

RAMAN SPECTRA OF ADDITION COMPOUNDS OF GLYCINE (DIGLYCINE HYDROCHLORIDE, DIGLYCINE HYDROBROMIDE AND DIGLYCINE NITRATE)

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1. INTRODUCTION

IN two papers which appeared in these *Proceedings*, Krishnan and Balasubramanyam (1958 *a, b*) reported the results obtained from a study of the Raman spectra of single crystals of α -glycine (G) and triglycine sulphate (G_3S). In continuation of this work, the Raman spectra of single crystals of three more addition compounds of glycine, namely, diglycine hydrochloride (G_2Cl), diglycine hydrobromide (G_2Br) and diglycine nitrate (G_2N) have been investigated and the results are presented here. These substances will hereafter be referred to by their respective shorter symbols as indicated in the brackets. The Raman effect in these substances has not been investigated so far. As they are transparent to the ultraviolet, the λ 2536.5 resonance radiation of mercury was used as exciter.

2. EXPERIMENTAL

Fairly large, transparent crystals of G_2Cl , G_2Br and G_2N were grown by slow evaporation of aqueous solutions of the constituents in stoichiometric proportions. The molecular formulæ of these crystals were established from density as well as X-ray measurements. Well-developed crystals were in the form of parallel-pipeds of 2 cm. \times $\frac{1}{2}$ cm. \times $\frac{1}{2}$ cm. in the case of G_2Cl and G_2Br and 1 cm. \times $\frac{1}{2}$ mm. \times $\frac{1}{2}$ mm. in the case of G_2N . The diglycine hydrohalides grow along the *c*-axis. The spectra were taken using a Hilger medium quartz spectrograph with 0.003 cm. slit width. Exposures of the order of 5 to 6 hours were found to be sufficient to get intense spectrograms using λ 2536.5 excitation. In the case of G_2Cl the scattering was taken at along the *c*-axis and the illumination was approximately 45° to the *b*-axis. In the case of G_2Br the *c*-axis was placed perpendicular to the plane of incidence and scattering. Scattered light along the *b*-axis was photographed in the case

of G_2N . The faces of G_2N used to get frosted due to exposure to the ultra-violet radiation and the crystal specimen had to be polished frequently. Frequency shifts of the very faint lines have been estimated from the microphotometer records.

3. RESULTS

Enlarged photographs of the Raman spectrum of single crystals of G_2Cl , G_2Br and G_2N together with their respective microphotometer records are reproduced in Figs. 1 to 3 in the accompanying plate. For the purpose of comparison the mercury arc spectrum in the ultraviolet region is also included. The principal Raman lines are marked in the microphotometer records. The frequency shifts have been listed in Tables I and II. The frequency shifts observed by the author in triglycine sulphate, and α -glycine are given in columns 5 and 6 respectively in Tables I and II.

TABLE I

Internal frequencies

Sl. No.	Diglycine hydrochloride	Diglycine hydrobromide	Diglycine nitrate	Triglycine sulphate	α -Glycine	Assignment		
1	330 (2 <i>d</i>)	330 (3 <i>d</i>)	311 (1 <i>d</i>)	330 (6 <i>d</i>)	358 (35)	C-C Torsion		
2	354 (6)	354 (6)	349 (3)	345 (2)				
3	504 (8) 518 (7)	504 (5) 518 (7)	505 (6)	450 (10) 463 (6) 500 (6)	499 (5 <i>bd</i>)	-COO ⁻ rocking		
			540 (2) 561 (2)	}			O-NO ₂	
			575 (4) 587 (3)					571 (4) 584 (3)
5	665 (3 <i>bd</i>)	660 (2 <i>d</i>)	689 (3)	665 (6 <i>d</i>) 697 (3)	677 (1) 697 (3 <i>d</i>)	-COO ⁻ bending		
6	878 (18)	873 (13)	869 (4)	870 (10)		-COOH ?		
7	890 (12)	889 (8 <i>b</i>)	898 (10)	890 (12)	896 (8 <i>b</i>)	CCN stretch		
8	914 (8)	913 (3)	924 (4)	902 (8)	925 (3)	OH out of plane bend ?		
9	1036 (8)	1034 (10)	1053 (5)	980 (20) 1009	1038 (3 <i>s</i>)	CCN stretch		
				1040 (6 <i>d</i>)			}	SO ₄ ⁻ - ν_4
				1092 (3 <i>d</i>)				
				1104 (6)				

TABLE I (Contd.)

Sl. No.	Diglycine hydrochloride	Diglycine hydrobromide	Diglycine nitrate	Triglycine sulphate	α -Glycine	Assignment
10	1106 (10)	1104 (12)	1132 (5)	1114 (8)	1112 (2s)	NH ₃ ⁺ rocking
11	1132 (12)	1124 (10)	1144 (3)	1134 (8) 1164 (4 d)	1140 (3s)	
	1249 } 1267 } (5 d)	1248 } 1264 } (3 d)				C-OH ?
12	1302 (8)	1301 (12)		1303 (10 d)	1320 (6)	CH ₂ Wagging and Twisting
13	1330 (16)	1327 (15)	1322 (10) 1339 (12) 1346 (12)	1321 (10 d)	1330 (10)	
14	1394 (6 d)	1396 (8 d)	1390 (10)	1375 (3 d)	1395 (2)	O-NO ₂ C-O stretch ?
15	1414 (20)	1412 (17)	1412 (10)	1414 (15)	1414 (6 d)	$\begin{array}{c} \text{O} \\ // \\ \text{C} \\ // \\ \text{O} \end{array}$ Valence
16	1453 (10) 1463 (4 d)	1450 (5) 1460 (5)	1443 (10)	1441 (12)	1441 (4 s) 1459 (4 d)	CH ₂ Scissoring
17	1507 (9)	1506 (10)	1512 (3)	1483 (6)	1505 (3 d)	NH ₃ ⁺ deformation
18	1599 (7)	1593 (8)	1584 (9) 1625 (5)	1609 (10)	1563 (4 d)	
19	1627 (4 d)	1610 (5 d)	1644 (5)	1648 (5)	1640 (1)	$\begin{array}{c} \text{O} \\ // \\ \text{C} \\ // \\ \text{O} \end{array}$ Valence
20	1671 (1)	1670 (1)	1675 (4)	1675 (10)	1668 (2)	C=O ionised carboxyl
21	1900 (1 d) 2030 (2 d) 2459 } (2 d)	1910 (0) 2000 (2 d)				
	2553 }			2528 (1 d)	2530 (1 d)	O...H...O
22	2613 (4 d)	2592 (3 d)	2620 (2 d) 2642 (2 d)	2651 (3 d)	2630 (3 d)	N-H hydrogen bonded
23	2652 (4 d)	2702 (3 d) 2724 (4 d)	2707 (3 d)			
				2763 (4 d)	2750 (2 d)	do.
24	2713 (3 d)	2785 (7 d)	2751 (3 d)			do.
25	2790 (4 d)	2874 (7 d)	2806 (3 d)	2874 (5 d)	2830 (2 d)	do.
	2853 (5 d)	2907 (8 d) 2917 (7 d)	2882 (4 d)	2930 (5 d)	2895 (2 d)	do.
26	2974 (19)	2967 (16)	2966 (15)	2962 (13)	2974 (5 d)	CH stretch
	2994 (20)	2986 (20)		2988 (15)		do.
27	3006 (11)	3002 (13)	3002 (13)	3004	3008 (8)	do.
28	3040 (8)	3029 (5)	3039	3022 (13)		NH ₃ ⁺
	3066 (3 d)	3067 (4 d)				do.
29	3126 (7 d)	3122 (7 d)	3143 (2 d)	3150 (6 d)	3145 (3 d)	do.
30	3229 (2 d)	3221 (4 d)	3252 (2 d)	3230 (5 d) 3270 (4 d)		do.
			3339 (1 d)			do.

TABLE II
External frequencies

Diglycine hydrochloride	Diglycine hydrobromide	Diglycine nitrate	Triglycine sulphate	α -Glycine
37 (6)	36 (2)			
	49 (5)	42 (4)	45 (6)	53 (7)
60 (5)	65 (7)	60 (4)	63 (10)	
73 (11)			73 (10)	74 (6 s)
	86 (8)	88 (20)		90 (1)
101 (8)	97 (11)	105 (9)	102 (10)	109 (9)
116 (3)	108 (6)			
141 (6)	139 (5)	141 (6)	129 (5)	
	158 (7)	153 (13)		
171 (7)	169 (5)	168 (5 d)	171 (8)	164 (5 s)
191 (4)	187 (4)	186 (4 d)		183 (4 s)
203 (2 d)	207 (3)	211 (3 d)	220 (4 d)	199 (3 s)
221 (2 d)		250 (1 d)		

Fifty-one Raman lines in the case of G_2Cl , 52 in the case of G_2Br and 46 in the case of G_2N have been recorded in the present investigation. Of these 10 in the case of G_2Cl , 11 in the case of G_2Br and 10 in the case of G_2N belong to the lattice spectra. The diffuse Raman line at 2030 appearing in G_2Cl falls on a weak mercury line. The presence of this could be easily seen by a comparative study of the photograph as well as the microphotometer record.

Edsall (1936) and Takeda *et al.* (1958) have recorded the Raman spectrum of glycine hydrochloride in aqueous solution and have reported the following frequency shifts 503, 577, 657, 871, 912, 1043, 1120, 1259, 1316, 1433, 1516, 1630, 1743, 2974 and 3017. These lines have been recorded by the author in the spectrum of single crystals of G_2Cl except 1743 cm^{-1} the presence of which is unfortunately masked by the triplet with the λ 2536.5 excitation.

4. STRUCTURE DATA

G_2Cl crystallises in the orthorhombic class in the space-group $P2_1 2_1 2_1$. The crystal structure has been determined by Theodor Hahn and Buerger (1957). The unit cell has 4 molecules of diglycine hydrochloride, with $a = 8.15 \text{ \AA}$, $b = 18.03 \text{ \AA}$ and $c = 5.34 \text{ \AA}$. According to these authors, slabs of glycine molecules are extending perpendicular to b , and zig zag Cl-Cl chains are along a screw parallel to c . The Cl chains are bonded on both sides to two molecules by means of hydrogen and Van der Waals bonds. The main effect of this

chain is to orient the molecules in such a way as to turn their NH_3 groups towards Cl forming $\text{N}\dots\text{Cl}$ hydrogen bonds. In the glycine molecules, strong forces are effective between the molecules, particularly the strong $\text{O}\dots\text{O}$ and $\text{N}\dots\text{O}$ hydrogen bonds. The chemical formula for G_2Cl is $(\text{NH}_3\text{CH}_2\text{COO}^-)(\text{NH}_2\text{CH}_2\text{COOH})\text{Cl}$.

G_2Br also crystallises in the orthorhombic symmetry in the space-group $\text{P2}_1\text{2}_1\text{2}_1$. The cell dimensions are: $a = 8.21 \text{ \AA}$, $b = 18.42 \text{ \AA}$ and $c = 5.40 \text{ \AA}$. The unit cell consists of 4 molecules of diglycine hydrobromide. The crystal structure was determined by Theodor Hahn, Elia Barney and M. J. Buerger (1956). Its chemical formula is similar to that of G_2Cl .

At room temperature G_2N crystallises in the monoclinic class, space-group $\text{P2}_1/a$ with $a = 9.496 \text{ \AA}$, $b = 5.107 \text{ \AA}$, $c = 9.35 \text{ \AA}$ and $\beta = 98.8^\circ$. The unit cell has 2 molecules of diglycine nitrate. The nitrate groups must be disordered or rotating in the room temperature phase, since the N-atoms of the nitrate groups are occupying the centres of symmetry. It goes into the ferroelectric phase below -67° C . The transition to the ferroelectric phase is of second order type (Pepinsky, Vedam, Okaya, 1958).

5. DISCUSSION

(i) Internal Frequencies

As is to be expected, there is a close correspondence between the frequency shifts observed in the various addition compounds of glycine. The common frequency shifts have been serially numbered in column 1. From a comparison of the frequency shifts observed in the Raman spectra of these compounds and those observed in similar organic compounds, the assignments for these common frequencies have been indicated in the appropriate column in Table II. The common frequency shifts numbered 10, 11, 16, 17, 18, 19, 21 and 22 exhibit appreciable variations from compound to compound. This may be attributed to the influence of the hydrogen bonds of different strengths in different compounds. The vibrations $-\text{COO}^-$ rocking (3), $-\text{COO}^-$ wagging (4) and CH_2 scissoring (16) are found to be split up and give rise to two frequencies each in G_2Cl and G_2Br . The CH_2 scissoring vibrations in G spectrum and NH_3 deformation (17) in G_2N are also found to split up. The splitting of the above lines may be due to the following: (i) larger number of molecules in the unit cell, and (ii) the effect of crystalline field. The CH stretching vibration appears as 3 lines in G_2Cl , G_2Br and G_3S , whereas only two lines are observed in G and G_2N . It should be mentioned that combination of any two intense lines in the region 1300–1600 will fall in the region of CH stretching vibrations. This might partly explain the intense background in this region,

or it may also be due to O...H...O oscillations. A series of discrete lines appear in the region (apart from the background) 2900–3270 cm^{-1} in all the above crystals. These frequencies may be due to N-H oscillations arising from zwitterion structure of the glycine group and N...H...O (hydrogen, bonded) oscillations. In the case of G_2Cl and G_2Br the N-H...Cl or N-H...Br oscillations can appear in this region for the bond distances observed in these crystals (Nakamoto, 1955; Pimental, 1956; Lord and Merrifield, 1953). In the region 2600–2950 cm^{-1} a series of well-defined broad and intense lines are observed in the spectra of glycine and its addition compounds. These are assigned as N-H hydrogen bonded stretching vibration. A faint band at about 2500 is observed in the case of G_2Cl spectrum. A band in the same region can also be seen with some difficulty in the spectra of G_2Br and G_2N although they have not been marked in the microphotometer. This may be attributed to O...H...O hydrogen bonds of very short distances.

The Raman lines 1900 and 2030 in G_2Cl and the corresponding lines at 1910 and 2000 in G_2Br appear to be peculiar to the halide addition compounds. In this connection, it is worthwhile to point out that in the case of NH_4Cl and NH_4Br , Krishnan (1947–48) observed frequency shifts at about 2000 cm^{-1} . He was unable to explain satisfactorily the existence of this line. In the case of glycine halides two more lines are observed in the region 1250. The diffuse lines around 1250 cm^{-1} may be due to C-OH vibrations. Similar bands are also observed in the infra red spectra of amino acid hydrohalides by Randall (1949), Josien *et al.*, in amino acids (1951), and Flett (1951) and Ananthanarayanan (1960) in the Raman spectra of dicarboxylic acids.

The principal frequency shifts of HCl acid and HBr acid are at about 2760 cm^{-1} and 2465 cm^{-1} respectively. A corresponding frequency may not appear in G_2Cl and G_2Br because of the presence of N-H...Cl and N-H...Br hydrogen bonds.

NO₃⁻ ion.—If the nitrate ion has the symmetry D_{3h} , it is expected to give rise to frequencies 1050 (totally symmetric oscillation observed as a very intense line), 720 and 1300 (doubly degenerate oscillations) and 830 (Theimer, 1950). The frequency 1053 observed in G_2N may correspond to 1036 line observed in all the other compounds both from the intensity point of view as well as the sharpness. Also in the spectrum one does not observe any line corresponding to 720 cm^{-1} . If the NO_3 ion is of the form O- NO_2 as in the case of alkyl nitrates it may give rise to frequencies in the region 1640–1628, 1285–1260 cm^{-1} (symmetrical) and ester deformation vibration near 610–560 cm^{-1} (West, 1956; Nibben, 1939). The spectrum of G_2N exhibits two feeble lines 540, 561, two very intense and broad lines 1339 and 1346 and a line of

moderate intensity at 1625 cm^{-1} . These are not recorded in the spectra of the other addition compounds. This observation seems to support the view of staggered configuration for NO_3 ion in G_2N . Fairly big crystals are being grown to undertake the orientation and polarisation work which could give some more information regarding the nature of the NO_3 ion.

The complete X-ray structure analysis should confirm the staggered configuration for NO_3 ion.

(ii) Lattice Spectrum

G_2Cl , G_2Br and G_2N exhibit nearly the same number of low frequency lines. There seems to be a close correspondence between the frequencies of G_2Br and G_2N , the only difference being in the G_2Br spectrum the lines are sharp, whereas in the G_2N spectrum the lines are broad. This is indeed surprising in view of the fact that both have got different crystal structures.

In the case of G_2Cl , G_2Br , one can work out group theoretically the number of lines that are allowed to appear in Raman effect for the space-group $\text{P2}_1\text{2}_1\text{2}_1$ taking the whole molecule as one unit. Nine translatory and 12 rotatory modes should be active in Raman effect. In organic crystals the oscillations of rotatory type are expected to appear more strongly. Actually 10 lines are observed in G_2Cl and 11 lines in G_2Br and these should be attributed to rotatory type of oscillations.

On the same basis in the case of G_2N only 6 rotational modes are permitted in Raman effect (space-group $\text{P2}_1/\alpha$). Actually one observes 10 frequency shifts. Taking the 2 glycines as 2 units and nitrate as the third unit, one finds that 6 translatory and 12 rotatory modes should be active in Raman effect. If the translatory modes as usual are of negligible intensity, twelve rotational modes will appear with appreciable intensity in the lattice spectrum.

6. SUMMARY

Raman spectra of single crystals of diglycine hydrochloride, diglycine hydrobromide and diglycine nitrate have been recorded for the first time. $\lambda 2536.5$ resonance radiation of mercury has been used as exciter. The spectrum of diglycine hydrochloride exhibits 10 low frequency lines and 41 lines due to internal oscillations, while that of diglycine hydrobromide exhibits 11 lines and 41 lines respectively. In the case of diglycine nitrate 46 lines have been recorded, of which 10 belong to the lattice spectrum. These spectra are compared with the Raman spectra of triglycine sulphate and α -glycine and proper assignments have been given to the internal oscillations.

7. ACKNOWLEDGEMENT

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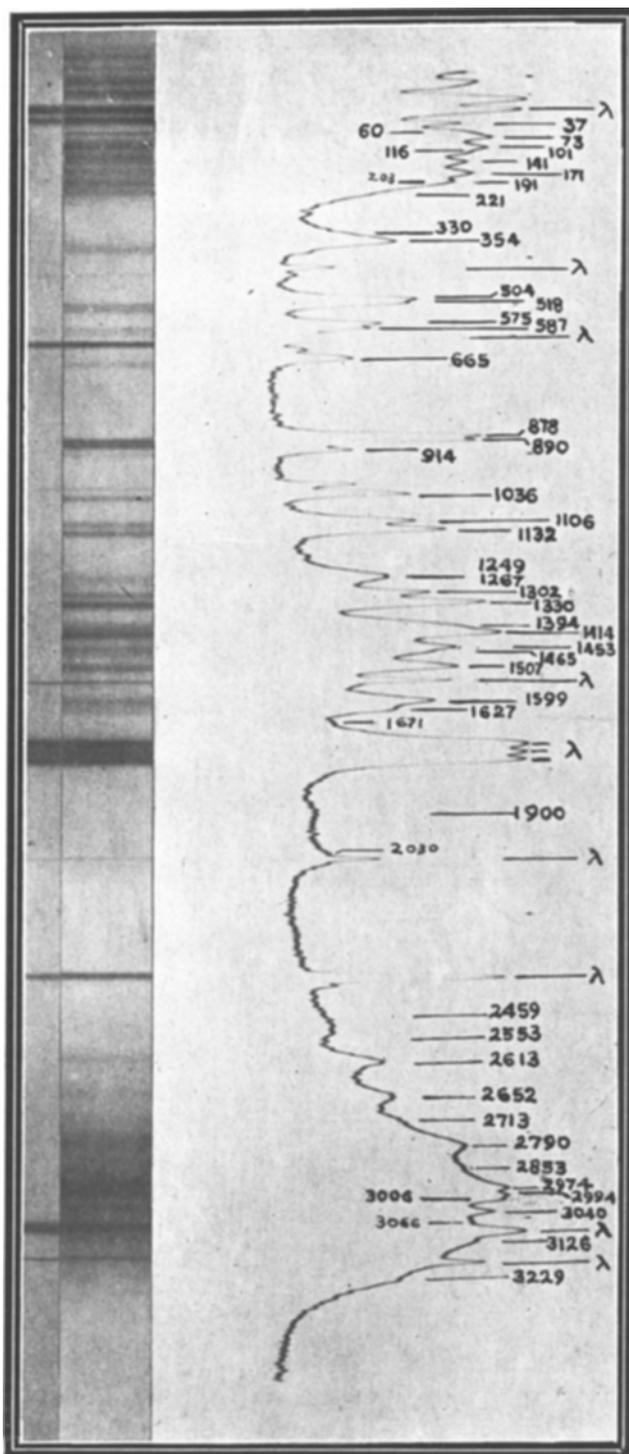


FIG. 1

- (a) Mercury Spectrum.
- (b) Raman Spectrum of Diglycine Hydrochloride.
- (c) Microphotometer Record.

(a)

(b)

(c)

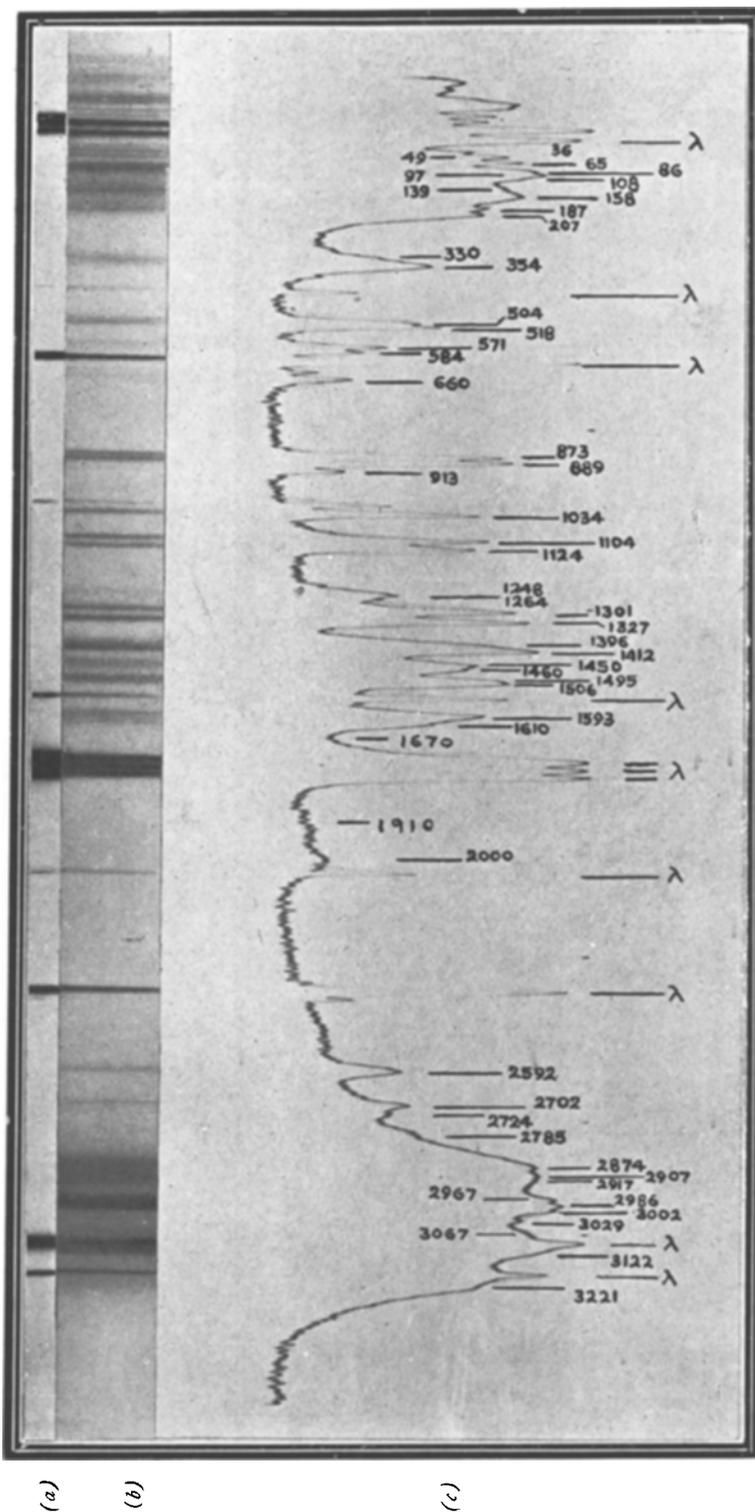
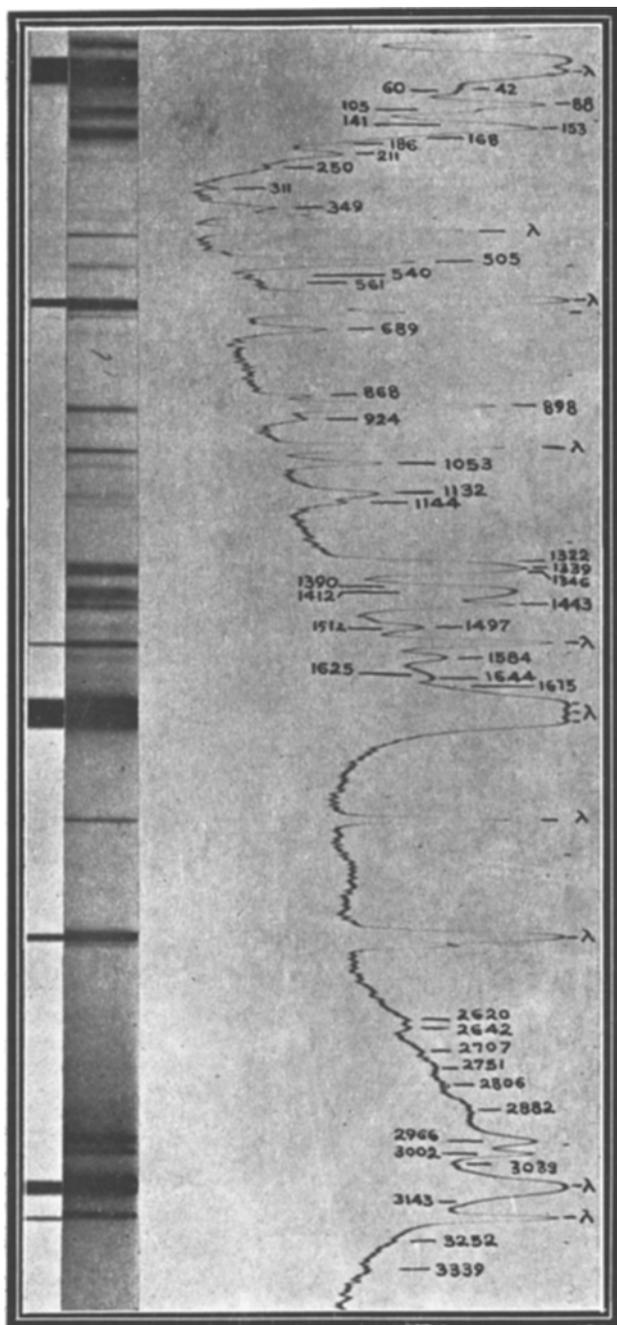


FIG. 2
(a) Mercury Spectrum.
(b) Raman Spectrum of Diglycine Hydrobromide.
(c) Microphotometer Record.



(a)
(b)

(c)

FIG. 3

- (a) Mercury Spectrum.
- (b) Raman Spectrum of Diglycine Nitrate.
- (c) Microphotometer Record.