Ab initio and density functional computations of the vibrational spectra, molecular geometries and other properties of 2-bromo-6-chloro-4-fluoroaniline

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ABSTRACT : *The FTIR and FT-Raman spectra of 2-bromo-6-chloro-4-fluoroaniline (BCFA) have been recorded in the regions 4000-400 cm^{-1} and 4000-50 cm^{-1}, respectively. The vibrational wavenumbers were computed at the HF and B3LYP levels of theory and tentative vibrational assignments were provided on the basis of combined theoretical and experimental infrared and Raman data of the molecule. A very small difference obtained between the observed and scaled wavenumber values. Optimized geometrical parameters and frontier molecular orbitals were carried out by HF and DFT/B3LYP methods combined with 6-31+G(d,p) basis set. Further, the first order hyperpolarizability and molecular electrostatic potential (MEP) was investigated using theoretical calculations. In addition, the Mulliken's charges analysis and several thermodynamic properties were calculated.*
Keywords: FTIR, FT-Raman, 2-bromo-6-chloro-4-fluoroaniline, DFT calculations, MEP.

I.INTRODUCTION

Aniline and its derivatives have been widely used as starting materials in a vast amount of chemicals, pharmaceuticals, dyes, electro-optical and many other industrial processes [1]. The conducting Polymer of aniline namely polyaniline is used in microelectronic devices as diodes and transistors. Particularly, aniline and its derivatives are used in the production of dyes, pesticides and antioxidants [2,3]. Wojciechowski et al. were investigated the theoretical Raman and infrared spectra, and vibrational assignment for para-halogen anilines [4]. The molecular structure, vibrational spectroscopy and HOMO, LUMO studies of 4-nitroaniline has been reported by Kavitha et al. [5]. The vibrational and non-linear optical properties of 2-(trifluoromethyl) aniline and 3-(trifluoromethyl) aniline were carried out by Arjunan et al. [6]. Moreover, the molecular structure and charge transfer contributions to nonlinear optical property of 2-Methyl-4-nitroaniline was studied by Femina Jasmine et al. [7]. More recently, Revathi et al. [8] deliberated the NLO properties of 4-Chloro-3-(trifluoromethyl)aniline, 4-bromo-3-(trifluoromethyl)aniline and 4-fluoro-3-(trifluoromethyl) aniline. However, to the best of our knowledge no Hartree-Fock (HF) and density functional theory (DFT) with 6-31+G(d,p) basis set calculations of 2-bromo-6-chloro-4-fluoro aniline (BCFA) have been reported so far. Therefore, in the present work an attempt has been made to study the detailed theoretical and experimental investigation of the vibrational spectra of BCFA.

II EXPERIMENTAL DETAILS

The fine polycrystalline sample of BCFA was obtained from Lancaster Chemical Company, UK and used as such for spectral measurements. The room temperature Fourier transform infrared spectra of the title compound were measured in the region 4000 - 400 cm^{-1} at a resolution of ± 1 cm^{-1} using KBr pellets on BRUKER IFS-66V FTIR spectrophotometer equipped with a cooled MCT detector. The FT-Raman spectrum was recorded on a computer interfaced BRUKER IFS model interferometer equipped with FRA 106 FT-Raman accessory in the region 4000 - 50 cm^{-1} using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW power. The reported wavenumbers are believed to be accurate within $\pm$ 1 cm^{-1}.

III COMPUTATIONAL DETAILS

The assignments of band in the vibrational spectra of molecule are an essential step in the application of vibrational spectroscopy for solving various structural and chemical problems. For the better understanding of IR and Raman spectra, reliable assignments of all vibrational bands are essential. In the present study, owing to the industrial importance of substituted anilines, an extensive spectroscopic study of BCFA has been undertaken by recording FTIR and FT-Raman spectra in an effort to provide possible explanations for the experimentally observed vibrational fundamentals and to understand the effect of halogen group substitution on the characteristic frequencies of the amino group. The optimized structural parameters, vibrational frequencies, optimized minimum energy, reduced mass, force constants, IR intensity and Raman activity have been carried out using the GAUSSIAN 09W [9] software package at the HF (Hartree-Fock) and B3LYP (Becke-3-Lee-Yang-Parr) levels

with 6-31+G(d,p) basis set. In order to improve the agreement of theoretically calculated frequencies with experimentally calculated frequencies, it is essential to scale down the theoretically calculated harmonic frequencies. Hence, the vibrational frequencies theoretically calculated are scaled down by using MOLVIB 7.0 version written by Tom Sundius [10,11].

IV RESULTS AND DISCUSSION

Molecular geometry

The optimized molecular structure of BCFA having C_s point group symmetry is shown in Fig. 1. The global minimum energy obtained by the HF and DFT structure optimization for BCFA is calculated as -3412.82303595 Hartrees and -3417.57716308 Hartrees. The optimized geometrical parameters obtained by HF and B3LYP methods with 6-31+G(d,p) basis set calculations in this study are presented in Table 1. It is observed that the various bond lengths are found to be almost equal at the HF and B3LYP methods. However, the B3LYP level of theory, in general slightly overestimates bond lengths but it shows bond angles in good agreement with the HF method. As seen from the Table 1, the bond length of C-Br is found to be 1.8954 Å by B3LYP method and is higher than other bond lengths, since bromine is highly electronegative in nature. The bond lengths of C-H lie in the characteristics region. For the title compound, the C-C bond lengths are calculated in between 1.3866 and 1.4095 Å by DFT/B3LYP method. In particular, the bond lengths of C3-C4 and C4-C5 are reduced slightly with other bond lengths in the skeleton. Asymmetry of the benzene ring is also evident from the positive deviation of C1-C2-C3, C3-C4-C5 and C1-C6-C5 bondangles from the normal value of 120^0. Other C-C-C angles are calculated bigger and smaller than the hexagonal angle due to the effect of substitutions in the benzene ring.

Vibrational Spectra

The title compound BCFA consists of 14 atoms and its 36 normal modes are distributed amongst the symmetry species as:

$$\Gamma_{3N-6} = 25 \text{ A' (in-plane)} + 11 \text{ A'' (out-of-plane)}$$

All the vibrations are active both in IR and Raman spectra. The detailed vibrational band assignments of BCFA calculated by the *ab initio* and DFT calculations with 6-31+G (d,p) basis set along with the calculated IR and Raman intensities and normal mode descriptions (Characterised by TED) are reported in Table 2. The experimental FTIR and FT-Raman spectra of BCFA are shown in Figs. 2-3.

Vibrational band assignments

IR and Raman spectra contain a number of bands at specific wavenumbers. The aim of the vibrational analysis is to decide which of the vibrational modes give rise to each of these observed bands.

C - H Vibrations

The C-H stretching vibrations of aromatic and heteroaromatic structure are normally appearing in the region 3000 - 3100 cm^{-1}[12]. In this region, the bands are not affected appreciably by the nature of the substituent. Hence, in the present investigation, the C–H stretching vibrations of BCFA are observed at 3083 cm^{-1} in both IR and Raman and 2929 cm^{-1} in IR spectrum. Generally, the bands due to C-H in-plane bending vibrations interact with ring vibrations, are observed as a number of sharp bands in the region 1300-1000 cm^{-1}. The FTIR bands observed at 1296 and 1193 cm^{-1} are assigned to C–H in-plane bending vibrations of BCFA and these modes are confirmed by their TED values. The C-H out-of-plane bending vibrations of BCFA have also been identified and listed in Table 2.

C - C Vibrations

The bands between 1400 and 1650 cm^{-1} in benzene derivatives are due to C-C stretching vibrations [13]. Therefore, the stretching vibrations of BCFA are observed at 1612, 1553, 1402 cm^{-1} in Raman and 1574, 1472, 1413 cm^{-1} in FTIR spectrum. Most of the ring vibrational modes are affected by the substitutions in the aromatic ring of the title compound. In the present study, the bands observed at 1089 cm^{-1} and 1079, 933 cm^{-1} in the FTIR and Raman spectra, respectively, have been designated to ring in-plane bending modes. These modes are confirmed by their TED values. The ring out-of-plane bending modes of BCFA are also listed in the Table 2. Due to the change in force constant and the vibrations of the functional groups, the ring out-of-plane bending frequencies are reduced.

C - F Vibrations

In the vibrational spectra of related compounds, the bands due to C-F stretching vibrations [14] may be found over a wide frequency range 1360-1000 cm^{-1}, since the vibration is easily affected by adjacent atoms or groups. In the present investigation, the FT-Raman band observed at 1301 cm^{-1} has been assigned to C-F stretching mode of vibration for BCFA. The Raman bands found at 476 and 402 cm^{-1} have been designated to C–F in-plane bending and out-of-plane bending modes, respectively.

C - Cl Vibrations

The C-Cl stretching frequency is generally observed in the region 850-550 cm^{-1} depending upon the

configuration and conformation of the compound [15]. Based on this, in the present study, the FTIR band of BCFA identified at 846 cm^{-1} is assigned to C-Cl stretching mode of vibration. The C-Cl in-plane and out-of-plane vibrational modes of BCFA are identified at 433 and 387 cm^{-1} in the Raman spectrum, respectively.

C - Br Vibrations

The assignment of C-Br stretching and deformation modes has been made through the comparison with assignments in other halogens substituted benzene derivatives [16]. Krishnakumar *et al*.[17] have assigned the C-Br vibrations in the frequency range 1300-550 cm^{-1}. In this study, the band observed at 562 cm^{-1} in FTIR spectrum has been assigned to C-Br stretching vibrations of BCFA. The C-Br in-plane and out-of-plane vibrational modes of BCFA are also identified and listed in Table 2.

NH$_2$ Group Vibrations

The frequencies of amino group appear around 3500 - 3300 cm^{-1} for NH$_2$ stretching, 1700-1600 cm^{-1} for scissoring and 1150 - 900 cm^{-1} for rocking deformation [16]. In the present study, the asymmetric and symmetric stretching modes of NH$_2$ group in BCFA are assigned at 3444 cm^{-1} in IR and 3365 cm^{-1} in Raman spectra. The bands appeared at 1627 cm^{-1} in IR has been assigned to scissoring modes of NH$_2$ group for BCFA. The Rocking, wagging and twisting vibrational modes of NH$_2$ for the title compound are also presented in Table 2. The theoretically computed values by B3LYP method for NH$_2$ vibrational modes give excellent agreement with experimental data.

V First hyperpolarizability

The quantum chemistry based prediction of non-linear optical (NLO) properties of a molecule has an essential role for the design of materials in modern communication technology, signal processing and optical interconnections [18,19]. Especially organic molecules are studied because of their larger NLO susceptibilities arising π-electron cloud movement from donor to acceptor, fast NLO response times, high laser damage thresholds and low dielectric constants. The components of dipole moment, polarizability and the first hyperpolarizability of BCFA are shown in Table 3. The total static dipole moment μ, the average linear polarizability $\overline{\alpha}$, the anisotropy of the polarizability $\Delta\alpha$, and the first hyperpolarizability β can be calculated by using the following Equations. [19]:

$$\overline{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2\right]^{1/2}$$

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

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}$$

The calculated values of total static dipole moment μ, the average linear polarizability $\overline{\alpha}$, the anisotropy of the polarizability $\Delta\alpha$, and the first hyperpolarizability β using the DFT-B3LYP/6-31+G(d,p) method are 1.3238 Debye, 16.25 Å^3, 33.05 Å^3 and 0.919×10^{-30} e.s.u.$^{-1}$, respectively. The values of μ, $\overline{\alpha}$ and β obtained by Sun *et al*. [20] with the B3LYP method for urea are 1.373 Debye, 3.831 Å^3 and 0.3729×10^{-30} e.s.u.$^{-1}$, respectively. The first hyperpolarizability of BCFA molecule is 3 times greater than that of urea. According to these results, the title compound may be a potential applicant in the development of NLO materials.

VI HOMO, LUMO analysis

The highest occupied molecular orbitals (HOMOs) and the lowest- lying unoccupied molecular orbitals (LUMOs) are named as frontier molecular orbitals (FMOs). The FMOs play an important role in the electric and optical properties, as well as in UV–Vis spectra and chemical reactions [21]. The atomic orbital HOMO and LUMO compositions of the frontier molecular orbital for BCFA computed at the B3LYP/6-31+G(d,p) are shown in Fig. 4. The calculations indicate that the title compound have 54 occupied MOs. The HOMO-LUMO energy gap for BCFA is found to be 5.797 eV. The decrease in energy gap between HOMO and LUMO facilitates intra molecular charge transfer which makes the material to be NLO active. The LUMO: of π nature, (i.e. benzene ring) is delocalized over the whole C-C bond. By contrast, the HOMO is located over NH$_2$ group and all halogen atoms; consequently the HOMO → LUMO transition implies an electron density transfer to C-C bond of the benzene ring, bromine and chlorine atoms from NH$_2$ group and fluorine atom. Moreover, these orbitals significantly overlap in their position of the benzene ring for BCFA. The LUMO as an electron acceptor represents the ability to obtain an electron, and HOMO represents the ability to donate an electron.

VII Mulliken Population Analysis

Mulliken atomic charge calculation [22] has an important role in the application of quantum chemical calculation to molecular system due to the change in dipole moment, polarizability, electronic structure, and much more properties of molecular systems. The total atomic charges of BCFA obtained by HF and B3LYP methods with 6-31+G(d,p) basis set are listed in Table 4. The charge distribution on the molecule has an important influence on the vibrational spectra. The graphical representation of the results has been done in Fig. 5 and it gives us information about the charge shifts relative to BCFA. More charge density was found at C1, C3 and C5 than that of other ring carbon atoms. The high positive charge at C2, C6 and C4 is due to the effect of electron releasing halogen group attached with these atoms. The electron donating character of the NH_2 group in the title compound is demonstrated by a decrease in electron density on C1 atom. From the result it is clear that the substitution of NH_2 and halogen groups in the aromatic ring leads to a redistribution of electron density.

VIII Electrostatic potential, total electron density and molecular electrostatic potential

The electrostatic potential has been used primarily for predicting sites and relative reactivities towards electrophilic attack, and in studies of biological recognition and hydrogen bonding interactions [23,24]. To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecule, the MEP at the B3LYP/6-31+G(d,p) optimized geometry was calculated. In the present study, the electrostatic potential (ESP), electron density (ED) and the molecular electrostatic potential (MEP) map figures for BCFA are shown in Fig. 6. The ED plots for the title molecule show a uniform distribution. However, the ESP figures shows that the negative potential is localized more over the bromine, chlorine, fluorine atoms and is reflected as a yellowish blob, the positive ESP is localized on the rest of the molecule. This result is expected, because ESP correlates with electro negativity and partial charges. The different values of the electrostatic potential at the surface are represented by different colours. Potential increases in the order red < orange < yellow < green < blue. In the Fig. 6, the negative (red and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity. As can be seen from the figure and the computed results, the MEP map shows that the negative potential sites are in between bromine and NH_2 group and the positive region is over the hydrogen atom of NH_2 group. The color code of these maps is in the range between -0.0399 a.u. (deepest red) to 0.0399 a.u. (deepest blue) in compound, where blue indicates the strongest attraction and red indicates the strongest repulsion. From these results, the H atoms of NH_2 group indicate the strongest attraction and space between bromine and NH_2 group indicates the strongest repulsion. The region of all halogen atoms are indicated by green, since they are neutral. These sites give information about the region from where the compound can have intermolecular interactions. Thus, it would be predicted that the BCFA molecule will be the most reactive site for both electrophilic and nucleophilic attack.

Other molecular properties

Normally, the thermo dynamical analysis on aromatic compound is very important since they provide the necessary information regarding the chemical reactivity. On the basis of vibrational analysis at the HF and B3LYP methods with 6-31+G(d,p) basis set, the standard statistical thermodynamic functions: heat capacity, zero point energy, entropy of BCFA have been calculated and are presented in Table 5. The difference in the values calculated by both the methods is only marginal. The variation in the ZPVE seems to be significant. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. The total dipole moment of BCFA determined by HF and B3LYP methods using 6-31+G(d,p) basis set are 1.3642 and 1.3238 Debye, respectively. The total energy and the change in the total entropy of the compound at room temperature are also presented. All the thermodynamic data are helpful for the further study on the BCFA. They can be used to compute the other thermodynamic energies and estimate directions of chemical reactions.

CONCLUSION

The molecular structural parameters and fundamental vibrational frequencies of 2-bromo-6-chloro-4-fluoroaniline have been obtained from *ab initio* and DFT calculations. The effect of halogen substituent on vibrational frequencies is analysed in detail. The assignments of most of the fundamentals provided in the present work are believed to be unambiguous. The TED calculation about the normal modes of vibration provides a strong support for the frequency assignment. The calculated first order hyperpolarizability was found to be 0.919×10^{-30} esu, which is 3 times greater than reported in literature for urea. The HOMO and LUMO energy gap shows that the charge transfer occur within the molecule, which are responsible for the bioactive property of the molecule. The MEP map predicts the reactive sites for electrophilic and nucleophilic attack the molecule and the results are discussed. Furthermore, the thermodynamic and Mulliken charge analysis of the compound have been calculated in order to get insight into the compound.

Table 1

Optimized geometrical parameters of 2-bromo-6-chloro-4-fluoroaniline obtained by B3LYP and HF calculations.

Bond length	Value (Å)		Bond angle	Value (°)	
	B3LYP/6-31+G(d,p)	HF/6-31+G(d,p)		B3LYP/6-31+G(d,p)	HF/6-31+G(d,p)
$C_1 - C_2$	1.4077	1.394	$C_1 - C_2 - C_3$	122.2713	122.1337
$C_2 - C_3$	1.3955	1.3849	$C_2 - C_3 - C_4$	118.081	118.305
$C_3 - C_4$	1.3866	1.3749	$C_3 - C_4 - C_5$	122.8996	122.5196
$C_4 - C_5$	1.3874	1.3758	$C_4 - C_5 - C_6$	117.2607	117.56
$C_5 - C_6$	1.3938	1.3826	$C_5 - C_6 - C_1$	123.1238	122.939
$C_6 - C_1$	1.4095	1.3957	$C_6 - C_1 - C_2$	116.3637	116.5428
$C_1 - N_7$	1.4243	1.4151	$C_6 - C_1 - N_7$	123.626	123.2606
$N_7 - H_8$	1.017	1.0	$C_2 - C_1 - N_7$	120.0103	120.1966
$N_7 - H_9$	1.017	1.0	$H_8 - N_7 - H_9$	107.1673	108.4273
$C_2 - Br_{10}$	1.8954	1.8829	$C_1 - C_2 - Br_{10}$	119.8058	120.3583
$C_3 - H_{11}$	1.0828	1.0722	$C_3 - C_2 - Br_{10}$	117.923	117.508
$C_4 - F_{12}$	1.3555	1.3284	$C_2 - C_3 - H_{11}$	121.5624	121.4895
$C_5 - H_{13}$	1.0828	1.0724	$C_4 - C_3 - H_{11}$	120.3567	120.2055
$C_6 - Cl_{14}$	1.7566	1.7409	$C_3 - C_4 - F_{12}$	118.654	118.8333
			$C_5 - C_4 - F_{12}$	118.4464	118.6472
			$C_4 - C_5 - H_{13}$	120.8788	120.7613

For numbering of atoms refer Fig. 1
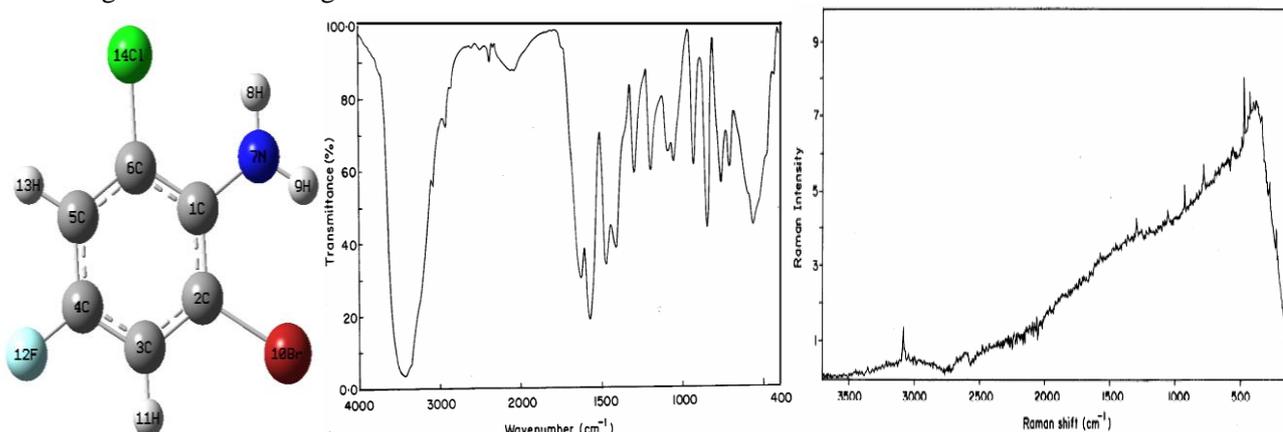
Fig1: Molecular structure of 2-bromo-6-chloro-4-fluoroaniline. **Fig2:** FTIR spectrum of 2-bromo-6-chloro-4-fluoroaniline.**Fig3:**FT-Raman spectrum of 2-bromo-6-chloro-4-fluoroaniline.
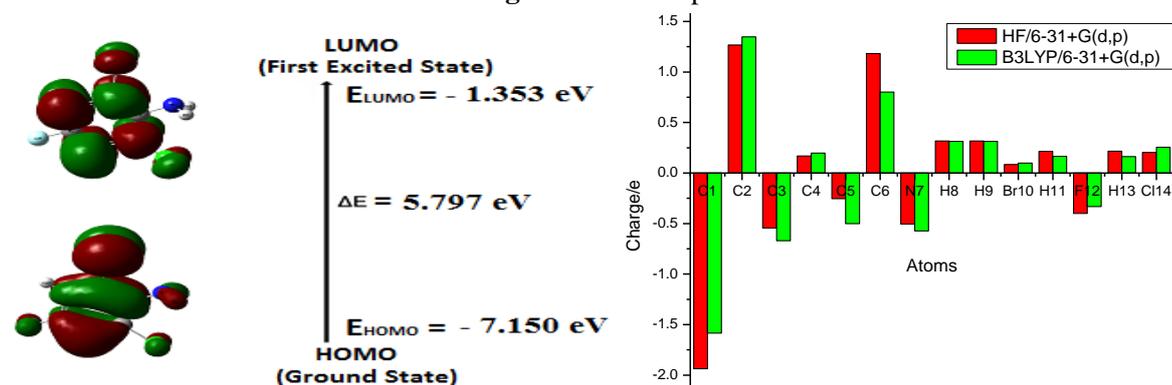
Fig4:HOMO and LUMO of2-bromo-6-chloro-4-fluoroaniline   **Fig 5:** Mulliken's plot for 2-bromo-6-chloro-4-fluoroaniline.

Fig 6: (a) Electrostatic potential (ESP);(b)Electron density (ED),(c)Molecular electrostatic potential (MEP) 2-bromo-6-chloro-4-fluoroaniline
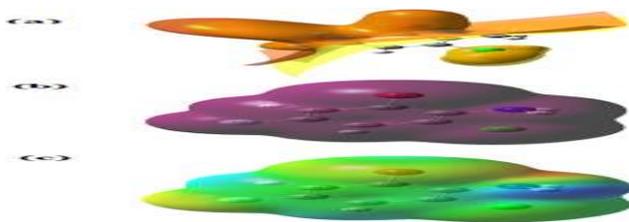
Table 2
Assignment of fundamental vibrational modes of 2-bromo-6-chloro-4-fluoroaniline based on SQM force field calculations using selectively scaled B3LYP/6-31+G(d,p) and HF/6-31+G(d,p) force field.

Symmetry species C_1	Observed frequencies (cm⁻¹)		Calculated frequencies (cm⁻¹)(Unscaled)		Scaling frequency (cm⁻¹)	Reduced mass(amu)		Force constant (m dyne A⁻¹)		IR intensity (km mol⁻¹)		Raman activity(A⁴ amu⁻¹)		Assignment (% TED)
	FTIR	FT-Raman	B3LYP	HF		B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	
A'	3444(vs)	-	3567	3951	3446	1.0589	7.1722	0.0533	0.0457	46.5548	1.1252	1.9228	0.5158	NH₂ ass (99)
A'	-	3365(w)	3494	3834	3369	6.7523	16.9532	0.0376	0.3545	0.5481	0.0823	0.2346	1.7289	NH₂ ss (98)
A'	3083(w)	3083(s)	3244	3405	3081	17.3029	8.8504	0.2928	0.2000	0.0378	0.7744	1.9344	0.8875	ν CH (97)
A'	2929(w)	-	3243	3403	2927	8.3936	3.9428	0.1490	0.1174	0.0024	1.2916	0.3117	2.8587	ν CH (96)
A'	1627(ms)	-	1663	1831	1623	4.7941	19.1717	0.1185	0.7214	0.7405	0.0798	1.8518	2.4565	NH₂ aciss (89)
A'	-	1612(vvs)	1644	1799	1616	17.3429	2.8910	0.5650	0.1539	0.3710	2.0803	2.1509	1.5131	ν CC (78)
A'	1574(ms)	-	1602	1773	1572	6.9293	1.7841	0.3250	0.1158	4.9412	15.1224	1.2574	3.3668	ν CC (82)
A'	-	1553(vvs)	1501	1634	1550	10.4026	3.8384	0.7151	0.3213	0.3388	5.8283	4.3125	3.4929	ν CC (80)
A'	1472(ms)	-	1422	1567	1474	4.9367	4.9763	0.3810	0.5188	3.0733	25.0309	2.7930	1.3930	ν CC (79)
A'	1413(w)	-	1319	1439	1420	7.2084	7.2312	0.8148	0.9512	8.2034	2.5820	3.0952	3.5893	ν CC (76)
A'	-	1402(vvs)	1296	1388	1407	10.7189	9.9521	1.4271	1.5626	1.1265	4.1206	9.3666	9.9383	ν CC (74)
A'	-	1388(vvs)	1233	1351	1380	5.2251	1.4042	0.9097	0.2684	0.0200	305.3903	0.7911	3.4134	ν CN (72)
A'	-	1301(s)	1222	1240	1300	4.2307	5.3139	0.8134	1.0370	7.8227	0.8356	1.3927	0.1292	ν CF (78)
A'	1296(s)	-	1194	1169	1294	3.8476	3.9207	0.8203	0.8768	0.8488	0.1370	0.0134	0.9976	b CH (81)
A'	1193(s)	-	1071	1159	1195	4.4873	3.3458	1.3766	0.8330	1.4929	2.9081	0.1335	0.0949	b CH (79)
A'	1089(w)	-	958	1029	1094	5.9994	7.2844	2.0706	2.8940	38.4729	24.9260	0.8919	2.0064	R asymd (80)
A'	-	1079(w)	884	1016	1070	6.0673	8.9165	2.2115	3.6072	38.9170	61.0777	11.8648	0.1680	R symd (72)
A'	1053(ms)	-	857	1001	1051	1.5167	5.0009	0.6494	2.1777	180.4590	29.0452	2.3145	10.9564	NH₂ rock (76)
A'	-	933(ms)	853	860	932	1.4078	1.4932	0.6088	0.8819	26.6467	43.8688	1.3436	1.2531	R trigd (70)
A'	929(s)	-	787	829	930	1.4077	1.3564	0.6479	0.8252	14.9722	3.3763	1.4376	0.7553	b CN (75)
A'	846(s)	-	765	821	848	9.6042	8.9294	5.1896	5.5752	45.6732	60.2388	11.5660	7.4457	ν CCl (78)
A'	562(s)	-	722	650	568	2.2812	2.5988	1.5411	2.0571	7.4643	91.8799	4.9588	4.6165	ν CBr (70)
A'	-	476(vs)	602	616	470	1.4979	2.5273	1.2576	2.0356	8.4193	60.0526	1.0252	8.1519	b CF (68)
A'	-	433(w)	571	576	427	1.2694	1.8914	1.1161	1.7136	0.1300	8.4884	1.5406	18.1321	b CCl (65)
A'	-	412(vvs)	544	570	410	2.1962	2.2233	1.9664	2.3898	21.7073	31.6464	6.8394	4.0016	b CBr (64)
A''	-	789(ms)	475	516	796	9.4935	1.4235	9.3986	1.6148	14.4510	3.2359	7.6470	2.4521	NH₂ wag (59)
A''	761(ms)	-	438	473	761	9.6626	8.4633	9.9056	10.3231	9.1005	3.8461	15.1108	20.2549	ω CH (60)
A''	706(w)	-	362	421	708	3.7786	4.0464	4.4999	5.8499	29.0370	13.2156	0.2468	0.4479	ω CH (58)
A''	-	689(vvs)	342	377	683	5.1964	4.8009	6.8986	7.5540	141.8888	267.9708	0.3409	1.5487	t R asymd (55)
A''	-	651(vvs)	282	332	655	4.7429	7.5968	7.1724	14.0627	50.8677	37.0129	10.8770	7.1264	t R trigd (57)
A''	-	602(vvs)	235	301	600	5.4756	1.8087	8.7238	3.4476	97.9144	178.4604	16.8159	1.8320	t R symd (58)
A''	-	485(w)	205	253	488	1.3020	2.1731	2.1219	4.2911	69.4586	20.6619	17.9909	18.3419	ω CN (54)
A''	-	402(vvs)	174	225	398	1.0931	1.0948	6.7728	7.4709	0.5409	0.6213	103.6561	92.5279	ω CF (53)
A''	-	387(w)	170	196	390	1.0930	1.0949	6.7770	7.4809	2.7188	1.8528	63.9063	63.3215	ω CCl (55)
A''	-	348(vvs)	97	188	352	1.0490	1.0479	7.5435	9.0774	7.5427	45.5971	141.9185	86.0398	NH₂ twist (53)
A''	-	235(w)	88	104	230	1.0924	1.1010	8.1891	10.1276	8.5050	44.7121	67.2380	27.1902	ω CBr (52)

Abbreviations: *w-weak, s-strong. ms-medium strong, vw-very weak, vs-very strong, R-ring, b-bending, v-streching, symd-symmetric deformation, ω-out-of-plane bending, asymd-antisymmetric deformation, trigd-trigonal deformation, ss-symmetric stretching ass-antisymmetric stretching, t-torsion.*

able 3

Calculated dipolemoment μ (Debye), polarizability (α) and the first hyperpolarizability (β) components (a.u.) for 2-bromo-6-chloro-4-fluoroaniline.

Components	Values	Components	Values
μ_x	0.4823	β_{xxx}	80.3571724
μ_y	-1.2327	β_{xxy}	-22.3534519
μ_z	0.00	β_{xyy}	-176.1690513
		β_{yyy}	59.4795737
α_{xx}	121.7934114	β_{xxz}	0.0
α_{xy}	5.269258	β_{xyz}	0.0
α_{yy}	144.6517728	β_{yyz}	0.0
α_{xz}	0.0	β_{xzz}	10.4549918
α_{yz}	0.0	β_{yzz}	26.4751129
α_{zz}	62.8895245	β_{zzz}	0.0

Table 4

The charge distribution calculated by the Mulliken method.

Atoms	Atomic charges (Mulliken)	
	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
C1	-1.93580	-1.583782
C2	1.268458	1.348139
C3	-0.543477	-0.669037
C4	0.168672	0.198111
C5	-0.253872	-0.499846
C6	1.183248	0.802730
N7	-0.504361	-0.572622
H8	0.317569	0.312497
H9	0.317569	0.312497
Br10	0.084397	0.099430
H11	0.215007	0.165116
F12	-0.399286	-0.332071
H13	0.215863	0.164018
Cl14	0.203356	0.254820

Table 5

Thermodynamic properties of 2-bromo-6-chloro-4-fluoroaniline.

Parameters	Method/Basis set	
	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
Optimized global minimum Energy (Hartrees)	-3412.82303595	-3417.57716308
Total energy(thermal), E_{total} (kcal mol^{-1})	65.408	61.451
Heat capacity, C_v (cal mol^{-1} k^{-1})	29.453	31.432
Entropy, S (cal mol^{-1} k^{-1})		
Total	91.958	94.083
Translational	42.108	42.108
Rotational	31.677	31.728
Vibrational	18.174	20.247
Vibrational energy, E_{vib} (kcal mol^{-1})	63.631	59.673
Zero point vibrational energy, (kcal mol^{-1})	60.37278	56.08642
Rotational constants (GHz)		
A	1.09166	1.06832
B	0.54370	0.53642
C	0.36363	0.35779
Dipole moment (Debye)		
μ_x	0.3576	0.4823
μ_y	-1.3165	-1.2327
μ_z	0.00	0.00
μ_{total}	1.3642	1.3238

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