

Article

The Behavior of the Deformation Vibration of NH₃ in Semi-Organic Crystals under High Pressure Studied by Raman Spectroscopy

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Abstract: Single-crystal samples of the semi-organic compounds mono-L-alaninium nitrate and monoglycine nitrate have been studied by Raman spectroscopy in a diamond-anvil cell up to 5.5 GPa, in order to observe the behavior of the deformation mode of NH₃ units. It was observed for these semi-organic crystals that increasing pressure produces a decrease in the wavenumber of the band associated with the deformation vibration, differently from most of the modes. Comparatively, mono-L-alaninium has a higher dv/dP than monoglycine nitrate, for the band associated with the deformation vibration. The anomalous behavior is explained in terms of the effect of high pressure in the short and linear intermolecular hydrogen bonds.

Keywords: semi-organic crystals; high-pressures; raman spectroscopy

1. Introduction

Hydrogen bonds (H-bond) play a very special role in the interactions among molecules of biological interest, including those with large applications and importance for pharmaceutical and medical sciences [1,2]. One way to gain insights about the behavior of H-bonds is approximating molecules through the application of high pressure. Unfortunately, there is the problem of obtaining accurate information on the H-atom positions and a complete picture of the effect of high pressure on H-bonds, which is a difficult experimental task. In fact, an H atom has only one electron, which makes them very hard to detect with X-rays accurately because X-rays are scattered from the electron density. On the other hand, thermal neutrons diffract strongly from the nuclei of H atoms, which make them detectable by using nuclear reactors, but the accessibility for researchers is limited.

Regarding the studies of amino acids from a structural point of view, only a few works have focused on the question of H-bonds. These investigations attempted to furnish a description of this interaction and to understand the stability of the crystal structure. For example, in the orthorhombic phase of L-cysteine, the values of the S-H•••O and the S-H•••S angles remain unknown and a complete picture of the effect of high pressure on H-bonds was not obtained [3]. On the other hand, an X-ray crystallographic study in L-alanine furnished a good picture about the high pressure effect in H-bonds [4]. In that work high-pressure single-crystal X-ray measurements were shown, which were carried out using L-alanine-h₇ combined with high-pressure neutron powder diffraction measurements, carried out with L-alanine-d₇ and DFT (Density functional theory) calculations. One of the main effects

of pressure in strong N-H...O bond is reducing significantly the bond angle, which varies from an average 155.75° at room pressure to 148.97° at 9.87 GPa [4].

Calculations on crystals using the DFT methodology have proven to be quite accurate [5]. A recent study on L-tyrosine under high pressure [6] showed that it is not possible to distinguish substantial differences between the theoretical spectrum and the experimental FT-IR spectrum. However, we are not using such calculations in the present work. Additionally, a complete picture of the effect of high pressure in H-bonds is not trivially obtained through high pressure crystallographic experiments. For example, deuteration, which requires a difficult procedure to obtain samples, is essential for neutron powder diffraction [4] due to the differences in scattering amplitude caused by the replaced H atom by the deuterium [7]. Thus, the main strength of Raman spectroscopy is the ability to provide a great wealth of easily analyzable qualitative information very rapidly, providing a powerful diagnostic of this process.

In other words, high-pressure Raman spectroscopy can provide interesting insights on the effect of high pressure in H-bonds. For example, we observed for the first time that the behavior of the NH_3^+ torsional mode in L-alanine is unusual because it presents a negative slope in wavenumber shifts with pressure ($dv/dp < 0$). We have interpreted this to be a consequence of the particular characteristics of H-bond geometry, where, on compression, the N-H...O bonds become less linear [8].

It is worth mentioning that a recent Raman scattering study, focusing on polymorphism [9], studied mono-L-alaninium nitrate under high pressure and observed a phase transition between 3.5 and 4.1 GPa. In another study, on monoglycine nitrate under high pressure [10], the occurrence of two phase transitions in the network modes between 1.1–1.6 GPa and 4.0–4.6 GPa was observed. In the present study, the focus is on the influence of the hydrogen bonds in a specific vibrational dynamic in the two semi-organic crystals. In addition, we try to show that the Raman spectroscopic technique is an easier way to obtain experimental results on these binding behaviors than crystallographic techniques.

This work is the continuation of a Raman spectroscopic investigation to monitor the effects of high pressure in H-bonds. Now we show a study about the behavior of the deformation mode of NH_3^+ unit, $\delta(\text{NH}_3^+)$, in two semi-organic compounds, mono-L-alaninium nitrate ($+\text{NH}_3\text{-CH}_3\text{-OH-COOH}$, NO_3^-), and monoglycine nitrate ($+\text{NH}_3\text{-CH}_2\text{-COOH}$, NO_3^-). The analysis allowed us to understand the change of geometry of H-bonds in the two compounds as a consequence of high pressure application.

2. Materials and Methods

Crystals of mono-L-alaninium nitrate were prepared by slow spontaneous evaporation of a solution of L-alanine 99%, Sigma-Aldrich (St. Louis, MO, USA) in nitric acid, Erba Lachema (Brun, Czech Republic), 1 mol/L (in a molar ratio of 1:1) at laboratory temperature. Crystals of monoglycine nitrate were prepared by reaction equimolar of glycine 98% Sigma-Aldrich (St. Louis, MO, USA), and nitric acid 65% Dinâmica (Diadema, Brazil), at laboratory temperature. To confirm the orthorhombic $P2_12_12_1$ structures of both crystals, X-ray diffraction patterns of crushed powder were recorded using a Philips Analytical X-ray diffractometer (Model PW1710) with Cu $K\alpha$ radiation. A Raman scattering experiment was performed from a small crystal in a membrane diamond anvil cell (MDAC), whose hole diameter in a stainless gasket was $\sim 130 \mu\text{m}$ pre-indented to a thickness of $\sim 54 \mu\text{m}$. The pressure in the cell was monitored using the shifts of the $\text{Cr}^{+3}:\text{Al}_2\text{O}_3$ lines. The pressure calibration is expected to be accurate to ± 0.08 GPa. The mineral oil Nujol was used as a hydrostatic pressure medium. The excited source was a semi-conductor Nd:YVO₄ laser, model Verdi V-5 of Coherent, with a line beam of 532 nm operating at 250 mW. However, due to the experimental laser assembly scheme, only a small fraction of the output power is absorbed by the sample. Therefore, the effect of the temperature increase of the sample in our work is neglected, an approximation commonly used in this type of experiment. The backscattering light was analyzed using a Jobin Yvon Triplemate 64,000 micro-Raman system equipped with an N_2 -cooled CCD system. The slits were set for a 2 cm^{-1} spectral resolution. The laser beam was focused on the sample surface using an Olympus BX40 microscope lens with

$f = 20.5$ mm. Spectra with six 90-s acquisitions were made. From this point, increasing numbers or acquisition time did not result in better spectrum performance.

3. Results and Discussions

In mono-L-alaninium nitrate (MAN), the structure molecule is in the form of a protonated alaninium cation ($+NH_3-CH_3-OH-COOH$). Each NH_3^+ group forms three conventional H-bonds. The bonds with lengths 2.830 and 2.900(1) Å, connect NH_3^+ group and nitrate anions (NO_3^-). The intermolecular bond with length 2.877(1) Å, connects the NH_3^+ group and $-COOH$ group [11].

In monoglycine nitrate (MGN) the molecule exists as $+NH_3-CH_2-COOH$, NO_3^- . Because H-bonds are long-range interactions, a group N-H is bonded to more than one acceptor (oxygen atom) at the same time and two of the hydrogen atoms of the NH_3 group form bifurcated hydrogen bonds (BH-bond). The third hydrogen atom of the NH_3^+ group forms a strong intermolecular conventional hydrogen bond (H-bond) with lengths 2.792 Å and angle 169° [12]. Figure 1 presents the local H-bond environment, with length and angle, of the NH_3^+ group in both (a) MGN and (b) MAN.

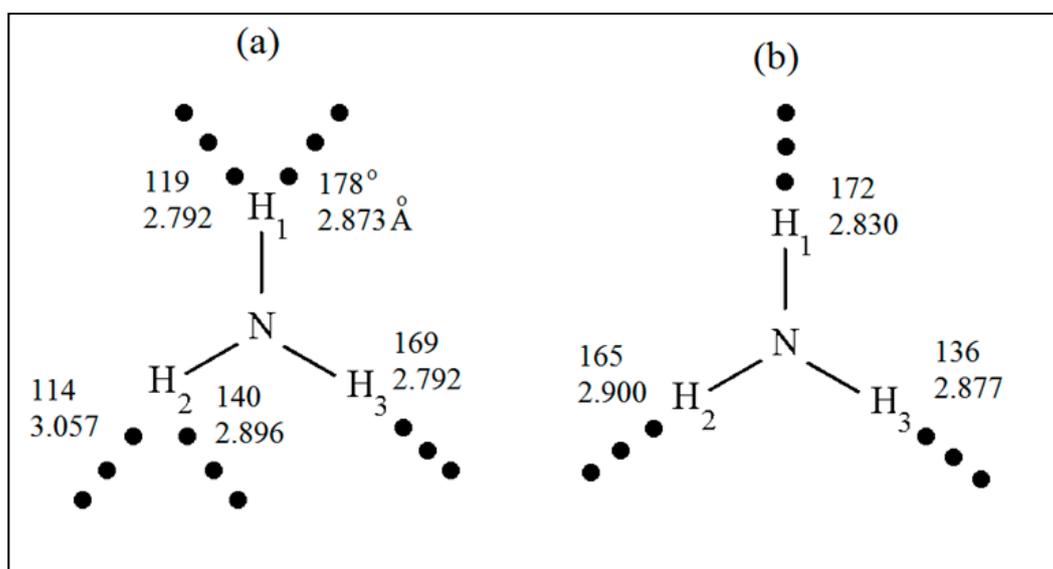


Figure 1. Representation of NH_3^+ group in (a) monoglycine nitrate and (b) mono-L-alaninium nitrate showing the hydrogen bonds with their respective lengths and angles.

An analysis and comparison of the H-bonds in both compounds reveals substantial differences. In fact, in MGN, the presence of two BH-bonds is observed, and these interactions are longer than most of the H-bonds in MAN, e.g., N-H...O. As a consequence, usually, the BH-bond has the characteristics of weak H-bonds [13].

Figure 2 presents the Raman spectra of MGN and MAN in the wavenumber region where the observation of deformation bending vibration of NH_3^+ , $\delta(NH_3^+)$ is expected, for two different pressure values. The pressure dependence of the wavenumber modes between 0.0 and 5.5 GPa is presented in Figure 3, where MGN is represented by the symbol (■) and MAN by the symbol (□). The wavenumber pressure dependence of the bands exhibits a linear behavior. In order to furnish a quantitative analysis of the behavior of the wavenumber pressure dependence, Table 1 shows the wavenumber values for $\delta(NH_3^+)$ (at atmospheric pressure) and the variation of the wavenumber as a function of pressure (dv/dP), for MGN and MAN.

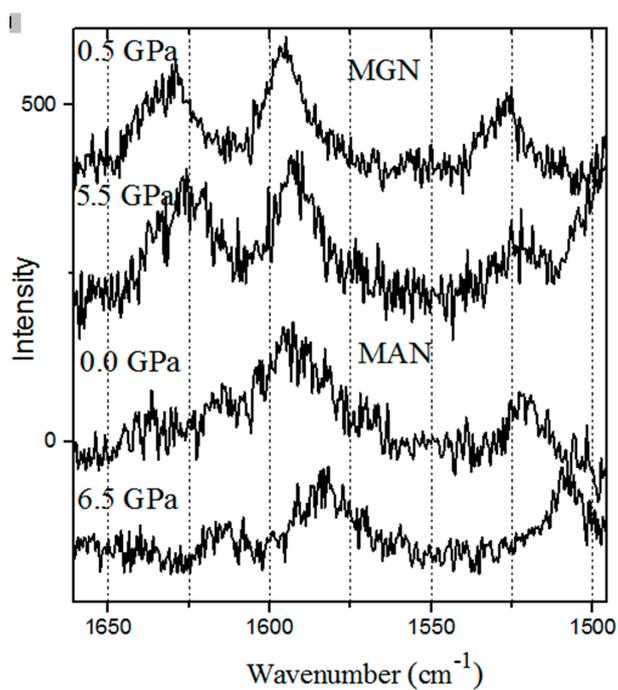


Figure 2. Raman spectra of monoglycine nitrate (MGN) and mono-L-alaninium nitrate (MAN) for two different pressures, showing the region where it is expected the observation of mode associated with the bending of NH₃⁺.

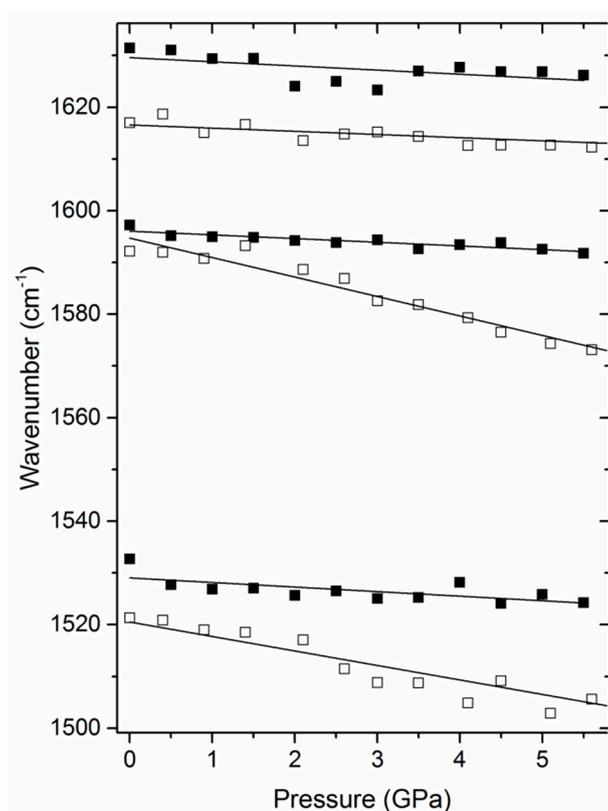


Figure 3. Wavenumber of the mode associated with bending of NH₃⁺ as a function of pressure for monoglycine nitrate (full symbols) and mono-L-alaninium nitrate (empty symbols).

Table 1. The wavenumber at atmospheric pressure ν (cm^{-1}) of the deformation mode of NH_3^+ unit and the variation of the wavenumber as a function of pressure ($d\nu/dP$).

MGN		MAN	
ν (cm^{-1})	$d\nu/dP$ ($\text{cm}^{-1}/\text{GPa}$)	ν (cm^{-1})	$d\nu/dP$ ($\text{cm}^{-1}/\text{GPa}$)
1533	−0.9	1521	−2.8
1597	−0.7	1592	−3.8
1631	−0.8	1617	−0.6

In general terms, the Raman bands are shifted to higher wavenumbers with increasing pressure because interatomic and intermolecular bonds stiffen as they shorten. The experimental result presented here indicated an anomalous behavior of the $\delta(\text{NH}_3^+)$ for both of the compounds with negative $d\nu/dP$ values. It is observable that the $\delta(\text{NH}_3^+)$ of H bond is influenced by the pressure effects, making it less linear and weakening the bonds. Additionally, for MAN, $d\nu/dP$ values vary more strongly. It is reasonable to affirm that the wavenumber of the NH_3^+ vibrations strongly depends on the local H-bond environment, as reported in [8] for the NH_3^+ torsional mode in L-alanine. In other words, the wavenumber behavior for the $\delta(\text{NH}_3^+)$ modes should be dominated by pressure effects on H-bonds set.

The NH_3^+ unit in MGN, is endowed with BH-bonds in two H-atoms (H1 and H2) and a strong H-bond (H3). Competitive interaction occurs between BH-bonds and strong H-bonds with compression having an effect on $d\nu/dP \sim -1.0 \text{ cm}^{-1}/\text{GPa}$ for $\delta(\text{NH}_3^+)$ bands. On the other hand, the NH_3^+ unit in MAN, endowed with three relatively strong H-bonds, having as an effect a higher variation in $d\nu/dP$ values than MGN, with $d\nu/dP \sim -4.0 \text{ cm}^{-1}/\text{GPa}$ for $\delta(\text{NH}_3^+)$ bands.

These results suggest a model to explain the unusual behavior of the $\delta(\text{NH}_3^+)$ mode for both compounds, where strong H-bonds become less linear with increasing pressure pointing to a weakening of the force constant at higher pressures. A similar effect occurs with H-bonds in L-alanine as verified through the behavior of the NH_3^+ torsional mode. In MGN, pressure has the effect of strengthening BH-bonds and weakening strong H-bonds resulting in a small variation of $d\nu/dP$ for $\delta(\text{NH}_3^+)$ bands. In MAN, which has three very strong H-bonds, the pressure increase causes the weakening not only of one h-bond, but of three, by decreasing linearity. Thus, this results in a large variation of $d\nu/dP$ for $\delta(\text{NH}_3^+)$ bands.

In a previous Raman spectroscopic work on MGN [10], we have studied the phase transition phenomenon, but we were not able to detail the effect of high pressure in the H-bonds. In that study, we have presented the behavior of the NH_3^+ torsional mode (at 506 cm^{-1} at atmospheric pressure) in MGN, that shows a positive slope in wavenumber shifts with pressure ($d\nu/dP = 1.1 \text{ cm}^{-1}/\text{GPa}$). According to our model, the NH_3^+ torsional mode in MGN is dominated by the effects of pressure on the weak BH-bonds, strengthening of the force constant at higher pressures. Unfortunately, the bands corresponding to the NH_3^+ torsional mode in MAN, which are very important for monitoring the hydrostatic pressure effects in the H-bonds and strengthen our model, are difficult to follow in the Raman spectra since they are too weak. In subsequent studies, the DFT investigation could contribute to elucidating what happens to the H bonds, completing the experimental observation.

The pressure or stress-induced wavenumber shifts $\Delta\nu/\nu$ are mainly determined by the associated deformation of volume, $\Delta V/V$. Pressure affects the equilibrium spacings between nuclei, distorts the electron clouds, and, through them, modifies the restoring forces. Interatomic potential containing power laws or exponential terms are strongly anharmonic, and are composed by attractive and repulsive terms [14]. Therefore, for short and linear N-H...O bonds, the approximation of the N, H, and O atoms, due to compression, is impeded by the repulsive terms of the interatomic potential having the effect of reducing the angle of the bond.

On one hand, our study showed the behavior of the H-bond geometry due to pressure effects. On the other hand, very recently, a study has shown that certain guest molecular inclusions result in

stronger H-bonds [15]. This means that H-bonds play a fundamental role in binding guest molecules to the respective host compounds, with a clear influence on the link of the host-guest complex [15]. So, we give as a suggestion for future works the investigation of host-guest compounds under high pressure conditions in order to draw a picture about the joint effects of strengthening H-bonds due to both the guest and the pressure effect itself.

4. Conclusions

We have presented a study on simple semi-organic compounds, mono-L-alaninium nitrate and monoglycine nitrate, in order to shed light on the problem of the effect of high pressure in H-bonds. Particularly, we have studied the pressure-dependence of the bending mode of the NH_3^+ unit under the scrutiny of a spectroscopic tool, an easier access tool than experimental methods used by [4]. The experimental results indicated that strong N-H...O bonds, at room temperature, become less linear and weak with increasing pressure, and, comparatively, the wavenumber behavior for the $\delta(\text{NH}_3^+)$ modes should be dominated by pressure effects on the H-bonds set. Additionally, the present study has improved the discussion about the effect of high pressure on H-bonds, complementing a previous work where the torsional vibrations of the same group in certain amino acids crystals were investigated.

Author Contributions: In this work, A.L.d.O.C. and R.J.C.L. conceived of the presented idea, R.A.S. and P.d.F.F.F. carried out the experiment, A.L.d.O.C. and R.J.C.L. wrote the manuscript with input from all authors. All authors discussed the results and contributed to the final manuscript.

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