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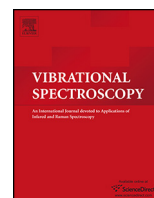**218** PUBLICATIONS **3,037** CITATIONS

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High pressure Raman spectra of D-threonine crystal

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ABSTRACT

Raman spectra of D-threonine crystal were recorded for pressures up to 8.5 GPa. Modifications in the lattice modes indicate that the crystal undergoes two structural phase transitions, the first in the 1.9–2.4 GPa pressure range and the second in the 5.1–6.0 GPa pressure range. Splitting of modes and changes in the intensity of several bands suggest a conformational reorientation of the molecule in the crystal framework between 3.5 and 4.3 GPa. We discussed ours results by comparing with previous high-pressure investigation on L-conformer.

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1. Introduction

Amino acids are the "bricks" that compose proteins, and they attract a lot of attention from biologists and biochemists. In addition, the complex hydrogen bonded (HB) network that stabilizes their crystalline structure in the solid state have made them a system that has also intrigued physicists. One way of studying and accessing the role of HB in amino acids crystal structure is by varying the thermodynamic parameters such as pressure and temperature. Besides the last years many papers on this subject have been published [1–10], but only few of them have focused on D (mirror image of L-form) and DL (racemic form) forms.

In particular, conformers L and DL of leucine were investigated by Raman spectroscopy. L-Leucine exhibits three phase transitions for pressures up to 6.0 GPa. The first (between 0.0 and 0.5 GPa) and the second (between 0.8 and 1.5 GPa) are characterized by the disappearance of lattice modes, appearance of internal modes and splitting of some vibrational bands [11]. Differently, the conformer DL-leucine undergoes only one phase transition in the 0.0–5.0 GPa pressure range, thus indicating that its structure is more stable than L conformer [12].

Raman scattering studies were reported for L and DL–valine conformers [13,14]. A phase transition close to 3 GPa was observed in both conformers, while a second phase transition (around 5 GPa) was only observed in the L-valine [13]. It is worth mentioning that although there is coincidence in the pressure value where a phase transition is observed for these two conformers, the changes in the

Raman spectra are different. In DL form of valine it was observed discontinuities in the $\omega \times P$ plot for many modes, changes in the intensity of NHO librational mode compared to the intensity of CO_2 rocking, and splitting of skeletal deformations modes [14]. In L-valine, changes in slopes of wavenumber vs. pressure plot were also reported, but the main change in the intensity was related to CH and CH_2 modes. The splitting of the CO_2 rocking mode and changes in the number of the lattice modes was also observed [13].

For serine the racemic form seems to be more stable than the L enantiomer. For DL-serine was reported to be stable up to 8.6 GPa while two phase transitions were observed in L-serine between 5.0 and 8.0 GPa [15,16].

Vibrational properties of DL-alanine crystal were also investigated for pressures higher than 10 GPa. Belo et al. [17] reported that this crystal undergoes phase transitions at about 1.0 GPa, and in 1.7–2.3 GPa, 6.0–7.3 GPa, 11.6–13.2 GPa pressure intervals. The phase transition at higher pressure is characterized by modifications in the lattice modes, red shift of bands associated with CCH_3 stretching and an increasing of line-width of bands associated with the wagging of CO_2 groups. This behavior is quite different from that observed for L-alanine in which phase transitions at about 2 [18] and at 9 GPa [19,20] were reported. Tumanov et al. [21] revisited L-alanine and established that the crystal does not undergo any phase transition for pressures below 12.3 GPa and explained that anomalies observed in the Raman spectra of the reference [18] are due to accidental coincidence of the parameters a and b in the unit cell. Recent X-ray experiments performed on L-alanine pointed out to a reversible crystal-amorphous phase transition at about 15.4 GPa [22].

The examples mentioned above clearly show that there is no rule to follow in order to predict the behavior of a particular

conformer based only in the behavior exhibited by similar crystals. Therefore, it is very important to compare the behavior of the three forms of each amino acid in order to better understand the mechanisms that govern the stability of an amino acid crystal framework.

More than 10 years ago a high-pressure experiment in the L form of threonine crystal was performed [23]. Based on Raman spectroscopy data, the authors of reference [23] proposed that a transition at about 2.2 GPa. In order to add knowledge and access the structural and vibrational properties of D-amino acids, we performed high-pressure Raman experiments in D-threonine crystal for pressures up to 8.5 GPa. The behavior of this form as well as similarities and differences in L and D conformers are discussed.

2. Experimental

Single crystals of the D-threonine were obtained by the slow evaporation of an aqueous solution at 300 K. The obtained crystals were colorless and the crystallographic structure was confirmed by single crystal X-ray diffraction experiments. The Raman spectra were obtained with a triple-grating spectrometer, Jobin Yvon T64000, which is equipped with an N_2-cooled charge-coupled device detection system. The 514.5 nm line of an argon laser was used as the excitation. An Olympus microscope lens with a focal distance of 20.5 mm and a numerical aperture of 0.35 was used to focus the laser beam on the sample surface. The spectrometer slits were set for a resolution of 2 cm^{-1}. In the high pressure experiment, we studied the sample increasing pressure between 0.0 GPa (ambient pressure) and 8.5 GPa using a membrane diamond anvil cell (MDAC) [24] with a stainless steel gasket with 200 μm of initial thickness and a 200 μm diameter hole. Nujol was used as pressure transmitting medium, and pressure was monitored using the ruby emission lines [25].

3. Results and discussion

Single crystal X-ray diffraction experiment was performed in order to identify the symmetry of the D-threonine crystal. It was found that the structure belongs to an orthorhombic symmetry with space group ($P2_12_12_1$) with four molecules in the unit cell. The cell parameters are $a = 5.1397$ Å, $b = 7.7091$ Å and $c = 13.6284$ Å which are compatible with crystallographic results reported for L-crystal [26].

Fig. 1 shows the Raman spectra of D-threonine recorded from 0.1 to 8.5 GPa in the 35–175 cm^{-1} spectral region. Most of the low-frequency modes observed in this region are often associated with lattice modes. Upon increasing pressure significant changes in the Raman spectra can be noticed. The first modification is the disappearance of two modes located at 50 cm^{-1} and 95 cm^{-1} (numbered as 1 and 4 in Fig. 1) which cannot be seen in the spectrum recorded at 2.4 GPa. We interpret this change to a phase transition undergone by D-threonine crystal. At 2.4 GPa it is possible to observe four modes with frequencies below 150 cm^{-1} whose intensities decrease with compression. Only three modes could be observed at 5.5 GPa. Again the disappearance of this mode at about 100 cm^{-1} can be related with another phase transition undergone by D-threonine. In this pressure range ($P > 5$ GPa) Nujol is not completely hydrostatic [27] and it is possible that the modifications are partially due to a phase transition or partially due to artifacts from not perfect hydrostatic conditions and new measurements using other transmitting medium should be performed in order to further clarify this point. For pressures up to 8.5 GPa the intensity of the modes continues to decrease and no additional change is observed. The wavenumber vs. pressure plot for the modes of this region is shown in Fig. 2, where the pressure range for each crystal
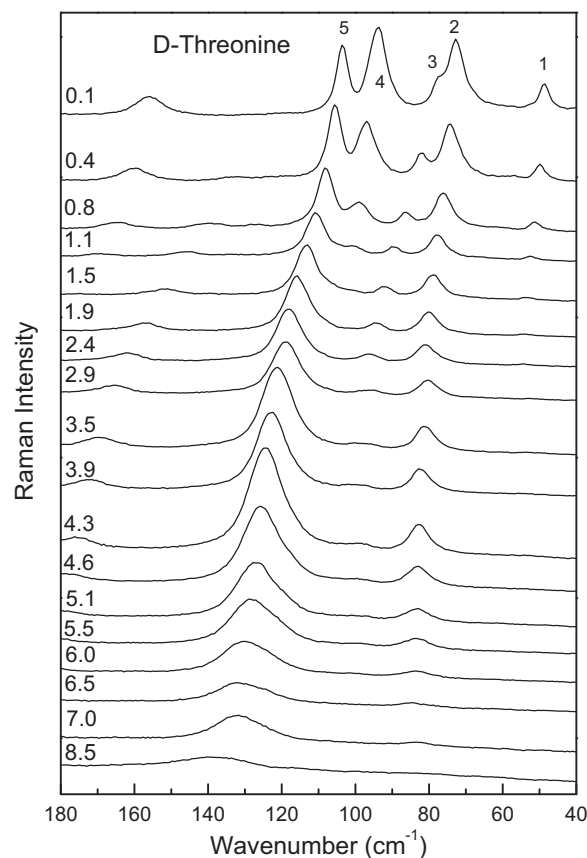
phase is limited by dashed lines. All the fit to experimental data are linear and discontinuities in $\omega \times P$ can be clearly observed.

Raman spectra of D-threonine in the 120–540 cm^{-1} recorded in the 0.1–8.5 GPa pressure range are shown in Fig. 3. The peak numbered as 6 is very weak at 0.1 GPa, but with increasing pressure its intensity increases up to 4.3 GPa and then starts to decrease until 8.5 GPa. This effect is probably due to some molecular rearrangement induced by pressure. We also observed that the most intense mode (numbered as 7) of this region also disappears at 2.4 GPa. This modification reinforces our hypothesis of the occurrence of a phase transformation in this pressure range. The two modes centered

Fig. 1. Raman spectra of D-threonine crystal in the spectral range 40–180 cm^{-1} for selected values of pressure. Values represent the pressure in GPa.
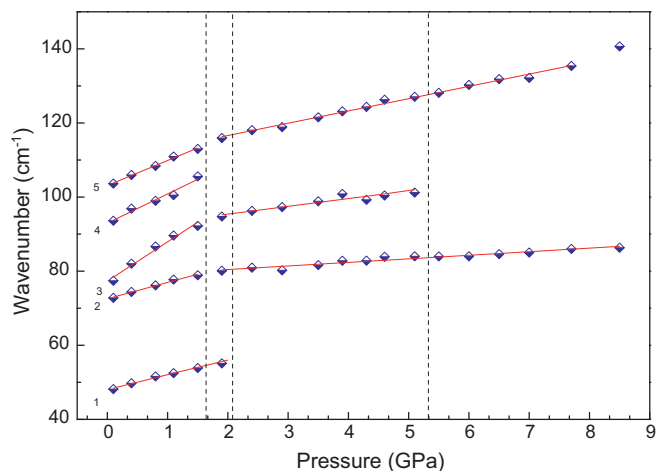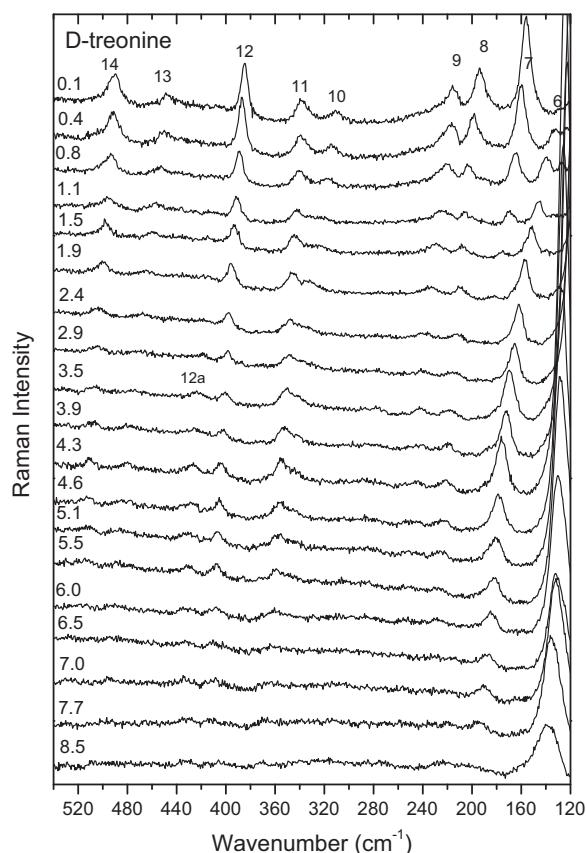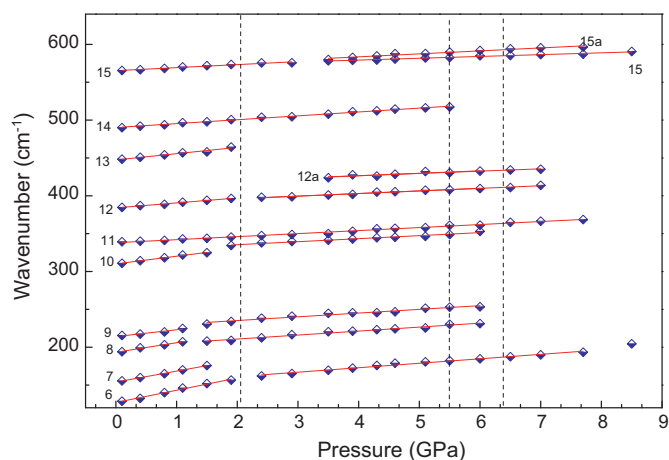

Fig. 2. Wavenumber vs. pressure plots of the bands appearing in the spectral range 40–150 cm^{-1}.

Fig. 3. Raman spectra of D-threonine crystal in the spectral range 120–540 cm^{-1} for selected values of pressure. Values represent the pressure in GPa.
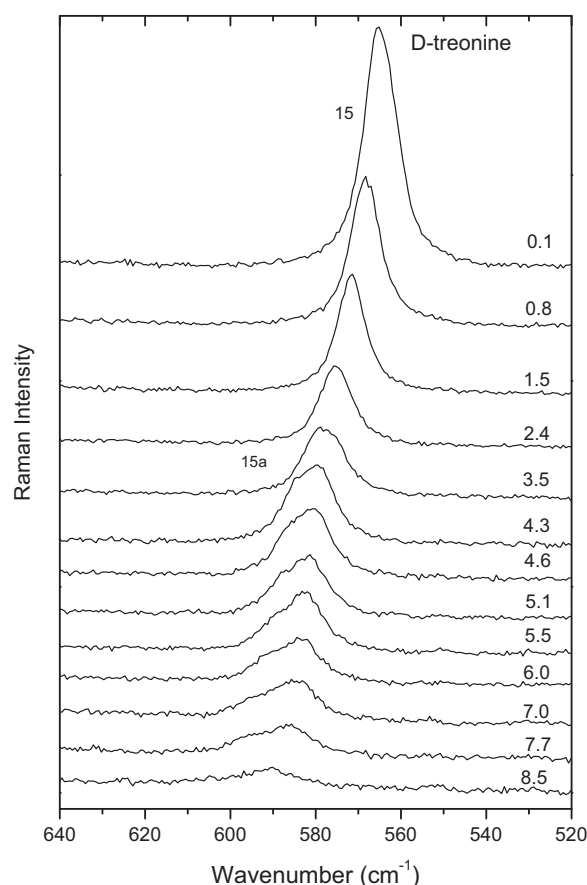

Fig. 5. Raman spectra of D-threonine crystal in the spectral range 520–640 cm^{-1} for selected values of pressure. Values represent the pressure in GPa.

at about 200 cm^{-1} decrease their intensities gradually and vanish at 6.0 GPa. In a similar way the two modes centered at 310 and 340 cm^{-1} decrease their intensities and at 4.3 GPa collapse forming a single band, being not possible to observe them for pressures higher than 6.0 GPa. The band observed at 385 cm^{-1} loses intensity with increasing pressure at 3.5 GPa and a band close to that appears and both could be observed up to 6.0 GPa. The last mode observed in this region is located at 490 cm^{-1}, which is assigned to NH$_3$ torsion vibration, and could be still observed even with low intensity, in the spectra recorded up to 4.6 GPa. Fig. 4 shows the

Fig. 4. Wavenumber vs. pressure plots of the bands appearing in the spectral range 120–640 cm^{-1}.

dependence of the frequency of the modes as function of pressure in the 120–640 cm^{-1} spectral range.

The pressure dependence of the rocking of CO$_2$ (r(CO$_2$)) can be seen in Fig. 5. The intensity of this mode decrease as pressure increases and at 3.5 GPa we can clearly observed a splitting. This phenomenon was already reported for other amino acids like L-methionine [28], and L-valine [13], but was not observed in the L conformer of threonine [23]. As the CO$_2$ is one of the units linked by hydrogen bonds it is possible to interpret such a splitting as due to conformational modifications of the molecules inside the unit cell, thus contributing to the phase transition mechanism at 5.1 GPa. As can be seen in Fig. 4 the frequency of this mode has a linear dependence with the pressure parameter, with no abrupt jump of the frequency close to the critical pressure. This suggests that the modification in the hydrogen bond network of D-threonine occurs continuously. This dynamic is completely different from what was reported, for L-methionine crystal, where an abrupt discontinuity of the r(CO$_2^-$) mode was verified [28].

It is also important to note that the band associated with NH$_3^+$ torsion mode, τ(NH$_3^+$), the band numbered as 13 in Fig. 3, presents pressure coefficient dω/dP > 0 with compression. This data can be partially related with the behavior of intermolecular hydrogen bonding. By considering the average hydrogen bond length as defined by the average N–O distance, where N belongs to the NH$_3^+$ group of a molecule and O belongs to the CO$_2^-$ group of a neighboring molecule; if the crystal is taurine (NH$_3$C$_2$H$_4$SO$_3$), the O atom is an oxygen of SO$_3^-$ group. In a comparative study performed using L-alanine, L-threonine and taurine, it was noted that if the average hydrogen bond dimensions among molecules in the unit cell of the crystal is higher than a certain value between 2.83 and 2.86 Å,

Table 1
Wavenumber of the peaks observed in the Raman spectra of D-threonine (Figs. 1, 3 and 5) for 0.1 GPa, and parameters obtained from linear fitting $\omega = \omega_0 + \alpha \cdot P$ to the experimental points. The assignment (based in Ref. [23]) of the modes is shown in the last column.

Peak	$\omega[P(0.1)]$ (cm^{-1})	0.1 GPa < P < 2.4 GPa		P > 2.4 GPa		Assignment
		ω_0 (cm^{-1})	α (cm^{-1} GPa^{-1})	ω_0 (cm^{-1})	α (cm^{-1} GPa^{-1})	
1	48	48.0	4.0			Latt.
2	73	72.6	4.4	78.5	0.9	Latt.
3	77	77.3	10.6	91.2	2.1	Latt.
4	94	92.9	7.9			Latt.
5	104	103.1	6.7	109.9	3.3	Latt.
6	129	126.9	16.2	149.3	5.9	Latt.
7	156	153.9	14.5			Latt.
8	194	193.3	12.6	200.2	5.3	$\tau(CO_2)$
9	216	214.0	8.9	225.4	4.9	–
10	311	310.1	10.1	327.4	4.0	–
11	339	338.1	4	338.1	4.0	δ(skel.)
12	385	384.0	6.6	389.2	3.4	δ(skel.)
12a				413.3	3.3	
13	448	447.4	8.3			–
14	490	490.2	5.1	490.2	5.1	$\tau(NH_3^+)$
15	565	565.3	4	569.6	2.4	r(CO_2^-)
15a				567.9	3.9	

Latt., lattice mode; skel, skeleton; τ, torsion; δ, deformation; r, rocking.

dω/dP of $\tau(NH_3^+)$ is positive; otherwise, dω/dP is negative [29]. In fact, the dω/dP < 0 situation is well fitted by L-alanine crystal which has N–O average distance equal to 2.83 Å, thus meaning that the main effect of high pressure on hydrogen bonding framework is to change the geometry of the bond. For the other cases studied in Ref. [29] dω/dP > 0, as it is verified for L-threonine and taurine crystals, meaning that the main effect of pressure is to decrease the length of hydrogen bond. D-threonine, the crystal studied in the present work, has as average N–O distance of 2.85 Å, which is a value compatible with positive dω/dP for torsion of NH$_3^+$, as observed experimentally. Therefore, D-threonine is another example where the behavior of dω/dP of $\tau(NH_3^+)$ can be correlated with the average hydrogen bond lengths in the unit cell.

It is also interesting to note that during compression the bands are continuously losing intensity in such a way that in the spectrum taken at 8.5 GPa most of the bands are hardly observed. This effect can be understood as consequence of increasing disorder in the system. Eventually, an amorphous state may be reached, as recently verified for L-alanine when the crystal was submitted to a pressure of 15 GPa [22].

After releasing pressure down to atmospheric pressure the original Raman spectrum was recovered thus showing that the pressure-induced phase transitions undergone by D-threonine are reversible.

Table 1 presents the experimental frequency at 0.1 GPa, the assignment of the modes and the frequency intercept ω_0 and pressure coefficients α obtained from linear fit to experimental data.

At this point it is worth commenting a previous study in the L enantiomer reported by Silva et al. [23]. The L-conformer is slightly different from the D-conformer and this can be appreciated in Fig. 6. It was observed that this conformer undergoes a phase transition at 2.2 GPa and this value is exactly inside the pressure range where the first phase transition in D-threonine is supposed to occur. However, modifications observed in the Raman spectra are different. In the L form the phase transition is characterized by appearance of one mode, discontinuities in the $\omega \times P$ plot and changes in the intensity of some bands. Otherwise for the D form the modifications observed are disappearance of lattice modes and discontinuities in the frequency of certain modes. Unfortunately, in the spectra reported by Silva et al. [23] the modes with frequencies below than 100 cm^{-1} were not recorded, and they performed the measurement for pressures up to 4.6 GPa, so a complete comparison is not possible to be made.
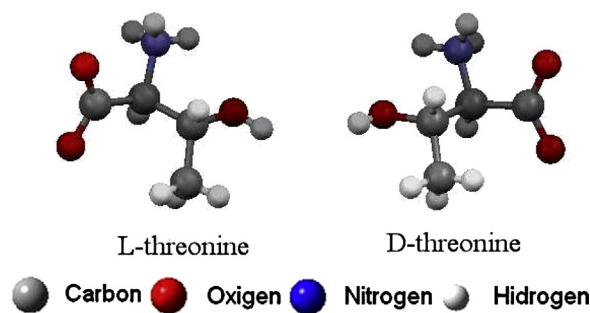

Fig. 6. L- and D-threonine molecules.

Discussing about structure modifications using only Raman spectroscopy results is a tough work, but in this case we can infer that pressure acts in a different way in L and D-threonine and even starting with the same structure, the pressure induced changes observed in the Raman spectra suggest that for pressures higher that 2.4 GPa the molecular conformations and almost certainly the symmetry of D-threonine at high-pressure are likely to be different from those of L-threonine.

4. Conclusion

Raman spectroscopy was used to study the vibrational properties of D-threonine crystal for pressures up to 8.5 GPa. Modifications in the lattice modes region indicate that the material undergoes two structural phase transitions, the first between 1.9 and 2.4 GPa and the second between 5.1 and 6.0 GPa. Discontinuities in the frequency plot and changes in the intensity of internal modes suggest that a conformational modification occurs between 3.5 and 4.3 GPa pressure range.

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