



Experimental and quantum chemical investigations on vibrational and molecular structural characteristics of vitamin B₇: Biotin Molecule

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Dedicated to Prof J R Durig

Experimental and theoretical investigations on the structural and the vibrational characteristics of biotin (vitamin B₇) are presented. The molecular structure and vibrational frequencies were obtained using the DFT/B3LYP calculations employing the 6-311++G** basis set available with the Gaussian 09 software. The computed spectra are compared with FTIR and FT-Raman spectra recorded in the regions 400–4000 and 100–4000 cm⁻¹, respectively. Optimized geometrical parameters suggest that the overall symmetry of the molecule is C₁. The molecule is found to possess twelve conformations. Conformational analysis was carried out to obtain the most stable configuration of the molecule. In order to assign the observed IR and Raman frequencies the potential energy distributions (PEDs) have also been computed using GAR2PED software. © Anita Publications. All rights reserved.

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1 Introduction

Biotin (also known as vitamin H or coenzyme R or vitamin B₇) is a water-soluble vitamin-B [1]. It is a heterocyclic, S-containing monocarboxylic acid and has an unusual structure, with two rings fused together via one of their sides. The two rings are ureido and thiophane moieties. A valeric acid is attached to one of the carbon atoms of the thiophane ring. It is a coenzyme for carboxylase enzymes, involved in the synthesis of fatty acids, isoleucine, and valine, and in gluconeogenesis. It is necessary for the cell growth, the production of fatty acids, and the metabolism of fats and amino acids [2-4]. It helps in maintaining a steady blood sugar level [5]. It is often recommended as a dietary supplement for strengthening hair and nails, though scientific data supporting this outcome are weak [6,7]. Nevertheless, it is found in many cosmetics and health products for the hair and skin [8,9]. Foods with a relatively high biotin content include Swiss chard, raw egg yolk, liver, kidney, Saskatoon berries, and leafy green vegetables.

Biotin is essential for all organisms but can only be synthesized by bacteria, yeasts, molds, algae, and some plant species [10]. After the initial findings of biotin, nearly 40 years of research were required to set up it as a vitamin [11-15]. It was isolated as a water-soluble vitamin in 1941 [16] and then induced considerable attention as a synthetic target because of its beneficial biological properties for human nourishment and animal health [17-19].

Though various theoretical and experimental results for the discussion of the molecular structure of biotin [20-26] have been reported, the detailed vibrational spectral features of biotin molecule have not been investigated so far. Therefore, in the present communication it is planned to calculate the optimized molecular geometries, APT and Natural charges and fundamental vibrational wavenumbers along with their intensities in the IR spectrum, Raman activities and depolarization ratios of the Raman lines using DFT (B3LYP) method employing the basis set 6-311++G** [27-31] available with Gaussian-09 software [32] for the lowest energy conformer of the biotin molecule. In addition the experimental IR and Raman spectra have been recorded and analyzed in light of the computed fundamentals and the corresponding PEDs using

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GAR2PED software [33].

2 Experimental

The vitamin Biotin was purchased from the Sigma-Aldrich Chemical Co. (USA). It forms a white solid at room temperature and was used as such without any further purification for recording the IR and Raman spectra. The IR spectrum has been recorded in KBr pellet on a Varian FTIR-3100 spectrometer in the spectral range 400–4000 cm^{-1} with the experimental parameters for recording the IR spectra: resolution - 4 cm^{-1} ; gain-20; scan-100.

Its Raman spectrum has been recorded in the region 100–4000 cm^{-1} , on a Jobin Yvon HORIBA HR 800 Raman spectrometer using 488 nm line of an Ar^+ laser for excitation with the parameters: laser spot size: 1 μm , resolution $\sim 1 \text{ cm}^{-1}$, power at the sample $< 10 \text{ mW}$, integration time: 10 s, one window covers $\sim 800 \text{ cm}^{-1}$, accuracy of measurements $- 2 \text{ cm}^{-1}$, slit-width fixed at the entrance of laser 200 μm .

3 Computational details

The most stable molecular structure of biotin in the ground state is optimized and the structural parameters, APT charges, natural charges and fundamental vibrational frequencies along with their corresponding intensities in IR spectrum, Raman activities and depolarization ratios of the Raman bands were computed at the B3LYP/6-311++G** level using the Gaussian 09 program package. Unscaled B3LYP/6-311++G** vibrational frequencies are generally larger than the experimental values. In order to obtain the reasonable frequency matching, scale factors proposed by Rauhut and Pulay [34] were employed. The assignments of all the normal modes of vibration have been made on the basis of the calculated potential energy distributions (PEDs). For the calculation of the PEDs the vibrational problem was set up in terms of internal coordinates using the GAR2PED software. The observed IR and Raman frequencies corresponding to the fundamental modes have been correlated to the calculated fundamental frequencies in light of the PEDs.

4 Results and discussion

4.1 Conformational analysis

In the optimized structure there are two possible orientations of each of the five C-C bonds and one C-O bond due to two orientations of single O-H bond which leads to 12 conformers of biotin molecule. These 12 conformers of biotin molecule have been optimized at the B3LYP/6-311G** level. The possible geometries of all the 12 conformers have been optimized. The conformer-1 (C-I) is found to be the most stable conformer. At room temperature (25.8 $\text{meV} \cong 300\text{K}$) conformers C-I–C-III are expected to exist while the remaining 9 conformers appear to be highly energetic. In the present work, for simplicity we have considered the vibrational characteristics of the most stable conformer (C-I) only. However, the observed spectra may contain stronger frequencies corresponding to the conformers C-II and C-III also. The total energies and relative energies (in different units) of all the possible 12 conformers of biotin molecule are given in Table 1.

Table 1. Total and relative energies of 12 conformers of Biotin

| Conformers | Total Energy (Hartree) | Relative Energy | | |
|------------|------------------------|-----------------|----------------|----------|
| | | Hartree | Temp. (Kelvin) | Kcal/mol |
| C-I | -1124.35780 | 0 | 0 | 0 |
| C-II | -1124.35655 | 0.00125 | 395 | 0.78 |
| C-III | -1124.35618 | 0.00162 | 512 | 1.02 |

| | | | | |
|--------|-------------|---------|------|------|
| C-IV | -1124.35504 | 0.00276 | 872 | 1.73 |
| C-V | -1124.35426 | 0.00354 | 1118 | 2.22 |
| C-VI | -1124.35337 | 0.00443 | 1399 | 2.78 |
| C-VII | -1124.35071 | 0.00709 | 2239 | 4.45 |
| C-VIII | -1124.34875 | 0.00905 | 2858 | 5.68 |
| C-IX | -1124.34755 | 0.01025 | 3237 | 6.43 |
| C-X | -1124.34715 | 0.01065 | 3363 | 6.68 |
| C-XI | -1124.34663 | 0.01117 | 3527 | 7.01 |
| C-XII | -1124.34496 | 0.01284 | 4055 | 8.06 |

4.2 Structural properties

The optimized geometrical structures and the atomic labelling scheme corresponding to the conformer (C-I) are shown in Fig 1. The optimized geometrical parameters of biotin (C-I) are collected in Table 2. Optimized geometric parameters of biotin are compared with the available X-Ray crystal diffraction data of the biotin molecule [35].

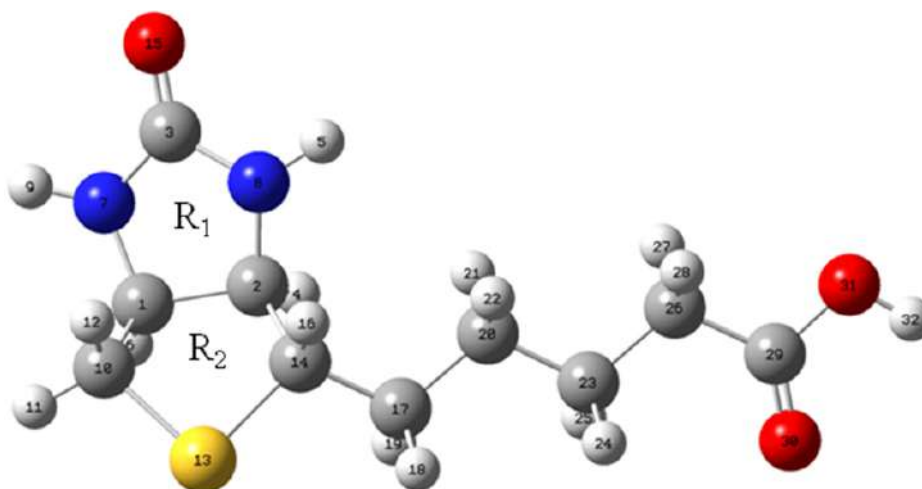


Fig 1. Optimized structure of Biotin (C-I)

Table 2. Geometrical parameters of the conformer (C-I) of Biotin

| S.No. | Parameters | Calculated ^a | Observed ^b |
|-------|-------------------------------------|-------------------------|-----------------------|
| 1 | r(C ₁ -C ₂) | 1.564 | 1.548 |
| 2 | r(C ₁ -H ₆) | 1.091 | 0.990 |
| 3 | r(C ₁ -N ₇) | 1.452 | 1.459 |
| 4 | r(C ₁ -C ₁₀) | 1.538 | 1.536 |
| 5 | r(C ₂ -H ₄) | 1.096 | 0.900 |
| 6 | r(C ₂ -N ₈) | 1.458 | 1.446 |
| 7 | r(C ₂ -C ₁₄) | 1.552 | 1.531 |
| 8 | r(C ₃ -N ₇) | 1.384 | 1.332 |

| | | | |
|----|---|-------|-------|
| 9 | r(C ₃ -N ₈) | 1.388 | 1.351 |
| 10 | r(C ₃ -O ₁₅) | 1.213 | 1.249 |
| 11 | r(H ₅ -N ₈) | 1.008 | 1.000 |
| 12 | r(N ₇ -H ₉) | 1.007 | 0.940 |
| 13 | r(C ₁₀ -H ₁₁) | 1.090 | 0.880 |
| 14 | r(C ₁₀ -H ₁₂) | 1.092 | 1.060 |
| 15 | r(C ₁₀ -S ₁₃) | 1.828 | 1.807 |
| 16 | r(S ₁₃ -C ₁₄) | 1.855 | 1.823 |
| 17 | r(C ₁₄ -H ₁₆) | 1.093 | 0.930 |
| 18 | r(C ₁₄ -C ₁₇) | 1.530 | 1.510 |
| 19 | r(C ₁₇ -H ₁₈) | 1.095 | 1.090 |
| 20 | r(C ₁₇ -H ₁₉) | 1.096 | 1.020 |
| 21 | r(C ₁₇ -C ₂₀) | 1.535 | 1.548 |
| 22 | r(C ₂₀ -H ₂₁) | 1.097 | 1.060 |
| 23 | r(C ₂₀ -H ₂₂) | 1.097 | 0.950 |
| 24 | r(C ₂₀ -C ₂₃) | 1.533 | 1.533 |
| 25 | r(C ₂₃ -H ₂₄) | 1.094 | 1.030 |
| 26 | r(C ₂₃ -H ₂₅) | 1.094 | 1.150 |
| 27 | r(C ₂₃ -C ₂₆) | 1.528 | 1.538 |
| 28 | r(C ₂₆ -H ₂₇) | 1.096 | 1.020 |
| 29 | r(C ₂₆ -H ₂₈) | 1.095 | 1.210 |
| 30 | r(C ₂₆ -C ₂₉) | 1.510 | 1.499 |
| 31 | r(C ₂₉ -O ₃₀) | 1.205 | 1.207 |
| 32 | r(C ₂₉ -O ₃₁) | 1.357 | 1.299 |
| 33 | r(O ₃₁ -H ₃₂) | 0.969 | 0.960 |
| 34 | α (C ₂ -C ₁ -H ₆) | 110.2 | - |
| 35 | α (C ₂ -C ₁ -N ₇) | 102.3 | 102.6 |
| 36 | α (C ₂ -C ₁ -C ₁₀) | 108.0 | 108.6 |
| 37 | α (H ₆ -C ₁ -N ₇) | 111.1 | - |
| 38 | α (H ₆ -C ₁ -C ₁₀) | 108.9 | - |
| 39 | α (N ₇ -C ₁ -C ₁₀) | 115.8 | 113.0 |
| 40 | α (C ₁ -C ₂ -H ₄) | 109.7 | - |
| 41 | α (C ₁ -C ₂ -N ₈) | 101.7 | 103.0 |
| 42 | α (C ₁ -C ₂ -C ₁₄) | 110.5 | 109.7 |
| 43 | α (H ₄ -C ₂ -N ₈) | 111.2 | - |
| 44 | α (H ₄ -C ₂ -C ₁₄) | 109.4 | - |
| 45 | α (N ₈ -C ₂ -C ₁₄) | 113.9 | 113.5 |
| 46 | α (N ₇ -C ₃ -N ₈) | 106.4 | 109.5 |

| | | | |
|----|---|-------|-------|
| 47 | $\alpha(\text{N}_7\text{-C}_3\text{-O}_{15})$ | 126.9 | 126.9 |
| 48 | $\alpha(\text{N}_8\text{-C}_3\text{-O}_{15})$ | 126.6 | 123.7 |
| 49 | $\alpha(\text{C}_1\text{-N}_7\text{-C}_3)$ | 112.8 | 112.5 |
| 50 | $\alpha(\text{C}_1\text{-N}_7\text{-H}_9)$ | 123.4 | - |
| 51 | $\alpha(\text{C}_3\text{-N}_7\text{-H}_9)$ | 118.8 | - |
| 52 | $\alpha(\text{C}_2\text{-N}_8\text{-C}_3)$ | 112.7 | 112.3 |
| 53 | $\alpha(\text{C}_2\text{-N}_8\text{-H}_5)$ | 122.0 | - |
| 54 | $\alpha(\text{C}_3\text{-N}_8\text{-H}_5)$ | 117.3 | - |
| 55 | $\alpha(\text{C}_1\text{-C}_{10}\text{-H}_{11})$ | 112.6 | - |
| 56 | $\alpha(\text{C}_1\text{-C}_{10}\text{-H}_{12})$ | 110.9 | - |
| 57 | $\alpha(\text{C}_1\text{-C}_{10}\text{-S}_{13})$ | 104.4 | 106.2 |
| 58 | $\alpha(\text{H}_{11}\text{-C}_{10}\text{-H}_{12})$ | 109.1 | - |
| 59 | $\alpha(\text{H}_{11}\text{-C}_{10}\text{-S}_{13})$ | 109.0 | - |
| 60 | $\alpha(\text{H}_{12}\text{-C}_{10}\text{-S}_{13})$ | 110.4 | - |
| 61 | $\alpha(\text{C}_{10}\text{-S}_{13}\text{-C}_{14})$ | 90.7 | 89.4 |
| 62 | $\alpha(\text{C}_2\text{-C}_{14}\text{-S}_{13})$ | 106.3 | 104.6 |
| 63 | $\alpha(\text{C}_2\text{-C}_{14}\text{-H}_{16})$ | 107.7 | - |
| 64 | $\alpha(\text{C}_2\text{-C}_{14}\text{-C}_{17})$ | 115.0 | 111.9 |
| 65 | $\alpha(\text{S}_{13}\text{-C}_{14}\text{-H}_{16})$ | 106.9 | - |
| 66 | $\alpha(\text{S}_{13}\text{-C}_{14}\text{-C}_{17})$ | 110.7 | 116.6 |
| 67 | $\alpha(\text{H}_{16}\text{-C}_{14}\text{-C}_{17})$ | 109.6 | - |
| 68 | $\alpha(\text{C}_{14}\text{-C}_{17}\text{-H}_{18})$ | 108.8 | - |
| 69 | $\alpha(\text{C}_{14}\text{-C}_{17}\text{-H}_{19})$ | 109.1 | - |
| 70 | $\alpha(\text{C}_{14}\text{-C}_{17}\text{-C}_{20})$ | 113.3 | 117.2 |
| 71 | $\alpha(\text{H}_{18}\text{-C}_{17}\text{-H}_{19})$ | 106.3 | - |
| 72 | $\alpha(\text{H}_{18}\text{-C}_{17}\text{-C}_{20})$ | 108.7 | - |
| 73 | $\alpha(\text{H}_{19}\text{-C}_{17}\text{-C}_{20})$ | 110.0 | - |
| 74 | $\alpha(\text{C}_{17}\text{-C}_{20}\text{-H}_{21})$ | 109.8 | - |
| 75 | $\alpha(\text{C}_{17}\text{-C}_{20}\text{-H}_{22})$ | 109.2 | - |
| 76 | $\alpha(\text{C}_{17}\text{-C}_{20}\text{-C}_{23})$ | 112.6 | 113.9 |
| 77 | $\alpha(\text{H}_{21}\text{-C}_{20}\text{-H}_{22})$ | 106.3 | - |
| 78 | $\alpha(\text{H}_{21}\text{-C}_{20}\text{-C}_{23})$ | 109.0 | - |
| 79 | $\alpha(\text{H}_{22}\text{-C}_{20}\text{-C}_{23})$ | 109.4 | - |
| 80 | $\alpha(\text{C}_{20}\text{-C}_{23}\text{-H}_{24})$ | 109.7 | - |
| 81 | $\alpha(\text{C}_{20}\text{-C}_{23}\text{-H}_{25})$ | 109.9 | - |
| 82 | $\alpha(\text{C}_{20}\text{-C}_{23}\text{-C}_{26})$ | 112.4 | 110.2 |
| 83 | $\alpha(\text{H}_{24}\text{-C}_{23}\text{-H}_{25})$ | 105.9 | - |
| 84 | $\alpha(\text{H}_{24}\text{-C}_{23}\text{-C}_{26})$ | 109.2 | - |

| | | | |
|-----|---|--------|--------|
| 85 | $\alpha(\text{H}_{25}\text{-C}_{23}\text{-H}_{26})$ | 109.3 | - |
| 86 | $\alpha(\text{C}_{23}\text{-C}_{26}\text{-H}_{27})$ | 111.3 | - |
| 87 | $\alpha(\text{C}_{23}\text{-C}_{26}\text{-H}_{28})$ | 111.3 | - |
| 88 | $\alpha(\text{C}_{23}\text{-C}_{26}\text{-C}_{29})$ | 113.5 | 110.9 |
| 89 | $\alpha(\text{H}_{27}\text{-C}_{26}\text{-H}_{28})$ | 105.3 | - |
| 90 | $\alpha(\text{H}_{27}\text{-C}_{26}\text{-C}_{29})$ | 107.3 | - |
| 91 | $\alpha(\text{H}_{28}\text{-C}_{26}\text{-C}_{29})$ | 107.4 | - |
| 92 | $\alpha(\text{C}_{26}\text{-C}_{29}\text{-O}_{30})$ | 126.3 | 123.9 |
| 93 | $\alpha(\text{C}_{26}\text{-C}_{29}\text{-O}_{31})$ | 111.2 | 113.6 |
| 94 | $\alpha(\text{O}_{30}\text{-C}_{29}\text{-O}_{31})$ | 122.3 | 122.5 |
| 95 | $\alpha(\text{C}_{29}\text{-O}_{31}\text{-H}_{32})$ | 107.2 | - |
| 96 | $\delta(\text{H}_6\text{-C}_1\text{-C}_2\text{-H}_4)$ | 19.3 | - |
| 97 | $\delta(\text{H}_6\text{-C}_1\text{-C}_2\text{-N}_8)$ | 137.1 | - |
| 98 | $\delta(\text{H}_6\text{-C}_1\text{-C}_2\text{-C}_{14})$ | -101.4 | - |
| 99 | $\delta(\text{N}_7\text{-C}_1\text{-C}_2\text{-H}_4)$ | -99.0 | - |
| 100 | $\delta(\text{N}_7\text{-C}_1\text{-C}_2\text{-N}_8)$ | 18.8 | -1.8 |
| 101 | $\delta(\text{N}_7\text{-C}_1\text{-C}_2\text{-C}_{14})$ | 140.2 | - |
| 102 | $\delta(\text{C}_{10}\text{-C}_1\text{-C}_2\text{-H}_4)$ | 138.2 | - |
| 103 | $\delta(\text{C}_{10}\text{-C}_1\text{-C}_2\text{-N}_8)$ | -103.8 | 118.1 |
| 104 | $\delta(\text{C}_{10}\text{-C}_1\text{-C}_2\text{-C}_{14})$ | 17.5 | - |
| 105 | $\delta(\text{C}_2\text{-C}_1\text{-N}_7\text{-C}_3)$ | -16.3 | -0.1 |
| 106 | $\delta(\text{C}_2\text{-C}_1\text{-N}_7\text{-H}_9)$ | -171.2 | - |
| 107 | $\delta(\text{H}_6\text{-C}_1\text{-N}_7\text{-C}_3)$ | -134.0 | - |
| 108 | $\delta(\text{H}_6\text{-C}_1\text{-N}_7\text{-H}_9)$ | 71.0 | - |
| 109 | $\delta(\text{C}_{10}\text{-C}_1\text{-N}_7\text{-C}_3)$ | 100.9 | -116.9 |
| 110 | $\delta(\text{C}_{10}\text{-C}_1\text{-N}_7\text{-H}_9)$ | -53.9 | - |
| 111 | $\delta(\text{C}_2\text{-C}_1\text{-C}_{10}\text{-H}_{11})$ | -158.5 | - |
| 112 | $\delta(\text{C}_2\text{-C}_1\text{-C}_{10}\text{-H}_{12})$ | 78.7 | - |
| 113 | $\delta(\text{C}_2\text{-C}_1\text{-C}_{10}\text{-S}_{13})$ | -40.3 | -27.7 |
| 114 | $\delta(\text{H}_6\text{-C}_1\text{-C}_{10}\text{-H}_{11})$ | -38.7 | - |
| 115 | $\delta(\text{H}_6\text{-C}_1\text{-C}_{10}\text{-H}_{12})$ | -161.4 | - |
| 116 | $\delta(\text{H}_6\text{-C}_1\text{-C}_{10}\text{-S}_{13})$ | 79.5 | - |
| 117 | $\delta(\text{N}_7\text{-C}_1\text{-C}_{10}\text{-H}_{11})$ | 87.3 | - |
| 118 | $\delta(\text{N}_7\text{-C}_1\text{-C}_{10}\text{-H}_{12})$ | -35.3 | - |
| 119 | $\delta(\text{N}_7\text{-C}_1\text{-C}_{10}\text{-S}_{13})$ | -154.3 | 85.5 |
| 120 | $\delta(\text{C}_1\text{-C}_2\text{-N}_8\text{-C}_3)$ | -16.8 | 3.3 |
| 121 | $\delta(\text{C}_1\text{-C}_2\text{-N}_8\text{-H}_5)$ | -165.1 | - |
| 122 | $\delta(\text{H}_4\text{-C}_2\text{-N}_8\text{-C}_3)$ | 99.9 | - |

| | | | |
|-----|---|--------|--------|
| 123 | $\delta(\text{H}_4\text{-C}_2\text{-N}_8\text{-H}_5)$ | -48.3 | - |
| 124 | $\delta(\text{C}_{14}\text{-C}_2\text{-N}_8\text{-C}_3)$ | -135.8 | 121.8 |
| 125 | $\delta(\text{C}_{14}\text{-C}_2\text{-N}_8\text{-H}_5)$ | 75.8 | - |
| 126 | $\delta(\text{C}_1\text{-C}_2\text{-C}_{14}\text{-S}_{13})$ | 12.8 | - |
| 127 | $\delta(\text{C}_1\text{-C}_2\text{-C}_{14}\text{-H}_{16})$ | -101.5 | - |
| 128 | $\delta(\text{C}_1\text{-C}_2\text{-C}_{14}\text{-C}_{17})$ | 135.9 | 158.9 |
| 129 | $\delta(\text{H}_4\text{-C}_2\text{-C}_{14}\text{-S}_{13})$ | -108.1 | - |
| 130 | $\delta(\text{H}_4\text{-C}_2\text{-C}_{14}\text{-H}_{16})$ | 137.5 | - |
| 131 | $\delta(\text{H}_4\text{-C}_2\text{-C}_{14}\text{-C}_{17})$ | 14.9 | - |
| 132 | $\delta(\text{N}_8\text{-C}_2\text{-C}_{14}\text{-S}_{13})$ | 126.7 | -82.7 |
| 133 | $\delta(\text{N}_8\text{-C}_2\text{-C}_{14}\text{-H}_{16})$ | 12.3 | - |
| 134 | $\delta(\text{N}_8\text{-C}_2\text{-C}_{14}\text{-C}_{17})$ | -110.2 | 44.4 |
| 135 | $\delta(\text{N}_8\text{-C}_3\text{-N}_7\text{-C}_1)$ | 6.5 | 2.2 |
| 136 | $\delta(\text{N}_8\text{-C}_3\text{-N}_7\text{-H}_9)$ | 162.6 | - |
| 137 | $\delta(\text{O}_{15}\text{-C}_3\text{-N}_7\text{-C}_1)$ | -173.4 | -177.0 |
| 138 | $\delta(\text{O}_{15}\text{-C}_3\text{-N}_7\text{-H}_9)$ | -17.3 | - |
| 139 | $\delta(\text{N}_7\text{-C}_3\text{-N}_8\text{-C}_2)$ | 7.4 | -3.6 |
| 140 | $\delta(\text{N}_7\text{-C}_3\text{-N}_8\text{-H}_5)$ | 157.4 | - |
| 141 | $\delta(\text{O}_{15}\text{-C}_3\text{-N}_8\text{-C}_2)$ | -172.5 | 175.7 |
| 142 | $\delta(\text{O}_{15}\text{-C}_3\text{-N}_8\text{-H}_5)$ | -22.5 | - |
| 143 | $\delta(\text{C}_1\text{-C}_{10}\text{-S}_{13}\text{-C}_{14})$ | 41.9 | 40.8 |
| 144 | $\delta(\text{H}_{11}\text{-C}_{10}\text{-S}_{13}\text{-C}_{14})$ | 162.6 | - |
| 145 | $\delta(\text{H}_{12}\text{-C}_{10}\text{-S}_{13}\text{-C}_{14})$ | -77.4 | - |
| 146 | $\delta(\text{C}_{10}\text{-S}_{13}\text{-C}_{14}\text{-C}_2)$ | -31.7 | -42.0 |
| 147 | $\delta(\text{C}_{10}\text{-S}_{13}\text{-C}_{14}\text{-H}_{16})$ | 83.1 | - |
| 148 | $\delta(\text{C}_{10}\text{-S}_{13}\text{-C}_{14}\text{-C}_{17})$ | -157.4 | -166.0 |
| 149 | $\delta(\text{C}_2\text{-C}_{14}\text{-C}_{17}\text{-H}_{18})$ | -170.9 | - |
| 150 | $\delta(\text{C}_2\text{-C}_{14}\text{-C}_{17}\text{-H}_{19})$ | -55.2 | - |
| 151 | $\delta(\text{C}_2\text{-C}_{14}\text{-C}_{17}\text{-C}_{20})$ | 67.76 | 171.5 |
| 152 | $\delta(\text{S}_{13}\text{-C}_{14}\text{-C}_{17}\text{-H}_{18})$ | -50.3 | - |
| 153 | $\delta(\text{S}_{13}\text{-C}_{14}\text{-C}_{17}\text{-H}_{19})$ | 65.3 | - |
| 154 | $\delta(\text{S}_{13}\text{-C}_{14}\text{-C}_{17}\text{-C}_{20})$ | -171.5 | -69.1 |
| 155 | $\delta(\text{H}_{16}\text{-C}_{14}\text{-C}_{17}\text{-H}_{18})$ | 67.4 | - |
| 156 | $\delta(\text{H}_{16}\text{-C}_{14}\text{-C}_{17}\text{-H}_{19})$ | -176.8 | - |
| 157 | $\delta(\text{H}_{16}\text{-C}_{14}\text{-C}_{17}\text{-C}_{20})$ | -53.8 | - |
| 158 | $\delta(\text{C}_{14}\text{-C}_{17}\text{-C}_{20}\text{-H}_{21})$ | -59.9 | - |
| 159 | $\delta(\text{C}_{14}\text{-C}_{17}\text{-C}_{20}\text{-H}_{22})$ | 56.2 | - |
| 160 | $\delta(\text{C}_{14}\text{-C}_{17}\text{-C}_{20}\text{-C}_{23})$ | 178.2 | 73.9 |

| | | | |
|-----|---|--------|-------|
| 161 | $\delta(\text{H}_{18}\text{-C}_{17}\text{-C}_{20}\text{-H}_{21})$ | 178.7 | - |
| 162 | $\delta(\text{H}_{18}\text{-C}_{17}\text{-C}_{20}\text{-H}_{22})$ | -65.0 | - |
| 163 | $\delta(\text{H}_{18}\text{-C}_{17}\text{-C}_{20}\text{-H}_{23})$ | 56.8 | - |
| 164 | $\delta(\text{H}_{19}\text{-C}_{17}\text{-C}_{20}\text{-H}_{21})$ | 62.5 | - |
| 165 | $\delta(\text{H}_{19}\text{-C}_{17}\text{-C}_{20}\text{-H}_{22})$ | 178.8 | - |
| 166 | $\delta(\text{H}_{19}\text{-C}_{17}\text{-C}_{20}\text{-C}_{23})$ | -59.2 | - |
| 167 | $\delta(\text{C}_{17}\text{-C}_{20}\text{-C}_{23}\text{-H}_{24})$ | -57.6 | - |
| 168 | $\delta(\text{C}_{17}\text{-C}_{20}\text{-C}_{23}\text{-H}_{25})$ | 58.4 | - |
| 169 | $\delta(\text{C}_{17}\text{-C}_{20}\text{-C}_{23}\text{-C}_{26})$ | -179.4 | 167.2 |
| 170 | $\delta(\text{H}_{21}\text{-C}_{20}\text{-C}_{23}\text{-H}_{24})$ | -179.9 | - |
| 171 | $\delta(\text{H}_{21}\text{-C}_{20}\text{-C}_{23}\text{-H}_{25})$ | -63.8 | - |
| 172 | $\delta(\text{H}_{21}\text{-C}_{20}\text{-C}_{23}\text{-C}_{26})$ | 58.2 | - |
| 173 | $\delta(\text{H}_{22}\text{-C}_{20}\text{-C}_{23}\text{-H}_{24})$ | 64.1 | - |
| 174 | $\delta(\text{H}_{22}\text{-C}_{20}\text{-C}_{23}\text{-H}_{25})$ | -179.7 | - |
| 175 | $\delta(\text{H}_{22}\text{-C}_{20}\text{-C}_{23}\text{-C}_{26})$ | -57.6 | - |
| 176 | $\delta(\text{C}_{20}\text{-C}_{23}\text{-C}_{26}\text{-H}_{27})$ | -58.7 | - |
| 177 | $\delta(\text{C}_{20}\text{-C}_{23}\text{-C}_{26}\text{-H}_{28})$ | 58.5 | - |
| 178 | $\delta(\text{C}_{20}\text{-C}_{23}\text{-C}_{26}\text{-C}_{29})$ | 179.9 | 175.8 |
| 179 | $\delta(\text{H}_{24}\text{-C}_{23}\text{-C}_{26}\text{-H}_{27})$ | 179.1 | - |
| 180 | $\delta(\text{H}_{24}\text{-C}_{23}\text{-C}_{26}\text{-H}_{28})$ | -63.5 | - |
| 181 | $\delta(\text{H}_{24}\text{-C}_{23}\text{-C}_{26}\text{-C}_{29})$ | 57.8 | - |
| 182 | $\delta(\text{H}_{25}\text{-C}_{23}\text{-C}_{26}\text{-H}_{27})$ | 63.6 | - |
| 183 | $\delta(\text{H}_{25}\text{-C}_{23}\text{-C}_{26}\text{-H}_{28})$ | -179.0 | - |
| 184 | $\delta(\text{H}_{25}\text{-C}_{23}\text{-C}_{26}\text{-H}_{29})$ | -57.6 | - |
| 185 | $\delta(\text{C}_{23}\text{-C}_{26}\text{-C}_{29}\text{-O}_{30})$ | 0.6 | 111.3 |
| 186 | $\delta(\text{C}_{23}\text{-C}_{26}\text{-C}_{29}\text{-O}_{31})$ | -179.3 | -79.4 |
| 187 | $\delta(\text{H}_{27}\text{-C}_{26}\text{-C}_{29}\text{-O}_{30})$ | -122.8 | - |
| 188 | $\delta(\text{H}_{27}\text{-C}_{26}\text{-C}_{29}\text{-O}_{31})$ | 57.1 | - |
| 189 | $\delta(\text{H}_{28}\text{-C}_{26}\text{-C}_{29}\text{-O}_{30})$ | 124.2 | - |
| 190 | $\delta(\text{H}_{28}\text{-C}_{26}\text{-C}_{29}\text{-O}_{31})$ | -55.7 | - |
| 191 | $\delta(\text{C}_{26}\text{-C}_{29}\text{-O}_{31}\text{-H}_{32})$ | -179.9 | - |
| 192 | $\delta(\text{O}_{30}\text{-C}_{29}\text{-O}_{31}\text{-H}_{32})$ | 0.0 | - |

Bond lengths in Å, bond angles and dihedral angles in degrees, ^a our work, ^b X-Ray single crystal diffraction data [35].

The geometrical structure shows that the atoms C_{14} , C_{17} , C_{20} , C_{23} , C_{26} , C_{29} , O_{31} and O_{32} are coplanar with the thiophane ring (R_2). Also the atoms H_{16} , H_{21} , H_{22} , H_{27} and H_{28} are almost coplanar. However, the molecule belongs to the C_1 point group. Optimized structure of the biotin molecule shows that the C-C ring bonds ($\text{C}_1\text{-C}_{10}$ and $\text{C}_2\text{-C}_{14}$) are slightly shorter than the $\text{C}_1\text{-C}_2$ bond. The four C-C bonds of the chain connected to the thiophane ring (R_2), $\text{C}_{14}\text{-C}_{17}$, $\text{C}_{17}\text{-C}_{20}$, $\text{C}_{20}\text{-C}_{23}$, $\text{C}_{23}\text{-C}_{26}$, have almost the same bond lengths (~ 1.53 Å) and the fifth one ($\text{C}_{26}\text{-C}_{29}$) is somewhat shorter (~ 1.51 Å). The magnitudes of the bond lengths $\text{N}_7\text{-H}_9$ and $\text{N}_8\text{-H}_5$ bond is equal (1.00 Å). Out of the two C=O bonds ($\text{C}_3\text{=O}_{15}$ and $\text{C}_{29}\text{=O}_{30}$) the $\text{C}_{29}\text{=O}_{30}$ bond

length is shorter (1.20 Å) than C₃=O₁₅ (1.21 Å) due to presence of OH group at the site C₂₉. No major changes are found in the bond lengths C-H and O-H from their corresponding usual bond lengths.

The bond angles $\alpha(\text{C}_2\text{-C}_1\text{-C}_{10})$, $\alpha(\text{C}_1\text{-C}_2\text{-C}_{14})$, $\alpha(\text{C}_{14}\text{-C}_{17}\text{-C}_{20})$, $\alpha(\text{C}_{17}\text{-C}_{20}\text{-C}_{23})$, $\alpha(\text{C}_{20}\text{-C}_{23}\text{-C}_{26})$ and $\alpha(\text{C}_{23}\text{-C}_{26}\text{-C}_{29})$ are found to be 108°, 111°, 113°, 113°, 112° and 114°, respectively in biotin in good agreement with the respective experimental values 109°, 110°, 117°, 114°, 110° and 111°, in the biotin molecule [35].

4.3 APT charges

Atomic polarizability tensor (APT) charge is interpreted as the sum of charge tensor and charge flux tensor [36]. APT charges at various atomic sites of biotin are collected in Table 3. Except C₂₆ atom, all the remaining 9 carbon atoms possess positive charges with different magnitudes. The carbon atom of the ureido ring (R₁), C₃, which is directly attached to the oxygen atom with double bond, bears highest APT charge with magnitude 1.41 a.u. The three O atoms (O₁₅, O₃₀ and O₃₁) possess negative charges with magnitudes 0.93, 0.76 and 0.77 a.u., respectively. The atom S₁₃ has negative APT charge with magnitude 0.19 a.u. The two N atoms (N₇ and N₈) have negative APT charges with magnitudes 0.72 and 0.71 a.u., respectively. Due to high electronegativity all the O, S and N atoms possess negative APT charges. There are 16 H atoms in the biotin molecule in which 11 H atoms (H₄, H₆, H₁₁, H₁₂, H₁₆, H₁₈, H₁₉, H₂₁, H₂₂, H₂₄, H₂₅) possess negative charges and remaining 5 H atoms (H₅, H₉, H₂₇, H₂₈, H₃₂) have positive charges.

Table 3. APT charges of Biotin (C-I conformer)

| Atom | APT charges |
|-----------------|-------------|
| C ₁ | 0.355 |
| C ₂ | 0.276 |
| C ₃ | 1.412 |
| H ₄ | -0.061 |
| H ₅ | 0.198 |
| H ₆ | -0.033 |
| N ₇ | -0.720 |
| N ₈ | -0.713 |
| H ₉ | 0.209 |
| C ₁₀ | 0.072 |
| H ₁₁ | -0.002 |
| H ₁₂ | -0.023 |
| S ₁₃ | -0.191 |
| C ₁₄ | 0.155 |
| O ₁₅ | -0.936 |
| H ₁₆ | -0.043 |
| C ₁₇ | 0.077 |
| H ₁₈ | -0.019 |
| H ₁₉ | -0.020 |
| C ₂₀ | 0.091 |
| H ₂₁ | -0.043 |
| H ₂₂ | -0.034 |

| | |
|-----------------|--------|
| C ₂₃ | 0.107 |
| H ₂₄ | -0.021 |
| H ₂₅ | -0.018 |
| C ₂₆ | -0.027 |
| H ₂₇ | 0.004 |
| H ₂₈ | 0.004 |
| C ₂₉ | 1.202 |
| O ₃₀ | -0.764 |
| O ₃₁ | -0.774 |
| H ₃₂ | 0.282 |

@in unit of e

4.4 Vibrational assignments

The biotin molecule is a 32 atomic molecule with 90 normal modes of vibration; Table 4. The calculated and observed vibrational frequencies along with the corresponding PEDs and normal mode assignments are collected in Table 5. The observed and calculated IR and Raman spectra of biotin are reproduced in Figs 2 and 3, respectively. The normal mode assignments could be discussed under the sections:

- (i) O-H modes (**3 modes**)
- (ii) CH₂ group modes (**30 modes**)
- (iii) N-H/C-H modes (**15 modes**)
- (iv) C-OH modes (**3 modes**)
- (v) C=O modes (**6 modes**)
- (vi) Ring modes (**18 modes**)
- (vii) C-C modes (**15 modes**)

Table 4. Normal modes distribution of Biotin (C-I conformer)

| S.No. | Modes | Total no. | Symbol | Groups | No. of modes |
|-------|---------------------------------|-----------|----------|---|---------------------------------------|
| 1. | Stretching | 33 | ν | C-H O-H C-O C-C C=O C-N N-H C-S | 13 1 1 8 2 2 4 2 |
| 2. | ^a Planar deformation | 11 | β | C ₃ =O, C ₂₉ =O N ₇ -H, N ₈ -H C ₁ -H, C ₂ -H, C ₁₄ -H | 2 2 3 |
| | | | α | R ₁ R ₂ | 2 2 |

| | | | | | |
|-----------------------|--------------------------------------|----|----------|---|---|
| 3. | ^a Non- planar deformation | 11 | γ | C ₃ =O, C ₂₉ =O | 2 |
| | | | | N ₇ -H, N ₈ -H | 2 |
| | | | | C ₁ -H, C ₂ -H, C ₁₄ -H | 3 |
| | | | | Ring R ₁ | 2 |
| | | | | Ring R ₂ | 2 |
| 4. | Twisting | 13 | τ | ¹⁰ CH ₂ , ¹⁷ CH ₂ , ²⁰ CH ₂ , | 5 |
| | | | | ²³ CH ₂ , ²⁶ CH ₂ | |
| | | | | O ₃₁ -H | 1 |
| | | | | C ₂₉ -OH | 1 |
| | | | | C ₁₄ -C ₁₇ , C ₁₇ -C ₂₀ , | 5 |
| | | | | C ₂₀ -C ₂₃ , C ₂₃ -C ₂₆ , | |
| | | | | C ₂₆ -C ₂₉ | 1 |
| Buffering mode (ring) | | | | | |
| 5. | Wagging | 5 | ω | ¹⁰ CH ₂ , ¹⁷ CH ₂ , ²⁰ CH ₂ , | 5 |
| | | | | ²³ CH ₂ , ²⁶ CH ₂ | |
| 6. | Scissoring | 5 | σ | ¹⁰ CH ₂ , ¹⁷ CH ₂ , ²⁰ CH ₂ , | 5 |
| | | | | ²³ CH ₂ , ²⁶ CH ₂ | |
| 7. | Rocking | 5 | ρ | ¹⁰ CH ₂ , ¹⁷ CH ₂ , ²⁰ CH ₂ , | 5 |
| | | | | ²³ CH ₂ , ²⁶ CH ₂ | |
| 9. | Angle Bending | 7 | α | S ₁₃ -C ₁₄ -C ₁₇ , | 5 |
| | | | | C ₁₄ -C ₁₇ -C ₂₀ , | |
| | | | | C ₁₇ -C ₂₀ -C ₂₃ , | |
| | | | | C ₂₀ -C ₂₃ -C ₂₆ , | |
| | | | | C ₂₃ -C ₂₆ -C ₂₉ | |
| | | | | C ₂₆ -C ₂₉ -OH | 1 |
| | | | | C ₂₉ -O ₃₁ -H | 1 |

^a with respect to the local plane

Table 5. Calculated and observed vibrational frequencies and assignments for Biotin (C-I conformer)

| S.No. | Calculated | Observed frequencies | | PEDs | |
|----------------|---|----------------------|----|-------|--|
| | | (intensities) | | | |
| | Unscaled freq. (IR, Raman) depolarisation ratio | Scaled freq.* | IR | Raman | |
| v ₁ | 17(1.9,1.1) 0.75 | 17 | - | - | $\tau(\text{C}_2\text{-C}_{14})(\mathbf{60})$, $\phi_2(\text{R}_2)(26)$, $\phi_1(\text{R}_2)(6)$, $\phi_2(\text{R}_1)(4)$ |
| v ₂ | 23(2.2,0.4) 0.75 | 23 | - | - | $\tau(\text{C}_2\text{-C}_{14})(61)$, $\phi_2(\mathbf{R}_2)(\mathbf{25})$, $\phi_1(\text{R}_2)(6)$, $\phi_2(\text{R}_1)(4)$ |
| v ₃ | 30(0.1,0.3) 0.75 | 29 | - | - | $\tau(\text{C}_2\text{-C}_{14})(49)$, $\delta(\text{S}_{13}\text{-C}_{14}\text{-C}_{17})(7)$, $\tau(\text{C}_{17}\text{-C}_{20})(7)$, $\phi_2(\text{R}_2)(5)$, $\tau(\text{C}_{20}\text{-C}_{23})(\mathbf{5})$, $\tau(\text{C}_{14}\text{-C}_{17})(5)$, $\tau(\text{C}_{23}\text{-C}_{26})(4)$, $\phi_1(\text{R}_2)(4)$ |
| v ₄ | 58(0.1,0.2) 0.75 | 57 | - | - | $\tau(\text{C}_2\text{-C}_{14})(52)$, $\phi_2(\text{R}_2)(31)$, $\phi_1(\mathbf{R}_2)(\mathbf{6})$, $\phi_2(\text{R}_1)(5)$, $\tau(\text{C}_1\text{-C}_{10})(5)$ |

| | | | | | |
|-----------------|------------------------|-----|-------------|-------------|--|
| v ₅ | 71(0.4,0.5) 0.74 | 69 | - | - | $\phi_2(\mathbf{R}_2)(40)$, $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(22)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(20)$, $\tau(\mathbf{C}_{26}\text{-}\mathbf{C}_{29})(5)$, $\tau(\mathbf{C}_{14}\text{-}\mathbf{C}_{17})(4)$ |
| v ₆ | 97(0.2,0.8) 0.75 | 95 | - | - | $\phi_1(\mathbf{R}_1)(30)$, $\alpha_1(\mathbf{R}_1)(18)$, $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(11)$, $\phi_2(\mathbf{R}_1)(7)$, $\phi_2(\mathbf{R}_2)(7)$, $\gamma(\mathbf{N}_7\text{-}\mathbf{H}_9)(6)$, $\gamma(\mathbf{N}_8\text{-}\mathbf{H}_5)(4)$, $\tau(\mathbf{C}_{23}\text{-}\mathbf{C}_{26})(3)$ |
| v ₇ | 110(2.3,1.0) 0.66 | 108 | - | - | $\phi_2(\mathbf{R}_2)(34)$, $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(33)$, $\phi_1(\mathbf{R}_1)(15)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(6)$, $\alpha_1(\mathbf{R}_1)(4)$ |
| v ₈ | 135(0.7,0.2) 0.49 | 132 | - | 125 (92) | $\phi_2(\mathbf{R}_2)(46)$, $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(27)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(15)$, $\phi_2(\mathbf{R}_1)(6)$, $\tau(\mathbf{C}_{17}\text{-}\mathbf{C}_{20})(6)$ |
| v ₉ | 149(2.2,0.2) 0.60 | 146 | - | - | $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(50)$, $\phi_2(\mathbf{R}_2)(42)$, $\phi_2(\mathbf{R}_1)(4)$ |
| v ₁₀ | 177(6.2,0.5) 0.23 | 173 | - | - | $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(59)$, $\phi_2(\mathbf{R}_2)(23)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(8)$, $\phi_1(\mathbf{R}_2)(6)$, $\tau(\mathbf{C}_{14}\text{-}\mathbf{C}_{17})(4)$ |
| v ₁₁ | 193(1.5,3.6) 0.25 | 189 | - | 164 (55) | $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(63)$, $\phi_2(\mathbf{R}_2)(16)$, $\phi_1(\mathbf{R}_2)(8)$, $\delta(\mathbf{S}_{13}\text{-}\mathbf{C}_{14}\text{-}\mathbf{C}_{17})(8)$ |
| v ₁₂ | 262(2.5,0.6) 0.26 | 256 | - | 246 (57) | $\phi_2(\mathbf{R}_1)(17)$, $\delta(\mathbf{C}_{17}\text{-}\mathbf{C}_{20}\text{-}\mathbf{C}_{23})(13)$, $\delta(\mathbf{S}_{13}\text{-}\mathbf{C}_{14}\text{-}\mathbf{C}_{17})(11)$, $\delta(\mathbf{C}_{26}\text{-}\mathbf{C}_{29}\text{-}\mathbf{OH})(10)$, $\delta(\mathbf{C}_{23}\text{-}\mathbf{C}_{26}\text{-}\mathbf{C}_{29})(10)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(9)$, $\alpha_1(\mathbf{R}_1)(4)$ |
| v ₁₃ | 306(2.4,1.5) 0.38 | 299 | - | 294 (63) | $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(42)$, $\phi_2(\mathbf{R}_2)(12)$, $\phi_2(\mathbf{R}_1)(11)$, $\phi_1(\mathbf{R}_1)(11)$, $\gamma(\mathbf{C}_{14}\text{-}\mathbf{H}_{16})(6)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(5)$ |
| v ₁₄ | 362(30.0,0.6) 0.25 | 354 | - | - | $\phi_2(\mathbf{R}_2)(27)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(16)$, $\alpha_2(\mathbf{R}_2)(16)$, $\gamma(\mathbf{C}_{14}\text{-}\mathbf{H}_{16})(8)$, $\phi_2(\mathbf{R}_1)(7)$, $\delta(^{10}\text{CH}_2)(6)$, $\phi_1(\mathbf{R}_2)(6)$, $\phi_1(\mathbf{R}_1)(5)$, $\gamma(\mathbf{N}_7\text{-}\mathbf{H}_9)(3)$ |
| v ₁₅ | 395(3.5,3.6) 0.29 | 386 | - | - | $\delta(\mathbf{S}_{13}\text{-}\mathbf{C}_{14}\text{-}\mathbf{C}_{17})(16)$, $\delta(\mathbf{C}_{20}\text{-}\mathbf{C}_{23}\text{-}\mathbf{C}_{26})(16)$, $\phi_2(\mathbf{R}_2)(13)$, $\alpha_2(\mathbf{R}_2)(13)$, $\delta(^{10}\text{CH}_2)(7)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(5)$, $\delta(\mathbf{C}_{14}\text{-}\mathbf{C}_{17}\text{-}\mathbf{C}_{20})(4)$, $\nu(\mathbf{C}_{10}\text{-}\mathbf{S}_{13})(4)$, $\alpha_2(\mathbf{R}_1)(4)$, $\alpha_1(\mathbf{R}_2)(3)$ |
| v ₁₆ | 405(10.8,6.1) 0.22 | 396 | - | 370 (70) | $\nu(\mathbf{S}_{13}\text{-}\mathbf{C}_{14})(15)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(13)$, $\delta(\mathbf{C}_{14}\text{-}\mathbf{C}_{17}\text{-}\mathbf{C}_{20})(13)$, $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(11)$, $\gamma(\mathbf{C}_{14}\text{-}\mathbf{H}_{16})(10)$, $\alpha_2(\mathbf{R}_2)(6)$, $\delta(\mathbf{S}_{13}\text{-}\mathbf{C}_{14}\text{-}\mathbf{C}_{17})(6)$, $\alpha_1(\mathbf{R}_2)(6)$, $\delta(^{10}\text{CH}_2)(5)$, $\gamma(\mathbf{N}_7\text{-}\mathbf{H}_9)(4)$, $\delta(\mathbf{C}_{20}\text{-}\mathbf{C}_{23}\text{-}\mathbf{C}_{26})(3)$ |
| v ₁₇ | 415(111.7,0.7) 0.32 | 406 | 426 (8) | - | $\alpha_1(\mathbf{R}_1)(42)$, $\gamma(\mathbf{N}_7\text{-}\mathbf{H}_9)(32)$, $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(8)$, $\phi_1(\mathbf{R}_2)(5)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(4)$ |
| v ₁₈ | 439(6.4,0.4) 0.15 | 430 | - | 429 (69) | $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(44)$, $\delta(^{10}\text{CH}_2)(17)$, $\phi_2(\mathbf{R}_2)(12)$, $\phi_2(\mathbf{R}_1)(7)$, $\alpha_1(\mathbf{R}_2)(7)$, $\alpha_1(\mathbf{R}_1)(3)$ |
| v ₁₉ | 454(40.3,1.0) 0.70 | 444 | 446 (18) | - | $\alpha_1(\mathbf{R}_1)(28)$, $\gamma(\mathbf{N}_8\text{-}\mathbf{H}_5)(25)$, $\phi_2(\mathbf{R}_1)(16)$, $\alpha_2(\mathbf{R}_1)(10)$ |
| v ₂₀ | 492(47.0,0.7) 0.67 | 481 | 465 (18) | - | $\tau(\mathbf{C}_1\text{-}\mathbf{C}_{10})(29)$, $\delta(\mathbf{C}_{26}\text{-}\mathbf{C}_{29}\text{-}\mathbf{OH})(20)$, $\phi_2(\mathbf{R}_2)(19)$, $\delta(^{10}\text{CH}_2)(9)$, $\alpha_1(\mathbf{R}_2)(6)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(5)$, $\gamma(\mathbf{N}_8\text{-}\mathbf{H}_5)(5)$, $\beta(\mathbf{C}_3\text{=}\mathbf{O}_{15})(4)$ |
| v ₂₁ | 520(31.0,2.0) 0.75 | 509 | - | - | $\gamma(\mathbf{C}_{29}\text{=}\mathbf{O}_{30})(43)$, $\tau(\mathbf{C}_{29}\text{-}\mathbf{O}_{31})(26)$, $\delta(^{26}\text{CH}_2)(23)$, $\tau(\mathbf{C}_{23}\text{-}\mathbf{C}_{26})(4)$ |
| v ₂₂ | 540(28.4,0.6) 0.35 | 528 | 521 (13) | - | $\alpha_1(\mathbf{R}_1)(24)$, $\phi_2(\mathbf{R}_2)(15)$, $\delta(^{10}\text{CH}_2)(13)$, $\beta(\mathbf{C}_3\text{=}\mathbf{O}_{15})(7)$, $\phi_1(\mathbf{R}_2)(6)$, $\tau(\mathbf{C}_2\text{-}\mathbf{C}_{14})(5)$, $\delta(\mathbf{S}_{13}\text{-}\mathbf{C}_{14}\text{-}\mathbf{C}_{17})(5)$, $\delta(\mathbf{C}_{17}\text{-}\mathbf{C}_{20}\text{-}\mathbf{C}_{23})(4)$, $\delta(\mathbf{C}_{26}\text{-}\mathbf{C}_{29}\text{-}\mathbf{OH})(4)$ |

| | | | | | |
|-----------------|------------------------|-----|-------------|--------------|---|
| v ₂₃ | 562(0.8,4.8) 0.71 | 550 | 560 (28) | 562 (76) | $\alpha_1(\text{R}_2)(23)$, $\delta(^{10}\text{CH}_2)(17)$, $\tau(\text{C}_1-\text{C}_{10})(9)$, $\phi_2(\text{R}_1)(6)$, $\gamma(\text{C}_2-\text{H}_4)(6)$, $\nu(\text{S}_{13}-\text{C}_{14})(6)$, $\beta(\text{C}_3=\text{O}_{15})(5)$, $\gamma(\text{C}_1-\text{H}_6)(4)$ |
| v ₂₄ | 635(24.5,3.2) 0.38 | 621 | 573 (23) | 607 (86) | $\beta(\text{C}_{29}=\text{O}_{30})(59)$, $\nu(\text{C}_{29}-\text{O}_{31})(10)$, $\delta(\text{C}_{23}-\text{C}_{26}-\text{C}_{29})(8)$, $\delta(\text{C}_{29}-\text{O}_{31}-\text{H})(6)$ |
| v ₂₅ | 649(86.6,0.5) 0.75 | 635 | 605 (35) | - | $\tau(\text{C}_{29}-\text{O}_{31})(63)$, $\gamma(\text{C}_{29}=\text{O}_{30})(17)$, $\delta(^{26}\text{CH}_2)(15)$ |
| v ₂₆ | 710(14.7,2.0) 0.51 | 695 | 650 (48) | 638 (81) | $\alpha_1(\text{R}_1)(45)$, $\nu(\text{C}_{10}-\text{S}_{13})(18)$, $\alpha_2(\text{R}_1)(18)$, $\tau(\text{C}_1-\text{C}_{10})(3)$ |
| v ₂₇ | 737(11.2,0.0) 0.33 | 721 | 683 (38) | 685 (100) | $\phi_2(\text{R}_2)(18)$, $\delta(^{10}\text{CH}_2)(14)$, $\tau(\text{C}_1-\text{C}_{10})(13)$, $\delta(^{20}\text{CH}_2)(12)$, $\alpha_1(\text{R}_1)(11)$, $\delta(^{23}\text{CH}_2)(9)$, $\delta(^{17}\text{CH}_2)(5)$ |
| v ₂₈ | 750(5.4,2.3) 0.67 | 734 | 734 (23) | 732 (79) | $\delta(^{10}\text{CH}_2)(25)$, $\phi_2(\text{R}_2)(19)$, $\alpha_1(\text{R}_1)(19)$, $\tau(\text{C}_1-\text{C}_{10})(18)$, $\gamma(\text{C}_1-\text{H}_6)(6)$ |
| v ₂₉ | 752(2.8,6.7) 0.17 | 736 | 751 (28) | - | $\phi_2(\text{R}_2)(27)$, $\alpha_1(\text{R}_1)(19)$, $\tau(\text{C}_1-\text{C}_{10})(15)$, $\delta(^{10}\text{CH}_2)(15)$, $\nu(\text{C}_{10}-\text{S}_{13})(10)$, $\alpha_1(\text{R}_2)(4)$ |
| v ₃₀ | 760(18.0,1.5) 0.51 | 744 | 761 (28) | - | $\gamma(\text{C}_3=\text{O}_{15})(29)$, $\phi_1(\text{R}_1)(19)$, $\alpha_1(\text{R}_1)(10)$, $\phi_2(\text{R}_2)(8)$, $\nu(\text{C}_{10}-\text{S}_{13})(7)$, $\alpha_1(\text{R}_2)(5)$, $\nu(\text{S}_{13}-\text{C}_{14})(4)$ |
| v ₃₁ | 774(3.9,15.0) 0.10 | 757 | - | - | $\nu(\text{S}_{13}-\text{C}_{14})(23)$, $\phi_1(\text{R}_2)(10)$, $\delta(\text{S}_{13}-\text{C}_{14}-\text{C}_{17})(8)$, $\tau(\text{C}_2-\text{C}_{14})(7)$, $\phi_2(\text{R}_2)(7)$, $\alpha_1(\text{R}_1)(7)$, $\nu(\text{C}_{10}-\text{S}_{13})(4)$, $\alpha_2(\text{R}_1)(4)$, $\gamma(\text{C}_3=\text{O}_{15})(4)$ |
| v ₃₂ | 794(5.18,1.74) 0.40 | 777 | - | - | $\phi_2(\text{R}_2)(17)$, $\delta(^{23}\text{CH}_2)(17)$, $\nu(\text{S}_{13}-\text{C}_{14})(14)$, $\delta(^{17}\text{CH}_2)(7)$, $\alpha_1(\text{R}_1)(6)$, $\gamma(\text{C}_{14}-\text{H}_{16})(6)$, $\alpha_1(\text{R}_2)(5)$, $\delta(^{10}\text{CH}_2)(4)$ |
| v ₃₃ | 845(7.0,5.7) 0.08 | 827 | 817 (13) | 818 (74) | $\tau(\text{C}_1-\text{C}_{10})(27)$, $\nu(\text{C}_1-\text{C}_2)(11)$, $\alpha_1(\text{R}_2)(9)$, $\tau(\text{C}_2-\text{C}_{14})(6)$, $\phi_1(\text{R}_2)(6)$, $\nu(\text{C}_1-\text{C}_{10})(5)$, $\alpha_1(\text{R}_1)(4)$, $\nu(\text{S}_{13}-\text{C}_{14})(4)$ |
| v ₃₄ | 880(3.5,8.3) 0.10 | 861 | 843 (28) | 842 (83) | $\nu(\text{C}_{26}-\text{C}_{29})(48)$, $\nu(\text{C}_{29}-\text{O}_{31})(9)$, $\delta(\text{C}_{23}-\text{C}_{26}-\text{C}_{29})(8)$, $\delta(\text{C}_{26}-\text{C}_{29}-\text{OH})(4)$, $\delta(\text{C}_{29}-\text{O}_{31}-\text{H})(4)$, $\delta(\text{C}_{20}-\text{C}_{23}-\text{C}_{26})(3)$ |
| v ₃₅ | 909(1.7,2.4) 0.17 | 890 | 887 (23) | 895 (77) | $\alpha_1(\text{R}_1)(22)$, $\tau(\text{C}_2-\text{C}_{14})(16)$, $\delta(^{17}\text{CH}_2)(15)$, $\delta(^{26}\text{CH}_2)(7)$, $\delta(^{10}\text{CH}_2)(6)$, $\gamma(\text{C}_{14}-\text{H}_{16})(6)$, $\delta(^{23}\text{CH}_2)(5)$, $\nu(\text{C}_1-\text{C}_2)(4)$, $\nu(\text{C}_2-\text{C}_{14})(4)$ |
| v ₃₆ | 952(4.1,1.0) 0.42 | 932 | 920 (23) | 919 (78) | $\delta(^{10}\text{CH}_2)(45)$, $\tau(\text{C}_1-\text{C}_{10})(41)$, $\phi_2(\text{R}_2)(7)$, $\alpha_1(\text{R}_1)(3)$ |
| v ₃₇ | 976(6.7, 6.0) 0.07 | 955 | 949 (23) | 948 (80) | $\delta(^{10}\text{CH}_2)(43)$, $\phi_2(\text{R}_2)(15)$, $\tau(\text{C}_1-\text{C}_{10})(9)$, $\nu(\text{C}_3-\text{N}_7)(5)$, $\nu(\text{C}_3-\text{N}_8)(5)$, $\tau(\text{C}_2-\text{C}_{14})(4)$ |
| v ₃₈ | 991(6.6,1.8) 0.44 | 970 | - | - | $\tau(\text{C}_1-\text{C}_{10})(30)$, $\phi_2(\text{R}_2)(24)$, $\delta(^{10}\text{CH}_2)(22)$, $\delta(^{26}\text{CH}_2)(20)$, $\tau(\text{C}_2-\text{C}_{14})(4)$ |
| v ₃₉ | 1022(7.3,1.1) 0.22 | 976 | 975 (13) | - | $\phi_2(\text{R}_2)(25)$, $\delta(^{10}\text{CH}_2)(20)$, $\nu(\text{C}_1-\text{C}_{10})(10)$, $\nu(\text{C}_{17}-\text{C}_{20})(6)$, $\tau(\text{C}_2-\text{C}_{14})(5)$, $\nu(\text{C}_{20}-\text{C}_{23})(5)$, $\nu(\text{C}_{23}-\text{C}_{26})(5)$, $\delta(\text{S}_{13}-\text{C}_{14}-\text{C}_{17})(4)$, $\gamma(\text{C}_2-\text{H}_4)(4)$ |

| | | | | | |
|-----------------|------------------------|------|--------------|--------------|---|
| v ₄₀ | 1037(5.0,6.0) 0.36 | 990 | - | 977 (77) | v(C₁₇-C₂₀)(18) , $\tau(\text{C}_1\text{-C}_{10})(13)$, $\tau(\text{C}_2\text{-C}_{14})(11)$, $\gamma(\text{C}_{14}\text{-H}_{16})(7)$, $\phi_2(\text{R}_2)(6)$, $\nu(\text{C}_1\text{-C}_{10})(5)$, $\nu(\text{C}_{23}\text{-C}_{26})(4)$, $\nu(\text{C}_{14}\text{-C}_{17})(4)$, $\nu(\text{C}_{20}\text{-C}_{23})(4)$ |
| v ₄₁ | 1051(34,13) 0.27 | 1004 | 1014 (40) | - | $\phi_2(\text{R}_2)(23)$, v(C₂₀-C₂₃)(20) , $\tau(\text{C}_1\text{-C}_{10})(11)$, $\nu(\text{C}_2\text{-N}_8)(6)$, $\tau(\text{C}_2\text{-C}_{14})(5)$, $\gamma(\text{C}_1\text{-H}_6)(5)$, $\nu(\text{C}_2\text{-C}_{14})(4)$ |
| v ₄₂ | 1072(24.1,6.7) 0.29 | 1024 | 1031 (38) | - | v(C₂₃-C₂₆)(23) , $\tau(\text{C}_2\text{-C}_{14})(14)$, $\nu(\text{C}_{17}\text{-C}_{20})(10)$, $\phi_2(\text{R}_2)(10)$, $\tau(\text{C}_1\text{-C}_{10})(6)$, $\nu(\text{C}_2\text{-C}_{14})(5)$, $\gamma(\text{C}_{14}\text{-H}_{16})(5)$, $\alpha_1(\text{R}_1)(4)$ |
| v ₄₃ | 1085(28.2,3.6) 0.37 | 1036 | - | 1022 (90) | $\phi_2(\text{R}_2)(34)$, v(C₁-N₇)(14) , $\gamma(\text{C}_1\text{-H}_6)(7)$, $\alpha_1(\text{R}_1)(7)$, $\gamma(\text{C}_{14}\text{-H}_{16})(5)$, $\alpha_1(\text{R}_2)(5)$, $\nu(\text{C}_1\text{-C}_{10})(4)$ |
| v ₄₄ | 1100(25.0,4.7) 0.52 | 1051 | - | 1049 (91) | $\delta(^{10}\text{CH}_2)(30)$, v(C₁₄-C₁₇)(13) , $\tau(\text{C}_2\text{-C}_{14})(9)$, $\nu(\text{C}_2\text{-C}_{14})(6)$, $\nu(\text{C}_1\text{-N}_7)(5)$, $\gamma(\text{C}_2\text{-H}_4)(4)$ |
| v ₄₅ | 1106(14.5,1.3) 0.73 | 1056 | 1061 (38) | 1065 (94) | $\delta(^{10}\text{CH}_2)(18)$, $\alpha_1(\text{R}_1)(12)$, $\tau(\text{C}_2\text{-C}_{14})(11)$, v(C₂-N₈)(9) , $\tau(\text{C}_1\text{-C}_{10})(8)$, $\gamma(\text{C}_{14}\text{-H}_{16})(6)$, $\gamma(\text{C}_1\text{-H}_6)(4)$, $\nu(\text{C}_2\text{-C}_{14})(4)$ |
| v ₄₆ | 1122(32.0,1.6) 0.46 | 1072 | 1075 (33) | - | $\gamma(\text{C}_{14}\text{-H}_{16})(17)$, v(C₂-C₁₄)(15) , $\tau(\text{C}_1\text{-C}_{10})(11)$, $\nu(\text{C}_1\text{-C}_2)(8)$, $\nu(\text{C}_1\text{-N}_7)(7)$, $\nu(\text{C}_2\text{-N}_8)(6)$, $\alpha_2(\text{R}_1)(6)$, $\tau(\text{C}_2\text{-C}_{14})(4)$ |
| v ₄₇ | 1141(95.6,1.7) 0.52 | 1090 | 1098 (33) | - | $\delta(^{10}\text{CH}_2)(30)$, $\tau(\text{C}_1\text{-C}_{10})(11)$, $\tau(\text{C}_2\text{-C}_{14})(11)$, $\phi_2(\text{R}_2)(7)$, $\gamma(\text{C}_2\text{-H}_4)(6)$, $\nu(\text{C}_{29}\text{-O}_{31})(6)$ |
| v ₄₈ | 1147(174,3) 0.61 | 1095 | 1117 (33) | - | $\delta(^{10}\text{CH}_2)(30)$, $\tau(\text{C}_1\text{-C}_{10})(17)$, v(C₂₉-O₃₁)(15) , $\phi_2(\text{R}_2)(6)$, $\gamma(\text{C}_2\text{-H}_4)(5)$, $\delta(\text{C}_{29}\text{-O}_{31}\text{-H})(4)$, $\tau(\text{C}_2\text{-C}_{14})(3)$ |
| v ₄₉ | 1172(1.1,0.6) 0.67 | 1119 | - | - | $\gamma(\text{C}_{14}\text{-H}_{16})(25)$, $\delta(^{10}\text{CH}_2)(18)$, $\phi_2(\text{R}_2)(12)$, $\tau(\text{C}_1\text{-C}_{10})(7)$, $\gamma(\text{C}_2\text{-H}_4)(5)$, $\delta(^{26}\text{CH}_2)(4)$, $\delta(^{17}\text{CH}_2)(4)$, $\delta(^{23}\text{CH}_2)(4)$ |
| v ₅₀ | 1221(2.3,1.5) 0.28 | 1166 | 1139 (33) | - | $\tau(\text{C}_2\text{-C}_{14})(47)$, $\beta(\text{C}_{14}\text{-H}_{16})(22)$, $\tau(\text{C}_1\text{-C}_{10})(7)$, $\gamma(\text{C}_1\text{-H}_6)(5)$, $\gamma(\text{C}_{14}\text{-H}_{16})(5)$, $\delta(^{10}\text{CH}_2)(5)$ |
| v ₅₁ | 1239(3.1,1.6) 0.37 | 1183 | 1154 (38) | - | $\tau(\text{C}_1\text{-C}_{10})(31)$, $\delta(^{10}\text{CH}_2)(22)$, $\gamma(\text{C}_1\text{-H}_6)(13)$, $\tau(\text{C}_2\text{-C}_{14})(12)$, $\gamma(\text{C}_{14}\text{-H}_{16})(6)$, $\beta(\text{C}_1\text{-H}_6)(4)$, $\beta(\text{C}_{14}\text{-H}_{16})(4)$ |
| v ₅₂ | 1260(18.1,2.6) 0.42 | 1203 | 1202 (35) | - | $\tau(\text{C}_2\text{-C}_{14})(23)$, $\gamma(\text{C}_2\text{-H}_4)(17)$, $\delta(^{10}\text{CH}_2)(13)$, $\beta(\text{C}_{14}\text{-H}_{16})(7)$, $\phi_2(\text{R}_2)(7)$, $\alpha_1(\text{R}_1)(6)$, $\gamma(\text{C}_{14}\text{-H}_{16})(4)$ |
| v ₅₃ | 1268(101,0.9) 0.63 | 1211 | - | 1204 (88) | $\gamma(\text{C}_1\text{-H}_6)(22)$, $\delta(^{23}\text{CH}_2)(20)$, $\tau(\text{C}_1\text{-C}_{10})(17)$, $\phi_2(\text{R}_2)(15)$, $\alpha_1(\text{R}_1)(9)$, $\gamma(\text{C}_{14}\text{-H}_{16})(4)$ |
| v ₅₄ | 1272(26.1,1.9) 0.75 | 1215 | 1236 (38) | - | $\phi_2(\text{R}_2)(23)$, $\delta(^{26}\text{CH}_2)(20)$, $\gamma(\text{C}_1\text{-H}_6)(12)$, $\tau(\text{C}_1\text{-C}_{10})(11)$, $\gamma(\text{C}_{14}\text{-H}_{16})(8)$, $\alpha_1(\text{R}_1)(8)$, $\tau(\text{C}_2\text{-C}_{14})(5)$, $\gamma(\text{C}_2\text{-H}_4)(4)$ |
| v ₅₅ | 1282(21.4,2.6) 0.70 | 1224 | - | - | $\gamma(\text{C}_1\text{-H}_6)(28)$, $\gamma(\text{C}_2\text{-H}_4)(25)$, $\tau(\text{C}_1\text{-C}_{10})(10)$, $\delta(^{10}\text{CH}_2)(10)$, $\phi_2(\text{R}_2)(4)$ |
| v ₅₆ | 1304(8.7,1.1) 0.43 | 1245 | - | - | $\delta(\text{C}_{29}\text{-O}_{31}\text{-H})(40)$, $\delta(^{20}\text{CH}_2)(14)$, $\delta(^{17}\text{CH}_2)(9)$, $\beta(\text{C}_{14}\text{-H}_{16})(9)$, $\delta(^{23}\text{CH}_2)(8)$, $\gamma(\text{C}_2\text{-H}_4)(6)$, $\delta(^{26}\text{CH}_2)(5)$ |

| | | | | | |
|-----------------|-------------------------|------|---------------|--------------|---|
| v ₅₇ | 1316(9.7,1.1) 0.73 | 1257 | 1251 (60) | - | $\gamma(\text{C}_{14}\text{-H}_{16})(30)$, $\delta(^{20}\text{CH}_2)(25)$, $\beta(\text{C}_2\text{-H}_4)(13)$, $\delta(^{26}\text{CH}_2)(7)$, $\tau(\text{C}_2\text{-C}_{14})(6)$, $\gamma(\text{C}_2\text{-H}_4)(4)$, $\delta(^{23}\text{CH}_2)(4)$ |
| v ₅₈ | 1332(2.8,11.1) 0.75 | 1272 | - | 1277 (84) | $\delta(^{23}\text{CH}_2)(43)$, $\delta(^{20}\text{CH}_2)(19)$, $\beta(\text{C}_2\text{-H}_4)(7)$, $\delta(^{26}\text{CH}_2)(7)$, $\gamma(\text{C}_1\text{-H}_6)(6)$, $\alpha_1(\text{R}_1)(5)$, $\gamma(\text{C}_2\text{-H}_4)(4)$ |
| v ₅₉ | 1339(8.0,5.5) 0.63 | 1279 | - | - | $\gamma(\text{C}_2\text{-H}_4)(23)$, $\beta(\text{C}_2\text{-H}_4)(20)$, $\delta(^{17}\text{CH}_2)(13)$, $\delta(^{20}\text{CH}_2)(10)$, $\gamma(\text{C}_1\text{-H}_6)(9)$, $\alpha_1(\text{R}_1)(9)$, $\tau(\text{C}_1\text{-C}_{10})(6)$ |
| v ₆₀ | 1353(4.0,3.4) 0.75 | 1292 | - | - | $\gamma(\text{C}_{14}\text{-H}_{16})(21)$, $\delta(^{17}\text{CH}_2)(20)$, $\gamma(\text{C}_1\text{-H}_6)(12)$, $\gamma(\text{C}_2\text{-H}_4)(11)$, $\alpha_1(\text{R}_1)(7)$, $\delta(^{20}\text{CH}_2)(6)$, $\delta(^{23}\text{CH}_2)(6)$, $\tau(\text{C}_1\text{-C}_{10})(4)$, $\beta(\text{N}_7\text{-H}_9)(4)$ |
| v ₆₁ | 1362(21.1,1.1) 0.72 | 1301 | 1292 (53) | - | $\gamma(\text{C}_{14}\text{-H}_{16})(17)$, $\gamma(\text{C}_1\text{-H}_6)(16)$, $\delta(^{17}\text{CH}_2)(16)$, $\gamma(\text{C}_2\text{-H}_4)(9)$, $\delta(^{23}\text{CH}_2)(6)$, $\beta(\text{C}_1\text{-H}_6)(5)$, $\beta(\text{N}_8\text{-H}_5)(4)$, $\phi_2(\text{R}_2)(4)$ |
| v ₆₂ | 1381(27.9,5.7) 0.67 | 1319 | 1318 (68) | 1312 (90) | $\gamma(\text{C}_{14}\text{-H}_{16})(30)$, $\beta(\text{C}_1\text{-H}_6)(28)$, $\tau(\text{C}_2\text{-C}_{14})(13)$, $\gamma(\text{C}_1\text{-H}_6)(6)$, $\delta(^{10}\text{CH}_2)(5)$, $\beta(\text{C}_2\text{-H}_4)(5)$ |
| v ₆₃ | 1394(6.7,1.0) 0.65 | 1331 | 1327 (58) | - | $\phi_2(\text{R}_2)(22)$, $\alpha_1(\text{R}_1)(14)$, $\beta(\text{N}_8\text{-H}_5)(14)$, $\beta(\text{C}_1\text{-H}_6)(12)$, $\gamma(\text{C}_{14}\text{-H}_{16})(9)$, $\gamma(\text{C}_2\text{-H}_4)(7)$, $\beta(\text{N}_7\text{-H}_9)(4)$, $\delta(^{10}\text{CH}_2)(4)$ |
| v ₆₄ | 1397(4.9,0.5) 0.45 | 1334 | - | - | $\delta(^{20}\text{CH}_2)(28)$, $\delta(^{17}\text{CH}_2)(23)$, $\gamma(\text{C}_{14}\text{-H}_{16})(12)$, $\nu(\text{C}_{17}\text{-C}_{20})(8)$, $\nu(\text{C}_{20}\text{-C}_{23})(4)$, $\nu(\text{C}_{14}\text{-C}_{17})(4)$, $\gamma(\text{C}_2\text{-H}_4)(3)$ |
| v ₆₅ | 1416(106.2,2.1) 0.62 | 1352 | 1338 (50) | - | $\delta(^{26}\text{CH}_2)(13)$, $\tau(\text{C}_2\text{-C}_{14})(12)$, $\delta(^{23}\text{CH}_2)(10)$, $\gamma(\text{C}_2\text{-H}_4)(9)$, $\beta(\text{C}_2\text{-H}_4)(8)$, $\gamma(\text{C}_{14}\text{-H}_{16})(6)$, $\nu(\text{C}_{26}\text{-C}_{29})(4)$, $\nu(\text{C}_3\text{-N}_8)(4)$, $\phi_2(\text{R}_2)(4)$, $\nu(\text{C}_{23}\text{-C}_{26})(4)$, $\alpha_1(\text{R}_1)(3)$ |
| v ₆₆ | 1418(11.7,1.3) 0.75 | 1354 | - | - | $\gamma(\text{C}_2\text{-H}_4)(11)$, $\gamma(\text{C}_{14}\text{-H}_{16})(11)$, $\tau(\text{C}_2\text{-C}_{14})(11)$, $\alpha_1(\text{R}_1)(10)$, $\beta(\text{C}_2\text{-H}_4)(8)$, $\nu(\text{C}_3\text{-N}_8)(6)$, $\nu(\text{C}_3\text{-N}_7)(5)$, $\delta(^{26}\text{CH}_2)(5)$, $\delta(^{23}\text{CH}_2)(4)$, $\beta(\text{C}_1\text{-H}_6)(4)$, $\tau(\text{C}_1\text{-C}_{10})(4)$ |
| v ₆₇ | 1423(13.1,4.0) 0.37 | 1359 | - | - | $\gamma(\text{C}_1\text{-H}_6)(38)$, $\beta(\text{N}_7\text{-H}_9)(20)$, $\tau(\text{C}_1\text{-C}_{10})(10)$, $\beta(\text{N}_8\text{-H}_5)(7)$, $\gamma(\text{C}_2\text{-H}_4)(6)$, $\alpha_1(\text{R}_1)(5)$, $\nu(\text{C}_3\text{-O}_{15})(3)$ |
| v ₆₈ | 1461(16.5,6.4) 0.75 | 1395 | - | 1383 (86) | $\delta(^{26}\text{CH}_2)(93)$ |
| v ₆₉ | 1484(6.3,6.3) 0.75 | 1417 | 1414 (30) | - | $\delta(^{10}\text{CH}_2)(92)$ |
| v ₇₀ | 1488(1.3,21.8) 0.58 | 1421 | 1430 (45) | - | $\delta(^{17}\text{CH}_2)(47)$, $\delta(^{20}\text{CH}_2)(43)$, $\delta(^{23}\text{CH}_2)(6)$ |
| v ₇₁ | 1493(0.6,1.3) 0.50 | 1426 | - | 1439 (95) | $\delta(^{23}\text{CH}_2)(54)$, $\delta(^{17}\text{CH}_2)(31)$, $\delta(^{20}\text{CH}_2)(11)$ |
| v ₇₂ | 1511(10.4,0.6) 0.70 | 1443 | 1430 (45) | 1448 (94) | $\delta(^{20}\text{CH}_2)(43)$, $\delta(^{23}\text{CH}_2)(37)$, $\delta(^{17}\text{CH}_2)(18)$ |
| v ₇₃ | 1804(866,15.1) 0.38 | 1722 | 1689 (100) | - | $\nu(\text{C}_3=\text{O}_{15})(60)$, $\alpha_1(\text{R}_2)(12)$, $\alpha_1(\text{R}_1)(8)$, $\nu(\text{C}_3\text{-N}_8)(8)$, $\nu(\text{C}_3\text{-N}_7)(7)$ |

| | | | | | |
|-----------------|--------------------------|------|---------------|--------------|--|
| v ₇₄ | 1813(288.4,8.8) 0.23 | 1731 | 1706 (100) | - | v(C ₂₉ =O ₃₀)(80), δ(C ₂₆ -C ₂₉ -OH)(6), v(C ₂₆ -C ₂₉)(6), δ(C ₂₉ -O ₃₁ -H)(4), v(C ₂₉ -O ₃₁)(3) |
| v ₇₅ | 2995(22.2,97.4) 0.04 | 2860 | - | - | v(C ₂₀ -H ₂₁)(61), v(C ₂₀ -H ₂₂)(34) |
| v ₇₆ | 3010(25.2,89.4) 1.17 | 2875 | 2837 (30) | - | v(C ₂ -H ₄)(87), φ ₂ (R ₂)(4), v(C ₂₀ -H ₂₂)(3) |
| v ₇₇ | 3019(11.5,56.4) 0.23 | 2883 | 2854 (30) | - | v(C ₁₇ -H ₁₉)(57), v(C ₁₇ -H ₁₈)(17), v(C ₂₀ -H ₂₁)(13), v(C ₂₀ -H ₂₂)(9) |
| v ₇₈ | 3022(13.5,64.4) 0.57 | 2886 | 2868 (33) | - | v(C ₂₀ -H ₂₂)(44), v(C ₁₇ -H ₁₈)(24), v(C ₂₀ -H ₂₁)(19), v(C ₂₃ -H ₂₄)(5), v(C ₁₇ -H ₁₉)(4) |
| v ₇₉ | 3028(3.8,185.8) 0.02 | 2892 | 2897 (35) | - | v(C ₂₆ -H ₂₇)(44), v(C ₂₆ -H ₂₈)(40), v(C ₂₃ -H ₂₄)(7), v(C ₂₃ -H ₂₅)(6) |
| v ₈₀ | 3040(27.9,27.4) 0.03 | 2903 | - | - | v(C ₂₃ -H ₂₄)(41), v(C ₂₃ -H ₂₅)(41), v(C ₂₆ -H ₂₇)(8), v(C ₂₆ -H ₂₈)(7) |
| v ₈₁ | 3047(12.2,27.8) 0.17 | 2910 | - | - | v(C ₁₄ -H ₁₆)(57), v(C ₁₇ -H ₁₈)(23), v(C ₁₇ -H ₁₉)(6), v(C ₂₃ -H ₂₅)(4) |
| v ₈₂ | 3050(13.3,154) 0.09 | 2913 | - | - | v(C ₁₀ -H ₁₂)(71), v(C ₁₀ -H ₁₁)(17), v(C ₁ -H ₆)(4) |
| v ₈₃ | 3052(1.8,62.9) 0.75 | 2915 | - | - | v(C ₂₆ -H ₂₈)(36), v(C ₂₆ -H ₂₇)(32), v(C ₁₄ -H ₁₆)(11), v(C ₂₃ -H ₂₄)(9), v(C ₂₃ -H ₂₅)(7) |
| v ₈₄ | 3064(12.2,22.1) 0.21 | 2926 | 2920 (43) | 2921 (71) | v(C ₃ -N ₈)(29), v(C ₁₇ -H ₁₈)(27), v(C ₁₄ -H ₁₆)(25), v(C ₂₆ -H ₂₈)(4), v(C ₂₆ -H ₂₇)(3), v(C ₁ -H ₆)(3) |
| v ₈₅ | 3068(30,51) 0.44 | 2930 | 2933 (43) | 2930 (64) | v(C ₁ -H ₆)(80), v(C ₁₀ -H ₁₁)(6), φ ₂ R ₂ (5) |
| v ₈₆ | 3081(49,6.8) 0.67 | 2942 | 2968 (33) | 2970 (43) | v(C ₂₃ -H ₂₄)(36), v(C ₂₃ -H ₂₅)(35), v(C ₂₆ -H ₂₈)(9), v(C ₂₆ -H ₂₇)(9), v(C ₂₀ -H ₂₂)(3) |
| v ₈₇ | 3116(11,104) 0.45 | 2976 | - | 2979 (34) | v(C ₁₀ -H ₁₁)(69), v(C ₁₀ -H ₁₂)(21), δ(¹⁰ CH ₂)(5) |
| v ₈₈ | 3641(38.3,74.2) 0.19 | 3477 | 3309 (68) | - | v(N ₈ -H ₅)(99) |
| v ₈₉ | 3650(44.1,130.1) 0.21 | 3486 | 3360 (55) | - | v(N ₇ -H ₉)(98) |
| v ₉₀ | 3759(71.7,180) 0.26 | 3590 | 3747 (3) | - | v(O ₃₁ -H ₃₂)(100) |

The numbers (in bracket) after the modes are the % potential energy calculated using normal coordinate analysis. The abbreviations are - v = stretching, ω = wagging, τ = twisting, ρ = rocking, σ = scissoring, γ = out-of-plane deformation, β = in-plane deformation, α = planar ring deformation, φ = non-planar ring deformation, δ = deformation. The mode in bold letters in the last column corresponds to the assigned mode.

*Calculated wave numbers below 1000 cm⁻¹ were scaled by the scale factor 0.9786 and those above 1000 cm⁻¹ by the scale factor 0.9550. [34].

4.4.1 O-H modes (3 modes)

The v(O-H) mode is identified as the computed wavenumber 3590 (v₉₀) cm⁻¹ corresponding to the mode v(O₃₁-H). The O-H stretching vibrations are pure and highly localized modes. The wavenumber 635

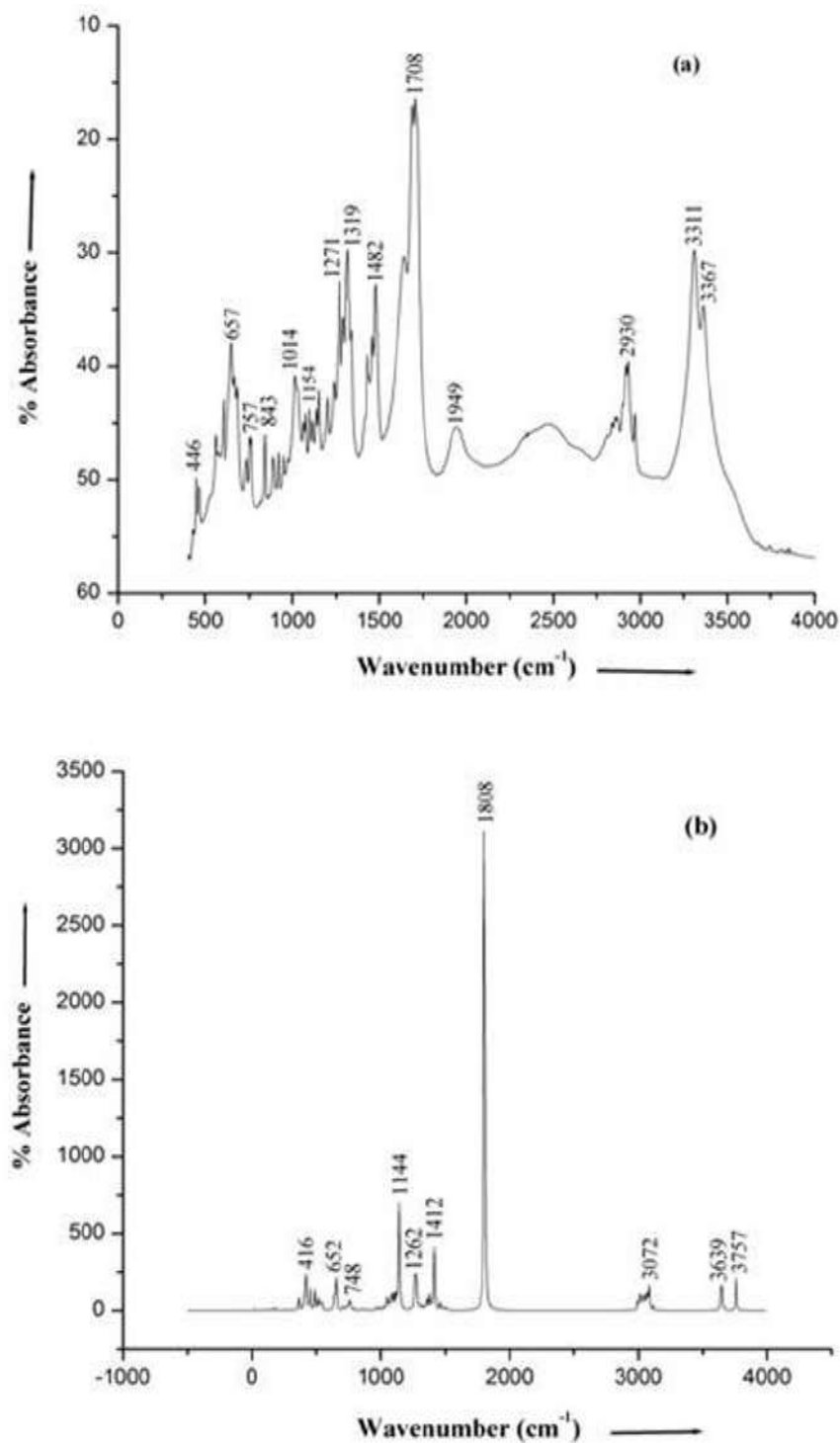


Fig 2. (a) Observed (b) Calculated IR spectra of Biotin (C-I)

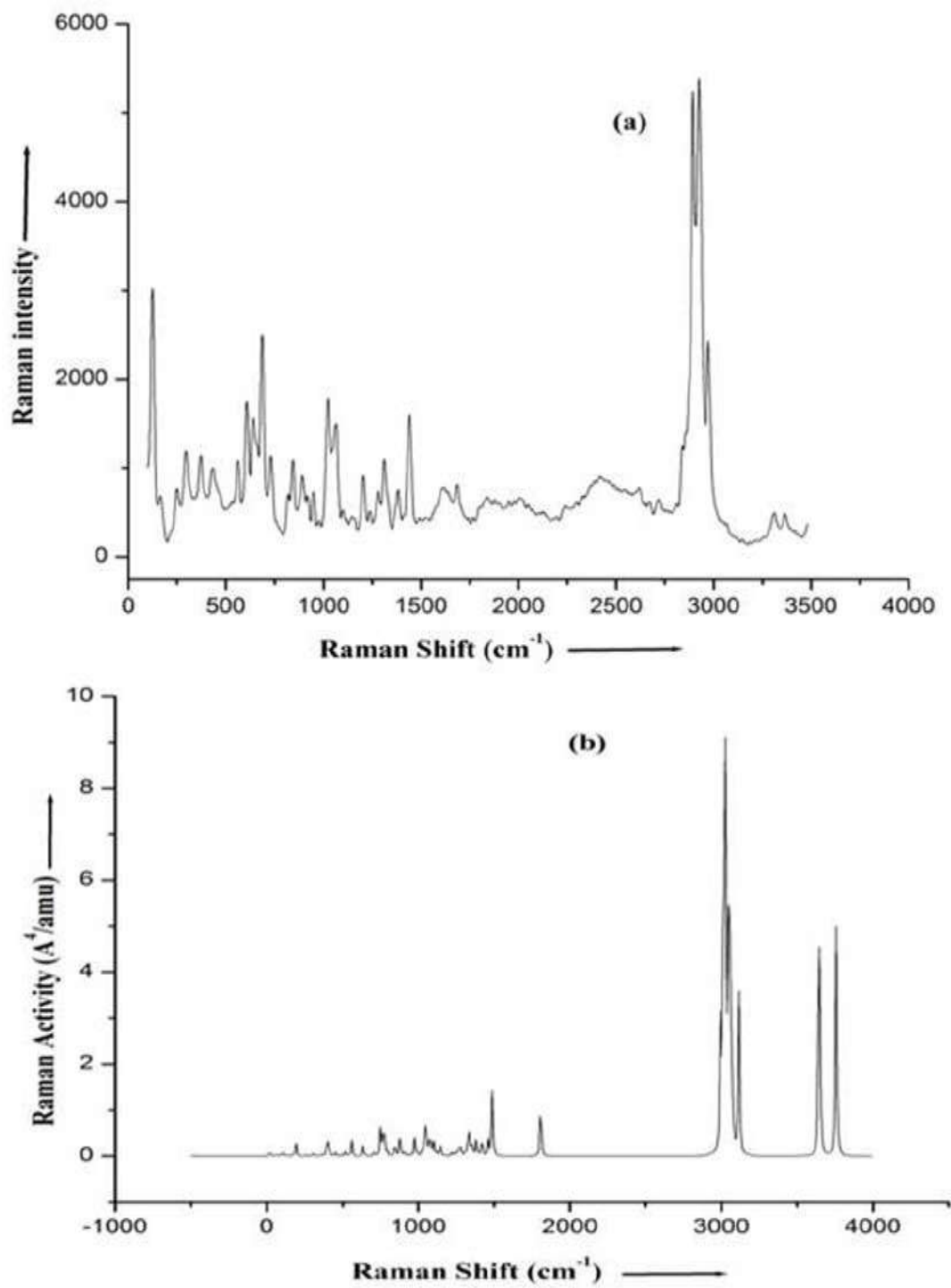


Fig 3. (a) Observed (b) Calculated Raman spectra of Biotin (C-I)

(ν_{25}) cm^{-1} corresponds to the mode $\tau(\text{O}_{31}\text{-H})$. The torsional modes are strongly coupled with many other modes. Assignment of the angle bending mode $\alpha(\text{C-O-H})$ is complicated due to coupling of these modes with the other modes. The mode ν_{56} corresponds to the $\alpha(\text{C}_{29}\text{-O-H})$ mode with the computed wavenumber 1245 cm^{-1} .

4.4.2 CH_2 group modes (30 modes)

The CH_2 stretching vibrations lie in the region $2800\text{--}3000 \text{ cm}^{-1}$. These bands are found to be unaffected by the nature of the substituent and are pure and highly localized modes. The $^{10}\text{CH}_2^*$ group has its stretching modes at 2913 cm^{-1} (ν_{82}) and 2976 cm^{-1} (ν_{87}) corresponding to the modes ν_s and ν_{as} , respectively whereas $^{17}\text{CH}_2$, $^{20}\text{CH}_2$, $^{23}\text{CH}_2$ and $^{26}\text{CH}_2$ groups have anti-symmetric stretching modes at 2926 cm^{-1} (ν_{84}), 2886 cm^{-1} (ν_{78}), 2942 cm^{-1} (ν_{86}) and 2915 cm^{-1} (ν_{83}), respectively. The symmetric stretching modes of $^{17}\text{CH}_2$, $^{20}\text{CH}_2$, $^{23}\text{CH}_2$ and $^{26}\text{CH}_2$ groups are strongly coupled and are identified as the calculated scaled wavenumbers 2883 cm^{-1} (ν_{77}), 2860 cm^{-1} (ν_{75}), 2903 cm^{-1} (ν_{80}) and 2892 cm^{-1} (ν_{79}). Out of the five scissoring modes of the CH_2 groups the $^{10}\text{CH}_2$ scissoring mode is calculated to have magnitude 1417 cm^{-1} (ν_{69}), the $^{17}\text{CH}_2$ and $^{20}\text{CH}_2$ scissoring modes are found at 1421 cm^{-1} (ν_{70}) and 1443 cm^{-1} (ν_{72}) while the $^{23}\text{CH}_2$ and $^{26}\text{CH}_2$ scissoring modes have magnitudes 1426 cm^{-1} (ν_{71}) and 1395 cm^{-1} (ν_{68}), respectively. The five normal modes of vibration arising due to the wagging of the CH_2 groups have wavenumbers 1183 cm^{-1} (ν_{51}), 1301 cm^{-1} (ν_{61}), 1334 cm^{-1} (ν_{64}), 1211 cm^{-1} (ν_{53}) and 1352 cm^{-1} (ν_{65}) and correspond to the modes $\omega(^{10}\text{CH}_2)$, $\omega(^{17}\text{CH}_2)$, $\omega(^{20}\text{CH}_2)$, $\omega(^{23}\text{CH}_2)$ and $\omega(^{26}\text{CH}_2)$, respectively. The $^{17}\text{CH}_2$ and $^{20}\text{CH}_2$ wagging modes are strongly coupled with each other as is evident from the Table 4. The wavenumbers 932 cm^{-1} (ν_{36}) and 890 cm^{-1} (ν_{35}) correspond to the $\rho(^{10}\text{CH}_2)$ and $\rho(^{17}\text{CH}_2)$ modes, 721 cm^{-1} (ν_{27}) to the $\rho(^{20}\text{CH}_2)$ mode, 777 cm^{-1} (ν_{32}) to the $\rho(^{23}\text{CH}_2)$ and 970 cm^{-1} (ν_{38}) to the $\rho(^{26}\text{CH}_2)$ mode. The twisting mode of the $^{10}\text{CH}_2$, $^{17}\text{CH}_2$, $^{20}\text{CH}_2$, $^{23}\text{CH}_2$ and $^{26}\text{CH}_2$ groups are found to have magnitudes 1090 cm^{-1} (ν_{47}), 1292 cm^{-1} (ν_{60}), 1257 cm^{-1} (ν_{57}), 1272 cm^{-1} (ν_{58}) and 1215 cm^{-1} (ν_{54}) cm^{-1} , respectively. The assignments of these modes are complicated as these are highly coupled modes.

4.4.3 N-H/C-H modes (15 modes)

The modes ν_{89} , ν_{67} , ν_{17} , calculated to have the wavenumbers 3486 , 1359 and 406 cm^{-1} , correspond to the modes $\nu(\text{N}_7\text{-H})$, $\beta(\text{N}_7\text{-H})$ and $\gamma(\text{N}_7\text{-H})$, respectively. Out of these 3 modes β and γ modes (ν_{67} and ν_{17}) appear to be strongly coupled with the other modes. The N-H stretching vibration is a pure and highly localized mode. Similarly, the modes ν_{88} , ν_{63} , ν_{19} , calculated to have the wavenumbers 3477 , 1331 and 444 cm^{-1} , correspond to $\nu(\text{N}_8\text{-H})$, $\beta(\text{N}_8\text{-H})$ and $\gamma(\text{N}_8\text{-H})$ modes, respectively.

The wavenumbers 2876 (ν_{85}), 1320 (ν_{81}) and 1263 (ν_{76}) cm^{-1} correspond to the modes $\nu(\text{C}_1\text{-H})$, $\nu(\text{C}_{14}\text{-H})$ and $\nu(\text{C}_2\text{-H})$, respectively. Out of the three, in-plane bending modes, the mode $\beta(\text{C}_1\text{-H})$ is calculated to have magnitude 1319 (ν_{62}) cm^{-1} while the wavenumbers 1279 (ν_{59}) and 1166 (ν_{50}) cm^{-1} correspond to the modes $\beta(\text{C}_2\text{-H})$ and $\beta(\text{C}_{14}\text{-H})$, respectively. The wavenumbers 1224 (ν_{55}), 1203 (ν_{52}) and 1119 (ν_{49}) cm^{-1} are assigned to the modes $\gamma(\text{C}_1\text{-H})$, $\gamma(\text{C}_2\text{-H})$ and $\gamma(\text{C}_{14}\text{-H})$, respectively.

4.4.4 C-O(H) group modes (3 modes)

The three normal modes of vibration arise due to the C-O(H) group and these are $\nu(\text{C-O(H)})$, C-C-O angle bending mode (α) and torsion about the C-C bond (τ). In the present case, an O(H) group is attached at the site C_{29} , hence, there are $\nu(\text{C-O(H)})$, $\tau(\text{C-CO(H)})$ and $\alpha(\text{C-C-O(H)})$ modes corresponding

*ⁿC means C atom with number n

to this group. The modes ν_{48} , ν_{20} , ν_5 with the wavenumbers 1095 , 481 and 69 cm^{-1} correspond to the $\nu(\text{C}_1\text{-O(H)})$, $\alpha(\text{C}_{26}\text{-C}_{29}\text{-O(H)})$ and $\tau(\text{C}_{26}\text{-C}_{29}\text{-O(H)})$, respectively.

4.4.5 C=O modes (6 modes)

The modes ν_{73} and ν_{74} at the wavenumbers 1722 cm^{-1} and 1731 cm^{-1} correspond to the $\nu(\text{C}=\text{O})$ vibrations. The higher frequency mode of these is assigned to the $\text{C}_{29}=\text{O}$ stretching vibrational mode, while the lower one represents the $\text{C}_3=\text{O}$ stretching vibrational mode. The two in-plane bending modes are calculated to have magnitudes $550 (\nu_{23})$ and $621 (\nu_{24})\text{ cm}^{-1}$ corresponding to the modes $\beta(\text{C}_3=\text{O})$ and $\beta(\text{C}_{29}=\text{O})$, respectively. The wavenumbers $744 (\nu_{30})$ and $509 (\nu_{21})$ are assigned to the modes $\gamma(\text{C}_3=\text{O})$ and $\gamma(\text{C}_{29}=\text{O})$. All of these modes are strongly coupled modes.

4.5.6 Ring modes (18 modes)

The ring modes can be divided into three categories: (i) Ureido ring modes (R_1) (9 modes); (ii) Thiophene ring modes (R_2) (8 modes) and (iii) Butterfly mode (1 mode).

(i) Ureido ring (R_1) (9 modes)

The present calculations place the five stretching modes of the ureido ring at $827 (\nu_{33})$, $955 (\nu_{37})$, $1036 (\nu_{43})$, $1056 (\nu_{45})$ and $1354 (\nu_{66})$ wavenumbers corresponding to the modes $\nu(\text{C}_1-\text{C}_2)$, $\nu(\text{N}_7-\text{C}_3)$, $\nu(\text{C}_1-\text{N}_7)$, $\nu(\text{N}_8-\text{C}_2)$ and $\nu(\text{C}_3-\text{N}_8)$, respectively. The mode (ν_{37}) is the breathing mode of the ureido ring. Out of the two planar ring deformations, the first one is assigned at the wavenumber $734 (\nu_{28})$, while the second is assigned at the wavenumber $695 (\nu_{26})\text{ cm}^{-1}$. The two normal modes of vibration corresponding to the non-planar ring deformations are calculated to have magnitudes $299 (\nu_{13})$ and $146 (\nu_9)\text{ cm}^{-1}$. All the 9 normal modes of the ureido ring are strongly coupled with the other modes.

(ii) Thiophene ring (R_2) (8 modes)

The 8 modes of vibration due to the ring R_2 are the 4 stretching modes- $\nu(\text{C}_1-\text{C}_{10})$, $\nu(\text{C}_{10}-\text{S}_{13})$, $\nu(\text{S}_{13}-\text{C}_{14})$ and $\nu(\text{C}_2-\text{C}_{14})$ modes; 2 in-plane ring deformation modes and 2 out-of-plane ring deformation modes. The C-S bond is highly polarisable and hence, it produces stronger spectral activity. The C-S stretching vibration is expected in the region $800-685\text{ cm}^{-1}$ [37]. The present calculation places the $\nu(\text{C}_{10}-\text{S}_{13})$ and $\nu(\text{S}_{13}-\text{C}_{14})$ modes at $736 (\nu_{29})$ and $757 (\nu_{31})\text{ cm}^{-1}$. The wavenumbers $976 (\nu_{39})$ and $1072 (\nu_{46})\text{ cm}^{-1}$ correspond to the stretching modes $\nu(\text{C}_1-\text{C}_{10})$ and $\nu(\text{C}_2-\text{C}_{14})$, respectively. The two in-plane ring deformation modes are calculated to have magnitudes $430 (\nu_{18})$ and $354 (\nu_{14})\text{ cm}^{-1}$. The wavenumbers $57 (\nu_4)$ and $23 (\nu_2)\text{ cm}^{-1}$ are found to two out-of-plane ring deformation modes of the thiophane ring (R_2).

(iii) Butterfly mode (R_1-R_2) (1 mode)

There is a single butterfly mode. The mode ν_7 having wavenumber 108 cm^{-1} corresponds to this vibration.

4.4.7 C-C modes (15 modes)

The $\text{C}_{14}-\text{C}_{17}$, $\text{C}_{17}-\text{C}_{20}$, $\text{C}_{20}-\text{C}_{23}$, $\text{C}_{23}-\text{C}_{26}$ and $\text{C}_{26}-\text{C}_{29}$ bonds give rise to 15 normal modes of vibration as: 5 $\nu(\text{C}-\text{C})$, 5 $\tau(\text{C}-\text{C})$ and 5 $\alpha(\text{C}/\text{S}-\text{C}-\text{C})$ modes. The wavenumbers $861 (\nu_{34})$, $990 (\nu_{40})$, $1004 (\nu_{41})$, $1024 (\nu_{42})$ and $1051 (\nu_{44})$ correspond to the C-C stretching vibrations. The lowest frequency mode of these is assigned as the $\text{C}_{26}-\text{C}_{29}$ stretching vibrational mode, while the lowest but one and the middle one represent the $\text{C}_{17}-\text{C}_{20}$ and $\text{C}_{20}-\text{C}_{23}$ stretching vibrational modes and the highest but one and the highest modes are assigned as the $\text{C}_{23}-\text{C}_{26}$ and $\text{C}_{14}-\text{C}_{17}$ stretching vibrational modes. The five twisting modes are calculated to have magnitudes $17\text{ cm}^{-1} (\nu_1)$, $29\text{ cm}^{-1} (\nu_3)$, $95\text{ cm}^{-1} (\nu_6)$, $132\text{ cm}^{-1} (\nu_8)$ and $173\text{ cm}^{-1} (\nu_{10})$ corresponding to the modes $\tau(\text{C}_{14}-\text{C}_{17})$, $\tau(\text{C}_{23}-\text{C}_{26})$, $\tau(\text{C}_{26}-\text{C}_{29})$, $\tau(\text{C}_{20}-\text{C}_{23})$ and $\tau(\text{C}_{17}-\text{C}_{20})$, respectively. Out of the five angle bending modes of the C/S-C-C groups, the modes $\alpha(\text{S}_{13}-\text{C}_{14}-\text{C}_{17})$ and $\alpha(\text{C}_{23}-\text{C}_{26}-\text{C}_{29})$ are calculated to have scaled magnitudes $204 (\nu_{11})$ and $204 (\nu_{12})\text{ cm}^{-1}$, $\alpha(\text{C}_{20}-\text{C}_{23}-\text{C}_{26})$ is assigned at $386 (\nu_{15})\text{ cm}^{-1}$, while $\alpha(\text{C}_{14}-\text{C}_{17}-\text{C}_{20})$ and $\alpha(\text{C}_{17}-\text{C}_{20}-\text{C}_{23})$ have the magnitudes $396 (\nu_{16})$ and $528\text{ cm}^{-1} (\nu_{22})$, respectively.

5 Conclusions

The detailed experimental and theoretical analyses of the vibrational spectrum of the most stable

conformer of biotin (C-I) have been studied for the first time. The optimized geometric parameters were seen to be in good agreement with the experimental data. The carbon atom C₃ of the ureido ring (R₁), directly attached to the oxygen atom with a double bond, bears highest APT charges. A complete vibrational assignments of the observed frequencies have been made on the basis of PEDs. Reasonably good agreement between the calculated and observed vibrational frequencies suggests the advantage of using the higher basis set for the present calculations.

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