Vibrational and Spectroscopic Analysis on 2,3-Dimercapto-1-Propanol by HF and DFT Calculations

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ABSTRACT

A combined experimental and theoretical study on molecular and vibrational structure of 2,3-Dimercapto-1-propanol have been undertaken in the present work. The FTIR Spectrum and FT-Raman spectrum of the molecule have been recorded in the region of 4000-400 cm⁻¹ and 4000-100 cm⁻¹. The optimized geometry, frequency and intensity of the vibrational bands of the molecule were obtained at HF and DFT (B3LYP) levels using 6-31G (d,p) basis set. A Complete vibrational assignments for the theoretical harmonic frequency were made and compared with the experimental frequencies recorded. HOMO-LUMO study confirms the charge transfer within the molecule. Mulliken population analysis and thermodynamic properties of the molecule were tabulated.

Key Words: 2, 3-Dimercapto-1-propanol, FT-IR, FT- Raman, DFT

INTRODUCTION

2,3 Dimercapto-1-Propanol is a clear colorless viscous Liquid which in boiling point at 248° F at 15 mm Hg pressure, has a specific gravity/density of 1.24. The molecular formula is C₃H₈OS₂. It acts as a chelating agent and is used in the treatment of arsenic, gold, and other heavy metal poisoning [1-3]. It is a metal chelating agent used as an antidote in arsenic, gold, lead, mercury and other heavy metal poisoning [4]. Metals form ligands in the body with the sulfhydryl groups. This leads to an inhibition of the normal functioning of these enzymes that are dependent on free sulfhydryl groups for their activity. It also reverses the enzyme inhibition by chelating the metal and regenerates free sulfhydryl groups, thereby preventing and reversing the metals toxic effects. The structure of 2,3-Dimercapto-1-Propanol is as shown in Figure 1.

EXPERIMENTAL DETAIL

High grade sample of 2,3-Dimercapto-1-Propanol was purchased from TCI chemicals and was used without further purification. The FTIR spectrum was recorded in the region

4000- 400 cm⁻¹ using Bruker IFS 66V spectrophotometer and FT Raman spectrum recorded using Bruker RFS27 recorded in the region 4000-100 cm⁻¹. The assignments were analogue with earlier assignments reported in the literature.

COMPUTATIONAL DETAILS

In the present work, the geometry optimization of the molecule was carried out by using Gaussian software employing density functional method (DFT) [5] with Becke's three parameter hybrid exchange functional and Lee-Yang -Parr correlation functional [6]. The entire calculations were performed at ab-initio Hartree Fock(HF) and DFT method using B3LYP levels at 6-31 G(d,p) basis sets on a Pentium V/ 1.6 GHz personal computer using Gaussian 09W program package [7-9].

Results and Discussion

Molecular geometry

The optimized structural parameters of 2,3-Dimercapto-1-Propanol have been calculated at DFT/B3LYP with 6-31 G(d,p) and the optimized structure was shown in Figure 2.

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From the calculated values shown in Table 1, it is clear that the bond lengths of S1 – H12 is less than the bond length of S2 – H13 which is far away from the electronegative oxygen atom. Also the hydrogen attached to Oxygen takes the lesser value when compared to hydrogen attached to sulphur atoms due to more electro negativity. The carbon attached to sulphur atoms have their bond length more when compared to carbon atoms attached with Oxygen atom. The bond angle of carbon attached with oxygen atom have more bond angle compared with carbon attached with sulphur atom [10].

Vibrational Assignment

The molecule 2,3-Dimercapto-1-Propanol has 14 atoms with 3N degrees of freedom corresponding to the Cartesian co-ordinates of each atom in the molecule. Therefore the net number of modes of vibrations is 36. The detailed vibrational analysis of fundamental modes is shown in Table 2 and FT-IR and FT-Raman spectra is shown in Figure 3 and Figure 4.

CH₂ Vibrations

The calculated bands observed at 2697, 2680 and 2669 cm⁻¹ in B3LYP/6-31G(d,p) and 2848, 2830 and 2810 cm⁻¹ in HF/6-31G(d,p) contribute to CH₂ Vibrations. A very strong intense band appear in the FT-Raman for CH₂ asymmetric stretching at 2919 cm⁻¹ and weak intense in FT-IR at 2873 cm⁻¹. A very strong intense band appears at 2557 cm⁻¹ in FT-Raman and weak intense in FT-IR at 2546 cm⁻¹ are assigned to CH₂ symmetric stretching vibration. The calculated bands are observed at 2649 and 2600 cm⁻¹ in B3LYP/ 6-31G(d,p) and 2795 and 2716 cm⁻¹ in HF/6-31G(d,p) method.

The CH₂ scissoring frequencies are observed at 1313 cm⁻¹ in FTIR and 1278 cm⁻¹ in FT-Raman. The theoretical observations in B3LYP/6-31G(d,p) at 1313 cm⁻¹ and HF/6-31G(d,p) at 1288 cm⁻¹. The CH₂ wagging frequencies are found at 1237 and 1170 cm⁻¹ in FTIR. The theoretical observations in B3LYP/6-31G(d,p) at 1232, 1209 and 1159 cm⁻¹ and HF/ 6-31G(d,p) at 1216, 1195 and 1137 cm⁻¹.

The CH₂ twisting vibrations are observed at 1040 cm⁻¹ (FTIR); 1030 cm⁻¹ (FT-Raman); 1118 and 1087 cm⁻¹ in B3LYP/6-31G(d,p); 1088 and 1061 cm⁻¹ in HF/6-31G(d,p). The CH₂ rocking vibrations are assigned at 1419 cm⁻¹ (FTIR); 1417 cm⁻¹ (FT-Raman); 1390 and 1366 cm⁻¹ in B3LYP/6-31G(d,p); 1357 and 1332 cm⁻¹ in HF/6-31G(d,p) [10]

C-C Vibrations

The C-C stretching frequencies are generally predicted in the region 650-1650 cm⁻¹. The bands occurring at 986 cm⁻¹ in FT-IR contribute to C-C vibrations and the theoretical observations at B3LYP/6-31G(d,p) level appears at 1011 cm⁻¹ and in HF/ 6-31G(d,p) at 1006 cm⁻¹. The frequencies 208 cm⁻¹ and 201 cm⁻¹ are assigned to C-C out of plane bending in B3LYP/6-31G(d,p) and HF/6-31G(d,p) respectively [11].

CH Vibrations

The 2,3-Dimercapto-1-Propanol theoretical observation for C-C stretching frequencies in B3LYP/6-31G(d,p) at 2830 cm⁻¹ and HF/ 6-31G(d,p) at 2680 cm⁻¹. The C-H in plane bending occurs at 1300-1000 cm⁻¹ respectively. The C-H in plane bending vibrations at 1313, 1270 and 1237 cm⁻¹ (FTIR); 1278 cm⁻¹ (FT-Raman); 1313, 1277, 1232, 1209, 1151, 1118, 1087, 1011 and 990 cm⁻¹ in B3LYP/6-31G(d,p); 1288, 1242, 1216, 1195, 1137, 1088, 1061, 1006 and 973 cm⁻¹ in HF/6-31G(d,p) are assigned to CH vibrations [11].

O-H vibrations

The 2,3-Dimercapto-1-Propanol gives rise to O-H stretching vibrations at 3428 cm⁻¹ in FTIR and the theoretical observations at B3LYP/6-31 G(d,p) level is 3428 cm⁻¹ and HF/6-31G(d,p) at 3428 cm⁻¹ respectively. The O-H in plane bending vibrations are observed at 1313, 1272, 1237, 1170, 1040, 986 and 783 cm⁻¹ (FTIR); 1278, 1030, 888, 564, 382 and 297 cm⁻¹ (FT-Raman); 1313, 1277, 1232, 1209, 1151, 1118, 1087, 1011, 972, 928, 849, 801, 549, 462, 415, 348, 288, 245, 208, 153 and 123 cm⁻¹ in B3LYP/6-31G(d,p); 1288, 1242, 1216, 1195, 1137, 1088, 1061, 1006, 941, 917, 836, 786, 549, 444, 366, 335, 280, 225, 201, 147 and 115 cm⁻¹ in HF/6-31G(d,p) [12].

S-H vibrations

The 2,3-Dimercapto-1-Propanol theoretical observation for C-C stretching frequencies in B3LYP/6-31G(d,p) at 2453 and 2437 cm⁻¹ and HF/ 6-31G(d,p) at 2382 and 2369 cm⁻¹. respectively. The S-H in plane bending vibrations at 1313, 1272, 1237, 1170, 1040, 986 and 783 cm⁻¹ (FTIR); 1278, 1030, 888, 564, 382, and 297 cm⁻¹ (FT-Raman); 1151, 1118, 1087, 1011, 990, 972, 928, 849, 801, 772, 549, 462, 415, 348, 288, 245, 208, 161, 153 and 123 cm⁻¹ in B3LYP/6-31G(d,p); 1137, 1088, 1061, 1006, 973, 941, 917, 836, 786, 759, 549, 444, 335, 280, 225, 201, 147 and 115 cm⁻¹ in HF/6-31G(d,p) levels.

Mulliken's charges

The bonding capability of a molecule depends on the electronic charge on the chelating atoms. The atomic charges values were obtained by mulliken population analysis. The atoms with their respected charges were properly tabulated and were shown in Figure 5.

The analysis shows the presence of electronegative oxygen atom (O₁) increases the charge on the carbon atom C₆ (0.089702 e). A small increase in the charge of atom H₁₀, H₁₁ (0.081832 e), (0.1112227 e) may be due to presence of carbon atmosphere [13]. In the title molecule, the charge on C₄, C₅ are negative. The result suggests that the carbon atom C₆ which is attached to oxygen atom are electron acceptor and also indicates the charge transfer from Oxygen atom to carbon atom. It is observed that the interaction between C₄ and S₂ atom may contribute to greater stability.

Thermodynamic properties

The thermodynamic parameters of the molecule have been computed at HF/6-31G(d,p) and DFT/B3LYP/6-31G(d,p) basis set and presented in Table 3. Thermodynamic data calculations provides useful information for further study of the molecule when used as a reactant in a new chemical process. These values can be taken as reference thermodynamic values in calculation of charges of entropies (ΔS_T) and changes of enthalpies (ΔH_T) of the reaction. The dipole moment and its principal inertial axes are strongly depending upon the conformation of the molecule.

CONCLUSION

The present work deals with the vibrational investigations of 2,3-Dimercapto-1-Propanol by using HF and DFT studies. The FTIR and FTRAMAN spectrum of the sample was analyzed. The optimized geometries, harmonic frequencies were determined and analysed both at HF and DFT/B3LYP levels of theories using 6-31 G(d,p) basis sets and it is confirmed that theoretical results computed using DFT/B3LYP/6-31 G(d,p) level compared is in good agreement with the experimental values. Thermo dynamic calculations have been tabulated.

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Figure 1: Structure of 2,3-Dimercapto-1-Propanol.

Figure 2: Geometry of 2,3-Dimercapto-1-Propanol optimized at DFT level.

Figure 3 & 4: FT-IR; FT-Raman spectra of 2,3-Dimercapto-1-propanol.

Table 1: Optimized geometrical parameters of 2,3-Dimercapto-1 Propanol

Bond Length / Å		Bond Angle / °	
S1 – H12	1.35115	H13-S2-C5	95.4180
S2 – H13	1.34898	H12-S1-C4	96.3255
O3 – H13	0.97029	H14-O3-C6	106.642
S2-C5	1.84900	C5-C4-C6	111.5102
S1-C4	1.85501	O3-C6-C4	112.93698
O3 – C6	1.40801	S2-C5-C4	112.14328

Figure 5: Mulliken Population analysis of 2,3-Dimercapto-1-propanol.

Table 2: Vibrational assignments of 2,3-Dimercapto-1-propanol

S. No	Observed frequencies		Calculated frequencies						Vibrational Assignments
			HF/6-31G (d,p)			DFT/B3LYP/6-31 G (d,p)			
	FTIR	Raman	Scaled	IR intensity	Raman Intensity	Scaled	IR intensity	Raman Intensity	
1	3428	2919	3428	53.656	35.457	3428	30.229	53.543	O-H STRETCHING
2	2873		2697	2.814	71.187	2848	18.270	67.174	CH ₂ ASYMMETRIC STRETCHING
3			2680	2.817	57.028	2830	2.077	57.999	CH ₂ ASYMMETRIC STRETCHING, CH STRETCHING
4			2669	31.281	86.319	2810	27.701	106.958	CH ₂ ASYMMETRIC STRETCHING
5			2649	28.499	82.646	2795	19.840	88.713	CH ₂ SYMMETRIC STRETCHING
6	2546	2557	2600	56.386	66.662	2716	56.432	71.347	CH ₂ SYMMETRIC STRETCHING
7			2382	19.221	183.29	2453	24.155	207.918	S-H STRETCHING
8			2369	9.5973	100.87	2437	10.860	91.5528	S-H STRETCHING
9	1419	1417	1357	0.5740	13.416	1390	0.6114	15.1801	CH ₂ ROCKING
10			1332	3.7843	7.5038	1366	3.1747	7.1600	CH ₂ ROCKING
11	1313	1278	1288	73.858	1.4425	1313	80.089	7.6744	CH ₂ SCISSORING, O-H BENDING, C-H BENDING

Table 2: (Continued)

12	1272		1242	13.090	9.9175	1277	7.5426	9.4471	O-H BENDING, C-H BENDING
13	1237		1216	16.076	2.7300	1232	12.134	3.8227	CH ₂ WAGGING, O-H BENDING, C-H BENDING
14			1195	39.960	6.7880	1209	36.216	5.1148	CH ₂ WAGGING, O-H BENDING, C-H BEND- ING, C-S BENDING
15	1170		1137	8.6622	9.0069	1151	7.9256	8.8808	CH ₂ WAGGING, O-H BENDING, C-H BEND- ING, S-H BENDING
16			1088	33.661	5.3241	1118	23.749	6.6008	CH ₂ TWISTING, O-H BEND- ING, C-H BENDING, S-H BENDING
17	1040	1030	1061	9.9505	8.3189	1087	7.5669	8.9093	CH ₂ TWISTING, O-H BEND- ING, C-H BENDING, S-H BENDING
18	986		1006	130.67	3.6696	1011	113.98	2.1355	C-O STRETCHING, C-C STRETCHING, O-H BENDING, C-H BENDING, S-H BENDING
19			973	4.6315	5.0010	990	2.7870	3.1092	S-H BENDING, C-H BENDING, CH ₂ TORSION
20			941	6.5793	6.5516	972	4.5372	8.1470	C- STRETCHING, C-S STRETCHING, O-H BENDING, S-H BENDING
21		888	917	12.495	9.8644	928	10.919	8.2113	C- STRETCHING, C-S STRETCHING, O-H BENDING, S-H BENDING
22			836	10.825	9.3457	849	7.1952	9.7744	CH ₂ TORSION, S-H BENDING, O-H BENDING
23	783		786	8.2631	7.9047	801	7.0982	7.5441	CH ₂ TORSION, S-H BENDING, O-H BENDING

Table 3: Thermodynamic properties of 2,3-Dimercapto-1-Propanol

Parameters	HF/6-31 G(d,p)	DFT/B ₃ LYP/ 6-31 G(d,p)
SCF energy (a.u.)	-988.1441	-990.7288
Total energy (thermal)E _{total} (Kcal mol ⁻¹)	78.214	73.204
Vibrational energy, E _{vib} (Kcal mol ⁻¹)	76.436	71.426
Zero point vibrational energy (Kcal mol ⁻¹)	73.21269	67.99513
Specific heat capacity, C _v (cal mol ⁻¹ K ⁻¹)	27.125	28.639
Entropy, S (cal mol ⁻¹ K ⁻¹)	88.095	89.451
Dipole moment μ (Debye)		
μ_x	0.4816	0.5592
μ_y	1.7018	-1.6507
μ_z	2.2132	1.8749
Total	2.8331	2.5598