Ethyl(S)-(−)-4-chloro-3-hydroxybutyrate Study by D.F.T

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Abstract: Active chiralS acids and esters are very important as chiral building blocks in pharmaceutical industries. Its enantiomers are precursors, being important to starting materials like enzyme inhibitors. The asymmetric reduction of ethyl 4-chloro-3-oxobutanoate using glucose, glycerol, or 2-propanol as a co-substrate in production of (S) and (R) 4-chloro-3-hydroxybutyrate was achieved by Hunt et.al. [Hunt, 1995]. Many studies have been reported on the microbial or enzymatic asymmetric reduction of similar acids and esters. Optically active 4-chloro-3-hydroxybutyrate, which is a chiral chloroalcohol having a C₂ structural skeleton, are employed in the synthesis of biologically and pharmacologically important compounds like (R)-carnitine, (R)-4-hydroxy-2-pyrrolidone. These are a physiologically significant agent, involved in the metabolism of long-chain fatty acids through the mitochondrial membrane in the human body. One such important molecule is Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate. Though hazardous to eyes and skin, it is useful as chiral building blocks for the synthesis of chiral pharmaceuticals, insect pheromones and others. The 4-chloro-3-hydroxybutyrate is synthesized from natural products like L-malic acid, dimethyl L-malic acid, l-ascorbic acid or L-asparatic acid [Suzuki, 1999], and synthesized further by microbial reduction with subsequent substitutions.

Keywords: Density Functional Theory, IR, Raman, Electronic Parameter, Thermodynamic parameter, Molecular Orbital, MESP.

I. INTRODUCTION

We present conformational and vibrational analysis of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate (C₆H₁₁O₃Cl). A broad IR band near 3450 cm⁻¹ is presumably due to the bonded O-H stretch. The C=O stretching mode is observed near 1729 cm⁻¹. The shift of these bands though not much (about 4% and 2% respectively) indicates that both the groups are involved in forming a dimer of the type O-H•••O=C hydrogen bond. Another IR band due to C=O stretch is observed at 1630 cm⁻¹. The proposed dimer model consists of four dimers arising from the combination of monomer conformers but unlike the one proposed for (R)-(+) Methylsuccinic acid there is a lack of local centre of inversion and hence the mutual exclusion rule is not satisfied because two IR bands are attributed to C=O vibration[1]. It will be shown that the most stable dimer has a population of ~90% while the remaining four have 10%. We do not rule out the existence of monomers as independent species completely as most of the dimer and monomer frequencies are nearer to each other.

A. Results and Discussion

1) Monomer and Dimer Analysis

![Molecular structure of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate](Fig1.1: Molecular structure of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate)

The molecular structure of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate is shown in Fig.

a) The experimental IR and Raman spectra, as shown in Fig1.2, are characterized by band features not amenable to straightforward spectral interpretation.
The IR region 3500 – 2500 cm\(^{-1}\) is dominated by broad structureless absorption with identifiable peaks at 3452 and 2982 cm\(^{-1}\). Further, there is an intense and rather broad absorption band near 1730 cm\(^{-1}\). Other absorption bands are somewhat sharp but covered in broad envelope with one isolated broad band near 1400-900 cm\(^{-1}\). The characteristic CH, CH\(_2\), CH\(_3\) and CC bands are all identified in absorption spectrum and correlated in the Raman spectrum. The bands are diffused and lumpy in nature because of the intermolecular influences.[2] In all the previous chapters where we have identified such similar characters in the vibration spectra in molecules like (R)-(−)-2-Pyrrolidinemethanol, (R)-(−)- Methylsuccinic acid, we have accounted for a DFT hydrogen bonded dimer model satisfactorily explaining the features. The down-shifted bands near 3430 and 1730 cm\(^{-1}\) are evidences in itself that the O-H and C=O are participating into forming a hydrogen bond of the type O-H…O=C bond. In molecules (R)-(−)-Methylsuccinic acid and (S)-(−)- Bromo-3-chloropropionic acid, we have seen the bands due to C=O stretching, appearing mutually exclusive in IR and Raman as asymmetric and symmetric modes near 1700 and 1650 cm\(^{-1}\). But unlike in the molecules (S)-(−)-Bromo-3-phenylpropionic acid and (R)-(−)- Methylsuccinic acid as discussed in Chapter 5 and 6 respectively, here we have a Raman mode at the same position as IR near 1730 cm\(^{-1}\), which rules out the idea that the molecule may form a centre of inversion upon hydrogen bonding. Investigation of the basis of these aspects we propose both monomer and dimer model to explain the observed spectra.

To investigate the structure of monomers we performed a relaxed potential energy surface scan (PES) at RHF/3-21G level of theory to confirm the orientation of O-H and C-Cl with respect to the skeleton of the molecule, we simultaneously varied the dihedral angle C5-C2*-C1-Cl16 (\(\tau_1\)) and C5-C2*-O17-H18 (\(\tau_2\)) (where C* refers to the carbon atom at chiral centre in the molecule C\(_6\)H\(_{11}\)O\(_2\)Cl).

![Fig. 1.2: Experimental IR and Raman spectra of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate](image)

We found three conformers on the PES curves as shown in Fig. 1.3. We further optimized the structures of the three conformers by performing harmonic frequency analysis at B3LYP/6-311+G(d,p) level by taking the PES results at RHF/3-21G level as input. The calculations yielded three conformers called \(C_1\), \(C_2\), and \(C_3\) that are shown in Fig. 1.4 (a), (b) and (c). The \(C_1\) is the most stable conformer with a population of 82.8%; the second most stable conformer is \(C_2\) with a population of 9.6%, being separated from \(C_1\) by 1.281 kcal/mol. The least populated conformer \(C_3\) with ~7% is separated from \(C_1\) by 1.427 kcal/mol. The Relative Gibbs energies and populations computed at B3LYP/6-31+G(d,p) level are given in Table 1.1. In Table 1.2 we present the optimized geometrical parameters of all the three conformers \(C_1\), \(C_2\), and \(C_3\).

From the conformers structures we see that the hydroxyl O-H is always oriented close to the carbonyl ‘O’. A possibility that the attraction here could be intra-molecular type cannot be ruled out. Thus we tried to model the hydrogen bonding considering the O-H…O=C type with-in the hydroxyl and carbonyl monomers of the same monomer. The energies for this modeling are the same as the ones presented in Table 1.1 for all the three conformers, and hence the frequencies are also reproduced.
Table 1.1: Conformers and their Relative Gibbs free energies, Boltzmann populations of conformers of Ethyl (S)-(-)-4-chloro-3-hydroxybutyrate

| Conformer | Relative ∆G (kcal/mol) | Population (%) |
|-----------|------------------------|----------------|
| C₁        | 0.0                    | 82.79          |
| C₂        | 1.281                  | 09.67          |
| C₃        | 1.427                  | 07.54          |

Fig. 1.3: PES scan curves for dihedral angles C5-C2*-C1-C16 and C5-C2*-O17-H18 yielding the most stable conformers C₁, C₂ and C₃.

(a): C5-C2-C1-C16= -66°, C5-C2-O17-H18= 57°
(b): C5-C2-C1-C16=55°, C5-C2-O17-H18=55°
(c): C5-C2-C1-C16= -168°, C5-C2-O17-H18=63°

Fig. 1.4: Conformers of Ethyl (S)-(-)-4-chloro-3-hydroxybutyrate at B3LYP/6-311+G(d,p) level.
Table 1.2: Optimized geometrical parameters of the conformers $C_1$, $C_2$, $C_3$.

| Parameters | Conformers |
|------------|------------|
| Bond Length (Å) | $C_1$ | $C_2$ | $C_3$ |
| C1-C2 | 1.525 | 1.523 | 1.522 |
| C2-C5 | 1.533 | 1.537 | 1.540 |
| C5-C7 | 1.512 | 1.513 | 1.516 |
| C10-C11 | 1.513 | 1.515 | 1.515 |
| C7-O20 | 1.222 | 1.222 | 1.341 |
| C10-O20 | 1.455 | 1.455 | 1.455 |
| C2-H6 | 1.098 | 1.105 | 1.100 |
| C1-H3/H4 | 1.089 | 1.090 | 1.091 |
| C5-H8/H9 | 1.096 | 1.096 | 1.098 |
| C10-H12/H13 | 1.091 | 1.093 | 1.094 |
| C11-H14/H15/H21 | 1.092 | 1.094 | 1.094 |
| C2-O17 | 1.422 | 1.415 | 1.417 |
| O17-H18 | 0.968 | 0.972 | 0.970 |
| C1-C16 | 1.814 | 1.817 | 1.811 |
| C7-O19 | 1.214 | 1.222 | 1.220 |

| Bond Angle (deg) |
| C2-C1-C16 | 112.0 | 114.1 | 112.4 |
| C1-C2-C5/C2-C5-C7 | 112.8 | 112.3 | 112.2 |
| C5-C7-O20 | 111.9 | 112.0 | 111.6 |
| C7-O20-C10 | 116.9 | 116.8 | 116.8 |
| C11-C10-O20 | 107.5 | 107.4 | 107.5 |
| H4-C1-H3 | 109.6 | 109.8 | 109.9 |
| C2-C1-H3 | 111.3 | 109.2 | 110.9 |
| C2-C1-H4 | 109.6 | 110.6 | 110.1 |
| C1-C2-H6 | 108.5 | 104.6 | 108.8 |
| C5-C7-O19 | 124.6 | 124.6 | 124.8 |
| O20-C7-O19 | 123.2 | 123.2 | 123.4 |
| C2-O17-H18 | 106.4 | 106.7 | 106.7 |

| Dihedral Angle (deg) |
| C5-C2-C1-C16 | -66.09 | 55.85 | -168.3 |
| C5-C2-O17-H18 | 57.18 | 54.40 | 63.02 |

Table 1.3: Relative Gibbs free energy and Boltzmann populations of four dimer species.

| Dimer | Monomer Pair | Relative $\Delta G$ (kcal/mol) | Population (%) |
|-------|--------------|-------------------------------|----------------|
| $D_1$ | $C_1$ with $C_1$ | 0.00 | 90.67 |
| $D_2$ | $C_1$ with $C_2$ | 1.703 | 5.21 |
| $D_3$ | $C_1$ with $C_3$ | 1.889 | 3.81 |
| $D_4$ | $C_2$ with $C_2$ | 3.401 | 0.31 |

In the next step we computed four dimer structures as -O-H•••O=C hydrogen bonded dimers from the three monomers. The four dimers $D_i$ ($i=1,2,3,4$) with relative Gibbs free energies and populations are presented in Table 7.3. The most stable dimer $D_1$ is the most populated at ~91%. It is noted that the dimers $D_2$ and $D_3$ thinly populated while $D_4$ is negligible. In Fig. 7.5 we show the most stable intra-molecular monomer in comparison with the most stable inter-molecular dimer labelled with respective H•••O distances. The intra and inter-molecular hydrogen bonding parameters are given in Table 1.4.
Fig. 1.5: Computed monomer and *inter*-molecular hydrogen bonded dimer with geometrical parameters of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate.

Table 1.4: Computed *intra*- and *inter*-molecular hydrogen bonding geometrical parameters of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate.

|                  | X-H***Y | X-H (Å) | H***Y (Å) | X***Y (Å) | ∠X-H***Y (Deg) |
|------------------|---------|---------|-----------|-----------|----------------|
| **Intra-molecular** |         |         |           |           |                |
| O–H***O=C monomer | 0.973   | 2.042   | 3.015     | 134       |                |
| **Inter-molecular** |         |         |           |           |                |
| O–H***O=C dimer   | 0.973   | 1.872   | 2.845     | 173       |                |

*Standard Values 0.969 2.724 3.694 -

In comparison we may say that the *inter*-molecular hydrogen bonded dimer agree better with the hydrogen bonding criteria, but we cannot rule out the possibility of *intra*- molecular monomer as well because the frequency correlation of monomer is also agreement with the observed which we will show in the next Section 1.2.2. This dilemma could be answered in some rigorous concentration dependent solution-phase IR spectral measurements. However, it has not been possible to ascertain by dimer calculations only as to which type of bonding is the determinant factor for the observed spectral features. Thus for tentative assignments we consider both *intra*- and *inter*-molecular hydrogen bonding. In nature *intra*-molecular hydrogen bonds are strong in comparison to *inter*-molecular hydrogen bonds. The H***O bond distances in both types fall under the strong hydrogen bonding criteria but it is the *inter*-molecular type that is more favoured. The shift in the O-H and C=O frequency is only −4% and 2% respectively, which contradicts the strength of the strong hydrogen bonding. Thus we characterize this as weak *inter*-molecular hydrogen bonding in Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate.
2) **Vibrational Analysis:** Observed IR and Raman spectrum of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate are presented in Fig. 1.2.

For a good agreement between experimental and theoretical spectra, we have plotted Boltzmann population-weighted IR spectra of monomers and dimers and are presented in Fig. 1.6 with experimental IR spectrum; likewise, the Fig. 1.7 give the Raman spectra, with lorentzian band width 4 cm\(^{-1}\). A complete assignment of all the observed bands with that of monomer and dimer are presented in Table 1.5.

The O-H stretching band computed near 3577 cm\(^{-1}\) for a monomer in Fig. 1.6(c) shift to 3550 and 3541 cm\(^{-1}\) for the dimers in Fig.1.6(b) agreeing with the observed bands at 3452 cm\(^{-1}\) in Fig. 1.6(a). The carbonyl bands for intra-molecular monomer and inter-molecular dimer are computed at 1692 cm\(^{-1}\). The observed band is at 1729 cm\(^{-1}\), it being the strongest band in the spectrum. The Raman counterpart is a medium weak band at 1727 cm\(^{-1}\). Another band is observed in IR at 1630 cm\(^{-1}\). This is a weak shoulder to the earlier mode. These bands are assigned as C=O asymmetric and symmetric stretch. The dimer’s bonded carbonyl band in Raman at 1692 cm\(^{-1}\) in Fig 1.7(b) is correlated to the observed band at 1727 cm\(^{-1}\) in Fig.1.7(a) and is assigned to the asymmetric carbonyl mode. The bands do not appear complimentary to each other, like we have already explained in the previous section about their lack of centre of inversion because the bands are not mutually exclusive. In Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate, there are two pairs of O-H and C=O groups, with both participating in the hydrogen bonding. Both the pairs give rise to bands with frequencies too close to be resolved in the dimer spectrum. For example, two computed bands at 1692 and 1690 cm\(^{-1}\) are merged into a single band, and we may conclude that the contribution from both the pairs is equal.

![Fig. 1.6: Experimental, simulated dimer and monomer IR spectrum of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate.](image)

![Fig. 1.7: Experimental (a), simulated dimer (b) and simulated monomer (c) Raman spectrum of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate (ordinate in Dimer spectrum is broken to adjust bands near 3500-3000 cm\(^{-1}\) from overshooting because of their large intensity.](image)
Table 1.5: Vibrational frequencies of Monomer and Dimer with experimental IR and Raman frequencies and assignments of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate.

| Computed Frequencies | Observed Frequencies | Assignments |
|----------------------|----------------------|-------------|
|                      | IR                   | Raman       |            |
| Intra-               | Inter-               |             |            |
| molecular            | molecular            |             |            |
| Monomer              | Dimer                |             |            |
| 3577                 | 3550                 | -           | -          | O-H asym stretch |
| -                    | 3541                 | 3452 br ms  | -          | O-H sym stretch  |
| 3053                 | 3049                 | -           | -          | CH₂ asym stretch (CH₂Cl) |
| 3016                 | 3016                 | -           | -          | CH₂ asym stretch (methyl-CH₂) |
| 3003                 | 3003                 | -           | -          | CH₁ asym stretch (methyl) |
| 2999                 | 2999                 | -           | -          | CH₁ asym stretch |
| 2993                 | 2993                 | -           | -          | CH₁ asym stretch (out of phase) |
| 2987                 | 2983                 | 2982 m      | 2964 s     | CH₂ sym stretch |
| 2953                 | 2953                 | -           | -          | CH₂ sym stretch (in phase) |
| -                    | 2945                 | -           | -          | CH stretch |
| 2933                 | 2943                 | 2929 m      | 2929 vs    | CH₂-CH (CHOH) stretch |
| 2897                 | 2933                 | 2910 m      | 2878 m, sh | Methyl sym stretch |
| 1693                 | 1692                 | 1729 vs     | 1727 mw    | C=O asym stretch |
| -                    | 1690                 | 1630 vw sh  | -          | C=O sym stretch |
| 1461                 | 1461                 | 1466 sh     | -          | CH₂ scissoring |
| 1445                 | 1445                 | 1445 v, sh  | 1449 mw    | CH₂ scissoring (methyl) |
| 1434                 | 1434                 | 1434 m sh   | -          | CH₂ asym deformation (methyl) |
| -                    | 1430                 | 1420 m, sh  | -          | CH₂ scissoring (CH₂Cl) |
| 1400                 | 1405                 | 1401 m      | 1403 sh    | CH₂ scissoring |
| 1390                 | 1386                 | 1375 ms     | -          | O-H in plane bend |
| 1377                 | 1379                 | 1360 w      | -          | CH₁ sym deformation (methyl, butterfly) |
| 1350                 | 1355                 | -           | -          | CH₂ wag |
| 1336                 | 1337                 | -           | -          | CH out of plane wag |
| 1311                 | 1310                 | 1305 ms     | 1299 w     | CH out of plane wag, O-H bend |
| 1270                 | 1274                 | 1261 m      | 1271 w     | O-H in plane bend |
| 1245                 | 1247                 | -           | -          | CH₂ twist (methyl, CH₂) |
| 1226                 | 1216                 | -           | -          | CH out of plane wag |
| 1198                 | 1210                 | 1191 s      | 1205 w     | CH out of plane wag |
| 1177                 | 1161                 | 1152 m      | 1156 w     | CHOH deformation |
| 1132                 | 1132                 | -           | -          | CH₂ rock (CH₂Cl-CH₂) |
| 1130                 | 1122                 | -           | 1112 w     | CH₂ twist (CH₂Cl) |
| 1091                 | 1092                 | 1093 m      | 1093 w     | Methyl rock |
| 1057                 | 1062                 | 1061 m      | 1059 w     | C-C-C stretch (CH₂Cl-CHOH-CH₂) |
| -                    | 1044                 | 1031 m      | 1031 w     | C-O stretch (CHOH) |
| 1019                 | 1013                 | -           | -          | C-O stretch (skeletal C-O) |
| 999                  | 993                  | 949 vw      | -          | Skeletal C-C-C asym stretch |
| 927                  | 932                  | 899 w       | 892 w sh   | C-C stretch (CH₂=C=O) |
| 877                  | 877                  | 863 w sh    | 862 w      | CH₂ rock (near C=O) |
| 845                  | 848                  | 848 w       | 850 w      | Skeletal C-C-O deformation |
The in-plane O-H deformation mode is a medium strong mode observed at 1375 cm\(^{-1}\). The DFT computed values in both intra- and inter-molecular bonding are fairly computed. Characteristically it would have been a test to decide the type of hydrogen bonding involved if the DFT value in either bondings is correlated. The out of plane deformation modes are also weak but can be identified at 598 and 566 cm\(^{-1}\), again the shift in the bands is negligible from where they are expected in the absence of hydrogen bonding. These modes due to CH, CH\(_2\) and CH\(_3\) have remained uninfluenced by the hydrogen bonding and are fairly accurately computed. The region 3000 - 2800 cm\(^{-1}\) is marked by a series of CH, CH\(_2\) and CH\(_3\) stretching modes [Belaidi, 2015; Guo, 2010]. Predicted bands agree very well with these modes though not all are observed. A very strong Raman mode at 2964 cm\(^{-1}\) and medium mode in IR at 2982 cm\(^{-1}\), is assigned to CH\(_2\) symmetric stretching and is also computed at the 2983 cm\(^{-1}\). The CH\(_2\)-CH stretch mode is observed at 2929 cm\(^{-1}\) as medium IR and very strong Raman band. The methyl symmetric stretch mode is observed at 2910 cm\(^{-1}\) in IR and 2878 cm\(^{-1}\) in Raman. The region 1500 – 1100 cm\(^{-1}\) shows several deformation modes arising from CH, CH\(_2\) and CH\(_3\) groups. The medium band 1449 cm\(^{-1}\) (Raman) is correlated to 1445 cm\(^{-1}\) (DFT) mode and is assigned as CH\(_2\) scissoring mode. Another medium strong mode at 1434 cm\(^{-1}\) (IR) is due to CH\(_2\) deformation coming from the methyl group. At 1360 cm\(^{-1}\) (Raman) is the CH\(_2\) symmetric deformation. It is computed at 1379 cm\(^{-1}\). Vibrations of skeletal stretching and deformation modes have appeared in 1100-850 cm\(^{-1}\) region. A medium IR band at 1061 cm\(^{-1}\) is a mode due to C-C-C stretching. Another weak IR mode is identified as the C-C-C asymmetric stretch. Two modes are further computed and assigned to C-O at 1031 cm\(^{-1}\) in both IR and Raman, and 1013 cm\(^{-1}\) DFT computed. The skeletal C-C-O deformation mode is identified at 899 cm\(^{-1}\). The skeletal and COOH deformation are weak in IR and Raman and observed at 848 cm\(^{-1}\).

We may say that though the O-H\(\cdots\)O modes are localized in the dimer structure, the vibrational structure in IR spectrum is considerably modified with visible features near 3550-3400 cm\(^{-1}\) and 1730 cm\(^{-1}\).

3) **IR And DFT-VCD Correlation:** Fig. 1.8 shows Boltzmann weighted-VCD spectrum for monomer and dimer, correlated with observed IR spectrum for the region 2000–400 cm\(^{-1}\) and the assignments are given in Table 1.6. The region is highly marked by the bands due to linear and oscillatory vibrations. From Fig.1.8 we can identify that the weak or shoulder bands in IR correspond to positive or negative bands. The assignments are as follows (Table 1.6).
Fig. 1.8: Experimental IR, Simulated Monomer and dimer VCD spectrum of Ethyl (S)-(−)-4-chloro-3-hydroxybutyrate

The 1729 cm\(^{-1}\) broad band in IR is split into two bisignate VCD dimer bands as 1, 1\(^{''}\). They are assigned to the C=O stretch asymmetric and symmetric stretch in the dimer. The intra-molecular monomer VCD has produced only band at 1693 cm\(^{-1}\). It is assigned as 1, because of the free C=O stretch in the unbound state. The band 2 is the O-H in plane bend coupled with CH wag, while band 3 is exclusively CH wag. Bands 4 and 4\(^{'}\) belong to the CH wag mode; the latter being a coupled mode with O-H bend. The band 5 is exclusively O-H in plane bend. Bands 6 and 6\(^{'}\) belong to CH wag of different CH groups while 7, 8 are individually contributing. Two bands 9 and 9\(^{'}\) are the C-C-C stretch modes in the dimer VCD.

| Band No. | Intra-molecular Monomer | Inter-molecular Dimer | IR | Assignments                      |
|----------|-------------------------|-----------------------|----|----------------------------------|
| 1        | 1693                    | 1695                  | 1729| C=O asymmetric stretch           |
| 1\(^{'}\)| -                       | 1687                  | 1630| C=O symmetric stretch            |
| 2        | 1390                    | 1383                  | 1375| O-H in plane bend, CH wag        |
| 3        | 1350                    | 1354                  | -  | CH\(_2\) wag                     |
| 4        | 1336                    | 1335                  | -  | CH out of plane wag              |
| 4\(^{'}\)| 1311                    | 1310                  | 1305| CH out of plane wag, O-H bend    |
| 4\(^{''}\)| 1282                   | 1297                  | -  | CH out of plane wag,             |
| 5        | 1270                    | 1274                  | 1261| O-H in plane bend                |
| 6        | 1226                    | 1216                  | -  | CH out of plane wag              |
| 6\(^{'}\)| 1198                    | 1210                  | 1191| CH out of plane wag              |
| 7        | 1177                    | -                     | 1152| CHOH deformation                 |
| 8        | 1130                    | 1122                  | -  | CH\(_2\) twist (CH\(_2\)Cl)      |
| 9        | 1057                    | 1062                  | 1061| C-C-C stretch                    |
| 9\(^{'}\)| -                       | 1044                  | -  | C-C-C stretch                    |
| 10       | -                       | 1013                  | 1031| C-O stretch (skeletal C-O)       |
| 11       | 999                     | 1005                  | 949 | Skeletal C-C-C asymmetric stretch|
| 12       | 877                     | -                     | 863 | CH\(_2\) rock (near C=O)         |
| 13       | 845                     | -                     | 848 | Skeletal C-C-O deformation       |
| 14       | 780                     | 783                   | 756 | C-Cl stretch                     |
| 15       | 712                     | -                     | 710 | CH\(_2\) twist (methyl)          |
| 16       | 587                     | 586                   | 598 | O-H out of plane deformation     |
| 16\(^{'}\)| 552                    | 541                   | 566 | O-H out of plane deformation     |
The band 14 is the C-Cl stretch band. It is a weak band in IR while we have not been able to identify the same in VCD because the rotational strength is very small. The bands 16 and 16' are the O-H out of plane bending vibration. We see that certain bands in VCD are not identified like bands 1 and 10 in monomer and 7, 12, 13 and 15 in dimer. These bands have been computed but the magnitudes of their corresponding rotational strengths are very small and hence they are difficult to place in the VCD spectra.

II. CONCLUSIONS
The DFT intra-molecular monomer and inter-molecular-dimer model proposed with O-H•••O=C type of hydrogen bonding has been satisfactory in accounting for the experimental IR and Raman spectral band features of Ethyl (S)-(−)-4-chloro-3- hydroxybutrate. Three stable monomers have shown the possibility of four dimer structures, with varying Boltzmann populations. The most stable monomer also forms the most stable dimer with ~90% population. It could be said that both intra- and inter- molecular hydrogen bondings may exist in the sample.

To resolve this further rigorous concentration-dependent solvent experiments and study, or near IR spectrum could be attempted based on the fact that inter-molecular hydrogen bonds are broken by dilution with non-polar solvents, whereas intra-molecular bonds are independent of the concentration; which is the future plan of work. The computed geometrical parameters for the hydrogen bond lengths are reasonably accurate and are in favor of O-H•••O=C type of hydrogen bonding but the shift in the bonded frequencies conclude the bonding as weak inter-molecular hydrogen bonding.

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