

# RAMAN AND INFRARED SPECTRA OF AMINO ACIDS

By R. S. KRISHNAN AND V. N. SANKARANARAYANAN  
(Department of Physics, Indian Institute of Science, Bangalore-560012)

AND

K. KRISHNAN  
(Department of Chemistry, Hunter College, New York, U.S.A.)

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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 studied are*

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

*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<sup>o</sup> cm<sup>-1</sup>. Some of the infra-red absorption spectra were recorded also at 100<sup>o</sup>K. The N-H stretching modes are influenced by hydrogen bonding. Raman lines characteristic of NH<sub>3</sub><sup>+</sup> and COO<sup>-</sup> groups have been identified in many of the amino acids. It has been shown that the appearance of band at 2100 cm<sup>-1</sup> which is assigned to a combination of the torsional oscillation and degenerate deformation of the NH<sub>3</sub><sup>+</sup> groups can also be used a "finger print" for the identification of NH<sub>3</sub><sup>+</sup> 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<sub>2</sub>-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  $\alpha$ -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<sup>1</sup>.

In most of the amino acids, the  $\alpha$ -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  $\alpha$ -carbon atom, irrespective of the sense of rotation of plane polarised light. Thus all protein derived amino acid are called L-amino acid 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  $\alpha$  carbon is not asymmetric exists only in one form which is optically inactive.

It has been observed that all amino acids exist as dipolar ions in their free state. Thus it is more appropriate to describe them with the general formula  $\text{NH}_3^+ - \text{CHR} - \text{COO}^-$ . 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  $\text{NH}_3^+$  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<sup>2</sup>. 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<sup>3</sup> 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  $\text{cm}^{-1}$ . The results are presented here.

## 2. REVIEW OF EARLIER WORK ON AMINO ACIDS

### A) Raman effect studies:

Edsall<sup>4</sup>, Kahovek and Kohlrausch<sup>5</sup> and Ananthakrishnan<sup>6</sup> recorded the Raman spectrum of glycine in crystalline powder form. The Raman spectrum of a single crystal of  $\alpha$ -glycine was first recorded by Krishnan and Balasubramanian<sup>7</sup> in this laboratory using the 2537A<sup>o</sup> 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  $\text{COO}^-$  ion, it was confirmed that in the crystal the molecular units exist as dipolar ions. Balasubramanian *et al*<sup>8</sup> recorded the Raman spectrum of  $\gamma$ -glycine which has a structure different from that of  $\alpha$ -glycine. As is to be expected, the lattice spectra of the two forms are different. Neelakantan *et al*<sup>9</sup> examined the Raman spectrum of C-deuterated  $\gamma$ -glycine and recorded the lattice lines. Balasubramanian and Krishnan<sup>10</sup> made polarization studies on the Raman spectrum of  $\alpha$ -glycine and from the observed depolarization values the classification of the Raman lines to the two different symmetry types  $A_g$  and  $B_g$  have been made. It was pointed out that the orientation of the  $\text{CH}_2$  groups deduced from these studies was slightly different from that given by the X-ray analysis.

The Raman spectra of triglycine sulphate<sup>11</sup> and triglycine selenate<sup>12</sup> were recorded using the 2537A<sup>o</sup> radiation. In the spectra of diglycine hydrochloride and hydrobromide the  $\text{COO}^-$  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<sup>13</sup>, while in the case of diglycine nitrate, the  $\text{NO}_3^-$  ion has a staggered configuration. In diglycine barium chloride monohydrate<sup>14</sup> no band characteristic of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  could be found. A strong sharp lattice line was seen at 121  $\text{cm}^{-1}$ . In this compound also the glycine units exist as zwitterions. The Raman spectrum of L-asparagine monohydrate was recorded by Krishnan and Krishnan<sup>15</sup>. The lines at 194, 245 and 296  $\text{cm}^{-1}$  were attributed to the hydrogen bond vibrations. The  $\text{NH}_2$  and  $\text{NH}_3^+$  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<sup>16</sup> proposed a correlation curve for the  $N^+ - H \dots O$  type bonds. The curve was found to be entirely different from the Nakamoto curve for the  $N - H \dots O$  type bonds. The straight line portion of the curve for  $N^+ - H \dots O$  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<sup>17</sup> investigated the Raman spectrum of  $\beta$ -alanine and found that the bands at 2651 and 2731  $\text{cm}^{-1}$  could be explained as due to the  $N^+ - H \dots O$  bonds as deduced from the proposed correlation curve. In this compound the low frequency hydrogen bond vibrations appear at 221 and 242  $\text{cm}^{-1}$ .

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<sup>18</sup> 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<sup>19</sup> recorded the Raman spectrum of  $\gamma$ -glycine. Herlinger and Long<sup>20</sup> 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<sup>21</sup> 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  $NH_3^+$  torsional 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 Storms<sup>21</sup> using laser excitation. Laser Raman spectra of L-proline hydrochloride, sodium proline and poly L-hydroxy proline in the solid state have been recorded by Deveney et al<sup>22</sup>. They reported the appearance of two lines at 1543 and 1374  $\text{cm}^{-1}$  and absence of lines at 1700 and 1750  $\text{cm}^{-1}$  in these amino acids indicating the existence of ionised carboxyl 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<sup>23</sup> and Wright<sup>24,25</sup> are significant. Wright studied the infrared



spectra of several amino acids in powder form from 400-3500  $\text{cm}^{-1}$ . 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.*<sup>26</sup> investigated the spectra in the solid state of 50 pairs of optically enantiomorphous amino acids in the region 650-5000  $\text{cm}^{-1}$ , 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  $\alpha$ -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  $\text{cm}^{-1}$ . Of these, the 1587 and 1408  $\text{cm}^{-1}$  bands were attributed to the carboxyl ion vibration. The 1515  $\text{cm}^{-1}$  line was attributed to an N-H deformation vibration, the peaks at 1444 and 1355  $\text{cm}^{-1}$  to methyl and methylene deformation and 1330  $\text{cm}^{-1}$  to  $\text{CH}_2$  wagging. The spectra of diastereomeric pairs were found to be different.

Leifer and Lippincott<sup>27</sup> who investigated the infrared spectra of several optically inactive amino acids, showed that the band at 2100  $\text{cm}^{-1}$  should be attributed to a bending vibration of the amino group rather than to a stretching mode attributed by Koegel *et al.*<sup>26</sup>. In the solid state the spectra of the optically active amino acids are found to differ from those of the corresponding inactive forms. This observation was made even by Wright<sup>25</sup> who studied several L and DL compounds. Koegel *et al.*<sup>28</sup> 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  $\alpha$ -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  $\text{cm}^{-1}$  for all the amino acids, a differentiation among them is rather difficult. However the region 400-700  $\text{cm}^{-1}$  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.*<sup>29</sup> have recorded the infrared spectra of cystine, serine, valine, leucine and tyrosine in the 400-4000  $\text{cm}^{-1}$  region and assigned bands in the range 560-770  $\text{cm}^{-1}$  to the deformation vibration of the carboxyl group. An investigation of the infrared absorption spectra of 49 amino acids in the 400-700  $\text{cm}^{-1}$  region was carried out by Warren *et al.*<sup>30</sup> who identified four characteristic bands, one at 740  $\text{cm}^{-1}$  ( $\text{COO}^-$  bending vibration), one at 650  $\text{cm}^{-1}$  ( $\text{COO}^-$  wagging mode) the third one at 540  $\text{cm}^{-1}$  (CCN bending mode) and the fourth one at  $\sim 480$   $\text{cm}^{-1}$  ( $\text{NH}_3^+$  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.*<sup>31</sup> have made complete assignments of the observed peaks in the region from 400-1800  $\text{cm}^{-1}$  by comparing the spectra of glycine, glycine hydrochloride and sodium glycinate and their N-deuterated analogues. Similar studies have been carried out in the case of DL-alanine by Fukushima *et al.*<sup>32</sup> Infrared spectral studies of C-deuterated alanine have been done by Oshima and Tamiya<sup>33</sup> who obtained the spectra of  $\text{CH}_3\text{CHNH}_3^+\text{COO}^-$ ,  $\text{CH}_3\text{CDNH}_3^+\text{COO}^-$ ,  $\text{CD}_3\text{CDNH}_3^+\text{COO}^-$  and  $\text{CD}_3\text{CDND}_3^+\text{COO}^-$ . Khanna *et al.*<sup>34</sup> have made a systematic analysis of the addition compounds of glycine,  $\text{NH}_2^+\text{DCH}_2\text{COO}^-$ ,  $\text{NHD}_2^+\text{CH}_2\text{COO}^-$  and  $\text{ND}_3^+\text{CH}_2\text{COO}^-$ . Suzuki *et al.*<sup>35</sup> have also studied the spectra of C-deuterated compounds of alanine. All vibrations involving the N atom in DL-alanine were identified by Tsuboi *et al.*<sup>36</sup> by substituting  $^{14}\text{N}$ , by  $^{15}\text{N}$  and observing the isotope shifts in the spectrum. Some studies on the spectra of metal amino acid complexes have been made<sup>37 38</sup>.

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<sup>32</sup> and glycine<sup>39</sup> 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  $\text{NH}_3^+$  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 frequencies of several amino acids, Tsuboi *et al.*<sup>40</sup> have tried to define some characteristic frequencies for the amino acids. They have identified the following vibrations: the  $\text{NH}_3^+$  degenerate deformation at  $\sim 1600 \text{ cm}^{-1}$ ,  $\text{NH}_3^+$  symmetric vibration at  $\sim 1510 \text{ cm}^{-1}$ ,  $\text{ND}_3^+$  deformation at  $\sim 1170 \text{ cm}^{-1}$ ,  $\text{NH}_3^+$  rocking at  $\sim 1130 \text{ cm}^{-1}$ ,  $\text{ND}_3^+$  rocking at  $800 \text{ cm}^{-1}$ , C-N stretching at  $\sim 1000 \text{ cm}^{-1}$ ,  $\text{COO}^-$  antisymmetric stretching at  $\sim 1600 \text{ cm}^{-1}$ ,  $\text{COO}^-$  symmetric stretching at  $\sim 1410 \text{ cm}^{-1}$ . In the hydrochlorides the C=O stretching appears  $\sim 1720 \text{ cm}^{-1}$  and the coupled O-H in plane bending and C-O stretching at  $\sim 1420 \text{ cm}^{-1}$  and  $\sim 1280 \text{ cm}^{-1}$ . The O-H out of plane bending of the COOH group has a frequency  $\sim 900 \text{ cm}^{-1}$ . The corresponding bends for COOD are at  $\sim 1710$ ,  $\sim 1380$ ,  $\sim 1040$  and  $\sim 600 \text{ cm}^{-1}$ .

In some cases it has been found that the infrared spectral bands of complicated molecules are well resolved if recorded at low temperature. Fairheller and Miller<sup>41</sup> recorded the infrared spectra of some amino acids and peptides from  $33 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  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  $\text{cm}^{-1}$ . In terms of spectral slit widths, these corresponded to 2.5  $\text{cm}^{-1}$  for the lattice region (0 - 150  $\text{cm}^{-1}$ ), 4.7  $\text{cm}^{-1}$  for the intermediate region (150 - 1700  $\text{cm}^{-1}$ ) and 7.5  $\text{cm}^{-1}$  for the high frequency hydrogenous stretching region (2800 - 3100  $\text{cm}^{-1}$ ). 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 occurred in the 400-700  $\text{cm}^{-1}$  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 been 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  $\text{NH}_3^+$  group. In the region from 700-1800  $\text{cm}^{-1}$ , 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 of their complete disappearance on deuteration. The symmetric deformation has a frequency  $1520 \pm 20 \text{ cm}^{-1}$ . 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  $1620 \pm 20 \text{ cm}^{-1}$  and this mode also gives more than one line. The  $\text{NH}_3^+$  rocking mode usually gives two lines lying between 1100 and 1200  $\text{cm}^{-1}$ .



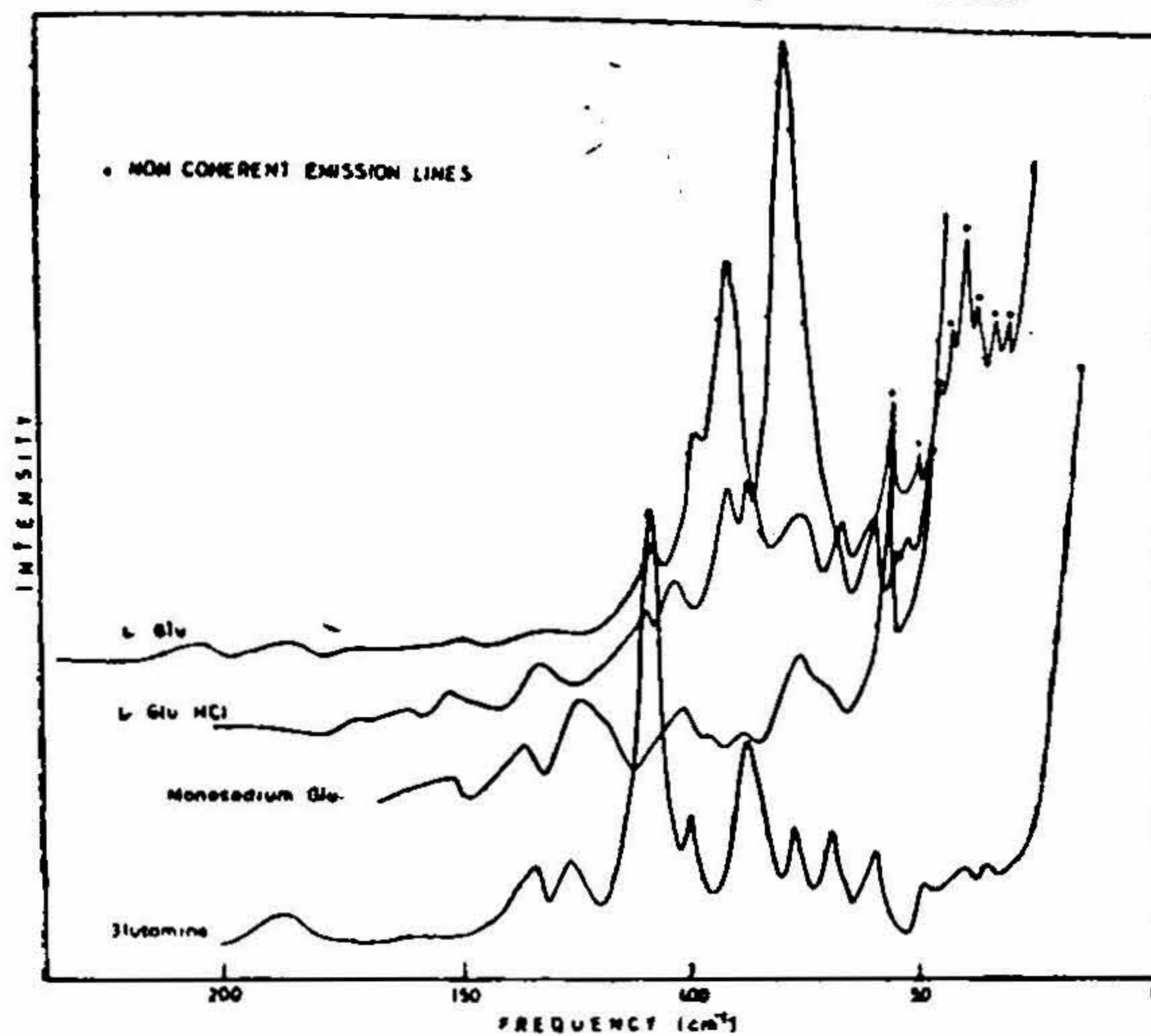


FIG. 1  
Lattice Spectra of some amino acids

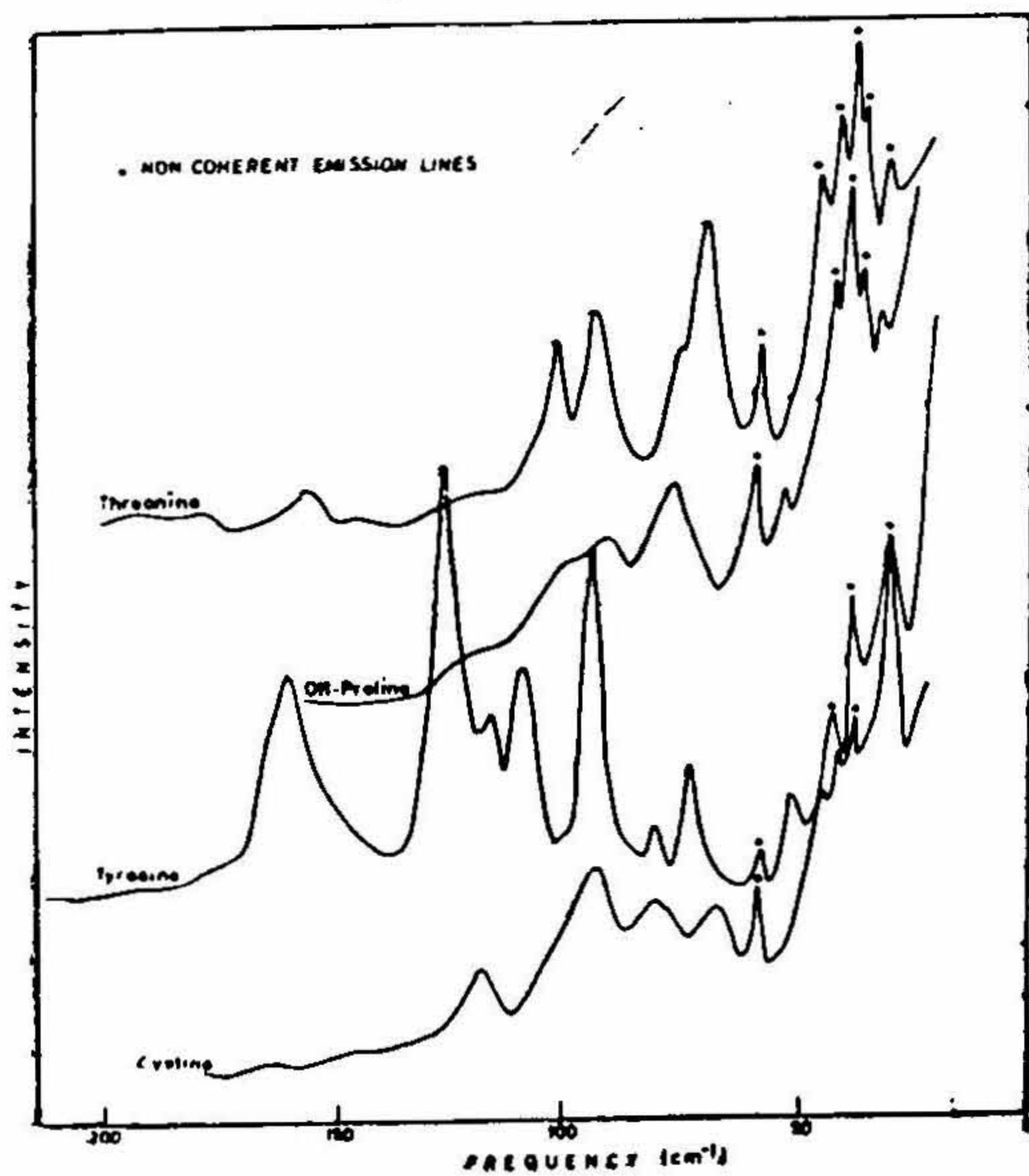


FIG. 2  
Lattice Spectra of some amino acids



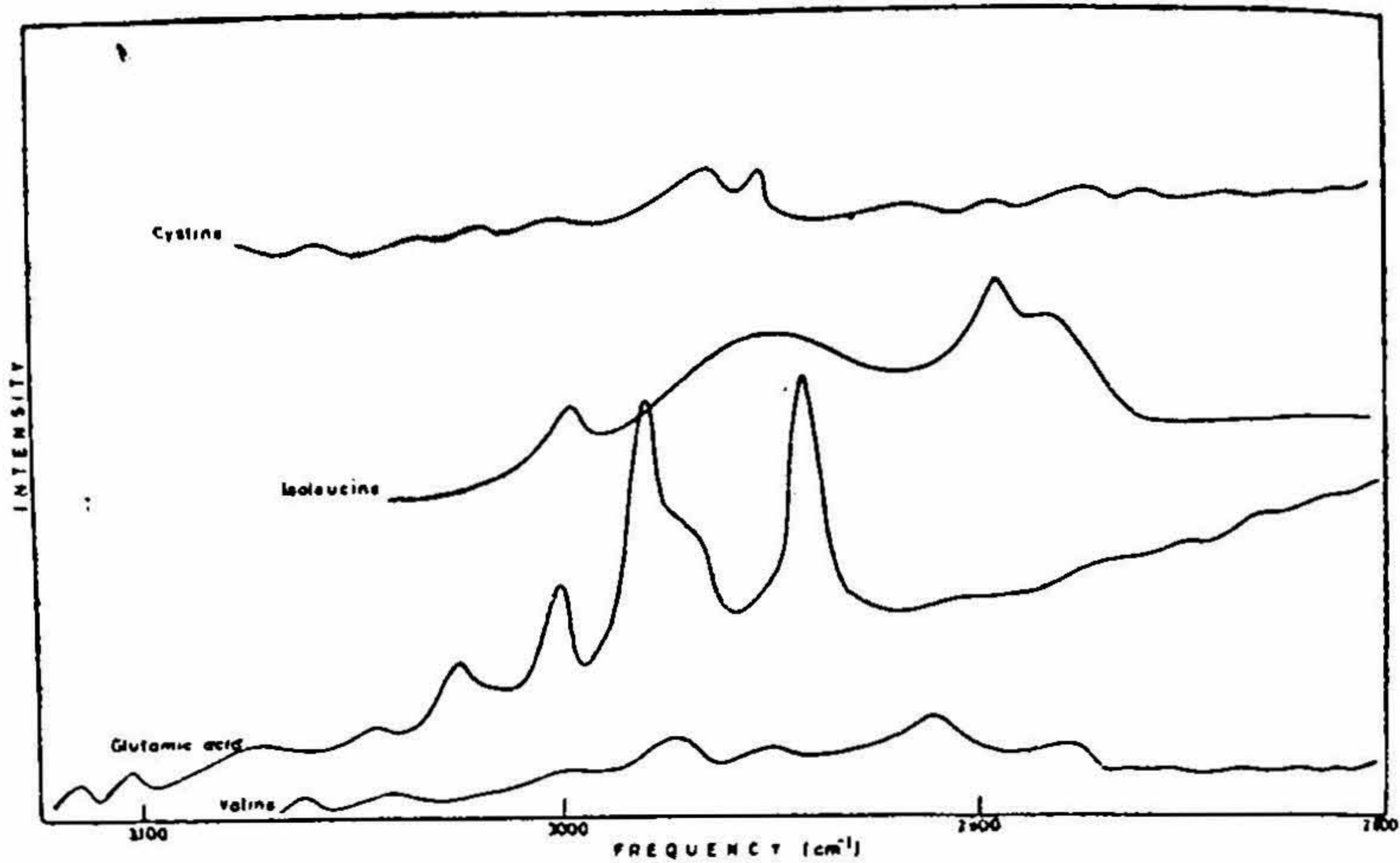


FIG. 3

High frequency Raman Spectre of amino acids

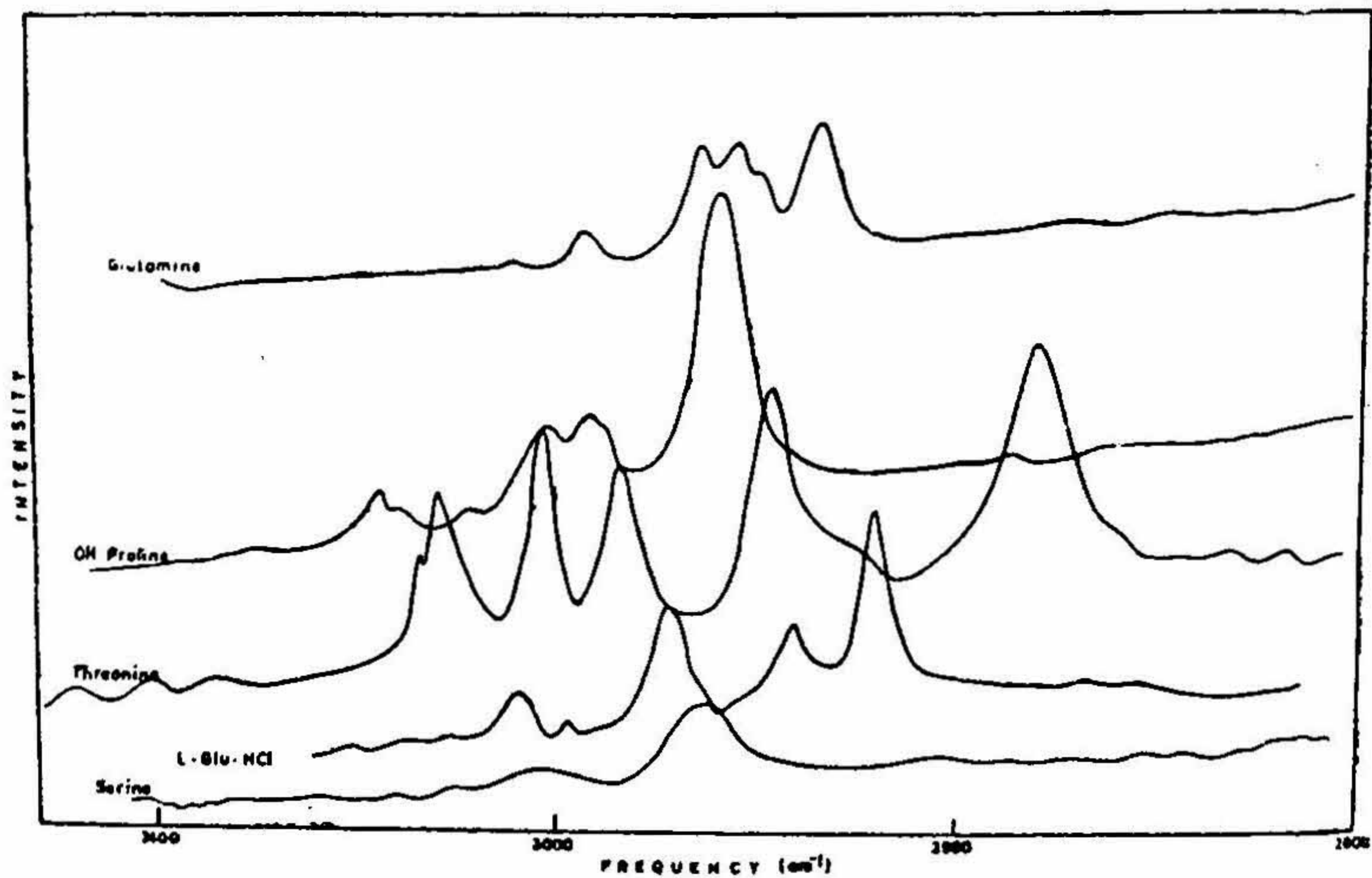


FIG. 4

High frequency Raman Spectra of amino acids



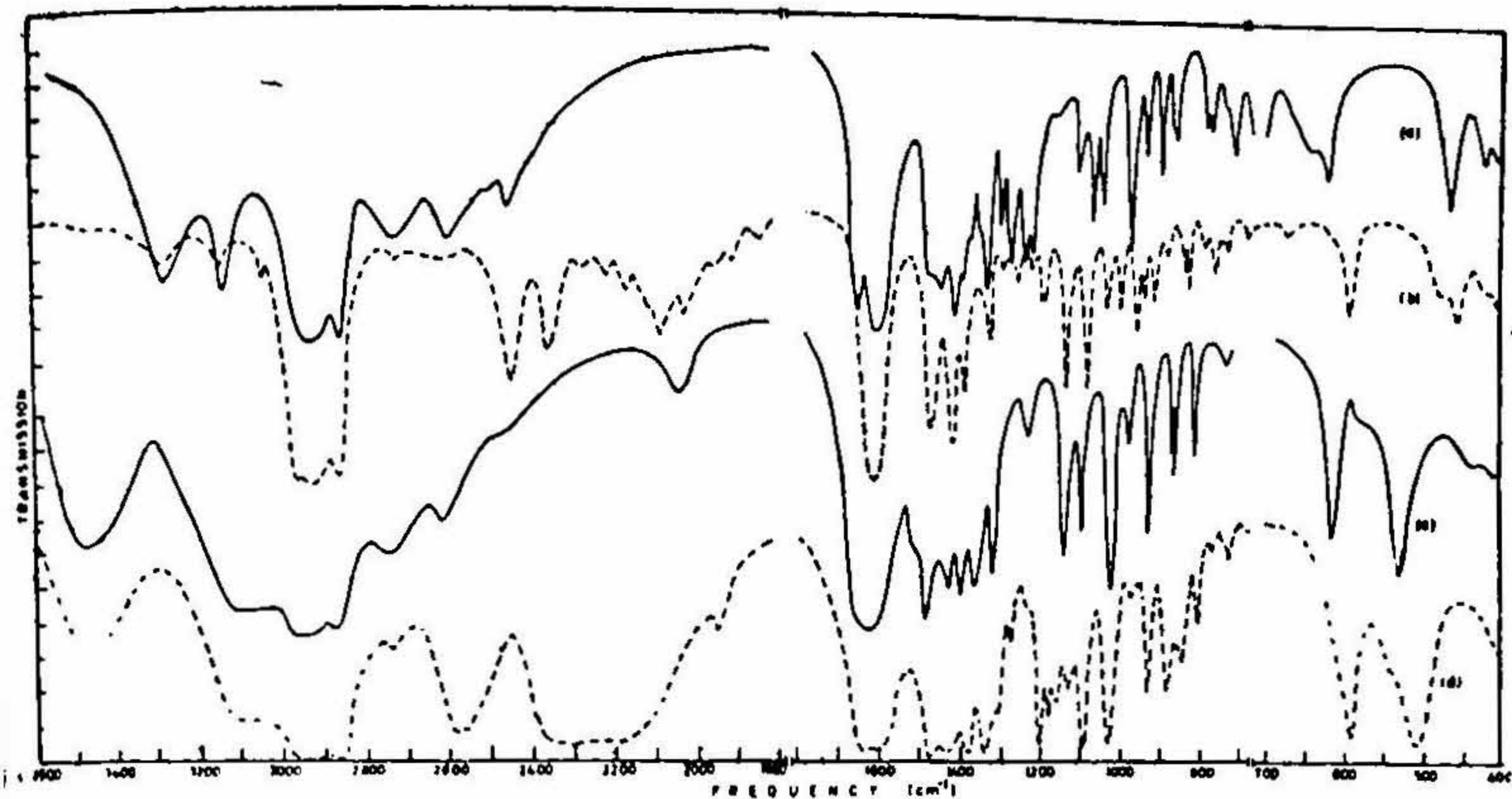


FIG. 5

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

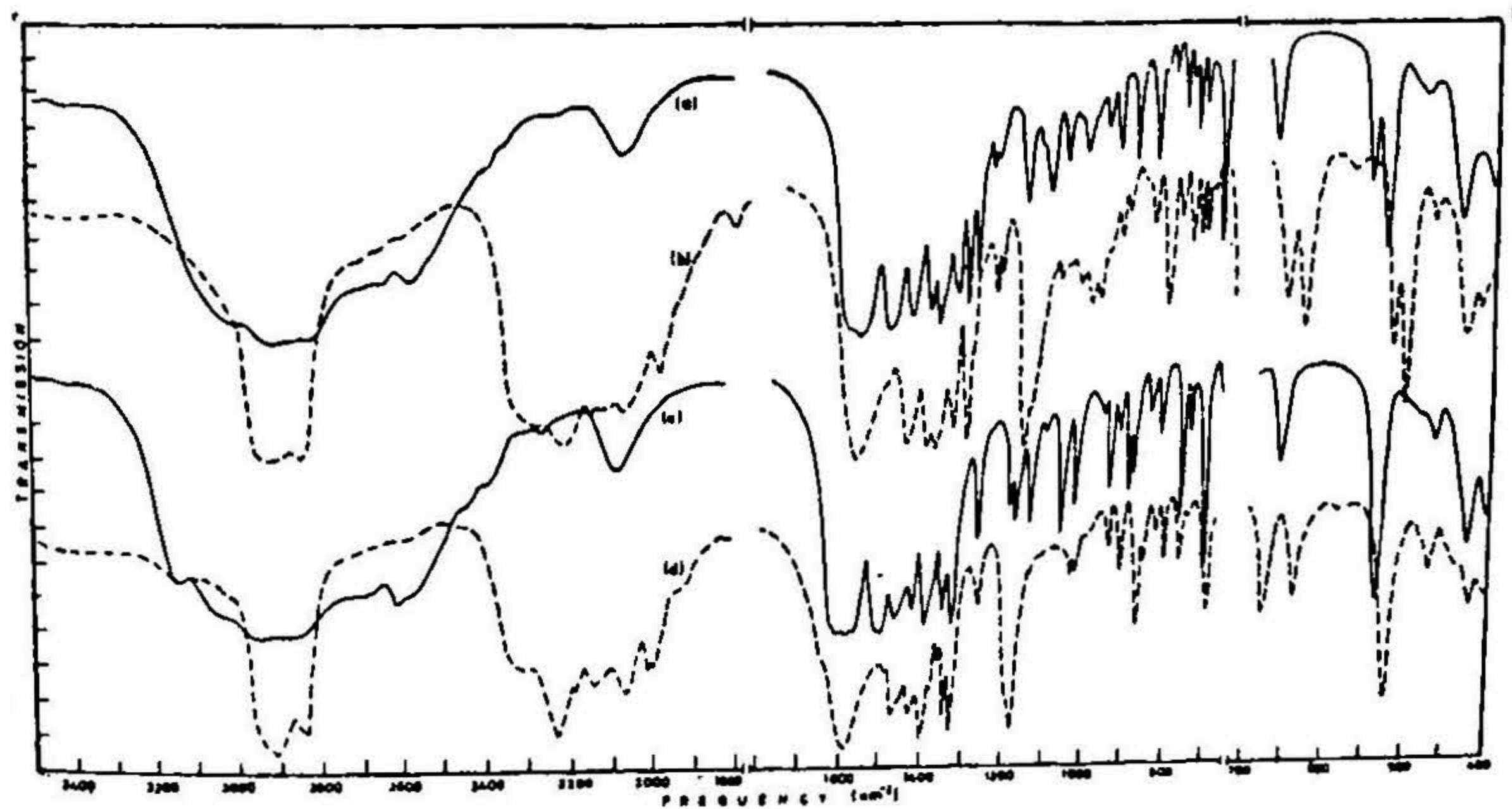


FIG. 6

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



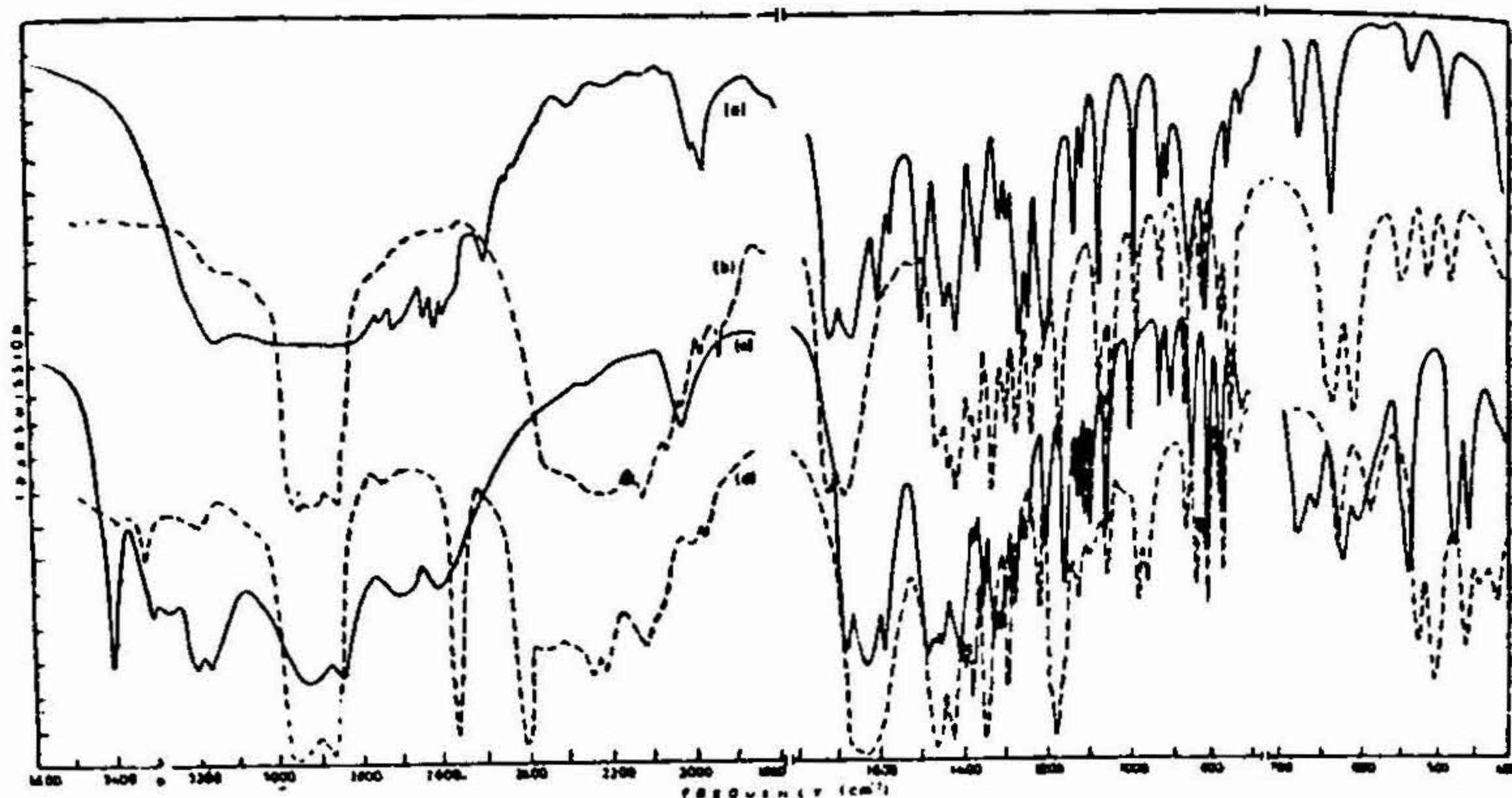


FIG. 7

Infrared Spectra of (a) Glu-HCl (b) Glu-HCl-deuterated (c) Glutamine and (d) Glutamine-deuterated

These are fairly broad and strong in the infrared absorption spectrum. On deuteration, bands corresponding to  $\text{ND}_3^+$  ions appear at  $\sim 1150$ ,  $\sim 1200$  and  $\sim 850 \text{ cm}^{-1}$  corresponding to the three vibrations respectively. The observed isotope ratios,  $\nu(\text{NH}_3^+)/\nu(\text{ND}_3^+)$ , 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<sup>40</sup>.

Proline and hydroxy-proline contain an  $\text{NH}_2^+$  group. Apart from stretching, these can give rise to bending, wagging, twisting and rocking frequencies. Of these twisting mode appears weak in infrared absorption. Though the Raman spectrum of hydroxy proline agrees fairly well with that reported by Deveney et al.<sup>22</sup> in the light of deuteration studies, some of their assignments had to be modified. Glutamine, which contains an  $\text{NH}_2$  group in addition to the  $\text{NH}_3^+$  group, shows bands at 1643, 1265, 1092 and  $675 \text{ cm}^{-1}$  corresponding to the former group. Arginine which has two uncharged  $\text{NH}_2$  groups and a charged  $\text{NH}_2^+$  group, shows several bands in the  $1500\text{-}1700 \text{ cm}^{-1}$  region.

In all the amino acids investigated, except in glutamic acid hydrochloride, there is at least one ionised carboxyl group. This group has two strong absorption bands, one near  $1600 \text{ cm}^{-1}$  corresponding to the asymmetric stretching and the other at



$\sim 1400\text{ cm}^{-1}$  corresponding to the symmetric stretching of the  $\text{COO}^-$  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 lengths differ only slightly and the OCO angle is about  $126^\circ$ . The oxygen 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  $30\text{ cm}^{-1}$ , the wagging vibration  $20\text{ cm}^{-1}$  and rocking vibration remaining almost constant. The approximate frequencies for these vibrations are  $700\text{ cm}^{-1}$ ,  $540\text{ cm}^{-1}$  and  $450\text{ cm}^{-1}$  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  $\text{COO}^-$  groups, several bands are present in the spectra assignable to the vibrations of these groups.

In glutamic acid and its hydrochloride, 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  $1240\text{ cm}^{-1}$  and another at  $1400\text{ cm}^{-1}$ . On deuteration, the corresponding bands move over to  $1350\text{ cm}^{-1}$  and  $1070\text{ cm}^{-1}$  respectively. The O-H out of plane bending appears at  $850\text{ cm}^{-1}$ . The C=O in plane bending appears as a strong band at  $680\text{ cm}^{-1}$ .

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  $800\text{-}900\text{ cm}^{-1}$ , which can be assigned to an almost pure C-C stretching mode. This is weak in infrared absorption. Similarly, between  $1000$  and  $1100\text{ cm}^{-1}$ , 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  $445\text{ cm}^{-1}$ . The C-S stretching gives two very strong lines in the Raman spectrum at  $640$  and  $695\text{ cm}^{-1}$ . In tyrosine, the ring vibration is assigned to the strong line at  $831\text{ cm}^{-1}$ . In hydroxy proline, the strong Raman line at  $883\text{ cm}^{-1}$  is due to ring vibration and its frequency increases to  $914\text{ cm}^{-1}$  on deuteration. The lone CH group on the  $\alpha$ -carbon atom gives rise to a bending frequency at  $1350\text{ cm}^{-1}$  in the spectra of amino acids. The skeletal deformation frequency lies below  $500\text{ cm}^{-1}$  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 contains an H<sub>2</sub>O group, the water bending and librational frequencies have been identified in the spectrum.

#### *Hydrogen Bonding:*

As has been pointed out, the NH<sub>3</sub><sup>+</sup> groups are strongly hydrogen bonded to the ionised carboxyl groups, resulting in a distortion of the NH<sub>3</sub><sup>+</sup> groups. Hydrogen bonding will also result in modifying the N<sup>+</sup>-H stretching frequency. The observed Raman lines in the region 2600 to 3400 cm<sup>-1</sup> 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<sub>3</sub><sup>+</sup> degenerate deformation mode with the C-N stretching mode or NH<sub>3</sub><sup>+</sup> 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<sup>+</sup> . . . O bonds given by Krishnan and Krishnan<sup>16</sup>, the N<sup>+</sup>-H stretching vibrations were calculated corresponding to different hydrogen bond distances. For crystals containing O-H . . . O type bonds, the correlation curves of Nakamoto et al.<sup>42</sup> 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<sup>-1</sup>. In hydroxy proline, with an O . . . O distance of 2.80 Å, the O-H stretching appears at 3300 cm<sup>-1</sup>. Similarly, the infrared spectrum of proline shows a broad peak at 3400 cm<sup>-1</sup>. This must be due to the stretching vibration of H<sub>2</sub>O 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<sup>-1</sup>. 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<sub>2</sub> group frequencies. Using the formula of Venkataramiah and Venkatachalapathy<sup>43</sup> for the non-bonded NH<sub>2</sub> groups in amides,

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

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



The band at  $3326\text{ cm}^{-1}$  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 $\text{NH}_3^+$ ;*

In all the amino acids containing the  $\text{NH}_3^+$  group there is a weak band in the infrared absorption at  $500\text{ cm}^{-1}$ . This band is seen in the Raman spectrum also. On cooling the sample, it increases in frequency and intensity. This band has therefore been assigned to  $\text{NH}_3^+$  torsional oscillation. In glycine it is known to occur at  $516\text{ cm}^{-1}$ (34).

The infrared absorption spectra of all amino acids containing the  $\text{NH}_3^+$  group, exhibit a band of medium intensity at  $2100\text{ cm}^{-1}$ . This band has been assigned by Koegel et al.<sup>26</sup> to a stretching frequency of the  $\text{NH}_3^+$  group. Later Leifer and Lippincott<sup>27</sup> suggested that this might be a bending vibration of the amino group. However, Krishnan and Krishnan<sup>16</sup> and Kanna et al.<sup>34</sup> have pointed out that this band is due to a combination of  $\text{NH}_3^+$  degenerate deformation and  $\text{NH}_3^+$  torsion. A similar band has been observed in the infrared spectra of methylammonium halides and interpreted by Cabana and Sandorfy<sup>44</sup> as due to such a combination. The results of the present study confirm this conclusion. In Table 16 are given the values of  $\text{NH}_3^+$  deformation,  $\text{NH}_3^+$  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  $\text{NH}_2$  groups or uncharged amino groups. This the band at  $\sim 2100\text{ cm}^{-1}$  forms a very interesting "indicator band" for the identification of charged  $\text{NH}_3^+$  group in amino acids since the region between  $1800\text{-}2400\text{ cm}^{-1}$  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  $\text{NH}_3^+$  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  $\text{NH}_2$  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 hydrochloride, the torsional frequency has gone below  $400\text{ cm}^{-1}$  and the frequency of the indicator band also has decreased. This is expected since the  $\text{N}^+\text{-H} \dots \text{Cl}$  bonds are weaker compared to the  $\text{N}^+\text{-H} \dots \text{O}$  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  $0\text{-}200\text{ cm}^{-1}$ .



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  $94\text{ cm}^{-1}$  in the spectrum of glutamic acid at  $83\text{ cm}^{-1}$  in glutamic acid HCl and at  $111\text{ cm}^{-1}$  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 frequency line is at  $73\text{ cm}^{-1}$ . 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  $300\text{ cm}^{-1}$ . Hurley et al.<sup>45</sup> have suggested criteria 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

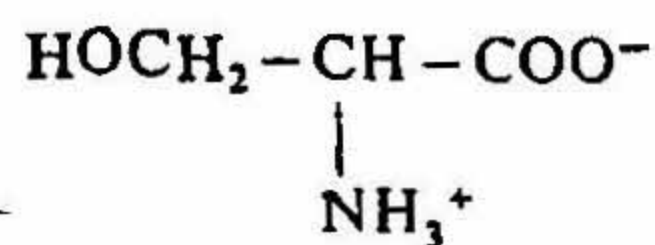
We wish to express our thanks to Prof. B. J. Bulkin of the Department of Chemistry, Hunter College, New York for permitting us to make use of the Laser Raman spectrometer. We are also grateful to Messrs Ajinomoto company, Japan for kindly supplying the samples of amino acids. Thanks are also due to K. Subramanya for the help in recording infra-red spectra. One of us, (V.N.S.) is grateful to the Council of Scientific and Industrial Research for financial support.

#### EXPLANATION OF THE SYMBOLS USED IN THE TABLES

$\nu$ - Stretching frequency	$\gamma$ - Out-of-plane bending
$\nu_s$ - Symmetric stretching	$\gamma_p$ - Rocking
$\nu_{as}$ - Asymmetric stretching	$\gamma_w$ - Wagging
$\delta$ - in-plane deformation	$\gamma_t$ - Twisting
$\delta_s$ - Symmetric deformation	$\tau$ - Torsion
$\delta_d$ - Degenerate deformation	



TABLE 1

*L*-Serine

Raman	Infrared	Infrared deuterated	Assignments
518(9)	433(m) 525(s)br	510(s) 540(sh)	$\tau \text{NH}_3^+$ $\gamma_w \text{COO}^-$
612(8)	570(m) 610(s)	592(s) 605(sh) 740(vw)	$\delta \text{COO}^-$ $\gamma \text{OD}$
751			
780			
809(10)	806(m)	807(m)	$\gamma \text{OH}$
815(26)			
850(10)		842(s)	
855(26)	859(m)	857(m) 879(m)	$\nu (\text{C}-\text{C})$ $\gamma_p \text{ND}_3^+$
925(4)	923(s)	930(s)	$\gamma_p \text{CH}_2$
970(8)	973(m)	973(w)	
1007(11)	1020(s)	1027(s)	
1012(14)			
1035(2)			
1090(2)	1089(s)		Skeletal $\delta \text{OD}$
1135(2)	1130(s)	1091(s) 1127(w) 1153 1179   1202	$\gamma_p \text{NH}_3^+$ $\delta_s \text{ND}_3^+$ $\delta_d \text{ND}_3^+$
1223(5)	1223(m)	1223(w) 1272(m) 1300(m)	$\nu \text{C}-\text{O} + \delta \text{O}-\text{H}$
1303(5)	1309(s)		$\gamma_s \text{CH}_2$
1318(4)			
1327(14)	1346(s)	1338(s)	$\delta \text{CCH}$
1386(2)	1386(s)	1380(s)	$\gamma_w \text{CH}_2$ , $\nu (\text{C}-\text{O})$
1418(5)	1420(s)	1425(s)	$\nu_s \text{COO}^-$
1464(9)	1479(s)	1460(s)	$\delta \text{CH}_2$
1480			$\nu \text{C}-\text{O} + \delta - \text{OH}$

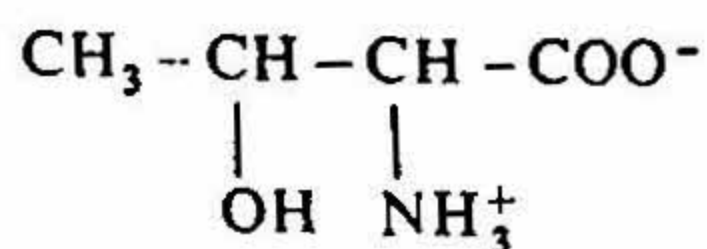


TABLE 1—(contd.)

Raman	Infrared	Infrared deuterated	Assignment
	1506(sh)		$\delta_s \text{NH}_3^+$
		1580(s)	
	1613(s)	1600(s)	$\nu_{as} \text{COO}^-$
	1638(s)	1640(s)	$\delta_d \text{NH}_3^+$
		1930(m)	Combinations
		1940(m)	
	2040(m)		$\delta_d \text{NH}_3^+ +$ $\tau \text{NH}_3^+$
	2089(m)		
		2030	$\nu (\text{N}-\text{D})$
		2120(s)	
		2180(s)	
		2300(s)	
		2350(s)	
		2580	$\nu (\text{O}-\text{D})$
	2270(w)		Combinations
	2455(m)		
	2590(s)		
	2606(s)		
	2700(s)		
	2725(s)		
	2870(s)		
2944(4)	2944(s)		$\nu_s \text{CH}_2$
2962(10)	2962(s)		$\nu_{as} \text{CH}_2, \nu \text{CH}$
3000(4)	3000(s)		$\nu (\text{N}-\text{H})$
	3100(s)		
	3466(s)		$\nu (\text{O}-\text{H})$



TABLE 2

*L*-Threonine

Raman	Infrared	Infrared deuterated	Assignments
421(7)	417(m)	407(m)	
436(6)			
449(13)	448(m)	432(w)	$\tau \text{ NH}_3^+$
494(10)	492(m)	487(m)	$\gamma_p \text{ COO}^-$
566(32)	562(s)	535(s)	$\gamma_w \text{ COO}^-$
		550 sh(m)	$\gamma \text{ OD}$
704(8)	708(s)	671(m)	$\delta \text{ COO}^-$
		684(m)sh	$\gamma \text{ OD}$
754(12)	750(m)		
	777(s)		$\gamma \text{ OH}$
	800(m)		
		807(m)	
		822(s)	
874(30)	877(m)		$\nu(\text{C}-\text{C})$
906(5)			
911(4)	912(m)	911(m)	
933(24)	940(s)	937(s)	
		950(s)	$\gamma_p \text{ ND}_3^+$
		1012(m)	
		1028(m)	
1032(7)			
1045(7)	1048(s)	1048(m)	$\gamma_p \text{ CH}_3$
1101(3)	1100(s)	1107(s)	"
1108(15)			
1118(20)	1118(s)		
1124(9)	1124(m)		
		1128(s)	$\delta_s \text{ ND}_3^+$
		1166(s)	$\delta_d \text{ ND}_3^+$
		1182(m)	"
			$\gamma_p \text{ NH}_3^+$
1196(7)	1190(m)		$\gamma_p \text{ CH}_3$
1253(3)	1253(m)	1254(m)	$\nu \text{ C}-\text{O} + \delta \text{ O}-\text{H}$
1308(3)	1328(s)		$\delta \text{ CCH}$
1342(16)	1350(s)	1338(s)	
1355(7)			
		1370(s)	$\nu (\text{C}-\text{O})$
		1388(s)	$\delta_s \text{ CH}_3$
	1393(s)		

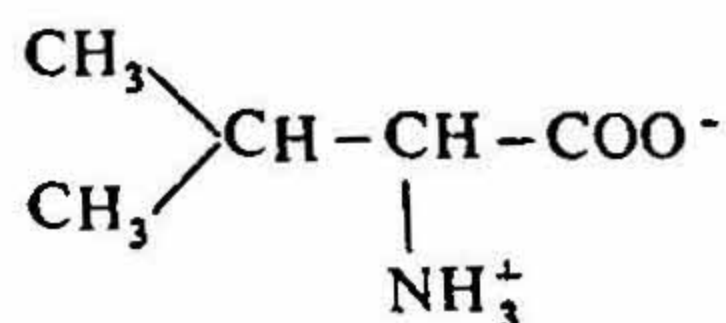


TABLE 2—(contd.)

Raman	Infrared	Infrared deuterated	Assignment
1420(6)	1425(s)	1422(s)	$\nu_s \text{COO}^-$
1454(9)		1465(s)	$\delta_d \text{CH}_3$
1468(6)	1463(s)		
1481(5)	1488(s)		$\nu(\text{C-O}) + \delta(\text{O-H})$
1549(2)	1549(m)		$\delta \text{NH}_3^+$
1601(1)	1612(s)	1621(s)	$\nu_{as} \text{COO}^-$
	1637(s)		$\delta_d \text{NH}_3^+$
1642(s)	1648(s)		
		1962(w)	Combination
	2051		$\delta_d \text{NH}_3^+ + \tau \text{NH}_3^+$
		2060(m)	
		2090(m)	
		2158(m)	$\nu(\text{N-D})$
		2200(s)	
		2250(s)	$\nu(\text{O-D})$
		2341(s)	
	2220(vw)		Combinations
	2550(m)		
	2600(m)		
	2635(m)		
	2668(s)		
	2721(s)		$\nu(\text{N-H})$
	2820(s)		
2878(26)	2878(s)	2878(s)	$\nu_s \text{CH}_3$
2923(8)	2920(s)		
2935(12)			$\nu_{as} \text{CH}_3$
2949(22)		2943(s)	
2980(20)	2980(s)	2980(s)	$\nu \text{CH}$
2997(22)			
3021(17)	3021(s)		$\nu(\text{N-H})$
	3123(s)		$\nu(\text{O-H})$
	3180(s)		



TABLE 3

*L*-Valine

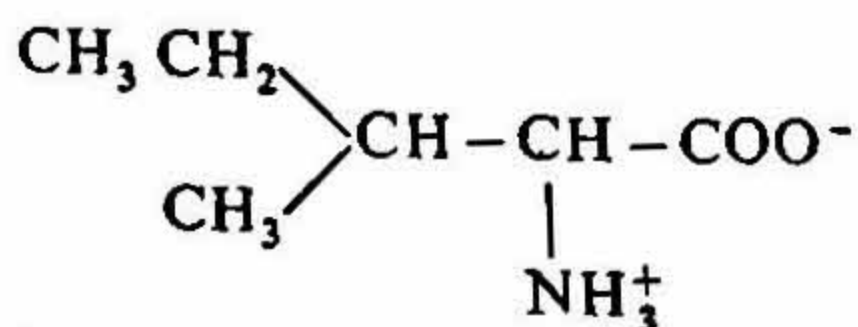
Raman	Infrared	Infrared deuterated	Assignment
	432(s)		
436(5)	428(s)	421(m)	$\gamma_p \text{COO}^-$
	436(m)	437(w)	
462(6)	473(m)	472(m)	
496(1)	490(w)		$\tau \text{NH}_3^+$
544(14)	543(s)	523(s)	$\gamma_w \text{COO}^-$
667(5)	665(m)	640(m)	$\delta \text{COO}^-$
718(5)	720(m)	675(m)	$\delta \text{COO}^-$
		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)	$\gamma_p \text{ND}_3^+$
887(2)	892(m)	898(m)	$\gamma_p \text{CH}_2$
903(2)	903(m)		$\gamma_p \text{CH}_2$
		924(m)	
		927(m)	
923(1)	920(m)		
956(7)	950(m)		
967(4)	970(m)	971(w)	$\gamma_p \text{CH}_3$
		978(w)	
		1018(m)	$\gamma_p \text{CH}_3$
1022(-)	1032(m)	1023(m)	
1035(-)	1039(m)		
1069(6)	1068(s)		
1129(4)	1110(w)	1129(w)	
	1147(m)	1146(m)	
		1158(m)	$\delta_s \text{ND}_3^+$
		1170(m)	$\delta_{as} \text{ND}_3^+$
		1178(m)	
1136	1180		$\gamma_p \text{NH}_3^+$
	1195		
1278(4)	1278(m)	1361(m)	$\gamma_p \text{CH}_3$
		1319(s)	
		1334(s)	$\delta \text{CCH}$
1330(5)	1337(s)		



TABLE 3 - (contd.)

Raman	Infrared	Infrared deuterated	Assignment
1347(4)			
1355(5)	1360(s)	1350(s)	$\delta_s$ CH <sub>3</sub>
	1380(s)	1379(s)	
1400(4)	1402(s)	1405(s)	$\nu_s$ COO <sup>-</sup>
1426(4)	1435(s)	1435(s)	
1457(6)	1455(s)	1466(s)	
1570(6)	1465(s)	1465(s)	$\delta_d$ CH <sub>3</sub>
		1478	
	1512(s)		$\delta_s$ NH <sub>3</sub> <sup>+</sup>
	1521(s)		
	1570(s)		
1602(2)	1591(s)	1595(s)	$\nu_{as}$ COO <sup>-</sup>
1620(2)	1621(s)		$\delta_d$ NH <sub>3</sub> <sup>+</sup>
1636(2)	1630(s)		$\delta_d$ NH <sub>3</sub> <sup>+</sup>
		1827(w)	
	2110(m)		$\delta_d$ NH <sub>3</sub> <sup>+</sup> + $\tau$ NH <sub>3</sub> <sup>+</sup>
		1927(m)	
		1942(m)	
		1957(m)	
		2000(s)	
		2018(s)	$\nu$ (N-D)
		2062(s)	and
		2092(s)	combinations
		2149(s)	
		2192(s)	
		2236(s)	
		2331(s)	
	2410		
	2600(s)		$\nu$ (N-H)
	2630(s)		
	2700(s)		
	2772(s)		$\nu$ (N-H)
2884(4)	2884(s)		
2909(8)	2903(s)		$\nu_s$ CH <sub>3</sub>
2952(4)	2941(s)		$\nu_s$ CH <sub>3</sub>
2975(6)	2960(s)		$\nu$ CH
3000(4)	2920(s)		
	3053(s)		$\nu$ (N-H)
	3152(s)		$\nu$ (N-H)

TABLE 4

*L*-Isoleucine

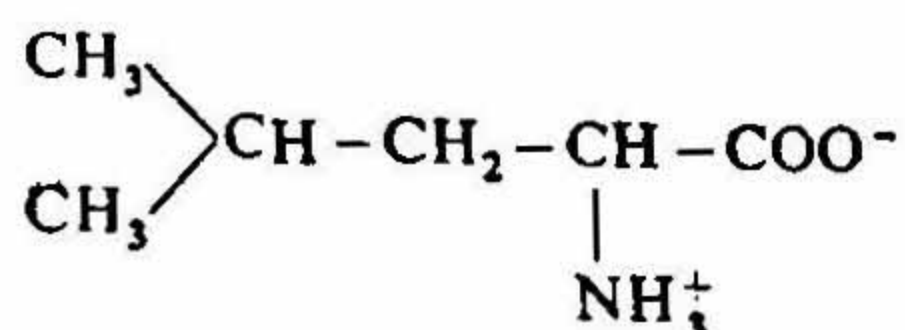
Raman	Infrared	Infrared deuterated	Assignment
411(1)			
428(3)		423(m)	
458(3)	440(m)	440(m)	$\gamma_p \text{COO}^-$
	488(w)	483(w)	
490(3)	495(w)		$\tau \text{NH}_3^+$
540(10)	537(s)	517(s)	$\gamma_w \text{COO}^-$
558(8)	556(s)	534(s)	
		584(w)	
677(3)	675(s)	645(s)	$\delta \text{COO}^-$
711(3)	708(s)	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)		$\nu(\text{C}-\text{C})$
		835(s)	$\gamma_p \text{ND}_3^+$
885(6)	854(w)		
877(4)	87(m)	873(m)	$\gamma_p \text{CH}_2$
925(4)	925(m)		
		938(w)	
950(2)	967(m)	951(m)	$\gamma_p \text{CH}_2$
996(5)	993(m)	1001(m)	$\gamma_p \text{CH}_3$
1024(4)	1027(w)	1029(m)	
1040(-)	1042(m)		
	1048(m)	1050(m)	
1092(3)	1090(m)	1099(w)	$\nu(\text{C}-\text{N})$
1126(2)	1133(m)		$\gamma_p \text{NH}_3^+$
1140(3)	1153(sh)		
1185(2)	1190(s)		
		1143(m)	$\delta_s \text{ND}_3^+$
		1173(s)	$\delta_d \text{ND}_3^+$
		1184(s)	
1233(1)		1246(w)	$\gamma_t \text{CH}_2$
1258(1)	1263(w)	1260(w)	
1277(1)	1275(w)		
	1299(w)		



TABLE 4 - (contd.)

Raman	Infrared	Infrared deuterated	Assignment	
1311(1)	1315(s)	1307(m)	$\gamma_w$ CH <sub>2</sub>	
1332(1)	1331(s)	1027(s)		
1357(4)	1354(s)	1357(s)	$\delta_s$ CH <sub>3</sub>	
1398(3)	1391(s)	1391(s)	$\delta$ CCH	
	1401(s)	1402(s)	$\nu_s$ COO <sup>-</sup>	
1420(1)	1427(s)	1423(s)		
1451(4)	1469(s)	1461(s)	$\delta$ CH <sub>2</sub>	
	1471(s)	1472(s)	$\delta_d$ CH <sub>3</sub>	
1519(1)	1518(s)		$\delta_s$ NH <sub>3</sub> <sup>+</sup>	
	1527(s)			
1582(2)	1590(s)	1593(s)	$\nu_{as}$ COO <sup>-</sup>	
1619(2)	1621(s)		$\delta_d$ NH <sub>3</sub> <sup>+</sup>	
		1825(w)		
	2119(m)		$\delta$ NH <sub>3</sub> <sup>+</sup> + $\tau$ NH <sub>3</sub> <sup>+</sup>	
		1955(m)		
		2007 m)		
		2057(s)	$\nu$ (N-D)	
		2078(s)		
		2091(s)		
		2140(s)		
		2180(s)		
		2239(s)		
		2320(s)	$\nu$ (N-D)	
	2400(s)		Combinations	
	2442(s)			
	2500(s)			
	2578(s)			
	2621(s)			
	2700(s)			
	2747(s)			
	2832(s)			
2882(9)	2881(s)			$\nu_s$ CH <sub>2</sub>
2895(12)	2895(s)			$\nu_s$ CH <sub>3</sub>
2948(16)	2945(s)		$\nu_{as}$ CH <sub>2</sub>	
2995(4)	2970(s)		$\nu_{as}$ CH <sub>3</sub>	
3008(3)				
	3063(s)		$\nu$ (N-H)	
	3110(s)			

TABLE 5

*L*-Leucine

Infrared	Infrared deuterated	Assignment
400[m]		
442[m]	440[m]	$\gamma_p \text{COO}^-$
452[m]	451[m]	
514[w]		$\tau \text{NH}_3^+$
536[s]	516[s]	$\gamma_w \text{COO}^-$
	531[sh]	
667[s]	638[s]	$\delta \text{COO}^-$
	665[m]	
771[m]	770[m]	
	803[m]	
	826[m]	$\gamma_p \text{ND}_3^+$
	837[m]	
851[m]	845[m]	(C-C)
	872[m]	
925[m]	928[w]	$\gamma_p \text{CH}_2$
947[m]	947[w]	
	967[vw]	
	982[vw]	
1009[w]	1005[w]	$\gamma_p \text{CH}_3$
1034[m]	1034[vw]	
	1072[w]	
1087[m]	1082[w]	Skeletal
	1134[m]	$\delta_s \text{ND}_3^+$
1142[s]		$\gamma_p \text{NH}_3^+$
1191[m]		
	1180[s]	$\delta_d \text{ND}_3^+$
	1237[m]	$\gamma_p \text{CH}_3$
1243[m]	1293[m]	
1302[s]	1317[s]	$\gamma_w \text{CH}_2$
1320[s]	1342[s]	$\delta \text{CCH}$
1332[s]	1355[s]	$\delta_s \text{CH}_3$
	1368[s]	
1370[s]	1415[s]	$\nu_s \text{COO}^-$
1417[s]	1450[s]	
1448[s]	1462[s]	$\delta \text{CH}_2$
1461[s]		

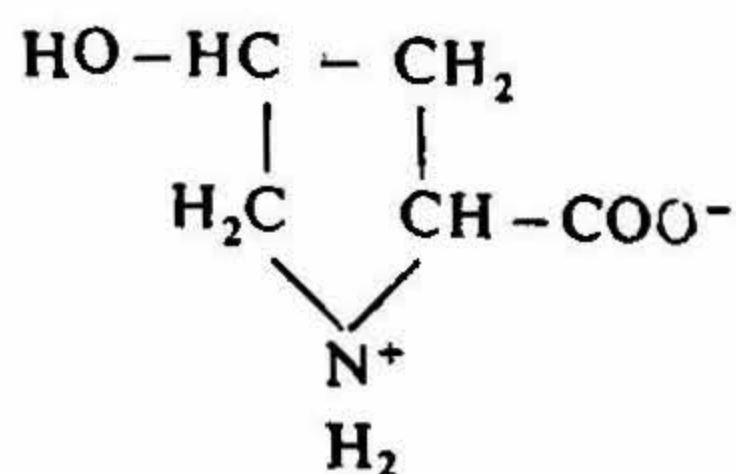


TABLE 5—(contd)

Infrared	Infrared deuterated	Assignment
1450[s]	1442[s]	$\delta_d \text{CH}_3$
1517[s]		$\delta_s \text{NH}_3^+$
1522[s]		
1595[s]	1590[s]	$\nu_{as} \text{COO}^-$
1625[s]		$\delta_d \text{NH}_3^+$
2130[m]		$\delta_d \text{NH}_3^+ + \tau \text{NH}_3^+$
	1818(w)	
	1990[m]	
	2020[m]	
	2078[s]	$\nu [\text{N} - \text{D}]$ and combinations
	2145[s]	
	2242[s]	
	2280[s]	
	2310[s]	
2450[m]		Combinations
2558[s]		
2600[s]		
2630[s]		
2700[s]		
2741[s]		
2823		$\nu_s \text{CH}_2$
2885		$\nu_s \text{CH}_3$
2950		$\nu [\text{C} - \text{H}]$
	3000[s]	$\nu [\text{N} - \text{H}]$
	3070[s]	$\nu [\text{N} - \text{H}]$

TABLE 6

Hydroxy-L-Proline



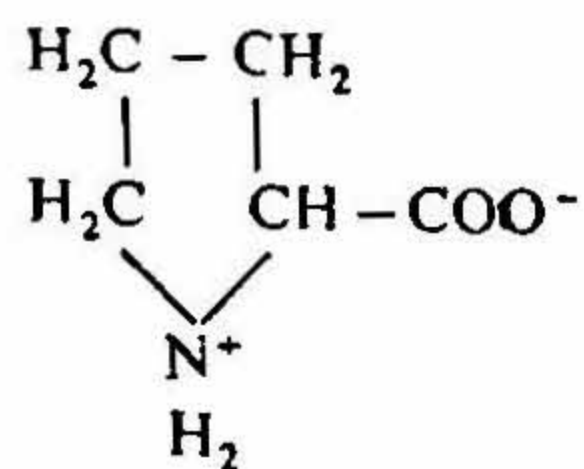
Raman	Infrared	Infrared deuterated	Assignment
425[16]	425[m]	415[w]	$\gamma_p \text{COO}^-$
468[3]	463[m]	457[w]	
	473[m]	474[m]	
618[8]	617[m]	593[m]	$\gamma_w \text{COO}^-$
	640[br]		$\gamma \text{OH}$
700[2]	703[m]		$\delta \text{COO}^-$
		738[w]	
757[6]	761[m]	757[m]	$\gamma_p \text{ND}_2^+$
	773[m]	783[w]	
		825[m]	
		835[m]	
853[52]	850[m]		$\nu [\text{C}-\text{C}]$
	857[m]		
865[10]	862[m]		$\gamma_p \text{CH}_2$
883[17]	884[m]	914[m]	ring vibration
920[6]	928[m]		
942[4]	959[s]	940[m]	$\gamma_p \text{CH}_2$
991[9]	971[s]	960[m]	
1016[2]			
1038[5]	1036[s]	999[m]	Skeletal
1060[10]	1063[s]	1030[m]	$\nu [\text{C}-\text{N}]$
1069[13]	1070[s]		
1070[10]	1090[m]		
		1083[s]	$\delta \text{OD}$
		1107[w]	$\delta \text{ND}_2^+$
		1133[s]	$\delta \text{ND}_2^+$
1189[10]	1189[m]		$\gamma_t \text{CH}_2$
1408[3]	1213[s]	1183[m]	$\gamma_t \text{CH}_2$
1229[9]	1230[s]	1192[m]	
1259[2]	1262[s]		$\nu [\text{C}-\text{O}] + \delta [\text{O}-\text{H}]$
1284[2]	1284[s]		$\gamma_p \text{NH}_2^+$



TABLE 6 - (Contd.)

Raman	Infrared	Infrared deuterated	Assignment
1324[14]	330[s]	1322[s]	$\gamma_w$ CH <sub>2</sub>
1354[8]	1340[m]	1334[m]	$\delta$ CCH
	1378[m]		$\gamma_w$ NH <sub>2</sub> <sup>+</sup>
1398[6]	1406[s]	1420[s]	$\nu_s$ COO <sup>-</sup>
1432[6]	1436[6]		$\delta$ CH <sub>2</sub>
1482[-]		1455[s]	
	1603[s]	1610[s]	$\nu_{as}$ COO <sup>-</sup>
	1648[s]		$\delta$ NH <sub>2</sub> <sup>+</sup>
		1843[w]	Combinations
		1912[w]	
		1957[m]	
		2033[m]	
		2022[m]	
		2115[m]	
		2167[m]	
		2218[m]	$\nu$ [N - D]
		2267[m]	
		2360[s]	
		2448[s]	$\nu$ [O - D]
	2442[s]		$\nu$ [N - H]
	2459[s]		
	2507[s]		
	2556[s]		
	2583[s]		
	2601[s]		
	2629[s]		
	2700[s]		
	2733[s]		
	2930[s]		
2959[36]	2950[s]		$\nu_s$ CH <sub>2</sub> , $\nu_{as}$ CH <sub>2</sub>
2991[12]	2987[s]		
3001[12]			$\nu$ [C - H]
3036[12]			
3043[6]			
3134[2]	3149[s]		$\nu$ [N - H]
	3298[s]		$\nu$ [O - H]

TABLE 7

*L-Proline*

[Raman spectrum taken from ref. 46]

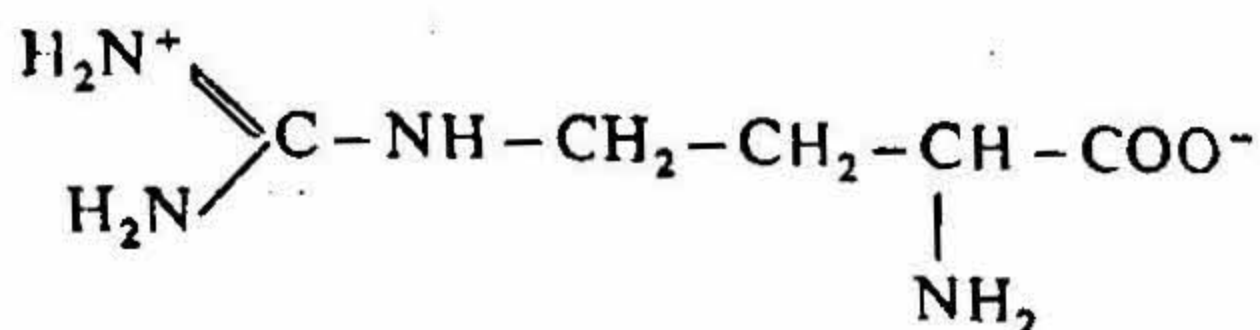
Raman	Infrared	Assignments
448	453[s]	$\gamma_p \text{COO}^-$
577	572[w]	
641	643[s]	$\gamma_w \text{COO}^-$
667	670[m]	
698	687[m]	$\delta \text{COO}^-$
	790[s]	
795	796[s]	
842	838[m]	
	851[s]	$\gamma_p \text{CH}_2$
866	864[m]	
	887[w]	
898	905[m]	$\gamma_p \text{NH}_2^+$
919	919[m]	$\gamma_p \text{CH}_2$
951	953[m]	
985	989[m]	
994		
1033	1040[s]	
1056	1052[m]	$\nu [\text{C} - \text{N}]$
1082	1052[m]	
1173	1177[m]	$\gamma_t \text{NH}_2^+$
1192		
1239		
1264	1261[m]	
1285	1302[s]	$\gamma_w \text{CH}_2$
1320	1328[s]	
1349		$\delta \text{CCH}$
1373	1383[s]	$\gamma_w \text{NH}_2^+$
1409	1410[s]	$\nu_s \text{COO}^-$
1441	1458[s]	$\delta \text{CH}_2$
1471	1482[s]	
1550	1557[s]	$\delta \text{NH}_2^+$



TABLE 7—(contd.)

Raman	Infrared	Assignments	
1624	1631[s]	$\nu_{as} \text{COO}^-$	
	2210[m]	Combinations	
	2390[s]		
	2507[s]		
	2590[s]		
	2645[s]		
	2685[s]		
	2748[s]		
	2783[s]		
	2810[s]		
2178	2925[s]		$\nu_s \text{CH}_2, \nu_{as} \text{CH}_2,$
2919			$\nu \text{CH}$
2952			
2976			
3001		2995[s]	
3051		3063[s]	$\nu [\text{N}-\text{H}]$
	3430 s [br]	$\nu \text{H}_2\text{O}$	

TABLE 8

*L*-Arginine

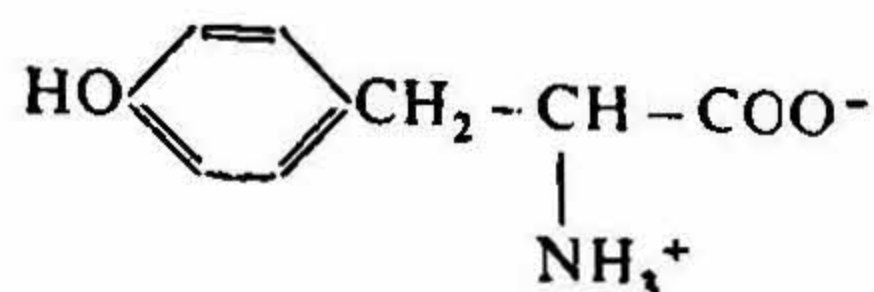
Raman	Infrared	Assignments
	468[w]	$\gamma_p \text{COO}^-$
495[1]	492[w]	
554[4]	551[m]	$\gamma_w \text{COO}^-$
	559[m]	
	611[m]	
	663[s]	$\delta \text{COO}^-$
	678[s]	$\gamma \text{NH}_2$
	757[m]	
	800[m]	$\gamma_p \text{CH}_2^+$
	814[m]	$\gamma_p \text{NH}_2$
876[3]	857[m]	$\nu [\text{C}-\text{C}]$
894[2]		
927[2]	931[w]	$\gamma_p \text{CH}_2$
979[4]		
989[6]		
1006[1]	1015[s]	
1084[3]	1081[m]	$\nu [\text{C}-\text{N}]$
1129[1]	1128[s]	$\gamma_w \text{NH}_2$
1154[1]	1128[s]	
1189[2]	1193[s]	$\gamma_w \text{NH}_2^+$
1314[2]	1320[m]	$\gamma_w \text{CH}_2$
1335[4]	1340[s]	$\gamma_w \text{CH}_2$
	1374[m]	
1385[2]	1384[s]	$\delta \text{CCH}$
1413[ ]		
1428[1]	1433[s]	$\nu_s \text{COO}^-$
1442[2]		
1476[1]	1472[s]	$\delta \text{CH}_2$
1488[1]		
1511[3]	1542[s]	$\delta \text{NH}_2$
	1625[s]	$\nu_{as} \text{COO}^-$
	1653[s]	$\nu [\text{C}=\text{N}]$
	1694[s]	$\delta \text{NH}_2^+$
	1710[s]	



TABLE 8 - (contd.)

Raman	Infrared	Assignments
	2300 [br] [w]	Combinations
	2700	
	2735	
	2784	
	2800	
	2872	$\nu_s \text{CH}_2$ $\nu \text{CH}$
	2954	
	3100 [s]	$\nu \text{[N-H]}$
	3290 [s]	
	3500 [m]	

TABLE 9

*L*-Tyrosine

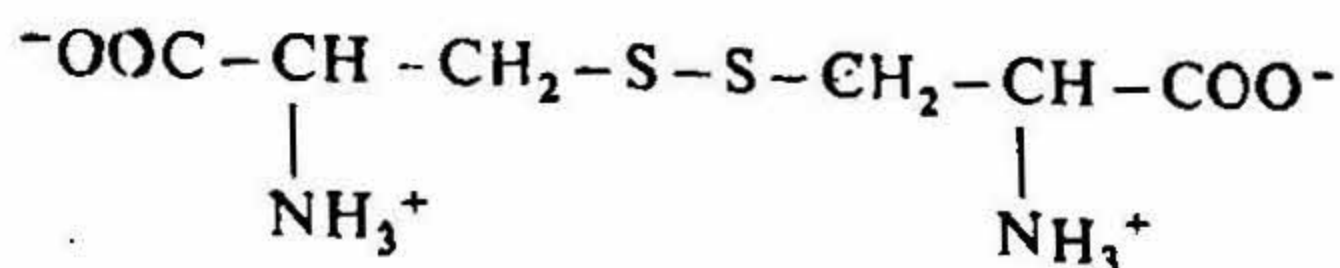
Raman	Infrared	Assignments
435[5]	432[m]	$\gamma_p \text{COO}^-$
	445[w]	
	471[w]	$\tau \text{NH}_3^+$
493[2]	493[m]	
527[1]	529[s]	$\gamma_w \text{COO}^-$
575[1]	576[s]	
645[6]	651[s]	Ring deformation
715[2]	717[m]	
744[1]	743[m]	$\delta \text{COO}^-$
758		
771		
800[5]	800[m]	
	809[m]	
831[17]	831	Ring stretch
849[5]	845[ ]	CH wagging of the ring?
	880[m]	
	901[m]	$\gamma_p \text{CH}_2$
	943[w]	
988[4]	989[w]	
	1022[w]	
1048[3]	1045[m]	$\nu [\text{C}-\text{N}]$
	1103[m]	
	1119[m]	
	1162[m]	$\gamma_p \text{NH}_3^+$
	1179[m]	
1183[6]	1202[m]	
1202[4]	1220[m]	
1216[4]	1250[s]	$\nu [\text{C}-\text{O}] + \delta [\text{O}-\text{H}]$
1249[4]	1271[m]	$\gamma_t \text{CH}_2$
1265[3]	1341[s]	$\gamma_w \text{CH}_2$
1329[5]	1372[s]	$\delta \text{CCH}$
1367[4]	1381[s]	$\delta \text{CCH}$
	1425[s]	$\nu_s \text{COO}^-$
1420[2]	1448[s]	$\nu [\text{C}-\text{O}] + \delta [\text{O}-\text{H}]$
1434[3]	1463[s]	$\delta \text{CH}_2$



TABLE 9—[contd.]

Raman	Infrared	Assignments
1515[2]	1525[s]	$\delta_s \text{NH}_3^+$
1590[1]	1598[s]	$\nu_{as} \text{COO}^-$
1615[1]	1620[s]	$\delta_d \text{NH}_3^+$
	2080	$\delta_d \text{NH}_3^+ + \tau \text{NH}_3^+$
	2495[m]	Combinations N—H Stretching hydrogen bonded
	2602[m]	
	2628[s]	
	2700[s]	
	2757[s]	
	2835[s]	
	2895	$\nu_s \text{CH}_2, \nu_{as} \text{CH}_2,$ $\nu \text{CH}$
	2937	
2931[5]	2937	
2960[5]	2967	
2970[5]		$\nu \text{CH}$
3020[3]	3026[s]	
3040[2]		
3060[5]		
	3140[s]	$\nu [\text{N}-\text{H}], \nu [\text{O}-\text{H}]$
	3213[s]	

TABLE 10

*L*-Cystine

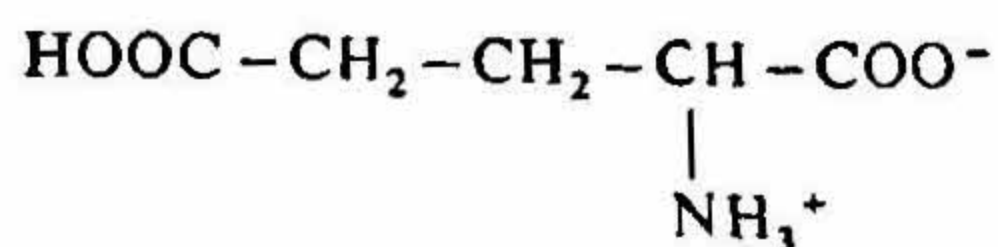
Raman	Infrared	Assignments	
416[5]			
436[8]		$\gamma_p \text{COO}^-$	
447[20]	445[s]	$\nu [\text{S-S}]$	
479[7]	465[m]	$\tau \text{NH}_3^+$	
498[7]			
538[17]	537[s]	$\gamma_w \text{COO}^-$	
640[60]	638[s]	$\nu [\text{C-S}]$	
695[44]	693[m]		
756[10]	757[m]	$\delta \text{COO}^-$	
775[26]	770[m]		
807[12]	810[m]		
827[19]	825[s]	Skeletal stretch	
857[12]	857[m]		
871[16]	870[s]		
915[6]	915[m]		$\gamma_p \text{CH}_2$
945[12]	945[s]		
996[6]	999[w]		
1008[6]	1010[w]		
1029[4]			
1044[-]			
1056[6]			
1069[11]	1069[m]	$\nu [\text{C-N}]$	
1108[6]	1108[m]		
1144[8]	1148[s]	$\gamma_p \text{NH}_3^+$	
1202[11]	1202[s]		
1241[4]			
1270[4]	1272[s]	$\gamma_t \text{CH}_2$	
1298[10]	1302[s]	$\gamma_w \text{CH}_2$	
1348[18]	1352[s]	$\delta \text{CCH}$	
1355			
1395[6]	1395[s]	$\nu_s \text{COO}^-$	
1402[14]	1400[s]		
1429[18]	1433[s]	$\delta \text{CH}_2$	
1493[4]			



TABLE 10—[contd.]

Raman	Infrared	Assignments
1524[5]	1547[s] } 1558[s] }	$\delta_s \text{NH}_3^+$
1577[3]	1593[s]	$\nu_{as} \text{COO}^-$
1621[1]	1618[s]	$\delta_d \text{NH}_3^+$
1653		
1579	2080[m]	$\delta_d \text{NH}_3^+ + \tau \text{NH}_3^+$
	2220[m]	
	2300[m] }	
	2410[m] }	
	2470[s] }	Combinations
	2512[s] }	
	2555[s] }	
	2600[s] }	
	2647[s] }	Combinations and
	2700[s] }	$\nu [\text{N-H}]$
	2725[s] }	
	2790[s] }	
	2840[s] }	
2878[2]	2870[s] }	
2899[2]		
2918[2]	2920[s] }	$\nu [\text{C-H}]$
2950[6]		$\nu_s \text{CH}_2, \nu_{as} \text{CH}_2$
2966[6]	2965[s] }	
2978[2]		
3001[1]	3000[s] }	
	3068[s] }	$\nu [\text{N-H}]$
	3186[s] }	

TABLE 11

*L*-Glutamic acid

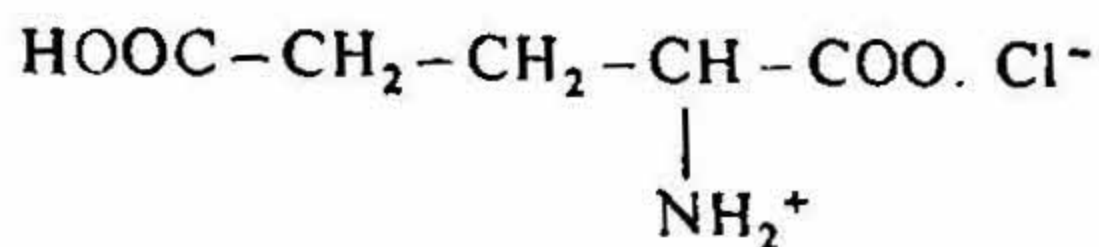
Raman	Infrared	Assignments
	402(m)	
	422(m)	$\gamma_p \text{COO}^-$
462(4)	463(m)	$\tau \text{NH}_3^+$
504(5)	506(m)	$\delta \text{COOH}$
542(8)	538(s)	$\gamma_w \text{COO}^-$
577(4)	577(w)	
	615(w)	
	673(m)	
	705(m)	
713(6)	718(m)	$\delta \text{COO}^-$
761(4)	763(w)	
806(4)	812(s)	$\delta \text{OH}$
834(3)	840(m)	
871(14)	871(m)	$\nu (\text{C}-\text{C})$
923(5)	917(m) }	$\gamma_p \text{CH}_2$
945(3)	951(m) }	
972(4)	973(m)	
	1062(s)	
1071(4)	1082(s) }	$\gamma_p \text{NH}_3^+$
1132(4)	1132(s) }	
	1157(s)	
1217(3)	1220(s)	$\nu (\text{C}-\text{O}) + \delta (\text{O}-\text{H})$
	1240(s) }	$\gamma_r \text{CH}_2$
	1265(s) }	
1313(2)	1318(s)	$\gamma_w \text{CH}_2$
1354(5)	1361(s)	$\delta \text{CCH}$
	1380(s)	
1410(5)	1417(s)	$\nu (\text{C}-\text{O}) + \delta (\text{O}-\text{H})$
	1420(s)	$\nu_s \text{COO}^-$
1441(4)	1445(s)	
	1500 }	$\delta_s \text{NH}_3^+$
	1525(s) }	
	1590(s)	$\delta_d \text{NH}_3^+$
	1610(s) }	$\nu_{as} \text{COO}^-$
	1625(s) }	



TABLE 11 - (contd.)

Raman	Infrared	Assignment
	1652(s) } 1675(s) }	$\nu$ (C=O)
	1840(m)	
	1960(m)	
	2081(m)	$\delta_d$ NH <sub>3</sub> <sup>+</sup> + $\tau$ NH <sub>3</sub> <sup>+</sup>
	2300(m)	$\nu$ (C-H)
	2490(m) } 2585(m) }	
	2660(s) } 2748(s) }	Combinations
2868(5)	2875(s) }	
2936(24)	2940(s) }	$\nu_s$ CH <sub>2</sub>
2965(10)	2970(s) }	$\nu_{as}$ CH <sub>2</sub>
2974(22) } 2995(12) }		$\nu$ CH
3009(4)		
3020(8)		
3039(4)		
3064(2)	3060(s) } 3150(s) }	$\nu$ (N-H)
	3260(m) }	

TABLE 12

*L*-Glutamic acid HCl

Raman	Infrared	Infrared deuterated	Assignment
· 03(9)	403(m)	400(m)	$\delta$ CCO
498(9)	490(m)	480(m)	$\delta$ CCO
532(8)	535(m)	511(m)	$\delta$ COOH
		542(m)	
642(6)	637(s)	605(s)	$\delta$ COOH
		628(s)	$\gamma$ OD
684(4)	678(m)	533(s)	$\delta$ COOH
751(6)	752(m)	755(s)	
777(4)	780(m)	782(m)	
	830(s)	827(m)	$\gamma$ OH
868(7)	870(s)	870(s)	$\nu$ (C-C),
	877		$\gamma_p$ ND <sub>3</sub> <sup>+</sup>
923(26)	927(m)	925(m)	
937(8)	940(m)		$\gamma_p$ CH <sub>2</sub>
1005(5)	1005(s)	983(m)	Skeletal
1074(7)	1070(sh)	1043(s)	$\nu$ (C-N)
		1065(s)	$\delta$ (O-D)
1084(16)	1087(s)	1078(s)	$\nu$ (C-N)
	1130(m)		$\gamma_p$ NH <sub>3</sub> <sup>+</sup>
1155(6)	1155(s)		$\delta_s$ ND <sub>3</sub> <sup>+</sup>
	1150(sh)		$\delta_d$ ND <sub>3</sub> <sup>+</sup>
	1172(s)		
	1217(m)		
1206(1)			$\nu$ (C-O) + $\delta$ (O-H)
1230(4)	1223(s)		
1254(4)	1250(s)	1238(s)	$\gamma_t$ CH <sub>2</sub>
1309(6)	1283(s)	1974(s)	
1314(6)	1314(m)		$\gamma_w$ CH <sub>2</sub>
1326(5)	1330(m)		
		1331(s)	$\nu$ (C-O)
1363(6)	1368(sh)	1362(s)	$\gamma_w$ CH <sub>2</sub>
1378(4)	1380(s)	1380(s)	$\delta$ CCH
1412(11)	1420(s)	1419(s)	$\nu$ (C-O) + $\delta$ (O-H)
1432(7)	1435(s)	1440(s)	$\delta$ CH <sub>2</sub>
	1460(s)	1462(s)	$\delta$ CH <sub>2</sub>
		1469(s)	

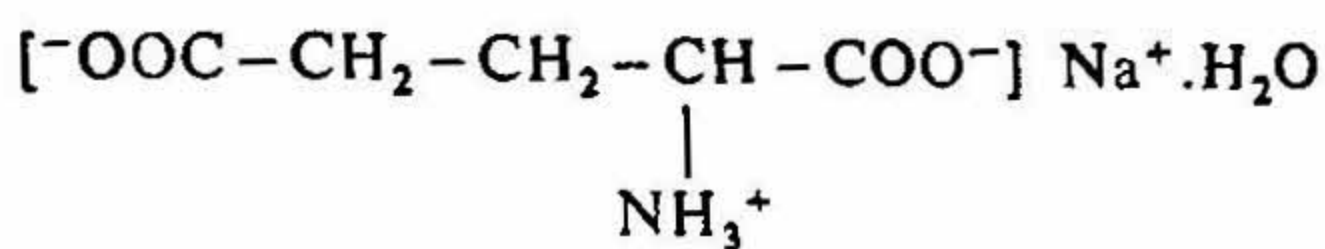


TABLE 12—(contd.)

Raman	Infrared	Infrared deuterated	Assignment
	1505(s) } 1510(s) }		$\delta_s \text{NH}_3^+$
1589(1)	1592(m) } 1620(s) }		$\delta_d \text{NH}_3^+$
1678(6)			
1687(4)	1689(s)	1681(s) }	$\nu (\text{C}=\text{O})$
1728(6)	1735(s)	1724(s) }	
		1911(m) }	Combinations
		1925(m) }	
		1945(m) }	
		1989(m) }	
		2038(m) }	
		2071(s) }	
		2128(s) }	
		2143(s) }	$\nu (\text{N}-\text{D})$ and $\nu (\text{O}-\text{D})$
		2200(s) }	
		2248(s) }	
		2350(s) }	
	1982(m)		$\delta_d \text{NH}_3^+ \tau \text{NH}_3^+$
	2005(m)		
	2290(w)		
	2502(s)		
	2580(s)		$\nu (\text{O}-\text{H})$
	2604(s)		$\nu (\text{N}-\text{H})$
2627(1)	2630(s)		Combinations
	2650(s) }		
	2722(s) }		
2752(1)	2745(s)		
2817(2)	2820(s)		
2858(2)	2875(s)		
2920(24)			$\nu_s (\text{CH}_2), \nu_{as} \text{CH}_2$
2933(8)			
2940(12)			
2970(14)			
2974(8)			
3009(8)			$\nu (\text{N}-\text{H})$
	3160(s) }		$\nu (\text{O}-\text{H})$
	3220(s) }		

TABLE 13

Monosodium Glutamate



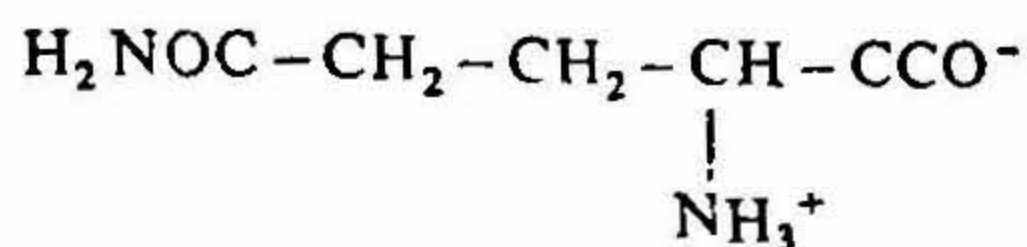
Raman	Infrared	Infrared deuterated	Assignment
437(7)	434(m)	434(m)	$\tau$ $\text{NH}_3^+$
482(2)	488(m)		$\gamma_p$ $\text{H}_2\text{O}$
504(12)	500(m)	486(m) }	$\gamma_p$ $\text{COO}$
533(10)	533(s)	521(s) }	
604(6)	600(s)	592(m)	
	628(s)	621(m) }	$\gamma_w$ $\text{COO}^-$
664(6)	655(s)	657(m) }	
	692(m)		$\gamma_w$ $\text{H}_2\text{O}$
731(5)	740(m)	727(w) }	$\delta$ $\text{COO}^-$
779(7)	772(m)	752(w) }	
		768(w)	
	798(m)	798(w)	
807(8)	805(m)	820(m)	$\gamma_p$ $\text{CH}_2$
		849(m)	$\gamma_p$ $\text{ND}_3^+$
861(16)	857(w)	861(w)	$\nu$ (C-C)
880(10)	871(w)	882(w)	$\nu$ (C-C)
927(8)	928(m)	990(m) }	$\gamma_p$ $\text{CH}_2$
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)	$\delta$ $\text{D}_2\text{O}$
		1963(w) }	$\nu$ (N-D) and $\nu$ (O-D)
		2018(w) }	
		2098(m) }	
		2110(m) }	
		2130(m) }	
		2256(m) }	
		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)			$\nu_s$ CH <sub>2</sub>
2928(10)			$\nu_{as}$ CH <sub>2</sub> and
2938(12)			$\nu$ CH
2955(5)			
2968(12)			
2975(19)	2978(s)		
2982(15)			
2994(6)			
	3065(s) } 3128(s) } 3273(s) } 3375(s) } 3420(s) }		$\nu$ (N - H) and $\nu$ (O - H)



TABLE 14

*L*-Glutamine

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

TABLE 14 - (contd.)

Raman	Infrared	Infrared deuterated	Assignments
1419(8)	1420(s)	1417(s) }	$\nu_s \text{COO}^-$
1426(4)	1430(s)	1426(s) }	
1453(10)	1462(s)	1449(s)	$\delta \text{CH}_2$
1498(2)	1492(s)		$\delta_s \text{NH}_3^+$
	1592(s)		$\delta_d \text{NH}_3^+$
1608			
1619(1)	1643(s)		$\delta \text{NH}_2$
	1692(s)	1659(s)	$\nu (\text{C}=\text{O})$
	1720(w)		
		1959(w)	
		1992(w)	
		2100(m) }	$\nu (\text{N}-\text{D})_{\text{d}}^{\text{H}}$
		2110(m) }	
	2040(m)		$\delta \text{NH}_3^+ + \tau \text{NH}_3^+$
		2206(s) }	$\nu (\text{N}-\text{D})$
		2230(s) }	
		2270(s) }	
		2320(s) }	
		2388(s) }	
		2459(s) }	
		2489(s) }	
		2562(s) }	
	2210(w) }		Combination
	2500(m) }		
	2550(m) }		
	2640(s) }		
	2733(s)		$\nu (\text{N}-\text{D})$
2876(1)	2880(s) }		$\nu_s \text{CH}_2$
2933(12)	2930(s) }		
2948(1)	2948(s) }		$\nu_s \text{CH}_2,$ $\nu_{\text{as}} \text{CH}_2,$ $\nu \text{CH}$
2954(12)			
2963(12)			
2994(6)	3000(s) }		
3009(2)			
	3186(s) }		$\nu (\text{N}-\text{H})$
	3219(s) }		
	3286(s)		$\nu_s \text{NH}_2$
3326(s)			
3420(s)			$\nu_{\text{as}} \text{NH}_2$

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
Hydroxy Proline	O-H . . O	2.80	(47)	3280	3298
	N <sup>+</sup> -H . . O	2.69		2459	2442
					2459
Threonine	N <sup>+</sup> -H . . O	3.17		—	3130
	O-H . . O	2.66	(48)	2750	2800
	N <sup>+</sup> -H . . O	2.90		3030	3021
	N <sup>+</sup> -H . . O	2.80		2750	2720
	N <sup>+</sup> -H . . O	3.10		3250	3180
	N <sup>+</sup> -H . . O	2.87	(49)	2920	2906
Valine	N <sup>+</sup> -H . . O	2.80		2750	2772
	N <sup>+</sup> -H . . O	2.86		2900	2906
	N <sup>+</sup> -H . . O	3.10		3250	3152
	N <sup>+</sup> -H . . O	2.81		2750	2772
	N <sup>+</sup> -H . . O	2.78		2660	2600
	N <sup>+</sup> -H . . O	2.91	(50)	3020	3009
Glutamine	N <sup>+</sup> -H . . O	2.79		2720	2700
	N <sup>+</sup> -H . . O	2.85		2890	2930
	N-H . . O	2.91		3150	3186
	N <sup>+</sup> -H . . O	2.94		3200	—
	N <sup>+</sup> -H . . O	2.87	(51)	2920	3100
Serine	N <sup>+</sup> -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 <sup>+</sup> —H . . O	2.87		2940	2936
	N <sup>+</sup> —H . . O	2.89		3015	3060
	N <sup>+</sup> —H . . O	2.92		3090	3150
	O—H . . O	2.63	(53)	2600	3200 2580 2604
L Glutamic acid HCl	N <sup>+</sup> —H . . Cl	3.16		3000	3009
	N <sup>+</sup> —H . . Cl	3.20		3050	
	N <sup>+</sup> —H . . O	2.90		3035	
	O—H . . Cl	3.04		3000	3160
	N <sup>+</sup> —H . . O	2.79	(54)	2710	2700 2725
	N <sup>+</sup> —H . . O	2.81		2760	2790
	N <sup>+</sup> —H . . O	2.87		2920	2920 3001
	N—H . . O	2.87	(55)	2955	2954
L Arginine	N—H . . O	2.91		3150	
	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	$\tau \text{ NH}_3^+$ $\text{cm}^{-1}$	$\delta_{\text{as}} \text{ NH}_3^+$ $\text{cm}^{-1}$	Calculated ( $\tau + \delta$ ) $\text{cm}^{-1}$	Observed $\text{cm}^{-1}$
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	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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