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Vibrational Spectra, First Orderhyperpolarizability, HOMO-LUMO and Molecularelectrostatic Potential Analysis of Methyl-2-Hydroxy-4-Methoxybenzoate

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Abstract: The Fourier transform infrared (FT-IR) and FT-Raman spectra of methyl-2-hydroxy-4-methoxybenzoate (M2H4MP) were recorded in the regions $4000-400$ cm^{-1} and $3500-100$ cm^{-1}, respectively. Utilizing the observed FT-IR and FT-Raman data, a complete vibrational assignment and analysis of the fundamental modes of the compounds was carried out. Extensive position of the substituent group in the benzene ring as well as its electron donor-acceptor capabilities plays a very important role on the molecular and electronic properties. The values of the total dipole moment (μ) and the first order hyperpolarizability (β) were computed using B3LYP/6-31+G (d) and B3LYP/6-311++G (d,p) calculations. The calculated HOMO-LUMO energies studies on the vibrational, structural, thermodynamic characteristics as well as the electronic properties of M2H4MP were carried out using DFT methods. In this kind of systems, the show that charge transfer occurs in the molecule. The influence of fluorine, amino and nitro group on the geometry of benzene and its normal modes of vibrations has also been discussed.
Keywords: Vibrational spectra, DFT calculations, HOMO-LUMO, DOS Spectrum, MEP Surface

I. INTRODUCTION

The sample name of methyl-2-hydroxy-4-methoxybenzoate is M2H4MP. It is a non-steroidal ant-inflammatory drug used for decades to relive pain, tenderness, swelling, and stiffness caused by rheumatoid arthritis has now been shown to reduce blood glucose leaves in individuals with type 2 diabetes. It has also been used as an alternative to narcotic pain medicine for people with spinal disc protrusion. The molecular formula for methyl-2-hydroxy-4-methoxybenzoate is $C_9H_{10}O_4$. It is a white crystalline powder and soluble in organic solvents such as ethanol, DMSO and acetone. The hydrogen bonding in M2H4MP crystal was described in literature [1]. The fluorimetric determination of M2H4MP in urine, serum and Pharmaceutical preparations were reported by Pulgarin and Bermejo [2]. The simultaneous TG-DTA study of the thermal decomposition of methyl-2-hydroxy-4-methoxybenzoate ester has been studied [3]. Haemostatic effects of M2H4MP were and changes in thyroid function tests during short-term M2H4MP were reported earlier [4, 5].

In spite of its importance for Pharmaceutical purpose, the reported spectroscopical studies on M2H4MP are scarce. The evolution of density function theory that includes electron correlation in an alternative way has affording opportunities of performing vibrational analysis of moderately large organic molecular. The results for DFT theory with results obtained from experiments has shown that the methods using B3LYP are the most promising in providing correct vibrational wave numbers. The kinetics and decomposing methy-2-hydroxy-4-methoxybenzoate have been studied with the help of thermogravimetry-differential thermal analysis (TG-DTA) and gas and liquid chromatography [6]. The hydrogen bonding in the M2H4MP crystal was previously carried out and the position of hydroxyl group in ortho position on an aryl ring with possible intermolecular hydrogen bonds are discussed with the crystal data collected at low temperature [7]. From the crystal data, the structure of the molecule was determined and there's no information about the structure conformation and vibrational analysis of the molecule. Literature survey reveals that so far there is no complete the oretical study for the title compound.M2H4MP in this study, we sat out experimental and theoretical investigation of the conformation, vibration and electron transition of M2H4MP.

In the ground state theoretical geometrical parameters, IR, Raman Detailed interpretations of the vibrational spectra of the basis of the calculate potential energy distribution (PED). The experimental results (IR, Raman) were supported by the computed results,

comparing with experimental characterization data, vibrational wave numbers and absorption wave length values are in fairly good agreement with the experimental results. The stable position with respect to pyridine ring was obtained by performing the potential energy surface (PES) scans with B3LYP/6-31+G (d) and B3LYP/6-311++G (d, p) level of theory. By analyzing the total density of state (TDOS) and partial density of state (PDOS), the molecular orbital compositions and their contributions to the chemical bonding were studied. The study of the HOMO and LUMO analysis has been used to elucidate information recording charge transfer within the molecule. Moreover, the Mulliken population analyses of the title compound have been reported. The experimental and theoretical results supported each other, and the calculations are valuable for providing a reliable inside in to the vibrational spectra and molecules properties.

II. EXPERIMENTAL DETAILS

The sample solid from provided by the Lancaster chemical company (USA) with a purity of greater than 98/ and was used as such without further purification. The FT-IR spectrum of this compound was recorded in the region 4000-400cm^{-1} spectrometers. The FT-Raman spectrum of the title molecule has been recorded excitation wavelength in the region 3500-100cm^{-1} spectrometer. The FT-Raman spectrum of M2H4MP has been recorded in frequency region 3500-100 cm^{-1} on NEXUS spectrophotometer equipped with Raman module accessory with some power continuously excitation. The reported wave number are expected to the accurate within ±-cm^{-1}.The date were recorded in the co-addition of 200 scans at ±-1cm^{-1} resolution with 250 mw of power at the sample in both the techniques.

III. COMPUTATIONAL DETAILS

Analysis of molecular geometry software package at the DFT(B3LYP)levels supplemented with the standard 6-31+G(d) and 6-311++G(d, p) basis sets. Cartesian representation of the theoretical force constants has been computed at optimized geometry. Vibrational modes were assigned by means of visual inspection using Gauss View [9] Data revealed that DFT calculation yielded results that are in better agreement with these experimental data. Prediction of Raman intensities was carried out by the following procedure. The transformation of force field, subsequent normal coordinate analysis and calculation of the PED were done on a PC with the MOLVIB program (Version 7.0–G77) written by Sundius [10].

The Raman activities (S_R) calculated with the GAUSSIAN 09W Program were converted to Raman intensities (I_R) using the following relationship derived from the intensity theory of Raman scattering.

$$I_R = \frac{f(\upsilon_0 - \upsilon_i)^4 S_R}{\upsilon_i[1 - \exp(-hc\upsilon_i/kT)]}$$

where υ_0 is the laser exciting frequency in cm^{-1} (in this work, we have used the excitation wavenumber υ_0=9398.5 cm^{-1}, which corresponds to the wavelength of 1064 nm of a Nd:YAG laser), υ_i is the vibrational wavenumber of the ith normal mode (in cm^{-1}) and S_R is the Raman scattering activity of the normal mode υ_i, f (is the constant equal to 10^{-12}) is a suitably chosen common normalization factor for all peak intensities. h, k, c, and T are Planck constant, Boltzmann constant, speed of light, and temperature in Kelvin, respectively.

A. Hyperpolarizabilty & Polarizability

The polarizabiliy (α), hyperpolarizability (β) and electric dipole moment (μ) of the title compound M2H4MP are calculated by B3LYP methods using with 6-31+G (d) and 6-311++G (d, p) basis sets, based on the finite field approach, polarizability and hyperpolarazability characterized the response of a system in applied electric field [8] To calculate all the electric dipole moment and the first hyperpolarizability tensor components for a given system will depend on the choice of the Cartesian co-ordinate system (x, y, z) = (0, 0, 0) was chosen at own centre of mass of molecule. The polarizability of this novel molecular system for which α_{xx}=α_{yy}=α_{zz} is said to be isotropic. The polarizability is isotropic or is the same in all direction for a molecular system whose electron density is spherically symmetrical. If the molecule is perfectly isotropic (P) and (E) will have the same direction and is then a simple scalar quantity .The polarizability of this novel molecular system for which α_{xx}≠α_{yy}≠α_{zz} (p) will no longer have the same direction as (E).The first hyperpolarizability (βtot) and related properties (α, β and Δα) of M2H4MP are calculated and it is based on the finite- field approach. The presence of external electric field (E) energy of the system is a function of the electric field the components of β are defined as the coefficients in the Taylor series expansion of energy in an external electric field. The external electric field is weak and homogeneous.

$$E = E^0 - \frac{\mu_i F_i}{1!} - \frac{\alpha_{ij} F_i F_j}{2!} - \frac{\beta_{ijk} F_i F_j F_k}{3!} - \frac{\gamma_{ijkl} F_i F_j F_k F_l}{4!} + \cdots$$

Where $E°$ is the energy of the unperturbed molecules Fi is the field at the origin hyperpolarizability respectively. The total static dipole moment (μ), the mean polarizability (α), the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyperpolarizability (β_{tot}) using the x, y, z components can be calculated using the following equation.

The total static dipole moment is

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}}$$

The isotropic polarizability is

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

The polarizability anisotropy invariant is

$$\Delta\alpha = 2^{-\frac{1}{2}}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{\frac{1}{2}}$$

The average hyperpolarizability

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}}$$

where

$$\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$$
$$\beta_y = (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})$$
$$\beta_z = (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})$$

The value of polarizability and hyperpolarizability of the Gaussian09 output are reported in atomic units (a.u) the calculated values have been converted into electrostastic units (e.s.u) (1a.u=8.639×10^{-33}e.s.u).The total molecular dipole moment, and first hyperpolarizability are 1.1212 debye, and 3.89×10^{-30} e.s.u B3LYP/6-31+G (d) and 1.1273 decay 3.67×10^{-30} e.s.u in 6-311++G (d, p) methods in Table 1, respectively.

Table 1

The electric dipole moment (μ) (debye), the mean polarizability (α) (e.s.u.), anisotropic polarizability $(\Delta\alpha)$ (e.s.u.) and first hyper polarizability (β_{tot}) (e.s.u) for methyl-2-hydroxy-4-methoxybenzoate at B3LYP/6-31+G (d) and B3LYP/6-311++G (d, p) methods.

Parameters	B3LYP/631+G (d)	B3LYP/6-311++G (d, p)
μ_x	0.447715	0.407328
μ_y	1.0279884	1.0511804
μ_z	-0.0008813	-0.000852
μ	1.121205056	1.127337893
α_{xx}	152.4996898	156.6261713
α_{xy}	29.791322	31.441391
α_{yy}	0.0016717	0.0020345
α_{xz}	154.2631567	158.2774315
α_{yz}	-0.0288533	-0.0284765
α_{zz}	71.571501	74.1609411
α	74.69095417	76.92304897

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$\Delta\alpha$	24961.43792	130123.0083
β_{xxx}	193.9161315	174.6481461
β_{xxy}	0.0508	0.0598374
β_{xyy}	-511.047863	-492.8572626
β_{yyy}	717.7889755	-165.1594534
β_{xxz}	0.2519039	0.2306008
B_{xyz}	0.3142405	-0.0731282
β_{yyz}	0.31424	-32.4496547
B_{xzz}	-33.4914381	0.2802466
β_{yzz}	57.8130864	56.334709
β_{zzz}	385.5366311	367.4280152
β_{tot}	3.89×10^{-30} e.s.u	3.67×10^{-30} e.s.u

IV. RESULTS AND DISCUSSION

A. Molecular Geometry

The Optimized molecular structure of M2H4MP belongs to c_1 point group symmetry. The most optimized geometry is performed at B3LYP/6-31+G (d) and B3LYP/6-311++G (d, p) basis sets of M2H4MP molecule with atom numbering scheme is shown in Fig. 1. The comparative optimized structural parameters such as bond length, bond angle are presents in Table 2. Comparing B3LYP/6-31+G (d) and B3LYP/6-311++G (d, p) levels, most of the bond lengths and bond angles of B3LYP/6-311++G (d, p) are slightly shorter due to the neglect of electron correlation. The inclusion of polarizability functions is important to have a good agreement with experimental geometry.
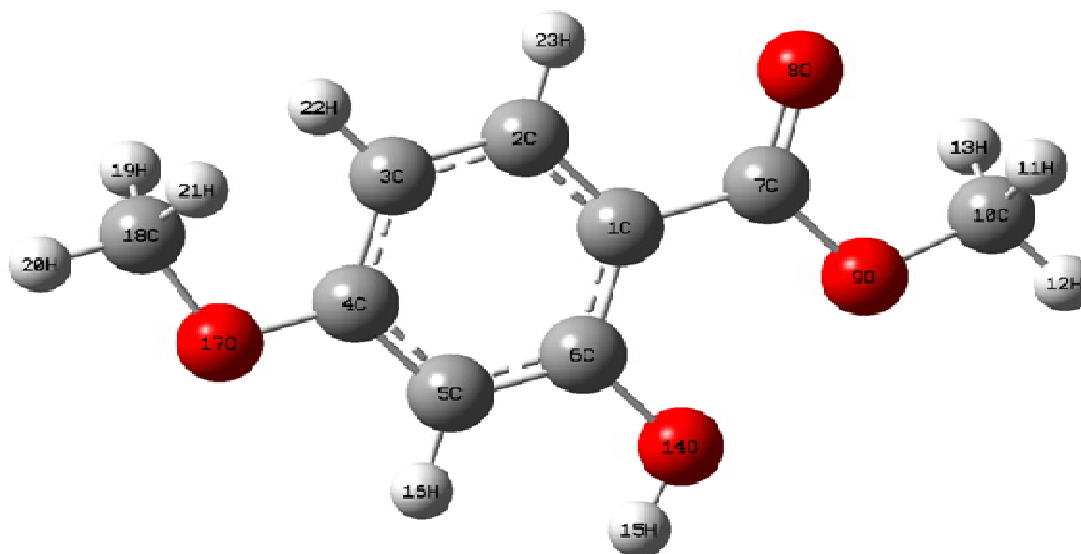

Fig. 1. The theoretical geometry structure and atomic numbering scheme of methyl-2-hydroxy-4-

B. Structural Properties

The optimized geometry of M2H4MP is calculated at B3LYP level with 6-31+G (d) and 6-311++G(d, p) basis sets and visualized using GAUSSIAN and GAUSSVIEW program in shown in Fig.1. The molecule consists of 23 atoms and expected to have 63 normal modes of fundamental vibrations out of which 22 modes are of stretching type and 21 and are of bending and 20 torsion. The optimized bond parameters of M2H4MP calculated by DFT method are listed in table 2. The C=O (C_7-O_8) band is shortened by experimental value and there is a deviations in (O_8-C_7-H_{23}) band angle due to the formation of inter molecular hydrogen band between C_7 and H_{23}. All bond lengths are in good agreement with the experimental data [12, 13]. Compared to DFT method yields

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the bond lengths close to experimental results. There is also in C_{15}-H_{16}-O_{17} band angle due to the presence of ether oxygen between phenol groups. The oxygen atom leads to the re-distribution of partial charges on the oxygen atom as the unpaired electron is delocalized.

Table 2 Optimized geometrical parameters of methyl-2-hydroxy-4-methoxybenzoate by B3LYP/6-31+G (d) and B3LYP/6-311++G (d, p) methods.

| Atoms | Bon lengths Å | | Atoms | Bon angles(degrees) | | Atoms | Dihedral angles (degrees) | |
| | B3LYP | | | B3LYP | | | B3LYP | |
	6−31+G (d)	6−311++G (d, p)		6−31+G (d)	6−311++G (d, p)		6−31+ G (d)	6−311++ G (d, p)
C_1-c_2	1.4006	1.3979	C_2-C_1-c_6	117.37	117.33	C_6-C_1-C_2-C_3	0.00	0.00
C_1-c_6	1.4149	1.4121	C_2-C_1-c_7	115.84	115.91	C_6-C_1-C_2-H_{23}	-180.00	180.00
C_1-c_7	1.4883	1.4869	C_6-C_1-c_7	126.79	126.76	C_7-C_1-C_2-C_3	-180.00	-180.00
C_2-c_3	1.3868	1.3839	C_1-c_2-c_3	123.19	123.20	C_7-C_1-C_2-H_{23}	0.00	0.00
C_2-H_{23}	1.0828	1.0800	C_1-c_2-H_{23}	116.94	116.92	C_2-C_1-C_6-C_5	0.00	0.00
C_3-C_4	1.3999	1.3975	C_3-c_2-H_{23}	119.88	119.88	C_2-C_1-C_6-O_{14}	180.00	-180.00
C_3-H_{22}	1.0805	1.0777	C_2-c_3-c_4	118.54	118.55	C_7-C_1-C_6-C_5	180.00	180.00
C_4-C_5	1.3957	1.3930	C_2-c_3-H_{22}	119.78	119.81	C_7-C_1-C_6-O_{14}	-0.01	0.00
C_4-O_{17}	1.3580	1.3574	C_4-c_3-H_{22}	121.68	121.64	C_2-C_1-C_7-O_8	-0.01	0.02
C_5-C_6	1.3929	1.3902	C_3-C_4-C_5	119.74	119.72	C_2-C_1-C_7-O_9	180.00	-179.98
C_5-H_{16}	1.0851	1.0824	C_3-C_4-O_{17}	124.72	124.72	C_6-C_1-C_7-O_8	180.00	-179.98
C_6-O_{14}	1.3596	1.3599	C_5-C_4-O_{17}	115.54	115.56	C_6-C_1-C_7-O_9	0.00	0.02
C_7-O_8	1.2144	1.2132	C_4-C_5-C_6	121.20	121.17	C_1-C_2-C_3-C_4	0.00	0.00
C_7-O_9	1.3450	1.3447	C_4-C_5-H_{16}	118.38	118.51	C_1-C_2-C_3-H_{22}	180.00	-180.00
O_9-C_{10}	1.4369	1.4362	C_6-C_5-H_{16}	120.42	120.31	H_{23}-C_2-C_3-C_4	180.00	-180.00
C_{10}-H_{11}	1.0911	1.0881	C_1-C_6-C_5	119.97	120.02	H_{23}-C_2-C_3-H_{22}	0.00	0.00
C_{10}-H_{12}	1.0880	1.0853	C_1-C_6-O_{14}	120.21	120.22	C_2-C_3-C_4-C_5	0.00	0.00
C_{10}-H_{13}	1.0911	1.0881	C_5-C_6-O_{14}	119.83	119.76	C_2-C_3-C_4-O_{17}	-180.00	180.00
O_{14}-H_{15}	0.9636	0.9623	C_1-C_7-O_8	123.26	123.18	H_{22}-C_3-C_4-C_5	180.00	180.00
O_{17}-C_{18}	1.4246	1.4240	C_1-C_7-O_9	114.23	114.31	H_{22}-C_3-C_4-O_{17}	0.00	0.00
C_{18}-H_{18}	1.0945	1.0914	O_8-C_7-O_9	122.52	122.52	C_3-C_4-C_5-C_6	0.00	0.00
C_{18}-H_{20}	1.0884	1.0856	C_7-O_9-C_{10}	115.74	115.35	C_3-C_4-C_5-H_{16}	-180.00	180.00
C_{18}-H_{21}	1.0945	1.0914	O_9-C_{10}-H_{11}	110.62	110.60	O_{17}-C_4-C_5-C_6	180.00	-180.00
			O_9-C_{10}-H_{12}	105.26	105.31	O_{17}-C_4-C_5-H_{16}	0.00	0.00
			O_9-C_{10}-H_{13}	110.62	110.60	C_3-C_4-O_{17}-C_{18}	0.01	0.01
			H_{11}-C_{10}-H_{12}	110.65	110.65	C_5-C_4-O_{17}-C_{18}	180.01	180.00
			H_{11}-C_{10}-H_{13}	109.03	109.01	C_4-C_5-C_6-C_1	0.00	0.00
			H_{12}-C_{10}-H_{13}	110.65	110.65	C_4-C_5-C_6-O_{14}	-180.00	180.00
			C_6-O_{14}-H_{15}	108.87	108.84	H_{16}-C_5-C_6-C_1	-180.00	-180.00
			C_4-O_{17}-C_{18}	118.78	118.52	H_{16}-C_5-C_6-O_{14}	0.00	0.00
			O_{17}-C_{18}-H_{19}	111.28	111.26	C_1-C_6-O_{14}-H_{15}	-180.02	180.00
			O_{17}-C_{18}-H_{21}	105.69	105.73	C_5-C_6-O_{14}-H_{15}	-0.02	0.00
			O_{17}-C_{18}-H_{21}	111.28	111.26	C_1-C_7-O_9-C_{10}	-180.01	179.99
			H_{19}-C_{18}-H_{20}	109.41	109.44	O_8-C_7-O_9-C_{10}	0.00	-0.01
			H_{19}-C_{18}-H_{21}	109.66	109.64	C_7-O_9-C_{10}-H_{11}	60.48	60.45
			H_{20}-C_{18}-H_{21}	109.41	109.44	C_7-O_9-C_{10}-H_{12}	-179.98	-179.98
			C_2-C_1-C_6	117.37	117.33	C_7-O_9-C_{10}-H_{13}	-60.44	-60.41
						C_4-O_{17}-C_{18}-H_{19}	61.31	61.28
						C_4-O_{17}-C_{18}-H_{20}	179.99	-180.01
						C_4-O_{17}-C_{18}-H_{21}	-61.32	-61.29
						C_6-C_1-C_2-C_3	0.00	0.00

Notes: Bon lengths re in Å- bon angles n iherl angles re in egress.

C. Vibrational Assignments

On the basis of theoretical investigation as discussed earlier, the atoms of these compounds occupy sites of the C1 symmetry. The compound has 23 atoms and the three Cartesian displacements of the compound provide 63 internal modes out of which 40 vibrations (stretching and deformation) are in plane and 20 vibrations are out of plane. The assignments of the experimental wave numbers based on normal mode analyses are provided in Table 3. The calculated harmonic force constants and frequencies are usually higher than the corresponding experimental quantities are due to combination of electron correlation effect and basis sets deficiencies. The polarized Raman wave numbers of M2H4MP with their respective IR counter parts are depicted in Fig. 2 and 3, respectively. Density functional theory (DFT) calculated frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation; basis sets deficiencies and anhormonicity [14].The values of uncertainties are insensitive to the theoretical method employed despite the neglect of electron correlation in the high level treatment of correlation in DFT theory. The uncertainties range from 0.05 to 0.7 cm^{-1} with a medium value of 0.2 cm^{-1}.

D. Ring Vibrations

The position and intensity of ring stretching vibrations depend on the natural of the ring and the type of substitution. In M2H4MP, FT-IR bands at 1593, 1506, 1462, 1377, 1348, 1267 cm^{-1} the frequency ranges given by Varsanyi [15] and FT-Raman bands at 1669, 1620, 1578, 1473, 1466, 1344, 1247 have been assigned to aromatic CC stretching vibrations. The carbon−carbon stretching modes of the phenyl group are expected in the region 1650−1200 cm^{-1} [16]. The ring in-plane and out of plane bending vibrations are assigned in the characteristic region. The ring stretching vibrations are all coupled vibrations, some vibrations coupled with C-H bending and some with O-H bending and some with C-O-C stretching vibrations. Small changes due to the change in force constant/reduced mass ratio resulting mainly due to the extent of mixing between ring and substituent group. The absorptions involves stretching of bands in ring and interaction between these stretching

E. C-C Vibrations

The C−C Stretching vibrations show absorption in the region 1260−700 cm^{-1} [17]. Accordingly, the bands observed at 1181, 1108, 1034 and 1000 cm^{-1} in FT-IR and observed at 1156, 1122, 1108 and 1000 cm^{-1} in FT-Raman spectra due to C−C stretching vibrations which are well comparable with the computer values. The theoretically calculated M2H4MP bending vibrations have been found to be consistent with the recorded spectral values and it is listed in Table 3 with contribution of PED, respectively.

C=O vibrational The band observed in the region 1700-1800 cm^{-1} is usually the most characteristics feature of carboxylic group. Also Koczen et al., [18] observed the range of 1800-1500 cm^{-1}, the C=O is group stretching vibrations. The C=O stretching vibration of the M2H4MP is observed at cm^{-1} in FT-IR and cm^{-1} in FT-Raman spectrum and these wave numbers are good coherent with empirical values. Also this mode is observed at and cm^{-1} in FT-IR and FT-Raman spectrum by Abkowicz et al., [19]. The C=O and C-O Vibrations also show fairly good coherent in literature.

Table 3

Vibrational assignments of FT-IR n FT-Raman peaks long the theoretically compute wave numbers- IR intensity I_{IR} n Raman intensity I_{Rmn} n the percentage of potential energy distribution of methyl-2-hydroxy-4-methoxybenzoate.

S. No	Observed wave number cm^{-1}		B3LYP/6-31+G (d)				B3LYP/6-311++G (d,p)				assignments with % of PED^C
	FT-IR	FT-Raman	Calculate wave number cm^{-1}		I_{IR}	I_{Raman}	Calculated wave number cm^{-1}		I_{IR}	I_{Raman}	
			Un scaled	Scaled			Un scaled	Scaled			
1	3179		3821	3514	60.42	111.74	3824	3516	60.18	109.25	υOH(97)
2		3083	3218	3081	6.25	106.72	3225	3086	5.86	104.57	υCH(97)
3			3198	3056	0.18	38.01	3206	3057	0.22	37.95	υCH(97)
4			3168	3023	5.22	99.83	3174	3026	4.96	97.59	υCH(98)
5		3016	3152	3015	15.96	77.58	3157	3017	14.55	74.44	CH$_3$ass(93)
6			3139	3006	19.32	133.81	3145	3011	17.50	129.40	CH$_3$ass(92)

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7		2970	3118	2976	21.29	61.73	3126	2972	18.81	61.02	CH$_3$ass(90)
8	2924		3076	2923	31.77	58.07	3084	2927	28.22	56.22	CH$_3$ass(92)
9			3047	2893	43.94	203.74	3058	2894	42.03	213.02	CH$_3$(91)
10	2854		3014	2452	53.94	171.09	3025	2955	50.81	179.29	CH$_3$ss(83)
11	1672	1669	1740	1670	335.95	89.42	1732	1668	317.50	86.45	υC=0(84)
12	1625	1620	1651	1626	414.94	171.37	1649	1621	411.41	170.79	υCC(84)βCH(8)
13	1593	1597	1612	1596	41.67	12.18	1611	1591	36.99	9.87	υCC(75)βCH(12)
14		1578	1593	1576	45.67	8.75	1598	1574	42.17	7.90	CH$_3$ipb(73)
15	1506		1524	1503	41.31	8.09	1529	1507	34.85	6.04	CH$_3$ipb(75)
16		1473	1497	1477	9.16	9.29	1501	1475	9.94	8.54	υCC(75)
17	1461	1466	1492	1467	9.93	14.32	1499	1462	9.05	10.14	υCC(71)βCH(11)
18			1481	1449	8.64	13.57	1487	1442	8.6	9.92	υCC(84)
19		1441	1475	1443	13.29	3.38	1479	1440	16.14	2.71	CH$_3$opb(66)
20	1377		1422	1379	74.96	7.79	1425	1378	57.91	8.40	CH$_3$opb(63)
21		1369	1410	1367	50.98	0.64	1413	1368	56.52	0.39	υC-O(71)
22	1348	1344	1376	1345	6.82	2.80	1375	1346	8.83	2.28	CH$_3$sb(65)
23	1299		1328	1295	57.16	1.71	1332	1298	69.32	0.87	CH$_3$sb (60)
24	1267		1282	1267	48.23	1.87	1292	1266	61.65	3.13	υC-O(71)
25		1247	1247	1283	776.32	156.44	1280	1284	736.70	149.54	βCH(60)υCC(12)
26	1224		1223	1223	171.56	8.34	1245	1221	149.05	8.99	βOH(45)
27	1204		1213	1206	35.76	5.23	1225	1207	34.73	3.78	υC-O(61)
28	1170	-	1195	1168	37.98	4.93	1197	1169	39.60	6.48	βOH(54)
29		-	1189	1159	68.76	11.27	1192	1157	76.63	9.84	βCH(43)υCC(12)
30	1150	-	1169	1149	0.89	3.07	1172	1151	1.07	1.66	υC-O(43)
31		-	1166	1146	0.67	2.75	1170	1143	0.77	1.55	υC-O(48)
32	1138	-	1157	1139	285.42	0.12	1157	1137	292.15	0.12	βCH(47)
33	1095		1119	1093	19.57	3.87	1120	1096	16.81	4.09	CH$_3$ipr(48)
34	1034	-	1058	1035	51.75	5.15	1057	1033	52.14	5.31	CH$_3$ipr(51)
35	954	-	988	957	9.89	2.96	991	958	1.02	0.03	γCH(54)
36	955		982	953	2.12	0.08	988	957	10.52	2.30	CH$_3$opr(63)
37	838		857	836	4.19	12.68	856	834	3.37	12.05	CH$_3$opr(62)
38		824	836	822	46.88	0.06	841	825	42.43	0.15	βC-O(61)
39	780		815	779	1.47	0.69	811	781	3.54	0.27	γCH(48)
40	771		811	772	3.80	16.77	809	770	3.49	17.83	βC-O(47)
41		736	754	737	26.23	0.54	775	735	21.31	0.57	βC-O(46)
42	723		746	724	4.84	16.35	747	722	4.53	16.81	βC=O(48)
43	698		713	697	11.44	0.05	725	700	15.60	0.11	γCH(47)
44		624	646	623	1.79	0.72	651	627	2.13	1.06	βC-O(48)
45			615	598	26.49	2.63	616	599	27.47	2.34	βC-O(47)
46		586	601	584	22.83	0.43	602	586	21.94	0.35	βCCC(45)
47	520		538	519	4.61	6.71	540	521	4.86	6.50	γC-O(46)
48	457		468	456	4.97	0.07	472	459	5.69	0.06	γC-O(53)
49			428	413	10.81	2.58	430	414	10.53	2.48	γC-O(51)
50			376	372	8.07	2.48	378	373	7.92	2.32	CH$_3$twist(46)

51			337	331	24.00	0.81	374	332	75.52	1.34	CH$_3$twist(48)
52			319	313	6.42	4.36	320	314	7.14	3.93	γC-O(42)
53			313	306	1.49	0.76	318	304	12.79	1.74	γOH(43)
54	252		262	251	70.98	2.41	271	254	0.76	1.00	γC=O(41)
55			229	214	1.41	0.41	233	216	0.03	0.50	γC-O(40)
56			228	210	4.10	2.07	229	212	3.67	2.17	βCCC(43)
57			213	206	0.00	1.18	217	207	0.09	1.07	βCCC(41)
58			156	148	5.31	0.33	160	149	5.39	0.23	βCCC(40)
59			139	132	2.78	0.07	140	133	2.74	0.07	βCCC(41)
60			125	119	0.73	0.64	136	121	1.30	0.33	γCCC(40)
61			92	86	0.73	0.07	94	87	1.09	0.06	γCCC(42)
62			66	60	1.77	0.33	67	61	1.21	0.31	γCCC(43)
63			16	15	2.32	0.10	18	16	2.12	0.07	γCCC(41)

ss – sym. stretching- ss – sym. stretching- ipb – in-plane-bending- opb – out-of-plane bending- sb – sym. bending- ipr – in-plane rocking- opr – out-of-plane rocking- sciss – scissoring- rock – rocking- wag – wagging- twist – twisting. Assignments: v - stretching- β - in-plane bending- γ- out-of-plane bending.
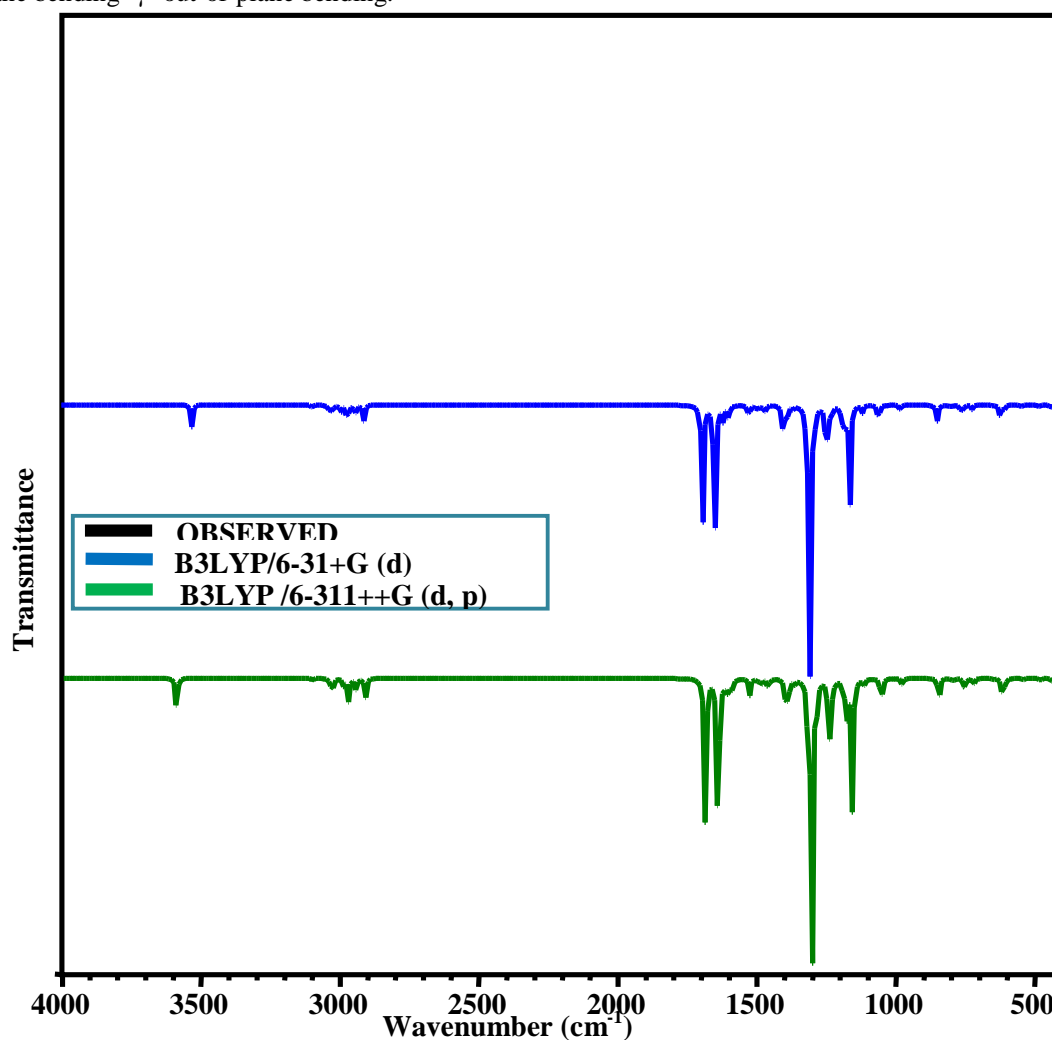
Fig. 2. Comparative representation of FT-IR spectra for methyl-2-hydroxy-4-methoxybenzoate.

F. C-H Vibration

Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000cm^{-1} [20] due to aromatic stretching vibrations. The IR bands at 3179, 2924, 2854cm^{-1} are assigned to C-H stretching vibrations of M2H4MP. All major contributions from C-C stretching vibrations and C-H deformation modes are assigned to absorptions at 1300-1100 cm^{-1}.The C-H out-of-plane bending occurs in the region 900-667 cm^{-1} [21]. In this region the bands are not affected appreciably by the nature of the substituent. FT-IR bands at 1377, 1348, 1299, 1267, 1138, 1034 and FT-Raman band at 824 cm^{-1} bending vibrations of M2H4MP are well identified in the recorded spectra within the characteristic region.
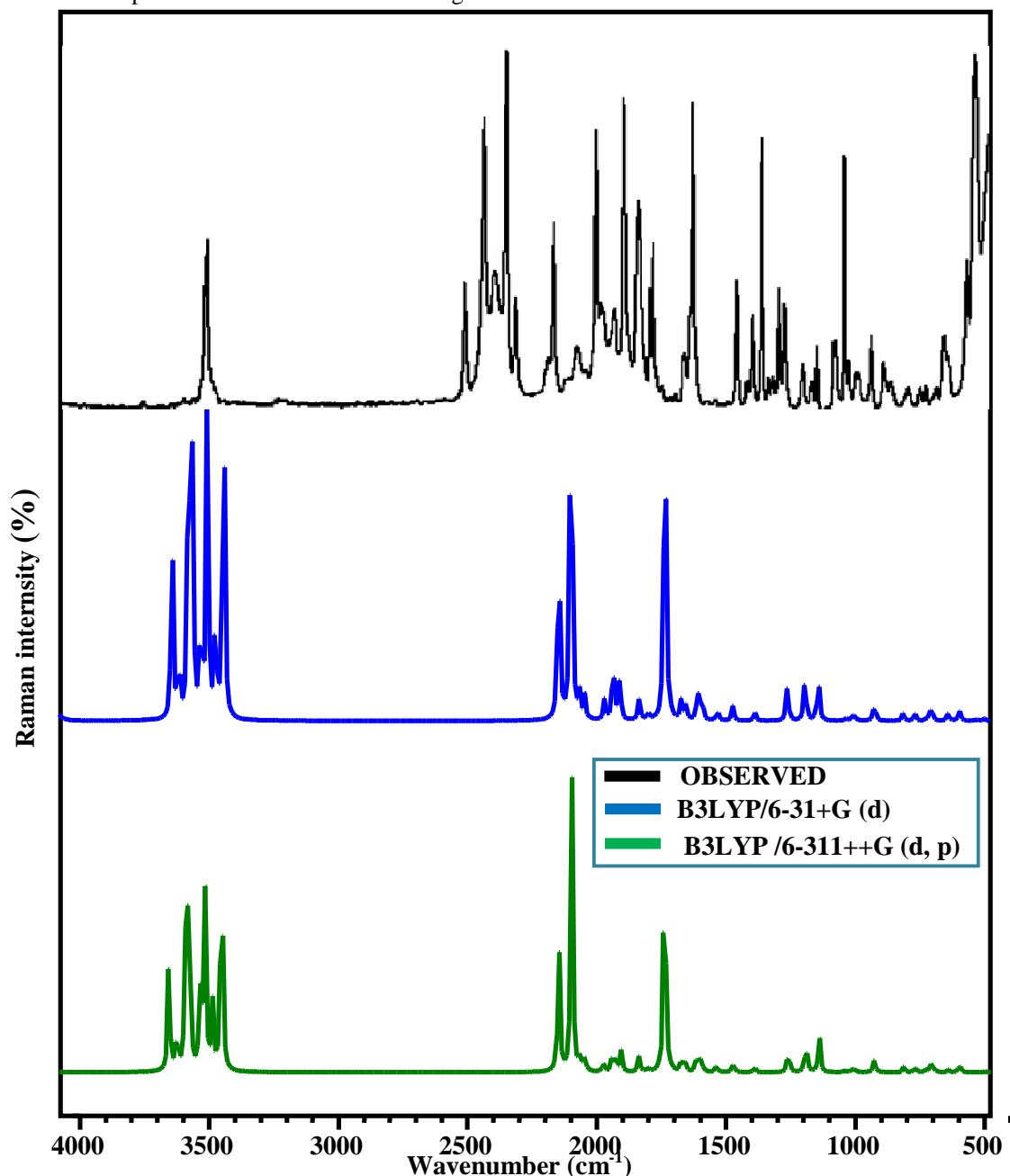
Fig. 3. Comparative representation of FT-Raman spectra for methyl-2-hydroxy-4-methoxybenzoate.

G. Methyl group Vibrations

The title molecule M2H4MP under consideration possesses a single CH$_3$ group in first position of the ring. For the assignments of CH$_3$ group frequencies, are can expect nine fundamentals can be associated to each CH$_3$ group, namely the asymmetrical stretching

(CH$_3$ass), symmetrical stretching (CH$_3$ss), in-plane bending (CH$_3$ipb), out-of plane bending (CH$_3$opb), symmetric bending (CH$_3$sb), the in-plane rocking (CH$_3$ipr), out-of-plane rocking (CH$_3$opr) and twisting mode in CH$_3$ (CH$_3$twist). Methyl groups are generally referred as electron donating substitution in the aromatic ring system [22]. In aromatic compounds, the CH$_3$ asymmetric stretching vibrations occurs at values greater than 3000 cm^{-1} and CH$_3$ Symmetric stretching vibrations occurs at values just below then 3000 cm^{-1} [23]. The CH$_3$ methyl groups stretching vibrations are generally observed in the range of 3000-2800 cm^{-1} [24]. The above results from asymmetric stretching CH$_3$ mode in which the two C-H bonds of the methyl group are extending while the third one is contracting it is symmetric stretching mode, in which all the three C-H bond extend and contract in space .In the present case, the FT-IR and FT-Raman band at 3068, 2954 and 3066 cm^{-1}represent asymmetric stretching mode.

 The calculated asymmetric modes are 3070, 3066, 2955 cm^{-1} B3LYP method good assignment observed data's. The symmetric mode was calculated at 2780 and 2782 cm^{-1} by B3LYP method respectively with PED contribution 95% two bending modes can occur within a methyl group. The first of these, the symmetric bending vibration, involves the in-phase bending of C-H bonds. The second the asymmetric bending vibration, involves out-of-phase bending of the C-H bonds. For M2H4MP the values observed at 1524 cm^{-1} and 1526 cm^{-1} in FT-Raman spectrum are contributed to CH$_3$ in-plane bending vibrations. The out-of-plane bending modes are calculated at 1404 and 1402 cm^{-1} by B3LYP method respectively with PED contribution of 98% .methyl rocking frequencies are mass sensitive and variable in position due to the skeletal stretching modes. Generally these band are observed in range 1120 -1050 cm^{-1} and 900-800 cm^{-1}, In the present molecule, the FT-IR and FT-Raman spectra source the bands at 1023 and 1028 cm^{-1} assigned in in-plane rocking and 960 cm^{-1} in out-of-plane rocking vibrations. As CH$_3$ twisting mode is expected below 400 cm^{-1}, the computed bands at 132 and 134 cm^{-1} in B3LYP method with 6-31+G (d) and 6-311++G (d, p) basis sets, respectively, are assigned to mode, for, no spectral measurements were possible in the region due to instrumental limits the C-CH$_3$ stretching vibration observed 1237 cm^{-1} the C-CH$_3$ in-plane and out-of-plane bending vibrations are assigned at 311 and 210 cm^{-1} respectively, in B3LYP method and it is in the expected range.`

H. Mulliken s Atomic Charge

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation molecular System because of atomic charges effect dipole moment, molecular polarizability, electronic structure and a lot of properties of molecular system [25].The charge distributions over the atoms suggest the formation of donor and acceptor pair involving The charge transfer in the molecule. The Mulliken population analysis in molecule is calculated using B3LYP level with 6-3+G (d) and 6-311++G (d, p) basis sets are listed. The plot Mulliken atomic charge is shown in fig.4. The Mulliken charge analysis of B3LYP shows that presence of four atoms (O$_8$=-0.2756), (O$_{14}$= -0.1949), (O$_{17}$=-0.1639), (O$_9$= -0.1357) are negative charges and imposes positive charges on C$_1$, C$_7$, H$_{11}$, H$_{12}$, H$_{13}$, H$_{15}$, H$_{16}$, H$_{19}$, H$_{20}$, H$_{21}$, H$_{22}$, H$_{23}$ atoms. Moreover the positive charge distribution (H$_{11}$, H$_{12}$, H$_{13}$, H$_{15}$, H$_{16}$, H$_{19}$, H$_{20}$, H$_{21}$, H$_{22}$ and H$_{23}$) are lsted in Table 4, respectively.
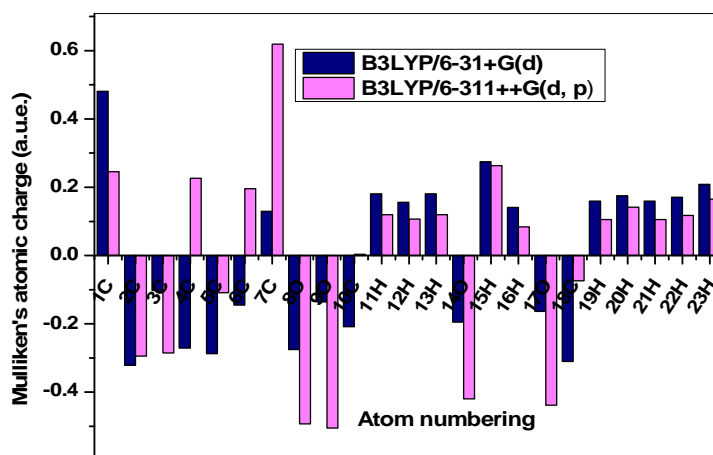

Fig. 4 Bar diagram representing the Mulliken atomic charge distribution of methyl-2-hydroxy-4-methoxybenzoate..

Table 4

Mulliken's population analysis of methyl-2-hydroxy-4-methoxybenzoate at B3LYP/c6-31+Gn B3LYP/6-3H11++G - p methods

Atom No.	Mulliken Atomic charge	
	B3LYP	
	631+G(d)	63H11++G (d, p)
1C	0.4813	0.2457
2C	-0.3218	-0.2947
3C	-0.1020	-0.2853
4C	-0.2710	0.2265
5C	-0.2878	-0.1087
6C	-0.1449	0.1957
7C	0.1292	0.6189
8O	-0.2756	-0.4928
9O	-0.1357	-0.5050
10C	-0.2087	0.0038
11H	0.1811	0.1193
12H	0.1557	0.1065
13H	0.1811	0.1193
14O	-0.1949	-0.4198
15H	0.2745	0.2634
16H	0.1409	0.0843
17O	-0.1639	-0.4385
18C	-0.3102	-0.0740
19H	0.1591	0.1055
20H	0.1751	0.1417
21H	0.1591	0.1055
22H	0.1708	0.1174
23H	0.2086	0.1653
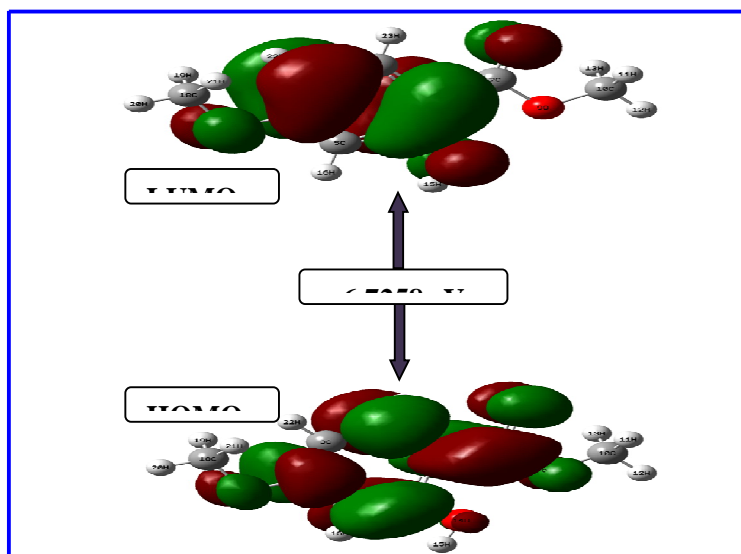
Fig. 5. The molecular orbital's and energies for the HOMO and LUMO of methyl-2-hydroxy-4-methoxybenzoate

I. Homo-Lumo

The HOMO-LUMO analysis for M2H4MP was conducted by B3LYP/6-31+G (d) and 6-311++G (d, p) level of theory. Using HOMO and LUMO energies, quantum chemical parameter s [26] where also calculated which are shown in Table 5. The frontier molecular orbital pictures are shown in Fig. 5, respectively. The orbital determine the way in which the molecule interacts with other species. HOMO is the orbital that acts as an electron donor, an LUMO is the orbital that acts as an electro deficient and hence most subject to nucleophilic attack [27]. A molecule with a small gap is more polarized and is known as soft molecule. In M2H4MP, the energy gap is small; hence it is thermodynamically favorable for an electron transfer to occur. Chemical potential are Fermi energy represented the change in Gibbs energy per atom. Low level of energy gap is also due to electron with drawn in groups that enter into conjugation. More ever, the Fermi energy lies exactly in the midst of the HOMO and LUMO in M2H4MP. Large value of electron a finite and electro philicity in M2H4MP confirm that it prefers to accept more number of electrons. Homo orbital is most heavily concentrated on Benzoic acid ring, meaning the electrophilic attack will likely occur here LUMO is over the carbonyl carbon consistent with the observation that carbonyl compounds undergo nucleophilic addition at the carbonyl carbon. LUMO is also slightly located over the oxygen.

The TDOS, PDOS and overlap population density of states, in terms of Mulliken population anlaysis were calculated and created by convoluting the molecular orbital information with Gaussian curves of unit height and a full width t half maximum of 0.3 eV using Gaussum 2.2. The main used of the DOS plots is to provide pictorial representation molecular orbital compositions and their contributions to chemical bonding through the PDOS plots which are also referred in the literature as crystal orbital overlap population diagram. The desity of electronic states have been calculated and they are displayed for the famotidine fig. 6 and 7.
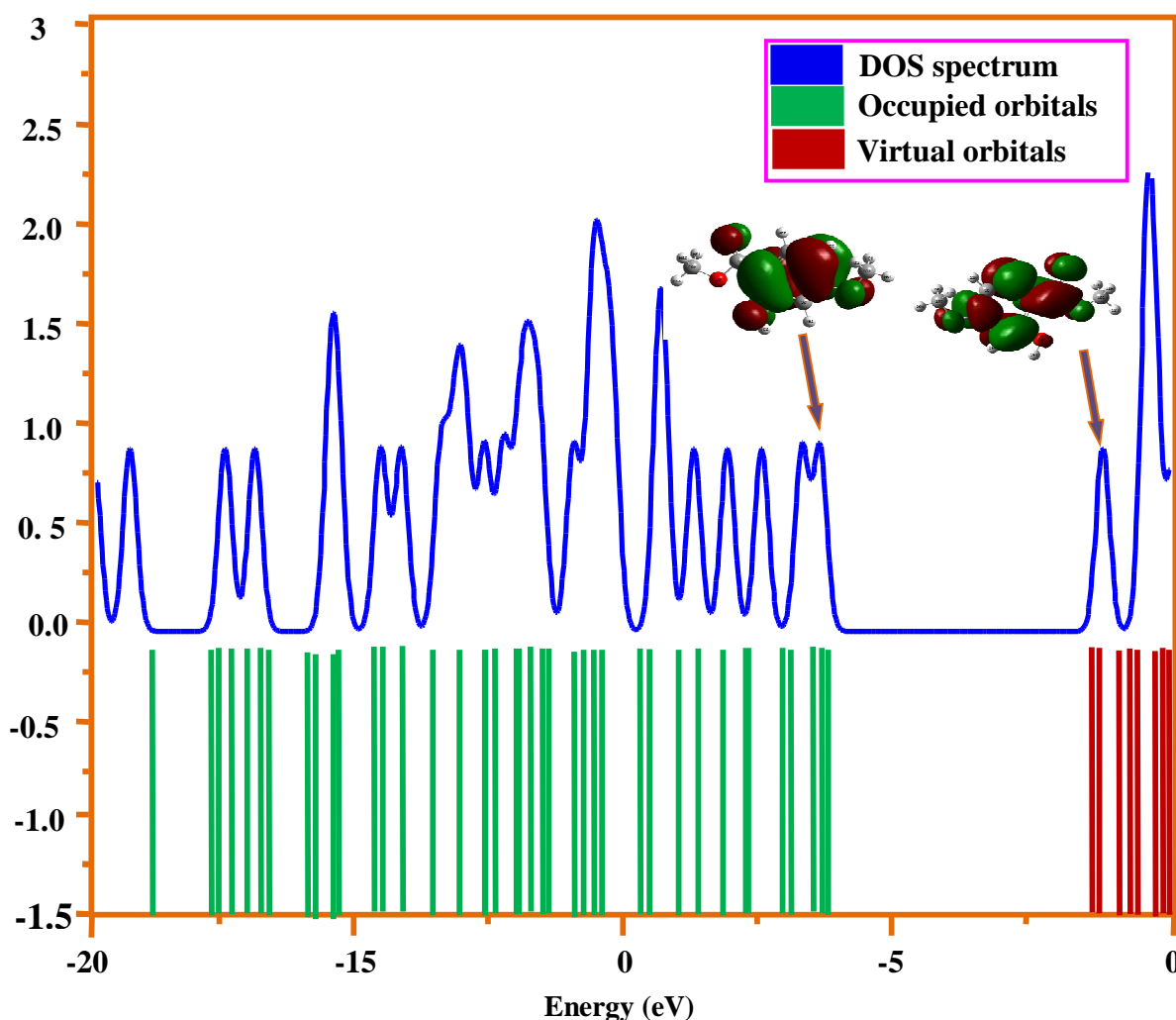

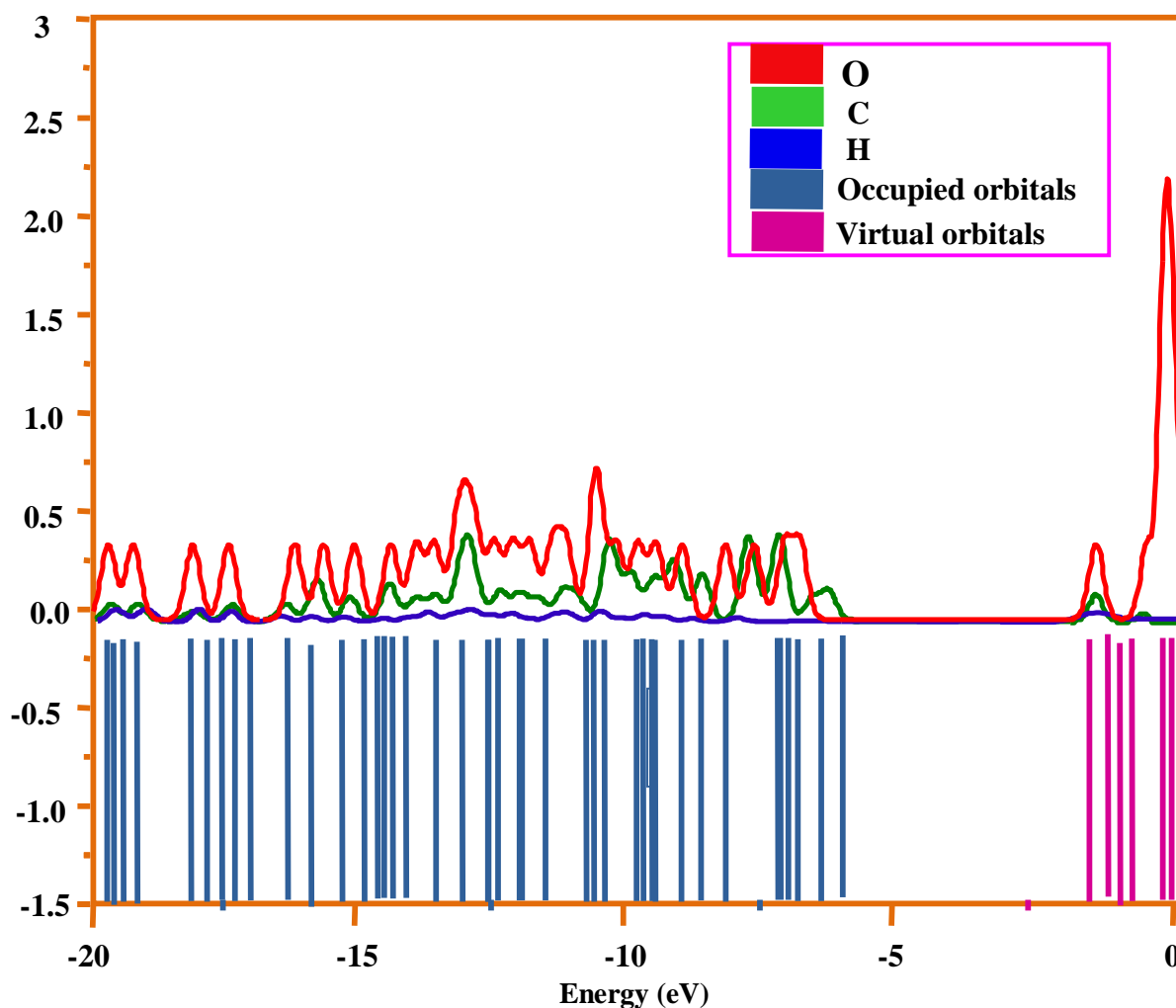Fig. 6 The calculate TDOS diagram of methyl-2-hydroxy-4-methoxybenzoate

Fig. 7. The calculated PDOS diagrams for methyl-2-hydroxy-4-methoxybenzoate

Table 5

Molecular properties	Energy (eV)	Energy gap (eV)	Ionization potential (I)	Electron affinity (A)	Global Hardness (η)	Electro negativity (χ)	Global softness (υ)	Chemical potential (μ)	Global Electrophilicity (ω)	Molecular electrostatic potential (MEP) at a molecule give information about
B3LYP/6-31+G (d)										
HOMO	-9.2491	6.7258	9.2491	2.5233	3.3629	5.8862	0.2974	-5.8862	5.1514	
LUMO	-2.5233									
B3LYP/6-311++G (d, p)										
HOMO	-8.1898	0.6422	8.1898	7.5476	0.3211	7.8687	3.1143	-7.8687	96.4130	
LUMO	-7.5476									

the net electrostatic effect produced at that point by total charge distribution of molecule [28].The interaction between the positive charge and some point in the molecule will be attractive if the point is negative charged; repulsive if it is positive charged, and the strength of interaction will depend on the magnitude of the charge. It is convenient to display this map using the colors of the rainbow from red to blue. Red is studied the MEP values are calculated as described previously [29].

$$V(r) = \sum \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r'-r|}dr$$

where the summation runs over all the neclei A in the compound and polarizability and reorganization effects are neglected. ZA is the charge of the nucleus A, located at RA and ρ(r) is the electron density function of the compound. The MEP surface provides necessary information about the reactive sites.mep surface is plotted over optimized geometry of the B3LYP method with6-31+G (d) and 6-311++G (d, p) basis sets. Electrostatic potential counter map along with the fitting point charge to the electrostatic potential, the electron density isosurface being 0.002 a.u the electrostatic potential map indicates that the atoms O_9, O_{14} and O_{17} the most electronegative atom in B3LYP method as shown in Fig. 8. The calculated point charge corresponding atoms H_{15}, H_{21} and H_{22} in the most electropositive atoms, respectively.

V. CONCLUSION

The present investigation thoroughly analyzed the HOMO-LUMO, and vibration spectra, both infrared and Raman of M2H4MBmolecules with B3LYP method with standard 6-31+G (d) and 6-311++G (d, p) basis sets. All the vibration bands are observed in the FT-IR and F-Raman spectra of the compound are assigned to various modes of vibration and most of the modes have wave numbers in the expected range. The complete vibration assignments of wave numbers are made on the basis of potential energy distribution (PED). The molecular electrostatic potential surfaces (MEP) together with complete analysis of the vibration spectra, both IR and Raman and electronic spectra help to identify the structure and symmetry. The excellent agreement of the calculated and observed vibration spectra reveals the advantages over the other method. The stabilization energy has been calculated from second order perturbation theory. Finally, calculated HOMO-LUMO energies show that the charge transfer occurs in the molecule, which are responsible for the bioactive properly of the biomedical compound M2H4MP.
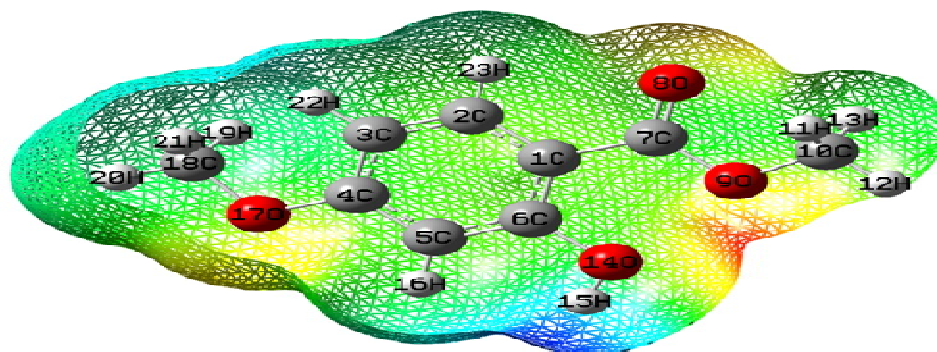

Fig. 8. The total electron density surface mapped with of methyl-2-hydroxy-4-methoxybenzoate.

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