Molecular Structure and Quantum Chemical Calculations of 2, 4-difluoroanisole

S. Jeyavijayan, Palani Murugan, M. S. Revathy, K. Gurushankar, K. Viswanathan

Abstract*: *FTIR / FT-Raman spectra in the regions 4000-400 cm^{-1}/3500-50 cm^{-1} are utilized for studying the molecular vibrations of 2,4-difluoroanisole (DFA). The optimized molecular structure and vibrational analysis of the DFA were estimated with the experimental as well as quantum chemical studies from ab initio and DFT calculations. The chemical shifts of ^1H and ^{13}C NMR were calculated. In addition, the thermodynamic and important electronic properties like HOMO-LUMO, NPA charge analyses have been examined. With the aid of NBO (Natural Bond Orbital) analysis, inter and intra molecular interactions are also illustrated.

Keywords*: *2,4-difluoroanisole, FTIR, FT-Raman, NMR, ab initio, B3LYP.

I. INTRODUCTION

Among the aromatic compounds, anisole possess simple structure with ether group. Being a synthetically processed material, it is usually a precursor for the formulation of new compounds. Anisole is a notable insect repellent and a part of Cresol type antiseptic compounds. In modern days, their derivatives are used as solvents, perfumery and extensive incorporation as intermediates in chemical reaction to acquire target materials such as agrochemicals, pharmaceuticals, perfumes,dyes and photo initiators. The orientation of methyl group in anisole was found to be important in governing the pharmacological propertiesof drugs. These interesting features of anisole and their derivatives have led to wide variety of research including spectroscopic investigations [1-4]. Hence, the vibrational spectroscopic literature on fluoro anisole derivatives motivated us to venture into the spectroscopic investigation on the title compound, namely, 2,4-difluoroanisole (DFA).

The present study seeks to portray the vibrational analysis of DFA by means of quantum mechanical method based on the *ab initio* HF/DFT calculations. Further, the ground state optimized geometries and the charge

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distribution associated with different atoms for DFA have been analyzed.The performance of the computational method for *ab initio* HF and DFT-B3LYP are compared.These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort.

II. MATERIAL AND METHODOLOGY

DFA, a fine polycrystalline specimen (98% purity) was procured commercially and utilized without extra purification. Spectroscopic tools such as room temperature FTIR(Fourier transform infrared spectra) by JASCO FTIR – 6300 spectrometer in recording range 4000–400 cm^{-1} of $\pm1cm^{-1}$ resolution and FT-Raman spectrum by BRUKER RFS 100/S model interferometer equipped with accessory FRA-106 FT-Raman in 3500–50 cm^{-1} range for the title compound was utilized and recorded.

III. COMPUTATION AND SIMULATION

In order to attain the complete geometry optimization, assessment was done through *ab initio* and density functional theoretical computations by Gaussian 09 program[5]. Hartree-Fock (HF) and DFT/B3LYP functionally [6] combined with the standard 6-311++G(d,p) basis set, was executed to look for the activities of IR, Raman and molecular global minimum energy in DFA. Initial geometry made 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 at DFT level employing the B3LYP method [7] with the same basis set for better description of the bonding properties. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum and the absence of the imaginary frequencies are guaranteed. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry. Scaled quantum mechanical (SQM) procedure [8] has been followed for better agreement between computational and the experimental data. The MOLVIB Program (Version V7.0-G77) by Sundius [9] has been used for the calculation of the PED (potential energy distribution).

IV. RESULT AND DISCUSSION

A. Molecular Geometry

In Fig.1, the molecular structure of DFA with numbering of atoms is shown. The values -545.42274825 and -545.39552894 Hartrees correspond to the global minimal energies acquired by *ab initio* HF and DFT/B3LYP with 6-311++G(d,p) basis set, respectively. The optimized geometrical parameters of DFA obtained by using the above methods are presented along with the experimental data of similar structures [10,11] in TableI. It is notified that the geometrical parameters computed by B3LYP method establish to be closer with the experimental ones. With the help of *ab initio* HF as well as DFT-B3LYP levels using 6-311++G(d,p) basis set, the thermodynamic properties like heat capacity, entropy, rotational constants, dipole moment and zero point vibrational energy (ZPVE) have been computed and the results are presented in Table II.
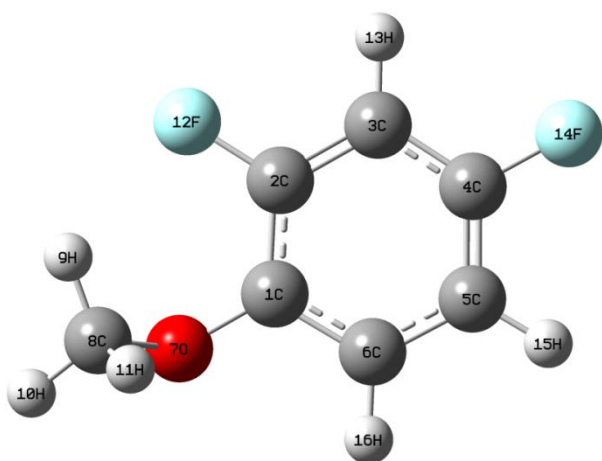

Figure 1. Molecular structure of 2,4-difluoroanisole

B. Vibrational Analysis

The molecule under investigation contains 16 atoms and therefore it has 42 modes (i.e)., (3N−6) of vibrations. The geometry of DFA is considered to have C_s point group symmetry. The 42 normal modes in DFA are disseminated amongst the symmetry species as,

$$\Gamma_{DFA} = 28A'_{\text{(in-plane)}} + 14A''_{\text{(out-of-plane)}}.$$

The experimental FTIR/FT-Raman spectra of DFA are revealed in Fig. 2. The detailed vibrational assignment along with calculated results is given in Table III.

Due to the electron correlation approximaticity, the anharmonicity effect and basis set deficiency, the frequencies of vibration attained by quantum chemical calculations with unscaled *ab initio* and DFT force fields are generally greater compared with experimental values [12]. Therefore, scaling is done to enhance the agreement between computed and experimental frequencies. After scaling, the theoretical frequencies are correlated and matched well with the experimental ones.

C-H Vibrations

The C-H stretching vibrations are normally found between 3100 and 3000 cm^{-1} [13]. The bands observed at 3087, 3084, 3013 cm^{-1} and computed at 3099, 3095, 3029

cm^{-1} and 3093, 3088, 3016 with 100% PED, by HF and B3LYP methods, respectively, in DFA have been assigned to C-H stretching mode of vibrations. Substitution sensitive C–H in-plane bending vibrations lie in the region 1000–1300cm^{-1} [14]. Bands observed at 1183, 1031, 955 cm^{-1} and calculated bands (HF method) at 1196, 1052, 971 cm^{-1} with almost 70% of PED are allocated to C-H in-plane bending mode of vibrations. Bands linking the out-of-plane C–H vibrations appear in the range 1000–675 cm^{-1}. Bands of 872, 810, 769 and 865, 804, 759 cm^{-1} by HF and B3LYP methods and the IR bands observed at 862, 801 and 754 cm^{-1} in DFA are attributed to C-H (out-of-plane) bending mode of vibrations.

Table I. Experimental (XRD) and optimized geometrical parameters of 2,4-difluoroanisole

Parameters	Expt[10,11]	HF	B3LYP
Bond length (A°)			
C1–C2	1.407	1.385	1.400
C1–C6	1.399	1.383	1.395
C1–O7	1.359	1.352	1.367
C2–C3	1.373	1.376	1.385
C2–F12	1.350	1.322	1.353
C3–C4	1.393	1.377	1.387
C3–H13	1.085	1.073	1.082
C4–C5	1.387	1.375	1.385
C4–F14	1.351	1.325	1.354
C5–C6	1.385	1.386	1.393
C5–H15	1.085	1.073	1.082
C6–H16	1.085	1.075	1.083
O7–C8	1.427	1.411	1.436
C8–H9	1.089	1.080	1.092
C8–H10	1.089	1.080	1.089
C8–H11	1.089	1.086	1.095
Bond angle (°)			
C1–C2–C3	123.5	122.34	122.46
C2–C3–C4	116.0	117.74	117.67
C3–C4–C5	123.6	122.24	122.32
C4–C5–C6	118.5	118.45	118.47
C1–C6–C5	120.2	121.27	121.40
C2–C1–C6	118.1	117.96	117.66
C2–C1–O7	124.9	121.27	122.80
C1–C2–F12	118.5	118.99	119.14
C3–C2–F12	118.5	118.66	118.39
C3–C4–F14	118.4	118.46	118.41
C5–C4–F14	118.3	119.30	119.26
C1–O7–C8	115.9	116.30	116.66

Table II. Theoretically computed thermodynamic parameters of 2,4-difluoroanisole

Parameter	HF	B3LYP
Zero-point vibrational Energy (kJ/mol)	326.134	303.599
	2.77732	2.78420
Rotational constants (GHz)	0.93582	0.91108
	0.73099	0.71184
Thermal energy (kJ/mol)		
Total	83.096	78.097
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	81.318	76.320
Heat capacity at constant volume (calmol^{-1}Kelvin^{-1})		
Total	30.177	32.592
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	24.215	26.630
Entropy (calmol^{-1}Kelvin^{-1})		
Total	89.958	92.880

Translational		40.806	40.806
Rotational		29.516	29.516
Vibrational		19.637	22.508
Dipole moment μ_{total} (Debye)		2.0675	1.8078

Table III. FTIR, Raman and calculated (unscaled and scaled) vibrational frequencies (cm^{-1}), IR intensity (km mol^{-1}),

No	Symm. Species	Experimental frequencies		HF 6-311++G(d,p)				B3LYP 6-311++G(d,p)				Characterization of normal modes with PED (%)
		FTIR	FT-Raman	Un Scaled	Scaled	IR intensity	Raman activity	Un Scaled	Scaled	IR intensity	Raman activity	
1	A′	3087	-	3374	3099	0.20	16.96	3215	3093	0.80	11.35	CH (100)
2	A′	-	3084	3368	3095	1.32	21.91	3210	3088	0.52	22.1	CH (100)
3	A′	3013	-	3350	3029	3.54	8.28	3194	3016	2.03	31.2	CH (100)
4	A′	2964	-	3285	2983	37.33	6.98	3138	2969	18.33	13.62	CH$_3$ ips (98)
5	A′	-	2934	3240	2951	36.21	7.07	3095	2937	25.89	15.55	CH$_3$ ss (98)
6	A″	2844	2837	3170	2862	55.08	11.5	3020	2840	57.32	23.92	CH$_3$ ops (97)
7	A′	1606	-	1815	1625	24.03	10.66	1653	1610	14.47	75.22	CC (89)
8	A′	1516	-	1787	1532	57.21	8.14	1634	1521	34.55	25.63	CC (87)
9	A′	1466	-	1685	1481	357.85	1.4	1534	1470	305.93	10.13	CH$_3$ ipb (87)
10	A′	1445	-	1626	1465	9.22	6.97	1507	1449	13.06	27.24	CC (84)
11	A′	1401	-	1617	1420	6.04	10.24	1491	1405	5.38	3.02	CC (81), bCH (14)
12	A′	1318	-	1603	1331	21.06	2.01	1474	1321	19.28	3.5	CC (82), Rasymd (17)
13	A′	-	1311	1577	1325	25.30	2.81	1450	1316	14.36	10.21	CH$_3$ sb (80)
14	A′	1298	-	1443	1317	52.85	37.26	1324	1303	36.70	1.53	CF (88)
15	A′	-	1292	1390	1310	138.04	1.72	1309	1298	26.92	17.92	Rtrigd (73), Rsymd (21)
16	A′	1286	-	1346	1299	33.15	2.65	1268	1290	92.81	2.28	CO (82)
17	A′	-	1279	1302	1291	41.32	4.43	1232	1283	70.96	5.49	Rasymd (74), CH (18)
18	A′	1261	-	1281	1273	55.49	1.94	1194	1266	35.11	5.38	CC (79), Rasymd (20)
19	A′	1219	-	1277	1231	44.80	2.52	1169	1224	1.56	7.8	CF (87)
20	A′	1183	-	1218	1196	20.53	4.28	1151	1187	67.37	28.17	bCH (70), CC(23)
21	A″	1143	-	1183	1153	10.33	2.84	1110	1140	31.99	2.5	CH$_3$opb (69)
22	A′	-	1119	1143	1131	113.58	15.12	1027	1113	81.55	2.56	Rsymd (73), Rasymd (21)
23	A′	1106	-	1072	1121	0.38	0.08	973	1111	70.18	11.16	O- CH$_3$ (75)
24	A′	-	1099	1051	1110	56.44	16.94	951	1094	2.64	56.3	CH$_3$ ipr (68)
25	A′	1031	-	973	1052	52.87	0.11	864	1036	49.09	1.38	bCH (69), CH (19)
26	A″	-	963	936	982	22.78	0.51	834	969	15.81	0.04	CH$_3$ opr (70)
27	A′	-	955	840	971	23.49	38.98	766	959	25.06	2.28	bCH (67), CC (23)
28	A″	862	-	810	872	3.93	35.11	736	865	18.59	1.65	ωCH (59)
29	A″	801	-	786	810	23.71	11.46	715	804	7.65	1.85	ωCH (53)
30	A″	754	761	690	769	11.16	4.79	618	759	10.14	1.67	ωCH (51)
31	A″	718	711	641	731	8.48	24.47	592	715	5.76	40.54	tRsym (59), ωCH (21)
32	A″	598	602	567	613	3.08	10.24	521	600	2.42	4.32	tRtrig (57), tRaysm (23)
33	A′	505	502	546	524	2.70	12.94	492	504	2.67	26.85	b O- CH$_3$ (75)
34	A″	498	-	497	519	3.59	6.23	454	503	3.83	7.49	tRaysm (53), ωCO (21)
35	A′	493	-	444	510	2.18	24.59	404	498	2.40	21.6	bCF (67), CC (23)
36	A″	466	-	368	479	6.69	0.57	339	470	4.31	2.35	ωO- CH$_3$ (65), CO (19)
37	A′	-	379	333	392	0.31	5.24	305	384	0.14	11.34	bCF (64) , CC (27)
38	A′	-	371	269	383	2.64	27.49	238	376	3.16	6.45	bCO (59), Rsymd (23)
39	A″	-	301	252	316	1.91	29.5	234	308	1.91	26.39	ωCF (59), ωCO (19)
40	A″	-	233	170	246	0.62	1.68	163	230	2.12	31.16	ωCF (53), tRaysm (23)
41	A″	-	150	122	168	1.19	50.97	112	153	0.59	28.72	ωCO (54), ω O- CH$_3$ (21)
42	A″	-	112	77	130	4.21	100	51	116	3.76	100	τ CH$_3$ (61)

Raman activity (Å^{4}amu^{-1}), and vibrational assignments of 2,4-difluoroanisole

C–C Vibrations

The spectral region ranging between 1600 and 1400 cm^{-1}, there are characteristic bands of C–C aromatic stretching vibrations have been studied in both the observed IR and Raman spectra [15]. In DFA, IR active bands at 1606, 1516,1445, 1401,1318 and 1261 cm^{-1} have been allocated to C-C stretching modes and they are computed at 1625, 1532, 1465, 1420, 1331, 1273 by HF method and at 1610, 1521, 1449, 1405, 1321, 1266 cm^{-1} by B3LYP method, employing 6-311++G(d,p) basis set. Similarly, the observed bands for in-plane and out-of-plane bending modes are in concurrence with the estimated ones as given in Table III.

C–F Vibrations

The vibrations associated with C–X (X = F, Cl, Br) bonds formed between the ring and the halogen atoms are important to discuss, since the presence of heavy atoms and lowering of molecular symmetry may yield mixed vibrations [16]. The absorption takes place in DFA, the IR bands at 1298 and 1219 cm^{-1} and computed at 1317, 1231, 1303 and 1224 cm^{-1} have been allocated to the mode C–F stretching vibrations. Also, IR and Raman bands (493 and 379 cm^{-1})and Raman bands(301, 233 cm^{-1})are assigned to C–F in-plane and out-of-plane bending mode, respectively. The consistency with the analyzed wavenumbers is revealed in Table III.
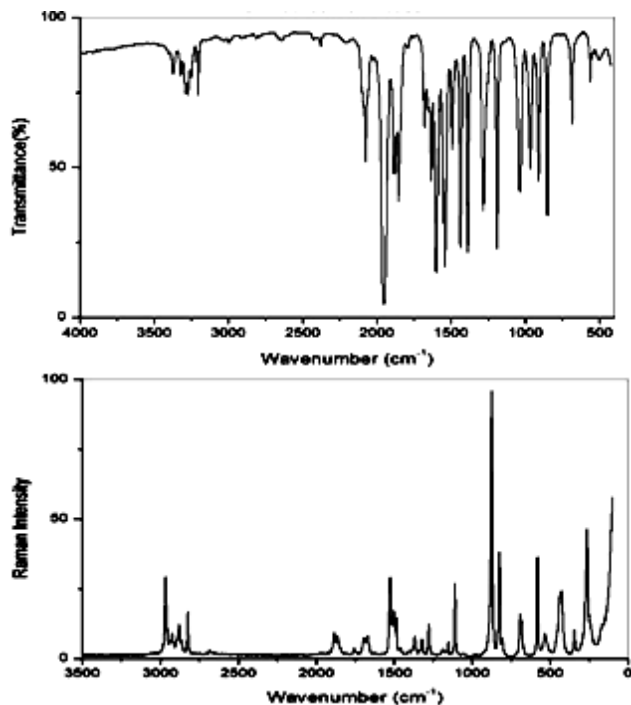
Figure 2. FTIR and FT-Raman spectra of 2,4-difluoroanisole

Methyl Group Vibrations

There are nine fundamental modes associated with each methyl group, out of which 5 modes are in-plane (A') and the remaining 4 modes are out-of-plane and are predictable as depolarized for symmetry class A″. At lower frequencies, the stretching in CH$_3$ occurs than those of aromatic ring (3000–3100 cm^{-1}). Around 2980 cm^{-1}, asymmetric CH$_3$ stretching mode and 2870 cm^{-1} corresponds to symmetric one is expected in the region of CH$_3$ group [17]. The asymmetric stretching frequency of –CH$_3$ is allocated at 2964 cm^{-1},for which 2983 cm^{-1} and 2969 cm^{-1} are HF and the B3LYP computed wave numbers, respectively. 2934 cm^{-1} Raman band in DFA is assigned to –CH$_3$ symmetric stretching for which the computed wave numbers are 2951 and 2937 cm^{-1}. The CH$_3$ out-of-plane stretching under A″ species are computed at 2862, 2840 cm^{-1} and observed at 2844, 2837 cm^{-1} in DFA. Good accordance between observed and calculated values of out-of-plane bending modes and rocking modes (in-plane and out-of-plane) are exhibited in Table III.

C. NPA Charge Distribution Analysis

Molecule's NPA Charge distribution plays vital role in the vibrational spectra and hence the NPA charge distributions of DFA were designed by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods and jointly presented in Table IV.

Table IV. Charge analysis for 2,4-difluoroanisole

ATOM	NPA charges	
	HF	B3LYP
C1	0.25125	0.23775
C2	0.44749	0.38557
C3	−0.32588	−0.31852
C4	0.47193	0.41138
C5	−0.27617	−0.27034
C6	−0.17439	−0.20247
O7	−0.62704	−0.56469
C8	−0.08518	−0.19845
H9	0.14632	0.17815
H10	0.16048	0.18721
H11	0.13727	0.16569
F12	−0.38382	−0.34838
H13	0.22588	0.23884
F14	−0.38860	−0.35072
H15	0.21332	0.22626
H16	0.20714	0.22273

From the NPA values listed in Table IV, we have examined the presence of electropositivenature in all hydrogen atoms and electronegative in all oxygen as well as fluorine atoms in DFA. The electro-positive as well as electro-negative scenario in carbon atoms depends upon the nature of atoms bonded with them. For example, C2 and C4 atoms in DFA are exhibiting strong electro positive nature since the strong electronegative fluorine atoms are bonded to it.

D. NMR Chemical Shifts

The reactive organic as well as ionic species identification was often done by isotropic chemical shifts [18]. Optimized geometry using B3LYP/6-311++G(d,p) method has been made by the Gauge-including atomic orbital (GIAO) ^{1}H and ^{13}C chemical shift calculations of the title compound and the results are presented in Table V. For DFA, the C-H protons chemical shifts are in the range 4.01-7.82 ppm. Among the C-H protons, the methyl protons are most deshielded and hence they have lower chemical shifts compared with other protons in the title compound. Usually, the typical range of ^{13}C NMR chemical shift in organic molecules is greater than the value of 100 ppm [19]. In Table V, the chemical shifts of carbon atoms are ranging from the values 78.43 ppm to 184.41 ppm. The carbon atoms attached to fluorine atoms F12 and F14 are found to be most deshielded and the carbon atom C8 (methyl group) is most shielded and hence it has the least chemical shift in the value 78.43 ppm.

Table V. The chemical shielding and shift (GIAO method) for 2,4-difluoroanisole

ATOM	Chemical shift (ppm)	ATOM	Chemical shift (ppm)
H9	5.08	C1	168.62
H10	4.56	C2	182.76
H11	4.01	C3	126.2
H13	7.54	C4	184.41
H15	7.51	C5	132.67
H16	7.82	C6	146.17
		C8	78.43

E. HOMO-LUMO Analysis
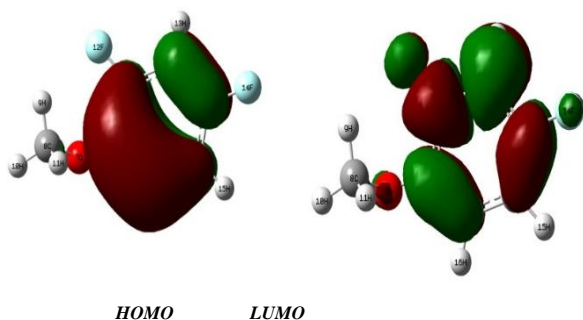
HOMO   LUMO

Figure 3. HOMO-LUMO of 2,4-difluoroanisole

The significant features of a molecule is decided by the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the energy gap between them [20]. In recent research, the energy gap laid by HOMO and LUMO has been utilized to demonstrate the bioactivity from intra-molecular charge transfer (ICT) [21]. The molecular orbital (MO) calculations indicate that the title compound DFA has 37 occupied MOs. The energies of HOMO and LUMO, their orbital energy gap iscalculated using the B3LYP/6-311++G(d,p)method. The HOMO-LUMO energy gap is found to be 7.4909 eV. The frontier molecular orbitals of DFA are shown in Fig. 3.

F. NBO Analysis

NBO (Natural Bond Orbital) analyses explain the intra and inter molecular bonding strength and bond interaction [22]. In Table VI, the perturbation energies of significant donor-acceptor interactions are presented for DFA. The strong interaction between electron donors and acceptors can be understood by the larger value of interaction energy, E(2). The intermolecular interaction between BD (2) C1 – C6 →BD* (2) C2 – C3 has been recognized as the interaction giving the strongest stabilization to the system since it has higher second order perturbation energy of the order of 22.79 kcal/mol. Further, the interactions initiated by lone pair parent NBOs like LP (2) O7 →BD* (2) C1 – C6, LP (3) F12 → BD* (2) C2 – C3 and LP (3) F14 → BD* (2) C4 – C5 are giving reasonable amount of stabilization because of their higher E(2) value.

Table VI. Significant donor – acceptor interactions in 2,4-difluoroanisole

Donor NBO (i)	Acceptor NBO (i)	E(2) (kcal/mol)	$(E_j – E_i)$ (a.u)	F(i,j) (a.u)
BD (2) C1 – C6	BD* (2) C2 – C3	22.79	0.28	0.072
	BD* (2) C4 – C5	18.57	0.28	0.065
BD (2) C2 – C3	BD* (2) C1 – C6	17.56	0.30	0.066
	BD* (2) C4 – C5	21.28	0.30	0.072
BD(2) C4 – C5	BD* (2) C1 – C6	21.14	0.29	0.071
	BD* (1) C2 – C3	18.90	0.28	0.066
LP (2) O7	BD* (2) C1 – C6	10.64	0.37	0.061
LP(3) F12	BD* (2) C2 – C3	17.92	0.43	0.086
LP(3) F14	BD* (2) C4 – C5	17.98	0.43	0.086

V. CONCLUSION

The optimized structure of 2,4-difluoroanisole(DFA) has been acquired and the bond length/bond angles are computed. The calculated geometric parameters are in good concurrence with the experimental values. The precisely assigned vibrational frequencies from the recorded FT-IR/ FT-Raman spectra for the fundamental modes of DFA are in concurrence with the calculated results. The NMRchemical shifts for hydrogen and carbon atoms have been calculated. The charge distribution on the molecule was furnished by NPA analysis. The energy gap of HOMO–LUMO and the second order perturbation energy calculations explains the eventual charge transfer interaction that occurs inside the molecule, which influences the spectral and biological activities of the molecule.

REFERENCES

1. V. Krishnakumar, and N. Prabavathi, "Simulation of IR and Raman spectra of p-hydroxyanisole and p-nitroanisole based on scaled DFT force fields and their vibrational assignments," *Spectrochim. Acta A Mol. Biomol. Spectrosc*., vol. 74 , 2009, pp. 154–161.
2. Ramalingam, and S. Periandy, "Spectroscopic investigation, computed IR intensity, Raman activity and vibrational frequency analysis on 3-bromoanisole using HF and DFT (LSDA/MPW1PW91) calculations," *Spectrochim. Acta A Mol. Biomol. Spectrosc*., vol. 78, 2011, pp. 835–843.
3. T. Prabhu, S. Periandy, and S. Ramalingam, "FT-IR and FT-Raman spectroscopic investigation, computed vibrational frequency analysis and IR intensity and Raman activity peak resemblance analysis on 2-nitroanisole using HF and DFT (B3LYP and B3PW91) calculations," *Spectrochim. Acta A Mol. Biomol. Spectrosc*., vol. 83, 2011, pp. 8–16.
4. M. Arivazhagan, and S. Prabhakaran, "DFT studies and vibrational spectra of 2-bromomethyl-4-nitroanisole," *Indian J. Pure & Appl. Phys*., vol.50, 2012, pp.26-33.
5. H.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, H.Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, K. Toyota, R. Fukuda, J.Hasegawa, M. Ishida, R. Nakajima, Y. Honda, O. Kilao, H. Nakai, T. Verven, J. A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V.N. Staroveror, R. Kobayashi, J. Normand, K. Ragavachari, A. Rendell, J.C. Burant, S. 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. Strattmann, O. Yazyev, A.J. Austin, R. Cammi, J.W. Ochetrski, R.L. Martin, K. Morokuma, V.G. Zakrazawski, G.A.Votn, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas and J.B. Foresman, Gaussian O.G., Revision A.O2, *Gaussian Inc., Wallingford*, CT. 2009.
6. A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys*., vol. 98, 1993, pp. 5648 – 5652.
7. C. Lee, W. Yang and R.G. Parr, "Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density," Phys. Rev. B., vol. 37, 1988, pp. 785–789.

8. G. Rahut and R. Pulay, "Transferable Scaling Factors for Density Functional Derived Vibrational Force Fields," *J. Phys. Chem.*, vol. 99, 1994, pp. 3093–3100, 1994 .

9. T. Sundius, Scaling of ab initio force fields by *MOLVIB, Vib. Spectrosc.*, vol. 29, 2002, pp. 89–95.

10. N.I. Giricheva, G.V. Girichev, J.S. Levina, and H. Oberhammer, "Molecular structures and conformations of 4-fluoranisole and 3,4-difluoroanisole: gas electron diffraction and quantum chemical calculations, J. Mol. Struct.," vol. 703, pp. 55–62, 2004.

11. L. Zhang, C. Dong, M. Cheng, L. Hu, Y. Du , Q. Zhu, and C. Zhang, "Resonance-enhanced two-photon ionization spectroscopy and theoretical calculations of 3,5-difluoroanisole and its Ar-containing complex," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 96, 2012, pp. 578–585.

12. M. Karaback, M. Cinar, and M. Kurt, "An experimental and theoretical study of molecular structure and vibrational spectra of 2-chloronicotinic acid by density functional theory and ab initio Hartree–Fock calculations," *J. Mol. Struct.*, vol. 885, 2008, pp. 28–35.

13. G. Varsanyi, Assignments for Vibrational Spectra of Seven Hundred Benzene Derivations, vol. 1, 1974, Adam Hilger, London.

14. G. Socrates, Infrared and Raman Characteristic Group Frequencies, *Tables and Charts*, 3rd ed., 2001, Wiley, Chichester.

15. V. Krishnakumar, and R.J. Xavier, "Molecular and vibrational structure of 2-mercapto pyrimidine and 2,4-diamino-6-hydroxy-5-nitroso pyrimidine: FT-IR, FT-Raman and quantum chemical calculations," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 63, 2006, pp. 454–463.

16. R. J. Xavier, and E. Gobinath, "Experimental and theoretical spectroscopic studies, HOMO–LUMO, NBO and NLMO analysis of 3,5-dibromo-2,6-dimethoxy pyridine," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 97, 2012, pp. 215–222.

17. M. T. Güllüoglu, M. Özduran, M. Kurt, S. Kalaichelvan, and N. Sundaraganesan, "Molecular structure and vibrational spectra of 2- and 5-methylbenzimidazole molecules by density functional theory," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 76, 2010, pp. 107–114.

18. S. Sebastian, N. Sundaraganesan, B. Karthikeyan, and V. Srinivasan, "Quantum mechanical study of the structure and spectroscopic (FT-IR, FT-Raman, 13C, 1H and UV), first order hyperpolarizabilities, NBO and TD-DFT analysis of the 4-methyl-2-cyanobiphenyl," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol.78, 2011, pp. 590–600.

19. K. Pihlager, E. Kleinpeter (Eds), Carbon[13] Chemical shifts in structure and Spectrochimical analysis, VCH publishers, Deerfiled Beach, 1994.

20. M. Amalanathan, V.K. Rastogi, I.H. Joe, M.A. Palafox, and R. Tomar, Density functional theory calculations and vibrational spectral analysis of 3,5-(dinitrobenzoic acid), *Spectrochim. Acta*, vol. A78, 2011, pp.1437 – 1444.

21. L. Padmaja, C. Ravi Kumar, D. Sajan, I.H. Joe, V.S. Jayakumar, and G.R. Pettit, Density functional study on the structural conformations and intramolecular charge transfer from the vibrational spectra of the anticancer drug combretastatin-A2, *J. Raman Spect.*, vol. 40, 2009 pp. 419–428.

22. A.E. Reed, L.A. Curtiss, and F. Weinhold, Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint, *Chem. Rev.*, vol. 88,1988, pp. 899–926.

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