High-pressure Raman study of Terephthalonitrile☆

DongFei Li [a,b], KeWei Zhang [a], MingXing Song [c], NaiCui Zhai [d], ChengLin Sun [b,*], HaiBo Li [a,*]

[a] *Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, Jilin Province, PR China*
[b] *State Key Laboratory of Superhard Materials, Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, Jilin Province, PR China*
[c] *College of Information and Technology, Jilin Normal University, Siping 136000, Jilin Province, PR China*
[d] *Institute of Translational Medicine, the First Hospital, Jilin University, Changchun 130061, Jilin Province, PR China*

ARTICLE INFO

ABSTRACT

The in situ high-pressure Raman spectra of Terephthalonitrile (TPN) have been investigated from ambient to 12.6 GPa at room temperature. All the fundamental vibrational modes of TPN at ambient were assigned based on the first-principle calculations. A detailed Raman spectroscopy analysis revealed that TPN underwent a phase transition at ~5.3 GPa. The frequencies of the TPN Raman peaks increase with increasing the pressure which can be attributed to the reduction in the interatomic distances and the escalation of effective force constants. The intensity of the C-C-C ring-out-plane deformation mode increases gradually as the frequency remains almost constant during the compression which can be explained by the existence of π-π interactions in TPN molecules. Additionally, the pressure-induced structural changes of TPN on the Fermi resonance between the $C\equiv N$ out-of-plane vibration mode and the $C-CN$ out-of-plane vibration mode have been analyzed.

1. Introduction

Terephthalonitrile (TPN) is an attractive aromatic compound and has been the subject of many experimental and theoretical studies for a long time owing to its peculiar structure and physicochemical properties [1–3]. On the one hand, the crystal structure of TPN changes upon heating below the melting temperature have been investigated, and the results, which obtained by X-ray diffraction studies of powder and single-crystal TPN samples, indicate that TPN is dimorphous, crystallizing in both triclinic and monoclinic form. The triclinic form is transformed into the monoclinic above 430 K. The single-crystal structure of the monoclinic form of TPN at room temperature has been obtained [4], as shown in Fig. 1. The cell dimensions are $a = 3.868(1)$, $b = 7.080(1)$, $c = 12.127(2)$ Å, $\beta = 97.21(3)°$, space group $P2_1/c$; $Z = 2$. On the other hand, the molecular structure of TPN has been studied in the solid state and gaseous phase, respectively [5–7]. These research work confirm that the TPN molecule belongs to the point group D_{2h} in both aggregation sates, although the TPN molecule is distorted slightly in the condensed phase due to the intermolecular interaction of TPN

molecules. In addition, an extensive study exploring the infrared, Raman and ultraviolet spectra of TPN has been conducted [8–11]. Recently, TPN has been used as a distinctive precursor for the synthetic metal-organic frameworks (MOFs) [12,13] and covalent organic frameworks (COFs) [14,15], which play important roles in science and technology fields and have been paid much attention as a useful platform for advanced functional material design. TPN has also led to a new wave of research in porous organic networks (PONs) [16–18], which can be applied in many fields such as gas storage [17], dye sorption [19], and catalyst [20,21].

Researches of pressure effect on the molecular materials have been the subject of considerable interest over many years and have attracted great attention of scientists from diverse fields ranging from physics, chemistry, materials science to biophysics and geophysics [22–26]. It is well known that, as two basic thermodynamic parameters, pressure and temperature have been widely used to develop a better understanding of material laws [27]. Pressure, being a continuous, reversible, and laboratory-controlled physical variable, can easily modify the distances between molecules and atoms; thus, they reorient themselves to counter steric hindrances and tend to achieve close packing, eventually resulting in new crystal structures which cannot be accessible at ambient conditions [28]. Moreover, with the significant advances in high-pressure techniques over the last half century, it has been proved that high pressure is one of the most ideal means of generating novel physical states [29–30]. High pressure can be considered as an efficient approach not only to tune the T_c of the superconductivity in elements [31] and compounds [32] but also to induce superconductivity with
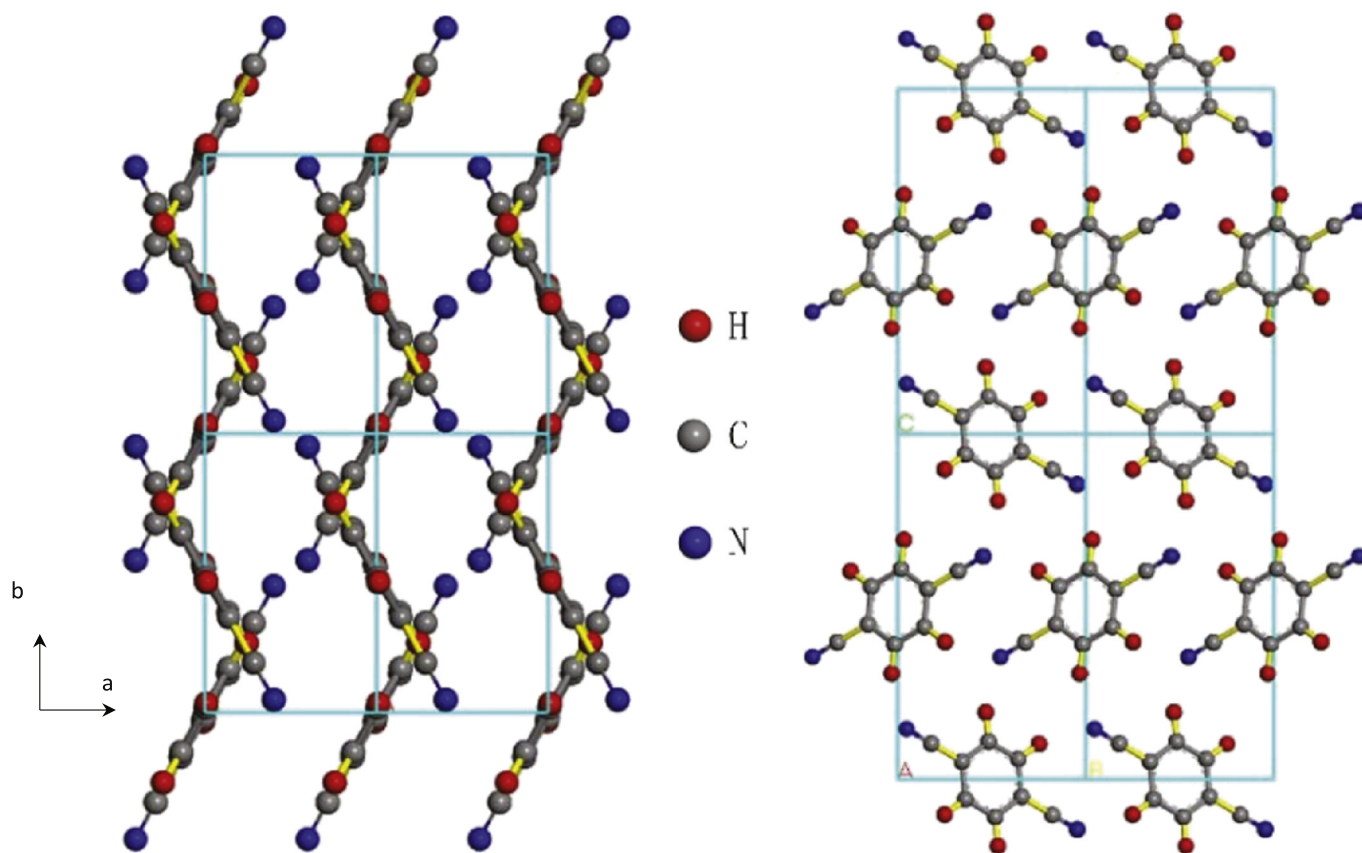
Fig. 1. The crystal structure of TPN under ambient conditions.

ferromagnetic or antiferromagnetic orders as their ground states at ambient conditions. As a powerful non-destructive spectroscopy technique, Raman spectroscopy has been widely applied to study the material properties including the structural phase transition of materials under high pressure [27,33,34].

In the present study, we have measured the high-pressure Raman spectra of TPN at room temperature with diamond anvil cells (DACs) from ambient to 12.6 GPa. One of the primary objectives is to give a tentative assignment of the fundamental Raman vibrational frequencies in the Raman spectrum of TPN based on the first-principles calculations. More importantly, the phase transition of TPN has been revealed according to the frequency-pressure curves at pressure ~5.3 GPa which has not been investigated so far. The detailed spectroscopic analysis based on Raman actives of the characteristic modes of TPN under high pressure will be helpful for a more in-depth understanding of the structure and stability of TPN.

2. Experimental and Computational Methods

The sample of TPN was purchased from Aldrich Chemical Company and it was used without further purification. Symmetric diamond anvil cells (DACs) with diamond anvils of 400 μm in diameter were used for in situ high-pressure Raman measurement. The powder samples were loaded in a 150 μm hole which was drilled in a T301 steel gasket pre-indented to ~55 μm thickness. The pressures in the DACs were calculated by applying the well-known pressure shift of Ruby luminescence R1 line [35,36], and a quasihydrostatic pressure condition in the sample chamber was confirmed by the sharp and well-separated ruby fluorescence peaks. High-pressure Raman spectra and ruby fluorescence spectra were collected at room temperature by a confocal microscope Raman spectrometer system (Renishaw InVia Raman microscope). The 532 nm line of diode-pumped solid state laser was

employed to excite the TPN sample. A Leica microscope with $50\times$ objective lenses enables measurements with back scattering geometry. The laser power was 4 mW and exposure time (CCD integration times) of 50s were used to collect all Raman spectra. The spectral resolution is ~1 cm^{-1}. Frequency calibration of the Raman spectrum is realized by using the characteristic 520 cm^{-1} line of silicon.

The first-principle calculation were carried out with the CASTEP code [37], based on density functional theory (DFT) method using norm-conserving pseudopotential [38]. Quantum-chemical calculations of a single TPN molecule were performed according to the same method reported by Liu et al. at B3LYP/6-31G* levels, as implemented in the Gaussian 03 program package [8]. All geometries were fully optimized using the minimum analytical gradient method. No geometry constraint was applied on the molecules.

3. Results and Discussion

The Raman spectrum of TPN obtained at room temperature and ambient pressure is shown in Fig. 2. TPN belongs to the D_{2h} point group. Under the D_{2h} point group, TPN has the following normal vibrations: $7A_g + B_{1g} + 4B_{2g} + 6B_{3g} + 2A_u + 6B_{1u} + 6B_{2u} + 4B_{3u}$. According to the selection rules, the A_g, B_{1g}, B_{2g}, B_{3g} modes are Raman active only, the A_u bands are infrared and Raman inactive, and the B_{1u}, B_{2u} and B_{3u} give only infrared bands; however, some of these Raman modes cannot be observed in our experiment due to the weak spectral intensity [10]. We calculated the vibrational modes of TPN in two ways because of two reasons. The first is to assay the Gaussian 03 calculation results based on the literature work. The second is to facilitate the assignment and description of the experimental vibration modes. Part of the calculation results by the CASTEP are listed in Table 1. Some of the calculated modes of the TPN crystals by CASTEP software occur in pairs owing to the effect of crystalline structure. The frequencies of TPN Raman