

# Ab Initio Determination of Molecular Geometry and Vibrational Frequencies of Benzotrifluoride

Anita Kushwaha<sup>1\*</sup>, R L Prasad<sup>2</sup> and R A Yadav<sup>3</sup><sup>1</sup>Department of Applied Chemistry, SoVSAS, Gautam Buddha University, Greater Noida-201310, India<sup>2</sup>Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi- 221005, India<sup>3</sup>Department of Physics, Institute of Science, Banaras Hindu University, Varanasi221005, India**\*Corresponding author**

Anita Kushwaha, Department of Applied Chemistry, SoVSAS, Gautam Buddha University, Greater Noida-201310, India.

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**Abstract**

Using Gaussian 05 Revision C.02 version of the quantum chemical program ab initio computations has been carried out to compute optimized geometry, harmonic vibrational frequencies along with intensities in IR and Raman spectra and atomic charges at rhf / 6-31+g\*, b3lyp / 6-31++g\*\* and b3lyp / 6-311++g\*\* levels. The optimized molecular structure is found to possess  $C_s$  point group symmetry with the plane of symmetry passing through the C atom, to which the  $CF_3$  group is attached, the centrally opposite C atom and the C atom of the  $CF_3$  group and perpendicular to the phenyl ring plane. One of the three F atoms of the  $CF_3$  group is found to be on one side of the ring plane and is situated on the plane of the symmetry while the other two F atoms are found to be on the other side of the ring plane placed symmetrically on either side of the symmetry plane. Vibrational assignments for the normal modes have been reviewed. To make vibrational assignments for the normal modes of vibration the Gauss View software was used. The  $CF_3$  group has the characteristic frequencies in the 340, 768, 1072, 1152 and 1318  $cm^{-1}$  which are due to the modes  $\delta_s(CF_3)$ ,  $V_s(CF_3)$ ,  $V_{as}(CF_3)$  ( $a'$ ),  $V_{as}(CF_3)$  ( $a''$ ) and  $V(C-CF_3)$  respectively. The torsional frequency of the  $CF_3$  group is found to be 16  $cm^{-1}$  which would lead to barrier height of  $\sim 0.5$  kJ / mol for the torsional motion of the  $CF_3$  group.

**Keywords:** Ab Initio Calculations, Geometrical Structure, Vibrational Assignments, Atomic Charges**Introduction**

Raman and IR spectra of benzotrifluoride (henceforth labelled as BTF) have been reported and vibrational assignments have been made assuming the  $CF_3$  group as a mass point [1]. Under this assumption the molecule BTF belongs to the  $C_{2v}$  point group. However, the above authors have pointed out that the symmetry group of the molecule could be  $C_s$  with the plane of symmetry either as the phenyl ring plane or as the plane perpendicular to the plane of the C atoms. Scott et al, studying the chemical thermodynamic properties and the internal rotation of the  $CF_3$  group, have also assumed this molecule to belong to the  $C_{2v}$  point group [2]. D'Cunha and Kartha remeasured the Raman and IR spectra and performed normal co-ordinate analysis by assuming this molecule to belong to the  $C_s$  point group with the plane of symmetry as the plane perpendicular to the plane of the C atoms [3]. Studying the vibrational spectra of mono-substituted BTFs, Green and Harrison recorded the IR spectra of liquid and vapour samples and the Raman spectra in solid, liquid and vapor phases and proposed vibrational analysis assuming the  $C_{2v}$  point group symmetry [4]. However, the tor-

sional mode of the  $CF_3$  group remained unassigned in the work of Green and Harrison [4]. This mode was assigned around 15  $cm^{-1}$  by D'Cunha and Kartha for BTF and around 50  $cm^{-1}$  for BTF derivatives [3, 5]. In addition to this there is controversy in the assignments of the  $\delta_s(CF_3)$ ,  $V_s(CF_3)$  and  $V(C-CF_3)$  modes amongst different group of workers. Uncertainty in the assignment of some of the normal modes of the  $CF_3$  group and orientation of the  $CF_3$  group with respect to the phenyl ring plane prompted us to carry out ab initio calculations of the molecular geometry and the vibrational frequencies of the BTF molecule and reanalyze the earlier reported IR and Raman data in light of the present calculations [1-4]. Using Gaussian 05 Revision C.02 version of the quantum chemical program ab initio computations has been carried out to compute optimized geometry, harmonic vibrational frequencies along with intensities in IR and Raman spectra, depolarisation ratios of the Raman lines and atomic charges at the rhf / 6-31+g\*, b3lyp / 6-31++g\*\* and b3lyp / 6-311++g\*\* levels. To make vibrational assignments for the normal modes of vibration the Gauss View software was used.

## Theoretical Computations

Calculations of structural parameters, atomic charges, vibrational frequencies, IR and Raman intensities of the BTF molecule were carried out on a PC model- Pentium IV, using Gaussian 03 Revision C.02 version of ab initio quantum chemical program [6]. Initially, the geometry optimization and calculation of other parameters were performed at restricted Hartree-Fock (rhf) level using 6-31+g\* basis set. Electron correlations were included using Becke3-Lee-Yang-Parr (b3lyp) procedure [7-9]. This includes Becke's gradient exchange corrections, Lee, Yang and Parr correlation functional and / or Vosko, Wilk and Nusair correlation functional [10]. The optimized geometry at rhf/6-31+g\* level was taken as the input structure for the density functional calculation

at b3lyp/6-31++g\*\* level. Finally, the optimized geometry at the b3lyp/6-31++g\*\* level was used as starting geometry for calculation at the b3lyp/6-311++g\*\* level. No symmetry constraints were applied in optimizing geometry.

## Results and Discussions

### Molecular Geometry

The optimized molecular structure at the highest level of our study i.e., at b3lyp /6-311++g\*\* level along with numbering scheme is given in Figs. 1(a) and 1(b). The optimized molecular structure of BTF possesses Cs point group symmetry. The symmetry plane passes through the atoms H<sub>9</sub>, C<sub>4</sub>, C<sub>1</sub>, C<sub>12</sub> and F<sub>13</sub> with the F<sub>14</sub> and F<sub>15</sub> atoms symmetrically on either side of this plane.

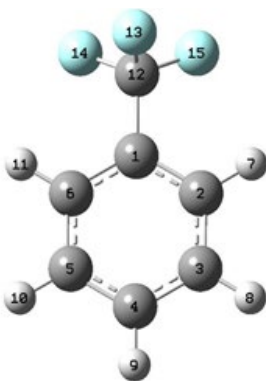


Figure 1(a): Atom Numbering Scheme in the Structure of BTF (Front View)



Figure 1(b): Atom Numbering Scheme in the Structure of BTF (Side View)

The optimized geometrical parameters, namely, bond lengths, bond angles and dihedral angles at the rhf /6-31+g\*, b3lyp /6-31++g\*\* and b3lyp /6-311++g\*\* levels are collected in Table 1.

Table 1: Geometrical Parameters of BTF (Distances in Å and Angles in degrees)

Parameters	rhf/31++g**	b3lyp /31++g**	b3lyp /311++g**
r (C <sub>1</sub> , C <sub>2</sub> )	1.387	1.399	1.396
r(C <sub>1</sub> , C <sub>6</sub> )	1.387	1.399	1.396
r(C <sub>1</sub> , C <sub>12</sub> )	1.505	1.506	1.504
r (C <sub>2</sub> , C <sub>3</sub> )	1.386	1.396	1.392
r (C <sub>2</sub> , H <sub>7</sub> )	1.074	1.085	1.083
r (C <sub>3</sub> , C <sub>4</sub> )	1.387	1.398	1.394
r (C <sub>3</sub> , H <sub>8</sub> )	1.075	1.086	1.084

r (C <sub>4</sub> , C <sub>5</sub> )	1.387	1.398	1.394
r (C <sub>4</sub> , H <sub>9</sub> )	1.076	1.086	1.084
r (C <sub>5</sub> , C <sub>6</sub> )	1.386	1.396	1.392
r (C <sub>5</sub> , H <sub>10</sub> )	1.075	1.086	1.084
r (C <sub>6</sub> , H <sub>11</sub> )	1.074	1.085	1.083
r (C <sub>12</sub> , F <sub>13</sub> )	1.329	1.362	1.359
r (C <sub>12</sub> , F <sub>14</sub> )	1.325	1.357	1.353
r (C <sub>12</sub> , F <sub>15</sub> )	1.325	1.357	1.353
r (H <sub>7</sub> ... F <sub>13</sub> )	3.272	3.301	3.295
r (H <sub>7</sub> ... F <sub>14</sub> )	3.906	3.952	3.942
r (H <sub>7</sub> ... F <sub>15</sub> )	2.480	2.495	2.489
r (H <sub>11</sub> ...F <sub>13</sub> )	3.272	3.301	3.295
r (H <sub>11</sub> ...F <sub>14</sub> )	2.480	2.495	2.489
r (H <sub>11</sub> ... F <sub>15</sub> )	3.906	3.952	3.942
r (F <sub>13</sub> ...F <sub>14</sub> )	2.128	2.177	2.172
r (F <sub>14</sub> ...F <sub>15</sub> )	2.134	2.183	2.176
r (F <sub>13</sub> ...F <sub>15</sub> )	2.128	2.177	2.172
α (C <sub>1</sub> ,C <sub>12</sub> , F <sub>13</sub> )	111.9	111.8	111.8
α (C <sub>1</sub> ,C <sub>12</sub> , F <sub>14</sub> )	112.1	112.4	112.3
α (C <sub>1</sub> ,C <sub>12</sub> , F <sub>15</sub> )	112.1	112.4	112.3
α (F <sub>13</sub> ,C <sub>12</sub> , F <sub>14</sub> )	106.6	106.4	106.4
α (F <sub>13</sub> ,C <sub>12</sub> ,F <sub>15</sub> )	106.6	106.4	106.4
α (F <sub>14</sub> ,C <sub>12</sub> ,F <sub>15</sub> )	107.2	107.1	107.1
δ(C <sub>12</sub> , C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> )	177.9	177.7	177.7
δ(C <sub>12</sub> , C <sub>1</sub> , C <sub>2</sub> , H <sub>7</sub> )	-2.4	-2.7	-2.9
δ(C <sub>12</sub> , C <sub>1</sub> , C <sub>6</sub> , C <sub>5</sub> )	-177.9	-177.7	-177.7
δ(C <sub>12</sub> , C <sub>1</sub> , C <sub>6</sub> , H <sub>11</sub> )	2.4	2.7	2.9
δ(C <sub>2</sub> , C <sub>1</sub> , C <sub>12</sub> , F <sub>13</sub> )	-88.9	-88.8	-88.7
δ(C <sub>2</sub> , C <sub>1</sub> , C <sub>12</sub> , F <sub>14</sub> )	151.4	151.7	151.7
δ(C <sub>2</sub> , C <sub>1</sub> , C <sub>12</sub> , F <sub>15</sub> )	30.7	30.8	30.9
δ(C <sub>6</sub> , C <sub>1</sub> , C <sub>12</sub> , F <sub>13</sub> )	88.9	88.8	88.7
δ(C <sub>6</sub> , C <sub>1</sub> , C <sub>12</sub> , F <sub>14</sub> )	-30.7	-30.8	-30.9
δ(C <sub>6</sub> , C <sub>1</sub> , C <sub>12</sub> , F <sub>15</sub> )	-151.4	-151.7	-151.7

Optimized structure yields identical bond length pairs for the bonds C<sub>1</sub> – C<sub>2</sub> and C<sub>1</sub> – C<sub>6</sub>, C<sub>2</sub> – C<sub>3</sub> and C<sub>5</sub> – C<sub>6</sub>, and C<sub>3</sub> – C<sub>4</sub> and C<sub>4</sub> – C<sub>5</sub> at all the three levels of calculations rhf /6-31+g\*, b3lyp /6-31++g\*\* and b3lyp /6-311++g\*\*. The magnitudes of all the 6-ring C – C bond lengths are in the range of partial double bond and have same magnitudes up to 2<sup>nd</sup> place of decimal indicating extensive involvement of these bonds in conjugation. The calculated bond length of C<sub>1</sub> – C<sub>12</sub> at all the levels of calculations are almost same and in the range of single C – C bond length (1.504 Ao). The C<sub>12</sub> – F<sub>13</sub> bond length has been calculated to be slightly higher than the other two C–F bonds (C<sub>12</sub> – F<sub>14</sub> and C<sub>12</sub> – F<sub>15</sub>) at all the levels of the calculations. The magnitudes of all the three C–F bond lengths increase from rhf /6-31++g\*\* to b3lyp /6-31++g\*\* and decrease from b3lyp /6-31++g\*\* to b3lyp /6-311++g\*\* level.

The C<sub>12</sub> – F<sub>14</sub> and C<sub>12</sub> – F<sub>15</sub> bond lengths are exactly equal (1.353 Ao) however, their magnitudes are smaller than C<sub>12</sub> – F<sub>13</sub> bond length (1.359 Ao). All these C–F bond lengths are slightly smaller than C – F bond length (1.37 Ao) for the Fluorine atom directly attached to the benzene ring suggesting stronger bonding between the C and F atoms in the CF<sub>3</sub> group as compared to the aromatic ring carbon- fluorine bond. Non - bonded distance H<sub>7</sub>.....F<sub>13</sub> is longer than H<sub>7</sub>.....F<sub>15</sub> and H<sub>11</sub>.....F<sub>13</sub> is longer than H<sub>11</sub>.....F<sub>14</sub>. The calculated distances F<sub>13</sub>.....F<sub>14</sub> and F<sub>13</sub>.....F<sub>15</sub> are found to have the same magnitudes ( 2.172 Ao) but these are slightly smaller than the distance F<sub>14</sub>.....F<sub>15</sub> ( 2.176 Ao). The bond angle C<sub>1</sub> – C<sub>12</sub> – F<sub>13</sub> decreases from rhf to b3lyp level of calculations and its magnitude is found to be (111.80). The bond angles C<sub>1</sub> – C<sub>12</sub> – F<sub>14</sub> and C<sub>1</sub> – C<sub>12</sub> – F<sub>15</sub> are equal in magnitudes (112.30). Their values increase from rhf /6-31++g\*\* to b3lyp /6-31++g\*\* and decrease

from b3lyp /6-31++g\*\* to b3lyp /6-311++g\*\* level. The magnitudes of the angles  $F_{13}-C_{12}-F_{14}$  and  $F_{13}-C_{12}-F_{15}$  are identical (106.40). Their magnitudes decrease from the rhf to the b3lyp level of calculations. The angle  $F_{14}-C_{12}-F_{15}$  (107.10) is higher than the angles  $F_{13}-C_{12}-F_{14}$  and  $F_{13}-C_{12}-F_{15}$  which is in conformity with larger non-bonded distance between  $F_{14}$  and  $F_{15}$  as compared to the non-bonded distances  $F_{13} \dots F_{14}$  and  $F_{13} \dots F_{15}$  discussed above. The dihedral angles  $C_{12}-C_1-C_2-C_3$  and  $C_{12}-C_1-C_6-C_5$  decrease from the rhf to the b3lyp /6-31++g\*\* to the b3lyp /6-311++g\*\* levels and are calculated to be 177.70. Thus, the  $C_{12}$  atom is found to be slightly out of phenyl ring-plane. The dihedral angles  $C_{12}-C_1-C_2-H_7$  and  $C_{12}-C_1-C_6-H_{11}$  increase from the rhf to the b3lyp /6-31++g\*\* to the b3lyp /6-311++g\*\* level and are calculated to be 2.90 which also indicates that the  $C_{12}$  atom is slightly out of phenyl ring-plane. The dihedral angles  $C_2-C_1-C_{12}-F_{13}$  and  $C_6-C_1-C_{12}-F_{15}$  decrease from the rhf to the b3lyp level

and each one of these is found to have a magnitude of 88.70. The dihedral angles  $C_2-C_1-C_{12}-F_{14}$  and  $C_6-C_1-C_{12}-F_{14}$  increase from the rhf to the b3lyp level and their magnitudes are found to be 151.70 and -30.90, respectively. The magnitudes of the dihedral angles  $C_2-C_1-C_{12}-F_{15}$  and  $C_6-C_1-C_{12}-F_{15}$  increase from the rhf to the b3lyp level and are calculated to be 30.90 and -151.70, respectively. Thus, it is clear that  $F_{14}$  and  $F_{15}$  are out of plane and are situated on one side of the phenyl ring-plane whereas the  $F_{13}$  atom resides on the opposite side of this plane. This can be viewed from the optimized structure at the highest level of calculation shown in Fig 1(b).

#### Atomic Charges

APT atomic charges at various atomic sites of the BTF molecule calculated at the rhf /6-31+g\*, b3lyp/6-31++g\*\* and b3lyp/6-311++g\*\* levels are collected in Table 2.

**Table 2: APT Atomic Charges at Various Atoms of the BTF Molecule**

S. No.	Atoms	rhf /6-31++g**	b3lyp /6-31++g**	b3lyp /6-311++g**
1	C <sub>1</sub>	-0.140	-0.165	-0.164
2	C <sub>2</sub>	-0.023	-0.017	-0.023
3	C <sub>3</sub>	-0.069	-0.043	-0.045
4	C <sub>4</sub>	0.029	0.009	0.004
5	C <sub>5</sub>	-0.069	-0.043	-0.045
6	C <sub>6</sub>	-0.023	-0.017	-0.023
7	H <sub>7</sub>	0.069	0.064	0.067
8	H <sub>8</sub>	0.044	0.038	0.041
9	H <sub>9</sub>	0.044	0.038	0.043
10	H <sub>10</sub>	0.044	0.038	0.041
11	H <sub>11</sub>	0.069	0.064	0.067
12	C <sub>12</sub>	1.873	1.771	1.805
13	F <sub>13</sub>	-0.638	-0.599	-0.610
14	F <sub>14</sub>	-0.605	-0.569	-0.579
15	F <sub>15</sub>	-0.605	-0.569	-0.579

APT charges at the atomic sites  $C_2$  and  $C_6$  are equal and similarly those at the atomic sites  $C_3$  and  $C_5$  are equal. These values are found to be -0.023 and -0.045, respectively. The magnitudes of the atomic charges decrease from the rhf /6-31++g\*\* to the b3lyp /6-31++g\*\* and increases from the b3lyp /6-31++g\*\* to the b3lyp /6-311++g\*\* level. The atomic charge at the site  $C_1$  increases from the rhf to the b3lyp level of calculation and possesses the value -0.164 whereas the magnitude of atomic charge at the site  $C_4$  decreases from the rhf /6-31++g\*\* to the b3lyp /6-31++g\*\* to the b3lyp /6-311++g\*\* and found to have the value 0.004. Thus, all the carbon atoms in the phenyl ring possess -ve charges except the carbon atom  $C_4$ . The order of magnitude of the negative charge on the ring carbon atoms are as  $C_1 > (C_3 / C_5) > (C_2 / C_6)$ . The carbon atom  $C_{12}$  possesses the highest positive charge (1.805). The magnitude of charge on  $C_{12}$  decreases from the rhf /6-31++g\*\* to the b3lyp /6-31++g\*\* and increases from the b3lyp /6-31++g\*\* to the b3lyp /6-311++g\*\* level. Amongst the three fluorine atoms

$F_{13}$  possesses the highest negative charge (-0.610) than the other two fluorine atoms which possess equal negative charges (-0.579). Since  $C_{12}$  is attached with highly electronegative fluorine atoms, it is expected to possess the highest +ve charge and therefore, it would exhibit electron withdrawing inductive effect on the benzene ring nucleus. Due to this withdrawing inductive effect of the  $CF_3$  group the highest electron charge accumulation takes place at the  $C_1$  carbon atom of the ring (-0.164). The charge density decreases at the ortho ( $C_2$ ,  $C_6$ ) and the para ( $C_4$ ) positions due to electromeric effect of the electron withdrawing  $CF_3$  group. Consequently,  $C_3$  and  $C_5$  meta position carbon atoms of the ring possess more -ve charge than all the ring carbon atoms except  $C_1$ . It is to be noted that the electron withdrawing effect is most prominent at the para position, resulting in positive charge (0.004) the site  $C_4$ .

## Vibrational Frequencies and Their Assignments

Optimized structure at the b3lyp /6-311++g\*\* level shown in the Figs. 1(a) and 1(b) of the BTF molecule shows that it is a non-planar molecule having Cs molecular symmetry. Its 39 normal modes of vibrations are distributed between the two symmetry species of the Cs point group as:

Phenyl ring: 17 a' + 13 a" CF<sub>3</sub> group : 5 a' + 4 a"

Under the Cs point group symmetry all the modes are Raman and IR active. The fundamental frequencies calculated at the rhf /6-31+g\*, b3lyp /6-31++g\*\* and b3lyp /6-311++g\*\* levels are collected in Table 3.

**Table 3: Calculated and Observed Fundamental Frequencies (cm<sup>-1</sup>) of BTF**

S. No.	Calculated			Observed#		Mode assignments
	rhf	b3	lyp	IR	Raman	
	6-31+g*	6-31++g**	6-311++g**	cm <sup>-1</sup> rel. int.	cm <sup>-1</sup> rel. int.	
1	6(0.03,3).75	4(0.04, 3).75	16(0.04, 3).75			τ (CF <sub>3</sub> ) (a'')
2	144(0.01,4).75	131(0.01, 4).75	131(0.01, 4).75	140(vw)	139(s,p)	γ(C-CF <sub>3</sub> ) (a')
3	214(1,0.04).75	195(1, 0.04).75	196(0.5,0.1).75	203(w)	199(vvw)	β(C-CF <sub>3</sub> ) (a'')
4	349(3,1)29	319(2,1).36	320(2,1).34	317(vvw)	321(vw,dp)	ρII(CF <sub>3</sub> ) (a')
5	366(3,3).23	339(3, 3).23	340(3,3).24	336(s)	339(m,p)	δ <sub>s</sub> (CF <sub>3</sub> ) (a')
6	431(1,0.4).75	390(1, 1).75	394(1, 1).75	393(m)		ρ <sub>⊥</sub> (CF <sub>3</sub> ) (a'')
7	451(0.01,0.01).75	412(0.001,0.01).75	409(0.02, 0.03).75	403(m)	400(w,dp)	φ (ring) (a'')
8	534(1,0.4).62	480(1, 1).64	483(1, 1).66	485(m)	485(vvwd,dp)	δ <sub>as</sub> (CF <sub>3</sub> ) (a')
9	626(0.4,1).75	563(0.03, 1).75	568(0.1, 1).75	585	583(vvwb)	δ <sub>as</sub> (CF <sub>3</sub> ) (a'')
10	652(11,0.2).53	590(7, 0.3).60	591(6, 0.3).67	596(s)		φ (ring) (a')
11	675(0.1,5).75	630(0.1, 5).75	632(0.1, 5).75	616(w sh)	618(m,dp)	α (ring) (a'')
12	715(24, 1)54	657(18, 1).74	662(18, 1).75	657(s)	658(w,p)	α (ring) (a')
13	771(59,0.03).44	707(44, 0.005).33	702(45, 0.02).32	695(s)		φ (ring) (a')
14	841(1, 12).02	766(0.5, 13).02	768(1, 13).03	763	770(s,p)	ν <sub>s</sub> (CF <sub>3</sub> ) (a')
15	863(58, 1).30	781(49, 1).07	780(52, 1).05	770(s)		γ(CH) (a')
16	956(0.1, 1).75	860(0.1, 0.1).75	857(0.2, 0.1).75	843(w)	844(vwd,dp)	γ(CH) (a'')
17	1057(7, 0.4).42	944(7, 0.2).49	941(8, 0.2).45	923(m)	925(vwd,dp)	γ(CH) (a')
18	1088(0.01, 44).03	1016(3, 30).04	1018(1, 34).04	1004(w)	1004(vs,p)	α (ring) (a')
19	1113(0.04, 0.01).75	990(0.1, 0.1).75	985(0.1, 0.01).75	970(vw)	972(vwd,p)	γ(CH) (a'')
20	1118(26, 14).08	1043(49,22).03	1042(52, 16).04	1028(s)	1027(m,p)	ν (ring) (a')
21	1132(0.1, 0.01).68	1010(0.1, 0.01).74	996(0.2, 0.01).72	990(vvw)	991(w)	γ(CH) (a')
22	1176(8, 0.1).75	1095(68, 1).75	1089(91, 1).75	1067		β(CH) (a'')
23	1177(82, 3).09	1081(73, 1).62	1078(84, 2).69	1031		β(CH) (a')
24	1215(29, 2).75	1188(0.1, 3).75	1187(0.1, 3).75	1156	1164(wd,dp)	β(CH) (a')
25	1296(5, 3).73	1207(4, 5).71	1205(4, 4).69	1180(vs)	1187(wd,p)	β(CH) (a')
26	1313(309, 3).68	1121(274, 4).45	1104(277, 4).41	1072(vs)	1080(w,p)	ν <sub>as</sub> (CF <sub>3</sub> ) (a')
27	1320(117, 0.3).75	1166(162, 1).75	1153(150, 1).75	1152(vs)	1164(wd,dp)	ν <sub>as</sub> (CF <sub>3</sub> ) (a'')
28	1369(95, 1).75	1363(0.4, 0.1).75	1339(1, 0.1).75	1303(vw)		ν (ring) (a'')
29	1468(378, 6).75	1325(328,19).13	1318(338, 20).14	1328(vs)	1324(m, p)	ν (C-CF <sub>3</sub> ) (a')
30	1471(9, 0.3).75	1348(3,0.3).75	1355(2, 0.2).75	1362(m)	1365(vvw)	β(CH) (a'')
31	1608(28, 0.2).75	1487(17,0.4).75	1483(18, 0.3).75	1459(vs)	1458(vvw,dp)	ν (ring) (a')
32	1667(0.2,1).65	1535(0.1,0.1).73	1530(0.03, 0.1).75	1502(vvw)		ν (ring) (a'')
33	1781(1,12).75	1638(0.3,9).75	1630(0.2, 8).75	1614(w)	1610(m, dp)	ν (ring) (a')
34	1809(10,21).75	1657(6,25).71	1648(6, 24).71	1614(w)	1593(w, p)	ν (ring) (a')
35	3349(0.3,45).75	3187(0.3,52).75	3170(0.2, 48).75		2995(w,p)	ν (CH) (a'')

36	3362(8,100).75	3198(8,111).75	3181(7, 104).75	3049(m)		$\nu(\text{CH})$ ( $a''$ )
37	3372(16,53).33	3207(13, 75).26	3190(11, 67).27		3022(w,p)	$\nu(\text{CH})$ ( $a'$ )
38	3383(11,6).75	3218(7, 8).75	3201(6, 6).75			$\nu(\text{CH})$ ( $a''$ )
39	3386(2,268).15	3220(2, 296).14	3203(2, 297).13	3076(m)	3076(s,p)	$\nu(\text{CH})(a'')$

# taken from Refs.2 and 4; rel. int.= relative intensity. The numbers left to the brackets under the columns 2, 3 and 4 correspond to the frequencies and those right to the brackets correspond to the values of depolarisation ratios.

The first numbers in the brackets correspond to the IR intensities and the second numbers to the Raman intensities.

s = strong, m = medium, v=very, w = weak, sh = shoulder, s = strong, b= broad, d= diffused, p= polarized, dp = depolarized.

$\Phi$  = non – planar ring deformation,  $\alpha$  = planar ring deformation,  $\nu$  = stretching,  $\beta$  = planar deformation,  $\gamma$  = non planar deformation,  $\rho_{\perp}$  = perpendicular rocking,  $\rho_{\parallel}$  = parallel rocking,  $\delta_s$  = symmetric deformation,  $\delta_{as}$  = antisymmetric deformation  $\tau$  = torsion,  $\nu_s$  = symmetric stretching,  $\nu_{as}$  = anti-symmetric stretching.

### C–H Modes

The 5 C–H bonds give rise to the 15 normal modes which are distributed under the  $C_s$  symmetry as:  $a' - 3 \nu(\text{CH}) + 2 \beta(\text{CH}) + 3 \gamma(\text{CH})$ ;  $a'' - 2 \nu(\text{CH}) + 3 \beta(\text{CH}) + 2 \gamma(\text{C–H})$ . Pictorial view of the normal modes shows that all the five  $\nu(\text{CH})$  modes are pure  $\nu(\text{CH})$  modes. It is to be noted that the calculated frequencies 3203, 3190 and 3170  $\text{cm}^{-1}$  belong to the symmetric species  $a'$  and the frequencies 3201 and 3181  $\text{cm}^{-1}$  to the anti-symmetric species  $a''$ . The five  $\beta(\text{CH})$  modes are identified as the calculated frequencies 1355, 1205, 1187, 1089 and 1078  $\text{cm}^{-1}$ . Out of these the frequencies 1205 and 1078  $\text{cm}^{-1}$  belong to the species  $a'$  and the remaining three frequencies to the species  $a''$ . It could be seen from the GaussView that the frequency 1205  $\text{cm}^{-1}$  is a pure CH planar bending mode whereas the frequency 1078  $\text{cm}^{-1}$  arises due to the mixing of the CH planar bending mode with the ring stretching and the symmetric  $\text{CF}_3$  stretching modes. Out of the three  $\beta(\text{CH})$  frequencies under the species  $a''$  the frequency 1187  $\text{cm}^{-1}$  appears to arise due to pure CH planar bending mode. However, the frequency 1355  $\text{cm}^{-1}$  arises due to the mixing of the CH planar bending mode with the ring stretching mode and the frequency 1089  $\text{cm}^{-1}$  originates due to the coupling of the CH planar bending mode with the ring stretching and the antisymmetric  $\text{CF}_3$  ( $a''$ ) stretching modes.

Out of the 5  $\gamma(\text{CH})$  frequencies calculated as 996, 985, 941, 857 and 780  $\text{cm}^{-1}$ , the frequencies 996, 941 and 780  $\text{cm}^{-1}$  belong to the species  $a'$  and the frequencies 985 and 857 to the species  $a''$ . The two higher frequencies under the symmetric species and the two frequencies under the anti-symmetric species appear to be pure  $\gamma(\text{CH})$  modes while the lowest frequency of the symmetric species appear to mix with the non-planar ring deformation mode slightly.

### $\text{CF}_3$ Group Modes

The pictorial view suggests that out of the nine modes of the  $\text{CF}_3$

group the modes  $\tau$ ,  $\rho_{\perp}$ ,  $\delta_{as}(a'')$  and  $\nu_{as}(a')$  are almost pure  $\text{CF}_3$  group modes and these are calculated to be 16, 394, 568 and 1104  $\text{cm}^{-1}$ . The other five  $\text{CF}_3$  group modes are coupled modes. The calculated frequency 340  $\text{cm}^{-1}$  contains contribution from the  $\delta^s$  and the planar ring bending modes. Similarly, the calculated frequency 483  $\text{cm}^{-1}$  arises due to the mode  $\nu_{as}(a')$  coupled with the non-planar ring bending mode. Assignment of the  $\nu_s(\text{CF}_3)$  mode has been controversial and has been widely discussed in the literature. It is to be noted that in the Raman spectra of benzene derivatives with  $\text{CF}_3$  group (s) one observes frequencies in the ranges 700–800  $\text{cm}^{-1}$  and 1300–1350  $\text{cm}^{-1}$  with good intensities and low depolarisation ratios. Some authors have assigned the  $\nu_s(\text{CF}_3)$  mode in the range 1300–1350  $\text{cm}^{-1}$  and the  $\delta_s(\text{CF}_3)$  mode in the range 700–800  $\text{cm}^{-1}$ , while some other group of workers have assigned the  $\nu_s(\text{CF}_3)$  mode in the range 700–800  $\text{cm}^{-1}$  and the  $\nu(\text{C–CF}_3)$  mode in the range 1300–1350  $\text{cm}^{-1}$  [1, 5]. The  $\delta_s(\text{CF}_3)$  mode has been assigned at a much lower frequency (in the range 275–350  $\text{cm}^{-1}$ ) by the latter group of workers. The present ab initio calculations favour the assignments of the latter group of workers and the most suitable candidate for the mode  $\nu_s(\text{CF}_3)$  is calculated to be 768  $\text{cm}^{-1}$ . It may be noted here that this mode also involves planar ring deformation and slight  $\nu(\text{C–CF}_3)$  modes. Similarly, the modes  $\nu_{as}(a')$  and  $\nu_{as}(a'')$  are identified as the calculated frequencies 1104 and 1153  $\text{cm}^{-1}$ . Usually C–F stretching appears with very large IR intensity. The calculated IR intensities for the  $\nu_{as}(a'$  and  $a''$ ) are found to be substantially large. The observed IR bands at 1072 and 1152  $\text{cm}^{-1}$  with very strong IR intensities are correlated to the calculated frequencies 1104 and 1153  $\text{cm}^{-1}$  respectively.

### C – $\text{CF}_3$ Modes

The C– $\text{CF}_3$  bond gives rise to the three normal modes, namely, the  $\nu(\text{C–CF}_3)$ ,  $\beta(\text{C–CF}_3)$  and  $\gamma(\text{C–CF}_3)$  modes. As discussed earlier, the mode  $\nu(\text{C–CF}_3)$  has been assigned in the range 1300–1350  $\text{cm}^{-1}$  for a number of benzene derivatives containing  $\text{CF}_3$  group (s). The present calculation places this mode at 1318  $\text{cm}^{-1}$ . Pictorial view suggests that this mode is coupled with  $\beta(\text{C–H})$  and  $\nu_s(\text{CF}_3)$  modes. The  $\beta$  and  $\gamma$  modes are calculated to be at 196 and 131  $\text{cm}^{-1}$  with the corresponding observed band at ~200 and 140  $\text{cm}^{-1}$  respectively and these are found to be pure modes.

### Phenyl Ring Modes

The six ring stretching modes are identified as 1648 1630, 1530, 1483, 1339 and 1042  $\text{cm}^{-1}$ . It could be seen that the first five frequencies involve mixing of the ring stretching with the planar CH bending modes while the last one is a result of the mixing of the ring stretching and the  $\nu_s(\text{CF}_3)$  modes. It corresponds to the ring breathing mode (993  $\text{cm}^{-1}$ ) of benzene. Assignment for this mode has been controversial in benzene derivatives and is widely discussed in the published literature. Though it is forbidden in IR spectrum under  $D_{6h}$  symmetry, in the present case it has good

IR intensity. The observed frequency corresponding to this mode is  $1028\text{ cm}^{-1}$ . Out of the three ring planar deformation modes the trigonal bending mode is one of the substituent sensitive modes, because in this mode the alternate three C atoms of the ring come closer to and the remaining three C atoms go farther from the ring center. Thus, one triangle formed by the alternate C atoms contract while the other one expands. Therefore, when one substituent is replaced for a H atom one of the triangles is loaded which makes the triangular motion of the triangle containing the substituent difficult. However, the other triangle remains unaffected. Thus, in mono substituted benzenes with a heavy substituent the trigonal ring bending remains practically unaffected. For BTF this mode is calculated to have the frequency  $1018\text{ cm}^{-1}$ . The other two ring planar bending modes are identified as the frequencies  $662$  and  $632\text{ cm}^{-1}$  corresponding to the species  $a'$  and  $a''$ . The torsional motions of the ring give rise to three modes in substituted benzenes. In the case of BTF the mode corresponding to the phenyl ring torsional mode 4 is calculated to be  $702\text{ cm}^{-1}$  and those corresponding to the mode 16 as  $591$  ( $a'$ ) and  $409$  ( $a''$ )  $\text{cm}^{-1}$ .

### Conclusions

The optimized geometry of the BTF molecule shows that the three F atoms of the  $\text{CF}_3$  group are found to be non-coplanar with the ring plane. In spite of their high electronegativity the F atoms are found to come closer compared to the perfect tetrahedral configuration. The  $\text{CF}_3$  group has a barrier height of  $\sim 5\text{ kJ/mol}$  in isomeric trifluoromethyl anilines [11]. It is proportional to the square of the torsional frequency. In the present case the torsional frequency  $16\text{ cm}^{-1}$  of the  $\text{CF}_3$  group is found to be quite low compared to the earlier estimated value for this mode in BTF derivatives. However, it is very close to that ( $15\text{ cm}^{-1}$ ) proposed by D'Cunha and Kartha for the BTF molecule [3]. Such a low value of the torsional frequency would lead to barrier height of  $\sim 0.5\text{ kJ/mol}$  for the torsional motion of the  $\text{CF}_3$  group. The  $\text{CF}_3$  group has the characteristic frequencies in the ranges  $285\text{--}350$ ,  $700\text{--}800$ ,  $1050\text{--}1200$  and  $1300\text{--}1350\text{ cm}^{-1}$  which are due to the modes  $\delta_s(\text{CF}_3)$ ,  $\nu_s(\text{CF}_3)$ ,  $\nu_{\text{as}}(\text{CF}_3)$  and  $\nu(\text{C--CF}_3)$  respectively.

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