



Structural, vibrational spectroscopic studies and quantum chemical calculations of 4-fluoro-3-methylphenol

S. Jeyavijayan¹ and J. Senthil Kumar²

¹Department of Physics, Kalasalingam University, Anand Nagar, Krishnankoil, Tamil Nadu, India

²PG & Research Department of Physics, Periyar EVR College, Tiruchirappalli, India

ABSTRACT

The FTIR and FT-Raman vibrational spectra of 4-fluoro-3-methylphenol (FMP) have been recorded in the regions 4000-400 cm^{-1} and 4000-50 cm^{-1} , respectively. The complete vibrational fundamental modes of the compound using the experimental FTIR and FT-Raman data have been analyzed on the basis of peak positions, relative intensities and quantum chemical studies. In the calculations performed to determine the optimum molecular geometry, harmonic vibrational frequencies, infrared intensities and Raman scattering activities, *ab initio* Hartree-Fock (HF) and Density functional theory (DFT/B3LYP) methods with 6-311++G(d,p) basis sets were used. The difference between the observed and scaled wavenumber values of most of the vibrational modes is very small. The normal modes are assigned with the help of total energy distribution (TED) analysis. Non-linear optical (NLO) behavior of FMP was investigated by determining of electric dipole moment, polarizability, and hyperpolarizability. The effects of frontier orbitals, HOMO and LUMO, transition of electron density transfer have been discussed. Decrease in HOMO and LUMO energy gap, explains the eventual charge transfer within the molecule which is responsible for the chemical reactivity of the molecule. Besides, Mulliken's charges analysis, and several thermodynamic properties were performed.

Keywords: FTIR, FT-Raman, DFT calculations, 4-fluoro-3-methylphenol, HOMO-LUMO

INTRODUCTION

Phenol derivatives are interesting molecules for theoretical studies due to their relatively small size and similarity to biological species. Phenol is also a versatile precursor to a large collection of drugs, most notably aspirin but also many herbicides and pharmaceuticals. It is used in the preparation of cosmetics including sunscreens, hair dyes and skin lightening preparations. Unlike normal alcohols, phenols are acidic because of the influence of the aromatic ring [1]. Phenol and its vapours are corrosive to the eyes, the skin and the respiratory tract. In recent years, phenol and substituted phenol have been the frequent subjects of experimental and theoretical work because of their significance in industry and environment. Evans [2] has extensively studied the vibrational assignments of infrared spectrum of phenol. Jianhan Huang *et al.* [3] have elucidated halogen effect and isotope effect of Chloro Phenol and Gui-xiangWang *et al.* [4] have obtained the vibrational analysis on nitro phenols. More recently, the vibrational spectroscopy investigation using *ab initio* (HF) and DFT (B3LYP) calculations on the structure of 3-bromo phenol have been studied by Mahadevan *et al* [5]. During the course of investigation on the samples of biological and pharmaceutical active compounds, our attention has been turned towards 4-fluoro-3-methylphenol (FMP). It is one of the most important organic intermediates, are widely used for the manufacture of pesticides, rubber, drugs, varnishes and dyestuffs. The assignment of the vibrational frequencies for substituted phenols becomes complicated problem because of the superposition of several vibrations due to fundamentals and due to substituents. However, a

comparison of the spectra with that of the parent compound gives some definite clues about the nature of the molecular vibrations.

Literature survey reveals that to the best of our knowledge, no *ab initio* / DFT frequency calculations for 4-fluoro-3-methylphenol have been reported so far. Therefore, the present investigation was undertaken to study the vibrational spectra of the molecule completely and to identify the various normal modes with greater wave numbers accurately. *Ab initio* (HF) and density functional theory (DFT) calculations have been performed to support our wave number assignments.

MATERIALS AND METHODS

The pure sample of FMP obtained from Lancaster chemical company, UK and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of the title compound is recorded in the region 4000-400 cm^{-1} , at a resolution of $\pm 1 \text{ cm}^{-1}$ using BRUKER IFS 66V model FTIR spectrometer equipped with an MCT detector, a KBr beam splitter and global source.

The FT-Raman spectrum of FMP is recorded on a computer interfaced BRUKER IFS 66V model interferometer equipped with FRA-106 FT-Raman accessories. The spectrum was measured in the Stokes region 4000-50 cm^{-1} using Nd: YAG laser operating at 200 mW power continuously with 1064 nm excitation. The reported wave numbers are expected to be accurate within $\pm 1 \text{ cm}^{-1}$.

Computational details

In order to provide information with regard to the structural characteristics and the normal vibrational modes of FMP, the *ab initio* HF and DFT-B3LYP correlation functional calculations have been carried out. The molecular geometry optimizations, energy and vibrational frequency calculations were carried out for FMP with the GAUSSIAN 09W software package [6]. Initial geometry generated from the standard geometrical parameters was minimized without any constraint on the potential energy surface at Hartree-Fock level adopting the standard 6-311++G(d,p) basis set. This geometry was then re-optimized again at DFT level employing the Becke 3LYP keyword, which invokes Becke's three-parameter hybrid method [7] using the correlation function of Lee *et al.* [8], implemented with the same basis set for better description of the bonding properties of methyl group. The multiple scaling of the force constants were performed according to SQM procedure [9,10] using selective scaling in the natural internal coordinate representation [11,12]. The transformation of force field, subsequent normal coordinate analysis and calculation of the TED were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [13,14]. By the use of GAUSSVIEW molecular visualization program [15] along with available related molecules, the vibrational frequency assignments were made by their TED with a high degree of confidence. The TED elements provide a measure of each internal coordinate's contributions to the normal coordinate.

RESULTS AND DISCUSSION

Molecular geometry

The optimized molecular structure of FMP is shown in Fig. 1. The global minimum energy obtained by the HF and DFT structure optimization for FMP are calculated as -443.5658 and -446.1541 Hartrees from 6-311++G(d,p) basis set, respectively. The optimization geometrical parameters of FMP are listed in the Table 1. From the structural data given in Table 1, it is observed that the geometrical parameters are found to be almost same at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. However, the B3LYP/6-311++G(d,p) level of theory, in general slightly over estimates bond lengths but it yields bond angles in excellent agreement with the HF method. According to the calculation (B3LYP/6-311++(d,p)), the order of the bond length is C4-C5 < C5-C6 = C3-C4 < C6-C1 < C1-C2 < C2-C3. From the order of the bond length, it is clear that the hexagonal structure of the benzene ring slightly distorted. This can be due to the influence of conjugation between the substituents and the ring. The ring carbon atoms in substituted benzenes exerts a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C-H force constants and a decrease in the corresponding bond length. It is evident from the C-H bond lengths in FMP vary from 1.085 to 1.074 Å and from 1.093 to 1.082 Å by HF and B3LYP methods, respectively. The benzene ring appears to be a little distorted because of the fluorine atom and methyl group substitutions as seen from the bond angles C3-C4-F14 and C2-C3-C4, which are calculated as 118.395° and 116.801°, respectively, by B3LYP method and are differ from their typical hexagonal angle of 120°.

Vibrational assignments

From the structural point of view the molecule is assumed to have C_1 point group symmetry and hence, all the calculated frequency transforming to the same symmetry species (A). The molecule consists of 16 atoms and expected to have 42 normal modes of vibrations. All the vibrations are active both in the Raman scattering and infrared absorption. The detailed vibrational assignment of fundamental modes of FMP along with the calculated IR

and Raman frequencies and normal mode descriptions (characterized by TED) are reported in Table 2. For visual comparison, the observed and calculated FTIR and FT-Raman spectra of FMP at the HF and B3LYP levels using 6-311++G(d,p) basis set are shown in Figs. 2 and 3, respectively.

Table 1 Optimized geometrical parameters of 4-fluoro-3-methylphenol obtained by HF and B3LYP with 6-311++G(d,p) basis set

Bond length	Value(Å)		Bond Angle	Value (°)		Dihedral Angle	Value (°)	
	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)		HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)		HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)
C1-C2	1.385	1.395	C1-C2-C3	121.295	121.359	C6-C1-C2-C3	0.00	0.00
C2-C3	1.390	1.398	C2-C3-C4	117.135	116.801	C6-C1-C2-C9	180.00	-179.99
C3-C4	1.380	1.391	C3-C4-C5	122.597	122.981	O7-C1-C2-C3	180.00	-179.99
C4-C5	1.375	1.384	C4-C5-C6	119.552	119.338	O7-C1-C2-H9	0.00	0.00
C5-C6	1.382	1.391	C5-C6-C1	119.364	119.353	C2-C1-C6-C5	0.00	0.00
C6-C1	1.384	1.393	C6-C1-C2	120.056	120.166	C2-C1-C6-H16	180.00	-179.99
C1-O7	1.353	1.371	C2-C1-O7	122.328	122.454	O7-C1-C6-C5	180.00	-179.99
O7-H8	0.940	0.962	C1-O7-H8	111.178	109.829	O7-C1-C6-H16	0.00	0.00
C2-H9	1.077	1.086	C1-C2-H9	119.643	119.711	C2-C1-O7-H8	-0.00	0.01
C3-C10	1.508	1.506	C3-C2-H9	119.062	118.929	C6-C1-O7-H8	-180.00	-179.98
C4-F14	1.336	1.363	C2-C3-C10	122.038	122.203	C1-C2-C3-C4	0.00	-0.00
C5-H15	1.085	1.083	C4-C3-C10	120.826	120.994	C1-C2-C3-C10	-180.00	179.99
C6-H16	1.083	1.082	C3-C10-H11	110.880	111.159	H9-C2-C3-C4	-180.00	179.99
C10-H11	1.085	1.093	C3-C10-H12	110.880	110.850	H9-C2-C3-C10	0.00	-0.00
C10-H12	1.074	1.091	C3-C10-H13	110.710	111.161	C2-C3-C4-C5	0.00	0.00
C10-H13	1.074	1.093	H12-C10-H13	108.419	108.312	C2-C3-C4-F14	180.00	-179.99
			H12-C10-H11	107.419	108.310	C10-C3-C4-C5	180.00	-179.99
			H11-C10-H13	108.419	106.897	C10-C3-C4-F14	0.00	0.00
			C3-C4-F14	118.669	118.395	C2-C3-C10-H11	120.38	-120.48
			C5-C4-F14	118.734	118.623	C2-C3-C10-H12	-120.38	0.034
			C4-C5-H15	119.391	119.473	C2-C3-C10-H13	0.00	120.56
			C6-C5-H15	121.057	121.187	C4-C3-C10-H11	-59.61	59.51
			C5-C6-H16	121.102	121.165	C4-C3-C10-H12	59.61	-179.96
			C1-C6-H16	119.534	119.481	C4-C3-C10-H13	180.00	-59.43
			C6-C1-O7	117.616	117.378	C3-C4-C5-C6	0.00	0.00
						C3-C4-C5-H15	180.00	179.99
						F14-C4-C5-C6	180.00	-180.00
						F14-C4-C5-H15	0.00	-0.00
						C4-C5-C6-C1	0.00	-0.00
						C4-C5-C6-H16	180.00	179.99
						H15-C5-C6-C1	-180.00	179.99
						H15-C5-C6-H16	0.00	-0.00

For numbering of atoms refer Fig. 1

The main focus of the present investigation is the proper assignment of the experimental frequencies to the various vibrational modes of FMP in correlation with the calculated harmonic vibrational frequencies at HF and B3LYP levels using the standard 6-311++G(d,p) basis set. Comparison of the frequencies calculated by HF and B3LYP methods with the experimental values reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. The results indicate that the B3LYP/6-311++G(d,p) calculations approximate the observed fundamental frequencies much better than the HF/6-311++G(d,p) results.

The vibrational analysis obtained for FMP with the unscaled HF and B3LYP force field is generally somewhat greater than the experimental values. These discrepancies can be corrected either by computing anharmonic corrections explicitly or by introducing a scaled field or directly scaling the calculated wavenumbers with proper factor. A tentative assignment is often made on the basis of the unscaled frequencies by assuming the observed frequencies so that they are in the same order as the calculated ones. Then, for an easier comparison to the observed values, the calculated frequencies are scaled by the scale to less than 1, to minimize the overall deviation. A better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different regions of vibrations. The resultant scaled frequencies are also listed in Table 2.

O-H vibrations

Bands due to O-H stretching are of medium to strong intensity in the infrared spectrum, although it may be broad. In phenols, the free O-H group absorbs at 3615 cm^{-1} while the associated group has a stretching frequency in the range $3145\text{--}3430\text{ cm}^{-1}$. This is due to the intermolecular hydrogen bonding [16]. The O-H stretching bands move to lower frequencies usually with increased intensity and band broadening in the hydrogen bonded species. In FMP, the FTIR band appeared at 3674 cm^{-1} is assigned to O-H stretching modes of vibration, which are further supported by the TED contribution of 100%. The O-H in-plane-bending vibration in phenol, in general, lies in the region $1150\text{--}1250\text{ cm}^{-1}$ and is not much affected due to hydrogen bonding unlike the stretching and out-of-plane deformation frequencies. The O-H out-of-plane deformation vibration in phenols lies in the region $290\text{--}320\text{ cm}^{-1}$ for free O-H and in the region $517\text{--}710\text{ cm}^{-1}$ for associated O-H [17]. Hence, in this study, the in-plane and out-of-plane bending

vibrations of hydroxy group in FT-Raman have been identified at 1164, 247 cm^{-1} for FMP, respectively. These bending modes show consistent agreement with the computed B3LYP results.

Table 2 Vibrational assignments of fundamental modes of 4-fluoro-3-methylphenol along with calculated IR intensity (km/mol), Raman activity ($\text{\AA} \text{amu}^{-1}$) and normal mode descriptions (characterized by TED) based on quantum mechanical calculations

Sl. No.	Species C_1	Observed fundamentals (cm^{-1})		Calculated frequencies ν_i (cm^{-1})								TED(%) among types of internal coordinates
		FTIR	Raman	HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)				
				Unscaled ν_i	Scaled	IR intensity	Raman activity	Unscaled ν_i	Scaled	IR intensity	Raman activity	
1	A	3674m	-	4191	3839	6.027	77.895	3840	3678	6.693	89.375	vOH(100)
2	A	-	3100 m	3365	3084	1.120	55.655	3205	3100	11.397	56.058	vCH(98)
3	A	-	3084 s	3348	3069	123.457	78.991	3192	3086	131.346	89.542	vCH(95)
4	A	-	3062s	3309	3033	36.975	66.698	3145	3041	0.714	96.166	vCH(94)
5	A	-	2997 vw	3252	2984	6.015	144.983	3111	2992	43.065	167.51	CH ₃ ops (83),CH ₃ ss(13)
6	A	-	2960 vw	3233	2967	43.209	62.103	3084	2962	14.852	68.371	CH ₃ ips(80),CH ₃ ops(13)
7	A	2917ms	-	3177	2915	1.681	5.427	3033	2917	173.272	0.038	CH ₃ ss(82),CH ₃ ips(18)
8	A	-	1659s	1809	1638	47.061	4.317	1657	1643	18.030	0.299	vCC(74), bCH(15)
9	A	1619ms	1620w	1795	1628	26.643	14.625	1645	1623	14.410	12.769	vCC(77),bCC(12)
10	A	1509vs	-	1673	1520	16.628	0.046	1535	1510	22.714	0.862	vCC(72),bCH(18)
11	A	-	1498w	1616	1486	21.430	3.229	1500	1471	12.910	3.185	vCH ₃ opb(75), bCC(25)
12	A	-	1446w	1599	1477	18.602	8.924	1480	1444	13.721	8.975	vCH ₃ ipb(78), CH ₃ ipr(16)
13	A	-	1390w	1581	1443	4.171	189.697	1460	1434	14.706	237.51	vCC(79), bCH(15)
14	A	-	1384m	1542	1420	0.736	19.275	1417	1382	13.979	17.547	vCH ₃ sb(76), bCC(18)
15	A	1336ms	1334w	1430	1304	7.924	6.782	1349	1336	11.610	7.971	vCC(72),bOH(12)
16	A	1294ms	1290m	1395	1272	209.082	0.624	1321	1293	167.026	16.476	vCC(73), bCH(15)
17	A	-	1253w	1343	1232	25.975	9.509	1280	1256	17.620	11.231	bCH(75), bCC(20)
18	A	1202vs	1201m	1342	1223	6.571	4.071	1224	1201	7.404	5.312	vCF(71), Rtrigd(20)
19	A	-	1164 w	1266	1153	29.578	14.759	1190	1168	67.768	9.311	bOH(74), bCC(16)
20	A	1144vw	-	1208	1103	24.833	3.115	1170	1148	1.622	0.317	bCH(70), bCO(18)
21	A	-	1105m	1200	1090	6.049	2.763	1122	1106	7.170	4.196	bCH(73), Rtrigd(17)
22	A	-	1043w	1158	1085	96.688	0.035	1057	1041	0.526	2.590	CH ₃ ipr(72),CH ₃ opr(19)
23	A	1003m	1003w	1083	999	3.102	4.314	1018	1004	3.548	1.214	CH ₃ opr(68), bCC(19)
24	A	945s	940m	1065	942	3.870	2.698	961	944	6.550	3.226	vCC(72), Rtrigd(13)
25	A	-	938 m	1029	923	72.999	0.321	943	918	61.287	4.199	ω CH(65),tRasynd(18)
26	A	826w	-	952	826	0.864	0.280	845	824	1.417	0.008	ω CH(64), tRasynd(15)
27	A	810s	808vs	927	809	1.700	1.229	825	805	2.935	2.237	ω CH(66), tRasynd(16)
28	A	748s	753w	831	750	0.955	17.442	773	760	1.477	6.618	vCO(70), Rasynd(19)
29	A	718w	718vs	787	718	23.950	9.016	736	720	13.127	11.032	Rtrigd(71), Rasynd(18)
30	A	-	676w	775	680	1.035	1.111	693	681	1.808	1.521	Rasynd(69), ω CF(18)
31	A	564mw	564w	642	568	28.949	2.389	578	567	5.289	18.585	bCF(67), Rasynd(25)
32	A	-	561ms	619	565	25.993	3.567	577	563	111.548	6.022	bCC(69),tRasynd(21)
33	A	496w	501ms	539	493	0.920	0.336	502	498	1.018	0.857	Rasynd(67),bCO(17)
34	A	-	450ms	497	452	25.068	1.062	453	445	24.361	0.407	tRtrigd(65),Rasynd(20)
35	A	443 ms	-	487	440	266.370	0.696	450	444	31.501	1.245	tRasynd(61), ω CC(16)
36	A	-	365ms	412	372	0.273	0.289	369	362	0.726	0.507	ω CF(60), tRtrigd(21)
37	A	-	327m	365	330	6.555	10.983	338	329	0.981	1.292	ω CC(63), bCC(18)
38	A	-	290w	288	263	0.077	0.009	269	260	0.045	0.740	bCO(69), Rasynd(17)
39	A	-	247m	234	228	0.142	0.267	267	250	0.146	0.483	ω OH(61), tRasynd(19)
40	A	-	167m	226	208	11.358	0.095	205	190	6.940	0.023	ω CO(59),tRasynd(17)
41	A	-	143w	166	151	6.822	0.732	149	147	11.384	0.010	tRasynd(62),tRasynd(14)
42	A	-	-	95	86	0.087	0.082	78	74	0.125	0.048	tCH ₃ (57), tRtrigd(16)

v-stretching; ss – symmetric stretching; ips – in-plane stretching; sb – symmetric bending; ipr – in-plane rocking; opr – out-of-plane rocking; ops – out-of-plane stretching; b-bending; ω -out-of-plane bending; R-ring; trigd-trigonal deformation; symd-symmetric deformation; asymd-antisymmetric deformation; t-torsion; s-strong; vs-very strong; ms-medium strong; w-weak; vw-very weak.

Table 3 Calculated HOMO-LUMO energy values of 4-fluoro-3-methylphenol using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods

Parameters	Method / Basis set	
	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
HOMO energy (eV)	-8.6082	-6.2925
LUMO energy(eV)	-0.9360	-0.7583
HOMO-LUMO energy gap(eV)	7.6722	5.5342

C-H vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000 cm^{-1} due to aromatic C-H stretching vibrations [18]. Hence, the FT-Raman bands appeared at 3100, 3084 and 3062 cm^{-1} in FMP has been assigned to C-H stretching vibrations and these modes are confirmed by their TED values of almost 100%. The bands due to C-H in-plane ring bending vibrations, interact somewhat with C-C stretching vibrations, are observed as a number of sharp bands in the region 1300-1000 cm^{-1} . The C-H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900-667 cm^{-1} . The FT-Raman bands at 1253, 1105 cm^{-1} and infrared bands at 1144 cm^{-1} are assigned to C-H in-plane bending vibrations of FMP. The out-of-plane bending vibrations of C-H group have also been identified for FMP and they were presented in Table 2. The theoretically computed values for C-H vibrational modes by B3LYP/6-311++G(d,p) method gives excellent agreement with experimental data.

Table 4 Thermodynamic parameters of 4-fluoro-3-methylphenol

Parameters	Method/Basis set	
	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
Optimized global minimum Energy (Hartrees)	-443.5658	-446.1541
Total energy(thermal), E_{total} (kcal mol ⁻¹)	87.590	82.450
Heat capacity, C_v (cal mol ⁻¹ K ⁻¹)	29.101	31.223
Entropy, S (cal mol ⁻¹ K ⁻¹)		
<i>Total</i>	86.643	88.641
<i>Translational</i>	40.408	40.408
<i>Rotational</i>	28.835	28.883
<i>Vibrational</i>	17.400	19.3494
Vibrational energy, E_{vib} (kcal mol ⁻¹)	85.812	80.672
Zero point vibrational energy, (kcal mol ⁻¹)	82.7055	77.2597
Rotational constants (GHz)		
<i>A</i>	3.0810	3.0378
<i>B</i>	1.3179	1.2946
<i>C</i>	0.9283	0.9129
Dipole moment (Debye)		
μ_x	0.6328	0.6759
μ_y	2.0961	2.0659
μ_z	0.0000	0.0005
μ_{total}	2.1895	2.1736

Table 5 The charge distribution calculated by the Mulliken method

Atoms	Atomic charges (Mulliken)	
	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
C1	-0.6168	-0.4610
C2	-0.7215	-0.7041
C3	1.5693	1.4078
C4	-0.9920	-0.9752
C5	0.2881	0.2595
C6	0.0978	0.0453
O7	-0.3097	-0.2366
H8	0.2752	0.2609
H9	0.1533	0.0933
C10	-0.4834	-0.3980
H11	0.1746	0.1735
H12	0.1746	0.1503
H13	0.1487	0.1734
F14	-0.2441	-0.1887
H15	0.2422	0.1968
H16	0.2435	0.2025

CH₃ group vibrations

For the assignments of CH₃ group frequencies one can expect nine fundamentals to be associated with each CH₃ group, namely the symmetrical stretching in CH₃ (CH₃ sym. stretching); asymmetrical stretching (i.e., in-plane hydrogen stretching mode); the symmetrical (CH₃ sym. deformation) and asymmetrical (CH₃ asy. deformation) deformation modes; the in-plane rocking (CH₃ ipr), out-of-plane rocking (CH₃ opr) and twisting t(CH₃) modes. In addition to that, CH₃ ops, out-of-plane stretch, and CH₃ opb, out-of-plane bending modes of the CH₃ group would be expected to be depolarized for asymmetry species. The C-H stretching in CH₃ occurs at lower frequencies than those of the aromatic ring (3100-3000 cm⁻¹). The vibrations of the methyl group in the FMP are observed in the typical range reported earlier [19]. The asymmetric and symmetric stretching vibrations are observed in the ranges 3010-2970 and 2940-2900 cm⁻¹. In the present study, the CH₃ symmetric and in-plane stretching frequencies are established at 2917 and 2960 cm⁻¹ in FTIR and Raman spectrum, respectively. We have observed the CH₃ in-plane bending mode of FMP at 1446 cm⁻¹ and CH₃ symmetric bending mode at 1384 cm⁻¹ in Raman spectrum. The CH₃ deformation modes mainly coupled with in-plane bending vibrations. The bands obtained at 1043 cm⁻¹ in Raman and 1003 cm⁻¹ in both IR and Raman are assigned to CH₃ in-plane and out-of-plane rocking modes. The CH₃ out-of-plane stretching and out-of-plane bending modes are observed at 2997 cm⁻¹ and 1498 cm⁻¹ in Raman, respectively. The calculated band at 78 cm⁻¹ by B3LYP method is attributed to CH₃ twisting mode. These assignments are substantiated by the reported literature [20].

C-C vibrations

The C-C aromatic stretching vibrations gives rise to characteristic bands in both the observed IR and Raman spectra, covering the spectral range from 1600 to 1400 cm⁻¹ [21,22]. Therefore, the C-C stretching vibrations of the title compound are found at 1619, 1509, 1336, 1294 and 945 cm⁻¹ in FTIR and 1659, 1620, 1390, 1334, 1290 and 940 cm⁻¹ in the FT-Raman spectrum and these modes are confirmed by their TED values. Most of the ring vibrational modes are affected by the substitutions in the aromatic ring of FMP. In the present study, the bands observed at 718, 496 cm⁻¹ and 718, 676, 501 cm⁻¹ in the FTIR and FT-Raman spectrum, respectively, have been designated to ring in-plane bending modes by careful consideration of their quantitative descriptions. The ring out-of-plane bending

modes of FMP are also listed in the Table 2. The reductions in the frequencies of these modes are due to the change in force constant and the vibrations of the functional groups present in the molecule.

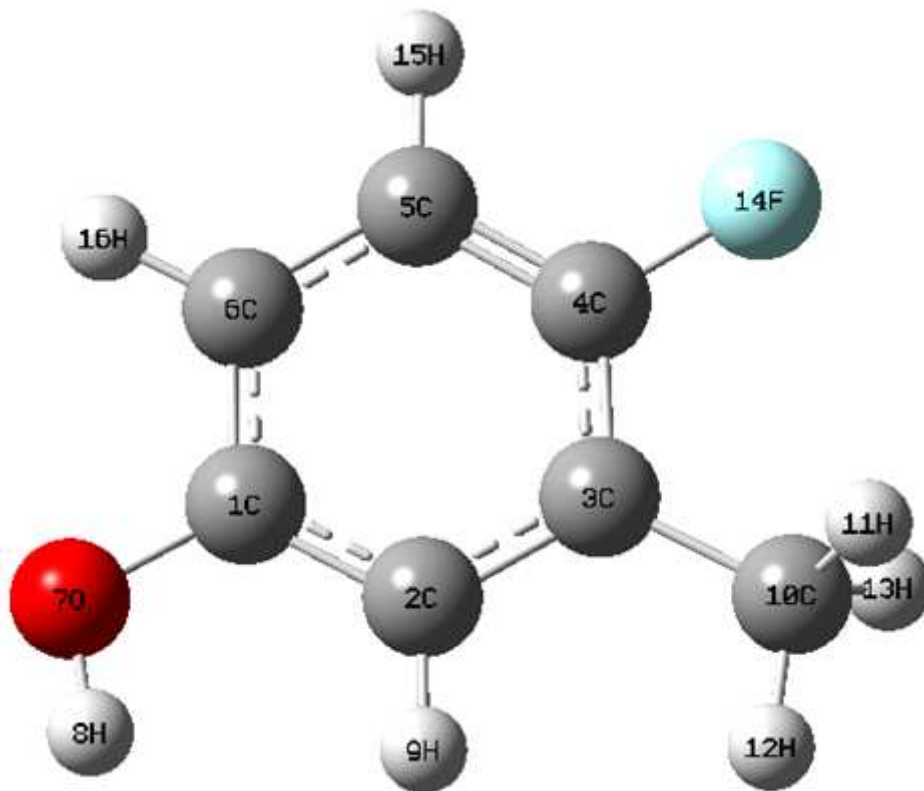


Fig.1. Molecular model of 4-fluoro-3-methylphenol along with numbering of atoms

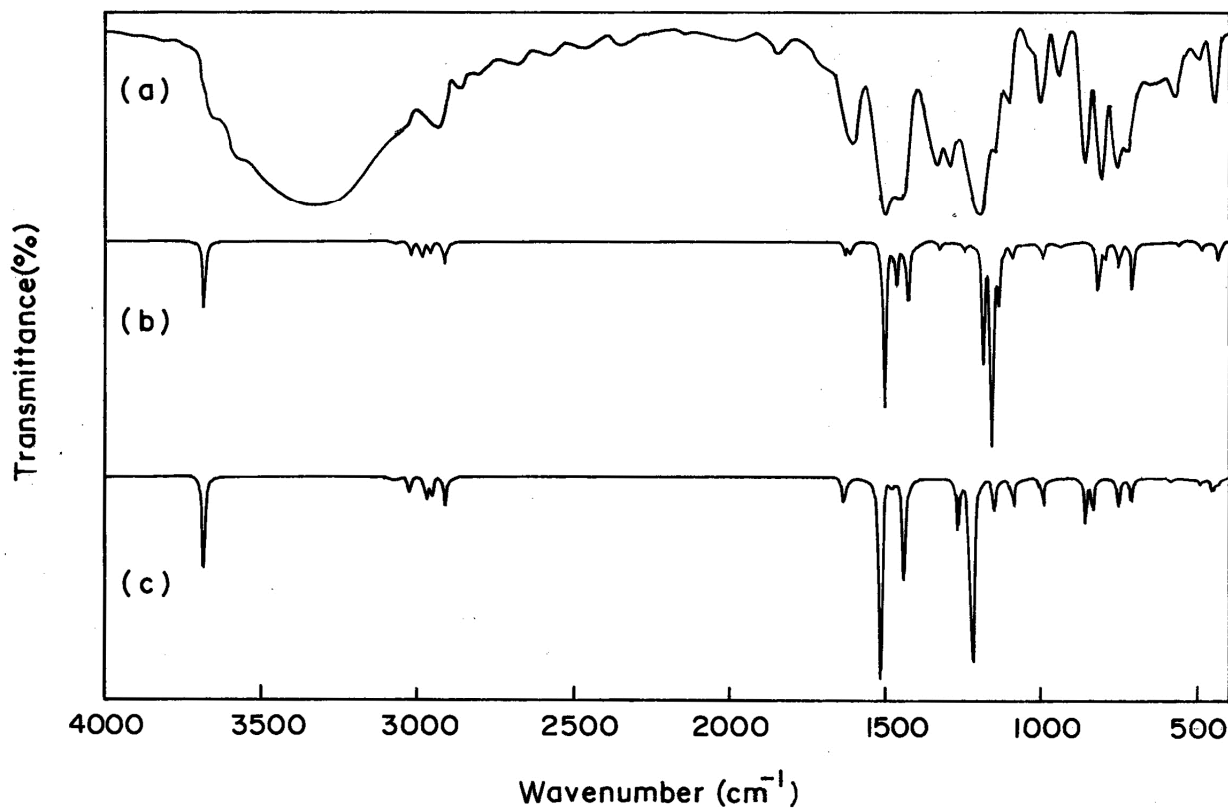


Fig.2. Comparison of observed and calculated FTIR Spectra of 4-fluoro-3-methylphenol (a) Observed in solid phase (b) calculated with B3LYP/6-311++G(d,p) and (c) calculated with HF/6-311++G(d,p)

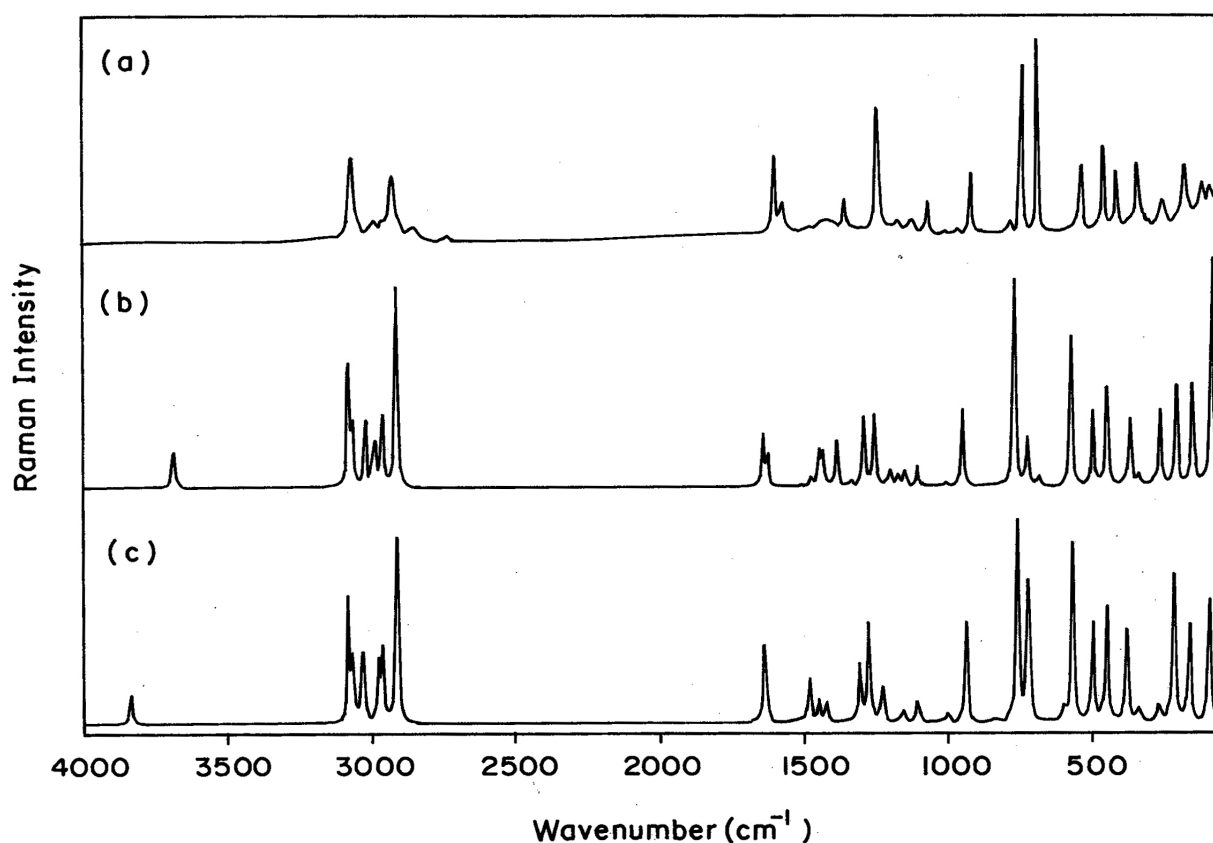


Fig.3. Comparison of observed and calculated Raman Spectra of 4-fluoro-3-methylphenol (a) Observed in solid phase (b) calculated with B3LYP/6-311++G(d,p) and (c) calculated with HF/6-311++G(d,p)

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 [23], 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 1000–1300 cm^{-1} for several fluoro-benzenes. Also, the C–F stretching vibrations strongly coupled with the C–H in-plane bending vibrations in the mono fluorinated benzene and are observed in the region 1100–1000 cm^{-1} . In the present study, the C–F stretching vibration is observed at 1202 cm^{-1} in IR and 1201 cm^{-1} in Raman spectrum. 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. The C–F in-plane bending vibrational mode for the mono fluorinated benzene normally assigned at 250–350 cm^{-1} . In the present case, the C–F in-plane bending has been assigned at 564 cm^{-1} in IR and Raman spectra and is supported by the above literature. The frequency of the C–F out-of-plane bending vibration assigned at 365 cm^{-1} in the Raman spectrum. According to the reported values [24], 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.

First hyperpolarizability

The quantum chemistry based on the prediction of non-linear optical (NLO) properties of a molecule has an important role for the design of materials in modern communication technology, signal processing and optical interconnections [25]. Especially organic molecules are studied because of their larger NLO susceptibilities arising π -electron cloud movement from donor to acceptor, fast NLO response times, high laser damage thresholds and low dielectric constants. Although the organic molecules have these advantages, they have several NLO disadvantages, too: they have generally low thermal stability and they may undergo a facile relaxation to random orientation [26]. In addition, in the UV–vis region, the low energy transitions result in a trade-off between the nonlinear efficiency and optical transparency [27,28]. But the usage of organic molecules as ligands can overcome these disadvantages. The first hyperpolarizability (β) of this novel molecular system is calculated using the DFT quantum mechanical method, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [29]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes,

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \dots$$

where E_0 is the energy of the unperturbed molecule; F^i is the field at the origin; and μ_i , α_{ij} , β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyperpolarizabilities and second hyperpolarizabilities, respectively. The calculated total dipole moment (μ) and mean first hyperpolarizability (β) of FMP using the B3LYP/6-311++G(d,p) method are 2.1736 Debye and 8.7855×10^{-30} esu, respectively. The values of μ and β obtained by Sun et al. [30] with the B3LYP/6-311++G(d,p) method for urea are 1.373 Debye and 3.729×10^{-31} e.s.u., respectively. The total dipole moment of FMP molecule is approximately 1.5 times greater than that of urea and first hyperpolarizability is 24 times greater than that of urea. The large value of hyperpolarizability, β which is a measure of the non-linear optical activity of the molecular system, is associated with the intramolecular charge transfer, resulting from the electron cloud movement through π conjugated frame work 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 we conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

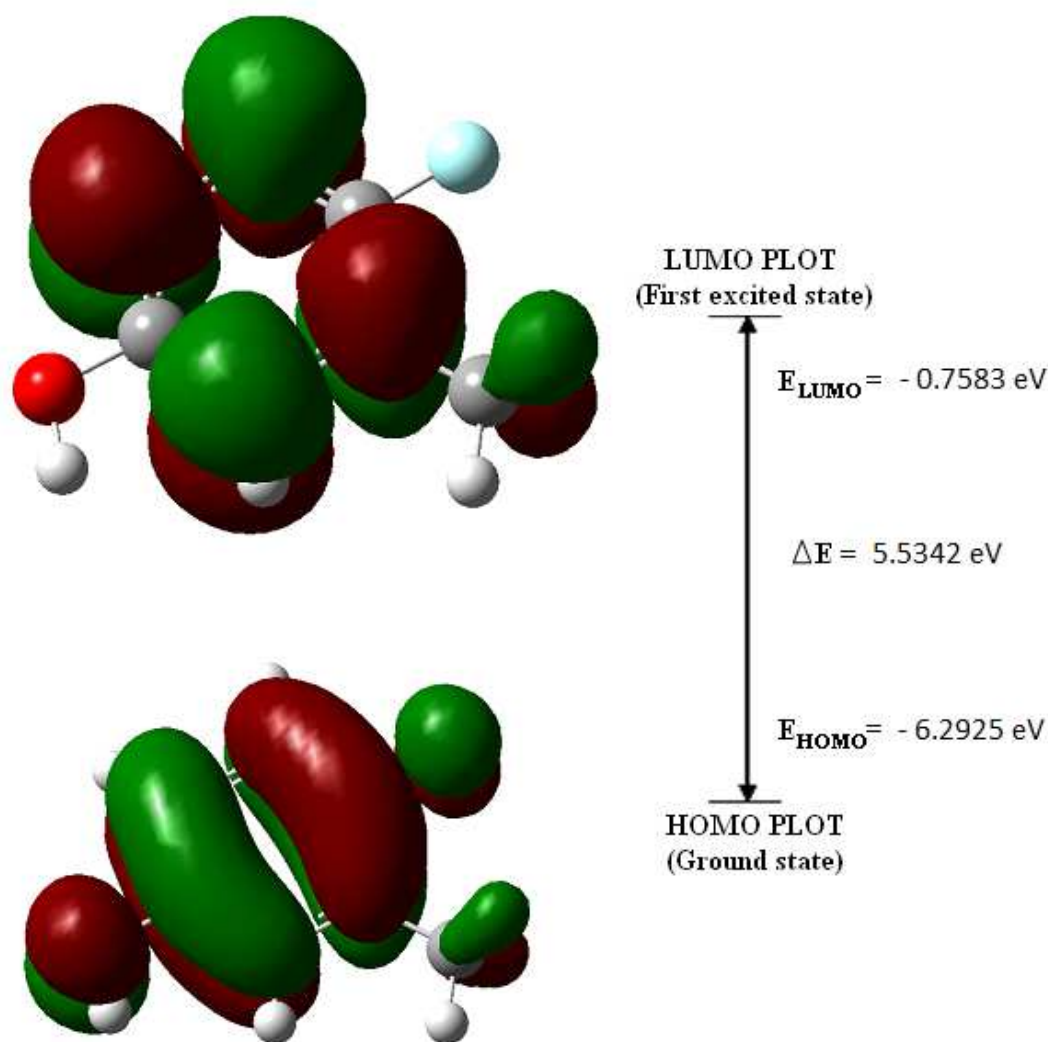


Fig.4. The atomic orbital compositions of the frontier molecular orbital for 4-fluoro-3-methylphenol

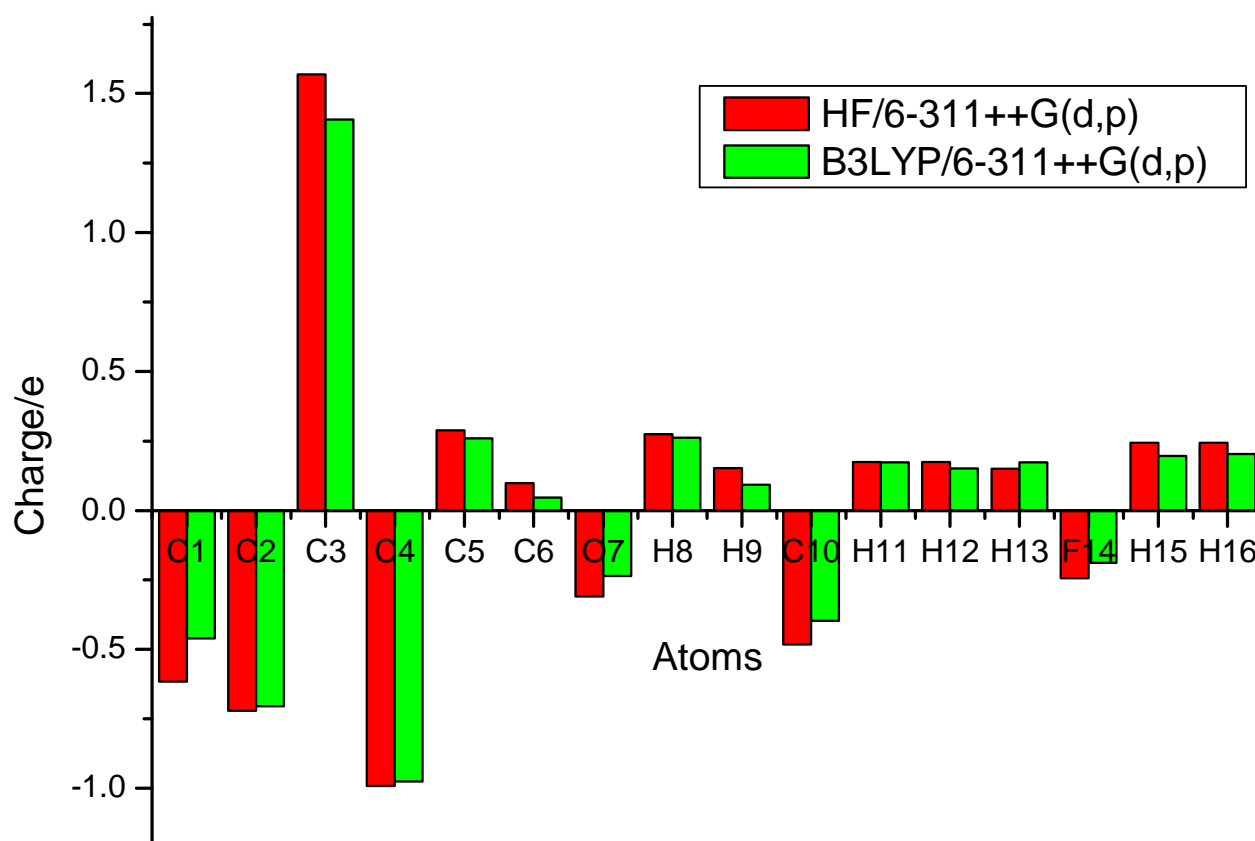


Fig.5. Mulliken's plot for 4-fluoro-3-methylphenol

HOMO, LUMO analysis

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are named as frontier molecular orbitals (FMOs). The FMOs play an important role in the electric and optical properties, as well as in UV-Vis spectra and chemical reactions [31]. The atomic orbital HOMO and LUMO compositions of the frontier molecular orbital for FMP computed at the B3LYP/6-311++G(d,p) are shown in Fig. 4. The calculations indicate that the title compound have 33 occupied MOs. The LUMO: of π nature, (i.e. benzene ring) is delocalized over the whole C-C bond. By contrast, the HOMO is located over OH group and fluorine atom; consequently the HOMO \rightarrow LUMO transition implies an electron density transfer to C-C bond of the benzene ring from OH group and fluorine atom. Moreover, these three orbitals significantly overlap in their position of the benzene ring for FMP. The HOMO-LUMO energy gap of FMP was calculated at HF and B3LYP methods using 6-311++G(d,p) basis set are shown in Table 3, which reveals that the energy gap reflects the chemical activity of the molecule. The LUMO as an electron acceptor represents the ability to obtain an electron, and HOMO represents the ability to donate an electron. Moreover, a lower HOMO-LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule.

Thermodynamic properties

Using the *ab initio* HF and DFT/B3LYP with 6-311++G(d,p) basis set calculations, several thermodynamic properties like heat capacity, zero point energy, entropy of FMP have been calculated and are presented in Table 4. The difference in the values calculated by both the methods is only marginal. Scale factors have been recommended [32] for an accurate prediction in determining the zero-point vibration energy (ZPVE), and the entropy (S_{vib}). The variation in the ZPVE seems to be insignificant. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. The total dipole moment of FMP determined by HF and B3LYP methods using 6-311++G(d,p) basis set are 2.1895 and 2.1736 Debye, respectively. The total energy and the change in the total entropy of the compound at room temperature are also presented.

Mulliken atomic charges

Mulliken atomic charge calculation [33] has an important role in the application of quantum chemical calculation to molecular system, because atomic charges affect dipole moment, polarizability, electronic structure, and much more properties of molecular systems. The total atomic charges of FMP obtained by Mulliken population analysis using HF and DFT/B3LYP with 6-311++G (d, p) basis set are listed in Table 5. The negative values on C1, C2 and C4 atom in the aromatic ring lead to a redistribution of electron density. Due to this strong negative charges, C3, C5 and C6 accommodate higher positive charge and the molecule becomes more acidic. In the benzene ring, all the hydrogen atoms have a net positive charge; in particular, the hydrogen atom H15 and H16 have charge of 0.2422 and 0.2435 respectively, owing to bound with more electronegativity atom of fluorine and oxygen atoms. The better represented graphical form of the results has been done in Fig. 5.

CONCLUSION

The optimized geometries, harmonic vibrational wavenumbers and intensities of vibrational bands of FMP have been carried out using the HF and B3LYP methods with the standard 6-311++G(d,p) basis set calculations. The theoretical results are compared with the experimental vibrations. The DFT based quantum mechanical approach provides the most reliable theoretical information on the vibrational properties of FMP. The assignments of most of the fundamentals provided in the present work are believed to be unambiguous. The TED calculation regarding the normal modes of vibration provides a strong support for the frequency assignment. Therefore, the assignments proposed at higher level of theory with higher basis set with only reasonable deviations from the experimental values seem to be correct. The calculated first hyperpolarizability results show that FMP may have microscopic nonlinear optical (NLO) behavior with non-zero values. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. Furthermore, the thermodynamic, total dipole moment and Mulliken atomic charge analysis of the compound have been calculated in order to get insight into the compound.

REFERENCES

- [1] N. Sundaraganesan, B. Anand, C. Meganathan, B. Dominic Joshua, *Spectrochim. Acta A*, **2007**, 68, 561.
- [2] J.C. Evans, *Spectrochim. Acta A*, **1960**, 16, 1352.
- [3] J. Huang, K. Huang, S. Liu, Q. Luo, W. Tzeng, *J. Photochem. Photobiol. A*, **2008**, 193, 245.
- [4] G. Wang, X. Gong, Y. Liu, H. Xiao, *Spectrochim. Acta A*, **2009**, 74, 569.
- [5] D. Mahadevan, S. Periandy, S. Ramalingam, *Spectrochim. Acta A*, **2011**, 78, 575.
- [6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian09, Revision A.02, Gaussian Inc, Wallingford CT, **2009**.
- [7] A.D. Becke, *J. Chem. Phys.*, **1993**, 98, 5648.
- [8] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B*, **1988**, 37, 785.
- [9] P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, *J. Am. Chem. Soc.*, **1983**, 105, 7037.
- [10] G. Rauhut, P. Pulay, *J. Phys. Chem.*, **1995**, 99, 3093.
- [11] G. Fogarasi, P. Pulay, in: J.R. Durig (Ed.), *Vibrational Spectra and Structure*, vol.14, p.125 (Chapter 3), Elsevier, Amsterdam, **1985**.
- [12] G. Fogarasi, X. Zhou, P.W. Taylor, P. Pulay, *J. Am. Chem. Soc.*, **1992**, 114, 8191.
- [13] T. Sundius, *Vib. Spectrosc.*, **2002**, 29, 89.
- [14] MOLVIB (V.7.0): Calculation of Harmonic Force Fields and Vibrational Modes of Molecules, QCPE Program No. 807, **2002**.
- [15] A. Frisch, A.B. Nielson, A.J. Holder, Gaussian user manual, Gaussian Inc., Pittsburgh, PA, **2009**.
- [16] B.S. Yadav, Israt Ali, Pradeep Kumar, Preeti Yadav, *Indian J. Pure Appl. Phys.*, **2007**, 45, 979.
- [17] N. Subramanian, N. Sundaraganesan, J. Jayabharathi, *Spectrochim. Acta A*, **2010**, 76, 259.
- [18] S. George, *Infrared and Raman characteristic group frequencies – Tables and Charts*, Third ed., Wiley, Chichester, **2001**.
- [19] J. Clemy Monicka, C. James, *J. Mol. Struct.*, **2015**, 1095, 1
- [20] V. Arjunan, S. Mohan, *Spectrochim. Acta A*, **2009**, 72, 436.

- [21] G. Socrates, *Infrared and Raman Characteristic Group Frequencies – Tables and Charts*, third ed., Wiley, Chichester, **2001**.
- [22] S. Prathap, M. Victor Antony Raj, J. Madhavan, *Der Chemica Sinica*, **2011**, 2(6), 173.
- [23] G. Subhapriya, S. Kalyanaraman, N. Surumbarkuzhali, S. Vijayalakshmi, V. Krishnakumar, *J. Mol. Struct.*, **2015**, 1083, 48.
- [24] N. Sundaraganesan, C. Meganathan, B. Dominic Joshua, P. Mani, A. Jayaprakash, *Spectrochim. Acta A*, **2008**, 71, 1134.
- [25] D. Sajan, J. Hubert, V.S. Jayakumar, J. Zaleski, *J. Mol. Struct.*, **2006**, 785, 43.
- [26] C.E. Powell, M.G. Humphrey, *Coord. Chem. Rev.*, **2004**, 248, 725.
- [27] K.S. Thanthiriwatte, K.M. Nalin de Silva, *J. Mol. Struct. (Theochem.)*, **2002**, 617, 169.
- [28] L. Fang, G.C. Yang, Y.Q. Qiu, Z.M. Su, *Theor. Chem. Acc.*, **2008**, 119, 329.
- [29] D.A. Kleinman, *Phys. Rev.*, **1962**, 126, 1977.
- [30] Y.X. Sun, Q.L. Hao, W.X. Wei, Z.X. Yu, L.D. Lu, X. Wang, Y.S. Wang, *J. Mol. Struct. (Theochem.)*, **2009**, 904, 74.
- [31] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, London, **1976**.
- [32] M. Alcolea Palafox, *Int. J. Quant. Chem.*, **2000**, 77, 661.
- [33] R.S. Mulliken, *J. Chem. Phys.*, **1955**, 23, 1833.