



## Experimental and Theoretical Studies of the Vibrational Spectra of 4-chloro-2-Bromoaniline

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### ABSTRACT

The FT-IR and FT-Raman spectra for 4-chloro-2-bromoaniline were recorded and analyzed. Ab initio (HF/6-311++G(d,p)) and DFT (B3LYP/6-311++G(d,p)) calculations have been performed giving energies, optimized structures, harmonic vibrational frequencies, IR intensities and Raman activities. The vibrational frequencies are calculated and scaled values are compared with FT-IR and FT-Raman experimental values. The differences between the observed and scaled vibrational frequencies values of most of the fundamentals are very small. The scaled B3LYP/6-311++G(d,p) results show the best agreement with the experimental values.

**Keywords:** FT-IR, FT-Raman, Ab initio, DFT, 4-chloro-2-bromoaniline.

### INTRODUCTION

Aniline and substituted anilines are widely used as starting materials in the manufacturing of a vast number of pharmaceuticals, dyestuffs, pesticides and also for several industrial and commercial purposes<sup>1-3</sup>. The conducting polymer of aniline namely polyaniline is used in microelectronic devices as diodes and transistors<sup>4</sup>. Some para-substituted derivatives of aniline are commonly used as local anesthetics, and among these molecules the amino group plays an important role in the interactions with the receptor. Therefore, in the view of understanding the properties of aniline and its derivatives, as well as their reaction mechanisms, extensive experimental<sup>5</sup>. The inclusion of a substituent in aniline leads to variation in the molecular charge distribution, and consequently greatly affects the electronic, structural and vibrational parameters<sup>6</sup>. Because of their spectroscopic properties and chemical significance, aniline and its derivatives were studied extensively by spectroscopic and theoretical methods. Vibrational assignment based FT-IR in the vapour, solution liquid phases and the Raman spectra in the liquid state have been reported for aniline<sup>7</sup>. The molecular structure of aniline is also known in the gas phase from microwave spectroscopy<sup>8,9</sup> and in the solid state from X-ray crystallography<sup>10</sup>. Vibrational analysis has been reported theoretically using semi-empirical<sup>11,12</sup>, Ab initio methods<sup>13,14</sup>. In this study, we recorded FT-IR and FT-Raman spectra of 4-chloro-2-bromoaniline compound and calculated the vibrational frequencies in the ground state to distinguish fundamentals from experimental vibrational frequencies and geometric parameters using Ab initio/HF and DFT/B3LYP (Becke 3-Lee-Yang-Parr) methods. A detailed quantum chemical study will aid in making definite assignments to fundamental normal modes of 4-chloro-2-bromoaniline molecule and in clarifying the experimental data for this important molecule.

### MATERIALS AND METHODS

The compound 4-chloro-2-bromoaniline was purchased from Sigma–Aldrich with a stated purity of 98 % and were used without further purification. FT-IR spectra of 4-chloro-2-bromoaniline has been recorded in the region 4000-400  $\text{cm}^{-1}$  using a Thermo Nicolet Nexus 870 FT-IR instrument. The instrument is equipped with a KBr beam splitter and an In GaAs detector. The spectral resolution is  $\pm 2 \text{ cm}^{-1}$ . The Raman spectra were measured using a dispersive Nexus 870 FT-Raman instrument. The instrument is equipped with Nd:YAG laser source operating at 1.064  $\mu\text{m}$  line widths with 200 mW powers. The spectra were recorded with scanning speed of 30  $\text{cm}^{-1} \text{ min}^{-1}$  of spectral width 2  $\text{cm}^{-1}$ .

### Computational methods

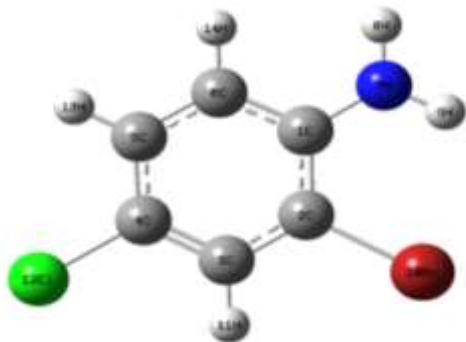
Many studies have shown that the DFT-B3LYP method in combination with the 6-311++G(d,p) basis set are able to give the accurate energies, molecular structures, and infrared vibrational frequencies<sup>15-17</sup>. The molecular structure optimization of the title compound and corresponding vibrational harmonic frequencies were calculated using HF and DFT with Beckee-3-Lee-Yag-Parr (B3LYP) with 6-311++G(d,p) basis set using GAUSSIAN 03 program package<sup>18</sup> without any constraint on the geometry. Geometries have been first optimized with full relaxation on the potential energy surfaces at HF/6-311++G(d,p) level and then re-optimized at B3LYP/6-311++G(d,p) level. The optimized geometrical parameters, rotational constants, vibrational frequencies, IR intensity, Raman activity and other thermodynamical parameters were calculated using the Gaussian 03 package. By combining the results of the GAUSS-VIEW<sup>19</sup> program with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. However, the defined coordinates forms complete set and matches quite well with the motions observed using GAUSS-VIEW program.



## RESULTS AND DISCUSSION

### Molecular geometry

The optimized molecular structure of 4-chloro-2-bromoaniline along with numbering of atoms is shown in Fig. 1. The optimized geometrical parameters of 4-chloro-2-bromoaniline obtained by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels are listed in Table 1. The global minimum energy obtained by Ab initio(HF) and DFT(B3LYP) structure optimization using 6-311++ G(d,p) basis set for 4-chloro-2-bromoaniline as -3316.3383794 and -3320.7085225 a.u., respectively.



**Figure 1:** Optimized geometry of 4-chloro-2-bromoaniline structure and atoms numbering.

The theoretical results show that the various bond angles are found to be almost the same at HF/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels. However, the B3LYP/6-311+G(d,p) level of theory in general slightly over estimates bond angles but it yields bond length in excellent agreement with B3LYP/6-311+G(d,p). The calculated geometric parameters can be used as foundation to calculate the other parameters for the compound. The change in bond length of the C–H bond on substitution due to a change in charge distribution on carbon atom of benzene ring from Table 1, It is observed that, C–C bond lengths in the ring in the optimized geometry of 4-chloro-2-bromoaniline calculated at B3LYP/6-311+G(d,p) level fall in the range 1.388–1.412 Å and this values are very close agreement with experimental value (1.395 Å). The average C–H bond length by B3LYP/6-311+G(d,p) is 1.079 Å. The optimized C–N bond length is 1.372 and 1.379 Å for 4-chloro-2-bromoaniline by HF and B3LYP methods, respectively. Both methods predict the C–N bond length very close to each other but shorter than the measured value (1.402 Å measured for a aniline)<sup>10</sup>. The optimized N–H bond length are calculated 0.986 Å and 1.003 Å by HF and B3LYP with 6-311++G(d,p) basis set, respectively. By comparing those values with experimental value of 1.001 Å, it is observed that B3LYP estimate the N–H bond length better than HF, which underestimates this bond than experimental values. The optimized C–Cl bond length indicates a considerable increase when substituted in place of C–H. This has been observed in benzene derivatives<sup>20</sup>. This bond length was also observed 1.735–1.744 Å range for

similar molecules<sup>21–23</sup>. The optimized C–Br bond lengths by two methods are 1.935 Å for HF/6-311++G(d,p) and 1.956 Å for B3LYP/6-311++G(d,p). The asymmetry of the benzene ring is evident by the bond angle order C2–C1–C6 < C2–C3–C4 < C4–C5–C6 < C3–C4–C5 < C1–C6–C5 < C1–C2–C3. The calculated bond angle of C1–C2–C3 and C3–C4–C5 are 122.106° and 121.217°, respectively at B3LYP/6-311++G(d,p) level which are differed from their experimental values<sup>24</sup>.

### Vibrational assignments

The maximum number of potentially active observable fundamentals of a non-linear molecule which contains N atoms is equal to (3N-6), apart from three translational and three rotational degrees of freedom. Hence, 4-chloro-2-bromoaniline molecule has 14 atoms with 36 normal modes of vibrations and considered under C1 point group symmetry. All the 36 fundamental vibrations are active in both Raman scattering and Infrared absorption. The detailed analysis of fundamental modes of vibration with FT-IR and FT-Raman experimental frequencies are tabulated in Table 2. Vibrational frequencies, IR intensity, Raman activity of 4-chloro-2-bromoaniline molecule using HF and B3LYP methods with 6-311++ G(d,p) basis set is reported in Tables 3. In this study, we followed two different scaling factors viz. 0.89 for HF and 0.96 for B3LYP to correct the theoretical error in this work<sup>25</sup>. The comparative graphs of the observed and simulated FT-IR and FT-Raman spectra for 4-chloro-2-bromoaniline molecule are presented in Figs. 2 and 3.

The hetero aromatic structure show the presence of C–H stretching vibrations in the region 3100–3000 cm<sup>-1</sup> which is the characteristic region for the ready identification of C–H stretching vibrations<sup>27</sup>. The C–H stretching vibrations in the region 3091–3040 cm<sup>-1</sup> at B3LYP/6-311++G(d,p) level show excellent agreement with FT-IR spectrum at 3088, 3071 cm<sup>-1</sup> and 3047 cm<sup>-1</sup> in FT-Raman spectrum. The aromatic C–H in-plane bending modes of benzene and its derivatives are observed in the region 1300–1000 cm<sup>-1</sup><sup>26</sup>. The bands are observed in the FT-IR spectrum at 1290 and 1153 cm<sup>-1</sup> and in the FT-Raman spectrum at 1295 and 1150 cm<sup>-1</sup> are assigned to C–H in-plane bending vibration. The theoretically computed B3LYP method at 1299, 1146 cm<sup>-1</sup> show good agreement with recorded as well as literature data<sup>27</sup>. The bands observed at 948 and 833 cm<sup>-1</sup> in FT-IR spectrum are (950 and 840 cm<sup>-1</sup> in FT-Raman spectrum) assigned to C–H out-of-plane bending vibrations for 4-chloro-2-bromoaniline. These also show good agreement with theoretically scaled harmonic wavenumber values at 951 and 836 cm<sup>-1</sup> at B3LYP/6-311++G(d,p) level. The ring carbon–carbon stretching vibration occurs in the region 1625–1430 cm<sup>-1</sup><sup>26,28</sup>. In the present work, the frequencies observed in the FT-IR spectrum at 1565 cm<sup>-1</sup> (1561 cm<sup>-1</sup> in FT-Raman) and predicted frequency by B3LYP/6-311++G(d,p) at 1565 cm<sup>-1</sup> were assigned to C–C stretching vibrations.

**Table 1:** Optimized geometrical parameters for 4-chloro-2-bromoaniline molecule (bond lengths in Å, angles in °).

Bond length (Å)	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Angles (°)	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
C1-C2	1.394	1.408	C2-C1-C6	117.115	116.947
C1-C6	1.401	1.412	C2-C1-N7	122.795	122.477
C1-N7	1.372	1.379	C6-C1-N7	120.089	120.575
C2-C3	1.383	1.391	C1-C2-C3	121.782	122.106
C2-Br10	1.935	1.956	C1-C2-Br10	120.170	119.492
C3-C4	1.375	1.388	C3-C2-Br10	118.046	118.400
C3-H11	1.067	1.078	C2-C3-C4	119.292	118.884
C4-C5	1.380	1.391	C2-C3-H11	120.069	120.268
C4-Cl12	1.806	1.828	C4-C3-H11	120.638	120.846
C5-C6	1.378	1.390	C3-C4-C5	120.856	121.217
C5-H13	1.069	1.079	C3-C4-Cl12	119.416	119.170
C6-H14	1.071	1.082	C5-C4-Cl12	119.727	119.612
N7-H8	0.986	1.003	C4-C5-C6	119.345	119.173
N7-H9	0.986	1.003	C4-C5-H13	120.400	120.493
			C6-C5-H13	120.247	120.333
			C1-C6-C5	121.608	121.671
			C1-C6-H14	118.899	118.842
			C5-C6-H14	119.492	119.486
			C1-N7-H8	120.457	120.794
			C1-N7-H9	121.614	121.032
			H8-N7-H9	117.927	118.173

**Table 2:** Experimental FT-IR, FT-Raman frequencies and assignment for 4-chloro-2-bromoaniline.

FT-IR frequency (cm <sup>-1</sup> )	FT-Raman frequency (cm <sup>-1</sup> )	Assignment
3600	3596	NH <sub>2</sub> stretch asym.
-	3480	NH <sub>2</sub> stretch sym.
3088	-	C-H stretch
3071	3047	C-H stretch
1630	1630	NH <sub>2</sub> (ip) bend
1565	1561	C-C-C deformation
1352	1350	C-N stretch
1290	1295	C-H (ip) bend
1153	1150	C-H (ip) bend
1066	1063	NH <sub>2</sub> (op) bend
948	950	C-H (op) bend
833	840	C-H (op) bend
671	670	C-C-C deformation
627	626	C-Cl stretch
553	551	C-Br stretch
456	460	C-C-C deformation
-	357	C-Cl (ip) deformation
-	235	C-Cl (op) deformation

**Table 3:** Calculated fundamental frequencies at HF/6-31++G(d,p) and B3LYP/6-31++G(d,p) levels calculated vibrational frequencies for 4-chloro-2-bromoaniline.

Mode of vibration	Calculated frequency (cm <sup>-1</sup> )							
	HF/6-31++G(d,p)				B3LYP/6-31++G(d,p)			
	Wave number		IR intensity	Raman activity	Wave number		IR intensity	Raman activity
Unscaled	Scaled	Unscaled			Scaled			
1	3997	3557	38.04	30.66	3748	3598	31.57	34.61
2	3860	3436	63.51	128.09	3618	3473	54.19	164.63
3	3386	3014	0.45	50.85	3219	3091	0.32	56.97
4	3373	3002	4.71	110.74	3207	3078	3.63	117.27
5	3336	2969	14.37	87.74	3167	3040	15.48	104.30
6	1841	1639	167.65	11.15	1697	1629	173.41	10.39
7	1770	1575	23.15	36.80	1630	1565	24.01	32.53
8	1743	1551	5.90	2.78	1595	1531	7.11	3.14
9	1648	1467	227.14	3.62	1524	1463	222.31	3.28
10	1537	1368	39.94	9.80	1411	1355	60.12	5.50
11	1448	1289	74.25	7.59	1353	1299	24.00	5.72
12	1410	1255	14.89	9.38	1341	1287	12.56	5.84
13	1323	1177	10.70	4.38	1301	1249	6.86	5.20
14	1262	1123	27.97	4.71	1194	1146	14.56	1.62
1	1205	1072	24.92	6.70	1114	1069	22.58	11.16
16	1159	1032	52.96	10.90	1070	1027	6.74	0.41
17	1129	1004	2.88	2.84	1046	1005	1.11	0.46
18	1124	1000	1.57	0.02	990	951	41.06	0.75
19	1080	962	5.05	0.18	939	902	7.70	0.07
20	971	864	89.73	0.49	870	836	67.62	0.35
21	918	817	8.91	25.64	857	822	9.36	32.84
22	865	770	2.18	0.27	775	744	0.14	0.18
23	751	669	47.31	7.77	699	671	43.21	6.14
24	705	628	33.38	4.61	655	629	31.58	2.12
25	648	577	5.08	0.69	580	557	4.57	0.62
26	511	455	0.83	0.17	473	454	1.29	3.17
27	511	455	0.92	4.14	458	440	0.89	0.16
28	446	397	351.91	0.26	418	402	240.96	0.24
29	403	358	3.79	14.04	397	381	58.31	0.09
30	388	346	1.71	0.12	372	358	4.95	12.24
31	353	314	20.10	0.09	326	313	8.94	0.07
32	350	311	1.24	10.19	322	309	0.92	7.72
33	262	233	1.80	3.60	243	234	2.59	2.71
34	172	153	0.39	0.82	158	152	0.33	3.57
35	171	152	0.45	3.38	156	150	0.54	1.05
36	3997	117	0.50	0.58	119	114	0.41	0.78

**Table 4:** Theoretically computed total energies (a.u.), zero-point vibrational energies (kcal mol<sup>-1</sup>), rotational constants (GHz) and entropies (cal mol<sup>-1</sup> K<sup>-1</sup>) for 4-chloro-2-bromoaniline.

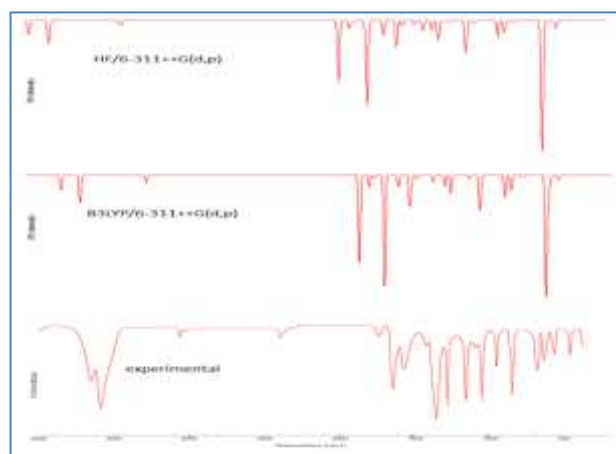
Parameters	HF/6-31++G(d,p)	B3LYP/6-31++G(d,p)
Total energy	-3316.3383794	-3320.7085225
Zero-point energy	60.030	61.562
Rotational constants	1.688	1.671
	0.537	0.526
	0.407	0.400
Entropy		
Total	90.462	92.422
Translational	41.857	41.857
Rotational	31.143	31.191
Vibrational	17.462	19.374

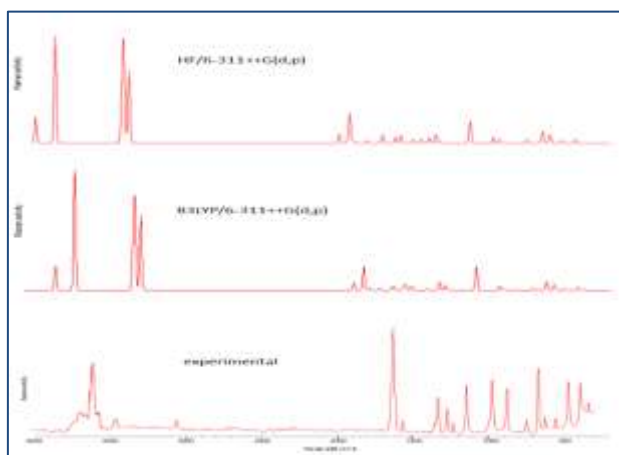
The bands at 671 cm<sup>-1</sup> and 456 cm<sup>-1</sup> in FT-IR (670 cm<sup>-1</sup> and 460 cm<sup>-1</sup> in FT-Raman) and the calculated value of 671 cm<sup>-1</sup> and 454 cm<sup>-1</sup> are assigned to C–C deformation of phenyl ring. In primary amines, usually the N–H stretching vibrations occurs in the region 3600–3300 cm<sup>-1</sup> 29,30. The NH<sub>2</sub> group has two vibrations one is being asymmetric and other symmetric. The frequency of asymmetric vibration is higher than that of symmetric one. In the present study, the asymmetric and symmetric of N–H stretching is assigned at 3600 cm<sup>-1</sup> in FT-IR and 3596, 3480 cm<sup>-1</sup> in FT-Raman. The N–H in-plane bending vibrations are usually observed in the region 1630–1610 cm<sup>-1</sup> and the out of plane bending vibrations are normally identified in the region 1150–900 cm<sup>-1</sup> 31,32. In the title molecule the N–H in-plane bending vibrations at 1630 cm<sup>-1</sup> in both FT-IR and FT-Raman spectra and the out of plane bending vibrations at 1066 cm<sup>-1</sup> and 1063 cm<sup>-1</sup> in the FT-IR and FT-Raman spectra, respectively. These values are consistent with the theoretically calculated value (1069 cm<sup>-1</sup>). The identification of C–N vibrations is very difficult because of the interference of many bands in the area where the vibration of this bond happens. For the aromatic amines, the C–N stretching appear in the region 1382–1266 cm<sup>-1</sup> 33. In the current study, a band appeared at 1352 cm<sup>-1</sup> and 1350 cm<sup>-1</sup> for the stretching vibration of the bond C–N in the FT-IR and FT-Raman, respectively. These values are consistent with the theoretically calculated value (1352 cm<sup>-1</sup>). The vibrations belonging to the bond between the ring and halogen atoms are worth to discuss here since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of the molecule<sup>34</sup>. The assignments of C–Cl stretching and deformation vibrations have been made by comparison with the halogen-substituted benzene derivatives<sup>35</sup>. The C–Cl stretching vibrations give generally bands in the region 710–505 cm<sup>-1</sup>. In the current study, in the FT-IR spectrum of 4-chloro-2-bromoaniline the band at 627 cm<sup>-1</sup> in FT-IR spectrum and at 626 cm<sup>-1</sup> in FT-Raman spectrum are assigned to C–Cl stretching vibration. The theoretical value by B3LYP/6-311++G(d,p) level

predict such a vibration at 629 cm<sup>-1</sup>. The C–Cl in-plane bending and out-of-plane bending vibrations are assigned to the FT-Raman bands at 357 and 235 cm<sup>-1</sup>. This is in agreement with the literature data<sup>35,36</sup>. Bromine compounds absorb strongly in the region 650–485cm<sup>-1</sup> due to the C–Br stretching vibrations<sup>37</sup>. Accordingly in the present case, the C–Br stretching vibration of the 4-chloro-2-bromoaniline is observed at 553 cm<sup>-1</sup> and 551 cm<sup>-1</sup> in the FT-IR and in the FT-Raman spectra, respectively. These values are consistent with the theoretically calculated value at B3LYP/6-311++G(d,p) level (557 cm<sup>-1</sup>).

#### Other molecular properties

Several calculated thermodynamical parameters such as the zero-point vibration energies (ZPVE), the entropy and rotational constants have been presented in Table 5. The variations in the ZPVEs seem to be insignificant. The total energies are found to decrease with the increase of the basis set dimension. The rotational constant values are somewhat higher when calculated in HF than B3LYP. From Table 4, the changes in the total entropy of 4-chloro-2-bromoaniline at room temperature at different basis sets are only marginal.

**Figure 2:** Comparison of experimental and calculated IR spectra of 4-chloro-2-bromoaniline.



**Figure 3:** Comparison of experimental and calculated Raman spectra of 4-chloro-2-bromoaniline.

### CONCLUSION

Based on the Ab initio(HF) and DFT(B3LYP) calculations at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels, complete vibrational properties of 4-chloro-2-bromoaniline have been investigated by FT-IR and FT-Raman spectroscopies. The assignments of the fundamental frequencies are confirmed by the qualitative agreement between the calculated and observed frequencies. The optimized structural parameter such as bond length and bond angle are also calculated and are compared among HF and B3LYP methods. The vibrational frequencies made by quantum mechanical calculation at B3LYP/6-311++G(d,p) level agree satisfactorily with FT-IR and FT-Raman experimental results. Assignments of all the fundamental vibrational modes were examined and proposed in this investigation and also the comparison with the literature support the validity of the background theory.

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