

**VIBRATIONAL ANALYSIS OF P-BROMO BENZOIC ACID AND P-FLUORO  
BENZOIC ACID AND SIMULATION OF FTIR AND FT-RAMAN SPECTRA  
BASED ON  
SCALED QUANTUM FORCE FIELDS**

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**Abstract**

A solid phase FTIR and FT-Raman spectra of p-bromo benzoic acid (p-BBA) and p-fluoro benzoic acid (p-FBA) were recorded in the region 4000-400cm<sup>-1</sup> and 4000-50cm<sup>-1</sup> respectively. The spectra were interpreted with the aid of normal coordinate analysis following full structure optimization and force field calculations based of DFT using standard B3LYP/6-31G\*\* basis set combination and was scaled using various scale factors yielding fairly good agreement between observed and calculated frequencies. The effects of bromo and fluoro substitutions on the structure and vibrational requences have been investigated. The Infrared and Raman spectra were also predicted from the calculated intensities.

Keywords: p-bromo benzoic acid and p-fluoro benzoic acid; Density functional theory; FTIR spectroscopy; FT-Raman spectroscopy; Vibrational spectra;

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## 1. Introduction

Vibrational spectroscopy is used extensively in organic chemistry, for the identification of functional groups of organic compounds, for studies on molecular conformation and reaction kinetics, etc. Due to the great biological and pharmaceutical importance, the vibrational studies of p-BBA and p-FBA have been carried out in this present investigation. The aromatic acids are crystalline substance, generally slightly soluble in water and well soluble in organic solvents like alcohol, chloroform, and benzene etc. One of the most common uses of benzoic acid is food preservatives [1]. It is also used in the manufacture of artificial flavors and perfumes and for the flavoring of tobacco. In medicine, the benzoic acid is used as an anti-microbial agent [2]. Benzoic acid and its derivatives inhibit the growth of mold, yeast and some bacteria [3]. Benzoic acid is found in toothpastes and mouthwashes, cosmetics and deodorants. In the present investigation, a complete study of vibrational spectra of p-BBA and p-FBA has been carried out. The fluorine and bromine substituent's present in the title compounds are highly electronegative and hence they withdraw the electrons from the ring, which results into the change in ionization potential, electronic affinity and excitation energies of the systems.

Quantum chemical computational methods have proven to be an essential tool for interpreting and predicting the vibrational spectra [4, 5]. In the SQM approach the systematic errors of the completed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules [5-7]. The vibrational analysis of p-BBA and p-FBA

using the SQM force field method based of DFT calculation has been presented [8]. The calculated infrared and Raman spectra of the title compounds are also simulated utilizing the scaled force fields and the computed dipole derivatives for IR intensities and polarizability derivatives for Raman intensities.

## 2. Experimental

The fine crystalline samples of p-BBA and p-FBA were obtained from Lancaster chemical company, UK and used as such for the spectral measurements. The Fourier transform infrared spectrum of the title compounds were recorded in the region 400–4000  $\text{cm}^{-1}$  using Perkin-Elmer spectrum RXI spectrophotometer equipped with He-Ne laser source, KBr beam splitter and  $\text{LiTaO}_3$  detector. The samples were prepared by pressing p-BBA and p-FBA with KBr into pellet form.

The FT-Raman spectra of p-BBA and p-FBA were recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory in the 4000-50  $\text{cm}^{-1}$  Stokes region using the 1064 nm line of a Nd:YAG laser for excitation operating at 200mW power. The reported frequencies' are believed to be accurate within  $\pm 1 \text{ cm}^{-1}$ .

## 3. Computational Details

Quantum chemical density functional calculations were carried out with the GAUSSIAN 98 W Program [9], using the Becke3-Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G\*\* basis set (referred to as DFT calculations) [10,11]. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming  $C_s$

point group symmetry. The multiple scaling of the force constants were performed by the quantum chemical method with selective scaling in the local symmetry coordinate representation [12], using transferable scale factors available in the literature [13]. The transformation of force field from Cartesian to symmetry coordinate, the scaling, the subsequent normal coordinate analysis, calculation of potential energy distribution (PED) and IR and Raman intensities were done on a PC with the version V7.0-G77 of the MOLVIB program written by Sundius [14, 15]. To achieve a close agreement between observed and calculated wave numbers, the least square fit refinement algorithm was used. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of  $10 \text{ cm}^{-1}$ .

### 3.1. Prediction of Raman intensities

The Raman activities ( $S_i$ ) calculated by the GAUSSIAN 98 W 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 [16-18].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i \left[ 1 - \exp\left(\frac{-hc\nu_i}{KT}\right) \right]} \quad (1)$$

Where,  $\nu_0$  is the exciting frequencies (in  $\text{cm}^{-1}$  units).  $\nu_i$  is the vibrational frequencies of the  $i^{\text{th}}$  normal mode,  $h$ ,  $c$  and  $k$  are the universal constants and  $f$  is a suitably chosen common normalization factor for all peak intensities.

## 4. Results and Discussion

### 4.1. Molecular geometry

The molecular structures of p-BBA and p-FBA having  $c_s$  symmetry are shown in Figs. 1(a) & 1(b), respectively. The global minimum obtained by the DFT structure optimization for p-BBA and p-FBA are calculated as -2991.9382 Hartrees and -520.0677 Hartrees, respectively.

The energy difference is clearly understandable, since the environments of the molecules are different. The calculated optimized geometrical parameters obtained in this study for p-BBA and p-FBA are presented in Table 1. All vibrational frequencies have been calculated and they were found to be positive.

### 4.2. Vibrational force constants

The output of the quantum-mechanical calculations contains the force constants matrix in Cartesian coordinates and in Hartrees/Bhor<sup>2</sup> units. These force constants were transformed to the force fields in the internal local symmetry coordinates; defined interims of the internal valence coordinates following the IUPAC recommendations [19, 20] are given in Table2 for p-BBA and p-FBA. The force fields determined were used to calculate the potential energy distribution (PED) among the normal coordinates.

The bonding properties of the title compounds are influenced by the rearrangements of electrons during substitutions and addition reactions. The values of the stretching force constants between carbon and bromine atoms of p-BBA are found to be lesser than the corresponding values between carbon and fluorine atoms of p-FBA because of fluorine atom which has higher

electronegative than bromine. The force constant of a bond increases numerically with bond order and consequently decreases with the increase in bond length. The stretching force constant of C=O is greater than C-O.

### 4.3. Vibrational spectra

The 39 normal modes of p-BBA and p-FBA are distributed amongst the symmetry species as

$$\Gamma_{\text{vib}} = 27A' \text{ (in-plane)} + 12A'' \text{ (out-of-plane)}$$

and in agreement with  $C_s$  symmetry, all the vibrations are active both in the Raman scattering and Infrared absorption. The detailed vibrational assignments of fundamental modes of p-BBA and p-FBA along with the observed and calculated frequencies, IR and Raman intensities and normal mode descriptions (characterized by PED) are reported in Tables 3&4. For visual comparison, the observed and simulated FTIR and FT-Raman spectra of p-BBA and p-FBA are presented in Figs 2-5 respectively. Root mean square (RMS) values were obtained in this study using the following expression

$$\text{RMS} = \sqrt{\frac{1}{(n-1)} \sum_i^n (\nu_i^{\text{calc}} - \nu_i^{\text{exp}})^2} \quad (2)$$

The harmonic frequencies (DFT-calculated) were found to be 10-15% more than that of the experimentally obtained frequencies (anharmonic). All vibrational assignments are based on the respective point group symmetry for each molecule.

Assignments were made through visualization of the atomic displacement representations for each vibration, viewed through GAUSSVIEW [21] and

matching the predicted normal frequencies and intensities with experimental data. It is convenient to discuss the vibrational spectra of p-BBA and p-FBA in terms of characteristic spectral regions as described below.

#### 4.3.1. C-H vibrations

Aromatic system exhibits the C-H stretching vibrations in the region 3100-3000  $\text{cm}^{-1}$ . In the present study, the C-H vibrations of the title compounds are observed at 3092, 3068, 3045  $\text{cm}^{-1}$  for p-BBA 3084,2997,2952  $\text{cm}^{-1}$  in the FTIR spectra. The bands observed at 3076  $\text{cm}^{-1}$  for p-BBA and 3094, 3078  $\text{cm}^{-1}$  for p-FBA in FT-Raman spectrum are assigned to C-H stretching vibration. The bands due to C-H in-plane bending vibration interacting some what with C-C stretching vibration are observed as a number of weak to medium intensity sharp bands in the region 1300-1000  $\text{cm}^{-1}$ . The C-H out-of plane bending vibrations give rise to intense bands in the region 900-667  $\text{cm}^{-1}$  [22]. The C-H in-plane and out-of-plane bending vibrations for the title compounds are found to be well with in the characteristic region which are depicted in tables 3&4.

#### 4.3.2. Carboxylic Acid

Due to the presence of strong intermolecular hydrogen bonding, carboxylic acid normally exists as dimer. Their spectra exhibit a broad band due to the O-H stretching vibration and a strong band due to C=O stretching vibration. In the presence of hydrogen bonding, carboxylic acids in the liquid and solid phases exhibit a broad band at 3300 to 2500  $\text{cm}^{-1}$ , due to the O-H stretching vibrations [23, 24]. In the present study, the bands identified at 3092  $\text{cm}^{-1}$  for p-BBA and 3094  $\text{cm}^{-1}$  for p-FBA are assigned to O-H stretching vibrations. The C=O

stretching bands of carboxylic acids are considerably more intense than ketonic C-O stretching bands. The characteristic infrared absorption wavenumbers of C=O in acids are normally strong in intensity and found in the region 1800-1690  $\text{cm}^{-1}$  [25-27]. In the case of dimers (solid or pure liquid state) strong hydrogen bonding and resonance lower the force constants of the C=O bond thus resulting in the absorption of C=O group at a lower frequency (1720-1680  $\text{cm}^{-1}$ ). The C=O formed by  $P_{\pi} - P_{\pi}$  bonding between C and O [28,29]. Internal hydrogen bonding reduces the frequency of the C=O stretching absorption to a greater degree than does intermolecular hydrogen bonding because of the different electro-negativities of C and O, the bonding are not equally distributed between the two atoms. The lone pair of electrons on oxygen also determines the nature of carbonyl groups. In this study, the FTIR band observed at 1692  $\text{cm}^{-1}$  in p-BBA and 1687  $\text{cm}^{-1}$  in p-FBA are assigned to C=O stretching vibrations.

The C-O-H in-plane bending appears as a weak band near 1420  $\text{cm}^{-1}$  and C-O stretching as a more intense band near 1300  $\text{cm}^{-1}$ . Since both the bands involve some interaction between them, they are referred to as coupled O-H in-plane bending and C-O stretching vibrations. This is also confirmed by PED output results from tables 1 & 2. The C-O stretching vibrations are assigned to 1134  $\text{cm}^{-1}$  in FT-Raman for p-BBA and 1096  $\text{cm}^{-1}$  in FTIR spectra for p-FBA. The in-plane bending and out-of-plane bending vibrations have been identified and presented in Tables 3 & 4.



#### 4.3.3. C-Br vibrations

The stretching vibrations of bromine compound have strong absorptions at 650- 395  $\text{cm}^{-1}$ . In the present study, the C-Br stretching vibration of p-BBA has been observed at 437  $\text{cm}^{-1}$ . The in-plane and out-of-plane bending vibrational assignments of C-Br are shown in Table 3. These assignments are in good agreement with the literature [30].

#### 4.3.4. C-F vibrations

Aromatic fluoro compounds have medium intensity bands in the region 1270-1100  $\text{cm}^{-1}$ , those with only one fluorine atom on the ring tending to absorb at 1230  $\text{cm}^{-1}$  [30]. In the present study, a weak band observed in FTIR spectrum at 1237  $\text{cm}^{-1}$  is assigned to C-F stretching vibrational mode of p-FBA. The C-F in-plane bending and out-of-plane bending vibrations have been identified and presented in Table 4.

#### 4.3.5. Ring vibrations

The ring stretching, in-plane and out-of-plane bending vibrations have been identified and presented in Tables 3&4. They are also supported by literature [31, 32].

### 5. Conclusion

A complete vibrational analysis of the title compounds were performed based on the SQM force field obtained by DFT calculations at B3LYP/6-31G\*\* level. The assignments of all the fundamentals were made unambiguously, taking advantage of FTIR and FT-Raman experimental data as well as effective scaling and the IR intensity information from DFT. The bromine and fluorine

substituents in the benzoic acid structure produce a remarkable effect on the geometry and spectroscopic properties of the title compounds. The  $-I > +M$  effect of the bromine and fluorine acted not only in the close environment of the place of the substitution but also on other parts of the ring through  $\pi$ -electron system. As a result of the halogen atoms substituents in the ring, remarkable changes are observed.

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**Table1**

**Optimized geometrical parameters of p-bromo benzoic acid (p-BBA) and p-fluoro benzoic acid (p-FBA) obtained by B3LYP6-31G\*\* density functional calculations.**

Bond length	Value(A°)		Bond angles	Value(°)	
	p-BBA	P-FBA		p-BBA	P-FBA
C1-C2	1.394	1.394	C1-C2-C3	119.994	119.994
C2-C3	1.395	1.395	C2-C3-C4	119.994	119.994
C3-C4	1.394	1.394	C3-C4-C5	120.0061	120.0061
C4-C5	1.395	1.395	C4-C5-C6	119.008	119.008
C5-C6	1.394	1.394	C6-C1-C7	119.984	119.984
C1-C7	1.540	1.540	C1-C2-H8	120.024	120.024
C2-H8	1.099	1.099	C2-C3-H9	119.993	119.993
C3-H9	1.099	1.099	C3-C4-Br10(F10)	120.010	120.010
C4-Br10(F10)	1.910	1.350	C4-C5-H11	119.997	119.997
C5-H11	1.099	1.099	C5-C6-H12	120.008	120.008
C6-H12	1.099	1.099	C1-C7-O13	119.996	119.996
C7-O13	1.301	1.301	C1-C7-O14	119.886	119.886
C7-O14	1.301	1.301	C7-O14-H15	109.500	109.500
O14-H15	0.960	0.960			

For numbering of atoms refer figure.1 (a) and figure.1 (b)

**Table 2**  
**Definition of local symmetry coordinates and diagonal force constants of p-bromo benzoic acid and p-fluoro benzoic acid**

No.	Symmetry coordinates <sup>a</sup>	Description		Diagonal force constants <sup>b</sup>	
		p-BBA	p-FBA	p-BBA	p-FBA
1	$S_1=r_{1,2}$	$\nu C1C2$	$\nu C1C2$	6.53	6.67
2	$S_2=r_{2,3}$	$\nu C2C43$	$\nu C2C43$	6.79	7.04
3	$S_3=r_{3,4}$	$\nu C3C4$	$\nu C3C4$	6.58	6.87
4	$S_4=r_{4,5}$	$\nu C4C5$	$\nu C4C5$	6.60	6.87
5	$S_5=r_{5,6}$	$\nu C5C6$	$\nu C5C6$	6.73	6.98
6	$S_6=r_{6,1}$	$\nu C6C1$	$\nu C6C1$	6.51	6.65
7	$S_7=r_{1,7}$	$\nu C1C7$	$\nu C1C7$	2.88	3.03
8	$S_8=r_{2,8}$	$\nu C2H8$	$\nu C2H8$	5.09	5.01
9	$S_9=r_{3,9}$	$\nu C3H9$	$\nu C3H9$	5.09	5.04
10	$S_{10}=r_{4,10}$	$\nu C4Br10$	$\nu C4F10$	3.34	5.82
11	$S_{11}=r_{5,11}$	$\nu C5H11$	$\nu C5H11$	5.09	5.09
12	$S_{12}=r_{6,12}$	$\nu C6H12$	$\nu C6H12$	5.11	5.11
13	$S_{13}=r_{7,13}$	$\nu C7O13$	$\nu C7O13$	10.89	11.17
14	$S_{14}=r_{7,14}$	$\nu C7O14$	$\nu C7O14$	5.11	5.22
15	$S_{15}=r_{14,15}$	$\nu O14H15$	$\nu O14H15$	5.36	5.36
16	$S_{16}=\beta_{1,2,3}+\beta_{2,3,4}-2\beta_{3,4,5}+\beta_{4,5,6}+\beta_{1,6,5}-2\beta_{6,1,2}$	$\delta Ring1$	$\delta Ring1$	1.28	1.29
17	$S_{17}=\beta_{1,2,3}-\beta_{2,3,4}+\beta_{3,4,5}-\beta_{4,5,6}+\beta_{1,6,5}-\beta_{6,1,2}$	$\delta Ring2$	$\delta Ring2$	1.91	1.62
18	$S_{18}=\beta_{12,3}-\beta_{2,3,4}+\beta_{4,5,6}-\beta_{1,6,5}$	$\delta Ring3$	$\delta Ring3$	1.11	1.24
19	$S_{19}=\beta_{6,1,7}-\beta_{2,1,7}$	$\delta C1C7$	$\delta C1C7$	1.28	1.02
20	$S_{20}=\beta_{1,2,8}-\beta_{3,2,8}$	$\delta C2H8$	$\delta C2H8$	0.50	0.51
21	$S_{21}=\beta_{2,3,9}-\beta_{4,3,9}$	$\delta C3H9$	$\delta C3H9$	0.51	0.49
22	$S_{22}=\beta_{3,4,10}-\beta_{5,4,10}$	$\delta C4Br10$	$\delta C4F10$	0.72	0.93
23	$S_{23}=\beta_{4,5,11}-\beta_{6,5,11}$	$\delta C5H11$	$\delta C5H11$	0.51	0.49
24	$S_{24}=\beta_{5,6,12}-\beta_{1,6,12}$	$\delta C6H12$	$\delta C6H12$	0.51	0.52
25	$S_{25}=\beta_{1,7,13}$	$\delta C7O13$	$\delta C7O13$	2.53	2.32
26	$S_{26}=\beta_{1,7,14}$	$\delta C7O14$	$\delta C7O14$	2.74	2.51
27	$S_{27}=\beta_{7,14,15}$	$\delta O14H15$	$\delta O14H15$	0.83	0.86
28	$S_{28}=\gamma_{7,1,6,2}$	$\gamma C1C7$	$\gamma C1C7$	0.04	0.38
29	$S_{29}=\gamma_{8,2,1,3}$	$\gamma C2H8$	$\gamma C2H8$	0.47	0.47
30	$S_{30}=\gamma_{9,3,2,4}$	$\gamma C6H9$	$\gamma C6H9$	0.44	0.42
31	$S_{31}=\gamma_{10,4,3,5}$	$\gamma C4Br10$	$\gamma C4F10$	0.56	0.31



32	$S_{32}=\gamma_{11,5,4,6}$	$\gamma_{C5H11}$	$\gamma_{C5H11}$	0.44	0.41
33	$S_{33}=\gamma_{12,6,5,1}$	$\gamma_{C6H12}$	$\gamma_{C6H12}$	0.44	0.45
34	$S_{34}=\tau_{13,7,1,6}-\tau_{13,7,1,2}$	$\tau_{C7O13}$	$\tau_{C7O13}$	0.10	1.07
35	$S_{35}=\tau_{14,7,1,2}-\tau_{14,7,1,6}$	$\tau_{C7O14}$	$\tau_{C7O14}$	0.11	0.01
36	$S_{36}=\tau_{15,14,7,1}$	$\tau_{O14H15}$	$\tau_{O14H15}$	0.15	0.14
37	$S_{37}=\tau_{1,2,3,4}+\tau_{2,3,4,5}-2\tau_{3,4,5,6}+\tau_{4,5,6,1}+\tau_{5,6,1,2}-2\tau_{6,1,2,3}$	$\tau_{Ring1}$	$\tau_{Ring1}$	0.41	0.48
38	$S_{38}=\tau_{1,2,3,4}-\tau_{2,3,4,5}+\tau_{3,4,5,6}-\tau_{4,5,6,1}+\tau_{5,6,1,2}-\tau_{6,1,2,3}$	$\tau_{Ring2}$	$\tau_{Ring2}$	0.30	0.35
39	$S_{39}=-\tau_{1,2,3,4}-\tau_{2,3,4,5}+\tau_{4,5,6,1}-\tau_{5,6,1,2}$	$\tau_{Ring3}$	$\tau_{Ring3}$	0.32	0.45

For numbering of atoms reference Fig. 1(a) and Fig. 1(b); Abbreviations:  $\nu$ : stretching;  $\delta$ : deformation in-plane;  $\gamma$ : deformation out-of-plane;  $\tau$ : torsion.

<sup>a</sup>definitions are made in terms of the standard valence coordinates:  $r_{ij}$  is the bond length between atoms  $i$  and  $j$ ;  $\beta_{i,j,k}$  is the valence angle between atoms  $i,j,k$  where  $j$  is the central atom;  $\gamma_{i,j,k,l}$  is the out-of-plane angle between the  $i-j$  bond and the plane defined by the  $j,k,l$  atoms;  $\tau_{i,j,k,l}$  is the torsional (dihedral) angle between the plane defined by  $i,j,k$  and  $j,k,l$  atoms.

<sup>b</sup>Stretching force constants are given in  $\text{mdyn \AA}^{-1}$ , bending and torsion force constants are given in  $\text{mdyn \AA}^0$ .

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**Table 3**

**Detailed assignment of fundamental vibrations of p-bromo benzoic acid by normal mode analysis based on SQM force field calculations**

Sl. No	Symmetry species C <sub>s</sub>	Observed wavenumbers cm <sup>-1</sup>		Calculated wavenumbers B3LYP/6-31G** force field cm <sup>-1</sup>		IR Intensity	Raman Activity	Characterization of normal modes with PED (%)
		FT IR	Raman	unscaled	scaled			
1	A'	3092	-	3767	3092	88.770	175.311	νOH(100)
2	A'	-	3076	3233	3056	0.665	171.452	νCH(99)
3	A'	3068	-	3229	3053	1.702	52.305	νCH(99)
4	A'	3045	-	3218	3042	0.473	64.694	νCH(99)
5	A'	1305	-	3217	3041	0.045	20.751	νCH(99)
6	A'	1680	-	1820	1687	290.361	66.303	νCO(64),bCO(16)
7	A'	-	1611	1646	1633	118.660	166.664	νCC (61), bCH(20),Rsymd(16)
8	A'	1572	-	1622	1571	21.034	11.174	νCC(70)
9	A'	1463	-	1528	1479	23.692	2.234	νCC (62),bCH(34),
10	A'	1430	-	1439	1408	26.879	4.492	νCC(46), bCH(36)
11	A'	1354	-	1392	1357	15.215	4.351	bCOH(51), νCO(23),bCO(12)
12	A'	1325	-	1350	1316	7.948	1.694	νCC(78),bCH(13)
13	A'	1280	-	1328	1293	1.060	0.473	bCH(65), νCC(32)
14	A'	1179	1179	1218	1173	9.770	3.504	bCH(69), νCC(23)
15	A'	-	1134	1194	1188	330.914	90.189	νCO(24),bCH(18),bCOH(17), νCC(16) νCCar(10)
16	A'	1110	-	1135	1098	47.448	17.632	bCH(51), νCC(31)
17	A'	1079	-	1117	1072	97.297	32.978	bCH(50), νCBr(21), νCC (16)

18	A'	1070	1070	1088	1056	80.064	9.172	vCC(40), vCO(33)
19	A'	-	1016	1028	1016	56.383	0.960	Rtrigd(71), vCC(17)
20	A''	961	-	1003	966	0.091	0.117	ωCH(92)
21	A''	928	-	991	947	0.040	1.807	ωCH(81), ttrig(17)
22	A''	852	-	871	830	2.830	4.673	ωCH(98)
23	A''	824	-	856	816	34.851	0.441	ωCH(79)
24	A'	818	-	786	802	17.986	17.463	vCC (53), Rsym (18), vCBr(10)
25	A''	750	-	774	747	1.328	0.088	ttrig(77),ωCH(10)
26	A'	-	685	714	666	47.997	2.465	bCO(48), vCO(17),bCOH (11)
27	A''	-	629	660	635	83.098	0.250	tCO(72),tOH(13)
28	A'	610	-	642	607	1.929	6.522	Rasymd(83)
29	A''	550	-	605	550	44.310	8.675	tOH(73)
30	A'	498	-	508	511	8.108	0.346	bCO(68),bCC(13)
31	A''	470	-	477	472	22.936	1.187	tRasym(45), ωCBr(35)
32	A'	430	-	461	437	11.864	0.689	vCBr(41), vCC(33),bCO(10)
33	A''	-	400	424	399	0.005	0.004	tRsym(67), ωCH(16),tRasym(13)
34	A'	-	279	283	280	0.097	0.101	bCBr(42),bCO(32),bCC(17)
35	A'	-	250	254	251	1.339	2.816	Rsym(36),vCBr(27), vCC (21)
36	A''	-	205	247	209	0.336	1.395	ωCBr(30),tRasym(21),tCO(21),tRsym(10))
37	A'	-	150	155	157	0.947	0.397	bCC(43),bCBr(27),bCO(23)
38	A''	-	79	80	66	03154	0.022	ωCC(48), ωCH(14),tRasym(12)
39	A''	-	70	73	61	0.832	0.975	tCO(99)

Abbreviations; R, ring; b, bending; d, deformation; sym, symmetric; asy, asymmetric; ω, wagging; t, torsion; trig, trigonal; v, stretching. Only contributions larger than 10% are given.

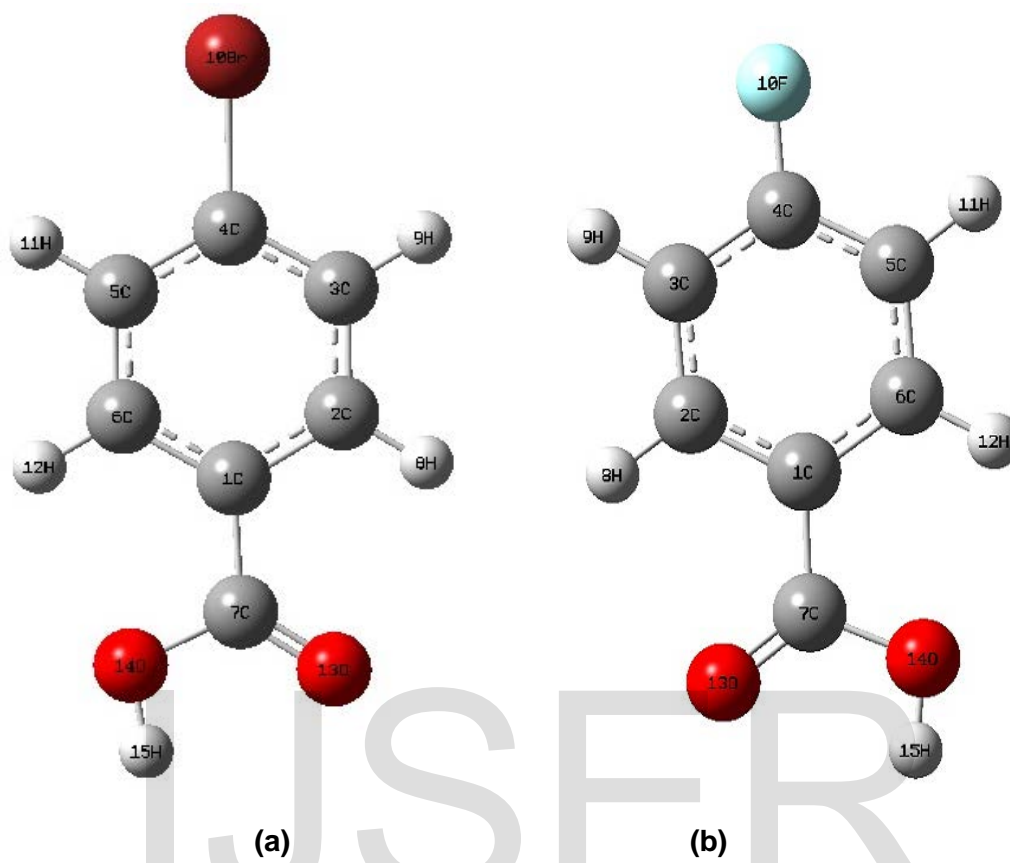
**Table 4**

**Detailed assignment of fundamental vibrations of p-fluoro benzoic acid by normal mode analysis based on SQM force field calculations**

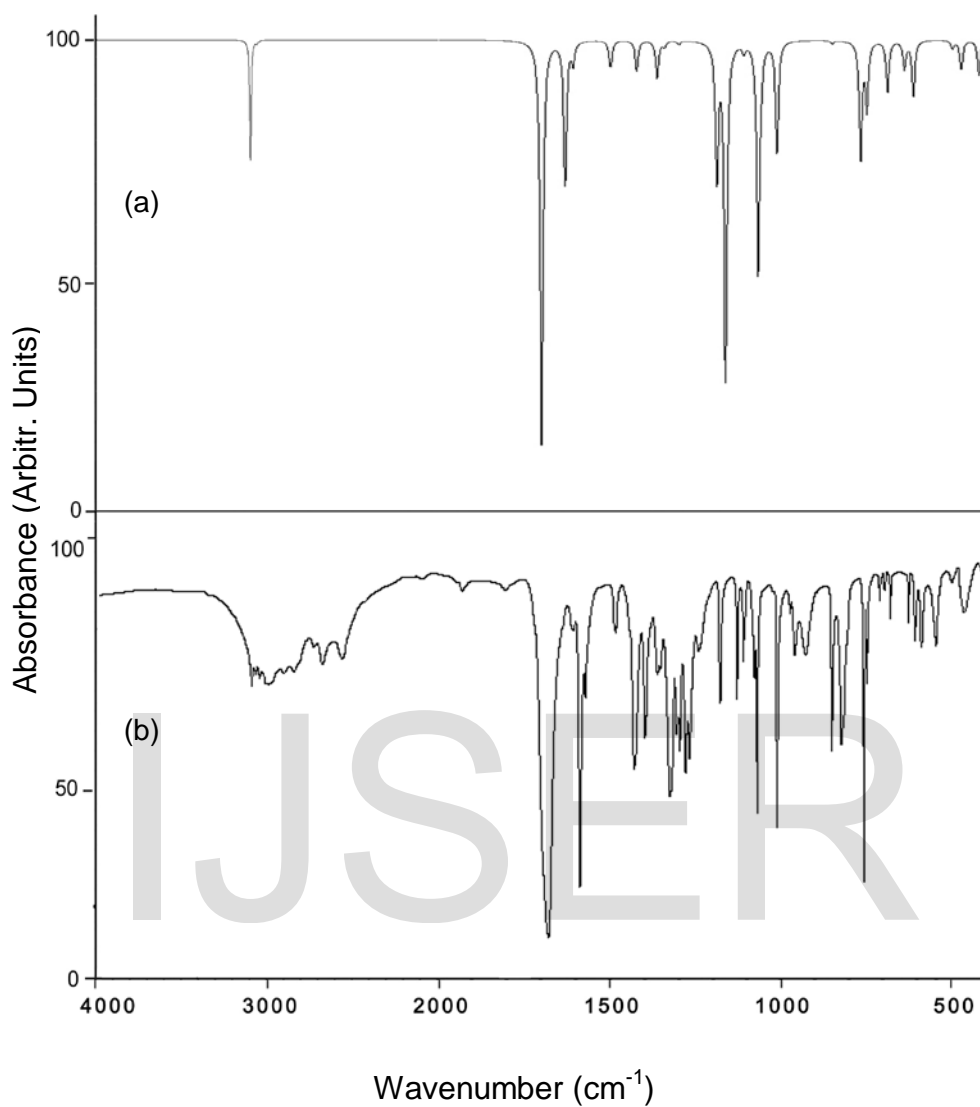
Sl. No	Symmetry species $C_s$	Observed wavenumbers $cm^{-1}$		Calculated wavenumbers B3LYP/6-31G** force field $cm^{-1}$		IR Intensity	Raman Activity	Characterization of normal modes with PED (%)
		FT IR	Raman	unscaled	scaled			
1.	A'	-	3094	3767	3094	80.658	151.598	$\nu$ OH(100)
2.	A'	3084	-	3233	3035	1.350	141.737	$\nu$ CH(99)
3.	A'	-	3078	3229	3031	2.479	85.614	$\nu$ CH(99)
4.	A'	2997	-	3218	3021	1.834	107.581	$\nu$ CH(99)
5.	A'	2952	-	3217	3013	285.969	23.650	$\nu$ CH(99)
6.	A'	1686	-	1819	1699	137.127	39.540	$\nu$ CO(67), bCO(13)
7.	A'	-	1634	1663	1650	11.243	77.967	$\nu$ CC(63), bCH(18), Rsymd(13)
8.	A'	1629	-	1642	1614	50.676	7.697	$\nu$ CC(71)
9.	A'	1511	1511	1555	1516	9.729	3.567	$\nu$ CC(52), bCH(37)
10.	A'	1431	-	1453	1429	7.451	1.542	$\nu$ CC(53), bCH(34)
11.	A'	1366	-	1393	1371	4.594	2.492	bCOH(59), $\nu$ CO(23), bCO(10)
12.	A'	1332	1332	1363	1342	4.734	2.458	$\nu$ CC(90)
13.	A'	1298	-	1317	1297	38.000	1.571	bCH(86)
14.	A'	1237	-	1286	1239	38.509	6.297	$\nu$ CF(50), $\nu$ CC(22), bCH(15), Rtrigd(11)
15.	A'	1161	-	1211	1166	389.522	18.465	bCH(52), $\nu$ CC(13)
16.	A'	-	1153	1177	1144	33.565	52.343	bCH(24), $\nu$ CO(21), $\nu$ CC(16), bCOH(12)
17.	A'	1108	-	1128	1102	107.536	8.771	bCH(60), $\nu$ CC(29)

18.	A'	1096	-	1112	1064	7.801	2.360	vCO(40), vCC(29)
19.	A'	1016	-	1031	1011	0.470	0.251	vCC(52), Rtrigd(32), bCH(14)
20.	A''	969	-	986	948	0.447	0.301	ωCH(91)
21.	A''	929	-	971	916	20.146	1.797	ωCH(87), tRtrig(11)
22.	A'	856	-	863	840	7.662	24.234	Rtrig(36),CC(29), CF(17)
23.	A''	-	829	854	816	0.036	0.167	ωCH(43),tRtrig(32), ωCC(14)
24.	A''	770	-	835	812	20.093	5.178	ωCH(97)
25.	A''	761	-	771	761	85.827	0.451	tRtrig(56),ωCH(33)
26.	A''	723	-	730	726	15.688	0.366	tCO(57),ωCH(35)
27.	A'	665	-	699	580	0.447	2.991	vCC (29), bCO(21), vCO(15),Rtrigd(11)
28.	A'	-	637	645	641	1.002	7.276	Rasymd(79), vCC(10),
29.	A'	600	-	603	583	56.482	0.865	bCO(37), Rsymd(27), vCF(12)
30.	A''	550	-	593	551	54.995	6.316	tOH(52),tRsym(28)
31.	A'	497	-	508	495	5.437	0.480	bCO(64),bCC(13)
32.	A''	490	-	504	487	32.698	3.119	tRasym(58), tOH(16), ωCH(14)
33.	A''	-	426	426	428	0.885	0.111	tRsym(74), ωCH(12)
34.	A'	-	386	399	390	5.717	0.294	bCF(54),bCO(28)
35.	A'	-	315	347	323	0.881	2.309	Rsymd(48), vCC (28)
36.	A''	-	245	299	245	2.252	2.479	ωCF(61), ωCC(31)
37.	A'	-	190	194	193	1.469	0.170	bCC(46),bCO(45)
38.	A''	-	98	111	104	0.192	0.001	ωCC(47), ωCF(18), ωCH(14)
39.	A''	-	70	73	71	0.818	1.084	tCO(99)

Abbreviations; R, ring; b, bending; d, deformation; sym, symmetric; asy, asymmetric; ω, wagging; t, torsion; trig, trigonal; v, stretching. Only contributions larger than 10% are given.



**Fig.1 Molecular model of (a) p-bromo benzoic acid and (b) p-fluoro benzoic acid along with numbering of atoms.**



**Fig.2** Comparison of observed and calculated FTIR spectra of  
p- bromo benzoic acid  
(a) calculated with B3 LYP/6-31G\*\*  
(b) observed with KBr disc

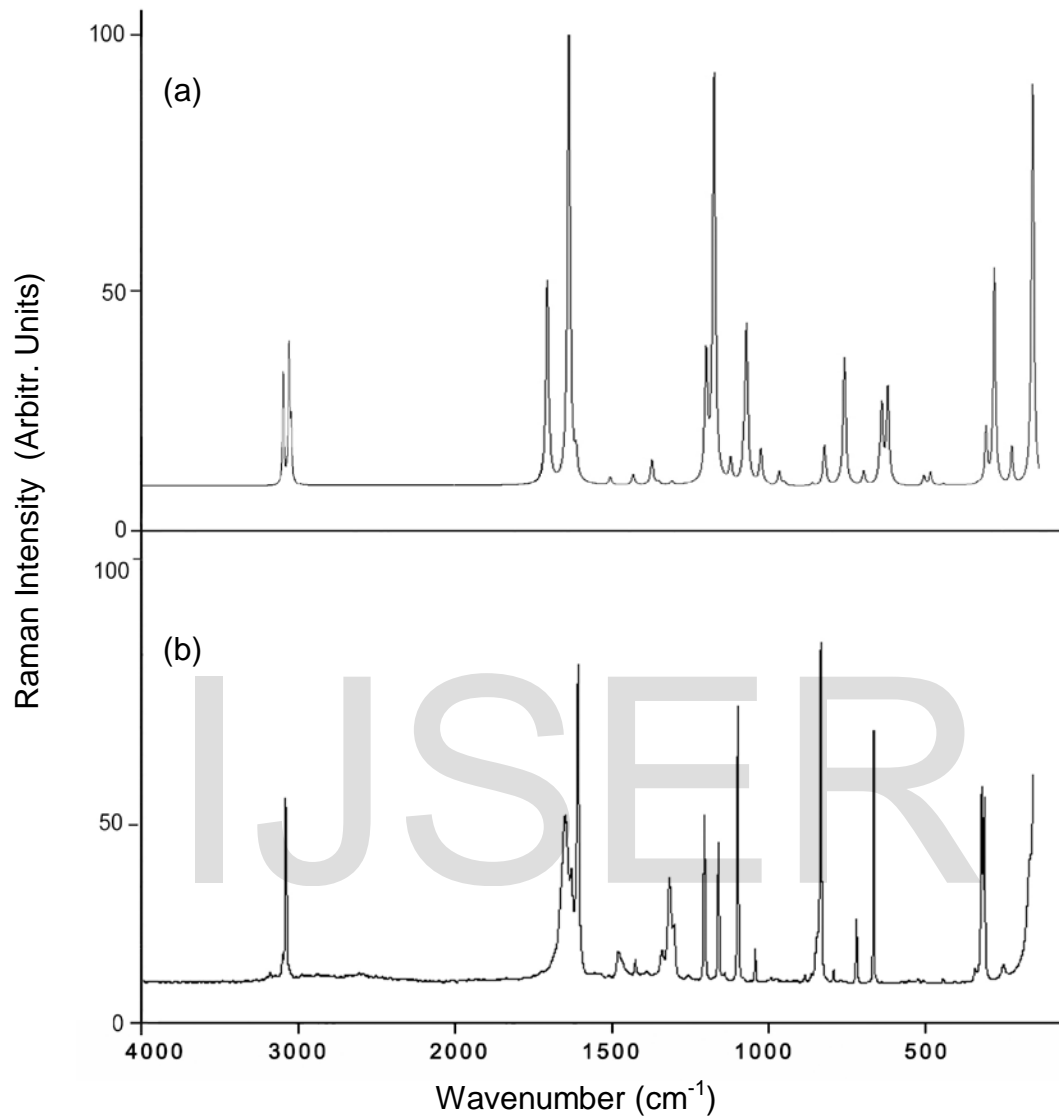


Fig. 3 Comparison of observed and calculated FT-Raman spectra of p-bromo benzoic acid  
(a) calculated with B3 LYP/6-31G\*\*  
(b) observed with KBr disc



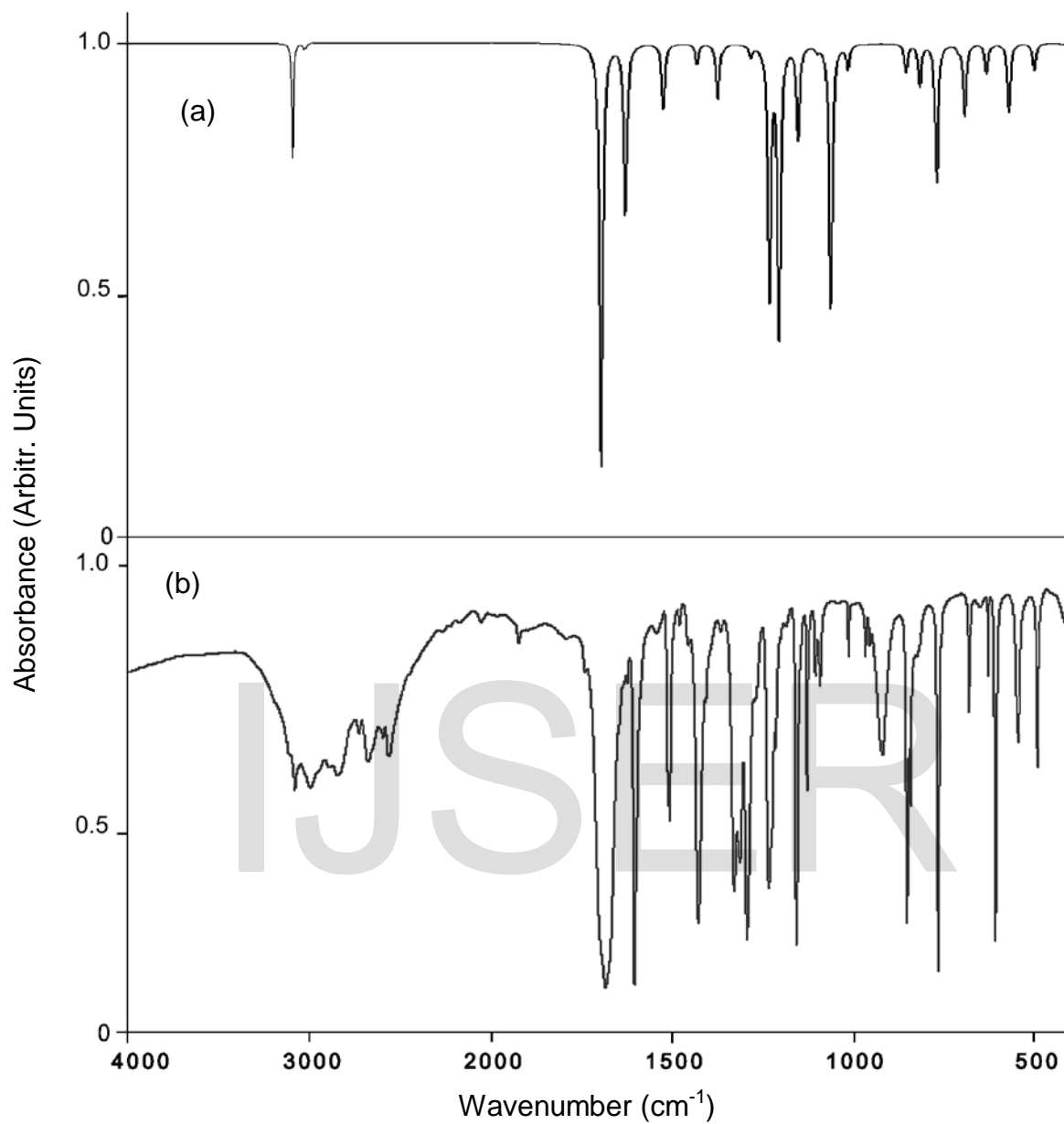


Fig.4 Comparison of observed and calculated FTIR spectra of p- fluoro benzoic acid

(a) calculated with B3 LYP/6-31G\*\*

(b) observed with KBr disc

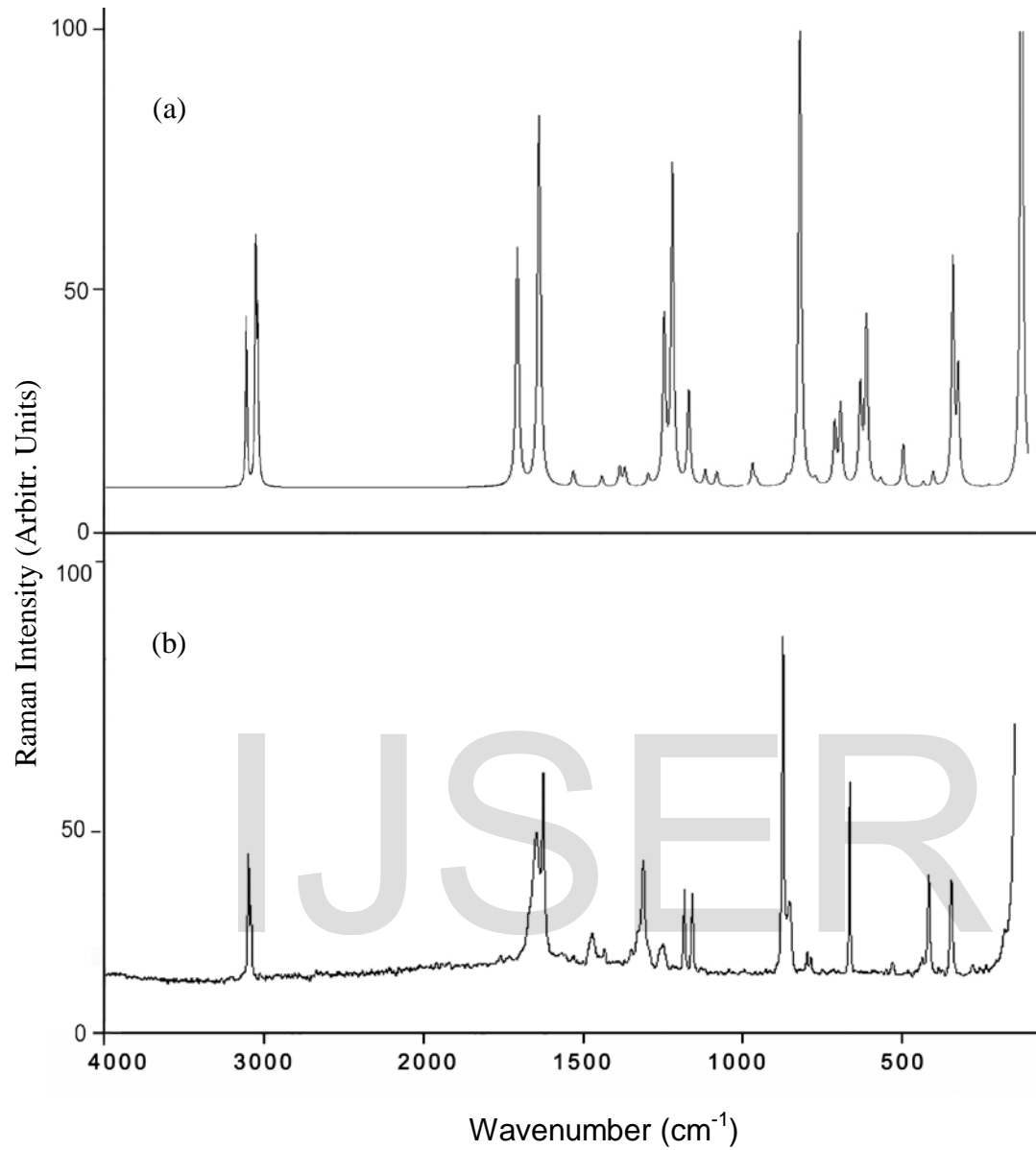


Fig.5 Comparison of observed and calculated FT-Raman Spectra of p- fluoro benzoic acid  
(a) Calculated with B3 LYP/6-31G\*\*  
(b) Observed with KBr disc