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Vibrational Spectroscopy

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Molecular Structure, Vibrational Investigation, First Hyperpolarizability, NBO and Homo-Lumo Analyses of O-Nitro Benzaldehyde

R. Senthilkumar¹, M. Arivazhagan² and N. Marudhaiveeran³

¹Department of School Educations, Government Higher Sec. School, Thirupainjeeli, Tiruchirappalli-621 005, TN, India. ²Department of Physics, Government Arts College, Thiruverumbur, Tiruchirappalli-620 022, TN, India. ³Department of Physics, Arignar Anna Government Arts College, Musiri-621 211, TN, India.

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ABSTRACT

The vibrational spectroscopy of o-nitrobenzaldehyde (ONBH) by means of quantum chemical calculation has been studied. The FT-Raman and FT-IR spectra of ONBH have been recorded in the region 3500-50cm⁻¹ and 4000-400cm⁻¹ respectively. The fundamental vibrational frequencies and intensity of vibrational bands have been evaluated using density functional theory (DFT) with standard B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p) basis set combinations for optimized geometries. The observed FT-IR and FT-Raman vibrational frequencies have been anlaysed and compared with theoretically predicted vibrational frequencies. The assignments of bands to various normal modes of molecule have also been carried out. The electric dipole moment (μ) and the first hyper polarazibility (β) values of the investigated molecule have been computed using DFT calculations. The calculated HOMO and LUMO energies show that charge transfer occur with in the molecule.

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Introduction

Benzaldehyde is an organic compound consisting of a benzene ring with a formyl substituent. It is the simplest aromatic aldehyde and one of the most industrially useful compounds. Substituted benzaldehydes such as vanillin, phydroxy-benzaldehyde, p-chlorobenzaldehyde and anisaldehyde are used in the synthesis of biologically active polymers, for example, in Chitosan derivatives, which are known for the application in cosmetics, textiles, as biomaterials and for antimicrobial activity [1]. Benzaldehyde and acetophenone derivatives are treated with base to form a substituted chalone, which has been found to have anti-cancer properties [2]. 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 experiment and or theoretical methods [3-8]. Hiremath et al have investigated about trisubstituted benzaldehydes [9]. Singh et al have studied about the vibrational spectra of three isomeric methoxy benzaldehyde [3] as well as four dihydroxybenzaldehydes [4] based on electronic structure calculations and normal coordinate analysis.

Literature survey reveals that to the best of our knowledge no DFT/B3LYP frequency calculations with the basis set of 6-31G+(d,p) and 6-31++G(d,p) of o-nitro benzaldehyde (ONBH) have been reported so far. Hence in the present investigation has been undertaken to study the vibrational spectra, highest occupied molecular orbital (HOMO), Lowest unoccupied molecular orbital (LUMO), Natural bond orbital analysis and First-order hyperpolarizability of these non-linear optically (NLO) active compounds and thermodynamical properties of the chosen compound.

The pure sample of ONBH was obtained from Lancaster chemical company, UK and used as such without any further purification to record FT-IR and FT-Raman spectra. The room temperature Fourier transform IR spectrum of the title compound was measured in the $4000 - 400 \text{ cm}^{-1}$ region at a resolution of ± 1 cm⁻¹ using BRUKER IFS-66V Fourier transform spectrometer equipped with an MCT detector, a KBr beam splitter and globar arc source. The FT-Raman spectrum was recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory. The FT-Raman spectrum is recorded in the 3500 - 50 cm⁻¹ stokes region using the 1064 nm line of Nd:YAG laser for the excitation operating at 200mW power. The reported wave numbers are expected to be accurate within $\pm 1 \text{ cm}^{-1}$.

Computational Methods

The molecular structure of ONBH in the ground state is computed using B3LYP with 6-31+G(d,p) and 6-31++G(d,p)basis set. All the computations have been done by adding polarization function and diffuse function on heavy atoms [10,11]. The calculated frequencies are scaled by 0.890 and 0.852 for B3LYP with 6-31+G (d, p) and 6-31++G (d,p) basis set by 0.934, 0.940, 0.982, 0.952, 0.899 and 0.969 [12]. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of the title compound. The DFT calculations for ONBH are performed using GAUSSIAN 09W program without any constraint on the geometry [13].

Result and Discussion

Molecular Geometry

The molecular structure of ONBH having C_1 symmetry is shown in Fig. 1. The ONBH compound consists of 16 atoms which lead to 42 normal modes. Detailed description of

vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 57 internal coordinates which contains 15 redundancies for the title compound is presented in Table 1.

Table 1. Definitions of Internal coordinates of onitrobenzaldehyde

S.No	Symbol	Туре	Definitions ^a
Stretching			
1-7	Pi	C–C	C ₁ -C ₂ , C ₂ -C ₃ , C ₃ -C ₄ , C ₄ -C ₅ , C ₅ -C ₆ ,
			C ₁ -C ₇
8-12	pi	С–Н	C ₃ -H ₁₃ , C ₄ -H ₁₄ , C ₅ -H ₁₅ , C ₆ -H ₁₆ ,
			C7-H9
13	Qi	C=O	C ₇ =O ₈
14	qi	C–N	C ₂ -N ₁₀
15-16	R _i	N-O	N ₁₀ -O ₁₁ , N ₁₀ -O ₁₂
Inplane	bending		
17-22	α_i	CCC	$C_1 - C_2 - C_3, C_2 - C_3 - C_4, C_3 - C_4 - C_5,$
		ring	$C_4 - C_5 - C_6, C_5 - C_6 - C_1, C_6 - C_1 - C_2$
23-30	β_i	С–С–Н	$C_2-C_3-H_{13}, C_4-C_3-H_{13}, C_3-C_4-H_{14},$
			$C_5 - C_4 - H_{14},$
			$C_4 - C_5 - H_{15}, C_6 - C_5 - H_{15}, C_5 - C_6 - H_{16},$
			C ₁ -C ₆ -H ₁₆
31-32	γ_i	C-C-N	$C_1 - C_2 - N_{10}, C_3 - C_2 - N_{10}$
33-34	σ_i	C-N-O	$C_2 - N_{10} - O_{11}, C_2 - N_{10} - O_{12}$
35	φ _i	0-N-0	O ₁₁ -N ₁₀ -O ₁₂
36	ε _i	C-C=O	$C_1 - C_7 = O_8$
37	ψ_i	С–С–Н	C ₁ -C ₇ -H ₉
38	Δ_{i}	О=С-Н	$O_8 = C_7 - H_9$
39-40	χ _i	С–С–С	$C_2 - C_1 - C_7, C_6 - C_1 - C_7$
Out of plane			
bending	1		
41-44	μ_{i}	С–С–Н	$H_{13}-C_3-C_4-C_2, H_{14}-C_4-C_5-C_3,$
			$H_{15}-C_5-C_6-C_4, H_{16}-C_6-C_1-C_5$
45	∇_{i}	C-C-N	$N_{10}-C_2-C_3-C_1$
46	λ_i	τNO_2	$(C_1, C_3) - C_2 - N_{10} - (O_{11}, O_{12})$
47	η_i	С–С–Н	$(C_2 - C_6) - C_1 - C_7 - H_9$
48	ω _i	С-С-О	$(C_2 - C_6) - C_1 - C_7 = O_8$
49–57	τ_i	Torsion	$C_1 - C_2 - C_3 - C_4, C_2 - C_3 - C_4 - C_5,$
			$C_3 - C_4 - C_5 - C_6,$
			$C_4 - C_5 - C_6 - C_1, C_5 - C_6 - C_1 - C_2,$
			$C_6 - C_1 - C_2 - C_3$

From these non-redundant set of local symmetry coordinates are presented in Table 2.

The calculated optimized geometrical parameters of ONBH are given in Table 3.



Fig 1. Molecular structure of o-nitrobenzaldehyde

Vibrational Frequencies

The detailed vibrational assignments of fundamentals modes of ONBH along with calculated IR and Raman frequencies, IR intensities, Raman activities, reduced mass and force constants are listed in Table 4. Total energy distribution (TED) is calculated by using the scaled quantum mechanical program (SQM) and Fundamental vibrational modes are characterized by their TED. The FTIR and FT-Raman spectra of ONBH are shown in Fig. 2 and 3 respectively.

Table 2. Definitions of Local symmetry coordinates of	0-
nitrohenzaldehyde	

No	Туре	Definitions
1-7	C–C	P ₁ , P ₂ , P ₃ , P ₄ , P ₅ , P ₆ , P ₇
8-12	С–Н	$p_8, p_9, p_{10}, p_{11}, p_{12}$
13	C=O	Q ₁₃
14	C–N	q_{14}
15	NO ₂ sym	$(R_{15}+R_{16})/\sqrt{2}$
16	No ₂ asym	$(R_{15} - R_{16})/\sqrt{2}$
17	R trig	$(\alpha_{17}-\alpha_{18}+\alpha_{19}-\alpha_{20}+\alpha_{21}-\alpha_{22})/\sqrt{6}$
18	R sym	$(-\alpha_{17}-\alpha_{18}+2\alpha_{19}-\alpha_{20}-\alpha_{21}+2\alpha_{22})/\sqrt{12}$
19	R asym	$(\alpha_{17} - \alpha_{18} + \alpha_{20} - \alpha_{21})/2$
20-23	b _{CH}	$(\beta_{23} - \beta_{24}) / \sqrt{2}, \ (\beta_{25} - \beta_{26}) / \sqrt{2} \ , \ (\beta_{27} -$
		$\left \beta_{28} \right / \sqrt{2}$, $\left(\beta_{29} - \beta_{30} \right) / \sqrt{2}$
24	b _{CN}	$(\gamma_{31} - \gamma_{32}) / \sqrt{2}$
25	NO ₂ rock	$(\sigma_{33} - \sigma_{34}) / \sqrt{2}$
26	NO ₂ twist	$(\sigma_{33} + \sigma_{34}) / \sqrt{2}$
27	NO ₂ scissoring	$(2\phi_{35}-\sigma_{33}-\sigma_{34})/\sqrt{6}$
28	b _{CO}	ε ₃₆
29	b _{CH}	Ψ ₃₇
30	b _{oH}	Δ_{38}
31	Xcc	$(\chi_{39} - \chi_{40}) / \sqrt{2}$
32-35	μ_{CH}	$\mu_{41},\mu_{42},\mu_{43},\mu_{44}$
36	$\nabla_{\rm CN}$	∇_{45}
37	τNO_2 wag	λ_{46}
38	η_{CH}	η ₄₇
39	ω _{CO}	ω ₄₈
40	τR_{trig}	$\left(\tau_{49}\!-\!\tau_{50}\!+\!\tau_{51}\!-\!\tau_{52}\!+\tau_{53}\!-\!\tau_{54}\right)/\sqrt{6}$
41	τR _{sym}	$\left(\tau_{49}\!-\!\tau_{51}\!+\!\tau_{52}\!-\!\tau_{54}\right)/\sqrt{2}$
42	τR _{asym}	$\left(-\tau_{49}+2\tau_{50}-\tau_{51}-\tau_{52}+2\tau_{53}-\tau_{54}\right)/\sqrt{12}$



Fig 2. FTIR spectrum of o-nitrobenzaldehyde



Fig 3. FT-Raman spectrum of o-nitrobenzaldehyde C–H vibrations

The aromatic carbon-hydrogen stretching vibrations appear in the region $3100 - 3000 \text{ cm}^{-1}$, C–H in-plane bending vibrations normally appear in the range $1000 - 1300 \text{ cm}^{-1}$ [14, 15]. In the present investigation, C–H stretching vibrations are observed at 3144, 3100, 2944, 2844 cm⁻¹ in the FT-IR spectrum and the corresponding Raman bands are observed at 3075 cm⁻¹. The in-plane C–H bending vibrations of ONBH compound is observed at 1133, 1000 cm⁻¹ in the FT-IR spectrum and 1175, 1138, 1038 and cm⁻¹ in FT-Raman spectrum which are mixed with other vibrations. The out-of-plane C–H bending vibrations of ONBH observed at 894, 867, 822, 789, 744 cm⁻¹ in FT-IR Spectrum and 825 cm⁻¹ Raman spectrum, are well supported by the computed values.

C–C vibrations

The bands observed between 1430 and 1650 cm⁻¹ in benzene derivatives are assigned to C–C stretching modes [16,17]. For ONBH, the IR bands obtained at 1594, 1528 and 1400 cm⁻¹ and the Raman bands at 1613, 1575, 1538 cm⁻¹ and 1444 cm⁻¹ are assigned to C–C stretching vibration modes. These vibrational positions are not very much affected by the nature of the substituent's attached with the ring. The C–C in plane and out-of-plane bending modes of ONBH is also assigned. All these vibrations have been found to be consistent with the experimental observations and in good agreement with the literature [18,19] and listed in Table 4.

Nitro group vibrations

Aromatic nitro compounds have strong absorptions due to the asymmetric and symmetric stretching vibrations of the NO₂ group at 1570 – 1485 cm⁻¹ and 1370 – 1320 cm⁻¹ region, respectively [20]. Hydrogen bonding has a little effect on the NO₂ asymmetric stretching vibrations [21]. For ONBH, the strong bands observed at 1567 cm⁻¹ and 1344 cm⁻¹ in IR spectra corresponds to symmetric and asymmetric stretching modes of nitro group, respectively.

The strong band observed at 694 cm⁻¹ in IR spectrum is assigned to NO₂ scissoring mode of ONBH. The deformation vibrations of NO₂ group (rocking, wagging and twisting) contribute to several normal modes in the low frequency region. In the present investigation, the NO₂ wagging and rocking vibrations of ONBH are observed at 306 and 206 cm⁻¹ in Raman spectra, respectively. These assignments are also supported by the literature [22] in addition to TED output.

Carbon-Nitrogen vibrations

The identification of C-N stretching vibrations is a very difficult task, since mixing of several bands are possible in this region. The C-N stretching absorption assigned in the region

 $1382 - 1266 \text{ cm}^{-1}$ for aromatic amines. The slight shift in wave number is due to the fact that force constants of the C–N bond increases due to resonance with the ring. Pyrimidine absorb strongly in the region $1600 - 1500 \text{ cm}^{-1}$ due to the C=C and C=N ring stretching vibrations [23]. In ONBH, the band observed at 1256 cm⁻¹ in FT-IR spectrum is assigned to C=N stretching vibration and the corresponding force constant contribute 72 % to the TED. The C–N in-plane and out-of-plane bending vibrations have also been identified and are listed in Table 4.

C=O vibrations

The carbonyl group vibrational frequencies are the significant characteristic bands in the vibrational spectra of ketones, and for this reason, such bands have been the subject of extensive studies [24]. The intensity of these bands can increase because of conjugation, therefore, leads to the intensification of the Raman lines as well as the increased infrared band intensities. The carbonyl stretching vibrations in ketones are expected in the region $1680 - 1715 \text{ cm}^{-1}$. In this case, the band observed at 1694 cm^{-1} in Raman spectra is assigned as C=O stretching vibration. The vibrational bands at 1194 cm^{-1} in Raman and 1189 cm^{-1} in IR spectra are assigned to C=O inplane and out-of-plane bending vibrations for ONBH, respectively. These vibrational assignments are in line with the literature [25].

HOMO-LUMO Analysis

In the aromatic compounds electronic transition is takes place from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Molecular orbital coefficients analysis based on optimized geometry indicate that, for ONBH, the frontier molecular orbitals are mainly composed of p-atomic orbitals, so the electronic transitions are mainly derived from the contribution of bands.

For the compound under study, the hips chromic shifts is caused by an increase in the gap between bonding and antibonding orbital's. The energy gap between the highest occupied and the lowest unoccupied molecular orbital's, is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one-electron excitation from HOMO to LUMO. The HOMO energy characterizes the ability of electron giving and the LUMO energy characterizes the ability of electron accepting, and the gap between HOMO and LUMO characterizes the molecular chemical stability. The energy gaps are largely responsible for the chemical and spectroscopic properties of the compound. This is also used by the frontier electron density for predicting the most reactive position in π -electron systems and also explains several types of reaction in conjugated system [26]. The energy value of HOMO and LUMO are computed as -0.34981 eV and -0.22119 eV by B3LYP/6-31G+(d,p) and the energy gap value noted as -0.12862 eV. Similarly for the same compound HOMO and LUMO values calculated by B3LYP/6-31G++(d,p) are -0.33735 and -0.22503 eV respectively and -0.11232 eV measured as its energy gap value. Surfaces for the frontier orbitals are drawn to understand the bonding scheme of present compound. The four important molecular orbital's (MO) for ONBH are outlined in Fig. 4 for ONBH.

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Bond Length	Value (Å)		Bond Angle	Value (Å)		Dihedral Angle	Value (Å)	
2 on a 2 ongoin	B3LYP/	B3LYP/	20110111910	B3LYP/	B3LYP/	2	B3LYP/	B3LYP/
	6-31+G(d,p)	6-31++G(d,p)		6-31+G(d,p)	6-31++G(d,p)		6-31+G(d,p)	6-31++G(d,p)
C ₁ -C ₂	1.4073	1.4073	$C_2 - C_1 - C_6$	117.262	117.2568	$C_6 - C_1 - C_2 - C_3$	-0.941	0.9872
C ₁ -C ₆	1.4028	1.4028	C ₂ -C ₁ -C ₇	125.3464	125.3518	$C_6 - C_1 - C_2 - N_{10}$	176.7138	-176.7613
C ₁ -C ₇	1.502	1.5019	$C_6 - C_1 - C_7$	117.242	117.2418	$C_7 - C_1 - C_2 - C_3$	174.4744	-174.4286
C ₂ -C ₃	1.3939	1.3939	$C_1 - C_2 - C_3$	122.1955	122.1998	$C_7 - C_1 - C_2 - N_{10}$	-7.8707	7.8228
C ₂ -N ₁₀	1.4756	1.4758	$C_1 - C_2 - N_{10}$	121.1246	121.1282	$C_2 - C_1 - C_6 - C_5$	-0.1294	0.1213
C ₃ –C ₄	1.3945	1.3944	$C_3 - C_2 - N_{10}$	116.641	116.6361	$C_2 - C_1 - C_6 - H_{16}$	179.3021	-179.2986
C ₃ -H ₁₃	1.0833	1.0832	$C_2 - C_3 - C_4$	119.1712	119.1676	$C_7 - C_1 - C_6 - C_5$	-175.9241	175.9166
$C_4 - C_5$	1.398	1.398	C ₂ -C ₃ -H ₁₃	119.2543	119.2551	$C_7 - C_1 - C_6 - H_{16}$	3.5074	-3.5033
C ₄ -H ₁₄	1.0853	1.0853	$C_4 - C_3 - C_5$	121.5672	121.5696	$C_2 - C_1 - C_7 - O_8$	166.1262	-166.3204
C ₅ -C ₆	1.394	1.394	$C_3 - C_4 - C_5$	119.9715	119.9734	$C_2 - C_1 - C_7 - H_9$	-16.2704	16.0456
C ₅ -H ₁₅	1.0856	1.0855	C ₃ -C ₄ -H ₁₄	119.5969	119.596	$C_6 - C_1 - C_7 = O_8$	-18.4575	18.2631
C ₆ -H ₁₆	1.085	1.085	$C_5 - C_4 - H_{14}$	120.431	120.4301	$C_6 - C_1 - C_7 - H_9$	159.1459	-159.3708
C ₇ =O ₈	1.2166	1.2166	$C_4 - C_5 - C_6$	120.083	120.0819	$C_1 - C_2 - C_3 - C_4$	1.2904	-1.3477
C7-H9	1.099	1.0998	C ₄ -C ₅ -H ₁₅	120.0969	120.0928	C ₁ -C ₂ -C ₃ -H ₁₃	-179.6777	179.645
H ₉ -O ₁₁	2.2983	2.2972	C ₆ -C ₅ -H ₁₅	119.8187	119.8238	N ₁₀ -C ₂ -C ₃ -C ₄	-176.4636	176.4962
N ₁₀ -O ₁₁	1.2331	1.2331	$C_1 - C_6 - C_5$	121.303	121.3056	N ₁₀ -C ₂ -C ₃ -H ₁₃	2.5682	-2.5111
N ₁₀ -O ₁₂	1.2304	1.2304	C ₁ -C ₆ -H ₁₆	117.5407	117.5351	$C_1 - C_2 - N_{10} - O_{11}$	-27.2381	27.366
			C5-C6-H16	121.1537	121.1567	$C_1 - C_2 - N_{10} - O_{12}$	153.6985	-153.5771
			$C_1 - C_7 = O_8$	121.6413	121.6433	C ₃ -C ₂ -N ₁₀ -O ₁₁	150.5417	-150.5027
			C ₁ -C ₇ -H ₉	117.3162	117.3182	$C_3 - C_2 - N_{10} - O_{12}$	-28.5216	28.5542
			O ₈ -C ₇ -H ₉	120.9983	120.9954	$C_2 - C_3 - C_4 - C_5$	-0.5559	0.5853
			C ₂ -N ₁₀ -O ₁₁	117.6232	117.6272	C ₂ -C ₃ -C ₄ -H ₁₄	179.1598	-179.1326
			C ₂ -N ₁₀ -O ₁₂	117.6431	117.6388	$H_{13}-C_3-C_4-C_5$	-179.5645	179.5688
			O ₁₁ -N ₁₀ -O ₁₂	124.7265	124.7266	$H_{13}-C_3-C_4-H_{14}$	0.1512	-0.1491
						$C_3 - C_4 - C_5 - C_6$	-0.4791	0.4861
						C ₃ -C ₄ -C ₅ -H ₁₅	179.9565	-179.9628
						$H_{14}-C_4-C_5-C_6$	179.8076	-179.7984
						$H_{14}-C_4-C_5-H_{15}$	0.2432	-0.2474
						$C_4 - C_5 - C_6 - C_1$	0.8296	-0.8473
						C ₄ -C ₅ -C ₆ -H ₁₆	-178.5814	178.5516
						$H_{15}-C_5-C_6-C_1$	-179.6048	179.6004
						H ₁₅ -C ₅ -C ₆ -H ₁₆	0.9842	-1.0007

Table 3. Optimized geometrical parameters of o-nitrobenzaldehyde obtained by B3LYP/6-31+G (d,p) and B3LYP/6-31++G(d,p) methods and basis set





Fig 4. HOMO – LUMO energy level diagram of onitrobenzaldehyde using (a) B3LYP/6-31+G(d,p)

(b) B3LYP/6-31++G(d,p) methods and basis set

The positive phase is red and the negative one is green. According to the Fig. 4, for HOMO, a charge density localized mainly some carbons of the ring and oxygen atom, however, the LUMO is characterized by a charge distribution on all structure, the HOMO presents a nonbonding character for some ring atoms and the LUMO exhibits a σ -anti-bonding character between some pairs of carbon atoms and hydro group.

						(d,p) and l	B3LYP/6	-31++G(d,p) calc	ulation	S				
S. No.	ecies	Obser Frequ	ved encies	B3LYP/6-31+G(d,p)				B3LYP/6-31++G(d,p)						Assignment % of TED		
	ry sp	(cm ⁻¹) FT-	FT-	Calculated	1	Reduce	Force	IR	Raman	Calculated	1	Reduce	Force	IR	Raman	
	net	IR	Rama	Frequenci	es (cm ⁻¹)	d Mass	Constant	Intensit	Activity	Frequenci	es (cm ⁻¹)	d Mass	Constant	Intensit	Activity	
			n	Unscale	Scale		s	У		Unsacle	Scale		s	У		
1	'Sy	2144		d	d	1.0020	6.7601	1.0600	100 2022	d	d	1.0020	6.7605	1.0610	100 2212	(0.0)
1.	A	3144	-	3239	3141	1.0938	6.7601	1.8688	108.2922	3239	3142	1.0938	6.7605	1.8610	108.3213	v _{CH} (98%)
2.	A	3100	-	3221	3095	1.0949	6.6924	5.0303	142.8940	3221	3097	1.0949	6.6923	5.0758	143.1471	v _{CH} (97%)
3.	A	-	3075	3212	3073	1.0921	6.6395	3.8664	117.0452	3212	3074	1.0921	6.6390	3.8623	117.1405	V _{CH} (99%)
4.	A	2944	-	3199	2940	1.0876	6.5564	2.5176	63.8344	3199	2942	1.0876	6.5556	2.5221	63.8687	$v_{CH}(96\%)$
5.	A	2844	-	3045	2841	1.0879	5.9418	37.7300	82.3238	3045	2841	1.0879	5.9428	37.8401	84.3084	$V_{CH}(9/\%)$
0. 7	A	1733	-	1770	1728	6 0058	11 2320	229.4880	52 7868	1651	1634	6 9979	11.2343	0.5868	52 0314	Rung (72%)
8	A	1700	-	1620	1693	5 9543	9 2083	64 2741	57 7169	1620	1695	5 9538	9 2066	64 0692	57 6563	Rasym (0970)
0.		1700		1020	1075	5.5545	9.2005	04.2741	57.7105	1020	1055	5.7550	9.2000	01.0072	57.0505	(68%)
9.	Α	-	1694	1600	1685	9.9478	15.0072	228.2072	15.9133	1600	1689	9.9479	15.0067	228.4443	15.9480	$v_{C=0}(83\%)$
10.	Α	-	1613	1507	1607	2.4533	3.2841	1.6818	1.6937	1507	1610	2.4534	3.2837	1.6762	1.7113	v _{CC} (91%)
11.	А	1594	-	1478	1598	2.1753	2.8005	13.0554	2.3589	1478	1597	2.1752	2.8002	13.1276	2.4024	v _{CC} (89%)
12.	Α	-	1575	1427	1581	1.3329	1.6000	38.7102	3.9379	1427	1582	1.3328	1.6001	38.6959	3.9659	v _{CC} (87%)
13.	А	1567	-	1384	1574	10.9176	12.3204	207.9786	132.1360	1384	1572	10.9472	12.3514	207.8335	131.3520	NO ₂ sym(82%)
14.	Α	-	1538	1364	1544	5.7650	6.3214	11.9683	5.4332	1364	1541	5.7666	6.3223	11.8936	5.4085	v _{CC} (88%)
15.	А	1528	-	1294	1533	1.6493	1.6261	22.1671	4.2775	1294	1530	1.6494	1.6261	22.2682	4.2915	v _{CC} (91%)
16.	Α	-	1444	1209	1449	2.2181	1.9107	60.0461	26.8809	1209	1451	2.2170	1.9098	60.0972	26.8042	v _{cc} (90%)
17.	Α	1400	-	1189	1406	1.1399	0.9490	3.2323	12.5677	1189	1403	1.1399	0.9490	3.2583	12.5575	v _{CC} (86%)
18.	А	1344	-	1161	1349	2.0129	1.5990	15.3043	23.9736	1161	1346	2.0117	1.5978	15.3862	23.9557	NO ₂ asym(88%)
19.	А	1256	-	1093	1263	3.6033	2.5368	1.7299	3.5872	1093	1261	3.6067	2.5390	1.7255	3.5994	v _{CN} (72%)
20.	Α	-	1194	1063	1199	2.3771	1.5835	0.0871	35.4727	1063	1198	2.3771	1.5835	0.0884	35.5768	bC=O (81%)
21.	А	1189	-	1021	1197	1.4570	0.8941	1.5138	0.9867	1020	1195	1.4510	0.8890	1.5593	1.1649	ωC=O (80%)
22.	Α	-	1175	1011	1183	1.5508	0.9342	0.8351	1.4675	1011	1182	1.5550	0.9366	0.8013	1.5106	bCH (78%)
23.	Α	-	1138	988	1146	1.4046	0.8072	1.2385	0.5213	988	1145	1.4014	0.8056	1.2506	0.4384	bCH (76%)
24.	Α	1133	-	906	1141	1.3561	0.6555	3.6240	0.3178	906	1139	1.3530	0.6542	3.6217	0.3611	bCH (77%)
25.	A	-	1038	863	1042	9.4597	4.1486	23.1394	7.5585	863	1040	9.4581	4.1471	23.1242	7.5583	bCH (79%)
26.	A	1000	-	830	1009	4./6/1	1.9362	39.4058	15.9311	830	1005	4.7826	1.9416	39.7996	16.2044	bCH (74%)
27.	A	867	-	804 752	899	2.4014	0.7280	23.0107	0.9732	804 752	897	2.5200	0.7178	29.6956	0.7770	0CH (59%)
20.	A	822	- 825	703	870	5 7600	1.6822	22 2102	0.2880	703	870	2.3390	1 7045	22 1701	0.4127	wCH (60%)
30	A	789	-	690	696	4 8421	1.0622	4 4719	0.1955	689	693	4 8356	1.7043	3 9858	0.1002	0CH (59%)
31.	A	744	-	648	752	6.0532	1.4998	10.9907	5.7059	648	751	6.0600	1.5007	10.9038	5.7404	ωCH (61%)
32.	A	694	-	569	699	5.6460	1.0769	0.6169	4.3937	569	697	5.6522	1.0781	0.6094	4.3021	NO ₂ sciss(65
33.	А	644	-	480	647	4.1160	0.5590	2.4551	1.4904	480	646	4.1462	0.5622	2.4012	1.4615	bcc (65%)
34.	Α	-	638	443	644	3.7783	0.4361	2.7966	2.0101	442	642	3.7849	0.4359	2.8213	2.2316	bCN (62%)
35.	Α	-	563	402	569	8.1355	0.7752	3.9373	3.7287	402	568	8.0628	0.7678	3.9211	3.6466	τRtrig (58%)
36.	А	489	-	376	493	7.7969	0.6503	2.9614	1.4019	376	494	7.8097	0.6508	2.9634	1.4032	τRsym (60%)
37.	А	-	475	293	481	3.4303	0.1730	8.0963	1.7685	292	480	3.4411	0.1730	8.0428	1.7997	τRasym (59%)
38.	Α	-	400	262	409	6.1002	0.2464	2.5413	0.7995	262	407	6.0853	0.2457	2.5564	0.7989	ωCN (62%)
39.	А	-	306	197	314	6.3071	0.1440	3.7039	1.4558	197	310	6.3154	0.1441	3.6850	1.4104	NO ₂ wag (55%)
40.	Α	-	263	123	271	4.5876	0.0411	1.7274	2.9741	123	273	4.5882	0.0409	1.7095	2.9350	ωCC (54%)
41.	А	-	206	98	213	5.7630	0.0323	5.0106	2.1455	97	211	5.7350	0.0320	5.0531	2.1868	NO ₂
42.	А	-	138	48	144	11.4246	0.0153	3.4466	0.5743	48	142	11.3990	0.0152	3.4751	0.5759	rock(52%) NO ₂ twist
											1	1			1	(51%)

Table 4. The observed (FT-IR and FT- Raman) and calculated (unscaled and scaled) frequencies, reduced mass, IR intensity (Km mol⁻¹) Raman activity (A4 amu⁻¹) and probable assignments (characterized by TED) of o-nitrobenzaldehyde using B3LYP/6-31+G (d n) and B3LYP/6-31++G(d n) calculations

Abbreviations: ν - stretching; asym - asymmetric stretching; ss - symmetric stretching; b - in-plane bending; ω - out-of-plane bending; τ - torsion.

Moreover lower value of HOMO and LUMO energy gap explains the eventual charge interactions taking place within the compound.

Non-Linear Optical Effects

Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [27]. Organic molecules with significant non-linear optical activity generally consist of a p electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end, forming a 'push–pull' conjugated structure [28]. The total static dipole moment (μ) and the first hyperpolarizability (β) using the x, y, z components are defined as [29].

$$\mu^{\mu} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$
$$\alpha^{\mu} = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$
$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$
$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$
$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

Table 5. The thermodynamic Properties of onitrobenzaldehyde along with global minimum energy calculated by B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p)

Parameter 6-31+G(d,p) 6-31++G(d,p) Global minimum energy -550.09520661 au -550.09529342 au Zero point correction 0.112160 0.112147 (Hartrees/particle) (Hartrees / particle) particle) Thermal correction to 0.121046 0.121036 energy 0.121990 0.121036 enthalpy 0.077152 0.077132 Gibbs free energy 0.0077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 I.20807 1.20770 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.889 Vibrational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_y (cal/mol-kelvin) Total Total 32.637 32.646 <t< th=""><th>meth</th><th>ous and Dasis set</th><th></th></t<>	meth	ous and Dasis set	
Global minimum energy -550.09520661 au -550.09529342 au Zero point correction 0.112160 0.112147 (Hartrees/particle) particle) Thermal correction to 0.121046 0.121036 energy 0.121090 0.121980 enthalpy 0.077152 0.077132 Gibbs free energy 0.0077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Nibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total Total 32.637 32.646 Electronic 0.00 0.000 <th>Parameter</th> <th>6-31+G(d,p)</th> <th>6-31++G(d,p)</th>	Parameter	6-31+G(d,p)	6-31++G(d,p)
Zero point correction 0.112160 0.112147 (Hartrees/ particle) $(Hartrees / particle)$ Thermal correction to 0.121046 0.121036 energy 0.121990 0.121980 Thermal correction to 0.077152 0.077132 Gibbs free energy 0.077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Vibrational 2.981 2.981	Global minimum energy	-550.09520661 au	-550.09529342 au
(Hartrees/ particle) (Hartrees / particle) Thermal correction to 0.121046 0.121036 energy 0.121990 0.121980 Thermal correction to 0.077152 0.077132 Gibbs free energy 0.077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Vibrational 2.981 2.981	Zero point correction	0.112160	0.112147
Image: marking learning		(Hartrees/ particle)	(Hartrees /
Thermal correction to energy 0.121046 0.121036 Thermal correction to enthalpy 0.121990 0.121980 Thermal correction to 0.077152 0.077132 Gibbs free energy 0.077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Vibrational 2.981 2.981			particle)
energy 0.121990 0.121980 Thermal correction to 0.077152 0.077132 Gibbs free energy 0.077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume $C_v (cal/mol-kelvim)$ Total 32.637 Total 32.637 32.646 Electronic 0.00 0.000 Translational 2.981 2.981 Vibrational 2.981 2.981	Thermal correction to	0.121046	0.121036
Thermal correction to enthalpy 0.121990 0.121980 Thermal correction to Gibbs free energy 0.077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K eal/mol) 70.37322 (K Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Vibrational 2.981 2.981	energy		
enthalpy 0.077152 0.077132 Thermal correction to Gibbs free energy 0.077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Notational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total 32.637 Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Vibrational 2.981 2.981	Thermal correction to	0.121990	0.121980
Thermal correction to Gibbs free energy 0.077152 0.077132 Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) rotal energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Notational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total Total 32.637 32.646 Electronic 0.00 0.000 Translational 2.981 2.981 Vibrational 2.981 2.981	enthalpy		
Gibbs free energy I.39848 I.39855 Rotational constant (GHz) 1.39848 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol) energy 70.38164 (Joules/mol) (Kcal/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Notational 74.180 74.174 Heat capacity at constant volume C_y (cal/mol-kelvin) Total 32.637 Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Kotational 2.981 2.981	Thermal correction to	0.077152	0.077132
Rotational constant (GHz) 1.39848 1.39855 1.20807 1.20770 0.66258 0.66256 Zero point vibrational 294476.8 (J/mol) 294441.5 energy 70.38164 (Joules/mol)(Kcal/mol) 70.37322 (K cal/mol) 70.37322 (KTotal energy 75.957 Electronic 0.000 0.000 0.000 Translational 0.889 Notational 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_y (cal/mol-kelvin)Total 32.637 Electronic 0.00 0.000 0.000 Translation 2.981 2.981 2.981 Notational 2.6676 26.676 26.684	Gibbs free energy		
1.208071.20770 0.66258 0.66256 Zero point vibrational294476.8 (J/mol)294441.5energy70.38164(Joules/mol)(Kcal/mol)70.37322 (Kcal/mol)70.37322 (KTotal energy75.95775.951Electronic0.0000.000Translational0.8890.889Notational0.8890.889Vibrational74.18074.174Heat capacity at constant volume C_y (cal/mol-kelvin)Total32.63732.646Electronic0.000.000Translation2.9812.981Rotational2.9812.981	Rotational constant (GHz)	1.39848	1.39855
0.66258 0.66256 Zero point vibrational energy294476.8 (J/mol) 70.38164 (Joules/mol) 70.37322 (K cal/mol)Total energy75.957Total energy75.957Total energy0.000Translational0.8890.8890.889Vibrational74.18070tal32.63722.646Electronic0.000.000Translational2.9812.9812.981Vibrational2.6676		1.20807	1.20770
Zero point vibrational energy294476.8 (J/mol) 70.38164 (Joules/mol) 70.37322 (K cal/mol)Total energy75.95775.951Electronic0.0000.000Translational0.8890.889Notational0.8890.889Vibrational74.18074.174Heat capacity at constant volume C_v (cal/mol-kelvin)32.63732.646Electronic0.000.000Total2.9812.981Rotational2.9812.981		0.66258	0.66256
energy 70.38164 (Kcal/mol) (Joules/mol) 70.37322 (K cal/mol) Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Notational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total 32.637 Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981	Zero point vibrational	294476.8 (J/mol)	294441.5
(Kcal/mol) 70.37322 (K cal/mol)Total energy 75.957 75.951 Electronic 0.000 0.000 Translational 0.889 0.889 Rotational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin)Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.6676 26.684	energy	70.38164	(Joules/mol)
cal/mol)Total energy75.95775.951Electronic0.0000.000Translational0.8890.889Rotational0.8890.889Vibrational74.18074.174Heat capacity at constant volume C_{γ} (cal/mol-kelvin)Total32.637Total32.63732.646Electronic0.000.000Translation2.9812.981Rotational2.9812.981Vibrational26.67626.684		(Kcal/mol)	70.37322 (K
Total energy75.95775.951Electronic 0.000 0.000 Translational 0.889 0.889 Rotational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_{γ} (cal/mol-kelvin)Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981 Vibrational 26.676 26.684			cal/mol)
Electronic 0.000 0.000 Translational 0.889 0.889 Rotational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981 2.981 Vibrational 2.6.676 26.684	Total energy	75.957	75.951
Translational 0.889 0.889 Rotational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin)Total 32.637 Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981 Vibrational 26.676 26.684	Electronic	0.000	0.000
Rotational 0.889 0.889 Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981 2.981 2.981 Vibrational 26.676 26.684 26.684	Translational	0.889	0.889
Vibrational 74.180 74.174 Heat capacity at constant volume C_v (cal/mol-kelvin) Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981 2.981 2.981	Rotational	0.889	0.889
Heat capacity at constant volume C_{v} (cal/mol-kelvin) Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981 Vibrational 26.676 26.684	Vibrational	74.180	74.174
Total 32.637 32.646 Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981 Vibrational 26.676 26.684	Heat capacity at constant volu	ume C _v (cal/mol-kelvin)
Electronic 0.00 0.000 Translation 2.981 2.981 Rotational 2.981 2.981 Vibrational 26.676 26.684	Total	32.637	32.646
Translation 2.981 2.981 Rotational 2.981 2.981 Vibrational 26.676 26.684	Electronic	0.00	0.000
Rotational 2.981 2.981 Vibrational 26.676 26.684	Translation	2.981	2.981
Vibrational 26.676 26.684	Rotational	2.981	2.981
	Vibrational	26.676	26.684
Entropy (cal/mol-kelvin) 94.369 94.391	Entropy (cal/mol-kelvin)	94.369	94.391
Translation 40.947 40.947	Translation	40.947	40.947
Rotational 30.041 30.042	Rotational	30.041	30.042
Vibrational 23.380 23.402	Vibrational	23.380	23.402
Dipole moment	Dipole moment		
μ_x (debye) -3.0014 -3.0014	μ _x (debye)	-3.0014	-3.0014
$\mu_{\rm y}$ (debye) -3.9820 -3.9820	μ _y (debye)	-3.9820	-3.9820
μ_z (debye) -0.4613 -0.4613	μ_z (debye)	-0.4613	-0.4613
μ _{Total} (debye) 5.0077 5.0077	µ _{Total} (debye)	5.0077	5.0077

The dipole moment (µ) and the first hyperpolarizability (β) have been calculated at the B3LYP/6-31G++(d,p) level using Gaussian 09W program package. The calculated dipole moment (µ) and first hyperpolarizability (β) for the title compound are 5.0077 debye and 3.030×10^{-30} esu respectively. The calculated values of the title compound are greater than those of urea. (The µ and β of urea are 1.3732 debye and 0.372×10^{-30} esu obtained by B3LYP/6-31G++(d,p) method). These results indicate that ONBH is a good non-linear optical material.

NBO Analysis

Natural bond orbital analysis provides an efficient method for studying intra- and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the secondorder micro-disturbance theory are reported [30,31]. Larger the E(2) value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the compounds at the B3LYP/6-31++G(d,p) level in order to elucidate the intramolecular, rehybridization and delocalization of electron density within the compounds which are listed in Table 6.

The intramolecular interaction are formed by the orbital overlap between bonding (C-C) and (C-C) antibond orbital which results intramolecular charge transfer (ICT) causing stabilization of the system. These interactions are observed as increase in electron density (ED) in C-C anti-bonding orbital that weakens the respective bonds. The electron density of six conjugated single bond of aromatic ring (\approx 1.6e) clearly demonstrates strong delocalization. In ONBH. the intermolecular hyper conjugative interaction of $\sigma(C_1-C_6)$ to $\sigma^*(C_1-C_2)$ and $\sigma(C_3-H_{16})$ to $\sigma^*(C_1-C_2)$ leading to stabilization of 4.15 Kcal/mol and 4.57 Kcal/mol respectively. The intermolecular interaction are formed by the orbital overlap between bonding C-C, C-N, C-H, antibond orbital which results intermolecular charge transfer (ICT) causing the stabilization of the system.

The energies for the interactions LP(1) $O_8 \rightarrow \sigma^*(C_2-C_7)$ gives the value of 0.90 Kcal/mole. These charge transfer interaction of ONBH is responsible for pharmaceutical and biological properties. Hence the ONBH structures is stabilized by the orbital interactions.

Mulliken's Population Analysis

The charge distributions calculated by the Mulliken method [32,33] for the equilibrium geometry using B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p) method and basis set are listed in Table 7. For ONBH the charge distribution on the compounds has an important influence on the vibrational spectra. The corresponding Mulliken's plots are shown in Fig.5.

The atomic charges obtained from B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) basis set shows that C_1 atom in ONBH is more acidic due to more positive charge whereas C_2 in ONBH is more negative which are listed in Table 7.

Donar (i)	Туре	occupancy	acceptor(j)	type	occupancy	E(z) kcal/mol	ε(j) - ε(i)	F (i , j)
							a.u.	a.u.
C1–C2	σ	1.97551	C1-C6	σ^*	0.02633	3.70	1.27	0.061
C1–C6	σ	1.97677	C1-C2	σ^*	0.02085	4.15	1.28	0.065
C1-N10	σ	1.98815	C2–C3	σ^*	0.09660	1.79	1.38	0.044
C2–C3	σ	1.97526	C1-N10	σ^*	0.01854	4.12	0.99	0.058
C2–C7	σ	1.98062	C3–C4	σ^*	0.32337	2.49	1.19	0.049
C3–C4	σ	1.98163	C2–C7	σ^*	0.01369	3.19	1.08	0.053
C3-H16	σ	1.97892	C1-C2	σ^*	0.01285	4.57	1.08	0.063
C4–C5	σ	1.98356	C6-H13	σ^*	0.01558	1.90	1.21	0.043
C4-H15	σ	1.98242	C2–C3	σ^*	0.01089	3.55	1.10	0.056
C5-C6	σ	1.97770	C1-N10	σ^*	0.01429	4.47	0.99	0.060
C5-H14	σ	1.98172	C1-C6	σ^*	0.01042	3.75	1.08	0.057
C6-H13	σ	1.97826	C4–C5	σ^*	0.0119	3.64	1.09	0.056
C7–O8	σ	1.99685	C1-C2	σ^*	0.00809	1.18	1.54	0.038
С7-Н9	σ	1.98843	C2–C3	σ^*	0.04727	2.86	1.10	0.050
N10-O11	σ	1.99586	C1-N10	σ^*	0.05459	0.55	1.35	0.025
N10-O12	σ	1.99544	C1-C6	σ^*	0.05591	0.84	1.61	0.033
LP(1)O8	σ	1.98539	C2-C7	σ^*	-	0.90	1.08	0.028

Table 6. NBO analysis of o-nitrobenzaldehyde using B3LYP/6-31++G(d,p) method and basis set.

Table 7. Mulliken's atomic charges of o-nitrobenzaldehyde performed by density functional calculations

Atoms	Atomic Charges					
	B3LYP					
	6-31+G(d,p)	6-31++G(d,p)				
C1	1.461507	1.629011				
C2	-1.973908	-1.918				
C3	0.630835	-0.44819				
C4	-0.28464	0.10737				
C5	0.053265	-0.31989				
C6	0.339009	0.43256				
C7	0.363152	O.358144				
08	-0.360184	-0.34708				
H9	0.142287	O.180064				
N10	-0.304287	-0.22333				
011	-0.031927	-0.05077				
012	0.002977	-0.01114				
H13	0.171761	-0.18269				
H14	0.147340	0.141297				
H15	0.145724	0.123729				
HH16	0.175102	0.16353				



Fig 5. Mulliken's atomic charges plot of onitrobenzaldehyde performed by density functional methods Thermodynamical Properties

Using the B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p) method, several thermodynamic properties of ONBH hae been calculated. The maximum number of potentially active observable fundamentals of non linear molecule which contains N atom is equal to (3N–6) apart from three translational and

three rotational degrees of freedom. Since the molecule do not possess any rotational, reflection or inversion symmetry the molecule is considered under C_1 point group symmetry. The zero point vibrational energy, rotational constants, vibrational energy, specific heat capacity (C_v) entropy and dipole moment by B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p) are presented in Table 5. The variation in the ZPVE seems to be insignificant. The total energy and the change in total entropy of ONBH at room temperature are also presented. **Conclusion**

Attempts have been done in the present work for the proper frequency assignment of the compound O-nitrobenzaldehyde from the FTIR and FT-Raman spectra. The molecular structural parameters thermodynamic properties and vibrational frequencies of the fundamental modes of the optimized geometry of O-nitrobenzaldehyde have been obtained from DFT techniques in the B3LYP approximation and two different basis set of atomic orbital. The bond length and bond angle are found to be almost basis set independent.

Comparison between the calculated vibrational frequencies and the experimental values indicates that both the methods can predict the FTIR and FT-Raman spectra of the title compound well. The influence of NO_2 group and the electron withdrawing nature of nitrogen atom in title compound were also discussed using Mulliken's charges. HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. NBO analysis shows that intermolecular charge transfer is responsible for biological activity.

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