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Vibrational Spectra and Phase Transition in Triglycine Sulpho-Phosphate

Infrared and single crystal Raman spectra for various polarization geometries of Triglycine Sulpho-Phosphate (TGSP) have been recorded and analysed. The bonds of hydrogen atoms in H_2SO_4 and H_3PO_4 groups are shown to be weak and the possibility of proton transfer from H_2SO_4/H_3PO_4 group is indicated. Two different types of glycinium ions are shown to be present in the unit cell. Temperature dependent Raman spectra of TGSP have been recorded. The phase transition detected around 325 K in TGSP is explained in terms of the flipping motion of the glycinium ion and of attaining a higher crystal symmetry.

Introduction

IR and Raman spectral investigations of Triglycine Sulphate (HADNI et al.; GRANDJEAN et al.; KHANNA et al.; TAUREL et al.; DODD.; WINTERFELDT et al.; BARKER Jr, TINKHAM; KRISHNAN, BALASUBRAMANIAN; GALUSTIAN) have received considerable attention because of its ferroelectric properties and its applications in developing infrared detectors. HADNI et al. studied the dielectric and thermal properties of TGS and triglycinefluoroberylate. The influence of inorganic ions has been studied by GAFFER et al. They have shown that doping with Cu^{2+}, Mg^{2+} and Cr^{3+} considerably reduced the ability of TGS to convert mechanical energy to electrical energy while this ability slightly increased at room temperature when admixed with Fe^{3+}. It has been found that the replacement of SO_4 by BeF_4 or SeO_4 group in TGS alters the transition temperature and other ferroelectric properties considerably (WINTERFELDT et al.; BLINC et al.). In the present study, an investigation has been made to analyse the vibrational spectra of $TGS_x P_{1-x}$ ($x = 0.5$) and the temperature dependence of low frequency modes above and below the transition temperature.

Experimental

Single crystals of triglycine sulpho-phosphate (TGSP) are synthesised from AR grade glycine, sulphuric acid, and orthophosporic acid (NATARAJAN et al.) in the stoichiometric ratio. Good optical quality single crystals are used to record the Raman spectra in the 90° scattering geometry, for the four orientations Z[YY[X, Z[XY]X, Z[YZ[X and Z[XZ]X using a Spex Ramalog 1401 spectrometer. The green line at 514.5 nm generated by an Ar^+ ion laser operating at 80 mw power, is used as the source. Bruker IFS-85 ($4000-500$ cm^{-1}) and Bio-Rad FTS-7 ($500-200$ cm^{-1}) FT-IR spectrometers are used to obtain the IR spectra with the sample in KBr.

The structural data are collected on a ENRAF-NONIVS diffractometer with MoK_α-radiation to confirm the crystal structure of TGSP.

Table 1

Factor group analysis of triglycine sulpho-phosphate space group $P2_1 = C_2^2; Z = 2$

Factor group species C_2	NH_3 (C_1 site)		CH_2 (C_1 site)		(P, S) O_4 (C_1 site)	
	Internal modes	External modes	Internal modes	External modes	Internal modes	External modes
A	18	9T, 9R	9	9T, 9R	9	3T, 3R
B	18	9T, 9R	9	9T, 9R	9	3T, 3R
	36	18T, 18R	18	18T, 18R	18	6T, 6R

Factor group species C_2	6 C C_1 site	12 O C_1 site	6 H C_1 site	Optical modes	Acoustic modes	Activity	
						Raman	IR
A	9T	18T	9T	114	−1	a	a
B	9T	18T	9T	114	−2	a	a
	18T	36T	18T	228	3		

T = translations; R = librations

Interpretation of the spectra

Crystal Structure and Factor group analysis

The comparison of the results of X-ray analysis and the calculation of Z-value from density measurements of TGSP with the corresponding values for TGS confirms that they are isostructural. Hence the space group of TGSP is taken as $P2_1$.

The structural parameters of TGSP are:

Space group $P2_1$; $Z = 2$

$a = 9.1651 \,\text{Å}$; $b = 12.6265 \,\text{Å}$; $c = 5.7348 \,\text{Å}$

$\beta = 105°63'$; $d = 1.863 \,\text{g/cm}^3$

The factor group analysis using the standard correlation method (Fateley et al.) has been carried out with NH_3, CH_2, (P,S)O_4 and the six hydrogen atoms in general positions. Excluding the acoustical modes 225 normal modes are predicted (Tab. 1).

(P, S)O_4 vibrations

Since the positions of P and S atoms are not distinguishable and the masses of S and P atoms are very close to each other, the frequencies of similar modes of PO_4 and SO_4 groups are expected to be very close with a possibility of overlapping of bands. Hence, independent assignments of PO_4 and SO_4 groups are very difficult.

Stretching modes of $(P, S)O_4$

As the symmetric stretching mode v_1 of $(P, S)O_4$ group is expected to be the most intense and polarized in the Raman spectrum, the band at 978 cm^{-1} is easily assigned to this mode. In IR this is observed as a weak band at 973 cm^{-1}. The activation of this inactive IR mode is due to the site symmetry effect.

When PO_4 and SO_4 groups go inside the unit cell to build up the crystal, forces due to the potential field of the neighbouring ions are likely to distort the tetrahedral symmetry of the groups thereby causing the removal of degeneracy of the degenerate vibrations. The triply degenerate asymmetric stretching mode v_3 expected to occur in the region 1100 to 1050 cm^{-1} (CHAPMAN et al.) is observed as two bands in the three polarization geometries [Z[YY]X: 1087, 1116 cm^{-1}; Z[XY]X: 1085, 1113 cm^{-1}: Z[XZ]X: 1095, 1110 cm^{-1}]. In Ir, all the expected components are observed at 1054, 1086, and 1128 cm^{-1}.

The degeneracy of the symmetric bending mode v_2 is lifted in IR (460, 488 cm^{-1}) due to crystal field effect. In the Z[XY]X, Z[YZ]X, Z[XZ]X spectra one band each is observed, whereas two bands are observed in the Z[YY]X spectrum. Two bands each are observed in the polarization geometries Z[YY]X, Z[XY]X, Z[XZ]X for the triply degenerate asymmetric bending mode. In IR also two bands (618 and 675 cm^{-1}) are observed. The complete assignments are listed in Table 2.

In compounds having H_2SO_4 und H_3PO_4 groups, polarized $(P, S) - O(H)$ stretching is expected around 860 cm^{-1} with high intensity (CHAPMAN et al.). In the present case, a wide range of frequencies (890 – 915 cm^{-1}) has been observed in the different orientation [Z[YY]X; 890 and 900 cm^{-1} Z[XY]X; 900 and 915 cm^{-1} and Z[XZ]X; 892 cm^{-1}]. The corresponding IR band is observed at 902 cm^{-1}. The high values obtained for the stretching frequencies show that the hydrogen atom is loosely bound to the oxygen atom of $(P, S)O_4$ group. As expected, the $(P, S) - O(H)$ in-plane and out-of-plane bending frequencies are observed in the regions 1200 – 1300 cm^{-1} and 800 – 820 cm^{-1}, respectively, with lower intensity.

Vibrations of glycine molecule

For the glycine cation (TAKEDA et al.); the $C = O$ stretching frequency of the un-ionized carboxylic group is usually found near 1740 cm^{-1} as an intense band in IR. The ionized carboxylic group is known to give rise to two principal stretching frequencies: an asymmetric stretching frequency in the region 1600 – 1560 cm^{-1} and a symmetric stretching frequency near 1400 cm^{-1} (RAO; PEARSON, SLIFKIN; TAKEDA et al.). The observed IR spectrum has three intense bands at 1738, 1703, and 1536 cm^{-1} and one medium intense band at 1423 cm^{-1}. This strongly suggests that TGSP contains both ionized and unionized carboxylic groups. From detailed analysis of the vibrational spectra of TGS it has been shown that the TGS contains the non-planar $NH_3^+CH_2COOH$ and the planar $NH_3^+CH_2COOH$ and $NH_3^+CH_2COO^-$ forms (WINTERFELDT et al.). These ions are inter-connected by a network of hydrogen bonds. As both TGS and TGSP have identical structure and ionized and unionized carboxylic groups are found to exist in TGSP, it is justified to assume that the glycinium group exist in the forms $NH_3^+CH_2COO^-$ and $NH_3^+CH_2COOH$. In the later form the protonation is at the expense of protons from the H_2SO_4/H_3PO_4 groups. This is supported by the absence of NH_2 in the spectrum as discussed below.

Table 2

Vibrational spectral data (in cm^{-1}) and band assignments[a] of triglycine Sulpho-Phosphate

Z[YY]X	Z[XY]X	Z[YZ]X	Z[XZ]X	IR	Assignments[b]
3153 w, br	3176 m, br			3200 vs 3100 s	ν NH$_3^+$
3018 m	3018 m	3018 m 3001 w	3015 w, br	3017 s	ν_{as} CH$_2$
2986 s	2985 s	2983 w	2981 w	2930 sh	
2960 m 2865 vw	2958 m	2960 w, br	2960 vvw	2888 sh	ν_s CH$_2$
	1945 vw, br			2745 w 2505 vw 2434 vw 2218 vvw 1867 w, br	Triobands Combinations
	1705 w, br			1738 s	ν C=O
1670 w, br	1680 vw			1703 s	
	1570 vw	1610 vw, br	1605 vw, br	1653 vvw 1623 w	δ_{as} NH$_3^+$
	1536 vw			1536 s 1502 s	ν_{as} COO$^-$ δ_s NH$_3^+$
	1485 vw	1440 w	1440 w	1465 w	δ CH$_2$
1430 w	1430 vw	1430 w	1411 vw	1423 m	ν_s COO$^-$
1415 w	1411 vw				
1335 m, br	1370 vw, br				
1302 sh	1324 w	1315 w, br	1320 w	1304 s	t, ω (CH$_2$)
1280 sh	1296 w				
					δ POH In-plane
				1212 sh	r NH$_3^+$
1116 w, br	1113 w		1110 w, br	1128 vvs	
1087 vvw	1085 vvw		1095 w	1086 s 1054 s	ν_3 (P,S)O$_4$
1036 w, br	1040 w, br	1040 w, br	1045 w, br	1019 s	ν_s C−N
978 vvs	979 vvs	980 w	981 w	973 vw	ν_1 (P,S)O$_4$
900 sh	915 sh		892 w, br	902 m	ν (P,S)-O(H)
890 m	900 m, br				
872 m	880 w			860 m	ν C−C
		815 vw, br		802 w	γ (P,S)-O(H) out-of-plane
			780 vw, br	748 vvw 720 vvw	δ COO$^-$
666 m, br	662 w, br		673 w, br	675 w	ν_4 (P,S)O$_4$
615 w	616 w, br	630 w	632 w	618 m	
580 w	588 w	582 vw, br	585 vw	571 w	ω COO$^-$
501 w	505 w	505 w, br	505 vw		r COO$^-$
467 sh				488 m	
453 m	450 m	460 vvw	463 vvw	460 vvw	ν_2 (P,S)O$_4$
330 w, br	330 w, br		338 vvw	328 vw 304 m 282 w	δ_s C−C
215 vvw				254 w 241 w	glyc/SO$_4$/PO$_4$ t/l
170 vw	175 vw	175 w, br	180 w		glyc: t/l
135 sh		130 sh	135 sh		glyc/SO$_4$/PO$_4$ t/l
105 s	105 s	106 s	105 s		
67 vs	67 vs	76 vvs 66 vs	76 vvs 66 vs		glyc: t/l

[a] s = strong, m = medium; w = weak, v = very; sh = shoulder; br = broad;

[b] δ = bending; ν = stretching; r = rocking; ω = wagging; l = librations, t = translations; γ = out-of-plane bending Subscripts as and s refer to asymmetric and symmetric vibrations, respectively

The stretching modes of CH_2 group usually occur in the $3100-2800$ cm^{-1} region (COLTHUP et al.). In the Raman spectra the v_s CH_2 is expected to be intense, sharp and polarized, whereas v_{as} CH_2 is unpolarized. The observed polarized bands at 2960 and 2986 cm^{-1} in the Z[YY]X orientation are easily assigned to the v_s CH_2 mode. Since the Raman band at 3018 cm^{-1} is unpolarized, it is assigned to v_{as} CH_2. In the IR sepctra there is a very intense broad band extending from $3600-2400$ cm^{-1} (FWHM~ 625 cm^{-1}) with peaks at 3017, 3110 and 3200 cm^{-1}. Since this broad frequency range contains NH_3^+ and CH_2 group vibrations, an unambiguous identification of their vibrational modes from the IR spectra has not been possible. The CH scissoring vibrations of the CH_2 group is observed at 1440 cm^{-1} in Raman and at 1465 cm^{-1} in IR. The CH wagging and twisting vibrations are observed in the region $1300-1370$ cm^{-1}. The frequencies observed here for these modes are in complete agreement with those of TGS and α-glycine (WINTERFELDT et al. KRISHNAN, BALASU-BRAMANIAN).

It is well established that the uncharged amino group NH_2 have stretching frequencies in the $3500-3300$ cm^{-1} range while the charged species NH_3 have stretching frequencies in the $3300-2500$ cm^{-1} range (EDSALL, SCHEINBERG; LINDGREN et al.; DURIG et al.). Furthermore the NH_3^+ stretching bands are broader and weaker than those arising from the uncharged NH_2 groups (BELLAMY; EDSALL, SCHEINBERG). In the Raman spectra, only a very broad medium intense band is observed at 3176 cm^{-1} for NH stretching modes. The position and broadness of this band clearly shows that it is due to NH_3^+ group. The bands observed at 3100 and 3200 cm^{-1} in the IR spectra also assigned to the stretching modes of NH_3^+. From a comparison of the spectrum of TGSP with those of TGS, triclycine, and α-glycine, the following assignments are made. The two IR bands at 1623 and 1653 cm^{-1} are assigned to δ_{as} NH_3^+ and the strong band at 1502 cm^{-1} is assigned to $\delta_s NH_3^+$. The band 1212 cm^{-1} is assigned to NH_3^+ rocking vibrations. The NH_3^+ rocking modes occur at much lower frequencies: 1112, 1114, 1135 and 1179 cm^{-1} in TGS; 1153 and 1162 cm^{-1} in triglycine and 1112 and 1140 cm^{-1} in α-glycine. The difference observed in these frequencies in TGSP could be due to the difference in the disposition and strength of hydrogen bonds.

The mode v_s CH_2 has two components in all the orientations and v_{as} CH_2 has two components (3001 and 3018 cm^{-1}) in the Z[YZ[X spectrum. v C=O which is expected to be a singlet appeared as a doublet (1703 and 1738 cm^{-1}) in IR. Two bands are observed also for the mode δ_{as} NH_3^+. If $NH_3^+CH_2COOH$ exists only in one form this doubling is improbable. This doubling is probably due to the existence of both planar and non-planar the (NCCOO$^-$ skeleton is non-planar) $NH_3^+CH_2COOH$ glycinium groups. Bands below 300 cm^{-1} are assigned to the external modes. The external modes include SO_4, PO_4 and glycine translations and librations.

Temperature effects

Recently, considerable progress has been made in relating phase transition of substance to softening of optical modes and variation in low frequency band profiles (MARCHON, NOVAK; OHNO, LOCKWOOD; MYLRAJAN, SRINIVASAN; RAIMBAULT et al.). In the present investigation, attention is focused on the effect of temperature variation on the external modes of TGSP.

The temperature dependent Raman Spectra (Fig. 1) of TGSP in the $50-300$ cm^{-1} region have been recorded with the help of the variable temperature Raman cell fabricated in our
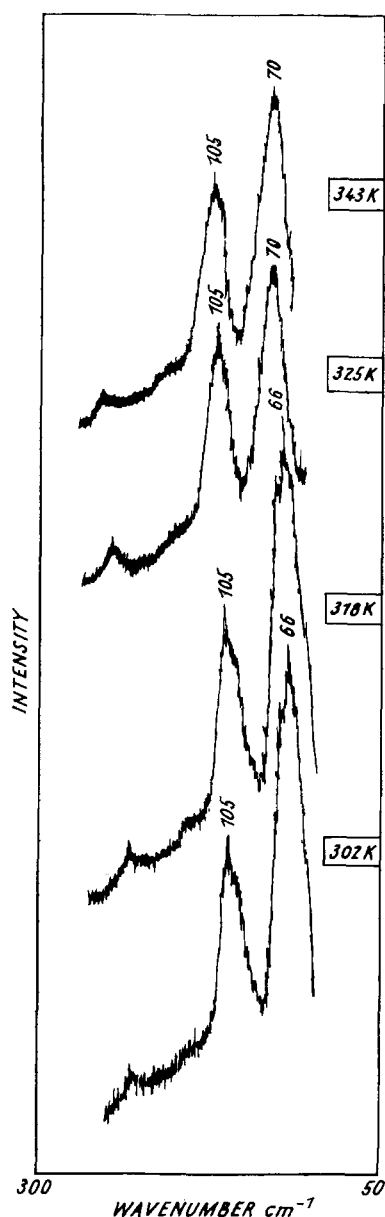
Fig. 1. Raman spectra of triglycine sulpho-phosphate single crystal using Z[YY]X geometry at different temperatures in the 50 – 300 cm^{-1} region

laboratory. Around 325 K, the intense band at 66 cm^{-1} is found to be shifted to 70 cm^{-1} with lowering of intensity. Also this band which showed upward shift in frequency with temperature is found to remain constant above T_c. In TGS, the glycinium groups as a whole are involved in the phase transition apart from the changes in the OH protons (BLINC et al.). Since TGS and TGSP are isostructual it is quite resonable to assume that the phase transition mechanism in both the compounds will be of identical nature. The unit cell of

TGS contains glycine $(NH_3^+CH_2COO)^-$ and protonated glycinium $(NH_3^+CH_2COOH)$ groups interconnected by hydrogen bonds. During phase transition the proton transfer between these groups results in polarization reversal and an exchange of the role of glycinium and glycine groups. Thus the proton transfer between glycinium and glycine groups around T_c may result in a frequency shift for internal and external modes. As in the case of TGS, the observed frequency shift is explained due to the flipping motion between glycine and glycinium groups, whereas the lowering of intensity could be due to the crystal attaining higher symmetry as it undergoes a phase transition. Since this phase transition is not accompanied by the presence of any prominent soft mode it is evident that the transition is of order-disorder type.

Results

1. Even though H_2SO_4 and H_3PO_4 groups do exist, the bonding of their hydrogen atom to the sulphate/phosphate oxygen is not strong.
2. The presence of both $(P, S)O_4$ and $(P, S)-O(H)$ stretching frequencies indicates the possibility of proton transfer between H_2SO_4/H_3PO_4 groups.
3. There are two different types of glycinium ions present in the unit cell.
4. TGSP is found to undergo a phase transition around 325 k which is detected from the changes in frequency and intensity in the Raman band. The observed frequency shift and intensity changes during phase transition are explained in terms of a flipping motion of the glycinium ion and of attaining a higher crystal symmetry.

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