Quantum Chemical study of Molecular structure, Non Linear Optical and Vibrational Properties of ortho and meta- Fluorobenzaldehyde

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ABSTRACT

The present communication is aimed at comparing the molecular structural properties, vibrational and energetic data of ortho and meta- Fluorobenzaldehyde, in gas phase, due to their commercial importance. The ground state properties of the title molecules have been calculated employing DFT/ B3LYP level of theory using the 6-311G(d,p) basis set. The dipole moment and mean polarizability are calculated to be 3.38 Debye and 74.679/a.u. in case of 'o'-Fluorobenzaldehyde and for 'm'- Fluorobenzaldehyde these values are 1.96 Debye and 75.052/a.u. calculated at same level of theory and basis set. The first static hyperpolarizability of 'm'- Fluorobenzaldehyde is found to be 4.6 times to that of 'o'-Fluorobenzaldehyde. MESP contours/surfaces have also been drawn and compared. In order to obtain a complete description of molecular dynamics, vibrational wavenumber calculation along with the normal mode analysis, have been carried out at the DFT level. The calculated spectra of both the molecules agree well with the experimental data.

Keywords : Frontier orbital band gap, Polarizability, Hyperpolarizability and Vibrational analysis.

INTRODUCTION

Benzaldehyde and its derivatives are the simplest representatives of the aromatic aldehydes. 'o'-Fluorobenzaldehyde and 'm'- Fluorobenzaldehyde are used essentially in the synthesis of organic compounds, extending from pharmaceuticals to plastic additives. Benzaldehyde and its derivatives have also shown antitumor activity in mice [1-2]. Recently it has been shown that the incorporation of the benzaldehyde increases the activity of the benzaldehyde-thiosemicarbazone which exhibits high anti-trypanosomal potential [3]. They are also important intermediaries for the processing of perfume and flavouring compounds and in the preparation of certain aniline

dyes. Although much work has been done on benzaldehyde and its derivatives [4-8], however a comprehensive comparative study of 'o'-Fluorobenzaldehyde and 'm'-Fluorobenzaldehyde on electronic structure, non-linear properties along with the detailed potential energy distribution of normal modes of vibrations has not been reported so far. Therefore the present communication is aimed at comparing the molecular structural properties, vibrational and energetic data of trans conformer of 'o'-Fluorobenzaldehyde and 'm'-Fluorobenzaldehyde, in gas phase, due to their commercial importance. Wasylishen and Schaefer [9] concluded on the basis of n.m.r. data and INDO calculations that the O-trans conformer was the more stable conformer for ortho- and meta-Fluorobenzaldehyde. The ground state properties of the title molecules have been calculated employing DFT/ B3LYP level of theory. The first static hyperpolarizability of both the molecules have been calculated and compared. The reported geometries, molecular properties along with the electrostatic potential surfaces and contours have also been used to understand the properties of the molecules.

EXPERIMENTAL SECTION

Structure and Spectra: The optimized molecular structure of 'o'-Fluorobenzaldehyde and 'm'-Fluorobenzaldehyde has been given in the Fig.1. The theoretically calculated IR and Raman spectra have been given Fig. 2. The calculated IR and Raman spectra of the two molecules agree well with the experimental spectral data reported by the Sigma Aldrich chemical website [10].
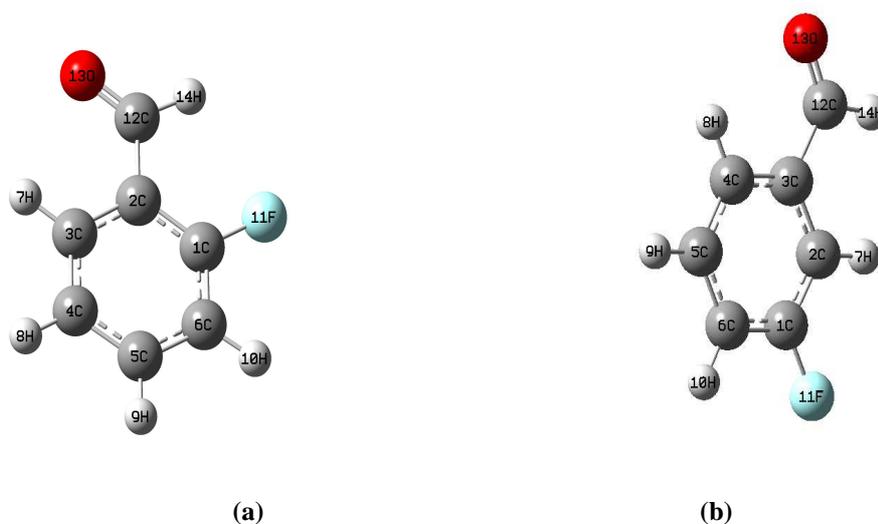

(a)   (b)
Figure: 1 Optimized structure of (a) 'o'-Fluorobenzaldehyde and (b)'m'- Fluorobenzaldehyde

Computational details

In the present communication the density functional theory [11] has been employed using Becke's three parameter hybrid exchange functionals [12] with Lee-Yang-Parr correlation functionals [13,14] to optimize the structure and calculate the electronic structure properties of both the molecules. The Gaussian 09 program [15] was used to calculate the dipole moment (μ), polarizability (α), the first static hyperpolarizability (β) of both the molecules, based on the finite field approach. The vibrational frequencies are also calculated and scaled down by the appropriate factor [16,17]. The vibrational wavenumber assignments have been carried out by combining the results of the Gaussview 5 program [18], symmetry considerations and the VEDA 4 program [19].

The Raman intensities were calculated from the Raman activities (S_i) obtained with the Gaussian 09 program, using the following relationship derived from the intensity theory of Raman scattering [20,21].

$$I_i = [f(v_0 - v_i)^4 S_i] / [v_i\{1- \exp(-hc \, v_i/kT)\}]$$

Where v_0 being the exciting wavenumber in cm^{-1}, v_i the vibrational wave number of ith normal mode, h,c and k universal constants and f is a suitably chosen common normalization factor for all peak intensities. Raman spectra has been calculated according to the spectral database reported by the Sigma Aldrich chemical website [10]. The calculated FTIR and Raman spectra have been plotted using the pure Lorentzian band shape with a band width of 10 cm^{-1} FWHM and are shown in Fig. 2. Density functional theory has also been used to calculate the dipole moment μ, mean polarizability <α> and first static hyperpolarizability β. Following Buckingham's definitions [22], the total dipole moment and the mean polarizability in a Cartesian frame is defined by

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$<\alpha> = 1/3 \, [\, \alpha_{xx} + \alpha_{yy} + \alpha_{zz}]$$

The total intrinsic hyperpolarizability β_{TOTAL} [23] is defined as

$$\beta_{TOTAL} = [\beta_x^2 + \beta_y^2 + \beta_z^2]^{1/2} \; ; \text{ where } \beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \, , \, \beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{yxx} \, , \, \beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}.$$
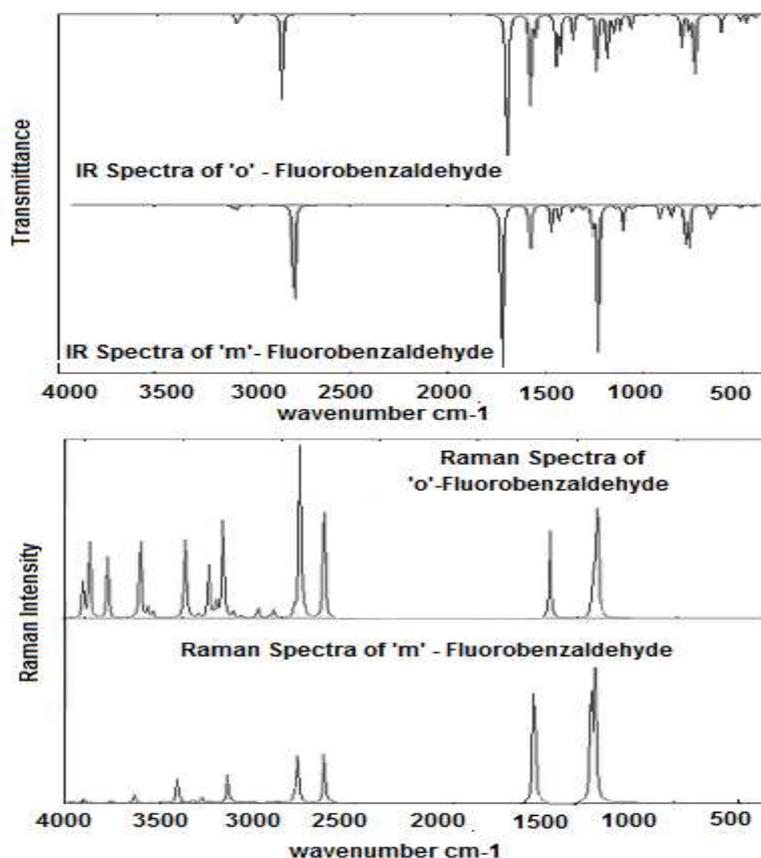

Figure 2 : Theoretical IR and RAMAN Spectra of 'o'- and 'm'- Fluorobenzaldehyde

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RESULTS AND DISCUSSION

Molecular geometry optimization and energies - The structure of 'm'-Fluorobenzaldehyde and 'o'-Fluorobenzaldehyde have been optimized to compare the variation in electronic and non-linear properties on substitution of halogen group (fluorine) at ortho and meta position. The equilibrium geometry optimization for both the molecules has been achieved by energy minimization, using DFT at the B3LYP level, employing the split valence basis set 6-311G(d,p). As all the atoms of aromatic nucleus and aldehyde group are situated in the molecular plane , the molecules were built using the Gaussview program package then optimized in steps. The optimized geometry of both molecules under study is confirmed to be located at the local true minima on potential energy surface, because of absence of imaginary wavenumber in the vibrational spectra. The optimized molecular structures thus obtained along with the numbering scheme of the atoms are shown in Fig. 1. The C-H   bond lengths vary in the range $1.08A^0$ - $1.10A^0$ and $1.08A^0$-$1.11A^0$ in ortho and meta Fluorobenzaldehyde respectively whereas C-C bond length varies in the range of $1.39A^0$-$1.48A^0$, for both ortho and meta isomers. The C-F bond length for both the molecules is calculated to be $1.35 A^0$.

Electronic properties - With the help of frontier orbital gap one can easily understand the characteristics of a molecule regarding its interaction with other species and to characterize the chemical and kinetic stability of the molecule. A molecule with small frontier orbital is more polarizable and is generally associated with high chemical reactivity, low kinetic stability due to which molecule termed as soft molecule [24]**.** The frontier orbital gaps of 'm'-Fluorobenzaldehyde/'o'-Fluorobenzaldehyde are to be 0.18996 a.u. and 0.18842 a.u. which clearly shows that ortho Fluorobenzaldehyde slightly more reactive than its meta isomer. The 3D plot of HOMO and LUMO and MEP are shows in the figure 3 and figure 4 respectively. The HOMO in case of meta isomer distributed over the ring while in ortho species it is shifted towards the aldehyde group mainly.

LUMO in both species spread uniformly over entire molecule. The importance of MEP is that it shows the size, shape as well as positive, negative and neutral electrostatic potential in terms of colour grading . The different values of the electrostatic potential at the surface are characterized by different colours; red represents regions of maximum negative electrostatic potential, blue represents regions of utmost positive electrostatic potential and green represents regions of zero potential. It is also very useful to correlate the molecular structure with its physiochemical property relationship [25-29]**.** The sliced 2D MESP contour maps of the title molecules have also been plotted in Fig. 4. Such a representation provides more detailed information regarding electrostatic potential distribution, by showing the values in a manifold of spatial location around the molecule. The MESP surface and 2D contour maps drawn in the molecular plane clearly suggests the different values of electrostatic potential in the two molecules. Moreover the red region has larger extent in case of 'm'- Fluorobenzaldehyde than 'o'-Fluorobenzaldehyde.
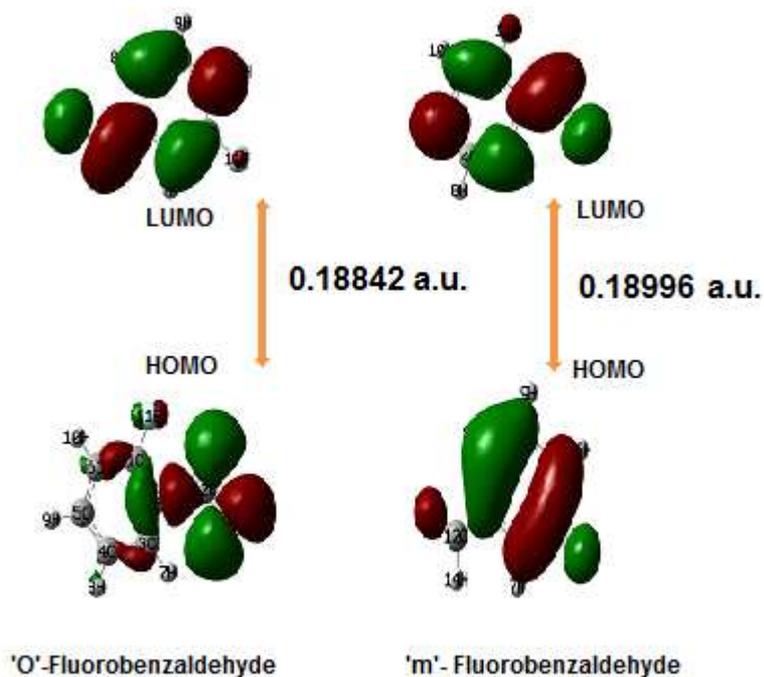
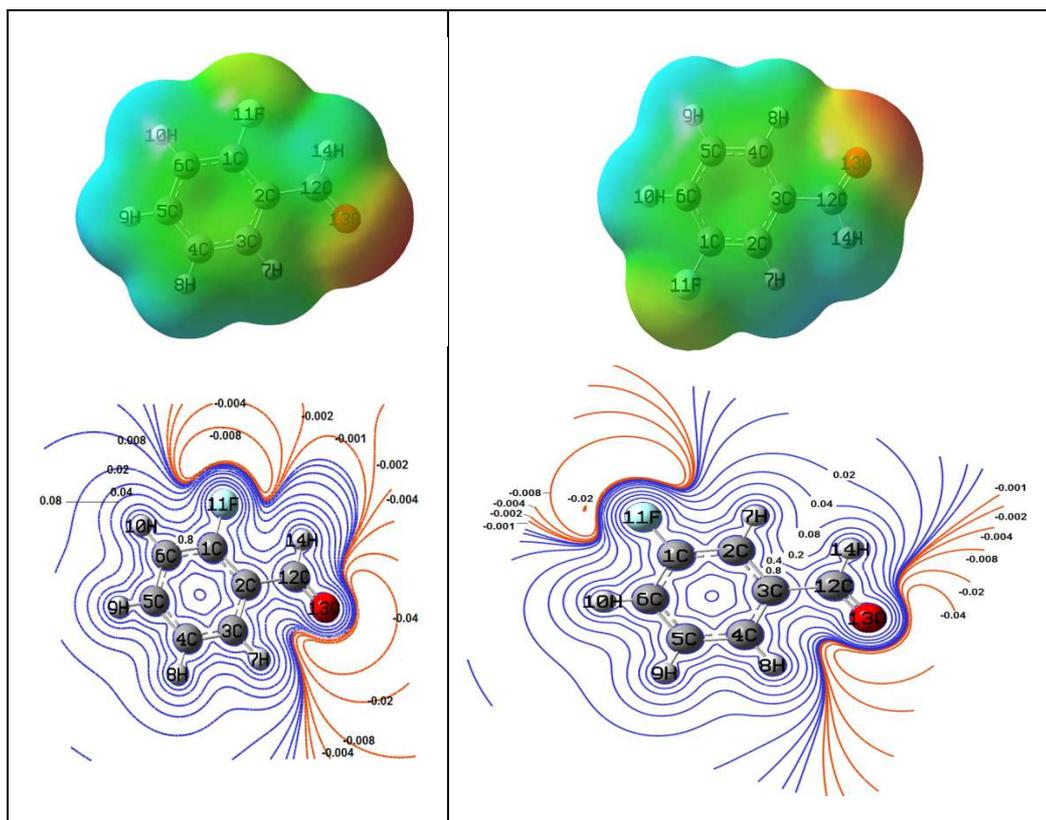**Figure 3 : HOMO-LUMO Plot of 'o' and 'm' Fluorobenzaldehyde**

Figure :4 MEP Surface and Contour Plots (values in a.u.) for 'o'-Fluorobenzaldehyde and 'm'-Fluorobenzaldehyde calculated at B3LYP/6-311G(d,p), in the molecular plane. The blue lines are representing positive isoptential and negative isoptential lines are red.

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Electric moments - The dipole moment in a molecule is   an   important property that is mainly used to study the intermolecular interactions involving the   non-bonded type dipole–dipole interactions, because higher the dipole moment, stronger will be the intermolecular interactions. The calculated value of dipole moment in case of 'o'-Fluorobenzaldehyde is found to be almost 1.7 times higher than that of the 'm'- Fluorobenzaldehyde (Table 1). The slightly lower frontier orbital energy gap and high dipole moment for 'o'-Fluorobenzaldehyde shows its higher activity and lesser stability as compared to 'm'- Fluorobenzaldehyde. The determination of electric polarizability   and hyperpolarizability   is of fundamental importance to study the phenomenon induced by intermolecular interactions, simulation studies and nonlinear optical effects. In the absence of experimental data, the values of polarizability and hyperpolarizability calculated at the same level of theory and the same basis set for the title molecules, can provide a satisfactory comparison of these quantities. Although the mean polarizability of 'o' and 'm'- Fluorobenzaldehyde is found to be almost same the total intrinsic hyperpolarizability β_{TOTAL} of meta isomer is 4.6 times than its ortho counterpart.

Table 1. Theoretically computed ground state optimized parameters

Parameter	'o'-Fluorobenzaldehyde B3LYP/6-311G(d,p)	'm'-Fluorobenzaldehyde B3LYP/6-311G(d,p)
Energy (in Hartree)	-444.92523 a.u.	-444.92597a.u.
Frontier orbital energy gap (in Hartree)	0.188 a.u	0.190 a.u.
Dipole moment (in Debye)	3.38	1.96
Polarizability / a.u.	74.679	75.052

Table 2. All β components and β total of 'o' and 'm' Fluorobenzaldehyde

	'o'-Fluorobenzaldehyde	'm'- Fluorobenzaldehyde
β_{XXX}	188.0	-202.1
β_{XXY}	41.5	-50.8
β_{XYY}	-47.1	-69.9
β_{YYY}	-69.2	-44.7
β_{XXZ}	0.0	0.0
β_{XYZ}	0.0	0.0
β_{YYZ}	0.0	0.0
β_{XZZ}	-14.1	8.2
β_{YZZ}	-1.6	3.2
β_{ZZZ}	0.0	0.0
β_{TOTAL}	141.8×10^{-30} e.s.u	653.7×10^{-30} e.s.u

Vibrational assignments - The experimental and computed vibrational   wavenumbers, their IR and Raman intensities and the detailed description of each normal mode of vibration of 'm'-Fluorobenzaldehyde and 'o'-Fluorobenzaldehyde carried out in terms of their contribution to the total potential energy are given in Table 3 and 4. DFT based calculations provide not only the qualitative but also the quantitative understanding of energy distribution of each vibrational mode on the basis of potential energy distribution (PED) and lead to an additional interpretation of the vibrational spectroscopic data as demonstrated in studies conducted by various groups [30-33]. The calculated FTIR and Raman spectra (Fig. 2) of both the molecules agree well with the FTIR and the FT-Raman data reported by the Sigma Aldrich chemical website [10]. The DFT calculated wavenumbers,   for the majority of the normal modes, are typically slightly higher than that of their experimental counterpart and thus proper scaling factors [16, 17] is employed to

have better agreement with the experimental wavenumbers. In the present study, vibrational wavenumbers calculated at B3LYP/6-311G(d,p) level have been scaled by 0.9679. There are total 14 atom which perform 36 normal modes of vibration Fundamental modes of vibrations of 'm'-Fluorobenzaldehyde/'o'-Fluorobenzaldehyde are distributed among the functional and the finger print regions. The phenyl ring spectral region predominantly involves the C–H, C–C and C=C stretching, and C–C–C as well as H–C–C-bending vibrations. Very intense band are found in the range 3100 -3000 cm^{-1} which is general observed in the case of aromatic compounds due to aromatic C-H stretching vibrations. The C–C stretching modes are observed as mixed modes in the wavenumber range 1600 cm^{-1} to 1000 cm^{-1} for both the molecules and are in good agreement with general appearance of C–C stretching modes. The modes appearing below 1000 cm^{-1} are mixed modes. The ring modes of both meta and ortho –Fluorobenzaldehyde are almost in the same range. The appearance of a strong band in IR spectra around 1700 cm^{-1} shows the presence of C=O stretch. The C=O stretch in m-Fluorobenzaldehyde/'o'-Fluorobenzaldehyde is calculated to be at 1730/1717 cm^{-1} and is assigned well with the experimental FTIR peak at 1734/1700 cm^{-1}. In the study of infra-red spectra of fluorinated aromatic compounds— pentaFluorobenzyl and pentaFluorobenzylidene halides, Mooney [34] have found that the v(C-F) modes are much more variable and are very sensitive to the nature of the substituent group Y in the pentaFluorophenyl derivative C_6F_5Y. The C-F stretching vibration in 'o'/'m' Fluorobenzaldehyde is calculated to be at 1203/1237 cm^{-1}.

Table 3: Theoretical and Experimental* wave-numbers (in cm^{-1}) of 'm'-Fluorobenzaldehyde

Calc. unsc. wave no. in cm^{-1}	Sc. wave. No in cm^{-1}	Exp.* FTIR waveno. in cm^{-1}	Exp.* Raman wave no in cm^{-1}	IR Intensity	Raman Intensity	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
3205	3102			4.3	9.12	v(C-H)R(99)
3200	3097	3096	3090	0.86	3.07	v(C-H)R(99)
3184	3082			0.7	5.90	v(C-H)R(92)
3181	3079			6.6	2.10	v(C-H)R(83)
2882	2789	2742	2735	128.09	10.34	v(C12-H14)(99)
1787	1730	1734	1720	239.12	14.47	v(C12-O13)(89)
1646	1593	1605	1495	4.89	17.52	v(C-C)R(54)+ β(H-C-C)R(12)
1632	1580	1527		74.62	3.04	v(C-C)R(48) + β(H-C-C)R(13)
1516	1467	1475	1470	32.22	0.43	β(H-C-C)R(44) + β(C-C-C)R(10)
1474	1427	1400		23.38	0.08	v(C-C)R(32)+ β(H-C-O)(12) + β(H-C-C)R(12)
1410	1365	1363		9.83	0.90	β(H-C-O)(74)
1352	1309	1315	1310	4.99	0.30	v(C-C)R(76)+β(H-C-O)(11)
1302	1260	1290	1250	21.51	0.95	β(H-C-C)R(59) + v(C-C)R(10)
1278	1237	1266		174.31	12.09	v(F-C)(30) + β(C-C-C)R(15) + v(C-C)R(12)
1182	1144	1150	1130	3.78	0.87	β(H-C-C)R(66)+ v(C-C)R(22)
1142	1105	1094		31.32	2.92	β(H-C-C)R(41) + v(C-C)R(17) + v(F-C)(11)
1095	1060		1073	5.61	1.52	β(H-C-C)R(49) + v(C-C)R(33)
1035	1002		1000	0.39	2.39	β $_{out}$(H-C-O)(95)
1016	983	974		0.46	14.49	β(C-C-C)R(61)+ v(C-C)R(24)
1000	968	955	960	0.02	0.02	ω(C-H)R(62) + ρ (C-C-C-C)R(13)
946	916			23.66	0.76	β(C-C-C)R(23)+v(C12-C3)(18)+v(F-C)(19)+v(C-C)R(10)
930	900	900		0.44	0.38	ω(C-H)R(88)
885	857			17.66	0.11	ω(C-H)R(70)+ ρ (C-C-C-C)R(10)

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810	784	790		46.8	0.31	ω(C-H)R(74)
788	763	760	770	56.41	7.85	β(C-C-C)R(27)+ β(O-C-C)(24) + ν(C-C)R(12)
690	668	660		15.97	0.01	ρ (C-C-C-C)R(64) +ω(C-H)R(34)
671	649		640	13.59	3.01	β(O-C-C)(33)+ β(C-C-C)R(16) + ν(C-C)R(12)
569	551	540		0.002	0.60	ρ (F-C-C-C)(42)+ ρ(C-C-C-C)R (38)
523	506			4.4	7.12	β(C-C-C)R(57) + ν (F-C)(18)
458	443		450	0.42	4.10	β(C-C-C)R(32)+ β(F-C-C)(23)+ ν(C12-C3)(14)

***Abbreviations**: ν -stretching; β-in plane bending; β$_{out}$ -out of plane bending; ρ - torsion;, ω-wagging.*
*Experimental FTIR and Raman data as reported in www.sigmaaldrich.com/united-states.html website.
Table 4 : Theoretical and Experimental* wave-numbers (in cm^{-1}) of 'o'-Fluorobenzaldehyde

Calc. unsc. wave no. in cm^{-1}	Sc. wave. No in cm^{-1}	Exp.* FTIR waveno. in cm^{-1}	Exp. * Raman wave no in cm^{-1}	IR Intensity	Raman Intensity	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
3205	3102	-	-	4.00	12.50	ν(C-H)R(92)
3199	3096	3096	-	6.82	2.34	ν(C-H)R(100)
3189	3087		3080	5.29	4.60	ν(C-H)R(91)
3176	3074	3033	-	2.24	3.20	ν(C-H)R(90)
2955	2858	2867	2875	85.85	8.79	ν(C12-H14)(100)
1774	1717	1700	1700	224.44	14.60	ν(C12-O13)(88)
1650	1597	1622	1615	91.90	17.46	ν(C-C)R(44)+ β(H-C-C)R(20)
1623	1571		1590	28.80	1.26	ν(C-C)R(49) + β(H-C-C)R(15)
1511	1462	1462	1490	55.17	0.95	β(H-C-C)R(36) + ν(C-C)R(16)
1488	1440		1474	41.51	0.32	β(H-C-C)R(53) + ν(C-C)R(13)+ ν(C-C)(10)
1429	1383	1402	1405	274.41	1.06	β(H-C-O)(82)
1342	1298	1304	1280	7.11	0.39	ν(C-C)R(78)+β(H14-C11-O13)(11)
1298	1256	1232	-	66.91	0.79	β(H-C-C)R(57) + ν(C-C)R(12)
1243	1203	1195	1226	54.26	12.21	ν(F-C)R(32) + β(H-C-C)R(20) + ν(C-C)R(11)
1208	1169	1157	1190	23.76	2.11	β(H-C-C)R(32)+ ν(C12-C2)(16)+ β(C-C-C)R(13)+ν(C-C)R(10)+ β(H-C-O)(10)
1174	1136	1130	1156	15.84	5.27	β(H-C-C)R(68) + ν(C-C)R(11)
1117	1081	-	-	18.41	0.63	β(H-C-C)R(35) +β(C-C-C)R(30)
1050	1016	1024	1030	1.83	9.54	ν(C-C)R(38)+ β(H-C-C)R(30)
1040	1008	1006	1006	0.15	1.91	β $_{out}$(H-C-O)(82)
1005	973		-	0.15	0.04	ω(C-H)R(83)
978	947	953	-	1.95	0.06	ω(C-H)R(78)+ β $_{out}$(H-C-O)(10)
881	853	847	-	0.76	0.75	ω(C-H)R(76) + β $_{out}$(C-C-C)(15)
852	825		800	34.23	1.11	β(C-C-C)R(47)+ ν(C12-C2)(15) + ν(F-C)(15)
813	787	800	-	20.10	10.04	β(O-C-C)(20) + β(C-C-C)R(18)+ ν(F-C)(13)
781	756	760	758	71.27	0.17	ω(C-H)R(73) + ρ(F-C-C-C)(10)
730	707	722	-	0.15	0.13	ρ(C-C-C-C)R(62)+ ρ(F-C-C-C)(12) + ω(C-H)R(11)
644	623	642	630	19.04	6.32	β(C-C-C)R(39) + β(O-C-C)(29) +β(H-C-C)R(14)
547	529	540	540	6.99	7.65	β(F-C-C)R(31) + β(C-C-C)R(10)+ β(H-C-C)R(10)
539	522	520	510	1.59	0.49	ρ (C-C-C-C)R(45)+ ρ(F-C-C-C) (29)
511	495		-	9.88	3.81	β(C-C-C)R(57) + β(F-C-C)(13) + ν(C12-C2)(10)
462	447		-	5.51	0.11	ρ (C-C-C-C)R(79)

***Abbreviations**: ν -stretching; β-in plane bending; β$_{out}$ -out of plane bending; ρ - torsion;, ω-wagging.*
*Experimental FTIR and Raman data as reported in www.sigmaaldrich.com/united-states.html website.

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CONCLUSION

In the present work we have calculated the geometric parameters, the vibrational frequencies, frontier orbital band gap, MESP surfaces and the non-linear optical properties of 'm'-Fluorobenzaldehyde and 'o'-Fluorobenzaldehyde using DFT/ B3LYP method. The lower frontier orbital energy gap and the higher dipole moment value make the 'o'-Fluorobenzaldehyde more reactive and more polar, hence lesser stable than 'm'-Fluorobenzaldehyde molecule. NLO behavior of both the title molecules were investigated by the determination of the dipole moment, polarizability and the first hyperpolarizability using the DFT/B3LYP/6-311G(d,p) method. In general, a good agreement between experimental and calculated normal modes of vibrations have been observed. The molecular electrostatic potential surfaces have also been drawn   to explain the activity of 'o'-Fluorobenzaldehyde over meta species. The present quantum chemical study may further play an important role in understanding of dynamics of these molecules.

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