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Structural, Spectroscopic Investigation and Quantum Chemical Calculation studies on Methyl L-α aspartyl -L-Phenyl alaninate (Aspartame) for pharmaceutical Application

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Abstract : The Fourier transform infrared (FTIR-ATR) and FT-Raman spectra of Methyl L-α aspartyl -L-Phenyl alaninate have been recorded in the range of 4000-400cm^{-1} and 4000-50cm^{-1} respectively. A detailed interpretation of the vibrational spectra of this compound has been made based on the calculated potential energy distribution (PED). The equilibrium geometries, harmonic frequencies and infrared intensities calculated by density functional B3LYP method with the 6-31G(d,p) basis set. The vibrational frequencies were calculated by this methods and were compared with the experimental frequencies which yield good agreement between observed and calculated frequencies. The calculated Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies show that the charge transfer occurs in the molecule. Stability of the molecule arising from hyper conjugative interactions, charge delocalization has been analyzed using natural bond orbital (NBO) analysis. The entropy of the title compound is also performed B3LYP/6-31G(d,p) levels of theory. The linear polarizability (α) and first order hyperpolarizability (β) values of the investigated molecules using DFT quantum chemicalcalculation was calculated. ^{13}C and ^{1}H nuclear magnetic resonance chemical shift of the molecule was calculated using gauge independent atomic orbit (GIAO) method. Molecular Electrostatic potential (MESP) was performed by the DFT method.
Keywords : FTIR, PED, HOMO, LUMO, Molecular DFT, Aspartame.

1. Introduction

Aspartame is a methyl ester of dipeptide natural amino acids L-aspartic acid and L-phenylalanine under strongly acidic or alkaline conditions, aspartame may generate methanol by hydrolysis under more severe conditions, the peptide bonds are also hydrolyzed, resulting in free amino acids [1]. Sickle cell disease is an inherited disorder of hemoglobin, resulting in abnormal red blood cells. These are rigid and may block blood vessels leading to acute painful crises and other complications. Recent research has focused on therapies to rehydrate the sickled cells by reducing the loss of water and ions from them [2]. Aspartame is an artificial sweetener with lower calorie benefit people who have problems with sugar metabolism. They are also cheaper and can significantly reduce the manufacturing costs of some beverages and food products.

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Nowadays, the common trend in food industry is to use sweetener combinations, so-called blends, to take advantage of the synergism that occurs with these combinations and to provide certain sensory profile [3,4].In the case of sweetener blends manufacturing, the control of sweeteners proportion in blends is essential to precisely reproduce the texture, sweetness profile and reduce the adverse health effects [5].

In this chapter, complete vibrational assignments of Methyl L-α aspartyl -L-Phenyl alaninatewas made with FTIR and FT-Raman techniques.Density functional B3LYP method with the 6-31G(d,p) basis set is used to compare theoretical and experimental vibrational frequency, to calculate HOMO and LUMO energies, to calculate linear polarizability (α) and first order hyperpolarizability (β), Stability of the molecules arising from hyper conjugative interaction and charge delocalization has been analyzed using Natural Bond Orbital (NBO) analysis, ^{13}C and ^{1}H nuclear magnetic resonance chemical shift of the molecule was calculated using a Gauge independent Atomic Orbit (GIAO) method. In addition, the thermodynamic properties of the compound were calculated.

2. Experimental

The spectroscopicallypure sample of Aspartame was procured from sigma Aldrich Pharmaceutical Company, USA with purity of greater than 98% and it was used as such without further purification. The FTIR spectrum of the title molecule has been recorded in the range 4000-450cm^{-1}using Perkin Elmer Spectrum Two FTIR-ATR spectrophotometer. UV-Visible Spectral measurement were carried out in the region 200-700nm using Perkin Elmer Lamda35 UV WINLAB V 6.0 Spectrophotometer. The spectral measurements were carried out SAIF, SPU, Chennai, India. The FT-Raman spectrum of aspartame was recorded in the range of 4000-50cm^{-1}on a computer interfaced BRUKER RFS 27: Stand alone spectrophotometer. ^{1}H NMR and ^{13}C NMR spectral measurements were recorded with base frequency of 400-100 MHz with Bruker AV III 500 MHz. All the spectral measurements were carried out at the Sophisticated Analytical Instrumentation Facility (SAIF), IIT, Chennai, India.

3. Computational Details

The computational methods are an important tool in the characterization of more complex molecules. Computational methods are adopted to get quality of information. Quantum chemical computational method has proven to be an essential tool for interpreting and predicting vibrational spectra. DFT method is now standard in virtually all of the most popular software packages. The most significant advantage to DFT methods is significant with increase in computational accuracy without additional increase in computing time. DFT method such as the B3LYP/6-31G(d,p) are often times considered to be a standard model for many chemistry applications. DFT method derives properties of molecule based on a determination of the electron density of the molecule.

In the present work, quantum chemical methods like Density Functional B3LYP method with the 6-31G (d,p) basis set are employed to study the complete vibrational spectra of the title compound and to identify the various normal modes with greater accuracy. The optimized molecular structures, vibrational frequencies, thermodynamics properties, HOMO-LUMO energy, UV-Visible and NMR spectra of the entitled compound were performed using the Gaussian 03W package program which is the modern computational chemistry software package with gauss view molecular visualization program at B3LYP/6-31G(d,p) level [6,7].

4. Results and discussions

In this study, the molecular geometry optimizations, calculations of energy, vibrational frequencies, IR intensities and Raman activities were carried out for Methyl L-α aspartyl -L-Phenyl alaninate with the GAUSSIAN 03W software package [8] using DFT /B3LYP functional combined with the standard 6-31G(d,p) basis sets. DFT employed the B3LYP keyword which invoke Becke's three parameter hybrid method [9]using correlation function of [10]. The optimized structural parameters were used in the vibrational frequency calculations at DFT level to characterize all stationary points as minima. The optimized structural parameters have been evaluated for the calculations of vibrational frequencies by assuming C_1 point group symmetry. The assignment of the calculated wavenumbers was aided by the animation option of Gauss view 5.0 graphical interface from Gaussian programs [11]. Furthermore, the

theoretical vibrational spectra of the title compound are interpreted by means of potential Energy Distribution (PED) using VEDA4 program [12]. The harmonic frequencies were calculated by B3LYP method using 6-31G (d, p) basis sets. However, the vibrational frequency values computed of this level contain known systematic errors [13,14], UV-Visible absorption energies, wave length, Oscillator strength of this compound were calculated by DFT method in gas phase. The NBO analysis was performed using the Gaussian 03W package at the B3LYP/6-31G (d, p) level in order to understand various second order interactions between the filled orbitals of the subsystem and vacant orbitals of another subsystem, which is a measure of the intra-molecular delocalization or hyper conjugation [15]. The natural charge analysis has been calculated. Finally,to show non -linear optic (NLO) activity of the title compound, the dipole moment, linear polarizability and first order hyperpolarizability have also been calculated and hence Molecular Electrostatic Potential(MESP) surface is plotted using DFT Method.

4.1 Molecular geometry

The optimized geometry ofMethyl L-α aspartyl -L-Phenyl alaninate obtained by B3LYP levels of calculations and the experimental values [16], in accordance with the atom numbering scheme given in **Fig.1**were listed in**Table 1.**The C_1-O_{11}Bond length is found to have the magnitude of 1.21^{o}which support the double character. The O_9-H_{36} bonds found to be shorter than other bands of the title compound. The average bond distances of C-C, C-H, C-N and C-O calculated by B3LYP method with 6-31G (d, p) basis sets values are 1.395, 1.09, 1.467 and 1.22A^{0}respectively.

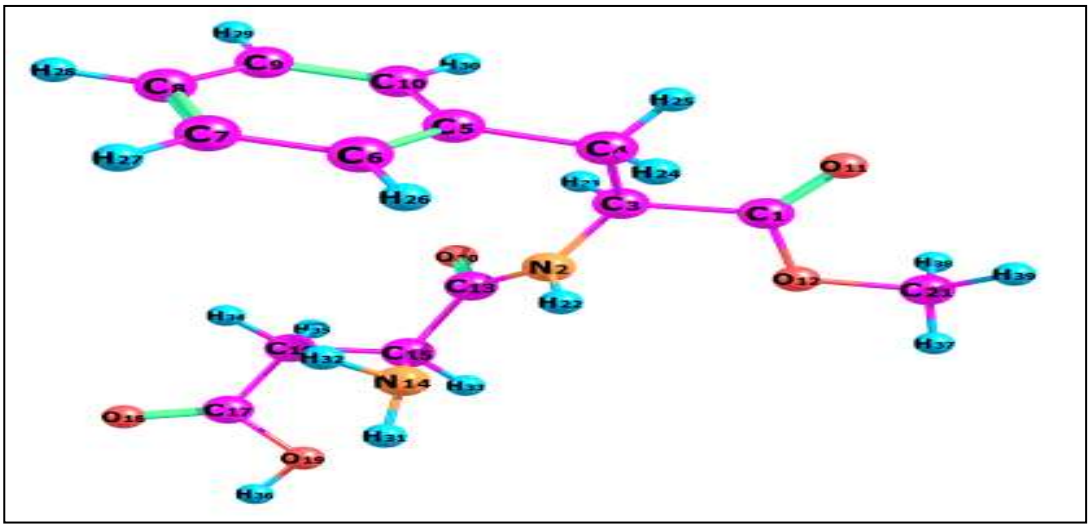

Fig. 1 Atom numbering Scheme of Aspartame

Table1.Optimized geometrical parameters [bond length (A^o), bond angle (^{o}) and dihedral angle (^{o})] of aspartame.

Bond Length (A)	B3LYP/6-31G(d,p)	Experimental	Bond Angle	B3LYP/6-31G(d,p)	Experimental	Dihedral Angle	B3LYP/6-31G(d,p)
C_1-C_3	1.533	1.53	C_3-C_1-O_{11}	123.0004	122.30	O_{11}-C_1-C_3-N_2	-174.501
C_1-O_{11}	1.212	1.20	C_3-C_1-O_{12}	113.131	115.60	O_{11}-C_1-C_3-C_4	-47.4812
C_1-O_{12}	1.345	1.35	O_{11}-C_1-O_{12}	123.8675	121.00	O_{11}-C_1-C_3-H_{23}	69.8023
N_2-C_3	1.442	1.459	C_3-N_2-C_{13}	122.466	123.62	O_{12}-C_1-C_3-N_2	5.8531
N_2-C_{13}	1.357	1.379	C_3-N_2-H_{22}	121.7326		O_{12}-C_1-C_3-C_4	132.8729
N_2-H_{22}	1.013	1.012	C_{13}-N_2-H_{22}	115.741	115.30	O_{12}-C_1-C_3-H_{23}	-109.8436
C_3-C_4	1.550	1.543	C_1-C_3-N_2	114.2463	117.30	C_3-C_1-O_{12}-C_{21}	178.4045
C_3-H_{23}	1.096	1.091	C_1-C_3-C_4	109.3607	110.70	O_{11}-C_1-O_{12}-C_{21}	-1.2378
C_4-C_5	1.512	1.510	C_1-C_3-H_{23}	105.6971	107.38	C_{13}-N_2-C_3-C_1	-107.5591
C_4-H_{24}	1.097	1.091	N_2-C_3-C_4	112.4449	110.13	C_{13}-N_2-C_3-C_4	127.0299
C_4-H_{25}	1.093	1.091	N_2-C_3-H_{23}	105.635	104.27	C_{13}-N_2-C_3-H_{23}	8.1738
C_5-C_6	1.400	1.395	C_4-C_3-H_{23}	109.0656	109.50	H_{22}-N_2-C_3-C_1	69.4934

C_5-C_{10}	1.401	1.400	C_3-C_4-C_5	113.1958	114.55	H_{22}-N_2-C_3-C_4	-55.9176
C_6-C_7	1.396	1.390	C_3-C_4-H_{24}	108.7729	109.50	H_{22}-N_2-C_3-H_{23}	-174.7737
C_6-H_{26}	1.087	1.080	C_3-C_4-H_{25}	107.0691	109.50	C_3-N_2-C_{13}-O_{20}	178.8792
C_7-C_8	1.395	1.390	C_5-C_4-H_{24}	109.8568	109.50	C_3-N_2-C_{13}-C_{15}	0.0765
C_7-H_{27}	1.086	1.080	C_5-C_4-H_{25}	110.9931	109.50	H_{22}-N_2-C_{13}-C_{15}	1.6621
C_8-C_9	1.396	1.390	H_{24}-C_4-H_{25}	106.7029	108.30	H_{22}-N_2-C_{13}-C_{15}	-177.1406
C_8-H_{28}	1.086	1.080	C_4-C_5-C_6	121.0145	120.17	C_1-N_2-C_{13}-C_{15}	172.6035
C_9-C_{10}	1.394	1.390	C_4-C_5-C_{10}	120.5834	120.87	C_1-N_2-C_{13}-H_{24}	-64.9876
C_9-H_{29}	1.086	1.084	C_6-C_5-C_{10}	118.3974	118.12	C_1-N_2-C_{13}-H_{25}	49.9677
C_{10}-H_{30}	1.087	1.085	C_5-C_6-C_7	120.9598	121.02	N_2-C_3-C_4-C_5	-59.3643
O_{12}-H_{21}	1.439	1.443	C_5-C_6-H_{26}	119.3318	119.00	N_2-C_3-C_4-H_{24}	63.0446
C_{13}-C_{15}	1.542	1.540	C_7-C_6-H_{26}	119.705	119.00	N_2-C_3-C_4-H_{25}	177.9998
C_{13}-O_{20}	1.227	1.210	C_6-C_7-C_8	120.0453	120.17	H_{23}-C_3-C_4-C_5	57.462
N_{14}-C_{15}	1.467	1.404	C_6-C_7-H_{27}	119.8427	119.00	H_{23}-C_3-C_4-H_{24}	179.871
N_{14}-H_{31}	1.016	1.010	C_8-C_7-H_{27}	120.1114	120.00	H_{23}-C_3-C_4-H_{25}	-65.1738
N_{14}-H_{32}	1.018	1.010	C_7-C_8-C_9	119.5645	119.65	C_3-C_4-C_5-C_6	102.5184
C_{15}-C_{16}	1.538	1.530	C_7-C_8-H_{28}	120.2424	120.00	C_3-C_4-C_5-C_{10}	-76.6735
C_{15}-H_{33}	1.096	1.097	C_9-C_8-H_{28}	120.1926	120.00	H_{24}-C_4-C_5-C_6	-19.285
C_{16}-C_{17}	1.510	1.510	C_8-C_9-C_{10}	120.1702	120.10	H_{24}-C_4-C_5-C_{10}	161.5231
C_{16}-H_{34}	1.093	1.086	C_8-C_9-H_{29}	120.0726	120.00	H_{25}-C_4-C_5-C_6	-137.0524
C_{16}-H_{35}	1.096	1.099	C_{10}-C_9-H_{29}	119.7568	119.00	H_{25}-C_4-C_5-C_{10}	43.7558
C_{17}-O_{18}	1.210	1.210	C_5-C_{10}-C_9	120.8625	120.70	C_4-C_5-C_6-C_7	-179.6716
C_{17}-O_{19}	1.362	1.350	C_5-C_{10}-H_{30}	119.4976	119.00	C_4-C_5-C_6-H_{26}	1.5068
O_{19}-H_{36}	0.972	0.964	C_9-C_{10}-H_{30}	119.6398	119.00	C_{10}-C_5-C_6-C_7	0.0376
C_{21}-H_{37}	1.089	1.080	C_1-O_{12}-C_{21}	115.051	115.86	C_{10}-C_5-C_6-H_{26}	-179.2841
C_{21}-H_{38}	1.092	1.090	N_2-C_{13}-C_{15}	114.1345	117.30	C_4-C_5-C_{10}-C_9	179.0227
C_{21}-H_{39}	1.092	1.090	N_2-C_{13}-O_{20}	124.403		C_4-C_5-C_6-H_{30}	-1.0826
-	-		C_{15}-C_{13}-O_{20}	121.4514	124.00	C_6-C_5-C_{10}-C_9	-0.19
-	-		C_{15}-N_{14}-H_{31}	109.9045		C_6-C_5-C_{10}-H_{30}	179.7047
-	-		C_{15}-N_{14}-H_{32}	110.3227		C_5-C_6-C_7-C_8	0.1502
-	-		H_{15}-N_{14}-H_{32}	107.2868		C_5-C_6-C_7-H_{27}	-179.5502
-	-		C_{13}-C_{15}-N_{14}	111.3439	117.30	H_{26}-C_3-C_4-C_5	179.4694
-	-		C_{13}-C_{15}-C_{16}	109.0455	114.80	H_{26}-C_6-C_7-H_{27}	-0.2311
-	-		C_{13}-C_{15}-H_{33}	105.4875	109.50	C_6-C_7-C_8-C_9	-01864
-	-		N_{14}-C_{15}-C_{16}	115.6962		C_6-C_7-C_8-H_{28}	-179.928
-	-		N_{14}-C_{15}-H_{16}	106.6185		H_{27}-C_7-C_8-C_9	179.5133
-	-		C_{16}-C_{15}-H_{33}	108.0802	109.50	H_{27}-C_7-C_8-H_{28}	-0.2284
-	-		C_{15}-C_{16}-C_{17}	114.8715	114.80	C_7-C_8-C_9-C_{10}	0.0355
-	-		C_{15}-C_{16}-H_{34}	111.1876	110.30	C_7-C_8-C_9-H_{29}	-179.7467
-	-		C_{15}-C_{16}-H_{35}	108.3418	109.50	H_{28}-C_8-C_9-C_{10}	179.7773
-	-		C_{17}-C_{16}-H_{34}	107.2407	109.50	H_{28}-C_8-C_9-H_{29}	-0.005
-	-		C_{17}-C_{16}-H_{35}	108.4347	109.50	C_8-C_9-C_{10}-C_5	0.1551
-	-		H_{34}-C_{16}-H_{35}	106.4103	109.00	C_8-C_9-C_{10}-H_{30}	-179.7394
-	-		C_{16}-C_{17}-O_{18}	125.5204	104.56	H_{29}-C_9-C_{10}-C_5	179.9381
-	-		C_{16}-C_{17}-O_{19}	112.6009	112.71	H_{29}-C_9-C_{10}-H_{30}	0.0435
-	-		O_{18}-C_{17}-O_{19}	121.8719	121.50	C_1-O_{12}-C_{21}-H_{37}	179.8797
-	-		C_{17}-O_{19}-H_{36}	105.7484		C_1-O_{12}-C_{21}-H_{38}	-60.4616
-	-		O_{12}-C_{21}-H_{37}	105.5889	109.00	C_1-O_{12}-C_{21}-H_{39}	60.0791
-	-		O_{12}-C_{21}-H_{38}	110.4706	110.00	N_2-C_{13}-C_{15}-N_{14}	18.4209
-	-		O_{12}-C_{21}-H_{39}	110.5959	110.00	N_2-C_{13}-C_{15}-C_{16}	147.2785
-	-		H_{37}-C_{21}-H_{38}	110.6433	110.00	N_2-C_{13}-C_{15}-H_{33}	-96.8505
-	-		H_{37}-C_{21}-H_{39}	110.7195	110.00	O_{20}-C_{13}-C_{15}-C_{14}	-162..7372
-	-		H_{38}-C_{21}-H_{39}	108.8365	109.00	O_{20}-C_{13}-C_{15}-C_{16}	-33.8796

-	-		-	-		O_{20}-C_{13}-C_{15}-H_{33}	81.9915
-	-		-	-		H_{31}-N_{14}-C_{15}-C_{13}	-161.4867
-	-		-	-		H_{31}-N_{14}-C_{15}-C_{16}	73.2854
-	-		-	-		H_{31}-N_{14}-C_{15}-H_{33}	-46.9158

Table 2. Calculated and Experimental wave numbers (cm^{-1}) of Aspartame

Frequency (cm^{-1})		**B3LYP/6-31g (d, p)**		**Vibrational assignment PED (%)**
FTIR	**FT Raman**	**Freq. (cm^{-1})**	**IR Intensity Km/mole**	
-	-	3749	57.6346	ν OH (100)
-	-	3587	1.5968	ν NH (97)
-	-	3578	76.6525	ν NH (99)
3428	3422	3493	0.2894	ν NH (99)
3331	3373	3344	0.2894	ν NH (99)
-	3247	3206	17.8378	ν CH (94)
-	-	3194	31.9591	ν CH (82)
-	-	3184	7.3982	ν CH (96)
-	-	3177	14.2711	ν CH (100)
-	-	3173	4.7368	ν CH (92)
-	-	3168	9.2243	ν CH (74)
-	3063	3146	17.3716	ν CH (99)
-	2975	3121	6.5140	ν CH (98)
2951	2950	3114	6.4184	ν CH (98)
-	2918	3077	7.8939	ν CH (94)
-	2852	3074	9.8701	ν CH (100)
-	2711	3070	1.2687	ν CH (100)
-	2466	3067	35.2847	ν CH (100)
-	-	3045	23.9538	ν CH (96)
1735	1736	1849	291.2970	ν OC(85)
	-	1815	223.0035	ν OC(89)
	-	1774	197.1427	ν OC (83)
1663	1664	1664	33.891	β HNH(72) + τ HNCC(22)
-	-	1663	2.9970	ν CC (33)
-	1603	1641	1.2089	ν NC(25) + β HNC(45)
1581	1584	1552	338.9334	ν NC(25) + β HNC(49)
1541	-	1541	12.5151	β HCC (66)+ β CCC (10)
-	-	1508	7.8805	β HCH (70) + τ HCOC (10)
-	-	1502	26.8166	β HCH(76)
1495	-	1495	5.4145	β HCH(84)
-	-	1480	10.4880	β HCN(40)
1446	1444	1470	5.6717	β HCH(87)
-	1403	1418	7.2395	β HNC(20) + β HCC(15) + τ HCCN(36)
-	-	1377	3.3658	ν CH(94)
-	-	1375	8.7285	ν CH(94) + β CH2
-	-	1368	25.7845	β HCC(20)+τ HCCO(18)
-	-	1362	1.5357	β HCC(44) + ν CC(33)
1361	1354	1361	28.9230	β HCC(12) + β OCO(13) + β HOC(23) + ν OC (15) + β HOCC(11)

-	-	1342	6.9810	τ HCCO(26) + τ HCCC(11)
-	-	1301	5.2560	β HCC(36) + τ HCCC(29)
-	-	1292	397.3262	ν CC(18) + β OCO(15)
-	1271	1278	2.0616	τ HCCN(11) + τ HCCO(39)
1258	-	1265	31.5042	β HNC(13) + β HCC(18)
-		1236	48.5672	ν NC(11) + β HNC(10) + β HCC(22)
1224		1229	10.0324	ν CC(30)
-		1220	42.5305	β HCC(12) + τ HCCO(10)
1205		1208	11.6808	β HCC(21) τ HCOC(21)
-	1196	1197	141.4051	ν OC(15) + β HOC(32) + β HNC(10)+ β HCC(15)
-		1187	0.1822	β HCC(76)
1154	1159	1178	1.8518	B HCH(27)+ τ HCOC(71)
-	-	1115		ν CC(32) + β HCC(21)
-	-	1058		ν CC(47)+ β HCC(10)
-	-	1017		ν CC(10) + β CCC(80)
-	-	908		ν OC(11) + τ HCCC(11)
-	-	894		ν OC(17) + ν CC(19) + τ HNCC(13)
-	-	887		ν NC(32) + ν CC(11) + γ OCOC(10)
		701	94.8551	τ HOCC(37) + τ HCCO(11) + γ OCOC(26)
		672	49.6214	τ HOCC(16) + τ HNCC(44)
667		664	81.9430	τ HNCC(17) + γ OCOC(25)
		636	0.0735	β CCC(78)
		624	22.1745	τ HNCC(23) + γ CNC(11)
607		603	33.6156	β OCO(53)
	-	575	8.6722	β CCC(16)
	-	556	9.7389	ν CC(10) + β CCN(10) + β CCN(10)+ τ HOCC(13) + γ OCOC(11)
546	-	535	65.5136	β OCO(14) + τ HOCC(10)
	-	503	4.4155	γ CCCC(14)
492	489	483	8.3683	β OCC(10) + γ NCCC(10)
	451	455	19.5680	β OCC(27) + γ NCCC(16)
	-	417	0.0376	τ HCCC(20)+ τ CCC(12) + τ CCCC(52)
	411	412	4.7872	β NCC(22)
	-	380	4.1415	β OCC(20) + β NCC(80)
	-	352	5.9378	β CCC(52)
	-	351	15.3774	β CCN(12) + β COC(40)
	-	333	45.5789	β CCC(13) + β CCN(10) + τ HNCC(28)
	-	277	1.8817	β CNC(10) + β CCN(11) + β CCC(10) + γ CCCN(14)
	-	255	3.3663	β OCC(20) + β COC(34) + β CCN(20)
	247	246	2.8492	β CCC(12)
	-	181	0.5373	β CNC(13) + β CCC(15) + τ COCC(36)
	-	158	3.3747	β CCC(16) + β CCN(10)
	-	139	0.4286	τ COCC(12) + γ CCCC(13)
	-	120	0.2276	τ HCOC(42)+ τ COC(25)
	-	112	4.4911	β CNC(16) + β CCN(24) +τ CCCN(14)
	86	75	0.8603	γ CCNC(10) + γ CCCC(16)

		64	0.5713	τ CCCN(36)
		54	0.5903	τ CCCN(36) + τ COC(11)
		44	0.3593	τ CCCN(33) + τ COC(25)
		28	1.7636	τ CNCC(15) + τ OCCC(54) + τCNC(12)
		23	0.3009	τ CCNC(12) + τ CCCC(61)
		18	2.6575	τ OCCC(64)
		13	1.5130	τ NCCC(27) + τ CCNC(45)

ν – Stretching, β – in plane bending, γ – out of plane bending, τ - torsion

4.2 Vibrational Band Assignments

The title compound aspartame has 39 atoms belong to C1 point group and possess 111 normal modes of vibrations. The vibrational spectral assignments have been performed based on the recorded FT-IR and FT-Raman spectra on the theoretically predicted wavenumbers of the title molecule. The harmonic vibrational frequencies are calculated for the title compounds by DFT/B3LYP level with 6-31G (d,p) basis set of theory in order to obtain the spectroscopic signature of the selected compounds. The observed and calculated frequencies using B3LYP level for the field along with their probable assignments and potential energy distribution (PED) of the title compound are summarized in **Table2.** The observed and stimulated FT-IR and FT-Raman spectra of aspartame compound are shown in **Fig.2 and 3**respectively. The calculated frequency is slightly higher than the observed values for the majority of the normal modes. Two factors may be the reason for all discrepancies between the experimental and computed spectra of this compound. The first is the influence of the environment and the second one is the fact that the experimental value is an anharmonic frequency. While the calculated value is a harmonic frequency. The calculated harmonic wave numbers are usually higher than the corresponding experimental quantities because of the combination of electron correlation effects and the basis set deficiencies. The maximum number of value is good agreement within the experimental values.

C-H Vibration

The heteroaromatic structure shows the presence of C-H stretching vibrations in the region 3250-3000cm^{-1} which is a characteristic region for theidentification of C-H stretching vibrations [17]. For hetero cyclic compound C-H vibration absorption bands are usually week; in many cases it is too weak for detection. In this region, the bands are not affected appreciably by the nature of substituents. In the present work, the bands observed at 3247, 3063cm^{-1} in FT-Raman are assigned to C-H stretching vibration. The B3LYP method gives the same frequency values at 3206 and 3067cm^{-1}. In general, the aromatic C-H stretching vibrations calculated theoretically are in good agreement with the experimentally reported values [18]for trisubstituted benzene in the region3250-3000cm^{-1}.

Methyl group vibrations

The title molecule Aspartame under consideration possesses a CH_3 group in the side substitution chain. For the assignments of CH_3 group frequencies one can expect that nine fundamentals can be associated to each CH_3 group. The C-H stretching are at lower frequencies than those of the aromatic ring. For CH_3 compound the mode appear in the region 3063cm^{-1} are assigned to CH_3 stretching modes of vibrations. The theoretically computed value shows an excellent agreement with the experimental results. The CH_3 deformations are found in both FTIR and FT-Raman spectra are in good agreement with the calculated B3LYP results. The experimental observation at 247cm^{-1}due to torsion vibrations are not observed in the FTIR spectrum because these appear at very low frequency. This assignment finds support with the frequency intervals given by (Varsanyi, 1973).

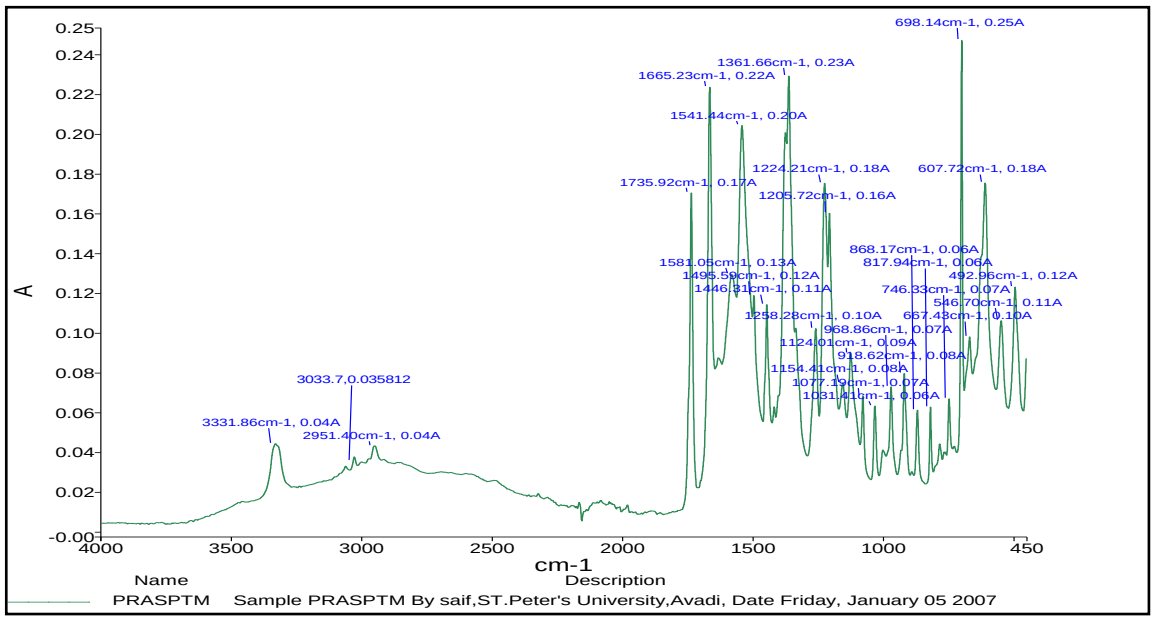

Fig.2 FTIR-ATR Spectrum of Aspartame

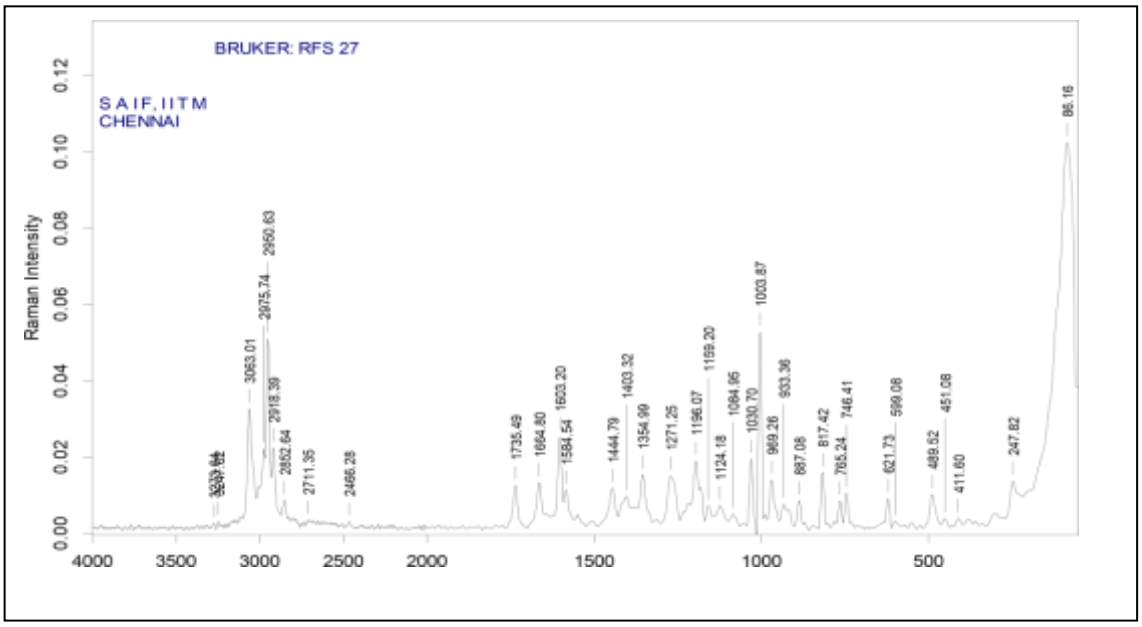

Fig.3 FT- Raman Spectrum of Aspartame

C-C Vibrations

The C-C aromatic stretching vibrations gives rise to characteristic bands in both the observed IR and Raman spectra, covering the spectral range[19] from 1625 to 1400cm^{-1}. Therefore, the C-C stretching vibration of the title are found at 1735, 1663,1581,1541,1495,1446cm^{-1} in FTIR and 1736,1664, 1603,1444,11403cm^{-1} in the FT-Raman spectrum and these modes are confirmed by their PED values. Most of the ring vibrational modes are affected by the substitutions in the aromatic ring of aspartame. In the resent present study, the bands observed at 1077,1031,968,918cm^{-1} and 1084,1030,969,933cm^{-1} in the FTIR and FT-Raman spectrum respectively have been designated toin-plane bending modes by careful consideration of their quantitative descriptions. The out-of-plane bending modes of aspartame are also listed in **Table2.** The reductions in the frequencies of these modes are due to the change in force constant and the vibrations of the functional groups present in the molecule.

C-O vibrations

If a compound contains a carbonyl group, the absorption caused by C-O stretching is generally among the strongest present and occur in the region1260-1000cm^{-1}. Hence the strongest FTIR and FT-Raman bands observed at 1258, 1224cm^{-1} and 1271, 1196cm^{-1} is assigned to the C-O stretching modes of vibrations. Thetheoretical in-plane and out-of-plane vibrations of C-O group are in very good agreement with the experimental values[20].

C-N vibrations

The identification of the C-N stretching vibration is a very difficult task since; the mixing of bands is possible in this region[21] (Gunasekaran et.al., 1993). The C-N stretching band is assigned at 1319cm^{-1} in 2,6-dibromo-4-nitroaniline by [22] have identified the FTIR band 1361cm^{-1} due to C-N in theophylline,[23]have observed the C-N stretching band at 1312cm^{-1} in benzocaine. Hence in the present investigation, the FTIR bands observed at 1361cm^{-1} and the bands at 1403, 1354cm^{-1} in the FT-Raman spectrum of aspartame are assigned to the C-N stretching mode of vibrations. The calculated value of 1361$cm^{-1}$is in excellent agreement with the observed value for the corresponding mode of vibration.

N-H vibration

It is stated that in in amines, the N-H stretching vibration occur in the region 3500-3000cm^{-1}. The asymmetric NH_2 stretching vibration appears from 3500 to 3420cm^{-1} and the symmetric NH_2 stretching is observed in the range 3420-3340cm^{-1}[24]. It is observed that, the N-H stretching band identified at 3462cm^{-1} in FTIR method the theoretically observed values with contribution of PED (100%). Similarly, one band identified in FT-Raman at 3428cm^{-1} and a band observed at 3422cm^{-1} in FTIR is assigned to the NH_2 symmetric stretching modes with maximum contribution of PED. For amino group the NH_2 scissoring identified at 1658cm^{-1} in FTIR and at1668cm^{-1} in FT-Raman spectrum.

5. Other Molecular Properties

5.1 Natural Bond Orbital analysis

Natural Bond Orbital (NBO) analyses provides an efficient method for studying intra and inter molecular bonding and interaction among bonds and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular system [25]. Higher magnitude of E(2) value indicates intensive interactions between electron donors and electron acceptors and hence greater will be the extent of conjugation. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond-Rydberg) non- Lewis orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the title molecule aspartame at the B3LYP/6-31G (d,p) level in order to elucidate the delocalization of electron density within the molecule. The intra molecular interaction are formed by the orbital overlap between bonding πC_5-C_6, $\pi C7$-C_8, πC_9-C_{10} and antibonding$\pi^* C_5$-C_6, $\pi^* C_7$-C_8, $\pi^* C_9$-C_{10} orbital with results in ICT causing stabilization of the system. The Second-Order perturbation theory of Fock matrix in the NBO analysis shows strong intermolecular hyper conjugate interactions and the interactions and the results are presented in **Table6**. The most important interaction observed areπC_5-$C_6$to $\pi^* C_5$-C_6, πC_7-$C_8$to $\pi^* C_7$-C_8, $\pi^* C_7$-$C_8$to $\pi^* C_7$-$C_8$and corresponding energies, 21.16, 21.10 and 20.12 KJ/mol respectively. The larger energy provides the stabilization to the molecular structure.

5.2 Molecular Electrostatic Potential

Molecular electrostatic potential (MESP) is a useful quantity to explain hydrogen bonding, reactivity and structural activity relationship of molecules including biomolecules and drugs [26]. Electrostatics potential correlates with dipole moment, electro negativity, partial charges and site of chemical reactivity of the molecule. It provides a visual method to understand the relative polarity of a molecule. While the negative electrostatic potential corresponds to an attraction of the proton by the concentrated electron density in the molecule represented in shades of red on the EPS surface, the positive electrostatic potential corresponds to repulsion of the proton by atomic nuclei in regions where low electron density exists and the nuclear charge is incompletely shielded represented in shades of blue. By definition, the electron density

isosurface is a surface on which molecule's electron density has a particular value and that encloses a specified fraction of the molecule's electron probability density. Coloring the isosurface with contours shows the electrostatic potential at different points on the electron density isosurface. The electron density isosurface where the electrostatic potential surface and contour has been mapped is shown in **Fig.4.** These electrostatic potential surface plots were obtained by Gauss View 03W programme. The different values of the electrostatic potential at the surface are represented by different colors; red represents regions of most negative electrostatic potential, blue represents regions of most positive electrostatic potential and green represents regions of zero potential. Potential increases in the order red < orange < yellow < green < blue. For the title molecule the most negative electrostatic, whereas the other surfaces with maximum positive potential on aspartame.

Table3.Second Order perturbation theory analysis of Fock in NBO Basis of aspartame

Donor(i)	**Type**	**Acceptor J)**	**Type**	**[b]E(2) (Kj mol^{-1})**	**[c]E(j)-E(i)(a.u)**	**F(ij) (a.u)**
C_5-C_6	Π	C7-C8	Π*	21.10	0.28	0.069
C_5-C_6	Π	C9-C10	Π*	19.34	0.28	0.066
C_7-C_8	Π	C5-C6	Π*	19.63	0.28	0.067
C_7-C_8	Π	C9-C10	Π*	20.28	0.28	0.068
C_9-C_{10}	Π	C5-C6	Π*	21.16	0.28	0.069
C_9-C_{10}	Π	C7-C8	Π*	20.12	0.28	0.067
N_2	LP(1)	C13-O20	Π*	59.25	0.30	0.121
O_{11}	LP(1)	C1	RY*	16.31	1.49	0.139
O_{11}	LP(2)	C1-C3	Π*	19.56	0.62	0.101
O_{11}	LP(2)	C1-O12	Π*	33.41	0.63	0.132
O_{12}	LP(2)	C1-O11	Π*	48.11	0.35	0.115
O_{18}	LP(2)	C16-C17	Π*	18.68	0.65	0.101
O_{18}	LP(2)	C17-O19	Π*	35.55	0.60	0.132
O_{19}	LP(2)	C17-O18	Π*	43.95	0.35	0.112
O_{20}	LP(2)	N2-C13	Π*	24.25	0.74	0.121
O^{20}	LP(2)	C13-C15	Π*	21.71	0.60	0.104

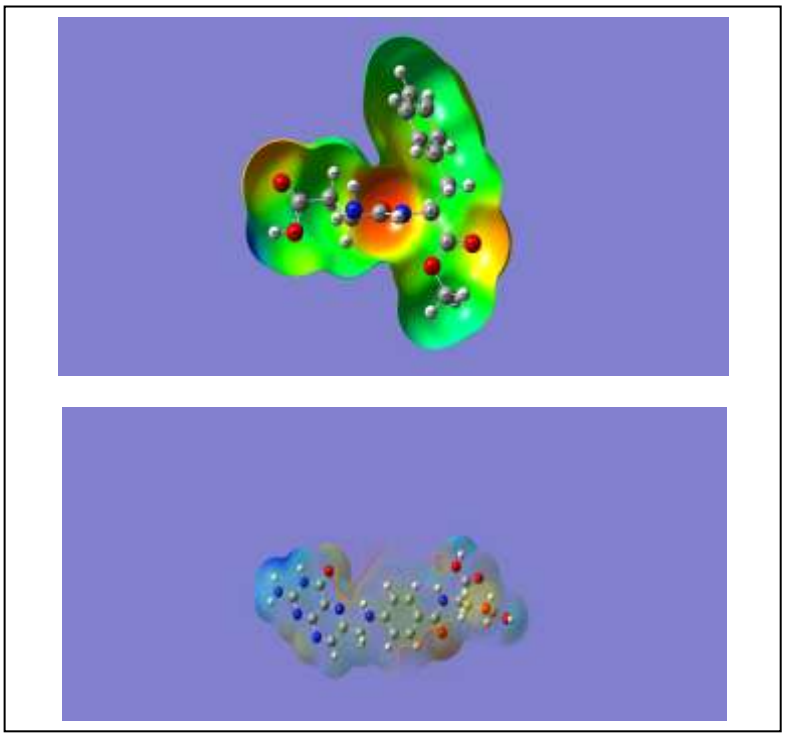

Fig.4 Molecular electrostatic potential of Aspartame

Table4.Mullikan atomic Charges ofAspartame

Parameter	**B3LYP/6-31G(d,p)**
C_1	0.617525
N_2	-0.515366
C_3	-0.009707
C_4	-0.273506
C_5	0.139635
C_6	-0.129050
C_7	-0.090371
C_8	-0.086212
C_9	-0.087409
C_{10}	-0.108179
O_{11}	-0.480922
O_{12}	-0.474243
C13	0.610945
N_{14}	-0.608775
C_{15}	-0.044136
C_{16}	-0.250549
C_{17}	0.573180
O_{18}	-0.482287
O_{19}	-0.500055
O_{20}	-0.525461
C_{21}	-0.074486
H_{22}	0.275511
H_{23}	0.172527
H_{24}	0.109536
H_{25}	0.129487
H_{26}	0.080072
H_{27}	0.085374
H_{28}	0.086935
H_{29}	0.091600
H_{30}	0.093122
H_{31}	0.262543
H_{32}	0.248641
H_{33}	0.137103
H_{34}	0.149211
H_{35}	0.173030
H_{36}	0.326371
H_{37}	0.116579
H_{38}	0.131956
H_{39}	0.129831

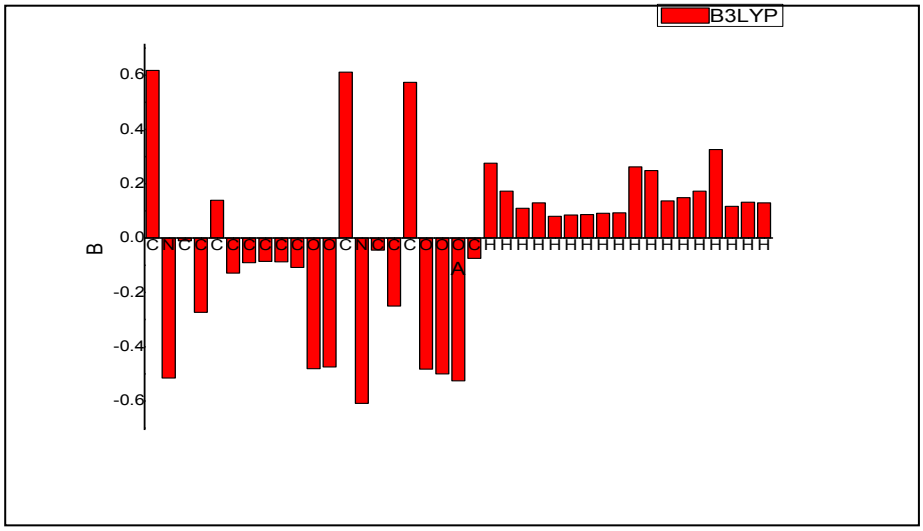

Fig.5 Mulliken Atomic Charges

6. Mulliken Atomic Charge

The Mulliken populations show one of the simplest pictures of charge distribution. The Mulliken charges provide net atomic populations in the molecule while electrostatic potentials yield the electric field out of the molecule produced by the internal charge distribution. Thus, in the reactivity studies, Mulliken populations and MESP are complementary tools, and correlation have between the schemes is expected[27]. However, Mulliken population has to be analyzed very carefully because it causes as large changes of the calculated atomic charges with small changes in the bases used and the over estimation of the covalent character of a bond are common. So, in general, the absolute magnitude of the atomic charges has little physical meaning, on the other hand, their relative values can after valuable information. **Table4** shows the Mulliken charge distribution of the molecule and **Fig.5**Shows the graphical representation.

For Mulliken charge distribution, the Gauss View adopts the follow colors scheme: bright red for more negative and bright green for more positive charge. The red hues illustrate negative charges while green hues expose positive charges. The charge distribution of the compound shows that carbon (C_3 and C_{15}) attached with nitrogen (N_2 and N_{14}) atom has negative charges. All the hydrogen has positive Mulliken charges and all the Oxygen atoms has negative Mulliken charges. The C_1 atom has the highest Mulliken charge (0.617525) when compared to other atoms. The Carbon C_1 atoms attached with the oxygen atoms O_{11} and O_{12} are much more negative than the other oxygen atoms. The smallest Mulliken charge value (-0.009707) was obtained for C_3 atom. The Mulliken charge distribution and the MESP information are concordant.

7. HOMO – LUMO analysis

The deeper understanding of chemical reactivity can be gained with electronic absorption that corresponds to the transition from the transition from the ground to the first excited state and it is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)[28]. The HOMO represents the ability to donate an electron and LUMO represents the ability to obtain an electron. The HOMO is located almost over the nitrogen atom and also slightly delocalized in hydrogen atom as well as carbon atom of benzene ring and hydrogen atom. The frontier molecular orbitals of aspartame were shown in **Fig.6.** The energy gap of the title molecule was calculated by B3LYP/6-31G(d,p) basis set.

The HOMO energy = 6.5286 eV

The LUMO energy = 0.21361 eV

Energy gap between HOMO and LUMO = 6.31499 eV

8. Global quantities

The energy gap between HOMO and LUMO is a critical parameter to determine molecular electrical transport properties. By using HOMO and LUMO energy values for a molecule, the global chemical reactivity descriptors of molecules such as hardness, chemical potential, softness electronegativity and electrophilicity index as well as local reactivity have been defined[29]. Pauling introduced the concept of electro negatively as the power of an atom in a molecule to attract electrons to it. Hardness (η), chemical potential (μ) and electronegativity (χ) and softness are defined as follows, Theoretically, the Ionisation potential (I) is defined as the amount of energy required to remove an electron from a molecule.

$I = -E_{HOMO}$

Electron affinity (A) is defined as the energy released when a proton is added to system.

$A = -E_{LUMO}$

The ionisation potential and elecgtron affinity by B3LYP/6-31G(d,p) for aspartame is -6.5286 respectively.

The electronativity is the measure of the power of an atom or group of atoms to attract electrons towards it [30].

$\chi = (I+A)/2$

Chemical hardness (η) measures the resistance of an atom to a charge transfer [31].

$\eta = (I-A)/2$

Chemical softness (S) is the measure of the capacity of an atom or group of atoms to receive electron[32].

$S = I/\eta$

The relationship between chemical potential with the first derivative of the energy € with respect to the number of electron (N) in the external potential of the system V®, is the electronegativity χ [33]can also be expressed as

$M = V(r) = -\chi$

Similarly, hardness (η) is defined as the second derivative of the energy E with respect to N as V(r) measures the stability and reactivity of the molecule.

$(\eta)^2E/dN^2)\ v(r)$

The electrophilicity is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a molecule within a relative scale. The electrophilicity index (ω) is defined as

$\omega = \mu^2/2\eta$

Using the above equations, the hardness (η), softness (S), electronegativity (χ) and electrophilicity (ω) were calculated for aspartame and the respective values are given in **Table5.** The usefulness of these quantities has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity[34]. The calculated value of electrophilicity index describes the biological activity.

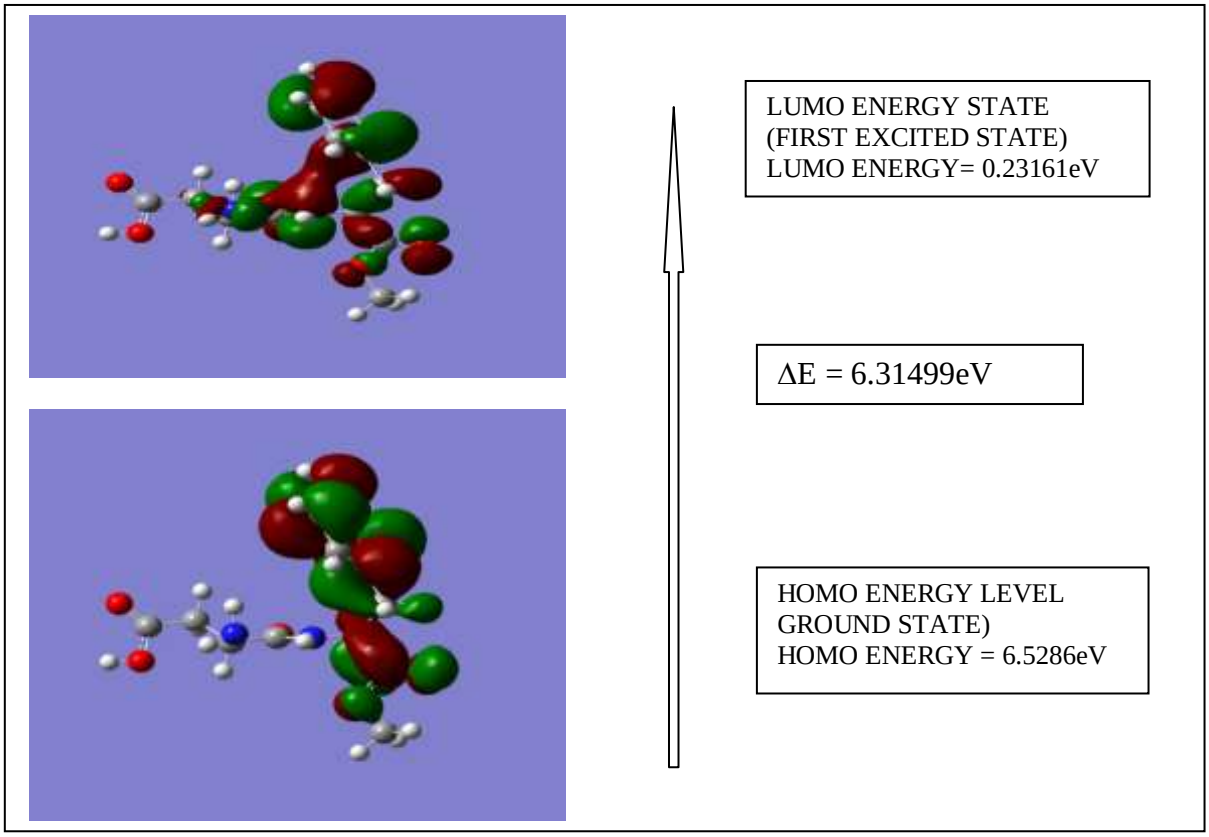

Fig.6 HOMO and LUMO energy structure of Aspartame

Table5. Comparison of HOMO, LUMO energy gaps and related molecular properties of aspartame.

Molecular Properties	**B3LYP/6-31G(d,p)**
EHOMO(ev)	6.5286
ELUMO(ev)	0.21361
EHOMO – LUMO gap (ev)	6.31499
Ionisation potential(I) (ev)	-6.5286
Electron affinity (A) (ev)	-0.21361
Chemical hardness (η)	-3.1574
Softness (S)	-0.31671
Chemical potential (μ)	3.3711
Electronegativity (χ)	-3.3711
Electrophilicity (ω)	5.6821

9. Thermodynamic properties

On the basis of vibrational analysis at B3LYP6-31G(d,p) levels of theory, several calculated thermodynamical parameter such as the zero-point vibrational energies, rotational constant , dipole moment, rotational temperature, specific heat capacity at constant volume and entropy have been presented in **Table 6.** Thermodynamic properties can be calculated from molecular quantities such as the electronic energy, the equilibrium geometry and the vibrational frequencies. The free energy of the molecule is calculated including the zero-point vibrational energy. The vibrational energy of a molecule atabsolute zero is called the zero-point energy. For the present compound, the zero point vibrational energy was obtained as 199.00003kcal/mol by B3LYP/6-31G(d,p) basis set. Even though, the zero-point vibrational energy of a single vibrational mode is rather than small, medium size or large molecule has many vibrational energies is substantial. Statistical mechanics gives the entropyas the sum of translational, rotational, vibrational and electronic contributions[35].

$E = E_t + E_r + E_v + E_e$

Thus,the molecular partition function is the product of the translational, rotational vibrational and electronic partition functions of the molecules[36]. In atomic level, the thermal energy is the kinetic energy of a system is constituent particles which can be molecules, electrons or particles in plasmas. In the present work the total thermal energy was obtained as 77.114 kcal/mol by B3LYP/6-31G(d,p) basis set. Dipole moment tells us about the charge separation in a molecule [37]. In case of polyatomic molecules like Aspartame, the dipole moment is calculated by adding all the individual dipoles of the bonds as their vector. The large value of the dipole moment of aspartame indicates the large charge separation and the influence of the electronegativity of bonded atoms. The larger the electro negativity of bonded atoms, the large the dipole moment[38].

Table 6. Thermodynamic parameters of Aspartame

Parameters	**B3LYP/6-31G(d,p)**
Zero-point Vibrational energy(kcal/mol)	199.00003
Rotational Constant(GHz)	
X	0.30287
Y	0.21824
Z	0.14126
Rotational Constant (Kelvin)	
X	0.01454
Y	0.01047
Z	0.00678
Energy (Kcal/mol)	
Total	77.114
Translational	2.981
Rotational	2.981
Vibrational	71.153
Specific Heat Capacity(Cal/mol/k)	
Total	167.907
Translational	42.934
Rotational	34.797
Vibrational	90.176
Entropy (Cv)	
Total	212.434
Translational	0.889
Rotational	0.889
Vibrational	210.657

10. UV-Visible Spectral analysis

UV-Visible spectroscopy is a useful tool to measure the number of conjugated double bond and also aromatic conjugation within the various molecules. The calculated absorption wavelength (λ), Excitation (E) and Oscillator frequency (*f*) calculated using TD-DFT/B3LYP compared with the experimental wavelength and tabulated in **Table7.** The UV-Vis spectrum of aspartame is presented in **Fig.6.** The electronic transition bands calculated at 207.13nm(f =0.0015) due to H→L, H→L+1, H+2→L, H+3→L+1, 206.03nm (f = 0.0133) is due to H+2→L, H+2→L+1, H+3→L+1 and 188.32nm (f = 0.0018) is due to H+2→L, H+2→L+1, H+3→L+1 excitation respectively. The present experiment revealed an absorption band at 223, 251, 256 and 262nm which implies the transition between π and π* electrons. However the theoretically calculated values are slightly lower than the observed electronic absorption bands of aspartame.

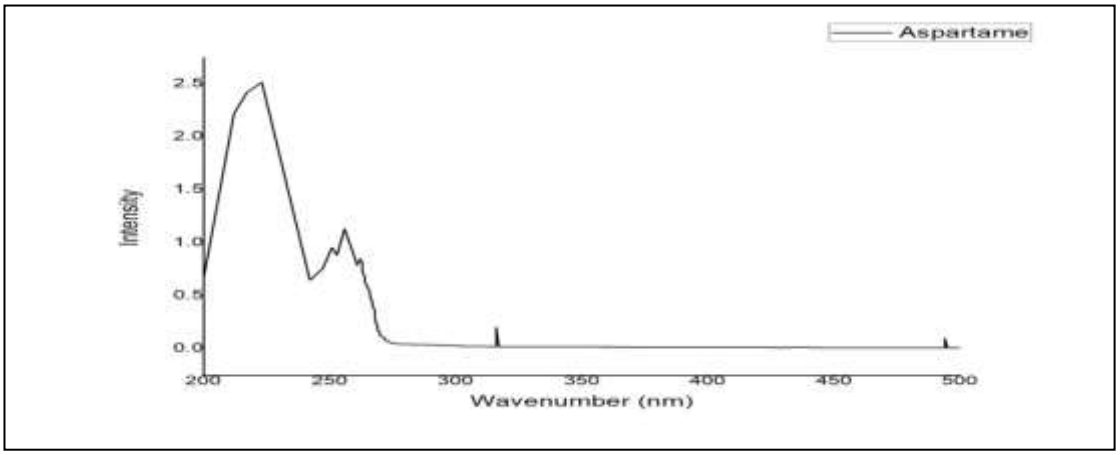

Fig.7 UV-Visible specyrum of Aspartame

Table7. Calculated absorption wavelength (k), excitation state, oscillator strength (f) and transition of aspartame by DFT method.

Excitation	**Singlet A**	**Calculated wavelength (nm)**	**Oscillator strength (f)**	**λ Expt (nm)**	**Transition**
Excited State – 1 77→79 77→80 78→79 78→80	 0.40692 0.32912 -0.37081 0.43794	207.13	0.0015	262	π – π*
Excited State – 2 77→79 77→80 78→79 78→80	 0.32818 -0.37285 0.41594 0.35484	206.03	0.0133	251	π – π*
Excited State – 3 72→79 72→82 72→83 76→79 76→82 76→83	 0.13909 034512 -0.32148 -0.11029 -0.24331 0.21680	188.32	0.0018	223	π – π*

11. ^{1}H-NMR and ^{13}C NMR chemical shift assignments

Nuclear Magnetic Resonance (NMR) analysis exploits the magnetic properties of atomic nuclei. It determines the physical and chemical properties of atom or the molecules. NMR has become one of the most powerful and versatile spectroscopic techniques for the analysis of pharmaceutical materials.

In this study ^{13}C and ^{1}H NMR chemical shifts of aspartame were calculated and depicted in **Table 8.** These calculations are obtained B3LYP/6-31G (d,P) levels for the optimized geometry were observed to be in good agreement with experimental results. The 1H isotropic chemical shift values were calculated from 2.318 to 10.192ppm by DFT method.While these values were observed from 2.061 to 9.246ppm. As seen from the table, all computations are good agreement with experimental data. The proton (H_{24}), which is observed to be about 8.305ppm was found to be 8.375ppm at B3LYP/6-31G(d,p) calculation level of theory.

In addition, ^{13}C isotropic chemical shifts with regard aspartame calculated at B3LYP/6-31G (d,p) basis set is gives in the same table. ^{13}C chemical shift values were obtained from 78.429 to 167.468ppm by DFT method where as these values were experimentally observed from 87.251 to 170.42ppm. The carbon atom C_4 connected with H_{24} and C_5 was observed to be 133.07ppm where it was noted to be 133.31ppm at B3LYP/6-31G (d,p) levels of theory. The Carbon atom C_{13} appearing at very higher chemical shift value (170.426ppm) than other carbon atoms and hence the shielding is very small. The carbon atomC_6 is highly shielded atom and hence appears downfield (lower chemical shift). The Carbon atom C_{13} connected with O_{20} is deshielded than other carbon atoms so that they have higher Chemical shift values. For visual comparison, the observed ^{13}C and ^{1}H NMR spectra of the titled compound were present in **Figs.6 &7.** Apart from that deviations are due to the theoretical calculations belong to isolated molecules in gaseous phases and experimental results belong to molecules in solid state.

Table 8. ^{13}C and ^{1}H isotopic chemical shifts of aspartame using DFT-B3LYP method with 6-31G (d,p) basis set.

Atom Number	DFT		Experimental values (ppm)
	Absolute Shielding	Chemical Shifts (ppm)	
C1	25.7276	86.8700	-
C3	135.8302	38.8594	36.805
C4	150.1298	26.6802	-
C5	57.8121	182.8437	175.717
C6	67.2858	149.7121	136.348
C7	69.8697	165.5741	-
C8	70.6096	168.4032	169.272
C9	68.1346	168.8966	169.272
C10	68.0336	160.7501	-
C13	30.8056	107.9302	127.230
C15	137.1249	20.6469	-
C16	150.3630	27.2114	-
C17	28.6165	92.9768	-
C21	140.2678	66.7277	-
H22	24.1657	11.3752	-
H23	26.8044	1.9660	1.780
H24	29.5433	4.6523	-
H25	28.0732	7.0386	7.116
H26	21.7074	6.8165	-
H27	24.5192	4.7706	4.700
H28	24.4961	3.7144	2.420
H29	24.3447	4.6148	4.072
H30	24.2717	8.0768	-
H31	30.4498	13.8828	-
H32	31.8879	11.7117	-
H33	28.1648	4.6703	4.082
H34	30.2390	3.7760	-
H35	28.2742	5.6402	-
H36	2..1624	12.2613	-
H37	28.2820	8.0908	-
H38	27.9833	9.3553	-
H39	27.9581	9.1037	-

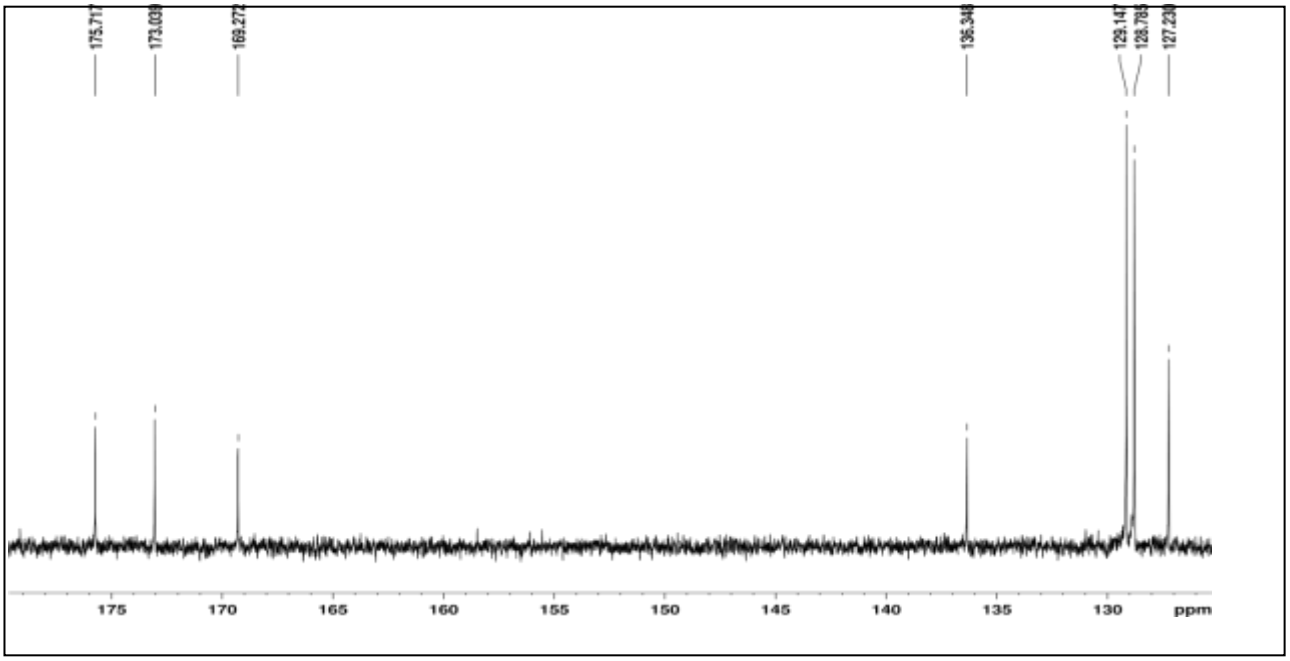

Fig.6. ^{13}C NMR spectrum of Ranitidine hydrochloride

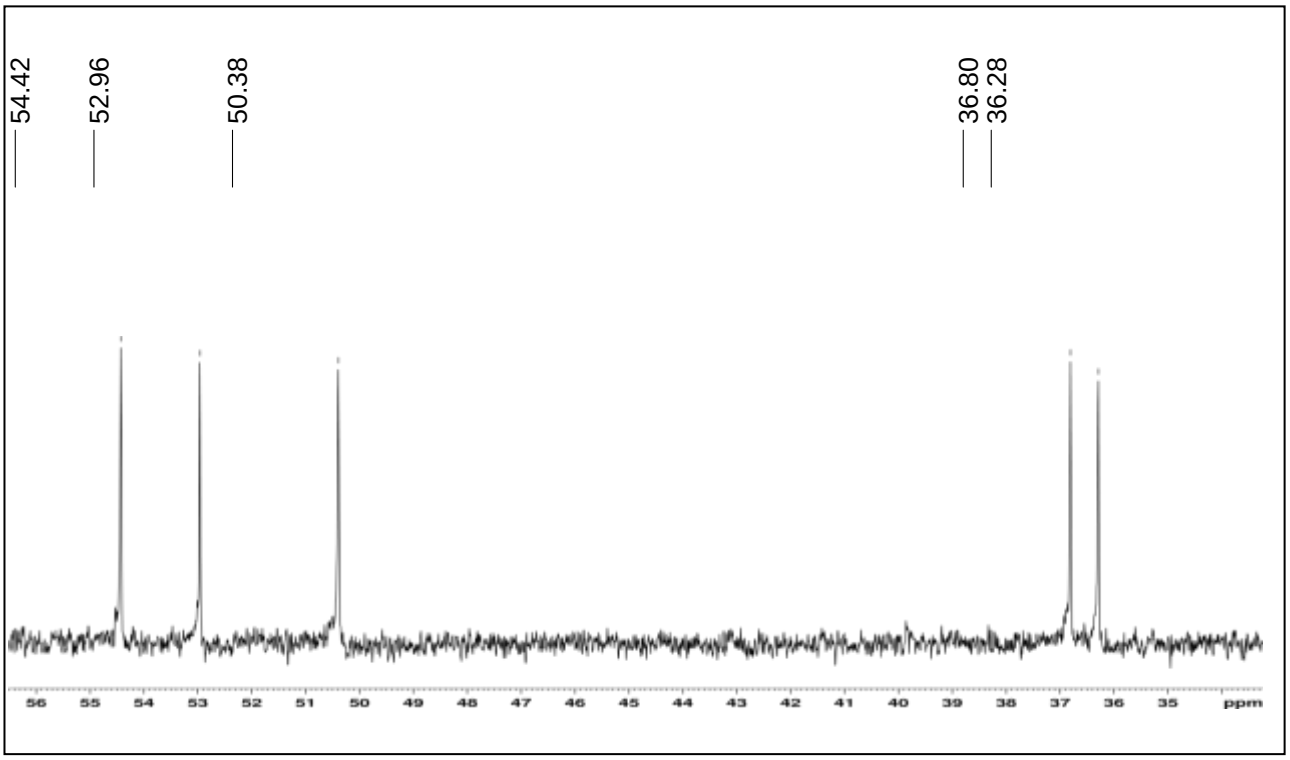

Fig.7. ^{1}H NMR spectrum of Ranitidine hydrochloride

12. Conclusion

The vibrational FTIR and FT-Raman spectra of Aspartame were recorded and compared with the computed vibrational wavenumbers. The fundamental assignment has been made on the basis of the calculated Potential Energy Distribution. The molecular structural parameters like bond length, bond angle, vibrational frequencies of the fundamental modes and thermodynamic properties has been determined using DFT-B3LYP calculations with 6-31G(d,p) basis set. The calculated HUMO-LUMO energies were used to analyze the charge transfer within the molecule. The Molecular Electrostatic Potential figure revealed the

negative and positive regions that were subjected to the electrophilic and nucleophilic attack of the molecule aspartame. Using NBO analysis the stability of the molecule arising from hyper conjugated interaction and charge delocalization was analysed. The electronic properties were also calculated and compared with the experimental UV-Vis spectrum. The chemical hardness, softness and other molecular parameters based on the Molecular orbital studies were outlined. The theoretical ^{1}H NMR and ^{13}C NMR chemical shift values were reported and compared with experimental data, showing a good agreement both for ^{1}H and ^{13}C NMR.Thus, the present investigation provides complete vibrational assignments, structural information's and electronic and electronic properties of the title compound which may be useful to upgrade the knowledge on Aspartame.

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