

Raman spectroscopic study of DL valine under pressure up to 20 GPa

F.S.C. Rêgo^a, J.A. Lima Jr.^{a,*}, P.T.C. Freire^a, F.E.A. Melo^a, J. Mendes Filho^a, A. Polian^b^a Departamento de Física, Universidade Federal do Ceará, C. P. 6030, CEP 60455-760, Fortaleza, CE, Brazil^b Institut de Minéralogie de Physique des Matériaux et de Cosmochimie, Sorbonne Universités, UPMC Univ Paris 06, UMR CNRS 7590, F-75005, Paris, France

ARTICLE INFO

Article history:

Received 18 September 2015

Received in revised form

24 November 2015

Accepted 12 December 2015

Available online 15 December 2015

Keywords:

DL-valine

High-pressure

Phase transition

Conformational changes

Raman scattering

ABSTRACT

DL-valine crystal was studied by Raman spectroscopy under hydrostatic pressure using a diamond anvil cell from ambient pressure up to 19.4 GPa in the spectral range from 40 to 3300 cm^{-1} . Modifications in the spectra furnished evidence of the occurrence of two structural phase transitions undergone by this racemic amino acid crystal. The classification of the vibrational modes, the behavior of their wavenumber as a function of the pressure and the reversibility of the phase transitions are discussed.

© 2015 Published by Elsevier B.V.

1. Introduction

Apart from glycine, all the twenty one protein amino acids are chiral, they exist in two pure enantiomers (L and D), and also can be exist in a racemic form (DL) in which a half of molecules are in the L chiral form and the other half in the D form. The number of papers dealing with vibrational and structural properties of the DL form of amino acid has increased in the last years [1–4], but it is still fewer than that on the L-forms [5–13]. Although L and DL are formed essentially by the same molecules, the way they are linked can provide very different properties. In this way high pressure is an useful tool that can be used to study the role of hydrogen bonds in the structure that compose amino acids as well as to compare the behavior of a chiral and a racemic form.

It is interesting to compare the vibrational behavior between the L and DL forms of amino-acids. For a long time it was believed that the L-alanine undergoes a phase transition at about 2.2 GPa [14]. The properties of this amino acid were revisited by X-ray diffraction by Tumanovet *al.* [3], who explained the anomaly observed around 2.0 GPa as a consequence of an accidental coincidence of the unit cell parameters, but no phase transition was observed for pressures up to 12.3 GPa. The first amorphisation in an amino acid crystal was observed in L-alanine. Funnell et al. [11] observed a reversible

crystal to amorphous phase transition in L-alanine crystal at about 15.0 GPa. Belo et al. [15] suggested that the DL-counterpart of alanine suffered pressure induced phase transitions but it is now recognized that the structure of DL-alanine remains stable up to 8.3 GPa [4].

L and DL leucine were also studied under high pressure and it was observed that differently from L and DL-alanine they have different behaviors. L-leucine undergoes three phase transitions up to 5.0 GPa. In the first two (at 0.46 GPa and between 0.8 and 1.46 GPa respectively) anomalies are characterized by the disappearance of lattice modes, the appearance of several internal modes, or the splitting of high wavenumber modes. The third modification, at about 3.2 GPa, is characterized by a discrete change of the slopes of the wavenumber *versus* pressure for most of the observed Raman modes [16]. The results for DL-leucine crystal indicate that it presents only one phase transition in the same range of pressure [17].

Meticulous studies on cysteine crystals have been performed [1,2,8,13,18]. The L form presents two polymorphs at ambient conditions, one monoclinic [19] and one orthorhombic [20] and under pressure up to 6.5 GPa both present phase transitions. The orthorhombic form of cysteine undergoes a phase transition at about 2.0 GPa [8,13] while the monoclinic one undergoes two phase transitions: (i) the first one at 2.9 GPa and the second at 3.9 GPa [8]. The monoclinic structure of the DL-cysteine undergoes three phase transitions up to 7.9 GPa: The first one at 0.1 GPa, the second one between 0.85 and 1.55 GPa and the last one at about 6.0 GPa [2]. The

* Corresponding author.

E-mail address: alves@fisica.ufc.br (J.A. Lima).

case of DL-cysteine is also interesting because it was found that the polymorph obtained in the first phase transition under pressure has the same structure as that obtained on cooling [2].

L enantiomer and racemic counterparts of serine were also compared and the results point out to a different scenario than that of cysteine. While DL-serine maintained its atmospheric pressure structure stable up to 8.0 GPa [21] the L form presented two phase transitions in the same pressure range [12].

Concerning the valine crystals a previous work showed that the L-form presents discontinuities in the wavenumber vs pressure plots at about 3 and 5.3 GPa, suggesting that the crystal undergoes phase transitions at these two pressure [22]. In another study performed using Raman spectroscopy, Murli et al. [23] suggested that the DL-valine presents changes in the nature of hydrogen bonds at about 3 GPa. However, the highest pressure reached in the experiment with the DL-forms was only 6.9 GPa (for the external modes). With the objective to investigate the vibrational properties of the material in a pressure range well above that of Ref [23], we present a detailed analysis of the Raman spectra of DL-valine up to 19.4 GPa. The pressure dependence of all the modes is presented and the observed modifications in the Raman spectra are discussed. Additionally, a comparison with a previous paper reporting the Raman spectra of the DL and L-valine under pressure is also done.

2. Experimental details

Single crystals of DL-valine ($\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}$ were obtained by slow evaporation of an aqueous solution at 298 K. Reagent of DL-valine was purchased from Sigma–Aldrich (99% purity) and the saturated solutions were also prepared at ambient conditions using 20 mL of deionized water. Platelet colorless crystals were obtained and their crystallographic structure was confirmed by X-ray diffraction experiments at 25 °C (See Supplementary Material). The Raman spectra were obtained with a triple-grating JobinYvon T64000 spectrometer equipped with a N_2 -cooled charge coupled device detection system with a resolution of 2 cm^{-1} . Lorentzian functions were used to fit the Raman spectra. The 514.5 nm line of an Ar^+ ion laser was used as the excitation source. In the high pressure experiment we studied the sample at increasing pressure between 0.0 GPa (ambient pressure) up to 19.4 GPa using a membrane diamond anvil cell (MDAC) [24]. We used diamond anvils with a culet of 400 μm in diameter. A 150 μm -diameter hole in a stainless-steel gasket (200 μm of thickness preindented to 40 μm) was loaded with argon [25]. The pressure and the hydrostaticity were monitored using the ruby fluorescence lines [26].

3. Results

At ambient conditions DL-valine crystal presents two polymorphs, one triclinic [27] and other monoclinic [28]. The crystallographic structure of the studied sample has been confirmed by X-ray diffraction experiments as being triclinic ($P\bar{1}$ - $N^\circ 2$ space group) in accordance with ref. [27]. The parameters obtained in our refinement are presented in Table S1 of the Supplementary Material. A molecule of valine, a projection of crystalline structure of DL-valine and the refinement of the structure are shown in the Supplementary Material (see Fig. S1 and S2).

Fig. 1 shows the Raman spectra of DL-valine crystal recorded from ambient pressure (0.1 MPa) up to 19.4 GPa in the 40–600 cm^{-1} spectral range. The low-wavenumber modes ($\omega < 150\text{ cm}^{-1}$) observed in this region are mainly associated with lattice modes. The lowest frequency mode has a wavenumber of 48 cm^{-1} at 0.1 MPa and its intensity gradually decreases with increasing pressure but it is still well observable at 19.4 GPa. The

two next modes (marked with two stars in the spectrum taken at 0.1 GPa) become closer and closer with pressure and from 1.4 GPa they merge into one band that can be observed up to 19.4 GPa.

The behavior of the fourth mode centered at 106 cm^{-1} is remarkable: up to 1.1 GPa its intensity is practically constant, then decreases at 1.4 GPa and increases at 1.8 GPa (it is almost quadrupled) and remains practically constant up to 6.6 GPa where it starts decreasing again. At 8.8 GPa this mode splits in two and remains so up to the highest pressure, although the bands appear with low intensities.

The three following modes (between 120 and 150 cm^{-1}) are the last ones to be classified as lattice modes. They have low intensity and for pressures higher than 10 GPa only one of them gains intensity, being observed up to 19.4 GPa. Between 150 and 250 cm^{-1} there are two modes. Both of them present a blue shift and are noted up to 19.4 GPa. The modes between 250 and 350 cm^{-1} have a very low intensity and their fitting are difficult so they will not be discussed. Four modes are present in the spectrum at 0.1 MPa between 350 and 500 cm^{-1} . It is remarkable that the first two change their relative intensity and at 10.0 GPa the mode centered at 370 cm^{-1} disappears. The other two modes, centered at 420 cm^{-1} (skeletal deformation) and at 473 cm^{-1} (torsion of NH_3) [29], can be seen for almost all values of pressure. The last two modes of this region were tentatively assigned as rocking of CO_2 (531 cm^{-1}) and librational mode of N–H–O (544 cm^{-1}), respectively [29,30]. They

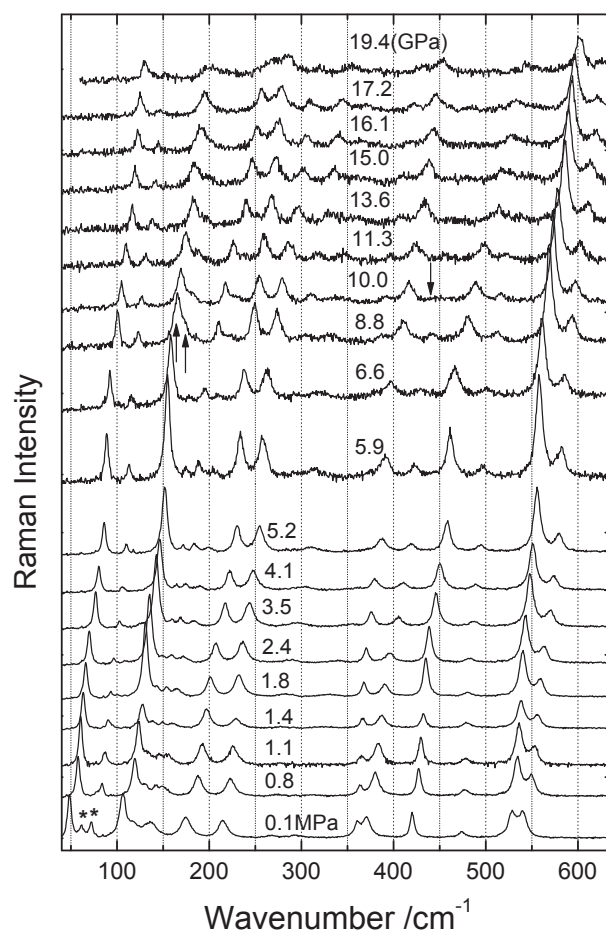


Fig. 1. Raman spectra of DL-valine crystal in the spectral range $40\text{--}600\text{ cm}^{-1}$ for selected values of pressure. Values represent the pressure in GPa, except for the bottom spectrum that was recorded at 0.1 MPa. Above 5.9 GPa spectra were multiplied by a factor of 5.

Download English Version:

<https://daneshyari.com/en/article/1409006>

Download Persian Version:

<https://daneshyari.com/article/1409006>

[Daneshyari.com](https://daneshyari.com)