

RAMAN SPECTRUM OF TRIGLYCINE SELENATE (G₃Se), [(NH₂CH₂COOH)₃ H₂SeO₄]

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1. INTRODUCTION

GLYCINE forms addition compounds very readily with inorganic acids. Such addition compounds are known to exhibit ferroelectric properties. Triglycine sulphate (G₃S) and triglycine selenate (G₃Se) are two such compounds (Mathias, Miller and Remeika, 1956). They form isomorphous crystals which belong to the space group $P2_1/m = C_2h^5$ in the non-ferroelectric phase and go over to $P2_1 = C_2^2$ in the ferroelectric phase. In the ferroelectric phase the [010] axis is the polar axis. The values of the transition temperatures for G₃S and G₃Se are 47° C. and 22° C. respectively. The values of the spontaneous polarization and coercive field for the two compounds are 2.2 and 3.2 μ coul./cm.² and 0.22 kV./cm. and 0.78 kV./cm. respectively at 10° C. below the Curie temperature. The substitution of the SeO₄⁻⁻⁻ for SO₄⁻⁻⁻ has marked influence on the ferroelectric properties. The Raman spectrum of triglycine sulphate in the form of single crystals has already been recorded by us (R. S. Krishnan and K. Balasubramanian, 1958 *b*). The Raman spectrum of triglycine selenate has not been recorded so far in spite of the fact that good crystals could be very easily grown. Therefore, it was considered desirable to have its Raman spectrum photographed and compared with that of triglycine sulphate and α-glycine. Since the crystals were found to be transparent to ultraviolet radiations, the Raman spectrum was recorded using λ 2537 radiation of mercury.

2. EXPERIMENTAL DETAILS

Single crystals of G₃Se were grown by the method of slow evaporation of the saturated aqueous solution of the constituents (glycine and selenic acid) in stoichiometric proportions. Crystals of the size 1½ cm. × 1 cm. × ½ cm. were used to photograph the spectrum. On exposure to ultraviolet radiations the crystals became coloured red and became opaque to the ultraviolet radiation. This difficulty was overcome by replacing the coloured specimen by a fresh one every half an hour. As the temperature of the crystal was about 25° C. the spectrum photographed is that of the crystal in the non-ferroelectric phase. The spectrum was photographed with a Hilger medium

Quartz spectrograph with a slit width of 0.04 mm. Exposures of the order of 10 to 12 hours were found to be necessary for getting a satisfactory spectrogram.

3. RESULTS

An enlarged photograph of the Raman spectrum of triglycine selenate and its microphotometer record are reproduced in Fig. 1 on Plate (XVII). The spectrum of triglycine sulphate is also included in Fig. 1, for comparison. The frequency shifts of the Raman lines observed in the case of triglycine selenate, triglycine sulphate and α -glycine are given in Table I.

TABLE I
Raman frequencies of triglycine selenate (G_3Se)

No.	G_3Se	G_3S	α -g	Infra-red G_3Se	Assignments
1	46 (7)	45	53		Lattice Oscillations
2	67 (35)	63 73	71 77		
3	94 (30)	102	109		..
4	117 (7)	129			..
5	154 (4)				..
6	164 (4)	171	164		..
7	185 (2d)		183		..
8	205 (2d)	210	199		N—H...O
9	225 (?)	220			N—H...O
10	330 (1)	330	358		N—H...O
11	339 (6)				C—C torsion
		345			SeO ₄ : ν_2
12	370 (3)				..
13	404 (?)				SeO ₄ : ν_2
14	438 (4)				..
15	446 (4)				SeO ₄ : ν_3
		450			SeO ₄ : ν_3
		463			SO ₄ : ν_2
		500	499		SO ₄ : ν_2
16	586 (1)	587	588		CCN bending
		610			NH ₃ ⁺ torsion
		629			SO ₄ : ν_3
		665			SO ₄ : ν_3
17	682 (1)	697	697	644	SO ₄ : ν_3
18	827 (?)			820	COO ⁻ sym. bend
19	835 (v.i.)			830	SeO ₄ : ν_4
	870 (?)	870		860	SeO ₄ : ν_1
					CCN stretch. (COOH glycine)

TABLE I (Contd.)

No.	G ₃ Se	G ₃ S	α -g	Infra- red G ₃ Se	Assignments
20	875 (25)			875	SeO ₄ : ν_4
21	896 (20)	890	896	890	CCN sym. stretch
22	920 (3)	902	925	905	CH ₂ rocking
		980		989	SO ₄ : ν_1
23	1029 (2)	1040	1038	1028	CCN antisym. stretch
				1044	..
		1092			SO ₄ : ν_4
		1104			SO ₄ : ν_4
		1114			SO ₄ : ν_4
24	1115 (4)	1134	1112	1117	NH ₃ ⁺ rocking
25	1146 (?)	1164	1140		NH ₃ ⁺ rocking
26	1305 (8)	1303	1320	1300	CH ₂ wagging
27	1325 (8)	1321	1330	1317	..
		1375	1395	1378	..
28	1414 (9)	1414	1414	1411	COO ⁻ sym. valence stretch
29	1440 (9)	1441	1441	1433	CH ₂ sym bend
			1459		CH ₂ sym. bend.
30	1486 (1)	1483	1497		NH ₃ ⁺ sym. deformation
			1506	1489	..
31	1596 (4)	1609	1563	1533	NH ₃ ⁺ deg. deformation
			1585(?)
32	1632 (2)	1648	1640	1611	COO ⁻ antisym. valence stretch
33	1680 (6)	1675	1668	1700	C=O of COO ⁻
				1744	..
				1856	..
				2227	..
				2318	..
				2373	..
		2532	2530	2500	N—H···O Hydrogen bonded
					O—H···O
34	2610	2651	2630	2591	do.
		2695			do.
35	2731 (1d)	2728	2750	2727	do.
		2773		2773	do.
36	2858 (1d)	2874	2830	2841	do.
37	2931 (3d)	2930	2895	2909	do.
38	2960 (28)	2962	2974		C—H stretch
39	2982 (40)	2988		3000	C—H stretch
40	3015 (35)	3022	3008		C—H stretch
41	3150 (4 d)	3150	3145	3183	NH ₃ ⁺ stretch
42	3230 (3 d)	3230			N—H···O
		3270		3273	N—H···O
				3364	..

v.i. = very intense; d = diffuse.

Note.—The values of the Raman frequency shifts for α -g and G₃S entered in Table I have been taken from the papers by Krishnan and Balasubramanian [(1958 a and 1958 b) respectively.]

Forty-two Raman lines have been identified in the spectrum of triglycine selenate. These are grouped as follows: 9 Raman lines in the region $0-250\text{ cm.}^{-1}$ come are classified as due to the external oscillations. The remaining 33 lines appearing in the region $300-3200\text{ cm.}^{-1}$ fall under one class and are due to the internal oscillations (the selenate ions and the glycine ions). As is to be expected the spectra of triglycine selenate and triglycine sulphate are similar in many respects. The points of difference are as follows: (1) The characteristic sulphate frequencies of the spectrum of G_3S are replaced by the corresponding selenate frequencies in the spectrum of G_3Se . These are indicated in Table I. (2) In the region $1543-1700\text{ cm.}^{-1}$ the frequencies in the spectrum of triglycine selenate are appreciably different from that found in triglycine sulphate and α -glycine. (3) The lines at 370, 438, 446 and 835 cm.^{-1} are found only in the spectrum of triglycine selenate. (4) The line at 500 cm.^{-1} observed in triglycine sulphate and α -glycine is not easily discernible in the spectrum of triglycine selenate. (5) Although the spectrum of triglycine selenate reproduced in Fig. 1 is not very intense, the Raman lines in the region $2500-2750\text{ cm.}^{-1}$ that are present in the spectra of triglycine sulphate and α -glycine are discernible in the spectrum of selenate with difficulty. (6) The line at 1038 cm.^{-1} in α -glycine which splits into a doublet with frequency shifts 1036 and 1043 in the spectrum of triglycine sulphate is shifted to a lower frequency and is observed at 1029 in triglycine selenate. (7) The lines at 1115 and 1146 cm.^{-1} in triglycine selenate are found at 1134 and 1164 cm.^{-1} in triglycine sulphate and at 1112 and 1140 cm.^{-1} in α -glycine respectively.

4. DISCUSSION

There are 6 glycine units and 2 selenic acid units in the unit cell of triglycine selenate. (Each glycine unit consists of 10 atoms and the H_2SeO_4 unit consists of 7 atoms.) Hence, a unit cell has altogether 222 degrees of freedom, 48 of which correspond to the lattice vibrations. The remaining 174 refer to the intramolecular vibrations.

(i) External Oscillations

The Raman spectrum of triglycine selenate exhibits 9 low frequency lines. The lines at 67 and 94 cm.^{-1} are the most intense; those at 46, 117 and 164 cm.^{-1} are of moderate intensity. All the other lines are of very low intensity. Of the 9 low frequency Raman lines, the lines at 185, 205 and 225 cm.^{-1} should be attributed to the vibrations of hydrogen bond, *i.e.*, $N-H\cdots O$ (Gross, 1959). The remaining 6 low frequency Raman lines belong to the lattice oscillations of rotatory and translatory types of glycine units.

Taking each glycine molecule as a separate unit and SeO_4 ion as another unit, and applying group theoretical methods to the unit cell of space group C_2^2 (ferroelectric phase) and C_{2h}^5 (non-ferroelectric phase) one can find out the number of external oscillations that are permitted to occur in both phases.

In the ferroelectric phase one should have 21 translatory type of external oscillations (11 totally symmetric *plus* 10 antisymmetric) and 24 rotatory type of external oscillations (12 totally symmetric *plus* 12 antisymmetric). All are active in Raman effect and infrared absorption.

In the non-ferroelectric phase 12 translatory (6 symmetric *plus* 6 anti-symmetric) and 12 rotatory (6 A_g *plus* 6 B_g) modes are permitted to occur in Raman effect. In infrared 9 translatory (5 A_u *plus* 4 B_u) and 12 rotatory (6 A_u *plus* 6 B_u) modes are allowed.

The Raman lines at 46, 67, 164, 205–225 cm^{-1} in triglycine selenate are observed at almost the same place in triglycine sulphate also. These frequencies could be due to the glycine units and $\text{NH}\dots\text{O}$ oscillations. The Raman lines at 94, 117 cm^{-1} in triglycine selenate may correspond to 102 and 129 cm^{-1} lines in triglycine sulphate. These frequencies might be due to the glycine units oscillating against the SeO_4^{--} or SO_4^{--} ions. The lines at 154 and 185 cm^{-1} in triglycine selenate are not observed in triglycine sulphate.

(ii) Internal Oscillations

SeO₄⁻⁻ frequencies.—From a comparison of the Raman lines observed in the spectra of triglycine selenate and triglycine sulphate the frequency shifts 336, 370, 438, 446, 827, 835 and 875 cm^{-1} can be assigned to the internal oscillations of SeO_4 groups. The free SeO_4^{--} ion has got the tetrahedral symmetry T_d and will have four frequencies: One totally symmetric, one doubly degenerate and two triply degenerate. (A. S. Ganesan, 1934). The relation between the observed SeO_4^{--} frequencies in triglycine selenate and the free ion is indicated below:

	ν_2	ν_3	ν_1	ν_4
In free state ..	342	415	835	875
In G_3Se ..	336, 370	438, 446	835	827, 875

The line at 370 cm^{-1} is broad and might possess another component. The line at 875 cm^{-1} is very much more intense because of its nearness to

the moderately intense Raman line due to the glycine units appearing at 870 cm.^{-1} . The symmetric oscillation appearing at 835 cm.^{-1} is very intense. As is to be expected because of the lower symmetry of the SeO_4^{--} ion inside the crystal the degeneracies of the modes are removed partly.

Glycine frequencies.—The assignments for the various group frequencies of the glycine ions were made after comparing the spectrum of triglycine selenate with that of triglycine sulphate and α -glycine. The presence of the zwitterion glycines is indicated by the existence of a band at 3150 cm.^{-1} and a line at 1680 cm.^{-1} which are due to the NH_3^+ stretching and $\text{C}=\text{O}$ stretching of COO^- groups respectively. The NH_3^+ rocking (1115 and 1146 cm.^{-1} in triglycine selenate (1134 and 1165 cm.^{-1} in triglycine sulphate) and deformation vibrational frequencies 1596 cm.^{-1} in triglycine selenate (1609 cm.^{-1} in triglycine sulphate) occur at lower frequency in triglycine selenate than in triglycine sulphate. Also, the COO^- antisymmetric vibration shows a similar behaviour: 1632 cm.^{-1} in triglycine selenate and 1648 cm.^{-1} in triglycine sulphate. The presence of a Raman line at 870 cm.^{-1} is due to the COOH group of the monoprotonated planar glycine. This feature was also observed in triglycine sulphate. In the spectrum of triglycine selenate also, one observes three frequencies 2960 , 2982 and 3015 cm.^{-1} which are attributed to the $\text{C}-\text{H}$ stretching vibrations; the corresponding lines in triglycine sulphate have the frequency shifts 2962 , 2988 and 3022 cm.^{-1} . In α -glycine and γ -glycine only two lines due to $\text{C}-\text{H}$ oscillations were observed. The multiplicity of the frequencies in triglycine sulphate and triglycine selenate might be a consequence of the presence of two types of glycine (planar monoprotonated glycine and zwitterion type of glycine).

The infrared absorption spectrum of triglycine selenate was investigated by Dodd (1959) and the frequency shifts corresponding to the absorption peaks recorded by him are entered in column 5 of Table I. The region investigated extends only from 640 cm.^{-1} to 3400 cm.^{-1} . There is a close correspondence between the frequency shifts of the Raman lines and the frequency shifts of the infrared absorption peaks. In infrared absorption there are five peaks at 1744 , 1856 , 2227 , 2318 and 2373 cm.^{-1} which do not appear in Raman effect. These peaks should therefore to be attributed to combinational modes.

5. SUMMARY

The Raman spectrum of a single crystal of triglycine selenate G_3Se which is ferroelectric below 22° C. has been photographed using $\lambda 2537$ excitation. 42 Raman lines have been recorded of which 6 belong to the lattice spectrum, 3 are due to $\text{NH}\dots\text{O}$ oscillations and the remaining 33 are due to internal

TRIGLYCINE SELENATE

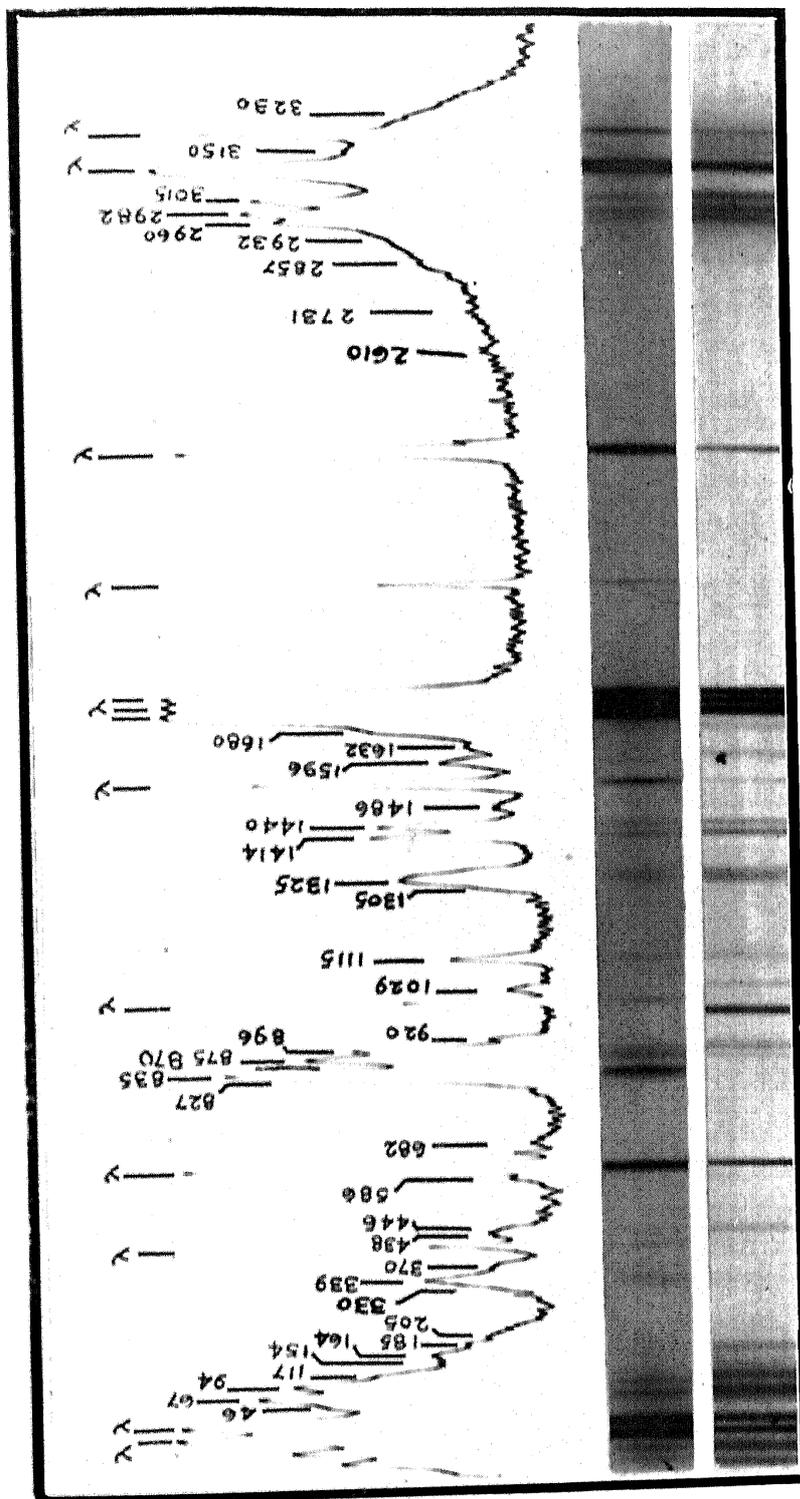


FIG. 1

oscillations of the ions of glycine and SeO_4^{--} . There is a close similarity between the spectrum of triglycine selenate and the spectrum of its isomorph, triglycine sulphate, the frequency shifts due to the SO_4^{--} ion being replaced by the frequency shifts due to the SeO_4^{--} ion. The existence of glycine in the zwitterion form in the structure of G_3Se is substantiated by the appearance in the Raman spectrum of lines which are attributable to NH_3^+ groups and COO^- groups. The appearance of the additional C—H line at 2982 cm.^{-1} in the spectrum of triglycine selenate which is absent in the spectrum of α -glycine indicates the existence of planar monoprotonated glycine also in the structure, as indicated by X-ray studies.

6. REFERENCES

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EXPLANATION OF PLATE XVII

FIG. 1

- (a) Raman spectrum of triglycine sulphate taken with Hilger medium Quartz Spectrograph.
- (b) Raman spectrum of triglycine selenate taken with Hilger medium Quartz Spectrograph.
- (c) Microphotometer record of the Raman spectrum of triglycine selenate.