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Raman and Infrared Spectra of β-Alanine

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The Raman spectrum of β-alanine has been recorded in the single crystal form employing λ 2537 technique. The infrared spectra in Nujol mull and KBr pellet have been taken for the range 400—4000 cm^{-1}. The spectra exhibit the characteristic lines of the zwitter ion and also hydrogen bond vibrations in the region 2400—3000 cm^{-1}. The tentative assignments of the observed lines are given and compared with those of other amino acids.

The study of the vibration spectra of amino acids by Raman and infrared spectroscopy is useful for getting information about their molecular configurations and the nature of hydrogen bonding in these substances. A systematic study of the Raman spectra of glycine and its addition compounds from this laboratory has been reported by Krishnan and Narayanan.[1] The infrared spectra of crystalline amino acids have been studied by Klotz and Green[2] and Thompson *et al.*[3] Edsall and his coworkers[4] have made extensive spectral measurements on a large number of amino acids in aqueous solution. Attempts have also been made to assign the vibrational frequencies of glycine molecule on the basis of the normal coordinate analysis.[5-7] The Raman and infrared spectra of β-alanine (β-amino propionic acid, $H_2N \cdot CH_2 \cdot CH_2 \cdot COOH$) in the crystalline state have, however, not been studied. The authors have recorded the Raman spectrum of β-alanine in the single crystal form and the infrared absorption spectrum in the powder form at the room temperature and the results are presented in this paper. A comparative study of the vibration spectra of α-glycine, γ-glycine, α-alanine and β-alanine has also been made.

Experimental

Single crystals of β-alanine were grown from aqueous solution of the pure substance. The biggest crystal grown had roughly the size, 6 mm^3. Using mercury λ 2537 excitation and a Hilger medium quartz spectrograph the Raman spectrum of the crystal was recorded on Ilford Zenith Astronomical plates with exposures of one day. The infrared absorption spectrum of the substance was recorded in the spectral region 4000—400 cm^{-1} in the form of the potassium bromide disc, using a Carl Zeiss UR-10 Infrared spectrometer.

Results

An enlarged photograph of the Raman spectrum of β-alanine is reproduced in Fig. 1, along with its microphotometer record. The positions and frequency shifts of the Raman lines are marked on the microphotometer tracing. The frequency shifts are also listed in Table I. The figures in brackets represent the relative intensities of the Raman lines estimated visually. Thirty nine Raman lines have been recorded. Some of these lines fall very near some mercury lines and are therefore not clearly separated. However, their

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[1] R. S. Krishnan and P. S. Narayanan, "Crystallography and Crystal Perfection," Academic Press Ltd., London (1963), and references therein.

[2] I. M. Klotz and D. M. Green, *J. Phys. Chem.*, **52**, 961 (1948).

[3] H. W. Thompson, D. L. Nicholson and L. N. Short, *Discussions Faraday Soc.*, **9**, 22 (1950).

[4] J. T. Edsall, *J. Am. Chem. Soc.*, **80**, 3807 (1958); **72**, 474 (1950); **62**, 1312, 1767 (1943).

[5] S. Suzuki, T. Shimanouchi and M. Tsuboi, *Spectrochimica Acta,* **19**, 1195 (1963).

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

[7] H. Baba, A. Mukai, T. Shimanouchi and S. Mizushima, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **70**, 333 (1949).

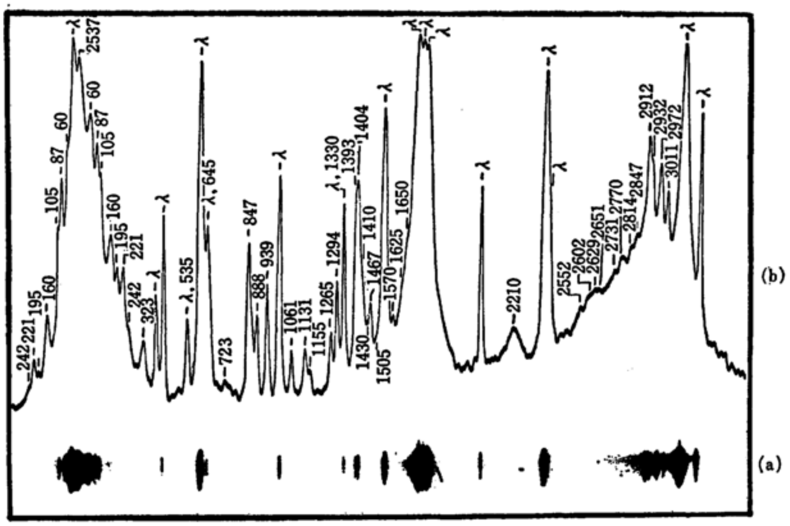

Fig. 1. (a) Raman spectrum of β-alanine, (b) Microphotometer record.

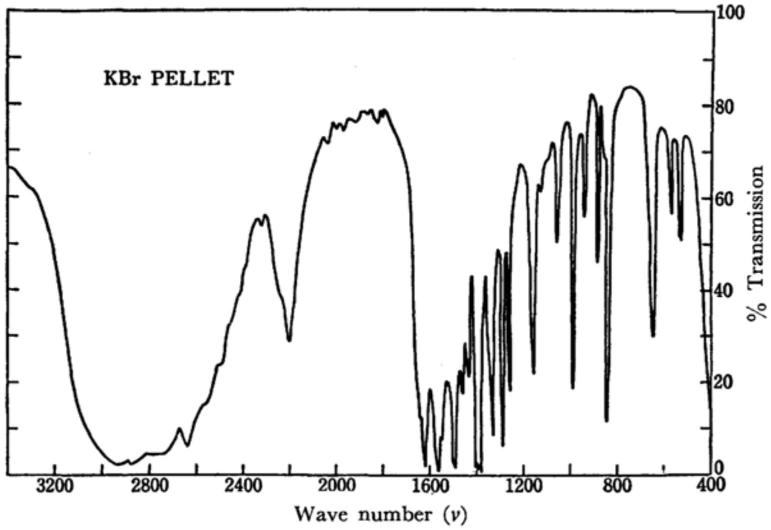

Fig. 2. Infrared absorption spectrum of β-alanine.

presence can be predicted from the infrared spectrum of the substance. The infrared absorption curve obtained for β-alanine is reproduced in Fig. 2. The observed infrared absorption frequencies are listed in Table 1. Forty nine absorption maxima have been identified.

Discussion

β-Alanine crystallises in the orthorhombic system (Jose and Pant[8]) with the space group D_{2h}^{15}-*Pbca*. The unit cell (a=9.865, b=13.8 and c= 6.07 Å), has eight molecules occupying general positions. The molecule as such does not have any symmetry and therefore all the internal vibrations of the molecule should be both Raman and infrared active. Exclusive of the long wavelength acoustic modes, there are a total of 309 factor group fundamentals. Each molecule of β-alanine has 33 internal vibrations. Since there are eight molecules in the unit cell, each internal vibration will be further split. Since the intermolecular forces in the crystal are relatively weak, the splitting of the degeneracies would be small and difficult to be experimentally observed. One can expect to observe at least 33 vibrations in Raman effect and in infrared absorption. This is actually the case. The remaining 45 fundamentals are known as the external vibrations and can further be divided into 24 rotatory type and 21 translatory type of oscilations. Since the crystal has got the centre of symmetry, only 12 translatory type and 12 rotatory type of oscillations will be Raman active.

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[8] P. Jose and L. M. Pant, *Acta Cryst.*, **18**, 806 (1965).

TABLE 1. VIBRATION FREQUENCIES OF β-ALANINE

Raman shifts (in cm^{-1})	IR absorption maxima (in cm^{-1})	Assignments
60(2)		Lattice lines
87(3)		
105(2)		
160(3)		
195(3)		
221(4)		N^+–H···O bonded
242(2)		
323(4)		C–CN^+ bending
535(—)	530(m)	COO^- rocking and NH_3^+ torsion
	537(m)	
	572(m)	COO^- wagging
645(—)	650(st)	COO^- bending
723(2)		
847(8)	850(st)	C–CN^+ stretch
888(6)	887(st)	
939(7)	947(m)	CH_2 rocking
	991(st)	
1061(5)	1060(m)	C–N^+ stretch
	1100(w)	
1131(4)	1130(w)	NH_3^+ rocking
1155(2)	1158(st)	
1265(5)	1261(st)	CH_2 wagging
1294(6)	1292(st)	CH_2 twisting
1330(—)	1332(st)	CH_2 wagging
1393(9)	1386(vs)	COO^- sym. stretching
1404(10)	1397(vs)	
1410(5)	1410(vs)	
1430(2)	1445(m)	CH_2 deformation
1467(5)	1462(st)	
1505(—)	1498(vs)	NH_3^+ sym. deformation
	1504(vs)	
1570(3)	1548(st)	NH_3^+ deg. deformation
	1565(vs)	
1625(—)	1623(vs)	COO^- asym. stretching
1650(—)	1645(w)	Combination frequencies
	1810(w)	
	1835(w)	
	1880(w)	
	1930(w)	
	1983(w)	
	2005(w)	
	2050(w)	
2210	2207(m)	
	2240(w)	
	2323(w)	
	2400(w)	
	2420(w)	
	2450(w)	
	2500(w)	
2552	2560(w)	
2602(3)		
2629(4)		
2651(4)	2640(vs)	N^+–H···O stretching
2731(4)		
2770(4)	2740—2800(vs)	N^+–H···O stretching
2814(2)		
2847(2)	2885(vs)	
2912(10)		
2932(9)	2932(vs)	CH_2 sym. stretching
2972(9)		
3019(8)	3025(vs)	CH_2 antisym. stretching
	3300(w)	Combination frequencies
	3400(w)	

The thirty three internal vibrations of the molecule can be classified as due to the vibrations of the various groups in the molecule. The assignments of the observed Raman and infrared frequencies are given in column 3 of Table 1. Theoretically the group $-CH_2-CH_2-$ should have two symmetric and two asymmetric CH_2 stretching vibrations. However, as one CH_2 group stretches in and out of phase, it disturbs the carbon atom of the next CH_2 group very little because of the insulating effect of the low frequency C–C vibration. Therefore the coupling between the two CH_2 groups is very weak. As a result, the two symmetric CH_2 stretching vibrations will have almost the same frequency and the two asymmetric stretching modes will also have nearly the same frequency which is somewhat higher than the symmetric stretching frequency. In the case of CH_2 bending vibrations such as wag and rock, the angle H–C–H does not change appreciably and the motions of the hydrogen atoms must be directly opposed by the motion of the carbon of the next CH_2 group which indicates a strong coupling between the two CH_2 groups and therefore they may be expected to have different rocking and wagging frequencies.

The absence of the C–O and NH_2 group frequencies and the presence of COO^- and NH_3^+ frequencies clearly indicate that the molecules exist in the zwitter ion form ($NH_3^+ \cdot CH_2 \cdot CH_2 \cdot COO^-$) in the crystal. Further, since the N–H stretching frequencies of NH_3^+ group are considerably lowered and are broad, the molecules are held together by strong hydrogen bonds of N^+–H···O type. According to Parimala Jose and Pant[8] the N···O distances are 2.76, 2.78 and 2.78 Å and three strong hydrogen bonds should therefore be present around the nitrogen atom. This view is confirmed in the present analysis. From the correlation curve of N^+–H···O stretching frequencies *versus* the H-bond lengths given by Krishnan and Krishnan,[9] the N^+–H···O stretching frequencies can be identified at 2651 and 2731 cm^{-1} in Raman spectrum corresponding to the N···O distances of 2.76 and 2.78 Å. The large number of subbands in this region quite possibly arises from an anharmonic interaction o the allowed overtone and summation frequencies. The presence of the hydrogen bonds must be accompanied by some low frequency N^+H···O stretching oscillations. These low frequency stretching oscillations are calculated using the formula given by Pimentel and Sederholm.[10] The results of the calculation show that the frequency shifts 221 and 242 cm^{-1} may be attributed to the motions of the hydrogen bonds N^+H···O. Similar low

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9) R. S. Krishnan and K. Krishnan, *Proc. Ind. Acad. Sci.*, **A60**, 11 (1964).

10) G. C. Pimentel and C. M. Sederholm, *J. Chem. Phys.*, **24** ,639 (1956).

TABLE 2. COMPARISON OF VIBRATION SPECTRA OF AMINO ACIDS

α-glycine Raman shifts (in cm^{-1})	γ-glycine Raman shifts (in cm^{-1})	α-alanine IR maxima (in cm^{-1})	β-alanine Raman shifts (in cm^{-1})	Assignments
3008	2995	—	3011	CH stretching
2974	2964		2972	
			2932	
			2912	CH stretching
1640	1629	1597	1625	COO^- stretching
1563	1586	1623	1570	NH_3^+ deg. deformation
			1548 IR	
1506	1500	1534	1505	NH_3^+ sym. deformation
			1498 IR	
—	—	1455	—	CH_3 deformation
1441	1441	—	1467	CH_2 deformation
1459			1430	—
1414	1405	1412	1410	COO^- sym. stretching
1395	1391		1404	
			1393	
—	—	1355	—	CH_3 sym. deformation
1330	1341	—	1330	CH_2 wagging
1320	1326	—	1294	CH_2 twisting
—	—	—	1265	CH_2 wagging
1140	1165	1237	1155	NH_3^+ rocking
1112	1141	1131		
1038	1045	1148	1061	C-N^+ stretching
—	—	1026	—	CH_3 rocking
		1015		
925	924	—	991 IR	CH_2 rocking
			939	
896	895	918	888	C-CN^+ stretching
		852	847	
677	686	771	645	COO^- bending
588	—	648	572 IR	COO^- wagging
499	503	540	537 IR	COO^- rocking and
—	516	492	530 IR	NH_3^+ torsion
358	362	—	323	CCN^+ bending

frequency shifts due to hydrogen bond oscillations have been observed by Gross,[11] Balasubramanian, Krishanan and Iitaka[12] and Krishnan and Krishnan[13] in hydrogen bonded crystals.

The tentative assignments of the other Raman frequencies have been made by comparing the vibration spectra of β-alanine with that of glycine. A comparative study of the vibration spectra of α-glycine,[1] γ-glycine,[12] α-alanine[14] and β-alanine has been made in the Table 2. It is to be noted that the group frequencies do not vary much in these crystals except some frequencies in the case of β-alanine. All these crystals exist as dipolar (zwitter) ions in the crystalline state. There are some weak bands observed in the infrared spectrum in the region from 1800 to 2500 cm^{-1}. These can be explained as the overtones and combinations of some of the fundamental vibration frequencies.

The low frequency Raman lines are due to the external oscillations of the molecules in the crystal.

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[11] E. Gross, "Hydrogen Bonding by Madzi," Pergamon Press, London, p. 202, (1959).

[12] K. Balasubramanian, R. S. Krishnan and Y. Iitaka, This Bulletin **35**, 1303 (1962).

[13] K. Krishnan and R. S. Krishnan, *Proc. Ind. Acad. Sci.*, **55**, 153 (1962).

[14] K. Fukushima, T. Onishi, T. Shimanouchi and S. Mizushima, *Spectrochimica Acta*, **14** ,236 (1959).