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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.

## 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 sugges 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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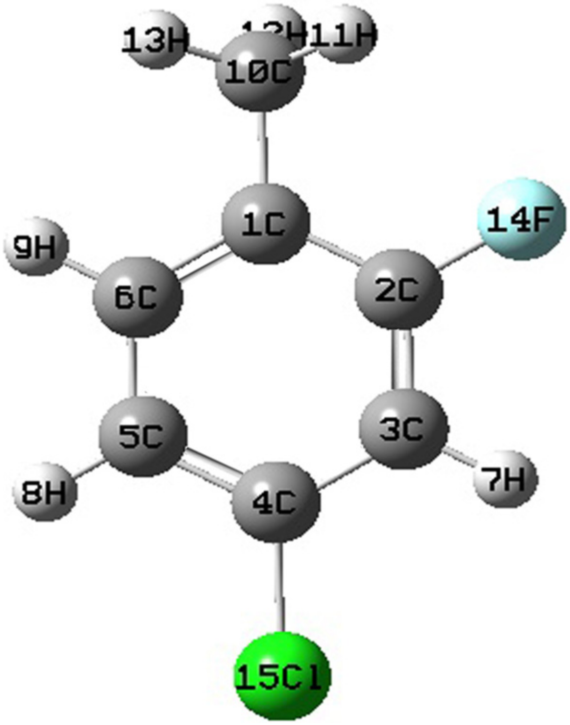

**Fig. 1.** Molecular structure of 4-chloro-2-fluoro toluene.

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 $\mathrm{cm}^{-1}$. The spectral resolution is ±2 $\mathrm{cm}^{-1}$. 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 $\mathrm{cm}^{-1}$ with scanning speed of 30 $\mathrm{cm}^{-1}\,\mathrm{min}^{-1}$ of spectral width 2 $\mathrm{cm}^{-1}$. The frequencies of all sharp bands are accurate to ±1 $\mathrm{cm}^{-1}$. 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 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.

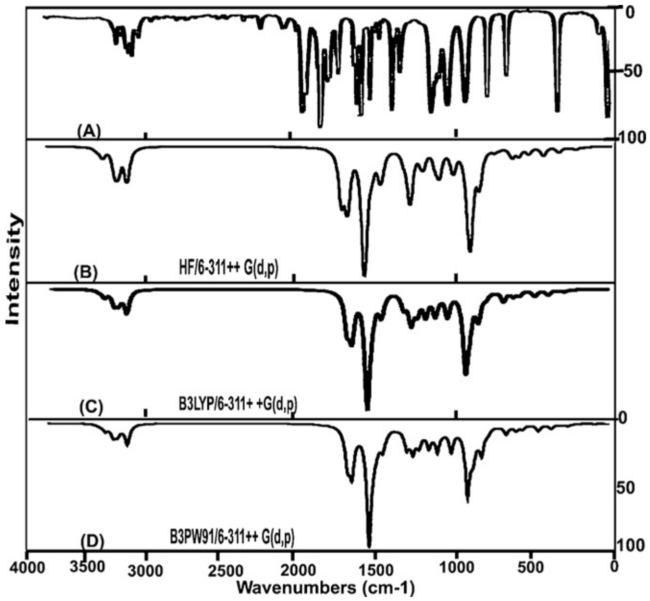

**Fig. 2.** Experimental (A), calculated (B), (C and D) FTIR spectra of 4-chloro-2-fluorotoluene.

## 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 GAUSSAN 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 J/mol

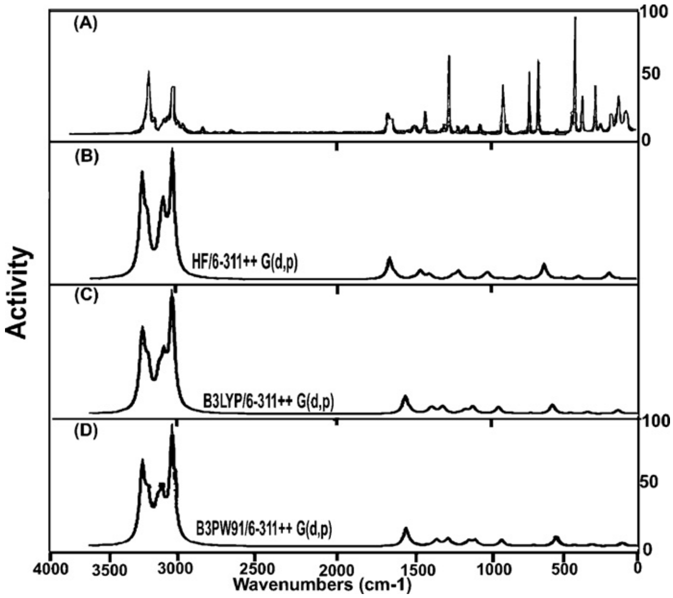

**Fig. 3.** Experimental (A), calculated (B), (C and D) FTRaman spectra of 4-chloro-2-fluorotoluene.