# FTIR, FT-RAMAN, Conformational Studies, the Molecular Geometry and Vibrational Frequencies of 5-Bromo-0-Anisaldehyde and 3-Fluoro-p-Anisaldehyde <br> D. Usha ${ }^{1}$, G. John James ${ }^{2}$ and L.F.A. Amirtharaj ${ }^{3}$ <br> ${ }^{1}$ Department of Physics, Women's Christian College, Nagercoil - 629 001, Tamil Nadu, India. <br> ${ }^{2}$ Department of Physics, Government Arts College, Tiruchirappalli - 620 022, Tamilnadu, India. <br> ${ }^{3}$ Department of Physics, Government Arts College, Karur - 639 005, Tamilnadu, India. 

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#### Abstract

The FTIR and FT-Raman spectra of 5-bromo-o-anisaldehyde (BOA) and 3-fluoro-panisaldehyde (FPA)have been recorded in the region $4000-400 \mathrm{~cm}^{-1}$ and $3500-50 \mathrm{~cm}^{-1}$, 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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## 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, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCH}_{3}$ (methyl phenyl ether), is a clear liquid that is soluble in ether and alcohol insoluble in water boiling point $155^{\circ} \mathrm{C}$. 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. pAnisaldehyde, an aromatic aldehyde with mothoxygruop, is a clear liquid may discolor to yellow on storage (limited shelf life for 6 months) melting at $-1^{\circ} \mathrm{C}$, boiling at $249.5^{\circ} \mathrm{C}$ 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 $180^{\circ} \mathrm{C}$, 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.

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 as benzaldehyde and formaldehyde may undergo 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].

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 $4000-400 \mathrm{~cm}^{-1}$ using BRUKER IFS 66 V FTIR spectrometer equipped with an MCT detector, a KBr beam splitter and globar source at a resolution of $\pm 1 \mathrm{~cm}^{-}$ ${ }^{1}$. The FT-Raman spectra were recorded on the same instrument with FRA 106 Raman accessories in the region $3500-100 \mathrm{~cm}^{-1}$. 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 $\mathrm{C}_{\mathrm{s}}$ 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 $10 \mathrm{~cm}^{-1}$.

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 $\left(S_{i}\right)$ calculated with the GAUSSIAN-03 program and adjusted during the scaling procedure with MOLVIB were converted to relative Raman
intensities $\left(I_{i}\right)$ using the following relationship derived from the basic theory of Raman scattering [19-21].

$$
\mathrm{I}_{\mathrm{i}} \quad=\frac{\mathrm{f}\left(v_{\mathrm{o}}-v_{\mathrm{i}}\right)^{4} \mathrm{~S}_{\mathrm{i}}}{v_{\mathrm{i}}\left[1-\exp \left(-\frac{\mathrm{hc} v_{\mathrm{i}}}{\mathrm{kT}}\right)\right]}
$$

... (1)
where $v_{o}$ is the exciting frequency (in $\mathrm{cm}^{-1}$ ), $v_{i}$ is the vibrational wavenumber of the $i^{\text {th }}$ normal 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 $\mathrm{C}_{\mathrm{s}}$ symmetry and were shown in Figs. 1 and 2, respectively.


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

| Conformer | Total energies (in Hartrees) |  |
| :--- | :--- | :--- |
|  | BOA | FPA |
| a | -3031.232151 | -559.345051 |
| b | -3031.080163 | -559.347346 |
| c | $-3031.236802^{*}$ | $-559.320102^{*}$ |
| d | -3031.157013 | -559.35236 |

*global minimum energy

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

| Parameters | Bond length ( A ) | Parameters | Bond angle( ${ }^{\circ}$ ) | Parameters | Dihedral angle $\left(^{\circ}\right.$ ) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| C1-C2 | 1.3997 | C2-C1-C6 | 119.9 | C6-C1-C2-C3 | -0.0003 |
| C1-C6 | 1.3891 | C2-C1-C7 | 121.1 | C6-C1-C2-O10 | 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 | -180.0 |
| C2-O10 | 1.3417 | C1-C2-O10 | 116.7 | C2-C1-C6-C5 | 0.0 |
| C3-C4 | 1.3853 | C3-C2-O10 | 123.7 | C2-C1-C6-H18 | 0.0 |
| C3-H15 | 1.0719 | C2-C3-C4 | 119.9 | C7-C1-C6-C5 | -179.9 |
| C4-C5 | 1.3830 | C2-C3-H15 | 121.1 | C7-C1-C6-H18 | 180.0 |
| C4-H16 | 1.0740 | C4-C3-H15 | 118.8 | C2-C1-C7-O8 | 0.0 |
| C5-C6 | 1.8919 | C3-C4-C5 | 120.4 | C2-C1-C7-H9 | -0.0008 |
| C5-Br17 | 1.3787 | C3-C4-H16 | 119.3 | C6-C1-C7-O8 | -0.0008 |
| C6-H18 | 1.0730 | C5-C4-H16 | 120.1 | C6-C1-C7-H9 | -180.0009 |
| C7-08 | 1.9370 | C4-C5-C6 | 120.0 | C1-C2-C3-C4 | 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 |
| C11-H11 | 1.0844 | C1-C6-C5 | 120.2 | O10-C2-C3-H15 | -0.0009 |
| C11-H12 | 1.0792 | C1-C6-H18 | 118.4 | C1-C2-O10-C11 | 180.0 |
| C11-H13 | 1.0844 | C5-C6-H18 | 121.3 | C1-C2-O10-C11 | 0.0033 |
|  |  | C1-C8-08 | 123.0 | C2-C3-C4-C5 | 0.0002 |
|  |  | C1-C7-H9 | 116.1 | C2-C3-C4-H16 | 180.0 |
|  |  | O8-C7-H9 | 120.8 | H15-C3-C4-C5 | -180.0 |
|  |  | C2-O10-C11 | 120.5 | C3-C4-C5-C6 | -0.0002 |
|  |  | O10-C11-H12 | 111.0 | C3-C4-C5-Br17 | -180.0 |
|  |  | O10-C11-H13 | 105.8 | H16-C4-C5-C6 | -180.0 |
|  |  | O10-C11-H14 | 111.0 | H16-C4-C5-Br17 | -0.0001 |
|  |  | 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 | -179.9 |
|  |  |  |  | C2-O10-H11-H14 | -61.2 |

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 ( ${ }^{\text {A }}$ ) | Parameters | Bond angle ${ }^{\circ}$ ) | Parameters | Dihedral angle $\left({ }^{\circ}\right.$ ) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 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 | C2-C1-C7-H9 | 0.0 |
| C5-H17 | 1.0833 | C3-C4-O12 | 116.3 | C6-C1-C7-08 | 0.0 |
| C6-H18 | 1.0851 | C5-C4-O12 | 125.6 | C6-C1-C7-H9 | -179.9 |
| C7-08 | 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-C8-08 | 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 $\Gamma_{\text {vib }}=33 \mathrm{~A}^{\prime}+$ $15 A^{\prime \prime}$. The $A^{\prime}$ and $A^{\prime \prime}$ 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-oanisaldehyde.

| No. (i) | Symbol | Type | Definition |
| :---: | :---: | :---: | :---: |
| Stretching |  |  |  |
| 1-3 | $\mathrm{r}_{\mathrm{i}}$ | C-H | C3-H15, C4-H16, C6-H18 |
| 4 | $\mathrm{R}_{\mathrm{i}}$ | C-C | C1-C7 |
| 5 | $\mathrm{r}_{\mathrm{i}}$ | C-H | C7-H94 |
| 6-7 | $\mathrm{p}_{\mathrm{i}}$ | C-O | C2-O10, C11-O10 |
| 8 | $\mathrm{P}_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{Br}$ | C5-Br17 |
| 9 | $\mathrm{p}_{\mathrm{i}}$ | $\mathrm{C}=\mathrm{O}$ | C7-08 |
| 10-12 | $\mathrm{r}_{\mathrm{i}}$ | C-H | C11-H12, C11-H13, C11-H14 |
| 13-18 | $\mathrm{q}_{\mathrm{i}}$ | C-C | C1-C2, C2-C3, C3-C4, C4C5, <br> C5-C6, C6-C1 |
| Bending |  |  |  |
| 19-24 | $\beta_{i}$ | bCH | $\begin{aligned} & \text { C1-C6-H18, C5-C6-H18, C5-C4- } \\ & \text { H16, C3-C4-H16, C4- } \\ & \text { C3-H15, C2-C3-H15 } \end{aligned}$ |
| 25-26 | $\alpha_{i}$ | bCC | C2-C1-C7, C6-C1-C7 |
| 27-28 | $\sigma_{i}$ | bCO | C1-C2-O10, C3-C2-O10 |
| 29-30 | $\rho_{i}$ | BCBr | C4-C5-Br17, C6-C5-Br17 |
| 31 | $\alpha_{i}$ | bCC | C1-C7-H9 |
| 32 | $\alpha_{i}$ | bCC | C1-C7-08 |
| 33 | $\delta_{i}$ | bOH | O8-C7-H9 |
| 34-36 | $\phi_{i}$ | bOC | $\begin{aligned} & \text { O10-C11-H12, O10-C11-H13, } \\ & \text { O10-C11-H14 } \end{aligned}$ |
| 37-39 | $\pi_{i}$ | $\begin{aligned} & \mathrm{H}-\mathrm{C}- \\ & \mathrm{H} \end{aligned}$ | $\begin{aligned} & \text { H12-C11-H13, H12-C11-H14, } \\ & \text { H13-C11-H14 } \\ & \hline \end{aligned}$ |
| 40-45 | $\gamma_{\mathrm{i}}$ | C-C-C | $\begin{aligned} & \text { C1-C2-C3, C2-C3-C4, C3-C4-C5, } \\ & \text { C4-C5-C6, C5-C6-C1, C6-C1-C2 } \\ & \hline \end{aligned}$ |
| Out-of-plane bending |  |  |  |
| 46-48 | $\omega_{\mathrm{i}}$ | C-H | $\begin{aligned} & \text { H15-C3-C2-C4, H16-C4-C3-C5, } \\ & \text { H18-C5-C1-C5 } \end{aligned}$ |
| 49 | $\varphi_{i}$ | C-C | C7-C1-C2-C6 |
| 50 | $\Phi_{i}$ | C-O | O10-C2-C1-C3 |
| 51 | $\psi_{i}$ | C-Br | Br17-C5-C4-C6 |
| 52 | $\theta_{i}$ | O-H | O8-C7-C1-C6 (C2) |


| 53 | $\omega_{\mathrm{i}}$ | C-H | H9-C7-C1-C6(C2) |
| :--- | :--- | :--- | :--- |
| 54 | $\tau_{\mathrm{i}}$ | t CO | C2-O10-C11-(H12, H13, H14) |
| 55 | $\tau_{\mathrm{i}}$ | t CO | H9-C7-O8-C1 |
| $56-61$ | $\tau_{\mathrm{i}}$ | t Ring | C1-C2-C3-C4, C2-C3-C4-C5, <br> C3-C4-C5-C6, C4-C5-C6-C1, <br> C5-C6-C1-C2, C6-C1-C2-C3 |

For numbering of atoms refer Fig. 2
Table 5.Definition of internal coordinates of 3-fluoro-panisaldehyde.

| No. (i) | Symbol | Type | Definition |
| :--- | :--- | :--- | :--- |


| No. (i) | Symbol |  | Type |
| :--- | :--- | :--- | :--- |
| Stretching |  |  |  |
| $1-3$ | $\mathrm{r}_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{H}$ | $\mathrm{C} 2-\mathrm{H} 10, \mathrm{C} 5-\mathrm{H} 17, \mathrm{C} 6-\mathrm{H} 18$ |
| 4 | $\mathrm{R}_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{C}$ | $\mathrm{C} 1-\mathrm{C} 7$ |
| 5 | $\mathrm{r}_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{H}$ | $\mathrm{C} 7-\mathrm{H} 94$ |
| $6-7$ | $\mathrm{p}_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{O}$ | $\mathrm{C} 4-012, \mathrm{C} 13-\mathrm{O} 12$ |
| 8 | $\mathrm{P}_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{Br}$ | $\mathrm{C} 3-\mathrm{F} 11$ |
| 9 | $\mathrm{p}_{\mathrm{i}}$ | $\mathrm{C}=\mathrm{O}$ | $\mathrm{C} 7-\mathrm{O} 8$ |
| $10-12$ | $\mathrm{r}_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{H}$ | $\mathrm{C} 13-\mathrm{H} 14, \mathrm{C} 13-\mathrm{H} 15, \mathrm{C} 13-\mathrm{H} 16$ |
| $13-18$ | $\mathrm{q}_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{C}$ | $\mathrm{C} 1-\mathrm{C} 2, \mathrm{C} 2-\mathrm{C} 3, \mathrm{C} 3-\mathrm{C} 4, \mathrm{C} 4-\mathrm{C} 5, \mathrm{C} 5-$ <br> $\mathrm{C} 6, \mathrm{C} 6-\mathrm{C} 1$ |


| In-plane Bending |  |
| :--- | :--- |
|  |  |


| $19-24$ | $\beta_{\mathrm{i}}$ | bCH | C1-C6-H10, C3-C2-H10, C1-C6-H18, <br> C5-C6-H18, C6-C5-H17, C4-C5-H17 |
| :--- | :--- | :--- | :--- |
| $25-26$ | $\alpha_{\mathrm{i}}$ | bCC | C2-C1-C7, C6-C1-C7 |
| $27-28$ | $\sigma_{\mathrm{i}}$ | bCO | C3-C4-O12, C5-C4-O12 |
| $29-30$ | $\rho_{\mathrm{i}}$ | bCBr | C2-C3-F11, C4-C3-F11 |
| 31 | $\alpha_{\mathrm{i}}$ | bCC | C1-C7-H9 |
| 32 | $\alpha_{\mathrm{i}}$ | bCC | C1-C7-O8 |
| 33 | $\delta_{\mathrm{i}}$ | bOH | O8-C7-H9 |
| $34-36$ | $\phi_{\mathrm{i}}$ | bOC | O12-C13-H14, O12-C13-H15, <br> O12-C13-H16 |
| $37-39$ | $\pi_{\mathrm{i}}$ | H-C- <br> H | $\mathrm{H} 14-\mathrm{C} 13-\mathrm{H} 15, \mathrm{H} 14-\mathrm{C} 13-\mathrm{H} 15, ~$ <br> H15-C13-H16 |
| $40-45$ | $\gamma_{\mathrm{i}}$ | C-C- <br> C | C1-C2-C3, C2-C3-C4, C3-C4-C5, <br> C4-C5-C6, C5-C6-C1, C6-C1-C2 |

Out-of-plane bending

| $46-48$ | $\omega_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{H}$ | H10-C2-C4-C3, H17-C5-C4-C6, <br> H18-C6-C1-C5 |
| :--- | :--- | :--- | :--- |
| 49 | $\varphi_{\mathrm{i}}$ | $\mathrm{C}-\mathrm{C}$ | C7-C1-C2-C6 |

For numbering of atoms refer Fig. 3
Table 6.Definition of local symmetry coordinates of 5-bromo-o-anisaldehyde.

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


|  |  | $1 \sqrt{2}$ |
| :---: | :---: | :---: |
| 22 | bCC | $\left(\alpha_{25}-\alpha_{26}\right) / \sqrt{2}$ |
| 23 | bCO | $\left(\sigma_{27}-\sigma_{28}\right) / \sqrt{2}$ |
| 24 | bCBr | $\left(\rho_{29}-\rho_{30}\right) / \sqrt{2}$ |
| 25 | bCC | $\alpha_{31}$ |
| 26 | bCC | $\alpha_{32}$ |
| 27 | bOH | $\delta_{33}$ |
| 28 | $\mathrm{CH}_{3} \mathrm{sb}$ | $\left(-\phi_{34}-\phi_{35}-\phi_{36}+\pi_{37}+\pi_{38}+\pi_{39}\right) / \sqrt{6}$ |
| 29 | $\mathrm{CH}_{3} \mathrm{ipb}$ | $\left(-\pi_{37}-\pi_{38}-2 \pi_{39}\right) / \sqrt{6}$ |
| 30 | $\mathrm{CH}_{3} \mathrm{Opb}$ | $\left(\pi_{38}-\pi_{39}\right) / \sqrt{2}$ |
| 31 | $\mathrm{CH}_{3} \mathrm{ipr}$ | $\left(2 \phi_{34}-\phi_{35}-\phi_{36}\right) / \sqrt{6}$ |
| 32 | $\mathrm{CH}_{3} \mathrm{Opr}$ | $\left(\phi_{35}-\phi_{36}\right) / \sqrt{2}$ |
| 33 | Rtrigd | $\left(\gamma_{40}-\gamma_{41}+\gamma_{42}-\gamma_{43}+\gamma_{44}-\gamma_{45}\right) / \sqrt{6}$ |
| 34 | Rsymd | $\left(-\gamma_{40}-\gamma_{41}+2 \gamma_{42}-\gamma_{43}-\gamma_{44}+2 \gamma_{45}\right) / \sqrt{12}$ |
| 35 | Rasymd | $\left(\gamma_{40}-\gamma_{4}+\gamma_{43}-\gamma_{44}\right) / 2$ |
| 36-38 | $\omega \mathrm{CH}$ | $\omega 46, \omega 47, \omega 48$ |
| 39 | $\omega \mathrm{CC}$ | Q49 |
| 40 | $\omega \mathrm{CO}$ | $\phi_{50}$ |
| 41 | $\omega \mathrm{CBr}$ | $\psi 51$ |
| 42 | $\omega \mathrm{OH}$ | $\omega_{52}$ |
| 43 | $\omega \mathrm{CH}$ | $\omega_{63}$ |
| 44 | $\omega \mathrm{CO}$ | $\tau 54$ |
| 45 | $\tau \mathrm{COH}$ | $\tau_{54}$ |
| 46 | tRtrig | $\left(\tau_{56}+\tau_{57}+\tau_{58}+\tau_{59}+\tau_{60}+\tau_{61}\right) / \sqrt{6}$ |
| 47 | tRsym | $\left(\tau_{56}+\tau_{57}+\tau_{59}+\tau_{60}\right) / 2$ |
| 48 | tRasy | $\left(-\tau_{56}+2 \tau_{57}-\tau_{58}-\tau_{59}+2 \tau_{60}-\tau_{61}\right) / \sqrt{12}$ |

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

| No. (i) | Symbol | Definition |
| :---: | :---: | :---: |
| 1-3 | CH | $\mathrm{r}_{1}, \mathrm{r}_{2}, \mathrm{r}_{3}$ |
| 4 | CC | $\mathrm{R}_{4}$ |
| 5 | CH | $\mathrm{r}_{5}$ |
| 6,7 | CO | $\mathrm{p}_{6}, \mathrm{p}_{7}$ |
| 8 | CBr | $\mathrm{P}_{8}$ |
| 9 | CO | $\mathrm{p}_{9}$ |
| 10 | $\mathrm{CH}_{3}$ ss | $\left(r_{10}+r_{11}+r_{13}\right) / \sqrt{3}$ |
| 11 | $\mathrm{CH}_{3} \mathrm{ips}$ | $\left(2 r_{10}-r_{11}-r_{13}\right) / \sqrt{6}$ |
| 12 | $\mathrm{CH}_{3} \mathrm{ops}$ | $\left(\mathrm{r}_{11}-\mathrm{r}_{12}\right) / \sqrt{2}$ |
| 13-18 | CO | $\mathrm{q}_{13,} \mathrm{q}_{14,} \mathrm{q}_{15}, \mathrm{q}_{16}, \mathrm{q}_{17,} \mathrm{q}_{18}$ |
| 19-21 | bCH | $\begin{aligned} & \left(\beta_{19}-\beta_{20}\right) / \sqrt{2},\left(\beta_{21}-\beta_{22}\right) / \sqrt{2},\left(\beta_{23}-\beta_{24}\right) \\ & / \sqrt{2} \end{aligned}$ |
| 22 | bCC | $\left(\alpha_{25}-\alpha_{26}\right) / \sqrt{2}$ |
| 23 | bCO | $\left(\sigma_{27}-\sigma_{28}\right) / \sqrt{2}$ |
| 24 | bCF | $\left(\rho_{29}-\rho_{30}\right) / \sqrt{2}$ |
| 25 | bCC | $\alpha_{31}$ |
| 26 | bCC | $\alpha_{32}$ |
| 27 | bOH | $\delta_{33}$ |
| 28 | $\mathrm{CH}_{3} \mathrm{sb}$ | $\left(-\phi_{34}-\phi_{35}-\phi_{36}+\pi_{37}+\pi_{38}+\pi_{39}\right) / \sqrt{6}$ |


| 29 | $\mathrm{CH}_{3} \mathrm{pb}$ | $\left(-\pi_{37}-\pi_{38-2} \pi_{39}\right) / \sqrt{6}$ |
| :--- | :--- | :--- |
| 30 | $\mathrm{CH}_{3} \mathrm{opb}$ | $\left(\pi_{38}-\pi_{39}\right) / \sqrt{2}$ |
| 31 | $\mathrm{CH}_{3} \mathrm{pr}$ | $\left(2 \phi_{34}-\phi_{35}-\phi_{36}\right) / \sqrt{6}$ |
| 32 | $\mathrm{CH}_{3} \mathrm{opr}$ | $\left.\phi_{35}-\phi_{36}\right) / \sqrt{2}$ |
| 33 | Rtrigd | $\left(\gamma_{40}-\gamma_{41}+\gamma_{42}-\gamma_{43}+\gamma_{44}-\gamma_{45}\right) / \sqrt{6}$ |
| 34 | Rsymd | $\left(-\gamma_{40}-\gamma_{41}+2 \gamma_{42}-\gamma_{43}-\gamma_{44}+2 \gamma_{45}\right) / \sqrt{12}$ |
| 35 | Rasymd | $\left(\gamma_{40}-\gamma_{4}+\gamma_{43}-\gamma_{44}\right) / 2$ |
| $36-38$ | $\omega \mathrm{CH}$ | $\omega 46, \omega 47, \omega_{48}$ |
| 39 | $\omega \mathrm{CC}$ | $\varphi_{49}$ |
| 40 | $\omega \mathrm{CO}$ | $\phi_{50}$ |
| 41 | $\omega \mathrm{CF}$ | $\psi_{51}$ |
| 42 | $\omega \mathrm{OH}$ | $\omega 52$ |
| 43 | $\omega \mathrm{CH}$ | $\omega 63$ |
| 44 | $\omega \mathrm{CO}$ | $\tau_{54}$ |
| 45 | $\tau \mathrm{COH}$ | $\tau_{54}$ |
| 46 | tRtrig | $\left(\tau_{56}+\tau_{57}+\tau_{58}+\tau_{59}+\tau_{60}+\tau_{61}\right) / \sqrt{6}$ |
| 47 | tRsymd | $\left(\tau_{56}+\tau_{57}+\tau_{59}+\tau_{60}\right) / 2$ |
| 48 | tRasym <br> d | $\left(-\tau_{56}+2 \tau_{57}-\tau_{58}-\tau_{59}+2 \tau_{60}-\tau_{61}\right) / \sqrt{12}$ |

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 $82.11 \mathrm{~cm}^{-}$ ${ }^{1}$, 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 $4.8 \mathrm{~cm}^{-1}$ for BOA and 4.3 $\mathrm{cm}^{-1}$ 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. 3.FT-IR Spectrum of 5-bromo-o-anisaldehyde.


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


Fig. 5.FT-IR Spectrum of 2-fluro-p-anisaldehyde.


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

The aromatic structure shows the presence of $\mathrm{C}-\mathrm{H}$ stretching vibrations in the region $3100-3000 \mathrm{~cm}^{-1}$ 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 $3103,3073,3015 \mathrm{~cm}^{-1}$ and $3051,3022,3000$ $\mathrm{cm}^{-1}$, respectively in BOA and FPA have been designated to $\mathrm{C}-\mathrm{H}$ stretching vibrations. The B3LYP level at $6-31+\mathrm{G}(\mathrm{d}, \mathrm{p})$ after scaling down give the frequency values at 3106,3082 , $3009 \mathrm{~cm}^{-1}$ and $3060,3026,3003 \mathrm{~cm}^{-1}$. In general the aromatic $\mathrm{C}-\mathrm{H}$ vibrations calculated theoretically are in good agreement with the experimentally reported values $[23,24]$ for trisubstituted benzene.

The in-plane aromatic $\mathrm{C}-\mathrm{H}$ deformation vibrations occur in the region $1450-990 \mathrm{~cm}^{-1}$. The bands are sharp but are weak to medium intensity. The $\mathrm{C}-\mathrm{H}$ in-plane bending vibrations computed at $1491,1466,1453 \mathrm{~cm}^{-1}$ and 1395, $1389,1345 \mathrm{~cm}^{-1}$ for BOA and FPA by B3LYP method shows good agreement with experimental value. The medium and very strong intensity bands at $1497,1480,1461 \mathrm{~cm}^{-1}$ and 1396, $1285 \mathrm{~cm}^{-1}$ 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 $1460 \mathrm{~cm}^{-1}$ with medium intensity for BOA and $1348 \mathrm{~cm}^{-1}$ in FT-Raman for FPA.

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

## C-C Vibrations

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

## Aldehyde group vibrations

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

## $\mathrm{CH}_{3}$ group vibrations

In the region of 3102-2843 $\mathrm{cm}^{-1}$, three bands have been observed at 2967, 2941 and $2843 \mathrm{~cm}^{-1}$ for BOA, have been assigned to two $\mathrm{CH}_{3}$ asymmetrical $\left(\mathrm{CH}_{3} \mathrm{ips}\right)$ and symmetrical $\left(\mathrm{CH}_{3} \mathrm{ss}\right)$ in-plane stretching modes, asymmetric $\left(\mathrm{CH}_{3} \mathrm{ops}\right)$ 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 $3251-2811 \mathrm{~cm}^{-1}$ were assigned to the $\mathrm{CH}_{3}$ asymmetric and symmetric in-plane stretches, $\mathrm{CH}_{3}$ asymmetric out-of-plane stretches, $\mathrm{CH}_{2}$ 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.

Table 8.The observed FTIR, FT Raman and calculated (Unscaled and Scaled) frequencies ( $\mathbf{c m}^{-1}$ ), IR intensity ( $\mathbf{k M ~ m o l}^{-1}$ ), Raman activity ( $\AA$ amu ${ }^{-1}$ ), Reduced masses ( $\mathbf{a m u}$ ) and force constant (mdyne $\AA^{-1}$ ) and probable assignments (characterized by TED) of 5-bromo-o-anisaldehyde using B3LYP/6-31+G(d,p).

| Symmetry species $\mathbf{C}_{\text {s }}$ | Fundamentals ( $\mathrm{cm}^{-1}$ ) |  | Calculated frequencies ( $\mathrm{cm}^{-1}$ ) |  | Reduced mass | Force constants | Infrared intensity | Raman activity | TED (\%) among types of internal coordinates |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Unscaled | Scaled |  |  |  |  |  |
| $\mathrm{A}^{\prime}$ | 3103 ms | Raman | 3403 | 3106 | 1.0945 | 7.400 | 8.24 | 141.13 | $\mathrm{v} \mathrm{CH}(99)$ |
| $\mathrm{A}^{\prime}$ | 3073ms | 3074w | 3402 | 3082 | 1.0935 | 7.4548 | 1.32 | 5.03 | $\mathrm{v}^{\mathrm{CH}}$ (99) |
| $\mathrm{A}^{\prime}$ | 3015ms | 3015w | 3379 | 3009 | 1.0915 | 7.3438 | 1.43 | 48.22 | ${ }^{\mathrm{v}} \mathrm{CH}(99)$ |
| $\mathrm{A}^{\prime \prime}$ | 2967 ms | - | 3319 | 2975 | 1.1028 | 7.1581 | 28.08 | 118.30 | $\mathrm{CH}_{3}$ as (85) |
| $\mathrm{A}^{\prime}$ | 2941 ms | - | 3265 | 2955 | 1.1078 | 6.9572 | 39.11 | 45.32 | $\mathrm{CH}_{3} \mathrm{as}(86)$ |
| $\mathrm{A}^{\prime}$ | 2878w | 2881w | 3236 | 2886 | 1.0892 | 6.7217 | 54.05 | 102.46 | ${ }^{2} \mathrm{CH}(97)$ |
| $\mathrm{A}^{\prime}$ | 2843w | 2848w | 3194 | 2849 | 1.0336 | 6.2125 | 54.21 | 132.27 | $\mathrm{CH}_{3} \mathrm{Ss}(88)$ |
| $\mathrm{A}^{\prime}$ | 1680vs | 1681vs | 1967 | 1685 | 9.8142 | 22.3657 | 378.79 | 93.39 | $\mathrm{v}^{\mathrm{CO}}$ (93) |
| $\mathrm{A}^{\prime}$ | 1634w | - | 1793 | 1641 | 5.8745 | 11.1221 | 87.96 | 74.42 | ${ }^{\nu} \mathrm{CC}(84), 8 \mathrm{CH}(12)$ |
| $\mathrm{A}^{\prime}$ | 1593w | 1596ms | 1764 | 1590 | 7.0906 | 12.9975 | 24.75 | 20.07 | $\nu^{2} \mathrm{CC}(75), \mathrm{\delta CH}(15), \mathrm{\delta CO}(10)$ |
| $\mathrm{A}^{\prime}$ | 1575vs | 1572ms | 1656 | 1578 | 2.2456 | 3.6285 | 185.55 | 10.05 | ${ }^{2} \mathrm{CC}(75), 8 \mathrm{CH}(20)$ |
| $\mathrm{A}^{\prime \prime}$ | 1561w | - | 1635 | 1566 | 1.0692 | 1.6847 | 50.08 | 8.05 | $\mathrm{CH}_{3} \mathrm{opb}$ (84) |
| $\mathrm{A}^{\prime}$ | 1533w | - | 1629 | 1530 | 1.0463 | 1.6367 | 8.06 | 14.79 | $\mathrm{CH}_{3} \mathrm{ipb}$ (85) |
| $\mathrm{A}^{\prime}$ | 1519w | - | 1612 | 1525 | 1.2457 | 1.9072 | 31.52 | 2.72 | $\mathrm{CH}_{3} \mathrm{sb}(84)$ |
| $\mathrm{A}^{\prime}$ | 1497vs | - | 1558 | 1491 | 2.2768 | 3.2583 | 16.41 | 3.12 | ¢CH (72), vCC (15) |
| $\mathrm{A}^{\prime}$ | 1480vs | - | 1541 | 1480 | 1.6056 | 2.2468 | 129.52 | 2.82 | ¢CH (74), vCC (12) |
| $\mathrm{A}^{\prime}$ | 1461 ms | 1460 ms | 1424 | 1466 | 2.1227 | 2.5387 | 268.18 | 10.98 | ¢CH (74), vCC (14) |
| $\mathrm{A}^{\prime}$ | 1455 ms | 1450w | 1393 | 1453 | 1.9488 | 2.2281 | 117.58 | 16.81 | ¢CH (74), vCC (10) |
| $\mathrm{A}^{\prime}$ | 1441w | - | 1332 | 1440 | 1.6899 | 1.7664 | 7.91 | 6.64 | $\mathrm{CH}_{3} \mathrm{ipr}(76), \mathrm{\delta CH}(20)$ |
| $\mathrm{A}^{\prime}$ | 1395vs | 1396ms | 1307 | 1394 | 1.6772 | 1.6882 | 19.43 | 2.07 | ${ }^{2} \mathrm{CC}(71), 8 \mathrm{CH}(15)$ |
| $\mathrm{A}^{\prime \prime}$ | 1298vs | 1300w | 1281 | 1299 | 1.2661 | 1.2242 | 3.34 | 2.08 | $\mathrm{CH}_{3} \mathrm{opr}(79)$ |
| $\mathrm{A}^{\prime}$ | 1267vs | 1265s | 1240 | 1263 | 2.2676 | 2.0536 | 84.72 | 4.01 | ${ }^{\nu} \mathrm{CC}(71), 8 \mathrm{CH}(16)$ |
| $\mathrm{A}^{\prime}$ | 1244w | - | 1234 | 1246 | 6.9153 | 6.2050 | 57.43 | 40.69 | ${ }^{2} \mathrm{CC}(70), 8 \mathrm{CO}(16)$ |
| $\mathrm{A}^{\prime}$ | 1179vs | 1180vs | 1194 | 1180 | 2.1117 | 1.7736 | 5.04 | 2.89 | $\nu \mathrm{CC}(75), \mathrm{\delta CH}(12)$ |
| $\mathrm{A}^{\prime \prime}$ | 1142ms | - | 1163 | 1145 | 1.8949 | 1.5121 | 0.00 | 3.57 | $\gamma \mathrm{CH}(37), \gamma \mathrm{CC}(19)$ |
| $\mathrm{A}^{\prime}$ | 1126w | 1125w | 1156 | 1128 | 6.2885 | 4.9540 | 55.97 | 6.11 | ${ }^{2} \mathrm{CO}(42), \mathrm{vCC}(18), 8 \mathrm{CH}(15)$ |
| $\mathrm{A}^{\prime \prime}$ | 1100w | 1095w | 1109 | 1106 | 1.4501 | 1.0524 | 0.10 | 0.16 | $\gamma \mathrm{CH}(37), \gamma \mathrm{CC}(25)$ |
| $\mathrm{A}^{\prime \prime}$ | 1020vs | - | 1082 | 1018 | 1.5028 | 1.0364 | 10.51 | 0.61 | $\gamma \mathrm{CH}(40), \gamma \mathrm{CC}(32)$ |
| $\mathrm{A}^{\prime}$ | 891ms | - | 961 | 890 | 5.7381 | 3.1273 | 25.73 | 3.01 | $\delta \mathrm{CO}(55), \mathrm{S} \operatorname{Ring}(32), \mathrm{vCBr}(12)$ |
| $\mathrm{A}^{\prime \prime}$ | 882vs | 885w | 938 | 884 | 1.6185 | 0.8381 | 41.69 | 0.38 | $\gamma \mathrm{CH}(29), \gamma \mathrm{CC}(19)$ |
| $\mathrm{A}^{\prime}$ | 824w | - | 859 | 823 | 5.2933 | 2.3019 | 8.11 | 23.06 | $\delta \mathrm{CO}(45), \mathrm{v} \mathrm{CC}(21), \delta \mathrm{CH}(15)$ |
| $\mathrm{A}^{\prime}$ | 803w | 799s | 829 | 804 | 3.0449 | 1.2318 | 4.03 | 1.42 | $\gamma \mathrm{CO}$ (35), $\gamma \mathrm{CH}$ (21) |
| $\mathrm{A}^{\prime}$ | 706 ms | 706w | 720 | 705 | 2.8092 | 0.8594 | 12.64 | 0.14 | ¢CC (55), $\delta$ CO (29) |
| $\mathrm{A}^{\prime}$ | 646s | 651 ms | 702 | 647 | 5.8549 | 1.7030 | 21.11 | 3.14 | $\delta \mathrm{Ring}(49)$, $\delta \mathrm{CO}(31)$ |
| $\mathrm{A}^{\prime}$ | 623s | 627s | 680 | 625 | 6.1708 | 1.6807 | 31.18 | 3.14 | $\mathrm{v} \mathrm{CBr}(61), 8 \mathrm{CC}(22), 8 \mathrm{CO}(10)$ |
| $\mathrm{A}^{\prime}$ | 539w | - | 565 | 540 | 5.9482 | 1.1222 | 33.98 | 2.18 | $\gamma \mathrm{CO}(55), \gamma \mathrm{CH}(19), \gamma \operatorname{Ring}(12)$ |
| $\mathrm{A}^{\prime}$ | 522s | 525 vw | 523 | 523 | 3.0381 | 0.4909 | 6.20 | 0.09 | $\delta \mathrm{Ring}(29), \delta \mathrm{CO}(13)$ |


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| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| A" | - | 425w | 432 | 425 | 6.0297 | 0.6619 | 1.06 | 4.79 | $\gamma \operatorname{Ring}(32), \gamma \mathrm{CO}(12)$ |
| $\mathrm{A}^{\prime \prime}$ | - | 410s | 419 | 413 | 4.4133 | 0.4582 | 0.18 | 1.32 | $\gamma \operatorname{Ring}(31), \gamma \mathrm{CO}(18)$ |
| $\mathrm{A}^{\prime}$ | - | 362w | 351 | 364 | 5.1865 | 0.3776 | 4.85 | 1.31 | $\delta \mathrm{CBr}(25), \delta \mathrm{CO}(16)$ |
| $\mathrm{A}^{\prime}$ | - | 318w | 295 | 320 | 9.7940 | 0.5051 | 2.33 | 8.06 | $\delta$ Ring(29), $\delta \mathrm{CO}(18)$ |
| $\mathrm{A}^{\prime \prime}$ | - | 258s | 265 | 256 | 1.1144 | 0.0464 | 0.98 | 0.15 | $\mathrm{tCH}_{3}$ (76) |
| $\mathrm{A}^{\prime \prime}$ | - | 201 ms | 209 | 200 | 2.8879 | 0.0744 | 5.45 | 2.06 | $\gamma \mathrm{CBr}(28), \gamma \mathrm{CC}(18)$ |
| $\mathrm{A}^{\prime \prime}$ | - | 188s | 201 | 189 | 4.3098 | 0.1031 | 0.14 | 0.86 | $\gamma \mathrm{CO}(33), \gamma \mathrm{CC}(15)$ |
| $\mathrm{A}^{\prime \prime}$ | - | - | 155 | 154 | 11.6713 | 0.1658 | 3.39 | 1.42 | $\gamma \mathrm{CO}(39), \gamma \operatorname{Ring}(20)$ |
| $\mathrm{A}^{\prime \prime}$ | - | - | 144 | 146 | 4.3950 | 0.0543 | 14.88 | 0.32 | $\gamma \mathrm{CO}(28), \gamma \operatorname{Ring}(15)$ |
| $\mathrm{A}^{\prime \prime}$ | - | - | 110 | 108 | 4.1382 | 0.0295 | 4.06 | 0.79 | $\gamma \mathrm{CO}(27), \gamma \operatorname{Ring}(15)$ |
| $\mathrm{A}^{\prime \prime}$ | - | - | 71 | 70 | 3.3912 | 0.0101 | 1.19 | 0.41 | $\gamma \mathrm{CO}(28), \gamma \operatorname{Ring}(13)$ |


 intensity in $\mathrm{Km} \mathrm{mol}^{-1}$. Raman scattering activity in $\mathrm{A}^{4} \mathrm{amu}^{-1}$. Depolarization rations for plane and unpolarised in amu. Reduced masses in AMU Force constants in $m$ Dyne A.

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

| Symmetry species $\mathrm{C}_{\text {s }}$ | Fundamentals ( $\mathrm{cm}^{-1}$ ) |  | Calculated frequencies ( $\mathrm{cm}^{-1}$ ) |  | Reduced mass | Force constants | Infrared intensity | Raman activity | TED (\%) among types of internal coordinates |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Unscaled | Scaled |  |  |  |  |  |
|  | FT-IR | Raman |  |  |  |  |  |  |  |
| $\mathrm{A}^{\prime}$ | 3051w | - | 3228 | 3060 | 1.0931 | 6.7100 | 5.68 | 112.08 | ${ }^{2} \mathrm{CH}(98)$ |
| $\mathrm{A}^{\prime}$ | 3022w | - | 3212 | 3026 | 1.0888 | 6.6191 | 0.23 | 39.17 | ${ }^{2} \mathrm{CH}(97)$ |
| $\mathrm{A}^{\prime}$ | 3000w | - | 3200 | 3003 | 1.0913 | 6.5844 | 1.70 | 88.8 | ${ }^{2} \mathrm{CH}(97)$ |
| $\mathrm{A}^{\prime \prime}$ | 2941ms | - | 3165 | 2940 | 1.1010 | 6.4987 | 14.17 | 133.61 | $\mathrm{CH}_{3}$ as(82) |
| $\mathrm{A}^{\prime}$ | 2847w | - | 3099 | 2844 | 1.1071 | 6.2645 | 29.79 | 56.95 | $\mathrm{CH}_{3} \mathrm{as}$ (82) |
| $\mathrm{A}^{\prime}$ | 2830w | - | 3029 | 2835 | 1.0337 | 5.5901 | 51.58 | 154.43 | ${ }^{2} \mathrm{CH}(95)$ |
| $\mathrm{A}^{\prime}$ | 2811 ms | - | 2914 | 2816 | 1.0836 | 5.4236 | 124.22 | 169.62 | $\mathrm{CH}_{3} \mathrm{ss}(85)$ |
| $\mathrm{A}^{\prime}$ | 1693vs | 1595vs | 1769 | 1690 | 9.8698 | 18.1933 | 304.39 | 179.94 | ${ }^{2} \mathrm{CO}(90)$ |
| $\mathrm{A}^{\prime}$ | 1610vs | 1611vs | 1652 | 1615 | 6.4768 | 10.42.14 | 215.55 | 270.26 | ${ }^{2} \mathrm{CC}(78), 8 \mathrm{CH}(12)$ |
| $\mathrm{A}^{\prime}$ | 1588s | 1588s | 1619 | 1583 | 7.8008 | 12.0513 | 58.81 | 5.45 | ${ }^{2} \mathrm{CC}(77), \delta \mathrm{CH}(15), \delta \mathrm{CO}(12)$ |
| $\mathrm{A}^{\prime}$ | 1586vs | - | 1555 | 1519 | 3.1947 | 4.5552 | 132.65 | 5.52 | ${ }^{\nu} \mathrm{CC}(75), \delta \mathrm{CH}(22)$ |
| $\mathrm{A}^{\prime \prime}$ | 1462w | - | 1506 | 1461 | 1.0572 | 1.4136 | 41.75 | 8.76 | $\mathrm{CH}_{3} \mathrm{ipb}$ (85) |
| $\mathrm{A}^{\prime}$ | - | 1452 ms | 1501 | 1452 | 1.0456 | 1.3874 | 9.79 | 15.17 | $\mathrm{CH}_{3} \mathrm{Opb}(86)$ |
| $\mathrm{A}^{\prime}$ | 1443s | - | 1484 | 1448 | 1.2934 | 1.6785 | 17.52 | 4.42 | $\mathrm{CH}_{3} \mathrm{sb}$ (84) |
| $\mathrm{A}^{\prime}$ | 1396ms | - | 1468 | 1395 | 2.5128 | 3.1852 | 11.76 | 1.43 | $\delta \mathrm{CH}(70), \mathrm{v} \mathrm{CC}(19)$ |
| $\mathrm{A}^{\prime}$ | 1388w | - | 1417 | 1389 | 1.5731 | 1.8605 | 2.77 | 9.07 | $\delta \mathrm{CH}(75), \mathrm{vCC}(18)$ |
| $\mathrm{A}^{\prime}$ | - | 1348 ms | 1364 | 1345 | 6.2128 | 6.8148 | 85.74 | 25.02 | $\delta \mathrm{CH}(74), \mathrm{vCC}(14)$ |
| $\mathrm{A}^{\prime}$ | 1285vs | 1289 ms | 1322 | 1286 | 4.2925 | 4.4190 | 434.57 | 39.02 | $\delta \mathrm{CH}(73), \mathrm{vCC}(12)$ |
| $\mathrm{A}^{\prime}$ | 1259w | 1260 ms | 1303 | 1257 | 1.7708 | 1.7725 | 30.69 | 9.56 | $\mathrm{CH}_{3} \mathrm{ipr}(77), \mathrm{\delta CH}(18)$ |
| $\mathrm{A}^{\prime}$ | 1226ms | 1230 ms | 1247 | 1228 | 2.8182 | 2.5820 | 30.82 | 29.10 | ${ }^{2} \mathrm{CF}(88), \delta \mathrm{CH}(10)$ |
| $\mathrm{A}^{\prime \prime}$ | 1186w | - | 1208 | 1185 | 1.3681 | 1.1767 | 2.84 | 5.94 | ${ }^{2} \mathrm{CC}(73), \delta \mathrm{CH}(17)$ |
| $\mathrm{A}^{\prime}$ | 1153w | - | 1179 | 1153 | 1.4722 | 1.2062 | 8.21 | 1.68 | $\mathrm{CH}_{3} \mathrm{Opr}(78)$, vCC (10) |
| $\mathrm{A}^{\prime}$ | 1121vs | 1121 ms | 1172 | 1124 | 1.2688 | 1.0271 | 0.97 | 1.87 | ${ }^{2} \mathrm{CC}(71), \delta \mathrm{CH}(16)$ |
| $\mathrm{A}^{\prime}$ | 1109s | - | 1132 | 1105 | 1.7526 | 1.3243 | 137.59 | 12.32 | ${ }^{2} \mathrm{CC}(68), \delta \mathrm{CO}(14)$ |



Abbreviations: t , torsion; R1 trigd, Ring 1 trigonal deformation; R2 trigd, Ring 2 trigonal deformation; asym, asymmetric; s, symmetric; $\omega$, 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 $\mathrm{cm}^{-1}$. The absolute IR intensity in $\mathrm{Km} \mathrm{mol}^{-1}$. Raman scattering activity in $\mathrm{A}^{4} \mathrm{amu}^{-1}$. Depolarization rations for plane and unpolarised in amu. Reduced masses in AMU Force constants in m Dyne A.

## $\mathrm{C}-\mathrm{Br}$ vibrations

Strong characteristic absorption due to the $\mathrm{C}-\mathrm{Br}$ 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 $\mathrm{C}-\mathrm{Br}$ stretching vibrations. According to these early reports $[33,34]$, the $\mathrm{C}-\mathrm{Br}$ stretching vibration gives generally strong band in the region $650-485 \mathrm{~cm}^{-1}$. In the present compound, a strong band is observed at $623 \mathrm{~cm}^{-1}$ in FT-IR spectrum and $627 \mathrm{~cm}^{-1}$ in FT-Raman spectrum are assigned to $\mathrm{C}-\mathrm{Br}$ stretching vibrations for BOA. The calculated $\mathrm{C}-\mathrm{Br}$ stretching bands are found at $625 \mathrm{~cm}^{-1}$ and this assignment is slightly above the literature value.
The theoretically computed value at $364 \mathrm{~cm}^{-1}$ is assigned to $\mathrm{C}-\mathrm{Br}$ in-plane by B3LYP/6-31+G(d,p) method. The $\mathrm{C}-\mathrm{Br}$ inplane bending bands are observed at $362 \mathrm{~cm}^{-1}$ in FT-Raman spectrum. The $\mathrm{C}-\mathrm{Br}$ out-of-plane bending bands are observed at $201 \mathrm{~cm}^{-1}$ in FT-Raman spectrum and is assigned to $\mathrm{C}-\mathrm{Br}$ out-of-plane bending of BOA. This shows that the other vibrations can hold back the $\mathrm{C}-\mathrm{Br}$ 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 $1270-1100 \mathrm{~cm}^{-1}$ [35]. The very strong band at 1226 $\mathrm{cm}^{-1}$ in FPA is assigned to C-F stretching vibration. The predicted band corresponding to C-F stretching mode is 1228 $\mathrm{cm}^{-1}$. C-F in-plane bending vibrations are expected in the range $420-254 \mathrm{~cm}^{-1}$ [23,35]. In FPA, a weak band at $504 \mathrm{~cm}^{-}$ ${ }^{1}$ and computed value $505 \mathrm{~cm}^{-1}$ is assigned to C-F in-planebending vibration. C-F out-of-plane bending vibrations were observed in the range $520-101 \mathrm{~cm}^{-1}[35,36]$. The observed FT-Raman band at $176 \mathrm{~cm}^{-1}$ 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 $4.8 \mathrm{~cm}^{-1}$ for BOA and for FPA, $4.3 \mathrm{~cm}^{-1}$ for the $6-31+G(\mathrm{~d}, \mathrm{p})$ 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.

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