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FT-IR and FT-Raman spectra and vibrational investigation of 4-chloro-2-fluoro toluene using ab initio HF and DFT (B3LYP/B3PW91) calculations

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ABSTRACT

FT-IR (4000–100 cm⁻¹) and FT-Raman (4000–100 cm⁻¹) spectra of solid sample of 4-chloro-2-fluoro toluene (4Cl2FT) have been recorded using Bruker IFS 66 V spectrometer. Ab initio-HF (HF/6-311++G (d, p)) and DFT (B3LYP/6-311++G and B3PW91/6-311++G (d, p)) calculations have been performed giving energies, optimized structures, harmonic vibrational frequencies, depolarization ratios, IR intensities, Raman activities. The vibrational frequencies are calculated and scaled values are compared with FT-IR and FT-Raman experimental values. The isotropic HF and DFT analyses showed good agreement with experimental observations. The differences between the observed and scaled wave number values of most of the fundamentals are very small in B3LYP than HF. Comparison of the simulated spectra provides important information about the ability of the computational method (B3LYP) to describe the vibrational modes. The influences of substitutions on the geometry of molecule and its normal modes of vibrations have also been discussed. The changes made by substitutions on the benzene are much responsible for the non-linearity of the molecule. This is an attractive entity for the future studies of non-linear optics.

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1. Introduction

Toluene is a common solvent, able to dissolve paints, paint thinners, many chemical reactants, rubber, painting ink, glues, lacquers, leather tanners, many disinfectants. It can also be used as fullerene indicator and is also a raw material for certain important products such as polyurethane foam, phenol and TNT. Toluene can be used as an octant booster in gasoline fuels used in internal combustion engine. Industrial uses of toluene include de-alkylation to benzene and disproportionation to a mixture of benzene and xylene. Toluene can be used to break open red blood cells in order to extract hemoglobin in biochemistry tests. Toluene is also known as methyl benzene or phenyl methane. It is a clear, water insoluble liquid with a typical smell of paint thinners, redolent of the sweet smell of the related compound benzene. It is an aromatic hydrocarbon that is widely used as an industrial feed stock and as a solvent.

Toluene reacts as a normal aromatic hydrocarbon towards electrophilic aromatic substitution [1,2]. Various spectroscopic studies of halogen and methyl substituted compounds have been reported in the literature [3–14] from time to time. Green and Harrison [3] and Dwivedi and Sharma [13] have studied the vibrational spectra

of few dihalogen toluenes of TXY type toluene halogens. Mohan and Feridoun [11] have reported the Raman spectral analysis of 2-fluoro 5-chloro toluene and 3-fluoro 6-chloro toluene.

More recently [15,16], FT-IR and FT-Raman spectra of ortho-, meta- and para-nitro toluene and chloro toluene have been reported together with the vibrational assignments of the vibrational modes. However, the detailed HF/B3LYP/B3PW91 at 6-311++G (d, p) comparative studies on the complete FTIR and FTRaman spectra of 4Cl2FT have not been reported so far.

In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for ab initio (RHF), hybrid density functional methods (B3LYP and B3PW91) at 6/311++G (d, p) basis sets is compared. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional ab initio Hartree–Fock calculations. The changes made by substitutions on the benzene molecule suggest an extended π -electron delocalization over the toluene moiety, which is responsible for the non-linearity of the molecule. This is an attractive entity for the future studies of non-linear optics. In DFT methods, Becke's three parameter exact exchange-functional (B3) [17] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [18,19] and

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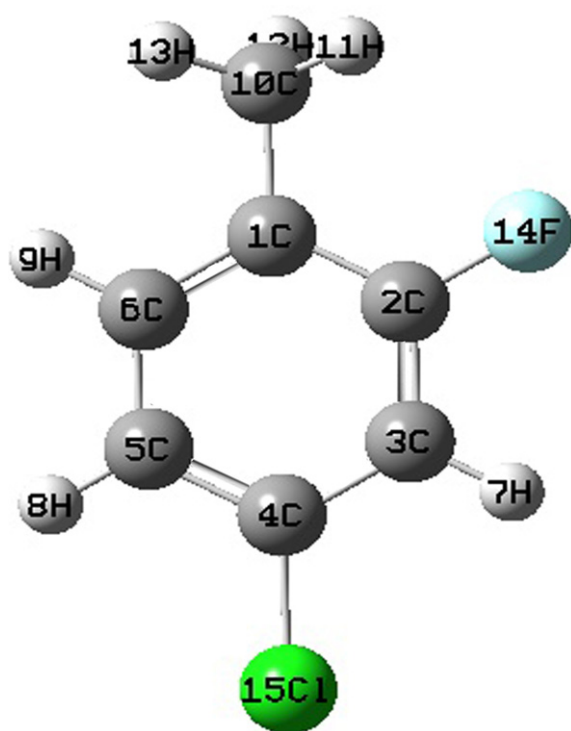


Fig. 1. Molecular structure of 4-chloro-2-fluorotoluene.

Perdew and Wang (PW91) [20,21] are the best predicting results for molecular geometry and vibrational wave numbers for moderately larger molecule [22–24].

2. Experimental details

The compound under investigation namely 4Cl2FT (Fig. 1) is purchased from Sigma–Aldrich Chemicals, U.S.A. which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FT-IR spectrum of the compound is recorded in Bruker IFS 66V spectrometer in the range of 4000–100 cm^{-1} . The spectral resolution is $\pm 2 \text{ cm}^{-1}$. The FT Raman spectrum of the compound is also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm excitation wavelength, line widths with 200 mW power. The spectra are recorded in the range of 4000–100 cm^{-1} with scanning speed of 30 $\text{cm}^{-1} \text{ min}^{-1}$ of spectral width 2 cm^{-1} . The frequencies of all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$. The comparative IR and Raman spectra of experimental and calculated HF and DFT (B3LYP/B3PW91) are given in Figs. 2 and 3 respectively.

3. Computational methods

The molecular structure of 4Cl2FT in the ground state is computed by performing both ab initio-HF and DFT/B3LYP and B3PW91 with 6-311++G (d, p) basis sets. The optimized structural parameters are used in the vibrational frequency calculations at HF and DFT levels. The minimum energy of geometrical structure is obtained using level 6-311++G (d, p) basis sets. The calculated frequencies are scaled by 0.909 for HF [25]. For B3LYP with 6-311++G (d, p) set is scaled with 0.952, 0.978, 0.950, 0.963 and 1.11 and B3PW91/6-311++G (d, p) basis set is scaled with 0.950, 0.941, 0.952, 0.968, 0.980, 0.957, 1.10, and 0.860 [26]. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of 4Cl2FT [27]. HF and DFT calculations are

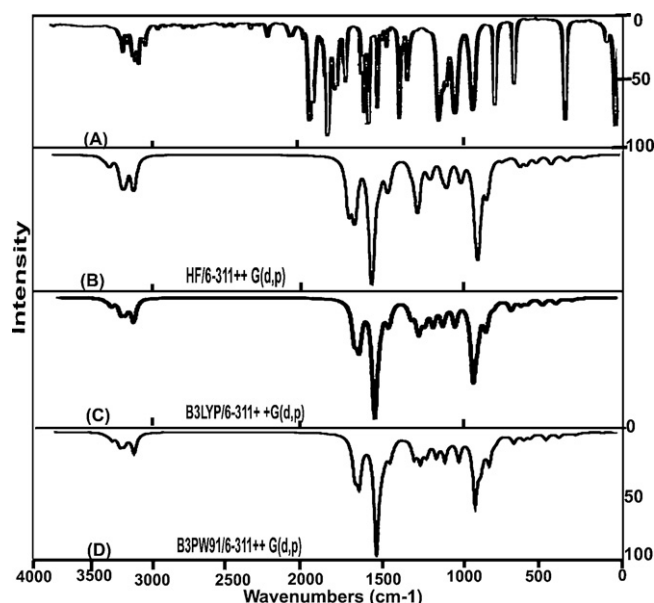


Fig. 2. Experimental (A), calculated (B), (C and D) FTIR spectra of 4-chloro-2-fluorotoluene.

performed using GAUSSIAN 03W program package on Pentium IV processor personal computer without any constraint on the geometry [28,29]. The comparative plots of IR intensities and Raman activities for four sets are presented in Figs. 4 and 5 respectively.

4. Results and discussion

4.1. Molecular geometry

The molecular structure of the 4Cl2FT belongs to C_s point group symmetry. The optimized molecular structure of title molecule is obtained from GAUSSIAN 03W and GAUSSVIEW programs are shown in Fig. 1. The molecule contains Cl, F and CH_3 with benzene ring. The structure optimization zero point vibrational energy of the title compound in HF, B3LYP/6-311++G (d, p) and B3PW91/6-311++G (d, p) are $-308,190.3$, $-288,276.8$ and $-289,221.8 \text{ J/mol}$

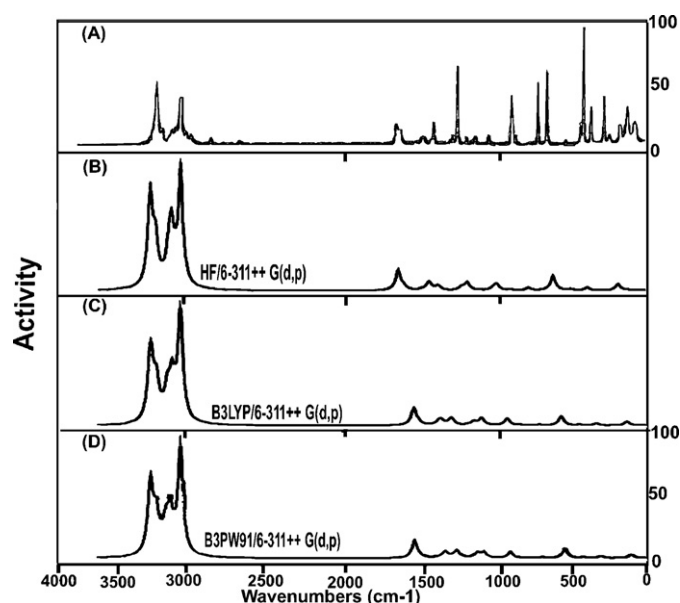


Fig. 3. Experimental (A), calculated (B), (C and D) FTRaman spectra of 4-chloro-2-fluorotoluene.

Table 1

Optimized geometrical parameters for 4-chloro-2-fluoro toluene computed at HF/6-311++G (d, p), B3LYP/6-311++G (d, p) and B3PW91/6-311++G (d, p) basis set.

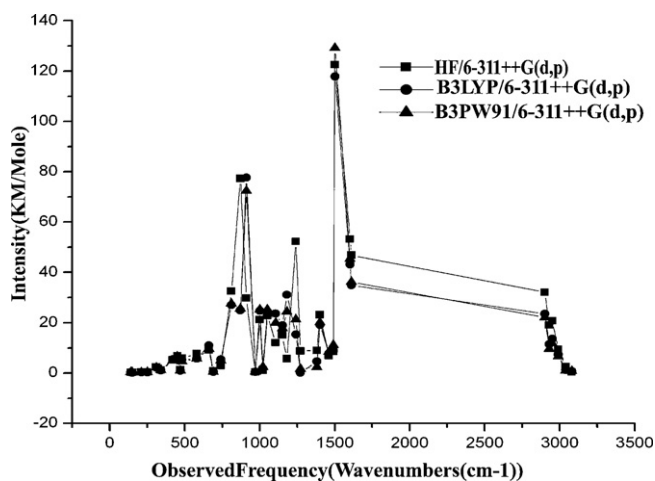
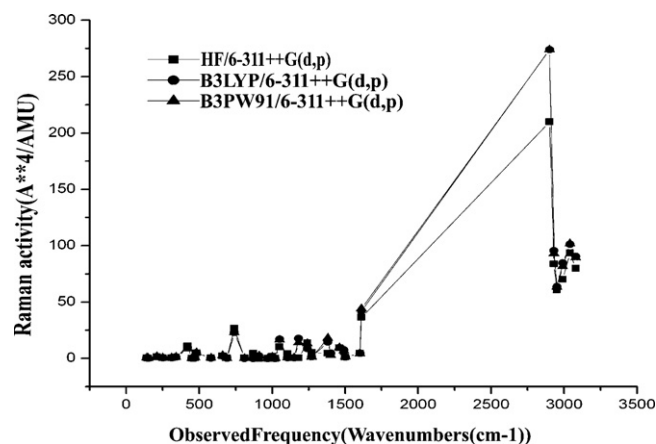
Bond length (Å) Exp (°) ^a	Value		Bond angle (°) Exp (°) ^a	Value		Dihedral angles (°)	Value	
	HF/6-311++G (d, p)	B3LYP/6- 311++G (d, p) B3PW91/6- 311++G (d, p)		HF/6-311++G (d, p)	B3LYP/6- 311++G (d, p) B3PW91/6- 311++G (d, p)		HF/6-311++G (d, p)	B3LYP/6- 311++G (d, p) B3PW91/6- 311++G (d, p)
C ₁ –C ₂ (1.384)	1.383	1.393/1.392	C ₂ –C ₁ –C ₆ (121.8)	116.30	116.08/116.10	C ₆ –C ₁ –C ₂ –C ₃	–0.02	–0.011/–0.012
C ₁ –C ₆ (1.394)	1.386	1.397/1.395	C ₂ –C ₁ –C ₁₀	120.89	121.06/121.06	C ₆ –C ₁ –C ₂ –F ₁₄	–179.96	–179.99/–179.98
C ₁ –C ₁₀	1.508	1.505/1.500	C ₆ –C ₁ –C ₁₀	122.79	122.84/122.82	C ₁₀ –C ₁ –C ₂ –C ₃	179.97	179.98/179.98
C ₂ –C ₃ (1.395)	1.374	1.384/1.383	C ₁ –C ₂ –C ₃ (119.2)	123.71	123.95/123.83	C ₁₀ –C ₁ –C ₂ –F ₁₄	0.03	0.002/0.01
C ₂ –F ₁₄ (1.337)	1.328	1.357/1.349	C ₁ –C ₂ –F ₁₄	118.39	118.28/118.34	C ₂ –C ₁ –C ₆ –C ₅	0.00	0.006/0.002
C ₃ –C ₄ (1.384)	1.382	1.391/1.389	C ₃ –C ₂ –F ₁₄	117.88	117.75/117.82	C ₂ –C ₁ –C ₆ –H ₉	–179.98	–179.98/–179.99
C ₃ –H ₇	1.072	1.081/1.082	C ₂ –C ₃ –C ₄ (119.7)	117.91	117.73/117.84	C ₁₀ –C ₁ –C ₆ –C ₅	–179.99	–179.99/–179.99
C ₄ –C ₅ (1.387)	1.379	1.389/1.388	C ₂ –C ₃ –H ₇	120.19	120.28/120.25	C ₁₀ –C ₁ –C ₆ –H ₉	0.01	0.011/0.015
C ₄ –Cl ₁₅ (1.737)	1.742	1.757/1.743	C ₄ –C ₃ –H ₇	121.88	121.98/121.90	C ₂ –C ₁ –C ₁₀ –H ₁₁	–59.85	–59.66/–59.67
C ₅ –C ₆ (1.383)	1.386	1.394/1.391	C ₃ –C ₄ –C ₅ (120.1)	121.02	121.07/120.99	C ₂ –C ₁ –C ₁₀ –H ₁₂	59.67	59.50/59.52
C ₅ –H ₈	1.073	1.081/1.083	C ₃ –C ₄ –Cl ₁₅ (124.7)	119.13	119.12/119.15	C ₂ –C ₁ –C ₁₀ –H ₁₃	179.92	179.93/179.93
C ₆ –H ₉	1.075	1.084/1.085	C ₅ –C ₄ –Cl ₁₅ (116.3)	119.83	119.79/119.84	C ₆ –C ₁ –C ₁₀ –H ₁₁	120.14	120.33/120.31
C ₁₀ –H ₁₁	1.085	1.093/1.093	C ₄ –C ₅ –C ₆ (121.6)	118.96	118.98/118.97	C ₆ –C ₁ –C ₁₀ –H ₁₂	–120.32	–120.49/–120.48
C ₁₀ –H ₁₂	1.085	1.093/1.093	C ₄ –C ₅ –H ₈	120.33	120.24/120.18	C ₆ –C ₁ –C ₁₀ –H ₁₃	–0.07	–0.066/–0.072
C ₁₀ –H ₁₃	1.083	1.091/1.093	C ₆ –C ₅ –H ₈	120.70	120.77/120.83	C ₁ –C ₂ –C ₃ –C ₄	0.02	0.005/0.011
–	–	–	C ₁ –C ₆ –C ₅ (117.7)	122.07	122.16/122.23	C ₁ –C ₂ –C ₃ –H ₇	–179.97	–179.99/– 179.98
–	–	–	C ₁ –C ₆ –H ₉	119.04	118.82/118.76	F ₁₄ –C ₂ –C ₃ –C ₄	179.96	179.99/179.98
–	–	–	C ₅ –C ₆ –H ₉	118.88	119.0/119.00	F ₁₄ –C ₂ –C ₃ –C ₇	–0.03	–0.007/–0.0164
–	–	–	C ₁ –C ₁₀ –H ₁₁	111.03	111.27/111.28	C ₂ –C ₃ –C ₄ –C ₅	–0.00	0.0005/0.0004
–	–	–	C ₁ –C ₁₀ –H ₁₂	111.05	111.28/111.29	C ₂ –C ₃ –C ₄ –Cl ₁₅	–179.99	–179.99/–179.9
–	–	–	H ₁ –C ₁₀ –H ₁₃	110.43	110.62/110.64	H ₇ –C ₃ –C ₄ –C ₅	179.99	179.99/179.99
–	–	–	H ₁₁ –C ₁₀ –H ₁₂	107.47	106.95/106.95	H ₇ –C ₃ –C ₄ –Cl ₁₅	0.00	0.002/0.002
–	–	–	H ₁₁ –C ₁₀ –H ₁₃	108.35	108.27/108.24	C ₃ –C ₄ –C ₅ –C ₆	–0.01	–0.009/–0.009
–	–	–	H ₁₂ –C ₁₀ –H ₁₃	108.36	108.28/108.25	C ₃ –C ₄ –C ₅ –H ₈	–179.99	179.99/179.99
–	–	–	–	–	–	Cl ₁₅ –C ₄ –C ₅ –H ₆	179.97	179.99/179.98
–	–	–	–	–	–	Cl ₁₅ –C ₄ –C ₅ –H ₈	–0.001	–0.002/–0.005
–	–	–	–	–	–	C ₄ –C ₅ –C ₆ –C ₁	0.01	0.002/0.008
–	–	–	–	–	–	C ₄ –C ₅ –C ₆ –H ₉	–179.99	–179.99/–179.99
–	–	–	–	–	–	H ₈ –C ₅ –C ₆ –C ₁	179.99	179.99/179.99
–	–	–	–	–	–	H ₈ –C ₅ –C ₆ –H ₉	–0.01	–0.005/–0.006

^a Ref. [32,33].

and 73.65, 68.89 and 69.12 kcal/mol respectively. The comparative optimized structural parameters such as bond lengths, bond angles and dihedral angles are presented in Table 1.

From the theoretical values, it is found 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 [30]. Comparing bond angles and lengths of B3LYP/B3PW91 with those of HF, as a whole the formers are bigger than later and the B3LYP/B3PW91 calculated values correlates well compared with the experimental data. Although the differences, calculated geometrical parameters represent a good approxima-

**Fig. 4.** Comparative graph of IR intensities by HF and DFT (B3LYP/B3PW91).**Fig. 5.** Comparative graph of Raman activities by HF and DFT (B3LYP/B3PW91).



The order of the optimized bond angles as $C_2-C_1-C_6 < C_2-C_3-C_4 < C_4-C_5-C_6 < C_3-C_4-C_5 < C_1-C_2-C_3$. The asymmetry of the benzene ring is also evident from the negative deviation of $C_1-C_2-C_3$, $C_1-C_6-C_5$ and $C_3-C_4-C_5$ and the positive deviation of $C_2-C_1-C_6$, $C_2-C_3-C_4$ and $C_4-C_5-C_6$ from the experimental values. The bond angle of C_1-C_2-F14 is 0.84° (B3LYP/6-311++G (d, p)) squeezed than the bond angle C_3-C_4-Cl15 since the substitution of chlorine and fluorine atom. The comparative graphs of bond lengths, bond angles and dihedral angles of 4Cl2FT for three sets are presented in Figs. 6–8.

Although basis set are marginally sensitive as observed in the HF and DFT values using 6-311++G (d, p), reduction in the computed harmonic vibrational frequencies are noted. With out affecting the basic level of calculations, it is customary to scale down the calcu-



Figure 1 is a scatter plot comparing Computed Frequency (cm⁻¹) on the y-axis versus Observed Frequency (cm⁻¹) on the x-axis. The plot shows three data series: HF/6-311++G(d,p) (squares), B3LYP/6-311++G(d,p) (stars), and B3PW91/6-311++G(d,p) (triangles). All three series show a strong linear correlation, with the HF/6-311++G(d,p) series generally having the highest values and the B3PW91/6-311++G(d,p) series having the lowest values for a given observed frequency.

Fig. 9. Comparative graph of experimental frequency and computed frequency (HF and DFT).

Table 2

Observed and HF/6-311++G (d, p), B3LYP/6-311++G (d, p) and B3PW91/6-311++G (d, p) level calculated vibrational frequencies of 4-chloro-2-fluoro toluene.

S. No.	Symmetry species C_s	Observed frequency		Calculated frequency (cm^{-1}) with HF/6-311++G (d, p)		Calculated frequency (cm^{-1}) with B3LYP/6-311++G (d, p)		Calculated frequency (cm^{-1}) with B3PW91/6-311++G (d, p)		Vibrational assignments
		FTIR	FTRaman	Unscaled value	Scaled value	Unscaled value	Scaled value	Unscaled value	Scaled value	
1	A'	3080vs	3080vs	3374	3066	3216	3061	3226	3064	(C–H) ν
2	A'	3040m	3040w	3366	3059	3206	3052	3216	3055	(C–H) ν
3	A'	2990s	–	3333	3029	3173	3008	3183	2995	(C–H) ν
4	A'	2950s	2950w	3253	2956	3113	2960	3133	2948	(C–H)(CH ₃) ν
5	A'	2930vs	2930m	3232	2937	3084	2932	3104	2920	(C–H)(CH ₃) ν
6	A'	2900w	2900w	3177	2887	3034	2885	3044	2897	(C–H)(CH ₃) ν
7	A'	1610vs	1610w	1798	1634	1645	1608	1662	1608	(C=C) ν
8	A'	1600vs	1600w	1762	1601	1614	1614	1630	1597	(C=C) ν
9	A'	1500vs	–	1653	1502	1517	1517	1524	1493	(C=C) ν
10	A'	1490vs	–	1611	1464	1494	1494	1489	1490	(C–C) ν
11	A'	1460vs	1460w	1600	1454	1482	1449	1474	1474	(C–C) ν
12	A'	1400s	1400w	1553	1411	1430	1398	1436	1407	(C–C) ν
13	A'	1380vs	1380w	1538	1398	1418	1386	1410	1381	(CH ₃) δ
14	A'	1270vs	–	1398	1270	1325	1296	1349	1290	(C–H) δ
15	A'	1240vs	1240vs	1360	1236	1288	1259	1290	1234	(C–H) δ
16	A'	1180vs	1180w	1294	1176	1241	1178	1249	1195	(C–CH ₃) ν
17	A'	1150w	–	1276	1160	1202	1142	1208	1156	(C–H) δ
18	A'	1105w	–	1194	1085	1150	1092	1149	1099	(C–H) δ
19	A'	1050vs	1050w	1174	1067	1089	1034	1095	1048	(C–F) ν
20	A'	1020w	–	1163	1057	1062	1008	1055	1009	(C–H) δ
21	A'	1000vs	–	1084	985	1012	1012	1008	1008	(C–H) δ
22	A''	970w	–	1073	975	955	964	953	962	(C–H) γ
23	A''	910vs	910s	986	896	898	906	905	905	(C–H) γ
24	A''	870vs	–	973	884	871	871	866	866	(C–H) γ
25	A''	810vs	–	917	833	817	817	816	816	(C–H) γ
26	A'	740vs	740s	817	742	768	739	773	739	(C–Cl) ν (C–H) γ
27	A'	690vs	690vs	790	718	713	686	714	683	(CCC) δ
28	A'	660w	–	705	640	658	658	663	663	(CCC) δ
29	A'	580vs	–	663	602	597	597	600	574	(CCC) δ
30	A'	480w	480w	600	545	557	447	558	479	(C–CH ₃) δ
31	A''	470vs	470vs	505	459	468	468	469	469	(CCC) γ
32	A''	450s	–	505	459	460	460	459	459	(CCC) γ
33	A''	–	420m	405	368	377	418	380	418	(CCC) γ
34	A'	–	340m	347	315	312	346	314	345	(C–F) δ
35	A'	–	310w	296	269	275	305	273	300	(C–Cl) δ
36	A''	–	250w	256	232	238	264	240	264	(C–CH ₃) γ
37	A''	–	210m	242	220	217	217	218	239	(C–F) γ
38	A''	–	150w	131	119	118	131	119	130	(C–Cl) γ
39	A''	–	140w	105	95	94	104	93	102	(CH ₃) τ

vs, very strong; s, strong; m, medium; w, weak; as, asymmetric; s, symmetric; ν , stretching; δ , in plane bending; γ , out plane bending; τ , twisting.

4.2.1. Computed IR intensity and Raman activity analysis

Computed vibrational spectral IR intensities and Raman activities of the 4Cl2FT for corresponding wave numbers by HF and DFT methods with B3LYP/B3PW91 at 6-311++G (d, p) basis sets are given in Table 3. Comparison of IR intensity and Raman activity calculated by HF and DFT with B3LYP/B3PW91 at 6-311++G (d, p) methods with experimental values shows the variation of IR intensities and Raman activities. In the case of IR intensity, the values of HF are found to be higher than B3LYP/B3PW91 at 6-311++G (d, p) levels whereas in the case of Raman activity the effect is reversed. The similar effect was also noticed in the earlier paper [32].

4.2.2. Computed vibrational frequency analysis

The comparative graph of calculated vibrational frequencies by HF and DFT methods B3LYP/B3PW91/6-311++G (d, p) basis sets for the 4Cl2FT are given in Fig. 9. From the figure, it is found that the calculated (unscaled) frequencies by B3LYP/B3PW91/with 6-311++G (d, p) basis sets are closer to the experimental frequencies. This observation is in line with our earlier work [33]. The standard deviation (SD) calculation made between experimental and computed frequencies DFT for the 4Cl2FT is presented in Table 4. According

to the SD, the computed frequency deviation decreases in going from HF to B3PW91/6-311++G (d, p) to B3LYP/6-311++G (d, p). The deviation ratio between HF/6-311++G (d, p) and B3LYP/6-311++G (d, p) is 2.64, HF/6-311++G (d, p) and B3PW91/6-311++G (d, p) is 2.45. It is also observed that the calculated frequencies by B3LYP/6-311++G (d, p) basis sets are closer to the experimental frequencies than B3PW91/6-311++G (d, p) basis sets in DFT method.

4.2.3. C–H vibrations

Normally, aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 cm^{-1} due to aromatic C–H stretching vibrations [34–37]. In halogen, dihalogen and trihalogen derivatives, the C–H stretching shifts to asymmetrical range due to inductive effect of halogen atom [38–40]. Greater the electro negativity of the halogen atom greater is the value of the C–H stretching. The 4Cl2FT possesses Cl and F in which the C–H stretching observed at 3080, 3040 and 2990 cm^{-1} . These assignments are in line with the literature. First two of the assigned frequencies have been found at asymmetrical range and last one slightly deviated down from the expected range. Thus, the inductive effect has been partially observed in the present molecule. All the computed

Table 3
Comparative values of IR intensity and Raman Activity between HF/6-311++G (d, p), B3LYP/6-311++G (d, p) and B3PW91/6-311++G (d, p) of 4-chloro-2-fluoro toluene.

S. No.	Calculated with HF/6-311++G (d, p)			Calculated with B3LYP/6-311++G (d, p)			Calculated with B3PW91/6-311++G (d, p)		
	Scaled frequency	IR intensity (Ai)	Raman activity (I)	Scaled frequency	IR intensity (Ai)	Raman activity (I)	Scaled frequency	IR intensity (Ai)	Raman activity (I)
1	3066	0.35	79.90	3061	0.67	90.54	3064	0.75	89.22
2	3059	2.53	93.50	3052	1.21	101.32	3055	0.95	101.85
3	3029	9.32	70.09	3008	7.32	84.59	2995	6.64	81.69
4	2956	20.72	60.72	2960	13.54	63.60	2948	11.67	63.31
5	2937	19.02	83.82	2932	11.44	95.59	2920	9.52	92.74
6	2887	32.05	209.91	2885	23.51	273.92	2897	21.97	273.81
7	1634	46.80	36.51	1608	34.84	41.80	1608	36.16	43.96
8	1601	53.16	4.71	1614	43.16	4.71	1597	45.34	4.19
9	1502	122.43	1.07	1517	117.84	1.25	1493	129.14	1.37
10	1464	8.46	6.13	1494	8.79	7.55	1490	11.13	7.01
11	1454	6.82	9.44	1449	7.73	9.53	1474	8.41	9.56
12	1411	23.18	3.55	1398	19.12	4.68	1407	20.07	2.81
13	1398	8.90	4.61	1386	4.61	14.59	1381	2.34	17.98
14	1270	8.75	5.24	1296	0.20	1.49	1290	1.61	1.32
15	1236	52.26	13.87	1259	15.30	8.63	1234	21.22	13.11
16	1176	5.69	0.60	1178	31.06	17.76	1195	24.36	13.80
17	1160	15.04	0.36	1142	18.97	0.47	1156	17.77	0.47
18	1085	12.09	4.17	1092	23.55	0.56	1099	19.90	0.57
19	1067	22.81	10.28	1034	23.14	17.08	1048	25.23	16.30
20	1057	0.94	0.01	1008	1.81	0.02	1009	2.32	0.02
21	985	21.24	1.60	1012	24.71	1.50	1008	25.12	1.30
22	975	0.31	0.04	964	0.40	0.03	962	0.44	0.02
23	896	29.75	0.02	906	77.68	2.07	905	72.35	2.33
24	884	77.31	4.27	871	24.88	0.03	866	25.49	0.04
25	833	32.47	0.31	817	27.03	0.06	816	27.54	0.06
26	742	2.92	26.71	739	5.42	22.86	739	4.99	22.81
27	718	0.79	0.28	686	0.41	0.14	683	0.36	0.09
28	640	9.07	2.19	658	10.94	2.20	663	9.53	2.43
29	602	7.71	0.40	597	5.72	0.35	574	5.66	0.41
30	545	5.82	4.96	447	5.23	5.16	479	4.53	5.20
31	459	1.31	0.51	468	0.91	0.45	469	0.83	0.52
32	459	6.73	0.23	460	6.00	0.11	459	6.41	0.12
33	368	5.20	10.97	418	5.53	9.62	418	4.83	8.65
34	315	1.14	1.33	346	1.01	1.17	345	1.16	1.07
35	269	2.45	0.28	305	2.13	0.48	300	2.12	0.51
36	232	0.31	0.47	264	0.28	0.60	264	0.25	0.59
37	220	0.34	1.48	217	0.27	1.58	239	0.20	1.58
38	119	0.16	0.15	131	0.16	0.15	130	0.19	0.17
39	95	0.18	0.33	104	0.22	0.61	102	0.25	0.60

bands for C–H vibrations by B3LYP/6-311++G (d, p) and B3PW91/6-311++G (d, p) methods shows excellent agreement with recorded spectrum as well as literature data.

The C–H in-plane and out-of-plane bending vibrations generally lies in the range 1000–1300 cm^{−1} and 950–800 cm^{−1} [41–43] respectively. In the present case, four bands are assigned to C–H in-plane bending vibrations of 4Cl2FT, identified at 1270, 1240 and 1150 cm^{−1}. The four C–H out-of-plane bending vibrations are observed at 970, 910 and 870 cm^{−1}. According to the literature, the in-plane and out-of-plane bending vibrational frequencies are found to be well within their characteristic region. The first band for C–H out-of-plane bending, the computed frequency by B3LYP/6-311++G (d, p) method being scaled up by 1.01(906 cm^{−1}) is nearly coincides with FT-IR experimental value (910 cm^{−1}) whereas in

B3PW91/6-311++G (d, p) the frequency (with out scaling (905)) is nearly coincides with same value.

4.2.4. Methyl group vibrations

The 4Cl2FT possesses only one CH₃ group in the ring. The C–H methyl group stretching vibrations are highly localized and generally observed in the range 3000–2900 cm^{−1} [44,45]. In the present investigation, the bands with sharp peaks are found at 2950, 2930 and 2900 cm^{−1} for the CH₃ stretching vibrations of methyl group. These observations agree well with the earlier work [46,47]. The C–H in-plane bending vibrations are observed at 1105, 1020 and 1000 cm^{−1}. The C–H out-of-plane bending vibrations are found at 810 and 740 cm^{−1}. These frequencies are in good agreement with those found in the characteristic group frequency table [48,49]. The

Table 4
Standard deviation of frequencies computed by HF/DFT (B3LYP/B3PW91) at 6-311++G (d, p) basis sets.

S. No.	Basic set levels	Total values	Average	Standard deviation average	Deviation ratio
1	Experimental	46,795	1227.7		
2	HF/6-311++(d, p)	51,509	1320.7	88.47	2.64
3	B3LYP/6-311++(d, p)	48,188	1235.5	33.48	
3	B3PW91/6-311++(d, p)	48,347	1239.6	36.08	2.45

theoretically computed value by B3LYP/B3PW91/6-311++G (d, p) method for C–H in-plane bending (with out scaling) is nearly coincides with FTIR experimental value.

In this investigation, the symmetrical methyl deformation (CH_3) δ found at 1380 cm^{-1} . This assignment authenticated by the literature [50,51]. This observed frequency lies in the symmetrical region which is purely due to the attraction of halogen in the ring. A strong IR band for C– CH_3 stretching vibration is identified at 1180 cm^{-1} . This assignment supported by the literature [52]. The bands at 480 and 250 cm^{-1} observed for C– CH_3 in-plane and out-of-plane bending vibrations respectively. According to the literature [53], the out-of-plane bending vibration slightly deviated down which is due to the influence of Cl atom.

4.2.5. C–C vibrations

Most of the computed frequencies by B3LYP/6-311++G (d, p) method are assigned for C=C and C–C stretching vibrations almost coincides with experimental without scaling. The bands between 1400 and 1650 cm^{-1} in benzene derivatives are usually assigned to C=C and C–C stretching modes [54]. In 4Cl2FT, the C=C stretching vibrations are found at 1610, 1600 and 1500 cm^{-1} and the C–C stretching vibrations are assigned at 1490, 1460 and 1400 cm^{-1} . These assignments are in line with the literature. These vibrational positions are not so much affected by the nature of the substituents attached with the ring. The CCC in-plane bending vibrations observed at 690, 660 and 580 cm^{-1} and the out-of-plane bending vibrations appeared at 470, 450 and 420 cm^{-1} . These assignments are in good agreement with the literature [55,56], which also indicate that the substitutions do not affect much the vibrations of these modes. With no scaling, computed value for CCC out-of-plane bending vibration by B3LYP/6-311++G (d, p) and B3PW91/6-311++G (d, p) methods nearly coincides with experimentally observed values.

4.2.6. C–Cl vibrations

The strong characteristic absorptions due to the C–X stretching vibrations are to be observed [57–60], with the position of the band being influenced by neighboring atoms or groups—the smaller the halide atom, the greater the influence of the neighbor. Bands of weak to medium intensity are also observed due to overtones of the C–X stretching vibrations. In Raman spectra, the vibration bands result in strong bands for Cl, Br and I atoms, but for F the bands are weaker. According to these early reports [61–63], the C–Cl stretching vibrations offer generally strong bands in the region $760\text{--}505\text{ cm}^{-1}$. Compounds with more than one chlorine atom exhibit very strong bands due asymmetric and symmetric modes. In compliance with above observation, a very strong band is present at 740 cm^{-1} for C–Cl stretching in 4Cl2FT.

The C–Cl in-plane and out-of-plane vibrations are assigned in the literature [64] at 321 and 260 cm^{-1} respectively. In the title molecule, two peaks observed at 310 and 150 cm^{-1} for C–Cl in-plane and out-of-plane bending respectively. The assignment of C–Cl in-plane bending is in line with the literature values whereas the assigned value of out-of-plane bending is deviated much and may be due to the proximity of methyl group. After scaled up (1.10) computed values for C–Cl in-plane and out-of-plane bending vibrations by B3LYP/6-311++G (d, p) and B3PW91/6-311++G (d, p) methods nearly coincides with experimental values.

4.2.7. C–F vibrations

Assignments of the C–F stretching modes are very difficult as these vibrations are strongly coupled with the other in plane bending vibrations of several modes. Normally [65–67], the observed bands of the C–F stretching vibrations have been found to be very strong in the FTIR spectra and these appear in the range $1000\text{--}1300\text{ cm}^{-1}$ for several fluoro-benzenes. And also the C–F

stretching vibrations strongly coupled with the C–H in-plane bending vibrations in the mono fluorinated benzene and is observed in the region $1100\text{--}1000\text{ cm}^{-1}$ [68]. The present molecule has one fluorine atom which is placed at para-position of the skeletal ring. The corresponding C–F stretching vibration observed at 1050 cm^{-1} . This assigned frequency is at the lower region of the expected range which implies that C–F vibration is favored in the presence of methyl group and Cl atom.

The C–F in-plane bending vibration mode for the mono fluorinated benzene normally assigned at $250\text{--}350\text{ cm}^{-1}$ [69–71]. In the present case, a band assigned to C–F in-plane bending at 340 cm^{-1} . This view supported by the above literature. The frequency of the C–F out-of-plane bending vibration assigned at 200 cm^{-1} . According to the reported values [72], this assignment is in line with the literature. The C–F in-plane bending is observed to be enhanced by the substitution, though the same has suppressed the stretching.

5. Conclusion

Based on the ab initio HF calculations at HF/6-311++G (d, p) and DFT with B3LYP/B3PW91/6-311++G (d, p) levels, complete vibrational properties of 4-chloro-2-fluoro toluene have been investigated by FT-IR and FT-Raman spectroscopies. The assignments of the fundamental frequencies are confirmed by the qualitative agreement between the calculated and observed frequencies. The optimized structural parameter such as bond length, bond angle and dihedral angles are also calculated and are compared among HF and DFT (B3LYP/B3PW91) methods. The vibrational frequencies made by quantum mechanical calculation of B3LYP/B3PW91 methods agree satisfactorily with FT-IR and FT-Raman experimental results. Assignments of all the fundamental vibrational modes were examined and proposed in this investigation and also the comparison with the literature support the validity of the background theory. From the discussion, it is clear that the substitution of CH_3 , Cl and F atoms distorts the ring geometry and their own modes to small extent.

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