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Vibrational spectroscopic (FT-IR and FT-Raman), Computational studies, thermodynamic functions, HOMO-LUMO analyses of 2-hydroxy-3,5dichlorobenzaldehyde

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ARTICLE INFO	ABSTRACT
Article history:	In this paper, we report a combined experimental and theoretical study on molecular
Received: 29 March 2013;	structure; vibrational spectra of 2-hydroxy-3,5-dichlorobenzaldehyde (HDCB) have been
Received in revised form:	recorded using Fourier transform infrared (FT-IR) and FT-Raman spectra in the region of
17 April 2013;	4000–400 cm ⁻¹ and 3500–100 cm ⁻¹ , respectively. The conformational stability, molecular
Accepted: 3 May 2013;	geometry and harmonic vibrational frequencies were obtained by HF/6-31++G(d,p) and
	B3LYP/ $6-31++G(d,p)$ basis set. The calculated harmonic vibrational frequencies were
Keywords	compared with experimental FTIR and FT-Raman fundamentals. The observed and
	colculated frequencies are found to be in good agreement. The colculated HOMO and

Conformation analysis; 2-hydroxy-3,5-dichlorobenzaldehyde; Density functional theory; Vibrational spectra.

calculated frequencies are found to be in good agreement. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. The thermodynamic functions from spectroscopic data by statistical methods were obtained for the range of temperature 100 - 1000K.

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1. Introduction

Benzaldehyde and acetophenone derivatives treated with base to form a substituted chalcone, which has been found to have anti-cancer properties. Substituted benzaldehydes such as p-hydroxybenzaldehyde, p-chlorobenzaldehyde, vanillin. anisaldehyde are used in the synthesis of biologically active polymers, for example, in Chitosen derivatives, which are known for application in cosmetics, textiles, as biomaterials and for anti-microbial activity [1]. Several workers have investigated vibrational spectroscopic properties, mutual influence of different types of substituents such as halogens, methyl, methoxy and hydroxyl through the benzaldehyde, the interactions between the ring and substituents, by the joint experimental and/or theoretical methods [2-5]. The conformational stability and vibrational spectral analysis of 2chloro-5-nitrobenzaldehyde have been investigated by Balachandran et al [6]. Nataraj et al. [7, 8] have investigated the structural conformations, intramolecular charge transfer and vibrational spectra of 4-hydroxy-3-methoxy-5nitrobenzaldehyde and 2-hydroxy-5-bromobenzaldehyde. The vibrational spectra of three isomeric methoxy benzaldehydes [8] as well as four dihydroxybenzaldehydes [2] have been investigated by Singh et al., based on electronic structure calculations and normal coordinate analysis. The existence of two rotational isomers between phenyl and formyl groups in 2chlorobenzaldehyde has been investigated by Akai et al [9]. In another study on the o- and m- substituted benzaldehydes by matrix isolation IR spectroscopy, Bednarek et al. have shown that the relative B3LYP/6-31G* energies of the cis and trans rotamers between oxygen of formyl group and chlorine of chlorobenzaldehyde decreases significantly from ortho to meta substitution [10]. By investigating three structural isomers (p-, m- and o-) of fluorobenzaldehyde (FB), Itoh [11] has shown that the formation of the intramolecular C-H.....F hydrogen

bond for the O-trans rotamer of o- FB results in the shortening of the aldehyde C-H bond length. The C-F and C=O bond lengths shortened for the O-cis rotamer of O-FB presumably due to the repulsion between the aldehyde O and F atoms. Likewise several vibrational spectroscopic studies on mono-, diand *tri*- substituted benzaldehydes have been reported [11–15]. It appears that methoxy, hydroxyl and nitro-substituted benzaldehyde has not been subjected to a systematic investigation of structure and vibrational assignments aided by DFT/B3LYP level with the 6-31++G(d,p) basis set. Hence, in the present study, we have undertaken a systematic vibrational spectroscopic investigation of HDCB. The present paper deals with a complete vibrational assignment of the infrared and Raman spectra of HDCB, aided by the electronic structure calculations, namely hybrid density functional method (B3LYP) with HF/6-31++(d,p) basis sets. Further, owing to coupling of different vibrations in normal modes, potential energy distribution (PEDs) and normal mode analysis have also been carried to ascertain the contributions of bond oscillators in each normal mode [16]. The motivation of this study is to give a description of the molecular vibrations, and HOMO-LUMO energy of HDCB based on DFT method.

2. Experimental Details

The compound HDCB is obtained from Lancaster Chemical Company, UK and used as such without further purification for the spectral measurements. The Fourier transform infrared spectrum of the title compound was recorded in the region 4000-400 cm⁻¹, at a resolution ± 1 cm⁻¹, using BRUKER IFS 66V Vacuum Fourier transform spectrophotometer equipped with an MCT detector, a KBr beam splitter and globar source. The FT-Raman was recorded on the same instrument with an FRA-106 Raman accessory in the region 3500-100 cm⁻¹. The 1064 nm Nd:YAG laser was used as an excitation source, and the laser power was set to 200mW.

3. Computational details

The entire quantum chemical calculations have performed at HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) basis sets using the Gaussian 09W program package [17]. The optimized structural parameters have been evaluated for the calculation of vibrational frequencies at Becke's three parameter hybrid model using the Lee-Yang-Parr [18, 19] correlation functional (B3LYP) method by assuming C_s point group symmetry. As a result, the unscaled calculated frequencies reduced mass, force constant, infrared intensity and Raman activity, are obtained. In order to fit the theoretical frequencies to the experimental frequencies, an overall scaling factor has been introduced by using a least-square optimization of the computed to the experimental data. The vibrational frequencies are scaled as 0.9963 for frequencies less than 1700 cm^{-1} and 0.8961 for higher frequencies for HF and B3LYP, respectively. The assignments of the calculated normal modes have been made on the basis of the corresponding PEDs. The PEDs are computed from quantum chemically calculated vibrational frequencies using MOLVIB program version 7.0 written by Sundius [20, 21]. Gauss view program [22] has been considered to get visual animation and also for the verification of the normal modes assignment.

4. Results and Discussion

4.1 Geometrical parameters

In order to find the most optimized geometry, the energy calculations were carried out for HDCB, using HF and B3LYP/6-31++G(d,p) basis set for various possible conformers. The computationally predicted various possible conformers obtained for the title compound are shown in Fig.1.



Fig. 1. Various possible conformers of 2-hydroxy-3,5dichlorobenzaldehyde

The total energies obtained for these conformers are listed in Table 1. It is clean from the Table 1, the DFT structure optimizations have shown that the conformers of Fig. 1(C2) of HDCB has produced the global minimum energy. The most optimized structural parameters were also calculated and they were depicted in Table 2.

4.2 Vibrational frequencies and normal coordinate analysis

The optimized structural parameter were used to compute the vibrational frequencies of the stable conformer of HDCB (Fig. 1(C2)) at HF and B3LYP/6-31++G(d,p) level of calculations. The molecule belongs to Cs point group symmetry. The HDCB molecule under investigation has 15 atoms give rise to 39 normal modes of fundamental vibrations, which span the irreducible representations: 27A'+12A'', all the 39 fundamental vibrations are active in both IR and Raman.

Normal coordinate analysis was carried out to provide a complete assignment of the fundamental vibrational frequencies for the molecule. For this purpose, the full set of 51 standard internal coordinates containing 14 redundancies for HDCB were defined as given in Table 3. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Puley et al.[23] and they were presented in Table 4. The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations. The observed FT-IR and FT-Raman spectra of the title compound were presented in Figs.2 and 3, respectively which helps to understand the observed spectral frequencies.



Fig. 2. Observed FT-IR spectrum of 2-hydroxy-3,5dichlorobenzaldehyde



Fig. 3. Observed FT-Raman spectrum of 2-hydroxy-3,5dichlorobenzaldehyde

O-H and **C-O** vibrations

The O–H group rises to three vibrations of HDCB compound (stretching, in-plane bending and out-of-plane bending vibrations). The O–H group vibrations are likely to be the most sensitive to the environment, so they show pronounced shifts in the spectra of the hydrogen bonded species. In this present study, the stable conformer Fig. 1(C2) shows the

attractive interaction between the hydrogen donor group and acceptor moiety leads to found new vibrational frequencies, they so called hydrogen bond modes. Such modes are connected with elongations of changing the A...B distance and/or the relative orientation of the hydrogen-bonded groups, Thus, they provide direct insight into the structure of hydrogen bonds and into processes of bond formation and cleavage. As such modes are characterized by a low reduced mass of the oscillator and a high force constant determined by the comparably strong attractive interaction along the hydrogen bond, hydrogen-bond modes occur at higher frequencies in the range between about 3450 cm⁻¹ and 3300 cm⁻¹. These intramolecular hydrogen bonds can be responsible for the geometry and the stability of the compound.

In the present study, the observed -OH stretching vibration at 3441 cm⁻¹ in IR lie close to the range suggested by Bellamy for intramolecular hydrogen bonds, in the range 3450 - 3200 cm⁻¹ [24]. The vibration assigned by Gauss view program package at 3452 cm⁻¹ by B3LYP/6-31++G(d,p) shows good agreement with observations of HDCB. The in-plane OH deformation [25] is expected in the region 1240 ± 60 cm⁻¹ and therefore in the present study, the band is observed at 1331 cm⁻¹ (IR), and 1333 cm⁻¹ (Raman) is assigned to in-plane bending mode of oxygen and hydrogen and this mode of vibration shows good agreement with the theoretical frequency at 1343 cm⁻¹.

The out-of-plane –OH deformation is dependent on the strength at hydrogen bond [26] and it is influenced by the nature of the substituents in the case of electron accepting or almost neutral groups, the band is found above 400 cm⁻¹ whereas with electron donating substituents the band occurs below 400 cm⁻¹ for the solid sample of compound [27–29]. In the present study, this band is observed in FT-Raman at 437 cm⁻¹. The theoretically computed value by HF/B3LYP/6-31++G(d,p) show the same kind of vibration at 518 and 448 cm⁻¹. The calculated values by B3LYP/6-31++G(d,p) is good agreement with recorded spectrum.

In the present study, the FT-Raman band observed at 1458 for the title compound is attributed to C–O stretching vibration in hydroxyl group. The observed IR frequency at 273 cm⁻¹ is attributed to C–OH (hydroxyl) out-plane bending mode. These assignments were also supported by the literature [30–32].

C-H vibrations

The aromatic structure shows the presence of C–H stretching at 3068, 2930 cm⁻¹ in IR and 3065 cm⁻¹ is observed in Raman spectrum. The band identified at 1271, 1221, 1188 (IR) and 1281, 1180 cm⁻¹ (Raman) are assigned for C–H in-plane bending mode. The C–H out-of-plane bending vibrations have been found at 1100, and 918 cm⁻¹ in theoretical value nearly coincides with experimental value at 1104, 919 and 872 cm⁻¹ in IR spectrum. These modes of vibrations are not affected appreciably by the nature of the substituents. These observations are in good agreement with the literature value [33].

C-CHO stretching and bending modes

The molecule under consideration possesses one C–CHO stretching vibration. Normally the band at appear around 1460 cm⁻¹ is assigned as C–CHO stretching vibration [34]. In our case also a strong band in FT-IR at 1430 cm⁻¹ is assigned to C–CHO stretching vibration. The theoretical frequency of this band at 1424 cm⁻¹ coincides well with the experimental as well as characteristic value [34] reported in literature. The C–CHO in-plane and out-of-plane bending modes also rise to bands at

340, 332 cm⁻¹ in theoretically calculated values, respectively. These are correlating very well with the literature [35]. –*CHO vibrations*

Group vibrations were determined in terms of the motions of the nuclei in the molecule undergo during vibrations and they appear in fairly constant regions of the spectrum. The strong band observed at 1663 cm⁻¹ in FT-IR and the very strong band observed at 1668 cm⁻¹ in FT-Raman have been assigned to C=O stretching in the –CHO group. The aldehydic C–H stretching vibration is the most important group frequency for aldehyde. The aldehydic C–H stretching frequency occurs lower than the most other C–H stretching vibrations. Two characteristic bands are usually observed due to the stretching vibration of the aldehydic C–H, both of which are of weak to medium intensity at about 2820 cm⁻¹ and the other in the region 2745–2650 cm⁻¹ [36].

The C–H stretching band although weak, is useful for characterization purposes. However, the overtone of the C–H inplane deformations may disturb the position of the C–H stretching band or result in some confusion. The presence of two bands in the region $2895-2650 \text{ cm}^{-1}$ is due to an interaction between the C–H stretching vibration and the overtone of C–H bending vibration near at 1180 cm^{-1} in FT-Raman and 1186 cm^{-1} in IR spectrum. This involves Fermi resonance since aldehyde for which the latter band is shifted have only one band, this being in the region $2895-2805 \text{ cm}^{-1}$. Thus, the strong and very weak intensity band at 2861 cm^{-1} in Raman is attributed to the aldehydic C–H stretching mode. The computed value at 872 cm^{-1} in infrared and 875 cm^{-1} in Raman spectrum is ascribed to the aldehydic out-of-plane deformational mode.

The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. This multiply bonded group is highly polar and therefore gives rise to an intense infrared absorption band. The carbon-oxygen double bond is formed by $p_{\pi-} p_{\pi}$ bonding between carbon and oxygen. Because of the different electro-negatives of carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms. The following two resonance forms contribute to the bonding of the carbonyl group:

 $>C=O \leftrightarrow C^+ - O^-$

The lone pair of electrons on oxygen also determines the nature of the carbonyl group. In the present study, the very strong band observed at 1663 cm⁻¹ in IR and 1668 cm⁻¹ in Raman for HDCB (Table 5) is assigned to C=O stretching vibration. The observed values for the in-plane and out-of plane bending vibrations of C=O bond are good agreement with the theoretical values and they are tabulated in Table 4. *C*–*Cl vibrations*

The presence of halogen on alkyl substituted aromatic ring can be detected indirectly from its electronic impact on the inplane C–Cl bending vibrations [37]. The substitution pattern in an aromatic is identified by looking at the C–Cl out-of-plane bending bands and also from the combination bands between 1650 and 2000 cm⁻¹. The position of absorption of the out-ofplane bending bands depends on the number of adjacent hydrogen atoms on the ring. A di-substituted benzene displays two very strong bands between 690–710 cm⁻¹ and 730–770 cm⁻¹ [38]. The C–Cl stretching vibrations give generally strong bands in the region 730–580 cm⁻¹ [39]. In this present work, the peaks at 720 in IR and 722 and 379 cm⁻¹ in Raman are due to C–Cl stretching vibrations and it may also imply that the compound is a di-chlorinated compound in the substituted aromatic ring. The theoretically computed values of C–Cl stretching vibrations are found to be 792 380, cm⁻¹ and 721, 377 cm⁻¹ by HF/6-31++G(d,p) and B3LYP/6-31++G(d,p), respectively and good agreement with experimental values.

The calculated frequencies at 204, 171 cm⁻¹ and 175, 163 cm⁻¹ by HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) methods are assigned to C–Cl in-plane bending vibrations which fall in the FT-Raman value at 179 cm⁻¹ which is good agreement with the literature [38]. The computed value predicted by HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) methods at 223, 136 and 208, 130 cm⁻¹ does not correlate with experimental observation for C–Cl out-of-plane bending deformation this may be due to substituent and conjugation effects.

5. HOMO-LUMO analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability [40]. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron the HOMO and LUMO energies were calculated by B3LYP/6-31++G(d,p) method. This electronic transition absorption corresponds to transition from the ground state to the first excited state and is mainly described by an electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

The HOMO is located over methoxy and OH group, the HOMO \rightarrow LUMO transition implies an electron density transfer to ring from OH group. Moreover, the orbital significantly overlap in their position for HDCB. The atomic orbital compositions of the frontier molecular orbital are sketched in Fig. 4.



HOMO-LUMO energy gap (B3LYP) = 0.09327 a.u

The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

6. Thermodynamic properties

The total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies. ie, E = Et + Er + ErEv + Ee. The statistical thermo chemical analysis of HDCB is carried out considering the molecule to be at room temperature of 298.15 K and one atmospheric pressure. The thermodynamic parameters, like rotational constant, zero point vibrational energy (ZPVE) of the molecule by DFT (B3LYP level) and HF methods were presented in Table 5 for HDCB. The title molecule is considered as an asymmetric top having rotational symmetry number 1 and the total thermal energy has been arrived as the sum of electronic, translational, rotational and vibrational energies. The variations in the zero point vibrational energy seem to be insignificant. The thermodynamic functions are determined from spectroscopic data by statistical methods. The thermodynamic quantities such as entropy S_{vib} , enthalpy (H-E)/T, and Gibb's free energy (G-E)/T for various ranges (100K-1000K) of temperatures are determined using the vibrational wave numbers and these results are presented in the Table 5. The correlation equations between these thermodynamic properties and temperatures were fitted by parabolic formula. All the thermodynamic data provide helpful information for the further study on the title compound. From the Table 8 it can be observed that the thermodynamic parameters are increasing with temperature ranging from 100K to 1000K, (Fig. 5) due to the fact that the vibrational intensities of molecule with temperature. For C2 conformer the following equations are used to predict approximately the values of heat capacity at constant pressure, entropy and internal energy for other range of temperature. The regression coefficient is also given in the parabolic equation.





Fig. 5 Temperature dependence with thermodynamic parameters of 2-hydroxy-3,5-dichlorobenzaldehyde For B3LYP method

 $(S) = 66.32 + 0.033T - 0.00002T^{2}(R^{2} = 0.993)$ $((H^{0} - E_{0}^{0})/T) = 8.451 + 0.004T - 0.00007T^{2}(R^{2} = 0.991)$ $(G^{0} - E_{0}^{0})/T) = -57.86 + 0.037T - 0.00008T^{2}(R^{2} = 0.994)$

Table 1. Calculated energies and energy difference for three conformers of 2-hydroxy-3, 5-dichlorobenzaldehyde with HF/6-31++G(d,p) and DFT/B3LYP/6-31++G(d,p) using 6-31++G(d,p) method								
	HF/6-311++G(d,p) B3LYP/6-311++G(d,p)							
Conformers	Energy (hartree)	Energy (kJmol ⁻¹)	Energy (hartree)	Energy (kJmol ⁻¹)				
C1	-1335.843521	-3507257.432971	-1339.800107	-3517645.448888				
C2	-1335.857334	-3507293.699085	-1339.812088	-3517676.905006				
C3	-1335.814973	-3507182.479929	-1339.767601	-3517560.104379				
C4	-1335.826379	-3507212.426385	-1339.774998	-3517579.525204				

*Energies of the other three conformers relative to the most stable C2 conformer.

Table 2. Internal co-ordinates of 2-hydroxy-3, 5-dichlorobenzaldehyde									
No	Symbol	Туре	Definition						
Stretching									
1-7	r _i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C1-C7						
8-10	ti	C-H	C4-H13, C6-H15, C7-H9						
11-12	si	C-Cl	C3-Cl12, C5-Cl14						
13	p _i	C-0	C2-O10						
14	q_i	O-H	O10-H11						
15	T _i	C=O	C7-O8						
In-plane	e bending								
16-21	α_i	Ring	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2.						
22-25	β_i	C-C-H	C3-C4-H13, C5-C4-H13, C5-C6-H15, C1-C6-H15						
26	β _i	С-С-Н	С1-С7-Н9.						
27-30	δi	C-C-Cl	C2-C3-Cl12, C4-C3-Cl12, C4-C5-Cl14, C6-C5Cl14.						
31-32	σ_{i}	C-C-O	C1-C2-O10, C3-C2-O10						
33-34	ρ_i	C-C-C	C2-C1-C7, C6-C1-C7.						
35	π_i	С-О-Н	C2-O10-H11						
36	φ _i	C-C-O	C1-C7-O8						
37	γ_i	O-C-H	O8-C7-H9						
Out-of-p	plane bendi	ng							
38-43	Γ_{i}	Ring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C1, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-						
			C3						
44-45	ω _i	C-H	H13-C4-C3-C5, H15-C6-C1-C5						
46-47	ω _i	C-C-CI	CI12-C3-C2-C4, CI14-C5-C4-C6						
48	ω	C-C	C7-C1-C2-C6						
49	ω _i	C-0	010-C2-C1-C3						
50	ω _i	O-H	H11-O10-C2-C3(C1)						
51	ω _i	H-C-O	H9-C7-O8-CI						

Table 3. Local symmetry co-ordinates of 2-hydroxy-3, 5-dichlorobenzaldehyde							
No	Symbol Definition						
Stretching		·					
1-7	C-C	r1, r2, r3, r4, r5, r6					
8-10	C-H	t8, t9, t10					
11-12	C-Cl	s11, s12					
13	C-0	p13					
14	O-H	q14					
15	C-0	T15					
In-plane b	ending						
16	Rtrigd	$(\alpha 16 - \alpha 17 + \alpha 18 - \alpha 19 + \alpha 20 - \alpha 21))/\sqrt{6}$					
17	Rsym	$(-\alpha 16 - \alpha 17 + \alpha 18 - \alpha 19 - \alpha 20 + 2\alpha 21)/\sqrt{12}$					
18	Rasym	$(\alpha 16 - \alpha 17 + \alpha 19 - \alpha 20)/\sqrt{2}$					
19-20	bCH	(β22-β23) √2, (β24-β25) √2					
21	bCH	β26					
22-23	bCCl	$(\delta 27 - \delta 28) \sqrt{2}, (\delta 29 - \delta 30)) \sqrt{2}$					
24	bCO	(σ31-σ32)/√2					
25	bCC	(p33-p34) √2					
26	bOH	π35					
27	bCO	ρ36					
28	bCH	ý37					
Out-of-pla	ne bending						
29	tRtrigd	(t38- t39+t40- t41+ t42- t43)/v6					
30	tRsym	$(\tau 38 - \tau 40 + \tau 41 - \tau 43)/2$					
31	tRasym	$(-\tau 38 + 2\tau 39 - \tau 40 - \tau 41 + 2\tau 42 - \tau 43)/\sqrt{12}$					
32-33	ωCH	ω44, ω47					
34-35	ωCCl	ω46, ω47					
36	ωCC	ω48					
37	ωCO	ω49					
38	ωOH	ω50					
39	ωCH	ω51					

	Table 4. Vibrational spectral analysis of 2-hydroxy-3,5-dichlorobenzaldehyde based on HF /6-31++G(d,p) and B3LYP /6-31++G(d,p)												
		Obsorv	od froquoney		Calculated	freque	ncy	IR in	toncity	Domon	intoncity		
No	Sno	Observ	(cm ⁻¹)		(cn	n ⁻¹)			mol^{-1}	(arb.unit)		Vibrational assignments/(%)TED	
110.	spe.		(cm)	Un	scaled	S	caled	(КШ	iiioi)			Vibrational assignments/(70)1ED	
		FT-IR	FT-Raman	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP		
1	A'	3441		4153	3751	3808	3452	166.30	121.61	43.35	45.92	vOH(99)	
2	A'	3068	3065	3403	3234	3121	3063	4.57	1.40	42.43	52.42	vCH(98)	
3	A'	2930		3399	3227	3117	2936	0.90	5.76	60.01	36.71	vCH(98)	
4	A'		2861	3238	3011	2969	2851	44.00	52.33	102.07	95.05	vCH(98)aldehyde	
5	A'	1663	1668	1974	1765	1694	1666	363.52	273.43	100.00	100.00	vCO(60)+δCC(18)+vCC(12)	
6	A'	1603	1609	1792	1634	1717	1609	64.93	56.69	59.40	58.54	vCC(62)+δCC(20)+vCO(10)	
7	A'		1583	1776	1617	1701	1593	8.11	9.20	14.75	14.80	vCC(63)+δCH(20)+δCH(10)	
8	A'		1458	1620	1487	1552	1465	295.55	254.47	3.08	3.62	vCO(65)+vCC(16)+δCH(12)	
9	A'	1430		1562	1446	1496	1424	5.01	25.41	5.16	7.20	vCC(65)+δCH(16)+δOH(10)	
10	A'	1372		1546	1426	1481	1375	59.68	52.95	2.33	3.30	δCO(68)+vCC(24)	
11	A'	1331	1333	1424	1363	1364	1343	138.62	80.43	2.44	2.51	δOH(63)+vCC(21)+δCH(11)	
12	A'	1279	1281	1394	1288	1335	1279	48.95	57.91	28.41	25.66	δCH (62)+vCC(22)+vCC(11)	
13	A'	1221		1323	1268	1267	1229	62.16	82.33	65.41	7.93	δCH (60)+δOH(24)+vCC(11)	
14	A'		1208	1286	1217	1232	1199	69.50	67.58	13.49	77.32	vCC(62)+δCH(20)+δOH(11)	
15	A'	1186	1180	1217	1199	1166	1181	35.35	111.94	37.55	11.10	δCH(61)+δOH(21)+vCCl(10)	
16	A'		1109	1201	1110	1151	1098	85.41	15.98	9.51	25.86	$\delta \text{Ring}(62) + v \text{CC}(24)$	
17	A"	1104		1142	1025	1094	1110	0.01	0.61	17.36	8.01	γCH (65)+γCC(23)	
18	A"	919		1061	929	1016	915	4.08	5.73	1.37	0.65	γ CH(64)+ γ Ring(25)	
19	A'		903	1029	925	986	911	23.73	8.05	0.23	17.38	$vCC(65)+vCCl(23)+\delta Ring(11)$	
20	A"	872	875	1000	886	958	873	10.44	21.58	36.70	0.07	$\gamma CH(82) + \gamma Ring(10)$	
21	A'	826	830	925	856	886	833	21.04	13.96	74.96	72.86	δ Ring(54)+vCCl(22)+vCO(20)	
22	A'	720	722	827	762	792	721	87.67	99.34	30.23	14.99	$vCCl(67)+\delta Ring(24)+\delta CO(10)$	
23	A"	688	680	791	688	758	678	9.77	2.71	8.11	5.95	$\gamma \text{Ring}(58) + \gamma \text{CCl}(21) + \gamma \text{CC}(13)$	
24	A'			718	667	688	657	27.82	22.08	1.95	5.23	$\delta \text{Ring}(73) + \delta \text{COH}(21)$	
25	A"	547		626	565	600	557	6.60	5.56	1.34	0.96	$\gamma \text{Ring}(73) + \gamma \text{CCl}(24)$	
26	A'	512	513	607	561	582	517	50.37	47.40	21.57	14.94	vCC(64)+δCH(21)	
27	A'		437	541	485	518	448	0.02	0.02	0.24	0.93	γOH (80)+γCC(11)	
28	A"			448	431	429	425	4.71	96.39	12.07	4.61	vCC (65)+δCO(20)+δCH(11)	
29	A'			414	413	417	407	0.60	4.15	92.63	5.87	δCO(75)+δCH(18)	
30	A'		379	397	383	380	377	3.73	1.11	40.39	76.36	vCCl(78)+δRing(16)	
31	A'		341	395	368	378	340	2.98	3.96	2.90	37.74	δCC(78)+δCH(18)	
32	A"			380	357	364	332	121.83	3.39	3.31	0.21	$\gamma CC(66) + \gamma CO(22) + \gamma Ring(12)$	
33	A"		273	328	300	314	296	0.88	1.38	6.81	3.76	γCO (73)+γRing(21)	
34	A"			233	211	223	208	6.26	3.27	13.05	8.99	γCCl (66)+ $\gamma CH(25)$ + $\gamma Ring(12)$	
35	A'		179	213	198	204	175	2.60	2.01	9.97	9.91	δCCl(76)+δCH(10)	
36	A'			179	165	171	163	3.77	3.26	13.10	12.58	δCCl(75)+δCOH(14)	
37	A"		140	169	161	162	149	8.98	10.15	8.50	11.05	γCO (75)+γCH(12)	
38	A"			142	132	136	130	5.53	2.52	0.75	0.00	γCCl (54)+γCO(20)+γCOH(12)	
39	A"			86	82	82	81	6.40	2.71	3.77	2.63	γ COH (38)+ γ Ring(27)	

v-stretching, β -in-plane bending, γ -out-of-plane bending, β Ring-in-plane ring, γ Ring-out-of-plane ring

Table 5. Statistical thermodynamic parameters of 2-hydroxy-3,5- dichlorobenzaldehyde at various temperatures									
S.No	Temperature (K)	Enthalpy (kcal/mol)	Gibbs free energy (cal/mol K)	Entropy (cal mol ⁻¹ K ⁻¹)					
1	100	7.95	-60.38	68.33					
2	200	7.95	-65.90	73.85					
3	300	7.95	-69.23	77.18					
4	400	7.97	-71.89	79.86					
5	500	8.07	-74.40	82.47					
6	600	8.31	-76.93	85.23					
7	700	8.72	-79.51	88.22					
8	800	9.32	-82.14	91.45					
9	900	10.12	-84.80	94.92					
10	1000	11.11	-87.47	98.58					

7. Electrostatic potential

Electrostatic potential (ESP) at a point in space around a molecule gives Information about the net electrostatic effect produced at that point by total charge distribution (electron+ proton) of the molecule and correlates with dipole moments, electro negativity, partial charges and chemical reactivity of the molecules. It provides a visual method to understand the relative polarity of the molecule. An electron density isosurface mapped with electrostatic potential surface depicts the size, shape, charge density and site of chemical reactivity of the molecules.



Fig. 6. Electrostatic potential surface of 2-hydroxy-3,5dichlorobenzaldehyde

The electrostatic potential at the surface are represented by different colors; red represents regions of most electronegative, blue represents regions of the most positive electrostatic potential and green represents region of zero potential. Potential decreases in the order red < orange < yellow <green < blue. Such mapped electrostatic potential surface have been plotted for title molecule in B3LYP/6-31++G (d,p) basis sets using the computer software Gauss view. Projections of these surfaces along the molecular plane and a perpendicular plane are given in Fig. 6. The hydroxyl group of H atom posses more positive in Nucleophilic region, lone pair of oxygen atom posses more electro negative. This figure provides a visual representation of the chemically active sites and comparative reactivity of atoms [4].

7. Conclusion

The FT-IR and FT-Raman spectra were recorded and the detailed vibrational assignments for HDCB has been proposed, aided by the hybrid density functional method (HF/B3LYP) using 6-31++G(d,p) basis set and PED analysis, for the first time. The most stable conformer of compound was determined with DFT/B3LYP/6-311++G(d,p) level of theory. The hydrogen bonding between -OH and chlorine groups of HDCB compound were determined. The vibrational frequencies were compared with experimental results. The differences between the corresponding frequencies (observed and calculated) are very small for most of fundamentals. Therefore, the results presented in this work for HDCB indicates that this level of theory is reliable for prediction of both infrared and Raman spectra of the title compound. The HOMO-LUMO energy gap for HDCB compound computed at B3LYP/6-311++G(d,p) is 0.16821 a.u. The HOMO-LUMO energies presented in this work shows the presence of charge transfer within the molecule. The correlations between the statistical thermodynamic and temperature are also obtained. It is seen that the heat capacity, entropy and enthalpy

increase with increasing temperature owing to the intensities of the molecular vibrations with increasing temperature. **References**

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