RAMAN AND INFRARED SPECTRA OF AMINO ACIDS

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ABSTRACT

Raman spectra of 12 *amino acids have been recorded using the* 6328 Å *radiation from a* He-Ne *laser as exciter. The substances studies are*

(1) *L-arginine,*
(2) *L-cystine,*
(3) *L-glutamic acid*
(4) *L-glutamtc acid*-HCl,
(5) *Monosodium glutamate,*
(6) *L-glutamine,*
(7) *Hydroxy-L-proline,*
(8) *L-isoleucine,*
(9) *L-serine*
(10) *L-threonine,*
(11) *L-tyrosine and*
(12) *L-valine.*

Eleven of them have been recorded for the first time. The infra-red spectra of these compounds and also of (13) *L-leucine and* (14) *L-proline have also been recorded in the region* 400-4000° cm^{-1}. *Some of the infra-red absorption spectra were recorded also at* 100°K. *The* N-H *stretching modes are influenced by hydrogen bonding. Raman lines characteristic of* NH_3^+ *and* COO^- *groups have been identified in many of the amino acids. It has been shown that the appearance of band at* 2100 cm^{-1} *which is assigned to a combination of the torsional oscillation and degenerate deformation of the* NH_3^+ *groups can also be used a "finger print" for the identification of* NH_3^+ *groups in amino acids.*

1. INTRODUCTION

Amino acids form a very important class of organic compounds which are of great biological significance. As the name itself suggests, any organic acid with one or more amino groups attached to it can strictly be called an amino acid. But the most important among these are the α-amino acids which form the constituents of proteins. These can be represented by the general formula NH_2-CHR.COOH where the amino group occupies a position alpha to the carboxyl group and R denotes a side group which may be of

diverse atomic composition and structure. It is this common feature of the α-amino acids that endows them with several interesting chemical properties like the capacity to form long chains. Excellent treatises on the chemistry of amino acids are available[1].

In most of the amino acids, the α−carbon atom is asymmetric, *i.e.*, the four groups attached to this carbon atom are different. Therefore the same amino acid can exist in two different forms depending on the geometrical configuration of these groups. These forms are indistinguishable chemically or physically, but they may be detected using polarised light. One form rotates the plane of polarised light to the right and the other to the left, but by an equal amount. It is an interesting fact that all protein-derived amino acids have the same configuration about the α−carbon atom, irrespective of the sense of rotation of plane polarised light. Thus all protein derived amino acid are called L−amino acid and and their antipodes D−amino acids. Also a mixture containing equal amounts of the D and the L forms of the amino acids will not show optical activity. It is obvious that glycine which is the first member of the amino acid series and in which the α carbon is not asymmetric exists only in one form which is optically inactive.

It has been observed that all amino acids exist as depolar ions in their free state. Thus it is more appropriate to describe them with the general formula $NH_3^+-CHR-COO^-$. It is the existence in the zwitterion form that endows them with many physical properties not possessed by similar chemical compounds. For example, in contrast with amines and carboxylic acids, amino acids are non-volatile crystalline solids with high melting points. They are insoluble in non-polar solvents and their aqueous solutions have high dielectric constant.

An important feature of amino acids in the crystalline state is the extensive system of hydrogen bonding that connects the molecules together. These hydrogen bonds give the structures cohesion in three dimensions. In the zwitterion structure the NH_3^+ group is a good hydrogen-bond donor and the carboxyl group an excellent acceptor and strong hydrogen bonds are formed between these groups. In some cases the same proton will be shared by two acceptors resulting in a bifurcated bond. It is the network in hydrogen bonds in the solid state that makes the amino acids particularly interesting for spectroscopic investigations. Vibrational spectroscopic methods of detecting and studying hydrogen bonds are well known[2]. Though both Raman and infrared spectroscopic methods give information regarding the hydrogen bonds, the infrared spectra in the hydrogen bond stretching region will be highly complicated due to the presence of overtone and combination bands. However, in the Raman spectra these bands will appear with poor intensity and so the fundamentals can be easily identified.

With this object in view, systematic investigations on the Raman spectra of amino acids and some addition compounds were started in this laboratory in 1958. Numerous studies[3] have already been carried out. In the present study the Raman spectra of 12 amino acids have been recorded. The substances investigated are (1) L-arginine, (2) L-cystine, (3) L-glutamic acid, (4) L-glutamic acid-HCl, (5) mono-sodium-L-glutamate, (6) L-glutamine, (7) hydroxy-L-proline, (8) L-isoleucine, (9) L-serine. (10) L-threonine, (11) L-tyrosine and (12) L-valine. The infrared spectra of these compounds and also of (13) L-leucine and (14) L-proline have also been recorded in the region of frequencies from 400-4000 cm^{-1}. The results are presented here.

2. REVIEW OF EARLIER WORK ON AMINO ACIDS

A) Raman effect studies:

Edsall[4], Kahovek and Kohlrausch[5] and Ananthakrishnan[6] recorded the Raman spectrum of glycine in crystalline powder form. The Raman spectrum of a single crystal of α-glycine was first recorded by Krishnan and Balasubramanian[7] in this laboratory using the 2537A° radiation as the exciting source. In addition to the internal frequencies of the glycine molecules, they recorded six intense lattice lines. From the observed frequencies attributable to the COO^- ion, it was confirmed that in the crystal the molecular units exist as dipolar ions. Balasubramanian *et al*[8] recorded the Raman spectrum of γ-glycine which has a structure different from that of α-glycine. As is to be expected, the lattice spectra of the two forms are different. Neelakantan *et al*[9] examined the Raman spectrum of C-deuterated γ-glycine and recorded the lattice lines. Balasubramanian and Krishnan[10] made polarization studies on the Raman spectrum of α-glycine and from the observed depolarization values the classification of the Raman lines to the two different symmetry types Ag and Bg have been made. It was pointed out that the orientation of the CH_2 groups deduced from these studies was slightly different from that given by the X-ray analysis.

The Raman spectra of triglycine sulphate[11] and triglycide selenate[12] were recorded using the 2537A° radiation. In the spectra of diglycine hydrochloride and hydrobromide the COO^- wagging and rocking modes were split and this was attributed to the effect of crystalline field and to the presence of a large number of molecules in the unit cell[13], while in the case of diglycine nitrate, the NO_3^- ion has a staggered configuration. In diglycine barium chloride monohydrate[14] no band characteristic of $BaCl_2-2H_2O$ could be found. A strong sharp lattice line was seen at 121 cm^{-1}. In this compound also the glycine units exist as zwitterions. The Raman spectrum of L−asparigine monohydrate was recorded by Krishnan and Krishnan[15]. The lines at 194, 245 and 296 cm^{-1} were attributed to the hydrogen bond vibrations. The NH_2 and NH_3^+ groups exhibited marked frequency differences in the spectrum.

From the available data on the lengths of hydrogen bonds in these amino acids and their addition compounds and the frequency shifts recorded in their Raman spectra, Krishnan and Krishnan[16] proposed a correlation curve for the $N^+-H-....O$ type bonds. The curve was found to be entirely different from the Nakamoto curve for the $N-H....O$ type bonds. The straight line portion of the curve for $N^+-H....O$ bonds can be described by the relation $\nu = 2.714\ (R-1.784) \times 10^3$ where R is the hydrogen bond length.

Krishnan and Katiyar[17] investigated the Raman spectrum of β-alanine and found that the bands at 2651 and 2731 cm^{-1} could be explained as due to the $N^+-H\ ...\ O$ bonds as deduced from the proposed correlation curve. In this compound the low frequency hydrogen bond vibrations appear at 221 and 242 cm^{-1}.

Apart from these investigations, there have not been many studies on the Raman spectra of amino acids, till the advent of lasers. However, mention may be made of the work of Stahlberg and Steger[18] who succeeded in recording the Raman spectrum of taurin.

Since the advent of the laser, a few investigations have been reported on the Raman spectra of amino acids. Khanna and Miller[19] recorded the Raman spectrum of γ-glycine. Herlinger and Long[20] recorded the Raman spectra of single crystals of L and DL-valine using an argon ion laser. The spectra of these two substances are different. Wang and storms [21] have made the interesting observation that many of the low frequency Raman lines in L-alanine show anomalous polarizations. They explain this as due to a protonic motion associated with the NH^+_3 group which introduces a dynamical disorder in the crystal, thus lowering the overall symmetry. The NH^+_3 torsinal mode is found to be very sensitive to temperature above 220°K. A detailed polarisation study of the Raman spectrum from the lattice phonons of a single crystal L-alanine was carried out by Wang and Stroms [21] using laser exciatation. Laser Raman spectra of L-proline hydrochloride, sodium prolinate and poly L-hydroxy proline in the solid state have been recorded by Deveney et al [22]. They reported the appearance of two lines at 1543 and 1374 cm^{-1} and absence of lines at 1700 and 1750 cm^{-1} in these amino acids indicating the existence of ionised caboxyl group.

B) Infrared Studies:

The amino acid molecules usually do not possess any symmetry and so all the internal vibrations will be both infrared and Raman active. However, in many cases the infrared method was preferred for routine analysis because of the ease with which the infrared spectra could be recorded. Among the early investigations on the infrared spectra of amino acids, the works of Gore et al[23] and Wright[24,25] are significant. Wright studied the infrared

spectra of several amino acids in powder form from 400-3500 cm^{-1}. It was the concept of group frequencies that helped the interpretation of the infrared spectra of amino acids. From a study of a large number of compounds containing the same functional groups, it was established that their spectra contained frequencies which could be attributed to the functional groups. Koegel et al[26] investigated the spectra in the solid state of 50 pairs of optically enantiomorphic amino acids in the region 650-5000 cm^{-1}, in an attempt to compare the frequencies of the functional groups and also to study the differences in the spectra of the D and L forms of α-amino acids. These investigations revealed that in the region studied, there was no difference in the spectra of the D- and L- forms. Most of the amino acids exhibited characteristic absorption peaks at 1587, 1515, 1444, 1408, 1355 and 1330 cm^{-1}. Of these, the 1587 and 1408 cm^{-1} bands were attributed to the carboxyl ion vibration. The 1515 cm^{-1} line was attributed to an N-H deformation vibration, the peaks at 1444 znd 1355 cm^{-1} to methyl and methylene deformation and 1330 cm^{-1} to CH_2 wagging. The spectra of diasteriomeric pairs were found to be different.

Leifer and and Lippincott[27] who investigated the infrared spectra of several optically inactive amino acids, showed that the band at 2100 cm^{-1} should be attributed to a bending vibration of the amino group rather than to a stretching mode attributed by Koegel *et al*[26]. In the solid state the spectra of the optically active amino acids are found to deffer from those of the corresponding inactive forms. This observation was made even by Wright[25] who studied several L and DL compounds. Koegel *et al*[28]. also have investigated the spectra of optically active and inactive forms of many amino acids. It has been found that the difference in their spectra varies from one compound to another. The spectrum of L-alanine was found to differ only very little from that of DL−alanine. However, the spectrum of active α−amino-n-butric acid was considerably different from that of the inactive form.

Because of the presence of a large number of strong absorption peaks in the region from 700-1800 cm^{-1} for all the amino acids, a differentiation among them is rather difficult. However the region 400-700 cm^{-1} does not contain many peaks and so a study of this region can, in principle, be used to distinguish one amino acid from another. Solinov *et al*.[29] have recorded the infrared spectra of cystine, serine, valine, leucine and tyrosine in the 400-4000 cm^{-1} region and assigned bands in the range 560-770 cm^{-1} to the deformation vibration of the carboxyl group. An investigation of the infrared absorption spectra of 49 amino acids in the 400-700 cm^{-1} region was carried out by Warren *et al*.[30] who identified four characteristic bands, one at in 740 cm^{-1} (COO^- bending vibration), one at 650 cm^{-1} (COO^- wagging mode) the third one at 540 cm^{-1} (CCN bending mode) and the fourth one at ~480 cm^{-1} (NH_3^+ rocking mode).

For a complete assignment of the bands in the spectra of amino acids, deuteration studies are extremely helpful. Such studies have been carried out in the case of glycine and alanine. In the case of glycine, Tsuboi *et al.*[31] have made complete assignments of the observed peaks in the region from 400-1800 cm^{-1} by comparing the spectra of glycine, glycine hydrocloride and sodium glycinate and their N-deuterated analogues. Similar studies have been carried out in the case of DL-alanine by Fukushima *et al.*[32] Iafrared spectral studies of C-deuterated alanine have been done by Oshima and Tamiya[33] who obtained the spectra of $CH_3CHNH_3^+COO^-$, $CH_3CDNH_3^+COO^-$, $CD_3CDNH_3^+COO^-$ and $CD_3CDND_3^+COO$. Khanna *et al.*[34] have made a systematic analysis of the addition compounds of glycine, $NH_2^+DCH_2COO^-$, $NHD_2^+CH_2COO^-$ and $ND_3^+CH_2COO$. Suzuki *et al.*[35] have also studied the spectra of C-deuterated compounds of alanine. All vibrations involving the N atom in DL-alanine were indentified by Tsuboi et al.[36] by substituting ^{14}N, by ^{15}N and observing the isotope shifts in the spectrum. Some studies on the spectra of metal amino acid complexes have been made [37 38].

Since the amino acids consist of a larger number of atoms, a normal coordinate analysis of the vibrational frequencies is rather difficult. However, in the cases of alanine[32] and glycine[39] such vibrational analyses have been done with considerable success. In the case of glycine, for example, the molecule was assumed a seven-body system with the NH_3^+ group assumed as a dynamical unit. A Urey-Bradley type potential field was assumed and the molecule was considered planar. The agreement between the calculated and observed frequencies was satisfactory.

In the light of the available data on the vibrational frequencie of several amino acids, Tsuboi et al [40] have tried to define some characteristic frequencies for the amino acids. They have identified the following vibrations: the NH_3^+ degenerate deformation at $\sim$1600 cm^{-1}, NH_3^+ symmetric vibration at$\sim$ 1510 cm^{-1}, ND_3^+ deformation at $\sim$1170 cm^{-1}, NH_3^+ rocking at $\sim$1130 cm^{-1}, ND_3^+ rocking at 800 cm^{-1}, C-N stretching at $\sim$1000 cm^{-1}, COO^- antisymmetric stretching at $\sim$1600 cm^{-1}, COO^- symmetric stretching at $\sim$1410 cm^{-1}. In the hydrochlorides the C=O stretching appears $\sim$1720 cm^{-1} and the coupled O-H in plane bending and C-O stretching at $\sim$1420 cm^{-1} and $\sim$1280 cm^{-1}. The O-H out of plane bending of the COOH group has a frequency $\sim$900 cm^{-1}. The corresponding bends for COOD are at $\sim$1710, $\sim$1380, $\sim$1040 and $\sim$600 cm^{-1}.

In some cases it has been found that the infrared spectral bands of complicated molecules are well resolved if recorded at low temperature. Feairheller and Miller[41] recorded the infrared spectra of some amino acids and peptides from 33 cm^{-1} to 4000 cm^{-1} at liquid nitrogen temperature. They found this technique quite useful in getting information on amino acids in the zwitterion form. Such studies are also useful in determining the assignments of several low frequency bands.

3. EXPERIMENTAL DETAILS

All the amino acids used in the present investigations were of high purity and were obtained as gift from Ajinomoto Co., Japan. Attempts to grow them in the form of single crystals were not quite successful and so the Raman spectra were recorded with the compounds in the powder form. A He-Ne laser of 75 mW power output and a Spex 1401 double monochromator were used for this purpose. Three slit-width settings were employed in the monochromator to cover the region 0-3000 cm^{-1}. In terms of spectral slit widths, these corresponded to 2.5 cm^{-1} for the lattice region (0 – 150 cm^{-1}), 4.7 cm^{-1} for the intermediate region (150 – 1700 cm^{-1}) and 7.5 cm^{-1} for the high frequency hydrogenous stretching region (2800 – 3100 cm^{-1}). Two samples, proline and leucine were highly fluorescent thereby rendering the recording of their Raman spectra difficult. All the infrared spectra were recorded using the Carl Zeiss UR-10 instrument. In the majority of the cases the spectra of the N-deuterated compounds were also recorded in order to assign the bands unambiguously. In a few cases, the infrared absorption spectra were recorded with the specimen cooled down to 110°K. It was found that while some changes occured in the 400-700 cm^{-1} region, no conspicuous change was discernable in the high frequency region.

4 RESULTS AND DISCUSSION

The Raman and infrared frequencies observed for the amino acids have keen tabulated in Tables 1 to 14. Assignments of the observed spectra of individual amino acids are given in the Tables. Some of the typical Raman spectra are reproduced in Fig. 1, 2, 3 and 4 to show the lattice spectrum and the high frequency region. Some typical infrared spectra are also shown along with those of the deuterated samples in figures 5, 6 and 7. As can be seen from these records, there is a fairly good percentage of hydrogen-deuterium exchange.

In the 14 amino acids studied, all except arginine, proline and hydroxyproline contain an NH_3^+ group. In the region from 700-1800 cm^{-1}, there are three characteristic frequencies belonging to this group. These are the symmetric deformation, the degenerate deformation and the rocking vibrations. All these modes can be easily identified because af their complete disappearance on deuteration. The symmetric deformation has a frequency 1520 ± 20 cm^{-1}. In some cases more than one line attributable to this vibration are seen in the spectra and these must be due to correlation splitting which is very prominent in such complex crystal containing several molecules in the unit cell. The degenerate deformation frequency has a value of 1620 ± 20 cm^{-1} and this mode also gives more than one line. The NH^+_3 rocking mode usually gives two lines lying between 1100 and 1200 cm^{-1}.

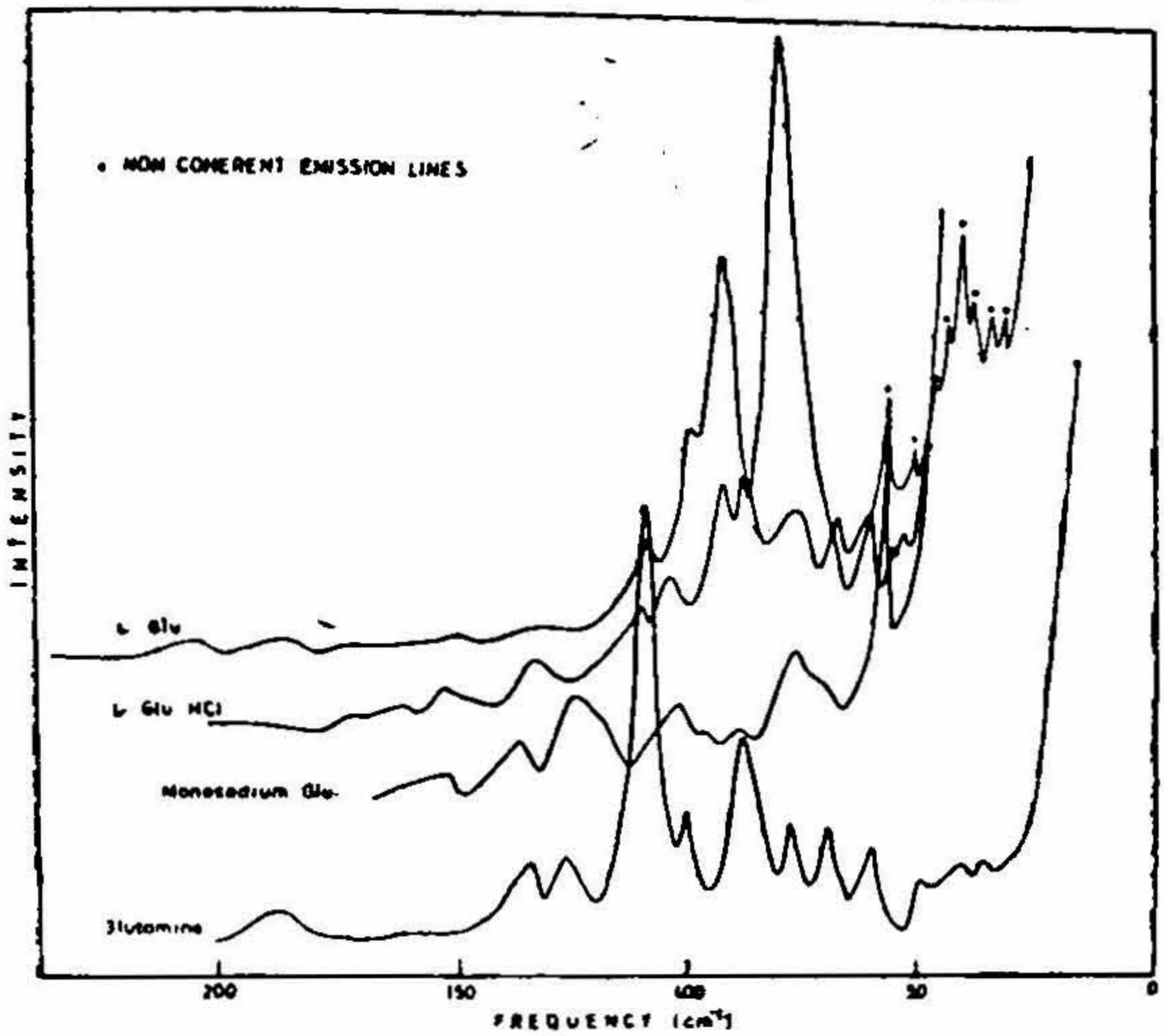

FIG. 1
Lattice Spectra of some amino acids

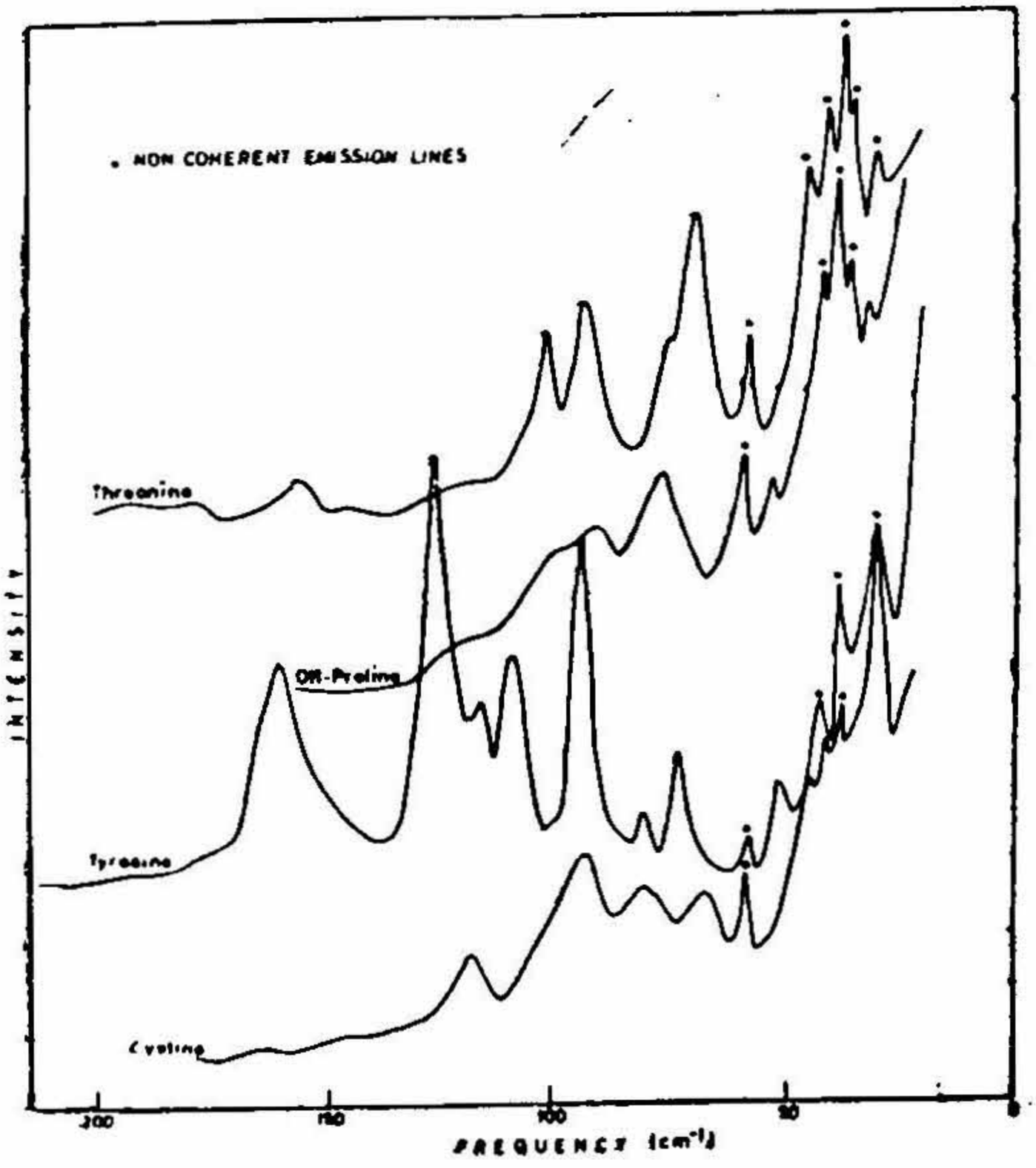

FIG. 2
Lattice Spectra of some amino acids

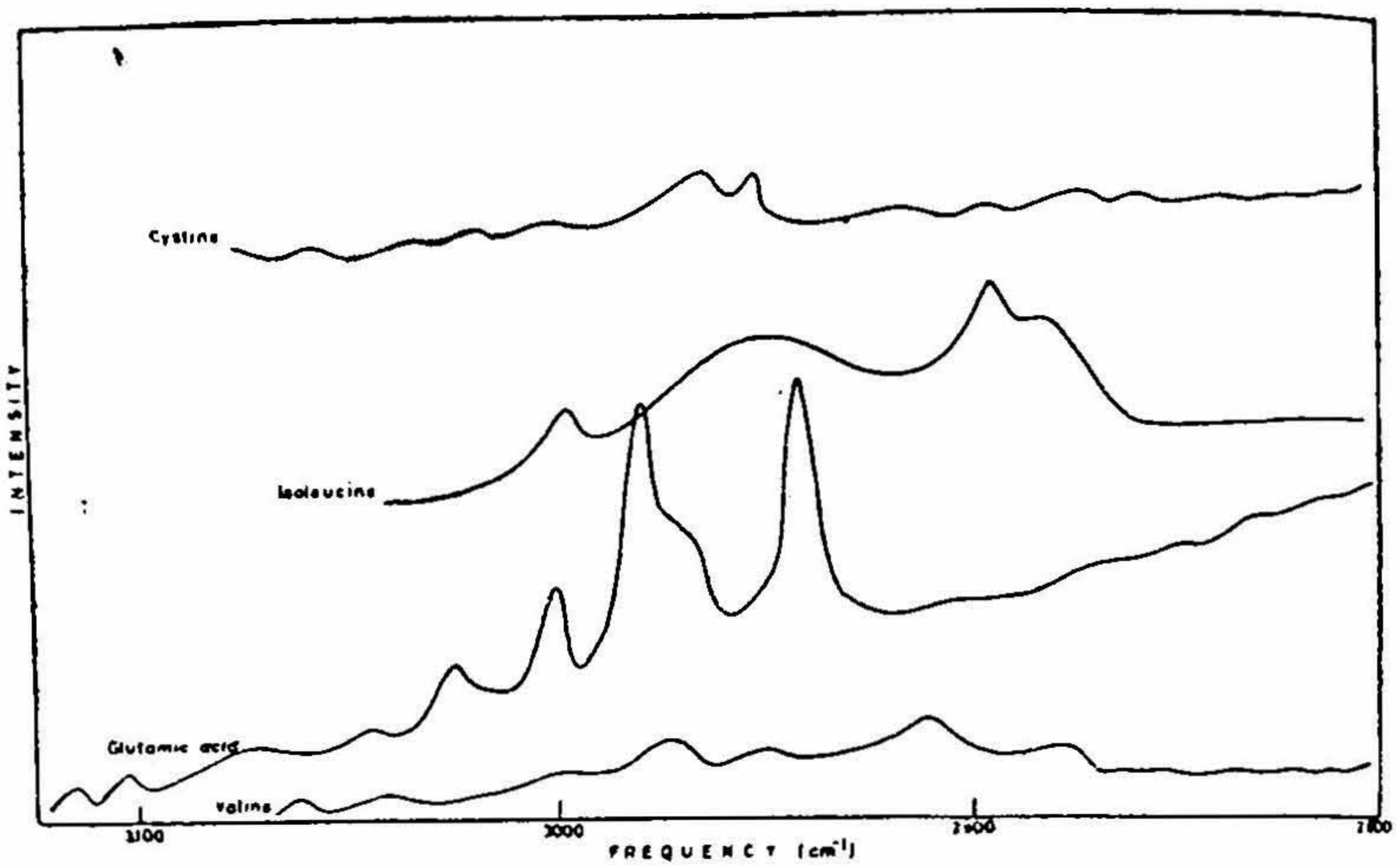

FIG. 3

High frequency Raman Spectre of amino aeids

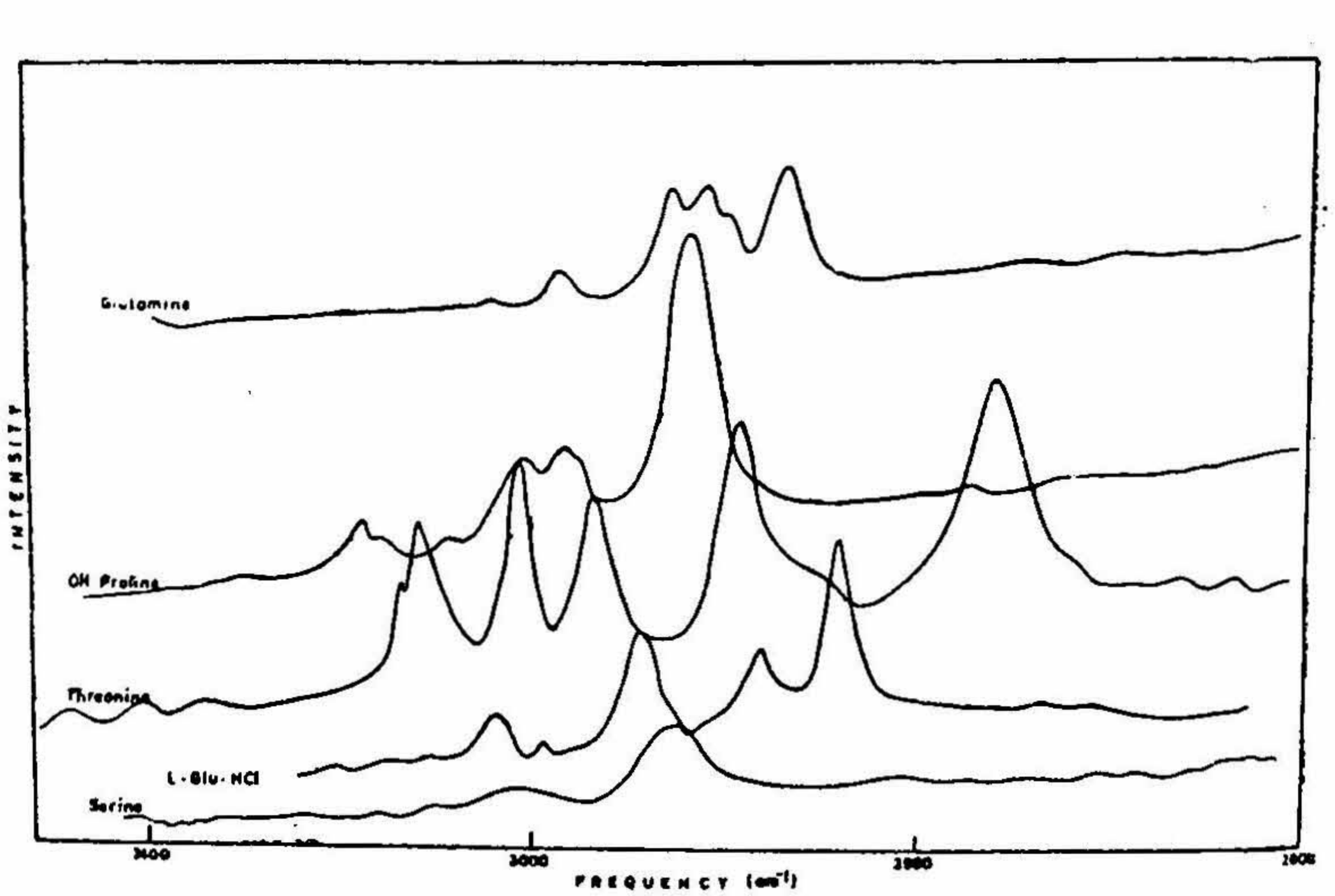

FIG. 4

High frequency Raman Spectra of amino acids

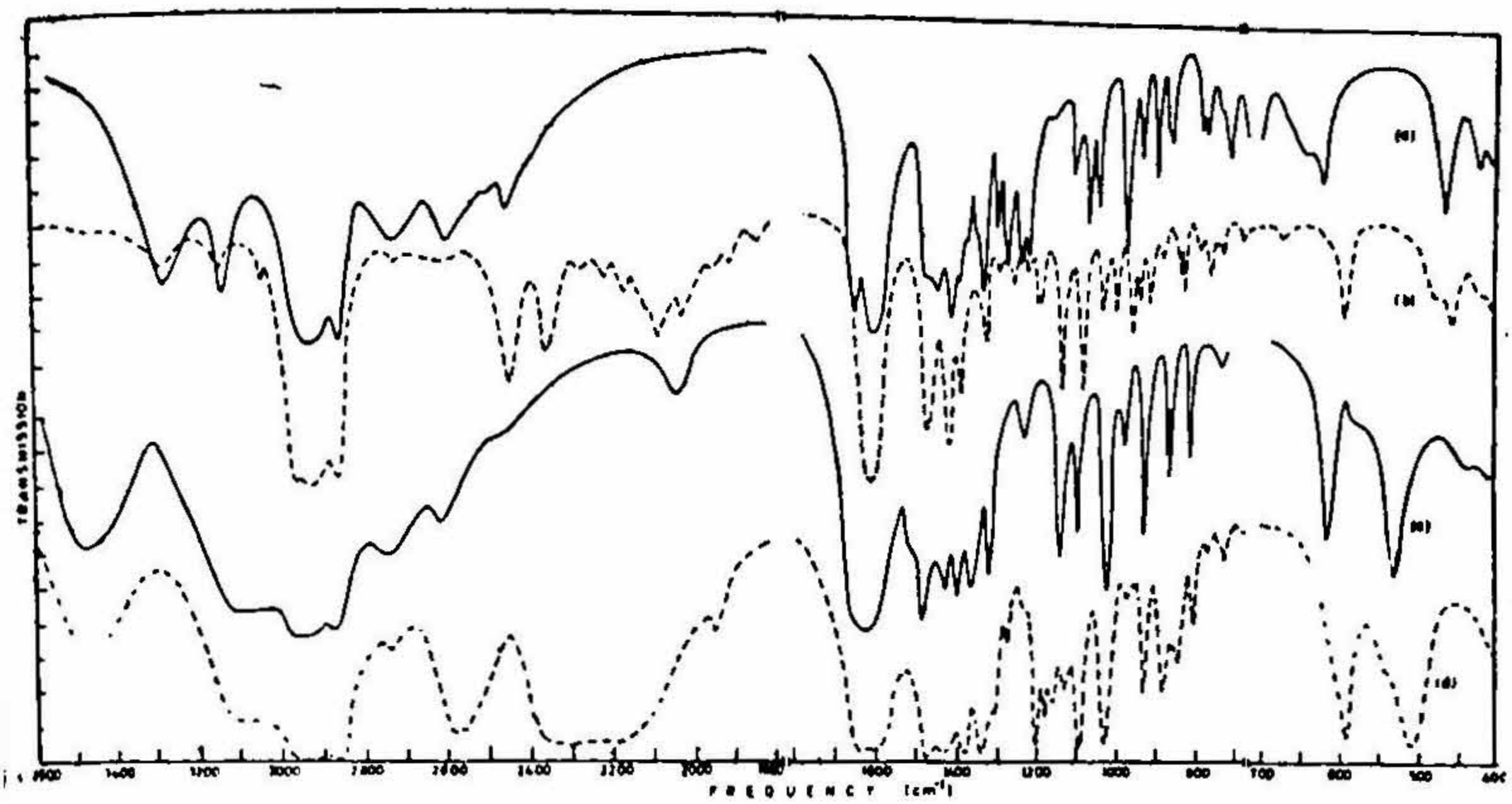

FIG. 5

Infrared Spectra of (a) Hydroxy Proline. (b) Hydroxy Proline-deuterated (c) Serine and (d) Serine-deuterated

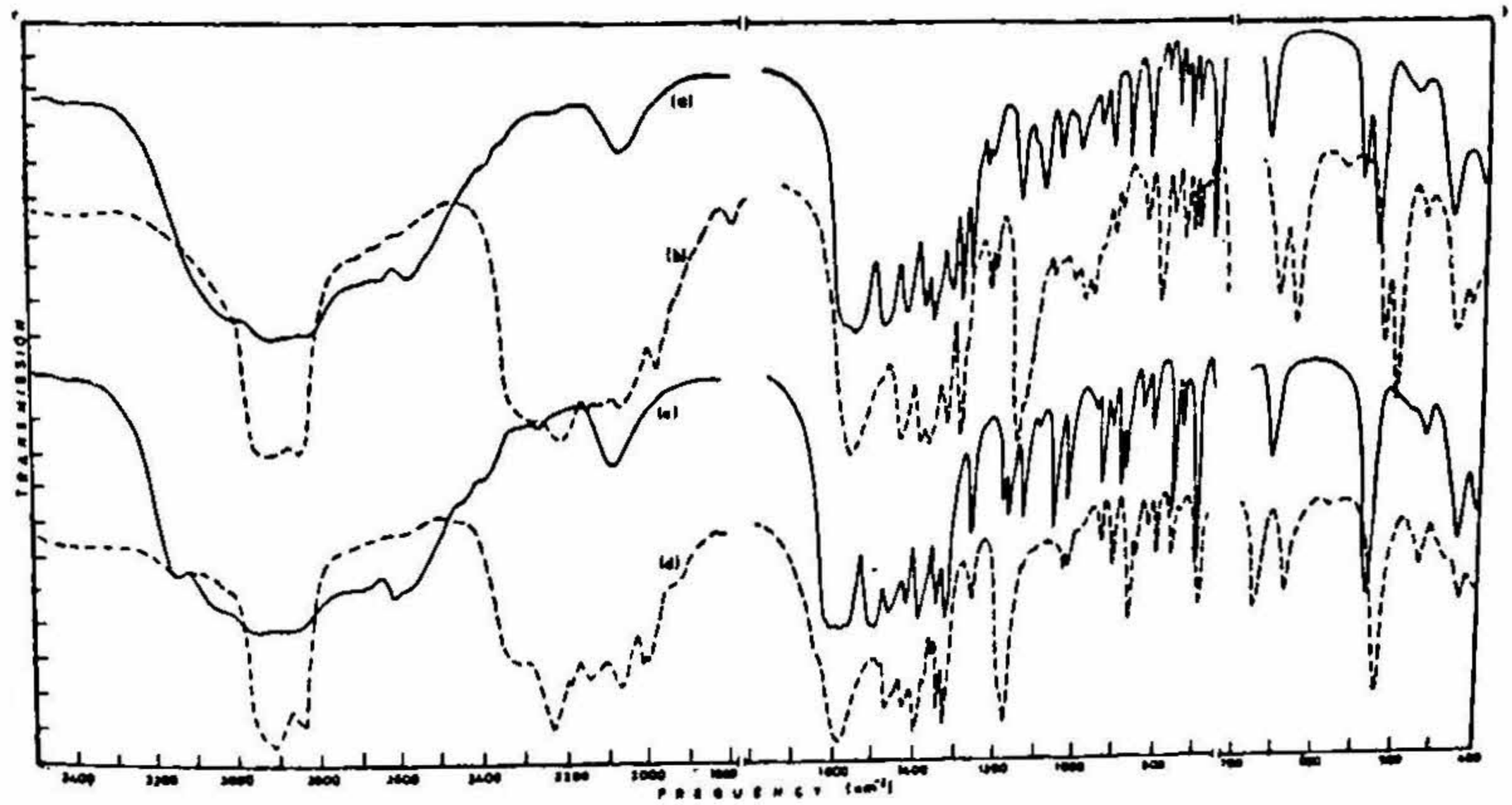

FIG. 6

Infrared Spectra of (a) Isoleucine (b) Isoleucine-deuterated, (c) Valine and (d) Valine-deuterated

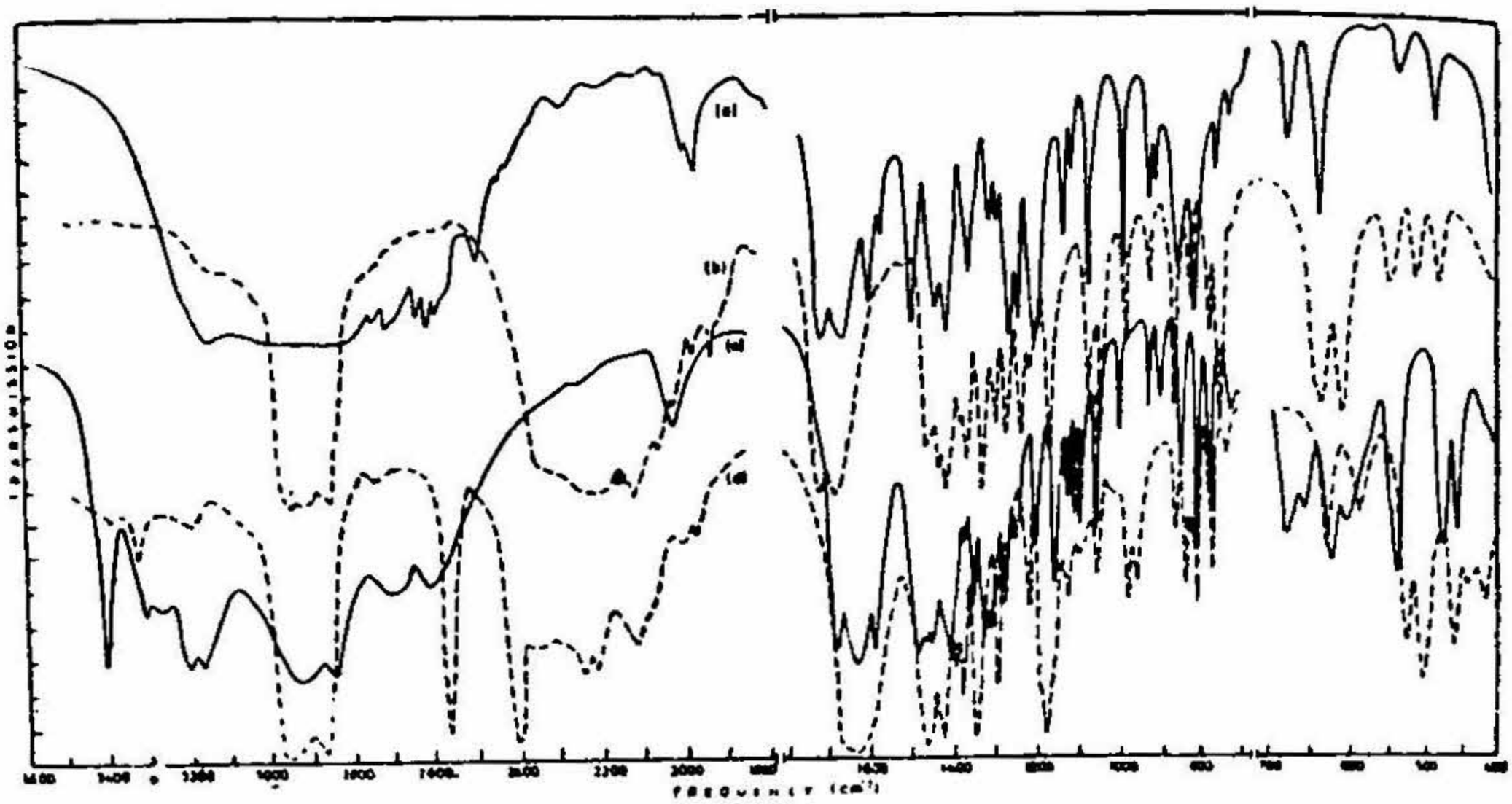

FIG. 7

Infrared Seectra of (a) Glu-HCl (b) Glu-Hcl-dcuterated (c) Glutamine and (d) Glutamine-deuterated

These are fairly broad and strong in the infrared absorption spectrum. On deuteration, bands corresponding to ND^+_3 ions appear at ~ 1150, ~ 1200 and ~ 850 cm^{-1} corresponding to the three vibrations respectively. The observed isotope ratios, $\nu(NH_3^+)/\nu(ND_3^+)$, are 1.32, 1.35 and 1.33 for symmetric deformation, degenerate deformation and rocking vibrations respectively. These values are in fair agreement with those estimated by Tsuboi[40].

Proline and hydroxy-proline contain an NH_2^+ group. Apart from stretching, these can give rise to bending, wagging, twisttng and rocking frequencies. Of these twisting mode appears weak in infrared absorption. Though the Raman spectrum of hydroxy proline agrees fairly well with that that reported by Deveney et al. [22] in the light of deuteration studies, some of their assignments had to be modified. Glutamine, which contains an NH_2 group in addition to the NH_3^+ group, shows bands at 1643, 1265, 1092 and 675 cm^{-1} corresponding to the former group. Arginine which has two uncharged NH_2 groups and a charged NH_2^+ group, shows several bands in the 1500-1700 cm^{-1} region.

In all the amino acids investigated, except in glutamic acid hydrochlo ride, there is at least one ionised carboxyl group. This group has twostrong absorption bands, one near 1600 cm^{-2} corresponding to the asymmetric stretching and the other at

~1400 cm^{-1} corresponding to the symmetric stretching of the COO^- group. On deuteration these bands increase slightly in frequency. This may be due to the decrease in the strength of the hydrogen bond. The other vibrations of the carboxyl group are the bending, wagging and rocking modes. In the literature there is considerable controversy regarding the assignments of the observed bands to these modes, but in the present case the following criteria have been used for the assignments. In all the amino acids whose structures have been solved, the two C-O bond legths differ only slightly and the OCO angle is about 126°. The oxgen atoms are hydrogen-bonded to the amino nitrogen atoms with nearly the same distances from them and hence in similar environments. Thus the frequencies are not expected to differ drastically from compound to compound. Also in comparison with glycine and alanine, in which the theoretically calculated values and observed values agree closely, the bending vibration is expected to show a deuteration shift of 30 cm^{-1}, the vagging vibration 20 cm^{-1} and rocking vibration remaining almost constant. The approximate frequencies for these vibration are 700 cm^{-1}, 540 cm^{-1} and 450 cm^{-1} respectively. The wagging mode is quite intense in all the spectra and is easily identified. In isoleucine, two frequencies each are observed for wagging and bending modes. In cystine and monosodium glutamate which contain two COO^- groups, several bands are present in the spectra assignable to the vibrations of these groups.

In glutamic acid and its hydrocloride, there are unionised carboxyl groups which are characterised by the strong C=O stretching frequency. The C-O stretching and O-H in-plane deformation are coupled and give two bands, one strong at 1240 cm^{-1} and another at 1400 cm^{-1}. On deuteration, the corresponding bands move over to 1350 cm^{-1} aud 1070 cm^{-1} respectively. The O-H out of plane bending appears at 850 cm^{-1}. The C=O in plane bending appears as a strong band at 680 cm^{-1}.

The skeletal vibrations of the amino acids are all coupled together. However, there is a very strong line in the Raman spectrum of all the compounds between 800-900 cm^{-1}, which can be assigned to an almost pure C-C stretching mode. This is weak in infrared absorption. Similarly, between 1000 and 1100 cm^{-1}, there is a line which can be assigned to a C-N stretching vibration. In cystine, the S-S stretching appears strongly in the Raman spectrum at 445 cm^{-1}. The C-S stretching gives two very strong lines in the Raman spectrum at 640 and 695 cm^{-1}. In tyrosine, the ring vibration is assigned to the strong line at 831 cm^{-1}. In hydroxy proline, the strong Raman line at 883 cm^{-1} is due to ring vibration and its frequency increases to 914 cm^{-1} on deuteration. The lone CH group on the α-carbon atom gives rise to a bending frequency at 1350 cm^{-1} in the spectra of amino acids. The skeletal deformation frequency lies below 500 cm^{-1} and could not be identified unambiguously in any of the cases.

In threonine, serine and tyrosine, there is an additional OH group present. This group also gives rise to absorption peaks similar to the OH groups of the carboxyl groups. In monosodium glutamate which contairs an H_2O group, the water bending and librational frequencies have been identified in the spectrum.

Hydrogen Bonding:

As has been pointed out, the NH_3^+ groups are strongly hydrogen bonded to the ionised carboxyl groups, resulting in a distortion of the NH_3^+ groups. Hydrogen bonding will also result in modifying the N^+-H stretching frequency. The observed Raman lines in the region 2600 to 3400 cm^{-1} other than those arising from the C–H oscillations, should be attributed to the hydrogen bonded N–H stretching oscillations. In infrared absorption, one observes many more absorption peaks in the same region. Some of them which do not appear in Raman effect may be attributed to combinations of NH_3^+ degenerate deformation mode with the C–N stretching mode or NH_3^+ rocking mode. Since for nine compounds, the crystal structures have been solved, the hydrogen bond distances in these are known. From the correlation curves for $N^+ \ldots O$ bonds given by Krishnan and Krishnan[16], the N^+-H stretching vibrations were calculated corresponding to different hydrogen bond distances. For crystals containing to O–H . . . O type bonds, the correlation curves of Nakamoto et al.[42] have been employed to get the O–H stretching frequency. The calculated values of the hydrogen bonded N–H stretching frequencies are given in Table 15 along with the hydrogen bond distances and the observed values of the same frequencies. It can be seen that the agreement is fairly good. In those cases where the deviation is considerable, the hydrogen bond may be taken to be far from linear. It is interesting to note that the hydroxyl group of serine forms only a very weak hydrogen bond giving a broad peak at 3500 cm^{-1}. In hydroxy proline, with an O . . . O distance of 2.80A°, the O–H stretching appears at 3300 cm^{-1}. Similarly, the infrared spectrum of proline shows a broad speak at 3400 cm^{-1}. This must be due to the stretching vibration of H_2O molecules which are easily absorbed by proline and may therefore be present as traces. In glutamine, there is a strong sharp band at 3420 cm^{-1}. This shows a clear isotope shift and may be assigned to the amide group. In the crystal structure, there are no nitrogen-oxygen distances which allow such a high value of the NH frequency. It must be concluded that the NH . . . O bonds weakened by some other mechanism. In such a case we can describe the vibrations in terms of NH_2 group frequencies. Using the formula of Venkataramiah and Venkatachalapathy[43] for the non-bonded NH_2 groups in amides,

$\nu_s = (1.12)\ (\nu_{as} - 3530) + 3415$ and taking

$\nu_{as} = 3420$, one gets $\nu_s = 3315$ cm^{-1}.

The band at 3326 cm^{-1} can then be assigned to this mode. The conclusion is that in glutamine the amide group appears to be only weakly hydrogen bonded.

The torsional frequency of NH_3^+ ;

In all the amino acids containing the NH^+_3 group there is a weak band in the infrared absroption at 500 cm^{-1}. This band is seen in the Raman spectrum also. On cooling the sumple, it increases in frequency and intensity. This band has therefore been assigned to NH_3^+ torsinal oscillation. In glycine it is known to occur at 516 cm^{-1}[34].

The infrared absorption spectra of all amino acids containing the NH_3^+ group, exhibit a band of medium intensity at 2100 cm^{-1}. This band has been assigned by Koegel et al.[26] to a stretching frequency of the NH_3^+ group. Later Leifer and Lippincott [27] suggested that this might be a bending vibration of the amino group. However, Krishnan and Krishnan[16] and Kanna et al. [34] have pointed out that this band is due to a combination of NH_3^+ degenerate deformation and NH_3^+ torsion. A similar band has been observed in the infrared spectra of methylammonium halides and interpreted by Cabana and Sandorfy[44] as due to such a combination. The results of the present study confirm this conclusion. In Table 16 are given the values of NH_3^+ deformation, NH_3^+ torsion and the calculated and observed values of the combinations. The remarkable agreement between the observed and calculated values points out the correctness of the assignment. It is also interesting to note that this band is absent in amino acids with only NH_2^+ groups or uncharged amino groups. This the band at ~2100 cm^{-1} forms a very interesting "indicator band" for the identification of charged NH_3^+ group in amino acids since the region between 1800-2400 cm^{-1} in most of the compounds are usually free from any absorption lines. The appearance of this band in the spectrum of monosodium glutamate indicates the presence of NH_3^+ group and the metal ion has displaced the hydrogen from one of the carboxy groups and not from the amino group, unlike in the case of sodium glycinate where there is only an NH_2 group. The value of the torsional oscillation frequency may give an indication of the strength of the hydrogen bonds formed by the amino groups. Thus in glutamic acid hydrocloride, the torsional frequency has gone below 400 cm^{-1} and the frequency of the indicator band indicator band also has decreased. This is expected since the N^+-H . . . Cl bonds are weaker compared to the N^+-H . . . O bonds.

The Lattice Spectra of Amino acids:

As can be seen from Table 16 and figures 1 and 2, there are strong lines in the Raman spectrum in all the amino acids in the lattice region 0-200 cm^{-1}.

These vibrations are due to the rotational and translational vibrations of the molecules and to the low frequency hydrogen bond vibrations. There is a very strong line at 94 cm^{-1} in the spectrum of glutamic acid at 83 cm^{-1} in glutamic acid HCl and at 111 cm^{-1} in glutamine. But in the spectrum of monosodium glutamate there is no line in this region, which is of comparable intensity. Similarly in threonine the strongest low freqnency line is at 73 cm^{-1}. In tyrosine there are several strong lines in this region. It is known that the rotatory type of lattice oscillations are stronger than the translatory types and so the strong lines can be attributed to such vibrations. The interesting point to note is that the lattice spectrum shows marked variation in frequency and intensity on going from compound to compound. Thus this region should provide a good test for the identification of amino acids whose high frequency spectra are crowded with lines due to the internal vibrations and which have many frequencies in common.

Not much is known regarding the low frequency hydrogen bond vibrations. These are expected to lie below 300 cm^{-1}. Hurley et al.[45] have suggested critera for identifying these bands ; the bands should be weak in the Raman spectrum and they should be broad and asymmetric. There are several weak lines in the low frequency Raman spectra of the amino acids, but a correct identification of the hydrogen bond vibrations could not be made since the compounds were studied in the powder form and no Raman spectra were recorded at low temperature. As the temperature is lowered, these vibrations are expected to increase in frequency due to an increase in the hydrogen bond strength.

ACKNOWLEDGEMENT

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EXPLANATION OF THE SYMBOLS USED IN THE TABLES

ν – Stretching frequency
ν_s – Symmetric stretching
ν_{as} – Asymmetric stretching
δ – in-plane deformation
δ_s – Symmetric deformation
δ_d – Degenerate deformation
γ – Out-of-plane bending
γ_ρ – Rocking
γ_w – Wagging
γ_t – Twisting
τ – Torsion

TABLE 1

L – Serine $HOCH_2-CH(NH_3^+)-COO^-$

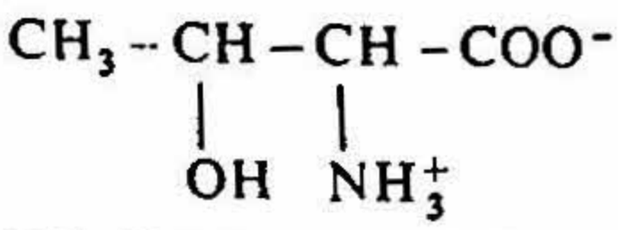
Raman	Infrared	Infrared deuterated	Assignments
	433(m)		$\tau\ NH_3^+$
518(9)	525(s)br	510(s)	$\gamma_w\ COO^-$
		540(sh)	
	570(m)		
612(8)	610(s)	592(s)	$\delta\ COO^-$
		605(sh)	γ OD
		740(vw)	
751			
780			
809(10)	806(m)	807(m)	γ OH
815(26)			
850(10)		842(s)	
855(26)	859(m)	857(m)	ν (C – C)
		879(m)	$\gamma_p ND_3^+$
925(4)	923(s)	930(s)	$\gamma_p\ CH_2$
970(8)	973(m)	973(w)	
1007(11)	1020(s)	1027(s)	
1012(14)			
1035(2)			
1090(2)	1089(s)		Skeletal
		1091(s)	δ OD
1135(2)	1130(s)	1127(w)	$\gamma_r NH_3^+$
		1153	$\delta_s ND_3^+$
		1179	$\delta_d\ ND_3^+$
		1202	
1223(5)	1223(m)	1223(w)	$\nu C-O+\delta O-H$
		1272(m)	
1303(5)	1309(s)	1300(m)	$\gamma_t CH_2$
1318(4)			
1327(14)			
	1346(s)	1338(s)	δCCH
1386(2)	1386(s)	1380(s)	$\gamma_w CH_2$, ν (C – O)
	1420(s)	1425(s)	$\nu_s\ COO^-$
1418(5)	1479(s)	1460(s)	$\delta\ CH_2$
1464(9)			$\nu C-O+\delta-OH$
1480			

TABLE 1—(*contd.*)

Raman	Infrared	Infrared deuterated	Assignment
	1506(sh)		$\delta_s NH_3^+$
		1580(s)	
	1613(s)	1600(s)	$\nu_{as} COO^-$
	1638(s)	1640(s)	$\delta_d NH_3^+$
		1930(m)	Combinations
		1940(m)	
	2040(m)		$\delta_d NH_3^+ +$
	2089(m)		τNH_3^+
		2030	
		2120(s)	
		2180(s)	ν (N – D)
		2300(s)	
		2350(s)	
		2580	ν (O – D)
	2270(w)		
	2455(m)		
	2590(s)		Combinations
	2606(s)		
	2700(s)		
	2725(s)		
	2870(s)		$\nu_s CH_2$
2944(4)	2944(s)		$\nu_{as} CH_2$, ν CH
2962(10)	2962(s)		
3000(4)	3000(s)		ν (N – H)
	3100(s)		
	3466(s)		ν (O – H)

TABLE 2

L – Threonine



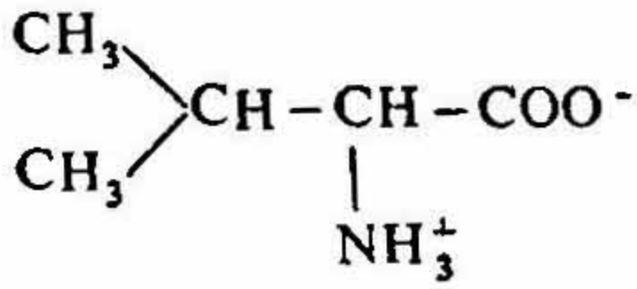
Raman	Infrared	Infrared deuterated	Assignments
421(7)	417(m)	407(m)	
436(6)			
449(13)	448(m)	432(w)	$\tau\ NH_3^+$
494(10)	492(m)	487(m)	$\gamma_p\ COO^-$
566(32)	562(s)	535(s)	$\gamma_w\ COO^-$
		550 sh(m)	γ OD
704(8)	708(s)	671(m)	$\delta\ COO^-$
		684(m)sh	γ OD
754(12)	750(m)		
	777(s)		γ OH
	800(m)		
		807(m)	
		822(s)	
874(30)	877(m)		ν(C – C)
906(5)			
911(4)	912(m)	911(m)	
933(24)	940(s)	937(s)	
		950(s)	$\gamma_p\ ND_3^+$
		1012(m)	
		1028(m)	
1032(7)			
1045(7)	1048(s)	1048(m)	$\gamma_p\ CH_3$
1101(3)	1100(s)	1107(s)	,,
1108(15)			
1118(20)	1118(s)		
1124(9)	1124(m)		
		1128(s)	$\delta_s\ ND_3^+$
		1166(s)	$\delta_d\ ND_3^+$
		1182(m)	,,
			$\gamma_p\ NH_3^+$
1196(7)	1190(m)		
1253(3)	1253(m)	1254(m)	$\gamma_p\ CH_3$
	1328(s)		ν C – O + δO – H
1308(3)			
1342(16)	1350(s)	1338(s)	δ CCH
1355(7)			
		1370(s)	ν (C – O)
	1393(s)	1388(s)	$\delta_s\ CH_3$

TABLE 2—(*contd.*)

Raman	Infrared	Infrared deuterated	Assignment
1420(6)	1425(s)	1422(s)	ν_s COO^-
1454(9)		1465(s)	δ_d CH_3
1468(6)	1463(s)		
1481(5)	1488(s)		ν(C-O) + δ(O-H)
1549(2)	1549(m)		δNH_3^+
1601(1)	1612(s)	1621(s)	ν_{as} COO^-
	1637(s)		δ_d NH_3^+
1642(s)	1648(s)		
		1962(w)	Combination $\delta_d NH_3^+ + \tau NH_3^+$
	2051		
		2060(m)	
		2090(m)	
		2158(m)	ν(N – D)
		2200(s)	
		2250(s)	ν(O – D)
		2341(s)	
	2220(vw)		
	2550(m)		
	2600(m)		Combinations
	2635(m)		
	2668(s)		
	2721(s)		ν(N – H)
	2820(s)		
2878(26)	2878(s)	2878(s)	ν_s CH_3
2923(8)	2920(s)		ν_{as} CH_3
2935(12)			ν CH
2949(22)		2943(s)	
2980(20)	2980(s)	2980(s)	
2997(22)			
3021(17)	3021(s)		ν(N – H)
	3123(s)		
	3180(s)		ν(O – H)

TABLE 3

L – Valine



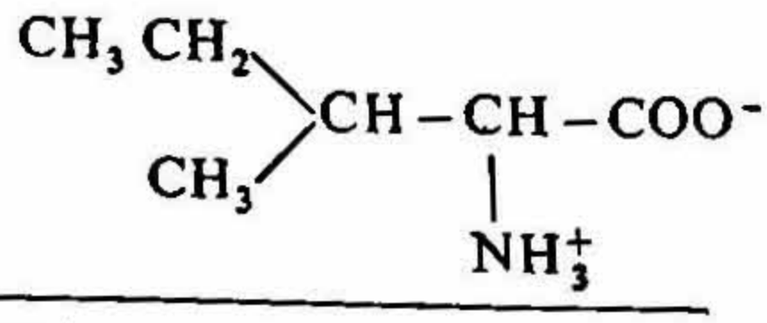
Raman	Infrared	Infrared deuterated	Assignment
	402(s)		
436(5)	428(s)	421(m)	$\gamma_p COO^-$
	436(m)	437(w)	
462(6)	473(m)	472(m)	
496(1)	490(w)		τNH_3^+
544(14)	543(s)	523(s)	$\gamma_w COO^-$
667(5)	665(m)	640(m)	δCOO^-
718(5)	720(m)	675(m)	δCOO^-
		746(m)	
		748(m)	
754(6)	757(m)		
780(12)	779(s)	784(m)	
828(4)	827(m)	806(m)	
852(7)	852(m)	838(m)	
		854(m)	$\gamma_p ND_3^+$
887(2)	892(m)	898(m)	$\gamma_p CH_2$
903(2)	903(m)		$\gamma_p CH_2$
		924(m)	
923(1)	920(m)	927(m)	
956(7)	950(m)		
967(4)	970(m)	971(w)	$\gamma_p CH_3$
		978(w)	
1022(–)	1032(m)	1018(m)	$\gamma_p CH_3$
1035(–)	1039(m)	1023(m)	
1069(6)	1068(s)		
1129(4)	1110(w)	1129(w)	
	1147(m)	1146(m)	
		1158(m)	$\delta_s ND_3^+$
		1170(m) }	$\delta_{as} ND_3^+$
		1178(m) }	
1136	1180 }		$\gamma_p NH_3^+$
	1195 }		
1278(4)	1278(m)	1361(m)	$\gamma_p CH_3$
		1319(s)	
1330(5)	1337(s)	1334(s)	δ CCH

TABLE 3 – (*contd.*)

Raman	Infrared	Infrared deuterated	Assignment
1347(4)			
1355(5)	1360(s)	1350(s)	δ_s CH_3
	1380(s)	1379(s)	
1400(4)	1402(s)	1405(s)	ν_s COO^-
1426(4)	1435(s)	1435(s)	
1457(6)	1455(s)	1466(s)	
1570(6)	1465(s)	1465(s)	δ_d CH_3
		1478	
	1512(s)		δ_s NH_3^+
	1521(s)		
	1570(s)		
1602(2)	1591(s)	1595(s)	ν_{as} COO^-
1620(2)	1621(s)		δ_d NH_3^+
1626(2)	1630(s)		δ_d NH_3^+
		1827(w)	
	2110(m)		δ_d NH_3^+ + τNH_3^+
		1927(m)	
		1942(m)	
		1957(m)	
		2000(s)	
		2018(s)	ν(N – D)
		2062(s)	and
		2092(s)	combinations
		2149(s)	
		2192(s)	
		2236(s)	
		2331(s)	
	2410		
	2600(s)		ν(N – H)
	2630(s)		
	2700(s)		
	2772(s)		ν(N – H)
2884(4)	2884(s)		
2909(8)	2903(s)		ν_s CH_3
2952(4)	2941(s)		ν_s CH_3
2975(6)	2960(s)		ν CH
3000(4)	2920(s)		
	3053(s)		ν (N – H)
	3152(s)		ν (N – H)

TABLE 4

L – Isoleucine



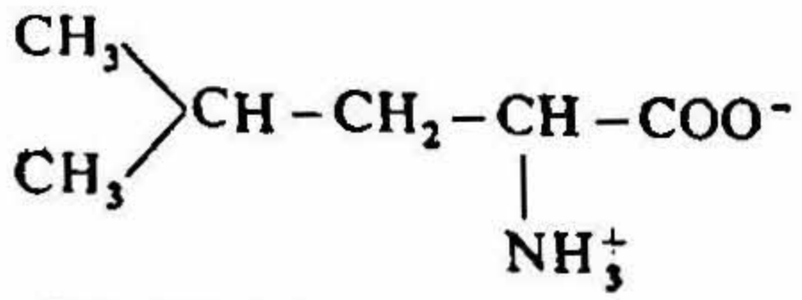
Raman	Infrared	Infrared deuterated	Assignment
411(1)			
428(3)		423(m)	
458(3)	440(m)	440(m)	$\gamma_p COO^-$
	488(w)	483(w)	
490(3)	495(w)		τNH_3^+
540(10)	537(s)	517(s)	$\gamma_w COO^-$
558(8)	556(s)	534(s)	
		584(w)	
677(3)	675(s)	645(s)	δCOO^-
711(3)	708(s)	668(s)	
753(8)	749(m)	742(m)	
772(6)	767(m)	758(m)	
	788(w)	778(m)	
806(2)	803(m)	809(m)	
828(6)	830(w)		$\nu(C-C)$
		835(s)	$\gamma_p ND_3^+$
885(6)	854(w)		
877(4)	87 (m)	873(m)	$\gamma_p CH_2$
925(4)	925(m)		
		938(w)	
950(2)	967(m)	951(m)	$\gamma_p CH_2$
996(5)	993(m)	1001(m)	$\gamma_p CH_3$
1024(4)	1027(w)	1029(m)	
1040(–)	1042(m)		
	1048(m)	1050(m)	
1092(3)	1090(m)	1099(w)	$\nu(C-N)$
1126(2)	1133(m)		$\gamma_p NH_3^+$
1140(3)	1153(sh)		
1185(2)	1190(s)		
		1143(m)	$\delta_s ND_3^+$
		1173(s)	$\delta_d ND_3^+$
		1184(s)	
1233(1)			
1258(1)	1263(w)	1246(w)	$\gamma_t CH_2$
1277(1)	1275(w)	1260(w)	
	1299(w)		

TABLE 4—(*contd.*)

Raman	Infrared	Infrared deuterated	Assignment
1311(1)	1315(s)	1307(m)	γ_w CH_2
1332(1)	1331(s)	1027(s)	
1357(4)	1354(s)	1357(s)	δ_s CH_3
1398(3)	1391(s)	1391(s)	δ CCH
	1401(s)	1402(s)	ν_s COO^-
1420(1)	1427(s)	1423(s)	
1451(4)	1469(s)	1461(s)	δ CH_2
	1471(s)	1472(s)	δ_d CH_3
1519(1)	1518(s)		δ_s NH_3^+
	1527(s)		
1582(2)	1590(s)	1593(s)	ν_{as} COO^-
1619(2)	1621(s)		δ_d NH_3^+
		1825(w)	
	2119(m)		δ NH_3^+ + τ NH_3^+
		1955(m)	
		2007 m)	
		2057(s)	
		2078(s)	ν (N – D)
		2091(s)	
		2140(s)	
		2180(s)	
		2239(s)	ν (N – D)
		2320(s)	
	2400(s)		
	2442(s)		
	2500(s)		
	2578(s)		Combinations
	2621(s)		
	2700(s)		
	2747(s)		
	2832(s)		
2882(9)	2881(s)		ν_s CH_2
2895(12)	2895(s)		ν_s CH_3
2948(16)	2945(s)		ν_{as} CH_2
2995(4)	2970(s)		ν_{as} CH_3
3008(3)			
	3063(s)		ν (N – H)
	3110(s)		

TABLE 5

L – Leucine



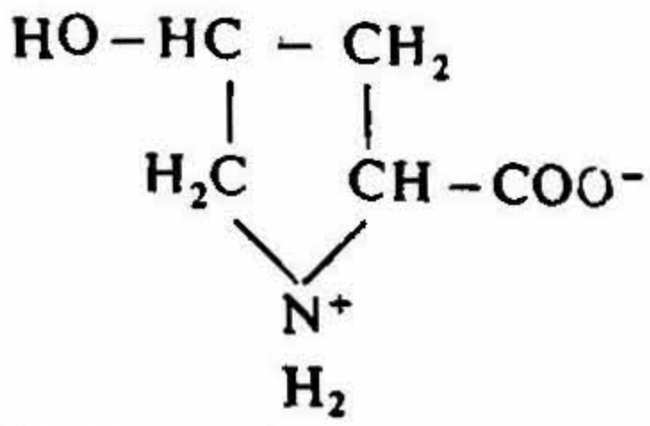
Infrared	Infrared deuterated	Assignment
400[m]		
442[m]	440[m]	γ_p COO⁻
452[m]	451[m]	
514[w]		τ NH_3^+
536[s]	516[s]	γ_w COO⁻
	531[sh]	
667[s]	638[s]	δ COO⁻
	665[m]	
771[m]	770[m]	
	803[m]	
	826[m]	$\gamma_p ND_3^+$
	837[m]	
851[m]	845[m]	(C – C)
	872[m]	
925[m]	928[w]	γ_p CH_2
947[m]	947[w]	
	967[vw]	
	982[vw]	
1009[w]	1005[w]	γ_p CH_3
1034[m]	1034[vw]	
	1072[w]	
1087[m]	1082[w]	Skeletal
	1134[m]	δ_s ND_3^+
1142[s]		γ_p NH_3^+
1191[m]	1180[s]	δ_d ND_3^+
1243[m]	1237[m]	γ_p CH_3
1302[s]	1293[m]	
1320[s]	1317[s]	γ_w CH_2
1332[s]	1342[s]	δ CCH
	1355[s]	δ_s CH_3
1370[s]	1368[s]	
1417[s]	1415[s]	ν_s COO⁻
1448[s]	1450[s]	
1461[s]	1462[s]	δ CH_2

TABLE 5—(*contd*)

Infrared	Infrared deuterated	Assignment
1450[s]	1442[s]	$\delta_d\ CH_3$
1517[s]		$\delta_s\ NH_3^+$
1522[s]		
1595[s]	1590[s]	$\nu_{as}\ COO^-$
1625[s]		$\delta_d\ NH_3^+$
2130[m]		$\delta_d\ NH_3^+ + \tau\ NH_3^+$
	1818(w)	
	1990[m]	ν [N – D] and combinations
	2020[m]	
	2078[s]	
	2145[s]	
	2242[s]	
	2280[s]	
	2310[s]	
2450[m]		
2558[s]		
2600[s]		Combinations
2630[s]		
2700[s]		
2741[s]		
2823		$\nu_s\ CH_2$
2885		$\nu_s\ CH_3$
2950		ν [C – H]
	3000[s]	ν [N – H]
	3070[s]	ν [N – H]

TABLE 6

Hydroxy-L-Proline



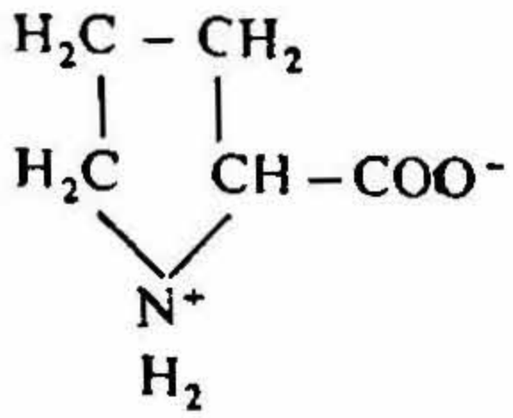
Raman	Infrared	Infrared deuterated	Assignment
425[16]	425[m]	415[w]	
468[3]	463[m]	457[w]	γ_p COO$^-$
	473[m]		
		474[m]	γ OD
618[8]	617[m]	593[m]	γ_w COO$^-$
	640[br]		γ OH
700[2]	703[m]		δ COO$^-$
		738[w]	
757[6]	761[m]		
		757[m]	γ_p ND_2^+
	773[m]	783[w]	
		825[m]	
		835[m]	
853[52]	850[m]		ν [C – C]
	857[m]		
865[10]	862[m]		γ_p CH_2
883[17]	884[m]	914[m]	ring vibration
920[6]	928[m]		
942[4]	959[s]	940[m]	γ_p CH_2
991[9]	971[s]	960[m]	
1016[2]			
1038[5]	1036[s]	999[m]	Skeletal
1060[10]	1063[s]	1030[m]	ν [C – N]
1069[13]	1070[s]		
1070[10]	1090[m]		
		1083[s]	δ OD
		1107[w]	δ ND_2^+
		1133[s]	δ ND_2^+
			γ_t CH_2
1189[10]	1189[m]	1183[m]	
1408[3]	1213[s]	1192[m]	γ_t CH_2
1229[9]	1230[s]		
1259[2]	1262[s]		ν[C – O] + δ[O – H]
1284[2]	1284[s]		γ_p NH_2^+

TABLE 6 – *(Contd.)*

Raman	Infrared	Infrared deuterated	Assignment
1324[14]	1330[s]	1322[s]	γ_w CH_2
1354[8]	1340[m]	1334[m]	δ CCH
	1378[m]		γ_w NH_2^+
1398[6]	1406[s]	1420[s]	ν_s COO^-
1432[6]	1436[6]	1455[s]	δ CH_2
1482[-]			
	1603[s]	1610[s]	ν_{as} COO^-
	1648[s]		δ NH_2^+
		1843[w]	Combinations
		1912[w]	
		1957[m]	
		2033[m]	
		20 2[m]	
		2115[m]	
		2167[m]	ν [N – D]
		2218[m]	
		2267[m]	
		2360[s]	
		2448[s]	ν [O – D]
	2442[s]		ν [N – H]
	2459[s]		
	2507[s]		
	2556[s]		Combinations
	2583[s]		
	2601[s]		
	2629[s]		
	2700[s]		
	2733[s]		
	2930[s]		ν_s CH_2,
2959[36]	2950[s]		ν_{as} CH_2
2991[12]	2987[s]		ν [C – H]
3001[12]			
3036[12]			
3043[6]			
3134[2]	3149[s]		ν [N – H]
	3298[s]		ν [O – H]

TABLE 7

L – Proline



[Raman spectrum taken from ref. [46]]

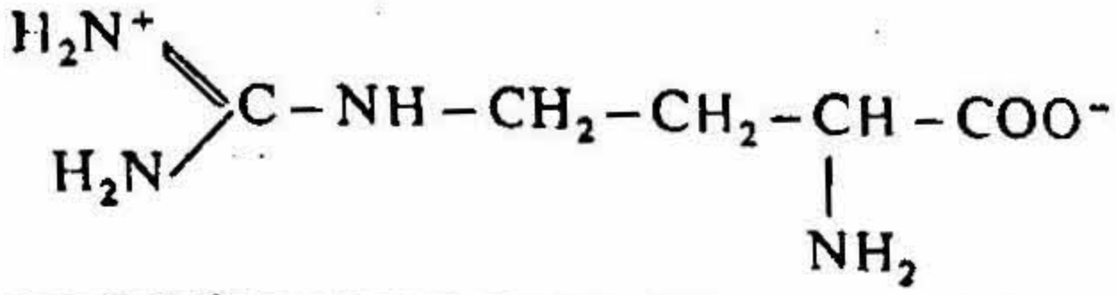
Raman	Infrared	Assignments
448	453[s]	γ_p COO⁻
577	572[w]	
641	643[s]	γ_w COO⁻
667	670[m]	
698	687[m]	δ COO⁻
	790[s]	
795	796[s]	
842	838[m]	
866	851[s], 864[m]	γ_p CH_2
	887[w]	
898	905[m]	γ_p NH_2^+
919	919[m]	γ_p CH_2
951	953[m]	
985	989[m]	
994		
1033	1040[s]	
1056	1052[m], 1052[m]	ν [C - N]
1082		
1173	1177[m]	γ_t NH_2^+
1192		
1239		
1264	1261[m]	
1285	1302[s], 1328[s]	γ_w CH_2
1320		δ CCH
1349		
1373	1383[s]	γ_w NH_2^+
1409	1410[s]	ν_s COO⁻
1441	1458[s], 1482[s]	δ CH_2
1471		
1550	1557[s]	δ NH_2^+

TABLE 7—(*contd.*)

Raman	Infrared	Assignments
1624	1631[s]	ν_{as} COO^-
	2210[m]	Combinations
	2390[s]	
	2507[s]	
	2590[s]	
	2645[s]	
	2685[s]	
	2748[s]	
	2783[s]	
	2810[s]	
2178		
2919	2925[s]	ν_s CH_2, ν_{as} CH_2, ν CH
2952		
2976		
3001	2995[s]	
3051	3063[s]	ν [N—H]
	3430 s [br]	ν H_2O

TABLE 8

L – Arginine



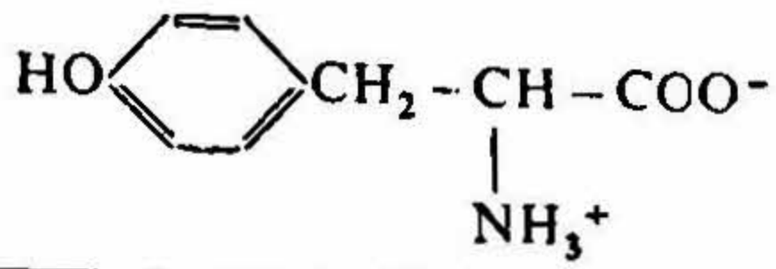
Raman	Infrared	Assignments
	468[w]	γ_p COO$^-$
495[1]	492[w]	
554[4]	551[m]	γ_w COO$^-$
	559[m]	
	611[m]	
	663[s]	δ COO$^-$
	678[s]	γ NH_2
	757[m]	
	800[m]	γ_p CH_{2+}
	814[m]	γ_p NH_2
876[3]	857[m]	ν [C – C]
894[2]		
927[2]	931[w]	γ_p CH_2
979[4]		
989[6]		
1006[1]	1015[s]	
1084[3]	1081[m]	ν [C – N]
1129[1]	1128[s]	γ_w NH_2
1154[1]	1128[s]	
1189[2]	1193[s]	γ_w NH_2^+
1314[2]	1320]m]	γ_w CH_2
1335[4]	1340[s]	γ_w CH_2
	1374[m]	
1385[2]	1384[s]	δ CCH
1413[ ]		
1428[1]	1433[s]	ν_s COO$^-$
1442[2]		
1476[1]	1472[s]	δ CH_2
1488[1]		
1511[3]		
	1542[s]	δ NH_2
	1625[s]	ν_{as} COO$^-$
	1653[s]	ν [C = N]
	1694[s]	δ NH_2^+
	1710[s]	

TABLE 8 – (*contd.*)

Raman	Infrared	Assignments
	2300 [br] [w]	Combinations
	2700	
	2735	
	2784	
	2800	
	2872	ν_s CH_2 ν CH
	2954	ν_{as} CH_2
	3100[s]	ν [N – H]
	3290[s]	
	3500[m]	

TABLE 9

L – Tyrosine



Raman	Infrared	Assignments
435[5]	432[m]	γ_p COO⁻
	445[w]	
	471[w]	τ NH_3^+
493[2]	493[m]	
527[1]	529[s]	γ_w COO⁻
575[1]	576[s]	
645[6]	651[s]	Ring deformation
715[2]	717[m]	
744[1]	743[m]	δ COO⁻
758		
771		
800[5]	800[m]	
	809[m]	
831[17]	831	Ring stretch
849[5]	845[ ]	CH wagging of the ring ?
	880[m]	
	901[m]	γ_p CH_2
	943[w]	
988[4]	989[w]	
	1022[w]	
1048[3]	1045[m]	ν [C – N]
	1103[m]	
	1119[m]	
	1162[m]	γ_p NH_3^+
1183[6]	1179[m]	
1202[4]	1202[m]	
1216[4]	1220[m]	
1249[4]	1250[s]	ν [C – O] + δ[O – H]
1265[3]	1271[m]	γ_t CH_2
1329[5]	1341[s]	γ_w CH_2
1367[4]	1372[s]	δ CCH
	1381[s]	δ CCH
1420[2]	1425[s]	ν_s COO⁻
1434[3]	1448[s]	ν [C – O] + δ[O – H]
	1463[s]	δ CH_2

TABLE 9 – [*contd.*]

Raman	Infrared	Assignments
1515[2]	1525[s]	$\delta_s\ NH_3^+$
1590[1]	1598[s]	$\nu_{as}\ COO^-$
1615[1]	1620[s]	$\delta_d\ NH_3^+$
	2080	$\delta_d\ NH_3^+ + \tau\ NH_3^+$
	2495[m]	Combinations
	2602[m]	Combinations
	2628[s]	N – H Stretching hydrogen bonded
	2700[s]	hydrogen bonded
	2757[s]	hydrogen bonded
	2835[s]	$\nu_s\ CH_2$, $\nu_{as}\ CH_2$, ν CH
	2895	$\nu_s\ CH_2$, $\nu_{as}\ CH_2$, ν CH
	2937	$\nu_s\ CH_2$, $\nu_{as}\ CH_2$, ν CH
2931[5]	2937	$\nu_s\ CH_2$, $\nu_{as}\ CH_2$, ν CH
2960[5]	2967	ν CH
2970[5]		ν CH
3020[3]	3026[s]	ν CH
3040[2]		ν CH
3060[5]		ν CH
	3140[s]	ν [N – H], ν [O – H]
	3213[s]	ν [N – H], ν [O – H]

TABLE 10

L – Cystine $^{-}OOC-CH(NH_3^+)-CH_2-S-S-CH_2-CH(NH_3^+)-COO^-$

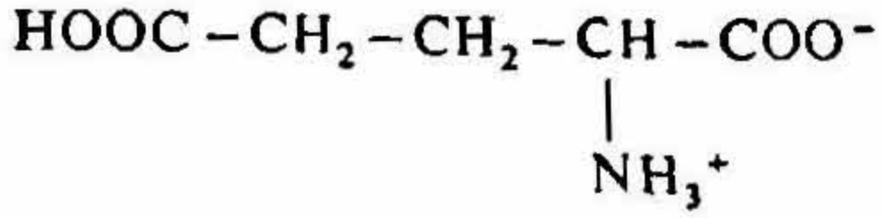
Raman	Infrared	Assignments
416[5]		
436[8]		γ_ρ COO⁻
447[20]	445[s]	ν [S – S]
479[7]	465[m]	τ NH_3^+
498[7]		
538[17]	537[s]	γ_w COO⁻
640[60]	638[s]	ν [C – S]
695[44]	693[m]	
756[10]	757[m]	δ COO⁻
775[26]	770[m]	
807[12]	810[m]	
827[19]	825[s]	Skeletal stretch
857[12]	857[m]	
871[16]	870[s]	
915[6]	915[m]	γ_p CH_2
945[12]	945[s]	
996[6]	999[w]	
1008[6]	1010[w]	
1029[4]		
1044[–]		
1056[6]		
1069[11]	1069[m]	ν [C – N]
1108[6]	1108[m]	
1144[8]	1148[s]	γ_ρ NH_3^+
1202[11]	1202[s]	
1241[4]		
1270[4]	1272[s]	γ_t CH_2
1298[10]	1302[s]	γ_w CH_2
1348[18]	1352[s]	δ CCH
1355		
1395[6]	1395[s]	ν_s COO⁻
1402[14]	1400[s]	
1429[18]	1433[s]	δ CH_2
1493[4]		

TABLE 10—[*contd.*]

Raman	Infrared	Assignments
1524[5]	1547[s], 1558[s]	$\delta_s NH_3^+$
1577[3]	1593[s]	$\nu_{as} COO^-$
1621[1]	1618[s]	$\delta_d NH_3^+$
1653		
1579		
	2080[m]	$\delta_d NH_3^+ + \tau NH_3^+$
	2220[m]	
	2300[m], 2410[m], 2470[s], 2512]s], 2555[s]	Combinations
	2600[s], 2647[s], 2700[s], 2725[s], 2790[s]	Combinations and ν [N–H]
	2840[s], 2870[s]	
2878[2]		
2899[2]		
2918[2]	2920[s]	ν [C–H]
2950[6]		$\nu_s CH_2$, $\nu_{as} CH_2$
2966[6]	2965[s]	
2978[2]		
3001[1]	3000[s]	
	3068[s], 3186[s]	ν [N–H]

TABLE 11

L – Glutamic acid



Raman	Infrared	Assignments
	402(m)	
	422(m)	γ_p COO^-
462(4)	463(m)	τ NH_3^+
504(5)	506(m)	δ COOH
542(8)	538(s)	γ_w COO^-
577(4)	577(w)	
	615(w)	
	673(m)	
	705(m)	
713(6)	718(m)	δ COO^-
761(4)	763(w)	
806(4)	812(s)	δ OH
834(3)	840(m)	
871(14)	871(m)	ν (C – C)
923(5)	917(m)	γ_r CH_2
945(3)	951(m)	
972(4)	973(m)	
	1062(s)	
1071(4)	1082(s)	γ_ρ NH_3^+
1132(4)	1132(s)	
	1157(s)	
1217(3)	1220(s)	ν (C – O) + δ(O – H)
	1240(s)	γ_t CH_2
	1265(s)	
1313(2)	1318(s)	γ_w CH_2
1354(5)	1361(s)	δ CCH
	1380(s)	
1410(5)	1417(s)	ν (C – O) + δ (O – H)
	1420(s)	ν_s COO^-
1441(4)	1445(s)	
	1500	δ_s NH_3^+
	1525(s)	
	1590(s)	δ_d NH_3^+
	1610(s)	ν_{as} COO^-
	1625(s)	

TABLE 11 – (*contd.*)

Raman	Infrared	Assignment
	1652(s), 1675(s)	ν (C=O)
	1840(m)	
	1960(m)	
	2081(m)	$\delta_d NH_3^+ + \tau NH_3^+$
	2300(m)	ν (C–H)
	2490(m), 2585(m), 2660(s), 2748(s), 2875(s)	Combinations
2868(5)		
2936(24)	2940(s)	$\nu_s CH_2$
2965(10)	2970(s)	$\nu_{as} CH_2$
2974(22), 2995(12), 3009(4)		ν CH
3020(8)		
3039(4)		
3064(2)	3060(s), 3150(s), 3260(m)	ν (N–H)

TABLE 12

L-Glutamic acid H Cl

$HOOC-CH_2-CH_2-\underset{\displaystyle NH_2^+}{\underset{|}{CH}}-COO.\ Cl^-$

Raman	Infrared	Infrared dueterated	Assignment
03(9)	403(m)	400(m)	δ CCO
498(9)	490(m)	480(m)	δ CCO
532(8)	535(m)	511(m)	δ COOH
		542(m)	
642(6)	637(s)	605(s)	δ COOH
		628(s)	γ OD
684(4)	678(m)	533(s)	δ COOH
751(6)	752(m)	755(s)	
777(4)	780(m)	782(m)	
	830(s)	827(m)	γ OH
868(7)	870(s)	870(s)	ν (C – C),
	877		$\gamma_p\ ND_3^+$
923(26)	927(m)	925(m)	
937(8)	940(m)		$\gamma_p\ CH_2$
1005(5)	1005(s)	983(m)	Skeletal
1074(7)	1070(sh)	1043(s)	ν (C – N)
		1065(s)	δ (O – D)
1084(16)	1087(s)	1078(s)	ν (C – N)
	1130(m)		$\gamma_p\ NH_3^+$
1155(6)	1155(s)		
	1150(sh)		$\delta_s\ ND_3^+$
	1172(s)		$\delta_d\ ND_3^+$
	1217(m)		
1206(1)			ν (C-O) + δ(O-H)
1230(4)	1223(s)		
1254(4)	1250(s)	1238(s)	$\gamma_t\ CH_2$
1309(6)	1283(s)	1974(s)	
1314(6)	1314(m)		$\gamma_w\ CH_2$
1326(5)	1330(m)		
		1331(s)	ν (C – O)
1363(6)	1368(sh)	1362(s)	$\gamma_w\ CH_2$
1378(4)	1380(s)	1380(s)	δ CCH
1412(11)	1420(s)	1419(s)	ν(C – O) + δ(O – H)
1432(7)	1435(s)	1440(s)	δ CH_2
	1460(s)	1462(s)	δ CH_2
		1469(s)	

TABLE 12 – (*contd.*)

Raman	Infrared	Infrared dueterated	Assignment
	1505(s)		$\delta_s NH_3^+$
	1510(s)		
1589(1)	1592(m)		$\delta_d NH_3^+$
	1620(s)		
1678(6)			
1687(4)	1689(s)	1681(s)	ν (C=O)
1728(6)	1735(s)	1724(s)	
		1911(m)	Combinations
		1925(m)	
		1945(m)	
		1989(m)	
		2038(m)	
		2071(s)	
		2128(s)	
		2143(s)	ν (N – D) and ν (O – D)
		2200(s)	
		2248(s)	
		2350(s)	
	1982(m)		$\delta_d NH_3^+ \tau NH_3^+$
	2005(m)		
	2290(w)		
	2502(s)		
	2580(s)		ν (O – H)
	2604(s)		ν (N – H)
2627(1)	2630(s)		
	2650(s)		Combinations
	2722(s)		
2752(1)	2745(s)		
2817(2)	2820(s)		
2858(2)	2875(s)		
2920(24)			
2933(8)			$\nu_s (CH_2)$, $\nu_{as} CH_2$
2940(12)			ν (CH)
2970(14)			
2974(8)			
3009(8)			ν (N – H)
	3160(s)		ν (O – H)
	3220(s)		

TABLE 13

Monosodum Glutamate $[^{-}OOC-CH_2-CH_2-\underset{\underset{NH_3^+}{|}}{CH}-COO^{-}]\ Na^+.H_2O$

Raman	Infrared	Infrared deuterated	Assignment
437(7)	434(m)	434(m)	$\tau\ NH_3^+$
482(2)	488(m)		$\gamma_p\ H_2O$
504(12)	500(m)	486(m)	γ_p COO
533(10)	533(s)	521(s)	
604(6)	600(s)	592(m)	
	628(s)	621(m)	$\gamma_\omega\ COO^-$
664(6)	655(s)	657(m)	
	692(m)		$\gamma_\omega\ H_2O$
731(5)	740(m)	727(w)	$\delta\ COO^-$
779(7)	772(m)	752(w)	
		768(w)	
	798(m)	798(w)	
807(8)	805(m)	820(m)	$\gamma_p\ CH_2$
		849(m)	$\gamma_p\ ND_3^+$
861(16)	857(w)	861(w)	ν (C – C)
880(10)	871(w)	882(w)	ν (C – C)
927(8)	928(m)	990(m)	$\gamma_p\ CH_2$
946(8)	928(m)	920(m)	
1006(6)	1010(m)		
	1024(m)		
1045(6)	1042(m)	1038(w)	Skeletal
1059(8)	1060(m)	1053(w)	
1080(7)	1081(m)	1075(m)	
		1081(sh)	$\delta\ D_2O$
		1963(w)	
		2018(w)	
		2098(m)	
		2110(m)	
		2130(m)	ν (N – D) and
		2256(m)	ν (O – D)
		2350(s)	
		2418(m)	
		2470(m)	
		2529(s)	
2480(m)			Combination
2540(m)			

TABLE 13—(*contd.*)

Raman	Infrared	Infrared deuterated	Assignments
	2632(m) 2744(m)		Combination
2849(8)			
2884(8)	2860(s)		
2894(8)			
2906(8)			ν_s CH_2
2928(10)			ν_{as} CH_2 and
2938(12)			ν CH
2955(5)			
2968(12)			
2975(19)	2978(s)		
2982(15)			
2994(6)			
	3065(s)		
	3128(s)		ν (N - H) and
	3273(s)		ν (O – H)
	3375(s)		
	3420(s)		

TABLE 14

L – Glutamine $H_2NOC-CH_2-CH_2-CH(NH_3^+)-CCO^-$

Raman	Infrared	Infrared deuterated	Assignments
		417(m)	
439(6)	430(w)	439(m)	
456(8)	457(s)	460(s)	COO^-
475(4)	475(m)		$\tau\ NH_3^+$
		504(s)	$\gamma_p\ ND_2$
546(7)	540(s)	525(s)	$\gamma_w\ COO^-$
	600(s)	582(m)	δ NCO
626(7)	623(s)	625(m)	γ (C=O)
653(4)	654(m)		
	675(s)		$\gamma_p\ NH_2$
780(10)	782(m)	762(m)	$\delta\ COO^-$
806(2)	813(s)	800(s)	
		809(w), 828(m)	$\gamma_w\ ND_2$
851(26)	850(m)	853(m)	ν (C–C)
900(14)	900(m)		$\gamma_p\ CH_2$
930(6)	928(m)	947(m)	$\gamma_p\ CH_2$
		966(m)	$\gamma_p\ ND_3^+$
1004(4)	1003(m)		
1055(3)	1056(m)	1044(m)	ν (C–N)
1089(6)	1092(m)		$\gamma_w\ NH_2$
1100(13)			
1108(8)	1109(m)	1113(m)	
1137(6)	1130(m)		
1155(4)	1166(s)		$\gamma_p\ NH_3^+$
1167(8)			
		1150(m)	
		1167(s)	$\delta_s\ ND_3^+$
		1180(s)	$\delta_d\ ND_3^+$
		1210(s)	$\gamma_t\ CH_2$
1209(5)	1210(s)		$\gamma_w\ NH_2$
1265(5)	1262(m)		
1289(7)	1288(s)	1282(s)	$\gamma_t\ CH_2$
1312(6)	1326(s)	1326(s), 1338(s)	δ CCH
1334(9)	1340(s)		
1361(7)	1366(s)	1370(s)	$\gamma_w\ CH_2$

TABLE 14 – (*contd.*)

Raman	Infrared	Infrared deuterated	Assignments
1419(8)	1420(s)	1417(s)	ν_s COO$^-$
1426(4)	1430(s)	1426(s)	
1453(10)	1462(s)	1449(s)	δ CH_2
1498(2)	1492(s)		δ_s NH_3^+
	1592(s)		δ_d NH_3^+
1608			
1619(1)	1643(s)		δ NH_2
	1692(s)	1659(s)	ν (C = O)
	1720(w)		
		1959(w)	
		1992(w)	
		2100(m)	ν (N – D)$_d^n$
		2110(m)	
	2040(m)		δ $NH_3^+ + \tau NH_3^+$
		2206(s)	
		2230(s)	
		2270(s)	
		2320(s)	ν (N – D)
		2388(s)	
		2459(s)	
		2489(s)	
		2562(s)	
	2210(w)		
	2500(m)		Combination
	2550(m)		
	2640(s)		
	2733(s)		ν (N – D)
2876(1)	2880(s)		ν_s CH_2
2933(12)	2930(s)		
2948(1)	2948(s)		ν_s CH_2,
2954(12)			ν_{as} CH_2,
2963(12)			ν CH
2994(6)	3000(s)		
3009(2)			
	3186(s)		ν (N – H)
	3219(s)		
	3286(s)		ν_s NH_2
3326(s)			
3420(s)			ν_{as} NH_2

TABLE 15

Bond length versus hydrogen bonded N–H stretching frequency in amino acids
(Hydrogen bond distances are taken from references given in column 4)

Crystal	Bond type	Bond distance (Å)	Ref.	Calculated frequency	Observed frequency
	O–H . . O	2.80	(47)	3280	3298
Hydroxy Proline	N^+–H . . O	2.69		2459	2442
					2459
	N^+–H . . O	3.17		–	3130
	O–H . . O	2.66	(48)	2750	2800
Threonine	N^+–H . . O	2.90		3030	3021
	N^+–H . . O	2.80		2750	2720
	N^+–H . . O	3.10		3250	3180
	N^+–H . . O	2.87	(49)	2920	2906
	N^+–H . . O	2.80		2750	2772
Valine	N^+–H . . O	2.86		2900	2906
	N^+–H . . O	3.10		3250	3152
	N^+–H . . O	2.81		2750	2772
	N^+–H . . O	2.78		2660	2600
	N^+–H . . O	2.91	(50)	3020	3009
Glutamine	N^+–H . . O	2.79		2720	2700
	N^+–H . . O	2.85		2890	2930
	N–H . . O	2.91		3150	3186
	N^+–H . . O	2.94		3200	–
	N^+–H . . O	2.87	(51)	2920	3100
Serine	N^+–H . . O	2.82		2860	3000
	O–H . . O	2.92		3500	3466
	O–H . . O	2.52	(52)	2200	2300

TABLE 15—(*contd.*)

Crystal	Bond type	Bond distance (Å)	Ref.	Calculated frequency	Observed frequency
Glutamic acid	N^+-H . . O	2.87		2940	2936
	N^+-H . . O	2.89		3015	3060
	N^+-H . . O	2.92		3090	3150
					3200
	O—H . . O	2.63	(53)	2600	2580
					2604
L Glutamic acid HCl	N^+-H . . Cl	3.16		3000	3009
	N^+-H . . Cl	3.20		3050	
	N^+-H . . O	2.90		3035	
	O—H . . Cl	3.04		3000	3160
	N^+-H . . O	2.79	(54)	2710	2700
					2725
	N^+-H . . O	2.81		2760	2790
	N^+-H . . O	2.87		2920	2920
					3001
	N—H . . O	2.87	(55)	2955	2954
	N—H . . O	2.91		3150	
L Arginine	N—H . . O	2.85		3100	3100
	N . . H . . N	2.90		3240	3290
	O—H . . O	2.74		3070	3100
	O—H . . O	2.87		3425	3500

TABLE 16

Compound	τNH_3^+ cm^{-1}	$\delta_{as} NH_3^+$ cm^{-1}	Calculated $(\tau+\delta)$ cm^{-1}	Observed cm^{-1}
Cystine	465	1618	2083	2080
Isoleucine . .	495	1621	2116	2119
Leucine . .	514	1635	2139	2130
Valine . .	490	1630	2120	2110
Tyrosine , .	471	1620	2091	2080
Glutamic acid . .	463	1590	2053	2081
Serine	433	1640	2073	2040 2080
Glu–HCl . .	373	1620	1993	1982 2005
Threonine . .	417	1648	2065	2052
Glutamine . .		1592 1608	2031 2047	2010 2040
Monosodium glutamate	488	1609	2097	2055

TABLE 17

Low Frequency spectra of amino acids

Serine	Threonine	Tyrosine	Valine
73[9]	73[28]	53[20]	67[5]
84[27] br	79[16]	76[16]	79[14]
94 } [11]	96[20]	82[10]	99[24]
100 }	99	96[42]	115[8]
119[18]	104[17]	112[44]	318[9]
141[14]	110[10]	117[28]	164[6]
164[6]	120[3]	128[50]	183[4]
173[3]	158[30]	149[16]	300[3]
198[6]	176[9]	156[24]	210[3]
236[5]	183[23]	161[32]	335[5]
264[2]	194[26]	176[6]	260[1]
300[3]	196	192[2]	384[1]
336[1]	217[14]	260[1]	399[4]
355[2]	314[4]	335[4]	
	337[7]	385[5]	
	386[7]		

TABLE 17 – (*contd.*)

Glutamic acid	Glutamic acid. HCl	Glutamine	Monosodium glutamate
68[14]	37[2]	39[2]	76[7]
78[14]	52[9]	43[2]	81[4]
82[2]	83[31]	50[6]	86[1]
94[36]	96[11]		93[1]
100[21]	111[6]	71[6]	100[3]
109[29]	135[20]	80[6]	107[5]
151[20]	156[14]	90[12]	111[14]
185[10]	200[8]	102[8]	120[9]
201[9]	268[14]	111[34]	128[8]
387[5]	290[10]	127[8]	139[4]
	329[12]	135[8]	155[10]
	373[5]	188[14]	179[9]
		194[7]	197[9]
		212[11]	213[6]
		238[9]	223[6]
		295[6]	286[4]
		346[5]	360[4]
			386[5]

TABLE 17—(*contd.*)

Isoleucine	OH—Proline	Arginine	Cystine
75[5]	55[4]	82[2]	32[46]
81[12]		96[4]	70[14]
95[10]	74[6]	103[4]	82[15]
99[10]	79[9]	117[6]	97[18]
118[2]	83[4]	124[17]	104[12]
138[1]	93[4]	144[2]	119[10]
165[12]	101[7]	153[20]	144[2]
196[12]	122[5]	212[5]	164[2]
285[6]	145[10]	245[5]	213[17]
303[3]	156[12]	256[5]	249[4]
341[3]	198[2]	273[3]	965[7]
366[6]	235[6]	300[4]	299[9]
391[3]	261[13]	340[1]	366[12]
	308[2]	371[4]	
	346[4]		
	375[5]		
	400[6]		

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