



**ADDITIONAL SUPPLEMENT  
SPECTROSCOPIC STUDIES OF SOME  
ORGANIC COMPOUNDS**

**THESIS**

**SUBMITTED IN PARTIAL FULFILMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF**

**Doctor of Philosophy**

**IN**

**PHYSICS**

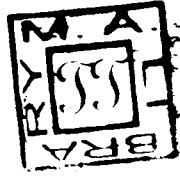
**BY**

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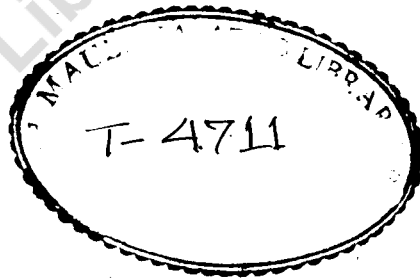
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## ADDITIONAL SUPPLEMENT

Vibrational spectroscopy is an important tool to investigate the various vibrations associated with a polyatomic molecules. Infrared, far-infrared and Raman spectra of polyatomic molecules give informations about the nature of the vibrations associated with polyatomic molecules in different frequency ranges. Near infrared spectra are obtained in the region  $250-4000\text{ cm}^{-1}$ . These spectra are important to know about various molecular vibrations corresponding to C-C, C=C and C-H atomic groups. Various stretching, in-plane and out-of-plane bending vibrations and their combinations are classified with the help of near infrared spectra.

Raman spectra obtained in the frequency region  $250-4000\text{ cm}^{-1}$  are used to confirm various assignments made about the molecular vibrations observed in the near infrared region. Depolarization ratios are calculated with the help of intensities obtained in the depolarized and polarized Raman spectra. With the help of depolarization ratios, the symmetries of various molecular vibrations are confirmed. Knowing the exact symmetry of the molecular vibrations, accurate nature of the molecular vibrations is obtained. With the help of the symmetries of vibrations, exact point group of a polyatomic molecule can be confirmed.

With the help of the far-infrared spectra of polyatomic molecules, the vibrations corresponding to lattice modes, difference frequencies and hydrogen bonding are obtained. These vibrations are very helpful in knowing the characteristics of complex biomolecules which change their structure even at the room temperature. Change in the geometry of the molecules gives rise to the change in the value of molecular vibrations in the far-infrared region i.e. between  $50-500\text{ cm}^{-1}$ , we can observe the nature of change in molecular vibrations of various molecules. In the case of biomolecules, these vibrations are important due to the fact that the occurrence of these vibrations are very frequent and some new species of the biomolecules can be predicted even with the observation of these low-lying vibrations.

We have given the theoretical consideration for vibrational spectroscopy of polyatomic molecules for molecular vibrations obtained in near infrared region. For far-infrared spectra interpretation, theoretical consideration has been described on the basis of lattice vibrations and vibrations associated with hydrogen bonding.

Spectroscopy of biomolecules involves the studies made in the far-infrared and low frequency Raman vibrations with respect to the conformational changes in such macromolecules.

These conformational changes give rise to low frequency molecular vibrations as well as some vibrational modes which are directly related with lattice vibrations.

Amino acids are of great biological significance as they form the basic constituents of proteins. The study of their vibrational spectra is necessary in order to get information on their molecular conformation and hydrogen bonding.

In the crystalline state and also in solution, amino acids exist as dipolar ions or zwitterions. The zwitterion structure leads to strong hydrogen bonds connecting the molecule together. The low frequency vibrations which are expected for amino acids in crystalline state consist of translational and rotational lattice vibrations, internal torsional modes of vibrations and low frequency hydrogen bond vibrations. It must be pointed out that the infrared, far-infrared and their corresponding Laser Raman spectra of amino acids exhibit important vibrations in the frequency and intensity on going from compound to compound.

In view of the above theoretical and other considerations infrared, far-infrared and Laser Raman spectra of DL-Phenyl alanine, L-Glutamic acid, DL-Aspartic acid, L-Tyrosine and DL-Tryptophan molecules

have been studied and explained. Help has been taken by analysing some of the vibrations with combination frequencies. However, some deviations are observed due to the fact that the big molecules, having a large number of atoms, do not follow exactly the selection rules due to their lower symmetry.

The molecules of L-Tyrosine, DL-Tryptophan, DL-Aspartic acid, L-Glutamic acid and DL-Phenyl alanine have been studied extensively in infrared and far-infrared region. The Laser Raman spectra of the compounds have also been obtained and studied widely. With the help of Laser Raman spectra with vertical and horizontal polarization, depolarization ratios of various fundamental modes of vibrations have been useful in assigning the symmetries of various fundamental.

**Table 3:** Analysis of the Laser Raman spectrum of DL-Phenyl alanine.

Frequency ( $\text{cm}^{-1}$ )	Intensity		Assignment
10	10.0		LA Mode
28	8.1		LA Mode
57	9.6		LA Mode
78	5.2	a'	tcc' Internal rotation
106	5.2	a''	tCN Internal rotation
126	4.8		COO torsion
145	4.7		
173	8.9		CC torsion
204	1.0		173 + 28
214	7.9	a'	tCN
265	1.1		
275	1.0		214 + 57
318	8.7		CCNC deformation
357	5.6		
408	1.1		CCNC deformation
473	9.8		
495	5.6		$\text{NH}^+_3$ torsion

Table 2 : Analysis of far-infrared spectrum of DL-Phenyl alanine.

Frequency ( $\text{cm}^{-1}$ )	Intensity	Assignment
57	0.5	LA Mode
63	1.0	LA Mode
65	1.0	LA Mode
73	1.6	LA Mode
80	1.7	a' tCC' internal rotation
97	3.0	
106	3.1	a'' tCN Internal rotation
127	4.3	a' COO torsion
145	4.9	80 + 63
190	8.1	a'' CC torsion
214	6.7	a' tCN
340	9.8	a' C-C-CH <sub>2</sub> trigonal bending
376	9.9	
431	3.9	
450	3.3	a' 106 + 340
475	7.4	



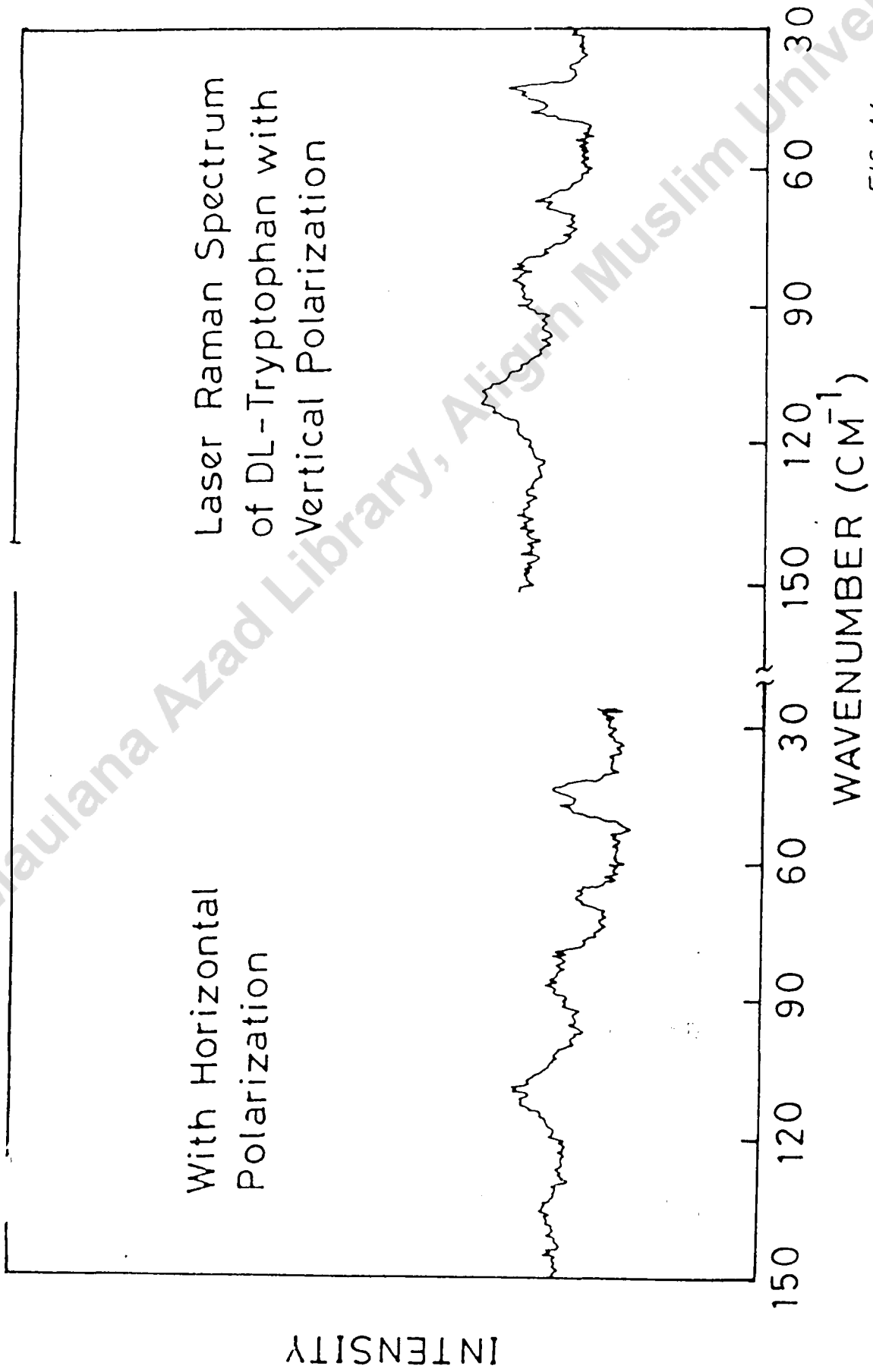


FIG. 14

Laser Raman Spectrum of  
L-Tyrosine with Vertical  
Polarization

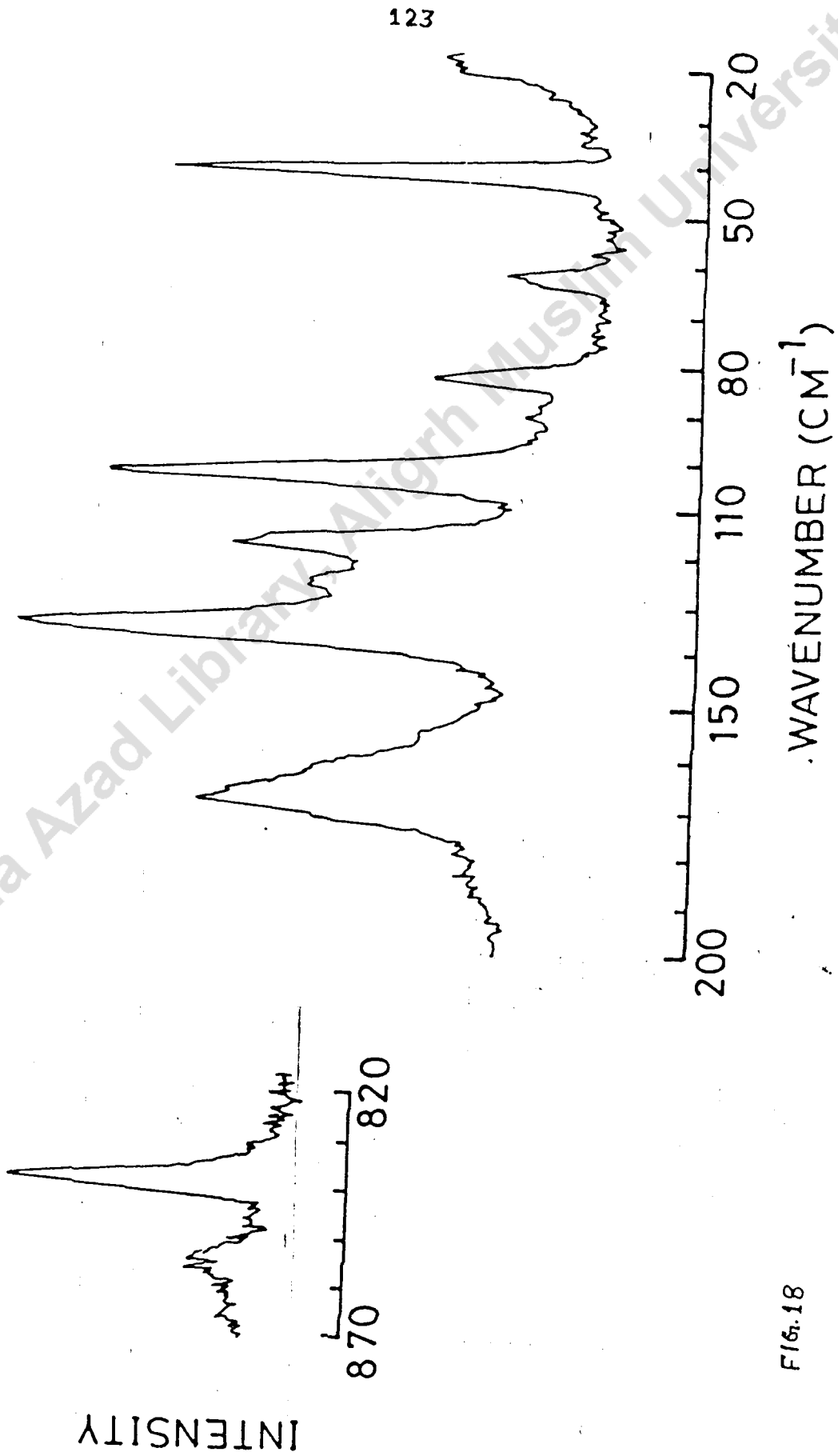


Fig. 18

# Laser Raman Spectrum of L-Tyrosine with Horizontal Polarization

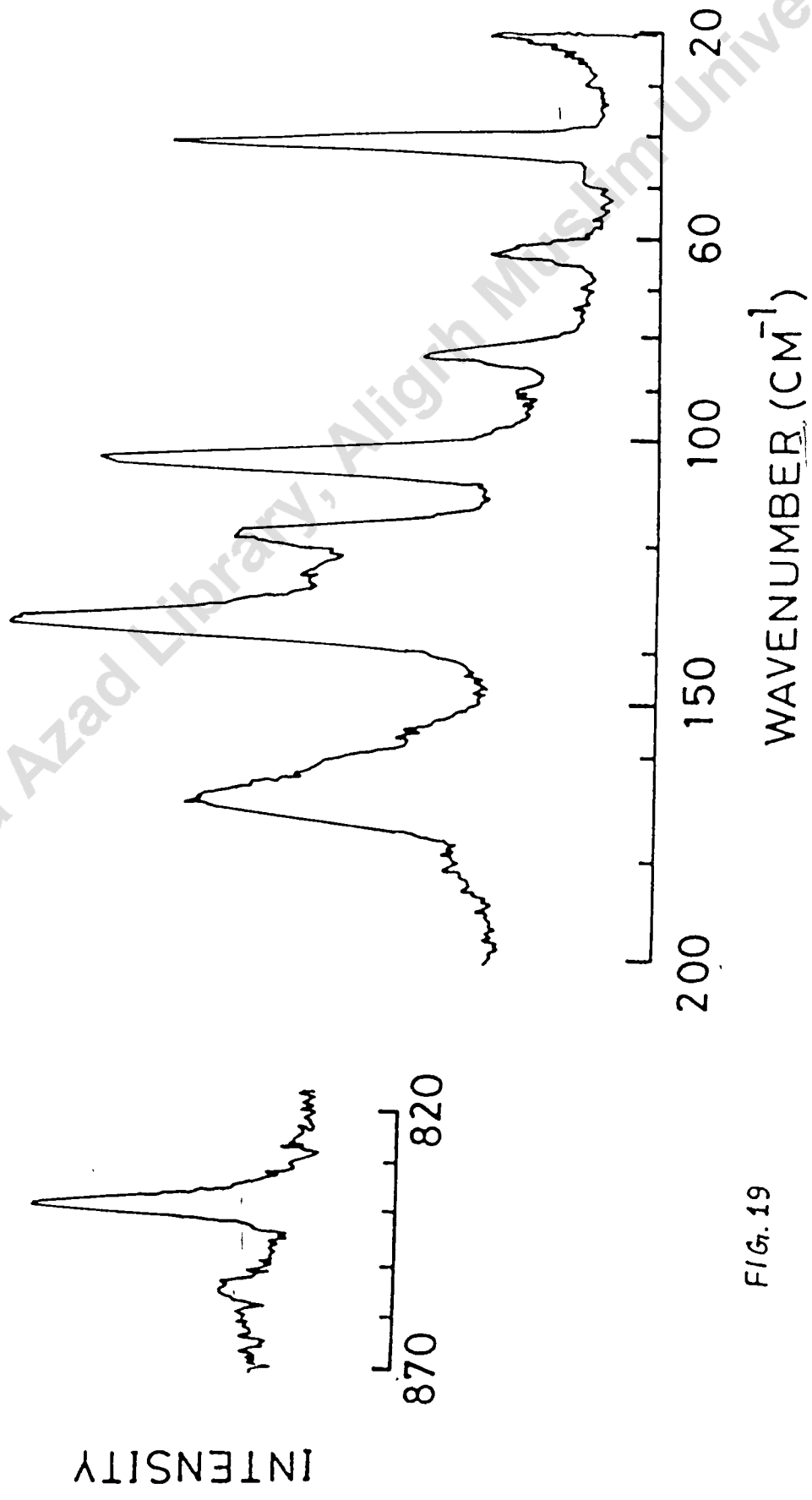


FIG. 19

1. Page No. 90 of Ph.D. thesis.

tcc internal rotation and tCN internal rotation have been assigned in the case of DL-Phenyl alanine molecule at 80 and 106  $\text{cm}^{-1}$  respectively. These vibrational assignments have been revised. Actually tCN vibration corresponds to the  $\text{NH}_2$  out-of-plane deformation vibration observed in aminoacids and that falls in the mid infrared region. LA modes have been assigned at 57, 63, 65 and 73  $\text{cm}^{-1}$ . Actually these modes are optically inactive. These vibrations may correspond to crystal vibrational modes. This has also been revised.

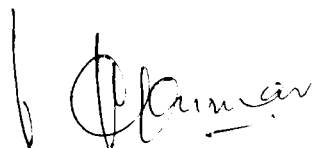
2. Page No. 105, 123, 124.

Laser Raman spectra of L-Tyrosine and DL-Tryptophan have been reported. Both the spectra appear approximately identical. There is very little difference between them.

It appears that there is very small effect of horizontal and vertical polarization. It has been agreed that measurements should be taken with a transparent sample. However, the observations of Raman spectra have been taken with the available samples.

3.  $C_s$  symmetry of most of the aminoacids have been taken under approximation. It has been revised considering the comment that molecules are still having the lower symmetries. In reality, it is correct that the aromatic ring is not coplanar with the N-C-COOH plane.
4. Assignments of very weak bands in Far-IR and low frequency Raman bands have been proposed. However, these may be noise of the instruments. It is agreed that some bands may be noise but resemblance of the occurrence of low frequency vibration in these complex molecules with very small intensity can not be completely ruled out.

All the points raised by foreign examiner have been considered in the revised form of this additional supplement of the Ph.D. dissertation.



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