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4-Chlorotoluene: Spectral studies and quantum chemical calculations

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ABSTRACT

In this work, the combined experimental and theoretical study on molecular and vibrational structure of 4-chlorotoluene (4CT) was studied based on Hartree-Fock (HF) and density functional theory (DFT) using the hybrid functional B3LYP. The Fourier Transform Infrared (FTIR) and Fourier Transform Raman (FT-Raman) spectra of 4CT were recorded in the solid phase. The optimized geometry was calculated by HF and B3LYP methods with 6-31G(d,p) and 6-311++G(d,p) basis sets. The harmonic vibrational frequencies, infrared intensities and Raman scattering activities of the title compound were performed at same level of theories. The thermodynamic functions of the title compound was also performed at HF/6-31G(d,p) and B3LYP/6-311++G(d,p) level of theories. A detailed interpretation of the infrared and Raman spectra of 4CT was reported. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed spectrograms.

Keywords: FT-IR and FT-Raman spectra; ab initio and DFT; 4-chlorotoluene; vibrational analysis.

INTRODUCTION

In recent times toluene and substituted toluenes have become very important on account of their wide range of applications in medicine and industry. 4-amino-3-bromotoluene derivatives find use in herbicidal activity [1] and central nervous system activity [2].

The IR and Raman spectra of toluene and m-xylene have been investigated by numerous workers and vibrational assignments have made by Pitzer and Scott [3]. The charecteristic ring vibrations of the o-chloro and bromotoluenes [4], p-chloro and bromotoluenes [5] and m-chlorotoluene [6] in the 800 - 1600 cm^{-1} region has been assigned. A comparative study of the gas and liquid IR spectra of $C_6H_5CH_3$, $C_6H_5CD_3$ and $C_6D_5CD_3$ and the liquid Raman spectra of the two former, leads to a vibrational assignment for these molecules consistent with the relative band intensities, vapour band contours, polarization data and Redlich-Teller isotope product rule [7]. The Raman and IR spectrum of o-fluorotoluenes has been investigated by Deb [8] in the liquid and in different aliphatic solvents viz., CCl_4, CS_2 and n-hexane solutions.

Sharma et al [9] analyzed the IR and Raman spectra of 2-fluoro-5-bromotoluene. The fundamentals of the observed bands have been assigned on the basis of C_s symmetry of the molecule. Attempts have been made to discuss the various modes of vibrations. The vibrational spectra of chloronitrotoluenes are studied by Singh and Rai [10]. The IR spectra of 2-amino-4-nitortoluene, 2-amino-5-nitrotoluene, 4-amino-2-nitrotoluene and 4-amino-3-nitrotoluene have been recorded in the region 200 - 4000cm^{-1}. The polarized and depolarized laser Raman spectra have also been recorded for 2-amino-4-nitrotoluene molecules. The assignments of the observed frequencies to the probable modes of vibration of the molecules are given [10].

The vibrational spectra of toluene, aniline and bromo benzene have been extensively studied and analysed [11-13]. Spectroscopic investigation on isomeric toluidines, nitrotoluenes and nitroanilines were reported by earlier workers [11, 14-17]. The vibrational spectra of certain fluoromethyl anilines [18, 19] and chloromethyl anilines [20] have been reported. Syam Sundar [21] has reported the vibrational spectral analysis of 4-amino-5-bromotoluene and 5-amino-2-bromotoluene by assuming C_s point group symmetry and in this no normal coordinate analysis has been found. The experimental vibrational spectra of 3-chloro-4-methyl aniline have been investigated in comparison with ab initio and DFT values recently by Kurt et al [22]. Recently the conformational behaviour and structural stability of chlorotoluene were investigated by utilizing ab initio calculations with 6-31G(d) basis set at RHF and DFT levels by Zhengyu Zhou et al [23]. They have also carried out vibrational frequencies calculation of chlorotoluene using HF and DFT methods. Tendative band assignmentswas also made by assuming C_s point group symmetry. It should be empasized that in our calculations we have included p-polarization functions on hydrogen atoms. It is anticipated that both ab initio HF and density functional level of theories are reliable for predicting the vibrational spectra of 4-chlorotoluene. 4-chlorotoluene is manufactured or used as a solvent, disinfectant, or as an intermediate for organic chemicals and dyes. Ortho nitrotoluene is used in the synthesis of intermediates for aze dyes, sulfur dyes, rubber chemicals and agricultural chemicals.

Therefore, the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wavenumber accuracy.

EXPERIMENTAL SECTION

The compound 4CT in the solid form was obtained from Sigma Aldrich Chemical Company (USA) with a stated purity of greater than 98% and it was used as such without further purification. The FT-Raman spectrum of 4CT has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 100-4000 cm^{-1} on a Brucker model IFS 66 V spectrophotometer. The FT-IR spectrum of this compound was recorded in the region 400-4000 cm^{-1} on IFS 66 V spectrophotometer using KBr pellet techinque. The data were recorded in the co-addition of 200 scans at ±4 cm^{-1} resolution with 250 mW of power at the sample in both the techniques. The observed experimental and theoretical FT-IR and FT-Raman spectra of the title compound are shown in Figs. 1-4. The spectral measurements were carried out at Central Electrochemical Research Institute (CECRI), Karaikudi, Tamil Nadu.

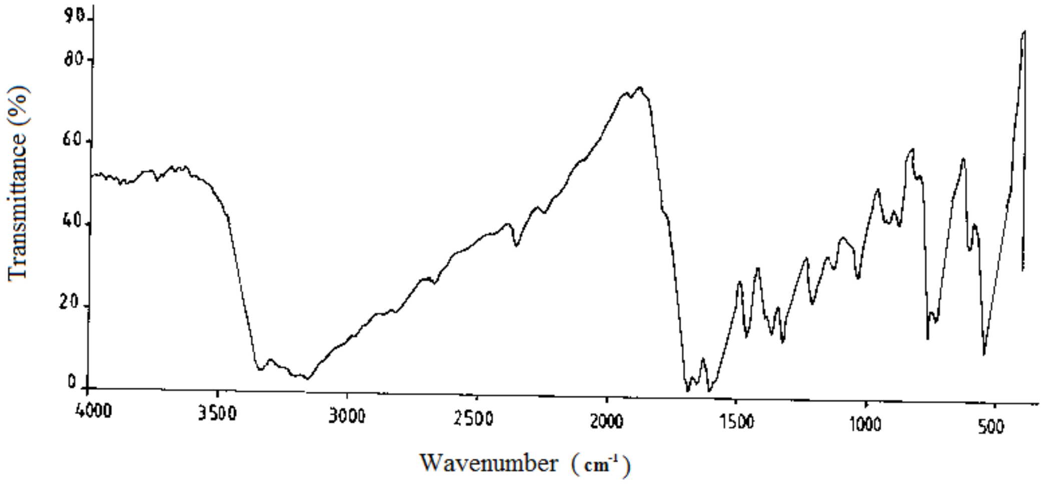

Fig.1. FT-IR Spctrum of 4-Chlorotoluene

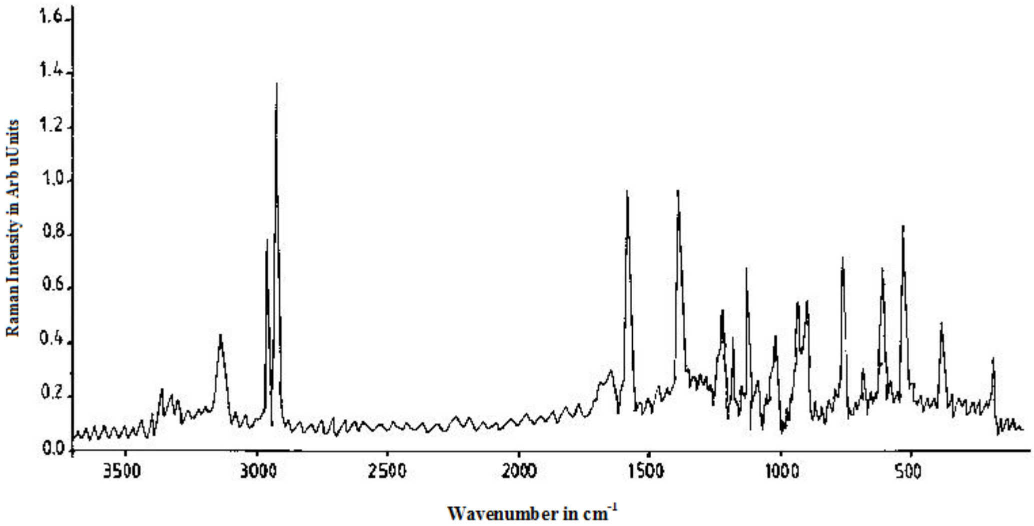

Fig.2. FT-Raman Sepctrum of 4-Chlorotoluene

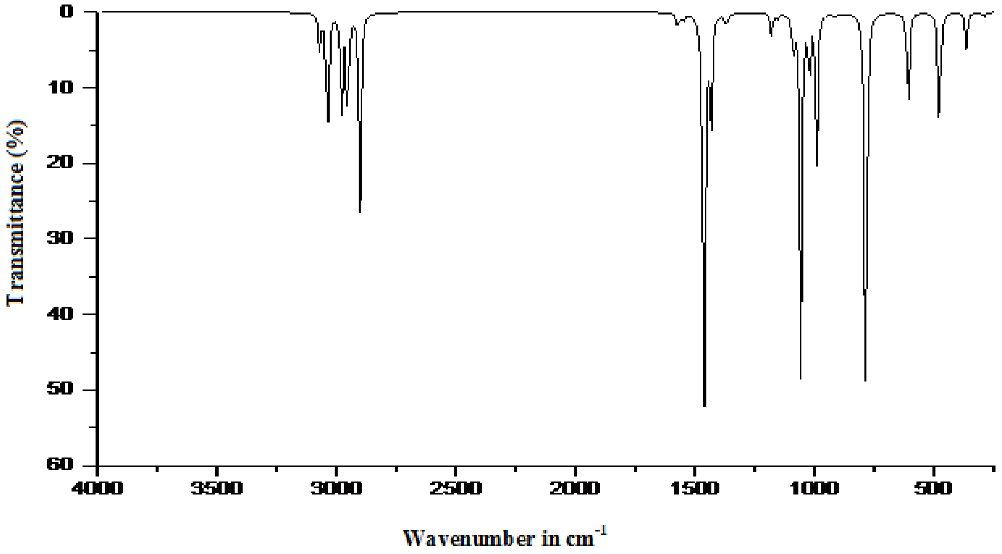

Fig.3. Scaled FT-IR Spectrum of 4-Chlorotoluene (B3LYP)

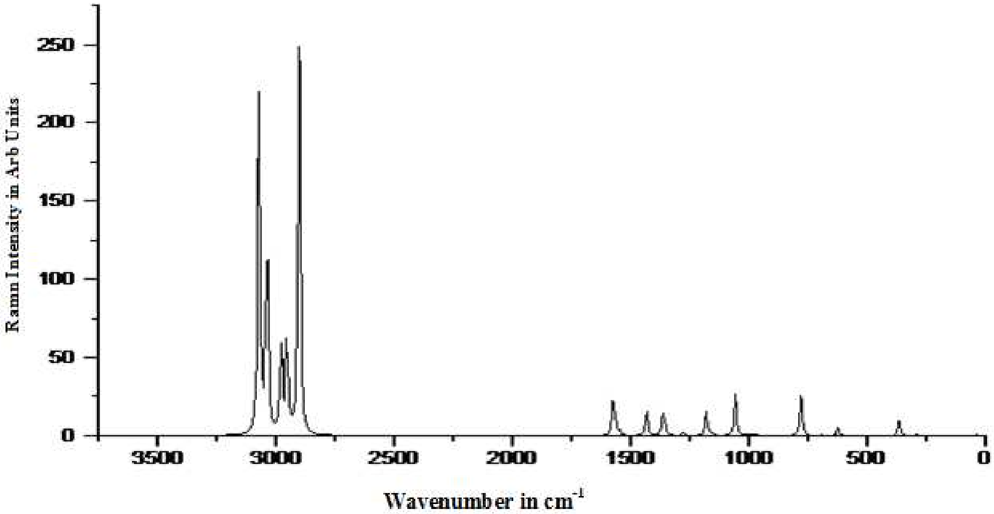

Fig.4. Scaled FT-Raman Spectrum of 4-Chlorotoluene (B3LYP)

Method of calculations

All calculations were performed at Hartree-Fock (HF) and B3LYP levels on a Pentium IV/3.02 GHz personal computer using Gaussian 03W [24] program package, invoking gradient geometry optimization [25]. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartree-Fock level, adopting the standard 6-31G(d,p) basis set. This geometry was then re-optimized again at HF and the gradient corrected density functional theory (DFT) [26] with the Becke's three parameter hybrid functional (B3) [27] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [28], accepted as a cost effective approach, for the computation of molecular structure, vibrational frequencies and energies of optimized structures. All the computations have been done by adding polarization function d and diffuse function on heavy atoms [29] and polarization function p and diffuse function on hydrogen atoms [30], in addition to triple split valence basis set (6-311++G(d,p)), for better treatment of polar bonds of methyl and chloro groups. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of 4CT were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. Vibrational frequencies computed at DFT level have been adjudicated to be more reliable than those obtained by the computationally demanding Moller-Plesset perturbation methods. Density functional theory offers electron correlation frequently comparable to second-order Moller-Plesset theory (MP2). Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics.

By combining the results of the GAUSSVIEW program [31] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the GAUSSVIEW program.

RESULTS AND DISCUSSION

4.1. Molecular Geometry

The Fig. 5, presents a schematic of 4CT molecule with its atoms numbered 1-15 to correspond with Table 2 and it shows the list of optimized structural parameters observed from HF and DFT computations and the corresponding experimental data [32]. All the geometries determined belong to a true minimum proven by real wavenumbers in the vibrational analysis.

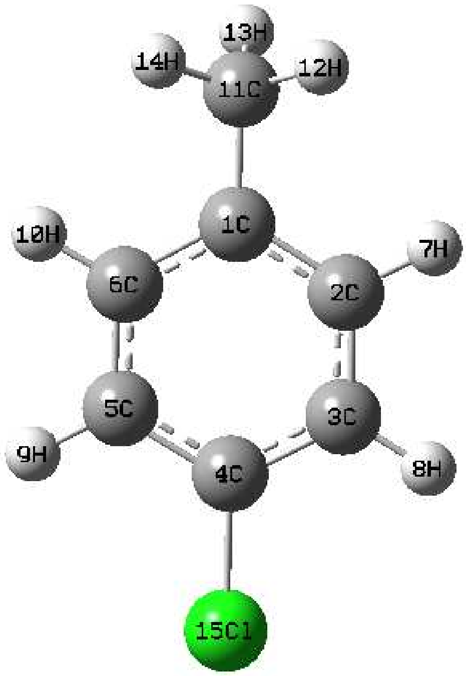

Fig. 5. Numbering system adopted in this study (4-chlorotoluene)

Table 2 Geometrical parameters optimized in 4-chlororoluene, Bond length (Å), angle (°)

Parameters	HF		B3LYP		Experimental [a]
	6-31G(d,p)	6-311++G(d,p)	6-31G(d,p)	6-311++G(d,p)	Toluene
Bond length (Å)					
C1-C2	1.390	1.389	1.401	1.399	1.399
C1-C6	1.389	1.389	1.401	1.399	1.399
C1-C11	1.511	1.511	1.510	1.510	1.511
C2-C3	1.384	1.385	1.395	1.393	1.399
C2-H7	1.076	1.076	1.087	1.085	1.098
C3-C4	1.382	1.381	1.393	1.391	1.399
C3-H8	1.074	1.073	1.084	1.083	1.098
C4-C5	1.382	1.381	1.393	1.390	1.399
C4-Cl15	1.746	1.747	1.761	1.761	---
C5-C6	1.385	1.385	1.395	1.393	1.399
C5-H9	1.074	1.073	1.084	1.083	1.098
C6-H10	1.076	1.076	1.087	1.085	1.098
C11-H12	1.084	1.084	1.094	1.093	1.120
C11-H13	1.087	1.087	1.097	1.096	1.120
C11-H14	1.084	1.084	1.094	1.093	1.120
Bond angle (°)					
C2-C1-C6	118.06	118.03	117.96	117.91	118.6
C2-C1-C11	120.96	120.97	121.01	121.03	---
C6-C1-C11	120.98	120.99	121.02	121.05	---
C1-C2-C3	121.37	121.38	121.50	121.50	120.9
C1-C2-H7	119.70	119.73	119.53	119.60	---
C3-C2-H7	118.93	118.89	118.98	118.90	---

C2-C3-C4	119.24	119.23	119.07	119.10	120.0
C2-C3-H8	120.65	120.63	120.81	120.75	---
C4-C3-H8	120.12	120.14	120.12	120.15	---
C3-C4-C5	120.74	120.76	120.90	120.88	119.5
C3-C4-Cl15	119.63	119.62	119.55	119.56	---
C5-C4-Cl15	119.63	119.62	119.55	119.56	---
C4-C5-C6	119.24	119.23	119.07	119.10	120.0
C4-C5-H9	120.12	120.15	120.12	120.15	118.7
C6-C5-H9	120.64	120.62	120.80	120.74	---
C1-C6-C5	121.37	121.38	121.50	121.50	120.9
C1-C6-H10	119.71	119.74	119.53	119.60	---
C5-C6-H10	118.93	118.88	118.97	118.90	---
C1-C11-H12	111.26	111.08	111.47	111.40	---
C1-C11-H13	110.90	110.71	111.17	110.97	---
C1-C11-H14	111.27	111.08	111.47	111.40	---
H12-C11-H13	107.63	107.85	107.25	107.41	---
H12-C11-H14	107.99	108.14	108.01	108.06	---
H13-C11-H14	107.63	107.85	107.26	107.42	---

[a] *Taken from Ref [32].*

Recently, the density functional theory (DFT) method has been extensively developed to study molecular structures [33-36], and it is believed that this theory has good geometrical prediction of a molecule. The comparisons among the various HF and DFT (B3LYP) are given in order of determine which calculation method is the most effective. For 4-chlorotoluene, two experimental parameters, namely 1.39 Å for the average ring C-C distance and 1.74 ± 0.01 Å for the C-Cl distance were given [37]. No matter what the calculation method selected, calculated bond lengths were very similar to the experimental ones.

As the influence of the substituents on the phenyl ring seems to be interesting. The benzene ring appears to be little distorted with C3-C4 and C4-C5 bond lengths were decreased; whereas the C1-C2 and C1-C6 bond lengths were increased when compared with the usually adopted bond length of C-C (1.39 Å) of the benzene ring [38]. The increase of the C-C bond lengths exactly at 4th position and decrease of bond lengths at 1st position is accompanied by slightly irregular hexagonal structure of the angles C2-C1-C6 and C3-C4-C5, 117.9 ° and 120.9 ° respectively at B3LYP/6-311++G(d,p) method. These results are in accordance with molecular geometry of substituted benzene derivatives [39]. Since the electron-withdrawing nature of Cl atom and electron-donating nature of CH_3 group may be the reason for different deviation of the C-C bond lengths and the C-C-C bond angles are observed in our title molecule.

From the theoretical values, we can find that most of the optimized bond lengths are slightly larger than the experimental values, due to that the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state. Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are bigger than later and the B3LYP calculated values correlates well compared with the experimental data. In spite of the differences, calculated geometrical parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and thermodynamics properties.

4.2. Vibrational assignments

With this assumed structural model, the molecule belongs to Cs point group and the 39 normal modes of fundamental vibrations which span the irreducible representations: 27A' + 12A". All the 39 fundamental vibrations are active in both IR and Raman. Vibrational assignments are based on comparison of calculated and observed Raman and IR frequencies and activities as well as the depolarisation ratios of Raman bands The assignments shown in Table 2 for several of phenyl ring modes along with substituents are briefly given in the present work.

The harmonic-vibrational frequencies calculated for 4CT at HF and B3LYP levels using the triple split valence basis set along with diffuse and polarization functions, 6-311++G(d,p) and observed FT-IR and FT-Raman frequencies for various modes of vibrations have been collected in Table 2. Comparison of the frequencies calculated at HF and B3LYP 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 extend makes the frequency values smaller in comparison with the HF frequency data. Reduction in the computed harmonic vibrations, though basis set sensitive are only marginal as observed in the DFT values using 6-311++G(d,p). Any way notwithstanding the level of calculations, it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experiment. The calculated frequencies were scaled by factors 0.8923 and 0.9623 for HF and DFT computation, respectively. These values minimize the root-mean square difference between calculated and experimental frequencies for bands with definite identifications. They are very close to the values recommended for HF/6-311++G(d,p) (0.8929) and DFT-/b3YLP/6-311++G(d,p) (0.9613) [40,41]. The descriptions concerning the assignment have also been indicated in Table 2.

4.3. C-H vibrations

The di-substituted benzenes, which form the subject of the recent investigation, gives rise to four C-H stretching, four C-H in-plane deformations and four C-H out-of-plane deformations. The aromatic structure shows the presence of C-H stretching vibrations in the region 3000 - 3100 cm^{-1} which is the charecteristic region for the identification of C-H stretching vibrations [42]. In this region, the bands are not affected appreciably by the nature of the substituents.

In benzene derivatives the C-H stretching frequencies arise from the modes a_{1g} (3062 cm^{-1}), e_{2g} (3047 cm^{-1}), b_{1u} (3060 cm^{-1}) and e_{1u} (3080 cm^{-1}). In the present investigation, the bands observed at 3139 cm^{-1} in FT-Raman are assigned to C-H stretchingmodes.

These assignments are in good agreement with earlier works [43-48]. The vibrations 36 - 39 assigned to aromatic C-H stretch in the region 3037 - 3071 cm^{-1} [48] are in agreement with experimental observations.

There are two degenerate e_{2g} (1178 cm^{-1}) and e_{1u} (1037 cm^{-1}) and two non-degenerate b_{2u} (1152 cm^{-1}) and a_{2g} (1340 cm^{-1}) modes of vibrations in benzene which involve C-H in-plane bending vibrations. In di-substituted benzenes, these modes should give rise to six planar bending vibrations, three involving the substituents and three involving the three hydrogen atoms. The aromatic C-H in-plane bending modes of benzene and its derivatives are observed in the region 1000 - 1300 cm^{-1} [49]. In this study the bands at 1140 and 1209 cm^{-1} in FT-IR have been assigned to C-H in-plane bending vibrations which belongs to A' species. These assignments are in agreement with values given in literature [43, 46, 50]. The theoretically calculated value of the C-H in-plane bending vibrations assigned at 1057 - 1277 cm^{-1} (mode nos. 20-24) even though found to be contaminated by CH_3 rocking are in the range found in literature.

Table 2. Vibrational wavenumbers obtained for 4-chlororoluene at HF/6-311++G (d,p) [harmonic frequency (cm^{1}), IR intensities (Km mol^{-1}), Raman scattering activities (Å^{4} amu^{-1}), Raman depolarization ratio and reduced masses (amu), force constants (m dyne Å^{-1})]

	Wavenumber		IR intensity		Raman intensity		Depolarization	Red	Force	
Number	unscaled	scaled	Rel	Abs	Rel	Abs	Ratios	mass	Constants	Vibrational assignments
1	32	29	0	0	1	0	0.75	1.0	0.00	t CH_3
2	130	116	0	0	0	0	0.67	4.6	0.05	γ C-Cl + γ CCC
3	268	238	0	0	0	0	0.75	4.7	0.20	β C-Cl
4	334	297	1	1	1	1	0.75	4.3	0.28	γ C-CH_3
5	403	358	0	0	0	0	0.74	3.0	0.28	β C-CH_3
6	406	361	4	6	12	6	0.25	9.6	0.93	β CCC
7	457	407	0	0	0	0	0.75	2.9	0.36	γ CCC
8	546	486	24	33	1	0	0.64	2.6	0.45	γ CCC
9	676	602	13	18	0	0	0.52	5.4	1.46	ν C-Cl
10	695	619	0	0	6	3	0.75	7.0	1.98	β CCC
11	785	699	0	0	1	0	0.29	3.0	1.10	γ CCC
12	860	766	12	16	35	17	0.05	5.1	2.24	ring breathing
13	913	812	60	82	0	0	0.72	1.4	0.68	γ CH
14	933	830	0	0	0	0	0.75	1.2	0.64	γ CH
15	1064	947	1	1	0	0	0.29	1.3	0.90	γ CH
16	1078	959	0	0	1	1	0.75	1.5	1.06	γ CH
17	1094	974	0	0	0	0	0.75	1.4	0.96	ω CH_3
18	1104	982	20	27	1	0	0.07	3.6	2.59	trigonal bending
19	1163	1035	7	10	1	0	0.38	1.6	1.25	γ CH
20	1173	1044	3	4	0	0	0.60	2.0	1.61	ρ CH_3

Table 2. Vibrational wavenumbers obtained for 4-chlororoluene at HF/6-311++G (d,p) [harmonic frequency (cm^1), IR intensities (Km mol^{-1}), Raman scattering activities (Å^4 amu^{-1}), Raman depolarization ratio and reduced masses (amu), force constants (m dyne Å^{-1})]

	Wavenumber		IR intensity		Raman intensity		Depolarization	Red	Force	
Number	unscaled	scaled	Rel	Abs	Rel	Abs	Ratios	mass	Constants	Vibrational assignments
21	1191	1060	53	73	22	11	0.04	3.4	2.86	β CH
22	1277	1136	2	2	0	0	0.75	2.4	2.28	β CH
23	1289	1147	1	1	1	1	0.47	1.2	1.17	γ C-CH$_3$
24	1311	1167	4	6	11	5	0.07	2.7	2.72	γ CC
25	1437	1279	0	0	1	1	0.75	1.3	1.57	β CH
26	1538	1369	2	3	2	1	0.40	2.1	2.87	CH$_3$ **umbrella mode**
27	1538	1369	1	1	8	4	0.35	1.4	1.91	γ CC
28	1608	1431	7	9	10	5	0.72	1.0	1.60	δ CH$_2$ **in** CH$_3$
29	1610	1433	10	14	6	3	0.75	1.1	1.67	CH$_3$ **asym. deform**
30	1653	1472	73	100	0	0	0.20	2.4	3.79	ν CC
31	1753	1560	0	1	6	3	0.75	6.0	10.88	ν CC
32	1787	1590	2	3	30	14	0.72	5.6	10.46	ν CC
33	3166	2818	36	49	208	100	0.04	1.0	6.14	ν$_s$ CH in CH$_3$
34	3222	2868	25	35	78	37	0.69	1.1	6.72	ν$_s$ CH in CH$_3$
35	3244	2887	23	31	61	29	0.75	1.1	6.84	ν$_{as}$ CH in CH$_3$
36	3326	2960	14	19	77	37	0.69	1.1	7.11	ν$_{as}$ CH
37	3326	2960	12	17	69	33	0.20	1.1	7.11	ν$_s$ CH
38	3362	2992	8	11	19	9	0.75	1.1	7.30	ν$_{as}$ CH
39	3363	2993	0	0	182	87	0.18	1.1	7.30	ν$_s$ CH

*ν–stretching; ν$_s$-**sym**. stretching; ν$_{as}$-asym. stretching; β – in-plane-bending; γ - out-of-plane bending; ω - wagging; ρ - rocking; t - twisting; τ - torsion; δ - scissoring.*

The C-H out-of-plane deformations are derived from b_{2g} (985 cm^{-1}), e_{2u} (970 cm^{-1}), e_{1g} (850 cm^{-1}) and a_{2u} (671 cm^{-1}) modes of benzene and they are expected in the region 600 - 1000 cm^{-1} [51]. In the di-substituted benzenes only four C-H out-of-plane bendings are expected. The C-H out-of-plane bending frequencies are independent of nature of substituents on the benzene ring [52]. The molecule has two adjacent free hydrogen atoms on the ring. It is observed that on reducing the number of free hydrogen atoms on the ring, the frequencies shift to higher values. Hence the bands observed at 606, 879 and 911 cm^{-1} in FT-IR are assigned to C-H out-of-plane bending vibrational modes. The calculated frequencies 787 - 933 cm^{-1} for the C-H out-of-plane bending falls within experimental observations.

4.4. C-C vibrations

Carbon stretching vibrations are very much prominent in the spectrum of benzene and its derivatives. There are two doubly degenerate vibrations of benzene e_{2g} (1596 cm^{-1}) and e_{1u} (1485 cm^{-1}) and two non-degenerate modes of benzene b_{2u} (1310 cm^{-1}) and a_{1g} (995 cm^{-1}) which have been attributed to C-C skeletal vibrations. In all substituted benzenes, four bands are usually observed in the region 1400 - 1650 cm^{-1} due to the splitting of the two doubly degenerate frequencies into four totally symmetric components. The actual positions are determined not so much by the nature of the substituents but by the form of substitution around the ring, as suggested by Bellamy [53]. The FT-IR and FT-Raman bands observed at 1605 and 1477, 1390 cm^{-1} have been assigned to degenerate modes by benzene C-C stretching mode, and finds support from the assignments of earlier workers [43,44,46]. These frequencies appear in the respective range and further it shows that these modes are almost pure.

Expect for ring breathing vibrations of benzene a_{1g} (995cm^{-1}) all of the skeletal C-C stretching frequencies are known to remain practically unaffected by substitution [54]. The frequency of the mode b_{2u} (1310 cm^{-1}) changes by a small magnitude on substitution in C_s symmetry [55]. The carbon vibration b_{2u} (1310 cm^{-1}) occurs [56] in asymmetric tri-substituted benzenes in the region 1240 - 1290 cm^{-1}. In the present molecule the band observed in IR at 1327 cm^{-1} has been assigned to this mode of vibration which is known as ‘Kekule mode’. This is in agreement with the literature value [46] and also agree with the assignment proposed by Sharma et al [57] in 2-fluoro-5-bromotoluene.

There are three modes associated with ring in-plane deformations are expected to occur on account of C_s symmetry, which correspond to vibrations b_{1u} (1010 cm^{-1}) and e_{2g} (606 cm^{-1}) of benzene. In the present work, the bands occuring at 941 and 536 cm^{-1} in FT-Raman are assigned to C-C-C in-plane bending. These assignments are in line with the earlier workers [46, 54].

The three C-C-C out-of-plane bending vibrations are derived from non-degenerate b_{2g} (703 cm^{-1}) and degenerate e_{2u} (404 cm^{-1}) modes of benzene the latter contributing two modes on substitution due to splitting [54]. The b_{2g} (703 cm^{-1}) vibration of benzene is found to be constant in substituted benzenes [58].

The ‘C-C-C puckering’ mode which was observed at 707 cm^{-1} in benzene [5]. The absorption band at 710 cm^{-1} in substituted benzenes [5] is assigned to this mode. Hence the C-C-C out-of-plane bending modes of 4CT under C_s symmetry is attributed to FT-IR frequencies observed at 685 cm^{-1}. Our assignments find support from the work of several workers [44, 46, 55]. Both the in-plane and out-of-plane bending vibrations are described as mixed modes.

Assignment of the ring breathing and C-C-C trigonal bending modes in benzene derivatives is a controversial one and has found some place for discussion in almost every article on the vibrational spectra of benzene derivatives. The ring breathing vibration a_{1g} (995 cm^{-1}) of benzene gives rise to a strong band in the Raman spectra of benzene derivatives. The frequency of this vibration is quite reduced in the C_s symmetry due to interaction with closely lying b_{1u} (1010 cm^{-1}) vibration of benzene, since under C_s symmetry both these vibrations belong to the same symmetry type A' [59]. In our title molecule a very strong IR band at 764 cm^{-1} and a medium strong FT-Raman band 766 cm^{-1} corresponds to ring breathing vibration. The theoretically scaled value by B3LYP/6-311++G(d,p) method at 777 cm^{-1} exactly correlates with experimental observation. The theoretically computed value of C-C-C trigonal bending vibrational mode at 990 cm^{-1} by B3LYP/6-311++G(d,p) method also in excellent agreement with experimental observation at 1029 cm^{-1} in FT-Raman spectrum.

4.5. C-CH_3 vibrations

It is noted from literature that the strong band around 1200 cm^{-1} appears due to valence oscillations in toluene and substituted toluenes [43]. Hence, the medium strong band at 1187 cm^{-1} in FT-Raman is attributed to C-CH_3 stretching mode, which agree with the literature value [43-45]. Bogamolov [60] predicted range for the CH_3 rocking frequency is 790 - 1050 cm^{-1}. The CH_3 rocking vibration has been identified in IR as 1042 cm^{-1} for 4CT. These agree well with assignments of similar molecules [46, 50, 55, 57].

4.6. C-Cl vibrations

The vibrations belonging 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 [61]. The assignments of C-Cl stretching and deformation vibrations have been made by comparison with similar molecules, para-bromophenol [62] and the halogen substituted benzene derivatives [63]. Mooney [64, 65] assinged vibrations of C-X group (X=Cl, Br and I) in the frequency range of 1129 - 480 cm^{-1}. The strong FT-Raman band at 614 cm^{-1} corresponds to C-Cl stretching mode. The theoretical wavenumber of C-Cl stretching vibration coupled with C=O in-plane bending vibration (mode no. 13) 608 cm^{-1} coincides very well with the experimental value. The C-Cl in-plane bending and out-of-plane bending vibrations are assigned to the FT-Raman bands at 342 and 252 cm^{-1} respectively. This is in agreement with the literature data [62-65].

4.7. CH_3 vibrations

There must be three CH_3 stretching modes (two asymmetric and one symmetric type). According to Colthup et al [66], these frequencies appear around fairly constant region of 2960 cm^{-1} and 2870 cm^{-1} respectively. Out of the two expected asymmetric stretching frequencies, only one in the region 2920 - 2930 cm^{-1} and the symmetric stretching in the region 2860 - 2865 cm^{-1} could be detected and assigned in the IR absorption spectra of aminonitrotoluene compound [50]. In the present case, the frequency at 2966 cm^{-1} in FT-Raman is taken as asymmetric CH_3 stretching mode and 2933 cm^{-1} as symmetric CH_3 stretching mode. These assignments agree well with Singh and Rai [50] and also find from the work of several workers [45, 54, 67].

The assignment of asymmetric and symmetric CH_3 deformation vibrations is more difficult as the spectra in the region are complex as several C-C stretching vibrations also appear in the same region. Mooney [68] has assigned the asymmetric and symmetric methyl deformations of halogenotoluens in the range (1466 -1488 cm^{-1}) and (1377 - 1380 cm^{-1}) respectively. The FT-IR band at 1464 cm^{-1} has been assigned to CH_3 asymmetric deformation mode in the present molecule. The IR frequency 1369 cm^{-1} has been assigned to CH_3 symmetric deformation mode. These assignments are in accordance with the assignments proposed by previous workers [45, 54, 57, 68].

The force constant values computed at HF and DFT level of theories at various basis sets have been collected in Tables 2. These force constant values on comparison with related molecules [69, 70] are found to deviate approximately by one unit.

5. Other molecular properties

Several calculated thermodynamic parameters are presented in Table 3. Scale factors have been recommended [71] 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 are found to decrease with the increase of the basis set dimension. The changes in the total entropy of 4CT at room temperature at different basis set are only marginal.

Table 3. Theoretically computed total energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal mol^{-1} K^{-1}) and dipole moment (D) for 4-chlororoluene

Parameters	HF		B3LYP	
	6-31G(d,p)	6-311++G(d,p)	6-31G(d,p)	6-311++G(d,p)
Total energy	-877.2259741	-877.3456395	-880.4192557	-880.5607311
Zero-point energy	71.68	71.11	66.54	66.14
Rotational constants				
	1.4908	1.4972	1.4525	1.4674
	1.1907	1.1858	1.1939	1.1809
	0.6792	0.6830	0.6563	0.6676
Entropy				
Total	90.153	90.382	94.325	92.473
Translational	41.044	41.044	41.044	41.044
Rotational	29.968	29.962	30.025	30.009
Vibrational	19.142	19.377	23.256	21.420
Dipole moment	2.133	2.176	1.728	2.103

CONCLUSION

We have carried out ab initio and density functional theory calculation on the structure and vibrational spectrum of 4CT. Comparison between the calculated and experimental structural parameters indicates that B3LYP are in good agreement with experimental ones. Vibrational frequencies, infrared intensities and Raman activities calculated by B3LYP/6-311++G(d,p) method agree very well with experimental results. On the basis of agreement between the calculated and observed results, assignments of all the fundamental vibrational modes of 4CT was examined and proposed for the first time in the literature. Therefore, the assignments made at higher level of theory with higher basis set with only resonable deviations from the experimental values, seem to be correct. This study demonstrates that scaled DFT/B3LYP calculations are powerful approach for understanding the vibrational spectra of medium sized organic compounds.

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