the ambient pressure and temperature responsible for the steric interference of the aromatic rings and π electron delocalization effects [22]. With respect to what condition can acquire the planar structural *para*-terphenyl and characteristic spectrum is important [23,24]. In this Letter, we investigate the high-pressure behavior of *p*-terphenyl by Raman spectroscopy. The structural information of *p*-terphenyl was obtained by frequency–pressure curve; meanwhile the Raman and infrared activities of different symmetric molecules are analyzed by group theory methods. The planar molecular structure could be reflected from the frequency–pressure curve of ring–ring stretching mode, provides new spectral evidence for the planar structure of polyphenyl material [9].

2. Experimental and computational methods

The sample of *p*-terphenyl was obtained from Aldrich Chemical Co. And it was used without further purification. The high-pressure cell used in this experiment is based on a symmetric diamond anvil cell (DAC) having two diamonds with 500 μm culet size. The sample with a small ruby chip (~ 10 μm) is loaded in a 200 μm hole drilled in a 250 μm thick T301 gasket preindented to 80 μm thickness. The micro Raman spectrometer (Renishaw InVia Raman microscope) equipped with a 514.5 nm Ar^+ ion excitation laser (Spectra Physics

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163-M42) was used to obtain Raman spectra. A Leica microscope with 50× objective lenses enables measurements with back scattering geometry. The laser power is 8 mW and exposure time (CCD integration times) of 30 s was used to collect all Raman spectra. The spectral resolution is 2 cm^{-1} . Frequency calibration of the Raman spectrum is realized using the characteristic 520 cm^{-1} line of silicon. The heating system connecting to the Raman spectrometer was Linkam THMS600.

The optimized geometries and the harmonic Raman frequencies Raman scattering activities of *p*-terphenyl were calculated using density functional theory (DFT), using Becke's three parameter exchange function (B3) in combination with LYP correlation functions and the 3-21G basis set. Calculations were performed with the GAUSSIAN 03 suite of programs. Internal coordinates were generated using the software Gauss view.

3. Results and discussion

3.1. Effect of pressure on the crystal structure of *p*-terphenyl

According to the high pressure XRD lattice parameters reported by Murugan and Yashonath [14], Figure 1 [14] shows the evolution of the unit cell volumes and lattice parameters with pressure, the curves change smoothed from ambient to 5 GPa, the lattice parameters *a*, *b* and *c* decreased with the increasing pressure and lattice parameters *a* shrinks about twice as much as *b*. This is closely related to an increase of the angle between *p*-terphenyl in the crystal. The compressibility along the long unit cell axis *c* is relatively small.

3.2. The Raman scattering activities of *p*-terphenyl

In non-planar molecular conformation, the symmetry of *p*-terphenyl can be characterized by three molecular point group C_2 , D_2 and C_{2h} . At ambient condition, the planar *p*-terphenyl belongs to the D_{2h} point group. For the molecule belonging to C_2 molecular group, all modes are Raman-active. In the case of D_2 symmetry, the vibrational modes are Raman-active as well. For the C_{2h} group, the vibrational modes are classified as $\Gamma = 21A_g \oplus 24B_g \oplus 21A_u \oplus 24B_u$. Here, only modes belonging to A_u and B_u representations are IR-active. For the planar configuration, *p*-terphenyl belongs to the D_{2h} point group. The vibrational modes are given by

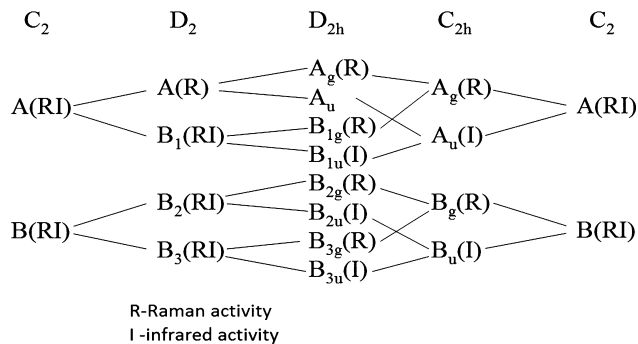


Figure 2. The relationship of vibrational modes and molecular group symmetry.

$\Gamma = 16A_g \oplus 6A_u \oplus 5B_{1g} \oplus 15B_{2g} \oplus 9B_{3g} \oplus 15B_{1u} \oplus 9B_{2u} \oplus 15B_{3u}$. Modes belonging to the A_g , B_{1g} , B_{2g} and B_{3g} are Raman-active. Figure 2 displays the relationship of vibrational modes and molecular group symmetry.

The change of Raman-active can be concluded that 45 Raman-active modes become Raman-forbidden when the symmetry of *p*-terphenyl transforms from C_2 to D_{2h} . 45 Raman-active modes become Raman-forbidden when it transforms from D_2 to D_{2h} . However, the number of Raman-active modes is unchanged when it transforms from C_{2h} to D_{2h} . Then it can be concluded that certain Raman-active peaks become Raman-forbidden when the molecular symmetry of *p*-terphenyl transforms from C_2 and D_2 to D_{2h} . The molecular symmetry transforms from C_{2h} to D_{2h} and C_2 to D_2 , the Raman-active have no change. Hence the information of Raman assignments and molecule symmetry could acquire by the transform of characteristic Raman band in experiment. The ambient pressure Raman spectrum of *p*-terphenyl is shown in Figure 3. The frequency and assignments are listed in Table 1.

The selected high pressure Raman spectra of *p*-terphenyl are shown in Figure 4. With the increase of pressure, the compression can induce changes of molecular bond lengths and angles, the vibrational frequencies move to the higher wavenumber region. When the pressure increased to about 0.4 GPa, the two bands at 399 cm^{-1} and 822 cm^{-1} disappeared (Figure 5). Based on the group theory analysis mentioned above, the symmetric changes can induce the Raman scattering actives changes. In order to know the correlations between the molecular symmetry and the Raman scattering

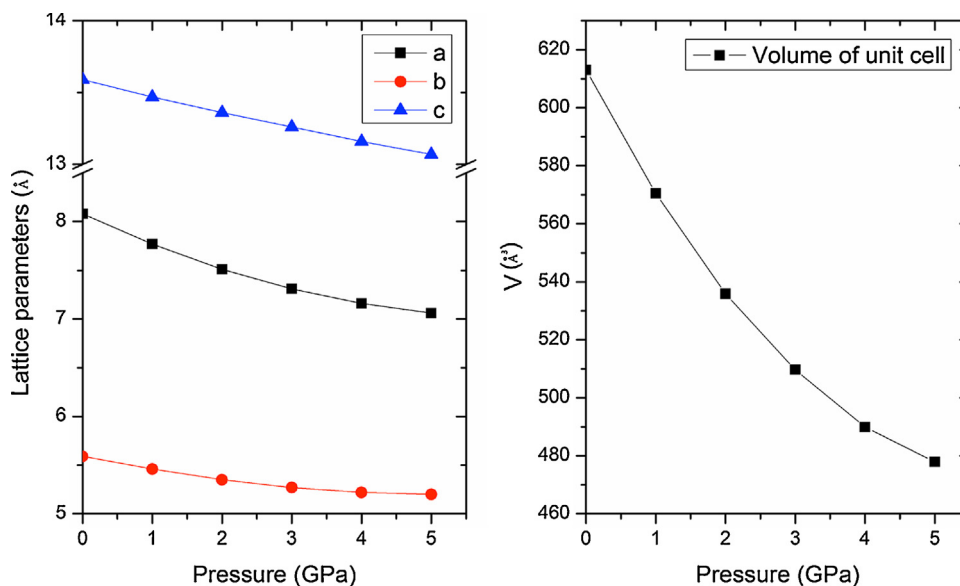


Figure 1. Evolution of the unit cell volumes and lattice parameters with pressure [14].

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