

Raman spectroscopy of L,L-diphenylalanine crystal under high pressure



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ABSTRACT

The L,L-diphenylalanine can self-assemble into long and stiff nanotubes with remarkable mechanical and chemical stability. In this work, Raman spectroscopy was used to investigate the vibrational properties of L,L-diphenylalanine single crystal under high-pressure conditions up to 7.4 GPa. The results show great modifications in the low-wavenumber bands accompanied by some changes in the internal mode vibrations between 3.9 and 4.6 GPa, indicating the occurrence of a structural phase transition. Since the coupling between water molecules and the nanochannels of the L,L-diphenylalanine crystal is extremely sensitive to the tubular arrangement, the vibrational changes observed in the spectral region of internal modes can be interpreted as conformational modifications in the dipeptide backbone. On decompression, we found that the phase transition is reversible since the ambient spectrum is recovered when the pressure is completely released.

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1. Introduction

Amino acids and small peptides are fundamental molecules to regulate a variety of physiological processes, including endocrine and paracrine mechanisms [1]. They may even act as neurotransmitters in the central nervous system or as cellular growth factors in some sites [2]. Additionally, exploiting their structural variability it is possible to design drugs that can be therapeutically useful against different biological targets [3]. As molecular building-blocks, peptides offer a great diversity of biochemical and physical properties to design distinct self-assembly structures, including tubes, micelles, vesicles and physical gels [4–7].

An active investigation of peptide-based nanostructures has been stimulated in recent years [8–10]. A major feature of self-assembly structures is the key role played by weak interactions (hydrogen bonds, van der Waals, and π – π stacking) in the formation and stability of these systems [6,11]. Thus, there is no surprise that most examples of self-assembly peptides are well established in water [12–16]. The intra- and intermolecular interactions are of great importance to determine specific structural properties. The conformation of peptide backbone in the crystalline structure can be probed by different methods [17]. Among them, vibrational spectroscopy such as infrared and Raman spectroscopy have been especially valuable to understand the conformational configurations in several studies [7,18–20].

The L,L-diphenylalanine is a short aromatic dipeptide and corresponds to the core recognition motif of Alzheimer's β -amyloid polypeptide [21]. This motif crystallizes in long and stiff nanotubes with remarkable mechanical, thermal and chemical stability [22,23]. In fact, L,L-diphenylalanine shows the presence of 12 Å wide channels where water molecules are positioned, aiding the stability of the crystal structure [10]. This peptide constitutes a system of interest because, from a biological point of view, models membrane pores and ion channels. Beyond this, a previous work showed that those self-assembly nanotubes have a pronounced nonlinear optical response of second harmonic generation [24,25], which makes them an excellent candidate for applications in electronic and optical devices. A follow-up study reported an irreversible phase transition at temperature of 140 °C, changing the crystal symmetry and consequently their physical properties [26]. In this work, we report a high-pressure study (0.0–7.4 GPa) of L,L-diphenylalanine crystals using Raman spectroscopy. The application of high-pressure leads to considerable modifications in the vibrational bands, mainly between 3.9 GPa and 4.6 GPa. This includes the disappearance of Raman bands in the spectral region associated with the lattice mode vibrations and changes in the relative intensities of some internal-mode lines.

2. Experimental

L,L-diphenylalanine single crystals were obtained by evaporation from a concentrated aqueous solution at 80 °C. These crystals were colorless and grew in a needle-like shape (approximately $0.200 \times 0.024 \times 0.026$ mm) as similar to the growth samples in

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ethanol or methanol [10]. Powder X-ray diffraction (XRD) pattern of the *L,L*-diphenylalanine sample was measured prior the high-pressure Raman experiment by using a $\text{CuK}\alpha$ (0.15406 nm) source (Bruker D8 diffractometer). Rietveld analysis of the XRD data was performed by Fullprof suite [27,28] with initial atomic parameters reported by Mason et al. [10]. The high-pressure Raman spectra were measured at room temperature using a triple grating spectrometer Jobin Yvon T64000 equipped with an N₂-cooled charge coupled device CCD detection system. A 532 nm beam of a Verdi laser (Coherent) focused through a 20X Olympus microscope was used as the excitation source. The spectrometer slits were set for a resolution of 2 cm^{-1} . The sample was loaded into a membrane diamond-anvil cell with a pre-indented stainless steel gasket of $120\ \mu\text{m}$ diameter hole. In order to ensure the hydrostatic conditions up to 7.4 GPa, mineral oil (Nujol) was used as the pressure transmitting medium. The R1 fluorescence line of a ruby was used for pressure calibration.

3. Calculations

The quantum chemical calculations were performed with the Gaussian09[®] suite [29]. The initial atomic coordinates of an isolated *L,L*-diphenylalanine molecule was taken from the X-ray diffraction data [10]. The relaxed geometry was calculated using density functional theory (DFT) approach with the hybrid Becke exchange with Lee, Yang, and Parr's (B3LYP) correlation functional and the 6-31++G(d,p) [30–33]. After the optimization, harmonic vibrational frequencies were evaluated at the same level of theory and then scaled by 0.955 (above 1800 cm^{-1}) and 0.977 (under 1800 cm^{-1}) [34,35]. The simulated Raman spectra (see Fig. S1 in the Supplementary material) were plotted using a pure Lorentzian band shape ($\text{FWHM} = 10\text{ cm}^{-1}$). Furthermore, theoretical vibrational spectra of the compound were interpreted by means of potential energy distribution (PED) using the VEDA 4 program [36]. The VEDA program does not scale the elements of force

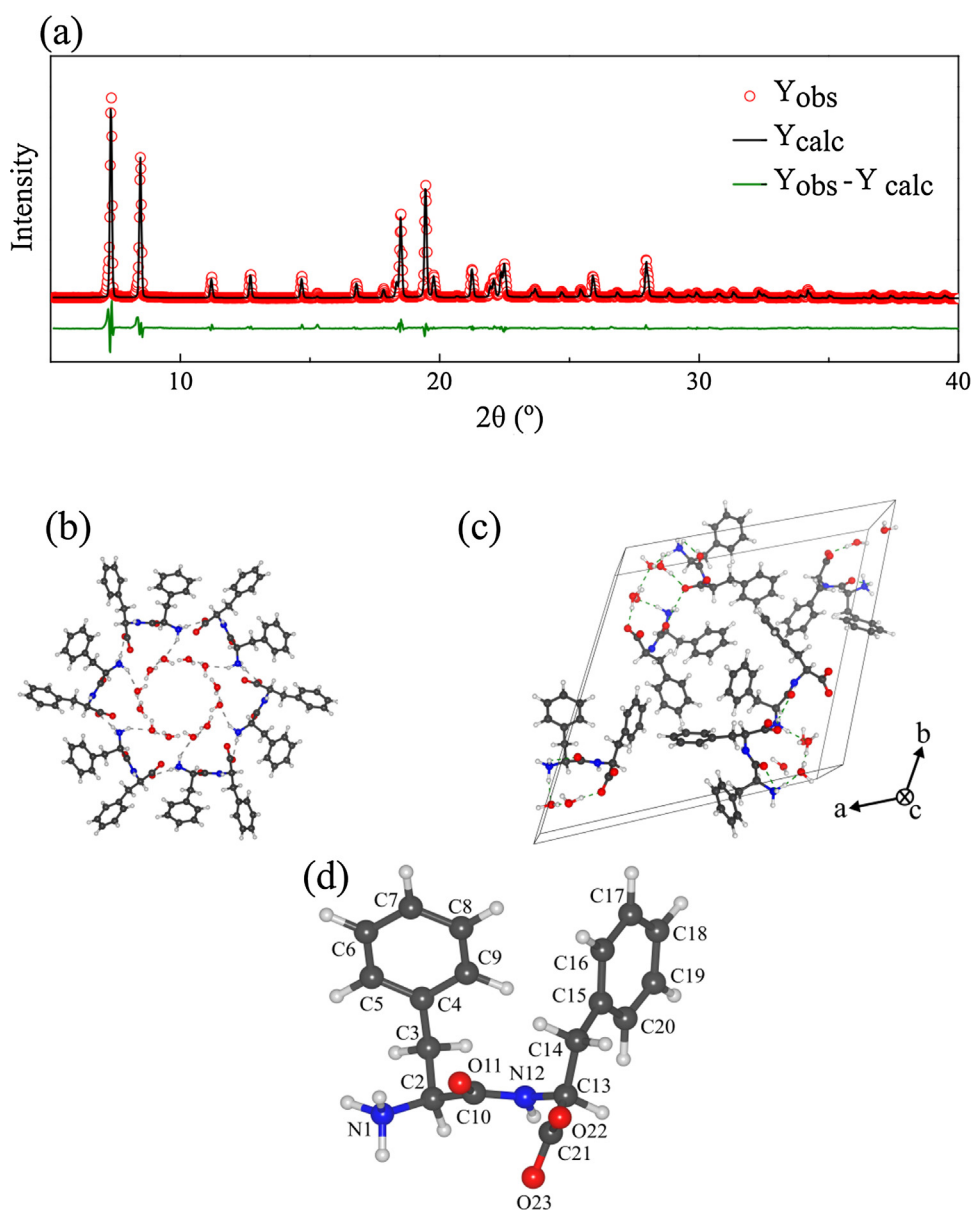


Fig. 1. (a) Rietveld-refined X-ray diffraction pattern of the *L,L*-diphenylalanine crystal. The black solid and red open circle lines represent theoretical and observed intensities, respectively. The green line denotes the difference between the observed and simulated profiles. (b) The cross-sectional view of the *L,L*-diphenylalanine nanotube partially filled by water (c) The hexagonal unit-cell of *L,L*-diphenylalanine viewed along the *c*-axis. (d) The isolated *L,L*-diphenylalanine scheme. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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