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High Pressure Raman Spectra of Amino Acid Crystals

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1. Introduction

Amino acids are molecules with general formula $HCCO_2^-NH_3^+R$, where R is a lateral chain characteristic of each molecule, which form the proteins of all living beings. Due the fact that both hydrogen bonding (HB) interactions play a central role on the secondary structure of proteins and the amino acids in crystal structure present complex networks of HB, they have been studied extensively in the last years (Barthes et al., 2004; Boldyreva et al., 2003a, 2003b, 2004, 2005a, 2007a, 2007b; Dawson et al., 2005; Destro et al., 1988; Façanha Filho et al., 2008, 2009; Freire, 2010; Funnel et al., 2010; Goryainov et al., 2005, 2006; Harding & Howieson, 1976; Hermínio da Silva et al., 2009; Lima et al., 2008; Migliori et al., 1988; Murli et al., 2003; Olsen et al., 2008; Sabino et al., 2009; Teixeira et al., 2000; Tumanov et al., 2010; Yamashita et al., 2007). These studies can be seen as important background to understand both static structure and dynamics properties of proteins such as denaturation, renaturation, folding itself, changes of folds, among others (Freire, 2010). The simplest protein amino acid is α-glycine, which was investigated by Raman spectroscopy under high pressure conditions, being discovered that up to 23 GPa the crystal structure does not undergo any phase transition, although modifications in the Raman spectra indicate changes in the intra-layer HB interactions (Murli et al., 2003). In this chapter we investigate the effect of high hydrostatic pressure on L-histidine hydrochloride monohydrate (HHM) and L-proline monohydrate (PM) crystals, in particular observing the effect of pressure on the vibrations related to hydrogen bonds observed in these amino acid crystals.

2. State of the art

Many works have investigated high pressure vibrational and structural properties of amino acid crystals. The simplest amino acid is glycine, which at atmospheric pressure presents at least three different polymorphs. When pressure is applied to the different polymorphs, different results are obtained. In this way, when α–glycine is submitted to high pressure, up to 23 GPa, no structural modification is verified (Murli et al., 2003). Relatively short N-H…O hydrogen bonds form layers parallel to the ac plane and the layers are connected by much

weaker bifurcated N-H…O hydrogen bond forming anti-parallel double layers (Murli et al., 2003). The difficult of rearranging the double layers in the crystal structure is an explanation for the stability of α-glycine with respect to pressure (Boldyreva, 2007b). Such a fact, the stability of the structure under high pressure conditions, is very different from what is observed with β- and γ-glycine. The β-glycine has a crystal structure very similar to the α-glycine, although this last polymorph is most stable and should be obtained from the β-polymorph under humid conditions (Dawson et al., 2005). For β-glycine it was observed through both Raman and polarizing spectroscopies a reversible phase transition at 0.76 GPa (Goryainov et al., 2005). Such a phase transition is accompanied by pronounced changes in the Raman spectra of the material, in particular by jumps and kinks at the curves of frequency versus pressure (for the band associated to NH$_3$ rock, the jump is higher than 10 cm^{-1}). Additionally, the transition is characterized by a rapid propagation of an interphase boundary accompanied by the crack formation in the crystal as verified by authors of Ref. (Goryainov et al., 2005). On decompression, the high pressure phase (β'-glycine) transforms back to the β-glycine without hysteresis (Goryainov et al., 2005), which is not a general result among amino acid crystals.

While the α– and β–forms of glycine crystallize in a monoclinic structure, respectively, with space groups *P2$_1$/n* and *P2$_1$*, γ-glycine crystallizes in a trigonal symmetry (*P3$_1$*) (Boldyreva et al., 2003a). Under ambient conditions the α– and γ-forms of glycine are stable for a very long time, but under high temperature (T ~ 440 K) it is observed a phase transition from the γ- to the α-polymorph of glycine. On the other hand, it is interesting to note that even the α-form being thermodynamically slightly less stable than the γ-form at low temperatures, its transformation to the γ-form is apparently kinetically hindered (Boldyreva et al., 2003b). Related to the behavior of γ-glycine under hydrostatic pressure some studies have investigated this subject. Under the scrutiny of X-ray diffraction authors of Ref. (Boldyreva et al., 2004) observed that γ-glycine undergoes a phase transition beginning at 2.7 GPa characterized by an abrupt change in the unit cell volume; such a phase transition is not completed even to pressures of 7.8 GPa. On compression up to 2.5 GPa, γ-glycine structure is changing anisotropically in such a way that the a/c ratio decreases. At 2.7 GPa the reflection of a new phase, δ-glycine, begins to appear, but when pressure is released even at ambient pressure, the new phase did not disappears completely. In other words, part of the high pressure δ-glycine phase remains down to the atmospheric pressure and the γ − δ transformation was not completely reversible (Boldyreva et al., 2005a). On decompression of the γ and δ phases, additionally, it was observed the appearance of another new phase at 0.62 GPa, ζ–glycine, which could be observed both by Raman and optical spectroscopies (Goryainov et al., 2006).

Among the amino acids, L-alanine is the most studied crystalline system and although a great number of works has visited its physical and chemical properties, there are some interesting non conclusive questions related to it. For example, although there is no indication for occurrence of temperature induced phase transition, it is known that the c lattice parameter of L-alanine increases with decreasing temperature (Destro et al., 1988) by a step-wise dynamics (Barthes et al., 2004). Under low temperature, authors of Ref. (Migliori et al., 1988) have observed an unusual behavior of the intensities of the low wavenumber modes at 41 and 49 cm^{-1}, associating the phenomenon to the occurrence of localized vibrational states. Such modes have also an intriguing behavior with high pressure conditions: between 0 and 2.3 GPa the lowest wavenumber band increases intensity while

the band at 49 cm^{-1} decreases; above the critical pressure of 2.3 GPa, an inverse effect is observed, e.g., the lowest wavenumber band decreases in intensity while the other band increases its intensity (Teixeira et al., 2000). Beyond this, under the scrutiny of the behavior of lattice modes of L-alanine through Raman spectroscopy it was reported the evidence of a structural phase transition at ~ 2.3 GPa (Teixeira et al., 2000), that seems to be confirmed by X-ray diffraction measurements (Olsen et al., 2008). However, very recent works reinterpreted X-ray diffraction measurements as conformational changes of the ammonia group (Funnel et al., 2010; Tumanov et al., 2010). Additionally, (i) the Raman scattering data were not correlated with a structural phase transition, only with continuous changes in the intermolecular interactions (Tumanov et al., 2010); (ii) at about 2 GPa the cell parameters *a* and *b* become accidentally equal to each other (Funnel et al., 2010; Tumanov et al., 2010), but maintaining the same orthorhombic structure ($P2_12_12_1$), differently from the work of ref. (Olsen et al., 2008) that interpreted the X-ray diffraction results as an orthorhombic → tetragonal phase transition.

There are three other aliphatic amino acids, which were investigated by Raman spectroscopy under high pressure conditions: L-leucine, L-isoleucine and L-valine. At atmospheric pressure and room temperature, L-leucine ($C_6H_{13}NO_2$) crystallizes in a monoclinic structure (C_2^2) (Harding & Howieson, 1976), although there are reports of a second phase for temperatures higher than 353 K (Façanha Filho et al., 2008) and a third polymorph resulting from residues of a solution at 200 Ma (Yamashita et al., 2007). A series of modifications on the Raman spectrum of L-leucine crystal were observed when it was submitted to high pressure conditions (Façanha Filho et al., 2009). The modifications occur in three different pressure ranges: (i) between 0 and 0.46 GPa, (ii) between 0.8 and 1.46 GPa, and (iii) at around 3.6 GPa. The first modification observed in the Raman spectra involves motions of the CH and CH$_3$ units, as can be understood from the behavior of the bands in the high wavenumber region (about 3000 cm^{-1}). It is worth to note that such a change is also associated to the hydrogen bond changes, because an increasing in the line width of a band associated with the torsion of CO$_2^-$ is verified across the pressure of 0.46 GPa, although there is no great change in the lattice modes. Differently, the changes observed between 0.8 and 1.46 GPa occurs both in the internal modes and in the lattice modes of the crystal, indicating a structural phase transition undergone by L-leucine. Finally, around 3.6 GPa change of the slopes of the frequency *versus* pressure plots associated with CO$_2^-$ moieties were observed, pointing to changes associated to hydrogen bonds (Façanha Filho et al., 2009).

The Raman spectrum of L-valine ($C_5H_{11}NO_2$) under high pressure conditions, presents several changes between 0.0 and 6.9 GPa (Hermínio da Silva et al., 2009). In particular, an extraordinary increase of intensity of the C – H stretching bands is verified at about 3 GPa and a decrease of intensity is observed at ~ 5.3 GPa. Simultaneously, discontinuities are observed in the frequency *versus* pressure plots for all modes of the Raman spectrum in these two pressure values, indicating possible phase transitions undergone by the crystal. L-isoleucine ($C_6H_{13}NO_2$) was another aliphatic amino acid whose Raman spectra were investigated under high pressure (Sabino et al., 2009). From this preliminary study, it were observed changes on bands associated with both the rocking of NH$_3^+$, r(NH$_3^+$), and the rocking of CO$_2^-$, r(CO$_2^-$), as well as to lattice modes at ~ 2.3 GPa and 5.0 GPa. Such modifications in L-isoleucine were associated with conformational change of molecules or to a phase transition undergone by the crystal. However, a confirmation of the occurrence of phase transitions for L-valine, L-leucine and L-isoleucine through X-ray diffraction or neutron diffraction is still lacking.

Two sulfur amino acids were investigated under high pressure conditions, L-methionine (Lima et al., 2008) and L-cysteine (Minkov et al., 2008, 2010; Moggach et al., 2006; Murli et al., 2006). L-methionine ($C_5H_{11}NO_2S$) crystallizes in a monoclinic structure and under compression undergoes a phase transition at about 2.2 GPa. This modification is realized by the observation of the appearance of a very strong peak between the bands associated to stretching of SC, ν(SC), and wagging vibration of CO_2^-, $\omega(CO_2^-)$. At P = 2.7 GPa, the intensity of the bands ν(SC) and $\omega(CO_2^-)$ goes to zero. Additionally, two new structures are observed around 540 cm^{-1}, in the region where it is expect to be observed the band associated to the rocking of CO_2^-, $r(CO_2^-)$. Such a picture was interpreted as a phase transition undergone by L-methionine crystal, with a hysteresis of about 0.8 GPa. On the other hand, L-cysteine can crystallize in two different polymorphs with orthorhombic and monoclinic symmetries (Minkov et al., 2010). For the monoclinic polymorph of L-cysteine it was observed phase transitions at about 2.9 and 3.9 GPa with the changes in the Raman spectra suggesting that the hydrogen bond network is distorted and the S-H…O bonding dominates over S-H…S bonding at high pressures. For the orthorhombic polymorph, a series of different phase transition occurs, but with no evidence that it transforms into the most dense monoclinic polymorph which is also stable at atmospheric pressure. It is worth to note that the phase transitions in the orthorhombic L-cysteine involve changes in molecular conformation while the pressure-induced phase transitions in the monoclinic phase are mainly related to changes in the hydrogen bond network (Minkov et al., 2010).

L-threonine ($C_4H_9NO_3$) (Silva et al., 2000) was investigated up to 4.3 GPa through Raman spectroscopy. From this study it was observed several modifications in the Raman spectrum, including the region associated to the lattice mode vibrations, mainly between 2 and 2.2 GPa. Other modifications above 3 GPa were also observed but no X-ray diffraction experiment was performed up to now, which would confirm the occurrence of eventual phase transition undergone by L-threonine crystal.

L-serine was also investigated under high pressure conditions (Boldyreva et al., 2005b, 2006a, 2006b; Moggach et al., 2005, 2006). From x-ray diffraction measurements (Moggach et al., 2005) it was observed that at ~ 4.8 GPa the crystal undergoes a phase transition with changes in the hydrogen bond network: while the low pressure phase is characterized by OH…OH hydrogen bond chains, in the high pressure phase it is observed shorter OH…carboxyl interactions. Yet, Ref. (Moggach et al., 2005) shows that the phase transition occurs with change in two torsion angles but with any major changes in the orientations of the molecules in the unit cell. Study of Ref. (Boldyreva et al., 2006b) confirms the phase transition previously reported in Ref. (Moggach et al., 2005), although with a transition pressure value of ~ 5.3 GPa, and points the existence of another phase transition at 7.8 GPa. In this second phase transition new OH…O(CO) hydrogen bond and a new NH…OH bond are formed, showing that OH-group becomes both a proton donor and a proton acceptor.

Finally, finishing this picture of the state of the art of vibrational and structural aspects of amino acid crystals under high pressure, we briefly discuss results on L-asparagine monohydrate, which was investigated both by Raman spectroscopy (Moreno et al., 1997) and by X-ray diffraction experiments (Sasaki et al., 2000). Both studies point to the occurrence of three different phase transitions between 0.0 and 1.3 GPa, which constitute, up to now, the most unstable amino acid crystal structure.

In all these investigations, the occurrence of phase transitions involving change in the dimension of the several HB in the unit cell seems to be the role. An extension of studies of

amino acid crystals under high pressure conditions investigated by Raman spectroscopy for L-histidine.HCl.H$_2$O and L-proline monohydrate is given here.

3. Experimental

The samples of HHM were grown from aqueous solution by the slow evaporation method at controlled temperature. The samples of PM polycrystals were obtained from reagent grade (Sigma Aldrich) and used without further purification. Raman experiments on HHM were performed in the backscattering geometry employing a Jobin Yvon Triplemate 64000 micro-Raman system equipped with a N$_2$-cooled charge-coupled device (CCD) detection system, while for Raman experiments on PM it was employed an HR 460 Jobin Yvon spectrometer. The slits were set for a 2 cm^{-1} spectral resolution. Raman spectra were excited with the 514.5 nm line of an argon ion laser. The high-pressure experiments at room temperature were performed on a small piece of sample compressed using a diamond anvil cell (model NBS — National Bureau of Standards). For the Raman experiments on PM it was used a membrane diamond anvil cell (MDAC) with a 400 µm culet diameter diamonds as the pressure device. A 150 µm-diameter hole in a stainless-steel (200 µm of initial thickness preindented to 40 µm) was loaded with argon, while a 200 µm-diameter hole in a stainless-steel with a 230 µm of initial thickness was loaded with mineral oil in the study of L-histidine.HCl.H$_2$O. An Olympus microscope lens with a focal distance f = 20.5 mm and a numerical aperture 0.35 was used to focus the laser beam on the sample surface, which was located in the pressure cell. The pressure in the cell was monitored using the standard shifts of the Cr^{3+}:Al$_2$O$_3$ emission lines.

4. Results

4.1 L-proline monohydrate
In this sub-section we present investigation of polycrystalline PM under hydrostatic pressure up to 11.8 GPa. It is important to state that the sample used in the experiment had a small quantity of anhydrous phase (about 8%, according to the Rietveld refinement) in such a way that the structure can be considered as monoclinic L-proline monohydrate.
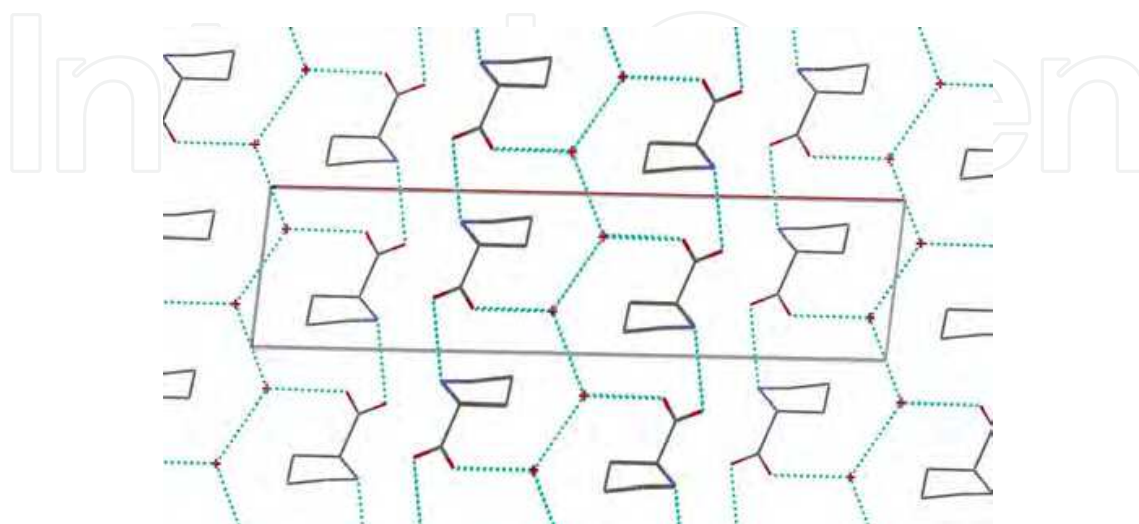

Fig. 1. Unit cell of PM seen along the *b*-axis.

PM (see Figure 1) crystal is found in a monoclinic structure, space group *C*2with a = 20.43 Å, b = 6.19 Å, c = 5.14 Å and β = 95.79° and Z=4 (Seijas et al., 2010). In such a material the hydrogen bonds play a special role in the stability of the crystal structure. X-ray diffraction study shows that there are interactions between amino and carboxylate groups through the hydrogen bonds N1-H1…O1, N1-H1…O2 and N1-H2…O1, with H1 atom acting as a bifurcated donor taking part in two hydrogen bonds. These hydrogen bonds link the proline molecules forming pairs of chains in opposite directions along the *c* axis. The water molecules form zigzag chains of O-H…O hydrogen bonds also parallel to the *c* axis (Seijas et al., 2010).

Figure 2 presents the Raman spectra of polycrystalline PM crystal in the spectral range 10 – 250 cm⁻¹ for pressures from 0.0 to 11.8 GPa. The spectrum taken at 0.0 GPa shows a complex profile indicating the occurrence of several bands; in fact, fitting with Lorentzian curves
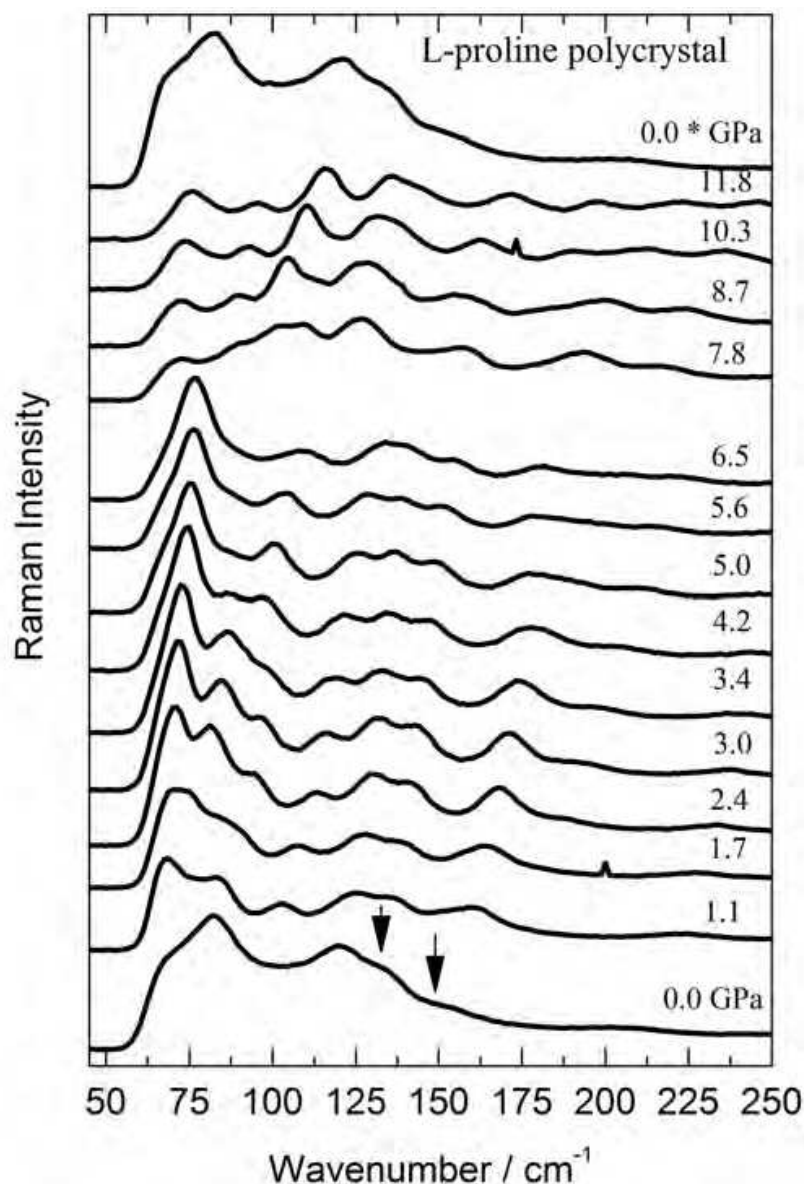

Fig. 2. Raman spectra of PM under several pressure conditions from 0.0 to 11.8 GPa in the spectral range 50 – 250 cm⁻¹.

points to the existence of six bands between 10 and 160 cm^{-1}. When pressure is increased great changes are observed in the Raman profile of the spectrum. At 1.1 GPa the Raman spectrum of L-proline is very different from that obtained at 0.0 GPa: (i) the mode peaked at ~ 68 cm^{-1} becomes the most intense band in the spectrum at 1.1 GPa; (ii) the most intense peak in the spectrum taken at 0.0 GPa decreases intensity and in the spectrum taken at 1.1 GPa it is only the second most intense peak in the region 10 – 250 cm^{-1}; (iii) the peaks marked by arrows in the spectrum at 0.0 GPa increase intensity. Such a set of modifications point to the possibility of the occurrence of a phase transition undergone by polycrystalline L-proline for pressures below 1.1 GPa. Results on other spectral regions of the Raman spectrum will reinforce this hypothesis.

It is observed a gradual change of intensity of all bands appearing in the Raman spectra of Figure 2 as well as continuous blue shifts of all wavenumbers when pressure is increased from 11.1 to 6.5 GPa. The gradual change of the profiles of the Raman spectrum can be interpreted as continuous changes of the conformation of the molecules of L-proline in the unit cell of the crystal. However, between 6.5 and 7.8 GPa it is observed a strong change in the profile of the Raman spectrum in the low wavenumber region. In particular, the most intense band observed in the spectrum taken at 6.5 GPa lost intensity becoming one of the peaks with lowest intensity. Additionally, jump in the wavenumber of almost all bands are also verified in this pressure interval (6.5 - 7.8 GPa). As a consequence, we have interpreted the changes of the Raman spectrum as a phase transition undergone by polycrystalline L-proline between 6.5 and 7.8 GPa. Other evidences will be shown in the next paragraphs. Finally, when we decrease pressure from the highest value obtained in our experiments down to atmospheric pressure we observe that the original spectrum – bottom spectrum in Figure 2 – is recovered (the final spectrum is marked as 0.0 * GPa).

Figure 3 presents the Raman spectra of PM crystal for several pressures in the spectral range 200 – 750 cm^{-1}. According to Ref. (Herlinger & Long, 1970) (see also Table 1) the band recorded close to 294 cm^{-1} in the 0.0 GPa spectrum can be associated to a deformation vibration of the skeleton of the structure, δ(skel). The bands observed at 377 and 447 cm^{-1} are associated, respectively, to the bending of CCN, δ(CCN), and rocking of CO_2^-, r(CO_2^-). In fact, for other amino acid crystals it has been reported that the r(CO_2^-) is the most intense band in the 200 – 700 cm^{-1} spectral range. However, for the other amino acids, differently from L-proline, the r(CO_2^-) mode is observed for wavenumber higher than 500 cm^{-1} (α-glycine: 503 cm^{-1} (Dawson et al., 2005); L-alanine: 532 cm^{-1}; L-valine, 542 cm^{-1} (Goryainov et al., 2005); DL-alanine, 543 cm^{-1}; etc.). Finally, in the spectrum taken at 0.0 GPa we can observe a band at 574 cm^{-1} which was associated to a bending of CO_2^-, group. Finally, bands at 641, 669 and 695 cm^{-1}, were associated, respectively, to wagging of CO_2^-, w(CO_2^-); δ(skel); and scissoring of CO_2^-, sc(CO_2^-).

By increasing the pressure we observe that between 0.0 and 1.1 GPa some important modifications are present. For example, the band δ(CCN) decreases intensity and seems to split. A clear splitting is observed for the band at 574 cm^{-1} and the r(CO_2^-) band at 447 cm^{-1} begins to present a shoulder in the high wavenumber side. Additionally, the δ(skel.) band at 669 cm^{-1} (marked by an asterisk in the spectrum of 0.0 GPa) disappears between the two lowest pressure spectra. This entire complex picture corroborates the fact that the crystal is undergoing a phase transition between 0.0 and 1.1 GPa.

If one continues to increase pressure on the PM crystal, it is possible to observe that all bands suffer blue shifts up to 6.5 GPa; also, in general terms, the linewidth increases for all bands. However, no great changes are observed, indicating that the crystal structure
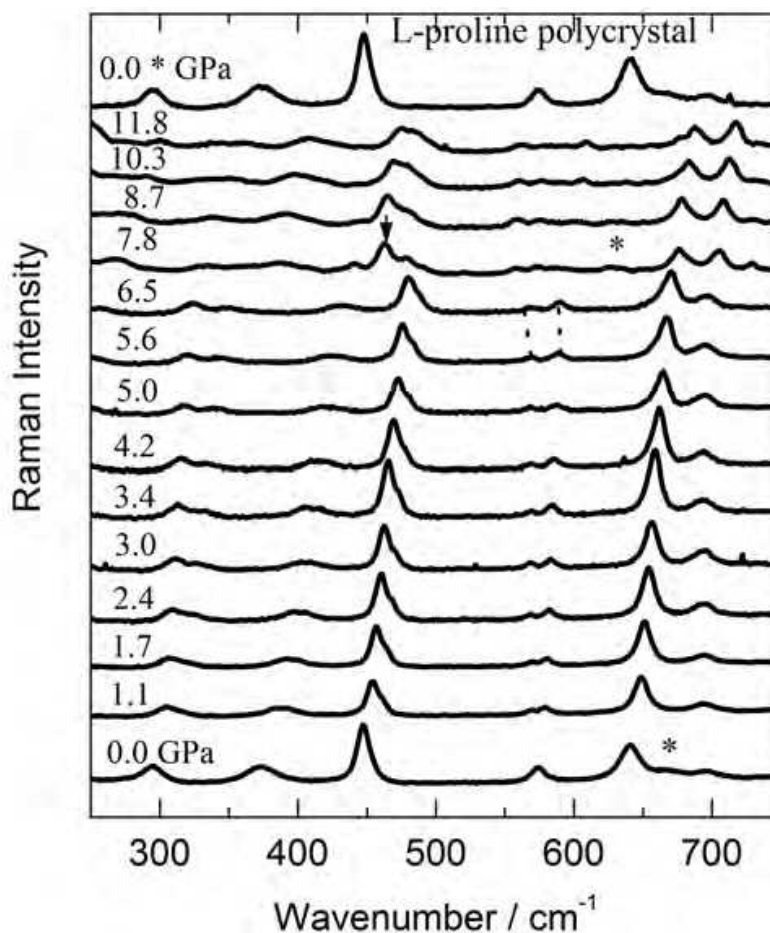
Fig. 3. Raman spectra of PM under several pressure conditions from 0.0 to 11.8 GPa in the spectral range 250 – 750 cm^{-1}.

remains the same of that observed at 1.1 GPa. In other words, the crystal seems to be stable between 1.1 to 6.5 GPa. But when pressure arrives to 7.8 GPa great modifications are observed in the 200 – 700 cm^{-1} spectral region. Let us state these modifications: (i) the appearance of a band (marked by an arrow in the spectrum taken at 7.8 GPa) in the region ~ 450 cm^{-1}; (ii) an impressive fall of intensity and a red shift of the band associated to r(CO$_2^-$); (iii) a red shift of the two bands in the region 550 – 600 cm^{-1}; (iv) the appearance of low intense bands (marked by an asterisk in the spectrum taken at 7.8 GPa) for wavenumbers higher than 600 cm^{-1}; (v) the increase of intensity of the band initially assigned as scissoring of CO$_2^-$; (vi) the appearance of a band at ~ 725 cm^{-1}. Again, the modifications in the spectra between 6.5 and 7.8 GPa presented in Figure 3 corroborate the fact that PM crystal undergoes a second phase transition, as discussed previously. When pressure is released down to 0.0 GPa, whose spectrum is marked by 0.0* GPa, we observe that the starting atmospheric spectrum is recovered, as already observed in Figure 2.

Figure 4 presents the Raman spectra of PM crystal under high pressure conditions, with argon as compression medium, in the region 600 to 1250 cm^{-1}. We have cut off the peaks in the region close to 900 cm^{-1} because there is a peak with high intensity that makes difficult the visualization of the bands close to it; this region will be discussed in Figure 5. In the Figure 4 we observe that several peaks are well defined (the peak marked by an asterisk is due a lamp used to calibrate the spectra). It is important to state that in the spectrum at 0.0

Wavenumber (cm⁻¹)	Assignment	Wavenumber (cm⁻¹)	Assignment
68	Lattice mode	950	$\nu(CCN)+\nu(CC)$
81	Lattice mode	982	$\nu(CCN)+\nu(CC)$
99	Lattice mode	991	$\nu(CCN)+\nu(CC)$
120	Lattice mode	1031	$\nu(CCN)+\nu(CC)$
134	Lattice mode	1055	$w(CH_2)$
149	Lattice mode	1079	$w(CH_2)$
203	-	1084	$r(CH_2)$
294	$\delta(skel.)$	1161	$t(CH_2)$
373	$\delta(CCN)$	1172	$t(CH_2)$
447	$r(CO_2^-)$	2876	$\nu(CH)$
574	(CO_2^-)	2898	$\delta(CH)$
641	$w(CO_2^-)$	2932	$\nu(CH)$
669	$\delta(skel.)$	2949	$\nu(CH)$
695	$sc(CO_2^-)$	2971	$\nu(CH)$
791	$\delta(skel.)$	2983	$\nu(CH)$
840	$r(CH_2)$	3006	$\nu(CH)$
863	$r(CH_2)$	3011	$\nu(CH)$
897	$r(NH_2^+)$	3041	$\nu(NH)$
918	$\nu(CCN)+\nu(CC)$	3068	$\nu(NH)$

Table 1. Wavenumber (in cm⁻¹) and approximate assignments of Raman bands for L-proline monohydrate crystal, where def., deformation; δ, bending; r, rocking ; w, wagging; sc, scissoring; ν, stretching ; t, twisting.

GPa there are two peaks between 975 and 1000 cm⁻¹ and in the spectrum taken at 1.1 GPa only one band is observed. Another aspect that worth note is the fact that the band of highest energy (~ 1172 cm⁻¹ at 0.0 GPa twisting of CH_2, $t(CH_2)$) splits in the spectrum taken at 1.1 GPa. Above this last pressure the intensity of the peaks remains approximately constant up to 6.5 GPa. Between 6.5 and 7.8 GPa the Raman spectrum presents great changes. The band associated to the rocking of CH_2, $r(CH_2)$, observed initially at ~ 840 cm⁻¹, presents both a jump to high wavenumbers and an increasing in its linewidth. A splitting is observed for the band marked by an star in the spectrum recorded at 6.5 GPa and observed initially at ~ 950 cm⁻¹, which is associated to the stretching of CCN and CC units, $\nu(CCN)$ + $\nu(CC)$. If one observe the band at 1033 cm⁻¹, which is associated to the wagging of CH_2, $w(CH_2)$, interestingly, between 6.5 and 7.8 GPa it changes intensity with the band marked by a down arrow in the spectrum taken at 6.5 GPa: so, the $w(CH_2)$ band lost intensity and the band marked by a down arrow increases intensity. Similarly, the low intense bands observed between 1080 and 1200 cm⁻¹ present great changes in their intensities between 6.5 and 7.8 GPa. All these changes corroborate the modification in the crystal structure which occurs above 6.5 GPa, which are reversible when pressure is released down to 0.0 GPa.
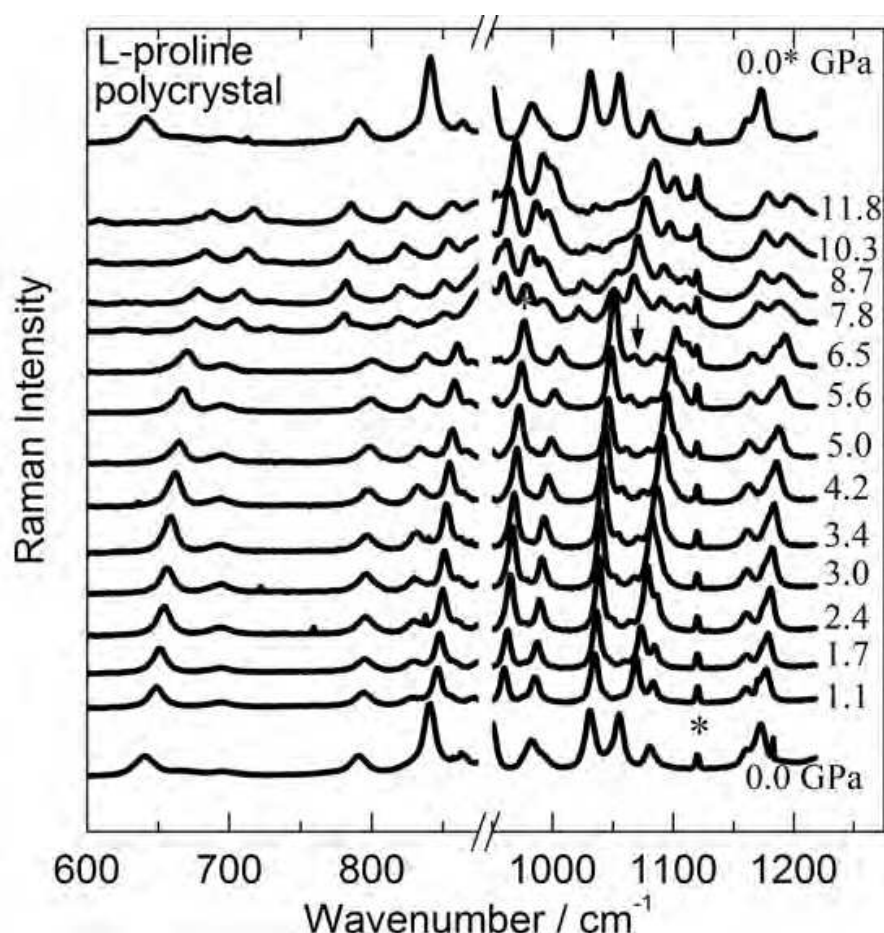
Fig. 4. Raman spectra of PM under several pressure conditions from 0.0 to 11.8 GPa in the spectral range 600 – 1250 cm^{-1}.

Figure 5 shows the Raman spectra of PM crystal in the 800 – 1100 cm^{-1} spectral region. The dominant band in the spectrum taken at 0.0 GPa observed at 897 cm^{-1} is associated to the rocking vibration of NH_2^+, $r(NH_2^+)$. The changes occurring in the first phase transition are not impressive but we note that between 6.5 and 7.8 GPa the band lost intensity and splits into two bands. Above 7.8 GPa blue shifts of the wavenumbers are verified but no great change is present up to the highest pressure arrived in the experiment. Decreasing pressure down to 0.0 GPa again, we observe that the original spectrum is also recovered in this region.

In the spectral region presented in Figure 6, it is expected to be observed bands associated to the stretching vibrations of CH and CH_2 units. A theoretical study performed on L-methionine showed that different profiles of the Raman spectrum in this wavenumber range are associated with different conformations of the molecule. In this sense, when we observe the Raman spectra of PM as a function of pressure we note that between 0.0 and 1.1 GPa, the most intense band at 0.0 GPa split into three bands (marked by up arrows). In the spectrum taken at 1.7 GPa the separation is very clear and when pressure is further increased, the bands become clearly distinct. But, between 6.5 and 7.8 GPa, the spectrum changes abruptly, indicating that between these two pressure values the proline molecules undergo a great conformational change. Because we have observed additionally, changes in the low wavenumber region we can understand that both, conformational change and structural phase transition take place for PM crystal. As observed in the other spectral regions, the original spectrum at 0.0 GPa is recovered when pressure is released.
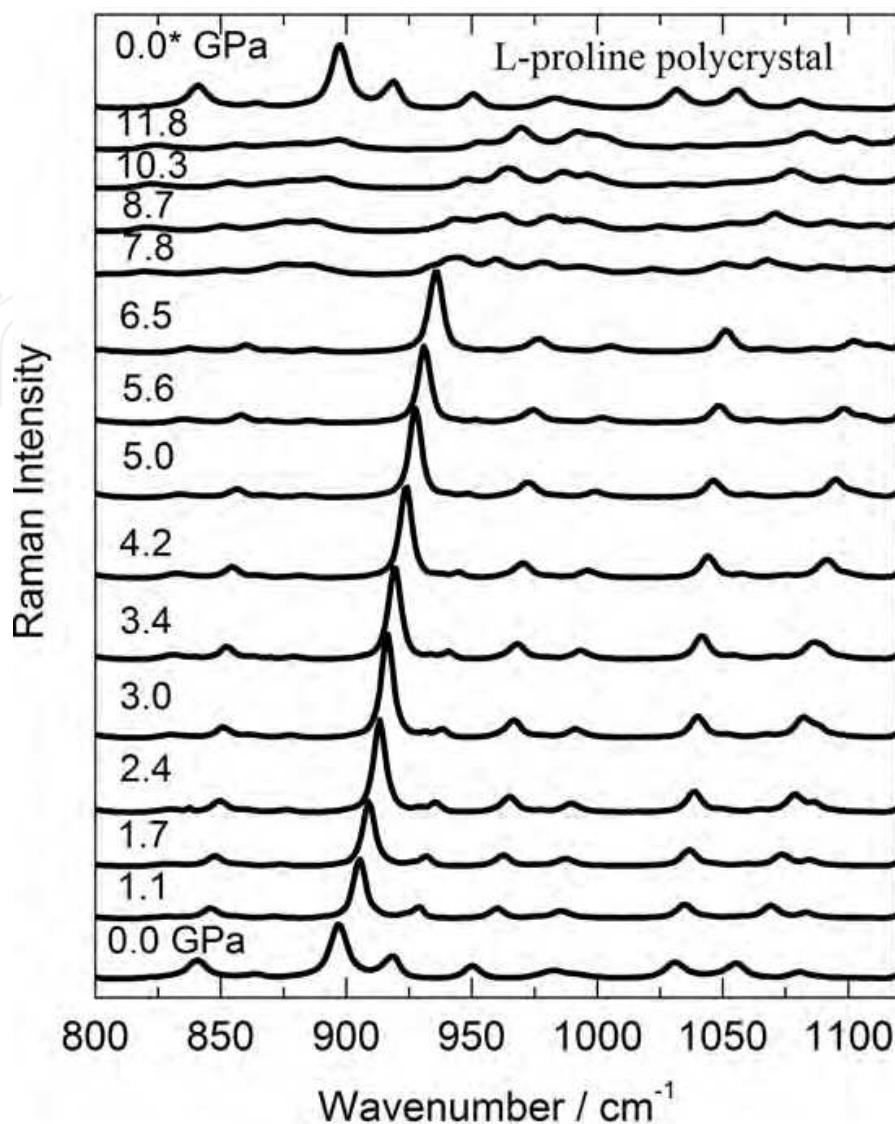
Fig. 5. Raman spectra of PM under several pressure conditions from 0.0 to 11.8 GPa in the spectral range 800 – 1100 cm^{-1}.

Data can give us some insights related to the behaviour of molecules of proline as the crystal is compressed. For example, in a previous study on α-glycine, the softening of a bending of CO_2^- was associated to a decrease in the intra-layer hydrogen bond strength, while the stiffening of the same vibration was associated to an increase in the bond strength (Dawson et al., 2005). For PM we have observed that the band associated to both bending of CO_2^-, $\delta(CO_2^-)$, and rocking of CO_2^-, $r(CO_2^-)$, increase wavenumbers from 1.1 to 6.5 GPa, and between 6.5 and 7.8 GPa decrease wavenumber; for $\delta(CO_2^-)$ the decreasing is represented by the two dashed lines in Figure 3 between the spectra of 6.5 and 7.8 GPa. We have also observed an additional increasing of wavenumbers for pressures higher than 7.8 GPa. This suggests that the intra-layer hydrogen bond strength is stiffened up to 6.5 GPa, between 6.5 and 7.8 GPa the hydrogen bond strength is softened and above 8.0 GPa, the hydrogen bond is stiffened. Additionally, our results suggest that between 6.5 and 7.8 GPa occurs a structural rearrangement in such a way that the behaviour of the hydrogen bond strengths is changed. This rearrangement is enough to change the symmetry of the crystal, because
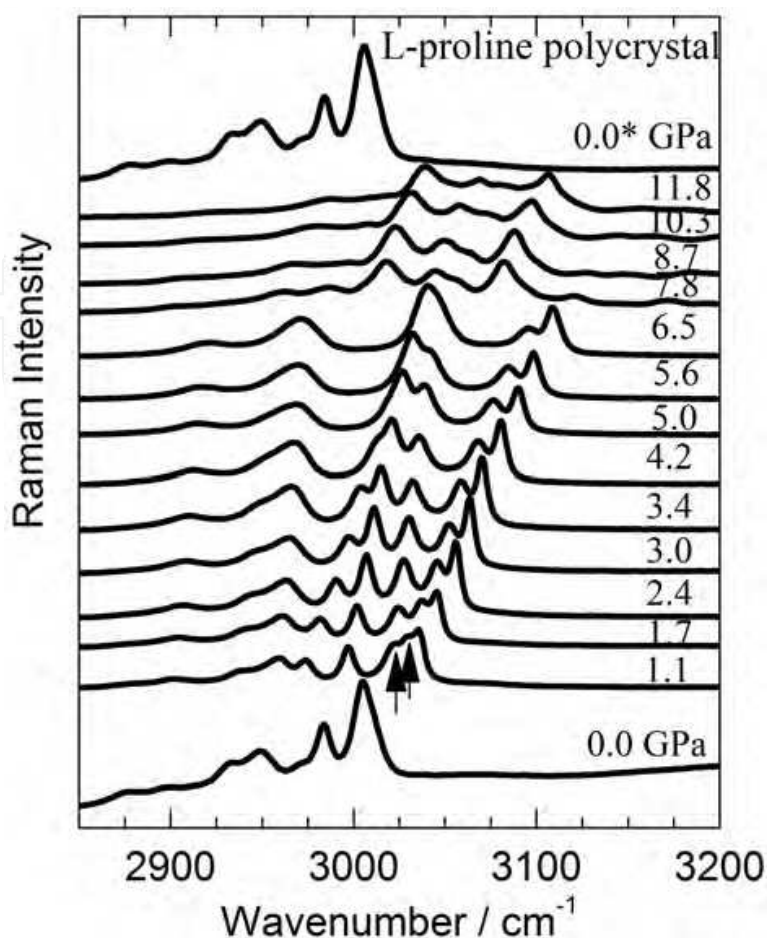
Fig. 6. Raman spectra of PM under several pressure conditions from 0.0 to 11.8 GPa in the spectral range 2850 – 3200 cm-1.

associated to it we observe great modifications in the Raman spectrum of low wavenumber region (Figure 2). Yet, related to the phase transition between 6.5 and 7.8 GPa, it is impressive the increase of intensity of a band in the spectrum taken at 6.5 GPa (marked by an arrow, see Figure 4) which can be assigned as wagging of CH_2, $w(CH_2)$; it change of intensity with the band close to it at ~ 1055 cm-1 at 0.0 GPa, which is also assigned as $w(CH_2)$, indicating that a conformational change in the ring may also occurs when the crystal undergoes the phase transition at 6.5 - 7.8 GPa.

It is also interesting to note that the first transition occurs from a monoclinic to a phase with lower symmetry (another monoclinic our a triclinic phase), because in several regions, including both internal and lattice mode spectral regions, the number of peaks in the spectrum taken at 1.1 GPa is greater than the number of Raman peaks in the spectrum taken at 0.0 GPa. It is also worth note that above 7.8 GPa almost all bands increases linewidth, indicating that some disorder is introduced in the high pressure phase. However, the disorder does not occur in a high degree because when pressure is released down to 0.0 GPa, the original spectrum is recovered. It is known that the amorphization process is preceded by some disorder in the crystal structure; however, due to recovered of the original Raman spectrum after releasing pressure we can infer that when we arrive to 111.8 GPa, we are far away from the pressure point where, eventually, the PM crystal should present amorphization.

4.2 L-histidine hydrochloride monohydrate

Related to the HHM (see Figure 8), which crystallizes in an orthorhombic structure belonging to the $P2_12_12_1$ (D_2^4) space group with four molecules of $C_6H_9N_3O_2.HCl.H_2O$ per unit cell, we were able to arrive up to 7.5 GPa and discovery a new polymorph of the material above 3.1 GPa. The strong bond between N-H of the imidazole ring and the carboxyl group of a neighboring molecule is the fundamental intermolecular link, resulting in a spiral arrangement along the c-axis (Donohue & Caron, 1964). The coupling of the four zwitterions in the unit cell leads to 297 optical normal modes decomposed into irreducible representations of the factor group D_2 as $\Gamma_{op} = 75\ A + 74\ (B_1 + B_2 + B_3)$ and the acoustic modes can be expressed as $\Gamma_{ac} = B_1 + B_2 + B_3$. Under high pressure conditions modifications, the Raman spectra are interpreted in terms of both conformational changes of the molecules in the unit cell and in terms of a phase transition.

Figure 9(a) presents the Raman spectra of HHM for several pressures in the spectral range from 50 to 660 cm^{-1}. The region for wavenumbers lower than 200 cm^{-1}, as previously stated, is characteristic of the lattice vibration modes. Increasing pressure we observe that the bands present blue shifts of their wavenumbers. However, between 2.7 and 3.1 GPa it is possible to note that a great change occurs in the Raman spectrum: the peak marked by a square, which is associated to torsion of CO_2^- ($\tau(CO_2^-)$), splits in two new peaks, which are marked by up arrows in the spectrum at 3.1 GPa. In Figure 9(b), which presents the plot of experimental wavenumber as function of pressure, we clearly observe the splitting of the band close to 180 cm^{-1}. Additionally we note that for other bands discontinuities of wavenumbers are observed between 2.7 to 3.1 GPa (De Sousa et al, 2011).
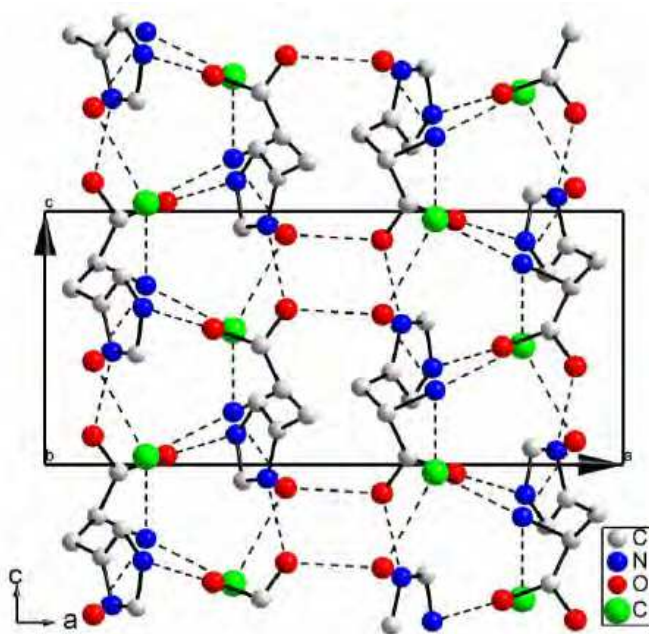

Fig. 8. Unit cell of HHM seen along the *b*-axis.

In this region, it is also possible to observe many internal vibrations of the histidine molecule, such as skeletal structure, at 442 and 490 cm^{-1}, torsion of NH_3^+, which is observed at 385 cm^{-1} and rocking of CO_2^- at 530 cm^{-1}. Again, as occurs with the spectra shown in the lattice mode region, modifications are observed in the spectral range 2.7 - 3.1 GPa. Among these changes we observed the disappearance of the bands at 276 and 500 cm^{-1} and the
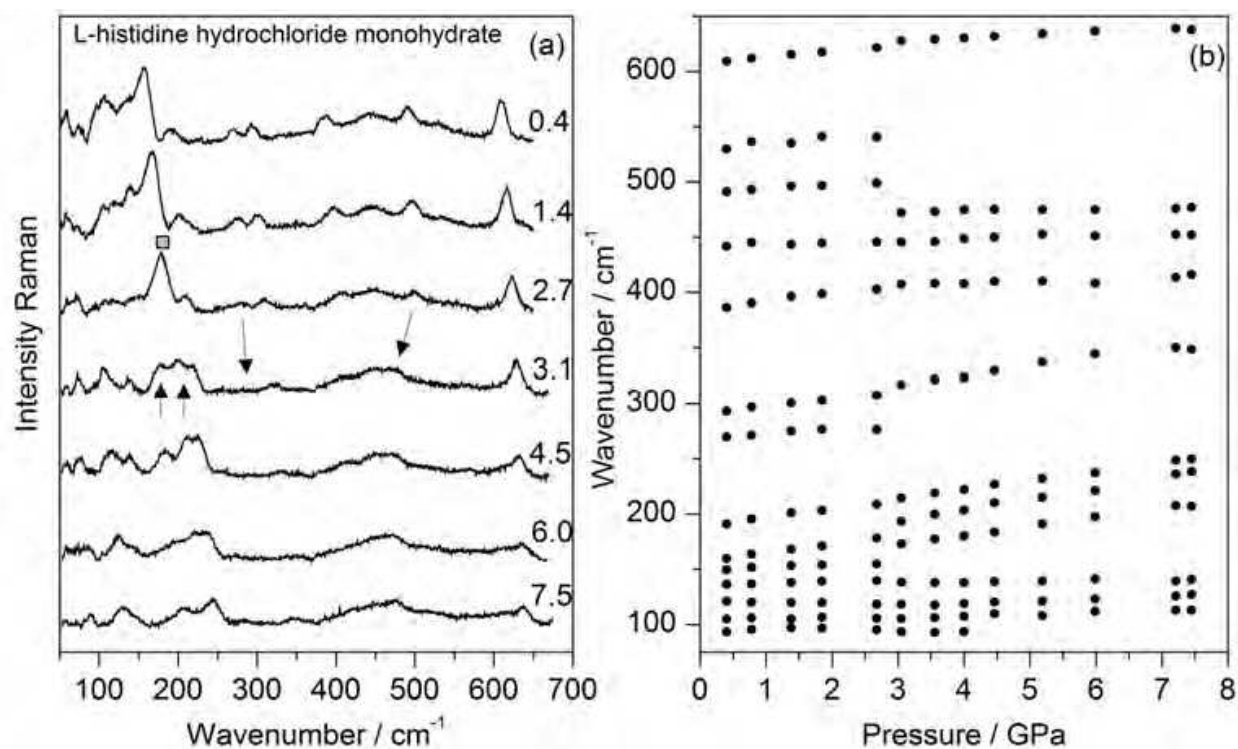
Fig. 9. (a) Raman spectra of HHM under several pressure conditions from 0.4 to 7.5 GPa in the spectral range 50 – 650 cm-1; (b) wavenumber versus pressure of the bands of HHM appearing in Fig. 9(a).

appearance of a band at 473 cm-1 in the spectrum taken at 3.1 GPa. We additionally note that the intensity of the band associated to torsion of NH_3^+ decreases with increasing pressure, indicating that there occurs a conformational change of histidine molecule. Such a conformational change can be understood as consequence of the change of the intermolecular hydrogen bond length. With increasing pressure, the band initially at 385 cm-1, which is associated with a torsion vibration of the NH_3^+ unit, shifts linearly toward higher wavenumbers; we can say that the pressure decreases the length of the hydrogen bonds, increasing the wavenumber of the band associated to torsional vibration of NH_3^+ unit.

Figure 10(a) presents the Raman spectra of HHM in the 650 – 1250 cm-1 interval for several pressure values up to 7.5 GPa. In this spectral region, it is expected to observe vibrations assigned to the deformation of CO_2^-, stretching of both C-C and C-N, wagging of H_2O and rocking of NH_3^+. The band observed at ~ 694 cm-1 is associated to a deformation vibration of CO_2^-, $\delta(CO_2)$, while the out-of-plane vibration of CO_2^-, $\gamma(CO_2)$, is observed at ~ 822 cm-1. The band at 807 cm-1 is associated with a wagging vibration of the water molecule, $w(H_2O)$. The bands recorded at 1191 and 1210 cm-1 can be assigned as the rocking of NH_3^+ unit, $r(NH_3^+)$. In this spectral region, some changes are observed in the range 2.7 – 3.1 GPa: (i) the disappearance of the band at 694 cm-1; (ii) the appearance of a new weak band at 717 cm-1 (marked by a star in the Figure 10(a)); (iii) the inversion of intensity of the two bands located at 807 and 822 cm-1 which are related to units directly involved in the hydrogen bonds and (iv) the inversion of intensity of the two bands associated to a rocking of NH_3^+ unit, $r(NH_3^+)$, located at 1191 and 1210 cm-1. The dependence of the wavenumber versus pressure plot for this spectral region is presented in Fig. 10(b) we note that many of the observed Raman modes show a small discontinuous change in the slope in the pressure-induced variation of its wavenumber in range 2.7 – 3.1 GPa.

Figure 11(a) shows the Raman spectra of the HHM crystal in the spectral range 1700-1400 cm^{-1} for pressure from 0,0 to 7,5 GPa; Fig. 11(b) shows the respective wavenumber *vs* pressure plots. In this region, one expects to observe vibrations assigned to a deformations of the imidazole ring of the histidine molecule, asymmetric stretching of the CO_2^- units, stretching of C=O, among others. In the Figure 11(a) two modifications are observed in the range 2.7 – 3.1 GPa. The first change is the decreasing of the relative intensity of the band originally at 1433 cm^{-1} and the second one is the appearance of a band at 1642 cm^{-1}. In the wavenumber versus pressure plot presented in Figure 11(b), a subtle discontinuity occurs in the range 2.7 – 3.1 GPa, with appreciably differences in slopes, where two modes change from positive to negative slopes.
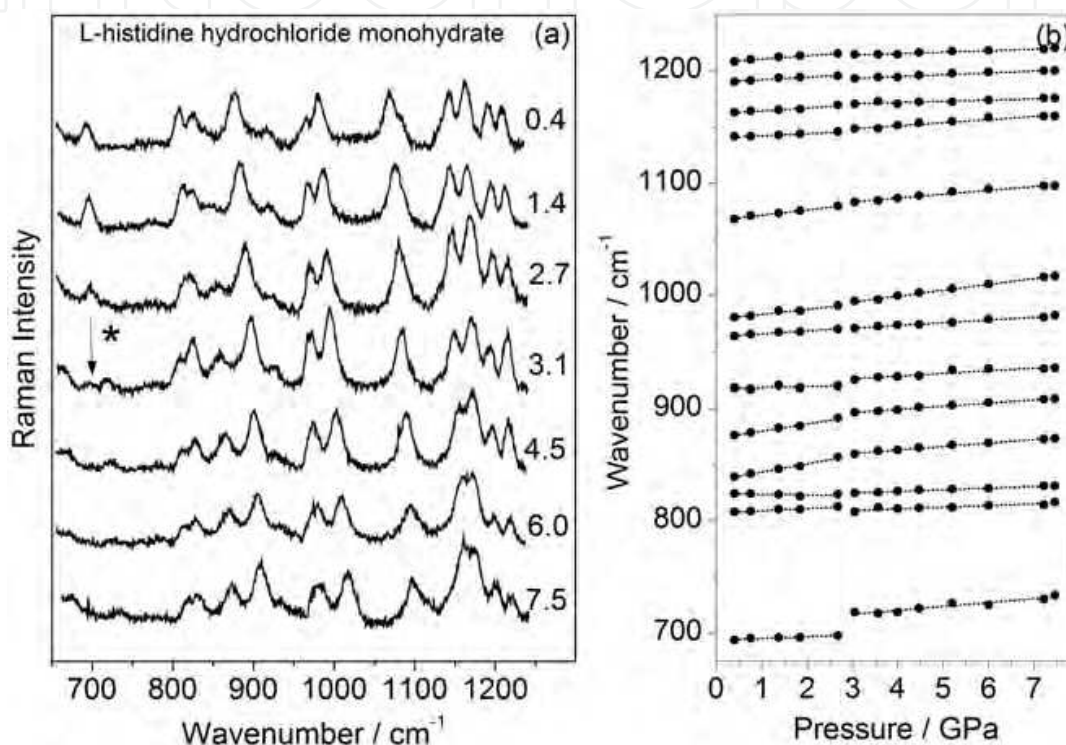

Fig. 10. (a) Raman spectra of HHM under several pressure conditions from 0.4 to 7.5 GPa in the spectral range 650 – 1250 cm^{-1}; (b) wavenumber versus pressure of the bands of HHM appearing in Fig. 10(a).

The Raman spectra of HHM crystal in the range 3450-3125 cm^{-1} are shown in the Figure 12(a) and in the Figure 12(b) the respective wavenumber *versus* pressure plots are given. In this region, we expected to observe stretching vibrations of several units of the amino acids and of the water molecule (CH, NH_3^+ and OH$^-$). It is important to note that for wavenumbers lower than 3000 cm^{-1} there are some modes related to the mineral oil used as compression media. In detail, the band at 3111 cm^{-1} can be associated to a stretching vibration of NH_3^+ unit, $\nu(NH_3^+)$, while the bands observed at 3155 and 3163 cm^{-1} are associated to a CH stretching vibration of imidazole ring. The bands observed at 3374 and 3408 cm^{-1} are related to the OH$^-$ stretching of the water molecules. In the pressure range 2.7 – 3.1 GPa, main changes are observed such as the disappearance of the bands related to a OH$^-$ stretching vibration (initially located at 3367 and 3393 cm^{-1}); the appearance of a band of weak intensity at 3424 cm^{-1} and discontinuities of the wavenumber curve of bands at 3155 and 3163 cm^{-1}, which are associated with the CH stretching vibration.
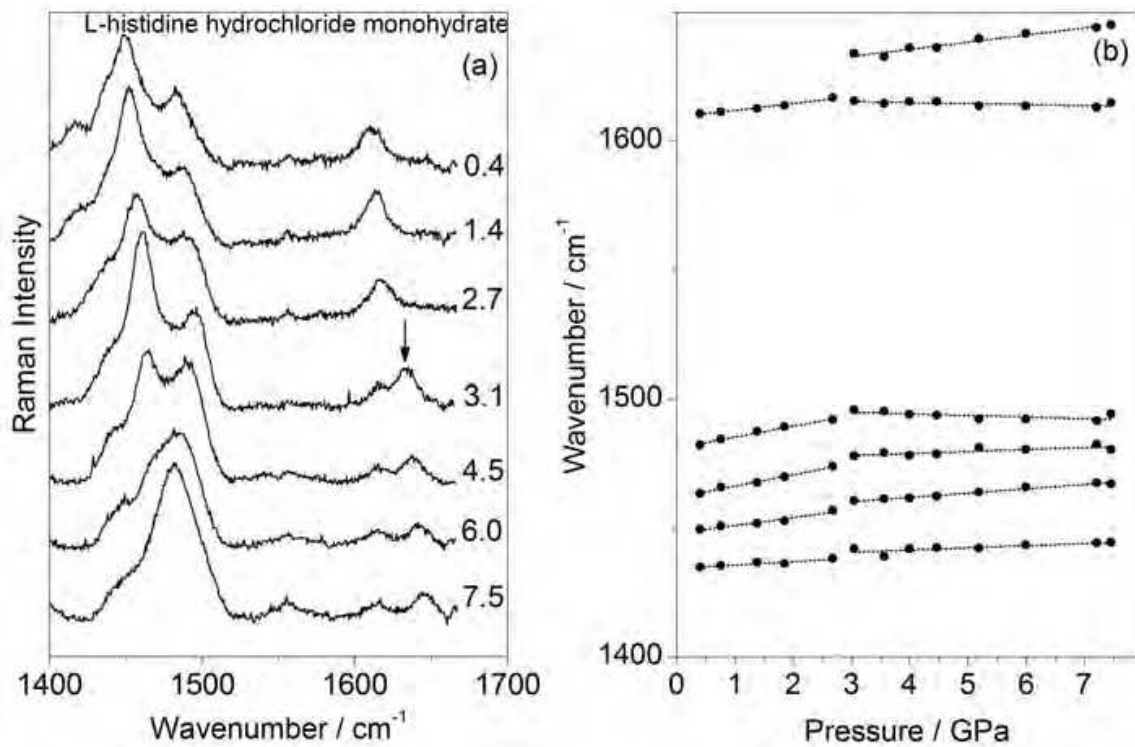
Fig. 11. (a) Raman spectra of HHM under several pressure conditions from 0.4 to 7.5 GPa in the spectral range 1400 – 1670 cm^{-1}; (b) wavenumber versus pressure of the bands of HHM appearing in Fig. 11(a).
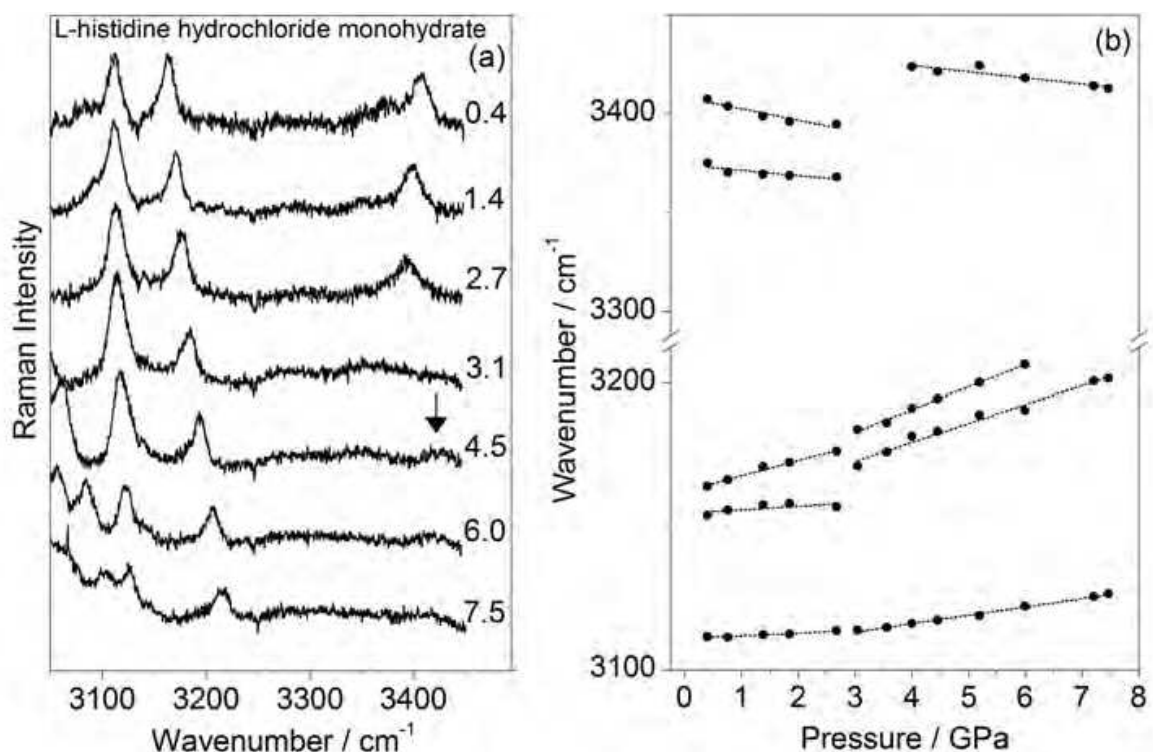

Fig. 12. (a) Raman spectra of HHM under several pressure conditions from 0.4 to 7.5 GPa in the spectral range 2950 – 3450 cm^{-1}; (b) wavenumber versus pressure of the bands of HHM appearing in Fig. 12(a).

Table 2 gives a quantitative analysis of the evolution of the Raman spectra of HHM crystal with pressure where fitting of all bands to a linear expression: $\omega = \omega_0 + \alpha \cdot P$ is furnished. In Table 2, the first column (ω_{obs}) represents the wavenumber of the Raman bands observed at room pressure, the second and third columns correspond to adjustment of data for pressure values between 0 and 2.7 GPa and the two last columns correspond to fitting of the high-pressure phase, that observed between 3.1 and 7.5 GPa.

A resume of the modifications observed in all spectral regions of the Raman spectra of HHM is as follows: (i) splitting of the band in the low-wavenumber lattice range; (ii) change in the number of bands associated to internal modes; (iii) wavenumber shifts with discontinuities; (iv) changes in the relative intensities of the vibrational bands. It is important to state that changes were observed for the deformation vibrations of the OH^- of the water molecule, as well as of the NH_3^+ and CO_2^- groups of the amino acid molecule. This picture indicates large conformational changes of the molecules in the unit cell.

Related to HHM, beyond the hydrogen bonds originated from the histidine molecule, there are two hydrogen bonds from the water molecule. It is interesting to note from Figure 12(b) that the wavenumber of OH^- stretching, $\nu(OH^-)$, decreases with increasing pressure. However, the OH units participate of hydrogen bonds, one to a carboxyl oxygen and another to the chloride ion. This means that between 0.0 and 3.1 GPa the hydrogen bond strength increases and the wavenumber of $\nu(OH^-)$ decreases in this pressure range. Also, after the phase transition, the wavenumber of $\nu(OH^-)$ suffers a jump and continues to decrease up to the highest pressure obtained in our experiments. Such a picture indicates a further increase of the hydrogen bonds formed by the water molecules and confirms that these bonds are playing an important role in the mechanism of the transition. It is interesting to note that similar changes in the low-wavenumber region were also observed for the same crystal, when subjected to low temperatures.

ω_{obs} (cm^{-1})	Phase 1 ($0 \leq P \leq 2.7$ GPa)		Phase 2 ($3.1 \leq P \leq 7.5$ GPa)	
	ω_0 (cm^{-1})	α (cm^{-1})/(GPa)$^{-1}$	ω_0 (cm^{-1})	α (cm^{-1})/(GPa)$^{-1}$
94	94.5	0.669	93.7	-0.103
105	105.2	0.276	100.2	1.771
121	121.4	-1.087	110.9	2.092
136	135.7	1.616	136.0	0.623
149	149.7	2.128	-	-
159	156.8	8.033	148.3	8.105
-	-	-	163.9	9.960
188	189.1	7.661	190.2	8.059
270	269.7	3.093	-	-
293	291.9	6.118	294.5	7.683
385	384.6	7.236	401.5	1.675
442	442.3	1.223	442.3	1.461

ω_{obs} (cm^{-1})	Phase 1 (0 ≤ P ≤ 2.7 GPa)		Phase 2 (3.1 ≤ P ≤ 7.5 GPa)	
	ω_0 (cm^{-1})	α (cm^{-1})/(GPa)$^{-1}$	ω_0 (cm^{-1})	α (cm^{-1})/(GPa)$^{-1}$
-	-	-	470.7	0.785
491	490. 5	3.319	-	-
530	530.4	4.335	-	-
609	607.8	5.312	620.8	2.463
693	693.5	1.529	-	-
-	-	-	706.4	3.449
807	806.7	2.042	804.7	1.467
824	824.0	-0.498	820.4	1.442
838	836.1	7.335	850.4	3.124
875	873.4	6.438	888.1	2.777
917	917.3	0.810	918.7	2.356
963	963.0	2.757	963.6	2.411
980	978.7	4.489	978.7	5.206
1068	1066.7	4.790	1073.2	3.418
1141	1140.3	1.890	1140.3	2.744
1162	1161.9	2.611	1167.4	1.120
1190	1190.0	2.277	1188.5	1.637
1208	1207.9	2.859	1210.1	1.341
1434	1434.5	1.316	1438.2	0.846
1448	1448.1	3.059	1455.4	1.677
1463	1462.1	4.415	1476.0	0.778
1481	1481.3	4.238	1497.0	-0.619
1609	1609.3	2.739	1616.6	-0.374
-	-	-	1624.9	2.736
3111	3111.0	0.919	3104.5	2.914
3154	3154.6	1.287	3153.2	6.564
3164	3162.6	5.305	3159.3	7.905
3375	3373.9	-2.638	-	-
3407	3408.1	-5.745	-	-
-	-	-	3437.1	-3.169

Table 2. Wavenumber values of the bands appearing in the HHM spectrum at 0.0 GPa (ω_{obs}) and adjustment data by linear fitting ($\omega = \omega_0 + \alpha.P$) for the two phases.

5. Conclusions

The results suggested that L-proline monohydrate undergoes two phase transitions, one between 0.0 and 1.1 GPa and a second between 6.5 and 7.8 GPa. In both transitions it was possible to observed changes in the spectrum profile, discontinuities in the wavenumber versus pressure plots in the lattice region of the spectrum and the appearance of news bands. By releasing the pressure after attaining a maximum of 11.8 GPa, the atmospheric pressure spectrum was fully recovered, showing that the pressure-induced transitions undergone by polycrystalline L-proline crystal are reversible. In the first transition it was observed the splitting of bands associated to $\delta(CCN)$, $\delta(CO_2^-)$ and $\nu(CH)$ vibrations. The band associated to $\delta(skel.)$ has disappeared. In the second one, we have observed the red shift of $r(CO_2^-)$, significant changes in the intensity of the bands associated to the $sc(CO_2^-)$ and $w(CH_2)$ vibrations and the splits of $\nu(CCN) + \nu(CC)$ and $r(NH_2^+)$ that also has lost intensity. These modifications were interpreted as conformational changes of molecules in the unit cell. Because these changes involve moieties that participate in hydrogen bonds, we suppose that these hydrogen bonds have also been modified. Modifications of hydrogen bonds can trigger some molecular rearrangements that lead to structural phase transitions. In our work this hypothesis was supported by the changes that were observed in the region of the lattice modes for both phase transitions. Therefore, the results suggested two structural phase transitions, one between 0.0 and 1.1 GPa, and another between 6.5 and 7.8 GPa, accompanied by significant conformational changes of molecules in the L-proline monohydrated crystal.

The results also suggest that HHM crystal undergoes a phase transition between 2.7 and 3.1 GPa when it is submitted to high pressure conditions, up to 7.5 GPa. The main changes observed in the Raman spectra was the splitting of the band in the low-wavenumber lattice range, change in the number of bands associated to internal modes and wavenumber shifts with discontinuities.

Having described the behavior of two amino acid crystals under pressure and looked back at the past fourteen years of research we can ask to ourselves what does the future hold. Based on the studies performed we believe that the use of several techniques such as neutron and Raman scattering as well as thermal and infrared analyses can help us to give a complete picture about hydrogen bond and the behavior of amino acids under pressure. Maybe, the study of peptide under similar external conditions should be the next road to be walked.

6. Acknowledgment

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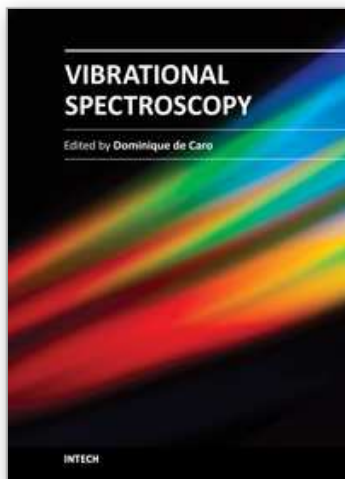
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