Molecular structure and vibration spectra of 2-amino-5-chloro benzophenone

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ABSTRACT

Molecular and Vibrational structure of 2A5CB were analyzed with the aid of density functional theory at B3LYP/6-31G(d, p) and 6-311G(d, p) level basis sets. Optimized geometrical structures, harmonic vibrational frequencies, intensities, reduced mass, force constants and depolarization ratio have been computed by the B3 based (B3LYP) density functional methods The calculation results also show that the synthesized molecule have microscopic nonlinear optical (NLO) behaviour with non zero values. The Fourier transform infrared (FT-IR) spectroscopic studies were performed for identifying different functional groups present in the compound and compared with the calculated vibrational frequencies. The important thermodynamical parameters were also reported. The simulated infrared spectrum of the title compound shows good agreement with observed spectra.

Keywords: 2A5CB, density functional theory, vibration mode, infrared spectrum
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INTRODUCTION

Many investigations are being conducted to synthesize new organic materials with large second-order optical nonlinearities in order to satisfy day-to-day technological requirements [1]. They have innumerable potential applications in optical computing, telecommunications, optical data storage, etc. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power as compared to inorganic materials [2]. The basic structure of organic nonlinear optical (NLO) materials is based on the π bond system. Due to the over-lap of π orbital, delocalization of electronic charge distribution leads to a high mobility of the electron density. Functionalization of both ends of the μ bond system with appropriate electron donor and acceptor groups can increase the asymmetric electronic distribution in either or both ground and excited states, leading to an increased optical nonlinearity [3, 4].

Vibrational spectral studies of the molecules can provide deeper knowledge about the relationships between molecular architecture, non-linear response and promote the discovery of new efficient materials for technological applications. It is delighting that density functional theoretical (DFT) methods can efficiently provide the molecule structure information, such as the vibrational assignment. Vibrational spectra combined with DFT calculations have been used as an effective tool in the study of NLO active compounds by numerous literatures [5-7].

In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for B3LYP at 6-31+G (d, p) and 6-311++G (d, p) basis sets is compared. In addition, HOMO, LUMO and thermodynamic properties have been used to elucidate the information regarding charge transfer within the molecule.

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MATERIALS AND METHODS

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Experimental Details
The commercially available AR grade 2A5CB (Merck) ($C_{13}H_{10}ClNO$) was purified by repeated recrystallization process using ethanol. The FT-IR spectra of 2A5CB was recorded on BRUKER IFS 66V FT-IR SPECTROMETER using KBr pellet in the range 4000 cm^{-1} to 400 cm^{-1}

Computational Details
Quantum chemical density functional theory calculations were carried out with the 03 version of the Gaussian program package [8] using B3LYP functions [9,10] combined with the standard 6-31G(d, p) and 6-311G(d, p) basis sets referred to as small and large basis sets, respectively. The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wavenumbers. The symmetry analysis for the vibrational modes of 2A5CB is presented in order to describe the basis for the assignments. The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, reduced mass, force constants and other Thermodynamic parameters were calculated

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RESULTS AND DISCUSSION

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Molecular Structure
The optimized structure parameter of 2A5CB calculated at DFT (B3LYP) level with the 6-31G (d, p) and 6-311G (d, p) basis set are listed in Table 1 in accordance with the atom numbering scheme given in Figure 1. All the geometries determined belong to a true minimum proven by real wavenumbers in the vibrational analysis.
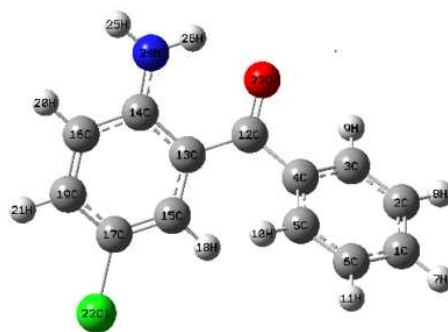

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Figure 1. Optimized Structure of 2A5CB

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The benzene ring appears to be little distorted with (C_{14}–C_{16}) and (C_{13}–C_{14}) bond lengths exactly at the substitution place 1.42 Å by B3LYP/6-31 and 1.43 Å B3LYP/ 6-311 method longer than the remaining bonds (C_{16}–C_{19}), (C_{17}–C_{19}), (C_{15}–C_{17}) and (C_{15}–C_{13}). The actual charge in the C–H bond length would be influenced by the combined effects of the inductive mesmeric interaction and the electron dipole field of the polar substituent. In this study, the C–H bond lengths were calculated as 1.08409, 1.08518, 1.08537, 1.08515 Å by B3LYP/6-31 and 1.08155, 1.08242, 1.08258, 1.08239 Å by B3LYP/6-311 methods. C- Cl single bond length is 1.83 Å by B3LYP/6-31 and 1.81 by B3LYP/6-311 methods.

Bond angles and bond lengths of B3LYP at 6-31+G (d, p) is higher than those of B3LYP at 6-311++G (d, p). The differences in calculated geometrical parameters represent a good approximation and they form the bases for calculating other parameters such as vibrational frequencies and thermodynamics properties.

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Table 1. Optimized geometrical Parameters of 2A5CB obtained by B3LYP/6-31 and 6-311 density functional calculations

Parameter	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311G(d,p)
Bond Distance (Å)		
C_1-C_2	1.40144	1.39681
C_2-C_3	1.39532	1.39103
C_3-C_4	1.40798	1.40267
C_4-C_5	1.40796	1.40295
C_5-C_6	1.39872	1.39424
C_4-C_{12}	1.49601	1.48975
$C_{12}-C_{13}$	1.47276	1.46612
$C_{13}-C_{14}$	1.43768	1.43245
$C_{13}-C_{15}$	1.41660	1.41225
$C_{15}-C_{17}$	1.37994	1.37501
$N_{24}-H_{26}$	1.01396	1.01088
C_3-H_9	1.08409	1.08155
C_2-H_8	1.08518	1.08242
C_1-H_7	1.08537	1.08258
$C_{15}-H_{18}$	1.08115	1.07925
$C_{19}-H_{21}$	1.08342	1.08082
$C_{16}-H_{20}$	1.08577	1.08318
Bond Angle		
$C_1-C_2-C_3$	120.07653	120.06643
$C_2-C_3-C_4$	120.53366	120.45335
$C_3-C_4-C_5$	119.00198	119.14879
$C_3-C_4-C_{12}$	117.80984`	117.97117
$C_{15}-C_{17}-C_{19}$	121.25998	121.19808
$C_{17}-C_{19}-C_{16}$	119.20479	119.27970
$C_{14}-C_{16}-C_{19}$	121.54935	121.59262
$C_{14}-C_{13}-C_{15}$	118.50087	118.69594
$C_{14}-N_{24}-H_{26}$	118.02576	118.16793
$C_{14}-N_{24}-H_{25}$	120.52009	120.61909
$C_1-C_6-H_{11}$	120.13777	120.12677
$H_7-C_1-C_2$	120.09030	120.08034
Dihedral Angle		
$C_1-C_2-C_3-C_9$	178.34667	178.18531
$H_8-C_2-C_3-C_4$	179.02559	179.05516
$C_2-C_3-C_4-C_{12}$	177.00580	176.97847
$O_{23}-C_{12}-C_4-C_5$	139.49235	137.83115
$O_{23}-C_{12}-C_{13}-C_{15}$	163.51258	163.07840
$N_{24}-C_{14}-C_{13}-C_{15}$	-176.33052	-176.19589
$N_{24}-C_{14}-C_{16}-C_{19}$	177.63421	177.48983
$C_{16}-C_{19}-C_{17}-Cl_{22}$	-178.17228	-178.01819
$C_{13}-C_{15}-C_{17}-Cl_{22}$	179.59039	179.41949
$H_{25}-N_{24}-C_{14}-C_{13}$	-177.20305	-176.68677
$H_{26}-N_{24}-C_{14}-C_{16}$	-173.90579	-173.79827
$C_6-C_5-C_4-C_{12}$	-175.82341	-175.78355

Vibration Spectra
Comparative vibrational frequency analysis:
The detailed vibrational assignments of fundamental modes of 2A5CB along with the calculated IR and Raman frequencies and normal mode descriptions are presented in Table 2. The FT-IR spectrum of the title compound is shown in Figure. 2, 3 and 4 respectively. The detailed discussion of our assignment is presented as follows.
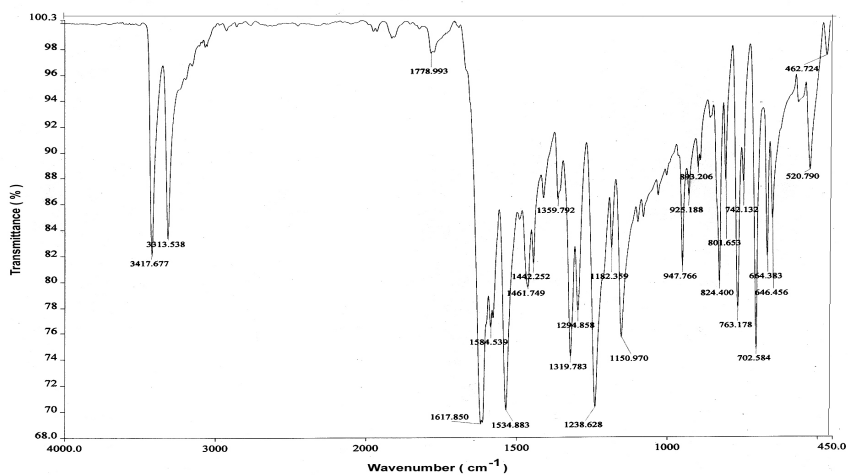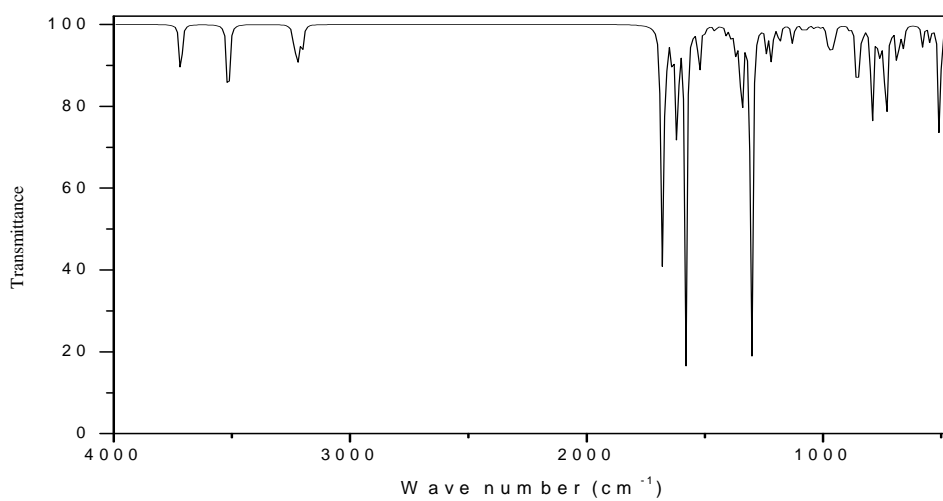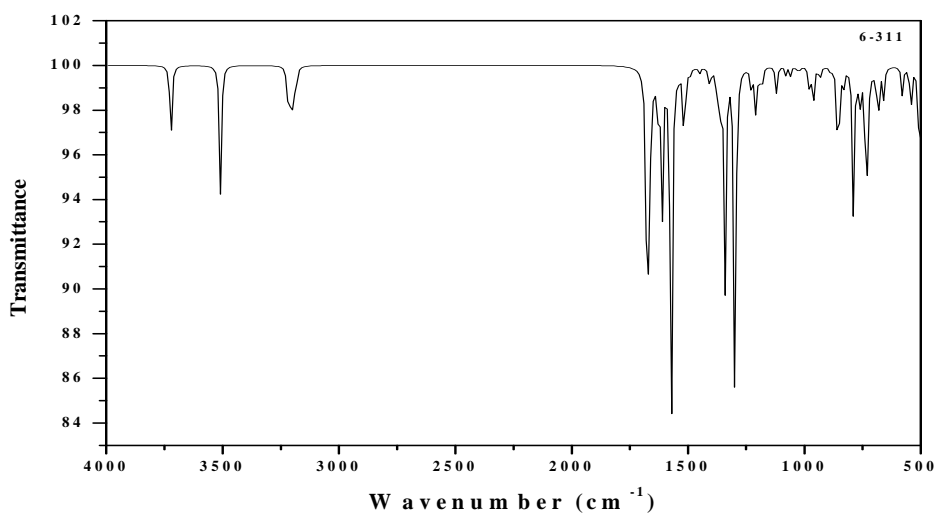
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Figure 2. Experimental FT-IR Spectrum of 2A5CB

Figure 3. Observed FT-IR Spectrum of 2A5CB by DFT (B3LYP/6-31G(d,p))

Figure 4. Observed FT-IR Spectrum of 2A5CB by DFT (B3LYP/6-311G(d,p))

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<p align="center">Table 2. Experimental and Calculated B3LYP/6-31 and 6-311 levels of vibrational frequencies of 2A5CB</p>

Experimental Frequency (cm^{-1})	Observed						Assignments
	B3LYP/6-31G(d,p)			**B3LYP/6-311G(d,p)**			
	FT-IR frequency	Reduced mass	Force constant	FT-IR frequency	Reduced mass	Force constant	
-	3715.94	1.0964	8.9202	3722.6831	1.0959	8.9478	OH st
3417.677	3515.0564	1.0528	7.6638	3509.2106	1.0542	7.6489	OH st in COOH
3313.538	3258.9633	1.0911	6.8277	3231.0783	1.0917	6.7151	CH$_2$ asy st
-	3239.7594	1.0944	6.7679	3222.5666	1.0950	6.6998	CH$_2$ asy st
-	3235.4790	1.0967	6.7644	3218.4139	1.0987	6.7052	CH$_2$ asy st
-	3228.2931	1.0954	6.7262	3210.5085	1.0958	6.6545	CH$_2$ asy st
-	3218.1065	1.0926	6.6669	3200.0910	1.0927	6.5932	CH$_2$ asy st
-	3207.0449	1.0887	6.5971	3189.8020	1.0886	6.5261	CH$_2$ asy st
-	3199.2617	1.0894	6.5695	3184.5796	1.0895	6.5102	CH st
-	3196.4633	1.0857	6.5357	3179.6772	1.0860	6.4690	CH str
1778.993	1681.4818	1.4084	2.3462	1674.7923	1.6277	2.6900	
-	1658.8693	5.3735	8.7124	1654.3186	5.4469	8.7828	C =N st
-	1636.7329	5.2184	8.2366	1631.9275	5.2908	8.3018	C=C st
1617.85	1616.9732	7.2730	11.2040	1611.9455	7.2635	11.1198	C-C st
1584.539	1580.0513	4.4907	6.6054	1572.5485	4.7160	6.8713	NH$_2$ sci
1534.883	1549.3657	2.0832	2.9463	1540.4816	2.1433	2.9967	C=C
-	1523.2954	2.4097	3.2945	1516.3844	2.4992	3.3859	COO asy st
-	1501.4285	2.0928	2.7796	1492.0977	2.0797	2.7280	CH ipb
1461.749	1456.8000	4.6333	5.7935	1450.9675	4.8355	5.9980	CH ipb
1359.792	1364.0269	5.9037	6.4717	1358.8914	4.1816	4.5494	CH opb
1319.783	1344.2491	2.5094	2.6716	1340.6243	2.4767	2.6226	CO st
1294.858	1302.4289	2.7076	2.7060	1297.9533	2.2292	2.2127	CH$_2$opb
1238.628	1238.0158	1.1405	1.0299	1226.9506	1.1372	1.0087	St of aromatic amines
1238.628	1224.7671	1.0813	0.9556	1213.9527	1.0911	0.9474	CO st
-	1217.6118	1.1831	1.0334	1207.8260	1.1969	1.0288	CH$_2$ roc
1182.359	1184.1741	3.7202	3.0736	1184.5540	3.5084	2.9005	CH$_3$ wag
1150.970	1129.2431	2.0640	1.5507	1121.3459	2.1032	1.5582	PhI
-	1126.7418	1.7152	1.2829	1118.7086	1.6457	1.2135	CN st
-	1085.1813	1.7955	1.2458	1080.2103	1.7836	1.2262	OH ipb
-	1066.6194	2.3259	1.5590	1059.7500	2.2972	1.5201	CH ipb
-	1040.1374	1.5194	0.9685	1037.0819	1.4099	0.8934	PhI
-	1035.0563	3.8984	2.4607	1030.4538	4.7481	2.9705	CH d
-	1013.1876	1.3704	0.8289	1018.1875	1.3812	0.8437	NH$_2$ t
947.766	968.5866	2.2222	1.2283	962.7714	3.0950	1.6903	R asyd
925.188	955.7554	1.8091	0.9736	933.7757	1.4444	0.7420	CCC ipb
893.206	887.2285	1.2508	0.5801	885.9578	1.2526	0.5793	CH d
-	856.0534	2.5804	1.1141	856.5765	2.5704	1.1112	CC st
824.400	852.4950	3.1897	1.3658	851.6505	3.4785	1.4865	CH$_3$ opb
801.653	835.3664	2.4462	1.0058	832.6577	2.4461	0.9992	CC st
-	793.0491	1.9205	0.7116	789.2583	1.9263	0.7070	Ring reathing
763.178	763.7355	3.7619	1.2928	763.0289	3.6600	1.2555	R opb
742.132	742.4243	1.3455	0.4370	741.1294	1.3370	0.4327	CN opb
-	729.9617	1.7715	0.5562	728.6383	1.8260	0.5712	CCC opb
702.567	709.8616	4.7147	1.3998	704.8951	4.8053	1.4068	C-Cl st
-	686.0444	6.0258	1.6710	683.8153	5.8764	1.6190	C-Cl st
664.383	662.6824	7.5140	1.9442	660.4432	7.4822	1.9229	C-C b
646.456	649.9636	6.4718	1.6108	646.8011	6.4575	1.5917	NH b
-	579.2447	4.4897	0.8876	579.2938	4.4977	0.8893	CN ipd
520.790	548.0090	3.1115	0.5506	542.8203	3.1846	0.5529	CN ipd
-	507.3123	1.3923	0.2111	504.5728	1.3549	0.2032	C-CO ipb
462.724	481.4718	3.1815	0.4345	479.1220	3.1199	0.4220	C-C b
-	459.4259	2.7401	0.3408	457.9920	2.8623	0.3537	C-C b
-	444.6180	4.0947	0.4769	443.4699	4.1704	0.4832	C-C opb
-	426.4146	2.8639	0.3068	423.5766	2.8300	0.2992	C-C opb
-	405.4540	8.7052	0.8432	401.7271	8.4821	0.8065	OH opb
-	366.8016	14.2011	1.1257	367.8265	14.2642	1.1371	C-Cl ipb
-	328.2700	5.1668	0.3280	324.1742	5.2014	0.3221	C-H d
-	315.0791	5.2373	0.3036	315.2057	5.2229	0.3057	OH opb
-	272.0342	5.6472	0.2462	270.3216	5.6542	0.2434	COO$^-$
-	231.9142	5.1673	0.1637	227.6552	5.1740	0.1580	CO opb
-	182.7593	7.5581	0.1487	183.5828	7.5197	0.1493	CN ipb
-	144.0436	6.5774	0.0804	142.9118	6.5649	0.0790	C-Cl opb
-	123.2750	5.8036	0.0520	121.0165	5.7703	0.0498	CC ipb
-	77.2702	5.8640	0.0206	75.0155	5.7483	0.0191	CNH$_2$ t

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The frequency values computed at B3LYP/6-31+G (d, p) and B3LYP/6-311+G(d, p) basis set contains known systematic error due to negligence of electron correlation. Therefore a linearity can be estimated by plotting the calculated versus experimental frequencies.

From the figure, it is found that the calculated (scaled) frequencies by B3LYP with 6-31G (d, p) basis set are closer to the experimental frequencies than B3LYP/6-311G (d, p).

Certain values obtained by DFT methods, are strongly under estimated. If the variations are omitted, the both B3LYP/6-31 and 6-311 calculations provide good linearity between the calculated and experimental frequencies. The small difference between the experimental and calculated vibrational modes is observed. This discrepancy could be attributed to the environment.

C-Cl Vibrations

In the lower region, C–Cl stretching vibrations appear at 760–505 cm^{-1} and C–Cl deformation vibrations appear in the region 420–250 cm^{-1} [11]. Compounds with more than one chlorine atom exhibit very strong bands due to the asymmetric and symmetric stretching modes. Vibrational coupling with other groups may results in a shift in the absorption to as high as 840 cm^{-1}. For simple organic chlorine compounds, C–Cl absorption is in the region 750–700 cm^{-1} [12]. The band observed at 709 cm^{-1} and 686 cm^{-1} computed by 6-31G(d, p) basis set and the frequencies obtained at 704 cm^{-1} and 683 cm^{-1} by 6-311G(d, p) basis set are assigned to C–Cl stretching vibrations for the title molecule. The sharp peak at 702 cm^{-1} in experimental spectrum is due to C–Cl stretching vibrations. From the above analysis it is found that B3LYP method with 6-311G (d, p) basis set yields better results in accordance with experimental results. The shifts to lower frequencies of 2A5CB, is due to the greater electro negativity of chlorine as compared with carbon atoms. Thus, chlorine atom acquires a small negative charge, and the carbon atom a small positive charge. The inductive effect of chlorine attracts electrons from C–Cl bond, which increases the force constant and leads to an increase in the absorption frequencies. The band is assigned at 366 and 367 cm^{-1} for C–Cl in-plane bending and 144 and 142 cm^{-1} is for out-of-plane bending vibrations respectively.

C-H Vibrations

In aromatic compounds, the carbon–hydrogen stretching vibrations normally occur at 3100–3000 cm^{-1} [13]. These vibrations are not found to be affected due to the nature and position of the substituent. Most of the aromatic compounds have nearly four infrared peaks in the region 3080–3010 cm^{-1} due to ring C–H stretching bands [14-16]. In the present work a sharp peak occurred at 3199 and 3196 cm^{-1} by B3LYP/6-31(d, p) method is due to C-H stretching vibrations. But 6-311(d, p) basis set yield C-H stretching vibrations at 3184 and 3179 cm^{-1}. The infrared peaks identified at 1501, 1456 cm^{-1} (6-31G(d, p) basis set) and 1492, 1450 cm^{-1}(6-311G(d, p) basis set) was due to the effect of C–H in-plane bending vibrations and an experimental counterpart is seen at 1461 cm^{-1} for this title molecule 2A5CB. The vibrations at 1388, 1371, 1364 cm^{-1}(6-31G(d, p) basis set) and 1379, 1367, 1358 cm^{-1} (6-311G(d, p) basis set) and a peak at 1359 cm^{-1} in experimental spectrum are assigned to C-H out of plane bending mode. Thus the candidate material exhibits a prominent C-H vibration which was due to its high organic nature.

C –C Vibrations

The ring C= C and C-C stretching vibrations, known as semicircle stretching occurs in the region 1625–1400 cm^{-1} and 1380–1280 cm^{-1} [17-19]. The C=C stretching vibrations for the title molecule 2A5CB occurred at 1636 cm^{-1}, 1549 cm^{-1}(6-31G(d, p) basis set) and 1549 cm^{-1} and 1540 cm^{-1}(6-311G(d, p) basis set). Experimental spectrum shows a peak at 1534 cm^{-1} which is due to C=C stretching vibrations. The actual positions of C-C stretching modes are determined not so much by the nature of the substituents but by the form of substitution around the ring. In general, the bands are of variable intensity and are observed at 1616 cm^{-1}, 856 cm^{-1}, 831 cm^{-1}(6-31G(d, p)) and 1611 cm^{-1}, 856 cm^{-1}, 832 cm^{-1} (6-311G(d, p)). Experimental values for C-C stretching are observed at 1617 cm^{-1} and 807 cm^{-1}. C–C in-plane and out-of-plane bending vibrations were the modes associated with smaller force constants than the stretching ones, and hence assigned to lower frequencies. The in-plane deformations were at higher frequencies than the out-of-plane vibrations. For this title molecule C-C in plane bending vibrations are observed at 555, 378, 102 cm^{-1} and out of plane bending is at 741 and 452 cm^{-1}.

Other Molecular Properties:
HOMO-LUMO Gap:

The interaction of two atomic (or) molecule orbital produces two new orbitals. One of the new orbitals is higher in energy than the original ones (the anti bonding orbital) and one is lower (the lower orbital). When one of the initial orbitals is filled with a pair of electrons (a Lewis base) and the other is empty (a Lewis acid), we can place the two electrons into the lower, energy of the two new orbitals. The "Filled - Empty" interaction therefore is stabilizing. When we are dealing with interacting molecular orbitals, the two that interact are generally the highest energy occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the compound. These

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orbitals are a pair of orbitals in the compound, which allows them to interact most strongly. These orbitals are sometimes called the frontier orbitals, because they lie at the outermost boundaries of the electrons of compound. The HOMO-LUMO energy gap of 2A5CB was calculated using B3LYP/6-31 G (d, p) and 6-311G (d, p) basis sets. The HOMO - LUMO gap value of the studied compound is -0.28388 a.u and -0.1399 a.u respectively. HOMO - LUMO orbital picture is shown in figure 5 and 6.

The HOMO-LUMO energy gap of 2A5CB reflects the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate an electron. Moreover the lower value in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule [20].
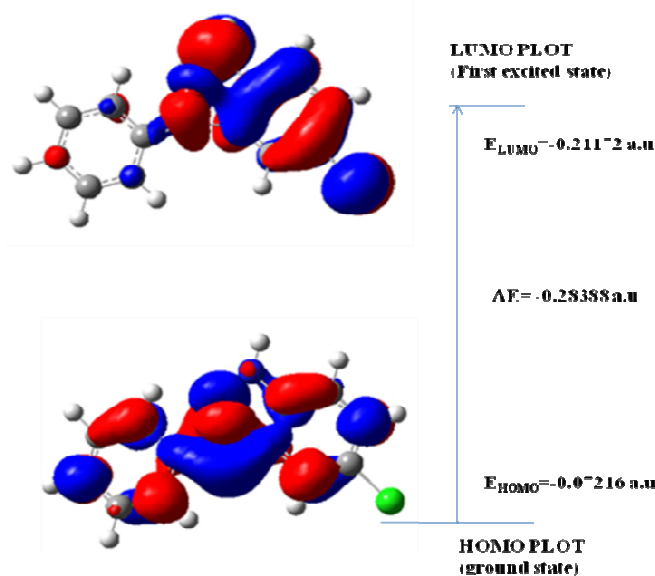

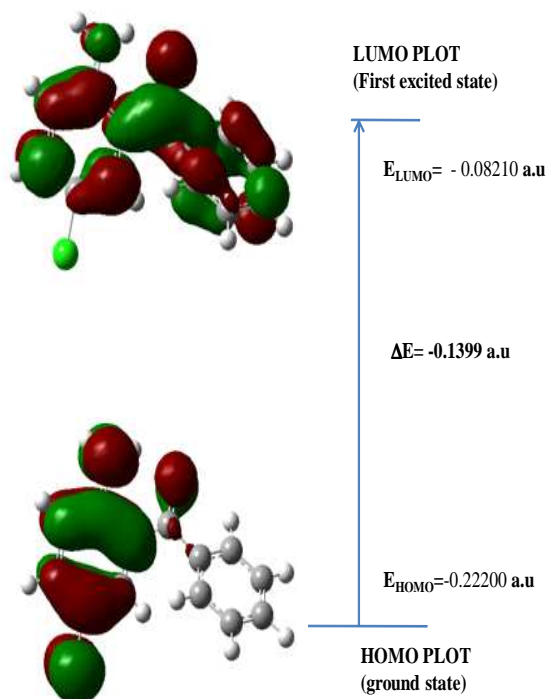**Figure 5. HOMO –LUMO plot of 2A5CB at B3LYP/6-31G(d,p)**

Figure 6. HOMO –LUMO plot of 2A5CB at B3LYP/6-311G(d,p)

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Thermodynamic Properties:

The calculated several thermodynamic parameters have been presented as shown in Table 3. The zero-point vibrational energies (ZPVE), rotational constants, rotational temperature, thermal energy, molar capacity at constant volume and entropy were calculated by B3LYP/6-31+G(d, p) and 6-311++G(d, p) basis sets. The rotational constants and the rotational temperatures were found to decrease with the increase of the basis sets. The important thermodynamical parameters are the thermal energy (134.576 kcal/mol), heat capacity (50.722 cal/mol K), entropy (114.234 cal/mol K) and dipole moment (1.6 Debye).

Table 3. Theoretically computed zero-point vibrational energy, rotational constant, rotational temperature, vibrational temperature, thermal energy, molar capacity at constant volume and entropy for 2A5CB

Parameters	B3LYP/6-31+G(d,p)	6-311++G(d,p)
Zero point vibration energy (kcalmol^{-1})	126.50077	125.93609
Rotational constants (GHz)		
A	0.66687	0.66961
B	0.32446	0.32823
C	0.22909	0.23201
Rotational temperature (k)		
A	0.03200	0.03214
B	0.01557	0.01575
C	0.01099	0.01113
Thermal energy (kcalmol^{-1})		
Total	134.576	134.050
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	132.799	132.273
Molar capacity at constant volume (calmol^{-1}k)		
Total	50.722	50.944
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	44.760	44.982
Entropy (calmol^{-1}k)		
Total	114.234	114.542
Translational	42.214	42.215
Rotational	33.139	33.111
Vibrational	38.881	39.217

CONCLUSION

The FT-IR spectral studies of 2A5CB were carried out and compared with simulated values for the first time. A complete vibrational and molecular structure analysis has been performed based on the quantum mechanical approach by DFT calculation. The difference between the basis set frequencies values of most of the fundamentals is very small. Therefore, the assignment made at DFT higher level at theory with higher basis set with only reasonable deviations from the experimental values, seems to be correct.

REFERENCES

[1] D. Sankar, VinayRajMenon, P.Sagayaraj, J. Madhavan, *Physica B*, January **2010** (405)192-197

[2] T. Sujatha , A. Cyrac Peter , M. Vimalan , J. Merline Shyla , J. Madhavan, *Physica B* , August **2010**,405, pp 3365–3370

[3] S. Senthil, S. Pari, R. John Xavier, J. Madhavan, *Optik*, **2011**, 123, pp 104

[4] M. Victor Antony Raj, J.Madhavan, M. Gulam Mohamed, *J. Comput. Method. Mol. Design*, **2011**, 1 (4):57-64

[5] S. Senthil , S.Pari , P.Sagayaraj , J.Madhavan, *Physica* B, **2009**, pp 1655- 1660

[6] A.CyracPeter , M. Vimalan , P. Sagayaraj , J. Madhavan, *Physica* B,**2010** (405), 65-71

[7] Nagalakshmi R, Krishnakumar V, Hans Hagemann, Muthunatesan S, *J. Molecular Structure*, 988(**2011**) 17-23

[8] M.J. Frisch, et al., Gaussian03, Revision C.02, Gaussian Inc., Pittsburgh, PA, **2003**.

[9] Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill,A.D. Becke, *J. Chem. Phys*. 98 (**1993**) 5648–5652.

[10] C. Lee, W. Yang, R.G. *Parr, Phys. Rev*. B 37 (**1998**) 785–789.

[11] J. Tonannavar, Jayashreeyenagi, *Spectrochim. Acta* A 77 (**2010**) 351–358.

[12] A.R. Krishnan, H. Saleem, S. Subashchandarabose, N. Sundaraganesan, S.Sebatain, *Spectrochim. Acta* A 78 (**2011**) 582–589.

[13] T. Sundius, Vib. Spectrosc. 29 (**2002**) 89–95.

[14] Y.R. Sharma, Elementary Organic Spectroscopy—Principles and Chemical Applications, S. Chand & Company Ltd., New Delhi, **1994**, p. 92.

_____

[15] F.B.S. Vogel, Text Book of Practical Organic Chemistry, 5th ed., Longman/Widely,New York, **1989**

[16] M. Pagannone, B. Formari, G. Mattel, *Spectrochim. Acta* 43A (**1986**) 621–625.

[17] Altun, K. Golcuk, M. Kumru, *J. Mol. Struct. (Theochem)* 155 (**2003**) 637–639.

[18] V. Krishnakumar, R. John Xavier, *Indian J. Pure. Appl. Phys*. 41 (**2003**) 95–98.

[19] N.P. Singh, R.V. Yadav, *Indian J. Phys.* B 75 (4) (**2001**) 347

[20] P.W. Atkins, Physical Chemistry, Oxford University Press, Oxford, **2001**.