International Journal of Education and Science Research Review
E-ISSN 2348-6457
Volume-7, Issue-5 Sep-Oct – 2020
P-ISSN 2349-1817
www.ijesrr.org
Email- editor@ijesrr.org

Vibrational (FT-IR and FT-Raman) and DFT analysis of 1,2,4,5-tetrachloro-3-nitrobenzene

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ABSTRACT

In the present work, FT-IR and FT Raman vibrational spectra of 1,2,4,5-tetrachloro-3-nitrobenzene (1,2,4,5-TC-3-NB) have been recorded in the range 4000–400 cm^{-1} and 3500–100 cm^{-1}, respectively. A detailed vibrational analysis has been carried out and assignments of the observed fundamental bands have been proposed based on peak positions and relative intensities. The optimized molecular geometry, vibrational frequencies, dipole moment, rotational constants and several thermodynamic parameters in the ground state were calculated using DFT (B3LYP) method with 6-31++G(d,p) and 6-311++G(d,p)basis sets. With the help of different scaling factors, the computed vibrational wavenumbers are compared with experimental values. Most of the modes have wave numbers in the expected range. The value of some thermodynamic parameters (such as enthalpy, heat capacity, free energy and entropy) of substituted benzenes is calculated using Statistical thermodynamics and spectroscopy. The mean Molecular Polarizabilities <α> and Anisotropic Polarizabilities Δα of substituted Benzenes have been evaluated using Density Functional theory.

Keywords: Vibrational Spectroscopy, 1,2,4,5-Tetrachloro-3-nitrobenzene (1,2,4,5-TC-3-NB), DFT.

1. Introduction

Molecular organic compounds with one or more aromatic systems in conjugated positions, leading to a charge transfer system, have been studied for the past two decades. Now-a-days, organic crystals are highly recognized as the materials of the future because their molecular nature combined with versatility can be used to alter their structure to maximize the non-linear properties [1–3]. Benzene derivates have been widely used to manufacture therapeutic chemicals, dyes, artificial leather and detergent products. Chlorobenzene once was used for manufacturing of certain pesticides, most notably DDT by reaction with chloral (trichloroacetaldehyde), but this application has declined with the diminished use of DDT. Additionally, chlorobenzene was the primary precursor for the production of phenol [4]. Chlorobenzene is nitrated on a large scale to give a mixture of 2- and 4-nitrochlorobenzene for the production of 2-nitrophenol, 2-nitroanisole,2-nitroaniline, 4-nitrophenol, 4-nitroanisole, 4-nitroaniline etc. [5] by nucleophilic displacement of chloride with sodium hydroxide, sodium methoxide, sodium disulfide and ammonia. Tetrachlorobenzene belongs to a group of organic halogen compounds that replace four hydrogen atoms in benzene with chlorine atoms. By taking all these facts into account, the present study has been aimed to investigate the vibrational spectra of 1,2,4,5-Tetrachloro-3-nitrobenzene. In the present work, the FT-IR and FT-Raman spectra of 1,2,4,5-TC-3-NB were studied experimentally and theoretically. The optimized structure of the titled molecule is shown in Figure 1. The Comparative Raman and IR spectra of experimental and calculated DFT(B3LYP)/6-31++G(d,p) and 6-311++G(d,p) of 1,2,4,5-TC-3-NB (Figures 2 and 3) are given. The DFT calculation is performed to obtain the ground state optimized geometries. In the DFT method, Becke's three-parameter exact exchange-functional (B_3) [6–8] combined with Parr (LYP) [9-14] are the best predicting results for molecular geometry and vibrational wavenumbers for larger molecules.

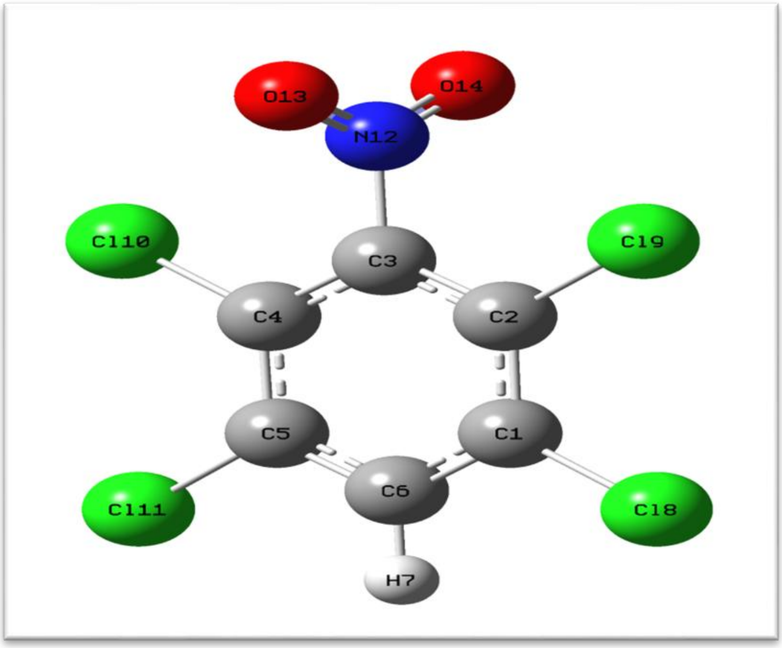

Figure 1: Optimized Molecular Structure of 1,2,4,5-tetrachloro-3-nitrobenzene.

2. Experimental details

The fine sample of 1,2,4,5-TC-3-NB was purchased from Sigma-Aldrich Chemicals, U.S.A. and used as such without further purification to record FT-IR and FT-Raman spectra. The FT-IR spectra of the titled compound were recorded on Perkin Elmer M-500 FTIR spectrophotometer in the region 4000-400 cm^{-1} using KBr pellets. The FT-Raman spectra of 1,2,4,5-TC-3-NB were recorded on a BRUKER IFS. 66V model interferometer equipped with an FRA-106 FT-Raman accessory in the 3500–100 cm^{-1} Stokes region using 1064 nm line of a Nd:YAG laser for excitation operating at 200mw power. The reported wave numbers are believed to be accurate within ±1 cm^{-1}.

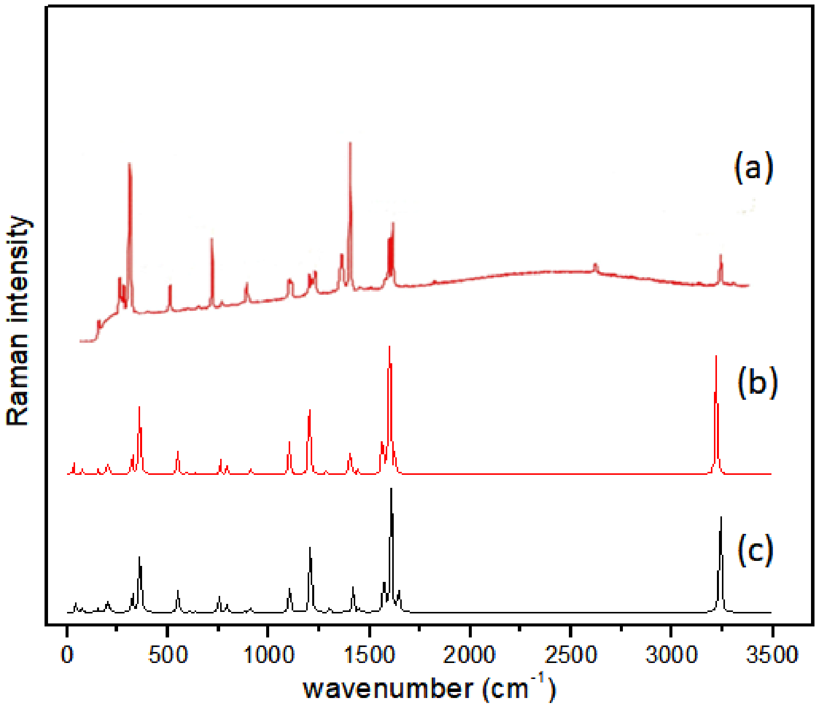

Figure 2: FT Raman spectra of 1,2,4,5-tetrachloro-3-nitrobenzene (a) Experimental, (b) 631++, (c) 6311++

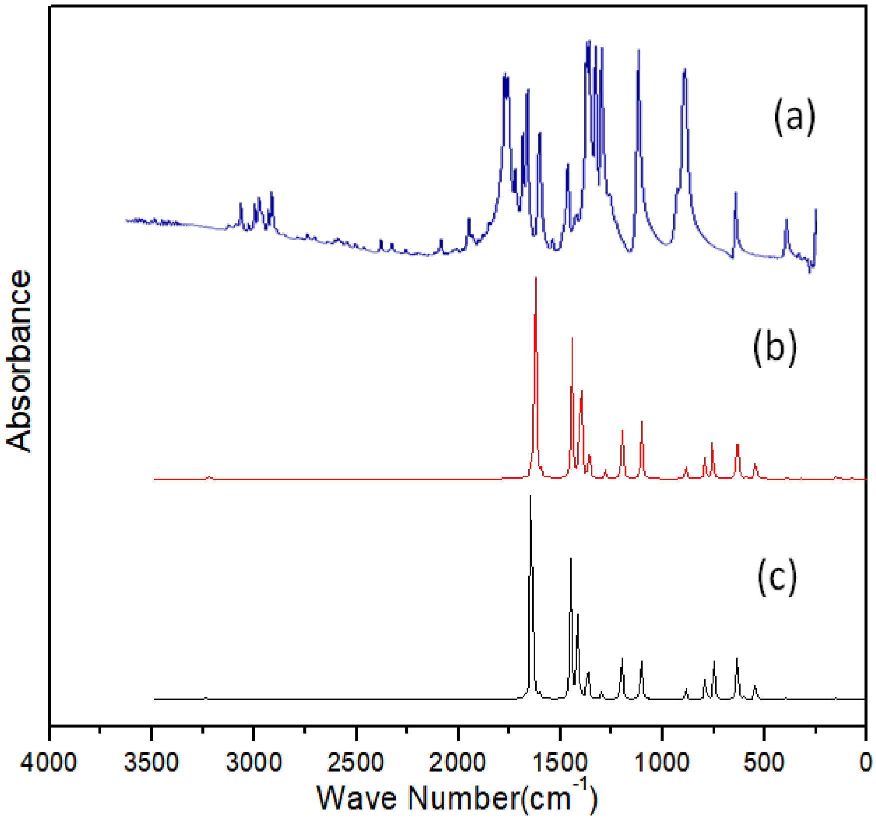

Figure 3: FT-IR spectra of 1,2,4,5-tetrachloro-3-nitrobenzene (a) Experimental, (b) 631++, (c) 6311++

3. Computational details

For meeting the requirements of both accuracy and computing economy, theoretical methods and basis sets should be considered. DFT has proved to be extremely useful in treating electronic structure of molecules. The DFT calculations have been carried out for 1,2,4,5-TC-3-NB with GAUSSIAN 09 W program package [10] and the corresponding vibrational assignments were studied using VEDA and Gauss view 6. Initial geometry generated from the standard geometrical parameters was minimized without any constraint on the potential energy surface at DFT level adopting the standard 6-31G++ (d,p) and 6-311G++ (d,p) basis sets. This geometry was then re-optimized again at DFT level employing the Becke3LYP keyword, which invokes Becke's three-parameter hybrid method [11, 12] using the correlation function of Lee et al. [14], implemented with the same basis sets for the better description of the bonding properties of nitro group. The minimum energy of geometrical structure is obtained using 6-31G++ (d,p). The calculated frequencies are scaled by 0.9613 for B3LYP basis set.

4. Results and discussion

4.1 Molecular geometry

The optimized geometrical parameters of the titled molecule, obtained by DFT(B3LYP)/6-31++G (d,p)/6-311++G (d,p) levels, are listed in Table 1. The experimental FT-IR and FT-Raman frequencies along with calculated data and vibrational assignments for 1,2,4,5-TC-3-NB are listed in the Table 2. From the table, it is clear that the various bond lengths are found to be almost the same at the B3LYP level. The calculated geometrical parameters can be used as a foundation to calculate the other parameters for the compound. The molecular structures of 1,2,4,5-TC-3-NB belong to C_s point group symmetry and molecular structures are obtained from GAUSSIAN 09W [18–23]. Inclusion of the NO_2 group and Cl atoms, known for their strong electron–withdrawing nature, is expected to increase the contribution of the resonance structure, in which the electronic charge is concentrated at this site. The bond lengths calculated by DFT/6-311++G(d,p) method are found to be 1.217 Å for each. The carbon atoms are bonded to the hydrogen atoms with a sigma bond in benzene and the substitution of chlorine atoms for hydrogen reduces the electron density at the ring carbon atom. The C-Cl bond length varies from 1.732 Å to 1.739 Å by the DFT/6-311++G(d,p) method. The ring carbon atoms in substituted benzenes exert a larger attraction on the valence electron cloud of the hydrogen atom, which gives an increment in the C-H force constants and a decrement in the corresponding bond length. From Table 1, it is clear that the C-H bond length varies from 1.070 Å to 1.072Å, C-C bond length from 1.390 Å to 1.400 Å by the DFT/6-311++G(d,p) method.

Table 1: Optimized geometrical parameters for 1,2,4,5-Tetrachloro-3-nitrobenzene computed at B3LYP/6-31++G (d, p) and B3LYP/6-311++G(d, p) basis sets.

Bond Length (	**B3LYP/6-31 (d, p)**	**B3LYP/6-311 (d, p)**	**Bond Angle (®)**	**B3LYP/6-31G (d, p)**	**B3LYP/6-311 (d, p)**
C1-C2	1.403	1.400	C2-C1-C6	120.2	120.2
C1-C6	1.394	1.390	C2-C1-Cl8	121.1	121.1
C1-Cl8	1.739	1.739	C1-C2-C3	118.0	118.0
C2-C3	1.397	1.393	C1-C2-Cl9	121.8	121.8
C2-Cl9	1.732	1.732	C6-C1-Cl8	118.7	118.7
C3-C4	1.397	1.393	C1-C6-C5	120.8	120.8
C3-N12	1.484	1.488	C1-C6-H7	119.6	119.6
C4-C5	1.403	1.400	C3-C2-Cl9	120.2	120.2
C4-Cl10	1.732	1.732	C2-C3-C4	122.8	122.8
C5-C6	1.394	1.390	C2-C3-N12	118.6	118.6
C5-Cl11	1.739	1.739	C4-C3-N12	118.6	118.6
C6-H7	1.083	1.081	C3-C4-C5	118.0	118.0
N12-O13	1.225	1.217	C3-C4-Cl10	120.2	120.2
N12-O14	1.225	1.217	C3-N12-O13	116.6	116.6
			C3-N12-O14	116.6	116.6
			C5-C4-Cl10	121.8	121.8
			C4-C5-C6	120.2	120.2
			C4-C5-Cl11	121.1	121.1
			C6-C5-Cl11	118.7	118.7
			C5-C6-H7	119.6	119.6
			C13-N12-O14	126.8	126.9

Table 2: Comparison of the experimental (FT-IR and FT-Raman) and computed vibrational frequencies of 1,2,4,5-tetrachloro-3-nitrobenzene.

Experimental		**Computational**				**Vibrational Assignments**
		DFT				
		B3LYP/6-31++G(D,P)		**B3LYP/6-311++G(D,P)**		
FT–IR	**FT-Raman**	**Unscaled**	**Scaled**	**Unscaled**	**Scaled**	
		40	38	29	28	τONCC (98)
		69	67	69	66	τCCCC (92)
		72	69	71	69	τCCCC (46)+γNCCC (28)
		131	126	129	124	τCCCC (12)+γCCCCl(68)+γNCCC(14)
		154	148	153	147	βNCC(64)+γOCON(18)
		195	187	194	187	βCCC(11)+βCCCl(78)
		200	192	199	192	βCCCl(72)
		212	204	208	200	βCCCl(88)
	220(vw)	213	204	212	204	βONC(12)+τCCCC(17)+γCCCCl(24)+γNCCC(15)
		319	306	319	306	νCCl(48)+βCCC(38)
		325	312	324	311	νNC(26)+βCCC(30)
	328(w)	339	326	332	319	γCCCCl(98)
350(w)	347(w)	360	346	359	345	νCCl(32)+βCCC(17)
378(vw)	363(vs)	400	384	395	379	βONC(39)+τCCCC(20)+γCCCCl(32)
418(vw)	451(vw)	524	504	523	503	βCCl(78)+γOCON(16)
466(w)	546(w)	547	526	545	524	νCCl(32)
		600	577	579	556	γCCCCl(90)
		604	581	591	568	βONC(20)+τHCCC(16)+τHCCC(20)+γCCCCl(24)+ γNCCC(10)
	637(vw)	634	610	633	609	νCCl(66)+γOCON(16)
662(m)	688(vw)	723	695	686	660	βONC(20)+τCCCC(13)+γCCCCl(20)+γNCCC(30)
	741(m)	749	720	756	727	νCC(11)+βONO(42)

	792(w)	790	759	792	761	βNCC(22)+γOCON(46)
849(vs)		881	846	877	843	νCCl(72)
858(vs)		884	850	885	850	τHCCl(77)+τCCCC (11)
880(w)	900(w)	908	872	910	875	νNC(26)+βONO(28)
1026(vs)	1097(w)	1102	1059	1100	1057	νCCl(20)+βCCC(55)
1168(vs)		1199	1152	1195	1149	βHCC(58)
	1193(w)	1207	1160	1201	1154	νCC(39)
1190(vs)	1213(m)	1300	1249	1282	1232	νCC(93)
1215(vs)	1337(m)	1368	1315	1362	1309	νCC(71)
1226(vs)	1375(vs)	1416	1361	1403	1348	$\nu_{s}NO_{2}(74)+\nu NC(11)+\beta NO_{2}(12)$
1406(s)	1415(w)	1449	1392	1443	1387	νCC(10)+βHCC(33)+βCCC(18)
1524(vs)	1473(w)	1571	1510	1564	1503	νCC(41)+βCCC(30)
1535(vs)	1547(m)	1605	1543	1597	1534	$\nu_{as}CC(83)$
1599(w)	1568(s)	1643	1579	1626	1563	$\nu_{as}NO_{2}(100)$
3123(w)	3133(w)	3238	3112	3219	3093	νCH(100)

Where ν – stretching, ν_{as}- asymmetric stretching, ν_{s} -symmetric stretching, β –in plane bending, γ-out of plane bending, τ-torsion

4.2 Other molecular properties

Several Thermodynamic properties like the heat capacity, zero-point energy, and entropy along with the minimum energy of 1,2,4,5-TC-3-NB have been obtained by the density functional theory method using 6-31++G(d,p) and 6-311++G(d,p) basis sets, as shown in Table 3. The difference in the values calculated by both methods is only marginal. The rotational constants and dipole moments for the titled compound are also listed in the table.

Table 3: Theoretically computed energies (a. u.), zero point vibrational energies (kcal/ mol), rotational constants (GHz), entropies (cal/mol-Kelvin), dipole moment (Debyes), thermal energy(kcal/mol) and specific heat(cal/mol-Kelvin) for 1,2,4,5-TC-3-NB

PARAMETER	DFT	
	B3LYP/6-31+G (d, p)	B3LYP/6-31++G (d, p)
Total Energy	-2275.115535	-2275.327075
Zero-Point Energy	39.98816	39.68825
Rotational Constants	0.57533	0.57676
	0.44764	0.44900
	0.26176	0.26240
Dipole Moment	3.5422	3.5460

ENTROPY

Total	112.640	113.623
Translational	42.553	42.553
Rotational	32.833	32.825
Vibrational	37.254	38.244

ENERGY(THERMAL ENERGY)

Total	47.536	47.294
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	45.758	45.517

SPECIFIC HEAT (Cv)

Total	41.297	45.517
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	35.335	35.551

1.4.3 C-H vibrations

The nitro group does not appear to affect the position of characteristic C-H bands in compound 1,2,4,5-TC-3-NB and these bands occur in the range 3100-3000 cm^{-1} [23]. The in plane bending vibrations appear in the range 1300-1000 cm^{-1} in the substituted benzenes and out of plane bending vibrations in the range 1000-750 cm^{-1} [30-35]. The weak bands of FT-IR vibrational frequencies at 3081 and 3123 cm^{-1} are assigned to C-H stretching vibrations. All values show good agreement with the calculated results. The Raman counterparts of C-H stretching vibrations are observed at 3070 and 3133 cm$^{-1,}$ which shows good agreement with the calculated results. Also, the FT-Raman bands at 1097, 1193 and 1213 cm^{-1} and infrared bands at 1026,1168,1190,1215,1226 and 1266 cm^{-1} are assigned to C-H in-plane bending vibrations. The C-H out-of-plane bending modes show consistent agreement with the computed B3LYP results.

4.4 C-C vibrations

The C-C aromatic stretching vibrations give rise to characteristic bands in both the observed IR and Raman spectra covering the range from 1600 to 1400 cm^{-1} [25]. C-C stretching vibrations of the compound are found at 1406, 1451, 1458, 1470, 1498, 1524, 1535, 1599 and 1623 cm^{-1} in FT-IR and 1599 and 1623 cm^{-1} in the FT-Raman spectrum. Most of the ring vibrational modes are affected by the substitutions in the aromatic ring [26]. The ring in plane bending modes are observed at 858, 880, 1026 cm^{-1} and 681, 741, 900 cm^{-1} in the FT-IR and FT-Raman respectively. The rings out of plane bending modes of the titled compounds are also listed in table 2. The reductions in the frequencies of these modes are due to a change in the force constant and the vibrations of functional group present in the molecules. The theoretically computed values for C-C vibrational modes by B3LYP/6-311++G(d,p) method gives excellent agreement with experimental data.

4.5 C-N vibrations

The identification of C-N vibrations is a difficult task since the mixing of vibrations is possible in this region. In aromatic compounds, the C-N stretching vibrations usually lie in the region 1400-1200 cm^{-1} [27]. In this study, the bands observed at 1298 and 1355 cm^{-1} in FT-IR and 1337 cm^{-1} in Raman spectrum have been assigned to C-N stretching vibration of 1,2,4,5-TC-3-NB. The assignments of C-N in-plane and out-of-plane bending vibrations are at 792 cm^{-1} and 220 cm^{-1} respectively [27, 28]. In this study, the theoretical values are supported by the literature. The remainder of the observed and calculated frequencies have been listed in Table 2.

4.6 NO_2 vibrations

The nitro group is substituted at the third position in the ring of the titled compound. The asymmetric stretching for the NO_2, NH_2 and CH_2 has a magnitude higher than that of the symmetric stretching [36,37]. Aromatic nitro compounds have strong absorptions due to the asymmetric and symmetric stretching vibrations of the NO_2 group at 1570-1500 cm^{-1} and 1370-1300cm^{-1}, respectively [38]. Hydrogen bonding has a little effect on the NO_2 asymmetric stretching vibrations [37, 38]. Hence, the asymmetric stretching mode of the nitro group for 1,2,4,5-TC-3-NB is identified at 1524 cm^{-1} (in FT-IR very strong band) and 1568 cm^{-1} (in Raman strong band) in good agreement with computed data. The symmetric stretching mode of the nitro group for the compound is assigned at 1355 cm^{-1} (in FT-IR very weak band) and 1337 cm^{-1} (in FT-Raman weak band). The NO_2 scissoring mode has been designated to the band at 741 cm^{-1} in Raman spectra. The other vibrations of NO_2 group (rocking, wagging and twisting) contribute to several normal modes in the low frequency region. Aromatic nitro compounds have a band of weak to medium intensity in the region 590-500 cm^{-1} due to the out-of-plane bending deformation mode of the NO_2 group and is observed at 466 cm^{-1}. The NO_2 deformation vibrations have a week to medium absorption in the region 775-660 cm^{-1} [38-40]. In the present case, the NO_2 deformation (in plane bending and wagging) is observed at 688 cm^{-1} in Raman band. Hence, it is clear that, the assignment is in line with the literature and the vibrational frequency is not affected. This is a unique occurrence of NO_2.

4.7 C-Cl vibrations

The vibration belonging to the link between the C-Cl is significant to discuss 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 the molecules [39, 40]. The assignments of C-Cl stretching and deformation modes have been made through comparison with similar assignments in other halogen-substituted benzene derivatives. The C-Cl stretching vibration generally gives a strong band in the region 750-580 cm^{-1} [41–56]. In 1,2,4,5-TC-3-NB, the C-Cl stretching vibration is observed at 858 cm^{-1} (in FT-IR band) and 637 cm^{-1} (in Raman band). C-Cl in-plane bending vibration compounds form a band in the region of 385-265 cm^{-1} [57, 58]. The same C-Cl in-plane bending vibration in compound 1,2,4,5-TC-3-NB is observed at 350 cm^{-1} (in FT-IR band) and 347 cm^{-1}, 363 cm^{-1} (in Raman band). The C-Cl out-of-plane bending vibration has been established at 124 cm^{-1}. These are in good agreement with literature data [59, 60].

4.8 Molecular polarizability calculation

The potential application of the substituted benzenes in the field of nonlinear optics demands the investigation of their structural and bonding features contributing to the hyperpolarizability enhancement, by analysing the vibrational modes using IR and Raman spectroscopy. The mean polarizability $\langle\alpha\rangle$ and anisotropic polarizability ($\Delta\alpha$) of substituted benzenes are calculated using the DFT-B3LYP method and

6-31++G(d,p) and 6-311++G(d,p) basis sets, based on the finite-field approach as shown in table 4. Also, the large values of polarizability and first order hyperpolarizability components indicate the substantial delocalization of charges in these directions. The large value of polarizability, α which is a measure of the non-linear optical activity of the molecular system, is associated with the intra-molecular charge transfer, resulting from the electron cloud movement through π conjugated framework from electron donor to electron acceptor groups. The physical properties of these conjugated molecules are governed by the high degree of electronic charge delocalization along the charge transfer axis and by the low band gaps. So, it can be concluded that the title compound is an attractive object for future studies of nonlinear optical properties.

Table 4: Theoretically computed Molecular Polarizability for 1,2,4,5-Tetrachloro-3-nitrobenzene.

Molecular Polarizability (Atomic unit)	**DFT**	
	B3LYP/6-31+G (d, p)	**B3LYP/6-31++G (d, p)**
α_{xx}	-98.1938	-98.0338
α_{xy}	-0.0002	0.0003
α_{yy}	106.2934	106.3868
α_{xz}	0.0002	0.0004
α_{yz}	0.000	0.0000
α_{zz}	-103.9284	-104.3197
Mean dipole Polarizability <α>	-102.8052	-102.9134
Anisotropic Polarizability Δα	7.213	7.534

5. Conclusion

Attempts have been made in the work for the proper frequency assignments for 1,2,4,5-terachloro-3-nitrobenzene from the FT-IR and FT-Raman spectra. The equilibrium geometries, vibrational frequencies, infrared intensities and Raman activities are calculated and analyzed by DFT(B3LYP) levels of theory utilizing 6-31++G(d,p) and 6-311++G(d,p) basis sets. Comparison between the calculated vibrational frequencies and the experimental values indicates that both methods can predict the FT-IR and FT-Raman spectra of the titled compound well. The influence of the nitro group and chlorine atom on the vibrational frequencies of the title compound was studied. Various quantum chemical calculations help us to identify the structural and symmetry properties of the titled molecule. The excellent agreement of the calculated and observed vibrational spectra reveals the advantages of a higher basis set for quantum chemical calculations. The scaling factors used in this study made a reliable agreement between the calculated and experimental values.

The atomic charges, molecular polarisability/hyperpolarisability and dipole moment in the titled molecule are also discussed elaborately. Several thermodynamic parameters of the titled molecules are comparatively discussed. The results may be of assistance in the quest of experimental and theoretical evidence for the title compound in reaction intermediates, nonlinear optical and photoelectric materials.

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