Molecular structure, vibrational spectroscopy, NBO and HOMO, LUMO studies of 3-Nitro Benzyl Chloride

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Abstract

In the present study, the FT-IR and FT-Raman spectra of 3-Nitro Benzyl Chloride (3NBC) have been recorded in the region 4000–400 cm^{-1} and 3500–50 cm^{-1}, respectively. The fundamental modes of vibrational frequencies of 3NBC are assigned. Theoretical information on the optimized geometry, harmonic vibrational frequencies, infrared and Raman intensities were obtained by means of *ab initio* Hartree–Fock (HF) and density functional theory (DFT) gradient calculations with complete relaxation in the potential energy surface using 3-21+G basis set. The vibrational frequencies which were determined experimentally from the spectral data are compared with those obtained theoretically from ab initio Hartree-Fock and DFT-B3LYP. A close agreement was achieved between the observed and calculated frequencies by refinement of the scale factors. The infrared and Raman spectra were also predicted from the calculated intensities. HOMO-LUMO energies, Mulliken's analyses, APT charges and calculation of thermodynamic properties have also been performed for both the compounds. Mulliken's population analysis reveals the σ-electron withdrawing character of chlorine atom in benzyl chloride. The calculated HOMO–LUMO energy gap reveals that charge transfer occurs within the molecule. It reflects the chemical activity of the molecule.

Keywords

3-Nitro Benzyl Chloride , DFT, *Ab initio,* HOMO–LUMO, Mulliken's analyses, APT charges

1. INTRODUCTION

The design of new molecular compounds exhibiting the spin crossover behavior is one of the growing importances in the research of functional materials, especially for applications in display devices [1], multi valued memory or switching devices [2-4], threshold indicators and biomedical imaging [5]. Benzyl chloride may be used in the synthesis of other organic compounds including pharmaceuticals. Industrially benzyl chloride is the precursor to benzyl esters which are used as plasticizers, flavourants and perfumes. Benzyl chloride reacts with water in a hydrolysis reaction to form benzyl alcohol and hydrochloric acid. Benzyl chloride and Tin are used in the synthesis of tribenzyl tinchloride. It is used in the synthesis of agrochemicals, dyes and plastic additives. Also it is used to

prepare benzyl alcohol, toluene and ester etc [6]. Owing to these greater pharmaceutical and industrial applications of benzyl chloride, an attempt has been made in this study to interpret the vibrational spectra 3-Nitro Benzyl Chloride (3NBC).

The assignments of band in the vibrational spectra of the molecules are an essential step in the application of vibrational spectroscopy for solving various structural chemical problems. In the present study, the detailed vibrational analysis of 3NBC has been performed by combining the experimental and theoretical information using Pulay's density functional theory (DFT) and HF methods [7].

The vibrational frequencies obtained by quantum chemical calculations are typically larger and they have to be scaled by empirical scaling factors ranging from 0.982 to 0.995. These scaling factors depend on both the method and basis sets and they are determined from the mean deviation between the calculated and experimental frequencies [8,9]. The complete vibrational analysis of benzyl chloride has been performed by Nagabalasubramanian et. al.,[10]. The analysis of vibrational spectra of chlorotoluene based on DFT theory calculations has been carried out by Zhou et. al., [11] and the internal rotation of o-chlorotoluene using microwave spectroscopy has been studied by Gerhard et. al., [12]. The NMR spectrum of o-chlorotoluene in a liquid crystal has been analyzed by Diehl et. al., [13]. The microwave spectrum of o-chlorotoluene has been studied by Nair and Epple [14] with a Stark spectrometer.

The literature survey reveals that no Density Functional Theory (DFT) calculation or detailed vibrational analysis has been performed on 3-Nitro Benzyl Chloride (3NBC). The aim of this work is to check the performance of HF and B3LYP density functional force field of 3NBC with the use of the standard 3-21+G basis set. HOMO-LUMO energies, Mulliken's analyses, APT charges and calculation of thermodynamic properties have also been performed for both the compounds.

2. EXPERIMENTAL PROCEDURES

The pure sample of 3NBC was purchased and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of the compounds were recorded in the region 4000–400 cm^{-1} at a resolution of $\pm$ 1 cm^{-1} using a BRUKER IFS – 66V FT-IR spectrometer.

The FT-Raman spectra of 3NBC were recorded on a computer interfaced BRUKER IFS model interferometer equipped with FRA-106 FT-Raman accessory in the 3500–50 cm^{-1} stokes region using the 1064 nm line of a Nd:YAG for the excitation operating at 200 mw power. The reported wave numbers were expected to be accurate within $\pm$ 1 cm^{-1} .

3. COMPUTATIONAL DETAILS

In order to provide information with regard to the structural characterics and the normal vibrational modes of 3NBC, the ab initio Hartree-Fock and DFT-B3LYP correlation functional calculations have been carried out. The entire calculations were performed using the GAUSSIAN 09W software package [15]. The ab initio HF and DFT

employing the Becke 3LYP keyword, which invokes Becke's three-parameter hybrid methods [16] have been computed using the correlation function of Lee et. al., [17], implemented with 3-21+G basis set. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wavenumber calculations. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry. Transformation of force field, the subsequent normal coordinate analysis including the least square refinement of the scale factors and calculation of the total energy distribution (TED) were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [18,19]. The symmetry of the molecules was also helpful in making vibrational assignments. By combining the results of the GAUSSVIEW program [20] with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. The systematic comparison of the results from DFT theory with results of experiments have shown that the method using B3LYP functional is the most promising in providing correct vibrational wavenumbers.

4. RESULTS AND DISCUSSION

4.1. Molecular Geometry

The optimized molecular structures of 3NBC are shown in Fig.1. Normal coordinate analysis is the mathematical procedure that gives the normal coordinates, their frequencies and the force constants. The detailed description of vibrational modes can be given by means of normal coordinate analysis. The internal coordinates describe the position of the atoms in terms of distances, angles and dihedral angles with respect to an origin atom. The symmetry coordinates are constructed using the set of internal coordinates. In the present investigation, the full set of 57 internal coordinates (each containing 12 redundancies) for 3NBC, and are defined and given in Table 1. From these, a non-redundant set of local symmetry coordinates are constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et. al., [21,22] and are summarized in Table 2 for 3NBC. The most optimized structural parameters (bond length, bond angle and diheadral angle) by HF and DFT with 3-21+G basis set are shown in Table 3.

From the experimental values of literature [23], the C–C single bond length is 1.5037Å, C–H single bond length is 1.0853Å and C–Cl bond length is 1.827Å for benzyl chloride. The C–Cl bond length (Cl atom of –CH2 Cl group) is 1.821Å in the earlier work done by Durig et. al., [24] and the bond distance is more consistent with the results from the electron diffraction study [25]. From the literature [26], the C-C bond length varies between the value 1.3752 and 1.3866Å, while the C–H bond length varies from 1.0705 to 1.0719Å. From the literature [27], C–C Single bond length is 1.4009Å, H–C Single bond length is 1.0875Å and C–Cl bond length is 1.8405Å for benzyl chloride. Taking account of the effect of conjugation, the calculated values of title molecules is in reasonable agreement with the above mentioned experimental data. The HF/3-21+G bond lengths are slightly exaggerated electron correlation effect. So, DFT/3-21+G bond lengths are quite agree with the experimental values.

4.2. Vibrational Assignment

The FT-IR and FT-Raman spectra of 3-Nitro Benzyl Chloride are shown in Figs. 2-3. The molecule 3NBC consists of 17 atoms, hence undergoes 45 normal modes of vibrations. In agreement with C1 symmetry most of the fundamental vibrations are active in both Raman scattering and IR absorption. In order to obtain a more complete description of the molecular motion involved in the fundamental modes 3NBC the normal coordinate analysis are carried out. The detailed vibrational assignment of fundamental modes of 3NBC along with the calculated IR and Raman frequencies and normal mode descriptions (characterized by TED) are reported in Table 4.

C–Cl Vibrations

The vibrations belong to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule [28]. Generally, the C–Cl absorption is obtained in the broad region between 850 and 550 cm–1 [29]. In 3NBC, the presence of C–Cl stretching is attributed at 743 cm^{-1} in FT-IR spectrum. The vibrational modes at 352 cm–1 and 61 cm–1 in FT-Raman spectrum have been assigned for the in-plane and out-of-plane vibrations, respectively. These are in good agreement with the literature data [30].

NO$_2$ Group Vibrations

The characteristic group frequencies of the 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 NO2 group at 1570–1485 cm^{-1} and 1370–1320 cm^{-1}, respectively [31]. Hence, In accordance with above conclusion, the very strong and weak bands at 1523 and 1318 cm^{-1} in FT-IR spectrum are assigned to NO$_2$ asymmetric and symmetric stretching vibrations of 3NBC, respectively. The NO$_2$ scissoring mode for 3NBC has been designated to the band at 813 cm^{-1} in FT-IR and supported by 812 cm^{-1} in FT-Raman spectra, respectively. The deformation vibrations of NO$_2$ group (rocking, wagging and twisting) contribute to several normal modes in the low frequency region [32]. These bands are also found well within the characteristic region and summarized in Table 4.

CH$_2$ Vibrations

For the assignments of CH$_2$ group frequencies, basically six fundamentals can be associated to each CH$_2$ group namely CH$_2$symmetric stretch; CH$_2$asymmetric stretch; CH$_2$ scissoring and CH$_2$ rocking which belong to in-plane vibrations and two out-of-plane vibrations, viz., CH$_2$wagging and CH$_2$twisting modes, which are expected to be depolarized [33]. The asymmetric CH$_2$stretching vibrations are generally observed above 3000 cm^{-1}, while the symmetric stretch will appear between 3000–2900 cm^{-1} [34 - 36]. In these molecules, the asymmetric and symmetric stretching vibrations were observed in 3088, 2972 cm^{-1} in FT-IR and 2971 cm^{-1} in FT-Raman for 3NBC, respectively.

For n-alkyl benzenes, the assignment of the fourth skeletal C−C stretching mode at about 1464 cm^{-1} is quite problematic, since this band is frequently masked by the more intense bands at 1446–1465 cm^{-1} arising from the CH2 scissoring vibrations [37,38]. For cyclohexane, the CH2 scissoring mode has been assigned to the medium intensity FT-IR bands at about 1450 cm^{-1} [39,40]. Thus a Similar band at 1445 cm^{-1} in FT-IR has been assigned to the CH$_2$ scissoring vibration for 3NBC. The band at 900 cm^{-1} in FT-IR spectrum has been assigned to CH$_2$ rocking in-plane bending vibration for 3NBC at 900   cm^{-1} in FT-IR and 994 cm^{-1} in FT-Raman. The CH$_2$ wagging and twisting out-of-plane bending vibrations at 1216 and 334 cm^{-1} for 3NBC are exactly coincide with the reported value of the earlier work [41].

5. MULLIKEN POPULATION ANALYSIS & CHARGE DISTRIBUTIONS

The total atomic charges of the title molecules obtained by Mulliken population analysis with HF and DFT methods with 3-21+G basis set for 3NBC have been plotted in Fig.4. From the result, it is clear that the substitution of CH$_2$Cl atoms in the aromatic ring leads to a redistribution of electron density. The -electron withdrawing character of the chlorine atom in CH$_2$–Cl is demonstrated by the decrease of electron density on C7 atom. The atomic charges in the CH$_2$ group are almost identical. The atomic charge obtained from HF/3-21+G shows that C1 atom is more basic due to more negative charges.

APT Charges at various atomic sites of the title molecule are computed at the HF and DFT methods with 3-21+G basis set have been plotted in Fig.5. The pattern of the charges is similar at both the levels.

6. HOMO & LUMO ANALYSIS

 Many organic molecules that containing conjugated   electrons are characterized hyperpolarizabilities and were analyzed by means of vibrational spectroscopy [42,43]. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. But the intra-molecular charge transfer from the donor to acceptor group through a single–double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for by ab initio calculations in conjugated system that predict exceptionally large FT-Raman and FT-IR intensities for the same normal modes. As observed in the title molecules the bands observed in FT-IR and FT-Raman Spectra show that the relative intensities in IR and Raman spectra are comparable resulting from the electron cloud movement through conjugated frame work from electron donor to electron acceptor groups. The analysis of the wave function indicates that the electron absorption corresponds to the transit from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The LUMO, of nature (ie. benzene ring) is molecular delocalized over chloro ethyl and one   of   the   two   chlorine   atoms,   consequently   the   HOMO LUMO   transition implies an electron density transfer to benzene ring of - conjugated system from chloro ethyl and one of the two chlorine atoms. Moreover, these three orbital significantly overlap in the different

positions of the benzene ring. The atomic orbital compositions of the frontier molecular orbital of   3NBC are sketched in Fig.6.

The HOMO-LUMO energy gap of 3NBC calculated at the DFT/3-21+ G level as shown below, reveals that the energy gap reflects the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron; HOMO represents the ability to donate an electron

$$HOMO \ energy = -0.30507 a.u.$$

$$LUMO \ energy = -0.15073 a.u.$$

$$HOMO\text{-}LUMO \ energy \ gap = 0.15434 \ a.u.$$

The calculated self-consistent field (SCF) energy of 3NBC is –930.9148 a.u. respectively. Moreover, the lower value in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

7. THERMODYNAMICAL PROPERTIES

Zero point vibrational energy, Rotational constants, Rotational temperatures, energy, entropy and Molar capacity at constant volume for   3NBC have been calculated and presented in Table 5. The variations in the Zero point vibrational energies are seem to be insignificant. The changes in the total entropy of 3NBC at room temperature at different methods are only marginal. The values of rotational constants and rotational temperatures have direct proportionate relationship. That is, as the rotational temperature increases, there will be an increase in rotational constant value.

8. CONCLUSION

 Attempts have been made in the present study for the proper frequency assignments for the title compound 3-Nitro Benzyl Chloride from the FT-IR and FT-Raman spectra. The equilibrium geometries, harmonic frequencies were determined and analyzed by ab initio HF and DFT/B3LYP levels of theory utilizing 3-21+G basis set. In particular, the results of B3LYP/3-21+G method indicate better fit to experimental ones than HF/3-21+G upon evaluation of vibrational frequencies. Mulliken's population analysis reveals the σ-electron withdrawing character of chlorine atom in benzyl chloride. Calculation of HOMO-LUMO gap reflects the chemical activity of the molecule. That is, it explains the eventual charge transfer taking place with in the molecule.

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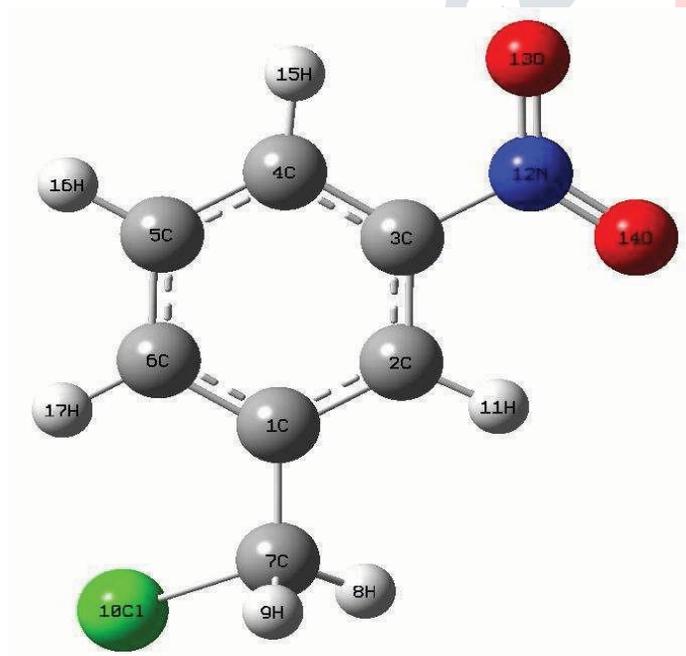
Fig.1: Molecular structure of 3-nitro benzyl chloride

Fig. 2: FT-IR Spectrum of 3-nitro benzyl chloride
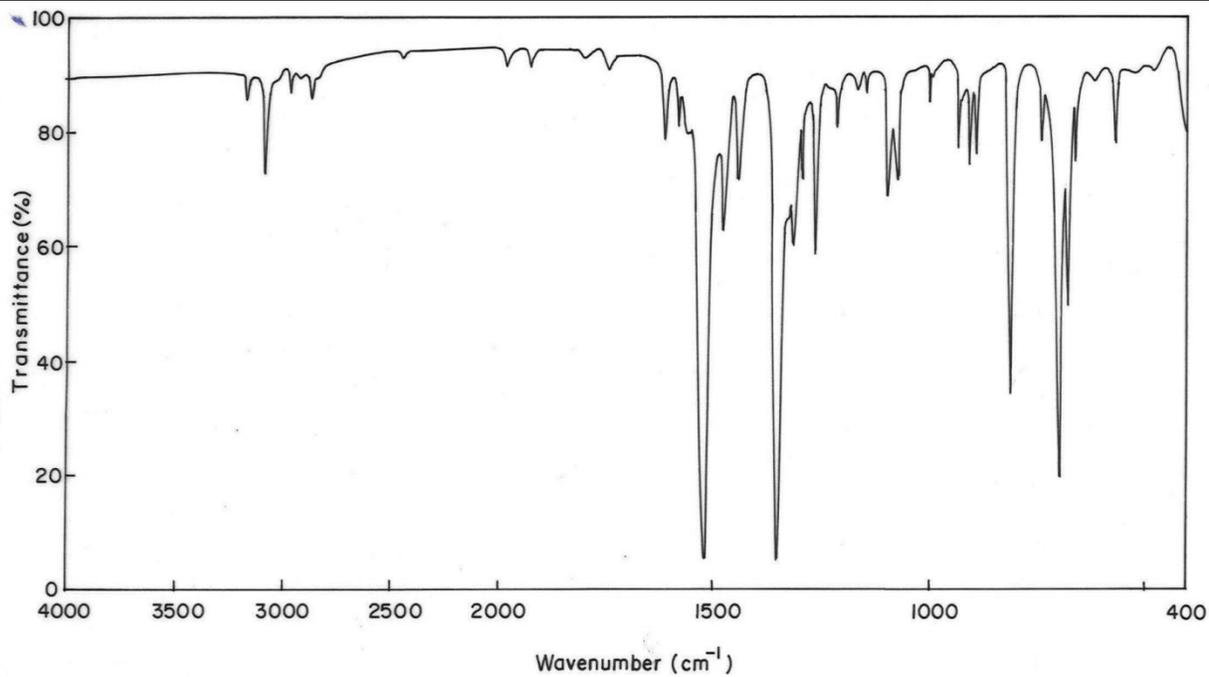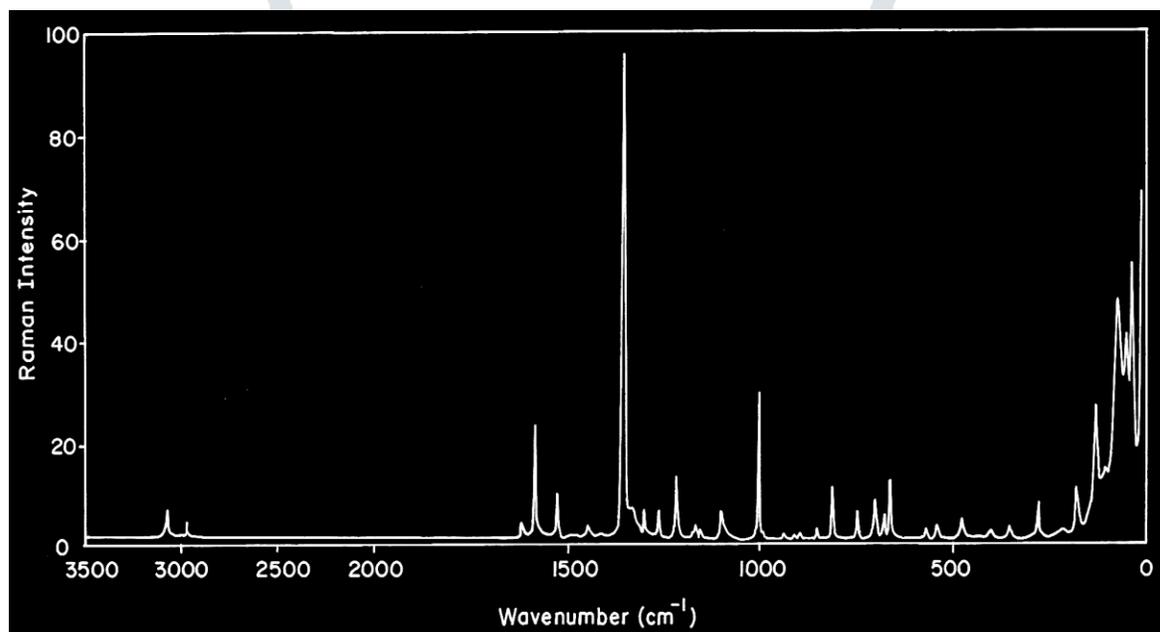

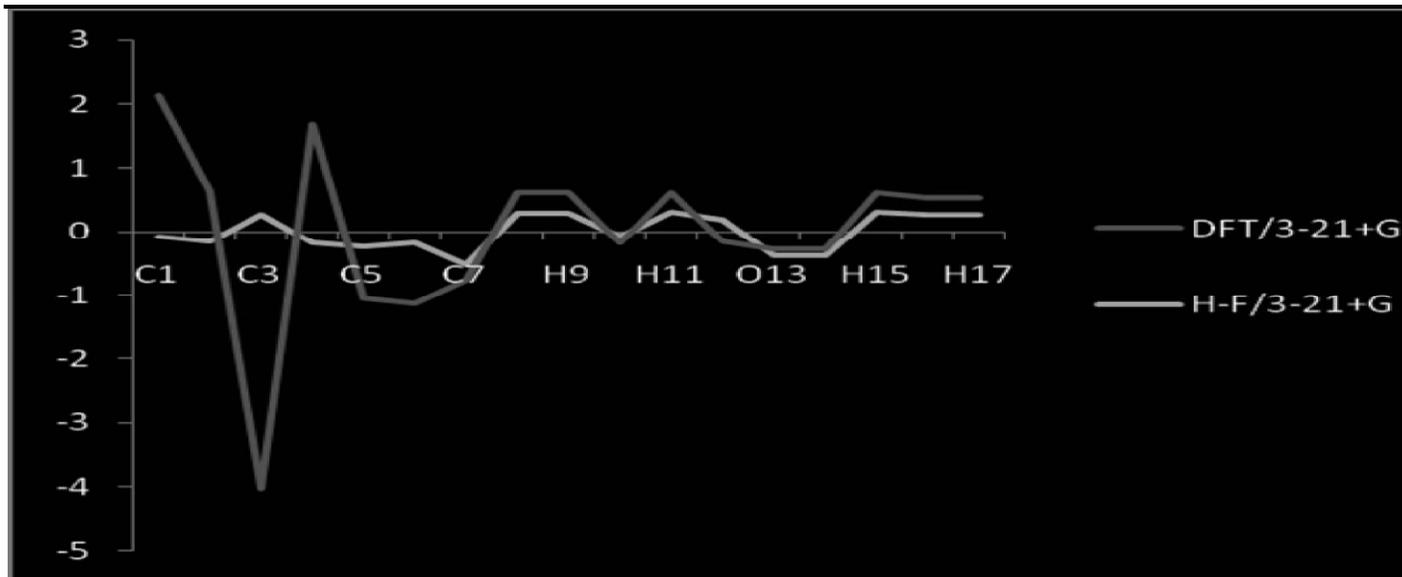Fig. 3: FT-Raman Spectrum of 3-nitro benzyl chloride

Fig. 4: Comparison of Mulliken charges at HF/ 3-21+G and DFT/3-21+G of 3-nitro benzyl chloride
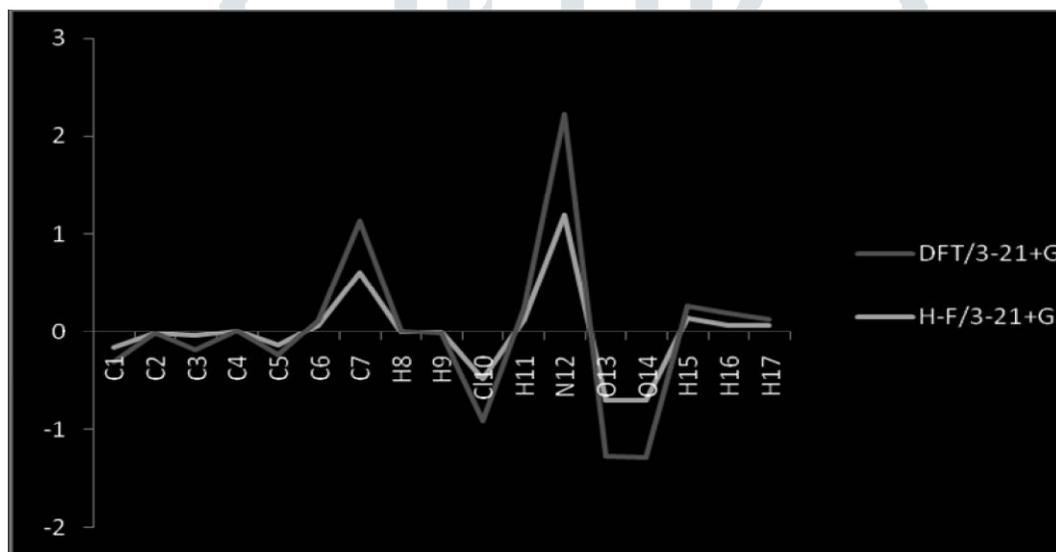

Fig. 5: Comparison of Atomic Charges at HF/ 3-21+G and DFT/3-21+G of 3-nitro benzyl chloride
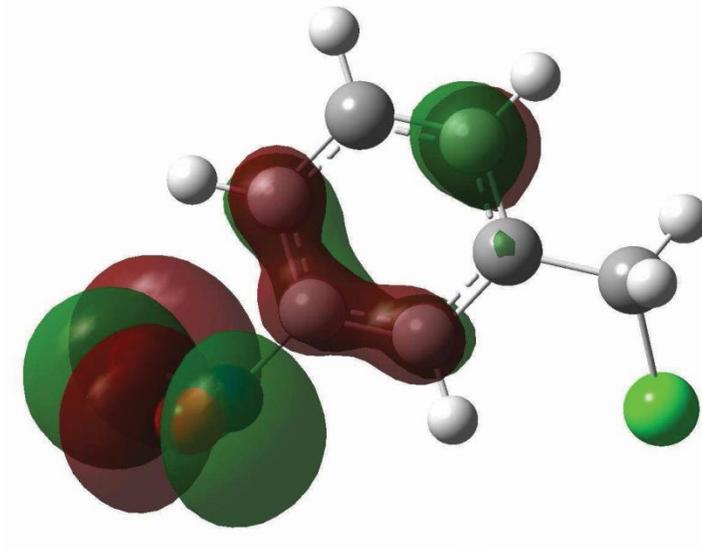
(a)   **HOMO**
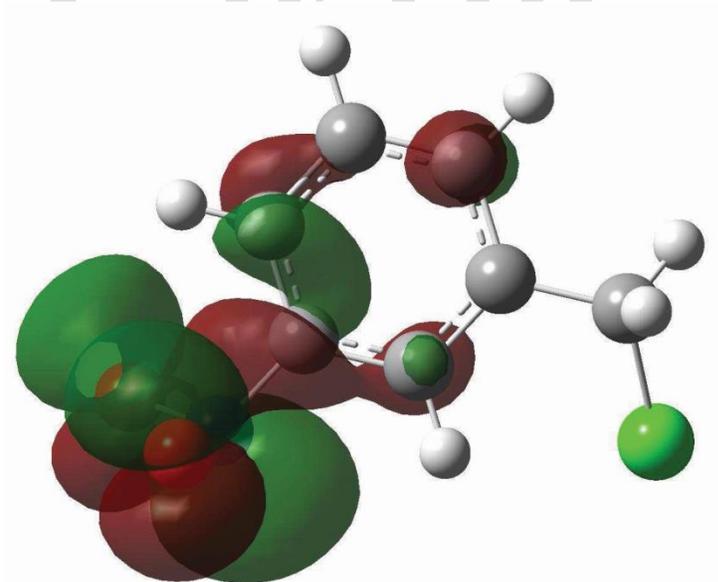
(b) **LUMO**
Fig. 6: (a) HOMO and (b) LUMO plot of 3-nitro benzyl chloride

Table 1: Definition of internal Co-ordinates of 3-nitro benzylchloride.

Number	Symbol	Type	Definition[a]
Stretching			
1-7	r_i	C-C	C_1-C_2, C_2-C_3, C_3-C_4, C_4-C_5, C_6-C_1, C_1-C_7
8-11	R_i	C-H	C_2-H_{11}, C_4-H_{15}, C_5-H_{16}, C_6-H_{17}
12	Q_i	C-Cl	C_7-Cl_{10}
13-14	R_i	C-H (ethyl)	C_7-H_8, C_7-H_9
15	P_i	C-N	C_3-N_{12}
16-17	P_i	N-O	N_{12}-O_{13}, N_{12}-O_{14}
In-plane bending			
18-23	a_i	Ring	C_1-C_2-C_3, C_2-C_3-C_4, C_3-C_4-C_5, C_4-C_5-C_6, C_5-C_6-C_1, C_6-C_1-C_2
24-25	y_i	CCC	C_7-C_1-C_2, C_7-C_1-C_6
26-33	$þ_i$	CCH	H_{11}-C_2-C_1, H_{11}-C_2-C_3, H_{15}-C_4-C_3, H_{15}-C_4-C_5, H_{16}-C_5-C_4, H_{16}-C_5-C_6, H_{17}-C_6-C_5, H_{17}-C_6-C_1
34-35	y_i	CCN	N_{12}-C_3-C_2, N_{12}-C_3-C_4
36-37	$þ_i$	CCH (ethyl)	C_1-C_7-H_8, C_1-C_7-H_9
38	6_i	HCH	H_8-C_7-H_9
39	0_i	CCCl	C_1-C_7-Cl_{10}
40-41	q_i	CNO	C_3-N_{12}-O_{13}, C_3-N_{12}-O_{14}
42	0_i	ONO	O_{13}-N_{12}-O_{14}
Out-of-plane bending			
43-46	m_i	C-H	H_{11}-C_2-C_1-C_3, H_{-12}-C_3-C_2-C_4, H_{13}-C_4-C_3-C_5, H_{14}-C_5-C_4-C_6
47	n_i	C-Cl	Cl_{10}-C_7-H_8-H_9
48	$\mathbf{;}_i$	CC	C_7-C_1-C_2-C_6
49	$\mathbf{;}_i$	CN	N_{12}-C_3-C_2-C_1
Torsion			
50-55	1_i	1 Ring	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
56	1_i	1 C-CH_2	C_1-C_7-H_8-H_9
57	1_i	1 C-NO_2	C_3-N_{12}-O_{13}-O_{14}

[a] For numbering of atoms refer Fig. 1.

Table 2:   Definition of local symmetry Co-ordinates of 3-nitro benzylchloride

No (i)	Symbol [a]	Definition [b]
1-7	C-C	$r_1, r_2, r_3, r_4, r_5, r_6, r_7$
8-11	C-H	R_8, R_9, R_{10}, R_{11}
12	C-Cl	Q_{12}
13	CH2ss	$(R_{13} + R_{14})/2$
14	CH2ass	$(R_{13} - R_{14})/2 \quad \surd$
15	CN	$P_{15} \quad \surd$
16	NO2ss	$(P_{16} + P_{17})/2$
17	NO2ass	$(P_{16} - P_{17})/2 \quad \surd$
18	Rtrigd	$(a_{18} - a_{19} + a_{20} - \surd a_{21} + a_{22} - a_{23})/6$
19	Rsymd	$(-a_{18} - a_{19} + 2a_{20} - a_{21} - a_{22} + 2a_{23})/2 \quad \surd$
20	Rasymd	$(a_{18} - a_{19} + a_{21} - a_{22})/2 \qquad \surd$
21	bCC	$(y_{24} - y_{25})/2 \qquad \surd$
22-25	bCH	$(\textrm{þ}_{26} - \textrm{þ}_{27})/2 , (\textrm{þ}_{28} - \textrm{þ}_{29})/2 ,$ $(\textrm{þ}_{30} - \textrm{þ}_{31})/2 , (\textrm{þ}_{32} - \textrm{þ}_{33})/2 \quad \surd$
26	bCN	$(y_{34} - y_{35})/2 \quad \surd \qquad \surd$
27	CH2twist	$(\textrm{þ}_{36} + \textrm{þ}_{37})/2 \quad \surd$
28	CH2rock	$(\textrm{þ}_{36} - \textrm{þ}_{37})/2 \quad \surd$
29	CH2sciss	$(2\textrm{6}_{38} - \textrm{þ}_{36} - \textrm{þ}_{37})/6 \quad \surd$
30	bCCl	θ_{39}
31	NO2twist	$(q_{40} + q_{41})/2 \quad \surd$
32	NO2rock	$(q_{40} - q_{41})/2 \quad \surd$
33	NO2sciss	$(2\textrm{0}_{42} - q_{41} - q_{42})/6 \quad \surd$
34-37	mCH	$m_{43}, m_{44}, m_{45}, m_{46}$
38	mCCl	n_{47}
39	mCC	T_{48}
40	mCN	T_{49}
41	tRtrig	$(1_{50} - 1_{51} + 1_{52} - 1_{53} + 1_{54} - 1_{55})/6 \qquad \surd$
42	tsym	$(1_{50} - 1_{52} + 1_{53} - 1_{55})/2 \quad \surd$
43	Tasym	$(-1_{50} + 2\textrm{1}_{51} - 1_{52} - 1_{53} + 2\textrm{1}_{54} - 1_{55})/12 \quad \surd$
44	CH2wag	1_{56}
45	NO2wag	1_{57}

[a] These symbols are used for description of normal modes.

[b] The internal coordinates used here are defined in Table 1.

Table 3: **Optimized geometrical parameters of 3-nitro benzylchloride by HF/3-21+G and B3LYP/3-21+G methods.**

Bond length	Value(Å)		Bond Angle	Value(°)		Dihedral Angle	Value(°)	
	HF/ 3-21+G	B3LYP/ 3-21+G		HF/ 3-21+G	B3LYP/ 3-21+G		HF/ 3-21+G	B3LYP/ 3-21+G
C1-C2	1.3813	1.3989	C2-C1-C6	119.2132	119.2752	C6-C1-C2-C3	-0.0031	-0.0587
C1-C6	1.3892	1.4058	C2-C1-C7	120.2725	120.1709	C6-C1-C2-H11	179.9354	179.9198
C1-C7	1.4932	1.4921	C6-C1-C7	120.5131	120.5538	C7-C1-C2-C3	-179.3216	179.977
C2-C3	1.3776	1.3942	C1-C2-C3	119.3005	119.0563	C7-C1-C2-H11	0.6125	-0.0446
C2-H11	1.0681	1.0831	C1-C2-H11	121.7306	121.2518	C2-C1-C6-C5	0.0089	0.0494
C3-C4	1.3765	1.396	C3-C2-H11	118.9688	119.6918	C2-C1-C6-H17	-179.9307	-179.938
C3-N12	1.4491	1.4686	C2-C3-C4	122.0147	122.2573	C7-C1-C6-C5	179.3318	-179.98
C4-C5	1.3836	1.3959	C2-C3-N12	118.8541	118.7441	C7-C1-C6-H17	-0.6078	0.0326
C4-H15	1.0672	1.0821	C4-C3-N12	119.1312	118.9982	C2-C1-C7-H8	153.6968	119.8315
C5-C6	1.3821	1.3978	C3-C4-C5	118.7031	118.4412	C2-C1-C7-H9	25.5826	-120.411
C5-H16	1.0703	1.0821	C3-C4-H15	119.309	119.8884	C2-C1-C7-Cl10	-90.3596	-0.3217
C6-H17	1.0722	1.0857	C5-C4-H15	121.9879	121.6703	C6-C1-C7-H8	-25.5858	-60.1329
C7-H8	1.0739	1.088	C4-C5-C6	119.9903	120.1786	C6-C1-C7-H9	-153.7	59.6247
C7-H9	1.0715	1.0881	C4-C5-H16	119.8253	119.7295	C6-C1-C7-Cl10	90.3577	179.7138
C7-Cl10	1.9072	1.9326	C6-C5-H16	120.1844	120.0918	C1-C2-C3-C4	-0.0234	0.0303
N12-O13	1.2441	1.2894	C1-C6-C5	120.7776	120.789	C1-C2-C3-N12	-179.9855	-179.981
N12-O14	1.2433	1.289	C1-C6-H17	119.4191	119.3707	H11-C2-C3-C4	-179.9639	-179.95

			C5-C6-H17	116.8009	119.84	H11-C2-C3-H12	0.0741	0.0386
			C1-C7-H8	113.2906	113.3695	C2-C3-C4-C5	0.1034	0.1474
			C1-C7-H9	113.3156	113.3684	C2-C3-C4-H15	-179.9108	-179.973
			C1-C7-Cl10	110.0314	109.9319	N12-C3-C4-C5	-179.8377	-179.649
			C8-C7-H9	111.2818	111.3078	N12-C3-C4-H15	0.1481	0.2307
			C8-C7-Cl10	104.2224	104.7972	C2-C3-N12-O13	-0.7396	-0.8523
			C9-C7-Cl10	103.8657	103.9082	C2-C3-N12-O14	179.4244	179.2851
			C3-N12-O13	117.4208	118.1248	C4-C3-N12-O13	179.2034	178.9513
			C3-N12-O14	117.4294	118.2048	C4-C3-N12-O14	-0.6326	-0.9113
			O13-N12-O14	125.1495	123.6703	C3-C4-C5-C6	0.06451	-0.0929
						C3-C4-C5-H16	-179.9068	-179.971
						H15-C4-C5-C6	-179.9209	-179.97
						H15-C4-C5-H16	0.1077	0.1511
						C4-C5-C6-C1	-0.0608	0.2718
						C4-C5-C6-H17	-179.4929	-179.528
						H16-C5-C6-C1	179.9104	-179.85
						H16-C5-C6-H17	0.4784	0.3501

For numbering of atoms refer Fig.1.

Table 4: Vibrational assignments of fundamental modes of 3-nitro benzylchloride along with calculated frequencies and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using HF and B3LYP methods

Modes	Symmetry Species	Observed fundamentals (cm⁻¹)		Calculated fundamentals (cm⁻¹)				Assignments with TED %
				HF/3-21+G		B3LYP/3-21+G		
		FT-IR	FT-Raman	Unscaled	Scaled	Unscaled	Scaled	
1	A	3088	-	3437	3098	3246	3101	ν_{ass} CH_2(92)
2	A	-	3079	3424	3088	3233	3088	νCH(93)
3	A	3067	-	3392	3079	3214	3079	νCH(94)
4	A	-	3059	3391	3072	3210	3071	νCH(97)
5	A	2972	2971	3367	2979	3193	2982	ν_{ss} CH_2(91)
6	A	2870	-	3316	2881	3137	2879	νCH(95)
7	A	-	1686	1786	1693	1629	1679	νCC(84)
8	A	1617	-	1761	1625	1604	1609	νCC(81)
9	A	1584	-	1661	1592	1529	1576	νCC(86)
10	A	1523	-	1648	1531	1521	1523	ν_{ass} NO_2 (82)
11	A	1480	-	1612	1489	1484	1482	νCN(82)
12	A	1445	-	1477	1453	1369	1435	νCH_2sciss(77)

13	A	-	1366	1416	1373	1351	1359	νCC(72)
14	A	1355	-	1397	1364	1310	1346	νCC(73)
15	A	1318	1305	1372	1327	1285	1306	vss NO_2 (71)
16	A	1297	1294	1357	1309	1252	1283	νCC(68)
17	A	1216	1216	1322	1227	1232	1225	CH_2wag(72)
18	A	1209	-	1304	1218	1183	1201	bCH(87)
19	A	1166	-	1243	1179	1173	1170	νC-CH_2(69)
20	A	1099	-	1202	1110	1107	1101	bCH(81)
21	A	1093	-	1198	1101	1058	1082	bCH(78)
22	A	1077	-	1160	1089	1033	1065	bCH (76)
23	A	994	-	1133	1003	1006	999	CH_2rock(73)
24	A	934	-	1111	948	985	942	bCN(73)
25	A	908	-	993	918	929	916	mCH(74)
26	A	892	-	962	905	892	892	mCH(72)
27	A	872	-	953	887	854	863	Rtrigd(62)
28	A	-	840	838	839	764	851	Rasymd(64)
29	A	820	-	804	814	747	809	Rsymd(67)
30	A	813	812	793	801	719	801	NO_2sciss(61)

31	A	743	-	743	743	678	732	$\tau CH_2\text{-}Cl(74)$
32	A	693	-	699	696	641	681	mCH(53)
33	A	686	-	630	679	580	675	mCH(55)
34	A	680	-	565	669	522	669	NO_2rock(69)
35	A	663	-	535	658	494	652	$bC\text{-}CH_2(73)$
36	A	616	-	498	605	450	601	mCN(65)
37	A	568	-	441	559	398	559	NO_2wag(62)
38	A	540	-	381	529	349	531	mC-CH2(58)
39	A	-	352	296	341	273	343	bC-Cl(63)
40	A	-	334	273	329	285	336	CH_2 twist
41	A	-	211	226	219	205	208	tRtrig(64)
42	A	-	180	205	189	188	184	tRsym(62)
43	A	-	131	120	125	110	124	tRasym(58)
44	A	-	77	64	69	63	71	NO2twist(61)
45	A	-	61	29	48	37	49	mCH2-Cl(62)

Abbreviations: ν - stretching; ss - symmetric stretching; ass - antisymmetric stretching; b - in-plane-bending; m - out-of-plane bending; t - torsion; R - Ring; 6 - scissoring; q - rocking; þ - wagging; ı - twisting.

Table 5 : Theoretically Computed Zero point vibrational energy (Kcalmol^{-1}), rotational constants (GHZ) rotational temperature (Kelvin) thermal energy (Kcalmol^{-1}) molar capacity at constant volume (calmol^{-1} k^{-1}) and entropy (calmol k^{-1}) of 3-nitro benzyl chloride.

Parameter	HF/3-21 + G	B3LYP/3-21 + G
Zero point vibrational energy	68.9953	76.27221
Rotational constants		
	0.9548	1.7760
	0.7591	0.5150
	0.4585	0.4267
Rotational temperatures		
	0.4558	0.08522
	0.0364	0.02474
	0.0220	0.02048
Energy		
Total	87.699	82.160
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	85.922	80.383
Entropy		
Total	31.820	98.827
Translational	2.981	41.317
Rotational	2.981	31.087
Vibrational	25.858	26.422
Molar capacity at constant volume		
Total	97.092	34.446
Translational	41.317	2.981
Rotational	31.005	2.981
Vibrational	24.770	28.484