FTIR and FT-Raman, normal coordinate analysis of the structure and vibrational spectra of o-nitrobenzaldehyde oxime

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ABSTRACT

The FTIR and FT-Raman spectra of the o-nitrobenzaldehyde oxime (ONBO) have been recorded in the regions 4000-400 and 3500-100 cm^{-1} respectively. The spectra were interpreted with the aid of normal coordinate analysis following full structure optimization and force field calculations based on density functional theory (DFT) using standard B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p) method and basis set combination. The geometries and normal modes of vibration obtained from the DFT method are in good agreement with the experimental data. The total energy distribution (TED) values obtained reflect the correctness of the vibrational assignments.

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Introduction

Oxime is an intermediate in the industrial production of caprolactam, a precursor to Nylon 6.[1] About half of the world's supply of cyclohexanone, more than a billion kilograms annually, is converted to the oxime. In the presence of sulfuric acid catalyst, the oxime undergoes the Beckmann rearrangement to give the cyclic amide caprolactam. Oxime compounds are used as antidotes for nerve agents. Oxime compounds can reactivate acetylcholinesterate by attaching to the phosphorus atom and forming an oxime-phosphonate which then splits away from the acetylcholinesterase molecule [2]. Owing to these applications of oxime, an attempt has been made in this study to interpret the vibrational spectra of O-nitrobenzaldehyde oxime.

For a proper understanding of IR and Raman spectra, a reliable assignment of all vibrational bands is essential. For this purpose, several theoretical methods are useful in analyzing vibrational spectra of organic molecules. These methods can be roughly divided in the following groups: classical mechanical method, semi-empirical quantum mechanical method, ab intio quantum mechanical method and density functional theory (DFT), each method having its own advantage [3-5]. Ab initio molecular orbital calculation is relatively successful approach to the calculation of vibrational spectrum of closed shell organic molecules. However, the Hartree – Fock ab intio methods are able to give good results provided a reasonable basis set and an appropriate correlation treatment is taken into account. The most popular and accurate scaled ab initio approach is scaled quantum mechanical (SQM) force field procedure, which employs different scale factors for different coordinates [3,6,7].

On the other hand, DFT methods, particularly hybrid functional method, [8-10] have evolved as powerful quantum chemical tool for the determination of the electronic structure of molecules. In the frame work of DFT approach, different exchange and correlation functionals, are routinely used. Among these, the B3LYP combination is widely used. Since it proved its ability in reproducing various molecular properties, including vibrational spectra, the combined use of B3LYP functional and standard basis set (6-31++G(d,p)) provide an excellent agreement between accuracy and computational efficiency of vibrational spectra for large and medium size molecules.

The vibrational frequencies obtained by quantum chemical calculations are typically larger and they have to be scaled by empirical scaling factors ranging from 0.8 to 1.0. These scaling factors depend on both the method and basis set and they are determined from the mean deviation between the calculated and experimental frequencies [4,11-13]. The aim of this work is to check the performance of B3LYP density functional force field for simulation of the IR and Raman spectra of title compound with the use of the standard 6-31+G(d,p) and 6-31++G(d,p) basis set.

Experimental analysis

Infrared absorption, emission and reflection spectra for molecular species can be rationalized by assuming that all arise from various changes in energy brought about by transitions of molecules from one vibrational (or) rotational energy state to the another. The phenomenon results from the same type of quantized vibrational changes that are associated with infrared absorption [14].

The fine sample O-nitrobenzaldehyde oxime, was obtained from Lancaster Chemical Company, UK and used as such for the study. The spectra were recorded on a computer interfaced BRUKER IFS model interferometer equipped with FRA 106 FT Raman accessory. The spectra were recorded in the region 3500-100 cm-1 with Nd:YAG laser operating at 200 mw power continuously with 1064 nm excitation and calibrated wave

numbers are accurate within ±1cm-1. The room temperature IR spectra of the title compound are measured in the region 4000-400 cm-1 at resolution of ±1 cm-1 using BRUKER IFS 66V vacuum Fourier transform spectrophotometer.

Computational details

The molecular geometry optimization energy and vibrational frequency calculations were carried out for ONBO with GAUSSIAN 09W software package [15] using the B3LYP functional [16,17] combined with the standard 6-31+G(d,p) and 6-31++G(d,p) basis set. The Cartesian representations of the theoretical force constant have been computed at optimized geometry by assuming Cs point group symmetry. Scaling of the force field was performed according to the SQM procedure [18-20] using selective scaling in the natural internal coordinate analysis including the least square refinement of the scaling factors and the calculation of the Total Energy Distribution (TED) were done on a PC with the MOLVIB PROGRAM (Version V7.0 – G77) written by Sundius [21-23].

The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using the standard procedure of decomposing the traces of the symmetry operation into the irreducible representations. The symmetry analysis for the vibrational modes of ONBO was presented in details in order to describe the basis for the assignments.

By combining the results of the GAUSSVIEW program [24] with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. There is always some ambiguity in defining internal coordinates. However, the defined coordinate form complete set and matches quite well with motions observed using the GAUSSVIEW program.

Results and discussion
Molecular geometry

The molecular structure of ONBO having Cs symmetry is shown in Fig1 The global minimum energy obtained by B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p) DFT structure optimization for ONBO is calculated as -605.39979188 Hartrees and -605.39256942 Hartrees, respectively. The calculated optimized geometrical parameters obtained in this study for the title compound is presented in Table 1.
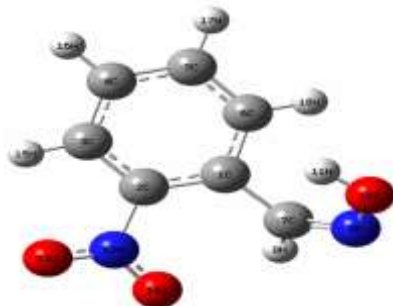

Fig 1. Molecular structure of O – Nitrobenzaldehyde Oxime

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose the full set of 60 standard internal coordinates (containing 12 redundancies) for the title compound are defined in Table 2. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi and Pulay [25,26] are summarized in Table 3. The theoretically calculated DFT force fields were transformed to this set of vibrational coordinates and used in all subsequent calculations.

Vibrational spectra

The title compound consists of 18 atoms and its 48 normal modes are distributed amongst the symmetry species as:

$$\Gamma_{3N-6} = \text{33 A}' \text{ (in-plane)} + \text{15 A}'' \text{ (out-of-plane)}$$

The detailed vibrational assignment of fundamental modes of ONBO along with the calculated IR and Raman frequencies and normal mode descriptions (characterized by TED) are reported in Table 4. The FTIR and FT Raman spectra of the title compound are shown in Figs 2 and 3 respectively.
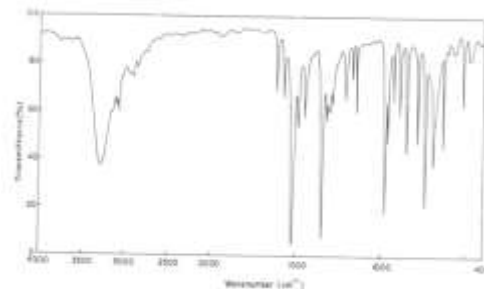

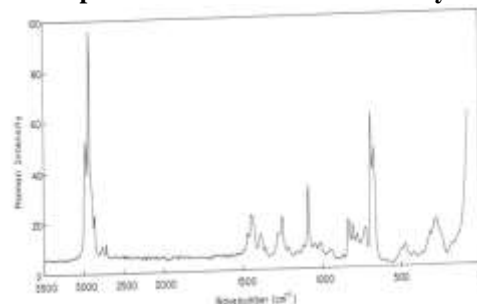**Fig. 2 FTIR spectrum of O – Nitrobenzaldehyde Oxime**

Fig. 3 FT-Raman spectrum of O – Nitrobenzaldehyde Oxime

O–H group vibrations

The O-H stretching vibrations are normally observed at about 3300 cm-1. The O-H in-plane bending vibration is observed in the region 1440 – 1260 cm-1 [27]. The FTIR band appeared at 3289 cm-1 was assigned to O-H stretching modes of vibrations. The in-plane and out-of-plane bending vibrations of hydroxy groups have been identified at 1286 cm-1 and 787 cm-1 for ONBO, respectively.

Carbon – Hydrogen vibrations

The heteroaromatic structure shows the presence of C–H stretching vibrations in the region 3000-3100 cm-1 which is the characteristic region for the ready identification of such C–H stretching vibrations [28]. Accordingly, in the present study, the C-H vibrations of the title compound are observed at 3108, 3081, 2935 and 2905 cm-1 in the FT-IR spectrum and at 2980, 2935 and 2900 cm-1 in the Raman for ONBO. The C-H in-plane and out-of-plane bending vibrations have also been identified and presented in table 4.

C-C vibrations

The ring stretching vibrations are very much prominent in the spectrum of pyridine and its derivatives and are highly characteristic of aromatic ring itself [29]. There are very wide fluctuations in intensity [30] in the absorption bands due to aromatic structures in the 1600-1500 cm-1 region. In this study the bands between 1612, 1573,1487,1448,1348 cm-1 and 1548, 1446, 1378 cm-1 in FTIR and FT- Raman spectra of title compound respectively. The higher percentage of total energy distribution (TED) obtained for this group encouraging and confirms the assignments proposed in this study for C-C stretching vibrations. The in-plane and out-of-plane bending vibrations of C-C group are also listed in table 4.

Carbon-Nitrogen vibrations

The IR and Raman bands appeared at 1320 and 1338 cm-1 in ONBO have been designated to C-N stretching vibrations respectively. The in-plane and out-of-plane bending vibrations assigned in this study are also supported by the literature [31,32]. The identification of C-N vibration is a difficult task since, it falls in a complicated region of the vibrational spectrum. However, with the help of force field calculations, the C-N vibrations were identified and assigned in this study.

Nitro group vibrations

The characteristics group frequencies of nitro group are relatively independent of the rest of the molecule, which makes this group convenient to identify. Aromatic nitro compounds have strong absorptions due to the asymmetric and symmetric stretching vibrations of the NO_2 group at 1570–1485 cm-1 and 1370-1320 cm-1, respectively [33]. Hydrogen bonding has little effect on the NO_2 asymmetric stretching vibrations [34,35]. The infrared and Raman band observed at 1523 cm-1 and 1306 cm-1 have been designated to asymmetric and symmetric stretching modes of NO_2 group, respectively. The scissoring modes of NO_2 group have been designated to the band at 696 cm-1 in Raman. The band at 290 cm-1 in Raman is attributed to NO_2 rocking mode. The bands observed at 320 cm -1 and the calculated frequency 36 cm-1 have been designated to NO_2 wagging and NO_2 twisting modes, respectively.

Other Molecular Properties

In addition to the vibrational assignments, several thermodynamic parameters are also calculated on the basis of vibrational analysis at B3LYP/6-31+G(d,p) B3LYP/6-31G++(d,p) . The calculated thermodynamic properties are presented in the Table 5. The self consistent field (SCF) energy, zero point vibrational energies (ZPVE), rotational constants, dipole moment and entropy SVib(T) are calculated to the extent of accuracy and the variations in the ZPVEs seem to be insignificant. The total energies and change in total entropy of o-nitrobenzaldehyde oxime at room temperature are only marginal.

Conclusion

Based on the SQM force field obtained by DFT calculations at B3LYP/6-31+G(d p) and B3LYP/6-31++G(d p) levels, the complete vibrational properties of o-nitrobenzaldehyde oxime have been investigated by FT-IR and FT-Raman spectroscopies. The role of methyl, nitro and other groups in the vibrational frequencies of the title compound has been discussed. The various modes of vibrations have unambiguously been assigned based on the results of the TED output obtained from normal coordinate analysis. The assignment of the fundamentals is confirmed by the qualitative agreement between the calculated and observed band intensities (especially with the large basis set) and the results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the title molecules in the solid phase. In addition, thermodynamic functions of ONBO were also presented.

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Table 1 Optimized geometrical parameters of O – Nitrobenzaldehyde Oxime obtained by B3LYP/6-31+G(d,p) and 6-31++G(d,p) density functional calculations

Parameter Bond length	Value (Å) B3LYP		Bond angle	Value (Å) B3LYP		Dihedral Angle	Value (Å) 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)
C1 – C2	1.4124	1.4091	C2 – C1 – C6	116.4556	116.6425	C6 – C1 – C2 – C3	-0.5063	0.0143
C1 – C6	1.4095	1.4079	C2 – C1 – C7	124.3247	125.4473	C6 – C1 – C2 – N12	178.6495	-179.4796
C1 – C7	1.4735	1.4928	C6 – C1 – C7	119.1606	117.891	C7 – C1 – C2 – C3	176.6651	-178.352
C2 – C3	1.3985	1.396	C1 – C2 – C3	122.1706	122.2399	C7 – C1 – C2 – N12	-4.1791	2.1541
C2 – N12	1.4745	1.4781	C1 – C2 – N12	122.1615	121.0403	C2 – C1 – C6 – C5	-0.8926	-0.4064
C3 – C4	1.3896	1.3926	C3 – C2 – N12	115.663	116.718	C2 – C1 – C6 – H18	178.7546	-179.119
C3 – H15	1.0828	1.0829	C2 – C3 – C4	119.7606	119.6265	C7 – C1 – C6 – C5	-178.2176	178.0878
C4 – C5	1.3999	1.3967	C2 – C3 – H15	118.7602	118.841	C7 – C1 – C6 – H18	1.4295	-0.6248
C4 – H16	1.085	1.085	C4 – C3 – H15	121.4747	121.5325	C2 – C1 – C7 – H8	-10.0525	60.965
C5 – C6	1.3901	1.3953	C3 – C4 – C5	119.4306	119.6607	C2 – C1 – C7 – N9	169.8844	-122.0294
C5 – H17	1.0857	1.0856	C3 – C4 – H16	119.8875	119.7715	C6 – C1 – C7 – H8	167.0475	-117.3829
C6 – H18	1.0838	1.0856	C5 – C4 – H16	120.6819	120.5678	C6 – C1 – C7 – N9	-13.0156	59.6227
C7 – H8	1.0906	1.0846	C4 – C5 – C6	120.4013	120.1288	C1 – C2 – C3 – C4	1.5052	0.4305
C7 – N9	1.2831	1.2835	C4 – C5 – H17	120.1278	120.2794	C1 – C2 – C3 – H15	-179.2551	-179.5385
N9 – O10	1.375	1.3862	C6 – C5 – H17	119.4678	119.591	N12 – C2 – C3 – C4	-177.7019	179.9451
O10 – H11	0.9789	0.9772	C1 – C6 – C5	121.7582	121.6989	N12 – C2 – C3 – H15	1.5377	-0.0239
N12 – O13	1.2311	1.2311	C1 – C6 – H18	117.7898	118.429	C1 – C2 – N12 – O13	155.3131	166.0951
N12 – O14	1.2353	1.2309	C5 – C6 – H18	120.4511	119.8595	C1 – C2 – N12 – O14	-25.6912	-14.2103
			C1 – C7 – H8	119.1554	118.9907	C3 – C2 – N12 – O13	-25.4797	-13.4257
			C1 – C7 – N9	119.3844	126.7765	C3 – C2 – N12 – O14	153.5161	166.2689
			H8 – C7 – N9	121.4602	114.1727	C2 – C3 – C4 – C5	-1.0936	-0.4866
			C7 – N9 – O10	116.4787	118.3188	C2 – C3 – C4 – H16	179.0007	179.4839
			N9 – O10 – H11	109.7996	110.3133	H15 – C3 – C4 – C5	179.6879	179.4816
			C2 – N12 – O13	117.6048	117.6	H15 – C3 – C4 – H16	-0.2178	-0.548
			C2 – N12 – O14	118.4046	117.9148	C3 – C4 – C5 – C6	-0.2706	0.1055
			O13 – N12 – O14	123.9822	124.4844	C3 – C4 – C5 – H17	-179.6343	179.7899
						H16 – C4 – C5 – C6	179.6343	-179.8647
						H16 – C4 – C5 – H17	0.2772	-0.1803
						C4 – C5 – C6 – C1	1.2958	0.3538
						C4 – C5 – C6 – H18	-178.3421	179.0483
						H17 – C5 – C6 – C1	-179.3429	-179.3328
						H17 – C5 – C6 – H18	1.0193	-0.6383
						C1 – C7 – N9 – O10	178.4609	6.0181
						H8 – C7 – N9 – O10	-1.6036	-176.8527
						C7 – N9 – O10 – H11	0.6226	4.7811

For numbering of atom refer Fig.1.

Table 2: Definition of Internal coordinates of O – nitrobenzaldehyde Oxime

No	Symbol	Type	Definition
Stretching			
1 – 5	P_i	CH	C3 – H15, C4 – H16, C5 – H17, C6 – H18, C7 – H8,
6 – 12	R_i	CC	C1 – C2, C2 – C3, C3 – C4, C4 – C5, C5 – C6, C6 – C1, C1 – C7
13, 14	U_i	CN	C7 = N9, C2 – N12
15	V_i	NO	N9 – O10
16	Q_i	OH	O10 – H11
17, 18	V_I	NO	N12 – O13, N12 – O14
In - plane - bending			
19 – 24	β_i	Ring	C1 – C2 – C3, C2 – C3 – C4, C3 – C4 – C5, C4 – C5 – C6, C5 – C6 – C1, C6 – C1 – C2
25 – 26	δ_i	CCC	C6 – C1 – C7, C6 – C1 – C7
27 – 34	α_i	CCH	C2 – C3 – H15, C4 – C3 – H15, C3 – C4 – H16, C5 – C4 – H16, C4 – C5 – H17, C6 – C5 – H17, C5 – C6 – H18, C1 – C6 – H18
35 – 38	γ_i	CCN HCN	C3 – C2 – N12, C1 – C2 – N12, C1 – C7 = N9, H8 – C7 = N9
39	σ_I	CNO	C7 = N9 – O10
40 – 42	σ_i	NO (Nitro)	C2 – N12 – O14, C2 – N12 – O13, O13 – N12 – O14
43	θ_i	NOH	N9 – O10 – H11
Out - of – plane bending			
44 – 49	τ_i	t Ring	C1 – C2 – C3 – C4, C2 – C3 – C4 – C5, C3 – C4 – C5 – C6, C4 – C5 – C6 – C1, C5 – C6 – C1 – C2, C6 – C1 – C2 – C3
50	ψ_i	CCC	C7 – C1 – C2 – C6
51 – 55	ω_i	CH	H15 – C3 – C2 – C4, H16 – C4 – C3 – C5, H17 – C5 – C6 – C4, H18 – C6 – C1 – C5, H8 – C7 – C1 – (C6, C2)
56, 57	ρ_i	CN	N12 – C2 – C1 – C3, N9 = C7 – C2 – (C6 – C2)
58	Σ_i	NO	O10 – N9 = C7 – C1
59	ϕ_i	OH	H11 – O10 – N9 – C7
60	τ_i	t NO₂	O13 – O14 – (N12, C2) – (C1 – C3)

Table 3: Definition of Local symmetry coordinates of O-nitrobenzaldehyde oxime

No	Type	Definition
1 – 5	CH	P_1, P_2, P_3, P_4, P_5
6 – 12	CC	$R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}$
13, 14	CN	U_{13}, U_{14}
15	NO	V_{15}
16	OH	θ_{16}
17	No₂ss	$(V_{17} + V_{18}) / \sqrt{2}$
18	No₂ass	$(V_{17} - V_{18}) / \sqrt{2}$
19	R trigd	$(\beta_{19} - \beta_{20} + \beta_{21} - \beta_{22} + \beta_{23} - \beta_{24}) / \sqrt{6}$
20	R symd	$(-\beta_{19} - \beta_{20} + 2\beta_{21} - \beta_{22} - \beta_{23} + 2\beta_{24}) / \sqrt{6}$
21	R asymd	$(\beta_{19} - \beta_{20} + \beta_{22} - \beta_{23}) / 2$
22	bCC	$(\delta_{25} - \delta_{26}) / \sqrt{2}$
23 - 26	bCH	$(\alpha_{27} - \alpha_{28}) / \sqrt{2}, (\alpha_{29} - \alpha_{30}) / \sqrt{2}, (\alpha_{31} - \alpha_{32}) / \sqrt{2}, (\alpha_{33} - \alpha_{34}) / \sqrt{2}$
27, 28	bCN	$(\gamma_{35} - \gamma_{36}) / \sqrt{2}, (\gamma_{37} - \gamma_{38}) / \sqrt{2}$
29	bNO	σ_{39}
30	No₂rock	$(\sigma_{40} - \sigma_{41}) / \sqrt{2}$
31	No₂twist	$(\sigma_{40} + \sigma_{41}) / \sqrt{2}$
32	No₂scis	$(2\sigma_{42} - \sigma_{41} - \sigma_{40}) / \sqrt{2}$
33	bOH	θ_{43}
34	t Rtrigd	$(\tau_{44} - \tau_{45} - \tau_{46} + \tau_{47} - \tau_{48} - \tau_{49}) / \sqrt{6}$
35	t Rsymd	$(\tau_{44} - \tau_{46} - \tau_{47} - \tau_{49}) / \sqrt{2}$
36	t Rasymd	$(-\tau_{44} + 2\tau_{45} - \tau_{46} - \tau_{47} + 2\tau_{48} + \tau_{49}) / \sqrt{12}$
37	ωCC	ψ_{50}
38 - 43	ωCH	$\omega_{51}, \omega_{52}, \omega_{53}, \omega_{54}, \omega_{55}$
44, 45	ωCN	ρ_{56}, ρ_{57}
46	ωNO	Σ_{58}
47	ωOH	ϕ_{59}
48	tNo₂	τ_{60}

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Table 4 The observed FTIR, FT Raman and calculated (Unscaled and Scaled) frequencies (cm⁻¹), IR intensity (KM mol⁻¹), Raman Activity (Å amu⁻¹), Reduced masses (amu) and and force constant (m dyne Å⁻¹) and probable assignments (characterized by TED) of O – nitrobenzaldehyde oxime using B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p)

Symm species Cₛ	Observed wave number (cm)		B3LYP/6-31+G(d,p)						B3LYP/6-31++G(d,p)						TED% among types of coordinates
	FTIR	FT Raman	Unscaled	Scaled	Reduced mass	Force Constants	IR intensity	Raman active	Unscaled	Scaled	Reduced mass	Force Constants	IR intensity	Raman active	
A'	3289 (s)	-	3609	3294	1.0660	8.1829	5.2494	224.1822	3626	3291	1.0665	8.2561	7.6033	77.6146	υOH (99)
A'	3108 (w)	-	3242	3114	1.0935	6.7724	2.1470	111.3537	3243	3111	1.0933	6.7750	3.4816	100.8624	υCH (98)
A'	3081(ms)	-	3229	3087	1.0935	6.7193	1.6010	81.7876	3217	3083	1.0949	6.6773	4.8835	250.8850	υCH (97)
A'	-	2980 (ms)	3213	2985	1.0933	6.6522	7.3749	166.9450	3216	2982	1.0907	6.6496	1.8230	50.2016	υCH (98)
A'	2935(w)	2935(vs)	3197	2940	1.0879	6.5551	3.2891	72.3635	3207	2937	1.0916	6.6178	2.1611	74.5731	υCH (99)
A'	2905(w)	2900(w)	3134	2909	1.0891	6.3051	23.8338	59.0261	3196	2906	1.0874	6.5464	0.9451	50.2286	υCH (96)
A'	1612(ms)	-	1664	1615	7.5124	12.2665	12.6687	108.5564	1663	1613	8.9281	14.5605	18.6626	122.5849	υCC (88)
A'	1573(ms)	-	1650	1577	6.8045	10.9624	74.4025	410.8145	1656	1575	7.2975	11.7946	41.5125	57.4610	υCC (86)
A'	-	1548(w)	1614	1551	6.2664	9.6267	52.0689	75.6874	1619	1550	6.2531	9.6579	89.6981	45.6951	υCC (89)
A'	1523(vs)	-	1589	1527	9.0269	13.4399	224.944	14.9313	1598	1525	8.5002	12.7891	151.2654	17.9363	No₂ass (81)
A'	1487(ms)	-	1516	1490	2.5499	3.4560	0.7288	15.8476	1509	1489	2.4871	3.3402	2.6098	2.4217	υCC (81)
A'	1448(ms)	1446(vw)	1474	1451	2.2685	2.9043	1.7788	20.7173	1471	1450	2.2149	2.8252	6.1222	1.5807	υCC (88)
A'	-	1378(w)	1451	1382	1.4791	1.8357	82.3044	1.3869	1388	1380	1.3445	1.5271	43.8579	29.8395	υCC (88)
A'	1348(vs)	-	1379	1353	7.2399	8.1200	226.6510	150.8927	1381	1351	5.8715	6.6031	228.3984	134.3314	υCC (89)
A'	-	1338(w)	1362	1342	4.6332	5.0658	46.8090	53.6468	1355	1341	3.3509	3.6296	34.5682	14.3021	υCN (78)
A'	1320(w)	-	1330	1326	1.3251	1.3819	14.2453	11.9465	1341	1323	1.4512	1.5382	12.6084	6.7267	υCN (79)
A'	1306(vw)	-	1305	1311	1.9600	1.9677	5.2656	99.1006	1292	1309	1.8267	1.7988	2.4038	3.8385	No₂sys (81)
A'	1300(w)	-	1234	1305	1.8100	1.6260	12.8256	74.6681	1212	1302	2.3422	2.0281	16.4497	26.6686	υNO (76)
A'	1286(ms)	-	1190	1293	1.1087	0.9253	1.3973	26.1363	1189	1291	1.1255	0.9381	2.4896	12.3968	bOH (72)
A'	-	1240(s)	1165	1247	1.9324	1.5465	9.4494	53.8977	1166	1244	2.0054	1.6067	13.5396	24.9645	bCH (73)
A'	1211(ms)	-	1096	1217	3.1323	2.2195	12.2765	4.6288	1093	1215	3.1942	2.2491	9.3744	3.4517	bCH (72)
A'	1169(s)	-	1068	1175	2.6364	1.7745	12.4665	56.3906	1065	1173	2.6351	1.7643	0.3223	39.5721	bCH (71)
A'	1146(s)	-	1027	1153	9.2539	5.7596	226.5576	1.8519	1014	1151	1.3107	0.7947	0.2098	0.2036	bCH (74)
A'	-	1085(w)	1013	1092	1.3347	0.8085	4.2373	0.3617	991	1086	1.3865	0.8034	6.2001	0.2947	Rtrigd (69)
A'	-	1058(vw)	987	1066	1.3636	0.7841	4.1838	0.1608	944	1063	5.0643	2.6616	137.5953	1.6485	Rsymd (70)
A'	-	1010(w)	938	1017	1.5683	0.8147	14.6198	11.6607	918	1015	1.9739	0.9820	16.4355	3.9609	Rasymd (68)
A'	979(ms)	-	902	986	1.8904	0.9073	6.2161	4.1883	881	983	2.0142	0.9224	3.2218	9.3677	bCH (70)
A'	962(ms)	-	893	970	2.2860	1.0754	6.1107	3.4640	865	968	3.0361	1.3391	31.9694	16.9276	bCC (66)
A'	-	940(vw)	856	950	9.0531	3.9163	24.7116	15.0819	859	947	2.2657	0.9868	13.3944	6.1821	bCN (68)
A'	928(s)	-	801	937	2.0675	0.7825	20.6513	1.3541	804	935	1.9315	0.7374	17.1077	2.3793	bCN (67)
A'	894(s)	-	758	903	2.2478	0.7613	35.6544	0.06449	760	901	4.1915	1.4287	18.2957	8.1078	bNO (64)
A'	787(s)	781(ms)	707	796	5.5432	1.6369	21.4554	0.6516	735	794	2.6959	0.8585	25.8426	0.2881	ωOH (50)
A'	742(vs)	-	705	751	5.5490	1.6281	10.5175	0.5187	687	748	5.3346	1.4867	5.9825	1.6922	ωCH (62)

A'	-	696(ms)	646	706	6.0557	1.4912	5.0932	7.0971	671	702	6.2182	1.6665	6.4511	1.9431	No₂sciss (70)
A"	609(w)	-	575	618	5.5742	1.0864	5.1432	1.8206	611	616	4.2550	0.9378	1.0460	10.1307	ωCH (64)
A"	571(s)	-	535	580	3.6204	0.6109	15.8312	0.9968	550	576	6.2272	1.1118	0.3901	5.0357	ωCH (65)
A"	477(w)	477(vw)	477	484	1.2414	0.1670	65.3854	2.8231	511	482	3.2186	0.4959	23.6938	2.9836	ωCH (63)
A"	-	417(w)	471	425	5.1755	0.6773	11.5003	2.4564	479	423	2.9414	0.3992	15.6291	2.7679	ωCH (64)
A"	-	-	432	440	4.4330	0.4852	1.1547	2.6740	442	439	3.0724	0.3540	7.2147	0.7100	t Rtrigd (60)
A"	-	320(w)	384	331	8.0999	0.7067	1.8400	2.8513	416	329	2.1704	0.2218	31.9031	0.7381	No₂wag (65)
A"	-	-	349	365	7.9898	0.5146	1.8363	1.2498	375	370	7.5861	0.6315	7.8208	2.2699	t Rsymd (62)
A"	-	-	308	321	4.9013	0.2744	2.3532	3.2884	312	316	5.6290	0.3233	2.4639	2.8935	t Rasymd (61)
A"	-	290(vw)	260	304	6.9150	0.2764	4.1002	0.8569	248	301	6.0153	0.2185	4.5890	1.5480	No₂rock (62)
A"	-	276(vw)	173	290	4.5850	0.0810	8.3367	0.7242	220	387	4.9064	0.1403	4.9012	1.3763	ωCC (60)
A"	-	-	159	173	5.4256	0.0810	19.5094	2.9878	162	170	5.5056	0.0850	2.1979	1.8412	ωCN (63)
A"	-	-	109	124	4.0614	0.0285	9.4710	2.4662	100	118	4.9287	0.0291	0.5232	5.0182	ωCN (62)
A"	-	-	70	85	4.7622	0.0140	16.0358	5.9083	60	81	7.4310	0.0163	1.9137	4.3697	ωNO (59)
A"	-	-	36	50	8.4314	0.0068	8.9248	0.6424	26	48	14.6155	0.0060	0.5344	3.0377	No₂twist (56)

Abbreviations: t,torsion; R1 trigd, Ring 1 trigonal deformation; R2 trigd, Ring 2 trigonal deformation; asym, asymmetric; s, symmetric; ω, bending out-of-plane; asymd,asymmetric deformation; symd, symmetric deformation; b, bending in-plane; s, strong; w, weak; m, medium; vs, very weak; -ms, medium strong, Harmonic Frequencies in cm⁻¹. The absolute IR intensity in Km mol⁻¹. Raman scattering activity in A⁴ amu⁻¹. Depola-rization rations for plane and unpolarised in amu. Reduced masses in AMU Force constants in m Dyne A.

Table 5. Thermodynamic properties of o-nitrobenzaldehyde oxime.		
Parameter	B3LYP/6-31G+(d,p)	B3LYP/6-31G++(d,p)
Self Consistent Field energy	-605.3997 a.u	-605.3925a.u
Zero point vibrational energy	80.4972 (Kcal/Mol)	80.5832 (Kcal/Mol)
Rotational constants	1.2312 GHz	1.1575 GHz
	0.7948 GHz	0.9474 GHz
	0.4897 GHz	0.5704 GHz
Entropy	101.179 Cal/Mol-Kelvin	101.178 Cal/Mol-Kelvin
Specific heat capacity at constant volume	37.586 Cal/Mol-Kelvin	37.342 Cal/Mol-Kelvin
Translational energy	0.889 KCal/Mol-Kelvin	0.889 KCal/Mol-Kelvin
Rotational energy	0.889 KCal/Mol-Kelvin	0.889 KCal/Mol-Kelvin
Vibrational energy	85.099 KCal/Mol-Kelvin	85.106 KCal/Mol-Kelvin
Dipole moment	3.0027 debye	3.0570 debye