

Vibrational assignments of α -acetyl - γ - butyrolactone by ab initio Hartree-Fock and Density Functional methods

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Abstract : The Fourier transform infrared and FT-Raman spectra of α -acetyl- γ -butyrolactone have been recorded in region 4,000–400 and 4,000–100 cm^{-1} respectively. A complete assignment and analysis of fundamental vibration modes of the molecule have been carried out. The observed fundamental modes have been compared with harmonic vibration frequencies computed using density functional theory calculations by employing B3LYP functional at 6-311+G(d,p) level. UV-Visible spectrum of the compound has been recorded and electronic properties, such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies have been calculated with B3LYP/6-311++G(d,p) level. These calculated energies show that charge transfer occurs within molecule. Mulliken population analysis and thermodynamic properties of title compound have also been calculated.

Keywords : α -acetyl- γ -butyrolactone, DFT, HF, FT-IR, FT-RAMAN, UV, HOMO-LUMO.

1. Introduction

α - acetyl - γ - butyrolactone (ABL) as a oxygen containing five- membered Lactone derivative heterocyclic compound. It is a clear slightly yellow liquid and solvable in water 200g/lit at 20⁰C. The α - acetyl - γ - butyrolactone synthesis, from γ - butyrolactone (GBL) with ethyl acetate (EtOAc), and there are two reaction mechanisms involved to produces this compound. One of the reaction mechanisms involves direct method of high cost and environmental pollution method. On other one, the use of synthon as the solvent is safe, minimum environmental pollution and low energy consumption method are performed in the literature [1].

α - acetyl - γ - butyrolactone and its derivatives are important synthon and intermediate products, in organic chemistry. They are used as an intermediate in the synthesis of vitamin B₁ and chlorophyll, to delay heartache and as an anti-angina agent [1]. Pyrodio [1,2-a] pyrimidine derivatives, synthesis from α - acetyl - γ - butyrolactone and its derivatives are used as antihypertensive, tranquillizers, and anti-allergic agent [2]. The microbial reduction of alpha-methyl, allyl and benzyl derivatives of alpha-acetyl-gamma-butyrolactone was carried out[3].

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The present investigation was undertaken to study the vibrational spectra of α - acetyl - γ - butyrolactone to identify the molecular structure and properties with support of FT-IR and FT-Raman experimental spectral data compared to that of theoretical observed data by using DFT/B3LYP/6-311+G(d,p) and HF/6-311+G(d,p). The electronic transition in UV-Vis spectra also analyzed for the molecule. The HOMO-LUMO analysis, Mulliken charge distribution and thermodynamic properties were obtained theoretically from the harmonic vibrations.

The aim of this work is to investigate the molecular structure, vibrational study of the molecule due to its biochemical importance. To the best our knowledge, no work on vibrational assignments, molecular structure and stability have been reported earlier.

2. Experimental Details

The pure sample was purchased from Avra synthesis India Pvt. Ltd., with started purity 98% and was used as such without further purification.

Infrared Spectra

The Fourier transform infrared spectrum of the title compound was carried out with anIR affinity model Shimadzu FT-IR spectrometer with a room temperature DLATGS detector. The spectra of the solids were recorded in technique of KBr pellets in the 4000-400 cm^{-1} spectral region at 4 cm^{-1} spectral resolution accumulating 32 scans.

Raman Spectra

The Fourier transform Raman spectrum was carried out with a Bruker IFS 66V FT-Raman spectrometer equipped with FRA-106 and 1064 nm line of Nd: YAG laser was used for excitation wavelength in the region 4000-50 cm^{-1} and 200 mW output powers. The reported wave numbers are expected to be accurate within $\pm 1 \text{ cm}^{-1}$. The FTIR, FT-Raman spectrums are presented in the Fig 3 and Fig.4 respectively.

UV-Visible Spectra

The Ultraviolet- Visible spectrum was recorded in the range of 200-800nm using with Jasco V-670 spectrometer. The Spectral measurement was carried out by the spectrometer. The response fast scans speed 2000 nm/min with using light source D₂/WI.

3. Computational Details

Quantum chemical calculation were carried out with GAUSSIAN suite of 09W program package on personal computer [4] using Ab initio HartreeFock (HF) and density functional theory (DFT) employing the Becke's Three-parameters hybrid functional[5] combined with Lee-Yang-Parr correction [6] functional (B3LYP) methods has been implemented with 6-311+G(d,p) basis sets. In the present study, the molecular geometry optimizations, vibrational frequency with intensity calculations and other molecular properties of Mulliken charge analysis, thermodynamic properties were carried out by using HF/6-311+G(d,p) and DFT/B3LYP/6-311+G(d,p). The vibrational frequencies are scaled down by the appropriate scaling factor [7] thereby the vibrational assignment are compared with observed values and HOMO-LUMO analysis were calculated by using DFT/B3LYP/6-311+G(d,p).

4. Result and Discussion

4.1 Molecular Structure

The α - acetyl - γ - butyrolactone ($\text{C}_6\text{H}_8\text{O}_3$) molecular structure is shown in the Fig 1. This molecule containing 17 (6 carbon, 8 hydrogen and 3 oxygen) atoms and its molecular weight is 128.127 g/mol.

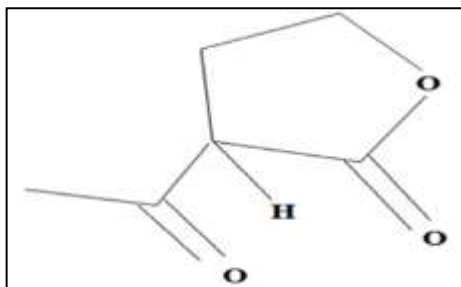


Fig 1 Molecular structure for α – acetyl - γ – butyrolactone

4.2 Molecular Geometry

The optimized structure parameters of ABL calculated by HF and DFT/B3LYP levels with 6-311+G(d,p) basis sets are listed in the Table 1 in accordance with the atom numbering scheme given in Fig. 2. In the table compares the calculated bond angles and bond lengths with experimental data.

The calculated bond length (C=O) of O₂-C₇ in B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) are 1.2007 Å⁰ and 1.1969 Å⁰ respectively which are in good agreement with experimental value 1.2213. Also bond length (C=O) of O₃ – C₈ in B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) are found be 1.2093 Å⁰ and 1.1862 Å⁰ which are in good agreement with experimental value 1.2300 Å⁰. The bond lengths (C-O) of O₁-C₆ and O₁ - C₇ are found to be 1.4483 Å⁰ (B3LYP), 1.4223 Å⁰ (HF) and 1.3517 Å⁰ (B3LYP), 1.3232 Å⁰ (HF) respectively which are in good agreement with experimental values 1.4311 Å⁰ and 1.3688 Å⁰.

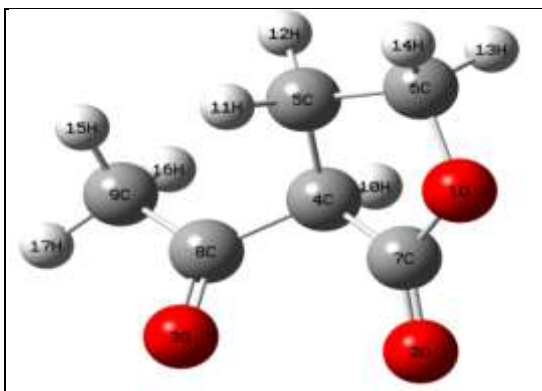


Fig 2. Molecular structure with Atom numbering for α – acetyl γ – butyrolactone

These calculated and experimental values of double bond (C=O) and single bond (C-O) lengths are indicating that its involvement of conjugation [8] and also the small difference between C-O bond lengths of O₁ - C₇ and O₁- C₆ can be attributed to the conjugation of the γ - butyrolactone ring and presence of C-H group in the neighboring position [9]. The O-C-C bond angles of O₁-C₆-C₅=105.7405 and O₃-C₈-C₉=120.5056 in B3LYP/6-311+G(d,p), which are shows interaction between Hydrogen and Oxygen atoms [10]. The CH group bond length are in the range of literature 1.0958-1.1119 Å⁰ for CH₂ and CH₃ groups, the C-H bond lengths are in the range of 1.0918-1.0951 Å⁰ [11]. All the CH bonds in our title molecule (CH₂, CH₃ and C-H) are good agreement with the experimental and literature values.

It is seen that, the C-C bond length of our title molecule are C₄-C₅= 1.5282 Å⁰ and C₅-C₆=1.5325 Å⁰ (B3LYP/6-311+G(d,p)) due to the presence of five atoms in the ring, which is slightly higher when compared to six membered benzene ring (C-C=1.40 Å⁰). Similarly, in our title molecule the bond angle of C-C-C is reduced by 103.0354° (C₄-C₅-C₆), when compared bond angle to benzene ring (C-C-C=120°).

4.3 Analysis of Vibration Spectra

The title compound, ABL consists of 17 atoms with 3N degrees of freedom corresponding to the Cartesian coordinates of each atom in the molecule. In a non linear molecule, 3 of these degrees belong to the

rotational, 3 of these degrees belong to translational motions and remaining (3N-6) corresponds to its vibrational motions [12]. Therefore the net number of modes of vibrations is 45. The detailed vibrational analysis of fundamental modes using HF/6-311+G(d,p) and DFT/6-311+G(d,p) with FT-IR and FT-Raman experimental frequencies of title molecule were presented in Table 2.

The calculated vibrational wave numbers are usually higher than the corresponding experimental quantities because of the combination of electron correlation effects and basis sets deficiencies [38]. Therefore, an empirical uniform scaling factor was used to offset the systematic errors caused by basis set incompleteness of electron correlation and vibrational anharmonicity. For DFT/B3LYP and HF levels with 6-311+G(d,p) basis set, the wave numbers are scaled with 0.95 and 0.91 respectively.

To understand at molecular level, both empirical and quantum chemistry calculations have been widely used in molecular modeling. Empirical approach uses simple models of harmonic potential, electrostatic interaction, and dispersion forces, allow for basic comparisons of energetic and geometry optimization. While quantum chemistry approaches based on explicit consideration of the electronic structure can be either *Ab initio* or semi empirical parameterized. In case of semi empirical model, some quantities can be taken from experiment or estimated by fitting to the data. Additionally, density functional method using electron density as a primary way of describing the system can also be used. In general, semi empirical density functional approximations were mostly used.

4.3.1 Lactone and ketone group vibration

Lactone shows two characteristic intense bands arising from C=O and C – O stretching modes and ketones are best characterized by the strong C=O stretching vibrations [13]. Their vibrations spread over a large range of wavenumber. Lactone and other ring are also found in several different substance of biological interest[14].

4.3.2 C=O (Carbonyl) Vibrations

The intense of C=O stretching vibration appears at higher frequency than that of normal ketones. The carbonyl stretching vibrations in ketones are expected in the region 1680-1715cm⁻¹ and γ - butyrolactone (five-membered ring) are expected in the region 1795-1760cm⁻¹ [15].

Accordingly, in the present study the very strong intense bands in FT-IR spectrum at 1762 and 1713cm⁻¹, which is also observed weak intense bands in FT-Raman spectrum at 1763 and 1719cm⁻¹. The theoretical calculation of B3LYP/6-31+G(d,p) method gives the C=O stretching vibration at 1749 and 1706cm⁻¹ and HF/6-311+G(d,p) gives at 1840 and 1810cm⁻¹.

Table 1 Optimized Geometrical parameters (bond length (Å), bond angles (°)) of α - acetyl- γ - butyrolactone

Parameters	Experiment	B3LYP	HF
Bond Length			
O ₁ -C ₆	1.4311	1.4483	1.4223
O ₁ -C ₇	1.3688	1.3517	1.3232
O ₂ -C ₇	1.2213	1.2007	1.1969
O ₃ -C ₈	1.2300	1.2093	1.1862
C ₄ -C ₅	1.5119	1.5282	1.5250
C ₄ -C ₇	1.5024	1.5418	1.5288
C ₄ -C ₈	1.4905	1.5411	1.5305
C ₄ -H ₁₀	1.0956	1.0967	1.0884
C ₅ -C ₆	1.5077	1.5325	1.5271
C ₅ -H ₁₁	1.0976	1.0913	1.0820
C ₅ -H ₁₂	1.0941	1.0904	1.0822
C ₆ -H ₁₃	1.0950	1.0933	1.0842
C ₆ -H ₁₄	1.0936	1.0890	1.0794
C ₈ -C ₉	1.5047	1.5066	1.5062
C ₉ -H ₁₅	1.0923	1.0955	1.0876
C ₉ -H ₁₆	1.0929	1.0935	1.0835
C ₉ -H ₁₇	1.0937	1.089	1.0811

Parameters	Experiment	B3LYP	HF
Bond Angle			
C ₆ -O ₁ -C ₇	109.5859	111.4617	112.3229
C ₅ -C ₄ -C ₇	101.7725	103.5983	102.6615
C ₅ -C ₄ -C ₈	111.3671	115.1755	115.9522
C ₅ -C ₄ -H ₁₀	111.6432	112.3620	111.4068
C ₄ -C ₅ -C ₆	102.4539	103.0354	101.9258
C ₄ -C ₅ -H ₁₁	110.9552	108.9286	109.5100
C ₄ -C ₅ -H ₁₂	113.5380	113.2241	113.4417
C ₆ -C ₅ -H ₁₁	109.8516	111.2637	110.9135
C ₆ -C ₅ -H ₁₂	112.3546	112.1941	112.5142
H ₁₁ -C ₅ -H ₁₂	107.6558	108.1445	108.4327
O ₁ -C ₆ -C ₅	105.0690	105.7405	105.1446
O ₁ -C ₆ -H ₁₃	108.4901	107.6457	108.2198
O ₁ -C ₆ -H ₁₄	109.7109	107.1842	107.6920
C ₅ -C ₆ -H ₁₃	112.3157	112.7501	112.4769
C ₅ -C ₆ -H ₁₄	112.0556	114.0122	113.9476
H ₁₃ -C ₆ -H ₁₄	109.0659	109.1182	109.0437
O ₁ -C ₇ -O ₂	124.3934	122.7956	123.4653
O ₁ -C ₇ -C ₄	109.6282	109.3068	109.2111
O ₂ -C ₇ -C ₄	125.9651	127.8967	127.3210
O ₃ -C ₈ -C ₄	121.6358	120.5056	120.4075
O ₃ -C ₈ -C ₉	121.6382	123.1447	122.8004
C ₄ -C ₈ -C ₉	116.7258	116.3494	116.7852
C ₈ -C ₉ -H ₁₅	110.0457	109.5984	109.1824
C ₈ -C ₉ -H ₁₆	109.7827	109.6194	110.0641
H ₁₅ -C ₉ -H ₁₇	108.8866	109.6009	109.4834
H ₁₆ -C ₉ -H ₁₇	108.3694	110.7706	110.532

The higher IR frequency at 1762 was assigned to C₇-O₁ stretching. The vibration frequency of ketone carbonyl group C₈-O₃ assigned at 1713 cm⁻¹, which is lower than that of C₇-O₁ bond due to its different position in the molecule. The C₇-O₁ band has in gamma position atom O₁ and belongs to the Lactone group; therefore its frequency is higher than the frequency of the ketone carbonyl group C₈-O₃. [16] The position of the C=O stretching vibration is very sensitive to various factors such as the physical state, electronic effects by substituent, ring strains, [17] etc.

The out of plane bending modes of C=O bonds are observed at 588,465cm⁻¹ in FT-IR and 453 cm⁻¹ in Raman; 567, 442, 58 cm⁻¹ in B3LYP/6-311+G(d,p) and 586, 461, 53 cm⁻¹ in HF/6-311+G(d,p).

4.3.3C – O Vibration

In the C – O stretching region, lactones shows a strong C – O stretching band where as a weaker band occurs for ketone. The 1200-950 cm⁻¹ regions are the C – O stretching region with contribution of C-C vibration [18].

In the present study the very strong bands occurring at 1148 and 1001 cm^{-1} in FTIR spectra are assigned to C – O stretching, and also observed very weak band in Raman spectra at 965 cm^{-1} . The theoretically computed frequencies for C – O stretching vibration at 1104 and 998 cm^{-1} by B3LYP/6-311+G(d, p) and HF/6-311+G(d,p) method gives at 1172 and 1068 cm^{-1} . The inplane bending in the ring of the C–O–C and O–C–C bands are observed at 1148,664 cm^{-1} in FTIR and 698 cm^{-1} in Raman; 1104, 668 cm^{-1} and 1172,700 cm^{-1} in B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) respectively. The out of plane bending of O–C–C bands are observed at 645 cm^{-1} in B3LYP/6-311+G(d,p) and 687 in HF/6-311+G(d,p).

4.3.4 C – H and C – C vibrations

The most characteristics vibrations are those of C – H and C – C stretching and bending. The bonding of CH_3 or CH_2 to atoms other than carbon or carbonyl group or aromatic or hetroaromatic ring may cause appreciable shifts the C – H stretching and bending frequencies.

4.3.5. CH_3 Vibrations

The methyl group is assigned to nine fundamental modes of vibration. Three stretching vibration, one being symmetric and other two asymmetric; three bending vibrations of scissoring, wagging and twisting; two rocking vibrations of inplane and out of plane and single torsion vibration describe the motion of the methyl group [19].

The CH_3 symmetric and asymmetric stretching vibrations generally occur at the region 2850-3000 cm^{-1} . This region is characterized for the confirmation of methyl stretching vibration. The CH_3 asymmetric stretching frequencies are expected in the regions $2985 \pm 20 \text{ cm}^{-1}$ and $2955 \pm 20 \text{ cm}^{-1}$ in which two C-H bonds are extending while the third one is contracting.

In the present study, CH_3 asymmetric stretching vibrations are observed at 3001 cm^{-1} weak intense in IR and very strong intense in Raman spectra at 3004 cm^{-1} . The B3LYP/6-311+G(d,p) gives the frequencies values for CH_3 asymmetric stretching at 3001 and 2950 cm^{-1} and the HF/6-311+G(d,p) method gives at 3001 and 2961 cm^{-1} . The CH_3 symmetric stretching vibrations is expected in the region $2845 \pm 45 \text{ cm}^{-1}$ in which all the three C-H extend and contract in phase.

Table 2. Vibrational assignments of ABL

SL No	Experimental frequencies		Calculated frequencies		Theoretical IR intensity		Theoretical Raman intensity		Assignment
	FTIR	RAMAN	B3LYP	HF	B3LYP	HF	B3LYP	HF	
1	3001	3004	3001	3001	6.59	9.59	69.97	60.97	$\nu_{\text{asy}} \text{CH}_3$
2			2984	2998	18.98	30.45	87.88	86.34	$\nu_{\text{asy}} \text{CH}_2$
3		2968	2972	2982	10.02	13.18	80.78	56.17	$\nu_{\text{asy}} \text{CH}_2, \nu_{\text{sy}} \text{CH}_2$
4			2950	2961	4.33	7.74	48.46	54.24	$\nu_{\text{asy}} \text{CH}_3$
5			2932	2940	10.18	19.42	88.69	122.88	$\nu_{\text{sy}} \text{CH}_2, \text{C-H}$
6			2911	2924	42.46	45.29	133.76	92.57	$\nu_{\text{sy}} \text{CH}_2, \text{C-H}$
7	2920	2923	2895	2900	6.86	11.56	154.66	122.95	$\nu_{\text{sy}} \text{CH}_3, \text{C-H}, \nu_{\text{asy}} \text{CH}_2$
8		2749	2889	2892	3.24	5.07	61.36	61.53	$\nu_{\text{sy}} \text{CH}_3, \text{C-H}$
9	1762	1763	1749	1840	349.04	468.31	12.86	11.26	$\gamma \text{C-O (ring)}$
10	1713	1719	1706	1810	236.69	321.98	9.55	11.48	$\gamma \text{C-O(CH}_2\text{C=O)}$
11		1485	1458	1514	1.13	1.26	6.72	5.07	ξCH_2
12	1423	1424	1435	1483	9.53	12.02	6.71	6.09	ξCH_2
13			1409	1458	16.93	14.14	7.34	6.49	ξCH_3
14			1400	1446	13.33	13.28	6.42	6.37	ξCH_3
15	1360		1334	1403	33.72	83.56	2.85	2.06	ωCH_2
16			1326	1394	47.32	31.30	1.47	0.46	ωCH_3
17		1279	1291	1368	10.30	9.76	1.62	3.17	$\omega \text{CH}_2, \beta_1 \text{CH}$
18			1249	1305	6.29	1.41	3.82	2.22	$\alpha \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
19	1217	1210	1200	1277	16.91	89.68	3.04	3.20	$\alpha \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
20			1178	1237	75.39	89.19	6.19	4.79	$\alpha \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
21			1155	1206	11.36	26.23	2.06	3.02	$\alpha \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
22			1134	1192	1.44	79.44	2.67	1.24	$\gamma \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
23	1148		1104	1172	328.31	144.27	0.66	2.51	$\gamma \text{C-O}, \beta_1 \text{C-O-C}$
24			1075	1118	15.31	3.69	1.25	2.62	$\omega \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
25	1022		1023	1081	5.55	100.91	0.62	2.45	$\gamma \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
26	1001	965	998	1068	73.76	11.15	2.15	0.50	$\gamma \text{C-O (ring)}, \gamma \text{CH}_3$
27			952	979	11.49	5.06	0.96	1.46	$\gamma \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
28			935	964	9.30	2.76	5.58	5.31	$\gamma \text{CH}_2, \beta_1 \text{CH}_2, \beta_1 \text{CH}$
29	937	938	900	939	4.32	16.89	1.88	2.49	$\gamma \text{C-C (ring)}$
30			884	917	17.75	11.08	0.89	2.19	$\beta_1 \text{C-C-C ring}, \gamma \text{C-O}$
31			828	860	1.93	1.43	1.99	1.87	$\gamma \text{CH}_2, \gamma \text{CH}_3$
32	785	784	754	796	2.92	5.48	7.43	7.84	$\gamma \text{CH}_2, \gamma \text{CH}_3$
33	664	698	668	700	3.24	8.51	13.68	12.40	$\beta_1 \text{C-O-C}, \gamma \text{CH}_2$
34			645	687	4.97	7.66	1.50	0.99	$\beta_1 \text{O-C-C}, \gamma \text{CH}_2$
35	588		567	586	26.18	33.23	3.11	3.88	$\beta_1 \text{C=O}$

The CH_3 symmetric stretching vibration found in Raman spectrum intense bands at 2920cm^{-1} which also found in FT-IR at 2923 cm^{-1} . The B3LYP/6-311+G(d,p) calculation frequencies at 2895cm^{-1} , 2889 cm^{-1} and HF/6-311+G(d,p) calculation frequencies $2900, 2892\text{ cm}^{-1}$.

The CH_3 scissoring vibration are assigned at 1409 and 1400 cm^{-1} in B3LYP/6-311+G(d,p); $1458, 1446$ in HF/6-311+G(d,p) (Not observed experimentally). The CH_3 wagging vibration observed in B3LYP/6-311+G(d,p) at 1326 cm^{-1} and HF/6-311+G(d,p) at 1394 cm^{-1} (not observed experimentally). The CH_3 rocking modes are expected in the region [40] $1100 \pm 95\text{cm}^{-1}$ and $1180 \pm 80\text{cm}^{-1}$. The experimental frequencies of methyl rocking are observed in FT-IR at $1022, 1001, 785\text{ cm}^{-1}$ and which also observed at $965, 784\text{ cm}^{-1}$ in FT-Raman. The B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) calculations gives the CH_3 rocking frequencies at $1023, 998, 828, 754\text{cm}^{-1}$ and $1081, 1067, 860, 796\text{ cm}^{-1}$ respectively. The CH_3 torsion vibration is assigned in FT-Raman at 70 cm^{-1} and theoretically observed at 136 cm^{-1} and 119 cm^{-1} in B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) calculations respectively.

4.3.6. CH₂ - Vibrations

The CH₂ group can assigned basically six fundamental modes of vibrations namely CH₂ symmetric and asymmetric stretching vibration, CH₂ bending vibrations of scissoring, rocking, wagging, and twisting modes [20].

The asymmetric CH₂ stretching vibration generally observed in the region 3000–2900cm⁻¹, while the CH₂ symmetric stretch will appear between 2900 and 2800cm⁻¹[50]. In the present study, Very strong intense band appear in the FT-Raman for CH₂ asymmetric stretching at 2968 and 2923 cm⁻¹ and weak intense in FT-IR at 2920 cm⁻¹. The calculated bands observed at 2984, 2972 cm⁻¹ in B3LYP/6-311+G(d,p) and 2998, 2982, 2900cm⁻¹ in HF/6-311+G(d,p). The symmetric CH₂ stretching vibration in FT-Raman very strong intense band appears at 2968 cm⁻¹. The calculated bands observed at 2971, 2910, 2895 cm⁻¹ in B3LYP/6-311+G(d,p) and 2981, 2940, 2923 cm⁻¹ in HF/6-311+G(d,p) method.

In the present assignment, the CH₂ bending modes follow, in decreasing wavenumber, the general order CH₂ scissoring > CH₂ wagging > CH₂ twist > CH₂ rock. Since the bending modes involving hydrogen atom attached to the central carbon falls into the 1485–645 cm⁻¹ range.

The scissoring frequencies are observed at 1423 cm⁻¹ in IR spectrum and 1485, 1424 cm⁻¹ in Raman spectrum. The CH₂ scissoring vibrations are assigned in B3LYP/6-311+G(d,p) at 1458, 1435 cm⁻¹ and 1514, 1483 cm⁻¹ in HF/6-311+G(d,p). The CH₂ wagging frequencies are found at 1360 in FTIR and 1279 cm⁻¹ in FT-Raman. The theoretical observations in B3LYP/6-311+G(d,p) at 1290, 1075 cm⁻¹ and HF/6-311+G(d,p) at 1403, 1368, 1118 cm⁻¹. The CH₂ twisting vibrations are observed at 1217 cm⁻¹(FTIR); 1210 cm⁻¹ (FT-Raman); 1249, 1200, 1178 and 1154 cm⁻¹ in B3LYP/6-311+G(d,p); 1305, 1277, 1237, 1206 cm⁻¹ in HF/6-311+G(d,p). The CH₂ rocking vibrations are assigned at 785 cm⁻¹(FTIR); 784cm⁻¹(FT-Raman); 1134, 952, 935, 828, 754, 255cm⁻¹ in B3LYP/6-311+G(d,p); 1192,978,964,860,796,259 cm⁻¹ in HF/6-311+G(d,p).

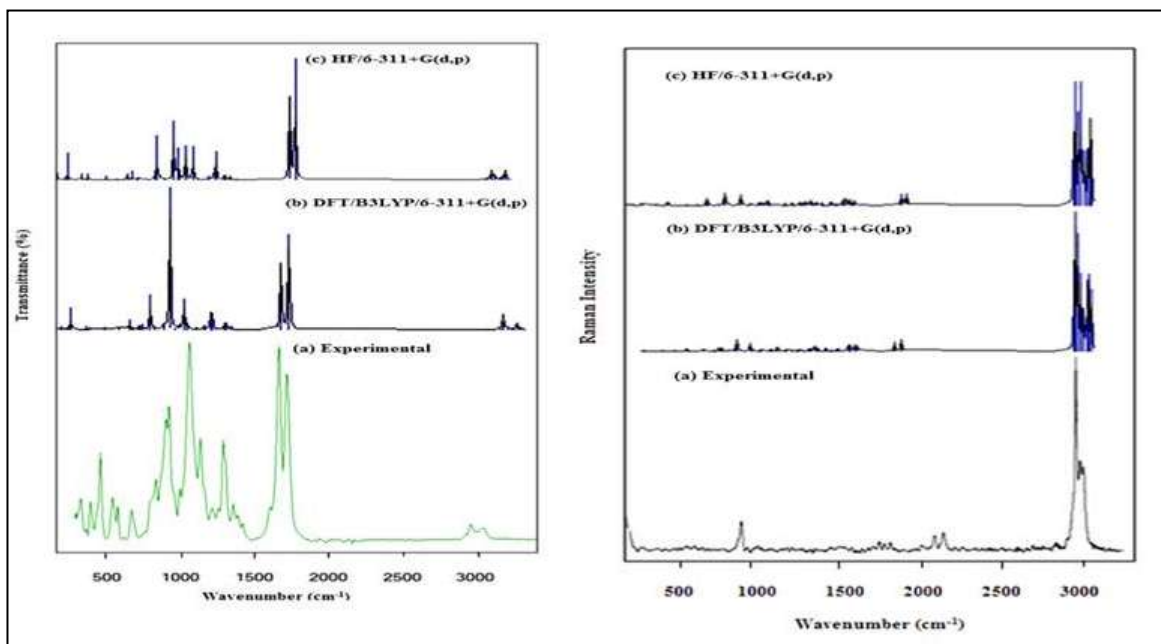


Fig.3 :Comparison of FTIR of ABL Fig.4 Comparison of FTR spectra of ABL

4.3.7 C – H Vibrations

The hetero cyclic organic compounds and its derivatives are commonly exhibit intense peaks in the region 3250-3000 cm⁻¹ due to C-H stretching vibration [21]. In the present study, the C-H stretching frequencies are observed in FT-IR at 2920 cm⁻¹ and 2923 cm⁻¹ in FT-Raman. B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) methods gives at 2932, 2911, 2895, 2889cm⁻¹ and 2940, 2924, 2900, 2892 cm⁻¹ respectively. The out of plane bending vibrations occur in the region 700-1000cm⁻¹, and inplane bending vibrations in the region 1000-1520 [22]. In our present study, the inplane bending experimental bands are observed at 1217 cm⁻¹ in FT-IR and

1279, 1210 cm^{-1} in FT-Raman. The theoretical calculated vibrations has been observed at $1200 \pm 90 \text{ cm}^{-1}$ in both B3LYP/6-311+G(d,p) and HF/6-311+G(d,p). The out of plane bending vibrations has been observed at $998 \pm 77 \text{ cm}^{-1}$ in both B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) methods. The experimental bands are observed at 1022 cm^{-1} in FT-IR.

4.3.8 C – C Vibrations

The C-C stretching frequencies are generally predicted in the region $650\text{-}1650 \text{ cm}^{-1}$ [22]. In our present study, C-C stretching vibrations are observed at 937 cm^{-1} in FT-IR spectrum and 938 cm^{-1} in FT-Raman spectrum. The theoretical C-C stretching vibrations are found at 900 and 939 cm^{-1} in B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) respectively. The bands occurring at 465 and 453 cm^{-1} in FT-IR and FT-Raman spectra have been assigned to C-C-C out plane bending vibrations. The frequencies $550, 519, 442, 336 \text{ cm}^{-1}$ and $581, 529, 461, 340 \text{ cm}^{-1}$ are assigned to C-C-C out of plane bending in B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) respectively. The inplane bending vibrations are found at 884 and 917 cm^{-1} in B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) respectively (Not observed experimentally)[23]

The comparison of experimental and calculated FT-IR and FT-Raman spectra of the title compound are given in the Fig 3.

5. Electronic absorption spectra analysis

The electronic absorption of the title compound was recorded within the $200\text{-}800 \text{ nm}$ range and the experimental UV absorption spectrum is given in the Fig 5.

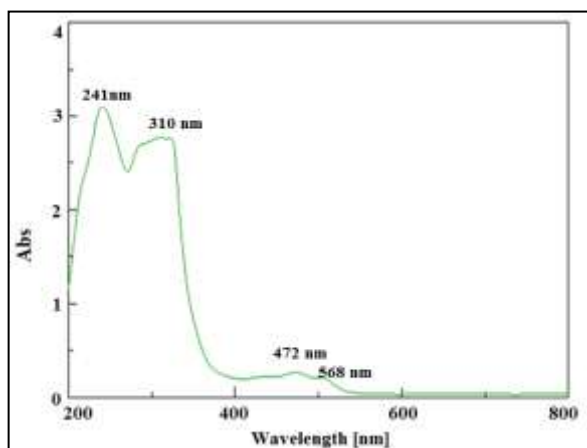


Fig 5 The experimental UV-Vis absorption spectrum of ABL

From this experimental UV spectrum, the maximum absorption values have been found to be 241, 310, 472 and 568 nm. these values may be slightly shifted by solvent effects. The broad absorption bands associated to a strong $\pi \rightarrow \pi^*$ and a weak $\sigma \rightarrow \sigma^*$ transition characterize the UV-Vis absorption spectra. The λ_{max} is a function of substituent, the stronger the donor character substitution, the more electrons transition into the molecules, the larger λ_{max} [24].

4.8 HOMO-LUMO Analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the most important parameters in quantum chemistry molecule [25-26]. HOMO, which can be thought as the outer orbital containing electrons, tends to give these electrons as an electron donor and hence the ionization potential (I_p) is directly related to the energy of the HOMO. On the other hand LUMO can accept electrons and the LUMO energy is directly related to electron affinity (E_A). Energy difference between HOMO and LUMO orbitals is called as energy gap (ΔE) that is an important stability for structures. From the HOMO-LUMO energy gap, one can find whether the molecule is hard or soft. The molecules having large energy gap are known as hard and molecules having a small energy gap are known as soft molecules. A molecule having a

small energy gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [27].

In the present study, the HOMO and LUMO energies are calculated by DFT/B3LYP/6-311+G(d,p) method. Accordingly to the results, the ABL molecule contains 34 occupied molecular orbitals and 212 unoccupied molecular orbitals. The few important molecular orbitals (MOs) were examined for the title compound, the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) which are given in Fig 6. The HOMO and LUMO energies have been focused in order to determine its correlations with interesting molecular/atomic properties and chemical quantities exist and which are, calculated by following expressions [28] and listed in Table 3.;

Ionization potential (I_p) = $-E_{HOMO}$ Electron affinity (E_A) = $-E_{LUMO}$ Global softness (S) = $1/2\eta$

Global hardness (η) = $\left(\frac{-E_{HOMO} + E_{LUMO}}{2}\right)$ Electronegativity (χ) = $-\left(\frac{E_{HOMO} + E_{LUMO}}{2}\right)$

Chemical potential or Fermi energy (μ) = $-\chi = \left(\frac{E_{HOMO} + E_{LUMO}}{2}\right)$ Electrophilicity (ω) = $\frac{\mu^2}{2\eta}$

Table 3. HOMO-LUMO energy values of ABL at DFT/ B3LYP/6-311+G(d,p)

Molecular properties	Calculated Energies (B3LYP/6-311+G(d,p))	
	In a.u.	In eV
HOMO (E_{HOMO})	-0.2760	-7.5112
LUMO (E_{LUMO})	-0.0449	-1.2219
Energy gap (E)	0.2311	6.2870
Ionization potential (I_p)	0.2760	7.5112
Electron affinity (E_A)	0.0449	1.2219
Global hardness (η)	0.1155	3.1447
Global softness (S)	4.3263	117.720
Electronegativity (χ)	0.1604	4.3666
Chemical potential	-0.1604	-4.3666
Electrophilicity (ω)	0.1114	3.0317

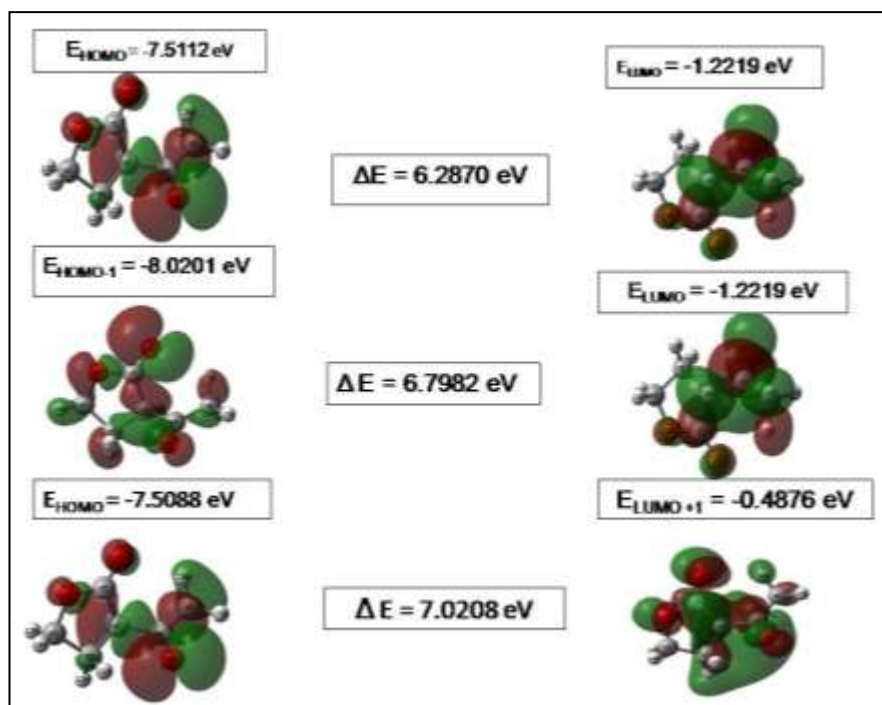


Fig 6 HOMO-LUMO analysis of ABL

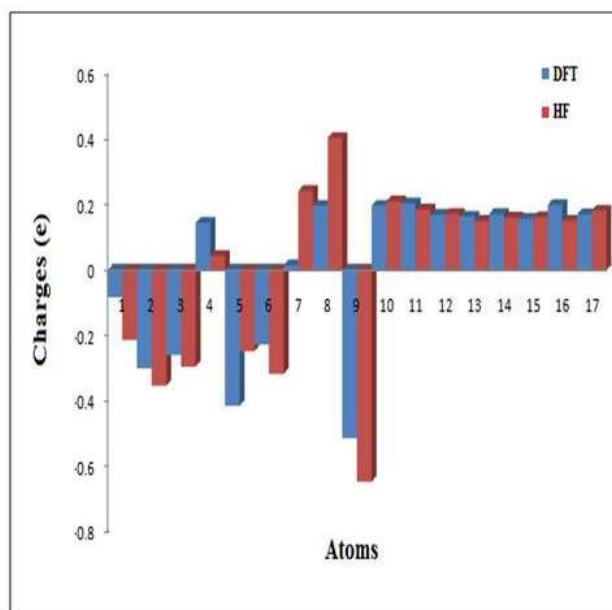
6. Mulliken Atomic Charges

Mulliken charges arise from the Mulliken population analysis [29] and provide a means of atomic charge distribution in the molecule from carried out computational methods. In the application of Quantum mechanical calculations to molecular system, the atomic charges calculations play an important role [30]. Mulliken atomic charge calculation values have been shown in the Table 4.4 using DFT/B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) methods.

Normally, the Carbon atom having negative charge but in our title molecule, carbon atoms show negative charge only that it is attached with Hydrogen atoms, whereas the remaining carbon atoms are positive [31] like C₇ and C₈ carbon atoms are bonded to oxygen atoms, which shows positive charge due to the electrons withdrawing nature of the oxygen atoms [32]. The atom O₂ and O₃ show greater negativity than the atom O₁, due to these O₂ and O₃ atoms are double bond attachment with Carbon atom. In our title molecule, all the Hydrogen atoms are having positive charge. These charge distribution on the molecule has an important influence on the vibrational spectra. The Mulliken charge distribution analysis graph is shown in the Fig 7 and listed in Table 4 using DFT/B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) methods.

Table.4. MPA of ABL

S. No	Atoms	Mulliken Charges	
		DFT/B3LYP/6-311+G(d,p)	HF/6-311+G(d,p)
1	O ₁	-0.082650	-0.212582
2	O ₂	-0.299897	-0.353141
3	O ₃	-0.258632	-0.294131
4	C ₄	0.144699	0.043762
5	C ₅	-0.414058	-0.247395
6	C ₆	-0.226800	-0.316570
7	C ₇	0.015439	0.242876
8	C ₈	0.197595	0.404815
9	C ₉	-0.512657	-0.645992
10	H ₁₀	0.197442	0.210881
11	H ₁₁	0.204356	0.185803
12	H ₁₂	0.170119	0.172620
13	H ₁₃	0.164406	0.150884
14	H ₁₄	0.171955	0.161260
15	H ₁₅	0.157627	0.162362
16	H ₁₆	0.200180	0.151801
17	H ₁₇	0.170876	0.182747

**Fig.6 MPA graph of ABL**

7. Thermodynamic Properties

On the basis of vibrational analysis at DFT/B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) level, several thermodynamic parameters are calculated and are presented in the Table 5. All the thermodynamic properties are helpful information for further study of the title molecule.

Table 5 .Thermodynamic properties of ABL

Parameters	DFT/B3LYP/6-11+G(d,p)	HF/6-311+G(d,p)
SCF Energy (a.u.)	-459.271	-456.569
Total thermal energy, E_{total} (Kcal mol ⁻¹)	90.226	96.330
Zero-point vibrational energy(Kcal/Mol)	84.81281	91.17094
Specific Heat Capacity,C(Cal/Mol-kelvin)	30.782	28.571
Entropy, S (Cal/Mol-Kelvin)	92.070	90.590
Rotational constants (GHZ) X	2.65527	2.75858
Y	1.41706	1.41012
Z	1.03103	1.04879
Dipole moment (Debye) μ_x	0.9550	1.0477
μ_y	2.2542	2.5554
μ_z	3.1491	3.5603
Total	3.9888	4.5060

This can be used to compute the other thermodynamic energies according to relationship of thermodynamic functions and estimate direction of chemical reactions according to second law of thermodynamical field. The value of zero point vibrational energy (ZPVEs) in B3LYP/6-311G(d,p) is lower than HF/6-311G(d,p) method but the value of specific heat capacity (C) and entropy (S) are in B3LYP/6-311G(d,p)

higher than HF/6-311G(d,p) method. Dipole moment reflects the molecular charge distribution and is given as vector in three dimensions [62]. Therefore it can be used as descriptor to depict the charge movement across the molecule depends on the centre of positive and negative charges. The total dipole moment of ABL is calculated by B3LYP/6-311G(d,p) and HF/6-311G(d,p) methods are 3.9888 and 4.5060 Debye, respectively.

8. Conclusion

In the present investigation thoroughly analyzed geometrical parameters, the vibrational spectra of both IR and Raman, HOMO-LUMO analysis of α - acetyl - γ - butyrolactone using DFT/B3LYP and HF methods with 6-311+G(d,p) basis sets. Atomic charge distribution and thermodynamic properties were also determined by using DFT/B3LYP and HF methods. The theoretical results were compared with experimental results. The small differences between experimental and theoretical values are observed due to fact that the experimental result belongs to solid phase and a theoretical calculation belongs to gaseous phase. It is clear that, most reliable theoretical information is provided by DFT/B3LYP/6-311+G(d,p) based quantum mechanical approaches for the molecule. The calculated HOMO and LUMO energy gap, chemical hardness and softness of the molecule are indication of the chemical stability of the molecule. The electronic transitions in UV-Vis spectra were analyzed for understanding the properties and activities of the molecule. In conclusion, all the calculated data and simulations not only show the way to the characterization of the molecule but also help for the application in fundamental researches in Chemistry, Pharmaceutical and biological industries in the future.

References

1. Wei Wang, Sheng-Wan Zhang, Mei-Ping Li, Ying-Yu Ren, (2012), "Mechanism of α -acetyl- γ -butyrolactone synthesis", Chemical Papers, pp i-vii.
2. Raghunath B. Toche, Pankaj B. Awarea, Satish M. Chavanb, Vasant M. Patila, Poonam S. Patila, "Simple route for the synthesis of pyrido [1, 2-a] pyrimidine derivatives", Der Pharma Chemica, (2016), Vol- 8(3), PP.146-151.
3. Ribeiro. Joyce B, Sousa. L.M.A, Fraga. C.A.M., Leite. Selma G.F, Ramos. M.C.K.V, Aquino Neto. F.R. de, Aguiar. L.C.S, Rodrigo O.M.A. de Souza, Antunes. O.A.C, (2008), "Microbial reduction of alpha-substituted-alpha-acetyl-gamma-butyrolactones",
4. Frisch.M.J, Trucks.G.W, Schlegel.H.B, Scuseria.G.E, Robb.M.A, Cheeseman.J. R, Scalmani .G, Barone.V, Mennucci .B, Petersson .G. A, Nakatsuji .H, Caricato.M, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, Ehara. M, Toyota. K, Fukuda. R, Hasegawa.J, Ishida. M, Nakajima.T, Honda. Y, Kitao.O, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, Heyd. J. J, Brothers. E, Kudin .K.N, Staroverov .V. N, Keith. T, Kobayashi.R,hi., Normand .J, Raghavachari. K, Rendell. A, Burant .J. C, Iyengar. S. S, Tomasi, Cossi. M, Rega. N, Millam. J. M, Klene .M, Knox. J. E, Cross. J. B, Bakken. V, Adamo. C, Jaramillo. J, Gomperts. R, Stratmann. R. E, Yazyev. O, Austin. A. J, Cammi. R, Pomelli.C, Ochterski. J. W, Martin. R. L, Morokuma.K, Zakrzewski. V. G, Voth. G. A, Salvador. P, Dannenberg, Dapprich. S, Daniels. A. D, Farkas. O, Foresman .J. B, Ortiz. J. V, Cioslowski .J. J, Fox D. J, (2013), "Gaussian Inc.," Wallingford CT, Gaussian 09.
5. Axel D. Becke, (1993), Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. Vol 98 (7), pp 5648-5652.
6. Burkhard Miehlich, Andreas Savin, Hermann Stoll and Heinz Werner Preussg, (1989), "Result obtained with the correlation energy Density Functionals of Becke and Lee, Yang and Parr, J. Chemical physics Letters, Volume 157, pp 200-206.
7. Anthony P. Scott and Leo Radom, (1996), Harmonic Vibrational Frequencies: An Evaluation of Hartree-Fock, Møller-Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors, J. Phys. Chem., Vol 100, pp 16502-16513.
8. Zhang Rui-Zhou, Li Xia-Hong, Zhang Xian-Zhou, (2012), "Molecular structure, vibrational spectra and theoretical NBO, HOMO-LUMO analysis of N-benzoyl glycine by DFT and ab-initio HF methods" Indian Journal of Pure & Applied Physics, Vol 50, pp 719-726.
9. Tomy Joseph, Hema Tresa Varghese, Yohannan Panicker. C, Thies Thiemann, Viswanathan.K, Christian Van Alsenoy, Manojkumar. T.K, (2014), "Spectroscopic (FT-IR, FT-Raman), first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis of 2,4-bis(2-methoxyphenyl)- 1-

- phenylanthracene-9,10-dione by ab initio HF and density functional methods", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol 117, pp 413–421.
10. Renjith. R, Sheena Mary. Y, Yohannan Panicker. C, HemaTresa Varghese, Magdalena Pakosinska-Parys, Van Alsenoy. C, Manojkumar. T.K, (2014), " Spectroscopic (FT-IR, FT-Raman), first order hyper polarizability, NBO analysis, HOMO and LUMO analysis of 1,7,8,9-tetrachloro-10,10-dimethoxy-4-[3-(4-phenylpiperazin-1-yl)propyl]-4-azatricyclo [5.2.1.0^{2,6}]dec-8-ene-3,5-dione by density functional methods", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol 124, pp 500–513.
 11. Rajalakshmi.K, Gunasekaran.S, Kumaresan.S, (2014) "Vibrational assignment, HOMO-LUMO and NBO analysis of (2S)-2-[(2S)-1-hydrxybutan-2-yl] amino}ethyl)amino]butan-1-ol by density functional theory ", *SpectrochimicaActa Part A: Molecular and Biomolecular spectroscopy*, Vol 130, pp 466-479.
 12. Sathyanarayana .D.N, (2004), "Vibrational spectroscopy Theory and Applications", New Age International Publishers, New Delhi, Cep 10, pp 413-454
 13. Bento.R.R.F, Freire P.T.C, Teixeira.A.M.R.,Silva.J.H., Lima Jr .J.A, de Oliveira M.C.F, Andrade-Neto. M, Romero.N.R, Pontes. F.M, (2009)," Vibrational spectra of pilocarpine hydrochloride crystals", *Brazilian Journal of Physics*, Vol 39, pp 62-68.
 14. Norman B. Colthup, Lawrence H. Daly, Stephen E. Wiberley (1990), "Introduction to Infrared and Raman spectroscopy", Harcourt Brace Jovanovich publishers -Academic Press Ltd., London, pp 307-308.
 15. Khaled Bahgat, (2006), "Scaled quantum chemical studies of the structural and vibrational spectra of acetyl coumarin", *Central European Journal of Chemistry*, Vol 4(4), pp 773-785.
 16. Zhang Rui-Zhou, Li Xia-Hong, Zhang Xian-Zhou, (2011), "Molecular structure, vibrational spectra and NBO analysis on 1N-acetyl-3-(2, 4dichloro-5-fluoro-phenyl)-5-(p-methyl-phenyl)-2-pyrazoline is using DFT method", *Indian Journal of Pure & Applied Physics*, Vol 49, pp 731-739.
 17. Betty Matsuhira, Igor O. Osorio-Románb, Rodrigo Torresa, (2012), "Vibrational spectroscopy characterization and anticoagulant activity of a sulfated polysaccharide from sea cucumber *Athyonidium chilensis*", *Carbohydrate Polymers*, Vol 88, pp 959- 965.
 18. Udhayakala.P, Rajendiran.T. V, Seshadri.S, Gunasekaran.S, (2011), "Quantum chemical vibrational study, molecular property and HOMO-LUMO energies of 3-bromoacetophenone for Pharmaceutical application", *J. Chem. Pharm. Res.*, Vol 3(3) pp 610-625.
 19. Chandraa.S, Saleemb.H, Sebastianc.S, Sundaraganesana.N, (2011), " The spectroscopic (FT-IR, FT-Raman), NCA, first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis of l-cysteine by ab initio HF and density functional method", *Spectrochimica Acta Part :A*, Vol 78, pp 1515–1524.
 20. Ramesh. R, Gunasekaran.S, Ramkumar.G.R, (2015), "Molecular Structure, Vibrational Spectra, UV-Visible and NMR Spectral Analysis on Ranitidine Hydrochloride using AB Initio and DFT Methods", *Int. J.Curr.Res.Aca.Rev*, Vol 3(11), pp 117-138.
 21. Chaitanya.K, Santhamma.C, Prasad. K.V, Veeraiah. V, (2012), "Molecular structure, vibrational spectroscopic (FT-IR, FT-Raman), first order hyperpolarizability, NBO, analysis, thermodynamic properties of 3, 5-dimethylbenzophenone by ab initio HF and density functional method" *J.At.Mol.Sci*, Vol 3, pp 1-22.
 22. Tomy Joseph , Hema Tresa Varghese, Yohannan Panicker.C, Viswanathan.K , Martin Dolezal, Christian Van Alsenoy, (2013), "Spectroscopic (FT-IR, FT-Raman), first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis of N-[(4-(trifluoromethyl)phenyl]pyrazine- 2-carboxamide by density functional methods", *Arabian Journal of Chemistry*, Production and hosting by Elsevier B.V. on behalf of King Saud University, pp 1-14.
 23. Prasad.M.V.S, UdayaSri.N, Veeraiah.A, Veeraiah.V, Chaitanya.K, (2013), "Molecular structure, vibrational spectroscopic (FTIR, FT-Raman),UV-Vis spectra, first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis, thermodynamic properties of 2,6-dichloropyrazine by ab initio HF and density functional method", *J. At. Mol. Sci.*, Vol 4, pp 1-17.
 24. Arivazhagan.M, Subhasini.V.P, Kavitha.K, (2014),"The spectroscopic (FT-IR, FT-Raman), MESP, First order hyperpolarizability, NBO analysis, HOMO and LUMO analysis of 1,5- dimethyl naphthalene by density functional method", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, pp 1-48.

25. Cecily Mary Glory.D, Madivanane.R, Sambathkumar.K, (2015), "Electronic Structure Investigations of 3 and 5- Diamino-1,2,4-Triazole By UV–Visible , NMR Spectral Studies and Homo-Lumo Analysis by AB Initio and DFT Calculations", *Elixir Comp. Chem.*, Vol 89 pp 36730-36741.
26. Sangeetha.C.C, Madivanane. R, Pouchaname.V, (2015), "Investigations of FT-IR, FT-Raman, UV-Visible, FT-NMR Spectra and Quantum Chemical Computations of Diphenylacetylene Molecule", *International Journal of Chemical and Physical Sciences*, Vol 4, pp 12-28.
27. Richa Sharma, Yadav.B.S, (2016), " Spectroscopic and Vibrational Characterization of Fluorinated Pyrimidine, NBO, NLO, Thermodynamic functions HOMO LUMO analysis based on density functional theory", *Global Journal of Advanced Research*, Vol 3, pp 601-619.
28. Pawar.A.B, Jadhav.K.D, Sarawadekar.R.G, (2015), "Vibrational study on the molecular structure of Zinc -Juglonate [Zn(5- hydroxy-1, 4-naphthoquinone)2] by DFT and HF calculations"*Der Pharma Chemica*, Vol 7(8), pp 233-240.
29. Sangeetha.C.C, Madivanane.R, Pouchaname.V, (2014), "The Vibrational Spectroscopic (FT-IR & FT Raman, NMR, UV) study and HOMO& LUMO analysis of Phthalazine by DFT and HF Studies", *International Journal of Engineering Research and General Science*, Vol 2, pp 222-250.
30. Gnanasambadan.T, Gunasekaran.S, Seshadri.S, (2013), "Quantum Chemical and Spectroscopic (FT-IR, FT-Raman) Study, First Order Hyperpolarizability, NBO Analysis, HOMO and LUMO Analysis of Selegiline by ab initio HF and DFT Method", *Orient. J. Chem.*, Vol-29(1), pp 185-200.
31. Balachandran.V, Lalitha.S, Rajeswari.S, RastogiV.K, (2014), "Theoretical investigations on the molecular structure, vibrational spectra, thermodynamics, HOMO–LUMO, NBO analyses and paramagnetic susceptibility properties of p-(p-hydroxyphenoxy)benzoic acid", *SpectrochimicaActa Part A: Molecular and Biomolecular spectroscopy*, Vol 121 pp 575-585.
