RAMAN SPECTRUM OF CRYSTALLINE TRI-GLYCINE SULPHATE $(NH_3.CH_2.COO)_3H_2SO_4$

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1. Introduction

In continuation of the work on the Raman spectrum of α-glycine (Krishnan and Balasubramanian, 1958), the authors have undertaken a systematic study of the Raman spectra of its derivatives. The present paper describes the results obtained with a single crystal of tri-glycine sulphate.

Tri-glycine sulphate is one of the few crystals which exhibit ferro-electricity at ordinary temperatures (Matthias *et al.*, 1956). Its transition temperature is in the neighbourhood of 48° C. The dielectric and thermal properties of this crystal have been studied in detail by Hoshino *et al.* (1957). The crystal is ferro-electric with low coercive field and has a simple domain structure. It appears therefore to be a very promising substance for use in memory devices of computers. The investigation of its Raman spectrum* and its variation with temperature would therefore be of very great interest. As it is transparent to the ultraviolet radiation, λ 2536·5 radiation could be used as exciter. Accordingly we started the investigation on its Raman spectrum. When the temperature variation of the Raman spectrum of tri-glycine sulphate was in progress, a short communication on the Raman spectrum of the same substance at room temperature by Taurel *et al.* (1958) appeared in *Comptes Rendus*. It was therefore considered desirable to publish immediately the results independently obtained by the authors at room temperature.

2. Experimental

Fairly large and clear crystals of tri-glycine sulphate were easily grown by the method of slow evaporation from aqueous solutions containing stoichiometric proportions of the two components, glycine and sulphuric acid. Crystals grown from solutions were colourless and were in the form of thick plates (about $1'' \times 1'' \times \frac{1}{4}''$) with the broad faces parallel to the *b*-axis (two-fold axis). They had only one cleavage face which is perpendicular to the *b*-axis. λ 2536·5 excitation was used to record the Raman

* The authors are grateful to Dr. K. Vedam for drawing their attention to the importance of this crystal.

spectrum. It was found that on exposure to the ultraviloet radiation for about half-an-hour the face of the crystal adjacent to the arc got frosted and the transparency decreased. This was a disturbing effect which was got over by polishing the crystal every half hour. Some specimens of the crystal got slightly coloured yellow after prolonged exposure. Using a Hilger medium quartz spectrograph and a slit width of 0·025 mm., a very intense spectrogram was obtained with the exposure of 5 hours. The illumination was normal to the broad face of the crystal plate and the scattered light was taken through one of the edges in a direction which was inclined at angle 45° to the *b*-axis.

3. Results

An enlarged photograph of the Raman spectrum of tri-glycine sulphate taken with a medium quartz spectrograph is reproduced in Fig. 1 *b* in Plate XVII. The corresponding microphotometer record is shown in Fig. 1 *c*. The spectrum of mercury arc is also included for purposes of comparison (Fig. 1 *a*). The positions and frequency shifts of the Raman lines are marked in the microphotometer record.

The spectrum recorded here exhibits 48 Raman lines. The frequency shifts of these are listed in Table I. Visual estimates of the intensities of the lines are also given within brackets in the table. Taurel *et al.* (1958) have reported only the existence of 36 Raman lines the frequency shifts of which are given in the same table. All the lines recorded by them except the frequency shift 131 have been confirmed and it is gratifying to note that in the majority of cases, the values of the frequency shifts are in very good agreement with those obtained by the present authors. The two low frequency lines 63 and 73 are not seen well resolved in the picture taken with medium quartz spectrograph (Fig. 1 *b*). In order to establish their doublet nature, the spectrum was photographed with the Hilger El large quartz spectrograph and the microphotometer record of a lightly exposed spectrogram is reporduced in Fig. 2. The two lines are clearly seen well separated not only on the Stokes side but also on the anti-Stokes side. The 63 line is broader than the 73 lines indicating thereby that the former might have a structure. The Raman line 610 and 1009 which have also been reported by Taurel and others fall adjacent to the mercury lines in the spectrogram taken with the λ 2536·5 excitation. The Raman spectrum exhibits an intense continuous band starting from 3100 cm.$^{-1}$ and extending over 200 cm.$^{-1}$ exhibiting 3 maxima at about 3150, 3230 and 3270 cm.$^{-1}$ There is also a weak band covering the region from 2874 to 3022 cm.$^{-1}$ The frequency

shifts of the Raman lines of crystalline glycine reported by the authors recently (Krishnan and Balasubramanian, 1958) have also been given in Table I.

TABLE I

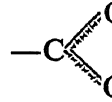
Tri-Glycine Sulphate			α-Glycine	Assignment
Sl. No.	Authors	Taurel *et al.*	Authors	
1	45 (6)	45		Lattice
2	63 (10)	64	53	,,
3	73 (10)	73	74	,,
4	102 (10)	100	109	,,
5	129 (5)	128		,,
		131		
6	171 (8)	170	164	,,
			183	
7	220 (4*d*)	207	199	,,
8	330 (6*d*)	330		C–C bending
9	345 (2)		358	C–C bending
10	450 (10)	450		SO_4^-—ν_2
11	463 (6)	463		SO_4^-—ν_2
12	500 (6)	499		C–CO bending
13	587 (3*d*)	578	588	C–CO bending
14	610	615		SO_4^-—ν_3
15	629 (6*d*)	623		SO_4^-—ν_3
16	665 (6*d*)	664		SO_4^-—ν_3
			677	
17	697 (1)		697	O–C–O bending
18	870 (10)	870		C–C Stretching
19	890 (12)	890	896	C–C Stretching
20	902 (8)	917	925	C–C Stretching
21	980 (20)	976		SO_4—ν_1
22	1009	1009		
23	1037 (1)	1037	1038	C–N Stretching
24	1043 (6*d*)	1042		SO_4^-—ν_4
25	1092 (3)			SO_4^-—ν_4
26	1114 (8)	1110	1112	C–CH_2 rocking
27	1134 (3)		1140	
28	1164 (4*d*)			SO_4^-—ν_4
29	1303 (10*d*)	1305	1320	C–H Wagging and
30	1321 (10*d*)		1330	Twisting
				Symmetric Valence
31	1375 (3*d*)	1377	1395	
32	1414 (15)	1405	1414	
33	1441 (12)	1435	1441	C–H Scissoring
			1459	

TABLE I (*Contd.*)

Sl. No.	Tri-Glycine Sulphate: Authors	Tri-Glycine Sulphate: Taurel *et al.*	α-Glycine Authors	Assignment
34	1483 (6)	1478	1506	Symmetric N–H bending
35	1609 (10)	1603	1563	C=O (ionised carboxyl)
36	1648 (5)		1640	Asymmetric N–H bending
37	1675 (10)	1678	1668	C=O (ionised carboxyl)
38	2528 (1)		2530	N–H Stretching NH_3^+
39	2651 (3)		2630	,,
40	2763 (4)		2750	,,
41	2874 (5*d*)		2830	,,
42	2930 (5*d*)		2895	,,
43	2962 (13)	2959		C–H Stretching
44	2988 (15)	2983 3012	2974	,,
45	3022 (13)	3019	3008	,,
46	3150 (6*d*)	3160	3145	N–H Stretching
47	3230 (5*d*)			—O.....H—
48	3270 (4*d*)			Hydroxyl Group

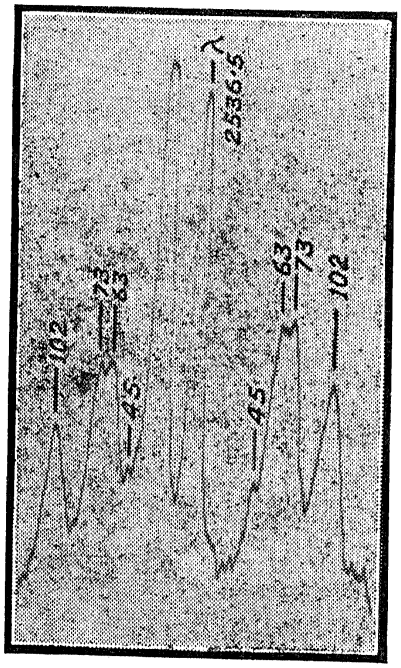


FIG. 2. Microphotometer record of the Raman spectrum (lathic region) of tri-glaycone sulphate taken with E.I. Spectrograph.

4. DISCUSSION

Tri-glycine sulphate crystallises in the monoclinic class with the space group C_2^2—$P2_1$. The crystallographic data have been determined by Wood and Holden (1957) and by Hoshino, Okaya and Pepinsky (1958). According to the latter group, the unit cell has got the following parameters $a = 9{\cdot}417$ Å, $b = 12{\cdot}643$ Å, $c = 5{\cdot}735$ Å and $\beta = 110° 23'$. The unit cell contains two molecules of tri-glycine sulphate situated symmetrically with respect to one another about the binary axis. There is no other element of symmetry at room temperature.

The observed Raman lines could be classified under 3 groups: (1) low frequency or lattice spectrum consisting of 7 Raman lines, (2) spectrum of the SO_4 ion consisting of 9 Raman lines and (3) spectrum of the internal oscillations of the glycine ion consisting of 32 Raman lines.

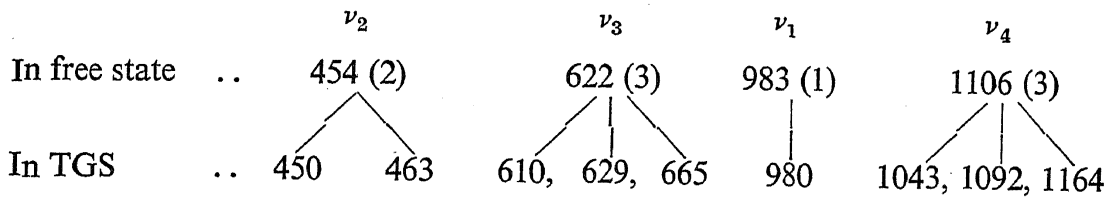
5. LATTICE SPECTRUM

Taking each glycine group as a unit and the SO_4 ion as another unit, one can work out the number of lattice oscillations on the basis of group theoretical analysis. The low frequency spectrum of tri-glycine sulphate should consist of 18 oscillations of the rotatory type and 21 oscillations of the translatory type, all of them being active in Raman effect. In actual practice this number may be reduced since in each molecule there are 3 units of glycine and consequently the frequencies of some of the oscillations may be nearly equal. Further, the oscillations of the rotatory type may be expected to appear strongly in the Raman spectrum. Only 7 lattice lines have been recorded in the spectrum of tri-glycine sulphate in the region from 45 cm.$^{-1}$ to 220 cm.$^{-1}$ Of these the prominent ones are 63, 73, 102 and 171 cm.$^{-1}$ The weaker lines are generally broader than the intense lines. In order to give proper assignments to the lattice lines, further investigations under high dispersion and for various orientations have to be carried out.

6. SO_4^- FREQUENCIES

From a comparison of the Raman lines observed in the spectra of tri-glycine sulphate and glycine (Table I), the following frequency shifts could be assigned to the internal oscillations of SO_4^- ion: 450, 463, 610, 629, 665, 980, 1043, 1092 and 1164 cm.$^{-1}$ Since 9 lines have been recorded, it follows that in crystalline tri-glycine sulphate the degeneracies of the frequencies belonging to the tetrahedral SO_4^- ion are completely removed. The relationship between the frequencies of the tetrahedral SO_4^- ion and those observed with tri-glycine sulphate are indicated below.

RAMAN FREQUENCIES OF SO_4^- ION



Since the splitting of the doubly degenerate frequency (454 cm.$^{-1}$) and the lowering of the totally symmetric frequency (983 cm.$^{-1}$) in the crystalline state are small, one can conclude that the influence of 3 glycine groups on the vibration of SO_4^- ion is not very much.

7. INTERNAL FREQUENCIES

The remaining 32 Raman lines with frequency shifts ranging from 330 cm.$^{-1}$ to 3270 cm.$^{-1}$ should be attributed to the internal oscillations of the glycine group. There is nearly a one-to-one correspondence between the Raman frequencies of tri-glycine sulphate and those of α-glycine as far as the internal oscillations are concerned. Since the frequency shifts for the corresponding Raman lines in both are nearly same, one can conclude that the glycine group in tri-glycine sulphate maintains its individuality. Proper assignments for the respective frequency shifts have been indicated in Table I. There are, however, certain characteristic differences between the two spectra due to the fact that the unit cell of tri-glycine sulphate contains six glycine groups whereas the unit cell of α-glycine contains only two glycine molecules.

(i) The spectrum of tri-glycine sulphate exhibits 3 intense lines due to C–H stretching oscillations, whereas the spectrum of glycine shows only two lines. Taurel *et al.* have reported the existence of another line 3012 $\pm$ 7. It is probable that the fairly intense continuum present in this region of the spectrum would have masked the detection of this line.

(ii) The spectrum of tri-glycine sulphate exhibits 3 intense lines due to C–C stretching vibration in place of one intense line observed in glycine.

(iii) The continuous band starting from 3100 cm.$^{-1}$ and extending upto 3300 cm.$^{-1}$ exhibiting a couple of maxima present in the spectrum of tri-glycine sulphate is absent in the spectrum of α-glycine. This might be due to the bonded — O....H—vibrations.

The absence of any Raman line corresponding to regular O–H frequency clearly indicates the absence of any water of crystallisation and the substance

that was crystallised from the aqueous solution had the formula $(NH_3CH_2COO)_3H_2SO_4$ and not $(NH_3.CH_2.COO)_2H_2SO_4.4H_2O$ (Wood and Holden, 1957).

8. SUMMARY

The Raman spectrum of a single crystal of tri-glycine sulphate $(NH_3.CH_2COO)_3H_2SO_4$ has been photographed using λ 2536·5 excitation. Fourty-eight Raman lines have been recorded. They have been classified as follows: Seven lines due to lattice vibrations, 9 lines due to SO^{-}_{4} ion oscillations and 32 due to internal oscillations of glycine group. As regards the latter, there is a close resemblance between the spectra of tri-glycine sulphate and glycine.

9. REFERENCES

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