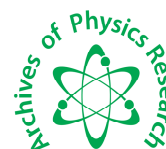




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FTIR spectra, Vibrational Spectroscopy of two Esters derivatives $C_9H_{10}O_2$ and $C_9H_9ClO_2$ of Benzene using DFT and HF methods

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ABSTRACT

Comparative studies of the infrared spectra of Ethyl benzoate ($C_9H_{10}O_2$) and Ethyl m-chloro benzoate ($C_9H_9ClO_2$ or 4-Chlorobenzoic acid) have been made. The spectra are interpreted with the aid of normal mode analysis following full structure optimization based on the DFT and HF method using 6-31G(d,p) basis sets combination. While making complete assignments of vibrational wave numbers some interesting observations in the vibrational spectra of these two molecules have been noticed. Following the quantum chemical calculation optimized geometries of the both molecules are predicted. The theoretical global minimum energy calculation helps to find the structural symmetries of the molecules.

Keywords: DFT; Ethyl benzoate; Ethyl m-chloro benzoate; Vibrational spectra.

INTRODUCTION

Vibrational spectroscopy has the potential to yield valuable structural and conformational information of organic compounds, if used in conjunction with accurate quantum chemical calculations. Prediction of vibrational frequencies of polyatomic molecules by quantum chemical computation has become very popular because of its accurate and consistent description of the experimental data. In this article, the performance of density functional theory (DFT) and HF employed 6-31G (d,p) basis sets has been evaluated. A close agreement between the observed and calculated wave number is achieved by introducing the scale factors. On comparing these two methods employed the reliability of DFT/B3LYP method with 6-31G (d, p) has been found to give the most accurate description of vibrational signatures in the present case. So to simplify the discussion we have only discussed all the results using DFT/B3LYP method.

MATERIALS AND METHODS

The molecular structure as seen by Gaussview using numbering scheme and experimental IR spectra of the ethyl benzoate ($C_9H_{10}O_2$) are given in Fig I and Fig II respectively, whereas for ethyl-m-chloro benzoate ($C_9H_9ClO_2$) these are given in Fig III and Fig IV respectively.

3. Computational details

All the calculations were performed on an AMD dual core/2.71 GHz personal computer using Gaussian 03W [1] program package, invoking gradient geometry optimization [2]. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartree-Fock level, adopting the standard 6-31G (d,p) basis set. This geometry was then re-optimized again at B3LYP level, using basis

set 6-31G (d, p) for better description. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT/B3LYP level to characterize all stationary points as minima. We have utilized the gradient corrected density functional theory (DFT) [3] with the three-parameter hybrid functional (B3) [4] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [5], accepted as a cost effective approach, for the computation of molecular structure, vibrational frequencies, and energies of optimized structures. Vibrational frequencies computed at DFT level have been adjudicated to be more reliable than those obtained by the computationally demanding Moller-Plesset perturbation methods. Density functional theory offers electron correlation frequently comparable to second-order Moller-Plesset theory (MP2) [6,7]. Finally, the calculated normal mode vibrational frequencies also provide the thermodynamic properties through the principle of statistical mechanics.

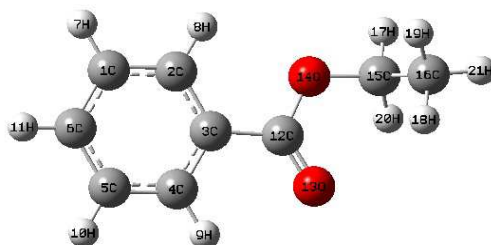


Fig. : Molecular Modeling Structure of Ethyl benzoate $C_9H_{10}O_2$

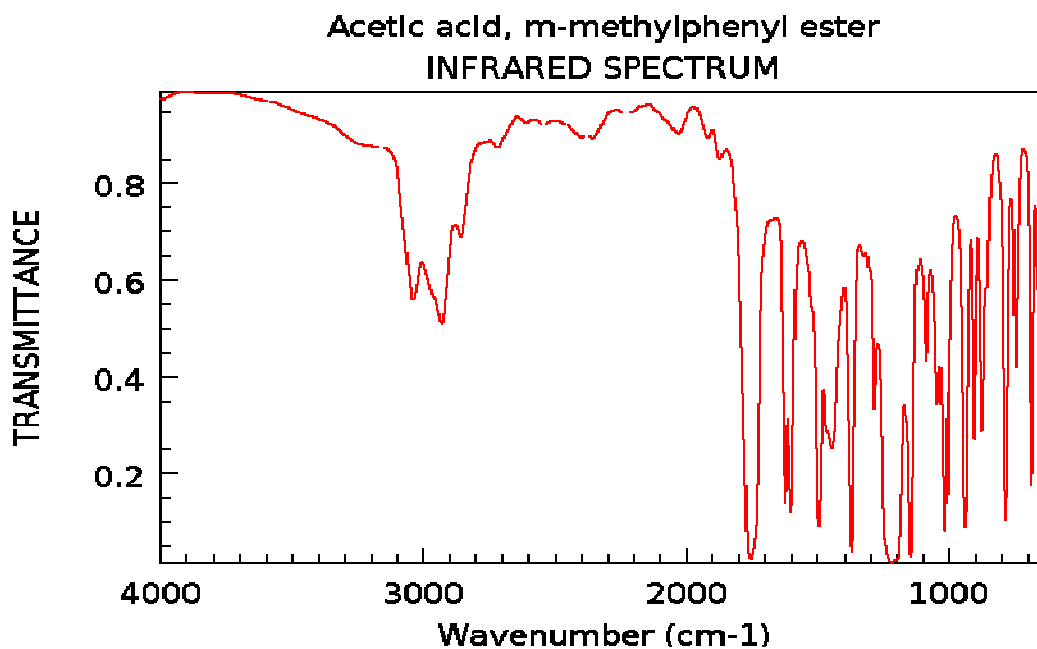


Fig. II : Theoretical FTIR spectra of Ethyl benzoate

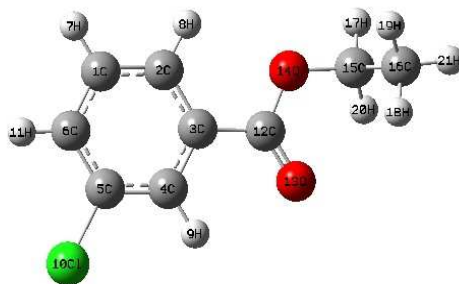


Fig 3: Molecular Modeling Structure of Ethyl m-choro benzoate

Fig III. Molecular Modeling Structure of Ethyl m-chloro benzoate $C_9H_9ClO_2$

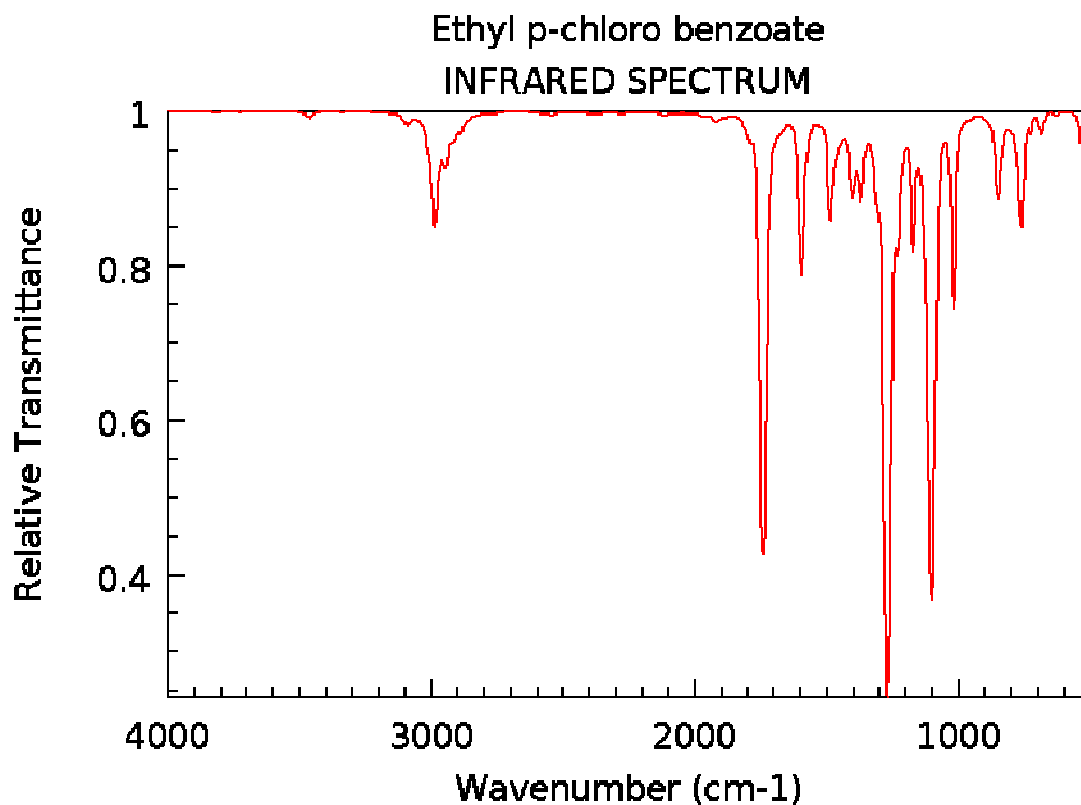


Fig IV. Theoretical FTIR spectra of Ethyl m-chloro benzoate $C_9H_9ClO_2$

Table-I Optimized geometrical parameters of Ethyl benzoate at HF and B3LYP level

Parameters	HF	B3LYP
Bond lengths		
C1-C2	1.3841	1.3937
C1-C6	1.3857	1.3967
C1-H7	1.0753	1.0859
C2-C3	1.3897	1.4016
C2-H8	1.0729	1.0837
C3-C4	1.3900	1.4014
C3-C12	1.4913	1.4913
C4-C5	1.3826	1.3922
C4-H9	1.0736	1.0846
C5-C6	1.3865	1.3972
C5-H10	1.0753	1.0859
C6-H11	1.0759	1.0862
C12=O13	1.1921	1.2167
C12-O14	1.3236	1.3538
O14-C15	1.4265	1.4473
C15-C16	1.5167	1.5209
C15-H17	1.0813	1.0926
C15-H20	1.0801	1.0923
C16-H18	1.0827	1.0924
C16-H19	1.0847	1.0939
C16-H21	1.0858	1.0951
Bond angles		
C2-C1-C6	120.0077	120.1329
C2-C1-H7	119.8824	119.8093
C6-C1-H7	120.1099	120.0579
C1-C2-C3	119.8924	119.8847
C1-C2-H8	120.3256	120.6325
C3-C2-H8	119.7820	119.4828
C2-C3-C4	119.9201	119.8222
C2-C3-C12	122.1240	122.4116
C4-C3-C12	117.9560	117.7662
C3-C4-C5	120.0799	120.1007
C3-C4-H9	118.9448	118.5098
C5-C4-H9	120.9753	121.3895
C4-C5-C6	119.8636	119.9776
C4-C5-H10	119.9888	119.9213
C6-C5-H10	120.1476	120.1011
C1-C6-C5	120.2364	120.0820
C1-C6-H11	119.8676	119.9464
C5-C6-H11	119.8960	119.9716
C3-C12=O13	123.5989	124.1339
C3-C12-O14	112.9439	112.3477
O13=C12-O14	123.4570	123.5181
C12-O14-C15	118.3039	116.4655
O14-C15-C16	111.4757	111.3585
O14-C15-H17	104.5011	104.3351
O14-C15-H20	109.1450	108.7855
C16-C15-H17	111.0387	111.5183
C16-C15-H20	111.2991	111.1340
H17-C15-H20	109.1400	109.4648
C15-C16-H18	110.8338	110.4970
C15-C16-H19	110.6318	110.8780
C15-C16-H21	109.6534	109.8193
H18-C16-H19	108.9593	108.9672
H18-C16-H21	108.3554	108.3021
H19-C16-H21	108.3397	108.3087

RESULTS AND DISCUSSION

4.1 Molecular Geometry

The optimized structure parameters of Ethyl benzoate and Ethyl m-chloro benzoate calculated by DFT/B3LYP and HF methods with the 6-31G (d, p) basis set are listed in Table.1, 2 and are in accordance with the atom numbering scheme as shown Fig. and II respectively. By allowing the relaxation of all parameters, the calculations converge to

the optimized geometries, which correspond to the true energy minima, as also revealed by the lack of imaginary frequencies in the vibrational mode calculation.

Table II Optimized geometrical parameters of Ethyl m-chloro benzoate at HF and B3LYP level

Parameters	HF	B3LYP
Bond lengths		
C1-C2	1.3842	1.3936
C1-C6	1.3841	1.3955
C1-H7	1.0749	1.0856
C2-C3	1.3880	1.4004
C2-H8	1.0724	1.0831
C3-C4	1.3895	1.4005
C3-C12	1.4938	1.4941
C4-C5	1.3792	1.3900
C4-H9	1.0723	1.0833
C5-C6	1.3844	1.3958
C5-Cl10	1.7433	1.7585
C6-H11	1.0739	1.0843
C12=O13	1.1910	1.2158
C12-O14	1.3212	1.3510
O14-C15	1.4285	1.4492
C15-C16	1.5164	1.5205
C15-H17	1.0811	1.0924
C15-H20	1.0800	1.0922
C16-H18	1.0828	1.0925
C16-H19	1.0847	1.0939
C16-H21	1.0857	1.0950
Bond angles		
C2-C1-C6	120.3991	120.5904
C2-C1-H7	120.0415	119.9964
C6-C1-H7	119.5594	119.4131
C1-C2-C3	119.6862	119.6538
C1-C2-H8	120.4397	120.7436
C3-C2-H8	119.8741	119.6036
C2-C3-C4	20.3128	120.2721
C2-C3-C12	122.2137	122.5611
C4-C3-C12	117.4736	117.1668
C3-C4-C5	119.1760	119.1238
C3-C4-H9	119.7336	119.3393
C5-C4-H9	121.0904	121.5368
C4-C5-C6	121.1118	121.2898
C4-C5-Cl10	119.5152	119.4199
C6-C5-Cl10	119.3730	119.2903
C1-C6-C5	119.3141	119.0700
C1-C6-H11	120.7602	120.9648
C5-C6-H11	119.9257	119.9652
C3-C12=O13	123.3637	123.9239
C3-C12-O14	112.7985	112.1852
O13=C12-O14	123.8376	123.8905
C12-O14-C15	118.3123	116.4929
O14-C15-C16	111.4298	111.3828
O14-C15-H17	104.4227	104.2556
O14-C15-H20	109.0483	108.6859
C16-C15-H17	111.1245	111.5855
C16-C15-H20	111.3794	111.2337
H17-C15-H20	109.1837	109.4876
C15-C16-H18	110.8765	110.5989
C15-C16-H19	110.6514	110.9354
C15-C16-H21	109.5928	109.7287
H18-C16-H19	108.9798	108.9727
H18-C16-H21	108.3315	108.2544
H19-C16-H21	108.3400	108.2776

Subsequently, the global minimum energy obtained for structure optimization of Ethyl benzoate with 6-31G (d, p) basis set is approximately -499.46 a. u. for DFT/ B3LYP and -496.40 a.u. HF methods. However in case of Ethyl m-chloro benzoate with 6-31G (d, p) basis set is approximately -959.05 a. u. for DFT/ B3LYP and -955.30 a.u. HF

methods. In case of Ethyl benzoate and Ethyl m-chloro benzoate least energy shifts to slightly higher values of roughly 3.60 a.u. and 3.75a.u. for HF method. The difference in energies between these two molecules is about 459.59 a.u. for B3LYP method. This drift in energy observed due to the chloro group attached at meta position enhance the more resonance (canonical) structure of the Ethyl m-chloro benzoate than Ethyl benzoate therefore the Ethyl m-chloro benzoate is more stable than the Ethyl benzoate.

All the observations are made without any symmetry restriction and the results are listed in Table I, II. In Ethyl m-chloro benzoate and Ethyl benzoate has no point group symmetry so called C1. Moreover, as described by the animated view of the output all carbons in the ring are in a plane in both molecule and also shows that, a single hydrogen atom of each methyl unit also lies in the plane of adjacent ring while other two are symmetrically positioned above and below the plane of adjacent ring. As seen methyl group attached with ring the C-H bond length which is in the plane are greater than other which are nonplaner e.g. bond length in between carbon and hydrogen which are nonplaner(in case of CH₃ which is attached to adjacent of ring) are 16C-19H, 16C-18H, are at 1.093 Å⁰ and 1.092 Å⁰ while bond length between carbon and hydrogen (in case of CH₃ which is attached to ring) lies in of plane are 1.095 Å⁰. Since large deviation from experimental X-H, bond length arises from low scattering factor of hydrogen atom in X-ray diffraction experiment hence; we have not discussed the C-H bond length. However comparison between B3LYP method and HF method it can easily seen that B3LYP method predicts bond length, which is systematically large, as in case of HF method [8-10]. Since all the carbon atoms in the benzene ring are sp² hybridized and having equal bond lengths and bond angles hence, substitution of hydrogen in benzene ring results in a perturbation of the valence electron distribution of the molecule followed by changes in the various chemical and physical properties. The angular changes in benzene ring geometry have proved to be a sensitive indicator of the interaction between the substituent and the benzene ring [11].

The bond length in the ring has also shown characteristic variation but they have been small and less well pronounced as compared to the angular changes. So the bond length between C-C of Ethyl m-chloro benzoate in the ring is nearly matched well with Ethyl benzoate. Bond length between C-C in case Ethyl m-chloro benzoate lies in between 1.390-1.405Å however bond length between C-C in case of ethyl benzoate lies in between 1.392-1.401 Å. The Bond length between C3-C12 is greater in case of Ethyl m- chloro benzoate than Ethyl benzoate this is due to the chlorine at meta position create electron efficiency at C3 position which causes weaker bond strength in case in C-C(out of ring) and hence increase bond length. And also it can seen that bond length between C-C are some shorter than usual bond length that is 1.54 Å. Dewar and Schmeising [12] is attributed this to the SP² hybrid state of C3. The NBO analysis [13] shows that σ_{c3-c12} NBO form sp^{1.84} hybrid on C3 interacting with SP^{2.23} hybrid on C12 is formed. All others bond length of one molecule are nearly same to the corresponding bond length of other molecule some deviation occurred due to chlorine attached at meta position in Ethyl m-chloro benzoate. Another aspect also arises that bond angle between carbon and hydrogen in methyl group that bond angle which are lies in a plane are different from which lies out of plane so shape of methyl group distorted from regular tetrahedral e.g. In case of Ethyl benzoate , Ethyl m-chloro benzoate bond angle between out of plane carbon and hydrogen (18H-16C-21H, 19H-16C-21H) are 108.3⁰,108.3⁰ and 108.2,108.2 however which corresponding in of plane 18H-16C-19H, 108.9⁰ and 108.9⁰ respectively. However, most of the substituents in the present study have a mixed σ/π character and the geometrical parameters of the ring are a result of superposition of overall effects. Based on above comparison although there are some difference between the theoretical values and experimental values, the optimized structural parameters can well reproduce the experimental ones and they are the basis for thereafter discussion.

4.2-Vibrational Analysis

Ethyl m-chloro benzoate and Ethyl benzoate have 21 atoms with 57 normal modes of fundamental vibration. Detailed description of vibrational modes can be given by means of normal coordinate analysis and vibrational assignments are achieved by comparing the band positions of calculated and experimental FT-IR of both molecules. In these cases the assignments are done following the animated view of normal mode description. It is to be emphasized that the calculated frequencies represent vibrational signatures of the molecules in its gas phase. Hence, the experimentally observed spectra of the solid/ liquid samples may differ to some extent from the calculated spectrum. Moreover, the calculated harmonic force constants and frequencies are usually higher than the corresponding experimental quantities, due to combination of electron-electron correlation [14] and basis set deficiencies. This is the reason to use scaling factor for theoretical calculations.

Table III Vibrational wave numbers obtained for Ethyl benzoate at HF/6-31G(d,p) in cm^{-1} , IR intensities ($K_m \text{ mol}^{-1}$), Raman scattering activities ($\text{A}^{04} \text{ amu}^{-1}$), Raman depolarization ratio and reduced mass (amu), force constants (m dyne A^{0-1})

S.No.	Calculated Freq.	Exp Freq	IR Inten.	Raman Acti.	Dep. Rat.	R.M	F.C	Vibrational Assignment	
	Unsc. Scal								
1.	52	46	----	1	4	0.7499	3.5157	0.0055	$\tau(\text{CC})\text{R}+\gamma(\text{CCO})\text{adjR}+\tau(\text{CC})\text{adj O}+\tau(\text{CC})\text{adj R}$
2.	65	57	----	2	2	0.7462	3.6593	0.0090	$\gamma(\text{COC})+\tau(\text{CC})\text{R}+\tau(\text{CC})\text{adj O}+\tau(\text{CO})$
3.	109	97	----	1	0	0.5297	4.7375	0.0335	$\gamma(\text{CC}=\text{O})+\gamma(\text{CCO})\text{adj R}+\gamma(\text{COC})+\tau(\text{CC})\text{adj O}$
4.	170	151	----	1	0	0.6959	2.4101	0.0410	$\tau(\text{CC})\text{adj O}+\tau(\text{CO})+\beta(\text{CCO})\text{adj R}+\beta(\text{CCC})\text{adj R}$
5.	193	172	----	1	4	0.7456	4.6592	0.1021	$\tau(\text{CC})\text{R}+\gamma(\text{CCC})\text{adj R}+\gamma(\text{CC}=\text{O})+\tau(\text{CC})\text{adj O}$
6.	251	223	----	2	0	0.5127	1.2918	0.0478	$\tau(\text{CC})\text{adj O}$
7.	351	313	----	3	3	0.1959	3.9517	0.2873	$\gamma(\text{COC})+\tau(\text{CO})+\beta(\text{CCO})+\tau(\text{CC})\text{R}$
8.	371	330	----	17	1	0.6339	3.8217	0.3097	$\beta(\text{COC})+\tau(\text{CC})\text{adj O}+\rho(\text{CH}_2)+\beta(\text{CCC})\text{adj R}$
9.	456	406	----	0	0	0.7264	2.9130	0.3573	$\gamma(\text{CCC})\text{R}$
10.	463	412	----	2	1	0.4674	3.8401	0.4846	$\beta(\text{CCO})+\gamma(\text{CCC})\text{R}+\tau(\text{CC})\text{adj O}$
11.	499	444	----	2	0	0.6935	4.1112	0.6032	$\gamma(\text{CCC})\text{R}+\gamma(\text{COC})+\beta(\text{CCO})$
12.	533	475	----	8	1	0.6877	4.6181	0.7742	$\beta(\text{CCO})+\beta(\text{CC}=\text{O})+\beta(\text{CCO})\text{adj R}+\omega(\text{CH}_3)$
13.	676	602	----	1	6	0.7489	6.4117	1.7278	$\beta(\text{CCC})\text{R}$
14.	739	658	----	10	2	0.1415	5.6678	1.8235	$\beta(\text{CCC})\text{R}+\beta(\text{OC}=\text{O})+\beta(\text{COC})+\beta(\text{CC}=\text{O})$
15.	758	675	----	5	0	0.7492	2.8342	0.9597	$\gamma(\text{CCC})\text{R}+\gamma(\text{OC}=\text{O})+\gamma(\text{CC}=\text{O})+\gamma(\text{CCO})\text{adj R}$
16.	803	714	712	115	2	0.7446	1.6581	0.6297	$\gamma(\text{CH})\text{R}+\gamma(\text{OC}=\text{O})+\gamma(\text{CC}=\text{O})+\gamma(\text{CCO})\text{adj R}$
17.	851	757	----	3	4	0.1263	1.3381	0.5709	$\rho(\text{CH}_2)+\rho(\text{CH}_3)+\text{R breath.}$
18.	905	805	----	0	0	0.7468	2.9892	1.4425	$\gamma(\text{CH})\text{R}+\gamma(\text{CCC})\text{R}+\gamma(\text{OC}=\text{O})+\gamma(\text{CC}=\text{O})$
19.	935	832	----	6	9	0.1538	3.0579	1.5743	$\beta(\text{COC})+\rho(\text{CH}_3)+\rho(\text{CH}_2)+\text{R breath.}+\beta(\text{OC}=\text{O})$
20.	958	853	850	8	10	0.3286	2.5698	1.3904	$\gamma(\text{CH})\text{R}+\gamma(\text{CCC})\text{R}$
21.	963	857	----	0	3	0.7500	1.2455	0.6811	$\omega(\text{CH}_3)+\nu(\text{CO})+\nu(\text{CC})\text{adj O}+\text{R breath.}$
22.	1076	958	----	1	2	0.7494	1.4160	0.9668	$\gamma(\text{CH})\text{R}+\gamma(\text{CCC})\text{R}$
23.	1092	971	----	1	31	0.0888	6.1546	4.3210	$\gamma(\text{CH})\text{R}+\gamma(\text{CCC})\text{R}$
24.	1113	991	----	4	6	0.2090	3.6969	2.7004	$\gamma(\text{CH})\text{R}+\gamma(\text{CCC})\text{R}$
25.	1118	995	----	0	0	0.3796	1.3670	1.0073	$\beta(\text{CCC})\text{R}$
26.	1131	1006	----	20	9	0.4349	2.2406	1.6880	$\nu(\text{CO})+\nu(\text{CC})\text{adj O}+\text{R breath.}+\beta(\text{CCO})$
27.	1135	1010	----	0	0	0.7484	1.3407	1.0181	$\text{R breath.}+\beta(\text{CH})\text{R}+\nu(\text{CO})+\nu(\text{CC})\text{adj O}$
28.	1178	1048	1027	4	1	0.7473	1.6864	1.3777	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\nu(\text{CO})$
29.	1209	1076	1071	6	5	0.6181	1.9463	1.6752	$\omega(\text{CH}_3)+\beta(\text{CCO})+\beta(\text{CH})\text{R}+\text{R breath.}+\nu(\text{CC})\text{adj O}$
30.	1226	1091	----	14	7	0.7497	1.8836	1.6692	$\text{R breath.}+\nu(\text{CO})+\beta(\text{CH})\text{R}+\rho(\text{CH}_3)$
31.	1251	1113	1109	136	15	0.1901	3.3549	3.0942	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}$
32.	1291	1149	----	32	4	0.5034	1.1649	1.1445	$\beta(\text{CH})\text{R}+\nu(\text{CO})\text{adj R}+\nu(\text{CC})\text{R}$
33.	1316	1171	1174	17	1	0.7197	1.8398	1.8771	$\rho(\text{CH}_2)+\rho(\text{CH}_3)+\beta(\text{COC})+\nu(\text{CO})\text{adj R}+\beta(\text{CH})\text{R}$
34.	1348	1199	----	11	0	0.6189	1.8297	1.9580	$\nu(\text{CC})\text{adj R}+\nu(\text{CO})\text{adj R}+\beta(\text{CC}=\text{O})+\beta(\text{CCC})\text{R}$
35.	1434	1276	1277	423	14	0.2388	2.0271	1.4565	$\tau(\text{CH}_2)+\rho(\text{CH}_3)+\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}$
36.	1454	1294	----	136	12	0.6100	1.3626	1.6983	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\tau(\text{CH}_2)+\beta(\text{CCC})\text{adj R}$
37.	1466	1304	----	184	8	0.3545	1.4946	1.8917	$\text{R Def.}+\beta(\text{CH})\text{R}$
38.	1533	1365	1367	53	3	0.2652	1.3243	1.8347	$\omega(\text{CH}_3)+\omega(\text{CH}_2)+\nu(\text{CO})\text{adj R}+\nu(\text{CC})\text{adj R}$
39.	1567	1395	----	8	2	0.7179	1.3800	1.9972	$\omega(\text{CH}_2)+\omega(\text{CH}_3)+\nu(\text{CC})\text{adj O}$
40.	1611	1433	----	26	2	0.4510	2.1726	3.3205	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\beta(\text{CCC})\text{adj R}$
41.	1614	1436	----	8	19	0.7241	1.0487	1.6089	$s(\text{CH}_3)+s(\text{CH}_2)$
42.	1630	1451	----	2	24	0.7379	1.0603	1.6596	$s(\text{CH}_2)+s(\text{CH}_3)$
43.	1642	1462	1452	18	2	0.6623	1.1084	1.7614	$s(\text{CH}_3)+s(\text{CH}_2)$
44.	1664	1481	----	4	1	0.2494	2.2350	3.6455	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\nu(\text{CC})\text{adj R}+\beta(\text{CCC})\text{R}$
45.	1783	1587	----	6	4	0.7021	5.4809	10.2653	$\nu(\text{CC})\text{R}+\beta(\text{CH})\text{R}+\beta(\text{CCC})\text{R}$
46.	1807	1608	1599	22	71	0.5438	5.3141	10.2258	$\nu(\text{CC})\text{R}+\beta(\text{CH})\text{R}+\beta(\text{CCC})\text{R}+\nu(\text{CC})\text{adj R}$
47.	1982	1764	1720	344	27	0.2313	11.8898	27.5066	$\nu(\text{C}=\text{O})+\beta(\text{CCO})\text{adj R}+\beta(\text{CCC})\text{adj R}+\beta(\text{CC}=\text{O})$
48.	3193	2842	----	24	118	0.0601	1.0378	6.2330	$\nu_s(\text{CH}_3)$
49.	3247	2890	----	21	108	0.2287	1.0683	6.6378	$\nu_s(\text{CH}_2)$
50.	3260	2901	----	55	95	0.5049	1.0971	6.8695	$\nu_{as}(\text{CH}_3)+\nu_{as}(\text{CH}_2)$
51.	3283	2922	----	19	64	0.7067	1.1007	6.9910	$\nu_{as}(\text{CH}_2)+\nu_{as}(\text{CH}_3)$
52.	3312	2948	----	30	22	0.7309	1.1095	7.1705	$\nu_{as}(\text{CH}_2)+\nu_{as}(\text{CH}_3)$
53.	3343	2975	----	1	57	0.7483	1.0874	7.1599	$\nu(\text{CH})\text{R}$
54.	3358	2989	----	18	99	0.7489	1.0921	7.2564	$\nu(\text{CH})\text{R}$
55.	3370	2999	2983	28	147	0.1348	1.0968	7.3368	$\nu(\text{CH})\text{R}$
56.	3394	3020	----	5	73	0.1792	1.0950	7.4304	$\nu(\text{CH})\text{R}$
57.	3399	3025	----	4	107	0.1672	1.0947	7.4498	$\nu(\text{CH})\text{R}$

Nevertheless, after applying the uniform scaling factor the theoretical calculation reproduce the experimental data well. The observed slight disagreement between the theory and the experiment could be a consequence of the anharmonicity [15] and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. Vibrational frequencies calculated at B3LYP and HF /6-31G (d, p) level were scaled by 0.9630 and .8929 respectively [16]. A good agreement between the theoretical and experimental consequences for the majority of bands is evident. The relative band intensities are also very satisfactory along with their positions. Some important modes are discussed here after. All the assignments for frequencies were done by gauss view [17]. Some important modes of vibration have been discussed as follows and are listed in Table III, IV.

4.2(a). C-H Stretching

In higher frequency region almost all vibrations belong to C-H stretching. The hetero aromatic structure shows the presence of C-H stretching vibrations in the region $3000-3100\text{ cm}^{-1}$, which is the characteristic region for the ready identification of the C-H stretching vibration [18]. In the present study the C-H stretching vibration of the Ethyl benzoate is observed in the range $3100-3055\text{ cm}^{-1}$, and the corresponding band in Ethyl m-chloro benzoate appears in between $3108-3070\text{ cm}^{-1}$ which are in good agreement with the characteristic region frequencies. In case of the Ethyl benzoate one medium polarized peak appears with polarization vector directed inward perpendicular to the plane of benzene ring due to the C-H stretching appears at 3077 cm^{-1} however there are no significant peak appears in the calculation due to C-H stretching in case of Ethyl m-chloro benzoate. As it can see that C-H stretching vibrational frequencies of Ethyl m-chloro benzoate are at some higher value than Ethyl benzoate. This can be possibly due

4.2.(b) C-C Ring Vibrations.

The C-C aromatic stretch known as semi-circle stretching are calculated at frequencies to the presence of Meta directing Cl which creates deficiency of electron at Meta position and hence the ring carbon extracts electron from the hydrogen atom and it reduces the bond strength of C-H. This effect does not occur in case of Ethyl benzoate. As seen in table-2 C-H stretching obtained by HF method are lies some lower value than obtained DFT.

4.2.(c). Carbonyl Absorption

Carbonyl absorptions are sensitive and both the carbon and oxygen atoms of the carbonyl group move during the vibration and they have nearly equal amplitude. In the present study a highly intense polarized peak with polarizing vector directed to the plane of benzene ring appears in case of ethyl benzoate and Ethyl m-chloro benzoate which is due to the C=O stretching vibration is observed at 1722 cm^{-1} and 1725 cm^{-1} respectively which is also supported by experimental FT-IR observed at 1720 cm^{-1} , 1724 cm^{-1} in case of Ethyl benzoate and Ethyl m-chloro benzoate respectively. As seen in table-2 C-H stretching obtained by HF method lies some higher value than obtained DFT.

4.2.(d). C-O vibrations

In this study the C-O stretching vibrations are observed in between $1352-853\text{ cm}^{-1}$ in case of Ethyl benzoate. In case of Ethyl m-chloro benzoate lies in between $1260-996\text{ cm}^{-1}$. Some deviation observed in C-O stretching modes of vibration in both This is due to the chloro group attached at meta position in case of Ethyl m-chloro benzoate. The various bending and torsional vibrations assigned in this study are also supported by the literature [19]. Any discrepancies observed in between experiment and theory this is due to intermolecular hydrogen bonding. Some other mixing of different modes of vibration along with C=O in plane and out of plane bending are also occurred at lower side of spectra are well matched with experimental data.

4.2.(e) C-C Vibrations

The C-C aromatic stretch known as semi-circle stretching, are calculated ranging from $1593\text{ cm}^{-1}-1060\text{ cm}^{-1}$ in case of Ethyl benzoate may be describe as opposite quadrant of ring stretching while intervening quadrants contract. In case of Ethyl m-chloro benzoate C-C aromatic stretch are obtained from $1582\text{ cm}^{-1}-1072\text{ cm}^{-1}$ and the corresponding experimental FTIR frequency of Ethyl benzoate and Ethyl m-chloro benzoate are ranging from $1599\text{ cm}^{-1}-1027\text{ cm}^{-1}$ and $1592\text{ cm}^{-1}-1021\text{ cm}^{-1}$. With heavy substituent, the band tends to shift somewhat lower wave number and greater the number of substituent on the ring broader the absorption region [20]. Ranges of these frequencies are nearly same in case of both molecules. One intense peak calculated at 1060 cm^{-1} for Ethyl benzoate (some lower intensity than in case of Ethyl m-chloro benzoate) and 1260 cm^{-1} for Ethyl m-chloro benzoate which are due to mixing of some mode of vibrations along with C-C stretching are supported by experimental FTIR frequencies at 1027 cm^{-1} and 1257 cm^{-1} of Ethyl benzoate and Ethyl m-chloro benzoate respectively.

Table IV Vibrational wave numbers obtained for Ethyl m-chloro benzoate at B3LYP/6-31G(d,p) in cm^{-1} , IR intensities ($\text{K}_m \text{mol}^{-1}$), Raman scattering activities ($\text{A}^{04} \text{amu}^{-1}$), Raman depolarization ratio and reduced mass (amu), force constants (m dyne A^{0-1})

S.No	C	alc	Exp. Freq	R Inten.	Raman acti.	Dep. Rat.	R.M	F.C	Vibrational Assignment
			Freq. Un sc. Scal		IR (Raman)				
1		36	35	--0	1	0.7420	4.3788	0.0033	$\gamma(\text{CCO})\text{adj O}+\gamma(\text{CCO})\text{adj R}+\gamma(\text{CC}=\text{O})$
2		59	57	-- 1	2	0.7487	3.6112	0.0074	$\gamma(\text{COC})+\gamma(\text{CCO})\text{adj O}+\tau(\text{CC})\text{adj O}+\tau(\text{CC})\text{R}$
3		91	87	-- 0	0	0.5650	5.3596	0.0260	$\gamma(\text{CC}=\text{O})+\gamma(\text{OC}=\text{O})+\gamma(\text{CCO})\text{adj R}+\gamma(\text{COC})$
4		132	127	-- 0	0	0.7416	3.5236	0.0361	$\tau(\text{CC})\text{adj O}+\rho(\text{CH}_3)+\rho(\text{CH}_2)+\beta(\text{CCO})\text{adj R}$
5		169	162	-- 1	2	0.7329	5.6686	0.0951	$\tau(\text{CC})\text{R}+\gamma(\text{CCC})\text{adj R}+\gamma(\text{CCC})\text{R}+\gamma(\text{CCCl})$
6		201	193	-- 0	3	0.7433	4.6079	0.1097	$\gamma(\text{CCCl})+\tau(\text{CC})\text{R}+\gamma(\text{CCC})\text{R}$
7		223	214	-- 2	1	0.6603	1.6267	0.0476	$\rho(\text{CH}_3)+\tau(\text{CC})\text{adj O}+\beta(\text{CCCl})$
8		256	246	-- 1	2	0.4664	2.7104	0.1049	$\tau(\text{CC})\text{adj O}+\rho(\text{CH}_3)+\beta(\text{CCCl})+\beta(\text{CCO})\text{adj R}$
9		333	320	-- 10	2	0.1642	2.9718	0.1940	$\tau(\text{CC})\text{adj O}+\gamma(\text{CCO})\text{adj O}+\gamma(\text{COC})+\tau(\text{CC})\text{R}$
10		368	353	-- 7	1	0.1258	5.8097	0.4649	$\beta(\text{CCCl})+\beta(\text{CC}=\text{O})+\beta(\text{CCC})\text{adj R}+\beta(\text{COC})$
11		412	396	-- 7	6	0.5119	10.0370	1.0065	$\nu(\text{CCl})+\beta(\text{CCC})\text{R}+\tau(\text{CC})\text{R}+\beta(\text{CC}=\text{O})$
12		427	410	-- 2	1	0.3815	3.4815	0.3747	$\gamma(\text{CCC})\text{R}+\beta(\text{CCO})\text{adj O}$
13		447	429	-- 1	1	0.4938	3.3964	0.4005	$\gamma(\text{CCC})\text{R}+\beta(\text{CCO})\text{adj O}+\gamma(\text{COC})+\tau(\text{CC})\text{adj O}$
14		509	489	-- 4	1	0.1806	5.7890	0.8854	$\gamma(\text{CCC})\text{R}+\gamma(\text{CCCl})+\beta(\text{CC}=\text{O})+\beta(\text{CCO})\text{adj R}$
15		520	499	-- 5	0	0.0860	5.1504	0.8217	$\gamma(\text{CCC})\text{R}+\gamma(\text{CCCl})+\gamma(\text{CCO})\text{adj R}+\beta(\text{CCO})\text{adj O}$
16		669	642	-- 3	5	0.3934	6.5856	1.7383	$\beta(\text{CCC})\text{R}+\nu(\text{CCl})+\beta(\text{OC}=\text{O})+\beta(\text{CCO})\text{adj R}$
17		684	657	-- 2	0	0.7323	3.2471	0.8963	$\gamma(\text{CCC})\text{R}+\gamma(\text{CCCl})+\gamma(\text{OC}=\text{O})+\gamma(\text{CCC})\text{adj R}$
18		741	711	-- 36	3	0.1272	4.5948	1.4853	$\nu(\text{CCl})+\beta(\text{CCC})\text{R}+\beta(\text{OC}=\text{O})+\rho(\text{CH}_2)+\beta(\text{COC})$
19		754	724	749 47	2	0.7480	2.8014	0.9383	$\gamma(\text{OC}=\text{O})+\gamma(\text{CH})\text{R}+\gamma(\text{CC}=\text{O})+\gamma(\text{CCO})\text{adj R}$
20		797	765	-- 23	4	0.2446	1.4584	0.5456	$\rho(\text{CH}_2)+\rho(\text{CH}_3)+\nu(\text{CCl})+\beta(\text{CCC})\text{R}$
21		818	785	-- 8	1	0.7486	1.7354	0.6835	$\gamma(\text{CH})\text{R}+\gamma(\text{OC}=\text{O})+\gamma(\text{CC}=\text{O})+\gamma(\text{CCC})\text{R}$
22		868	833	-- 8	9	0.1117	2.9552	1.3109	$\beta(\text{COC})+\nu(\text{CH}_2)+\rho(\text{CH}_3)+\nu(\text{CCl})+\beta(\text{CCC})\text{R}$
23		898	862	-- 27	7	0.4883	2.8917	1.3752	$\omega(\text{CH}_3)+\nu(\text{CO})+\nu(\text{CC})\text{adj O}+\nu(\text{CCl})+\beta(\text{CCC})\text{R}$
24		929	892	891 3	1	0.7499	1.3500	0.6869	$\gamma(\text{CH})\text{R}+\gamma(\text{CCC})\text{R}$
25		943	905	-- 4	2	0.7496	1.4273	0.7476	$\gamma(\text{CH})\text{R}+\gamma(\text{CCC})\text{R}+\gamma(\text{OC}=\text{O})+\gamma(\text{CC}=\text{O})$
26		992	952	---0	0	0.7479	1.3004	0.7541	$\gamma(\text{CH})\text{R}+\gamma(\text{CCC})\text{R}$
27		1015	974	--- 1	33	0.1287	6.1950	3.7594	$\beta(\text{CCC})\text{R}+\nu(\text{CC})\text{adj O}+\nu(\text{CCl})$
28		1037	996	--- 48	5	0.5039	3.6645	2.3210	$\nu(\text{CO})+\nu(\text{CC})\text{adj O}+\text{R breath.}+\nu(\text{CCl})$
29		1103	1059	1021 19	8	0.1750	1.9264	1.3804	$\nu(\text{CCl})+\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\beta(\text{CCC})\text{R}+\beta(\text{CCCl})$
30		1117	1072	--- 2	1	0.5506	1.6859	1.2398	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\omega(\text{CH}_3)+\nu(\text{CC})\text{adj O}$
31		1121	1076	1082 21	3	0.5552	1.8390	1.3620	$\omega(\text{CH}_3)+\beta(\text{CCO})\text{adj O}+\beta(\text{CH})\text{R}+\nu(\text{CCl})$
32		1148	1102	1127 89	9	0.2154	3.9683	3.0806	$\beta(\text{CCC})+\nu(\text{CCl})+\beta(\text{CH})\text{R}+\nu(\text{CO})+\rho(\text{CH}_3)$
33		1195	1147	-- 17	3	0.6952	1.1230	0.9448	$\beta(\text{CH})\text{R}$
34		1204	1156	1170 18	1	0.7476	1.8535	1.5841	$\rho(\text{CH}_2)+\rho(\text{CH}_3)+\nu(\text{CO})+\beta(\text{COC})+\beta(\text{CH})\text{R}$
35		1289	1237	518	49	0.2457	2.6209	2.5643	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{adj R}+\beta(\text{OC}=\text{O})+\beta(\text{CC}=\text{O})$
36		1312	1260	1257 137	16	0.2299	1.7724	1.7983	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\nu(\text{CC})\text{adj R}+\nu(\text{CO})+\omega(\text{CH}_2)$
37		1337	1284	1287 23	12	0.7115	1.1298	1.1892	$\tau(\text{CH}_2)+\omega(\text{CH}_3)$
38		1358	1304	3	2	0.6751	5.4882	5.9605	$\nu(\text{CC})\text{R}+\beta(\text{CCC})\text{R}+\beta(\text{CH})\text{R}+\beta(\text{CCCl})$
39		1408	1352	1352	15 4	0.2260	1.2752	1.4896	$\omega(\text{CH}_2)+\omega(\text{CH}_3)$
40		1432	1375	8	4	0.6207	1.3372	1.6157	$\omega(\text{CH}_2)+\omega(\text{CH}_3)+\nu(\text{CC})\text{adj O}$
41		1464	1405	57	7	0.4750	3.1034	3.9167	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\beta(\text{CCC})\text{adj R}+\beta(\text{CCCl})$
42		1499	1439	1424 11	34	0.6619	1.0563	1.3985	$s(\text{CH}_3)+s(\text{CH}_2)$
43		1502	1442	11	17	0.6964	1.0853	1.4425	$s(\text{CH}_2)+s(\text{CH}_3)$
44		1514	1453	7	5	0.3759	2.2984	3.1041	$\beta(\text{CH})\text{R}+\nu(\text{CC})\text{R}+\nu(\text{CC})\text{adj R}+s(\text{CH}_3)+\beta(\text{CCCl})$
45		1522	1461	1471 7	7	0.7379	1.0658	1.4541	$s(\text{CH}_3)+s(\text{CH}_2)$
46		1628	1563	1592 28	6	0.7248	6.2530	9.7606	$\nu(\text{CC})\text{R}+\beta(\text{CH})\text{R}+\beta(\text{CCC})\text{R}+\beta(\text{CCCl})$
47		1648	1582	3	85	0.5143	6.1535	9.8506	$\nu(\text{CC})\text{R}+\beta(\text{CH})\text{R}+\beta(\text{CCC})\text{R}+\beta(\text{CCCl})$
48		1797	1725	1724 190	57	0.2410	11.6995	22.2670	$\nu(\text{C}=\text{O})+\beta(\text{CCO})\text{adj R}+\beta(\text{CC}=\text{O})+\beta(\text{OC}=\text{O})$
49		3056	2934	17	135	0.0508	1.0360	5.6995	$\nu_s(\text{CH}_3)$
50		3085	2962	2985 31	103	0.1161	1.0588	5.9384	$\nu_s(\text{CH}_2)$
51		3125	3000	21	106	0.6508	1.1028	6.3470	$\nu_{as}(\text{CH}_3)+\nu_{as}(\text{CH}_2)$
52		3135	3010	9	85	0.7235	1.1042	6.3958	$\nu_{as}(\text{CH}_2)+\nu_{as}(\text{CH}_3)$
53		3154	3028	24	5	0.5969	1.1072	6.4914	$\nu_{as}(\text{CH}_2)+\nu_{as}(\text{CH}_3)$
54		3198	3070	7	86	0.5121	1.0885	6.5585	$\nu(\text{CH})\text{R}$
55		3221	3092	3	122	0.2673	1.0938	6.6884	$\nu(\text{CH})\text{R}$
56		3236	3107	--- 1	61	0.2231	1.0928	6.7422	$\nu(\text{CH})\text{R}$
57		3237	3108	--- 4	81	0.1670	1.0924	6.7432	$\nu(\text{CH})\text{R}$

Note: Abbreviations used here have following meaning. ν : stretching; ν_{symm} : symmetric stretching; ν_{asym} : asymmetric stretching; β : in-plane bending; ω : out-of-plane bending; τ : torsion; R: Ring; adj: adjacent.

The theoretically calculated C-C-C bending modes and C-C torsional modes have been found to be consistent with the recorded spectral values and literature [21].

4.2.(f). Methyl group vibrations

The asymmetric CH₃ stretching vibrations are calculated at 3028-3009cm⁻¹ in case of Ethyl benzoate and 3028-3000 cm⁻¹ in case of Ethyl m-chloro benzoate. The symmetric CH₃ stretching vibrations are calculated at 2933 cm⁻¹ in case of Ethyl benzoate and 2934 cm⁻¹ in case of Ethyl m-chloro benzoate. These assignments are also supported by the literature [22]. In the present study various bending vibrations of CH₃ group are also summarized in Table 3 and are supported by literature [22]. As seen in table-2 and 3 CH₃ stretching obtained by HF method are lies some lower value than obtained DFT.

4.2.(g.) Methylene Group Vibrations

The asymmetric CH₂ stretching vibrations are generally observed in the region 3100-3000 cm⁻¹, while the symmetric stretching vibrations are generally observed between 3000-2900 cm⁻¹ [23]. In present study asymmetric CH₂ stretching vibrations are obtained in between 3028 cm⁻¹-2999 cm⁻¹, 3028 cm⁻¹-3000 cm⁻¹ for Ethyl benzoate and Ethyl m-chloro benzoate respectively. Two calculated medium intense peak due to CH₂ asymmetric stretching vibration are calculated at 3028 cm⁻¹, 2999 cm⁻¹ in case of Ethyl benzoate and 3028 cm⁻¹, 3000 cm⁻¹ in case of Ethyl m-chloro benzoate. Whereas one medium intense peak due to CH₂ symmetric stretching vibrations is also calculated at 2960 cm⁻¹ in case of Ethyl benzoate. In case of Ethyl m-chloro benzoate corresponding bands are obtained at 2962cm⁻¹ which are good agreement with experimental FTIR peak observed at 2985 cm⁻¹ in case of Ethyl m-chloro benzoate. The bands corresponding to different bending vibrations of CH₂ group are summarized in Table-3&4 and are supported by literature [23]. This mode of vibration is also in good agreement with our earlier work reported [24]. As seen in table-3 and 4 CH₂ stretching obtained by HF method are lies some lower value than obtained DFT.

4.2.(h). C-Cl Vibration

Vibration belonging to bond between ring and other group are important as mixing of vibration is possible due to the presence of heavy atom which shows lower absorption frequencies as compared to C-H, due to the increase reduced mass [25]. C-Cl-Stretching is calculated at 1076 cm⁻¹, 862 cm⁻¹, 996 cm⁻¹ which is at a lower frequency than the frequency observed in IR-spectra. The frequency in case of (C-Cl) comes out to be higher in aromatic benzene ring because of the presence of -COOC₂H₅ group which decreases the bond order between (C-Cl) group, and hence decrease bond strength factor K and consequently there is an decrease in the corresponding frequency.

Table V Theoretically computed energies (a.u), zero-point Vibrational energies (kcal mol⁻¹), rotational constants (GHz), entropies (Cal mol⁻¹ K⁻¹) and dipole moment (D) for Ethyl benzoate

Parameters	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
Total energy	496.40740070	-499.46250246
Zero-point energy	115.69722	108.14173
	3.03638	2.96959
Rotational Constants	0.61194	0.60452
	0.53408	0.52693
Entropy		
Total	99.602	99.602
Translational	40.928	40.928
Rotational	30.161	30.209
Vibrational	26.105	28.465
Dipole moment	1.829	2.019

5. Other molecular properties

Several calculated thermodynamic properties at HF and B3LYP level are listed in Table 5,6. These thermodynamic parameters clearly indicate that vibration motion play a crucial role in order to access the thermo dynamical behavior of title compound. Because all frequencies are real in both the molecules hence, both compounds have stable structure.

Entropy of Ethyl benzoate molecule at 99.6(Cal/Mol- Kelvin) is less than entropy of Ethyl m-chloro benzoate 106.9(Cal/Mol- Kelvin) and hence more probably ethyl benzoate has a well ordered structure than ethyl m-chloro

benzoate as seen in Table IV. In this study total energy is greater for B3LYP method, while zero point energy is greater for HF method. Values of all rotational constants and dipole moment are also greater for HF method, while entropy is greater for B3LYP method.

Table VI Theoretically computed energies (a.u), zero-point Vibrational energies (kcal mol⁻¹), rotational constants (GHz), entropies (Cal mol⁻¹ K⁻¹) and dipole moment (D) for Ethyl m-chloro benzoate

Parameters	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
Total energy	-955.30430968	-959.05595022
Zero-point energy	109.35291	102.03695
	2.01368	1.97330
Rotational Constants	0.38120	0.37624
	0.33070	0.32609
Entropy		
Total	104.051	106.908
Translational	41.536	41.536
Rotational	31.516	31.563
Vibrational	30.999	33.809
Dipole moment	3.685	3.318

CONCLUSION

The equilibrium geometries and harmonic frequencies of Ethyl m-chloro benzoate and Ethyl benzoate were determined and analyzed at both HF and DFT level of theories. The difference between the observed and scaled wave numbers values of most of the fundamentals is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. As it can also be seen from table some lower frequencies along with intensities are very near to experimental one in case of HF/6-31G(d,p) method than DFT/6-31G(d,p). This is due to the sample impurities deficiencies of basis set, anharmonicity, and some other factor are responsible for this.

Theoretical mode description makes easy to identify the relatively weak Raman or IR bands more accurately. Furthermore, yet again it is established obviously that the scaled quantum mechanical method in combination of DFT may be used as a reliable tool for the interpretation of vibrational signatures.

As we can see that Ethyl benzoate has low entropy than Ethyl m-chloro benzoate so corresponding band of frequency shifts to lower side in case of Ethyl benzoate.

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