RAMAN SPECTRUM OF CRYSTALLINE
α-GLYCINE

By R. S. Krishnan, F.A.Sc. and K. Balasubramanian

(*Department of Physics, Indian Institute of Science, Bangalore-3*)

1. Introduction

Glycine (amino-acetic acid $NH_2CH_2CO_2H$) is the simplest representative of the important class of amino-acids characterised by exceptional properties. All the compounds of this series belong to the class of amphoteric electrolytes. They are supposed to exist in the undissociated state as salt-like " zwitter ions " or dipolar ions, $^+NH_3.R.COO^-$. Glycine, like all the amino-acids, possesses both the properties of an amine and an acid. Because of their very interesting properties, a study of the Raman spectra of amino-acids in the form of single crystals is of very great importance. In the present paper are reported the results obtained from the study of the Raman spectrum of a single crystal of glycine.

Raman spectrum of solid glycine was investigated by Edsall (1936), Kahovec and Kohlrausch (1936), Ananthakrishnan (1937) and Baba *et al.* (1949). The substance used by them was in the form of crystal powder and the spectrum was excited by λ 4046 radiation of the mercury arc. It is not surprising therefore to find that the results obtained by them are far from being complete, even as regards the internal frequencies. Besides no data are available concerning the lattice (low) frequency spectrum of crystalline glycine. A reinvestigation of the Raman spectrum of crystalline glycine was therefore called for. This has now been carried out by us under more favourable conditions.

2. Experimental Details

Single crystals of α-glycine, in the form of colourless rhombic prisms, were easily grown from aqueous solutions of the pure substance. Samples of average size 1 cm. long were used for the present investigation. They were, however, not very clear. λ 2536·5 excitation was used to record the Raman spectrum. Using a Hilger medium quartz spectrograph and a slit width of 0·025 mm. satisfactory spectrograms were obtained with the exposures of the order of a few hours.

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3. RESULTS

A typical photograph of the Raman spectrum of glycine taken with the medium quartz spectrograph is reproduced in Fig. 1 (*b*) in the accompanying Plate XII together with the corresponding microphotometer record, Fig. 1 (*c*). A spectrum of the mercury arc is also reproduced in Fig. 1 (*a*). The positions and frequency shifts of the principal Raman lines are marked in Fig. 1 (*c*). They are listed in Table I below. Some of the Raman lines listed in the table fall on or adjacent to some of the faint mercury lines. This fact has been taken into consideration and the existence of all the Raman lines, listed in column 2 of Table I, has been established from a comparison of their relative intensities. The frequency shifts reported by Edsall, Kahovec and Kohlrausch and Ananthakrishnan have been included in the same table. We had no access to the original paper by Baba *et al.* and hence their results could not be included in the table.

The spectrum recorded here exhibits not less than 35 Raman lines, of which 17 including all the 7 lattice lines, have been recorded for the first time. The values of the frequency shifts obtained by the present authors agree reasonably well with those reported by the previous workers. Visual estimates of the relative intensities of the lines are also given in the same table. The orientation used was such that the illumination was parallel to the *b*-axis and the observation was perpendicular to the same axis.

The frequencies of the infra-red absorption maxima reported by Lenormant (1946) in the region 5–8 μ have been included in the column 6 of Table I. They agree reasonably well with some of the Raman frequencies observed in this region.

4. DISCUSSION

Glycine crystallises in two different crystal forms, namely, α- and β-forms, the ordinary one being the α-form. Both of them belong to the monoclinic class. α-glycine is usually crystallised from aqueous solution at room temperature, whereas β-glycine is obtained by adding alcohol to the glycine solution. The unit cell of α-glycine belongs to the monoclinic centro-symmetric class, with $a_0 = 5 \cdot 10$ Å, $b_0 = 11 \cdot 96$ Å, $c_0 = 5 \cdot 46$ Å and $\beta = 111° \ 42'$ (Marsh, 1957). The unit cell contains 4 molecules of glycine and the space group is $C_{2h}^5 - P2_1/n$. According to Albrecht and Corey (1939), the structure consists of nearly flat glycine molecules held together by hydrogen bonds between adjacent nitrogen and oxygen atoms to form continuous layers throughout the crystal. The atomic arrangement suggests a " zwitter ion " structure for glycine molecules in the crystal also ($^+NH_3 \cdot CH_2 \cdot COO^-$).

TABLE I

Raman frequencies of crystalline α-glycine

Sl. No.	Authors	Edsall	Kahovec and Kohlrausch	Anantha-krishnan	Infra-red (Lenormant)
1	53 (7s)	..	..	..	..
2	74 (6s)	..	..	..	..
3	90 (1)	..	..	...	..
4	109 (9)	..	..	..	..
5	164 (5s)	..	..	..	..
6	183 (4s)	..	..	..	..
7	199 (3s)	..	..	..	..
8	358 (3s)	..	..	..	..
9	499 (4bd)	507	..	507	..
10	588 (1)	589	..	..	..
11	677 (1)	..	..	..	..
12	697 (3d)	..	..	..	..
13	896 (8b)	891	870	893	..
14	925 (1)	..	..	..	..
15	1038 (3s)	1033	1020	1047	..
16	1112 (2s)	1112	..	1121	..
17	1140 (3s)	..	1130	1132	..
18	1320 (6)	1323	1320	1319	..
19	1330 (10)	..	..	1336	1332
20	1395 (2)	..	..	..	1388
21	1414 (6d)	1404	1400	1397	1408
22	1441 (4s)	..	1440	1437	1442
23	1459 (3s)	..	..	..	1460
24	1506 (3d)	..	1510	1499	1518
25	1563 (4d)	..	1570	1577	1562
26	1640 (1)	..	1650	1650	1613
27	1668 (2)	..	..	..	1627
28	2530 (1)	..	..	..	..
29	2630 (3)	..	..	2592	..
30	2750 (2)	..	..	..	..
31	2830 (2)	..	..	..	..
32	2895 (2)	..	..	2870	..
33	2974 (10)	2968	2960	2959	..
34	3008 (8)	3002	..	2999	..
35	3145 (3)	..	..	3113	..

(a) *External oscillations.*—The recorded spectrum exhibits 7 low frequency Raman lines with frequency shifts 53, 74, 90, 109, 164, 183 and 199 cm.$^{-1}$ Of these, the line at 90 cm.$^{-1}$ is very faint. The line at 109 cm.$^{-1}$ is the most intense. Of the 6 prominent lattice lines, the first three fall under one group and the remaining three fall under another group of closely spaced lines. All of them are reasonably sharp. From the fact that the unit cell belongs to the space group C_{2h}^5, and that it contains 4 molecules of glycine, taking each molecule as a unit, it is possible to work out the number of possible external or lattice oscillations [that are active in Raman effect. The full character table is given in Table II. The symbols given in the table have the usual significance. It is seen from the table that excluding the 3 translations (T) of the unit cell as a whole, there are 12 rotatory modes (R') and 9 translatory modes (T') of lattice oscillations. Of these, 6 rotatory modes and 6 translatory modes are active in Raman effect. In the case of organic crystals of the molecular type where the individual units are of the same kind as in naphthalene and held together by forces weaker than those in inorganic crystals like calcite, it is generally found that the translatory type of lattice oscillations appear very feebly in almost all the crystals studied (Kastler and Rousset, 1941; Fruhling, 1951) and the intense low frequency shift lines appearing in the Raman spectra of organic crystals should rarely be attributed to the translatory type of oscillations (*see* page 22 of Rousset's Book on "La Diffusion De La Lumiere par les Molecules Rigides", 1947). It is obvious therefore that the six intense lattice lines recorded in the spectrum of glycine may be attributed to the six rotational modes of the glycine molecule permitted to appear in Raman effect. Of these six, three are of the symmetrical class A_1 (symmetric with reference to two-fold axis) and the rest are of the anti-symmetric class A_2. It is well known that in the case of a monoclinic crystal Raman lines coming under the symmetric class A_1 should exhibit a variation in intensity with the orientation of the crystal (Saksena, 1940). In order to find out the class to which the observed lattice lines belong, preliminary studies were made of the effect of crystal orientation on the intensity of the Raman lines. For this purpose the crystallographic axes of the crystal were identified. The following two orientations were used: (1) Illumination along α and observation along γ, and (2) Illumination along β and observation along γ. It is observed that the set of lattice lines, namely, 164, 183 and 199 cm.$^{-1}$ exhibited marked variation in intensity with the orientation, and these three may therefore be attributed to the three modes of symmetric class A_1. Accurate polarisation studies are being carried out. The first three lattice lines 53, 74 and 109 should therefore belong to asymmetric class A_2. The feeble line near 90 cm.$^{-1}$ may be a translatory type of lattice oscillation.

TABLE II

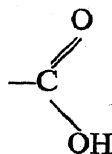| C_{2h}^{5}	E	C_2	i	σ_h	T	R'	T'	Selection Rule Raman	Selection Rule Infra-red
A_1	1	1	1	1	0	3	3	p	f
A_2	1	−1	1	−1	0	3	3	p	f
B_1	1	1	−1	−1	1	3	2	f	p
B_2	1	−1	−1	1	2	3	1	f	p
U_R (s) ..	4	0	0	0					
U_R (s—v) ..	4	0	0	0					
$h_\rho \chi_\rho'$ (R') ..	12	0	0	0					
$h_\rho \chi_\rho'$ (T') ..	9	1	3	−1					

p = permitted;   f = forbidden.

(b) *Internal oscillations.*—The 28 Raman lines of frequency shifts varying from 358 cm.$^{-1}$ to 3145 cm.$^{-1}$ can be classified as the internal oscillations of the glycine molecule and are analysed as follows:

The two intense lines with frequency shifts 3008 cm.$^{-1}$ and 2974 cm.$^{-1}$ should be assigned to the C—H stretching vibrations. The 2974 line which is more intense is nearly twice as broad as the 3008 line. The 2974 line can therefore be attributed to the symmetric stretching vibration. On either side of those two intense lines there are a few diffuse bands with mean frequency shifts 3145, 2895, 2830, 2750, 2630 and 2530 cm.$^{-1}$ They may be attributed to N—H stretching vibrations. The fact that there are no frequency shifts above 3145 cm.$^{-1}$ clearly shows the absence of trivalent nitrogen as in amines. This observation supports the conclusions of earlier investigators that there is no free amino group in crystalline glycine and that the constitution of the glycine molecule is $^+NH_3 \cdot CH_2 \cdot COO^-$. This is supported also by the investigations on the infra-red carried out by Lenormant (1946). Two bands are commonly observed in the spectra of $^-NH_3$ compounds due to the N—H bending vibrations. They usually occur in the ranges 1640–1535 and 1520–1490. The lower of the two bands is usually more intense. In the spectrum of glycine there are two lines at 1640 and 1506 and these could therefore be assigned to the asymmetrical and symmetrical

N—H bending vibrations. Both of them are broad and might possess a structure.

The non-appearance of any Raman line with a frequency shift in the 1700 region indicates the absence of the carboxyl group
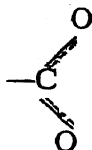
$$\underset{\text{OH}}{\overset{\displaystyle O}{\underset{\diagdown}{-\overset{\diagup\diagup}{C}}}}$$

in the crystalline glycine. The two feeble lines 1668 and 1563 may be attributed to the C = O oscillation of the ionised carboxyl group. The lines at 1459 and 1441 are extremely sharp but weak, and can be attributed to the C—H scissoring vibrations. The lines 1414 and 1395 form a close doublet, the former being more intense. These may be attributed to the symmetrical valence vibrations of the

$$\underset{\text{O}}{\overset{\displaystyle O}{\underset{\diagdown}{-\overset{\diagup}{C}}}}$$

group. The 1330 and 1320 lines which also form a very close doublet may be attributed to C—H wagging and twisting vibrations. The 1140 and 1112 cm.$^{-1}$ might arise from the C—CH$_2$ rocking vibrations, while the 1038 line can be assigned to the C—N stretching vibration. The 896 line which is very intense is due to the C—C stretching vibration. The 697 line is in all probability due to the C—N bending vibrations. The 499 and 358 lines are due to the C—C bending and torsional oscillations. The 499 is more intense and broad.

5. SUMMARY

Raman spectrum of a single crystal of α-glycine has been photographed using λ 2536·5 excitation. 35 Raman lines have been recorded with frequency shifts 53, 74, 90, 109, 164, 183, 199, 358, 499, 588, 677, 697, 896, 925, 1038, 1112, 1140, 1320, 1330, 1395, 1414, 1441, 1459, 1506, 1563, 1640, 1668, 2530, 2630, 2750, 2830, 2895, 2974, 3008 and 3145. Of these 17 have been recorded for the first time. The 6 intense lattice lines 53, 74, 109, 164, 183 and 199 have been attributed to the rotational oscillations of the 4 molecules of glycine contained in the unit cell of the crystal. Assignments have also
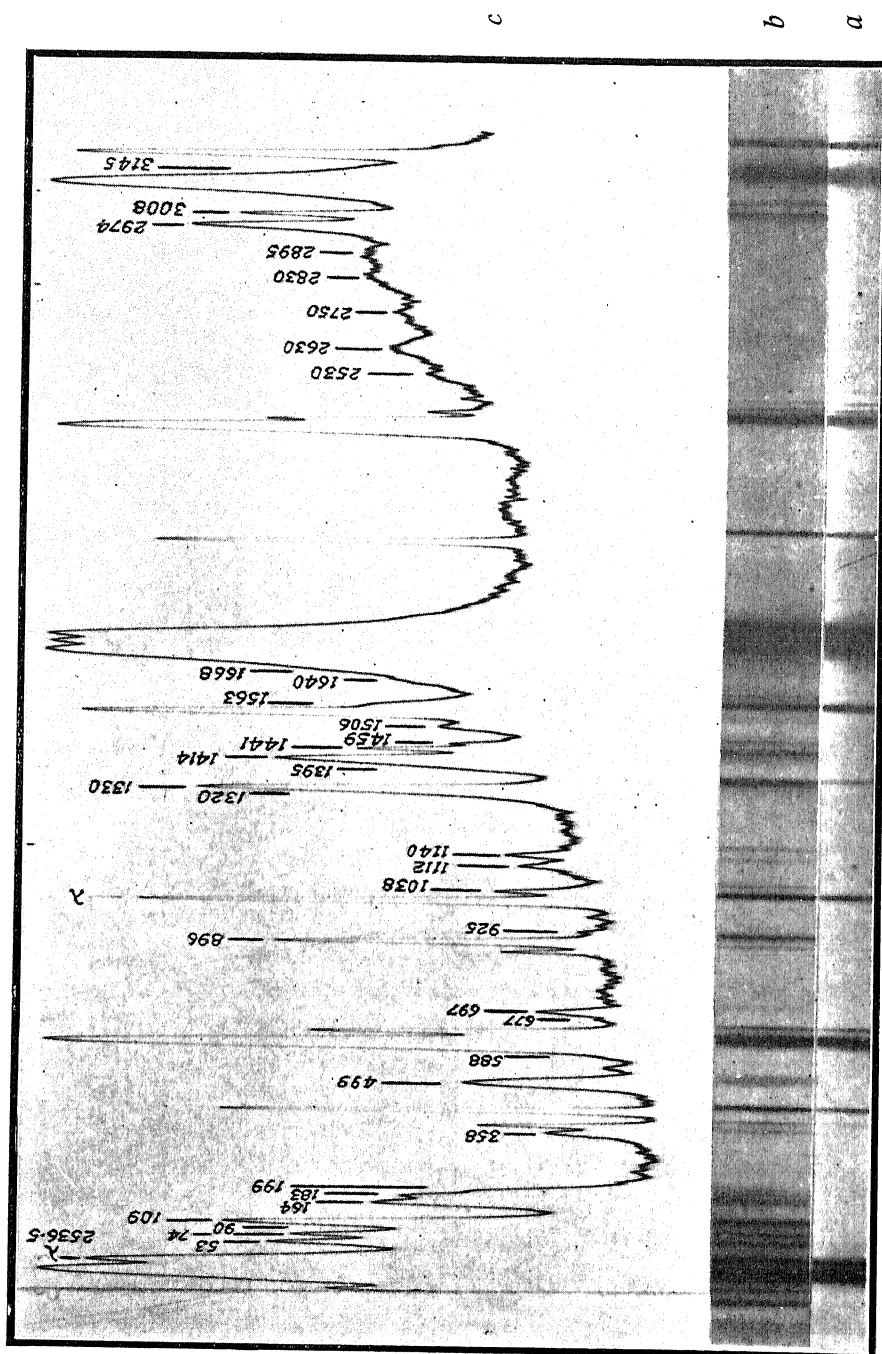
FIG. 1. (a) Spectrum of the mercury arc. (b) Raman spectrum of crystalline α-glycine taken with medium quartz spectrograph. (c) Its microphotometer record.

been made for all the prominent internal frequencies. The present study confirms the existence of $-^+NH_3$ groups and the ionisation of the carboxyl group even in the crystal.

6. REFERENCES

1.	Albrecht, G. and Corey, R. B.	*Jour. Am. Chem. Soc.*, 1939, **61**, 1087.
2.	Ananthakrishnan, R.	.. *Proc. Ind. Acad. Sci.*, 1937, **5 A**, 200.
3.	Baba, H. Shimanouchi, T. and Mizushima, S.	*Jour. Chem. Soc. Japan Pure Chem. Sec.*, 1949, **70**, 333.
4.	Edsall, J. T.	.. *Jour. Chem. Phys.*, 1936, **4**, 1.
5.	Fruhling, A.	.. *Ann. de Phys.*, 1951, **6**, 401.
6.	Kahovec, L. and Kohlrausch, K. W. F.	*Mon. f. Chemie*, 1936, **68**, 359.
7.	Kastler, A. and Rousset, A.	.. *C. R. Acad. Sci.*, 1941, **212**, 645; *Journal de Physique*, 1941, **2**, 49.
8	Lenormant, H.	.. *Comp. Rend.*, 1946, **222**, 1432.; *Jour. Chem. Phys.*, 1946, **43**, 327.
9.	Marsh, R. E.	.. *Acta Cryst.*, 1957, **10**, 814.
10.	Saksena, B. D.	.. *Proc. Ind. Acad. Sci.*, 1940, **11 A**, 229.