Raman Spectrum of γ-Glycine

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A study of Raman spectra of crystalline glycine and its addition compounds is of great interest because of the existence of strong hydrogen bonding in these substances. A systematic study of Raman effect in single crystals of these substances was therefore undertaken in the Department of Physics of the Indian Institute of Science a few years ago. The Raman spectra of α-glycine(1), triglycine sulfate(2), diglycine nitrate(3), diglycine hydrochloride(3) and diglycine hydrobromide(3) have already been reported. It is well known that besides the α-form, two other polymorphic forms of glycine exist. These are (1) an unstable β-form first described by Fischer(4) and (2) γ-form the existence of which was reported by one of us(5). The crystal structure of the γ-form has been determined very accurately(6). This γ-variety can be obtained in single crystal form and is quite stable. It is therefore considered desirable to have its Raman spectrum photographed and compared with that of α-glycine.

Experimental Details

Single crystals of γ-glycine were grown in the following way(5,6). A saturated aqueous solution of α-glycine was prepared at 60 to 80°C. This was made acidic with 15% acetic acid and was cooled slowly in an ice-box with seeding γ-glycine crystals. They usually grow in massive aggregates; but, with some difficulty single crystals of small size could be obtained. Two specimen of roughly 5 mm. in size were used for taking the Raman spectrum using λ 2536.5 excitation. Exposure for about one day was found to be necessary for recording a satisfactory spectrogram with a Hilger medium quartz spectrograph. The crystals did not get spoiled due to irradiation with ultraviolet light.

Results

An enlarged photograph of the Raman spectrum of γ-glycine obtained with λ 2536.5 excitation is reproduced in Fig. 1 (b) and the corresponding microphotometer record is shown in Fig. 1(c). Fig. 1(a) represents the Raman spectrum of α-glycine taken under identical conditions. The frequency shifs in cm^{-1} of the observed Raman lines are marked in the microphotometer record. They are also tabulated in Table I, column 2. The figures given in brackets are the intensities of the lines for the unspecified orientation that was used. These intensities are estimated spectrophotometrically. The Raman frequency shifts of α-glycine(1) are also entered in column 1 of Table I. On the whole 39 Raman lines are

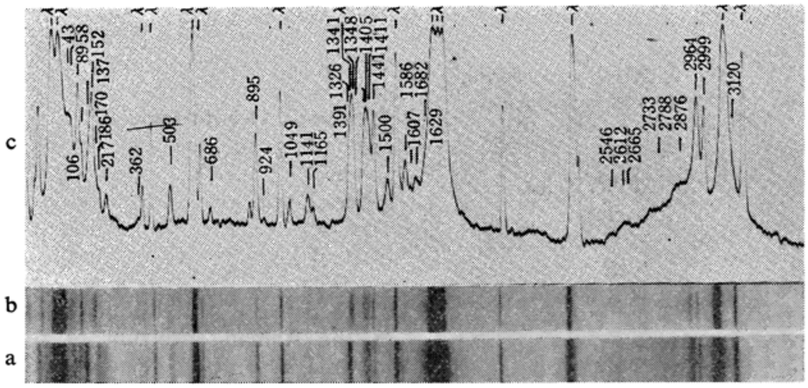

Fig. 1. (a) Raman spectrum of α-glycine with λ 2536 excitation.
(b) Raman spectrum of γ-glycine with λ 2536 excitation.
(c) Microphotometer record of Raman spectrum of γ-glycine.

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1) R. S. Krishnan and K. Balasubramanian, *Proc. Ind. Acad. Sci.*, **48A**, 55 (1958).

2) R. S. Krishnan and K. Balasubramanian, ibid., **48A**, 138 (1958).

3) K. Balasubramanian, ibid., **53A**, 105 (1961).

4) E. Fischer, *Ber. dtsch. chem. Ges.*, **38**, 2917 (1905).

5) Y. Iitaka, *Proc. Japan Acad.*, **30**, 109 (1954).

6) Y. Iitaka, *Acta Cryst.*, **14**, 1 (1961).

TABLE I. RAMAN FREQUENCIES OF CRYSTALLINE γ-GLYCINE

α-Glycine	γ-Glycine Raman effect	γ-Glycine Infrared	Assignment
	43(10)		Lattice
53(30)	58(15)		
74(23)	89(48)	90.3(i)	
90(?)		101(w)	
109(61)	106(20)	105(i)	
588		116(w)	
		127(w)	
	137(15)	138(i)	
164(33)	152(40)		
	170(6)	173(i)	
183(25)	186(8)		NH……O
199(15)	217(9)	243	NH……O
358(11)	362(2)	357	NCC
499(18)	503(14)	503	COO^- nocking
588		557, 560	NH_3^+ torsion
		602, 607	-COO^- wagging
697(7)	686(4)	684, 689	-COO^- sym. bend.
896(42)	895(27)	888, 893	CCN sym. stretch.
925	924(?)	924, 929	CH_2 rocking
1038(12)	1045(?)	1044	CCN antisym. stretch.
	1049(8)	1050	
		1126	
1112(9)	1141(10)	1135	NH_3^+ rocking
1140(10)	1165(6)	1154	〃
1320(60)	1326(25)	1317	CH_2 wagging
1330(60)	1341(35)	1324	〃
		1340	
	1348(35)		〃
1395	1391(30)	1389	-COO^- sym. stretch.
	1405(30)	1397	〃
1414(41)	1411(25)		〃
1441(27)	1441(31)	1435	CH_2 sym. bend.
1459(20)			
1506(14)	1500(7)	1492	NH_3^+ sym. defmn.
1563(25)	1586(10)	1575	NH_3^+ deg. defmn.
		1585	
	1607(5)	1620	
1640(12)	1629(5)		-COO^- antisym. stretch.
1668(8)	1682(?)	1660	NH_3^+ deg. defmn.
2530(5)	2546(3)		N-H bonded oscillations
2630(11)	2612(5)		〃
	2663(5)		〃
2750(10)	2733(8)		〃
	2788(8)		〃
2830(14)	2876(11)		〃
2895(17)			〃
2974(47)	2964(41)		C-H stretch.
3008(36)	2999(35)		C-H stretch.
3145(15)	3120(5)		NH_3^+ stretch.

i, Intense; w, Weak

recorded in γ-glycine of which the first nine lines (43~270 cm^{-1}) belong to low frequency spectrum and the remaining 30 lines belonging to internal oscillations. The Raman spectrum of α-glycine reproduced in Fig. 1 (a) is more intense than that of γ-glycine. This is due to the fact that the specimen of γ-glycine used was less perfect than that of α-glycine.

Discussion

γ-Glycine crystallizes in hexagonal class with space group $P3_1$ or $P3_2$ and shows piezoelectric properties along the c-axis. The cell dimensions are $a=7.037$ Å and $c=5.483$ Å. There are 3 molecules in the unit cell. Here also the glycine units exist in the zwitter ion form as in α-glycine. According to the detailed structure analysis carried out by one of us (Iitaka[6]) the N atom is 0.309 Å (12.8°) out of the best plane through C_{I}, C_{II}, O_{I}, O_{II} as against 0.436 Å (18.6°) in α-glycine. The N atoms are surrounded by 5 oxygen atoms at short distances out of which 3 short distances are attributed to be making hydrogen bonds (N–H···O); these hydrogen bond (N–H···O) distances are as follows; 2.801 Å, 2.817 Å and 2.970 Å. In α-glycine two hydrogen atoms are participating in strong hydrogen bonds which hold the molecule in a sheet and the third hydrogen atom forms a weak bifurcated bond with glycines in the next sheet. Whereas, in γ-glycine there is no such bifurcated bond and all these bonds are nearly of equal strength. The directional properties of the hydrogen bonds are more fully satisfied in γ-glycine than that in the other form. The hydrogen bonding between amino N and carboxyl O atoms links the molecules in helical chains about the 3-fold screw axis. These chains are linked together by lateral hydrogen bonds forming the 3-dimensional network of hydrogen bonds.

Internal Oscillations.—The frequencies corresponding to the absorption maxima of γ-glycine in infrared reported by Tsuboi and others[7] are given in column 3 of Table I. The data on the far-infrared absorption spectrum of γ-glycine (85~200 cm^{-1}) was supplied by Tsuboi[8]. There is a very close correspondence between the frequency shifts observed in the Raman spectrum of γ-glycine and its infrared absorption frequencies. This is not surprising because the crystal belongs to the hexagonal class $P3_1$ or $P3_2$ for which the selection rules are such that the Raman effect and infrared absorption are not mutually exclusive. Some additional maxima are observed in the

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[7] M. Tsuboi, T. Onishi, I. Nakagawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta.*, 12, 253 (1958).

[8] M. Tsuboi, unpublished work.

infrared. The Raman line corresponding to the absorption 602∼607 cm^{-1} in infrared can not be identified in the spectrum taken with λ 2536.5 excitation as it falls very close to the mercury line λ 2576.3 Å. In the infrared absorption, above 1700 cm^{-1} no data are available for comparison with the observed Raman frequencies.

As is to be expected there is a close agreement between the Raman frequencies of γ-glycine and α-glycine. From a comparative study of the two spectra the assignments have been given for most of the internal oscillations. Many of the internal oscillations are influenced by the hydrogen bonds and especially those which contain N–H group. A very careful comparison of the spectra of α-glycine and γ-glycine reveals the fact that the influence of hydrogen bonds on some of the internal frequencies is different in the two crystals. This is not surprising if one remembers the fact that in γ-glycine there are 3 equally strong hydrogen bonds, whereas in α-glycine there are only two strong hydrogen bonds and one comparatively weaker bond. As in the case of α-glycine and other glycine addition compounds, a large number of Raman frequency shifts are observed in the spectrum of γ-glycine in the region 2500∼2900 cm^{-1}, the intensity increasing with increasing frequency shift. They are all assigned to N–H···O oscillations. The presence of the Raman line at 3120 cm^{-1} adjacent to intense mercury line λ 2752.8 clearly indicates the existense of NH_3^+ group. This supports the X-ray evidence that the glycine molecules in γ-glycine exist in the zwitter ion configuration. The planarity of the glycine molecule is different in the α and γ forms. This appears to have some influence on the C–H stretching frequency. The C–H frequencies in γ-glycine, in which the glycine molecule is more planar, are lower than the corresponding frequencies of α-glycine, whereas the difference in the frequency shifts between the symmetric and antisymmetric (C–H) oscillations remains the same. Similar observations have also been made with addition compounds of glycine (Balasubramanian[3]).

Low Frequency Spectrum.—In the Raman spectrum, one observes 9 distinct lines in this region, some of them being very intense. Of these the lines at 186 and 217 which are also observed in the spectrum of α-glycine should be attributed to the vibrations of hydrogen bond i.e., NH···O (Gross[9]). The remaining seven low frequency Raman lines belong to the lattice oscillation of rotatory and translatory types of glycine units. There is practically no similarity between the lattice spectra of α- and γ-glycine. This is not surprising because they belong to two different crystal systems. In infrared absorption, Tsuboi[8] has also observed seven maxima. However, only four of them with frequencies 90.3, 105, 138 and 173, which are the intense ones, agree closely with those observed in Raman effect.

From a group theoretical analysis, taking each glycine molecule as an individual unit, it can be shown that there are, on the whole (for the unit cell of γ-glycine) only 10 external oscillations, which are active both in infrared and Raman effect. These are as follows: 2 translatory and 3 rotatory oscillations coming under the symmetric class, and 2 translatory and 3 rotatory coming under the doubly degenerate class. Taking all the observed frequencies in infrared as well as in Raman effect, one observes that they are actually twelve in number. Therefore, at least two of them should be assigned to combination or overtones. The oscillations with frequencies 101, 116 and 127 appear very weakly in infrared absorption and do not appear in Raman effect. It is possible that with a better and more clear specimen of γ-glycine and a longer exposure these faint lines may also be recorded in Raman effect. The appearance of two lowest frequency lines 43 and 58 in infrared absorption is yet to be confirmed. Tsuboi's observations in infrared extends only up to 85 cm^{-1}. The Raman line at 152 cm^{-1} is extremely intense and sharp while the corresponding frequency is absent in infrared absorption. This might be due to the fact that for this particular oscillation though there might be a great change in polarizability, the change in dipole moment may not be appreciable.

Summary

Using λ 2536.5 excitation the Raman spectrum of single crystal of γ-glycine has been recorded for the first time. Thirty-nine Raman frequencies have been reported. Comparing the spectrum of γ-glycine with its infrared absorption spectrum and also with the Raman spectrum of α-glycine, proper assignments have been given to the internal frequencies. The lattice lines observed in Raman effect and infrared absorption have been satisfactorily accounted for.

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[9] E. F. Gross, "Hydrogen Bonding" by D. Hadži, Pergamon Press (1959), p. 203.