

Spectroscopic (FT-IR, FT-Raman And UV-Visible) Investigations Of Calcium Acetylaminopropane Sulfonate Using Density Functional Theory

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Abstract: Calcium Acetylaminopropane Sulfonate(CAS) otherwise commonly called as Acamprosate is a drug used for the treatment of alcohol dependence. The drug is a receptor maintains a balance in the human brain. The spectroscopic properties were investigated by FT-IR, FT-Raman. The FT-IR spectrum ($4000-400\text{ cm}^{-1}$) and FT-Raman spectrum ($4000-100\text{ cm}^{-1}$) in solid phase was recorded for CAS. The equilibrium geometry harmonic vibrational frequencies, infrared intensities and Raman scattering activities were calculated by Hartee Fock(HF) and density functional theory(DFT) B3LYP methods with 6-31+G(d,p) basis set, using Gaussian 03W program package on a Pentium IV/1.6 GHz personal computer. Theoretical vibrational frequencies are calculated using HF and DFT methods. UV-vis spectrum of the molecule was recorded and the electronic properties, such as highest occupied molecular orbitals (HOMO) and the lowest-lying unoccupied molecular orbitals (LUMO) energies were performed by DFT using 6-31+G(d, p) basis sets. The calculated HOMO and LUMO energies show that, the charge transfer occurs within the molecule. The first-order hyperpolarizability and other related properties of CAS are calculated using density functional theory (DFT) on a finite field approach. The calculated results also show that the CAS molecule may have microscopy nonlinear optical (NLO) behavior with non zero values. Thermodynamic properties of CAS were calculated.

Keywords: DFT, CAS, FTIR, FT-RAMAN, HOMO-LUMO.

1. Introduction

Alcoholism is a broad term for problems with alcohol, and is generally used to mean compulsive and uncontrolled consumption of alcoholic beverages, usually to the detriment of the drinker's health, personal relationships, and social standing. It is medically considered a disease, specifically an addictive illness, and in psychiatry several other terms are used, specifically "alcohol abuse" and "alcohol dependence," which have slightly different definitions. CAS, also known as *N*-acetyl homotaurine[1]. and by the brand name Campral, is a drug used for treating alcohol dependence. Campral was manufactured and marketed in the United States by Forest Laboratories, while Merck KGaA markets it outside the US. It is sold as 333 mg white and odorless tablets of acamprosate calcium, which is the equivalent of 300 mg of acamprosate [2]. CAS is a white, odorless or nearly odorless powder. It is freely soluble in water, and practically insoluble in absolute ethanol and dichloromethane. CAS was first made available in the UK in 1996. It is used in the UK, Republic of Ireland, Australia and many other countries

2. Experimental Details

The pure compound CAS was purchased from Sigma-Aldrich Chemical company, USA with more

than 98% purity and was used as such without further purification to record FTIR and FT Raman spectra. The FTIR spectrum of the compound is recorded in the region 4000–400 cm^{-1} in evacuation mode on Bruker IFS 66V spectrophotometer using KBr pellet technique (solid phase) with 4.0 cm^{-1} resolution. The FT Raman spectrum is recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 3500–100 cm^{-1} on Bruker IFS 66V spectrometer equipped with FRA 106 FT Raman module accessory. The spectral measurements were carried out at Sophisticated Instrumentation Analysis Facility, IIT, Madras, India. The experimental FTIR and FT Raman spectra of CAS are presented in the Figs. 1 and 2.

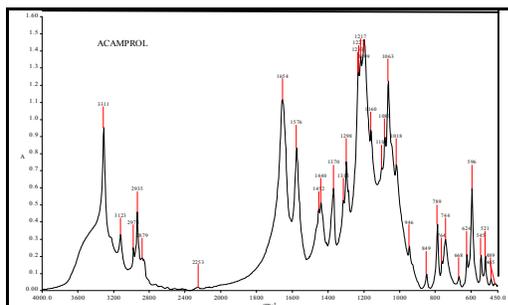


Fig.1. FTIR spectrum of CAS

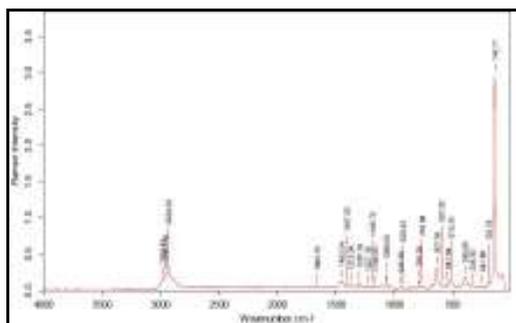


Fig.2. FT-Raman spectrum of CAS

3. Computational Methods

In the present work, the density functional method (DFT) has been employed using Becke's three parameter hybrid exchange functional [3] with the Lee–Yang–Parr correlation functional [4] to optimize the structure of the molecule and also to calculate the electronic structure of the title molecule. The entire calculations were performed at ab initio Hartree Fock (HF) and DFT method using B3LYP levels at 6-31+G(d,p) basis sets on a Pentium V/1.6 GHz personal computer by using Gaussian 03W program package [5] and applied geometry optimization [6]. Initial geometry generated, was minimized at the Hartree Fock level using 6-31+G(d,p) basis set and also optimized at DFT/B3LYP levels at 6-31+G(d,p) basis set. The vibrational modes are assigned using Gauss-View molecular visualization program package. The vibrational frequencies were calculated and scaled down by the appropriate scaling factor and thereby the vibrational assignments are compared with observed values. Gauss View 4.1 program have been used to study HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) orbital energy distribution, frontier orbital energy gaps (a.u.) of the title molecule were calculated by DFT method based on the finite field approach.

4. Results and Discussion

4.1 Vibrational Assignments

The aim of the vibrational analysis is to decide which of the vibrational modes give rise to each of these observed bands. The molecule has 22 atoms and 60 normal modes of fundamental vibrations ($3N-6$). A satisfactory vibrational band assignment has been done and shown in Table 1. Chemcraft [7], a graphical

interface, was used to assign the calculated harmonic wavenumbers using scaled displacement vectors to identify the motion of modes. On the whole, the predicted vibrational wavenumbers are in agreement with the experimental results.

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42	596	597	668	618	11.7589	0.7826		608	10.09	0.7370	$\beta(\text{C}=\text{O})$ $\tau(\text{CH}_2)$
43	545	541	617	562	84.0295	1.6808	625	558	55.62	1.4042	$\omega(\text{CH}_2)$ $\gamma(\text{C}-\text{H})$ $\beta(\text{N}-\text{H})$ $\beta(\text{C}=\text{O})$ $\beta(\text{C}-\text{O})$
44	521		572	537	41.2452	1.1829	514	532	101.78	0.4361	$\beta(\text{C}-\text{C})$ $\beta(\text{S}=\text{O})$ $\beta(\text{S}-\text{O})$ $\omega(\text{CH}_2)$
45	489		517	502	10.6028	0.7253	486	493	71.87	0.2081	$\beta(\text{C}-\text{CH}_3)$ $\beta(\text{C}=\text{O})$ $\beta(\text{N}-\text{H})$ $\beta(\text{C}-\text{C})$
46	465		475	487	13.7981	0.6428	454	478	32.23	0.7834	Ring breathing
47		395	452	419	115.1376	0.1399	420	411	36.35	0.3583	$\beta(\text{C}-\text{S})$ $\beta(\text{C}-\text{C})$ $\gamma(\text{O}-\text{H})$
48		322	434	338	27.9872	0.3658	392	331	45.57	0.3643	$\beta(\text{O}-\text{H})$ $\beta(\text{C}-\text{CH}_3)$ $\beta(\text{S}=\text{O})$
49		247	349	268	2.8633	0.2350	320	259	25.69	0.1574	$\gamma(\text{O}-\text{H})$ $\beta(\text{C}-\text{S}=\text{O})$ $\rho(\text{CH}_2)$
50		193	316	220	16.9361	0.1796	286	208	17.67	0.1445	Lattice Vib
51		175	310	199	20.2766	0.1787	274	182	10.85	0.2285	Lattice Vib
52		171	255	197	1.7050	0.1711	233	183	89.52	0.0491	$\gamma(\text{O}-\text{H})$ + Lattice vib.
53		142	203	157	99.5465	0.0343	226	152	58.40	0.1180	$\gamma(\text{O}-\text{H})$ + Lattice vib.
54		140	155	158	1.7621	0.0634	138	153	5.46	0.0559	$\tau(\text{C}-\text{CH}_3)$ $\beta(\text{S}-\text{O})$
55		127	121	149	3.2122	0.0209	110	138	1.91	0.0166	$\beta(\text{C}-\text{C})$ $\beta(\text{C}-\text{S}=\text{O})$
56		115	81	130	1.3810	0.0160	78	127	7.47	0.0066	$\tau(\text{CH}_3)$
57		98	67	110	10.4923	0.0078	75	108	3.05	0.0060	$\tau(\text{CH}_3)$ + Lattice vib.
58		90	39	108	9.2505	0.0029	57	101	14.25	0.0059	$\rho(\text{CH}_2)$
59		80	35	100	5.7344	0.0020	39	97	1.74	0.0053	Butterfly vib.
60		50	30	80	3.8986	0.0011	26	63	9.36	0.0025	$\rho(\text{CH}_2)$ + Lattice vib.

Abbreviations: δ – stretching; δ_{sym} – symmetric stretching; δ_{asym} – asymmetric stretching; β – in-plane bending; $\tilde{\alpha}$ – out-of-plane bending; $\hat{\alpha}$ – scissoring ; $\tilde{\eta}$ – rocking ; $\tilde{\omega}$ – wagging; $\hat{\delta}$ – twisting;

O-H vibrations

Generally the O-H stretching bands of hydroxyl group is characterized by a very broad band appearing around 3400 cm^{-1} [8]. In the present study the calculated band at 3312 cm^{-1} from DFT/B3LYP may be assigned as O-H stretching vibration. The corresponding band is observed at 3311 cm^{-1} in the FTIR spectrum of CAS. The in plane deformation vibration gives rise to the presence of strong band in the region 1440 cm^{-1} to 1260 cm^{-1} [9]. In CAS the O-H in-plane bending vibrations calculated at 1322 cm^{-1} , 1305 cm^{-1} and 1235 cm^{-1} from the DFT/B3LYP method and is observed at 1315 cm^{-1} , 1298 cm^{-1} and 1227 cm^{-1} in the FTIR spectrum and at 1297 cm^{-1} , 1227 cm^{-1} in the FT raman spectrum.

N-H vibrations

Normally the vibrational bands due to the N–H stretchings are sharp than those of O–H stretching vibrations by virtue of which they can be easily identified [10]. By observing the position of the bands in the proper region, the vibrational bands present at 3125 cm^{-1} in the DFT/B3LYP calculation and at 3123 cm^{-1} in the FTIR spectra of the compound is assigned as N-H stretching.

C-H vibrations

The symmetric stretching vibrations of CH_2 has been observed at $2,750\text{ cm}^{-1}$ and $2,684\text{ cm}^{-1}$ and the CH_2 asymmetric stretching modes are observed between $2,736\text{ cm}^{-1}$ and $2,719\text{ cm}^{-1}$. The CH_2 in-plane and out of plane bending are observed in the region $750\text{--}770\text{ cm}^{-1}$ and the CH_2 twisting modes in the regions $943\text{--}873\text{ cm}^{-1}$ [11]. The asymmetric CH_2 stretching vibrations are generally observed in the region $3100\text{--}3000\text{ cm}^{-1}$, while the symmetric stretch will appear between 3000 and 2900 cm^{-1} [12]. In this compound the asymmetric stretching vibration occurs at 3002 cm^{-1} in FTIR spectrum. The results well agree with the DFT method. The CH_2 wagging is observed at 1370 cm^{-1} in FTIR, 1372 cm^{-1} in Raman and it is equal to 1378 cm^{-1} in the DFT method. The CH_2 scissoring is observed at 1452 cm^{-1} in FTIR spectrum, 1453 cm^{-1} in Raman and the calculated band for CH_2 scissoring is at 1460 cm^{-1} [13]. The twisting mode of CH_3 vibrations are observed at 1227 cm^{-1} in the FTIR and Raman spectra and it is found to be at 1235 cm^{-1} in the DFT method. If a CH_3 group is present in a compound, it provokes to exhibit two asymmetric and one symmetric stretching vibrations. In the present study, one methyl group is present. The CH_3 asymmetric stretching vibration is observed at 2835 cm^{-1} in the raman spectrum and 2840 cm^{-1} from the DFT method

C-N vibrations

The identification of C–N vibrations is a difficult task, since the mixing of vibrations is possible in this region. However, with the help of the animation option of chemcraft graphical interface for Gaussian programs

the C–N vibrations was identified. Silverstein et al. [14] have assigned C-N stretching absorption in the region 1300–800 cm^{-1} . In this study C-N stretching bands is found at 1100 cm^{-1} in the FTIR spectrum.

C=O vibrations

The carbonyl group shows a strong absorption band due to C=O stretching vibrations and is observed in the region 1850-1550 cm^{-1} . Because of its high intensity and relatively interference-free region in which it occurs, this band is reasonably easy to recognize. In the present work the bands are observed at 1654 cm^{-1} in FTIR spectrum and 1660 cm^{-1} . FT Raman spectrum are assigned to C=O stretching mode of vibration, respectively and it well agrees with the values of DFT method.

C-S vibration

In general the assignment of the band due to the C-S stretching vibration is different compound is difficult. Since it is of variable intensity and may be found over the wide region 1035–245 1227 cm^{-1} both in aliphatic and aromatic [15] sulfides have a weak to medium band due to C-S stretching vibration in the region 710–570. In the present work the band observed at 764 cm^{-1} in FTIR and 762 cm^{-1} in FT Raman are assigned to C-S stretching vibration. Theoretically computed values are found to be in good agreement with experimental results.

4.2 Uv-Spectral Analysis and Homo–Lumo Band Gap

Table.2 Experimental and calculated absorption wavelength (λ),Excitation energies (E),oscillator strength (f) of CAS by TD-DFT method.

States	Wavelength(nm)		E(ev)	Frequency
	Experimental	Calculated		
Excited state-S1	250	223	5.5377	0.0005
Excited state-S2		209	5.9149	0.0023
Excited state-S3		205	6.0450	0.0083

Ultra-violet spectral analysis of CAS has been investigated by TD-B3LYP method. Table 2. presents the experimental and calculated absorption wavelength (λ), excitation energies (E) and oscillator strength(f). The maximum absorption peak observed in UV–Visible spectrum corresponds to vertical transitions according to Frank-Condon principle [16]. The experimental λ_{max} is observed at 250 nm while the corresponding calculated λ_{max} is at 223 nm. This corresponds to π – π^* transition. The other two less intense calculated bands are at 209 nm and 205 nm. The excitation energies for the absorption wavelengths are calculated to be 5.5377, 5.9149 and 6.0450 and their corresponding oscillator strengths are 0.0005, 0.0023 and 0.0083 respectively. Fig.4. shows the UV–Visible spectrum of CAS. The highest occupied molecular orbitals (HOMO) and the lowest-lying unoccupied molecular orbitals (LUMO) are named as Frontier molecular orbitals (FMOs). The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to accept an electron. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity and optical polarizability and chemical hardness–softness of a molecule. 3D plots of the HOMO-2, HOMO-1, HOMO, LUMO, LUMO + 1 and LUMO + 2 orbitals computed at the B3LYP/6-31+G(d,p) level for CAS molecule are illustrated in Fig.4. It is clear from the figure that while the HOMO is localized on almost the whole molecule, LUMO is especially localized on the methyl group. Both the HOMOs and LUMOs are mostly antibonding type orbitals. The energy value of the HOMO-2, HOMO-1, HOMO and LUMO, LUMO+1, LUMO+2 were calculated using B3LYP/6-31+G(d,p) are presented in Table.3. The energy gap between HOMO and LUMO indicates molecular chemical stability.

Table.3 Calculated energy values of B3LYP/6-31+G (d,p)

Basis set	B3LYP/6-31+G(d,p)
EHOMO (eV)	-0.345
ELUMO (eV)	-0.117
(EHOMO - ELUMO) (eV)	-0.228
EHOMO-1 (eV)	-0.365

ELUMO+1 (eV)	-0.047
(EHOMO-1 - ELUMO+1) (eV)	0.318
EHOMO-2(eV)	-0.373
ELUMO+2 (eV)	-0.027
(EHOMO-2- ELUMO+2) (eV)	-0.346

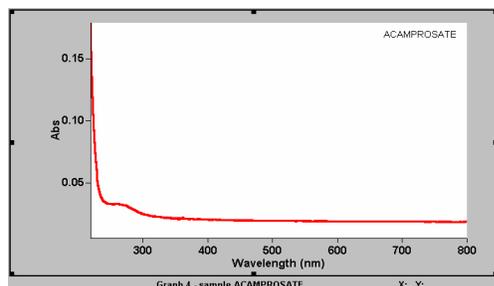


Fig.3. UV –vis spectrum of CAS

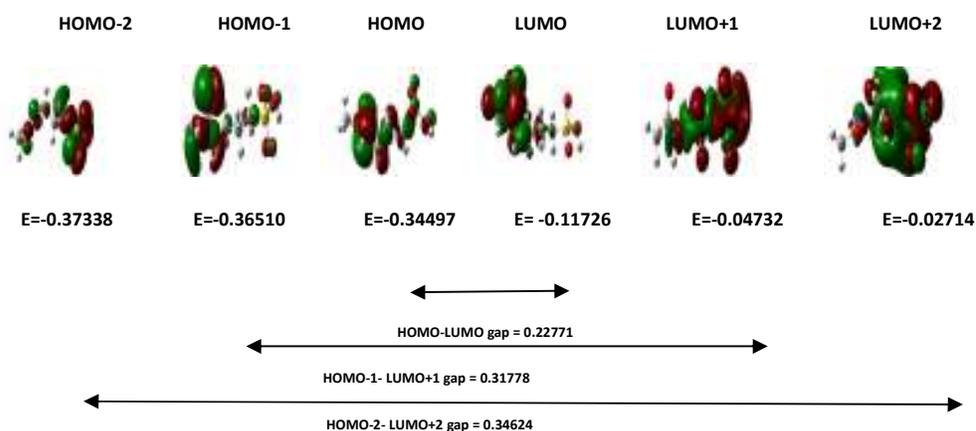


Fig. 4 .Molecular orbitals and energies for the HOMO-2, HOMO-1, HOMO and LUMO, LUMO + 1, LUMO + 2 of CAS

4.3 Thermodynamic Properties

Several calculated thermodynamic parameters such as, rotational constants, zero point thermal energy, specific heat capacity, entropy, dipole moment, Gibbs free energy have been presented in Table.4. The highest value of ZPVE of CAS is $117.660 \text{ kcal mol}^{-1}$ obtained by HF/6-31+G (d,p), whereas the lowest one is $109.162 \text{ kcal mol}^{-1}$, obtained by B3LYP/6-31+G(d,p) method. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as an illustrator to depict the charge movement across the molecule. As a result, the dipole moment of CAS was observed at 0.7199D in HF/6-31+G(d,p) method whereas 1.3042D in B3LYP/6-31+G(d,p) method. On the basis of vibrational analysis and statistical thermodynamics, the standard thermodynamic functions heat capacity (C) entropy (S) and enthalpy changes (ΔH) for the title molecule where calculated using Perl script THERMO.PL [17] and are listed in Table 5. The values of C, S and ΔH all increase of temperature from 100 to 1000 K, which is attributed to the enhancement of the molecular vibration as the temperature increase. The correlation equations between heat capacity, entropy, enthalpy changes and temperatures were fitted by quadratic formulas, and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9997, 0.9998 and 0.9996, respectively.

Table.4 Thermodynamic properties of CAS

Parameter	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
Zero point vibrational energy(Kcal/Mol)	117.6608	109.16275
Gibbs free energy	0.1456	0.131877
zero point correction	0.1875	0.173962
Thermal free energy	-946.999	-950.8875
Rotational constant (GHz)	2.61373	2.51913
	0.33478	0.32577
	0.32975	0.32075
Rotational temperatures (Kelvin)		
	0.12544	0.1209
	0.01607	0.01563
	0.01583	0.01539
Dipole moment		
μ_x	0.0283	0.6696
μ_y	-0.7193	-1.1192
μ_z	-0.0007	-0.0009
μ_{total}	0.7199	1.3042
Entropy (Cal/Mol-Kelvin)		
Total	116.696	118.36
Translational	41.487	41.487
Rotational	31.388	31.48
Vibrational	43.82	45.392
Energy (KCal/Mol)		
Total	125.566	117.45
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	123.789	115.673
Molar capacity at constant volume (Cal/Mol-Kelvin)		
Total	42.682	45.712
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	36.72	39.751

Table.5 Thermodynamic properties at different temperatures at the B3LYP/6-31+G(d,p) level for CAS

T (K)	S (J/mol.K)	C (J/mol.K)	ΔH (kJ/mol)
100	408.98	171.7	10.86
200	559.23	271.57	33.11
298.15	685.25	365.89	64.39
300	687.52	367.66	65.07
400	806.08	459.51	106.51
500	917.43	539.05	156.55
600	1021.71	604.62	213.85
700	1119.09	658.48	277.09
800	1210.03	703.33	345.24
900	1295.12	741.21	417.52
1000	1374.93	773.57	493.3

$$S = 272.666 + 1.4847T - 3.869 \times 10^{-4}T^2 \quad (R^2 = 0.9998)$$

$$C = 51.723 + 1.2117T - 4.9213 \times 10^{-4}T^2 \quad (R^2 = 0.9997)$$

$$\Delta H = -15.147 + 0.1772T + 3.357 \times 10^{-4}T^2 \quad (R^2 = 0.9996)$$

All the thermodynamic data supply helpful information for the further study on the CAS. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemicals reactions according to the second law of thermodynamics in thermochemical field. Notice: all thermodynamic calculations were done in gas phase and they could not be used in solutions.

4.4. Hyperpolarizability Calculations

Table .6 The values of calculated dipole moment (μ_D), polarizability (α_0), first hyperpolarizability (β_{tot}) components of Calcium Acetylaminopropane Sulfonate(CAS)

Parameters	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
μ_x	-2.03681	-1.7686
μ_y	-1.3968	-1.1081
μ_z	-0.92868	-0.7951
μ_D	2.6892	2.23334
α_{xx}	1.197×10^{-23}	1.2850×10^{-23}
α_{xy}	1.0078×10^{-24}	1.5313×10^{-24}
α_{yy}	1.4509×10^{-23}	1.6342×10^{-23}
α_{xz}	3.1569×10^{-25}	3.3580×10^{-25}
α_{yz}	-5.088×10^{-26}	-4.3793×10^{-26}
α_{zz}	1.0001×10^{-23}	1.0419×10^{-23}
α_0 (esu)	1.216×10^{-23}	1.3203×10^{-23}
$\Delta\alpha$ (esu)	2.10986×10^{-23}	2.2845×10^{-23}
β_{xxx}	-50.4652	-62.334
β_{xxy}	13.8893	10.726
β_{xyy}	-27.3261	-27.956
β_{yyy}	-124.7396	-88.826
β_{xxz}	-11.5619	-16.542
β_{xyz}	-3.7478	-4.3384
β_{yyz}	-10.1509	-16.912
β_{xzz}	15.3134	17.62
β_{yzz}	-48.1917	-48.691
β_{zzz}	-6.05701	-8.154
β_{tot} (esu)	2.1509×10^{-30}	1.7721×10^{-30}

The potential application of the title compound in the field of non-linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement by analyzing the vibrational modes using IR and Raman spectroscopy. The first hyperpolarizability (β_0) of this novel molecular system and related properties ($\beta_{tot}, \alpha, \Delta\alpha$) of CAS are calculated using HF and DFT-B3LYP methods with B3LYP/6-31+G(d,p) basis set, based on the finite-field approach. First, hyperpolarizability is a third-rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [18]. DFT has been extensively used as an effective method to investigate the organic NLO materials. In addition, the polar properties and dipole moment of the title compound were calculated using the HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) methods using Gaussian 03W program package. The calculated electronic dipole moment, polarizability, and first order hyperpolarizability values obtained from HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) methods are collected in Table.6. Urea is one of the prototypical molecules used in the study of the NLO properties of the molecular systems. Therefore it was used frequently as a threshold value for comparative purposes. The total molecular dipole moment of CAS from HF and B3LYP with 6-31+G(d,p) basis set are 2.6892D and 2.23334D respectively, which is greater than the value of urea ($\mu = 1.3732$ D). Similarly the first order hyperpolarizability of CAS with B3LYP/6-31+G(d,p) basis set is 1.7721×10^{-30} which is greater than the value of urea ($\beta_{tot} = 0.372 \times 10^{-30}$ esu). From the computation, the high values of the hyperpolarizability of CAS are probably attributed to the charge transfer existing between the phenyl rings within the molecular skeleton. This is evidence for nonlinear optical (NLO) property of the molecule.

5. Conclusion

In the present work, the calculated vibrational wavenumber, frontier molecular orbitals, of Calcium Acetylaminopropane Sulfonate (CAS) using DFT/B3LYP method were discussed. The FT-IR and FT-Raman spectra have been recorded and the detailed vibrational assignment is presented for Calcium Acetylaminopropane Sulfonate (CAS). The simulated FT-IR and Raman spectra of the CAS show good

agreement with the observed spectra. The difference between the observed and scaled wavenumber values of the most of the fundamental is very small. Therefore the assignments with reasonable deviation from the experimental value seem to be correct. This study demonstrates that scaled DFT (B3LYP) calculations are powerful approach for understanding the vibrational spectra of the title molecule. Increased HOMO and LUMO energy gap explains the eventual charge transfer within the molecule which is responsible for the chemical reactivity of the molecule. NLO properties of CAS are much greater than those of urea. The calculated normal-mode vibrational frequencies provide thermodynamic properties by the way of statistical mechanics. The electronic properties were also calculated and compared with the experimental UV-Vis spectrum. This study demonstrates that scaled B3LYP calculations are powerful approaches for understanding the vibrational spectra of CAS.

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