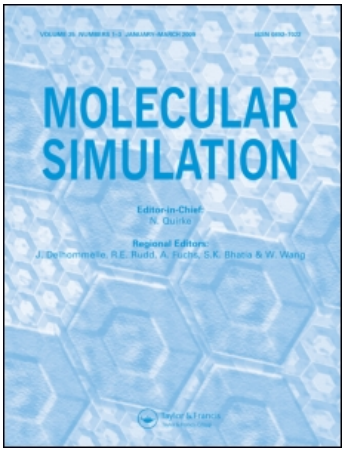

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Molecular structure and vibrational spectra of 4-nitrobenzylchloride by *ab initio* Hartree-Fock and density functional methods

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Molecular structure and vibrational spectra of 4-nitrobenzylchloride by *ab initio* Hartree–Fock and density functional methods

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The Fourier transform Raman and Fourier transform infrared spectra 4-nitrobenzylchloride of (NBC) were recorded in the solid phase. The Fourier transform gas phase infrared spectrum of NBC was also recorded. The equilibrium geometry, harmonic vibrational frequencies, infrared intensities and Raman scattering activities were calculated by HF/DFT (B3LYP and BLYP) and SVWN methods with the 6-31G(d,p) basis set. The scaled theoretical wave numbers by B3LYP showed very good agreement with the experimental ones. A detailed interpretation of the infrared and Raman spectra of NBC is reported on the basis of the calculated potential energy distribution. The theoretical spectrograms for the IR spectrum of the title molecule have been constructed.

Keywords: Hartree–Fock; density functional theories; 4-nitrobenzylchloride; vibrational spectra

1. Introduction

4-nitrobenzylchloride ($O_2NC_6H_4CH_2Cl$) is a well known organic compound. The synthesis of this crystal was performed recently [1–3]. The title compound is highly toxic and corrosive and causes burns very destructive to mucous membranes. It has been reported in the literature [4] that the reaction of *p*-nitrobenzylchloride with thiophenoxideion did indeed use a single electron transfer (SET) mechanism. The vibrational spectrum of liquid benzyl alcohols has been assigned by Bellanato and Schmid [5]. The internal hydrogen in the *o*-substituted benzyl alcohols and in *o*-and *p*-substituted 1,2-diarylethanols (1-*x*-phenyl-2-*y*-pheylehthol) has been studied by IR spectroscopy and with chloro, methoxy and nitro groups as substituents [6]. The observation of two OH stretching bands in the IR spectrum of aryl alcohols ($C_6H_5(CH_2)n$OH) in dilute solutions has been generally interpreted as evidence for intramolecular OH$\cdots\cdots\pi$ bonding [7–9]. Abraham and Bakke [10] studied the confirmations of benzyl alcohol and the *o*- and *p*-nitro and methoxy derivatives and benzyl methyl ester have been investigated by NMR in CCl_4 and DMSO solutions.

During the past decade, the density functional theory (DFT) has emerged as a powerful tool for studying vibrational spectra of fairly large molecules. In our earlier works, we have shown that the DFT methods reproduce vibrational frequencies and infrared intensities well, even for these aromatic molecules, where MP2 method fails [11,12].

The literature search has revealed that *ab initio* Hartree–Fock (HF) and density functional theory calculations and vibrational analysis have not been reported so far on NBC. Therefore, the present investigation was undertaken to study the vibrational spectrum of this molecule completely and to identify the various normal modes with greater wave number accuracy. The *ab initio* HF and DFT calculations have been performed to support our wave number assignments.

2. Experimental

The compound NBC in the light yellow powder form was obtained from Department of Chemistry, Annamalai University, with a stated purity of greater than 99% and it was used as such without further purification. The FT-Raman spectrum of NBC has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 50–3500 cm^{-1} on a Brucker model IFS 66 V spectrophotometer. The FT-IR spectrum of this compound was recoded in the region 400–4000 cm^{-1} on IFS 66 V spectrophotometer using KBr pellet technique. The FT-IR gas phase spectrum was also recorded in the region 400–4000 cm^{-1}. The spectrum was recorded at

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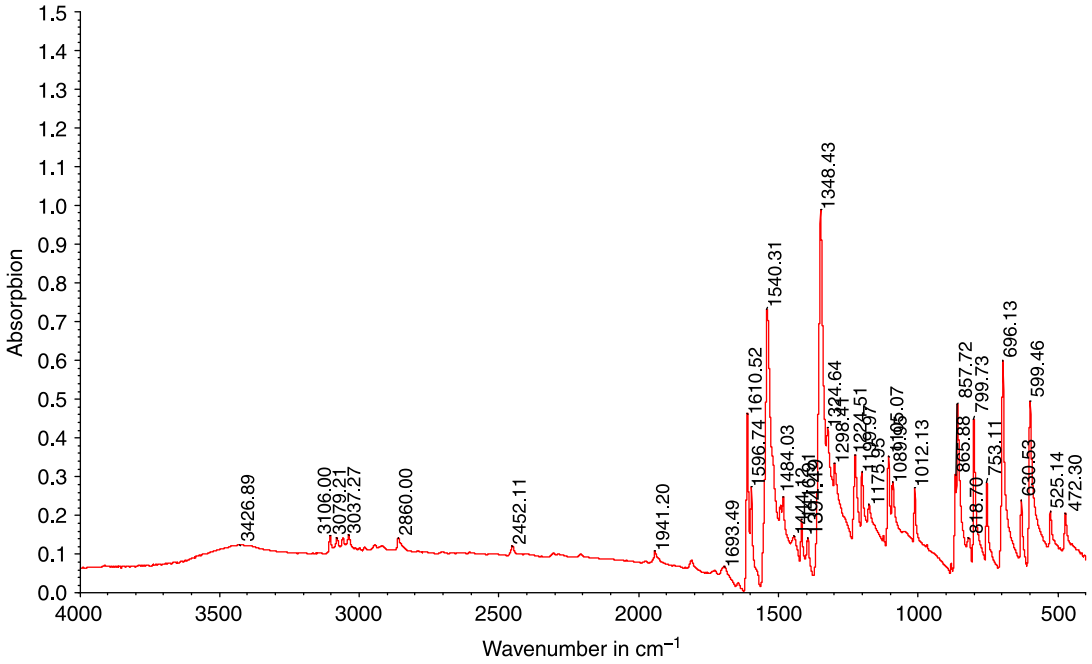

Figure 1. FT-IR solid phase spectrum of 4- nitrobenzylchloride.

room temperature, with scanning speed of 30 cm^{-1}min^{-1} and the spectral resolution of 2.0 cm^{-1}. The observed experimental solid and gas phase FT-IR and FT-Raman spectra of the title compound are shown in Figures 1–3 and scaled FT-IR spectra of all the methods are shown in Figure 4. The spectral measurements were carried out at Central Electrochemical Research Institute (CECRI), Karaikudi, Tamil Nadu.

3. Method of calculations

Calculations were carried out at the Hartree–Fock [13,14] and density functional theory levels (DFT) using the SVWN [15,16] and B3LYP, BLYP [17,18] exchange correlation functional implemented in Gaussian 03 program [19]. Functional SVWN consists of local electron spin density exchange proposed by Slater [15] in conjunction with the correlation function of

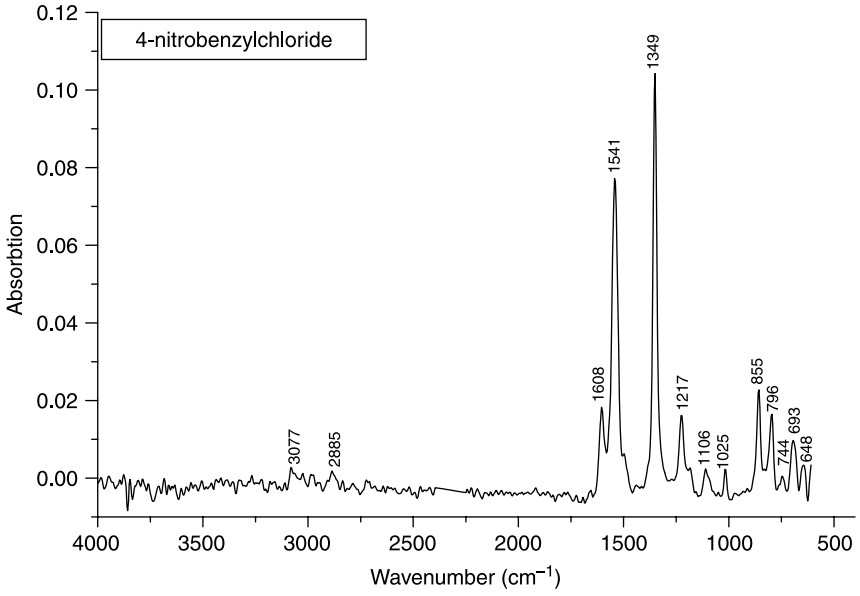

Figure 2. FT-IR gas phase spectrum of 4-nitrobenzylchloride.

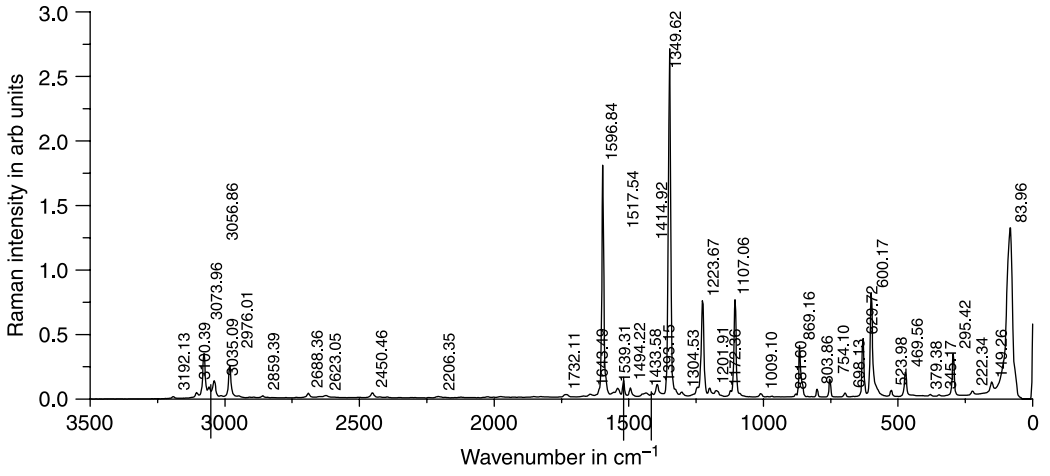

Figure 3. FT-Raman spectrum of 4-nitrobenzylchloride.

Vosko et al. [16] LDA approximation. The latter two functionals, B3LYP and BLYP are hybrid methods consisting of Becke's [18] three parameter function as a linear combination of (1) local density approximation, (2) Becke's gradient correlation [20], and (3) Hartree–Fock exchange energy based on Kohn–Sham orbitals [21]. Additionally, the Lee–Yang–Parr [17] and Perdew–Wang 91 [22] gradient-corrected correlation functionals are used in B3LYP and B3PW91 methods, respectively. These two functionals, called also non-local, involve both the values of electron spin densities and their gradient [23]. All calculations were performed with the 6-31G(d,p) basis set. Polarisation functions were added for better description of polar bonds of NO_2 and Cl groups in molecules.

All calculations were performed assuming C_s group symmetry for 4-NBC molecules. Thus, obtained frequencies were multiplied by empirical factors of 0.8929, 0.9833, 0.9613 and 0.994 for HF, SVWN, B3LYP [23] and BLYP [24] methods, respectively. This procedure is necessary for the HF method to correct for overestimation of vibrational frequencies due to vibrational anharmonicity and neglecting electron correlation [25,26]. In the case of DFT methods, scaling factors are used to compensate for incomplete incorporation of electron correlation, as well as to account for vibrational anharmonicity. It would thus be a difficult problem to make assignments on the basis of 'group frequencies concept' and *ab initio* spectra alone. Therefore, to aid the assignments normal coordinate calculations were performed using MOLVIB program [27]. By taking B3LYP/6-31G(d,p) results as input, we computed general valance force-fields, normal modes and potential energy distributions (PEDs); the frequencies were reported to within $1-2\,cm^{-1}$.

4. Results and discussion

4.1 Molecular geometry

The optimised structure parameters of NBC calculated by *ab initio* HF, B3LYP, BLYP and SVWN levels with the 6-31G(d,p) basis set are listed in Table 1 in accordance with the atom numbering scheme given in Figure 5. Since the crystal structure of the title compound was not available till now, the optimised structure can only be compared with other similar systems for which crystal structures have been solved. Therefore optimised geometrical parameters of NBC are compared to those of 4-chlorobenzyl alcohol [28]. As discussed in the literature [29], it is well known that HF and SVWN methods underestimate bond lengths and BLYP methods predict bond lengths which are systematically too long, particularly C—H bond lengths. Since large deviation from experimental C—H bond lengths may arise from the low scattering factors of hydrogen atoms in the X-ray diffraction experiment we did not discuss C—H bond lengths. In our case, B3LYP method leads to geometric parameters, which are much closer to experimental data. Because of these reasons we take into account B3LYP/6-31G(d,p) level for geometric parameters of NBC in present discussion.

As expected, the geometrical parameters of NBC presented in Table 1 vary with the method used in calculations. It is generally accepted that bond lengths and angles depend also upon the basis set used in calculations. To avoid this problem we present data obtained with the 6-31G(d,p) basis set only. As is evident from Table 1, the C—C bond lengths of NBC have approximately identical length of 1.390 Å, while introduction of the substituent group causes slight difference between them. The breakdown of hexagonal

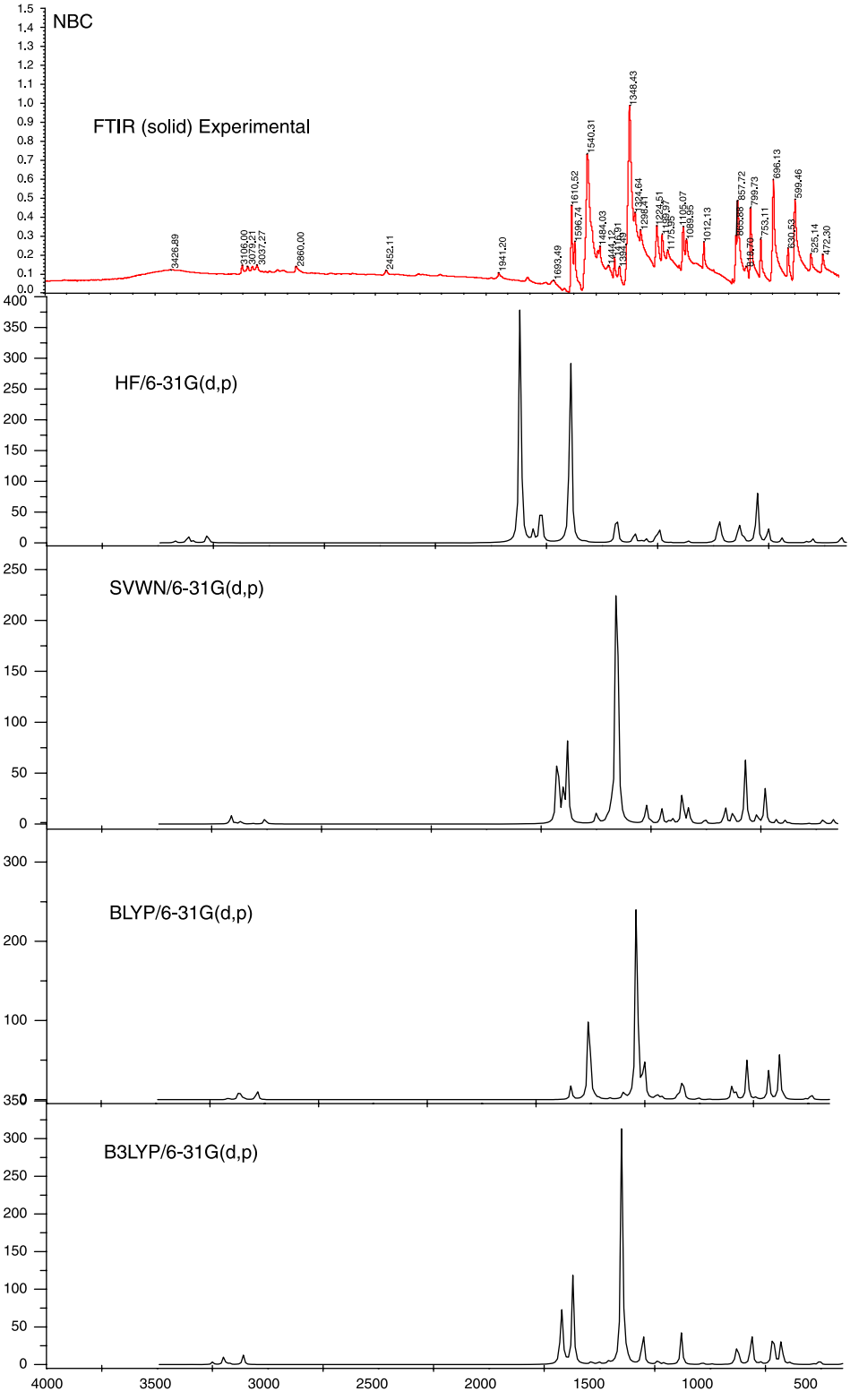

Figure 4. Comparison of observed and calculated infrared spectra of 4-nitrobenzylchloride.

Table 1. Geometrical parameters optimised in 4-nitrobenzylchloride, bond length (Å), bond angle (°) and dihedral angle (°).

Parameters	HF/6-31G(d,p)	SVWN/6-31G(d,p)	BLYP/6-31G(d,p)	B3LYP/6-31G(d,p)	Experimental[a] (4-chlorobenzyl alcohol)
Bond length (Å)					
C1—C2	1.389	1.398	1.413	1.402	1.387
C1—C6	1.389	1.393	1.413	1.402	1.378
C1—C11	1.505	1.492	1.507	1.501	1.509
C2—C3	1.382	1.383	1.401	1.391	1.379
C2—H7	1.075	1.097	1.093	1.086	
C3—C4	1.382	1.387	1.404	1.393	1.377
C3—H8	1.071	1.094	1.089	1.083	
C4—C5	1.382	1.385	1.404	1.393	1.383
C4—N15	1.459	1.452	1.490	1.473	
C5—C6	1.382	1.386	1.401	1.391	1.373
C5—H9	1.071	1.094	1.089	1.083	1.010
C6—H10	1.075	1.095	1.093	1.086	1.010
C11—H12	1.078	1.103	1.097	1.090	
C11—H13	1.078	1.104	1.097	1.090	
C11—Cl14	1.800	1.778	1.863	1.831	
N15—O16	1.194	1.228	1.250	1.230	
N15—O17	1.194	1.228	1.250	1.230	
Bond angle (°)					
C2—C1—C6	119.48	119.60	119.13	119.25	118.5
C2—C1—C11	120.26	117.71	120.44	120.37	
C6—C1—C11	120.26	122.66	120.43	120.37	121.6
C1—C2—C3	120.65	120.64	120.83	120.77	120.9
C1—C2—H7	119.95	119.61	119.64	119.69	119.9
C3—C2—H7	119.40	119.75	119.53	119.54	119.2
C2—C3—C4	118.55	118.33	118.56	118.53	
C2—C3—H8	121.39	123.12	122.02	121.95	121.1
C4—C3—H8	120.06	118.55	119.42	119.52	
C3—C4—C5	122.12	122.41	122.10	122.15	
C3—C4—N15	118.94	118.71	118.95	118.93	118.6
C5—C4—N15	118.94	118.88	118.95	118.93	
C4—C5—C6	118.55	118.59	118.56	118.53	
C4—C5—H9	120.06	118.52	119.42	119.52	
C6—C5—H9	121.39	122.89	122.02	121.95	121.8
C1—C6—C5	120.65	120.43	120.83	120.77	
C1—C6—H10	119.95	118.91	119.64	119.69	
C1—C6—C11	119.40	120.66	119.53	119.54	
C1—C11—H12	111.51	110.44	112.24	111.90	
C1—C11—H13	111.51	110.29	112.23	111.89	111.3
C1—C11—Cl14	111.88	114.61	111.82	111.84	
H12—C11—H13	109.17	107.43	109.73	109.40	
H12—C11—Cl14	106.25	107.27	105.18	105.73	
H13—C11—Cl14	106.25	106.49	105.18	105.73	
C4—N15—O16	117.63	117.42	117.59	117.61	
C4—N15—O17	117.63	117.38	117.59	117.61	
O16—N15—O17	124.74	125.20	124.83	124.78	

[a] The X-ray data from [28].

symmetry of the benzene ring is obvious from the elongation of C1—C2 (~1.40 Å) and C1—C6 (~1.40 Å) from the remaining C—C bond lengths (~1.39 Å). The asymmetry of the benzene ring is also evident from the negative deviation of C2—C1—C6 and the positive deviation of C3—C4—C5 from the normal value of 120°. The C—Cl bond length is found 1.831 Å (B3LYP), 1.800 Å (HF) and 1.863 Å (BLYP). The correlation between the experimental and calculated geometric parameters obtained by the HF, SVWN, and DFT (B3LYP and BLYP) methods is given in Table 4. Based on our calculations, DFT/B3LYP method correlates ($r = 0.9996$) well for the bond length compared with other three methods. The bond angles provided by SVWN method are much closer to the experimental values ($r = 0.9833$). As a result, the optimised bond lengths obtained by the DFT-B3LYP/631-G(d,p) method and bond angles by *ab initio* SVWN/6-31G(d,p) method

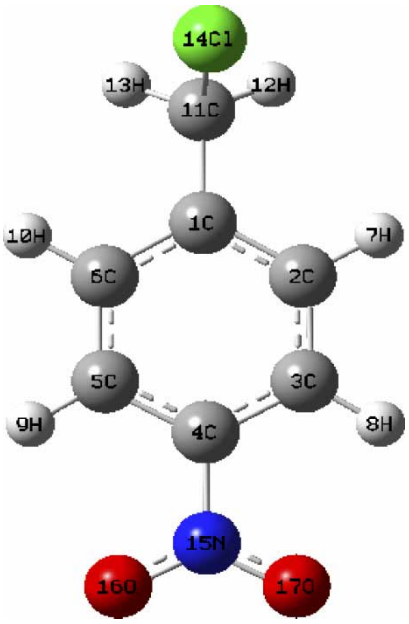

Figure 5. Numbering system adopted in the study (4-nitrobenzylchloride).

show the best agreement with the experimental values. The difference between experimental and calculated geometric parameters comes from the environment of the compound. It is clear that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

4.2 Vibrational assignments

With this assumed structural model, the molecule NBC may be assumed to possess C_s point group symmetry, because two of the H atoms and the Cl atom of the methylene group are slightly out of the molecular plane. The title molecule NBC has 17 atoms and it has 45 normal vibrational modes. 31 of these modes should be symmetric, A′, and 14 antisymmetric, A″, in respect to reflection on the symmetry plane. For the atoms located in the plane of the molecule, the A′ vibrational displacements take place in the plane of the molecule and the A″ modes correspond to displacement out of the plane of the molecule. All of the calculated normal modes are numbered from the smallest to the largest frequency within each fundamental wave number. All the 45 fundamental vibrations are active in both IR and Raman.

The assignments shown in Table 2 for several of benzene ring modes along with substituents are briefly given in the present work. The harmonic vibrational frequencies calculated for NBC at HF, DFT (B3LYP and BLYP) and SVWN levels using 6-31G(d,p) basis set have been collected in Table 2. In the last column is given a detailed description of the normal modes based on the potential energy distribution (PED). The observed FT-IR and FT-Raman frequencies for various modes of vibrations are also presented in Table 2. On the basis of our calculations, and experimental infrared (solid and gas phase) and Raman spectra, we made a reliable one-to-one correspondence between our fundamentals and any of our frequencies calculated by the HF, DFT (B3LYP and BLYP) and SVWN methods. The assignments are based on the PED and the vibrational animations of the fundamentals using the Gauss-View package program [30] in the HF/B3LYP/BLYP/SVWN/6-31G(d,p) calculations.

Comparison of the frequencies calculated at HF, B3LYP, BLYP and SVWN levels with experimental values (Table 2) reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with the HF frequency data. In the NBC, the B3LYP method leads to vibrational frequencies which are much closer to experimental data.

In order to investigate the performance and vibrational frequencies for the title molecule, mean absolute deviation, standard deviation (SD), root mean square value (RMS) and correlation coefficient (r) between the calculated harmonic and observed fundamental vibrational frequencies for each method and basis set were also calculated and given in Table 3. The root mean square (RMS) values were obtained in the study using the following expression [31] (Table 4).

$$\mathrm{RMS} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(\upsilon_i^{\mathrm{cal}} - \upsilon_i^{\mathrm{exp}})^2}.$$

The results indicate that the fundamental frequencies calculated (DFT-both BLYP and B3LYP) for the title molecule show quite good agreement with experimental values. Furthermore, the B3LYP method calculations approximate the observed fundamental frequencies much better than the BLYP method. A small difference between experimental and calculated vibrational modes is observed. This discrepancy can come from the formation of intermolecular hydrogen bonding. The nitro group in the molecule will have a residual negative charge localised on the two oxygen and will certainly have intermolecular H bonded interaction with the hydrogens of the near by molecules. Similarly, the chloride on the $-CH_2Cl$ group will also be able to show inter molecular H-bonding interaction. However, X-ray structure of the compound will be able to quantify such interactions completely. Also, we note that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

Table 2. Fundamental vibrations of 4-nitrobenzylchloride (in cm^{-1}): Comparison between the experimental data, HF, SVWN, BLYP and B3LYP results.

Assignment	Experimental in this work			HF/6-31G(d,p) (scaled)	SVWN/6-31G(d,p) (scaled)	BLYP/6-31G(d,p) (scaled)	B3LYP/6-31G(d,p) (scaled)	Force constant	PED (%) (>5% taken)
	IR	IR(GAS)	Raman						
υ_1 τCH_2				25	16	30	30	0.01	D11(18), D14(18), D9(16), D13(15), D12(15), D10(15)
υ_2 τNO_2				51	76	62	62	0.04	D30(22), D27(22), D29(22), D28(22)
υ_3 $\gamma C{-}Cl$				66	94	64	64	0.13	A21(18), D7(11), D3(11), D8(6), D4(6), D20(5)
υ_4 $\gamma C{-}Cl + \gamma C{-}NO_2$			149w	165	141	160	160	0.08	A21(36), D20(6), D25(6)
υ_5 $\beta C{-}Cl$			222vw	215	232	212	212	0.07	A11(21), A12(21), A3(9), A2(9)
υ_6 $\gamma C{-}NO_2$			295m	300	267	297	297	0.14	R15(13), R9(8), D27(8), D30(8), A21(5)
υ_7 CH_2 deform			345vw	336	313	334	334	0.23	A2(26), A3(26)
υ_8 βNH_2			379vw	378	404	373	373	0.11	R9(30), A10(10), A21(9)
υ_9 γCCC				409	412	405	405	0.56	D31(14), D15(14), D16(5), D33(5), D17(5), D32(5)
υ_{10} γCCC	472w		469w	493	459	485	485	0.35	R15(23), D27(7), (D30(7)
υ_{11} ρNO_2	525m		524w	516	522	513	513	0.59	A25(31), A26(31), A11(9), A12(9)
υ_{12} βCCC	599ms		600ms	616	609	613	613	1.21	R9(19), A1(13), R3(11), A21(7), A27(7)
υ_{13} βCCC				619	628	621	621	0.34	A16(16), A4(16), A7(16), A13(16)
υ_{14} $\nu C{-}Cl$	631m	644m	630m	672	668	651	651	0.69	R15(69)
υ_{15} t NO_2	696ms	694m	698 vw	716	718	688	688	0.87	R15(26), A21(9), D29(7), D28(7), D27(6), D30(6)
υ_{16} ωNO_2	753m	745w	754w	772	754	743	743	1.47	D29(16), D28(16), R15(15)A21(7)
υ_{17} βCCC	800m	798m	804w	789	806	781	781	1.58	R3(26), A27(15), A10(10), R2(7), R1(7)
υ_{18} γCH	819ms			848	809	820	820	0.52	D32(9), D17(9), D33(9), D16(9), D8(8), D4(8)
υ_{19} ringbreathing	858ms	858ms		864	815	841	841	0.67	A27(21), R9(15), R3(6), R8(5), R6(5)
υ_{20} γCH	866ms		869m	875	861	849	849	0.65	D4(7), D8(7), D17(5), D32(5)
υ_{21} ρCH_2			882w	893	898	889	889	1.28	A19(19), A20(19), A24(11), A23(11), D13(6), D9(6)
υ_{22} γCH				992	932	949	949	1.10	D34(23), D18(23), D26(5), D22(5)
υ_{23} γCH				994	949	954	954	0.97	D18(22), D34(22), D22(7), D26(7)
υ_{24} trigonal bending	1012m	1018m	1009w	999	987	994	994	1.03	A13(9), A7(9), A16(9), A4(9), R2(7), R1(7)
υ_{25} βCH				1065	1060	1086	1086	1.29	A15(13), A7(9), A16(9), A4(9), R2(7), R1(7)
υ_{26} βCH	1090m			1108	1088	1086	1086	1.14	R9(34), R8(12), R6(11), A8(8), A15(6), A10(5)
υ_{27} tCH_2	1105m		1107m	1120	1133	1129	1129	1.65	A19(18), A20(18), A23(15), A24(15), R1(5), R2(5)
υ_{28} βCH				1162	1148	1161	1161	1.96	A6(12), A18(12), A5(10), A17(10), R4(9), R10(9)
υ_{29} βCCC	1176m	1186w	1172w	1182	1182	1187	1188	1.68	A6(12), R3(50), R2(5), R1(5), R4(5), R10(5)
υ_{30} ωCH_2	1225m	1226m	1224ms	1209	1234	1246	1253	4.27	A23(18), A24(18), A20(17), A19(17), R3(12)
υ_{31} βCH				1281	1251	1280	1282	3.75	A9(12), A14(12), A8(11), A15(11), A18(10), A6(10)
υ_{32} νCC	1298w			1297	1376	1288	1323	1.52	R2(16), R1(16), R8(14), R6(14), R10(13), R4(13)
υ_{33} ν_s NO_2	1348vs	1348vs	1350vs	1406	1383	1339	1345	2.77	R16(34), R17(34), R9(19), A27(8)
υ_{34} νCC	1394w		1393w	1454	1404	1400	1401	1.37	R10(16), R4(16), A5(7)A17(7)
υ_{35} δ CH_2	1444w	1445vw	1435w	1466	1421	1454	1445	1.82	A22(58), A20(12), A19(12), R3(6)
υ_{36} νCC	1484w		1494w	1496	1472	1474	1477	4.34	R8(9), R6(9), A8(8), A15(8), A9(7), A14(7)
υ_{37} ν_{as} $NO_2 + \nu CC$	1540s	1544s	1539 w	1585	1603	1497	1557	9.32	R17(30), R16(30), R6(8), R8(8), R2(7), R1(7)
υ_{38} νCC	1597m		1597 s	1616	1622	1579	1593	2.08	R4(21), R10(21), R1(7), R2(7)
υ_{39} νCC	1611ms	1606m		1668	1648	1580	1608	7.15	R17(24), R16(24), R8(11), R6(10)
υ_{40} ν_s C11—H			2976m	2925	2957	3015	2990	5.63	R13(50), R14(50)
υ_{41} ν_{as} C11—H	3037w	3025w	3035w	2983	3012	3077	3051	6.19	R14(50), R13(50)
υ_{42} ν_{as} CH	3060w		3057w	3003	3065	3096	3074	6.33	R5(54), R12(44)

Table 2 – *continued*

Assignment	Experimental in this work			HF/6-31G(d,p) (scaled)	SVWN/6-31G(d,p) (scaled)	BLYP/6-31G(d,p) (scaled)	B3LYP/6-31G(d,p) (scaled)	Force constant	PED (%) (>5% taken)
	IR	IR(GAS)	Raman						
υ_{43} ν_s CH	3079w	3085w	3074w	3004	3085	3097	3075	6.37	R12(54), R5(44)
υ_{44} ν_{as} CH				3055	3109	3146	3123	6.43	R7(68), R11(31)
υ_{45} ν_s CH	3106w	3110w	3100w	3055	3110	3147	3123		R11(67), R7(30)

[a] vs, very strong; s, strong; ms, medium strong; w, weak and vw, very weak. [b] υ, stretching; υ_s, sym.stretching; υ_{as}, asym.stretching; β, in-plan-bending; γ, out-of-plane; ω, wagging; ρ, rocking; t, twisting; τ, torsion; δ, scissoring and PED, potential energy distribution.

R1:C1−C2, R2:C1−C6, R3:C1−C11, R4:C2−C3, R5:C2−H7, R6:C3−C4, R7:C3−H8, R8:C4−H5, R9:C4−N15, R10:C5−C6, R11:C5−H9, R12:C6−H10, R13:C11−H12, R14:C11−H13, R15:C11−Cl14, R16:N15−O16, R17:N15−O17, A1:C2−C1−C6, A2:C2−C1−C11, A3:C6−C1−C11, A4:C1−C2−C2, A5:C1−C2−H7, A6:C3−C2−H7, A7:C2−C3−C4, A8:C2−C3−H8, A9:C4−C3−H8, A10:C3−C4−C5, A11:C3−C4−N15, A12:C5−C4−N15, A13:C4−C5−C6, A14:C4−C5−H9, A15:C6−C5−H9, A16:C1−C6−C5, A17:C1−C6−H10, A18:C1−C6−C11, A19:C1−C11−H12, A20:C1−C11−H13, A21:C1−C11−Cl14, A22:H12−C11−H13, A23:H12−C11−Cl14, A24:H13−C11−Cl14, A25:C4−N15−O16, A26:C4−N15−O17, A27:O16−N15−O17,D1:C6−C1C2−C3,D2:C6−C1−C2−H7,D3:C11−C1−C2−H7, D5:C2−C1−C6−C5,D5:C2−Cl−C6−C5,D6:C2−C1−C6−H10,D7:C11−C1−C6−C5, D8:C11−C6−H10, D9:C2−C1−C11−H12, D10:C2−C1−C11−H13, D11:C2−C1−C11−Cl14, D12:C6−C1−C11−H12, D13:C6−C1−C11−H13, D14:C6−C1−Cl14, D15:C1−C2−C3−C4, D16:C1−C2−C3−H8, D17:H7−C2−C3−C4, D18:H7−C2−C3−H8, D19:C2−C3−C4−C5, D20:C2−C3−C4−N15, D21:H8−C3−C4−C5, D22:H8−C3−C4−N15, D23:C3−C4−C5−C6, D24:C3−C4−C5−H9, D25:N15−C4−C5−C6, D26: N15−C4−C5−H9, D27:C3−C4−N15−O16, D28:C3−C4−N15−O17, D29:C5−C4−N15−O16, D30:C5−C4−N15−O17, D31:C4−C5−C6−C1, D32:C4−C5−C6−H10, D33:H9−C5−C6−C1, D34:H9−C5−C6−H10.

4.3 C—H vibrations

The hetero aromatic structure shows the presence of C—H stretching vibrations in the region 3100–3000 cm^{-1} which is the characteristic region for the ready identification of the C—H stretching vibrations [32]. In this region, the bands are not affected appreciably by the nature of the substituents. Hence, in our present work, the FT-IR bands observed at 3106, 3079 and 3060 cm^{-1} are assigned to C—H stretching vibration. The same vibrations in gas phase IR and Raman spectra are at 3110 and 3085 cm^{-1} and at 3100, 3074 and 3057 cm^{-1}, respectively. The majority of these bands are weak in both IR and Raman spectra. The scaled vibration mode nos. 45–42, by B3LYP/6-31G(d,p) method predicted at 3123, 3123, 3075 and 3074 cm^{-1} are assigned to C—H vibration. The HF level at 6-31G(d,p) after scaling down gives the frequency values of 3055, 3004 and 3003 cm^{-1} of (mode nos. 45–42) Table 2 are assigned to C—H stretching. For the same vibration the BLYP/6-31G(d,p) and SVWN/6-31G(d,p) methods also show very good agreement with FT-IR gas phase experimental observation. As expected these four modes are pure modes, as is evident from the last column of Table 2.

The title molecule NBC has out-of-plane and in-plane aromatic C—H bending vibrations, corresponding to C2—H, C3—H, C5—H and C6—H. The out-of-plane bending mode of C2—H is found to be well within the experimentally predicted [33,34] region of 900–840 cm^{-1} at B3LYP/6-31G(d,p), while the calculations at HF level give the frequency value of 992–848 cm^{-1} (mode nos. 22–18) which coincides with experimental observation. The observed FT-IR values of 866 and 869 cm^{-1} in FT-Raman are in excellent agreement with HF/6-31G(d,p) results. The computed C—H out-of-plane bending vibration by BLYP/6-31G(d,p) and SVWN/6-31G(d,p) shows good agreement with experimental observation. The out-of-plane C5—H and C6—H deformation vibrations experimentally predicted in the region 813–873 cm^{-1} [35] coincide satisfactorily with the calculated values in the region 849–820 cm^{-1} (mode nos. 20 and 18) by B3LYP/6-31G(d,p). The bands corresponding to in-plane C—H deformations are observed in the region 1000–1300 cm^{-1}. In *p*-substituted benzene the C—H in-plane bending mode can be expected in the region 1000–1300 cm^{-1}. The bands are sharp but are weak to medium intensity. The frequency observed in FT-IR at 1090 cm^{-1} is due to in-plane C—H bending. The theoretically scaled values of C—H in-plane bending also fall in the region 1086–1282 cm^{-1} by B3LYP/6-31G(d,p) method.

4.4 Internal vibrations of the NO_2 group

NO_2 asymmetric and NO_2 symmetric stretching vibrations generally give rise to bands in the regions

1500–1570 cm^{-1} and 1300–1370 cm^{-1} in nitrobenzene and substituted nitrobenzenes, respectively. In our previous study of 5-bromo-2-nitropyridine [11,36] we assigned the frequencies at 1529 and 1350 cm^{-1} to NO_2 asymmetric and NO_2 symmetric stretching vibrations, respectively. In accordance with the above conclusion the medium strong band at 1540 cm^{-1} in FT-IR and the weak band at 1539 cm^{-1} in FT-Raman correspond to NO_2 asymmetric stretching vibrations. The same vibration in FT-IR gas phase as a very strong band at 1544 cm^{-1}. The intensity of Raman bands corresponding to the symmetric stretching vibrations is very strong for ν_s NO_2 at 1350 cm^{-1}. The same vibration in FT-IR solid and gas phase both at 1348 cm^{-1} as a very strong band. The theoretically scaled values at 1557 and 1345 cm^{-1} by B3LYP/6-31G(d,p) method exactly correlate with experimental observations. The PED of this mode is contributing 30% for NO_2 asymmetric stretching and 34% for NO_2 symmetric stretching.

The deformation vibrations of NO_2 group (rocking, wagging, twisting and torsion) contribute to several normal modes in the low frequency region. The strong band observed at 525 and 524 cm^{-1} in FT-IR and FT-Raman, respectively, are assigned to the rocking mode of NO_2 group. However, for the gas phase infrared spectrum show no such band. The band observed at 753 cm^{-1} in FT-IR is assigned to wagging mode of NO_2 group. It should be emphasised that the wave number calculated by the B3LYP/6-31G(d,p) method for the rocking and wagging modes (513 cm^{-1} – mode no. 11) and (743 cm^{-1} – mode no. 16) is in very good agreement with the corresponding experimental data.

The NO_2 twisting vibration contributes mainly to the normal mode (mode no. 15), which is observed as a medium band at 696 and 694 cm^{-1} in the FT-IR solid and gas phase spectra, respectively. The theoretically scaled value by B3LYP/6-31G(d,p) method at 688 cm^{-1} shows very good agreement with FT-IR gas phase experimental data.

4.5 Phenyl ring vibrations

There are six equivalent C—C bonds in benzene and consequently there will be six C—C stretching vibrations. In addition, there are several in-plane and out-of-plane bending vibrations of the ring carbons. However, due to high symmetry of benzene, many modes of vibrations are infrared inactive. In general the bands around 1400–1650 cm^{-1} in benzene derivatives are assigned to skeletal stretching C—C bands. The same vibrations in FT-Raman spectrum are at 1597–1393 cm^{-1}. The bands observed at 1611–1298 cm^{-1} in FT-IR solid phase are attributed to C—C stretching vibration. The theoretically scaled C—C stretching vibration at B3LYP/6-31G(d,p) is 1608–1323 cm^{-1} shows excellent agreement with recorded spectral data.

The scaled frequencies of DFT values 485 and 405 cm^{-1} (mode nos. 10 and 9) show the semicircular out-of-plane bending modes of the ring carbons. The observed FT-Raman spectrum shows the frequency band at 469 cm^{-1} is in very good agreement with computed values. The band observed at 472 cm^{-1} in FT-IR solid phase can be attributed to C—C—C out-of-plane bending vibrations.

In di-substituted benzenes, the assignments of the ring breathing mode and trigonal C—C—C in-plane bending modes have also been the subject of controversy for a long time. We believe that because of its most symmetric nature of the ring breathing mode should appear with good intensity and low depolarisation ratio in the Raman spectrum like 992 cm^{-1} frequency of benzene. Under the C_s point group both the vibrations will have the same symmetry species A'. As the energies of these vibrations are very close, there is an appreciable interaction between these vibrations and consequently their energies will be modified. In the case of 3-methoxybenzaldehyde the Raman frequency at 996 cm^{-1} assigned to ring breathing mode [37]. For a number of mono-, ortho- and para-substituted benzene the ring breathing mode is assigned at ~1040 and ~800 cm^{-1}, respectively [38–40]. In the present case, the medium band at 858 cm^{-1} in FT-IR solid and 858 cm^{-1} FT-IR gas phase, respectively, are assigned to ring breathing mode. The theoretically predicted wave number at 841 cm^{-1} by B3LYP/6-31G(d,p) method deviate by ~17 cm^{-1}.

The trigonal C—C—C in-plane bending mode in substituted benzenes is sensitive to the positions and natures of the substituents and is at some time drastically affected due to its interaction with other modes. The frequencies 825, 806 and 1019 cm^{-1} are assigned to

Table 3. Mean absolute deviation, SD, root mean square (RMS) and correlation coefficient (*r*) between the calculated and observed fundamental frequencies for the title molecule.

	HF 6-31G(d,p)	SVWN 6-31G(d,p)	BLYP 6-31G(d,p)	B3LYP 6-31G(d,p)
Mean absolute deviation	25.2647	19.8823	16.9117	11.7647
SD	20.2967	16.8658	11.7707	6.9918
RMS	32.8951	26.4643	20.9146	13.8913
r	0.9994	0.9995	0.9998	0.9998

Table 4. Mean absolute deviation, SD, root mean square (RMS) and correlation coefficient (r) between the calculated and observed structural parameters (bond lengths and bond angles).

	HF 6-31G(d,p)	SVWN 6-31G(d,p)	BLYP 6-31G(d,p)	B3LYP 6-31G(d,p)
Bond lengths				
Mean absolute deviation	0.0178	0.0267	0.0358	0.0280
SD	0.0243	0.0311	0.0255	0.0252
RMS	0.0320	0.0435	0.0467	0.0399
r	0.9994	0.9996	0.9994	0.9996
Bond angles				
Mean absolute deviation	0.4522	0.8322	0.5422	0.5088
SD	0.3989	0.5632	0.3626	0.3532
RMS	0.6396	1.0653	0.6918	0.6570
r	0.9810	0.9833	0.9816	0.9813

the trigonal C—C—C in-plane bending modes for *o*-, *m*-and *p*-trifluoromethyl benzaldehyde. Our theoretical calculations by B3LYP/6-31G(d,p) method predicted at 994 cm^{-1} are assigned for trigonal bending vibration. The experimental observation shows that 1012 (1018) and 1009 cm^{-1} in FT-IR solid phase (gas phase) and FT-Raman spectra are assigned to trigonal C—C—C in-plane bending vibration.

4.6 C—Cl vibrations

The vibrations belonging to the bond between the ring and the halogen atoms are worth discussing here, since mixing of vibrations is possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule [41]. The assignments of C—Cl stretching and deformation vibrations have been made by comparison with similar molecules, 5-amino-2-chlorobenzoic acid [42] and the halogen substituted benzene derivatives [43]. Mooney [44,45] assigned vibrations of C—X group (X = Cl, Br and I) in the frequency range of 1129–480 cm^{-1}. The medium FT-IR band at 631 cm^{-1} and medium strong band at 630 cm^{-1} in FT-Raman correspond to C—Cl stretching mode. However, the gas phase infrared spectrum for C—Cl vibration shows at 644 cm^{-1}as a medium band. The scaled wave number of C—Cl stretching vibration (mode no. 14) at 651 cm^{-1} coincides very well with experimental observation. As it is evident from PED, this is pure stretching vibration and it almost contributing to 69%. The C—Cl in-plane bending and out-of-plane bending vibrations are assigned to the FT-Raman bands at 222 and 149 cm^{-1}, respectively. This is in agreement with the literature data [41–45].

4.7 CH_2 vibration

A major coincidence of theoretical values with those of experimental evaluation is found in the symmetric and asymmetric vibration of the methylene (—CH_2—) moiety. PED of these modes shows that they are pure stretching modes. The —CH_2— wagging mode at 1252 cm^{-1} also exactly coincides with the reported value of ~1250 cm^{-1} [45]. 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 CH_2 scissoring vibrations [7,46]. For cyclohexane, the CH_2

Table 5. Theoretically computed total energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal mol^{-1}) and dipolemoment (D) for 4-nitrobenzylchloride.

Parameters	HF/6-31G(d,p)	SVWN/6-31G(d,p)	BLYP/6-31G(d,p)	B3LYP/6-31G(d,p)
Total energy	−402.2259741	−404.5607311	−404.4192557	−402.3456395
Zero-point energy	70.68	72.14	72.54	70.11
Rotational constants				
	5.4908	5.4674	5.4525	5.4972
	2.1907	2.1809	2.1939	2.1858
	1.9792	1.8976	1.8963	1.9830
Entropy				
Total	90.153	92.473	94.325	90.382
Translational	41.044	41.044	41.044	41.044
Rotational	30.009	30.009	30.025	29.962
Vibrational	19.142	21.420	23.256	19.377
Dipole moment	2.133	1.913	1.998	2.176

scissoring mode has been assigned to the medium intensity IR band at about 1450 cm^{-1} [47,48]. In 3-aminobenzyl alcohol [49] medium intensity FT-IR band at 1464 cm^{-1} and FT-Raman band at 1465 cm^{-1} have been assigned to the CH_2 scissoring vibration. This band probably obscures the C—C vibration of phenyl mode. In our title molecule the scaled vibrational frequency 1445 cm^{-1} exactly coincides with the FT-IR gas phase experimental observation of 1445 cm^{-1}. The PED of this mode contributes 58%. Methylene wagging and twisting (called CH_2 deformation) generate bands at 1225 and 1105 cm^{-1} in the FT-IR spectrum. The theoretically calculated CH_2 deformation vibration has been found to be consistent with recorded spectral data.

The force constant values computed at B3LYP level of theory have been collected in Table 2. These force constant values on comparison with related molecules [50,51] are found to deviate approximately by one unit.

5. Other molecular properties

Several calculated thermodynamic parameters are presented in Table 5. Scale factors have been recommended [52] for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy, S_{vib} (T). The variations in the ZPVEs seem to be insignificant. The total energies and the change in the total entropy of NBC at room temperature at different methods are also presented.

6. Conclusions

Comparison of the observed fundamental vibrational frequencies of NBC and the results calculated by density functional B3LYP, BLYP, SVWN and HF methods indicate that B3LYP is superior to the scaled HF and SVWN approach for molecular vibrational problems. On the basis of the calculated results, assignments of the fundamental vibrational frequencies have been proposed. The good agreement between frequencies calculated by B3LYP/6-31G(d,p) and experimental results indicate that the density functional methods are reliable and provide valuable information in understanding the vibrational spectra of the title molecule. The optimised geometry parameters calculated at HF/6-31G(d,p) are slightly shorter than those calculated at B3LYP/6-31G(d,p) level and the B3LYP-SVWN/6-31G(d,p) calculated values coincides well compared with the crystal structure data on the whole.

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