

High-pressure Raman study of taurine crystal

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Single-crystal samples of taurine, $\text{NH}_3\text{C}_2\text{H}_4\text{SO}_3$, were studied by Raman spectroscopy in a diamond-anvil cell up to pressures of 5.6 GPa. From the analysis of the results we observed that the crystal undergoes a phase transition at about 0.7 GPa. The transition is accompanied by the appearance of a phonon in the external mode region of the spectrum and by changes of both the wavenumber of the CCN bending and of the CSH torsional vibrations. Additionally evidence for a second phase transition occurring at 5.2 GPa was observed. Pressure coefficients for all modes observed in this work are also given. Copyright © 2001 John Wiley & Sons, Ltd.

INTRODUCTION

It is well known that in the solid state, the packing of the molecules is determined both by their shape and by the variety of intermolecular forces present. Among the different kinds of forces, the hydrogen bond deserves particular attention because of the role played by it in the biological molecules and in the life molecular processes themselves. Through the observation of molecular vibrational modes it is possible to obtain some information about the molecular conformation and about the bond between the molecules. The vibrational spectra of certain amino acids, peptides and other relatively simple organic substances have been studied and assignments for the fundamental vibrations have been proposed.^{1–8} These studies have included considerations of the effects of some types of intermolecular forces on the vibrational wavenumbers in the crystal,⁹ derivation of the force constants for amino acid molecules and normal coordinate analyses for several isotopomers,¹⁰ the nature of the coordination in specific groups of amino acids,¹¹ and the role played by hydrogen bonding in their molecular configuration.^{10,12}

On the other hand, high-pressure studies are revealing new and important aspects of biological systems as structure and function of molecules, and are aiding the understanding of exceptionally complicated biological functions of living organisms.¹³ We have recently been investigating the effects of variable pressures on the Raman spectra of some

biological crystals, in particular amino acid crystals such as monohydrated L-asparagine¹⁴ and L-alanine.¹⁵ In this paper we present and discuss the spectra of taurine, an aminosulfonic crystal (a structure very similar to the structure of amino acid crystals) under high hydrostatic pressure conditions.

Taurine (2-aminoethylsulfonic acid) is a substance found in several organs of the human body such as heart, brain, liver, muscle and some fluids such as bile.¹⁶ It is believed that taurine plays a fundamental role in neuronal mechanisms and its low concentration in the body can be associated with neurological abnormalities.¹⁷ In water solution taurine has a zwitterion configuration and in the crystal the molecules are held by a three-dimensional network of N—H...O hydrogen bonds.^{18,19}

EXPERIMENTAL

Crystals of taurine used in the experiments were grown from aqueous solution by slow evaporation at 294 K. High-pressure experiments at room temperature were carried out with small single crystals of taurine along the [010] direction, selected by x-ray analysis. Raman spectra were measured for a small crystal in a standard diamond-anvil cell. 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 excitation source for the Raman experiments was 514.5 nm radiation from an argon ion laser operating at 100 mW (output power) and less than 10 mW on the sample. The backscattering light was analyzed using a Jobin Yvon Triplemate 64000 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 a lens with $f = 20.5$ mm. To ensure focusing of laser on the sample when Raman spectra were recorded or on the

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ruby chip when pressure was calibrated, an image of the pressure compartment, the hole in the gasket, was recorded by a CCD camera.

RESULTS AND DISCUSSION

The taurine crystal crystallizes in a monoclinic structure in a C_{2h}^5 space group with four molecules per unit cell.¹⁹ All ions occupy C_1 local sites symmetries. The 168 vibrations of a taurine crystal can be decomposed into irreducible representations of the factor group C_{2h} as $\Gamma = 42(A_g + B_g + A_u + B_u)$, where A_g and B_g modes are Raman active and A_u and B_u modes are infrared active. At room temperature and atmospheric pressure, 38 modes in the A_g representation and 37 modes in the B_g representation were observed.²⁰ In the Raman-active representations the external modes of the crystal are observed at about 45, 71, 77, 98, 112, 137, 187 and 233 cm^{-1} .

In Fig. 1(a) we show the Raman spectra of taurine crystal in the low-wavenumber region for six different pressure values. The peak marked by an asterisk corresponds to a plasma line of the laser serving the purpose of calibration. The peak marked C (at $P = 0.00\text{ GPa}$), centered at 137 cm^{-1} , is the only band observed between 120 and 170 cm^{-1} in both A_g and B_g representations of the C_{2h}^5 factor group.²⁰ With increasing pressure, the wavenumber of peak C increases to 0.52 GPa . The positive pressure shift observed for external modes, as the mode associated with peak C, is to be expected since the strength of the interactions between the adjacent molecules should increase as the distance between the molecules is decreased. No new feature is observed in this pressure range in the spectral region of Fig. 1(a). For a pressure of 0.78 GPa an additional feature is clearly observed: a large band at

about 125 cm^{-1} . In fact, a new band is appearing in the spectrum of 0.78 GPa . This new band is marked with an arrow in Fig. 1(a). In Fig. 2(a) we plot the wavenumber of the bands of low energy as function of pressure up to a pressure value where it is possible to observe the bands with a reasonable intensity allowing the fitting procedure. In Fig. 1(b) we show the Raman spectra for different pressures in the wavenumber region $160\text{--}300\text{ cm}^{-1}$. Bands marked D and E are centered at ~ 187 and 233 cm^{-1} , respectively. The wavenumbers of these two bands are plotted as a function of pressure in Fig. 2(b). From this figure, a clear discontinuity of the wavenumber $\tilde{\nu}$ curve is also observed for pressures between 0.52 and 0.78 GPa .

When pressure is applied to a crystal the Raman spectra can suffer mainly three effects: (i) band wavenumber shifts to higher values, in a general way; (ii) lineshape changes; (iii) when a phase transition is induced, selection rules change and this will come to light through the appearance of new features in the spectra because either forbidden excitations become Raman active or degeneracies are lifted. The set of the changes in the low-wavenumber spectra of taurine crystal [e.g. the appearance of a new line in the external mode region, and the discontinuity of the $\tilde{\nu}(P)$ curves] allows one to visualize them as evidence for a pressure-induced phase transition undergone by the taurine crystal between 0.52 and 0.78 GPa . In Fig. 2(b) the vertical dashed line at about 0.7 GPa corresponds to the boundary between the region of the low-pressure phase (C_{2h}^5) and the region of the high-pressure phase, which we called β -phase. The second vertical dashed line at $\sim 5.3\text{ GPa}$ will be discussed later. Table 1 gives the coefficients for the linear fittings for the external and the internal modes observed in this work. In this table, $\tilde{\nu}_{0\text{ obs}}$ represents the wavenumber of

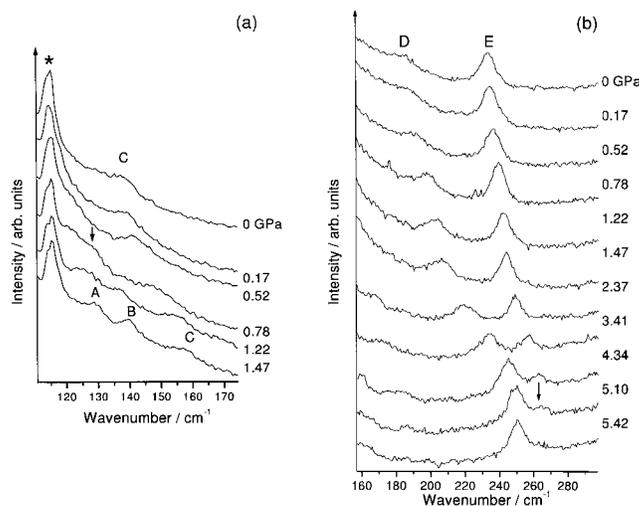


Figure 1. (a) Pressure Raman spectra of the taurine crystal in the low-wavenumber region obtained with increasing pressure at room temperature. The asterisk above the peak at about 117 cm^{-1} represents a plasma line and the band marked with an arrow is the band B, which is clearly observed in the spectrum at 1.47 GPa . (b) Pressure Raman spectra of the taurine crystal in the wavenumber region $160\text{--}300\text{ cm}^{-1}$.

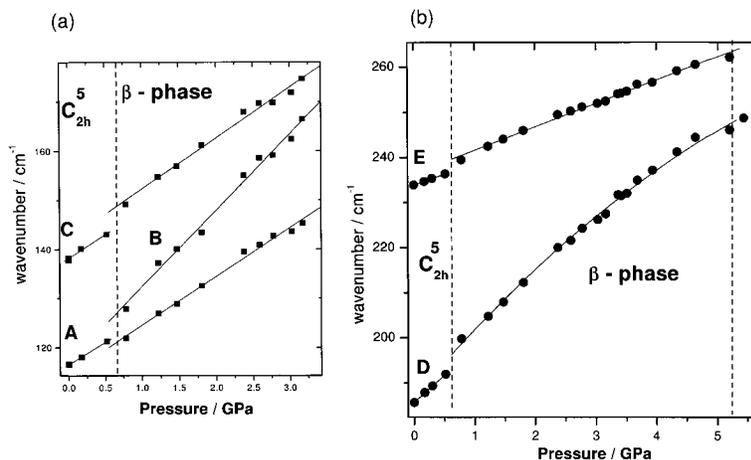


Figure 2. (a) Wavenumber of the low-energy bands of the taurine crystal as function of pressure. (b) Pressure dependence of the Raman peak wavenumber of the taurine crystal for bands D and E (see text). The two dashed vertical lines represent the pressure-induced phase transition judged by various changes in the Raman spectral features.

the Raman bands as observed at 0.00 GPa, $\tilde{\nu}_0$ fit represents the wavenumber of the Raman bands obtained by the linear fitting to experimental data and $d\tilde{\nu}/dP$ represents the variation of the wavenumber as a function of pressure. For the low-wavenumber modes the fittings are different in the two phases presented by the crystal. In fact, the behavior of band D as a function of pressure at the β -phase is not linear but a good fit for its wavenumber is obtained assuming a quadratic behavior given by

$$\tilde{\nu} = 187.3 \text{ cm}^{-1} + 15 \text{ cm}^{-1} \text{ GPa}^{-1} \times P - 0.07 \text{ cm}^{-1} \text{ GPa}^{-2} \times P^2$$

where P is the pressure value (in GPa). For almost all the internal modes, mainly for those with wavenumber higher than 350 cm^{-1} , only one linear fitting is sufficient to support all experimental points between 0.0 and 5.6 GPa. In Table 1, the $d\tilde{\nu}/dP$ values for the modes with $\tilde{\nu} > 350 \text{ cm}^{-1}$ (except for the modes at 896 and 1258 cm^{-1}) appearing in the column corresponding to the C_{2h}^5 phase are also valid for the β -phase.

Figure 3(a) shows the Raman spectra for several pressure values in the spectral region between 300 and 650 cm^{-1} and Fig. 3(b) shows the linear fit to experimental data. The band at 326 cm^{-1} is assigned as the torsion of CSH structure, $\tau(\text{CSH})$.²⁰ For the other bands appearing in Fig. 3, a linear behavior of the wavenumber as a function of pressure is manifested. The bands observed at 367 and $467\text{--}475 \text{ cm}^{-1}$ were assigned as deformation of NCC, $\delta(\text{NCC})$ and torsion of NH_3 , $\tau(\text{NH}_3^+)$, respectively.²⁰ The changes in the hydrogen bonds of a crystal where such a bond plays an important role in the structural stability can be determined to a great extent by the observation of torsional vibration of NH_3 , $\tau(\text{NH}_3^+)$, and the stretching of NH , $\nu(\text{NH}_3^+)$. Many studies dwell on the various aspects of Raman band profile of both $\nu(\text{NH}_3^+)$ ^{21,22} and $\tau(\text{NH}_3^+)$,²³ and the thrust of these investigations lies mainly in the mechanisms responsible for the band broadening as temperature is raised.²⁴ It would be

of great value to observe the linewidth of the torsional NH_3 vibration of the taurine crystal at high pressure. However, the low intensities of the two bands associated with $\tau(\text{NH}_3^+)$ did not allow us to perform a rigorous study of the band linewidths and quantitative results cannot be obtained from the present spectra. Consequently, the distortion of the hydrogen bond (as occurs with the L-alanine crystal²³) in the taurine crystal submitted to high pressure will continue to be an open problem.

The band at 528 cm^{-1} is associated with a bending vibration of SO_3 .²⁰ At $P = 0.00 \text{ GPa}$ it appears as a peak of high intensity with a shoulder at the low-energy side; this set of two bands is plotted in Fig. 3(b). With increasing pressure, the shoulder increases in intensity and the splitting of the bands becomes more evident at a pressure of about 2.4 GPa . Above this pressure two new bands appear in the SO_3 bending region. The four bands are seen in a clear way in the spectra at 5.2 and 5.4 GPa . The splitting of internal modes when pressure is applied in a crystal can be interpreted in two different ways: (a) inducing a phase transition by increasing the crystal field effects or (b) increasing the strength of the intermolecular bonds via a decrease in the lattice spacing.²⁵ The latter can be used to interpret the behavior of the SO_3 bending vibration because no significant change is observed in the lattice mode of the crystal in the $2.5\text{--}3.0 \text{ GPa}$ pressure range. In other words, the splitting of SO_3 bending cannot be used to support an eventual phase transition undergone by the taurine crystal between 2.4 and 2.6 GPa .

In Fig. 4(a) we show the pressure Raman spectra of the taurine crystal in the region $700\text{--}1280 \text{ cm}^{-1}$ for various pressures between 0.00 and 5.6 GPa . The band marked as P corresponds to a rocking of the CH_2 structure, while the rock of NH_3 is observed at 1179 cm^{-1} (Ref. 20) (the band V with weak intensity). In this region the stretchings of the CC and CN structures are also expected. Figure 4(b) gives the pressure dependence of the wavenumbers of

Table 1. Assignment of the modes, atmospheric pressure wavenumber values of the bands appearing in Figs 1–5, $\tilde{\nu}_{0 \text{ obs}}$, the wavenumber values of the Raman bands obtained by the linear fitting to experimental data, $\tilde{\nu}_{0 \text{ fit}}$, and the variation of the wavenumber as a function of pressure, $d\tilde{\nu}/dP$, for taurine crystal in both C_{2h}^5 and β -phases

Mode	Assignment (tentative)	$\tilde{\nu}_{0 \text{ obs}}/\text{cm}^{-1}$	C_{2h}^5 $\tilde{\nu}_{0 \text{ fit}}/\text{cm}^{-1}$	C_{2h}^5 $d\tilde{\nu}/dP/cm^{-1} \text{ GPa}^{-1}$	β -Phase $\tilde{\nu}_{0 \text{ obs}}/\text{cm}^{-1}$	β -Phase $d\tilde{\nu}/dP/cm^{-1} \text{ GPa}^{-1}$
A	Lattice	112.0	112.5	9.1	114.7	10.0
B	Lattice	—	—	—	116.9	15.5
C	Lattice	138.2	138.1	9.7	142.0	10.0
D		185.6	185.7	12.0		
E		233.9	233.9	4.8		
F		307.7	307.8	−1.5	308.9	3.1
G	$\tau(\text{CSH})$	324	323.5	8.4		
H	$\delta(\text{NCC})$	367	368.3	7.0		
I	$\tau(\text{NH}_3^+)$	467	466.9	3.3		
J	$\tau(\text{NH}_3^+)$	473.4	474.6	3.8		
L		522	521.7	1.0		
M		—	—	—	525.7	1.8
N		530	529.6	3.4		
N'	Bend(SO_3)	—	—	—	536.1	4.0
O		592	592.5	2.2		
P	$r(\text{CH}_2)$	736	736	4.9		
Q		849	848.9	3.9		
R		895	895.5	−0.3	893	1.8
S		964	963.6	2.7		
T		1032	1032.0	3.1		
U		1050	1049.6	3.7		
V	$r(\text{NH}_3)$	1179	1179.7	1.8		
X	$w(\text{CH}_2)$	1248	1247.5	0.2		
Z		1257	1257.8	−0.5	1254.5	2.4
1	CH and NH_3 stretch	2940.6	2935.6	6.4		
2	CH and NH_3 stretch	2977	2971	7.3		
3	CH and NH_3 stretch	2987.4	2982	7.4		
4	CH and NH_3 stretch	3013	3006	9.1		

bands appearing in the spectra in Fig. 4(a). From this figure a linear behavior of the wavenumber of all bands is observed. In Fig. 5(a) and (b), the high-wavenumber bands of the taurine crystal are shown. The spectral region corresponding to Fig. 5 is characterized by many bands due to the stretching of CH, $\nu(\text{CH})$, and to $\nu(\text{NH}_3^+)$. This can cause considerable uncertainty in the baseline necessary for the accurate determination of linewidth, as occurs for amino acid crystals such as L-threonine⁷ and monohydrated

L-asparagine.⁸ Although allowing for the existence of some limitation in the linewidth determination, we investigated the band linewidths of those appearing in the last spectral region in order to determine changes due to the mechanisms outlined in the discussion of the $\tau(\text{NH}_3^+)$ mode. The results of our analysis show no substantial variation in the high-wavenumber band linewidths, indicating that the factors producing the band linewidths in the taurine crystal due to change of temperature²⁶ are not present (or present to

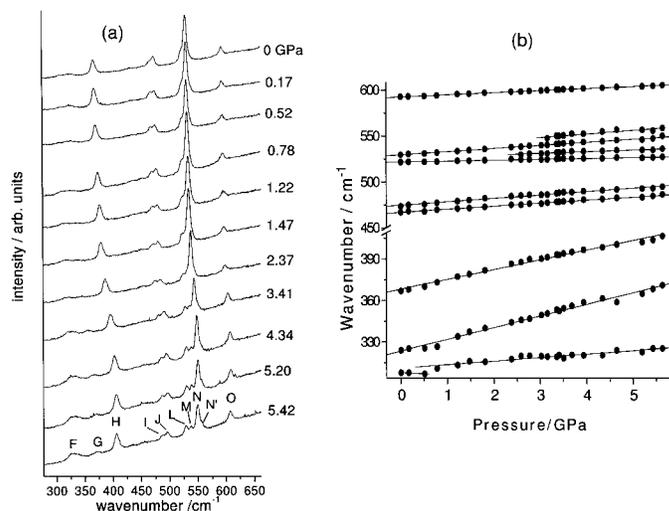


Figure 3. (a) Pressure Raman spectra of the taurine crystal in the 300–650 cm^{-1} region obtained with increasing pressure at room temperature. (b) Pressure dependence of the Raman peak wavenumber of the taurine crystal for bands appearing in (a).

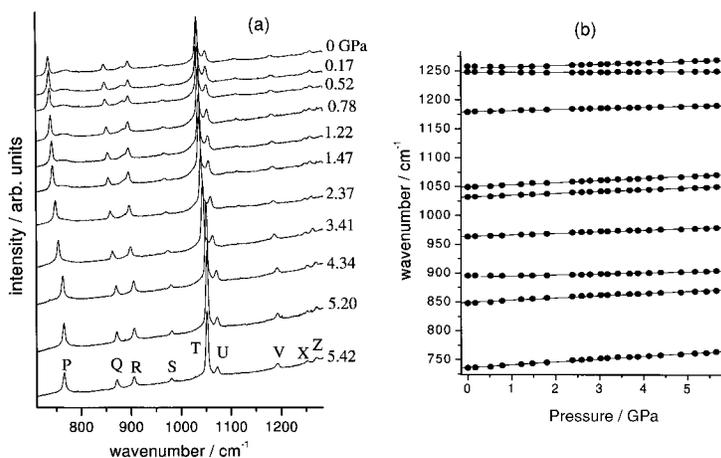


Figure 4. (a) Pressure Raman spectra of the taurine crystal in the 700–1280 cm^{-1} region obtained with increasing pressure at room temperature. (b) Pressure dependence of the Raman peak wavenumber of the taurine crystal for bands appearing in (a).

a contemptible negligible extent) in the crystal constrained to high-pressure conditions (we must bear in mind that hydrostatic pressure produces only volume variations, whereas temperature is a more complex thermodynamic parameter for the crystal because it is manifested through the parallel effects of phonon population and thermal expansion).

Finally, the evolution of the Raman spectra presented in Fig. 1(b) suggests that taurine can undergo a second phase transition at pressures higher than 5.2 GPa. This is seen by the disappearance of the band marked E, which in the spectrum at 5.42 GPa is completely absent. Such a band is assigned as a bending of NCC structure.²⁰ It is worth mentioning that in experiments performed at low temperature (between 10 and 300 K) a discontinuity of the wavenumber of this band at about 230 K is also associated with a phase transition (RJC Lima, AMR Teixeira, PTC Freire *et al.*, UFC

High Pressure Laboratory, personal communication and work to be published). This is an interesting result because in many cases low temperatures and high pressures give similar conditions to a crystal. We emphasize that one of the aspects characterizing the first phase transition observed in this work is the discontinuity of the wavenumber at $P \approx 0.7$ GPa for the bending of NCC. In other words, the band marked E in Fig. 1(b) is very sensitive to the change in structure, which is induced either by pressure (at the two transitions) or by temperature. However, in the temperature phase transition only a discontinuity of the wavenumber of band E is observed, whereas in the pressure-induced phase transition between 0.52 and 0.7 GPa the appearance of a new band is verified in the low-wavenumber region. Also, the disappearance of band E at 5.42 GPa does not fit with the temperature phase transition in taurine crystal. The second vertical dashed line in Fig. 2 represents the boundary

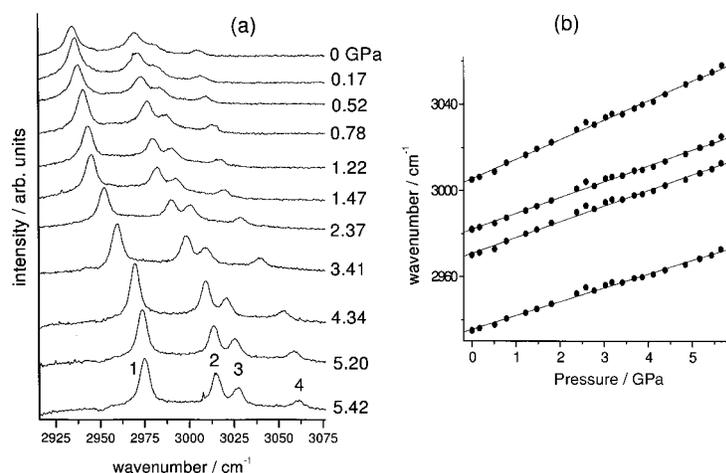


Figure 5. (a) Pressure Raman spectra of the taurine crystal in the 2920–3075 cm^{-1} region obtained with increasing pressure at room temperature. (b) Pressure dependence of the Raman peak wavenumber of the taurine crystal for bands appearing in (a).

between the β -phase and a third different phase (γ -phase) that we assume exist for the taurine crystal at pressures higher than 5.2 GPa.

The results described above reveal a certain complexity in the high-pressure behavior of the taurine crystal. In particular, an issue that needs to be addressed is the structure of the β -phase and the structure of the phase for $P > 5.2$ GPa (if, in fact, the second phase transition does exist). Obviously, a correct answer to this question must come from high-pressure x-ray diffraction studies, preferably on single crystals. Recently, a study of x-ray diffraction from a synchrotron radiation source [JM Sasaki, PTC Freire, AJD Moreno *et al.*, Presented at the 17th International Conference on High Pressure Science and Technology (to be published)] was performed on monohydrated L-asparagine, confirming the results of Raman spectroscopy¹⁴ and giving additional insights in to the problem.

CONCLUSION

We have studied the Raman spectra of the taurine crystal at pressures up to 5.6 GPa. From this study a phase transition at ~ 0.7 GPa was detected and possibly a second phase transition occurs for the taurine crystal above 5.2 GPa. The pressure coefficients for all modes observed in this work are given. In future work we shall investigate the temperature behavior of these modes and will calculate the Grüneisen parameter for this organic crystal. The temperature study can throw light on the anharmonic effects due to the hydrogen bond dynamics.

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