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FTIR, FT–RAMAN, Conformational Studies, the Molecular Geometry and Vibrational Frequencies of 5–Bromo–o–Anisaldehyde and 3–Fluoro–p–Anisaldehyde

D. Usha¹, G. John James² and L.F.A. Amirtharaj³

¹Department of Physics, Women's Christian College, Nagercoil – 629 001, Tamil Nadu, India. ²Department of Physics, Government Arts College, Tiruchirappalli – 620 022, Tamilnadu, India. ³Department of Physics, Government Arts College, Karur – 639 005, Tamilnadu, India.

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Introduction

Anisole is one of the simplest aromatic compound to which ether group is linked. But it is different with aromatic compounds like furan where the oxygen is a part of the ring. Anisole, $C_6H_5OCH_3$ (methyl phenyl ether), is a clear liquid that is soluble in ether and alcohol insoluble in water boiling point 155°C. Anisole and its derivatives are used as solvents and in perfumery. Anisole can be obtained from anise seed. Anisic acid, p-methoxybenzoicacid, is a part of cresol class antiseptic compounds. It is also used as an insect repellent and ovicide. Anisole, anisic acid, and their derivatives are also widely used in chemical reaction as intermediates to obtain target materials such as dyes, pharmaceuticals, perfumes, photoinitiators and agrochemicals. p-Anisaldehyde, an aromatic aldehyde with mothoxygruop, is a clear liquid may discolor to yellow on storage (limited shelf life for 6 months) melting at -1°C, boiling at 249.5°C insoluble in water, soluble in alcohol and ether. It is used in the synthesis of other organic compounds including pharmaceuticals (especially antihistamines), agrochemicals, dyes and plastic additives. It is an important intermediate for the processing of perfumes and flavouring compounds.

Benzaldehyde (also called Benzenecarbonal) is the simplest representative of the aromatic aldehydes. It is a colorless liquid aldehyde with a characteristic almond odor. It boils at 180°C, is soluble in ethanol, but is insoluble in water. Benzaldehyde is formed by partial oxidation of benzyl alcohol and readily oxidized to benzoic acid and is converted to addition products by hydrocyanic acid or sodium bisulfite. It is also prepared by oxidation of toluene or benzyl chloride or by treating benzal chloride with an alkali, e.g., sodium hydroxide.

ABSTRACT

The FTIR and FT-Raman spectra of 5-bromo-o-anisaldehyde (BOA) and 3-fluoro-panisaldehyde (FPA)have been recorded in the region 4000-400 cm⁻¹ and 3500-50 cm⁻¹, respectively.The structural and spectroscopic data of the molecule in the ground state were calculated by using density functional theory (DFT) employing B3LYP 6-31+G(d,p) basis set.The geometry of the molecule was fully optimized, vibrational spectra were calculated and fundamental vibration were assigned on the basis of potential energy distribution (TED) of the vibrational modes calculated with scaled quantum mechanical (SQM) method.

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It is used chiefly in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives and benzaldehyde is an important intermediate for the processing of perfume and flavouring compounds and in the preparation of certain aniline dyes. It is the first step in the synthesis for fragrances. It undergoes simultaneous oxidation and reduction with alcoholic potassium hydroxide, giving potassium benzoate and benzyl alcohol. It is converted to benzoin with alcoholic potassium cyanide, with anhydrous sodium acetate and acetic anhydride, giving cinnamic acid. Compounds which do not have alpha-hydrogen atoms cannot form an enolate ion and do not undergo electrophilic alphasubstitution and aldol condensation. Aromatic aldehydes such benzaldehyde and formaldehyde may undergo as disproportionation in concentrated alkali(Cannizaro's reaction)one molecule of the aldehyde is reduced to the corresponding alcohol and another molecule is simultaneously oxidized to the salt of a carboxylic acid. The speed of the reaction depends on the substituents in the aromatic ring. Two different types of aldehydes (aromatic and aliphatic) can undergo crossing reaction to form fomaldehyde and aromatic alcohols.

The assignment of bands in the vibrational spectra of aromatic and another conjugated systems are an essential step in application of vibrational spectroscopy for solving various structural chemical problems. Assignments for complex systems can be proposed on the basis of frequency agreement between the computed harmonics and the observed fundamentals. Density functional theory (DFT) is becoming increasingly popular among experimentalists and theoreticians in the present chemical literature [1, 2].

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Numerous reports have been made citing the success of DFT compared with the conventional ab initio methods in computing molecular and chemical properties such as geometries, harmonics frequencies, and energies [3-6]. DFT is superior to the conventional methods such as Hartree-Fock (HF) and second-order Moller-Plesset perturbation theory (MP2), for the calculation of polyatomic vibrational frequencies with empirical scaling factors approaching unity [3,7]. The cost effectiveness of DFT over conventional methods is an additional feature.

In this study, the conformational behaviour and vibrational analysis of 5-bromo-o-anisaldehyde (BOA) and 3-fluoro-p-anisaldehyde (FPA) have been carried out by the application of the Becke3-Lee-Yang-Parr (B3LYP)/6-31+G(d,p) basis sets-based on scaled quantum mechanical (SQM) method [8]. The energies have been carried out for the various possible conformers of the title compounds and the optimized geometrical parameters also obtained by the DFT calculations.Based on these calculations, the calculated frequencies were obtained. The observed and the calculated frequencies agree well.

2. ExperimentaL PROCEDURES

BOA and FPA were purchased from Lancaster Chemical Company, UK and used without further purification. Fourier transform infrared spectra for the title compounds were recorded in the region 4000 - 400 cm⁻¹ using BRUKER IFS 66V FTIR spectrometer equipped with an MCT detector, a KBr beam splitter and globar source at a resolution of ± 1 cm⁻¹. The FT-Raman spectra were recorded on the same instrument with FRA 106 Raman accessories in the region 3500 - 100 cm⁻¹. The 1064 nm Nd:YAG laser was used as excitation source, and the laser power was set to 200 mW.

3. Computational METHODS

The molecular geometry optimizations and vibrational frequency calculations were performed with the Gaussian 03W software package [9] with B3LYP-DFT functional and the standard 6-31+G(d,p) basis set [10,11]. The normal grid (12,13) was used for numerical integration. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming C_s point group symmetry. Scaling of the force fields was performed by the scaled quantum mechanical (SQM) procedure with selective scaling in the local symmetry coordinate representation [14] using transferable scale factors available in the literature [8]. The transformations of the force field and the subsequent normal coordinate analysis including the least square refinement of the scaling factors calculation of the total energy distribution (TED), and the prediction of IR and Raman intensities were done on a PC with the MOLVIB program (Version V7.0 - G77) written by Tom Sundius [15,16]. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 10 cm⁻¹.

The vibrational modes were assigned by means of visual inspection using the GAUSSVIEW program [17]. The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using standard procedure [08,18] of decomposing the traces of the symmetry operations into the irreducible represents. The symmetry analysis for the vibrational modes of BOA and FPA were presented in some detail in order to better describe the basis for the assignments.

The Raman activities (S_i) calculated with the GAUSSIAN-03 program and adjusted during the scaling procedure with MOLVIB were converted to relative Raman

intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [19-21].

$$\frac{f(v_{o} - v_{i})^{4}S_{i}}{v_{i}\left[1 - \exp\left(-\frac{hcv_{i}}{kT}\right)\right]}$$
...(1)

where v_o is the exciting frequency (in cm⁻¹), v_i is the vibrational wavenumber of the *i*thnormal mode, *h*, *c* and *k* are fundamental constants, and *f* is a suitably chosen common normalization factor for all peak intensities.

4. Results and discussion 4.1. Geometrical parameters

The molecular structures and stable conformers of BOA and FPA were belong to C_s symmetry and were shown in Figs. 1 and 2, respectively.



(c) (d) Fig. 1.Molecular structure and various conformers of 5-bromo-o-anisaldehyde.



Fig. 2.Molecular structure and variable conformers of 3-fluoro-p-anisaldehyde.

Table 1.Total energies of different conformations of 5bromo-o-anisaldehyde and 3-fluoro-p-anisaldehyde, calculated at the DFT (B3LYP)/6-31+G(d,p) level of theory.

theory.						
Conformer	Total energies (in Hartrees)					
	BOA	FPA				
а	-3031.232151	-559.345051				
b	-3031.080163	-559.347346				
с	-3031.236802*	-559.320102*				
d	-3031.157013	-559.35236				

*global minimum energy

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Bond length (Å) **Parameters Parameters** Bond angle(°) **Parameters Dihedral angle(°)** C1-C2 1.3997 C2-C1-C6 119.9 C6-C1-C2-C3 -0.0003C6-C1-C2-O10 C1-C6 1.3891 C2-C1-C7 121.1 180.0 C1-C7 1.4868 C6-C1-C7 118.8 C7-C1-C2-C3 0.0 C2-C3 1.3907 C1-C2-C3 119.4 C7-C1-C2-O10 -180.0116.7 C2-O10 1.3417 C1-C2-O10 C2-C1-C6-C5 0.0 C3-C2-O10 C3-C4 1.3853 123.7 C2-C1-C6-H18 0.0 C3-H15 1.0719 C2-C3-C4 119.9 C7-C1-C6-C5 -179.9C4-C5 1.3830 C2-C3-H15 C7-C1-C6-H18 180.0 121.1 C4-H16 1.0740 C4-C3-H15 118.8 C2-C1-C7-O8 0.0 C3-C4-C5 C2-C1-C7-H9 C5-C6 1.8919 120.4 -0.0008C5-Br17 1.3787 C3-C4-H16 119.3 C6-C1-C7-O8 -0.0008C6-C1-C7-H9 C6-H18 1.0730 C5-C4-H16 120.1 -180.0009C4-C5-C6 C1-C2-C3-C4 C7-08 1 9370 120.0 0.0001 C7-H9 1.0876 C4-C5-Br17 119.8 C1-C2-C3-H15 180.0007 O10-C11 1.4059 C6-C5-Br17 120.1 O10-C2-C2-C4 179.9 120.2 C11-H11 1.0844 C1-C6-C5 O10-C2-C3-H15 -0.00091.0792 C1-C2-O10-C11 C11-H12 C1-C6-H18 118.4 180.0 C1-C2-O10-C11 C11-H13 1.0844 C5-C6-H18 121.3 0.0033 C2-C3-C4-C5 C1-C8-O8 123.0 0.0002 C1-C7-H9 C2-C3-C4-H16 116.1 180.0 O8-C7-H9 120.8 H15-C3-C4-C5 -180.0C3-C4-C5-C6 C2-O10-C11 120.5 -0.0002O10-C11-H12 111.0 C3-C4-C5-Br17 -180.0O10-C11-H13 105.8 H16-C4-C5-C6 -180.0H16-C4-C5-Br17 O10-C11-H14 -0.0001111.0 H12-C11-H13 109.3 C4-C5-C6-C1 0.0 H12-C11-H14 109.9 C4-C5-C6-H18 180.0 H13-C11-H14 109.3 Br17-C5-C6-H18 180. Br17-C5-C6-C1 0.0001 C2-O10-H11-H12 61.4 C2-O10-H11-H13 -179.9C2-O10-H11-H14 -61.2

Table 2.Optimized geometrical parameters of 5-bromo-o-anisaldehyde obtained by B3LYP/6-31+G(d,p) density functional calculations.

for numbering of atom refer Fig. 2.

Table 3.Optimized geometrical parameters of 3-fluoro-p-anisaldehyde obtained by B3LYP/6-31+G(d,p) density functional calculations.

Parameters	Bond length (Å)	Bond length (Å) Parameters B		Parameters	Dihedral angle(°)
C1-C2	1.4069	C2-C1-C6	119.3	C6-C1-C2-C3	0.0011
C1-C6	1.4014	C2-C1-C7	119.5	C6-C1-C2-H10	179.9
C1-C7	1.4755	C6-C1-C7	121.1	C7-C1-C2-C3	-179.9
C2-C3	1.3792	C1-C2-C3	119.5	C7-C1-C2-H10	-0.001
C2-H10	1.0863	C1-C2-H10	121.3	C2-C1-C6-C5	-0.0012
C3-C4	1.4085	C3-C2-H10	119.1	C2-C1-C6-H18	-180.0
C3-F11	1.3532	C2-C3-C4	121.9	C7-C1-C6-C5	-180.0
C4-C5	1.4055	C2-C3-F11	119.7	C7-C1-C6-H18	-0.0023
C4-O126	1.3515	C4-C3-F11	118.2	C2-C1-C7-O8	-179.9
C5-C6	1.3929	C3-C4-C5	118.0	С2-С1-С7-Н9	0.0
C5-H17	1.0833	C3-C4-O12	116.3	C6-C1-C7-O8	0.0
C6-H18	1.0851	C5-C4-O12	125.6	С6-С1-С7-Н9	-179.9
C7-O8	1.2198	C4-C5-C6	120.3	C1-C2-C3-C4	0.0
C7-H9	1.1114	C4-C5-H17	120.0	C1-C2-C3-F11	-180.0
O12-C13	1.4274	C6-C5-H17	119.5	H10-C2-C2-C4	180.0
C13-H14	1.0898	C1-C6-C5	120.7	H10-C2-C3-F11	0.0
C13-H15	1.0961	C1-C6-H18	118.7	C2-C3-C4-C5	-0.0018
C13-H16	1.0961	C5-C6-H18	120.3	C2-C3-C4-O12	-179.9
		C1-C8-O8	124.8	F11-C3-C4-C5	179.9
		C1-C7-H9	114.7	F11-C3-C4-O12	0.0
		O8-C7-H9	120.3	C3-C4-C5-C6	0.0
		C4-O12-C13	118.6	C3-C4-C5-H17	180.0
		O12-C13-H14	105.4	O12-C4-C5-C6	-180.0
		O12-C13-H15	111.1	O12-C4-C5-H17	-0.0005
		O12-C13-H16	111.1	C3-C4-O12-C13	180.0
		H14-C13-H15	109.5	C5-C4-O12-C13	0.071
		H14-C13-H16	109.5	C4-C5-C6-C1	-0.0002
		H15-C13-H16	109.8	C4-C5-C6-H18	-179.9
				H17-C5-C6-C1	-180.0
				H17-C5-C6-H18	-0.0014
				C4-O12-C13-H14	-180.0
				C4-O12-C13-H15	-161.3
				C4-O12-C13-H16	-61.2

For numbering of atom refer Fig. 3.

In order to find the most optimized geometry, the energy calculations were carried out for various possible conformers. The global minimum energy calculations of the title compounds were found using 6-31+G(d,p) (for four different possible conformers. The total energies obtained for these conformers were listed in Table 1. The stable conformers Fig. 1(c) of BOA and Fig. 2(c) of FPA have produced the global energy minimum. The most optimized geometrical parameters for BOA and FPA were also calculated and they were listed in Table 2 and 3, respectively.

4.2. Vibrational band assignments

Both the molecules BOA and FPA having 18 atoms give rise to 48 normal modes of vibrations and they were distributed among the symmetry species as $\Gamma_{vib} = 33A' + 15A''$. The A' and A'' represents the in-plane and out-ofplane vibrations, respectively. All vibrations are active both in the infrared absorption and Raman scattering.

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full sets of (61 for both BOA and FPA) standard internal coordinates (containing 13 redundancies for both the title compounds) were defined as given in Tables 4 and 5, respectively. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi and Pulay [22] and they were presented in Tables 6 and 7. The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations.

Table 4.Definition of internal coordinates of 5-bromo-oanisaldebyde

No. (i)	Symbol	Туре	Definition
Stretchir	ig		·
1-3	r _i	C-H	C3-H15, C4-H16, C6-H18
4	R _i	C-C	C1 – C7
5	r _i	C-H	C7 – H94
6-7	pi	C-0	C2-O10, C11-O10
8	Pi	C-Br	C5 – Br17
9	pi	C=O	C7 – O8
10-12	r _i	C-H	C11 - H12, C11 - H13, C11 - H14
13-18	\mathbf{q}_{i}	C-C	C1 - C2, C2 - C3, C3 - C4, C4 -
			С5,
			C5 - C6, C6 - C1
Bending	1		
19-24	βi	bCH	С1 - С6-Н18, С5-С6-Н18, С5-С4-
			H16, C3-C4-H16, C4-
		1.99	C3-H15, C2-C3-H15
25-26	αi	bCC	C2-C1-C7, C6-C1-C7
27-28	σi	bCO	C1-C2-O10, C3-C2-O10
29-30	ρι	BCBr	C4-C5-Br17, C6-C5-Br17
31	αί	bCC	С1-С7-Н9
32	αi	bCC	C1-C7-O8
33	δi	bOH	О8-С7-Н9
34-36	φi	bOC	O10-C11-H12, O10-C11-H13,
	1-		O10-C11-H14
37-39	π_{i}	H-C-	H12-C11-H13, H12-C11-H14,
		Н	H13-C11-H14
40-45	γi	C-C-C	C1-C2-C3, C2-C3-C4, C3-C4-C5,
	-		C4-C5-C6, C5-C6-C1, C6-C1-C2
Out-of-p	lane bending	3	
46-48	ωi	C-H	H15-C3-C2-C4, H16-C4-C3-C5,
			H18-C5-C1-C5
49	φi	C-C	C7-C1-C2-C6
50	Φ_{i}	C-0	O10-C2-C1-C3
51	ψi	C-Br	Br17-C5-C4-C6
52	θ_i	O-H	08-C7-C1-C6 (C2)

-			
53	ωi	C-H	H9-C7-C1-C6(C2)
54	τi	t CO	C2-O10-C11-(H12, H13, H14)
55	τi	t CO	H9-C7-O8-C1
56-61	τι	t Ring	C1-C2-C3-C4, C2-C3-C4-C5,
			C3-C4-C5-C6, C4-C5-C6-C1,
			C5-C6-C1-C2, C6-C1-C2-C3
г	1	C	E' 0

For numbering of atoms refer Fig.2

Table 5.Definition of internal coordinates of 3-fluoro-p-
anisaldehyde.

No. (i)	Symbol	Туре	Definition
Stretchi	ing		
1-3	r _i	C-H	C2-H10, C5-H17, C6-H18
4	R _i	C-C	C1-C7
5	r _i	C-H	С7-Н94
6-7	p _i	C-0	C4-O12, C13-O12
8	Pi	C-Br	C3-F11
9	pi	C=O	C7-O8
10-12	r _i	C-H	C13-H14, C13-H15, C13-H16
13-18	q_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-
			C6, C6-C1
In-plane	Bending		1
19-24	β_i	bCH	С1-С6-Н10, С3-С2-Н10, С1-С6-Н18,
			С5-С6-Н18, С6-С5-Н17, С4-С5-Н17
25-26	α_i	bCC	C2-C1-C7, C6-C1-C7
27-28	σ_{i}	bCO	C3-C4-O12, C5-C4-O12
29-30	ρ_i	bCBr	C2-C3-F11, C4-C3-F11
31	α_{i}	bCC	С1-С7-Н9
32	α_i	bCC	C1-C7-O8
33	δi	bOH	O8-C7-H9
34-36	φ _i	bOC	O12-C13-H14, O12-C13-H15,
			O12-C13-H16
37-39	π_{i}	H-C-	H14-C13-H15, H14-C13-H15,
		Н	H15-C13-H16
40-45	γ_i	C-C-	C1-C2-C3, C2-C3-C4, C3-C4-C5,
		С	C4-C5-C6, C5-C6-C1, C6-C1-C2
Out-of-p	plane bendi	ng	
46-48	ω _i	C-H	H10-C2-C4-C3, H17-C5-C4-C6,
			H18-C6-C1-C5
49	ϕ_i	C-C	C7-C1-C2-C6
50	Φ_{i}	C-0	012-C4-C3-C5
51	ψ_i	C-F	F11-C3-C2-C4
52	θ_{i}	O-H	O8-C7-C1-C6 (C2)
53	ω _i	C-H	H9-C7-C1-C6(C2)
54	τ_{i}	t CO	H9-C7-O8-C1
55	τ	t CO	C4-O12-C13-(H14, H15, H16)
56-61	τ _i	t	C1-C2-C3-C4, C2-C3-C4-C5,
		Ring	C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-
			C1-C2, C6-C1-C2-C3

For numbering of atoms refer Fig. 3

Table 6.Definition of local symmetry coordinates of 5bromo-o-anisaldehyde.

No. (i)	Symbol	Definition
1-3	CH	r_1, r_2, r_3
4	CC	R ₄
5	СН	r ₅
6,7	CO	p ₆ , p ₇
8	CBr	P ₈
9	CO	p ₉
10	CH ₃ ss	$(r_{10}+r_{11}+r_{13})/\sqrt{3}$
11	CH ₃ ips	$(2r_{10}-r_{11}-r_{13})/\sqrt{6}$
12	CH ₃ ops	$(r_{11}-r_{12}) / \sqrt{2}$
13-18	CO	$q_{13}, q_{14}, q_{15}, q_{16}, q_{17}, q_{18}$
19-21	bCH	$(\beta_{19}-\beta_{20})/\sqrt{2}, (\beta_{21}-\beta_{22})/\sqrt{2}, (\beta_{23}-\beta_{24})$

		$\sqrt{\sqrt{2}}$
22	bCC	$(\alpha_{25} - \alpha_{26}) / \sqrt{2}$
23	bCO	$(\sigma_{27} - \sigma_{28}) / \sqrt{2}$
24	bCBr	$(\rho_{29} - \rho_{30}) / \sqrt{2}$
25	bCC	α31
26	bCC	α32
27	bOH	δ ₃₃
28	CH ₃ sb	$(-\phi_{34} - \phi_{35} - \phi_{36} + \pi_{37} + \pi_{38} + \pi_{39})/\sqrt{6}$
29	CH ₃ ipb	(- m ₃₇ -m ₃₈ - 2m ₃₉)/ $\sqrt{6}$
30	CH ₃ opb	(_{π38} - _{π39}) / $\sqrt{2}$
31	CH ₃ ipr	$(2\phi_{34} - \phi_{35} - \phi_{36}) / \sqrt{6}$
32	CH ₃ opr	$(\phi_{35} - \phi_{36}) / \sqrt{2}$
33	Rtrigd	$(\gamma_{40} - \gamma_{41} + \gamma_{42} - \gamma_{43} + \gamma_{44} - \gamma_{45}) / \sqrt{6}$
34	Rsymd	$(-\gamma_{40} - \gamma_{41} + 2\gamma_{42} - \gamma_{43} - \gamma_{44} + 2\gamma_{45}) / \sqrt{12}$
35	Rasymd	$(\gamma_{40} - \gamma_{4+} \gamma_{43} - \gamma_{44}) / 2$
36-38	ωCH	W46, W47, W48
39	ωCC	Φ49
40	ωCO	φ50
41	ωCBr	Ψ51
42	ωOH	ω52
43	ωCH	ω63
44	ωCO	τ54
45	τСОН	τ54
46	tRtrig	$^{(\tau_{56}+\tau_{57}+\tau_{58}+\tau_{59}+\tau_{60}+\tau_{61})/}\sqrt{6}$
47	tRsym	$(\tau_{56}+\tau_{57}+\tau_{59}+\tau_{60})/2$
48	tRasy	$(-\tau_{56}+2\tau_{57}-\tau_{58}-\tau_{59}+2\tau_{60}-\tau_{61})/\sqrt{12}$

 Table 7.Definition of local symmetry coordinates of 3fluoro-p-anisaldehyde.

No. (i)	Symbol	Definition
1.2	СЦ	
1-5	СП	D
4	CC GV	K ₄
5	СН	r ₅
6,7	CO	p ₆ , p ₇
8	CBr	P ₈
9	CO	p9
10	CH ₃ ss	$(r_{10}+r_{11}+r_{13})/\sqrt{3}$
11	CH ₃ ips	$(2r_{10}-r_{11}-r_{13})/\sqrt{6}$
12	CH ₃ ops	$(r_{11}-r_{12}) / \sqrt{2}$
13-18	СО	$q_{13}, q_{14}, q_{15}, q_{16}, q_{17}, q_{18}$
19-21	bCH	$(\beta_{19} - \beta_{20}) / \sqrt{2}, (\beta_{21} - \beta_{22}) / \sqrt{2}, (\beta_{23} - \beta_{24})$
		/ √2
22	bCC	$(\alpha_{25} - \alpha_{26}) / \sqrt{2}$
23	bCO	$(\sigma_{27} - \sigma_{28}) / \sqrt{2}$
24	bCF	$(\rho_{29} - \rho_{30}) / \sqrt{2}$
25	bCC	α ₃₁
26	bCC	α32
27	bOH	δ ₃₃
28	CH ₃ sb	$(-\phi_{34} - \phi_{35} - \phi_{36} + \pi_{37} + \pi_{38} + \pi_{39})/\sqrt{6}$

29	CH ₃ ipb	$(-\pi_{37}-\pi_{38}-2\pi_{39})/\sqrt{6}$
30	CH ₃ opb	$(\pi_{38} - \pi_{39}) / \sqrt{2}$
31	CH ₃ ipr	$(2\phi_{34} - \phi_{35} - \phi_{36}) / \sqrt{6}$
32	CH ₃ opr	$\phi_{35} - \phi_{36}) / \sqrt{2}$
33	Rtrigd	$(\gamma_{40} - \gamma_{41} + \gamma_{42} - \gamma_{43} + \gamma_{44} - \gamma_{45}) / \sqrt{6}$
34	Rsymd	$(-\gamma_{40} - \gamma_{41} + 2\gamma_{42} - \gamma_{43} - \gamma_{44} + 2\gamma_{45}) / \sqrt{12}$
35	Rasymd	$(\gamma_{40} - \gamma_{4+} \gamma_{43} - \gamma_{44}) / 2$
36-38	ωCH	ω 46, ω 47, ω 48
39	ωCC	φ49
40	ωCO	φ50
41	ωCF	Ψ51
42	ωОН	ω52
43	ωCH	ω 63
44	ωCO	τ ₅₄
45	τСОН	τ54
46	tRtrig	$(\tau_{56} + \tau_{57} + \tau_{58} + \tau_{59} + \tau_{60} + \tau_{61}) / \sqrt{6}$
47	tRsymd	$(\tau_{56}+\tau_{57}+\tau_{59}+\tau_{60})/2$
48	tRasym d	$(-\tau_{56}+2\tau_{57}-\tau_{58}-\tau_{59}+2\tau_{60}-\tau_{61})/\sqrt{12}$

The observed, calculated frequencies, calculated IR and Raman intensities and normal mode descriptions (characterized by TED) for the conformers (Figs. 1 (c) and 2(c)) of the title compounds were presented in Tables 8 and 9, respectively. The observed FT-IR and FT-Raman spectra of the title compounds were presented in Figs. 3 - 6, which helps to understand the observed spectral features.

Root mean square error of the frequencies (unscaled) observed for BOA and FPA were found 84.45 and 82.11 cm⁻¹, respectively. In order to reproduce the observed frequencies, refinement of scaling factors were applied and optimized via least square refinement algorithm which resulted a weighted RMS deviation 4.8 cm^{-1} for BOA and 4.3 cm^{-1} for FPA, respectively, between the experimental and scaled quantum frequencies for 6-31+G(d,p) basis set. The vibrational frequencies of the various functional groups present in the title compounds were discussed below:



Fig. 4.FT-Raman Spectrum of 5-bromo-o-anisaldehyde.



Fig. 6.FT-Raman Spectrum of 2-fluro-p-anisaldehyde. C–H Vibrations

The aromatic structure shows the presence of C–H stretching vibrations in the region $3100-3000 \text{ cm}^{-1}$ which is the characteristic region for the ready identification of the C–H stretching vibrations. In this region, the bands are not affected appreciably by the nature of the substitutents. Hence, in the present investigation, the FT-IR and FT-Raman bands are observed at 3103, 3073, 3015 cm⁻¹ and 3051, 3022, 3000 cm⁻¹, respectively in BOA and FPA have been designated to C–H stretching vibrations. The B3LYP level at 6-31+G(d,p) after scaling down give the frequency values at 3106, 3082, 3009 cm⁻¹ and 3060, 3026, 3003 cm⁻¹. In general the aromatic C–H vibrations calculated theoretically are in good agreement with the experimentally reported values [23,24] for trisubstituted benzene.

The in-plane aromatic C–H deformation vibrations occur in the region 1450–990 cm⁻¹. The bands are sharp but are weak to medium intensity. The C–H in-plane bending vibrations computed at 1491, 1466, 1453 cm⁻¹ and 1395, 1389, 1345 cm⁻¹ for BOA and FPA by B3LYP method shows good agreement with experimental value. The medium and very strong intensity bands at 1497, 1480, 1461 cm⁻¹ and 1396, 1285 cm⁻¹ in FT-IR spectra are due to in-plane C–H deformations for BOA and FPA, respectively. The same vibrations appear in the Raman spectra at 1460 cm⁻¹ with medium intensity for BOA and 1348 cm⁻¹ in FT-Raman for FPA.

C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm⁻¹ [25]. Theoretically computed frequencies at 1145, 1106, 1018 cm⁻¹ and 1020, 949, 885 cm⁻¹ for BOA and FAP by B3LYP/6-31+G(d,p) method are assigned to C–H out-of-plane bending vibrations coincides with experimental value. In this current work, the peaks at 1142, 1100, 1020 cm⁻¹ in IR, and 1095 cm⁻¹ in FT-Raman while the peaks at 1021, 949, 884 cm⁻¹ in IR counterpart confirms the C–H out-of-plane bending vibration for BOA and FPA, which agrees with the above said literature values [26,25].

C–C Vibrations

The bands 1430–1650 cm⁻¹ were assigned to C–C stretching modes [27]. Socrates [28] mentioned that the presence of conjugate substituents such as C=C causes a heavy doublet formation around the region 1625–1575 cm⁻¹. The six ring carbon atoms undergo coupled vibrations, called skeletal vibrations and give a maximum of four bands with region 1660–1220 cm⁻¹ [29]. As predicted in the earlier references, in this title compounds also there are prominent peaks at 1634, 1593, 1575, 1395, 1267, 1244, 1179 cm⁻¹ for BOA and 1610, 1588, 1586, 1186, 1121 cm⁻¹ for FPA due to strong C–C stretching vibrations. The C–C in-plane bending results 705 cm⁻¹ and 750 cm⁻¹ harmonic frequencies calculated by B3LYP/6-31+G(d,p) method for the title molecules show good agreement with experimental results. **Aldehvde group vibrations**

The C–H stretching vibrations of the aldehyde group [30] usually appear in the region 2806–2871 cm⁻¹. Hence, in the present work, the C-H stretching vibrations computed by B3LYP/6-31+G(d,p) method at 2886 cm^{-1} for BOA and 2835 cm⁻¹ for FPA show very good agreement with recorded value. The weak band observed in the FT-IR spectra 2878 and 2830 cm⁻¹ for BOA and FPA, respectively are due to C-H stretching vibration of the aldehyde group. The in-plane C-H deformation mode of aldehyde group is observed at 1480 and 1388 cm⁻¹ with weak intensity both in the FT-IR spectra for the title molecules. The carbonyl (C=O) stretching vibrations in the substituted benzaldehydes is reported near 1700 cm^{-1} [28]. The very strong band centered at 168 cm⁻¹ in FT-IR and 1681 cm⁻¹ in FT-Raman for BOA and 1693 cm⁻¹ in FT-IR spectrum for FPA are attributed to C=O stretching vibrations of the aldehyde group. Singh et al., [31] have assigned the C=O in-plane bending vibrations for isomers of methoxybenzaldehydes in the region $585-820 \text{ cm}^{-1}$. Hence, in the present investigation, the strong bands observed at 824 cm⁻¹ and 836 cm⁻¹ for BOA and FPA, respectively, could be assigned to C=O in-plane bending vibrations. Hankenet al., [32] have assigned the band at 173 cm^{-1} in the Raman spectrum of chlorobenzalddehyde as aldehyde out-of-plane bending vibration. In BOA and FPA, respectively the very weak band centered at 188 cm⁻¹ and 230 cm⁻¹ in Raman spectra could be due to C=O out-of-plane bending vibrations of aldehyde groups. A weak to medium intensity band due to the aldehyde group CHO deformation vibration [33] is found in the region 975-780 cm⁻¹. In consonance with this, the medium and weak intensity band at 803 cm⁻¹ and 813 cm⁻¹ could be assigned to CHO out-of-plane deformation for MHB and HMB, respectively.

CH₃ group vibrations

In the region of $3102-2843 \text{ cm}^{-1}$, three bands have been observed at 2967, 2941 and 2843 cm⁻¹ for BOA, have been assigned to two CH₃ asymmetrical (CH₃ips) and symmetrical (CH₃ ss) in-plane stretching modes, asymmetric (CH₃ ops) out-of-plane stretch modes of methyl group and three CH stretching vibrations. In FPA, there were 6 bands have been observed between the region $3251-2811 \text{ cm}^{-1}$ were assigned to the CH₃ asymmetric and symmetric in-plane stretches, CH₃ asymmetric out-of-plane stretches, CH₂ asymmetric and symmetric stretches and CH stretches based on the calculated frequencies and Raman activities. The bands due to the scissoring, rocking, wagging and twisting modes of methylene group and rocking and wagging modes of methyl groups of the title compounds have also been assigned and listed in Tables 8 and 9.

Symmetry species C _s	C _s Fundamentals (cm ⁻¹)		Calculated frequencies (cm ⁻¹)		Reduced mass	Force constants	Infrared intensity	Raman activity	TED (%) among types of internal coordinates
		r	Unscaled	Scaled					
	FT-IR	Raman							
A'	3103ms	3100ms	3403	3106	1.0945	7.400	8.24	141.13	vCH(99)
A'	3073ms	3074w	3402	3082	1.0935	7.4548	1.32	5.03	vCH(99)
A'	3015ms	3015w	3379	3009	1.0915	7.3438	1.43	48.22	vCH(99)
A″	2967ms	-	3319	2975	1.1028	7.1581	28.08	118.30	CH ₃ as(85)
A'	2941ms	-	3265	2955	1.1078	6.9572	39.11	45.32	CH ₃ as(86)
A'	2878w	2881w	3236	2886	1.0892	6.7217	54.05	102.46	vCH(97)
A'	2843w	2848w	3194	2849	1.0336	6.2125	54.21	132.27	CH ₃ ss(88)
A'	1680vs	1681vs	1967	1685	9.8142	22.3657	378.79	93.39	vCO(93)
A'	1634w	-	1793	1641	5.8745	11.1221	87.96	74.42	_V CC(84), δCH(12)
A'	1593w	1596ms	1764	1590	7.0906	12.9975	24.75	20.07	_V CC(75),δCH(15), δCO(10)
A'	1575vs	1572ms	1656	1578	2.2456	3.6285	185.55	10.05	_V CC(75),δCH(20)
Α″	1561w	-	1635	1566	1.0692	1.6847	50.08	8.05	CH ₃ opb (84)
A'	1533w	-	1629	1530	1.0463	1.6367	8.06	14.79	CH ₃ ipb (85)
A'	1519w	-	1612	1525	1.2457	1.9072	31.52	2.72	CH ₃ sb (84)
A'	1497vs	-	1558	1491	2.2768	3.2583	16.41	3.12	δCH (72), _V CC (15)
A'	1480vs	-	1541	1480	1.6056	2.2468	129.52	2.82	δCH (74), _V CC (12)
A'	1461ms	1460ms	1424	1466	2.1227	2.5387	268.18	10.98	δCH (74), vCC (14)
A'	1455ms	1450w	1393	1453	1.9488	2.2281	117.58	16.81	δCH (74), vCC (10)
A'	1441w	-	1332	1440	1.6899	1.7664	7.91	6.64	CH ₃ ipr(76),δCH(20)
A'	1395vs	1396ms	1307	1394	1.6772	1.6882	19.43	2.07	_V CC(71), δCH(15)
A″	1298vs	1300w	1281	1299	1.2661	1.2242	3.34	2.08	CH ₃ opr(79)
A'	1267vs	1265s	1240	1263	2.2676	2.0536	84.72	4.01	vCC(71), δCH(16)
A'	1244w	-	1234	1246	6.9153	6.2050	57.43	40.69	_V CC(70), δCO(16)
A'	1179vs	1180vs	1194	1180	2.1117	1.7736	5.04	2.89	_V CC(75), δCH(12)
Α″	1142ms	-	1163	1145	1.8949	1.5121	0.00	3.57	γCH(37), γCC(19)
A'	1126w	1125w	1156	1128	6.2885	4.9540	55.97	6.11	vCO(42), vCC(18), δCH(15)
Α″	1100w	1095w	1109	1106	1.4501	1.0524	0.10	0.16	γCH(37), γCC(25)
A″	1020vs	-	1082	1018	1.5028	1.0364	10.51	0.61	γ CH(40), γ CC(32)
A'	891ms	-	961	890	5.7381	3.1273	25.73	3.01	$\delta CO(55), \delta Ring(32), VCBr(12)$
A″	882vs	885w	938	884	1.6185	0.8381	41.69	0.38	γCH(29), γCC(19)
A'	824w	-	859	823	5.2933	2.3019	8.11	23.06	δCO(45), vCC(21), δCH(15)
A'	803w	799s	829	804	3.0449	1.2318	4.03	1.42	γCO (35), γCH (21)
A'	706ms	706w	720	705	2.8092	0.8594	12.64	0.14	δCC (55), δCO (29)
A'	646s	651ms	702	647	5.8549	1.7030	21.11	3.14	δRing(49), δCO(31)
A'	623s	627s	680	625	6.1708	1.6807	31.18	3.14	vCBr(61), δCC(22), δCO(10)
A'	539w	-	565	540	5.9482	1.1222	33.98	2.18	γCO(55), γCH(19), γRing(12)
A'	522s	525vw	523	523	3.0381	0.4909	6.20	0.09	δRing(29),δCO(13)

Table 8.The observed FTIR, FT Raman and calculated (Unscaled and Scaled) frequencies (cm⁻¹), IR intensity (kM mol⁻¹), Raman activity (Å amu⁻¹), Reduced masses (amu) and force constant (mdyne Å⁻¹) and probable assignments (characterized by TED) of 5-bromo-o-anisaldehyde using B3LYP/6-31+G(d,p).

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A″	-	425w	432	425	6.0297	0.6619	1.06	4.79	γRing(32), γCO(12)
A″	-	410s	419	413	4.4133	0.4582	0.18	1.32	γRing(31), γCO(18)
A'	-	362w	351	364	5.1865	0.3776	4.85	1.31	δCBr(25), δCO(16)
A'	-	318w	295	320	9.7940	0.5051	2.33	8.06	δRing(29), δCO(18)
A″	-	258s	265	256	1.1144	0.0464	0.98	0.15	tCH ₃ (76)
A″	-	201ms	209	200	2.8879	0.0744	5.45	2.06	γ CBr(28), γ CC(18)
A″	-	188s	201	189	4.3098	0.1031	0.14	0.86	γCO(33), γCC(15)
A″	-	-	155	154	11.6713	0.1658	3.39	1.42	γCO(39), γRing(20)
A″	-	-	144	146	4.3950	0.0543	14.88	0.32	γCO(28), γRing(15)
A″	-	-	110	108	4.1382	0.0295	4.06	0.79	γCO(27), γRing(15)
A″	-	-	71	70	3.3912	0.0101	1.19	0.41	γCO(28), γRing(13)

Abbreviations: t, torsion; R1 trigd, Ring 1 trigonal deformation; R2 trigd, Ring 2 trigonal deformation; asym, asymmetric; s, symmetric; w, bending out-of-plane; asymd, asymmetric deformation; symd, symmetric deformation; b, bending in-plane; s, strong; w, weak; m, medium; vs, very weak; ms, medium strong, Harmonic Frequencies in cm⁻¹. The absolute IR intensity in Km mol⁻¹.Raman scattering activity in A⁴ amu⁻¹. Depolarization rations for plane and unpolarised in amu. Reduced masses in AMU Force constants in m Dyne A. **Table 9.The observed FTIR, FT Raman and calculated (Unscaled and Scaled) frequencies (cm⁻¹), IR intensity (kM mol⁻¹), Raman activity (Å amu⁻¹), Reduced masses (amu) and**

force constant (mdyne $Å^{-1}$) and probable assignments (characterized by TED) of 3-fluoro-p-anisaldehyde using B3LYP/6-31+G(d,p).

Symmetry species C _s	Fundamentals (cm ⁻¹)		Calculated frequencies (cm ⁻¹)		Reduced mass	Force constants	Infrared intensity	Raman activity	TED (%) among types of internal coordinates
			Unscaled	Scaled					
	FT-IR	Raman							
A'	3051w	-	3228	3060	1.0931	6.7100	5.68	112.08	vCH(98)
A'	3022w	-	3212	3026	1.0888	6.6191	0.23	39.17	vCH(97)
A'	3000w	-	3200	3003	1.0913	6.5844	1.70	88.8	_V CH(97)
A″	2941ms	-	3165	2940	1.1010	6.4987	14.17	133.61	CH ₃ as(82)
A'	2847w	-	3099	2844	1.1071	6.2645	29.79	56.95	CH ₃ as(82)
A'	2830w	-	3029	2835	1.0337	5.5901	51.58	154.43	vCH(95)
A'	2811ms	-	2914	2816	1.0836	5.4236	124.22	169.62	CH ₃ ss(85)
A'	1693vs	1595vs	1769	1690	9.8698	18.1933	304.39	179.94	vCO(90)
A'	1610vs	1611vs	1652	1615	6.4768	10.42.14	215.55	270.26	νCC(78), δCH(12)
A'	1588s	1588s	1619	1583	7.8008	12.0513	58.81	5.45	νCC(77),δCH(15),δCO(12)
A'	1586vs	-	1555	1519	3.1947	4.5552	132.65	5.52	_V CC(75),δCH(22)
A″	1462w	-	1506	1461	1.0572	1.4136	41.75	8.76	CH ₃ ipb (85)
A'	-	1452ms	1501	1452	1.0456	1.3874	9.79	15.17	CH ₃ opb (86)
A'	1443s	-	1484	1448	1.2934	1.6785	17.52	4.42	CH ₃ sb (84)
A'	1396ms	-	1468	1395	2.5128	3.1852	11.76	1.43	δCH(70), vCC (19)
A'	1388w	-	1417	1389	1.5731	1.8605	2.77	9.07	δCH(75), vCC (18)
A'	-	1348ms	1364	1345	6.2128	6.8148	85.74	25.02	δCH(74), vCC (14)
A'	1285vs	1289ms	1322	1286	4.2925	4.4190	434.57	39.02	δCH(73), vCC (12)
A'	1259w	1260ms	1303	1257	1.7708	1.7725	30.69	9.56	CH ₃ ipr(77),δCH(18)
A'	1226ms	1230ms	1247	1228	2.8182	2.5820	30.82	29.10	_V CF(88), δCH(10)
A″	1186w	-	1208	1185	1.3681	1.1767	2.84	5.94	_ν CC(73), δCH(17)
A'	1153w	-	1179	1153	1.4722	1.2062	8.21	1.68	CH ₃ opr(78), vCC (10)
A'	1121vs	1121ms	1172	1124	1.2688	1.0271	0.97	1.87	νCC(71), δCH(16)
A'	1109s	-	1132	1105	1.7526	1.3243	137.59	12.32	_ν CC(68), δCO(14)

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A″	1021s	1020w	1052	1020	7.8689	5.1401	43.96	1.78	vCC(75), δCH(13)
A'	971w	-	1023	974	1.7681	1.0913	1.52	2.45	γCH(37), γCC(14)
A″	949ms	-	968	949	1.3201	0.7282	0.09	0.16	_ν CO(40), _ν CC(18), _δ CH(11)
A″	894ms	-	963	897	3.6270	1.9832	20.26	6.65	γCH(39), γCC(25)
A'	884ms	-	893	885	1.3627	0.6402	22.51	0.16	γCH(44), γCC(28)
A″	836ms	-	828	838	1.4446	0.5840	35.73	0.14	δCO(54), δRing(35),
A'	813ms	-	790	810	6.0791	2.2361	54.72	13.57	γCH(29), γCC(19)
A'	783ms	785ms	773	785	4.6440	1.6352	11.41	15.56	δCO(45), _V CC(21), _δ CH(15)
A'	745ms	-	714	750	4.4641	1.3429	0.13	0.12	γCO (37), γCH (20)
A'	637ms	638ms	638	639	6.6337	1.5927	18.74	1.03	δCC (55), δCO (29)
A'	586ms	-	592	590	5.741	1.1859	10.89	3.79	δRing(47),δCO(30)
A'	-	571w	586	573	4.0021	0.8101	5.78	0.43	γ CO(52), γ CH(20), γ Ring(12)
A'	504w	-	490	505	7.1179	1.0090	9.39	5.67	δCBr(55), _v CC(20), _δ CH(14)
A″	486w	-	467	489	3.1919	0.4107	0.90	0.44	δRing(30),δCO(12)
A″	410w	-	380	412	10.0494	0.8559	0.46	7.51	γRing(36), γCO(15)
A'	-	369w	349	370	4.3054	0.3101	2.81	1.58	γRing(30), γCO(13)
A'	-	321w	339	322	4.7476	0.3221	0.18	4.24	δRing(32),δCO(12)
A″	-	255w	260	256	3.1101	0.1244	4.23	0.31	tCH ₃ (74)
A″	-	236w	236	236	1.1603	0.0381	0.24	0.45	γCO(31), γCC(17)
A″	-	230w	233	231	5.6465	0.1813	3.66	0.34	γCO(36), γRing(22)
A″	-	176w	167	175	5.5559	0.0920	8.55	1.23	γ CF(33), γ Ring(20)
A″	-	116w	159	163	3.5416	0.0530	0.58	2.39	γ CO(27), γ Ring(16)
A″	-	106w	113	105	4.5260	0.0345	14.52	1.43	γCO(23), γRing(17)
A″	-	-	79	59	4.2170	0.0156	0.00	0.39	$\gamma CO(25), \gamma Ring(19)$

Abbreviations: t, torsion; R1 trigd, Ring 1 trigonal deformation; R2 trigd, Ring 2 trigonal deformation; asym, asymmetric; ω , bending out-of-plane; asymd, asymmetric deformation; b, bending in-plane; s, strong; w, weak; m, medium; vs, very weak; ms, medium strong, Harmonic Frequencies in cm⁻¹. The absolute IR intensity in Km mol⁻¹. Raman scattering activity in A⁴ amu⁻¹. Depolarization rations for plane and unpolarised in amu. Reduced masses in AMU Force constants in m Dyne A.

C-Br vibrations

Strong characteristic absorption due to the C–Br stretching vibration is observed [28] with the position of the band being influenced by neighboring atoms or groups, the smaller the halide atom, the greater the influence of the neighbour. Bands of weak to medium intensity are also observed for the C–Br stretching vibrations. According to these early reports [33,34], the C–Br stretching vibration gives generally strong band in the region 650–485 cm⁻¹. In the present compound, a strong band is observed at 623 cm⁻¹ in FT-IR spectrum and 627 cm⁻¹ in FT-Raman spectrum are assigned to C–Br stretching vibrations for BOA. The calculated C–Br stretching bands are found at 625 cm⁻¹ and this assignment is slightly above the literature value.

The theoretically computed value at 364 cm^{-1} is assigned to C–Br in-plane by B3LYP/6-31+G(d,p) method. The C–Br inplane bending bands are observed at 362 cm^{-1} in FT-Raman spectrum. The C–Br out-of-plane bending bands are observed at 201 cm⁻¹ in FT-Raman spectrum and is assigned to C–Br out-of-plane bending of BOA. This shows that the other vibrations can hold back the C–Br vibrations due to its weak force constant [35]. The influence of other substitution on C– Br stretching and deformation band is significant in this compound.

C-F vibration

Aromatic fluorine compounds give stretching bands in the region 1270-1100 cm⁻¹ [35]. The very strong band at 1226 cm⁻¹ in FPA is assigned to C-F stretching vibration. The predicted band corresponding to C-F stretching mode is 1228 cm⁻¹. C-F in-plane bending vibrations are expected in the range 420-254 cm⁻¹ [23,35]. In FPA, a weak band at 504 cm⁻¹ and computed value 505 cm⁻¹ is assigned to C-F in-planebending vibration. C-F out-of-plane bending vibrations were observed in the range 520-101 cm⁻¹ [35,36]. The observed FT-Raman band at 176 cm⁻¹ is assigned to C-F out-of-plane vibration.

5. Conclusion

In this study, the SQM force field method based on DFT calculations at the B3LYP/6-31+G(d,p) level have been carried out to analyse the vibrational assignments of BOA and FPA. Refinement of the scaling factors applied in this study achieved a weighted RMS deviation of 4.8 cm⁻¹ for BOA and for FPA, 4.3 cm⁻¹ for the 6-31+G(d,p) basis set, respectively, between the experimental and SQM frequencies. The close agreement established between the experimental and scaled frequencies obtained using the basis set (6-31+G(d,p)) calculation are proved to be more reliable. This accuracy is desirable for resolving disputes in vibrational assignments and provides valuable insight for understanding the observed spectral features.

References

01. W.Kohn, A.D.Becke, R.G.Parr, J. Phys.Chem.,100 (1996) 12974.

02. R.G.Par, W.Yang, Density - Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

03. A.P.Scott, l.Radom, J. Phys. Chem., 100 (1996) 16502.

04. B.G.Johnson, P.M.W.Gill, J.A.Peple, J. Chem. Phys., 98 (1993) 5612.

05. M.W.Wong, Chem. Phys. Lett., 256 (1996) 391.

06. F.De Proft, G.M.L Martin, P.Geerlings, Chem. Phys. Lett., 250 (1996) 393.

07. P Pulay, J. Mol. Struct., 347 (1995) 293.

08. G.Rauhut, P.Pulay, J. Phys. Chem., 99 (1995) 3093.

09. M.J.Frisch, G.W.Trucks, H.B.Schlegal, G.E.Scuseria,

M.ARobb, J.R.Cheesman, V.G.Zakrzewski, J.A.Montgomerg,

Jr., R.E.Stratmann, J.C.Burant, S.Dapprich, J.M.Millam,

A.D.Daniels, K.N.Kudin, M.C.Strain, O.Farkas, J.Tomasi, V.Barone, M.Cossi, R.Cammi, B.Mennucci, C.Pomelli, C.Adamo, S.Clifford, J.Ochterski, G.A.Petersson, P.Y.Ayala, Q.Cui, K.Morokuma, N Rega, P.Salvador, J.J. Dannenberg, D.K.Malich, A.D.Rabuck, K.Raghavachari, J.B.Foresman, J.Cioslowski, J.V.Ortiz, A.G. Baboul, B.B.Stetanov, G.Liu, A.Liashenko, P.Piskorz, I.Komaromi, R.Gomperts. R.L.Martin, D.J.Fox, T.Keith, M.A.Al-Laham, C.Y.Peng, A. Nanayakkara, M.Challacombe, P.M.W.Gill, B.Johnson, W.Chen, M.W.Wong, J.L.Andres, C.Gonzalez, M.Head-Gordon, E.S.Replogle and J.A.Pople, GAUSSIAN 03, Revision A 11.4, Gaussian, Inc, Pittsburgh PA, 2003. 10. A.D.Becke, J. Chem. Phys., 98 (1993) 5648.

11. C.Lee, W. Yang, R.G. Parr, Phys. Rev., 37 (1998) 785.

12. P.Pulay, W.Mayer, J. Mol. Spectrosc., 40 (1971) 59.

13. Sundaraganesan N, Ayyappan S, Umamaheswari H, Dominic Joshua B, *Spectrochim. Acta*. A 66 (2007) 17.

14. G.Fogarasi, X.Zhou, P.W. Taylor, P.Pulay, J. Am. Chem. Soc., 114 (1992) 8191.

15. T.Sundius, J.Mol. Struct. 218 (1990) 321; MOLVIB: A Program for Harmonic Force Field Calculations, QCPE Program No.604 (1991).

16. T.Sundius, Vibr. Spectrosc., 29 (2002) 89.

17. M.J.Frisch, A.B.Nielson, A.J.Holder, GaussviewUsers Manual, Gaussian Inc., Pittsburgh, PA, 2000.

18. G.Fogarasi, P.G.Szalay, P.L.Liescheski, J.E.Boggs, P.Pulay, J. Mol. Struc., 105 (1983) 7037.

19. P.L. Polavarapu, J. Phys. Chem., 94 (1990) 8106.

20. G.Keresztury, S.Holly, J.Varga, G.Besenyei, A.Y.Wang, J.R.Durig, Spectrochim. Acta Part A, 49 (1993) 2007.

21. G.Keresztury, Raman Spectroscopy :Theory in : J.M. Chalmers, P.R.Griffiths (Ed.), Handbook of vibrational spectroscopy, Vol.1, Wiley, 2002.

22. P.Pulay, G.Fogarasi, F.Pong, J.E. Boggs, J. Am. Chem. Soc., 101 (1979) 2550.

23. N.B.Colthup, L.H.Daly, S.E.Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964.

24. M.Fox, Journal of Chemical Society (1939) 318.

25. P.S.Kalsi, Spectroscopy of organic compounds, Willey Eastern Ltd, New Delhi, 1993.

26. Jag Mohan, Organic Spectroscopy - Principles and Applications, second ed., Narosa, Publishing House, New Delhi, 2001.

27. D.N. Sathyanarayana, Vibrational Spectroscopy - Theory and Applications, second ed., New Age International (P) Limited Publishers, New Delhi, 2004.

28. G.Socrates, Infrared and Raman Characteristic Group Frequencies - Tables and charts, third ed., Wiley, Chichester, 2001.

29. V.R.Dani, Organic Spectroscopy, Tata-McGraw Hill Publishing Company, New Delhi.1995, P.139.

30. P.K Syed Tariq, Verma, Rashid Aquell, Indian Journal of Pure and Applied Physics 20 (1982) 974.

31. D.N.Singh, I.D.Singh, R.A.Yadav, Indian Journal of Physics 763 (2002) 307–318.

32. S.H.W.Hanken, O.S.Khalil, L.Goodman, Journal of Molecular Spectroscopy 72 (1978) 383.

33. D.H.Wiffen, Spectrochimica Acta Part A 7(1955) 253.

34. V.Sortu, J.JayashreeYengai, V.B.Tonannavar, M.V. Jadhav, Kulkarni, Spectrochimica Acta Part A 71(2008) 688–694.

35. V.K Rastogi, C.b.Arora, S.K.Singhal, D.N.Singh, R.A. Yadav, spectrochimi. Acta A 53 (1997) 2005.

36. P.J.A.Ribeiro-Claro, M.P.M.Marques, A.M.Amado, Chem PhysChem 3 (2002) 599.

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