Vibrational and PED analysis of o-Nitro Phenol-a DFT Study

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Abstract-The present study of optimum molecular geometry and Vibrational spectra of o-Nitro Phenol has been carried out by the density functional theory (DFT/B3LYP) method with 6-31* G(d,p) basis set. We have also calculated the infrared intensities, reduced mass and force constant. The descriptions of the motions and the force constants have been discussed in terms of bond lengths and bond angles. The assignment of the vibrational frequencies calculated on the basis of the potential energy distribution (PED) using Vibration Energy Distribution Analysis (VEDA) 4 program. Several thermodynamic properties like heat capacity, zero point energy, entropy have also been calculated. The Highest Occupied Molecular Orbital (HOMO)- Lowest Unoccupied Molecular Orbital (LUMO) study has been used to interpret the information of charge transfer within the molecule.The present study suggests that it the calculated vibrational frequencies are found very close to the experimental values and therefore this method may be applied to study vibrational spectra for such moleculs.

Keywords: DFT- Calculations, IR Spectra, PED, o-Nitro Phenol, HOMO, LUMO

1. INTRODUCTION

Nitrophenols, in combination with mineral oil, were used to fight mites in orchards by eliminating their overwintering eggs. When 2-nitrophenol is reduced with iron, red insoluble color lakes are formed as by products that decrease the yield. Therefore, the iron reduction of 2-nitrophenol is of minor industrial importance today[1]. o-Nitro Phenol is the organic compound with the formula $C_6H_6NO_3$ which relates to 1- hydroxyl, 2-Nitro Benzen by replacement of one H centres with hydroxyl (-OH) and replacement of one H centres with Nitro (-NO_2) group. Nitro phenols constitute a class of volatile organic compounds that is increasingly presented in urban as well as in natural environments. Nitrocompounds has to be considered to play a significant role as atmospheric pollutants of environmental concern[2]. Title molecule poses significant health risks since it is a toxic to mammals, microorganisms and anaerobic bacteria. Its toxicity is thought to be due to the nitro group being easily reduced by the enzymes into nitro anion radical, nitroso and hydroxylamine derivatives [3-5].

Vibrational spectroscopy has been demonstrate to be a competent investigation of the structural properties of o-Nitro Phenol. The dipole moment of the molecules may change periodically in the various vibrational states therefore the transition between thesestates may result in absorption or emission of light[6].

Analysis of vibrational spectra of organic molecules has played an important role for a long time in determining their molecular structure, intramolecular and intermolecular forces. Spectroscopy in the middle infrared region is extremely useful for the study of organic compouonds. Infrared spectroscopy utilize the details that molecules absorb specific frequencies that are feature of their structure[7]. Molecular vibration have a very complex nature and different atoms move in complicated ways. However, such vibration can be decomposed as a superposition of some of the 3N-6 normal vibrations[8]. The calculation is facilitated by the

ovservation that in the spectra of the o-Nitro Phenol there are stable frequencies and substituent-sensitve frequencies.

The aim of present study was to investigate of inter- and intra-molecular interation with the help of vibrational analysis and PED percentage of o-Nitro Phenol. The vibrational spectra of the molecule o-Nitro Phenol have studied completely and recognized the various normal modes with a greater wave number accurately. In the present study, the DFT calculations have been done to support the wave number assignments[9-10].

2. COMPUTATIONAL DETAILS

In the present study, we adopted density functional theory (DFT) to theoretically predict the IR spectrum, thermo dynamical parameter. DFT studies have been accepted as a popular approach for molecular computation. All the calculations have been done using the Gaussian 03 program package[11]. The optimized geometry was first obtained by a semi empirical method, and then by using HF with 6-31G*(d, p) then by using DFT Becke-Lee-Young–Parr the geometry optimizations and calculation of frequency were carried out by using DFT-B3LYP hybrid functional[12] and 6-31*G (d,p) basis set. The scaling of the theoretical wave numbers was done by CCCBDB[13]. The vibrational problem was set-up in terms of symmetry and internal coordinates. The Cartesian representation of the theoretical force constants has been computed using the completely optimized geometry by assuming C_1 point group symmetry. In making vibrational assignments the symmetry of the molecule was also helpful. Using the GAUSSVIEW molecular visualization program [14], the vibrational frequency assignments were calculated on the basis of PED by VEDA 4[15] program a great degree of confidence along with available related molecules.

3. RESULT AND DISCUSSION

3.1. MOLECULAR GEOMETRY

The optimized molecular geometry represents an isolated molecule with a stationary point at the potential energy surfaces under the ideal conditions; the convergence was confirmed by observing no imaginary vibrational wave numbers. The optimized molecular structure of o-Nitro Phenol is shown in Fig. 1.
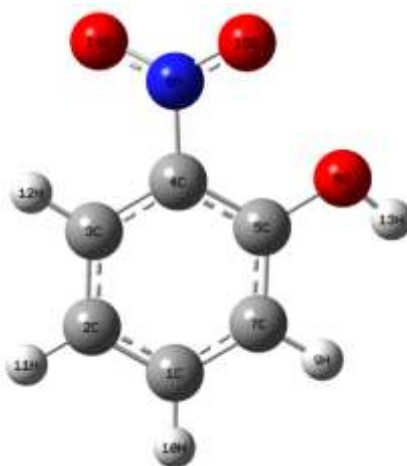

Figure 1: Molecular structure of o-Nitro Phenol

The computed geometry parameters; bond lengths, bond angles and dihydral angle respectively, for o-Nitro Phenol molecule unit in solid phase alongwith presented thedensity functional theory (DFT/B3LYP) method with 6-31* G (d, p) basis set optimized molecule [16] are listed in Table 1.This molecule has one O-H bond length, one C=O bond length,one C-N bond length, twoN-O bond lengthsix C-C bond length, and four C-H bond lengths. In the present study, the C-Hbond length calculated as 1.0844 A^0. According to the calculation theorder of the bond length, it is clear that the hexagonal structure of the benzene ring is slightly distorted. The bond angles C_1-C_2-C_3, C_4-C_5-C_7 and C_1-C_7-C_5 are 119.199°, 117.8461°and 121.1275°respectively deviated from the typical hexagonal angle of 120°. This is due to substitution of nitro and hydroxy group attached to C_4 and C_5 of thering. The calculated geometrical parameters are the basis for calculating other parameters such as vibrational frequencies and thermodynamics properties of the compound.

Table 1 Optimized geometrical parameters of o-Nitro Phenol by DFT-B3LYP method with 6-31*G(d,p)

S.No	Bond Length	Value (A$^\circ$)	Bond Angle	Value (A$^\circ$)	Dihedral Angle	Value (A$^\circ$)
1.	C_1-C_2	1.3995	C_2-C_1-C_7	120.4707	C_7-C_1-C_2-C_3	0.0177
2.	C_1-C7	1.3916	C_2-C_1-H_{10}	120.2466	C_7-C_1-C_2-H_{11}	179.9509
3.	C1-H_{10}	1.0858	C_7-C_1-H_{10}	119.2823	H_{10}-C_1-C_2-C_3	-179.7455
4.	C_2-C_3	1.3898	C_1-C_2-C_3	119.199	H_{10}-C_1-C_2-H_{11}	0.1877
5.	C_2-H_{11}	1.0844	C_1-C_2-H_{11}	120.6928	C_2-C_1-C_7-C_5	0.6391
6.	C_3-C_4	1.3987	C_3-C_2-H_{11}	120.1081	C_2-C_1-C_7-H_9	-179.2104
7.	C_3-H_{12}	1.0833	C_2-C_3-C_4	120.4992	H_{10}-C_1-C_7-C_5	-179.5954
8.	C_4-C_5	1.4099	C_2-C_3-H_{12}	121.4994	H_{10}-C_1-C_7-H_9	0.5552
9.	C_4-N_6	1.4676	C_4-C_3-H_{12}	118.001	C_1-C_2-C_3-C_4	-0.9599
10.	C_5-C_7	1.4041	C_3-C_4-C_5	120.8455	C_1-C_2-C_3-H_{12}	179.2664
11.	C_5-O_8	1.3538	C_3-C_4-N_6	117.2623	H_{11}-C_2-C_3-C_4	179.1065
12.	N_6-O_{14}	1.2356	C_5-C_4-N_6	121.8922	C_1-C_2-C_3-H_{12}	-0.6672
13.	N_6-O_{15}	1.229	C_4-C_5-C_7	117.8461	C_2-C_3-C_4-C_5	1.2667
14.	C_7-H_9	1.0876	C_4-C_5-O_8	120.5671	C_2-C_3-C_4-N_6	-178.7413
15.	O_8-H_{13}	0.9672	C_7-C_5-O_8	121.5619	H_{12}-C_3-C_4-C_5	-178.9518
16.			C_4-C_6-O_{14}	117.0669	H_{12}-C_3-C_4-N_6	1.0402
17.			C_4-C_6-O_{15}	118.378	C_3-C_4-C_5-C_7	-0.6029
18.			O_{14}-C_6-O_{15}	124.5425	C_3-C_4-C_5-O_8	177.6105
19.			C_1-C_7-C_5	121.1275	N_6-C_4-C_5-C_7	179.4055
20.			C_1-C_7-H_9	120.1368	N_6-C_4-C_5-O_8	-2.3811
21.			C_5-C_7-H_9	118.7355	C_3-C_4-N_6-O_{14}	-25.094
22.			C_5-O_8-H_{13}	109.5463	C_3-C_4-N_6-O_{15}	153.6682
23.					C_5-C_4-N_6-O_{14}	154.8979
24.					C_5-C_4-N_6-O_{15}	-26.3399
25.					C_4-C_5-C_7-C_1	-0.342
26.					C_4-C_5-C_7-H_9	179.5095
27.					O_8-C_5-C_7-C_1	-178.5366
28.					O_8-C_5-C_7-H_9	1.3149
29.					C_4-C_5-O_8-H_{13}	-175.5599

30.					C_7-C_5-O_8-H_{13}	2.5862

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full sets of 39 standard internal coordinates for the o-Nitro Phenol are defined in Table 2. From these, a non redundant set of local symmetry coordinates is constructed from suitable linear combinations of internal coordinates following the recommendations of Fogarasi et. al. [17-20] are summarized in Table 3[21].

Table 2 Definition of internal coordinates of o-Nitro Phenol

No. (i)	Symbol	Type	Definition
		Stretching	
1-6	r_i	C-C	C_1-C_2, C_2-C_3, C_3-C_4, C_4-C_5, C_5-C_7, C_7-C_1
7-10	R_i	C-H	$C=$-H_{10}, C_2-H_{11}, C_3-H_{12}, C_7-H_9
11,12	P_i	N-O	N_6-O_{14}, N_6-O_{15}
13	Q_i	O-H	O_8-H_{13}
14	L_i	C-N	C_4-N_6
15	J_i	C-O	C_5-O_8
		In plane bending	
16-21	α_i	bRing	C_1-C_2-C_3, C_2-C_3-C_4, C_3-C_4-C_5, C_4-C_5-C_7, C_5-C_7-C_1, C_7-C_1-C_2
22-29	β_i	bCCHdef	C_1-C_2-H_{11}, C_2-C_3-H_{12}, C_5-C_7-H_9, C_7-C_1-H_{10}, C_3-C_2-H_{11}, C_4-C_3-H_{12}, C_1-C_7-H_9, C_2-C_1-H_{10}
30	γ_i	bONOsciss	O_{14}-N_6-O_{15}
31,32	σ_i	bCCNrock	C_3-C_4-N_6, C_5-C_4-N_6
33-34	θ_i	bCCOrock	C_4-C_5-O_8, C_7-C_5-O_8
35	π_i	bCOH	C_5-O_8-H_{13}
36-37	ρ_i	bCONrock	C_4-N_6-O_{14}, C_4-N_6-O_{15}
		Out of plane bending	
38	η_i	C-Owagg	O_8-C_5-C_4-C_7
39	Ω_i	C-Nwagg	N_6-C_4-C_3-C_5
40	ω_i	TNO_2wagg	(C_3,C_5)-C_4-N_6-(O_{14},O_{15})
		Torsion	
41-46	τ_i	Tring	C_1-C_2-C_3-C_4, C_2-C_3-C_4-C_5, C_3-C_4-C_5-C_7, C_4-C_5-C_7-C_1, C_5-C_7-C_1-C_2, C_7-C_1-C_2-C_3
47-50	τ_i	TCH	H_{10}-C_1-C_5-C_7, H_{11}-C_2-C_7-C_1, C_1-C_2-C_3-H_{12}, H_{12}-C_3-C_4-N_6
51	τ_i	TON	O_{14}-N_6-C_4-C_3
52	τ_i	TOH	H_{13}-O_8-C_5-C_4
rock-rocking; sciss-scissoring; wagg-wagging			

Table 3 Definition of local symmetry coordinates of o-Nitro Phenol

No.(i)	Description	Definition
1-6	C-C	$r_1, r_2, r_3, r_4, r_5, r_6$
7-10	C-H	R_7, R_8, R_9, R_{10}
11,12	O-N	P_{11}, P_{12}
13	O-H	Q_{13}
14	C-N	L_{14}
15	C-O	J_{15}
16	R trigd	$(\alpha_{16}-\alpha_{17}+\alpha_{18}-\alpha_{19}+\alpha_{20}-\alpha_{21})/\sqrt{6}$
17	Rsymd	$(-\alpha_{16}-\alpha_{17}+2\alpha_{18}-\alpha_{19}-\alpha_{20}+2\alpha_{21})/\sqrt{12}$
18	Rasymd	$(\alpha_{16}-\alpha_{17}+\alpha_{19}-\alpha_{20})/2$
19-22	bHCC	$(\beta_{22}-\beta_{23})/\sqrt{2}, (\beta_{24}-\beta_{25})/\sqrt{2}, (\beta_{26}-\beta_{27})/\sqrt{2}, (\beta_{28}-\beta_{29})/\sqrt{2}$
23	bONO	γ_{30}
24	bNCC	$(\sigma_{31}-\sigma_{32})/\sqrt{2}$
25	bOCC	$(\theta_{33}-\theta_{34})/\sqrt{2}$
26	bHOC	π_{35}
27	bNOC	$(\rho_{36}-\rho_{37})/\sqrt{2}$
28	C-O	η_{38}
29	C-N	Ω_{39}
30	NO2	ω_{40}
31	TRtrigd	$(\tau_{41}-\tau_{42}+\tau_{43}-\tau_{44}+\tau_{45}-\tau_{46})/\sqrt{6}$
32	TRsymd	$(-\tau_{41}-\tau_{43}+\tau_{44}-\tau_{45})/\sqrt{2}$
33	TRasymd	$(-\tau_{41}+2\tau_{42}-\tau_{43}-\tau_{44}+2\tau_{45}-\tau_{46})/\sqrt{2}$
34-37	TCH	$\tau_{47}, \tau_{48}, \tau_{49}, \tau_{50}$
38	TON	τ_{51}
39	TOH	τ_{52}

R-ring; trigd- triggering; symd-symmetric deformation

The title molecule o-Nitro Phenol consists of 15 atoms and hence it has 39 normal modes of vibrations. For a proper understanding of IR of molecules with modes of vibration more than 50, the DFT method gives the more precise prediction than other theoretical calculation method [22]. The 39 normal modes of vibration distributed as $\Gamma = 27A'(\text{Planar}) + 12A''(\text{non}-\text{planar})$ in which 15 stretching modes, 12 bending modes (inplane) and 12 tours (out of plane) [23]. These species are best characterized by group-theoretical methods. For any molecule of given symmetry, each symmetry species is defined, and its species label assigned, to correspond to a characteristic behavior under each of the various "classes" of symmetry operations of the symmetry group[24]. The thirty modes are associated with the benzene ring in which 12 stretching modes -ν, 3

planar ring deformation -α, 3 non planar ring deformation -τ, 4 planar deformation modes -β(C-H) and 4 non-planar deformation modes -τ(C-H),out of which 2 of each i.e. β(C-H) and τ(C-H) become σ(C-N), θ(C-O) and Ω(C-N), η(C-O) respectively. The four normal modes of OH-group are: OH stretching -ν(OH), OH torsion -τ(OH), πCOH and ρCON angle bending. The six normal modes of the nitro group are: two symmetric NO_2 stretching -$\nu_{ss}(NO_2)$, NO_2 rocking -$\gamma(NO_2)$, NO_2 wagging -$\omega(NO_2)$, and NO_2 torsion -$\tau(NO_2)$.

3.2. VIBRATIONAL ASSIGNMENTS

The computed vibrational frequencies unscaled and scaled of o-Nitro Phenol, infrared intensities and force constants are reported alongwith corresponding PEDs [25-29] and vibrational assignments in Table 4. The vibrational analysis obtained for o-Nitro Phenol with the scaled B3LYP force field is, generally, somewhat less than the computational values. These discrepancies can be corrected either by computing anharmonic corrections explicitly or by introducing a scaled field or directly scaling the calculated wavenumber with proper factor. For an easier comparison to the observed values, the calculated frequencies are scaled by the scale of less than 1, to minimize the overall deviation; the scaling factor of 0.96 [30] for all the fundamental modes has been utilized to obtain the scaled frequencies of the compound namely o-Nitro Phenol[31-33].

Table 4 Calculated (Unscaled and scaled) frequencies (cm^{-1}), force constant (mdyn A-1) and IR intensity (km/mol) use DFT-B3LYP method with 6-31*G (d, p) basis set and vibrational assignment based on the potential energy distribution (PED) for o-Nitro Phenol.

S.No	Frequency Unscaled	Frequency Scaled	Frequency Exp.	IR Intensity	Reduced mass	Force constant	Assignments PED (%>10)	Vibrational Assignment
1	3813	3660	3467	73.81	1.07	9.13	$\nu O_8 H_{13}$ (100)	νOH
2	3239	3109	3113	2.65	1.09	6.76	$\nu C_1 H_{10}$ (86)	νCH
3	3218	3089	3091	6.33	1.09	6.67	$\nu_{ss} C_2 H_{11}$ (79)+ $\nu_{ss} C_1 H_{10}$ (11)	νCH
4	3201	3073	3071	6.30	1.09	6.58	$\nu_{asym} C_3 H_{12}$ (79)+ $\nu_{ss} C_7 H_9$ (11)	νCH
5	3174	3047	3049	8.51	1.09	6.47	$\nu_{asym} C_7 H_9$ (86)	νCH
6	1663	1597	1614	156.43	7.18	11.70	$\nu O_{15} N_6(52)$ + $R\nu_{asym} C_1 C_7$ (11) + $\tau_{asym} H_{10} C_1 C_7 C_5$ (13)	$\nu_{sym}NO_2$
7	1638	1572	1589	36.95	6.04	9.54	$\nu_{asym} O_{14} N_6$ (62) + $\pi_{asym} H_{13} O_8 C_5$(13)	$\nu_{asym}NO_2$
8	1598	1534	1532	215.72	10.25	15.41	$R\nu_{asym} C_1 C_7$(76)	νR
9	1531	1470	1477	18.88	2.52	3.48	$R\nu C_3 C_2(44)$ + $\beta_{ss} H_{11} C_2 C_1(11)$ + $\beta_{asym} H_{10}C_1C_7(11)$+ $\beta_{ss} H_{12} C_3 C_4$(10)	νR
10	1488	1429	1447	25.29	2.60	3.40	$R\nu C_5 C_4(31)$+ $\beta_{ss} H_{11} C_2C_1(11)$ (14)+ $\beta_{ss} H_{10}C_1C_7$ (12)	νR
11	1391	1336	1373	200.09	8.56	9.76	$R\nu_{ss} C_4C_3$(63)	νR
12	1369	1315	1312	127.31	5.19	5.73	$R\nu_{ss} C_7 C_5$ (63)	νR

13	1335	1282	1266	80.74	1.54	1.62	$R\nu_{ss}$ C$_5$ C$_4$ (51) + $R\nu_{ss}$ C$_2$C$_1$ (16)	νR
14	1300	1248	1236	64.82	3.46	3.45	ν_{ss}O$_8$C$_5$(38) + ν_{ss}O$_{15}$N$_6$(11) + $R\nu_{asym}$C$_3$ C$_2$ (18)	νCO
15	1195	1147	1177	21.51	1.20	1.01	νC$_6$ N$_4$(47) + νC$_2$ C$_1$(28)	νCN
16	1186	1139	1133	12.53	1.14	0.95	πH$_{13}$O$_8$C$_5$(63) + ν_{asym}O$_{14}$N$_6$ (13)	πOH
17	1163	1116	1027	66.97	2.08	1.63	β_{ss} H$_{10}$C$_1$C$_7$ (30)+ ν_{asym}N$_6$C$_4$(18)+ νC$_2$C$_1$(15)+ α_{asym}C$_4$ C$_3$C$_2$(18)	αR
18	1100	1056	988	39.98	2.78	1.98	β_{aysm} H$_{11}$C$_2$C$_1$ (31)+ τ_{Ring} C$_3$ C$_2$C$_4$C$_5$(18)+ν_{asym} O$_{14}$ N$_6$C$_4$(11)+ τ_{Rin} C$_3$C$_2$C$_4$ C$_5$ (18)	βCH
19	1066	1023	956	0.59	2.42	1.62	β_{ss} H$_{12}$C$_3$C$_4$ (65)+ν_{asym}C$_3$C$_2$(17)	βCH
20	993	953	868	0.48	1.29	0.75	βH$_9$ C$_7$C$_1$ (75)	βCH
21	968	930	818	2.42	1.36	0.75	γO$_{15}$N$_6$O$_{14}$(71)+ τ_{asym}H$_9$C$_7$C$_1$C$_2$(11)	γNO2
22	874	839	748	38.23	7.85	3.53	ρO$_{14}$N$_6$C$_4$(66)	ρNO2
23	858	824	664	1.67	1.51	0.65	α_{asym}C$_2$C$_1$C$_7$(85)	αR
24	826	793	546	14.88	7.52	3.02	τ H$_{13}$O$_8$C$_5$C$_4$ (19) + $\tau_{Ringasym}$ C$_3$C$_2$C$_4$ C$_5$(15) + νO$_8$C$_5$ (15) + βH$_{10}$ C$_1$C$_7$(14)+ RνC$_4$ C$_3$(12)	βCH
25	784	753	523	25.14	2.15	0.78	αC$_7$C$_5$C$_4$(49) + θO$_8$C$_5$C$_7$(26)	αR
26	754	724	421	59.23	2.17	0.73	θO$_8$C$_5$C$_7$ (46) + α_{asym}C$_7$C$_5$C$_4$ (35)	θCO
27	690	663		10.08	4.56	1.28	σN$_6$C$_5$C$_4$ (58)	σCN
28	672	645		8.56	6.24	1.66	τH$_{13}$O$_8$C$_5$C$_4$(54) + σ_{asym}N$_6$C$_4$C$_5$(12)	τOH
29	575	552		7.42	6.18	1.20	τ H$_{10}$C$_1$C$_7$C$_5$ (48)	τCH
30	555	533		0.85	5.61	1.02	τ_{asym}H$_{11}$C$_2$C$_1$C$_7$ (60)	τCH
31	533	512		10.00	3.57	0.60	τ_{asym}H$_{12}$C$_3$C$_4$N$_6$(59)	τCH
32	446	428		6.40	3.96	0.46	τ_{aysm} H$_9$C$_7$C$_1$C$_2$(42) + τO$_{14}$N$_6$C$_4$ C$_3$ (30)	τCH
33	399	383		17.61	3.58	0.34	τ_{aysm} H$_9$C$_7$C$_1$C$_2$ (30) + τ_{aysm} O$_{14}$N$_6$C$_4$ C$_3$ (23) + $\tau_{ringasym}$C$_1$C$_7$C$_2$C$_3$(11)	τNO2
34	380	365		88.67	1.31	0.11	$\tau_{ringasym}$C$_1$C$_7$C$_2$C$_3$ (80) + α_{aysm}C$_4$C$_3$C (11)	$\tau_{ringasym}$
35	362	348		2.96	7.51	0.58	$\tau_{ringasym}$C$_1$C$_7$C$_2$C$_3$ (45) + ν_{asym} N$_6$C$_4$(23)	$\tau_{ringasym}$
36	243	233		0.80	5.61	0.20	τ_{ring}C$_5$C$_4$C$_7$C$_1$(64) + τ_{asym} O$_{15}$C$_4$O$_{14}$N (15)	τ_{ring}
37	238	229		0.60	7.00	0.23	ωO$_{15}$C$_4$O$_{14}$N$_4$ (61)	ωNO2
38	132	126		0.05	5.32	0.05	ηO$_8$C$_4$C$_7$C$_5$(84)	ηCO

39	40	38		0.61	11.78	0.01	$\Omega_{asym}N_6C_3C_5C_4$ (91)	ΩCN

Abbreviations: ν-stretching; s-symmetric stretching; asym-anti symmetric, α, β, γ,σ, θ, π, ρ-in plane bending; ω, Ω, η-out of plane bending;; τ-torsion;.τ$_{ring}$ - ring torsion, R-Ring

The comparison of computed scaled and unscaled IR spectra of o-Nitro Phenol at B3LYP level using 6-31*G (d, p) basis set are shown in Fig. 2 and Fig. 3 as well as Fig. 4 and Fig. 5 respectively.
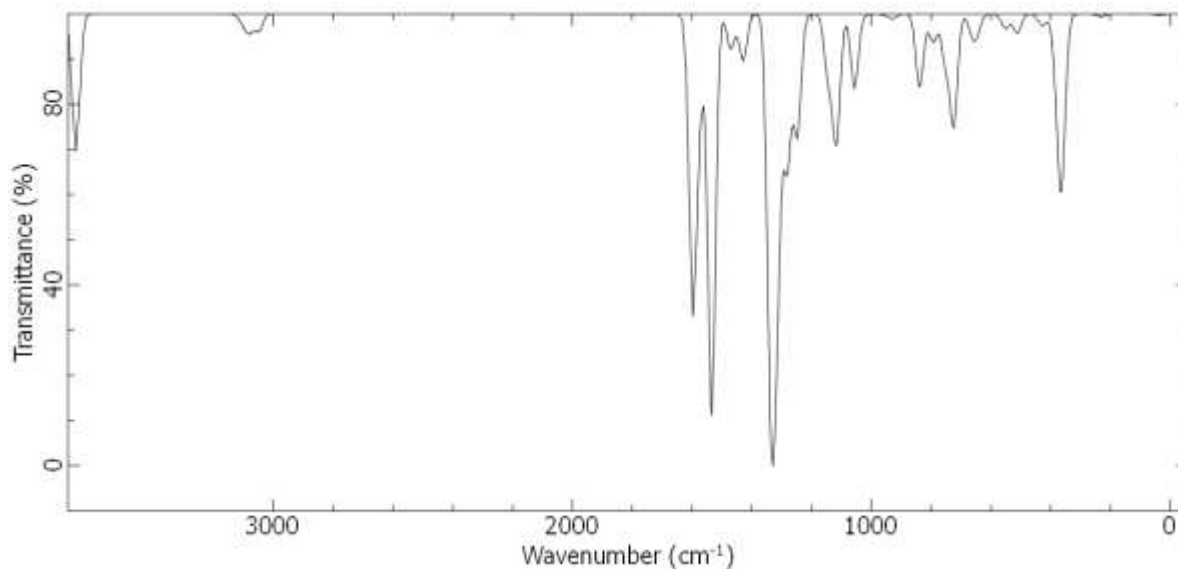

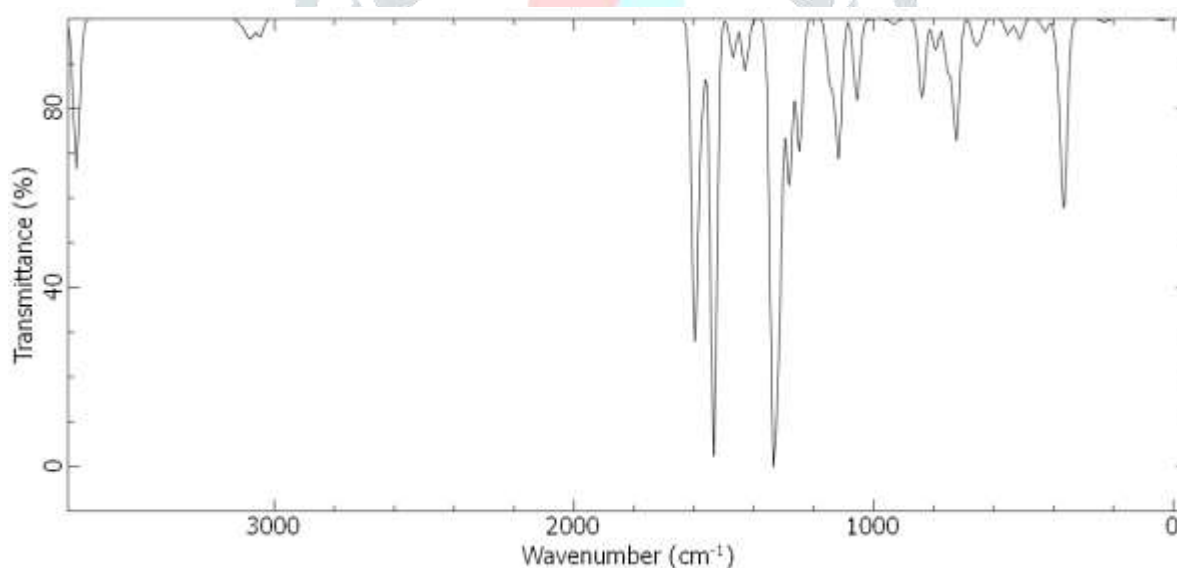Figure 2 IR spectra of O-Nitro Phenol calculated with B3LYP/6-31*G(d,p) Scaled

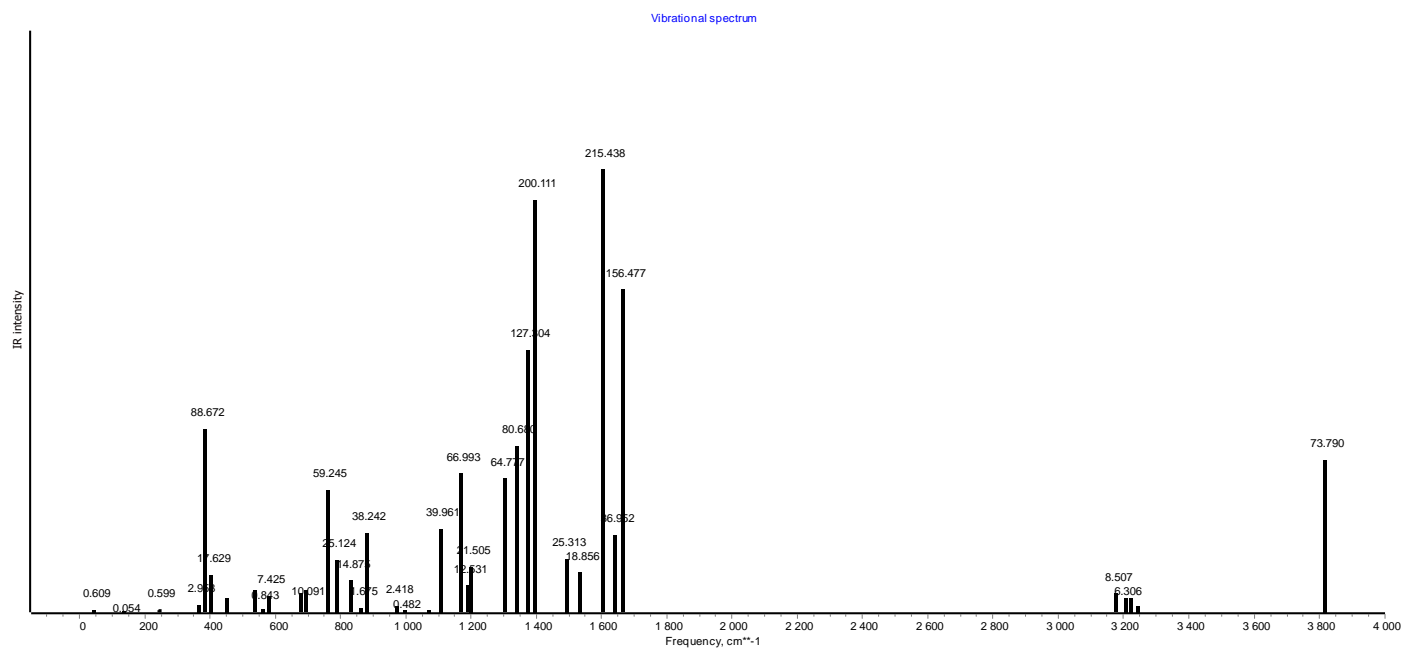Figure 3 IR spectra of o-Nitro Phenol calculated with B3LYP/6-31G*(d, p) Unscaled

Figure 4 IR spectra of o-Nitro Phenol calculated with B3LYP/6-31G*(d, p) scaled
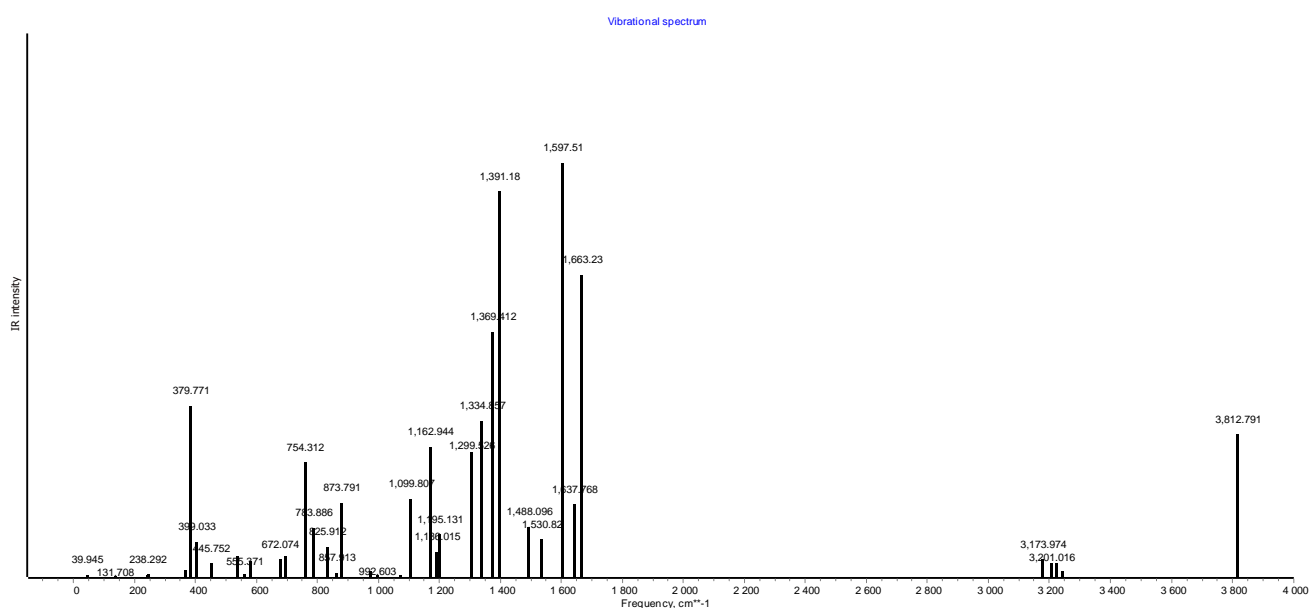

Figure 5 IR spectra of o-Nitro Phenol calculated with B3LYP/6-31G*(d, p) Unscaled

Phenyl Ring Modes:

The four C-H stretching modes ν (C-H) are assigned to the frequencies 3239, 3218, 3201 and 3174 cm^{-1} respectively. The C-H stretching modes ν (CH) were assigned to the frequencies 3222,3204, 3197 and 3178 cm^{-1} [32]. The C-H stretching vibrations are pure and highly localized modes. There are 6 C-C stretching modes ν(R) due to the phenyl ring which are identified as the computed frequencies 1598, 1531,1488, 1391, 1369 and 1335cm^{-1}. These modes are strongly coupled with many other modes. These modes were assigned to the frequencies 1661, 1620, 1487, and1413, cm^{-1} [32]. The C-N and C-O streching modes occur at frequencies 1195, 1300 cm^{-1} corresponding to the modes ν(C$_4$-N$_{13}$) and ν(C$_3$-O$_{11}$) respectively. These modes are also

coupled with many other modes. The C-N and C-O stretching mode in the literature was found to be corresponding to the frequency 1101 and 1284cm^{-1}[32].

There are three ring planar deformation modes which we assign as the frequencies 1163, 858 and 784 cm^{-1}. These modes are coupled with other modes as shown in the Table-4. The three ring nonplanar deformation modes are correlated to the frequencies 380, 362 and 243 cm^{-1} corresponding to modes 4 and 16(a,b) of the benzene molecule. These modes were found to occur at frequencies 1049, 837, 682 and 698, 524, 144[32].

The four C-H planar deformations β(C-H) and four C-H nonplanar deformations τ(C-H) are assigned at the frequencies 1100, 1066, 993, 826, 575, 555, 533 and 446 cm^{-1} respectively.These modes were found to occur at frequencies 1510, 1319, 1232, 1158, and 1000, 977, 867, 776[32]. These modes are coupled with many other modes. The modes σ(C-N), Ω(C-N), θ(C-O) and η(C-O) correspond to the frequencies 690, 40, 754 and 132 cm^{-1} respectively. These modes are strongly coupled modes. The modes β(C-N) and β(C-O) were assigned to the frequencies 245, 291 and 422, 554 cm^{-1} [32].

O-H group modes (3 modes): The OH stretching ν(O_8-H_{13}) mode corresponds to the frequency 3813 cm^{-1}. The O-H stretching vibration is pure and highly localized mode. The O-H stretching mode was found to correspond to the frequency 3472 [32]. The C-O-H angle bending- π(C_5-O_8-H_{13}) mode and one -OH tour in plane is found to correspond to the frequency 1186 and 672 cm^{-1} and also to the frequencies 1185 and 422 cm^{-1} [32], which is also strongly coupled with many modes.

NO₂ group modes (6 modes): There are six modes of vibrations due to the NO_2 group , namely, symmetric NO_2 stretching-vs(NO_2), asymmetric NO_2 stretching -vas(NO_2), NO_2 rocking-γ(NO_2), NO_2 scissoring -ρ(NO_2), NO_2 torsion-τ(NO_2) and wagging-ω(NO_2) which correspond to the frequencies 1663, 1638, 968, 874, 399 and 238 respectively. The NO_2 torsion-τ(NO_2)is slightly coupled with τ(C_3-O_{11}) and the other five modes strongly coupled with various vibrational modes. The modes vas(NO_2), vs(NO_2), ω(NO_2), δ(NO_2) and τ(NO_2) were found to correspond to the frequencies 1582, 1368, 884, 736 and 571 cm^{-1} [32].

4.3 OTHER MOLECULAR PROPERTIES

Using the DFT/B3LYP with 6-311*G(d,p) basis set calculations, several thermodynamic properties like heat capacity, zero point energy, entropy of o-Nitro Phenol have been calculated and are presented in Table 5.

Table 5 Thermodynamic parameters of o-Nitro Phenol calculated at DFT-B3LYP method with 6-31*G (d, p) basis set

Optimized global minimum energy (Hartrees)	0.107046
Total energy (thermal) E_{total}(K cal mol^{-1})	72.214
Heat capacity, C_v(cal mol^{-1}k^{-1})	30.397
Entropy, S (cal mol^{-1}k^{-1})	89.529
Zero point vibrational energy (K cal mol^{-1})	67.17262
A	2.33109
B	1.25123
C	0.83160

Scale factors have been recommended for an accurate prediction in determining the zero point energy (ZPVE) and entropy (S_{vib}). The variation in the ZPVE seems to be insignificant. The total energy and the change in the

total entropy of the title compound at room temperature are also presented. All the thermodynamic data supply helpful information for further study on the o-Nitro Phenol. They can be used to compute the other thermodynamic energies according to the relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermochemical field.

4.5 HOMO-LUMO ANALYSIS

The highest occupied molecular orbital (HOMOs) and the lowest unoccupied molecular orbital (LUMOs) are named as frontier molecular orbital (FMOs). The frontier molecular orbital (FMOs) plays an important role in optical and electrical properties. The atomic orbital compositions (HOMO and LUMO) of frontier molecular orbital for o-Nitro Phenol at B3LYP/6-31+G(d,p) are shown in Fig.6.
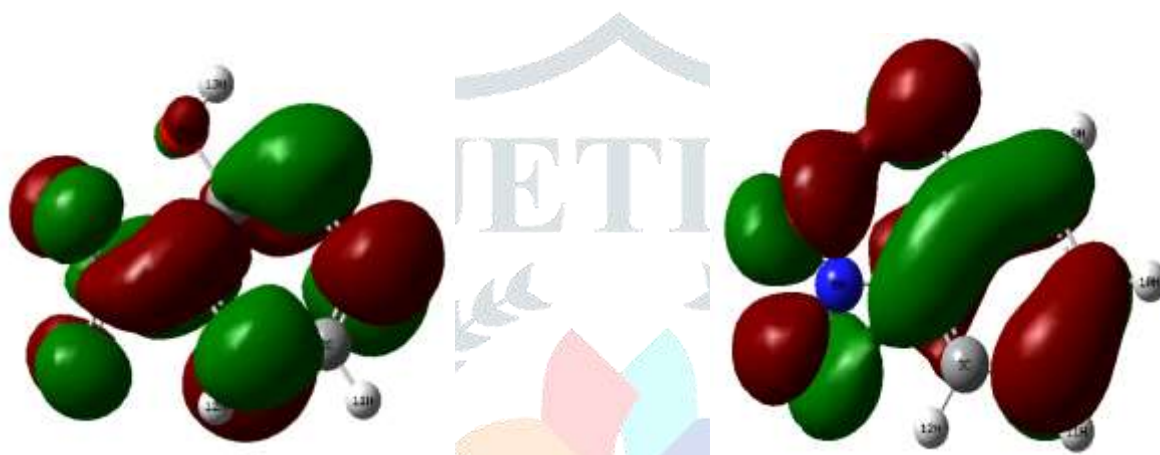

Figure 6: Atomic orbital compositions (HOMO and LUMO) of the frontier molecular orbital for o-Nitro Phenol

The LUMO, of nature, (i.e. benzene ring) is delocalized over the whole C-C bond. By contrast, the HOMO is located over the NO_2 group; consequently the HOMO→LUMO transition implies an electron density transfer to C-C bond of the benzene ring from NO_2 group. Moreover, these orbital significantly overlaps in their position of the benzene ring for o-Nitro Phenol. The HOMO-LUMO energy gap of title molecule reflects the chemical activity of the molecule. The HOMO represents the ability to donate an electron and LUMO represents the ability to obtain an electron. Moreover, a lower HOMO-LUMO energy gap explains the fact that ultimate charge transfer interaction is taking place within the molecule and is calculated as[33-35].

HOMO energy E_{HOMO}= -0.3296

LUMO energy E_{LUMO}= -0.1916

HOMO-LUMO energy gap ΔE= 0.1380

5 CONCLUSION

The optimized molecular geometries, the harmonic vibrational wavenumber and intensities of vibrational bands of o-Nitro Phenol have been carried out using B3LYP level using 6-31+G (d,p) basis set calculations. The DFT based quantum mechanical method provides the most reliable theoretical information on the

vibrational properties of o-Nitro Phenol. The assignments of most of fundamentals provided in the present work are believed to be unambiguous. Therefore, the assignment proposed at a higher level of theory with a higher basis set with only reasonable deviations from the experimental values seems to be correct. The calculated HOMO and LUMO energies reveal that charge transfer occurs within the molecule. In addition, the thermodynamic parameter and total dipole moment properties of the compound have been calculated in order to get insight into the compound.

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