Vibrational study of 2,4-Dichlorobenzoic acid by DFT

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Abstract- The FTIR and FTRaman spectrum of 2,4–Dichlorobenzoic acid have been recorded in the region 4000-400 cm^{-1} and 3500-250cm^{-1}, respectively. The theoretical vibrational frequencies and geometry parameters have been calculated and compared with the experimental values. A satisfactory band assignment has been obtained by ab - initio Hatree –Fock (HF) and Density Functional Theory (DFT) methods. Optimized geometries were obtained using the global optimization procedure. Theoretical investigations of harmonic vibrational frequencies, HOMO-LUMO analysis and thermodynamic properties like zero point vibrational energy (ZPVE), entropy, heat capacity have been tabulated.

Keywords: 2,4–Dichlorobenzoic acid, .FTIR, FT Raman spectra, HF, DFT

I. INTRODUCTION

2,4–Dichlorobenzoic acid ($C_7H_4Cl_2O_2$) is a halogenated carboxylic acid and it is white to slightly yellowish powder. It is used as an intermediate in the synthesis of spirodiclofen, a tetronic acid acaricide fungicide used in controlling red mites. It is insoluble in water and soluble in ethanol. It is very stable, incompatible with strong oxidizing agents.

The aim of the work is to investigate the molecular structure, vibrational study of the molecule due to its biological and pharmaceutical importance. The structure and the ground state energy of the drug under investigation has been analyzed by using Density functional theory in B3LYP basis sets. In order to obtain the complete description of the molecular vibrations of the title molecule, complete vibrational frequency calculations have been carried out and it provides the detailed information about the intra molecular vibrations in the fingerprint region.

II.Experimental details

High grade sample of 2,4-Dichlorobenzoic acid was purchased from Loba chemicals and was used without further purification. The 2,4-Dichlorobenzoic Acid data was taken from SDBS [1]. The molecular structure of the molecule optimized at DFT/B3LYP/6-31 +G(d, p)level has been given in Fig.1. The xperimental and calculated FT-IR spectrum and FT-Raman spectrum are shown in Fig. 2(a) and Fig. 2(b).

III.Computational details

In the present work, the density functional method (DFT) [2] has been employed using Becke's three parameter hybrid exchange functional with the Lee-Yang –Parr correlation functional [3-4] to optimize the structure of the molecule and also to calculate the electronic structure of the title molecule.

The entire calculations were carried at DFT/B3LYP levels at 6-31G (d, p) basis set. Initial geometry generated was minimized at the Hartree Fock level using 6-31 G(d, p) basis set and again reoptimized at 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/ 1.6GHz personal computer using Gaussian 03W program package and vibrational modes are assigned using Gauss-View molecular visualization program package [5-7].The optimized structural parameters were used in the vibrational frequency calculations at HF and DFT levels to characterize all stationary points as minima. The vibrational frequencies are calculated and scaled down by the appropriate scaling factor thereby the vibrational assignments are compared with observed values.

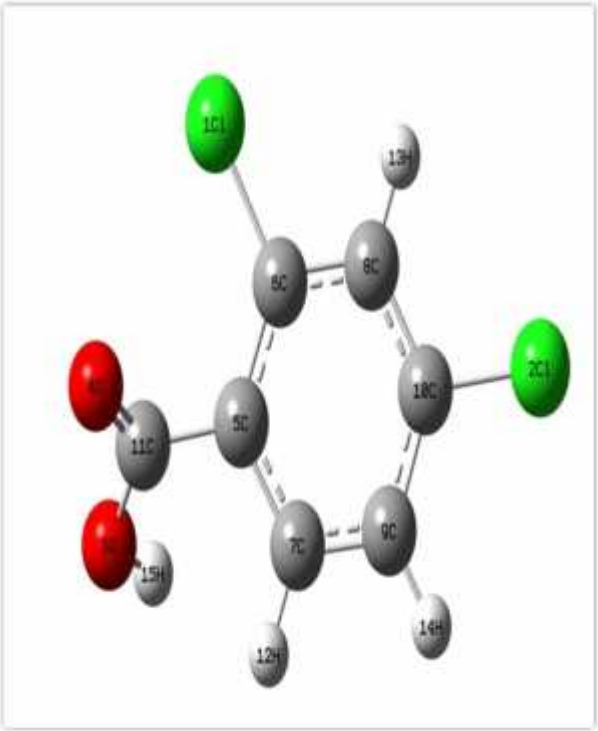

Fig 1. Optimized structure of 2,4-Dichlorobenzoic Acid at DFT / B3LYP/6-31 +G(d,p) leve

IV.RESULTS AND DISCUSSION

4.1 Molecular Geometry

The optimized structure parameters (bond length and bond angles) of the title molecule calculated by quantum mechanical methods of ab initio HF and DFT-B3LYP levels with the 6-31+G (d, p) basis sets are listed in Table 4.1. The experimental and calculated geometric parameters agree well with almost all

The optimized parameters like bond length and bond angles were obtained by HF/6-31 +G (d,p)and DFT/B3LYP with 6-31 +G (d,p) levels and the values were compared with experimental values. The theoretical values are very closer to the experimental values. The value of bond lengths C –C obtained from DFT/B3LYP/6-31 +G (d,p) levels is found equal to 1.400Ǻ and it matches well with the experimental values. The value of C-H obtained from DFT/B3LYP/6-31 +G (d, p)levels is equal to 1.00Ǻ. The average bond lengths of C–Cl bond obtained from DFT/B3LYP/6-31 +G (d, p) levels is nearly equal to 1.73 Ǻ and it is closer to the experimental values. It is clear that the bond angles calculated at DFT/B3LYP with 6-31 +G (d, p) levels agree well with the literature values.

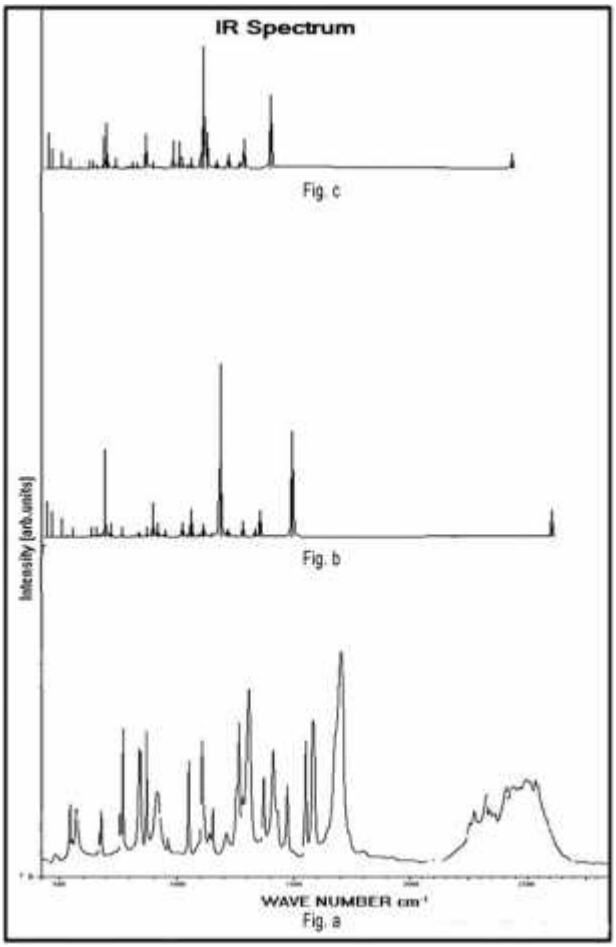

Fig.2(a). FT-IR of 2,4-Dichlorobenzoic acid

The small deviations are probably due to the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state. B3LYP calculations provide good linearity between the calculated and experimental frequencies.

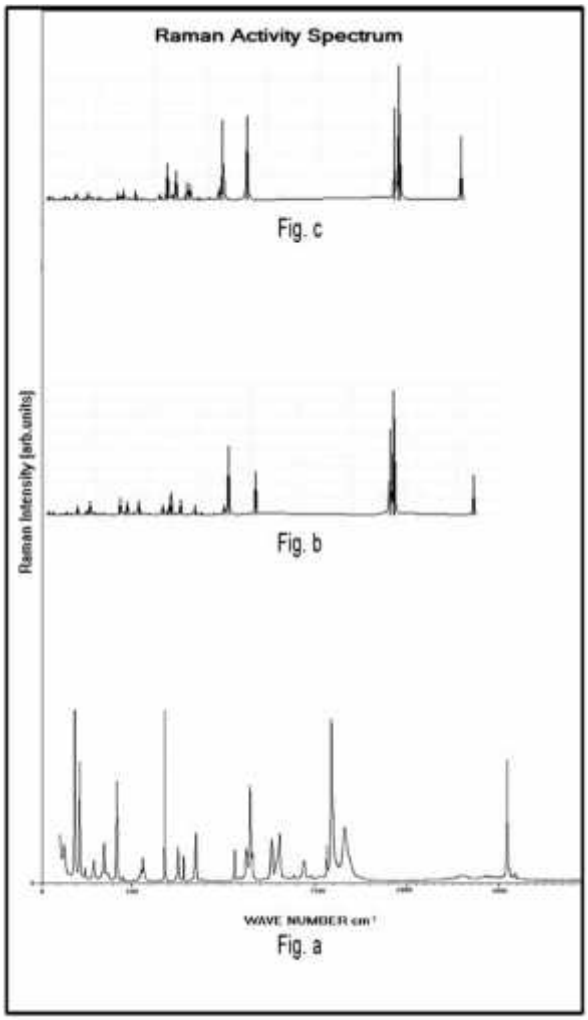

Fig.2(b). FT-Raman of 2,4-Dichlorobenzoic acid

4.2 Vibrational assignments

The molecule 2, 4-Dichlorobenzoic acid has 15 atoms and it has 39 normal modes of vibration. The aim of the vibrational analysis is to decide which of the vibrational modes gives rise to each of these observed bands. The assignments for the fundamental modes of vibration have been made on the basis of position, shape and intensity. The scaling factor of 0.95 is used for getting theoretical vibrational frequencies. Comparison of frequencies calculated at DFT method using 6-31 +G (d, p) basis set with experimental values reveal that the DFT/ B3LYP/6-31 G (d, p) method shows very good agreement with experimental observation and it is presented in Table 4.2.

Table 4.1 Optimized bond parameters of 2,4-Dichlorobenzoic acid

S. No	Atom numbering	X-ray	HF/6-31 + G(d,p)	DFT/B3LYP/ 6-31 +G (d,p)
Bond length (A)				
1	Cl_1- C_6	1.699	1.747	1.734
2	Cl_2- C_{10}	1.693	1.751	1.735
3	O_3- C_{11}	1.227	1.362	1.333
4	O_3- H_{15}	0.879	0.968	0.944
5	O_4- C_{11}	1.221	1.204	1.179
6	C_5- C_6	1.423	1.391	1.404
7	C_5- C_7	1.421	1.391	1.404
8	C_5- C_{11}	1.393	1.506	1.406
9	C_6- C_8	1.412	1.396	1.400
10	C_7- C_9	1.405	1.393	1.400
11	C_7- H_{12}	1.024	1.086	1.076
12	C_8- C_{10}	1.406	1.394	1.383
13	C_8- H_{13}	1.023	1.083	1.072
14	C_9- C_{10}	1.404	1.395	1.383
15	C_9- H_{14}	1.023	1.083	1.073
Bond Angles (A^o)				
1	C_{11} -O_3- H_{15}	120.514	112.635	110.721
2	C_6 -C_5- C_7	117.603	117.541	118.213
3	C_6 -C_5- C_{11}	123.671	122.675	122.684
4	C_7 -C_5- C_{11}	118.724	118.561	119.021
5	Cl_1 -C_6 -C_5	124.307	121.201	121.281
6	O_3 -C_{11} -O_4	113.801	121.122	120.428
7	O_3 -C_{11} -C_5	122.779	115.124	115.056
8	O_4 -C_{11} -C_5	123.418	123.768	124.398
9	C_{10} -C_8 -H_{13}	118.919	120.697	120.679

O – H vibrations

The unassociated O –H groups absorbs strongly in the region 3670- 3580 cm^{-1}. The hydrogen bonding in the hydroxyl group band appears at 3590-3400 cm^{-1}. These bands are the result of presence of hydrogen bonding, and the degree of vibration increases with concentration. In the present investigation, the FT-IR band observed at 3486 cm^{-1} is assigned to O-H stretching vibrations. The bands observed at 3505 cm^{-1} in DFT/B3LYP / 6-31 +G (d, p) and 3542 cm^{-1} at HF/ 6-31 +G (d, p) levels are assigned to O-H stretching vibrations. The bending vibrations are assigned at 1755, 1263, 1239, 1217 cm^{-1} in DFT/B3LYP / 6-31 +G (d, p) levels and assigned at 1886, 1341, 1283, 1216 cm^{-1} in HF/ 6-31 +G (d, p) levels. These assignments are in good agreement with the literature value [8-10].

C-H vibrations

The substituted benzene molecules gives rise to C-H stretching. The C-H stretching vibrations of benzene derivatives generally appear above 3000 cm^{-1} [11]. The hetero aromatic structure shows the presence of C-H vibrations in the region 3100 – 2900 cm^{-1}. For the title molecule, the bands observed at 3072 and 2995 cm^{-1} in FT-IR spectra are assigned to C-H stretching vibrations. In the Raman spectrum, the band observed at 3079 cm^{-1} is attributed to the C-H stretching vibrations. The bands obtained at 3072 and 3067 cm^{-1} in DFT/B3LYP with 6-31 +G (d,p) levels correspond to C-H stretching vibrations. The C-H deformation vibration at two distinct regions 1300-1000 cm^{-1} and 700 – 610 cm^{-1} are due to in plane and out of plane bending vibrations respectively. The band at 1239, 1217, 1141, 1112, 1067 cm^{-1} assigned to C-H in plane bending vibrations agrees well with the value reported by previous work on benzene [12].

C = O vibrations

A strong absorption band due to C = O stretching occurs in the region 1850 – 1550 cm^{-1} [13]. A strong band at 1684 cm^{-1} in FT-IR spectrum and a band observed at 1664cm^{-1} in FT-Raman are assigned to C = O stretching vibrations. The bands calculated at 1755 cm^{-1} in DFT/B3LYP /6-31 +G (d,p) levels and 1886cm^{-1} in HF/6-31 +G (d, p) levels corresponds to C = O stretching vibrations.

C - C vibrations

The C-C aromatic stretching vibrations gives rise to characteristic bands both in the observed IR and Raman spectra in the spectral range 1684 -1267 cm^{-1}. It has been reported that the ring carbon-carbon stretching vibrations occur in the region 1625-1430 cm^{-1} region. In general, the bands are of variable intensity and are observed in the range 1625 - 1590, 1590 – 1575, 1540 – 1470, 1465 1430 cm^{-1} as given by five bands in this region [8]. The sharp bands observed at 1555 and 1427 cm^{-1} in FT-IR spectrum and at 1458 and 1433 cm^{-1} in FT-Raman are assigned to C-C stretching vibrations. The bands are observed at 1547, 1515 and 1428 cm^{-1} in DFT/B3LYP / 6-31 +G (d,p) levels are assigned to C-C stretching vibrations. The bands are observed at 1644, 1603 and 1515 cm^{-1} in HF/ 6-31 +G (d, p) levels are assigned to C-C stretching vibrations.

C-Cl vibrations

The C-Cl stretching vibrations are assigned at 750 and 683 cm^{-1}. In the present investigation, spectrum bands observed at 772, 760, 679 and 671 cm^{-1} in FT-IR and band observed at 745 and 673 cm^{-1} in FT-Raman are assigned to C–Cl stretching vibrations. The bands are observed at 793, 730, 692 and 668 cm^{-1} in DFT/B3LYP/ 6-31 +G (d, p) levels are assigned to C-Cl stretching vibrations. The bands are observed at 837,793, 736 and 723 cm^{-1} in HF/ 6-31 +G (d, p) levels are assigned to C-Cl stretching vibrations. The calculated bands are in good agreement with the literature values [14].

C – O vibrations

The absorption region for C-O group due to stretching vibration will appear at 1200 to 1000 cm^{-1}. Hydrogen bonding has the effect of decreasing the frequency of this band. Saturated primary alcohols absorb in the region 1085 - 1030 cm^{-1}. Secondary alcohols absorb at 1125 – 1085 cm^{-1} and tertiary alcohols absorb at 1205 – 1125 cm^{-1} [14]. In the present investigation, the bands observed at 1267 916, and

772 cm^{-1} in FT-IR spectrum and band observed at 1255 cm^{-1} is assigned to C – O stretching vibrations. The bands are observed at 1255, 1000, 1755 and 920cm^{-1} in DFT/B3LYP/ 6-31 +G (d, p) levels are assigned to C-O stretching vibrations. The bands observed at 1341, 1058, and 1010cm^{-1} in HF/6-31 +G (d, p) levels are assigned to C-O stretching vibrations. These assignments are in good agreement with the literature value [15].

4.3 HOMO – LUMO ANALYSIS

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the two main orbital that take part in chemical stability. The HOMO represents the ability to donate an electron and LUMO represents the ability to obtain an electron. The HOMO and LUMO energy calculated by DFT/B3LYP/6-31 +G(d, p) method is shown in Figure 4.3. The positive phase is represented in red color and the negative phase is represented in green colour. The energy gap of HOMO–LUMO explains the eventual charge transfer interaction within the molecule [10].

4.4 Thermodynamic Properties

. Thermo dynamical parameters such as the zero-point vibrational energy (ZPVE), the rotational constants, the specific heat, the entropy and dipole moment were computed by HF/6-31 +G(d, p) and DFT/B3LYP/6-31 +G(d,p) levels were presented in Table 4.3 It is clear that SCF energy and the dipole moment obtained from DFT/B3LYP/6-31 +G (d, p) level is minimum when compared to HF/ 6-31 +G (d, p) level.

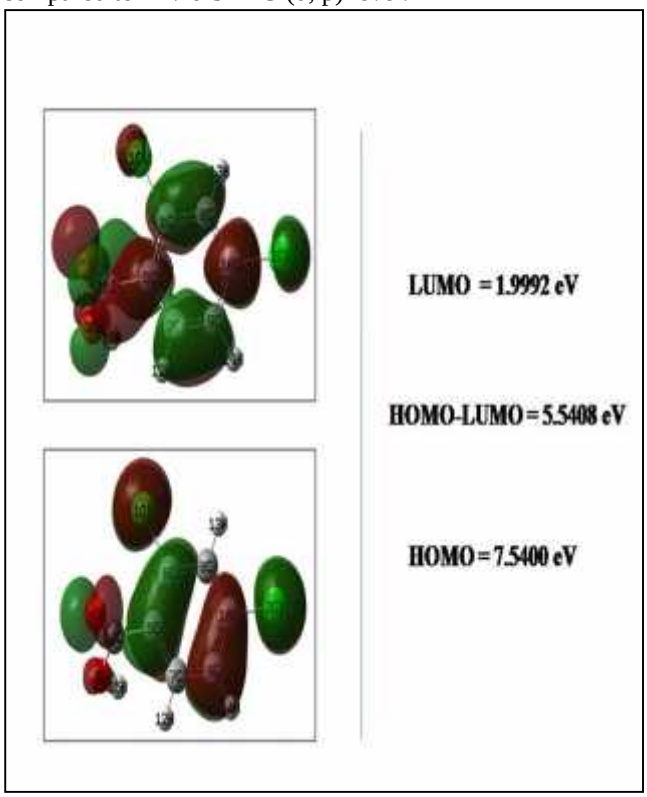

Fig. 4.3 HOMO-LUMO analysis of 2,4-Dichlorobenzoic acid

Table 4.3. Thermodynamic parameters of 2,4-Dichlorobenzoic acid

S. No	Thermodynamic Parameters	HF/6-31 +G(d,p)	DFT/B3LYP/ 6-31 +G (d,p)
1	SCF energy (a.u.)	-1336.1209	-1340.0211
2	Total energy (Thermal) E ($Kcalmol^{-1}$)	70.634	66.069
3	Heat Capacity at Constant Volume C_v ($calmol^{-1}K^{-1}$)	33.077	35.401
4	Entropy S (calmol-1K-1)	97.751	99.884
5	Vibrational Energy Evib (Kcalmol-1)	68.857	64.292
6	Zero Point Vibrational Energy (Kcalmol-1)	64.8648	59.9457
7	Rotational constants (GHz)		
	A	1.49591	1.46818
	B	0.5118	0.50461
	C	0,39866	0.39105
8	Dipole Moment (Debye)		
	μ_x	3.384	3.2974
	μ_y	-2.1561	-2.0365
	μ_z	-2.2955	-2.0029
	μ_{total}	4.6227	4.3626

Table 4.2 : Vibrational assignments of 2,4-Dichlorobenzoic acid

S. No	Experimental frequencies (cm^{-1})		Calculated Frequencies (cm^{-1})		Vibrational Assignment
	FTIR	FT Raman	HF/ 6-31+G (d,p)	DFT/B3LYP/ 6-31 +G (d,p)	
1	3486		3542 (s)	3505 (s)	O-H Stretching
2	3072	3079	3132 (s)	3072 (w)	C-H Stretching
3			3122 (s)	3067 (vw)	C-H Stretching
4	2995		3088 (s)	3032 (w)	C-H Stretching
5	1684	1664	1886 (s)	1755 (vs)	C = O Stretching+C-O Bending+O-H Bending
6	1555	1558	1644 (s)	1547(vs)	C-C Stretching + C-H Bending + Ring stretching
7			1603 (s)	1515 (s)	C-C Stretching+ C-H Bending + Ring stretching
8	1427	1433	1515 (s)	1428 (s)	C-C Stretching+ C-H Bending
9	1311	1299	1402 (s)	1337(s)	C-C Stretching+ C-H Bending
10	1267	1255	1341(s)	1263 (vs)	C-O Stretching+ O-H Bending + C-H Bending
11			1283 (s)	1239 (vs)	C-C Stretching + O-H Bending + C-H Bending
12	1214		1216 (s)	1217(s)	C-H Bending + O-H Bending
13	1138	1139	1185 (s)	1141(s)	C-H Bending + O-H Bending
14	1111	1117	1131(s)	1112(m)	C-H Bending + O-H Bending
15	1063		1124 (s)	1067(s)	C-H Bending+ C-C Stretching
16		1055	1104 (s)	1055(s)	C-H Bending + C-C Stretching + O-H Bending + O-H Bending
17			1058(s)	1000(s)	C-H Bending + O-H Bending + C-O Stretching
18	916		1010(s)	920 (w)	C-O Stretching + Ring stretching
19	847	844	931(s)	844(m)	C-H Out of Plane Bending
20			871(s)	797(s)	C-H Out of Plane Bending
21	772		837(s)	793(s)	C-Cl Stretching + C-H Bending + O-H Bending + C-O Stretching
22	760	745	793(s)	730 (m)	C-C Bending + C-H Bending +C=O Bending + C-Cl Stretching +Ring stretching
23	679		736(s)	692(m)	C-Cl Stretching + C = O bending + O-H Bending
24	671	673	723(s)	668(w)	C-Cl Stretching + C-C Bending + O-H Bending
25		663	673(s)	641(w)	C-H Bending + C-C Bending + C = O Bending
26	570		600(s)	561(m)	C = O Bending + C-Cl Bending
27			523(s)	498(m)	O-H Out of Plane Bending + C = O Bending
28			509(s)	491(s)	O-H Bending + C-O Bending + C-Cl Stretching
29			477(s)	473 (s)	O-H Bending + C-O Bending + C=O Bending
30		413	435(s)	413 (w)	C-Cl Stretching + C -H bending + Ring Torsion
31			404(s)	385(w)	O-H Bending + C-O Bending + C=O Bending
32		344	375 (s)	355 (w)	C-H Bending + C-O Bending + C-Cl Bending + C=O Bending + Ring Torsion
33		288	293 (s)	281(vw)	C-C Stretching + C -H bending + Ring Torsion
34		210	229 (s)	216 (w)	O-H Out of Plane Bending + C-Cl Bending
35		183	193 (s)	186 (vw)	C-Cl Bending + C-O Bending + C=O Bending
36			173(s)	162 (vw)	C-Cl Bending + C-O Bending + C=O Bending
37		126	152 (s)	146 (w)	C-C Out of Plane Bending + Ring Torsion
38			76 (s)	72 (w)	O-H Bending + C-O Bending + C=O Bending
39			39 (s)	44 (w)	O-H Bending + C-O Bending + C=O Bending

CONCLUSION

The geometry of 2, 4-Dichlorobenzoic acid was optimized with HF and DFT-B3LYP methods using 6-31 +G(d, p) basis sets. The complete molecular structural parameters and thermodynamic properties of the optimized geometry of the compound have been obtained from ab initio HF and DFT calculations. The bond order and atomic charges of the title molecule have been studied by both methods. The vibrational frequencies of the compound have been precisely assigned and analyzed and the theoretical results were compared with the experimental vibrations. The spectral studies such as FT-IR, FT-Raman for 2, 4-Dichlorobenzoic acid was carried out with quantum chemical computations. A complete vibrational and molecular structure analysis has been performed based on the quantum mechanical approach by B3LYP calculations in 6-31 +G (d, p) basis set. The difference between the observed and scaled wave number values of the most of the fundamental is very small. The complete vibrational assignment was calculated. The theoretically constructed FT-IR and FT-Raman spectra had good correlation with experimentally observed FT-IR and FT-Raman spectra. HOMO-LUMO analysis shows that charge transfer takes place in the molecule. Thus the present investigation provides the complete vibrational assignments, structural information and thermodynamic properties of the compound which may be useful to upgrade the knowledge on the molecule.

REFERENCES

[1] http://sdbs.db.aist.go.jp/sdbs/cgibin/direct_frame_top.cgi.

[2] W. Kohn, L. J. Sham, Self-consistent equations including exchange and correlation effects 140 , pp A1133–A1138, 1965.

[3] A. D. Becke, J. Chem. Phys. 98, pp 5648–5652, 1993.

[4] C. Lee, W.Yang, R.G.Parr, Phys. Rev. B 37 pp 785–789, 1988.

[5] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, B.Johnson, W.M. Chen, W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Wallingford, CT, 2004.

[6] H.B. Schlegel, J. Comput. Chem. 3, pp 214 -218, 1982.

[7] A.Frisch, A.B.Nielsen, A.J. Holder. Gaussview Users Manual, Gaussian Inc., Pittsburgh, 2000.

[8] Varsanyi G., Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives, Vol.1 and 2, Academial Kiado, Budapest, 1973.

[9] Vander Maas J.H, Lutz E.T.G, " Structural information from OH stretching frequencies monohydric saturated alcohols", Spectrochimica Acta Part A, 30, pp 2005–2019, 1974.

[10] Rajalakshmi.K, Gunasekaran.S, Kumaresan.S, " Vibrational spectra, electronic and quantum mechanical investigations on ciprofloxacin ", Ind J. Pure &Applied Phys. 88, pp 733-742, 2014.

[11] Silverstein M., Glayton Basseler G., Morill C., Spectrometric Identification of Organic Compounds, Wiley, New York, 1981.

[12] M.Arivazhagan, K.Sambathkumar, S.Jeyavijayan, Ind. J.Pure & Appl. Phys. 48, 869-874, 2010.

[13] M Szafran, AKomasa and E B AdamskaJ. Mol. Struct. Theochem .**827,** 101, 2007.

[14] Gunasekaran S, Thilak kumar R, Ponnusamy S, "Vibrational Spectra and Normal Co-ordinate analysis of Aderenaline and Dopamine ", Ind J. Pure &Applied Phys. 45, pp 884 -892, 2007.

[15] G.Socrates, Infrared Characteristic Group Frequencies, Wiley, Interscience Publications, New York, 1980.