

HF, DFT Computations and Spectroscopic study of Vibrational frequency, HOMO-LUMO Analysis and Thermodynamic Properties of Alpha Bromo Gamma Butyrolactone

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Abstract

The molecular vibrations of Alpha Bromo Gamma Butyrolactone have been investigated by Fourier transform infrared (FTIR) and Fourier transform Raman (FT Raman) spectroscopy. The FTIR, FT Raman and UV spectra of the title compound have been recorded in the regions 4000-400, 4000-100 and 800-200 cm^{-1} . The theoretical investigations were carried out using Hartree-Fock (HF) with 6-311 ++G(d,p) basis set and Density functional theory (DFT) method at B3LYP level with 6-311++G(d,p) basis set. The investigation shows clearly that the DFT values are in good agreement with the experimental values. The optimized geometric parameters, the electronic properties such as HOMO and LUMO energies were performed using DFT approach. The thermodynamic properties and Mulliken charge density analysis were also done and their values were tabulated.

Keywords: alpha-Bromo-gamma-butyrolactone, FTIR, FTRaman, HF, DFT, Mulliken

INTRODUCTION

The alpha-Bromo-gamma-butyrolactone is a colourless liquid which boils at from 94 to 106 ° C at 1 mm absolute pressure, has a density at 25° C of 1.79, and has an index of refraction, n of 1.509. The molecular formula is $\text{C}_6\text{H}_5\text{BrO}_2$. Its chemical name is 2-bromo-4 butanolide. The yield of alpha-Bromo-gamma-butyrolactone was 85 percent of theoretical, based on the gamma-butyrolactone as starting material. A solution of 71 grams of phosphorus tri bromide and 1120 grams of gamma-butyrolactone was heated to a temperature of 100° C and 1975 grams of bromine were added gradually and with stirring [1]. The bromine was added at a rate of about 1 gram per second over a period of about 2.5 hours, after which the rate of bromine addition was reduced somewhat to avoid vaporization of free bromine from the mixture. Considerable heat was evolved during the reaction carried out for temperatures of between 120 and 130° C. After th

addition of bromine, the mixture was heated at 130°C, for a period of 4 hours to assure substantial completion of the reaction. The crude product weighed 3100 grams was approximately 98 percent of theoretical. After distillation, the resultant product is alpha-Bromo-gamma-butyrolactone.

EXPERIMENTAL DETAIL

High grade sample of alpha-Bromo-gamma-butyrolactone was purchased from Avira chemicals and was used without further purification. The FTIR spectrum of the sample was recorded using Burker IFS 66V spectrophotometer in the region 400-4000 cm^{-1} and UV absorption spectrum using Jasco V-670 spectrometer in the region 200-800 cm^{-1} . The FT Raman spectrum was taken from IIT using Burker RFS27 recorded in the region 100-4000 cm^{-1} . The assignments were analogue with earlier assignments reported in the literature.

COMPUTATIONAL DETAIL

The entire calculations in the present study were performed at Hartree-Fock (HF) and DFT/B3LYP levels included in the Gaussian 09W package [2] program with the 6-311++G(d,p) basis set function utilizing gradient geometry optimization. The vibrational modes assigned using Gauss-view molecular visualization program package [2-4] for motions observed against fundamental frequencies. B3LYP represents Becke's three parameter hybrid functional method with Lee-Yang-Parr's correlation functional (LYP) [5-7]. Gauss view 5.0 program, a graphical interface was used to study the vibrational assignments, highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO), orbital energy distribution and other thermodynamic properties of the molecule.

RESULTS AND DISCUSSION

Molecular Geometry

The molecule Alpha-Bromo-gamma-butyrolactone has 12 atoms with 30 modes of vibration. The optimized structural parameters have been calculated at B3LYP with 6-31++ G(d,p) and the optimized structure was shown in Figure 4.1. The optimized bond parameters of Alpha Bromo gamma butyrolactone calculated by HF and DFT/B3LYP method using 6-311++G(d,p) basis sets are listed in Table 4.1. In the molecule, optimized bond length of C-O ranges from 1.35-1.44 Å (HF/B3LYP/6-311++G(d,p)). The 6C -2O bond length is slightly higher than 7C-2O, this is because of the presence of double bond in 7C with 3O atom. The C-X (F, Cl, Br etc.) bond length indicates a considerable increase when substituted in place of C-H.

The C-Br bond length is found to be 1.9584 Å which is larger than the C-H bond length which ranges from 1.075-1.094 Å. The C-C bond length is in good agreement with the literature data [8]. The optimized bond angle C-C-C fall in the range from 101.66° to 103.35° which is smaller than the literature value 120°. This is due to the presence of electronegative element Br and O attached to the carbon atoms.

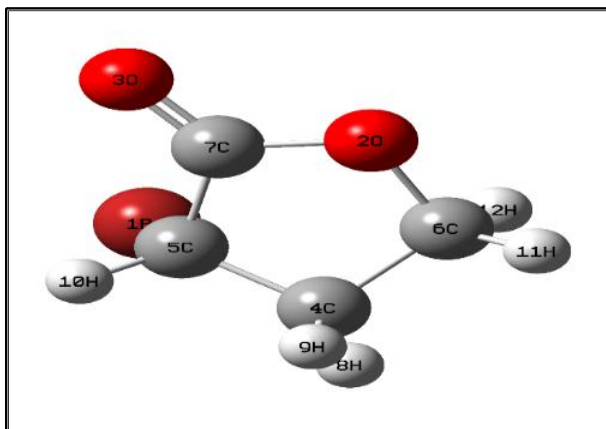


Fig 4.1 Geometry of alpha-Bromo-gamma-butyrolactone at DFT/B3LYP/6-31++G(d,p) level

Table 4.1

Optimized parameters bond length (Å) and bond angle (°) of alpha-Bromo-gamma-butyrolactone

Optimized parameters	Method/basis sets		Experimental
	HF/6-311++G(d,p)	DFT/B3LYP/6-311++G(d,p)	
Bond length (Å)			
R (1,5)	1.99	1.9584	1.93316
R (2,6)	1.4211	1.4468	1.43148
R (2,7)	1.3274	1.3586	1.36857
R (3,7)	1.1723	1.1947	1.22171
R (4,5)	1.5912	1.5091	1.50588
R (4,6)	1.5282	1.5033	1.50962
Bond angle (°)			
A (6,2,7)	112.4075	111.2694	109.7893
A (5,4,6)	101.6683	102.0329	103.3551
A (5,4,8)	114.323	114.2775	115.4495
A (5,4,9)	108.4053	108.3907	108.8743
A (6,4,8)	113.5254	113.4388	112.7821
A (6,4,9)	109.9485	110.0189	108.6855
A (8,4,9)	108.7147	108.4656	107.4912

VIBRATIONAL ASSIGNMENT

The assignments of the experimental wave numbers based on normal mode analysis are tabulated in Table 4.2. Vibrational assignments are based on the observations of the animated modes in Gauss view 5.0 and assignments reported in literature. To overcome discrepancies between the calculated and observed wavenumbers, the calculated values are scaled down to improve the agreement with experimental values. On comparing the HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) value with the experimental value, DFT calculations provide excellent agreement with experimental vibrational frequencies. The Observed and experimental FTIR and FT-Raman spectra are shown in Figure 4.2. and Figure 4.3.

Table 4.2
 Vibrational assignments of fundamental modes of Alpha Bromo gamma butyrolactone

S. No	Observed fundamentals		Calculated frequencies						Vibrational assignments
			HF/6-311++G(d,p)			DFT/B3LYP/6-311++G(d,p)			
	FTIR cm ⁻¹	FT Raman cm ⁻¹	Scaled	IR intensity	Raman Intensity	Scaled	IR intensity	Raman Intensity	
1	2970	3014	3103	1.409	1.407	2970	1.282	1.780	ν (CH)
2		2921	3066	3.706	1.851	2936	2.581	1.955	ν_{as} (CH ₂)
3	2916	2887	3054	3.305	0.350	2929	3.020	0.487	ν_{as} (CH ₂), γ (CH)
4		2856	3007	1.465	2.795	2873	1.290	3.268	ν_s (CH ₂)
5		2773	2970	13.42	9.180	2849	9.750	8.637	ν_s (CH ₂)
6	1766	1777	1907	25.98	12.96	1740	16.78	9.875	ν (C=O)
7	1497	1438	1543	9.940	2.666	1426	6.711	2.687	ξ (CH ₂)
8	1373	1373	1499	11.12	4.013	1388	5.713	5.252	ξ (CH ₂)
9	1311	1313	1433	7.810	3.537	1308	3.327	3.433	ω (CH ₂)
10		1291	1369	0.885	7.881	1256	1.181	7.759	ω (CH ₂)
11	1199	1226	1299	26.61	4.141	1195	35.48	2.277	ω (CH ₂), γ (CH)
12	1151	1208	1268	4.225	6.002	1158	4.259	6.344	τ (CH ₂), ν (C-C), γ (CH)
13			1256	8.032	4.188	1148	26.63	2.756	τ (CH ₂), ν (C-C)
14		1120	1222	22.35	1.325	1120	68.01	3.274	τ (CH ₂)
15	1031	1030	1213	103.7	2.686	1087	21.53	1.148	τ (CH ₂)
16			1107	98.91	3.438	1005	174.7	3.036	ξ (CH ₂), ξ (C-C-C)
17	987	987	1090	78.18	4.317	987	23.17	6.885	ω (CH ₂)
18		939	1015	90.87	3.082	943	46.66	3.634	ν_{as} (C-C-C)
19	889	892	932	54.84	7.388	874	7.115	6.225	Ring breathing
20	837	838	916	9.825	5.102	840	2.550	5.308	γ (CH ₂)
21	742	749	867	11.92	0.471	792	4.868	0.655	γ (CH ₂)

22	675	678	775	37.18	1.432	699	12.99	2.374	ρ (CH ₂)
23			682	8.547	6.753	634	9.601	8.844	ρ (CH ₂)
24	547	551	673	4.230	5.392	625	5.116	7.208	γ (C-C-C)
25			564	572.5	16.30	509	408.9	21.46	C=O oscillation
26	464	467	470	16.48	132.2	430	9.236	174.1	Deformation bending
27		296	298	30.26	88.71	278	24.84	85.93	C-Br deformation
28			196	9.556	69.75	188	8.042	88.06	Deformation bending
29		173	164	24.73	82.85	149	13.21	85.71	Deformation bending
30		71	97	3.326	75.52	95	1.312	83.16	Deformation bending

Abbreviations : ν -stretching, ν_s -symmetric stretching, ν_{as} -asymmetric stretching, β -in plane bending, γ -out of plane bending, ξ -scissoring, ρ -rocking, ω -wagging and τ -twisting.

C-H vibrations

The title molecule gives rise to C-H stretching vibrations at 2970 cm⁻¹ in IR and 3014 cm⁻¹ in Raman which is in good agreement with the literature value 2850-3000 cm⁻¹. The calculated values obtained from DFT method is 2970 cm⁻¹ and 3103 cm⁻¹. The C-H in plane and out of plane bending occurs at 1300-1000 and 1000-750 cm⁻¹ [9] respectively. The FTIR bands at 1311,1119,1151, 1100cm⁻¹ and FT Raman bands at 1313,1291,1226,1208,1120 cm⁻¹ and 1433,1369,1299,1268,1222 cm⁻¹ in HF/6-311++G(d,p) are assigned to C-H in plane bending vibrations of the molecule. The peaks at 1031,1010,943,837 and 742 cm⁻¹ in FTIR and 1040,1030,939,838 and 749 cm⁻¹ in FT Raman and 1087,1005,943,874 and 792 cm⁻¹ in the DFT/B3LYP/6-311++G(d,p) computed value represents the C-H out of plane bending vibrations.

Carbonyl group stretching

The C=O stretching vibration is expected in the region 1750-1680 cm⁻¹ [10]. In the present study, it had been observed at 1740 cm⁻¹ in DFT/B3LYP/6-311++G(d,p) level and at 1907 cm⁻¹ in HF/6-311++G(d,p). A strong band is observed at 1766 cm⁻¹ in FTIR and at 1777 cm⁻¹ in FT Raman were observed representing the presence of C=O in the molecule.

C-Br vibrations

The assignments of C-Br stretching vibrations appear at longer wavelength region (200-480 cm⁻¹) [11]. The assignments of the C-Br stretching vibrations have been made based on the

calculated DFT/B3LYP/6-311++G(d,p) and HF/6-311++G(d,p). The Raman band 467 cm^{-1} , FTIR band 464 cm^{-1} and the calculated value at 430 cm^{-1} (DFT/B3LYP/6-311++G(d,p)), 470 cm^{-1} (HF/6-311++G(d,p)) correspond to C-Br stretching mode. The deformation bending of C-Br occurs at 296 cm^{-1} in FT Raman, 298 cm^{-1} in HF/6-311++G(d,p) and at 278 cm^{-1} in DFT/B3LYP/G(d,p).

CH₂ Vibration

A major coincidence of theoretical values with that of experimental evaluations is found in the symmetric and asymmetric stretching vibrations of the methylene (-CH₂-). The calculated values for symmetric and asymmetric stretching vibrations show good agreement with obtained data (2856 cm^{-1} and 2773 cm^{-1} in FT Raman for symmetric stretching and 2916 cm^{-1} in FTIR and $2921, 2887\text{ cm}^{-1}$ in FT Raman for asymmetric stretching) [12]. The deformation vibrations of -CH₂- group (scissoring, wagging, twisting and rocking) contribute to several normal modes in the low frequency region

C-C vibrations

In general, C-C stretching vibrations give the band in the region of 1430 to 1650 cm^{-1} [13]. The band observed at $1426, 1388, 1158\text{ cm}^{-1}$ (DFT/B3LYP/6-311++G(d,p), $1438, 1373, 1208\text{ cm}^{-1}$ (FT Raman), $1497, 1373, 1151\text{ cm}^{-1}$ (FTIR) and at $1543, 1499, 1268\text{ cm}^{-1}$ (HF/6-311++G(d,p) correspond to C-C stretching mode. From the above discussion it is clear that the experimental values are in good agreement with the theoretical value of DFT/B3LYP/6-311++G(d,p) rather than that of HF/6-311++G(d,p). The ring breathing mode at 874 cm^{-1} coincides quite good with FTIR band at 889 cm^{-1} and with FT Raman at 892 cm^{-1} . The theoretically calculated C-C-C bending mode too is consistent with the recorded spectral values. The in plane C-C-C bending occurs at a higher frequency than the out of plane bending.

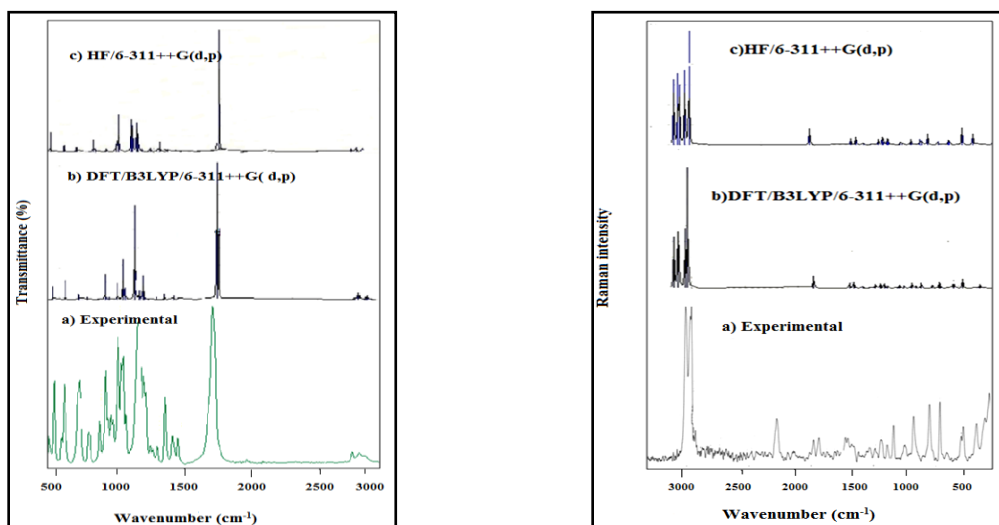


Fig 4.2 Comparison of FTIR spectra and FT-Raman (a) experimental (b) DFT (c) HF

MULLIKEN'S PLOT

The total atomic charges of Alpha Bromo gamma butyrolactone obtained by Mulliken [14] using DFT/B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels have been shown in Figure 3. The presence of bromine atom, an electronegative element makes the carbon atom C₅ positive and the presence of oxygen atom bonded to carbon atom C₇ makes it to be positive.

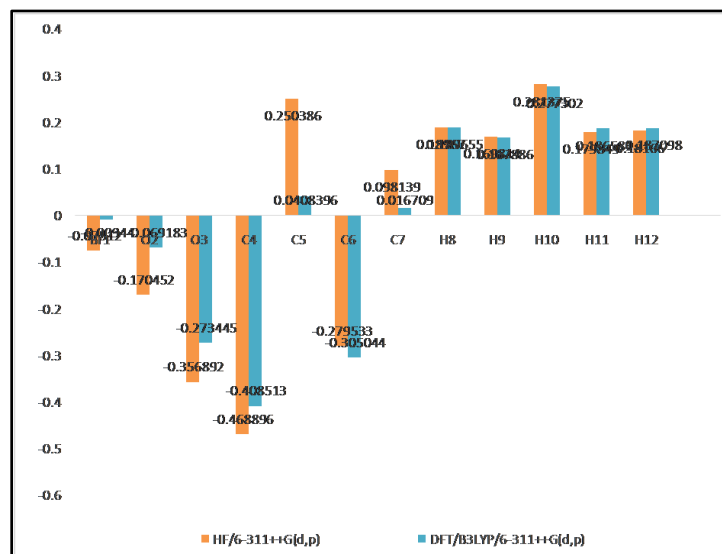


Figure 3: Mulliken's plot of alpha gamma bromo gamma butyrolactone

THERMODYNAMIC PROPERTIES

The thermodynamic properties of the molecule calculated using HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) are presented in Table 3. The energy is minimum at DFT level and other parameters are tabulated.

CONCLUSION

Attempts have been made in the present study for assigning of vibrational frequency for the molecule. The FTIR and FT Raman spectra have been recorded and analysed. The optimized geometries, harmonic frequencies were determined and analysed both at HF and DFT/B3LYP levels of theories using 6-311++G(d,p) basis sets. The theoretical results have been compared with experimental vibrations and values obtained from DFT/B3LYP/6-311++G(d,p) level is in good agreement with the experimental values. Muliken's plot and thermodynamic properties calculated.

Table 3
 Thermodynamic properties of Alpha Bromo gamma butyrolactone

Parameters	HF/6-311++G(d,p)	DFT/B3LYP/6- 311++G(d,p)
SCF energy (a.u.)	-2876.5588	-2880.1191
Total energy (thermal) E_{total} (Kcal mol ⁻¹)	63.707	59.531
Vibrational energy, E_{vib} (Kcal mol ⁻¹)	61.929	57.753
Zero point vibrational energy (Kcal mol ⁻¹)	59.94381	55.55400
Specific heat capacity, C_v (cal mol ⁻¹ K ⁻¹)	20.501	22.251
Entropy, S (cal mol ⁻¹ K ⁻¹)	81.392	82.663
Rotational constant (GHz) X	3.0304600	2.95009
Y	1.3511886	1.32741
Z	1.0778615	1.0894701
Dipole moment μ (Debye) μ_x	0.3559	0.2331
μ_y	-5.2097	-4.6125
μ_z	1.5959	1.4468
Total	5.4603	4.8392

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