Spectrochimica Acta Part A 78 (2011) 1321–1328

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# Vibrational spectroscopic (FTIR and FTRaman) investigation using ab initio (HF) and DFT (LSDA and B3LYP) analysis on the structure of Toluic acid

P. David Suresh Babu[a,*], S. Periandy[b], S. Ramalingam[c]

[a] Wyckoff Junior College, Muttathur, Villupuram, Tamilnadu, India
[b] Department of Physics, Tagore Arts College, Puduchery, India
[c] Department of Physics, A.V.C. College, Mayiladuthurai, Tamilnadu, India

ARTICLE INFO

*Article history:*
Received 19 November 2010
Accepted 5 January 2011

*Keywords:*
Toluic acid
LSDA and B3LYP
IR intensities
Raman activities
Benzoic acid and methyl substitutions

ABSTRACT

The FTRaman and FTIR spectra for Toluic acid (TA) have been recorded in the region 4000–100 $cm^{-1}$ and compared with the harmonic vibrational frequencies calculated using HF/DFT (LSDA and B3LYP) method BY employing 6-311G (d, p) basis set with appropriate scale factors. IR intensities and Raman activities are also calculated by HF and DFT (LSDA/B3LYP) methods. Optimized geometries of the molecule have been interpreted and compared with the reported experimental values for benzoic acid and some substituted benzoic acids. The experimental geometrical parameters show satisfactory agreement with the theoretical prediction from HF and DFT. The scaled vibrational frequencies at B3LYP/6-311G (d, p) seem to coincide with the experimentally observed values with acceptable deviations. The theoretical spectrograms (IR and Raman) have been constructed and compared with the experimental FT-IR and FT-Raman spectra. Some of the vibrational frequencies of the TA are effected upon profusely with the methyl substitutions in comparison to benzoic acid and these differences are interpreted.



## 1. Introduction

Human beings have been experiencing pain for centuries. Commonly used non steroidal anti-inflammatory drugs on the market show some side effects to a certain extent, including gastrointestinal disorders, kidney damage and hematological toxicities. Therefore, the design of new active anti-inflammatory compounds have attracted the attention of medicinal chemists. As a result, there are many heterocyclic compounds have been investigated for anti-inflammatory activity and suppressing side effects by these drugs is a challenge for many years [1,2]. A recent patent reported that benzoic acid derivatives have good anti-tumor properties and their activity being related to novel synergistic compositions that selectively control tumor tissue [3].

Derivatives of benzoic acid have been the subject of investigation for many reasons. A derivative of benzoic acid is an essential component of the Vitamin B complex. Benzoic acid occurs widely in plants and animals tissues along with Vitamin B complex and is used in miticides, contrast media in urology, cholocystrographic examinations and in the manufacture of pharmaceuticals.

Toluic acid (TA) is used as an intermediate for polymer stabilizers, pesticides, light sensitive compounds, animal feed supplements and other pharmaceuticals, pigments and dyestuff. There are almost infinite esters obtained from thousands of potential starting materials. Esters are formed by removal of water from an acid and an alcohol, e.g., carboxylic acid esters, phosphoric acid esters, and sulfonic acid esters. Carboxylic acid esters are used as in a variety of direct and indirect applications.

Lower chain esters are used as flavoring base materials, plasticizers, solvent carriers and coupling agents. Higher chain compounds are used as components in metalworking fluids, surfactants, lubricants, detergents, oiling agents, emulsifiers, wetting agents textile treatments and emollients. They are also used as intermediates for the manufacture of a variety of target compounds. Because of its wide applications, the surface enhanced Raman scattering studies [4], vibrational spectra of benzoic acid [5] and methyl derivatives have been extensively investigated.

Mohan and Arul Dhass [6] have recorded the Fourier transform infrared and laser Raman spectra of para-chlorobenzoic acid in the regions of 200–4000 and 30–4000 $cm^{-1}$, respectively. Richards and Xin [7] investigated the antibacterial activity of 4-amino benzoic acid and its effect on bacterial DNA synthesis. Recently, Chaman and Verma [8] have recorded laser Raman and FT-IR spectra of 2,3,5-tri-iodobenzoic acid. Recently, Swaminathan et al. [9] have recorded the FTIR and FTRaman spectra of 2-Bromobenzoic acid and Sundaraganesan et al. [10] have recorded the FT-IR and FT-Raman spectra of 5-amino-2-chlorobenzoic acid and methyl benzoate.

* Corresponding author. Tel.: +91 9443800764; fax: +91 9443800764; mobile: +91 9443800764.
*E-mail address:* davidsureshbabu@yahoo.com (P.D.S. Babu).

1386-1425/$ – see front matter. 
doi:10.1016/j.saa.2011.01.008

Literature survey reveals that to the best of our knowledge no ab initio HF/DFT with 6-311G (d, p) basis sets calculations of TA have been reported so far. Therefore, an attempt has been made in the present work to study the detailed theoretical (HF/DFT) and experimental (FTIR and FTRaman) investigation of the vibrational spectra of TA. In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performances of the computational methods for ab initio (HF) and hybrid density functional methods (B3LYP and LSDA) at 6-311G (d, p) basis sets are 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. In DFT methods, local-spin density approximation LSDA [11–14] generally gives good molecular structures, vibrational frequencies and charge densities in strong bound systems [15–17] and Becke's three parameter hybrids functional combined with the Lee–Yang–Parr correlation functional (B3LYP) predict best results for molecular geometry and vibrational wave numbers for moderately larger molecule [18,19].

## 2. Experimental details

The compound under investigation namely TA 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 FTIR spectra of the compounds are recorded in Bruker IFS 66V spectrometer in the range of 4000–100 $cm^{-1}$. The spectral resolution is $\pm 2\ cm^{-1}$. The FTRaman spectra of these compounds are 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 $cm^{-1}$ $min^{-1}$ of spectral width 2 $cm^{-1}$. The frequencies of all sharp bands are accurate to $\pm 1\ cm^{-1}$.

## 3. Computational methods

The molecular structure of the TA in the ground state is computed by performing both ab initio-HF and DFT (LSDA and B3LYP) with 6-311G (d, p) basis sets. The optimized structural parameters are used in the vibrational frequency calculations in HF and DFT methods. The minimum energy of geometrical structure is obtained by using level 6-311G (d, p) basis sets. The calculated frequencies are scaled by 0.904, 0.778 and 0.852 for HF/6-311G (d, p) [20,21]. For LSDA with 6-311G (d, p) set is scaled with 0.820, 0.920, 0.889, 1.02and 1.07 and B3LYP/6-311G (d, p) basis set is scaled with 0.945, 0.926, 0.900, 0.892, 1.047, and 0.960 [22]. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of the title molecule [23]. HF/DFT calculations for TA are performed using GAUSSIAN 03 W program package on Pentium IV processor personal computer without any constraint on the geometry [24–27].

## 4. Results and discussion

### 4.1. Molecular geometry

The molecular structure of the TA 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 COOH and $CH_3$ connected with benzene ring. The structure optimization

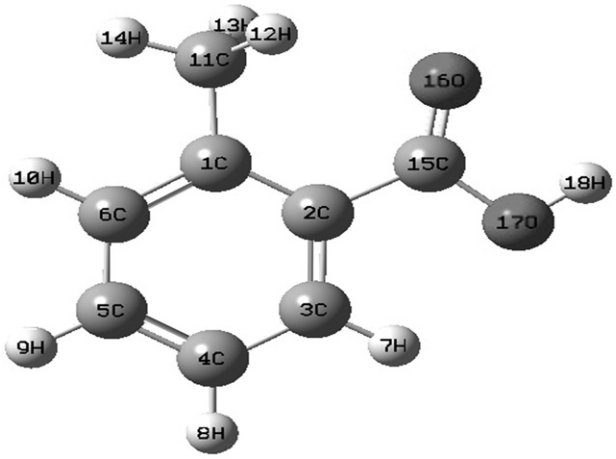


**Fig. 1.** Molecular structure of Toluic acid.

zero point vibrational energy of the title compound in HF/6-311G (d, p), LSDA/6-311G (d, p) and B3LYP/6-311G (d, p) are −402312.3, −359361.0 and −369592.3 J/mol and 96.15, 85.88 and 88.33 kcal/mol, respectively. The experimental and calculated FTIR spectra of TA are given in Fig. 2. Fig. 3 represents the observed and calculated FTR spectra of TA. The comparison plot of IR intensities by HF/DFLT is presented in Fig. 4. Raman activity for TA by HF/DFLT is given in Fig. 5.

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 belonging to isolated molecules in gaseous phase while the experimental results belong to molecules in solid state [28]. Comparing bond angles and lengths of LSDA/B3LYP with those of HF, as a whole the former is larger than later while LSDA/B3LYP calculated values correlates well compared with the experimental data. The calculated geometrical parameters represent a good approximation and they are the bases for the calculating other parameters, such as vibrational frequencies and thermodynamics properties. The comparative graphs of bond lengths, bond angles and dihedral angles of TA for four sets are presented in Figs. 6–8, respectively.

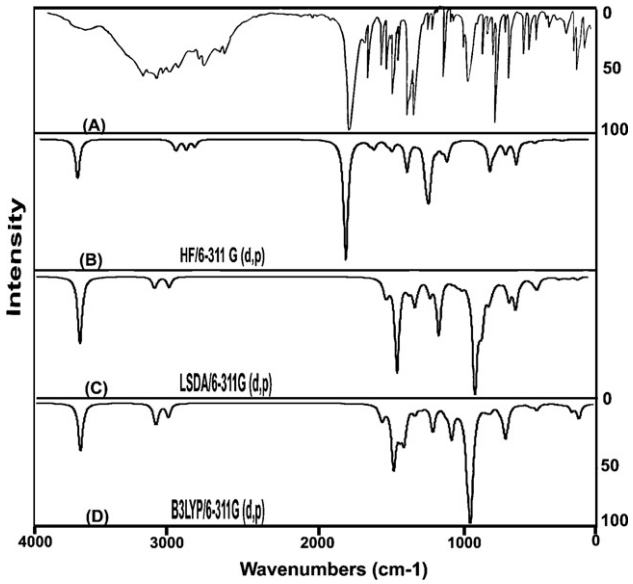


**Fig. 2.** Experimental (A), calculate (B), (C) and (D) FTIR spectra of Toluic acid.