Original Article

Quantum Chemical Calculation And Spectroscopic Approach For The Analyses Of 2-Oxovaleric Acid, Methyl Ester

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Abstract

In ancient times, certain plants and their parts were used to cure most of the kinds of human diseases. Hybanthus, an eternal medicinal herb has been used in traditional medicine for treating ailments such as diarrhoea, urinary infections, and anti-allergic remedy which have been reported. Since the plant has many pharmacological activities, further research work in the field of drug discovery could be carried out on the active compounds other than this angelic herb. The chief chemical constituents present in Hybanthus are alkaloids, flavonoids, steroids, terpenoids, phenols, dipeptide, isoarborinol, and sugars tannins. In the current investigation, infrared spectroscopic techniques are employed for the identification and assignment of common functional groups present in the medicinally important 2-oxovaleric acid, methyl ester compound. It is used to strengthen the milk secretion in women and utilized in external exercise of the herb relieves for ulcer and hemicrania. The internal standard ratio of the specific modes of the vibration in the IR spectra of the sample has been analyzed between the sample stored in the suitable storage condition and the sample exposed to environmental hazards. 2-Oxovaleric acid is a secondary metabolically or physiologically non-essential metabolites that serve a prominent role of signal-ling molecules, the incomplete metabolism of other secondary metabolites. 2-oxovaleric acid carries oxo- and methyl substituents at C-2 and C-3, respectively. 2-Oxovaleric acid is known to possess the structure of alpha-keto acid which is the constituent of the metabolite of isoleucine in man, animals and bacteria. The fresh liquid extract that is derived from the hybanthus leaves of PN could be utilized as blood tonic and clinical marker of maple syrup which is used for curing urine diseases. 2-oxovaleric acid, methyl ester molecules have been analyzed using FTIR, and DFT (B3LYP) method using the extended 6-311++G (d,p). UV-Visible spectroscopic investigation on this compound has also been made to study the variation in the light absorption activity of λ_{max} of the drug with various concentrations and at different storage conditions.

Keywords: 2-oxovaleric acid, Methyl ester, UV-Visible, Homo-Lumo

1. Introduction

Over the years, quantum chemical calculations as well as spectroscopic investigations are consistently in the limelight as most of the characteristic nature of materials that are used for various purposes and particularly for medical applications are authenticated by virtue of the outcomes whereby these investigations continue to be the narrative of progressive research. WHO continue to provide priority for the medical plants which consistently contribute a substantial role in healthcare in such a way that they are predominantly recognized to be a key factor for the world health. Plants have been consistently used by humans and animals for their food and health purposes from ancient days. In India, large numbers of medicinal plants have been constantly used from ancient days to this day for serve diseases which include the modern day covid-19. Medicinal plants have bio-active ingredients that are present in typical plants which are constantly screened and used in the pharmacological activities and formulated as drugs for therapeutic resolution. A lot of natural bio-active compounds have been recognized to be used for the cure of diseases in brutal nature [1]. Hybanthus enneaspermus (L) F. Muell (Syn. Ionidium suffruticosum), known to be in Violaceae family is a foremost medicinal herb that has been used from ancient times. The chief chemical constituents present in Hybanthus are alkaloids, flavonoids, steroids, terpenoids, phenols, dipeptide, isoarborinol, sugars tannins [2], amino acids, cardiac glycosides, cyanogenic glycosides, anthraquinone glycosides, saponins, tannins, D-mannitol, tetradecanediol, phytol, 2-piperdinone, cedarn-diol, 2-mono linoleo glycerol trimethyl silyl ether and silane [3]. Ayurvedic medicine of the hybanthus plant is used to treat ailments like, urinary calculi, painful dysentery, vomiting, burning sensation, blood troubles, asthma, epilepsy and breast tone [4]. According to Siddha literature, it is used to strengthen milk secretion in women and used in external exercise of the herb relieves for ulcer and hemicrania. Hybanthus in albino mice has been proved to possess the anti-allergic activity by milk-induced leucocytosis and eosinophilia methods. The flavonoids and polar constituents in the plant primarily contribute for the anti-allergic activity [5]. Moreover, infectious diseases are anti- bacterial activity [6] and anti-viral (anti-HIV) [7] medicines that are taken from hybanthus plant. To find the structural information, bond-length as well as bond-angles, [8] functional groups and other quantum level parameters, the analyses of FTIR, UV-Vis spectroscopy with the blend of density functional theory (DFT) have been implemented. The data obtained from experimental as well as calculated IR and UV-Vis spectra of the 2-oxovaleric acid, methyl ester compounds are known to be in good agreement with each other. The vibrational spectra of pharmaceutically viable 2-oxovaleric acid, methyl ester molecules could be obtained from FTIR, FTIR analyses and DFT (B3LYP) method using the extended 6-311++G(d,p) level of theory[9]. The vibrational frequencies of the experimental compound at B3LYP functional and vibrational assignments were prepared with the assistance of computed data assisted by Potential Energy Distribution (PED) experimental values [10]. Natural Bond Orbital (NBO) analysis has been performed to identify the possible intra- and intermolecular interactions present in the abovementioned compounds. The HOMO-LUMO energies have been computed for analyzing the intramolecular charge transfer. The main intension of the present study is to investigate and attribute the vibrational spectra of the important assignments involved in the chemical molecule.

2. Sample and chemical preparation

In the month of June 2021, fresh Hybanthus leaves were taken from Ammakullam village, Villupuram district in Tamilnadu, and they were then dehydrated at room temperature for future study. Dehydrated Hybanthus leaves were contrived into powder form and converted into collodial suspension. Next part of work was progressed with the mixture of the Hybanthus of 1 kg and 3 kg of Methanol constituting the ratio of 1:3 and the resultant solution was stirred well utilizing a magnetic stirrer and allowed to settle down. After 24 hours the product was filtered thereby the excess Methanol was removed. The process of filtration was periodically repeated for 2nd and 3rd times and the resultant compound was filtered by lab A1 qualitative filter paper such that the extract was separated from methanol. The collected extract was heated up to 30 to 60 degree Celsius using Soxhlet extractor. Soxhlet apparatus can be used in order to accomplish the simple filtration so as to separate the compounds from an insoluble mixture. After that, the extract was collected from the Soxhlet equipment such that it was again added to Methanol thereby this by-product was treated by column chromatography. From the column chromatography the mixture of Hybanthus extract and Methanol was separated based on their differentials partitioning between a mobile phase and stationary phase. The filtered product was added with carbon tetra chloride and heated to 50- 60 degree Celsius such that the final product was pure without any impurities whereby it was utilized for further identification, as illustrated in Fig:1.

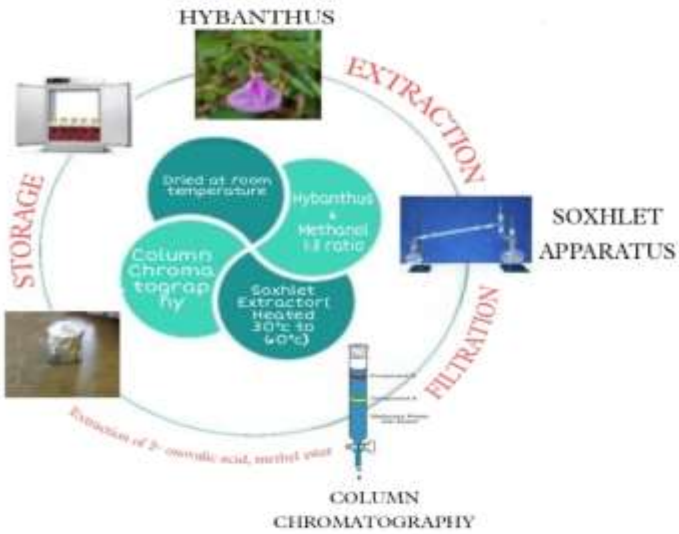

Fig 1: Scheme of preparation of 2-oxovaleric acid, methyl ester.

3.Computational details

The quantum chemical calculation was performed with the B3LYP/HSEH1PBE functional, 6-311ppG(d,p) level of theory employing Gaussian 09W program package [50]. Moreover, the structurally optimized compound was scrutinized by using Gaussview 5.0 software.The optimized geometry parameters of this compound were carried out using B3LYP functional within 6-31+G(d,p) and 6- 311+G(d,p) basis sets such that conceivable correlations were investigated between observed and theoretical data. Also, quantum chemistry methods based on DFT could predict new organic molecules, accomplish the theoretical spectroscopic analysis, arrive at optimal structure, locate the vibrational frequencies, and establish their PED assignments of 2-oxovaleric acid, methyl ester . The experimental data of the given compound as reflected in UV-Vis and IR spectra could provide certain physical values [11-18]. The 2-Oxovaleric acid, methyl ester was designed and it's geometrical parameters are calculated by made use of UV-Vis, IR spectra and DFT (PBE1PBE/6-31+G(d) level of theory [19]. The molecular structure is optimized and employed for the calculation of vibrational assignments, IR intensities such as computation of the potential energy distribution (PED) were calculated utilizing the VEDA 4.0 program [20] and consequently we have applied the scaling factor estimation of 0.967 for the B3LYP/6-311++G (d,p) and carried out the calculation for Dipole moment (D) as well as geometrical parameters such as bond length (Å) and symmetry. The value of nucleophilicity index (N), chemical potential (μ), and electrophilic index (ω) were computed by implementation of solution combination of Crystal explorer 17.5 [21]. The donor - acceptor interactions in the natural bond orbitals (NBO) were calculated with the implementation of second - order Fock matrix [22, 23]. The next part of the paper deals with the analyses charge distribution and electronic characteristics along with HOMO - LUMO energy gap.

4. Result and Discussion

4.1Geometry Optimization

The optimized structural parameters of 2-oxovaleric acid, methyl ester have been established by DFT, B3LYP. The optimized molecular structure has been formulated for the 2-oxovaleric acid, methyl ester in such a way that the numbering of atoms could be accomplished and these aspects have been ascertained by making use of Gaussian 09 and Gauss view program [24, 25] which are displayed in Fig. 2. The computed optimized structural parameters such as bond length, bond angle and an interior angle of the molecule are listed in Table 1.

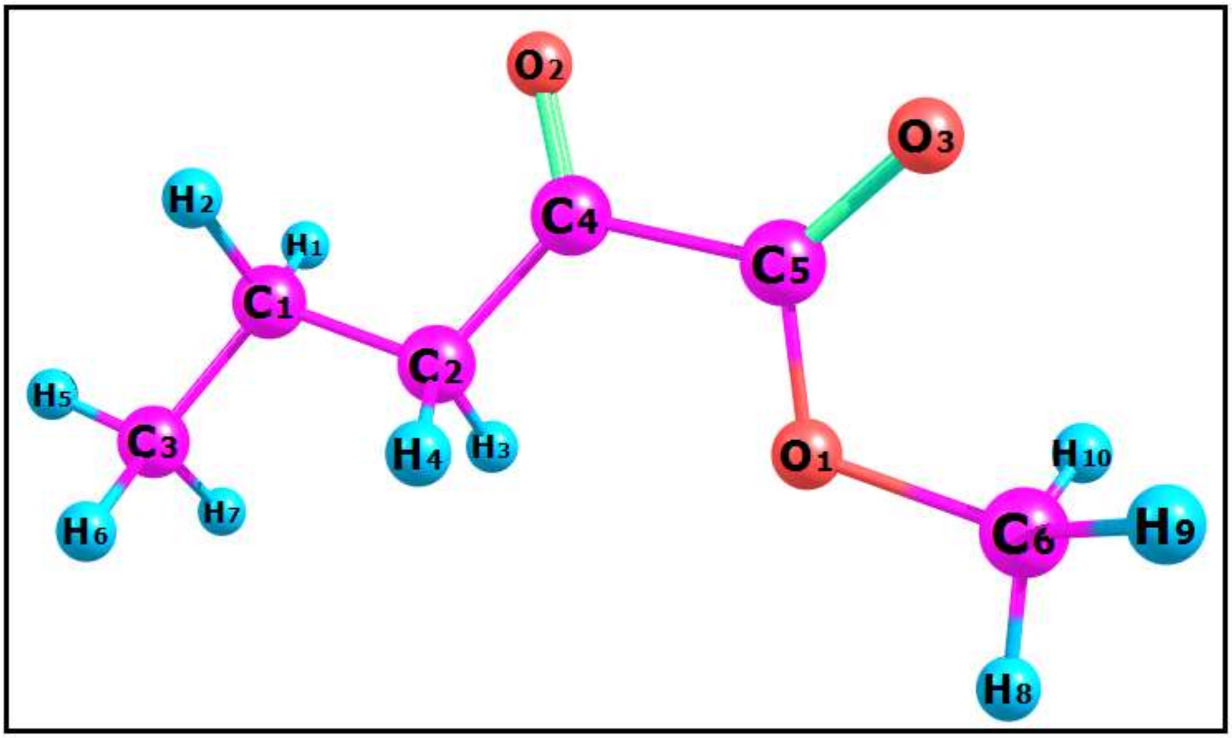

Fig 2: Structure of 2 - Oxovaleric acid, methyl ester.

Table 1: Selected optimized geometrical parameters (bond length & bond angles)

Atoms	Bond length (A^0)		Atoms	Bond Angle (^{0})	
	B3LYP/6-311++G(d,p)	Experimental*		B3LYP/6-311++G(d,p)	Experimental*
C_1 - H_4	1.05	-	C_7-C_6-H_6	119.3	116.49
C_1 - C_2	1.495	-	C_5-C_6-H_6	120.6	116.49
C_1 - H_1	1.06	-	C_5-C_6-C_7	120	116.49
C_1 - H_2	1.064	-	O_2-C_4-C_5	116.2	116.49
C_2 - C_3	1.408	-	C_4-C_3-H_3	121.3	116.49

C3 - H3	1.076	-	O_2-C_4-C_3	121.2	116.49
C_3 - C_4	1.402	-	O_1-C_2-C_3	122	-
C_4 - O_2	1.293	1.26	O_1-C_1-C_1	117.3	115.56
O_2 - H_5	1.247	1.26	C_1-C_2-C_1	120.7	116.49
O_1 - H_5	1.325	1.35	H_1-C_1-H_2	108.4	107.31
C_2 - O_1	1.286	1.26	H_1-C_1-H_4	107.2	107.31
C_4 - C_5	1.481	-	H_2-C_1-H_4	107.5	107.31
C_5 - C_6	1.402	-	C_2-C_1-H_4	109.8	111.34
C_6 - H_6	1.079	-	C_2-C_1-H_1	110.7	111.34
C_6 - C_7	1.391	1.35	C_2-C_1-H_1	113	111.34
C_7 - H_7	1.087	-	C_2-O_1-H_5	101.1	-
C_7 - C_8	1.395	1.35	C_4-O_2-H_5	102.6	-
C_8 - C_9	1.395	1.35	O_1-O_2-H_5	152.7	-
C_9 - C_{10}	1.392	1.35	C_2-C_3-C_4	119.8	116.49
C_5 - C_{10}	1.405	-	C_3-C_4-H_3	118.8	116.49
C_{10} - H_{10}	1.081	-	C_3-C_4-C_5	122.7	-
C_9 - H_9	1.092	-	C_4-C_5-C_6	121.7	-
C_8 - H_8	1.086	-	C_6-C_5-C_{10}	118.9	116.49
			C_9-C_8-H_8	119.4	116.49
			C_8-C_9-C_{10}	119.6	116.49
			C_8-C_9-H_9	120.3	116.49
			C_{10}-C_9-H_9	120.2	116.49
			C_5-C_{10}-C9	119.5	116.49

C_5-C_{10}-H_{10}	120.1	116.49
C_9-C_{10}-H_{10}	119.2	116.49
C_7-C_8-H_8	120.7	116.49
C_7-C_8-C_9	120.7	116.49
C_8-C_7-H_7	119.7	116.49
C_6-C_7-H_7	120.2	116.49
C_6-C_7-C_8	119.3	116.49

The calculated bond length between various combination are (C4-O2) 1.293A^0, (O2-H5) 1.247A^0, (O1-H5) 1.325A^0, (C1-O1) 1.286A^0, (C6-C7) 1.391A^0, (C7-C8) 1.395A^0, (C8-C9) 1.395A^0 and (C9-C10) 1.392A^0 for which the corresponding experimental values lie between 1.26A^0 and 1.35A^0. The highest calculated bond length is found to be (C1-C2) 1.495A^0 whereas the least value is identified to be (C1-H4) 1.05A^0 and DFT (B3LYP/6-311++G(d,p)) for all basis sets. The comparative analysis between the calculated and experimental values of the bond angles are (C7-C6-H6) 119.3^0 , (C5-C6-H6) 120.6^0 , (C5-C6-C7) 120^0 , (O2-C4-C5) 116.2^0 , (C4-C3-H3) 121.3^0 , (O2-C4-C3) 121.2^0 , (O1-C1-C1) 117.3^0 , (C1-C2-C1) 120.7^0 , (H1-C1-H2) 108.4^0 , (H1-C1-H4) 107.2^0 ,(H2-C1-H4) 107.5^0 , (C2-C1-H4) 109.8^0 ,(C2-C1-H1) 113^0 , (C2-C3-C4) 119.8^0 , (C3-C4-H3) 118.8^0 , (C6-C5-C10) 116.49^0 , (C9-C8-H8) 119.4^0 , (C8-C9-C10) 119.6^0 , (C8-C9-H9) 120.3^0 , (C10-C9-H9) 120.2^0 , (C5-C10-C9) 119.5^0 , (C5-C10-H10) 120.1^0 , (C9-C10-H10) 119.2^0 , (C7-C8-H8) 120.7^0 , (C7-C8-C9) 120.7^0 , (C8-C7-H7) 119.7^0 , (C6-C7-H7) 120.2^0 and (C6-C7-C8) 119.3^0 are 116.49^0 , 115.56^0 ,107.31^0 and 111.34^0 , respectively. The highest value of bond angle is found to be for O1-O2-H5 which is 152.7^0 and DFT (B3LYP/6-311++G(d,p)).

4.2. Vibrational spectral analysis

The 2-oxovalic acid molecule has an oxo group that is positioned at 2 and 19 atoms which undergo 51 detailed normal vibrational modes. Vibrational Spectroscopic investigation of the molecule has been accomplished by FT-IR and the comparative analysis has been theoretically inferred for the observed spectra. The appearing frequencies in the spectra and theoretically determined frequencies are shown in Table 2. It is also determined the PED for each of the normal mode under the symmetrical coordinates of the molecule. Furthermore, a complete allocation of the fundamental frequencies is established according to the determined PED values.

Table 2: Experimental and Theoretical (DFT B3LYP/6-311ppG(d,p) basis set) vibrational spectroscopic data with vibrational assignments.

Wavenumber					
Experimental	Theoretical		IR Intensity		
IR	Unscaled	Scaled*	Absolute	Relative**	Vibrational assignments(%PED)

-	3164	3060	10.72	4	υ CH (93)
3128	3130	3027	14.49	5	υ CH (100)
-	3090	2988	38.36	14	υ CH (92)
-	3087	2985	57.27	21	υ CH(94)
-	3063	2962	0.45	1	υ CH (98)
-	3054	2953	24.78	9	υ CH (93)
-	3041	2941	17.12	6	υ CH(88)
-	3036	2936	3.19	1	υ CH (91)
-	3019	2919	24.89	9	υ CH (92)
3001	3014	2915	14.38	5	υ CH (88)
-	1813	1753	96.04	35	υ OC (81)
1804	1804	1744	273.56	100	υ OC (85)
-	1508	1458	8.45	3	δ HCH (82)
1500	1501	1451	8.33	3	δ HCH (88)
-	1495	1446	9.55	3	δ HCH (75)
1466	1467	1419	2.37	1	δ HCH (15) + δ HCO (62) + τ HCOC (15)
1440	1492	1443	10.33	4	δ HCH (80) + τ HCCH (10)
1472	1483	1434	3.97	1	δ HCH (92)
-	1203	1163	20.27	7	δ HCO (18) + δ HCO (13) + τ HCOC (48)
1440	1442	1394	1.33	1	δ HCH (88)
-	1415	1368	25.90	9	γ CHHH (95)
1400	1400	1354	15.92	6	δ HCC (70) + υ CC (10)
1325	1325	1281	1.43	1	δ HCC (69)
1320	1322	1278	0.11	1	δ HCC (79)
1266	1246	1205	262.28	96	δ HCC (75)

-	1231	1190	5.86	2	δ HCO (16) + υ CC (16) + υ CC (33)
823	833	806	0.96	1	δ HCO (13) + υ CC (42)
-	749	724	69.67	25	δ HCO (25) + δ HCC (13)
1157	1169	1130	0.46	1	δ HCO (88)
1129	1129	1092	76.36	28	τ HCCH (28) + υ CC (12) + υ CC (19)
910	909	879	8.14	3	τ HCCH (20) + υ CC (49)
-	1107	1070	24.44	9	δ HCC (72)
1060	1052	1017	9.07	3	δ HCC (10) + υ CC (51)
-	388	375	0.20	1	δ HCC (47) + υ CC (25)
-	1046	1011	12.37	5	υ CC (53)
980	990	957	0.29	1	υ OC (76)
-	311	301	32.35	12	υ CC (10) + δ HCC (20) + δ CCC(20)
-	888	859	12.63	5	τ HCCC (64)
752	766	741	3.61	1	τ HCCC (60)
678	678	656	9.52	3	τ HCCC (42) + δ HCC (30)
-	245	237	1.95	1	τ HCCC (11) + τ HCCH (79)
480	488	472	5.60	2	δ HCC (51) + τ HCCO (11)
-	426	412	5.12	2	δ HCC (14) + τ HCCO (51)
-	109	105	0.09	1	δ CCC (65)
-	340	329	5.18	2	δ CCC (62)
-	228	220	1.97	1	δ CCC (76)
-	66	64	0.53	1	τ HCCO (17) + τ HCCC (66)
-	160	155	1.21	1	τ HCOC (70) + τ HCOC (12)
-	127	123	1.68	1	τ HCOC (12) + τ HCOC (76)
-	87	84	0.01	1	τ HCCC (71)
-	12	12	0.03	1	τ CCCO (91)

* Scaling factor: .967 above and below 3000 cm B3LYP/6-311ppG(d,p).
** Relative IR intensities normalized with highest peak absorption equal to 100.
υ - stretching, δ - in-plane bending, γ - out-of-plane bending and τ - torsion

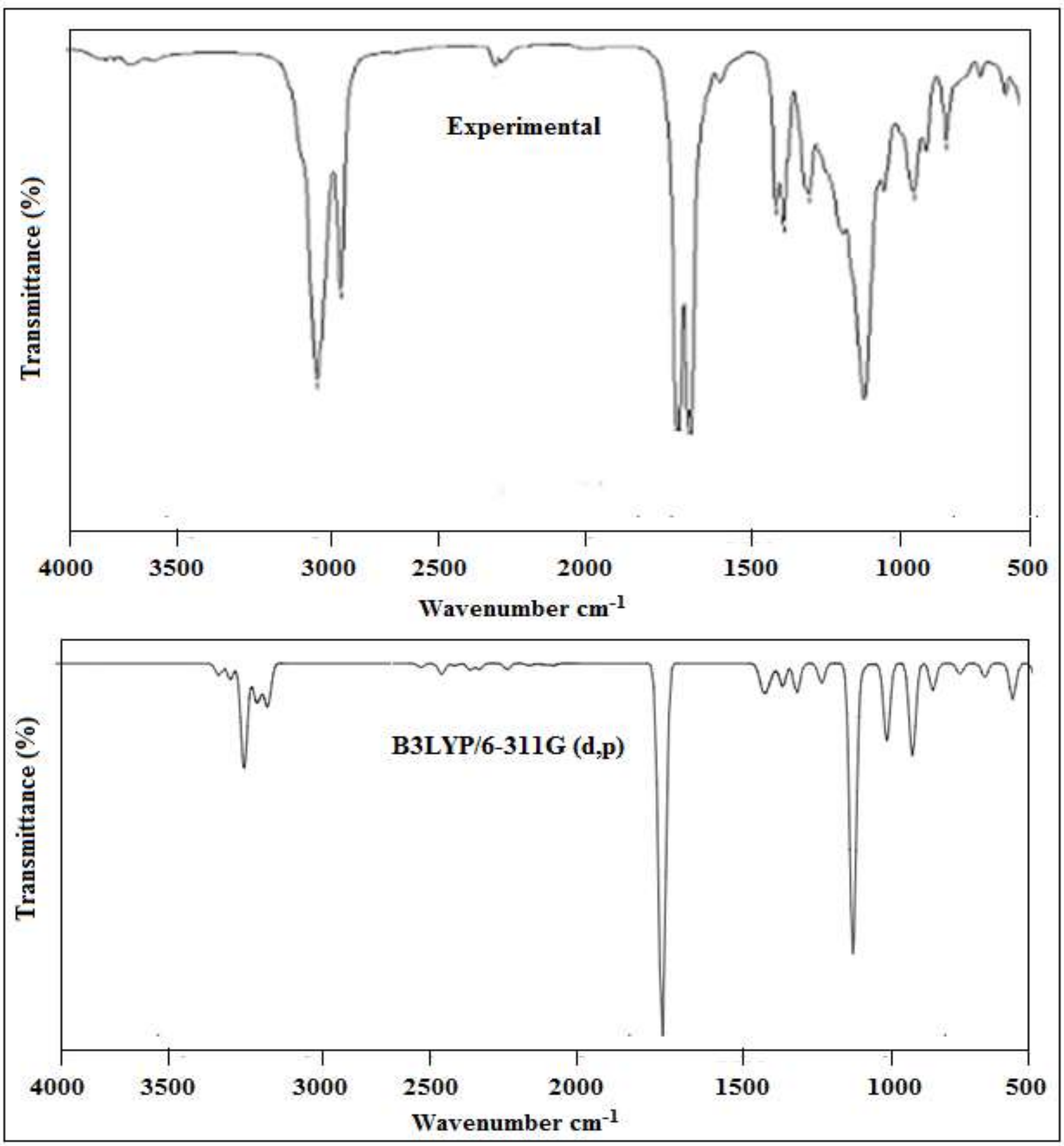

Fig 3: Experimental and calculated FTIR spectra of 2-oxovaleric acid, methyl ester.

4.3 CH vibrations

The bands that are tracked down in the high frequency region of spectra of 2-oxovalic acid are quite clearly pinpointed to be because of CH stretching modes. The corresponding wavenumbers of aromatic CH stretching vibrations are identified to be lying in the range between 3200 and 3000 cm^{-1}, which is known to be the characteristic range of detection such that the rapid recognition of CH stretching vibrations is ensured [26, 27]. The bands appearing for the title compound for the wavenumbers 3164, 3130, 3090, 3087, 3063, 3054, 3041, 3036, 3019 and 3014 cm^{-1} which represent CH stretching modes are experimentally observed at 3128 and 3001 cm^{-1} in the FTIR spectrum. The existing CH vibrations are supported by the potential energy contribution which has a maximum value of 95%.

4.4 CC vibrations

Ring (CC) vibrations are primarily identified in the typical range of 1400 - 1000 cm^{-1} [28, 29]. The observed FTIR spectrum possesses the characteristic vibrations detected at 1266, 1129 and 1060 cm^{-1} for which the theoretical data are found to be 1400,1231, and 1046 cm^{-1} by theory of the B3LYP feature 6-311++G(d,p) level that was captured at 1129 cm^{-1}. The maximum contribution of the PED is 53%.

4.5 Other vibrations

In the case of bending vibration of HCH, the obtained theoretical estimates for the 2-oxovalic acid, methyl ester molecule are found to be in the ranges of 1442, 1467,1483,1492,1495 and 1501 cm^{-1} while the HCH bending peak appears at 1500 cm^{-1} in the experimented FTIR wherein the most extreme potential energy has the spread of 92%. Moreover, in the case of HCC band, the corresponding vibrations are located to occur in the ranges of values such as 245,311,388,488,678,1052,1246,1322, and 1325 cm^{-1} whereas the respective experimental HCC modes are located at 1325 cm^{-1} of the FTIR wherein the contribution of PED is estimated to be 79%. Other bending vibrations such as (CH, OC, HCO, CC, HCC, CCC) are also observed for the 2-oxovalic acid, methyl ester molecule. The presence of torsional vibrations of HCOC, HCCO, HCCC, HCCH, CCCO are identified for the 2-oxovalic acid, methyl ester molecule wherein out of plane bending could also be observed such as CHHH with PED of 95%. Almost all types of vibrations of 2-oxovalic acid, methyl ester have been processed such that the obtained values are found to be in positive agreement with the experimental values [30, 31, 32].

4.6 Electronic properties

Table 3: Selected donor - acceptor interactions and their second order perturbation energies of C6H10O3.

DONOR	TYPE	ED/e	ACCEPTOR	TYPE	ED/e	E(2)	E(j) - E(i)	F(i,j)
BD (1) C1 - O7	π	1.99143	BD*(1) C5 - H12	π*	0.35541	4.66	1.58	0.78
BD (1) C2 - H10	π	1.95253	BD*(2) C1 - O6	σ*	0.59213	4.61	0.51	0.045
BD (1) C2 - H10	π	1.95253	BD*(2) C3 - O4	σ*	0.00862	4.37	0.56	0.044
BD (1) C2 - H11	π	1.95257	BD*(2) C1 - O6	σ*	0.20110	4.6	0.51	0.045
BD (1) C2 - H11	π	1.95257	BD*(2) C3 - O4	σ*	0.01696	4.37	0.56	0.044
BD (1) C5 - H12	π	1.96152	BD*(1) C3 - O4	π*	0.01696	4.89	1.10	0.066
BD (1) C5 - H12	π	1.98734	BD*(1) O7 - C8	π*	0.04575	5.59	0.74	0.057

BD (1) C5 - H13	π	1.96665	BD*(2) C3 - O4	σ*	0.03238	5.11	0.50	0.046
BD (1) C5 - H14	π	1.96668	BD*(2) C3 - O4	σ*	0.03238	5.10	0.50	0.046
BD (1) O7 - C8	π	1.98734	BD*(1) C1 - C2	π*	0.05026	4.02	1.25	0.064
BD (1) C9 - H17	π	1.98327	BD*(1) O7 - C8	π*	0.04575	4.66	0.79	0.054
LP (2) O4	LP (2)	1.97806	BD*(1) C2 - C3	π*	0.06666	22.36	0.64	0.108
LP (2) O4	LP (2)	1.89270	BD*(1) C3 - C5	π*	0.05281	19.47	0.66	0.103
LP (2) O6	LP (2)	1.97664	BD*(1) C1 - C2	π*	0.05026	17.31	0.65	0.097
LP (2) O6	LP (2)	1.85769	BD*(1) C1 - O7	π*	0.10599	35.10	0.63	0.134
LP (1) O7	LP (1)	1.88270	BD*(1) C1 - O6	π*	0.20110	5.20	1.20	0.072
LP (1) O7	LP (1)	1.88270	BD*(1) C5 - H12	π*	0.09758	78.88	1.22	0.278
LP (2) O7	LP (2)	1.81140	BD*(2)C1 - O6	σ*	0.20110	44.87	0.37	0.115
LP (2) O7	LP (2)	1.81140	BD*(1) C8- H15	π*	0.02186	4.85	0.79	0.058
LP (2) O7	LP (2)	1.81140	BD*(1) C8 - H16	π*	0.02186	4.85	0.79	0.058
BD*(1) C1 - O7	π*	1.99143	BD*(1) C1 - C2	π*	0.35541	13.61	0.02	0.046
BD*(1) C1 - O7	π*	1.99143	BD*(1) C2 - C3	π*	0.39937	7.45	0.04	0.055
ED(e) is the electron density of donor and acceptor in the NBO analysis								
E(2) means Stabilization energy in kj/mol								
E(j) - E(i) is the Energy difference between donar and acceptor i and j NBOs in a.u								
F(i,j) is the Fock matrix element between i and j NBOs in a.u								

The energy of excitation state of a molecule could be represented by the difference between HOMO and LUMO analysis such that the bandgap signifies an imperative position in identifying the chemical stability of any given molecular structure [33,34]. Energy gap of HOMO-LUMO 2-oxovaleric acid, methyl ester molecule is enumerated by using B3LYP functional with the help of 6-311++G(d,p) level of theory whereby the representation of the chemical properties could be ensured for the molecules [35]. The Highest Occupied Molecular Orbital (HOMO) is known to be the orbital whose principal role is to act as an electron-donor and the (ED/e) interaction value is calculated to be 1.99143e and the Lowest Un-occupied Molecular Orbital (LUMO) is the orbital whose principal role is to act as an electron-acceptor and the (ED/e) interaction value is identified to be .01696e [36] such that HOMO-LUMO variables could be accomplished.

Table 4. Acquired energy values of 2-oxovaleric acid by B3LP/6-3++G (d,p) method.

Variables	values
HOMO energy (i)	-7.3966
LUMO energy (j)	-2.275
Energy gap (eV)	5.1216
Ionization potential (I)	7.3966
Electron affinity (A)	2.275
Chemical Hardness (η)	2.56
Chemical Softness (δ)	0.3906
Chemical potential (μ)	-4.8358
Electrophilicity (ω)	29.935
Electronegativity (χ)	4.8358
Electron acceptor power ($\omega+$)	2.468
Electron donor power ($\omega-$)	4.839

In (Table 4) which can be acquired from the following relationship:

Chemical potential (μ) $=1/2$ (LUMO + HOMO) $= 1/2 (i+j)$ (1)

Chemical Hardness (η) $=1/2$(LUMO - HOMO) $=1/2 (I-j)$ (2)

Chemical Softness (δ) $= 1/\eta$ (3)

Electronegativity (χ) = (LUMO+ HOMO) $- \mu = (i+j) - \mu$ (4)

Electrophilicity (ω) $= \mu^2/2\eta$ (5)

Electron acceptor power ($\omega+$) $= (i+3j)^2 / 16 (i-j)$ (6)

Electron donor power ($\omega-$) $= (3i+j)^2 /16 (i-j)$ (7)

The HOMO-LUMO energy esteems could be utilized such that these are very much associated to the Ionization potential (i) and Electron affinity (j) of the molecules. In addition, other variables such as Chemical Potential (μ), Chemical Hardness (η), Chemical Softness (δ), Electronegativity (χ), Electrophilicity(ω), Electron acceptor power ($\omega+$) and Electron donor power ($\omega-$) have been anticipated for the 2-oxovaleric acid, methyl ester molecules. The ionization potential that exists in a compound can directly influence the proposed HOMO energy. On the other hand, LUMO energy could be treated as an outcome constituted by the electrons such that LUMO energy is regarded as a direct contribution which arises out of the electron affinity [37]. Moreover, two prominent molecular orbitals constituted by HOMO-LUMO can be investigated whereby the molecular properties represented by HOMO and LUMO are showcased in Fig.3. The enumerated value of HOMO-LUMO energy gap is 5.1216 eV. The chemical hardness is known to be a good criterion by which the chemical stability can be identified. The values of higher chemical hardness and lower softness could reflect the stability of the molecules. The chemical hardness of the compound is found to be 2.560 while the softness value is estimated to be 0.3906. The electrophilicity index value is calculated as 29.935and the calculated values of Electron acceptor power (ω+) and Electron donor power (ω-) are 2.468 and 4.839, respectively with which the biological activity of the title compound could be indicated [38,39,40].

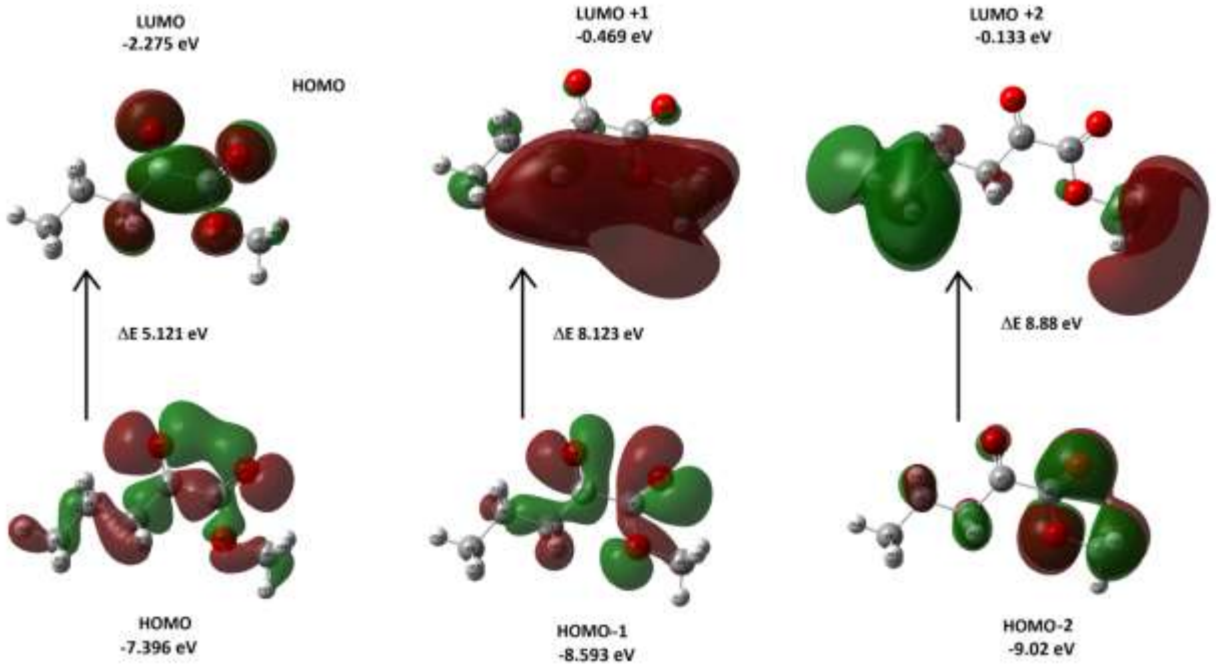

Fig 4: Atomic orbital HOMO - LUMO Composition of 2-oxovaleric acid, methyl ester.

4.7 Donor- acceptor interactions

NBO analysis is one of the most efficient methods to portray intra- and intermolecular bonding, charge transfer, conjugation contraction and stabilization energies that exist in molecular systems. This analysis was performed on the 2-oxovalic acid, methyl ester molecule as shown in Table 3. NBO analysis is performed so as to find electron donor-electron acceptor interaction energies in 2-oxovalic acid methyl, ester molecules. A second-order Fock matrix was adopted to calculate the donor-acceptor interaction during the course of NBO analysis. The stabilization energy E(2) for each electron donor (i) and electron acceptor (i) have been analyzed. The intermolecular hyper connect interactions are identified to be (C5-H12)π to (O7-C8)π*, (C5-H13)π to (C3-O4)σ* and (C5-H14)π to (C3-C4)σ* whereby it is established that the highest stabilization energies for the respective cases are 5.59, 5.11 and 5.10 kj/mol with ED/e values being 1.98734e, 1.96665e and 1.96668e. Another set of data are obtained from LP(O7) to (C5-H12)π*, LP(O7) to (C1-O6)σ* and LP(O6) to (C1-O7)π* by stabilization energies that are identified to be 78.88,44.87 and 35.10kj/mol with ED/e values to be 1.88270e, 1.81140e and 1.85769e, respectively. [41,42,43]

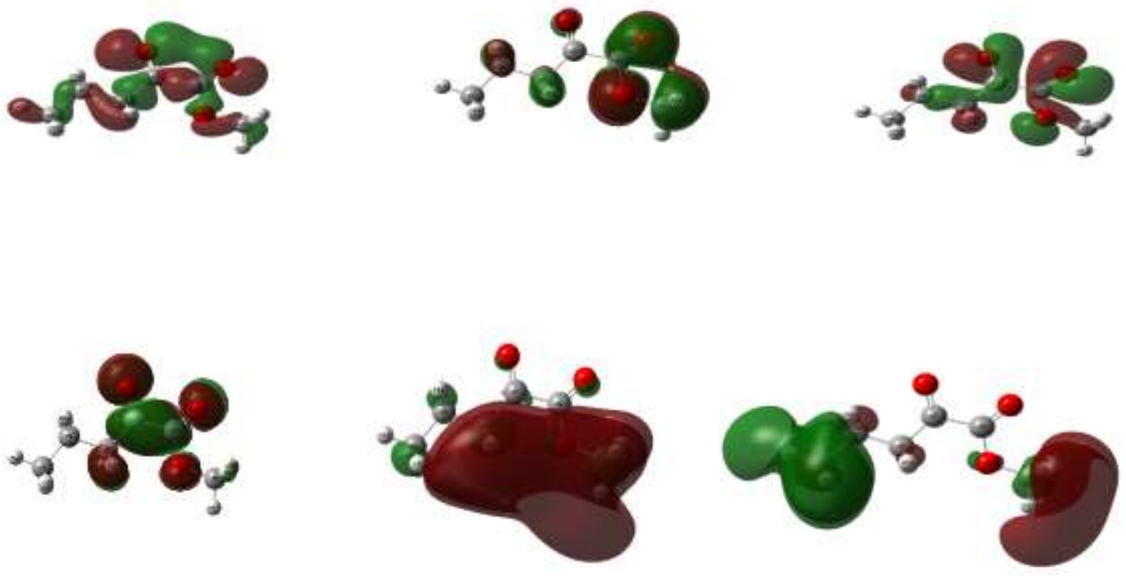

Fig 5: Different pictures of HOMO - LUMO of 2-oxovaleric acid, methyl ester.

4.8 Mulliken analysis

Mulliken charge analysis could enable the manipulation of molecular properties and changes in the dipole moment of chemical bonds displayed within the molecule. The Mulliken atomic charge distribution of the 2-oxovalic acid, methyl ester molecule inferred by the B3LYP/6-311++G(d,p) level is shown in Table 5 and The Mulliken atomic changes of atoms of oxygen (O1-O3) (C4-C9) are found to be negative (nucleophilic attack) and H10-H19 are identified to have positive (electrophilic attack) values. Mulliken atomic charge distribution analysis can contribute to the prediction of the involved intermolecular hydrogen bonds. Frontier molecular orbitals' calculations that have been undertaken can pave the way for the HOMO-LUMO band gap energy (Δ E= 5.121 eV) thereby the probable reactivity properties can be examined for the compound.

Mulliken atomic charges	
Atoms	Charges
O1	-0.093112
O2	-0.199001
O3	-0.231311
C4	-0.212464
C5	-0.263844
C6	-0.587964

C7	0.217910
C8	-0.034228
C9	-0.218727
H10	0.164192
H11	0.167453
H12	0.178350
H13	0.165508
H14	0.147982
H15	0.134877
H16	0.135814
H17	0.159828
H18	0.183291
H19	0.185447

Table 5: Mulliken atomic charges.

Table 6. UV – Vis Excitation Energy and oscillator strengths of 2-oxovaleric acid:

States	B3LYP/6-311++G(d,p)			Experimental value (nm)
	Gas Phase			
	λ cal (nm)	E(eV)	Oscillation strength.	
S1	320.04	3.8741	0.0002	-
S2	269.78	4.5957	0.0028	-
S3	232	5.3528	0.0004	231

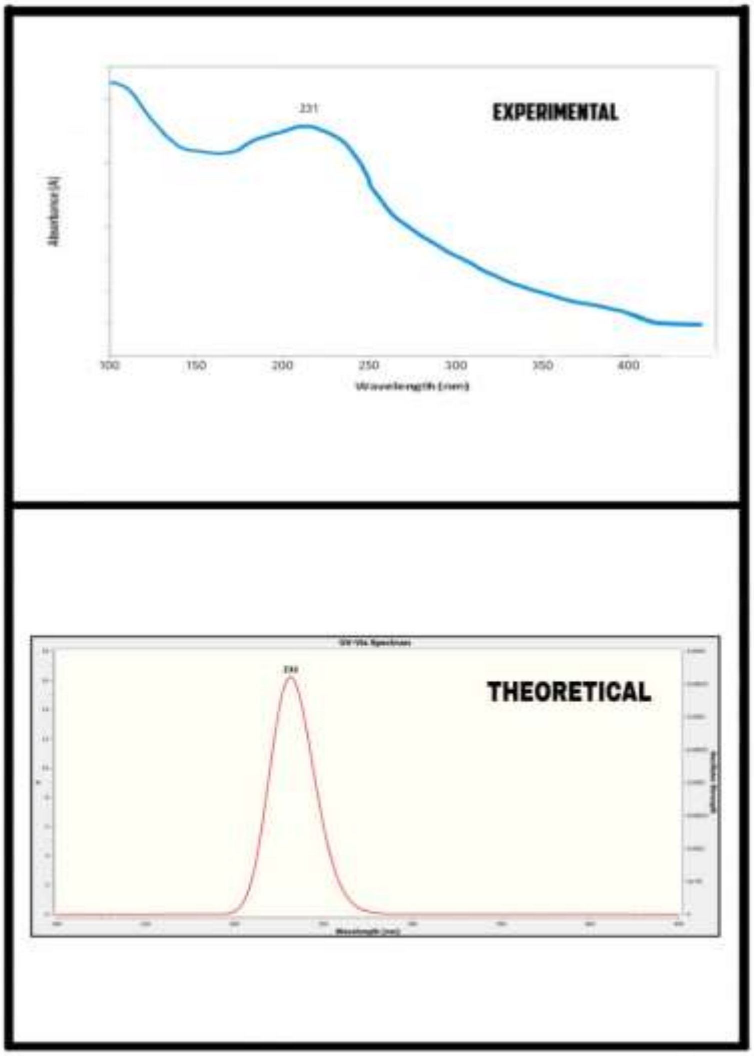

Fig 6: UV - Vis experimental and calculated spectrum of 2-oxovaleric acid, methyl ester.

The transitions that occur for the lowest computed energies are listed together with their vertical excitation energies, oscillator strengths, wavelengths and transition assignments. The visual absorption maxima of the molecule has been accomplished by implementing the calculations of the molecular orbital geometry by which a clear picture of an electron moving from one frontier orbital to another could be established such as from HOMO to LUMO. The obtained spectrum of absorption maximum reveals one broad band which has a long wavelength band spreading across the range between 100 and 450 nm. Fig 6 showcases the UV–visible absorption spectrum that has been recorded in the 450–100 nm region. Intense primary absorption is observed to be at 232 nm, 269.78 nm and 320.04nm. The experimental value of UV - Visible absorption spectrum is obtained to be at 269 nm which is corroborated with the calculated value of 231nm. UV - Vis Excitation energy maximum is located at 5.3528 eV with the wavelength of 232 nm (minimum) while the Excitation energy minimum is identified to be at 3.8741eV with the wavelength of 320.04 nm (maximum).

5. Conclusion

With the outcome of the current work, the molecular structure, vibrational frequency (FTIR) and quantum chemical calculations have been formalized for 2-oxovaleric acid, methyl ester such that its structural as well as spectroscopic features are authenticated. The title compound has been theoretically evaluated using B3LYP functional with 6-311++G (d,p) level of theory thereby the optimized geometrical values are tabulated whereby the comparison with the experimental values at DFT level of theory could be established. The vibrational frequency calculation manifests that both the observed structures are strong. The calculated HOMO-LUMO energy gap reveals that the prevailing charge transfer is because of the interaction occurring within the molecule. Molecular Electrical properties and Mulliken analysis of 2-oxovaleric acid, methyl ester represents the negative potential site which is known to be nucleophilic attack, while the positive potential sites are around the electrophilic attack. The occurring interaction could set out the strongest stabilization energy of the system. The obtained experimental values have been recorded in the presence of the existing intermolecular interactions. Therefore, these calculated frequencies could be a stepping stone for the researches and especially for the experimentalists.

Declarations

Author contribution statement

M. **Lawrence, P. Rajesh -** dream up and map out the demonstration; Performed the demonstration; Analyzed and interpreted the data; subscribe reagents, materials, analysis tools or data; providing the consequential imputation. **S. Sahaya Jude Dhas -** done work of the project administration, Investigation, review and editing, corresponding author of the research paper.

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