

DENSITY FUNCTIONAL THEORY AND *AB INITIO* HARTREE-FOCK CALCULATIONS THE STRUCTURE OF METHYL SALICYLATE

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The compound Methyl Salicylate characterized by elemental analysis, IR, UV-Vis, Mass and NMR. Density functional theory (DFT) calculations have been carried out for the title compound by performing HF and DFT levels of theory using the standard 6-311+G(d,p) basis set. The calculated results show that the predicted geometry can well reproduce the structural parameters. Predicted vibrational frequencies have been assigned and compared with experimental IR spectra and they are supported each other. The theoretical electronic absorption spectra have been calculated by using CIS, TD-DFT, ZINDO methods. ¹³C, ¹H NMR of the Methyl Salicylate have been calculated by means of B3LYP density functional theory method with 6-311+G(d,p) basis set. Comparison between the experimental and the theoretical results indicates that density functional theory B3LYP method is able to provide satisfactory results for predicting NMR properties. On the basis of vibrational analyses, the thermodynamic properties of the title compound at different temperatures have been calculated.

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1. Introduction

Salicylates are the class of compounds that are widely valued for their pain killing, antipyretic and anti-inflammatory properties [1]. The most commonly known and used salicylates are salicylic acid. They are used extensively for the relief of headache, inflammation, arthritis pain, and some are employed in the treatment of heart attacks and strokes in the elderly [2]. Recently, salicylic acid has been used primarily as an intermediate in the production of agrochemicals, dyes and colorants products [3]. In addition to analgesic, antipyretic, and antiinflammatory properties, salicylates possess also some other actions that have been proven to be therapeutically beneficial [4].

Gaseous methyl salicylate (MeSA), a major volatile produced in tobacco mosaic virus TMV- inoculated tobacco plants, was recently shown to be an airborne defense signal. Using an assay developed to measure the MeSA present in tissue, have shown that in TMV-inoculated tobacco plants the level of MeSA increases dramatically, paralleling increases in salicylic acid (SA). MeSA accumulation was also observed in upper, noninoculated leaves[5].

Methyl salicylate is a typical molecule having an intramolecular hydrogen bond between its hydroxyl and carbonyl groups [6]. Methyl salicylate (oil of wintergreen) is used for relieving muscle aches and pains by applying externally to the affected area. It is an ingredient in numerous commercially available products [7].

We performed HF and DFT calculations on title compound. In this paper, we wish to report the experimental values as well as the calculated results and so have studied ¹H and ¹³C chemical shifts of Methyl salicylate from both experimental and theoretical point of view. Recently reported us the DFT calculation of the 4-substituted aminoazo-benzenesulfonyl azides [8]

Therefore, the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wave number accuracy. Ab initio HF and density functional theory (DFT) calculations have been performed to support our wave number assignments.

On the basis of vibrational analyses, the thermodynamic properties of the Methyl salicylate at different temperatures have been calculated, revealing the correlations between $C_{p,m}^{\circ}$, S_m° , H_m° and temperatures.

2. Computational details

The molecular structures of this compound in the ground state are also optimized by Hartree-Fock (HF), Becke 3-Lee-Yang-Parr (B3LYP) level on a Pentium IV/3.06 GHz personal computer using Gaussian 98W [10,11,12].

Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartree-Fock level, adopting the standard 6-311G(d) basis set. This geometry was then re-optimized again at B3LYP and B3PW91 level, using basis set 6-311G(d), 6-311+G(d,p) for better description. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of this compound were used for harmonic vibrational frequency calculations resulting in IR frequency together with intensities.

Chemical shifts of the considered compounds were calculated at the same level using the Gauge-Included Atomic Orbital (GIAO) approach [13,14]. 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 [15].

The convergence is set to 0.001 kcal mol⁻¹, vibrational frequencies for these species were calculated using these methods and then scaled by 0.8991 and 0.9663 for HF/6-311G(d) and B3LYP/6-311G(d), respectively [16].

3. Results and discussion

3.1. Molecular structure, optimized geometry

The labelling of atoms in Methyl salicylate is given in Fig. 1. The optimized geometrical parameters (bond length, angles and dihedral angles) by HF, DFT/B3LYP with 6-311+G(d,p) and as basis sets are listed in Table 1. The aim of this study is to give optimal molecular geometry and vibrational modes of this compound.

Since the crystal structure of this compound is not available, the optimized structure can be only be compared with other similar systems for which the configurations have been optimized [17,18]. For example, the optimized bond lengths of C-C in phenyl ring fall in the range from 1.373-1.404 Å for HF/6-31G* method and 1.384-1.414 Å for B3LYP/6-31G* method, which are in good agreement with a similar molecular structure, (phenyl ring with arensulfonyl group) 1.385-1.400 Å [18]. Based on above comparison, although there are some differences between our values and the literature data, the optimized structural parameters can well reproduce the literature ones and they are the bases for thereafter discussion.

There are two types of CC bonds involved in these species, i.e. bonds, strained C=C C-C single bonds (e.g. C(1)-C(2)). The CC bond lengths of Methyl salicylate are in the order: $r < r_{C-C}$, C=C e.g. C(2)-C(3) < C(1)-C(2).

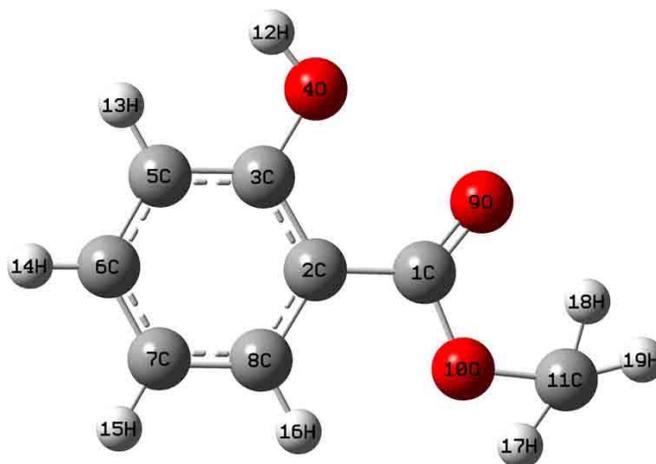


Fig. 1. Numbering system adopted in this study (Methyl salicylate).

Table 1. Selected bond distances (Å), bond angles (°) and torsional angles (°) of the Methyl salicylate optimized.

Entry	HF/6-311+G(d,p)	B3LYP/6-311+G(d,p)
Bond lengths (Å)		
C11-O10	1.367	1.342
O10-C1	1.236	1.296
C1-O9	1.317	1.351
C1-C2	1.461	1.440
C2-C3	1.401	1.421
C3-O4	1.343	1.366
C3-C5	1.389	1.397
C5-C6	1.379	1.393
C6-C7	1.380	1.397
C7-C8	1.376	1.386
C8-C2	1.400	1.416
Bond angles (°)		
C11-O10-C1	130.9	130.0
O10-C1-O9	120.5	119.5
O9-C1-C2	120.5	122.0
O10-C1-C2	118.9	118.3
O4-C3-C5	120.4	120.8
O4-C3-C2	119.8	118.9
C8-C2-C1	118.1	119.4
C1-C2-C3	123.7	123.4
Dihedral angles (°)		
C11-O10-C1-O9	0	0
C11-O10-C1-C2	180	180
O10-C1-C2-C8	0	0
O10-C1-C2-C3	180	180
O9-C1-C2-C3	0	0
O9-C1-C2-C8	180	180
O4-C3-C2-C1	0	0
O4-C3-C2-C8	180	180
O4-C3-C5-C6	180	180

3.2. The Vibrational frequency

The observed experimental FT-IR spectra and theoretically predicted IR spectra are shown in Figs. 2-5. The vibrational frequency and approximate description of each normal modes obtained using HF and DFT/B3LYP methods with 6-311+G(d,p) basis set are given for this compound in Table 2.

In our study, vibrational frequencies calculated at HF/6-311+G(d,p) level were scaled by 0.904 ± 0.025 and B3LYP/6-311+G(d,p) level were scaled by 0.964 ± 0.023 [15]. On the basis of the comparison between calculated and experimental results, assignments of fundamental modes were examined. The assignment of the experimental frequencies are based on the observed band frequencies in the infrared spectra of this species confirmed by establishing one to one correlation between observed and theoretically calculated frequencies.

The calculated frequencies are slightly higher than the observed values for the majority of the normal modes. Two factors may be responsible for the discrepancies between the experimental and computed spectra of this Methyl Salicylate. The first is caused by the environment and the second reason for these discrepancies is the fact that the experimental value is an anharmonic frequency while the calculated value is a harmonic frequency [19]. A linearity between the experimental and calculated wave numbers (i.e. for the whole spectral range considered), can be estimated by plotting the calculated versus experimental wave numbers (Fig. 6). The values of correlation coefficients provide good linearity between the calculated and experimental wave numbers (correlation coefficients of 0.899-0.999).

In the spectra of methyl esters the overlap of the regions in which both asymmetric stretching absorb with a weak to medium intensity (3020 ± 30 and 2990 ± 40 cm^{-1}) is not large [20]. Both normal modes are usually observed separately. Methyl formate displays the stretching vibrations in the neighbourhood of 3037 and 3010 cm^{-1} and methyl acetate at 3030 and 3001 cm^{-1} [20]. With methyl esters of unsaturated carboxylic acid $\nu_{\text{asymm}}\text{CH}_3$ cannot always be attributed unambiguously because the CH stretching modes also occur in the vicinity of 3000 cm^{-1} [20]. The experimentally observed bands at 2954 and 2920 cm^{-1} in the IR spectrum is assigned to $\nu_{\text{asymm}}\text{CH}_3$ modes. The calculations give 3346 and 3332 (HF) 2960 and 2958 (B3LYP) cm^{-1} as $\nu_{\text{asymm}}\text{CH}_3$ modes. The symmetric stretching mode $\nu_{\text{symm}}\text{CH}_3$ is expected in the region 2905 ± 65 cm^{-1} [20] in which all three of the CH bonds extend and contract in phase. In IR spectrum, a weak band at 2864 cm^{-1} is assigned as $\nu_{\text{symm}}\text{CH}_3$ mode and the ab initio calculation gives a value 2600 and 2800 cm^{-1} for this mode. With methyl esters the overlap of the regions in which the methyl asymmetric deformation are active (1460 ± 25 and 1450 ± 15 cm^{-1}) is quite strong, which leads to many coinciding wave numbers. This is obvious, not only for the asymmetric deformations, but also for the symmetric deformation mostly displayed in the range 1435 ± 15 cm^{-1} [20]. The intensity of these absorptions is only weak to moderate. Experimentally no bands are observed for these modes in the IR spectrum.

The methyl rocking modes are active in the region 1170 ± 50 cm^{-1} [20] with a band intensity which is sometimes weak although the band can also be of medium intensity or some times even be strong. The vibrational modes are generally observed separately and reported at 1202 and 1159 cm^{-1} for $\text{ClC}(=\text{O})\text{OMe}$ and at 1194 and 1163 cm^{-1} for $\text{MeC}(=\text{O})\text{OMe}$ [20]. The strong band seen at 1159 cm^{-1} in the IR spectrum and is assigned as ρCH_3 . Ab initio calculations gives 1189 and 1136 cm^{-1} as ρCH_3 modes. For $\text{C}(=\text{O})\text{OMe}$ group, the twisting modes of CH_3 (τCH_3) are expected in the region 225 ± 65 cm^{-1} [20].

The most characteristic band of esters arises from the C=O stretching vibration occurring at 1750 ± 50 cm^{-1} with a strong to very strong intensity [20]. Methyl esters of unsaturated and aromatic carboxylic acids show the $\nu\text{C}=\text{O}$ at 1725 ± 20 cm^{-1} . Seth Paul and Van Duyse [21] identified the region 1730 ± 15 cm^{-1} for mono and di-substituted methyl benzoates and Nyquist [22] proposed 1733 ± 5 cm^{-1} for *o*-phtalic esters. In the spectra of salicylic acid Volosek et al [23] have reported C=O stretch as intense band at 1660 cm^{-1} (IR). For the title compound, the νCO mode is seen as a strong band at 1682 cm^{-1} in IR and at 1692 and 1651 cm^{-1} theoretically. The C(=O)-O stretching vibration, often considered as the C-O asymmetric stretch, appears strongly at 1255 ± 60 cm^{-1} , a region in good agreement with that of the $\nu\text{C}-\text{O}$ in carboxylic acids (1250 ± 80 cm^{-1}) [20]. The strong band seen at 1255 cm^{-1} in IR spectrum and 1297 and 1214 cm^{-1} theoretically is

assigned to this mode. The O–C stretching vibration of the O–Me group appears in the wide range $975\pm 125\text{ cm}^{-1}$ with an intensity varying from weak to strong [20]. The mode is often called the symmetric C–O–C stretching vibration which is seen at 1121 and 1063 cm^{-1} theoretically and as a strong band at 1092 cm^{-1} in the IR spectrum. The hydroxyl OH group provides three normal vibrations νOH , δOH and πOH , of which not only the stretching vibration but also the out-of-plane deformation are good group vibrations [20]. Ab initio calculation give the νOH mode at 3568 and 3357 cm^{-1} . The moderate to strong absorption at $1350\pm 40\text{ cm}^{-1}$ in the spectra of phenols is assigned to the δOH mode. The region $1395\pm 55\text{ cm}^{-1}$ in the spectrum of carboxylic acid is also assigned as well to this OH in-plane deformation [24]. The medium band at 1339 cm^{-1} in the IR, and 1401 and 1320 cm^{-1} (calculated) are assigned to this δOH mode. The O–H out-of-plane deformations in the spectra of phenols takes up the whole region $685\pm 115\text{ cm}^{-1}$ [20]. Carbonyl substituted phenols give high values in the range $750\pm 50\text{ cm}^{-1}$, for 2-MeC(=O)PhOH at 800 cm^{-1} , 4-MeC(O)PhOH at 780 cm^{-1} as πOH deformation with weak, broad band disturbed by ring vibrations [20].

For 1,2 light–heavy disubstituted benzenes, the CH stretching modes of the ring are expected in the region $3110\text{--}3000\text{ cm}^{-1}$ [20]. The calculated values are $3217, 3204, 3190, 3175\text{ cm}^{-1}$ (HF) and $3129, 3111, 3092, 3015\text{ cm}^{-1}$ (B3LYP). These vibrations are observed at 3073 and 3004 cm^{-1} in the IR spectrum. The bands observed at $1616, 1586, 1488, 1442$ and 1307 cm^{-1} in the IR spectrum is assigned to the ring stretching modes. The calculated values for these modes are $1679, 1586, 11573, 1519, 1396\text{ cm}^{-1}$ (HF) and $1613, 1490, 1459, 1375, 1316\text{ cm}^{-1}$ (B3LYP). These vibrations are expected in the range $1620\text{--}1260\text{ cm}^{-1}$ [20]. For 1,2 light–heavy disubstituted benzenes δCH modes are seen in the range $1300\text{--}1240$ and $1170\text{--}1010\text{ cm}^{-1}$ [20]. We have observed theoretical values at $1267, 1170, 1070\text{ cm}^{-1}$ (HF) and $1204, 1129, 1030\text{ cm}^{-1}$ (B3LYP). The experimental values are $1218, 1137, 1034\text{ cm}^{-1}$ in the IR spectrum. The out-of-plane CH deformation bands πCH are expected in the region $995\text{--}720\text{ cm}^{-1}$ [20]. As seen from the Table 2, the ab initio calculations give wave number at 1057 cm^{-1} (HF) and 947 cm^{-1} (B3LYP). The bands at 965 cm^{-1} in IR spectrum is assigned to this mode.

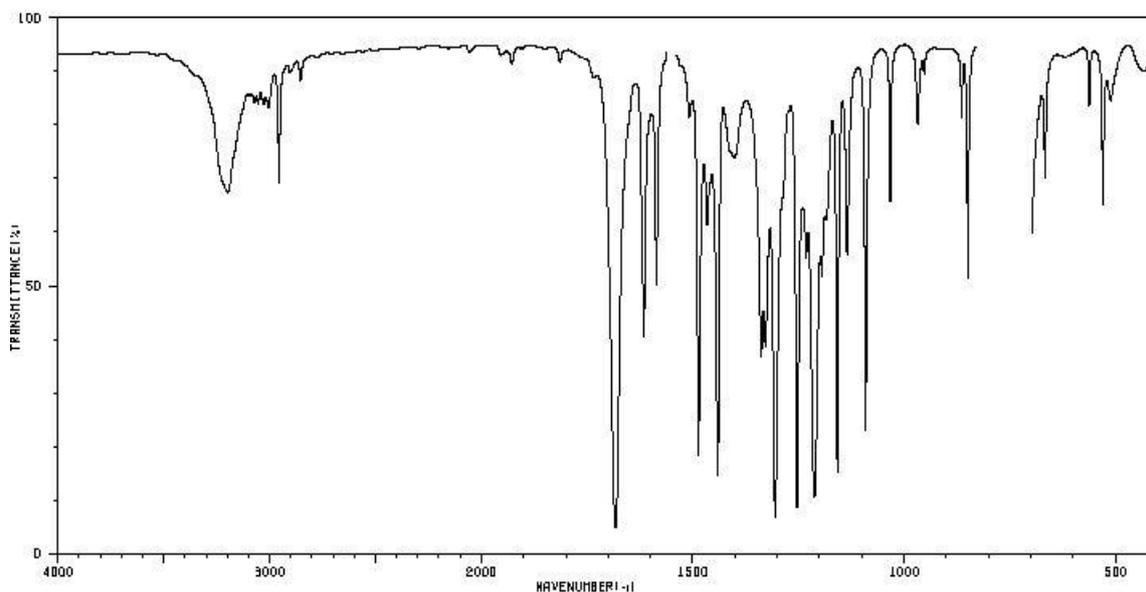


Fig. 2. FT-IR spectra of Methyl Salicylate

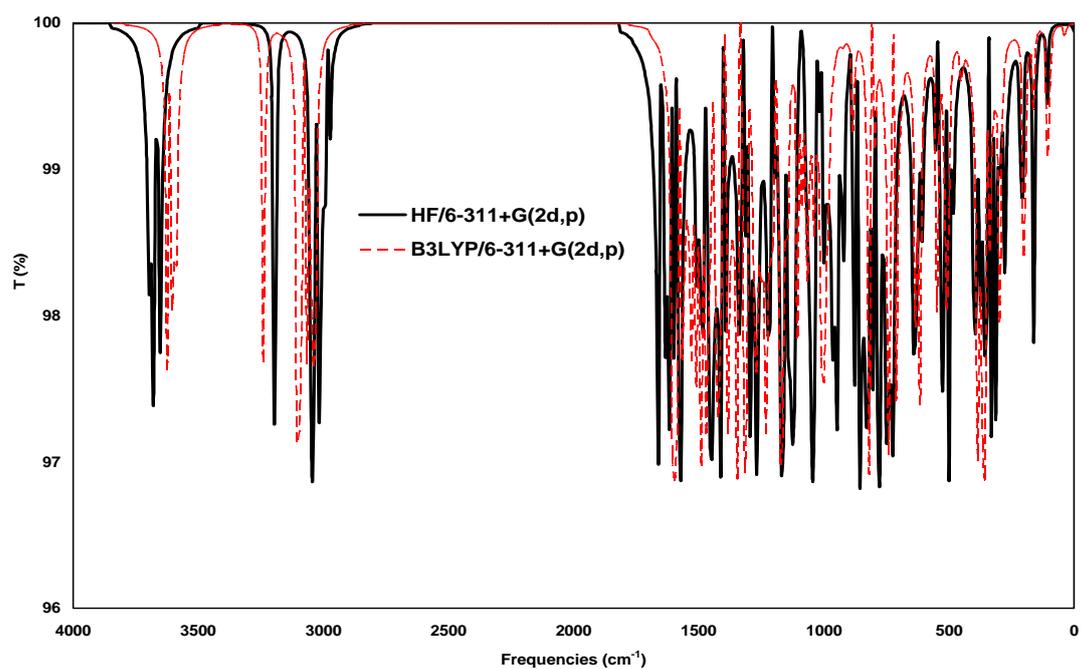


Fig. 3. Predicted spectrum at HF/6-311+G(*d,p*) & B3LYP/6-311+G(*d,p*) level for the Methyl Salicylate

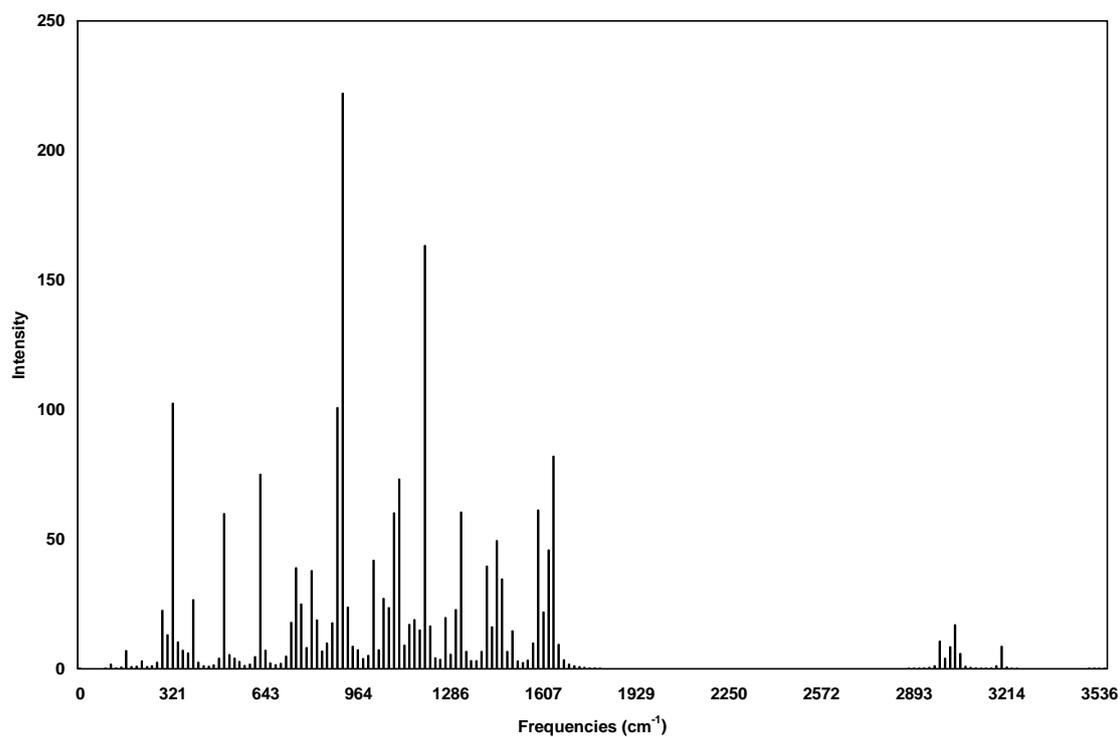


Fig. 4. HF/6-311+G(*d,p*) level for the Methyl Salicylate

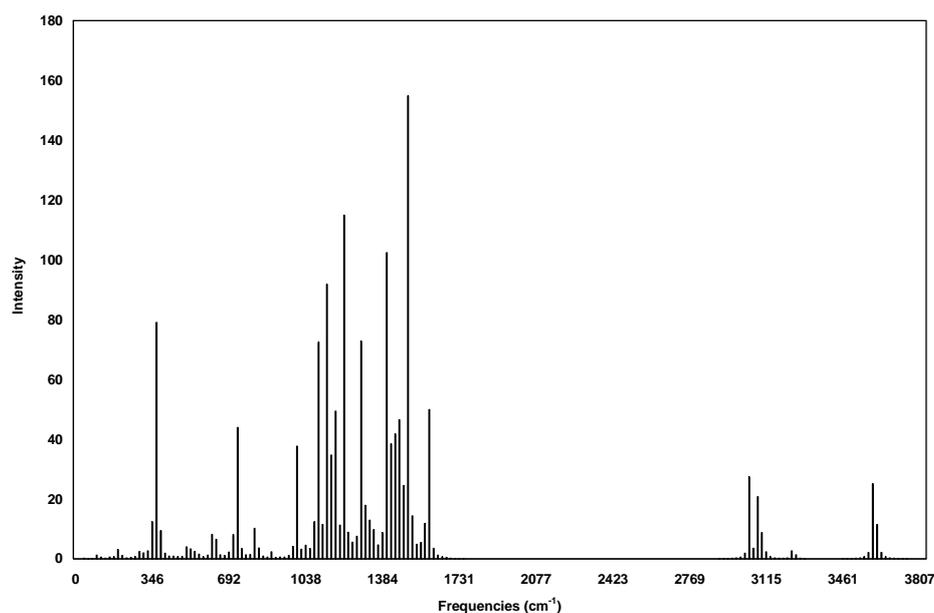


Fig. 5. B3LYP/6-311+G(d,p) level for the Methyl Salicylate

Table 2. Comparison of the observed and calculated vibrational spectra of the Methyl Salicylate

	HF /6-311+G(d,p)	B3LYP /6-311+G(d,p)	Exp ^a	Assignment
1	3576(12.5817)	3368(8.6924)	3199(64)	ν OH
2	3217(4.9782)	3129(7.3329)	3073(81)	ν CH
3	3204(14.4146)	3111(21.1415)	3054(81)	ν CH
4	3190(24.0681)	3092(16.4938)	3030(81)	ν CH
5	3175(7.4447)	3015(6.1184)	3004(79)	ν CH
6	3346(23.0324)	2960(26.9203)	2955(66)	$\nu_{\text{asym}}\text{CH}_3$
7	3332(293.625)	2958(56.6545)	2905(86)	$\nu_{\text{asym}}\text{CH}_3$
8	2800(10.8708)	2633(19.02)	2864(84)	$\nu_{\text{sym}}\text{CH}_3$
9	1692(13.0467)	1651(65.1189)	1682(4)	$\nu\text{C}=\text{O}$
10	1679(196.479)	1613(106.006)	1616(36)	ν Ph
11	1586(79.1942)	1490(125.939)	1586(47)	ν Ph
12	1573(172.029)	1459(37.4872)	1488(58)	ν Ph
13	1519(17.3682)	1375(151.173)	1442(70)	ν Ph
14	1401(163.137)	1320(113.037)	1339(35)	δ OH
15	1396(35.4094)	1316(73.5913)	1307(6)	ν Ph
16	1297(62.1862)	1214(9.2138)	1255(53)	$\nu\text{C}(=\text{O})-\text{O}$
17	1267(165.443)	1204(86.0009)	1218(10)	δ CH
18	1189(95.3729)	1136(121.247)	1159(50)	ρCH_3
19	1170(39.3397)	1129(2.6385)	1137(53)	δ CH
20	1121(2.6063)	1063(0.1956)	1091(22)	$\nu\text{O}-\text{Me}$
21	1082(722.899)	1030(2.6185)	1034(62)	δ CH
22	1057(2.7318)	947(27.627)	965(86)	π CH
23	951(81.7652)	860(19.1842)	850(49)	δ Ph
24	660(59.7844)	559(16.032)	563(81)	δ Ph
25	608(0.0416)	505(0.9471)	511(81)	τ OH

^aReference [19]

ν , stretching; δ , in-plane bending; π , out of plane bending; ρ , rocking; ω , wagging; τ , twisting. Subscript: asym, asymmetric; sym, symmetric.

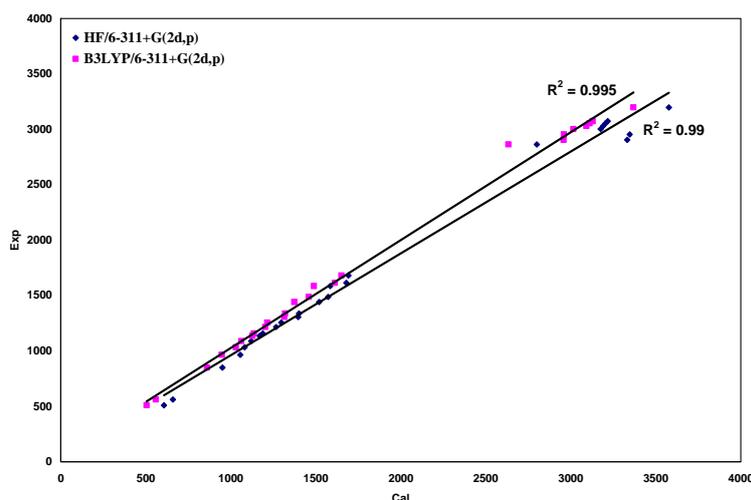


Fig. 6. Graphic correlation between the experimental and the theoretical frequencies obtained by HF/6-311+G(d,p) and B3LYP/6-311+G(d,p) method.

3.3. Electronic absorption spectra

Experimental electronic spectra measured in methanol solution along with the theoretical electronic absorption spectra calculated on the B3LYP/6-311+G(d,p) level optimized structure are listed in Table 3. In addition, the theoretical electronic spectra have a broad band from 259 to 766 nm [5], which is different from the experimental peak at 305 nm. Molecular orbital coefficients analyses based on the optimized geometry indicate that the frontier molecular orbitals are mainly composed of *p* atomic orbitals, so electronic transitions corresponding to above electronic spectra are mainly LUMO and HOMO-LUMO for the title compound. Fig. 7 shows the surfaces of HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital), in the HOMO, electrons are mainly delocalized on carboxyl with methyl group, while in the LUMO, electrons are all delocalized on phenyl ring with methyl group. So, the electronic spectra are corresponding to electronic transition of the phenyl ring (transition of π - π^* type). Absorption maximum (λ_{max}) this compound were calculated by the CIS, TD, ZINDO methods.

Table 3. Experimental and theoretical electronic absorption spectra values.

Exp ^a	Calculated λ_{cal} (nm) CIS		Calculated λ_{cal} (nm) TD		Calculated λ_{cal} (nm) ZINDO	
	wave length (nm)	oscillator strength	wave length (nm)	oscillator strength	wave length (nm)	oscillator strength
305.3	307.15	0.0001	321.15	0.0002	766.19	0.0016
237.9	259.28	0.1095	275.47	0.1436	602.31	0.0548

^aReference [5]

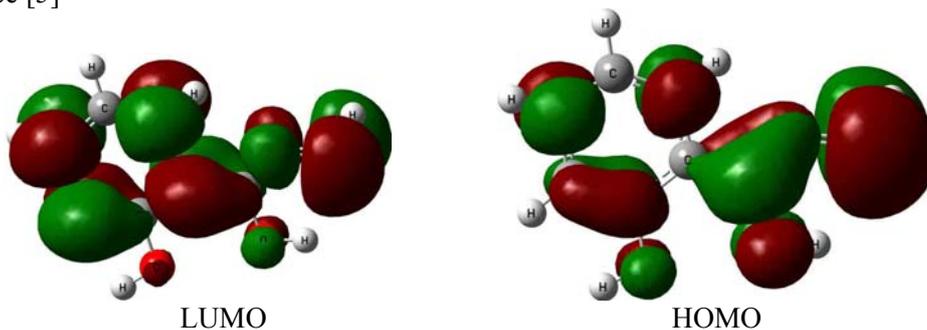


Fig. 7. Surfaces of HOMO, LUMO for the Methyl salicylate

3.4. NMR spectra

The experimental and theoretical values for ^1H , ^{13}C NMR, and calculated structural parameters of the Methyl Salicylate are given in Tables 4–5. We have calculated the theoretical ^1H , ^{13}C NMR chemical shifts, and structural parameters of the Methyl Salicylate.

The theoretical ^1H and ^{13}C NMR chemical shifts of Methyl Salicylate have been compared with the experimental data. According to these results, the calculated chemical shifts are in compliance with the experimental findings. In order to compare the experimental chemical shifts, the correlation graphics based on the calculations have been presented in Fig. 8. The correlation values carbon and proton chemical shifts are found to be 0.904 ± 0.025 and 0.964 ± 0.023 for HF and B3LYP with the 6-311+G(d,p) basis set, respectively [25–27].

Methyl Salicylate shows eight different carbon atoms, which is consistent with the structure on the basis of molecular symmetry. Chemical shifts were reported in ppm relative to TMS for ^1H and ^{13}C NMR spectra (Table 4,5). ^1H and ^{13}C NMR spectra were obtained at a base frequency of 125.76 MHz for ^{13}C and 500.13 MHz for ^1H nuclei. Relative chemical shifts were then estimated by using the corresponding TMS shielding calculated in advance at the same theoretical level as the reference.

Calculated ^1H and ^{13}C isotropic chemical shielding for TMS at the HF/6-31G(d), B3LYP/6-311+G(d,p) level in methanol were 31.87 ppm and 183.97 ppm, respectively.

The experimental values for ^1H and ^{13}C isotropic chemical shifts for TMS were 30.84 ppm and 188.1 ppm, respectively [28]. All the calculations were performed by using Gaussian 98W program package on a personal computer.

There is an excellent linear relationship between experimental and computed results. The experimental points, however, are above the line $y = x$, also shown (fig. 8).

Table 4. Experimental and calculated ^{13}C NMR chemical shifts (ppm) of the Methyl Salicylate

Carbon	HF/6-31G(TMS)	B3LYP/6-311+G(d,p)(TMS)	Exp ^a
C11	51.266	53.336	52.21
C3	160.3055	162.813	161.75
C1	168.1988	170.5924	170.59
C6	133.9246	137.5712	135.69
C8	130.1339	133.5969	129.98
C7	118.6574	120.292	119.17
C5	115.1465	117.6781	117.59
C2	111.2913	115.6153	112.48

^a Reference [19]

Table 5. Experimental and calculated ^1H NMR chemical shifts (ppm) of the Methyl Salicylate

Poroton	HF/6-31G(TMS)	B3LYP/6-311+G(d,p)(TMS)	Exp ^a
H18	3.7651	3.29	3.926
H19	3.2617	3.284	3.926
H17	3.81208	3.287	3.926
H12	10.28859	10.719	10.74
H16	7.83021	7.783	7.814
H14	7.33248	7.417	7.43
H15	6.83323	6.815	6.87
H13	6.56284	6.923	6.97

^a Reference [19]

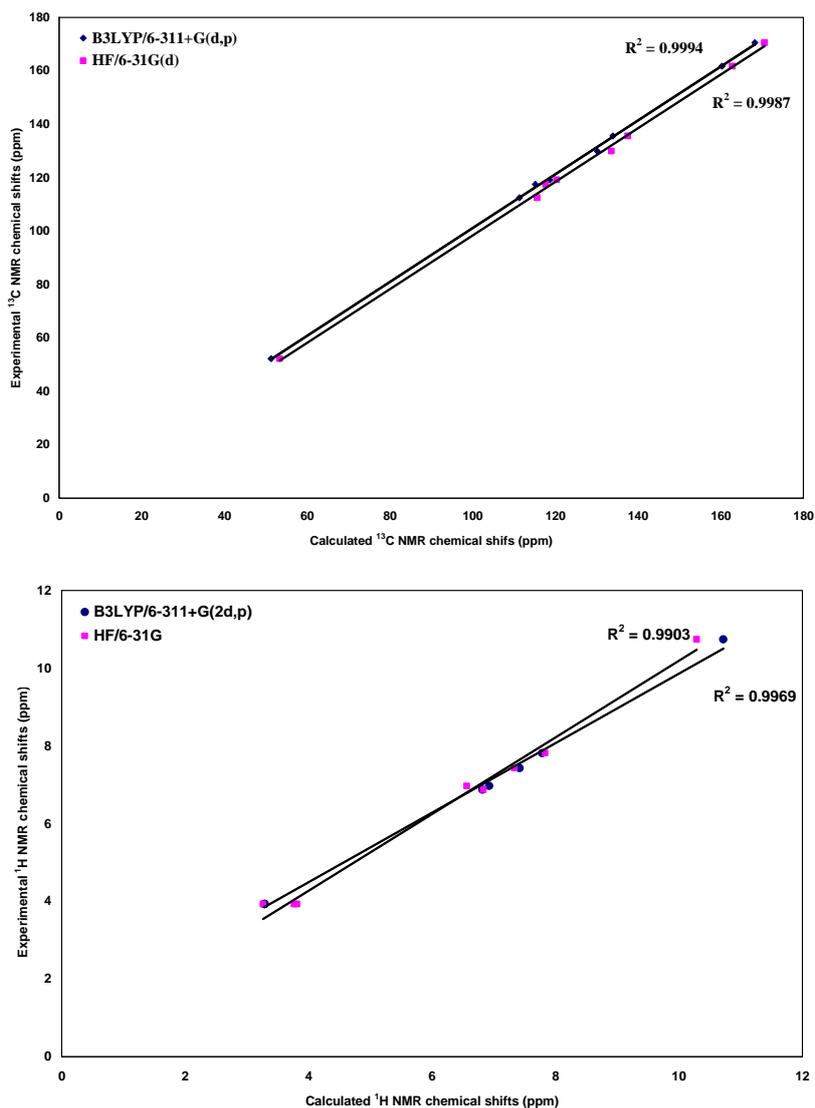


Fig. 8. Plot of the calculated vs. the experimental ^{13}C NMR, ^1H NMR chemical shifts (ppm)

3.5. Thermodynamic properties

On the basis of vibrational analyses and statistical thermodynamics, the standard thermodynamic functions: heat capacity ($C_{p,m}^\circ$), entropy (S_m°) enthalpy (H_m°) were obtained and listed in Table 6. The scale factor for frequencies is still 0.96.

Table 6: Thermodynamic properties at different temperatures at B3LYP/6-311+G(d,p) level

T (K $^\circ$)	$C_{p,m}^\circ$ (cal.mol $^{-1}$ K $^{-1}$)	S_m° (cal.mol $^{-1}$ K $^{-1}$)	H_m° (Kcal.mol $^{-1}$)
100	12.774	66.427	87.541
200	22.002	79.435	89.40871
300	31.664	90.993	92.292
400	40.571	101.924	96.112
500	48.042	112.251	100.754
600	54.085	121.927	106.07
700	58.983	130.951	111.93

As observed from Table 6, all the values of $C_{p,m}^{\circ}$, S_m° and H_m° increase with the increase of temperature from 100.0 to 700.0 K, which is attributed to the enhancement of the molecular vibration while the temperature increases because at a constant pressure ($dp=1\text{atm}$) values of $C_{p,m}^{\circ}$, S_m° and H_m° are equal to the quantity of temperature [29].

The correlations between these thermodynamic properties and temperatures T are shown in Fig. 9. The correlation equations are as follows:

$$C_{p,m}^{\circ} = 0.9047 + 0.1189 T - 5 \times 10^{-5} T^2 \quad (R^2 = 0.9994)$$

$$S_m^{\circ} = 53.365 + 0.1362 T - 4 \times 10^{-5} T^2 \quad (R^2 = 1)$$

$$H_m^{\circ} = 86.132 + 0.0089 T + 4 \times 10^{-5} T^2 \quad (R^2 = 0.9998)$$

These equations could be used for the further studies on the title compound. For instance, when we investigate the interaction between the title compound and another compound, thermodynamic properties $C_{p,m}^{\circ}$, S_m° and H_m° could be obtained from these equations and then used to calculate the change of Gibbs free energy of the reaction, which will assist us to judge the spontaneity of the reaction.

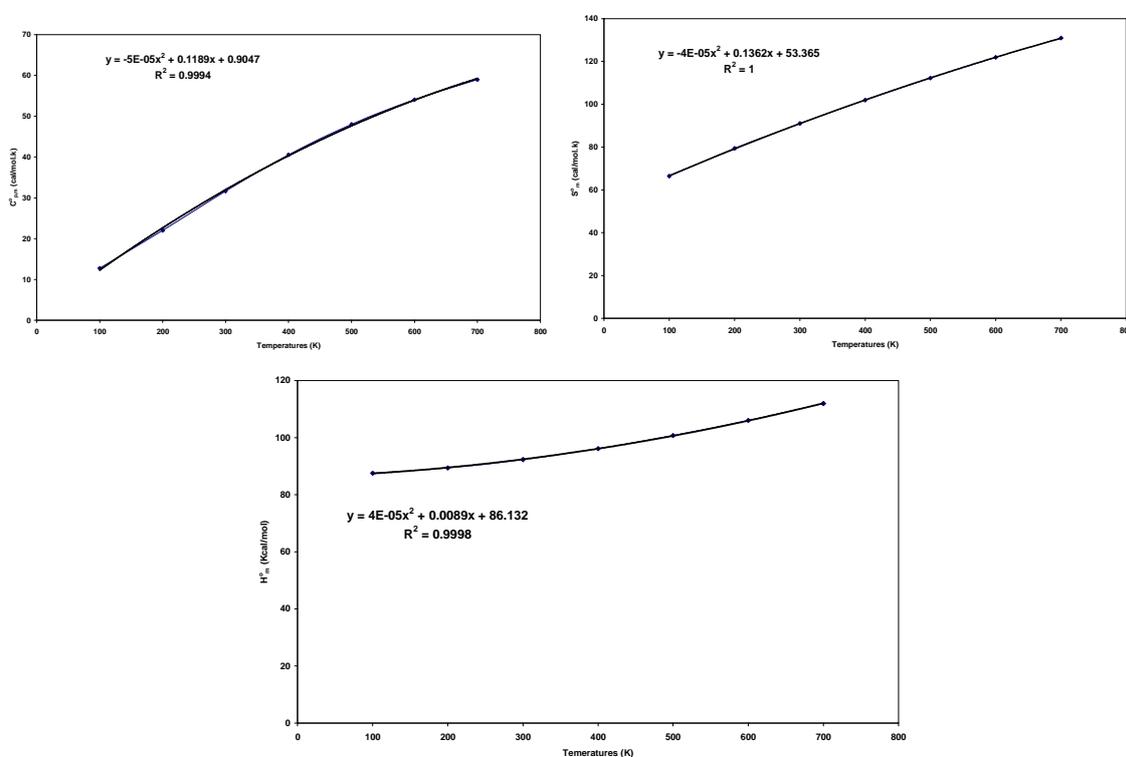


Fig. 9. Correlation graphics of thermodynamic properties and temperatures for the title compound.

Scale factors have been recommended [30] for an accurate prediction in determining the zero-point vibration energies, heat capacities, entropies, enthalpies, Gibbs free energies. All of this thermodynamic parameters and dipole moment at room temperature (298.15 K°) at different methods are also presented (table 7).

Table 7. Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), heat capacities ($\text{cal mol}^{-1} \text{K}^{-1}$), entropies ($\text{cal mol}^{-1} \text{K}^{-1}$), enthalpies (Kcal. mol^{-1}), Gibbs free energies (Kcal. mol^{-1}) and dipole moment (D) for Methyl Salicylate

Parameters	HF/6-311+G(d,p)	B3LYP/6-311+G(d,p)
Total energy	-532.024	-535.21
Zero-point energy	96.605	89.815
Rotational constant	2.11588	2.06581
	0.85028	0.83878
	0.60654	0.59656
Heat capacity	32.287	36.843
Entropy	88.864	96.564
Enthalpy	102.312	96.447
Gibbs free energy	75.818	67.657
Dipole moment	1.202	1.262

4. Conclusions

The HF/6-311+G(d,p), B3LYP/311+G(d,p) calculations were performed for methyl salicylate. The calculated results show that the predicted geometry can well reproduce the structural parameters. Predicted vibrational frequencies have been assigned and compared with experimental IR spectra and they are supported each other. The theoretical electronic absorption spectra have been calculated by using CIS, TD-DFT and ZINDO methods. ^1H , ^{13}C NMR of the methyl salicylate have been calculated by means of HF and B3LYP density functional method with 6-311+G(d,p) basis set. Comparison between the experimental and the theoretical results indicates that B3LYP/6-311+G(d,p) method is able to provide satisfactory results for predicting NMR properties. After the study of vibrational analyses, the thermodynamic properties of the methyl salicylate at different temperatures have been calculated, revealing the correlations between $C_{p,m}^\circ$, S_m° and H_m° and temperatures are obtained.

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