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Molecular structure, NMR, UV-Visible, Vibrational Spectroscopic and HOMO, LUMO analysis of methyl m-hydroxy benzoate and methyl salicylate

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ABSTRACT

Vibrational spectral analysis was carried out for Methyl m-hydroxy benzoate (MMHB) and Methyl salicylate (MS) by using the FTIR and FT-Raman spectroscopy in the range of 4000cm^{-1}-400cm^{-1} and 4000cm^{-1}-50cm^{-1} respectively. The theoretical computational density functional theory (DFT/B3LYP) was performed at 6-31G** levels to derive equilibrium geometry, vibrational wavenumbers, infrared intensities and Raman scattering activities. The complete vibrational assignment was performed on the basis of the potential energy distribution (PED), calculated with scaled quantum mechanics (SQM) method. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), chemical potential (P_i), global hardness (η),and the softness (σ), were calculated. The theoretical electronic absorption spectra have been calculated by using CIS methods. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated by using gauge invariant atomic orbital (GIAO) method. The total atomic charges, natural charges and thermodynamic parameters were also calculated. As expected, the results show the greater stability and stronger hydrogen bond between oxygen and ester group.

1. Introduction

In the past two decades, quantum chemical computational methods have been proven to be an essential tool for interpreting and predicting vibrational spectra [1,2]. A significant advancement in this area was made by combining semi-empirical quantum mechanical method; ab initio quantum mechanical method and density functional theory (DFT), each method having its own advantages [3-6]. In the SQM approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules [2, 7].

Methyl benzoate, derivative of benzoic acid is an essence or oil of Niobe with molecular formula $C_6H_5COOCH_3$. It is colourless, oily transparent liquid with a pleasant odour. Methyl benzoate is obtained by heating methyl alcohol and benzoic acid in presence of sulfuric acid and passing dry hydrogen chloride through a solution of benzoic acid in methanol. It occurs naturally in oils of dove and tubercose. It is also used as a perfume and dye carrier. It is also used as solvent for cellulose esters, ether, resins, rubber and flavoring [8].

Methyl m-hydroxy benzoate is typically used in pharmaceutical and perfumery industry. More than 90% of commercial benzoic acid is converted directly to phenol and caprolactam. Its use in the production of glycol benzoates for the application of plasticizer in adhesive formulation is increasing. It is also used in the manufacture of drilling mud additive for crude oil recovery applications. Esters of hydroxy benzoic acid are recognized as antiseptics. Especially parabens, substituted at 1,4 positions, are widely used as preservatives in food and pharmaceuticals [9].

Methyl Salicylate is a chemical cousin of aspirin. Thus, drugs belong to a category of anti inflammatory analgesics known as “salicylates”. However, it is very dangerous to administer methyl salicylate orally, because it is more toxic than aspirin. The ingredient in the sports creams responsible for Newman’s death is methyl salicylate. The common name for methyl salicylate is oil of wintergreen. It is widely available as a component in many over-the-counter brands of creams, ointments, lotions and medicated oils intended for topical application to relieve musculo skeletal aches and pains [10-12].

In this study, we recorded FTIR, FT-Raman spectra and calculated the vibrational frequencies of Methyl m-hydroxy benzoate and methyl salicylate in the ground state to distinguish fundamentals from experimental vibrational frequencies and geometric parameters using DFT/B3LYP (Becke3-Lee-yang-Parr) method. Natural bond orbital (NBO) analysis of the title molecules are also carried out. In addition, the gauge-invariant atomic orbital (GIAO) ^{13}C and ^{1}H chemical shifts calculations of the title compounds were calculated by using B3LYP/6-31G** basis set [13]. The calculated quantum chemical parameters are E_{HOMO}, E_{LUMO}, ΔE and those parameters that give valuable information about the reactive behavior such as chemical potential (P_i), global hardness (η),and the softness (σ) [14]. A detailed quantum chemical study will aid in making definite assignments to fundamental normal modes of MMHB and MS in clarify the experimental data for these important molecules.

2. Experimental

The compound MMHB in the solid form was purchased from sigma-Aldrich company (USA) with a stated purity of 99% and it was used as such without further purification. The

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compound MS in the liquid form was obtained. Fourier transform infrared (FTIR) were measured in the region of 4000-400cm^{-1}. The FT-Raman spectra of MMHB and MS were recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 and FT-Raman accessory. The spectra were recorded in the 4000-50cm^{-1} stokes region using 1064-nm line of a Nd:YAG laser for excitation operating at 200-mW power. The reported wavenumbers are believed to be accurate within ±1cm^{-1}.

The ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ solution and all signals were referenced to TMS on a BRUKER FT-NMR spectrometer. All NMR spectra were measured at room temperature.

3. Calculations

All the calculations were performed by using Gaussian 03 program [15] package on the personal computer. The Becke's three-parameter hybrid density functional, B3LYP was used to calculate both harmonic and anharmonic vibrational wavenumbers with 6-31G** basis set. It is well known in the quantum chemical literature that the B3LYP functionals yields a good description of harmonic vibrational wavenumbers for small and medium sized molecules.The optimized structural parameters were used in the vibrational frequency calculations at the DFT levels to characterize all stationary points as minima. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming C_s point group symmetry respectively for MMHB and Ms. The theoretical DFT force field were transformed from Cartesian into the local coordinates and then scaled empirically according to the SQM procedure [16].

$$F_{ij}^{Scaled} = (C_i C_j)^{\frac{1}{2}} F_{ij}^{B3LYP}$$

Where C_i is the scale factor of coordinate i, F_{ij}^{B3LYP} is the B3LYP/6-31G** force constant in local coordinate and F_{ij}^{Scaled} is the scaled force constant.

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities (S_i) calculated by the Gaussian 03 program and adjusted during the scaling procedure with the MOLVIB program were converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [17-19].

$$I_i = \frac{f(\upsilon_o - \upsilon_i)^4 S_i}{\upsilon_i \left[1 - \exp\left(\frac{-hc\upsilon_i}{KT}\right)\right]}$$

Where υ_0 is the exciting frequency (in cm^{-1} units), υ_i the vibrational wavenumber of the ith normal mode,h,c and k are the fundamental constants and f is the suitably chosen common normalization factor for all the peak intensities.

The calculated quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), chemical potential (P_i), global hardness (η) and the softness (σ) were calculated. The concepts of these parameters are related to each other [20-23]. Where,

$P_i = -\chi$

$P_i = (E_{HOMO} + E_{LUMO}) / 2$

$\eta = (E_{LUMO} - E_{HOMO}) / 2$

The inverse values of the global hardness is designated as the softness σ, as follows:

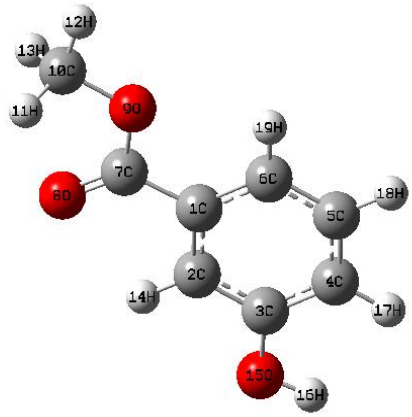
$\sigma = 1/\eta$

For NMR calculations, the title molecules are firstly optimized and after optimization, ^{1}H and ^{13}C NMR chemical shifts (H and C) were calculated using the GIAO method in $CDCl_3$ at B3LYP method with 6-31G** basis set [24,25]. Absolute isotropic magnetic shieldings were transformed into chemical shifts by referencing to the shieldings of a standard compound (TMS) computed at the same level. It has been shown that B3LYP applications were successful in shielding calculations on carbon atoms [25].

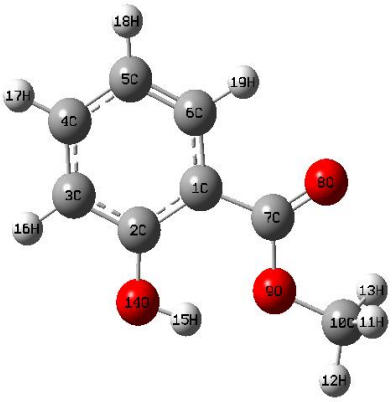
4. Results and Discussion

4.1 Molecular geometry

The molecular structures of MMHB and MS with C_S symmetry are shown in Figs 1(a) and (b) respectively. The global minimum energies obtained by the DFT structure optimization for MMHB and MS are calculated as -535.36013 and -535.36736hartrees, respectively. The energy difference is clearly understandable, since the environments of the molecules are different. In the title compounds, the introduction of two substituent group on the benzene ring causes some changes in the ring C-C bond distances.



(a)



(b)

Fig.1. Optimized structure of (a) Methyl m-hydroxybenzoate and (b) Methyl Salicylate

The substitution of $COOCH_3$ with OH group in the MMHB and MS leads to intermolecular hydrogen bonding and intramolecular hydrogen bonding, respectively. As the consequence of the inter and intra molecular hydrogen bonding formation in the MS, C7-O8 bond length is shorter than the C7-O8 bond length in MMHB. The strong intra and inter molecular hydrogen bonding evident from the optimized structure for the title compounds. In MMHB and MS both inductive (-I) and mesomeric effects (+M) operate. Mesomeric effect dominates

over inductive effect. Thus stretching C=O absorption occurs at lower wavenumber. Mesomeric effect causes lengthening of C=O bond leading to lowering of absorption frequency. In esters the +M effect OR group means that electrons are donated to the acyl group, lowering its reactivity to nucleophiles [26].

The optimized geometrical parameters of MMHB are compared to those of mainly Methyl p-hydroxy benzoate (MPHB) [27] which exhibit very strong intermolecular hydrogen bonding when compared with MMHB. The C=O bond length in MPHB is C12-O13 (1.353) which is greater than C7-O8 (1.21) in MMHB. This decrease of bond length is due to mesomeric effect.

4.2. Vibrational force constants

Quantum-mechanical calculations contain the force constant matrix in Cartesian coordinates and in Hartree/Bohr^2 units. These force constants were transformed to the force fields in internal local-symmetry coordinates. The local-symmetry coordinates defined interms of the internal valence coordinates following the IUPAC recommendations [28, 29] are given in Table 5 for the title compounds.

Intramolecular hydrogen bonding is within the same molecule, hence it is not affected by change in intermolecular distance. Thus, intramolecular hydrogen bonds are unaffected by dilution, and so the absorption band is also unaffected. Intramolecular hydrogen bonding (chelation) is very strong in Methyl salicylate due to resonance stabilization of the chelate ring. The molecule MMHB having the intermolecular hydrogen bonding which is concentration dependent [30].

The stretching force constant of the C=O bond in ester is increased due to the –I effect of the adjacent oxygen. Thus, stretching $\upsilon_{C=O}$ band of ester appear at a higher wavenumber than that of a ketone. The stretching force constant of C=O is greater than C-O. The force constant of carbonyl stretching C=O in MMHB is found to be greater than MS due to stronger intermolecular hydrogen bonding. The most important diagonal force constants (stretching only) of MMHB and MS are listed in Table 5.

4.3. Assignment of Fundamentals

The molecules MMHB and MS are disubstituted aromatic system. The vibrational bands observed in the IR region are very sharp, broad and less intense. The title compounds belong to C_s point group. The 19 atoms composing for MMHB and MS structure, each molecule has 51 fundamental modes of vibration. For molecules of C_s symmetry, group theory analysis indicates that the 51 fundamental vibrations are distributed among the symmetry species as,

Γ_{vib} =35A'(in–plane) +16A"(out–of–plane)

for both MMHB and MS respectively. From the structural point of view of the molecules, MMHB and MS have 18 stretching vibrations, 33 bending vibrations, respectively. All the vibrations were found to be active both in Raman scattering and infrared absorption.

The observed and calculated wave numbers, calculated IR and Raman intensities and normal mode descriptions (characterized by potential energy distribution (PED)) for the fundamental vibrations of MMHB and MS are depicted in Tables 6 and 7. For visual comparison, the observed and simulated FTIR and FT-Raman spectra of the compounds are presented in Figs. 2-5, which help to understand the observed spectral features. The root mean square (rms) error of the observed and calculated wavenumbers (unscaled/ B3LYP/6-31G**) of MMHB and MS was found to be 98.6 cm^{-1} and 102 cm^{-1}, respectively. This is understandable since the mechanical force fields usually differ appreciably from the observed ones. This is partly due to the neglect of anharmonicity and partly due to approximate nature of the quantum mechanical methods. However for reliable information on the vibrational properties, the use of selective scaling is necessary. The calculated wavenumbers are scaled using the set of transferable scale factors recommended by Rauhut and Pulay [31]. The SQM treatment has resulted in an rms deviation of 8.58cm^{-1} and 9.79cm^{-1} for MMHB and MS, respectively. The rms values of wavenumbers were obtained in this study using the following expression,

$$RMS=\sqrt{\frac{1}{(n-1)}\sum_{i}^{n}\left(\upsilon_i^{calc}-\upsilon_i^{\exp}\right)^2} \quad - (5)$$

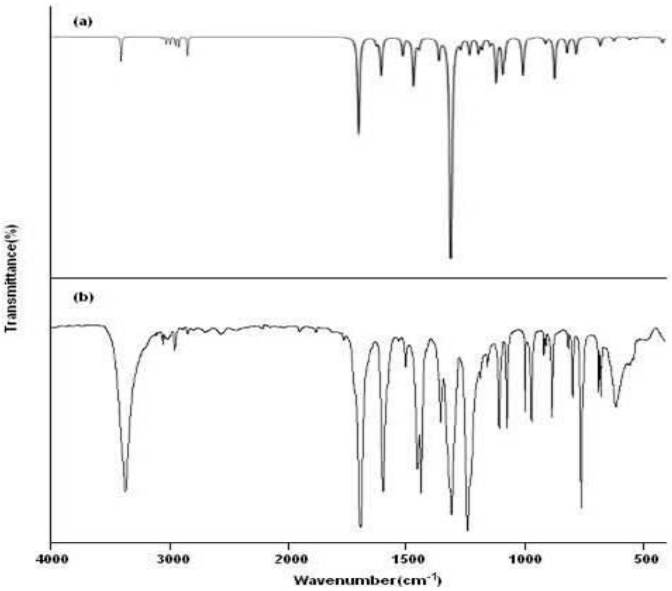


Fig.2. FTIR Spectra of Methyl m-hydroxybenzoate (a) Observed (b) Calculated with B3LYP/6-31G**

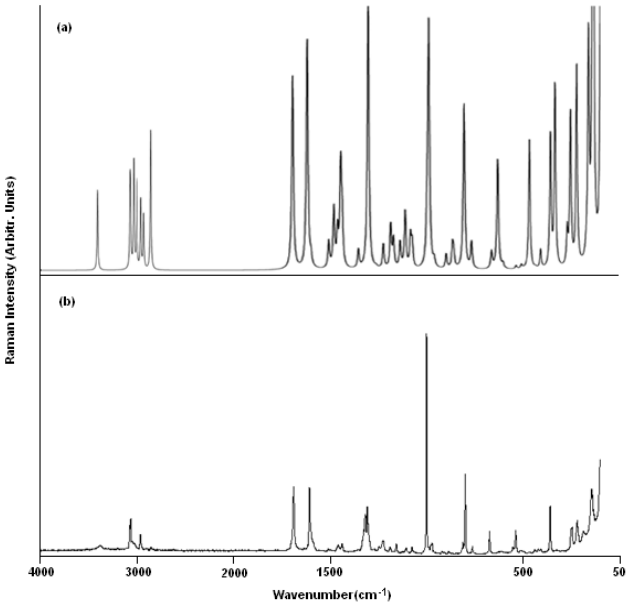


Fig.3. FT- Raman Spectra of Methyl m-hydroxybenzoate (a) Observed (b) Calculated with B3LYP/6-31G**

4.3.1. CH Vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000cm^{-1} [32] due to aromatic C-H stretching vibrations. According to the PED analysis, the bands

observed in experimental spectrum at 3016, 3030, 3064, 3065cm^{-1} in MMHB and 3120, 3100, 3080, 3074cm^{-1} in MS were assigned to stretching vibrations of C-H bond. According to these studies, all the C-H stretching vibrations are not mixed with other types of vibrations.

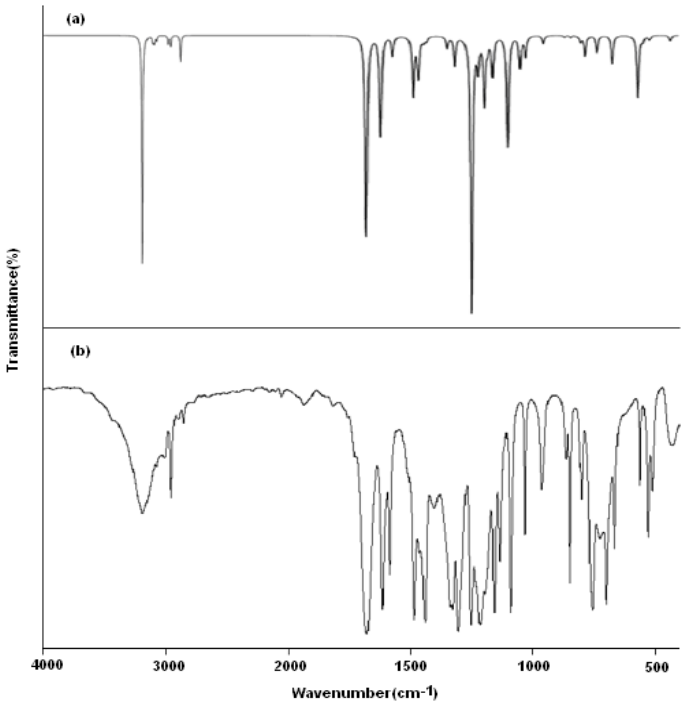


Fig.4. FTIR Spectra of Methyl Salicylate (a) Observed (b) Calculated with B3LYP/6-31G.**

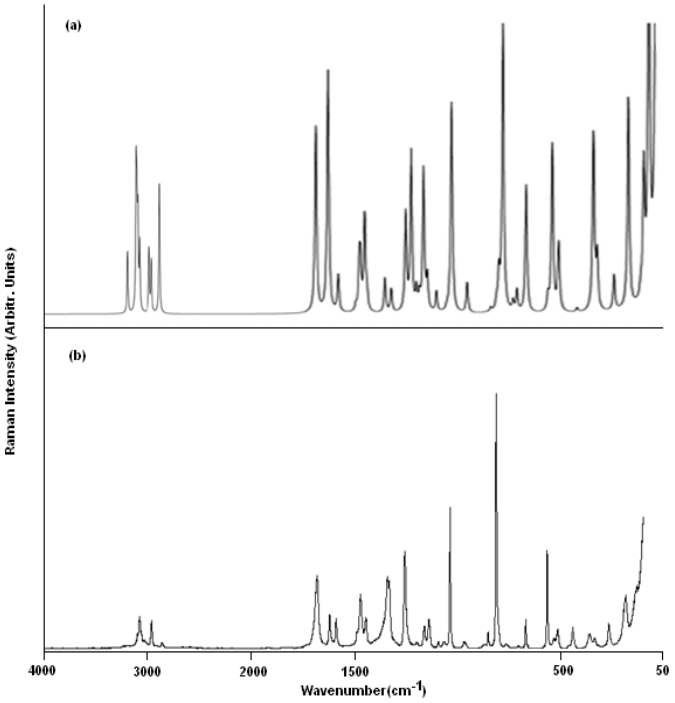


Fig.5. FT-Raman Spectra of Methyl Salicylate (a) Observed (b) Calculated with B3LYP/6-31G.**

The C-H in-plane deformation vibrations assigned in the region 1100-1400cm^{-1} [30].The in-plane deformations of C-H groups are noticed on PED analysis at 1460, 1225, 1155, 1108 in MMHB and 1487, 1471, 1446, 1217cm^{-1} in MS. There is slightly increase in the C-H in-plane deformation frequency because of mesomeric effect in MMHB and steric effect in MS. These values of calculated frequencies are typical and in very good agreement with experimental data. The in-plane C-H deformation vibrations are slightly mixed in both MMHB and MS.

The C-H out-of-plane deformation vibrations assigned in the region 900-600cm^{-1} [32,33].The bands appeared at 976, 911, 886, 770cm^{-1} in MMHB and 865, 849,801,667cm^{-1} in MS were assigned to out-of-plane deformation type of vibration (ω) of C-H groups. There is slightly increase in the C-H out-of-plane deformation frequency because of intermolecular hydrogen bonding in MMHB. In these bands, the pronounced participation of other types of vibrations is observed. These are also supported by the literature.

4.3.2. C=O, C-O stretching vibrations

Carbonyl group vibrations give rise to characteristic bands in vibrational spectra and for this reason, such bands have been subject of extensive studies [34,35]. When inductive and mesomeric effects oppose each other in the same substituent such as in esters, the relative importance of the two effects decides the fate of the carbonyl absorption [36]. The carbonyl stretching vibrations in saturated esters are expected in the region 1750cm^{-1}-1735cm^{-1}. The IR band at 1695cm^{-1} in MMHB and Raman band at 1681 cm^{-1} are assigned as C=O stretching vibrations. Conjugation of a carbonyl group with an aromatic ring lowers the stretching frequency of the C=O groups by about 30cm^{-1} due to mesomeric effect [30]. The C-O bond of saturated esters shows strongly in the 1210-1163cm^{-1} region. It is often broader and stronger than the C=O stretching absorption [37]. The bands observed at 1235, 880cm^{-1} in MMHB and 1254, 767cm^{-1} in MS are assigned to C-O stretching mode. When a C=C or an aromatic ring is attached to the oxygen of the C-O group of an ester, there is a marked increase in the carbonyl frequency along with a decrease in the C-O frequency, because of the mesomeric effect for the title compounds [30]. The present assignments agree very well with the values available in the literature.

4.3.3. Methyl group vibrations

The title molecules MMHB and MS under consideration possess one CH_3 group. For the assignments of CH_3 group one can expect that 9 fundamentals can be associated to each CH_3 group, namely the symmetrical stretching (CH_3 symmetric stretch) and asymmetrical stretching (CH_3 asymmetric stretch), in-plane stretching modes (ie, in-plane hydrogen stretching modes), the symmetrical (CH_3 symmetric deform) and asymmetrical (CH_3 asymmetric deform) deformation modes; in-plane rocking ($CH_{3\ ipr}$) out-of-plane rocking (CH_3 opr) and twisting (tCH_3) bending modes.

For the ester group compounds [34], the asymmetric stretching mode appeared in the range 2950-3050cm^{-1}, symmetric stretching mode appeared in the range of 3000-2860cm^{-1}. The IR bands at 2850cm^{-1} for MMHB, 2890cm^{-1} for MS are symmetric stretching. The asymmetric methyl stretching band appeared at 2962, 2924cm^{-1} in MMHB and 2965, 2963cm^{-1} in MS respectively. The asymmetric deformation of CH_3 group is usually observed around at 1450cm^{-1} for methyl substituted benzenes. The FT-Raman band at 1515cm^{-1} in MMHB and FT-Raman band 1199cm^{-1} in MS are assigned as asymmetric deformation vibration. The asymmetric deformation vibrational frequency is higher in MMHB and lower in MS due to steric effect. The CH_3 deformation absorption occurs at 1439cm^{-1} and 1199cm^{-1}, this vibration is known as umbrella mode overlaps with CC ring stretching vibrations for the title compounds.

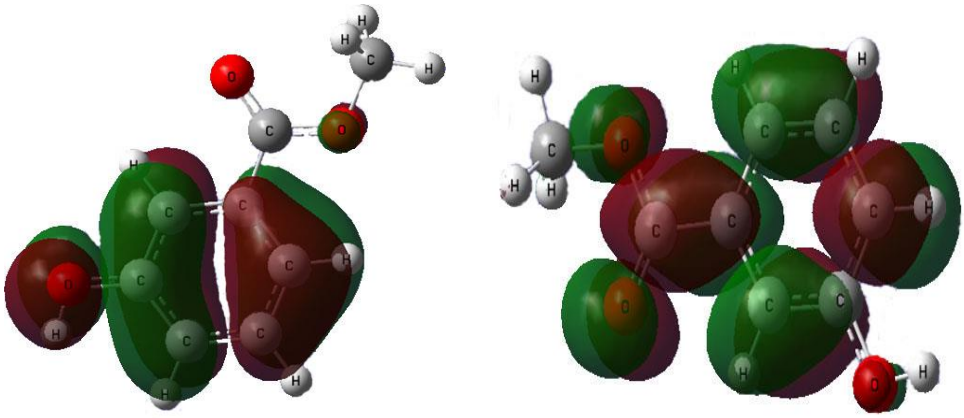


Fig.6. Surfaces of HOMO, LUMO for the Methyl m-hydroxybenzoate

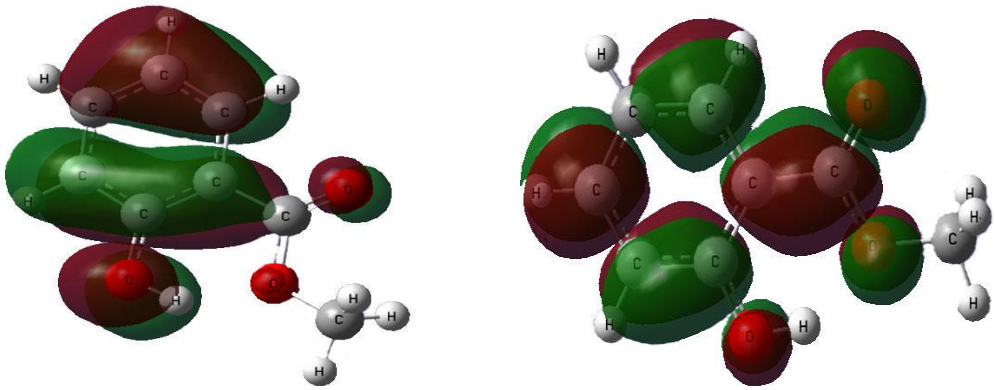


Fig.7. Surfaces of HOMO, LUMO for the Methyl Salicylate

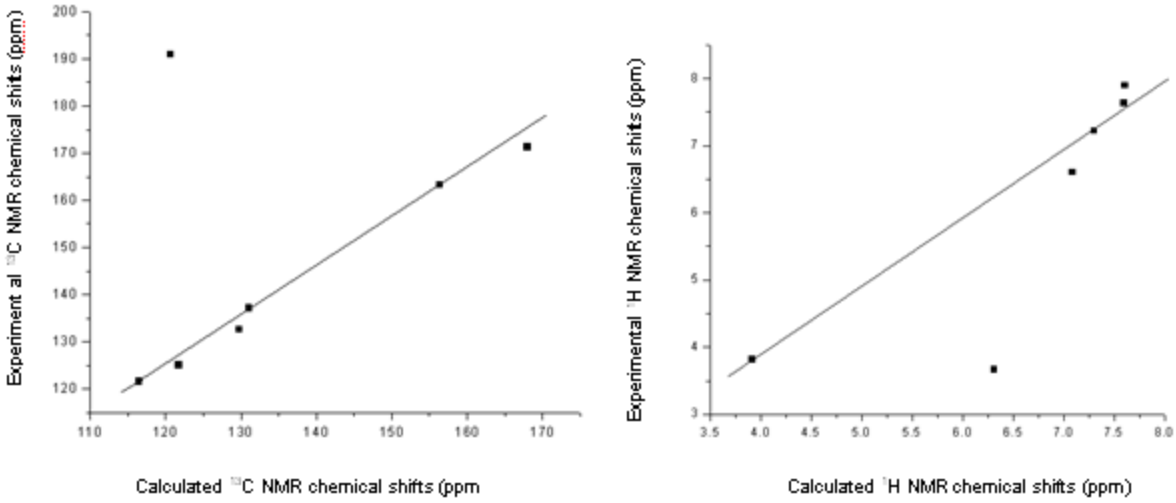


Fig.8. Plot of the calculated vs. the experimental ^{13}C NMR, ^{1}H NMR chemical shifts (ppm) for Methyl m-hydroxy benzoate

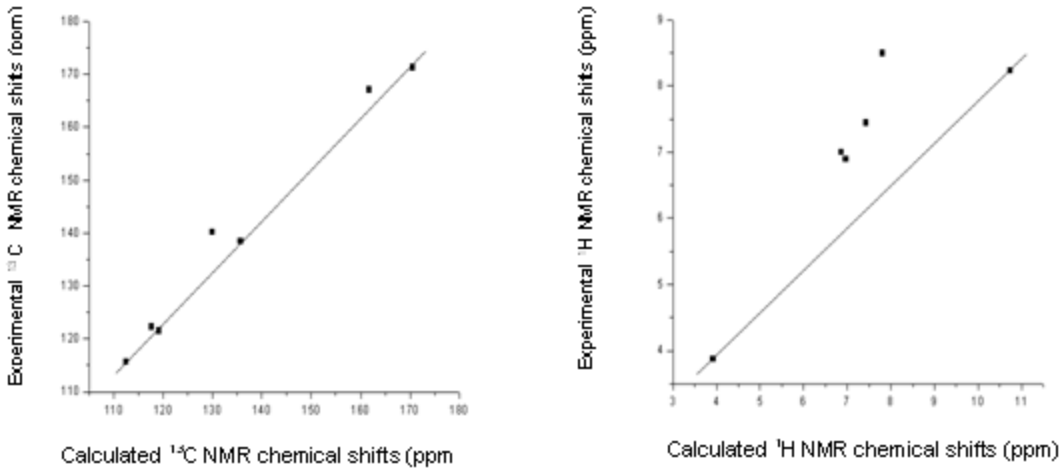


Fig.9. Plot of the calculated vs. the experimental 13C NMR, 1H NMR chemical Shifts (ppm) for Methyl Salicylate

The methyl deformational modes mainly coupled with the C-H in-plane bending vibrations. These are also supported by the literature.

The torsional modes of ester group, which are strongly coupled with other vibrations, are observed at 120cm^{-1} in MMHB and 110cm^{-1} in MS which are in agreement with the calculated results also.

4.3.4. OH Vibrations

The OH group gives rise to three vibrations-stretching, in-plane bending and out-of-plane bending vibrations. The OH group vibrations are sensitive to the chemical environment. For the dimeric associated intermolecular hydrogen bonding appeared in the range 3550-3450cm^{-1} [34] and monomeric intramolecular hydrogen bonding appeared in the range 3200-2500cm^{-1} [36] for the title compounds, respectively.

The probability of strong intramolecular hydrogen bonding in MS but weak in MMHB. The title molecules both exhibiting inter molecular hydrogen bonding. In our case, a band at 3410cm^{-1} in MMHB, 3190cm^{-1} in MS are assigned as OH stretching vibrations. There is a slightly decrease in the OH frequency because of mesomeric effect in MMHB. This shift in frequencies towards lower wavenumbers due to this reflects the strength of hydrogen bonding. The OH in-plane bending vibration generally lies in the region of 1500-1300cm^{-1} [34]. The bands appeared at 1120cm^{-1} in MMHB, 1338cm^{-1} in MS are assigned to OH in-plane bending vibration. The OH out-of-plane bending vibrations normally occur in the region of 710-570cm^{-1} [34]. The bands appeared at 360cm^{-1} in MMHB and 565cm^{-1} in MS are assigned to OH out-of-plane bending vibration. The OH out-of-plane bending vibrations in MMHB decrease due to intermolecular hydrogen bonding. The present assignments agree very well with the values available in the literature.

4.3.5. Ring Vibrations

The ring C-C stretching vibrations occur in the region of 1600-1400cm^{-1} [37]. The bands appeared at 1607, 1600, 1504, 1367, 1310, 1076, 639cm^{-1} in MMHB and 1620, 1588, 1306, 1226, 1091, 1033, 1037 cm^{-1} in MS were assigned to C-C stretching vibrations. The shift in the frequency of C-C vibrations towards lower wave number may be due to the hydroxyl and $COOCH_3$ groups. Many ring modes are affected by the substitutions in the aromatic ring. The bands at 145cm^{-1} and 150cm^{-1} for MMHB and MS were assigned to C-C bending vibrations. The out-of-plane and in-plane deformations of the phenyl ring are observed below 1000cm^{-1}, and these modes are sensitive by the addition of functional groups. The out-of-plane bending vibrations were observed at 97cm^{-1} and 50cm^{-1} for MMHB and MS. Small changes in the wavenumbers observed due to the presence of steric effect in MS and mesomeric effect in MMHB. The computed wavenumbers are in good agreement with experimental data.

4.4. Electronic properties

Atomic charges on the various atoms of MMHB and MS obtained by Mulliken population analysis [38] is given in Table 8. From the listed atomic charge values, the oxygen [O8, O9] and O14 in MS, O15 in MMHB atoms had a large negative charge and behaved as electron acceptor. It was also observed that there is a large accumulation of charge on O15 in MMHB, O14 in MS molecules. Therefore, C7, O15 in MMHB and C7, O14 in MS had a greater ionic character.

Natural bond orbital analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Natural charge analysis is given in Table 9 for the title compounds. The results show that substitution of OH and $COOCH_3$ group in MMHB and MS leads to a redistribution of electron density. The C7 atom in MMHB and MS is more positive charge (+0.81612, +0.81424).

The theoretical electronic absorption spectra for the title compounds were calculated at B3LYP/6–31G** using CIS method and absorption maxima are listed in Table 10. The theoretical electronic excitation energies, oscillator strengths, absolute energies, and nature of the singlet-singlet excitations were also calculated for the water solvents. Calculations of the molecular orbital geometry show that the visible absorption maxima of the molecule correspond to the electron transition between frontier orbitals such as translation from HOMO to LUMO. We performed an analysis of all the molecular orbitals involved, taking into consideration that orbital 40 is the HOMO and orbital 41 is the LUMO for MMHB and MS, respectively.

Highest occupied molecular orbital and lowest unoccupied molecular orbital are very important parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most reactive position in π-electron systems and also explains several types of reaction in conjugated system [39]. The conjugated molecules are characterized by a small highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) separation, which is the result of a significant degree of intermolecular charge transfer from the end-capping electron-donar groups to the efficient electron-acceptor groups through π conjugated path [40]. Both the highest occupied molecular orbital and lowest unoccupied molecular orbital are the main orbitals take part in chemical stability [41]. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures which are given in Table 11.

Many organic molecules that contain conjugated π electrons are characterized as hyper-polarisabilities and are analyzed by means of vibrational spectroscopy. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground state to the first excited state and is mainly described by the one-electron excitation from the HOMO to the LUMO. The HOMO, of π nature (ie, aromatic ring) is delocalized over the whole C-C bond. By contrast, the LUMO is located over the aromatic ring. Consequently, the HOMO-LUMO transition implies an electron density transfer to hydroxyl and ester group from the aromatic ring. The atomic orbital compositions of the frontier molecular orbitals are sketched in Figs. 6 and 7.

4.5. NMR spectra

DFT methods treat the electronic energy as a function of the electron density of all electrons simultaneously and thus include electron correlation effect [42]. In this study, molecular structure of the MMHB and MS was optimized by using B3LYP method in conjunction with 6-31G**. ^{13}C and ^{1}H chemical shift calculations of the title compounds have been made by using GIAO method and same basis set. The isotropic shielding values were used to calculate the isotropic chemical shifts δ with respect to tetramethylsilane (TMS). The isotropic chemical shifts are frequently used as an aid in identification of reactive ionic species. The B3LYP method allows calculating the shielding constants with the proper accuracy, and the GIAO method is one of the most common approaches for calculating nuclear magnetic shielding tensors.

Table 1. Optimized geometrical parameters of Methyl m-Hydroxy Benzoate (MMHB) and Methyl Salicylate (MS) obtained by B3LYP/6-31 G density functional calculations**

Bond length[a]	Bond length[b]		Value(Å)		Bond angle[a]	Value(°)	
		MPHB	MMHB	MS		MMHB	MS
C1-C2	C1-C2	1.39	1.39	1.41	C1-C2-C3	119.77	119.19
C2-C3	C1-C6	1.40	1.39	1.40	C2-C3-C4	119.90	120.61
C3-C4	C1-C12	1.48	1.39	1.38	C3-C4-C5	119.92	120.70
C4-C5	C2-C3	1.38	1.39	1.40	C4-C5-C6	120.67	119.08
C5-C6	C2-H7	1.03	1.39	1.38	C2-C1-C7	117.20	124.85
C1-C7	C3-C4	1.39	1.49	1.48	C1-C7-O8	124.64	125.67
C7-O8	C3-H8	1.08	1.21	1.21	C1-C7-O9	112.40	113.12
O9-C7	C4-C5	1.39	1.35	1.37	C7-O9-C10	115.07	115.59
O9-C10	C5-C6	1.38	1.43	1.44	O9-C10-H11	110.62	110.30
C10-H11	C5-H10	1.08	1.09	1.09	O9-C10-H12	105.66	105.62
C10-H12	C6-C11	1.08	1.08	1.08	O9-C10-H13	110.62	110.30
C10-H13	C12-O13	1.35	1.09	1.09	C3-C2-H14(O14)	120.30	116.39
C2-H14(O14)	C12-O14	1.36	1.08	1.35	O15-C3-C4	122.71	-
C3-O15	O14-C15	1.43	1.36	-	(C2-O14-H15)	-	108.22
(O14-H15)	C15-H16	1.08	-	0.97	C3(C4)-O15(C3)-H16	109.24	121.60
O15(C3)-H16	C15-H17	1.09	0.96	1.08	C5-C4-H17	120.13	119.98
C4-H17	C15-H18	1.09	1.08	1.08	C6-C5-H18	120.02	120.37
C5-H18			1.08	1.08	C1-C6-H19	119.90	117.28
C6-H19			1.08	1.08			

[a]The atoms indicated in the parenthesis belong to MS.
[bT]The atoms belong to MPHB. Experimental values taken from reference 27
For numbering of atoms refer Figs.1 (a) and (b).

Table 2. Definition of internal coordinates of Methyl m-Hydroxy Benzoate (MMHB)

No.(i)	Symbol	Type	Definition
Stretching			
1-4	r_i	C-H	C2-H14,C4-H17,C5-H18,C6-H19.
5-11	r_i	C-C	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1,C1-C7.
12-14	r_i	C-O	C7-O8,C7-O9,C3-O15.
15	r_i	O-C	O9-C10.
16	r_i	O-H	O15-H16.
17-19	r_i	C-H(methyl)	C10-H11,C10-H12,C10-H13.
Bending			
20-21	β_i	C-C	C2-C1-C7,C6-C1-C7.
22-29	β_i	C-C-H	C1-C2-H14,C3-C2-H14,C3-C4-H17,C5-C4-H17, C4-C5-H18,C6-C5-H18,C5-C6-H19,C1-C6-H19.
30-32	β_i	C-C-H(methyl)	O9-C10-H11,O9-C10-H12,O9-C10-H13.
33-35	β_i	H-C-H	H11-C10-H12,H12-C10-H13, H11-C10-H13.
36-37	β_i	C-C-O	C2-C3-O15,C4-C3-O15.
38	β_i	C-O-H	C3-O15-H16.
39-40	β_i	C-C-O	C1-C7-O8,C1-C7-O9.
41	β_i	C-O-C	C7-O9-C10.
42-47	β_i	C-C-C (Ring)	C1-C2-C3,C2-C3-C4,C3-C4-C5,C4-C5-C6, C5-C6-C1,C6-C1-C2.
Out-of-plane bending			
48-51	ω_i	C-H	H14-C2-C3-C1,H17-C4-C5-C3,H18-C5-C6-C4,H19-C6-C1-C5.
52	ω_i	C-C	C7-C1-C6-C2.
53	ω_i	C-O	O15-C3-C4-C2.
Torsion			
54-55	τ_i	C-O	C2-C1-C7-O8,C2-C1-C7-O9.
56	τ_i	C-O-C	C1-C7-O9-C10.
57-59	τ_i	C-H(methyl)	C7-O9-C10-H11,C7-O9-C10-H12,C7-O9-C10-H13.
60-61	τ_i	O-H	C2-C3-O15-H16,C4-C3-O15-H16.
62-67	τ_i	tring	C1-C2-C3-C4,C2-C3-C4-C5,C3-C4-C5-C6, C4-C5-C6-C1,C5-C6-C1-C2,C6-C1-C2-C3.

For numbering of atoms refer Fig.1 (a).

Table 3. Definition of internal coordinates of Methyl Salicylate (MS)

No.(i)	Symbol	Type	Definition
Stretching			
1-4	r_i	C-H	C3-H16,C4-H17,C5-H18,C6-H19.
5-11	r_i	C-C	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1,C1-C7.
12-14	r_i	C-O	C7-O8,C7-O9,C2-O14.
15	r_i	O-C	O9-C10.
16	r_i	O-H	O14-H15.
17-19	r_i	C-H(methyl)	C10-H11,C10-H12,C10-H13.
Bending			
20-21	β_i	C-C	C2-C1-C7,C6-C1-C7.
22-29	β_i	C-C-H	C4-C3-H16,C2-C3-H16,C3-C4-H17,C5-C4-H17, C4-C5-H18,C6-C5-H18, C5-C6-H19,C1-C6-H19.
30-32	β_i	C-C-H(methyl)	O9-C10-H11,O9-C10-H12,O9-C10-H13.
33-35	β_i	H-C-H	H11-C10-H12,H12-C10-H13,H11-C10-H13.
36-37	β_i	C-C-O	C1-C2-O14,C3-C2-O14.
38	β_i	C-O-H	C2-O14-H15.
39-40	β_i	C-C-O	C1-C7-O8,C1-C7-O9.
41	β_i	C-O-C	C7-O9-C10.
42-47	β_i	C-C-C(Ring)	C1-C2-C3,C2-C3-C4,C3-C4-C5,C4-C5-C6, C5-C6-C1,C6-C1-C2.
Out-of-plane bending			
48-51	ω_i	C-H	H16-C3-C4-C2,H17-C4-C5-C3,H18-C5-C6-C4,H19-C6-C1-C5.
52	ω_i	C-C	C7-C1-C6-C2.
53	ω_i	C-O	O14-C2-C3-C1.
Torsion			
54-55	τ_i	C-O	C2-C1-C7-O8,C2-C1-C7-O9.
56	τ_i	C-O-C	C1-C7-O9-C10.
57-59	τ_i	C-H(methyl)	C7-O9-C10-H11,C7-O9-C10-H12,C7-O9-C10-H13.
60-61	τ_i	O-H	C3-C2-O14-H15,C1-C2-O14-H15.
62-67	τ_i	tring	C1-C2-C3-C4,C2-C3-C4-C5,C3-C4-C5-C6, C4-C5-C6-C1,C5-C6-C1-C2,C6-C1-C2-C3.

For numbering of atoms refer Fig.1 (b).

Table 4. Definition of natural internal coordinates of Methyl m-Hydroxy Benzoate (MMHB) and Methyl Salicylate (MS)

No. (i)	Symbol[a]	Definition[b]
1-4	C-H Stretch	r_1,r_2,r_3,r_4
5-11	C-C Stretch	$r_5,r_6,r_7,r_8,r_9,r_{10},r_{11}$
12-14	C-O Stretch	r_{12},r_{13},r_{14}
15	O-C Stretch	r_{15}
16	O-H Stretch	r_{16}
17	CH_3 ss	$(r_{17}+r_{18}+r_{19})/\sqrt{3}$
18	C H_3 ips	$(2r_{17}-r_{18}-r_{19})/\sqrt{6}$
19	C H_3 ops	$(r_{18}-r_{19})/\sqrt{2}$
20	bC-C	$(\beta_{20}-\beta_{21})/\sqrt{2}$
21-24	bC-H	$(\beta_{22}-\beta_{23})/\sqrt{2},(\beta_{24}-\beta_{25})/\sqrt{2},(\beta_{26}-\beta_{27})/\sqrt{2},(\beta_{28}-\beta_{29})/\sqrt{2}$
25	CH_3 sb	$(-\beta_{30}-\beta_{31}-\beta_{32}+\beta_{33}+\beta_{34}+\beta_{35})/\sqrt{6}$
26	CH_3 ipb	$(-\beta_{33}-\beta_{34}-2\beta_{35})/\sqrt{6}$
27	CH_3 opb	$(\beta_{33}-\beta_{34})/\sqrt{2}$
28	CH_3 ipr	$(2\beta_{30}-\beta_{31}-\beta_{32})/\sqrt{6}$
29	CH_3 opr	$(\beta_{31}-\beta_{32})/\sqrt{2}$
30	bC-O	$(\beta_{36}-\beta_{37})/\sqrt{2}$
31	bC-O-H	β_{38}
32-33	bC-C-O	β_{39},β_{40}
34	bC-O-C	β_{41}
35	Rtrigd	$(\beta_{42}-\beta_{43}+\beta_{44}-\beta_{45}+\beta_{46}-\beta_{47})/\sqrt{6}$
36	Rsymd	$(-\beta_{42}-\beta_{43}+\beta_{44}-\beta_{45}-\beta_{46}+2\beta_{47})/\sqrt{12}$
37	Rasymd	$(\beta_{42}-\beta_{43}+\beta_{45}-\beta_{46})/2$
38-41	ωC-H	$\omega_{48},\omega_{49},\omega_{50},\omega_{51}$
42	ωC-C	ω_{52}
43	ωC-O	ω_{53}
44-45	tC-O	τ_{54},τ_{55}
46	tC-O-C	τ_{56}
47	tCH_3	$1/3(\tau_{57}+\tau_{58}+\tau_{59})$
48	tO-H	$1/2(\tau_{60}+\tau_{61})$
49	Ttrigd	$(\tau_{62}-\tau_{63}+\tau_{64}-\tau_{65}+\tau_{66}-\tau_{67})/\sqrt{6}$
50	Tsymd	$(\tau_{62}-\tau_{63}+\tau_{65}+\tau_{66})/2$
51	Tasymd	$(-\tau_{62}+2\tau_{63}-\tau_{64}-\tau_{65}+\tau_{66}-\tau_{67})/\sqrt{12}$

[a]These symbols are used for description of the normal modes by PED in Table.
[b]The internal coordinates used here are defined in Table.

Table 5. Diagonal force constants (10^2 Nm^{-1}) of Methyl m-Hydroxy Benzoate (MMHB) and Methyl Salicylate (MS)

Description[a]	Force constants[b]	
	MMHB	MS
C1-C2	6.91	6.49
C2-C3	6.92	6.28
C3-C4	6.77	6.83
C4-C5	6.94	6.35
C5-C6	7.04	6.89
C6-C1	6.72	6.18
C1-C7	4.80	4.76
C2-H14(O14)	5.16	5.90
C4-H17	4.94	5.20
C5-H18	5.04	5.24
C6-H19	5.17	5.29
C7-O8	11.20	11.04
C7-O9	5.31	4.57
C3-O15(H16)	5.62	5.27
O9-C10	4.76	4.67
O15-H16	6.51	-
(O14-H15)	-	5.69
C10-H11	4.64	4.73
C10-H12	4.75	4.81
C10-H13	4.64	4.73

[a]The atoms indicated in the parenthesis belong to MS.
[b]Stretching force constants are given in mdyn $Å^{-1}$.
For numbering of atoms refer Figs.1 (a) and (b).

Table 6. Detailed assignment of fundamental vibrations of Methyl m-Hydroxy Benzoate (MMHB) by normal mode analysis based on SQM force field calculations

Sl. No	Symmetry species C_s	Observed wavenumbers cm^{-1}		Calculated wavenumbers B3LYP/6-31G** force field cm^{-1}		IR *Intensity*	Raman Activity	Characterization of normal modes with PED (%)
		FT IR	Raman	unscaled	scaled			
1.	A'	3410	-	3283	3410	49.471	135.201	υOH(100)
2.	A'	-	3065	3239	3065	2.277	88.960	υCH(99)
3.	A'	3064	-	3234	3064	2.267	53.237	υCH(99)
4.	A'	3030	-	3197	3030	14.396	127.566	υCH(99)
5.	A'	3016	-	3172	3016	15.330	100.192	υCH(99)
6.	A'	2962	-	3162	2962	16.927	75.669	υCH_3ips(99)
7.	A"	2924	-	3140	2924	20.972	57.658	υCH_3ops(99)
8.	A'	2850	-	3063	2850	38.261	138.041	υCH_3ss(100)
9.	A'	1695	-	1802	1695	194.611	39.448	υCO(64) , bCCO(21), υCC(10)
10.	A'	-	1607	1671	1607	13.424	64.879	υCC(74), bCH(13)
11.	A'	1600	-	1643	1600	76.750	2.679	υCC(70), bCH(10)
12.	A'	-	1515	1528	1515	6.731	6.685	CH_3 ipb(86)
13.	A'	1504	-	1515	1504	3.172	14.440	υCC(49), bCH(35)
14.	A'	-	1460	1509	1460	97.255	8.425	bCH(44), υCC(34), υCO(10)
15.	A"	1455	-	1494	1455	6.035	23.365	CH_3 opb(92)
16.	A'	1439	-	1479	1439	18.965	10.177	CH_3 sb(63) , υCC (33)
17.	A'	1367	-	1379	1367	41.530	3.841	υCC(85)
18.	A'	1310	-	1339	1310	599.937	51.134	υCC(32), υCO(25), bCCO(19)
19.	A'	-	1255	1322	1255	16.128	0.336	bCH(72)
20.	A'	-	1235	1275	1231	32.963	4.295	υCO(40), bCH(16) , υCC(13) bCCO(13)
21.	A'	1188	-	1215	1188	30.412	7.259	CH_3 ipr(84)
22.	A'	-	1180	1202	1180	0.554	4.737	CH_3 opr(91)
23.	A'	-	1155	1192	1155	3.990	4.057	bCH(80) υCC(12)
24.	A'	1120	-	1178	1120	88.830	8.640	bCOH(61), bCH(17) υCC(15)
25.	A'	1108	-	1127	1108	65.199	4.550	bCH(39), υCC(23), υOC(19), υCO(11)
26.	A'	1076	-	1116	1076	26.157	3.539	υCC(46), bCH(42)
27.	A'	-	1001	1027	1001	75.180	4.525	υOC(58), υCC(13), bCCO(13)
28.	A'	998	-	1013	998	3.146	30.799	Rtrigd(62), υCC(35)
29.	A"	976	-	973	972	1.591	0.915	ωCH(86), ttrigd(11)
30.	A"	911	-	925	911	12.310	1.597	ωCH(78)
31.	A"	886	-	912	886	0.001	2.370	ωCH(89)
32.	A'	-	880	893	880	83.255	1.438	υCO(40), υCC(24)
33.	A'	816	-	808	815	1.327	15.532	bCCO(37), υCO(28)
34.	A"	-	770	805	770	33.865	2.343	ωCH(79)

35.	A"	-	673	757	673	18.117	1.237	tCO(67), ωCC(16)
36.	A'	-	639	686	639	0.165	7.352	υCC(31) , Rsymd(26), Rasymd(17)
37.	A"	-	614	683	614	8.099	0.317	ωCO(15), ttrigd(34)
38.	A'	550	-	556	550	5.955	0.178	bCCO(62), Rasymd(10)
39.	A"	-	535	551	531	3.837	0.194	ttrigd(31) , tasymd(21), ωCH(14) ωCO(12), ωCC(10)
40.	A'	480	-	501	480	1.541	5.644	Rasymd(56), bCO(16)
41.	A"	-	440	445	440	0.718	0.055	tsymd(56), tCO(14), ωCH(11)
42.	A'	-	407	409	407	11.154	0.646	bCO(36), Rsymd(27), bCO(23)
43.	A"	-	360	348	360	118.014	3.561	tOH(94)
44.	A'		350	346	350	0.673	4.360	Rsymd(37), υCC(29), bCCO(16)
45.	A'	-	248	296	248	8.214	0.560	bCOC(66), bCC(22)
46.	A"	-	219	236	219	0.377	2.113	tasymd(46), ttrigd(15), tCO(14) ωCH(14)
47.	A"	-	190	205	190	1.029	2.050	tCOC(50), tCO(19), ωCC(10)
48.	A'	-	145	148	140	2.900	0.027	bCC(46), bCCO(25), bCOC(20)
49.	A"	-	120	127	120	0.009	0.991	tCH_3(77), tCO(11)
50.	A"	-	97	105	97	2.667	2.182	ωCC(47) , tCOC(33)
51.	A"	-	50	49	50	1.606	0.379	tCO(99)

Abbreviations; R, ring; b, bending; deform, deformation; sym, symmetric; asy, asymmetric; ω, wagging; t, torsion; trig, trigonal; υ, stretching; ips, in – plane stretching; ipb, in –plane bending; ops, out - of - plane stretching; opb, out - of - plane bending; sb, symmetric bending; ipr, in - plane rocking; opr, out – of – plane rocking.
Only contributions larger than 10 % are given.

Table 7. Detailed assignment of fundamental vibrations of Methyl Salicylate (MS) by normal mode analysis based on SQM force field calculations

Sl. No	Symmetry species C_s	Observed wavenumbers cm^{-1}		Calculated wavenumbers B3LYP/6-31G** force field cm^{-1}		IR *Intensity*	Raman Activity	Characterization of normal modes with PED (%)[a]
		FT IR	Raman	unscaled	scaled			
1.	A'	3190	-	3651	3190	314.092	83.440	υOH(100)
2.	A'	3120	-	3223	3120	7.391	163.707	υCH(99)
3.	A'	3100	-	3216	3100	6.703	99.639	υCH(99)
4.	A'	-	3080	3206	3080	10.157	103.64	υCH(99)
5.	A'	3074	-	3187	3074	7.461	79.451	υCH(99)
6.	A'	2965	-	3179	2965	12.204	70.568	υCH_3ips (100)
7.	A"	-	2963	3155	2963	15.695	56.450	υCH_3ops (99)
8.	A'	2890	-	3072	2890	36.787	130.674	υCH_3ss (100)
9.	A'	-	1681	1807	1682	275.884	55.582	υCO(63), bCCO(21), υCC(10)
10.	A'	-	1620	1675	1620	139.161	68.247	υCC(62), bCH(20)
11.	A'	1588	-	1633	1588	27.266	9.755	υCC(63) , bCH(17)
12.	A'	1487	-	1527	1487	81.978	1.372	bCH(51) , υCC(36)
13.	A'	-	1471	1523	1471	18.530	10.493	bCH(31), CH_3 ipb(26), υCC(22)
14.	A'	-	1446	1510	1446	49.171	10.023	bCH(38), υCC(21), CH_3 ipb (17) bHCH(14)
15.	A"	-	1442	1491	1442	6.780	21.790	CH_3 opb(94)
16.	A'	1441	-	1476	1441	6.892	3.468	CH_3 ipb(50), υCC (45)
17.	A'	1338	-	1416	1338	16.638	7.041	bCOH(41), υCC(34), bCH(20)
18.	A'	1306	-	1366	1306	40.559	4.596	υCC(56) , bCH(21)
19.	A'	1254	-	1312	1254	400.451	17.501	υCO(32), υCC(27), bCCO(12) bCOH(11)
20.	A'	-	1226	1277	1226	39.065	27.486	υCC(35), bCH(27), υCO(21) bCCO(11)
21.	A'	1217	-	1238	1217	92.604	3.441	bCH(32), υCC(27), bCOH(19)
22.	A'	-	1199	1210	1199	13.921	2.274	CH_3sb(41), bCH(38), υCC(14)
23.	A'	1159	-	1182	1159	53.714	22.656	CH_3ipr(52) bCH(18) υCC(12)
24.	A'	1135	-	1177	1135	0.593	5.098	CH_3opr(93)
25.	A'	1091	-	1144	1091	153.619	3.034	υCC(30), υOC(18), bCH(16), υCO(15)
26.	A'	-	1037	1111	1037	44.303	0.412	υCC(28), υOC(19), Rtrigd(19), υCO(10), bCH(10)
27.	A'	1033	-	1063	1033	28.259	27.620	υCC(61), bCH(16), υOC(15)
28.	A'	964	-	992	964	11.613	3.546	υOC(37), bCCO(23), υCC(14) Rtrigd(12), υCO(10)
29.	A"	865	-	986	864	2.299	0.040	ωCH(80), ωCO(10)
30.	A"	849	-	976	849	2.459	0.421	ωCH(79), ttrigd(10)

31.	A'	-	814	877	814	0.516	0.733	Rtrigd(37), υCO(21), bCCO(15)
32.	A''	801	-	866	801	8.994	3.258	ωCH(42) , ttrigd(27), ωCO(21)
33.	A'	767	-	806	767	28.280	25.028	υCO(39), bCCO(19), υCC(16)
34.	A''	726	-	791	726	23.752	0.844	ttrigd(31), ωCH(28), tCO(90), ωCO(13)
35.	A''	702	-	760	702	0.169	1.678	tCO(49), ωCH(27), ωCO(11)
36.	A'	-	670	701	670	5.786	6.657	Rsymd(47), υCC(22), Rasymd(15)
37.	A''	667	-	669	667	33.790	2.290	ωCH(56), ttrigd(32)
38.	A''	-	565	613	565	85.384	0.811	tOH(80)
39.	A'	-	540	564	540	7.106	8.740	Rasymd(63), υCC(15)
40.	A''	531	-	543	531	5.247	0.593	ωCO(30), ωCH(25), ttrigd(23), tsymd(18)
41.	A'	512	-	540	512	1.117	2.978	bCCO(58), bCO(13), υCC(13)
42.	A''	431	-	443	431	7.725	0.158	tasymd(71), ωCH(11), υCC(11)
43.	A'	-	360	401	360	5.382	4.922	bCCO(40) bCO(31), υCC(11)
44.	A'	-	340	354	340	2.887	1.354	bCO(44), Rsymd(22), υCC(19)
45.	A'	-	268	330	268	9.779	0.621	bCOC(53), bCC(24), bCCO(18)
46.	A''	-	186	263	186	1.616	2.347	tsymd(39), tCO(29), ωCC(14)
47.	A'	-	150	186	150	0.461	0.058	bCC(70), bCOC(17)
48.	A''	-	130	175	130	2.602	0.686	tCOC(47), tCH_3(27), tsymd(10)
49.	A''	-	110	121	110	1.681	1.481	tCH_3(60), tCO(24)
50.	A''	-	99	100	99	0.309	1.243	tCO(92)
51.	A''	-	50	60	50	2.895	1.972	ωCC(14), tCO(23), tOH(11)

Abbreviations; R, ring; b, bending; deform, deformation; sym, symmetric; asy, asymmetric; ω, wagging; t, torsion; trig, trigonal; υ, stretching; ips, in – plane stretching; ipb, in –plane bending; ops, out - of - plane stretching; opb, out - of - plane bending; sb, symmetric bending; ipr, in - plane rocking; opr, out – of – plane rocking.
Only contributions larger than 10 % are given.

Table 8. Atomic charges for optimized geometry of Methyl m-Hydroxy Benzoate (MMHB) and Methyl Salicylate (MS) obtained by B3LYP/6-31 G density functional calculations**

Atoms [a]	Mulliken		Atoms [a]	Mulliken	
	MMHB	MS		MMHB	MS
C_1	0.011	-0.009	H_{11}	0.124	0.133
C_2	-0.111	0.292	H_{12}	0.118	0.123
C_3	0.322	-0.100	H_{13}	0.138	0.140
C_4	-0.120	-0.079	H_{14} (O_{14})	0.126	-0.565
C_5	-0.097	-0.100	O_{15} (H_{15})	-0.554	-0.565
C_6	-0.102	-0.103	H_{16}	0.317	0.1007
C_7	0.599	0.620	H_{17}	0.079	0.093
O_8	-0.489	-0.485	H_{18}	0.092	0.089
O_9	-0.480	-0.534	H_{19}	0.107	0.119
C_{10}	-0.081	-0.081			

[a]The atoms indicated in the parenthesis belong to MS.

Table 9. Natural atomic charges of Methyl m-Hydroxy Benzoate (MMHB) and Methyl Salicylate (MS) Calculations performed at the B3LYP/6-31G levlel of theory**

Atoms[a]	MMHB	MS	Atoms[a]	MMHB	MS
C_1	-0.15001	-0.25669	H_{11}	0.2253	0.22919
C_2	-0.24124	0.37419	H_{12}	0.22509	0.22768
C_3	0.32470	-0.29216	H_{13}	0.22353	0.22919
C_4	-0.30040	-0.19748	H_{14} (O_{14})	0.27153	-0.69276
C_5	-0.22359	-0.27542	O_{15} (H_{15})	-0.68756	0.51847
C_6	-0.23036	-0.17122	H_{16}	0.49193	0.25350
C_7	0.81612	0.81424	H_{17}	0.23439	0.24365
O_8	-0.59946	-0.59330	H_{18}	0.24446	0.24444
O_9	-0.54727	-0.58706	H_{19}	0.25757	0.26175
C_{10}	-0.33296	-0.33021			

[a]The atoms indicated in the parenthesis belong to MS. For numbering of atoms refer Fig.1 (a) & (b).

Table 10. Theoretical electronic absorption spectra values

Calculated/λ_{cal} (nm) CIS					
Excitation Energies(ev)		Oscillator strength		Wavelength (nm)	
MMHB	MS	MMHB	MS	MMHB	MS
5.7032	5.6338	0.0975	0.1511	217.39	220.07
6.0852	6.1278	0.0575	0.0661	203.75	202.33
6.3984	6.6446	0.0007	0.0005	193.77	186.59

Table 11. Calculated quantum chemical parameters of the Methyl m-Hydroxy Benzoate (MMHB) and Methyl Salicylate (MS) derivatives

Parameters	MMHB	MS
E_{HOMO}	-0.229	-0.227
E_{LUMO}	-0.043	-0.045
ΔE	0.186	0.182
X	0.136	0.136
η	0.093	0.091
σ	10.752	10.989

Table 12. Calculated ^{13}C NMR Chemical shifts (ppm) of Methyl m-Hydroxy Benzoate (MMHB) and Methyl Salicylate (MS)

Carbon	Exp		B3LYP/6-31G**	
	MMHB	MS	MMHB	MS
C_1	131.04	161.75	137.13	167.06
C_2	116.50	112.48	121.55	115.73
C_3	156.24	129.98	163.31	140.16
C_4	120.66	119.17	190.88	121.51
C_5	129.77	135.69	132.60	138.48
C_6	121.78	117.59	125.05	122.29
C_7(=o)	168.01	170.59	171.26	171.26
C_{10}	52.51	52.21	52.90	52.34

Table 13. Experimental and calculated ^{1}H NMR Chemical shifts (ppm) of Methyl m-Hydroxy Benzoate (MMHB) and Methyl Salicylate (MS)

Proton[a]	Exp		B3LYP/6-31G**	
	MMHB	MS	MMHB	MS
H_{14} (H_{15})	7.61	7.814	7.893	8.493
H_{16}	6.31	6.87	3.664	6.996
H_{17}	7.089	7.43	6.609	7.440
H_{18}	7.300	6.97	7.218	6.893
H_{19}	7.60	10.74	7.636	8.235
H_{11},H_{12}, H_{13}	3.918	3.926	3.813	3.870

[a]The atoms indicated in the parenthesis belong to MS.

Table 14. Theoretically computed Energies (a.u.), Zero-point vibrational energies (kcal mol^{-1}), Rotational constants (GHz), Entropies (cal mol^{-1} K^{-1}), Nuclear repulsion energy (hartrees) and Dipole moment (Debye) for MMHB and MS

Parameters	B3LYP/6-31G**	
	MMHB	MS
Zero-point energy	92.70396	93.16864
Rotational constants	2.63041	2.25791
	0.65118	0.82693
	0.52368	0.60758
Entropy		
Total	98.694	96.904
Translational	40.967	40.967
Rotational	30.262	30.028
Vibrational	27.465	25.909
Dipole moment	2.992	1.1860
Nuclear repulsion energy	577.82272	593.17684

Theoretical and experimental chemical shifts of MMHB and MS in ^{1}H and ^{13}C NMR spectra are gathered in Tables 12 and 13. The range of the ^{13}CNMR chemical shifts for typical organic molecules usually is >100 ppm [43, 44] and the accuracy ensures reliable interpretation of spectroscopic parameters. In the present study, the ^{13}CNMR chemical shifts in the ring are >100 ppm, as they would be expected.

A nearby electronegative atom withdraws electron density (due to Inductive (–I) effect) from the neighbourhood of the proton, so the NMR signal of such deshielded proton (the proton surrounded by less electron density) will appear downfield (higher δ value). Thus the greater the electronegativity of the atom, the greater is the deshielding of the proton [30]. The carbon atom of the carbonyl group is strongly deshielded and has a characteristic chemical shift of around 160-210 ppm [26]. The chemical shift value of C7 (MMHB and MS) which has bigger value than the other carbons due to the electronegative property of oxygen atom. The linear correlations between calculated and experimental data of ^{13}CNMR and ^{1}HNMR spectra are determined as 0.8240, 0.8382 for MMHB and 0.9891, 0.8758 for MS, respectively. There is an excellent linear relationship between experimental and computed results which are shown in Figs. 8-9.

4.6. Thermodynamic Properties

Several calculated thermodynamical parameters are presented in Table 14 for MMHB and MS, respectively. Scale factors have been recommended [45] for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy *S*vib(T). The total energies and the change in the total entropy at room temperature using B3LYP/6–31G** method are presented.

5. Conclusion

Attempts have been made in the present work for the molecular parameters and frequency assignments for the compounds MMHB and MS from the FTIR and FT-Raman spectra. The equilibrium geometries, harmonic and anharmonic frequencies for the title compounds were determined and analyzed at DFT level of theory utilizing 6-31G** basis set. The assignments of most of the fundamentals of the title compounds provided in this work are quite comparable. The excellent agreement of the calculated and observed vibrational spectra reveals the advantages of a smaller basis set for quantum chemical calculations. The absorption wavelength (λ), excitation energies and oscillator strengths (f) were calculated. HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The experimental and theoretical investigation of the title compounds have been performed successfully by using ^{1}H and ^{13}C NMR. The various modes of vibrations were unambiguously assigned on the basis of the result of the PED output obtained from normal coordinate analysis. These studies conforms the presence of OH and ester group. The role of stretching frequency of OH is a test for hydrogen bonding as well as measure of strength of hydrogen bonding. The obtained data and simulations both show the way to the characterization of the molecule and help for spectra studies in the future.

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