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Spectroscopic studies of valine and leucine molecules a comparative study

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ABSTRACT

The infrared and Raman spectra of valine and Leucine molecules have been recorded in nujall mull in the range 4000-400 cm^{-1} . Large number of bands belonging to different modes of vibration could be observed and assigned. The electronic absorption spectra of these molecules have also been measured at different pH values. It is observed that absorption peak shifts with the change in pH value of the solutions. A tentative explanation of the peak shift is given.

Introduction

Among the 20 standard amino acids valine and leucine are the two most important aliphatic type amino acids molecule. These molecules do not contain heteroatom and chromophors in their chains.

This interest in these molecules are due to following facts:

(a) These data are useful to discuss the importance of intermolecular bonding in life process.

(b) Vibrational spectra of these molecules are well studied. These studies are useful to get information about the molecular conformers. This provides Insights into the structure and properties of peptides and proteins [1-3] Valine molecule contains 19 atoms and has 51modes of vibrations. The molecule belongs to Cs point group and therefore all the vibrations are infrared as well as Raman active. Stepanian et al.[1]studied the conformational behavior of nonionised α valine. Raman optical activity of L-Valine has been reported by Garago et al [2]. The structural and electronic properties of L-Valine have also been studies by Tulip et al [3]. Raman scattering of L- valine crystal was studied by Lima et al[4].Leucine has monoclinic structure with space group P_{21}.There are four molecules per unit cell. Herlinger et al [5] have at preliminary level the IR spectrum of L-Leucine. Similarly Simson et al [6] have observed few bands in the Raman spectra of L-Leucine. These studies were carried out at room temperature. Filho et al [7] studied the Raman spectra of L- leucine at higher temperature. Almost-in all these studies there are large number of unassigned bands both in IR and Raman spectra of both these molecules. Which needs a further study in more details of the two. We have also monitored the electronic absorption spectra of these molecules at several pH values. The effect of change of pH on band shift has also been studies.

The main objective of this paper are:

(I)To present the Raman &IR spectra of both molecule through the range of 4000-400 cm^{-1} and give a tentative assignment of them.

(II) To present the electronic absorption spectra of both these molecules.

(III)To observe the effects of change of pH on band shift.

Experimental

The sample of valine and leucine molecules obtained from Merk (99%) has been used as such to record the Infrared and Raman spectra of the two. The IR spectra of these samples have been recorded in nujoll mull using a Fourier Transform IR spectrophotometer (JASCO FTIR-5300) in the range of 4000-400 cm^{-1}. Different quantities of the powder samples were mixed in nujoll mull and several batches of the same were prepared. The spectra were recorded at least for five different concentrations for each sample to get well developed vibrational structure. The Raman spectra of the same materials were recorded using an ISA Jobin-Yvon, HR-320; F/4 monochromatic (600g/mm grating).The excitation Laser source used was SDL-8530 with pump wavelength785 nm and 140mw power. For electronic absorption spectrum we have used Systronic -117 model UV-VIS-NIR Spectrophotometer. The pH of the solution was changed by adding HCl to make the medium acidic and NaOH for basic. The pH values were measured by pH meter.

Results and discussion

The IR and Raman spectra of valine & leucine molecules are shown in Figs.1-4 respectively. A broad band appears in the IR spectrum of valine at 2927 cm^{-1} and at 2957 cm^{-1} in leucine and is due to asymmetric stretch of CH_2 group. No peak appears at these energies in Raman spectrum in any of the two. However, there are three peaks at 2888, 2842, 2800 cm^{-1} in Raman spectrum of leucine due to asymmetric stretch of CH_2 group. Similar peaks are also seen in valine molecule at 2880, 2865, 2835 and 2810 cm^{-1} due to Asymmetric stretch of CH_2 group. These peaks do not appear in IR spectrum in these two molecules. There appears a peak at 2670 cm^{-1} in Raman spectrum in leucine molecule due to symmetric stretch of NH_3 group ,which is absent in IR as well as Raman spectrum of valine molecule. A broad band is seen at 2104 cm^{-1} in IR spectrum of valine molecule. This is due to combination CH3 bend and the rocking vibration of NH2 group (1065+1032). A band is seen at 2131 cm^{-1} in the IR spectrum of leucine molecule similar to band at 2104 cm^{-1} in valine and is due to combination of two fundamental modes. Three bands has been observed at

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1583,1600 and 1630 cm^{-1} in IR and Raman spectrum of leucine molecule but only one peak is observed at 1640 cm^{-1} in Raman spectrum for valine molecule. All these bands are associated to stretching vibrations of CO_2^- [7].Within the frequency range 1400-1600 cm^{-1} there are six bands in Raman spectrum of leucine molecule at 1400,1408,1444,1500,1516&1540 cm^{-1} , and only a single IR peak at 1408 cm^{-1} . These bands are symmetric CH_3 bending and due to HCH bend. Similarly in valine molecule five peaks have been observed in Raman and IR spectra at 1394, 1400, 1423, 1448&1480 cm^{-1} due to symmetric bending of CH_3. There appear peaks within the frequency region 1400-1300 cm^{-1} viz. at 1360, 1352&1329 cm^{-1} in valine molecule. These bands in leucine molecule are found at 1361, 1315&at 1340 cm^{-1} . These bands are associated with bending mode of CH_3, stretching of CC and rocking of CH. In the frequency range of 1300-1200 cm^{-1} , the IR and Raman bands at 1177, 1200,1271 and1288 cm^{-1} respectively in valine molecule are associated with bending of CH vibrations, whereas in leucine molecule corresponding IR and Raman bands are at 1296 , 1256 ,1238 and 1200 cm^{-1} respectively. They are due to rocking of NH_3 and bending of COH. The IR and Raman peaks are seen at 1140 and 1152 cm^{-1} in valine molecule and the corresponding peaks in leucine molecule are at 1134 and1152 cm^{-1}.

These peaks are contributed to CC stretch. Some additional IR and Raman peaks have been observed in valine molecule at 1080, 1065, 1048 and 1032 cm^{-1} .They are contributed by bending vibration of CH_3. These peaks are not seen in leucine molecule. In leucine molecule there is single band at 1005 cm^{-1} due to stretch of CN group. In valine molecule there is a Raman active CC stretch band which appear at 968 cm^{-1} .The bands observed at 949 (in IR) and at 928 cm^{-1}(in Raman) respectively in valine are assigned CN to be due to stretch. Similar peak is not seen in leucine molecule. Two bands appear in IR spectra in both the molecules at 900 and 918 cm^{-1} associated with stretch of CC bond [8]. A band due to NH2 bending band at 872 cm^{-1} is present in the Raman spectrum in both molecules. Bands are seen at 823, 840 cm-1 in the IR and Raman spectra respectively in valine due to torsion of OH group. No corresponding peaks are found in leucine molecule.

A IR peak is seen in valine as well as in leucine at 775 cm^{-1} and 769 cm^{-1} respectively due to bending of CO_2. In valine molecule a peak appear in IR at 715 cm^{-1}. The corresponding Raman band is seen at 710 cm^{-1} due to stretch of CC bond along with the bending of CO. These peaks do not appear in leucine. There appears a band in IR spectra at 665 cm^{-1} and a corresponding band is at 633 cm^{-1} in valine molecule due to bending of CO_2^- . The Corresponding peaks in leucine appear at 669 and 668 cm^{-1} due to bending of CO_2^- also.

A IR rocking band of CO_2 is seen in valine at 543 cm^{-1}. No such band is seen in the Raman spectrum of this molecule. However, in leucine molecule, there appears band in IR as well as in Raman at 534 and 535 cm^{-1} respectively due to rocking of CO_2 group. There also appears a peak at 490 cm^{-1} in Raman spectrum of leucine molecule which has been assigned as rocking of CO_2.

The peak seen at 472 cm^{-1} in valine molecule is due to bending of CO. The Raman spectra of valine show a peak at 428cm^{-1} and another peak at 435 cm^{-1}. These peaks are due to bending of NCC and torsion of CC bond respectively. However in leucine molecule a single peak is observed at 441 cm^{-1} and is assigned as twisting of NH_3 group.

Electronic absorption spectrum

Valine Molecule

The electronic absorption spectrum of valine molecule has been recorded in the region 200-400 nm, at different pH values and the spectra obtained is shown in Fig 5. For valine molecule 0.01 gm of sample material was dissolved in 2ml of triply distilled water and a peak is observed due to electronic transition at 212 nm (Table 3a). On increasing the dilution of sample (two times) the peak position was found to shift towards higher energy side. The electronic peak also shifts on changing the pH value. Thus at pH = 10, this peak appear at 220 nm.

Leucine Molecule

The Solution of leucine molecule prepared by dissolving 0.2 gm of leucine in 4 ml of triply distilled

Water was used to record the spectrum in the region 200-400 nm is shown in Fig 6. Two peaks observed at 238 and 278 nm at pH=7.A shift is observed in peak position when the pH of the samples changed. Thus at pH=2 the peak appear at 234 and 276 nm and at pH=10 the position of the Peaks are at 232 and 278 nm (table 3b).

Conclusions:

In the present paper a detailed vibrational structure analysis has been carried out by recording FT-IR and Raman spectra of valine and leucine molecules. The vibrational assignments of large number of the unreported bands as well as reported one have been made. IR and Raman spectra manifest all the characteristics bands expected for the compounds. A critical analysis of both the molecules has been done simultaneously. Maximum modes of vibrations are in good agreement. In addition to this the electronic absorption spectra of both these molecules have been studies at different pH and concentrations. The change in pH and concentrations reveal the shift of peak positions.

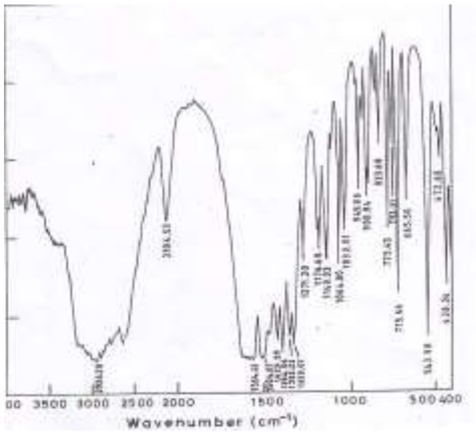

Figure 1 – IR Spectrum of Valine

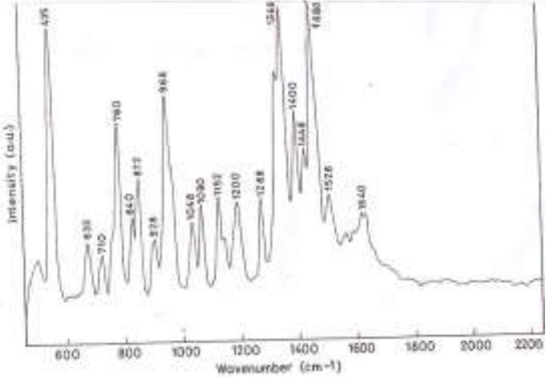

Figure 2

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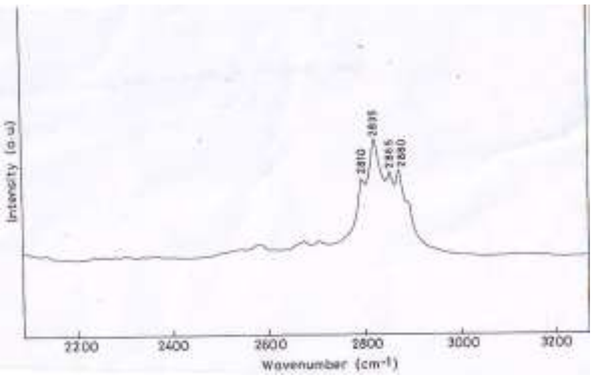

Figure 2 – Raman Spectrum of Valine

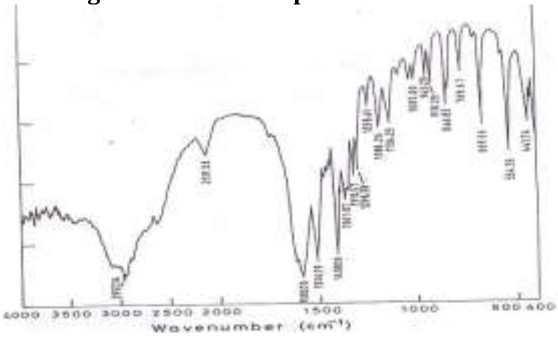

Figure 3 - IR Spectrum of Leucine

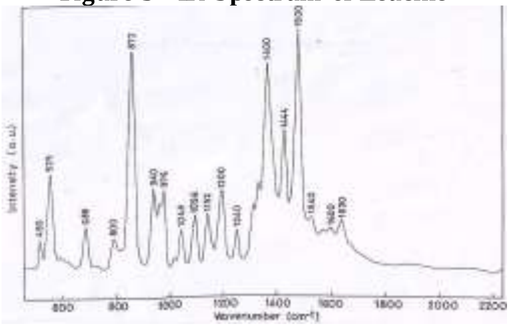

Fig 4
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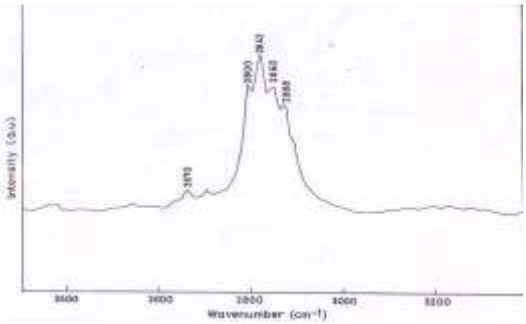

Figure 4 - Raman Spectrum of Leucine

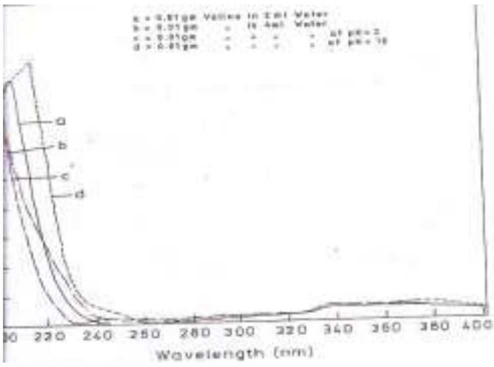

Figure 5 –Electronic Absorption Spectrum of Valine

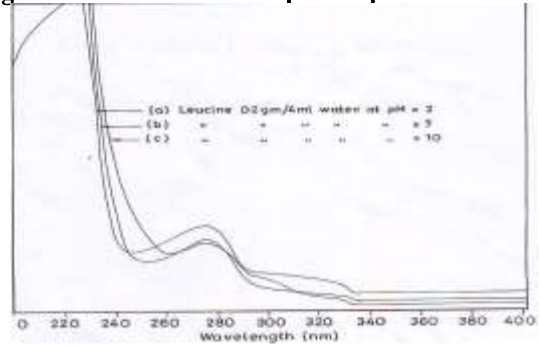

Figure 6 - Electronic Absorption Spectrum of Leucine

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References

1. S. G. Stepanian, I. D. Reva, E. D.Radchenko, and L. Adamowicz, J. Phys. Chem. A103, 4404 (1999).

2. A. R. Garago, L. D. Barron, L. Hecht, J. Raman Spectrosc, 24, 91, (1993).

3. P. R. Tulip Physical Review B 71, 195117(2005).

4. J. A. Lima Jr, P.T.C.Freire, R. J. C. Lima, A. J. D. Moreno, J. Mendes Filho and F. E. A. Melo, J. Raman Spectrosc. 36,1076-1081, (2005).

5. A. W. Herlinger, S. L. Wenhold and T. Veach Long II, J. Am. Chem. Soc.,92,6474(1970).

6. L. Simons, G. Bergstrom, G. Blomfeld, S. Fross, H. Stenback and G. Wansen, Comment. Phys-Math., 42, 3 (1973).

7. 7 P. F. Facanha Filho, P.T. C. Freir, K. C. V. Lima, J. Mendes fieho, F.E. A. Melo, Brazilian Journal of Physics 38(1) March (2008).

8. Santosh Kumar and S B Rai , Indian Journal of Pure and aapplied Physics, 48, April 251-255,(2010)

Table 1. A comparison of IR and Raman frequencies of valine

S. NO.	I.R. Frequency(cm^{-1})	Raman Frequency(cm^{-1})	Assignment
1	2927	2880	Asym CH_2 Str
2	------	2865	Asym CH_2 Str
3	-------	2835	Sym CH_2 Str
4	--------	2810	Sym CH_2 Str
5	2104	----------	Combi(1065+1032)
6	-------	1640	Asy Str CO_2
7	-------	1480	HCH Bend
8	1423	1448	HCH Bend
9	1394	1400	OH Bend + CH Bend
10	1352	--------	CH_3 Bend
11	1329	1360	CC Str, OH Bend
12	1271	1288	CH Bend
13	1177	1200	CH Bend
14	1140	1152	CC Str
15	1065	1080	CH_3 Bend
16	1032	1048	CH_3 Bend
17	-----	968	CC Str
18	949	928	CN Stre
19	900	--------	CC str
20	--------	872	NH_2 Bend
21	823	840	OH Tor
22	775	-----	Co_2 Bend
23	715	710	CC Stre, C=OBend
24	665	633	Co_2^- Bend
25	543	-----	Roc Co_2
26	472	-----	CO Bend
27	428	435	NCC Bend, CC Tor

Table2 A comparison of IR and Raman frequencies of L- Leucine molecule

S.NO.	I.R. Frequencies (cm^{-1})	Raman Frequencies (cm^{-1})	Assignment
1	2957	-----	Asy str CH_2,
2	….	2888	Asy str CH_2
3.	---	2842	Asy str CH_2
4.	---	2800	Sym str CH_2
5.	----	2670	Sym str NH_3
6.	2131	----	Combi (1134+1005)
7.	----	1630	Str Co_2^-
8.	1583	1600	Str Co_2^-
9.	----	1540	Asy Bend NH^+_3
10.	1516	1500	Asy Bend CH_3
11.	----	1444	Asy Bend CH_3
12.	1408	1400	Sym Bend CH_3
13.	1361	----	Sym Bend CH_3
14.	1315	1340	Rock CH
15.	1296	----	NH Bend
16.	1238	1256	COH Bend
17.	1188	1200	Roc NH_3^+
18.	1134	1152	C-C Str
19.	1005	----	C-N Str
20.	943	940	Rock CH_3
21.	918	----	Rock CH_3, Str C-C
22.	----	872	NH_2 Bend
23.	769	----	Str C-C=O
24.	669	668	Bend CO_2^-
25.	534	535	Rock COO
26.	----	490	Rock COO
27.	441	----	Twist of NH_3

Table 3 Electronic absorption spectrum Valine and Leucine molecules.

Valine (a)

S.No	Concentration(gm/ml)	pH Value	Peaks value(nm)
1	0.01/2	7	212
2	0.1/4	7	204
3	0.1/4	2	204
4	0.1/4	10	220

Leucine (b)

S.No	Concentration(gm/ml)	pH Value	Peaks value(nm)
1	0.2/4	7	238,278
2	0.2/4	2	234,276
3	0.2/4	10	232,278

Str. - Stretching, Asy. - Asymmetric,Sym.-Symmetric,Rock.-Rocking , Bend.- Bending ,Combi.-Combination,Tor- Torsion