Electronic Structure, Nonlinear Optical Properties, and Vibrational Analysis of Ethyl benzoate by Density Functional Theory

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ABSTRACT

This work deals with the vibrational spectroscopy of Ethyl benzoate (C9H10O2). The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT) using standard HF/6-31G(d,p) and B3LYP/6-31G(d,p) methods and basis set combinations. The vibrational spectra were interpreted, with the aid of normal coordinate analysis based on a scaled quantum mechanical force field. The infrared and Raman spectra were also predicted from the calculated intensities. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes.

Key words - *Hartree-Fock; DFT; Ethyl benzoate; Vibrational spectra*

1. INTRODUCTION

Vibrational spectroscopy has the potential to yield valuable structural and conformational information of organic compounds, if used in conjugation 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 for Ethyl benzoate. 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.

2. MATERIALS AND METHODS

The molecular structure as viewed by Gaussian software using numbering scheme of the title compound Ethyl benzoate is given in figure 1. The experimental FTIR or Raman spectra of the compound are not yet reported so here the theoretically plotted FTIR spectra are shown in fig 2.

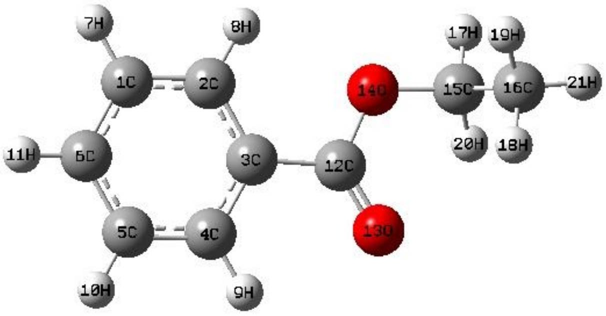

Fig.1. Molecular Modeling Structure of Ethyl benzoate

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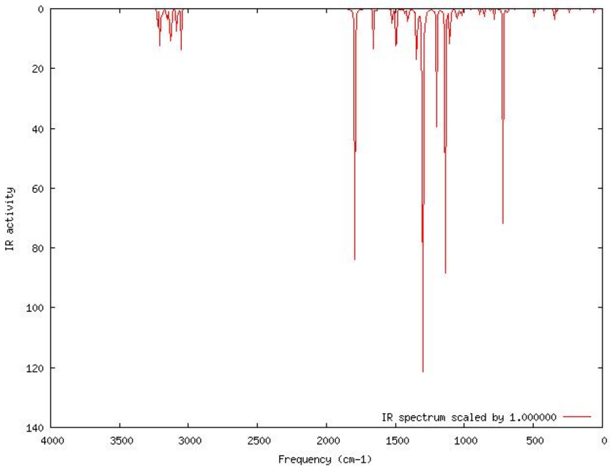

Fig. 2. Theoretical FTIR spectra of Ethyl benzoate

3. COMPUTATIONAL DETAILS

The entire calculations were performed at Hartree-Fock (HF) and DFT/B3LYP level 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 Hatree-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 provide thermodynamic properties also through the principle of statistical mechanics.

4. RESULT AND DISCUSSION

4.1 Molecular Geometry

The optimized structure parameters of Ethyl benzoate calculated by DFT/B3LYP and HF methods with the 6-31G (d, p) basis set are listed in Table 1 and are in accordance with the atom numbering scheme as shown Fig.1. 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. 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.

All the above observations are made without any symmetry restriction and the results are listed in Table 1. 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 the 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 A^0 and1.092 A^0 while bond length between carbon and hydrogen(in case of CH3 which is attached to ring)lies in of plane are 1.095 A^0.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 in case of 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 sp^2 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 benzoate lies in between 1.392-1.401 Å. 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 SP^2 hybrid state of C3. The NBO analysis[13] shows that $\sigma_{c3\text{-}c12}$ NBO form $sp^{1.84}$ hybrid on C3 interacting with $SP^{2.23}$ hybrid on C12 is formed. 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. In case of Ethyl benzoate, bond angle between out of plane carbon and hydrogen (18H-16C-21H, 19H-16C-21H) are 108.3^0,108.3^0 and 108.2^0,108.2^0. 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.

Table-1

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

4.2 Vibrational Analysis

Ethyl benzoate has 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 the present molecule. In this case 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. 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 2 and Table 3.

Table-2

Vibrational wave numbers obtained for Ethyl benzoate at HF/6-31G(d,p) in cm-1, IR intensities(Km mol-1), Raman scattering activities (A04 amu-1), Raman depolarization ratio and reduced mass (amu), force constants (m dyne A0-1)

S.No	Calculated Freq.		Exp Freq	IR Inten.	Raman Acti.	Dep. Rat. Un sc.	R.M Scal	F.C	Vibrational Assignment
1.	52	46	----	1	4	0.7499	3.5157	0.0055	τ(CC)R+γ(CCO)adj R+τ(CC)adj O+τ(CC)adj R
2.	65	57	----	2	2	0.7462	3.6593	0.0090	γ(COC)+τ(CC)R+τ(CC)adj O+τ(CO)
3.	109	97	----	1	0	0.5297	4.7375	0.0335	γ(CC=O)+γ(CCO)adj R+γ(COC)+τ(CC)adj O
4.	170	151	----	1	0	0.6959	2.4101	0.0410	τ(CC)adj O+τ(CO)+β(CCO)adj R+β(CCC)adj R
5.	193	172	----	1	4	0.7456	4.6592	0.1021	τ(CC)R+γ(CCC)adj R+γ(CC=O)+τ(CC)adj O
6.	251	223	----	2	0	0.5127	1.2918	0.0478	τ(CC)adj O
7.	351	313	----	3	3	0.1959	3.9517	0.2873	γ(COC)+τ(CO)+β(CCO)+τ(CC)R
8.	371	330	----	17	1	0.6339	3.8217	0.3097	β(COC)+τ(CC)adj O+ρ(CH_2)+β(CCC)adj R
9.	456	406	----	0	0	0.7264	2.9130	0.3573	γ(CCC)R
10.	463	412	----	2	1	0.4674	3.8401	0.4846	β(CCO)+γ(CCC)R+τ(CC)adj O
11.	499	444	----	2	0	0.6935	4.1112	0.6032	γ(CCC)R+γ(COC)+β(CCO)
12.	533	475	----	8	1	0.6877	4.6181	0.7742	β(CCO)+β(CC=O)+β(CCO)adj R+ω(CH_3)
13.	676	602	----	1	6	0.7489	6.4117	1.7278	β(CCC)R
14.	739	658	----	10	2	0.1415	5.6678	1.8235	β(CCC)R+β(OC=O)+β(COC)+β(CC=O)
15.	758	675	----	5	0	0.7492	2.8342	0.9597	γ(CCC)R+γ(OC=O)+γ(CC=O)+γ(CCO)adj R
16.	803	714	712	115	2	0.7446	1.6581	0.6297	γ(CH)R+γ(OC=O)+γ(CC=O)+γ(CCO)adj R
17.	851	757	---	3	4	0.1263	1.3381	0.5709	ρ(CH_2)+ρ(CH_3)+R breat.
18.	905	805	---	0	0	0.7468	2.9892	1.4425	γ(CH)R+γ(CCC)R+γ(OC=O)+γ(CC=O)
19.	935	832	---	6	9	0.1538	3.0579	1.5743	β(COC)+ρ(CH_3)+ρ(CH_2)+Rbreath.+β(OC=O)
20.	958	853	850	8	10	0.3286	2.5698	1.3904	γ(CH)R+γ(CCC)R
21.	963	857	----	0	3	0.7500	1.2455	0.6811	ω(CH_3)+ν(CO)+ν(CC)adj O+R breat.
22.	1076	958	----	1	2	0.7494	1.4160	0.9668	γ(CH)R+γ(CCC)R
23.	1092	971	----	1	31	0.0888	6.1546	4.3210	γ(CH)R+γ(CCC)R
24.	1113	991	----	4	6	0.2090	3.6969	2.7004	γ(CH)R+γ(CCC)R

S.No	Calculated Freq.	Exp Freq	IR Inten.	Raman Acti.	Dep. Rat. Un sc.	R.M Scal	F.C	Vibrational Assignment
26. 1131	1006	----	20	9	0.4349	2.2406	1.6880	ν(CO)+ν(CC)adj O+R breat.+β(CCO)
27. 1135	1010	----	0	0	0.7484	1.3407	1.0181	R breat.+β(CH)R+ν(CO)+ν(CC)adj O
28. 1178	1048	1027	4	1	0.7473	1.6864	1.3777	β(CH)R+ν(CC)R+ν(CO)
29. 1209	1076	1071	6	5	0.6181	1.9463	1.6752	ω(CH$_3$)+β(CCO)+β(CH)R+Rbreat.+ν(CC)adj O
30. 1226	1091	----	14	7	0.7497	1.8836	1.6692	R breat.+ν(CO)+β(CH)R+ρ(CH$_3$)
31 1251	1113	1109	136	15	0.1901	3.3549	3.0942	β(CH)R+ν(CC)R
32 1291	1149	----	32	4	0.5034	1.1649	1.1445	β(CH)R+ν(CO)adj R+ν(CC)R
33. 1316	1171	1174	17	1	0.7197	1.8398	1.8771	ρ(CH$_2$)+ρ(CH$_3$)+β(COC)+ν(CO)adj R+β(CH)R
34. 1348	1199	----	11	0	0.6189	1.8297	1.9580	ν(CC)adjR+ν(CO)adj R+β(CC=O)+β(CCC)R
35. 1434	1276	1277	423	14	0.2388	2.0271	1.4565	t(CH$_2$)+ρ(CH$_3$)+β(CH)R+ν(CC)R
36. 1454	1294	----	136	12	0.6100	1.3626	1.6983	β(CH)R+ν(CC)R+t(CH$_2$)+β(CCC)adj R
37. 1466	1304	----	184	8	0.3545	1.4946	1.8917	R Def.+β(CH)R
38. 1533	1365	1367	53	3	0.2652	1.3243	1.8347	ω(CH$_3$)+ω(CH$_2$)+ν(CO)adj R+ν(CC)adj R
39. 1567	1395	----	8	2	0.7179	1.3800	1.9972	ω(CH$_2$)+ ω(CH$_3$)+ν(CC)adj O
40. 1611	1433	----	26	2	0.4510	2.1726	3.3205	β(CH)R+ν(CC)R+β(CCC)adj R
41. 1614	1436	----	8	19	0.7241	1.0487	1.6089	s(CH$_3$)+s(CH$_2$)
42. 1630	1451	----	2	24	0.7379	1.0603	1.6596	s(CH$_2$)+s(CH$_3$)
43. 1642	1462	1452	18	2	0.6623	1.1084	1.7614	s(CH$_3$)+s(CH$_2$)
44. 1664	1481	----	4	1	0.2494	2.2350	3.6455	β(CH)R+ν(CC)R+ν(CC)adj R+β(CCC)R
45. 1783	1587	----	6	4	0.7021	5.4809	10.2653	ν(CC)R+β(CH)R+β(CCC)R
46. 1807	1608	1599	22	71	0.5438	5.3141	10.2258	ν(CC)R+β(CH)R+β(CCC)R+ν(CC)adj R
47. 1982	1764	1720	344	27	0.2313	11.8898	27.5066	ν(C=O)+β(CCO)adj+R+β(CCC)adj R+β(CC=O)
48. 3193	2842	----	24	118	0.0601	1.0378	6.2330	ν_s(CH$_3$)
49. 3247	2890	----	21	108	0.2287	1.0683	6.6378	ν_s(CH$_2$)
50. 3260	2901	----	55	95	0.5049	1.0971	6.8695	ν_{as}(CH$_3$)+ν_{as}(CH$_2$)
51. 3283	2922	----	19	64	0.7067	1.1007	6.9910	ν_{as}(CH$_2$)+ν_{as}(CH$_3$)

S.No	Calculated Freq.		Exp Freq	IR Inten.	Raman Acti.	Dep. Rat. Un sc.	R.M Scal	F.C	Vibrational Assignment
52.	3312	2948	----	30	22	0.7309	1.1095	7.1705	$\nu_{as}(CH_2)+\nu_{as}(CH_3)$
53.	3343	2975	----	1	57	0.7483	1.0874	7.1599	ν(CH)R
54.	3358	2989	----	18	99	0.7489	1.0921	7.2564	ν(CH)R
55.	3370	2999	2983	28	147	0.1348	1.0968	7.3368	ν(CH)R
56.	3394	3020	----	5	73	0.1792	1.0950	7.4304	ν(CH)R
57.	3399	3025	----	4	107	0.1672	1.0947	7.4498	ν(CH)R

4.2.1 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 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 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}.

Table - 3

Vibrational wave numbers obtained for Ethyl benzoate at B3LYP/6-31G(d,p) in cm^{-1}, IR intensities(K$_m$ mol^{-1}), Raman scattering activities (A^{04} 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. Un sc.	R.M Scal	F.C	Vibrational Assignment
1	46	45	--	0	4	0.7492	3.1837	0.0041	τ(CC)R+γ(CCO)adj R+τ(CC)adj O+τ(CC)adj R
2	63	61	--	2	2	0.7461	3.8055	0.0090	γ(COC)+τ(CC)R+τ(CC)adj O+τ(CO)
3	94	90	--	0	0	0.5260	4.9785	0.0260	γ(CC=O)+γ(CCO)adj R+γ(COC)+τ(CC)adj O
4	158	151	--	1	0	0.6801	2.6799	0.0392	τ(CC)adj O+τ(CO)+β(CCO)adj R+β(CCC)adj R
5	179	172	--	1	4	0.7440	4.4751	0.0845	τ(CC)R+γ(CCC)adj R+γ(CC=O)+τ(CC)adj O
6	241	232	--	2	0	0.4894	1.2575	0.0432	τ(CC)adj O
7	330	317	--	2	3	0.2048	4.1382	0.2656	γ(COC)+τ(CO)+β(CCO)+τ(CC)R
8	347	334	--	15	1	0.6920	3.4887	0.2482	β(COC)+τ(CC)adj O+ρ(CH$_2$)+β(CCC)adj R
9	417	400	--	0	0	0.6992	2.9695	0.3043	γ(CCC)R
10	427	410	--	2	1	0.4298	3.8670	0.4149	β(CCO)+γ(CCC)R+τ(CC)adj O
11	463	444	--	1	0	0.6855	4.2247	0.5326	γ(CCC)R+γ(COC)+β(CCO)
12	496	476	--	4	1	0.7337	4.6400	0.6724	β(CCO)+β(CC=O)+β(CCO)adj R+ω(CH$_3$)

S.No		Calculated Freq.	Exp Freq	IR Inten.	Raman Acti.	Dep. Rat. Un sc.	R.M Scal	F.C	Vibrational Assignment
13	631	606	--	1	6	0.7486	6.4026	1.5042	β(CCC)R
14	686	659	--	6	1	0.2185	5.5058	1.5275	β(CCC)R+β(OC=O)+β(COC)+β(CC=O)
15	700	672	--	1	0	0.6609	3.6149	1.0426	γ(CCC)R+γ(OC=O)+γ(CC=O)+γ(CCO)adj R
16	721	693	712	72	2	0.7435	1.6708	0.5124	γ(CH)R+γ(OC=O)+γ(CC=O)+γ(CCO)adj R
17	786	755	--	4	8	0.1416	1.4499	0.5282	ρ(CH_2)+ρ(CH_3)+R breath.
18	812	780	----	2	0	0.4073	2.6936	1.0469	γ(CH)R+γ(CCC)R+γ(OC=O)+γ(CC=O)
19	858	824	----	3	10	0.1341	2.6631	1.1553	β(COC)+ρ(CH_3)+ρ(CH_2)+R breat.+β(OC=O)
20	869	834	----	0	5	0.7500	1.2460	0.5546	γ(CH)R+γ(CCC)R
21	888	853	850	4	8	0.4515	2.7084	1.2592	ω(CH_3)+ν(CO)+ν(CC)adj O+R breat.
22	957	918	----	1	2	0.7499	1.4009	0.7556	γ(CH)R+γ(CCC)R
23	989	950	----	0	0	0.7419	1.3526	0.7799	γ(CH)R+γ(CCC)R
24	1011	970	----	0	0	0.7379	1.2719	0.7654	γ(CH)R+γ(CCC)R
25	1018	978	----	2	27	0.1111	6.2825	3.8401	β(CCC)R
26	1031	989	----	9	5	0.2237	3.7017	2.3170	ν(CO)+ν(CC)adj O+R breat.+β(CCO)
27	1054	1012	----	23	12	0.2042	2.1935	1.4354	R breat.+β(CH)R+ν(CO)+ν(CC)adj O
28	1104	1060	1027	31	0	0.7390	1.5985	1.1484	β(CH)R+ν(CC)R+ν(CO)
29	1120	1075	1071	5	4	0.5819	2.0112	1.4864	ω(CH_3)+β(CCO)+β(CH)R+R breat.+ν(CC)adj O
30	1140	1094	----	165	5	0.1107	3.2597	2.4945	R breat.+ν(CO)+β(CH)R+ρ(CH_3)
31	1188	1141	----	0	8	0.7489	1.1055	0.9196	β(CH)R+ν(CC)R
32	1201	1153	1109	49	5	0.3226	1.1664	0.9916	β(CH)R+ν(CO)adj R+ν(CC)R
33	1204	1156	1174	21	2	0.7495	1.7942	1.5327	ρ(CH_2)+ρ(CH_3)+β(COC)+ν(CO)adj R+β(CH)R
34	1301	1249	1277	491	63	0.2751	3.9643	3.9547	ν(CC)adj R+ν(CO)adj R+β(CC=O)+β(CCC)R
35	1335	1282	----	10	11	0.7435	1.1424	1.2002	t(CH_2)+ρ(CH_3)+β(CH)R+ν(CC)R
36	1346	1292	----	24	4	0.3639	1.4354	1.5314	β(CH)R+ν(CC)R+t(CH_2)+β(CCC)adj R
37	1365	1311	----	3	1	0.6724	5.3473	5.8731	R Def.+β(CH)R
38	1408	1352	1367	18	4	0.2443	1.2827	1.4984	ω(CH_3)+ω(CH_2)+ν(CO)adj R+ν(CC)adj R

S.No	Calculated Freq.		Exp Freq	IR Inten.	Raman Acti.	Dep. Rat. Un sc.	R.M Scal	F.C	Vibrational Assignment
39	1432	1375	----	8	3	0.5612	1.3433	1.6226	$\omega(CH_2)+\omega(CH_3)+\nu(CC)\text{adj O}$
40	1492	1432	----	14	3	0.4324	2.2667	2.9720	$\beta(CH)R+\nu(CC)R+\beta(CCC)\text{adj R}$
41	1500	1440	1452	13	36	0.6556	1.0637	1.4094	$s(CH_3)+s(CH_2)$
42	1502	1442	----	7	15	0.7229	1.0690	1.4219	$s(CH_2)+s(CH_3)$
43	1522	1461	----	7	7	0.7500	1.0591	1.4456	$s(CH_3)+s(CH_2)$
44	1535	1473	----	1	4	0.2847	2.2564	3.1310	$\beta(CH)R+\nu(CC)R+\nu(CC)\text{adj R}+\beta(CCC)R$
45	1639	1573	----	5	4	0.5708	5.8337	9.2328	$\nu(CC)R+\beta(CH)R+\beta(CCC)R$
46	1659	1593	1599	14	93	0.4984	5.6360	9.1401	$\nu(CC)R+\beta(CH)R+\beta(CCC)R+\nu(CC)\text{adj R}$
47	1794	1722	1720	209	60	0.2470	11.6120	22.0134	$\nu(C=O)+\beta(CCO)\text{adj R}+\beta(CCC)\text{adj R}+\beta(CC=O)$
48	3055	2933	----	18	132	0.0518	1.0361	5.6973	$\nu_s(CH_3)$
49	3083	2960	----	32	102	0.1137	1.0587	5.9305	$\nu_s(CH_2)$
50	3124	2999	2983	21	102	0.6626	1.1028	6.3421	$\nu_{as}(CH_3)+\nu_{as}(CH_2)$
51	3134	3009	----	10	83	0.7266	1.1043	6.3926	$\nu_{as}(CH_2)+\nu_{as}(CH_3)$
52	3154	3028	----	25	4	0.6454	1.1067	6.4861	$\nu_{as}(CH_2)+\nu_{as}(CH_3)$
53	3183	3055	----	0	58	0.7398	1.0857	6.4796	$\nu(CH)R$
54	3195	3067	----	15	111	0.7492	1.0900	6.5543	$\nu(CH)R$
55	3205	3077	----	22	159	0.1509	1.0951	6.6282	$\nu(CH)R$
56	3222	3093	----	5	88	0.1539	1.0936	6.6898	$\nu(CH)R$
57	3229	3100	----	3	107	0.1613	1.0933	6.7153	$\nu(CH)R$

4.2.2 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 which is due to the C=O stretching vibration is observed at 1722 cm^{-1} which is also supported by experimental FT-IR observed at 1720 cm^{-1}. As seen in Table 2, C-H stretching obtained by HF method are lies some higher value than obtained DFT.

4.2.3 C-O vibrations :

In this study the C-O stretching vibrations are observed in between 1352-853cm^{-1} in case of Ethyl 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.

4.2.4 C-C Vibrations :

The C-C aromatic stretch known as semi-circle stretching, is calculated ranging from 1593 cm^{-1}-1060 cm^{-1} in the present molecule which may be described as oppositive quadrant of ring stretching while intervening quadrants contract. The corresponding experimental FTIR frequency are ranging from 1599 cm^{-1}-1027 cm^{-1}. With heavy substituent, the band tend to shift somewhat lower wave number and greater the number of substituent on the ring broader the absorption region [20]. One intense peak calculated at,1060 cm^{-1} 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}. 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].

4.2.5 Methyl group vibrations :

The asymmetric CH_3 stretching vibrations are calculated at 3028-3009cm^{-1} in case of Ethyl benzoate. The symmetric CH_3 stretching vibrations are calculated at 2933 cm^{-1}. These assignments are also supported by the literature [22]. In the present study various bending vibrations of CH_3 group are also summarized in Table 2 and are supported by literature [22]. As seen in Table 2, CH_3 stretching obtained by HF method lies some lower value than obtained DFT.

4.2.6 Methylene Group Vibrations :

The asymmetric CH_2 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 CH_2 stretching vibrations are obtained in between 3028 cm^{-1} -2999 cm^{-1} . Two calculated medium intense peak due to CH_2 asymmetric stretching vibration are calculated at 3028 cm^{-1} ,2999 cm^{-1} , whereas one medium intense peak due to CH_2 symmetric stretching vibrations is also calculated at 2960 cm^{-1} for the current molecule. The bands corresponding to different bending vibrations of CH_2 group are summarized in Table 2 and are supported by literature [23]. As seen in Table 2 and 3, CH_2 stretching obtained by HF method lies some lower value than obtained DFT.

5. Other molecular properties :

Several calculated thermodynamic properties at HF and B3LYP level are listed in Table 4. 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 the present molecule hence, it has a stable a structure. In this study total energy is greater for B3 LYP 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 - 4

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

6. CONCLUSION

The equilibrium geometries and harmonic frequencies of 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 seen from table 2 and 3 some lower frequencies along with intensities are very near to experimental one in case of HF/6-13G(d,p) method than DFT/6-31G(d,p).This is due to the sample impurities deficiencies of basis set, anharmonicity, and some other factors 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.

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