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MOLECULAR STRUCTURE, SPECTROSCOPIC (FT-IR, FT-RAMAN) AND HOMO–LUMO ANALYSES OF SOME ACNE VULGARIS DRUGS

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ABSTRACT

The FT-IR and FT-Raman spectra for salicylic acid and benzoyl peroxide have been recorded in the range 4000–400 cm^{-1}. DFT (B3LYP/6-311++G(d,p)) calculations have been performed giving energies, optimized structures, harmonic vibrational frequencies, IR intensities and Raman activities. The computed vibrational frequencies have been scaled and compared with corresponding experimental FT-IR and FT-Raman values. The differences between the observed and scaled wave number values for most of the fundamentals are very small. The calculated HOMO–LUMO energies show that charge transfer occurs in the molecules.

Keywords: DFT, FT-IR, FT-Raman, HOMO, LUMO, Salicylic acid, Benzoyl peroxide.

INTRODUCTION

It was argued that Acne vulgaris may be viewed as the most common skin disorder, characterized by the inflammation of the pilosebaceous glands.[1] Also, acne vulgaris may be involved in both emotional and physiological distress, and it can affect negatively on the overall quality of life.[2-5] From the pharmaceutical point of view, acne vulgaris can be administered either orally or topically. Topical administration of anti-acne agents comprises an important part of the therapy. However ,Acne vulgaris treatment in most mild and moderate cases begins by topical therapy.[6,7] Salicylic acid and benzoyl peroxide are the most significant drugs widely used in acne therapy and it may be considered as the simplest aromatic carboxylic acid (2-hydroxybenzoic acid), which contains the hydroxyl group and the carboxyl group together. It is widely used either as an antimicrobial agent or antifungal agent.[8] Due to its biological effect and its biotransformation pathways, it is recently used in medicinal and enzyme chemistry.[9–12] Furthermore, salicylic acid and its derivatives are characterized by their pharmacological effects and biotransformation pathways, as well as by their effect on physical and chemical properties.[13-19] Raman spectra of salicylic acid were reported experimentally.[20,21] Both FT-IR and NMR spectra were obtained for salicylic acid and its derivatives.[22,23] Also, its crystal structure was studied by X-ray.[24]

Benzoyl peroxide which is known to have a keratolytic effect, may be considered as an antibacterial agent releasing free radical oxygen species which has the ability to oxidize bacterial proteins . It is widely described as a drug in acne therapy. There are many acne products containing benzoyl peroxide including creams, gels, lotions, and washes from 2.5% to 10%. Benzoyl peroxide may cause skin dryness and irritation.[25] To reduce irritation and dryness of benzoyl peroxide, an emollient may be used in its formulations.[26] The IR and UV spectroscopy are successfully used to establish the structure of the synthesized peroxides as well as for their identification and kinetic studies.[27,28] The IR spectra also work as an indicator of the oxidative stability and peroxide value in the foods oxidative modification.[28] An important feature of the IR spectroscopy is the absence of damaging effects of the infrared light quanta on the peroxide molecule. This method allows one to investigate peroxides in any aggregate state.[28] The development of quantum chemistry and the growth of computing power have led to the fact that modern semi-empirical, density-functional theory (DFT) and ab initio methods of the quantum chemistry can

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significantly improve the speed and accuracy of calculations for various physical and chemical characteristics of the objects or processes and in many cases allow to achieve precise agreement with the experimental data.[28]

In the present work, based on quantum chemistry the optimized structures of salicylic acid and benzoyl peroxide were obtained using DFT- Beckee-3-Lee-Yag-Parr (B3LYP) with the 6-311++G(d,p) basis set. The FT-IR and FT-Raman spectra along and Highest Occupied Molecular Orbital–Lowest Unoccupied Molecular Orbital (HOMO–LUMO) energies were carried out. Theoretically predicted values were compared with the experimentally measured data and the results were discussed. DFT method has been chosen because it gives accurate results which are close to the experimental values of organic compounds. The method supports the allocation of the vibrational frequencies at the same time does not take much too long in the calculation process compared to other methods which may give good results but consume more time. Thus, DFT has been used to obtain more accurate results in a shorter time.

EXPERIMENTAL

Both salicylic acid and benzoyl peroxide samples were used without any other purification after purchasing from Sigma–Aldrich (99% purity). In order to record FT-IR spectrum for samples in the range 4000-400 cm^{-1}, I used a Thermo Nicolet Nexus 870 FT-IR instrument. The instrument is equipped with a KBr beam splitter and an In GaAs detector. The spectral resolution is ±2 cm^{-1}. The Raman spectra were measured using a dispersive Nexus 870 FT-Raman instrument. The instrument containing Nd:YAG laser source with 200 mW powers and 1.064 μm line widths. The scanning speed was 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}.

Computational Details

The molecular structure optimization of salicylic acid and benzoyl peroxide compounds and corresponding vibrational frequencies were calculated using the DFT with B3LYP combined with 6-311++G(d,p) basis set using GAUSSIAN 09W program package without any constraint on the geometry.[29] I calculated fundamental vibrational frequencies, optimized geometrical parameters, IR intensity and Raman activity..

By combining both the results of the GAUSS-VIEW program and symmetry considerations, vibrational frequency assignments were certainly obtained with a high degree of accuracy.[30]

RESULTS AND DISCUSSION

Molecular Geometry

Figure-1 represents the molecular structure of salicylic acid and benzoyl peroxide obtained from GAUSS VIEW program with the numbering of atoms. The Calculated energy using B3LYP/6-311++ G(d,p) for salicylic acid as -496.1903041 a.u., and -840.5625022 a.u for Benzoyl peroxide. The most optimized structural parameters (bond length and bond angle) calculated by B3LYP with 6-311++G(d,p) basis set are represented in Tables-1 and 2. Due to the steric and electronic effects of COOH and OH groups the theoretical results show that the aromatic ring of salicylic acid is distorted from the regular hexagon. Table-1, shows that C1-C2 bond length is 1.5101 Å. The breakdown of hexagonal symmetry of the benzene ring is obvious from the elongation of C2–C3 (1.4044 Å) and C2-C8 (1.4011 Å) from the remaining C–C bond lengths (1.3900 Å) while other C-C bonds are compatible with the experimental values.[31] For salicylic acid, the asymmetry of the benzene ring is also evident from the negative deviation of C3–C5–C6 and C6–C7–C8 (119) and positive deviation of C2–C8–C7 (121) from the normal value of 120. Substitution with the carboxylase group at C2 atom and Hydroxyl group at C3 atom leads to some changes of the bond lengths and bond angles in the aromatic ring. The C1-O9 (C=O group) bond length is found 1.2049 Å. The average C–H bond length in the aromatic ring calculated by B3LYP/6-311++G (d,p) level is 1.0839 Å which conformed to the experimental values.[32] The optimized O4-H11 (Hydroxyl

group) bond length was calculated 0.9629 Å While O10-H16 (carboxylase group) bond length was 0.9713 Å for Salicylic acid.
The experimental O-O was 1.4500 Å, which proved the creditability of our calculated results 1.4498 Å.[33] As seen from Table-2, The average bond distances of C–C and C–H in the aromatic ring calculated are 1.3952 Å and 1.0833 Å, respectively for Benzoyl peroxide by the B3LYP method .The optimized C3-O10 and C11-O18 (C=O group) bond lengths are calculated at 1.1970 Å and these values are very close agreement with experimental value 1.3950 Å.[33] The optimized C11–O1 and C3-O2 bond lengths is 1.3900 Å and 1.3932 Å respectively. The computed C–O bond lengths are very close to each other.

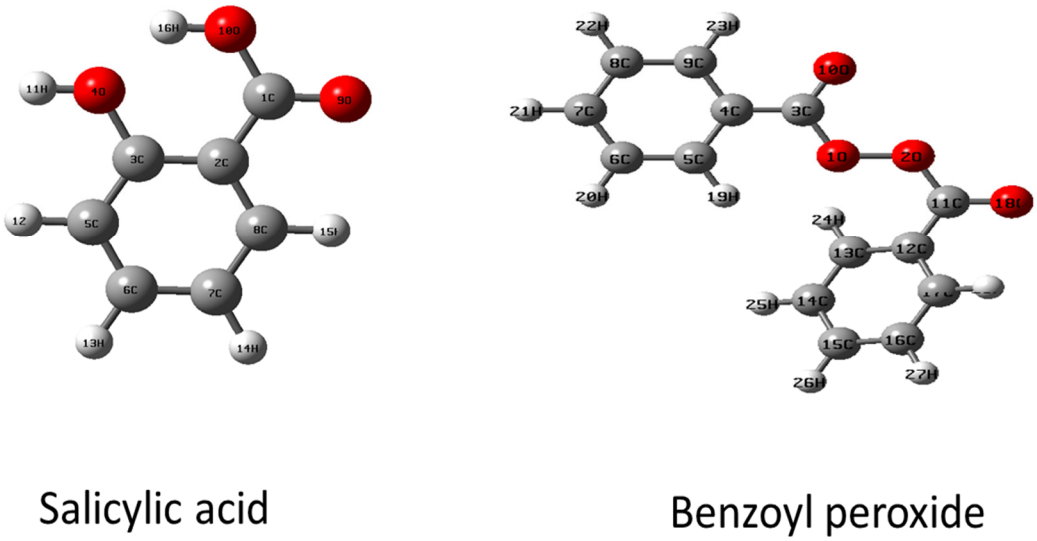

Fig.-1:Molecular structure of Salicylic acid and Benzoyl peroxide.

Table-1: Optimized geometrical parameters of the salicylic acid molecule (bond lengths in Å , angles in ◦).

Bond	length (Å)	Bond Angles	Angles (◦)
C1-C2	1.5101	C2-C1-O9	121.6072
C1-O9	1.2049	C2-C1-O10	118.1531
C1-O10	1.3470	O9-C1-O10	120.2398
C2-C3	1.4044	C1-C2-C3	125.6631
C2-C8	1.4011	C1-C2-C8	116.5886
C3-O4	1.3777	C3-C2-C8	117.7483
C3-C5	1.3936	C2-C3-O4	118.3869
O4-H11	0.9629	C2-C3-C5	120.9807
C5-C6	1.3902	O4-C3-C5	120.6323
C5-H12	1.0860	C3-O4-H11	111.1414
C6-C7	1.3930	C3-C5-C6	119.9676
C6-H13	1.0839	C3-C5-H12	119.6709
C7-C8	1.3920	C6-C5-H12	120.3615
C7-H14	1.0830	C5-C6-C7	120.1053
C8-H15	1.0827	C5-C6-H13	119.4518
O10-H16	0.9713	C7-C6-H13	120.4429
		C6-C7-C8	119.4638
		C6-C7-H14	120.3681

		C8-C7-H14	120.1682
		C2-C8-C7	121.7343
		C2-C8-H15	117.0689
		C7-C8-C15	121.1968
		C1-O10-H16	111.0158

Table-2: Optimized geometrical parameters of benzoyl peroxide molecule (bond lengths in Å , angles in ◦).

Bond	length (Å)	Bond Angles	Angles (◦)
O1-O2	1.4498	O2-O1-C3	110.9437
C11-O1	1.3900	O1-O2-C11	112.8209
C3-O2	1.3932	O1-C3-C4	109.7534
C3-C4	1.488 9	O1-C3-O10	123.7356
C3-O10	1.1970	C4-C3-O10	126.4968
C4-C5	1.4011	C3-C4-C5	123.0837
C4-C9	1.4005	C3-C4-C9	116.9635
C5-C6	1.3915	C5-C4-C9	119.9523
C5-H19	1.0817	C4-C5-C6	119.7340
C6-C7	1.3945	C4-C5-H19	120.0896
C6-H20	1.0837	C6-C5-H19	120.1755
C7-C8	1.3953	C5-C6-C7	120.1894
C7-H21	1.0842	C5-C6-H20	119.7143
C8-C9	1.3899	C7-C6-H20	120.0961
C8-H22	1.0838	C6-C7-C8	120.1336
C9-H23	1.0820	C6-C7-H21	119.9222
C11-C12	1.486 9	C8-C7-H21	119.9440
C11-O18	1.1970	C7-C8-C9	120.0067
C12-C13	1.3993	C7-C8-H22	120.1427
C12-C17	1.3990	C9-C8-22	119.8506
C13-C14	1.3915	C4-C9-C8	119.9838
C13-H24	1.0830	C4-C9-H23	118.9156
C14-C15	1.3947	C8-C9-H23	121.1001
C14-H25	1.0838	O2-C11-C12	119.8456
C15-C16	1.3944	O2-C11-C18	114.7039
C15-H26	1.0841	C12-C11-C18	125.4221
C16-C17	1.3911	C11-C12-C13	122.2465
C16-H27	1.0838	C11-C12-C17	117.5208
C17-H28	1.0833	C13-C12-C17	120.0076
		C12-C13-C14	119.7156
		C12-C13-H24	120.2245
		C14-C13-H24	120.0264
		C13-C14-C15	120.2235
		C13-C14-H25	119.6657
		C15-C14-H25	120.1106
		C14-C15-C16	120.0647
		C14-C15-H26	119.9438
		C16-C15-H26	119.9893
		C15-C16-C17	120.0009
		C15-C16-H27	120.1860
		C17-C16-H27	119.8100
		C12-C17-H16	119.9579
		C12-C17-H28	119.3563
		C16-C17-H28	120.6858

Vibrational assignments

Salicylic acid consists of 16 atoms having 42 normal modes of fundamental vibrations, and benzoyl peroxide consists of 28 atoms, having 78 normal modes of fundamental vibrations. All these fundamental vibrations are active both in Raman scattering and IR absorption. These molecules belong to the Cs and C1 symmetry group for salicylic acid and benzoyl peroxide, respectively. The detailed analysis of fundamental modes of vibration with FT-IR and FT-Raman experimental frequencies are tabulated in Table-3 for salicylic acid and benzoyl peroxide. Tables-4 and 5 show the vibrational frequencies, IR intensity and Raman activity of salicylic acid and benzoyl peroxide using the B3LYP method with 6-311++G(d,p) basis set respectively. In this study, the scaling factor 0.96 was applied for B3LYP to correct the theoretical error in this work.[34] The comparative graphs of the observed and simulated FT-IR and FT-Raman spectra for salicylic acid are presented in Figs.-2 and 3, respectively and Figs.-4 and 5, respectively for benzoyl peroxide.

For salicylic acid, the OH band in FT-IR spectrum at 3225 cm^{-1} (3223 cm^{-1} in FT-Raman spectrum) is assigned to OH stretching vibration. The calculated value by in B3LYP/6-311++G(d,p) of this vibration at 3227 cm^{-1} shows excellent agreement with experimental results. The O-H bending peak appeared at 1334 cm^{-1} and 1330 cm^{-1} in FT-IR and FT-Raman spectra, respectively which in good agreement with calculated value 1339 cm^{-1}. In the present work, The band in FT-IR spectrum at 833 cm^{-1} (830 cm^{-1} in FT-Raman spectrum) is assigned to O–O stretching vibration of benzoyl peroxide. The calculated value by in B3LYP/6-311++G(d,p) of this vibration at 830 cm^{-1} shows excellent agreement with experimental results. The aromatic compounds show the presence of C–H stretching vibrations in the region 3000–3100 cm^{-1} which are the characteristic region for the ready identification of C–H stretching vibrations. This permits the ready identification of the structure. The FT-IR band for Salicylic acid at 3000 cm^{-1} (3062 cm^{-1} for benzoyl peroxide) and FT-Raman band at 3010 cm^{-1} (salicylic acid) and at 3060 cm^{-1} (benzoyl peroxide) assigned to C–H aromatic stretching modes. The calculated frequencies of the C–H stretching vibrations by B3LYP/6-311++G(d,p) method at 3008 cm^{-1} and 3062 for salicylic acid and benzoyl peroxide, respectively show very good agreement with experimental data. The calculated frequencies 700–753 cm^{-1} (salicylic acid) and 685–711 cm^{-1} (benzoyl peroxide) for the C–H bend falls in the FT-IR/FT-Raman values of 700-755 cm^{-1} (salicylic acid) and 690-712 cm^{-1} (benzoyl peroxide). For salicylic acid, the C=O asymmetric and symmetric stretching vibration occurs at 1664-1687 cm^{-1} and 1380 cm^{-1} in FT-IR, respectively. The same bands in the FT-Raman spectrum at 1661-1680 cm^{-1} and 1380 cm^{-1}, respectively. The computed values at 1659-1683 cm^{-1} for C=O asymmetric stretching vibration and 1382 cm^{-1} for C=O symmetric stretching vibration by B3LYP method exactly correlates with measured FT-IR and FT-Raman values. The (C–O) COO^- stretching and C–OH (phenolic) stretching was assigned to FT-IR peaks appeared at 1298 cm^{-1} (1296 cm^{-1} in the FT-Raman spectrum) and 1270 cm^{-1} (1260 cm^{-1} in the FT-Raman spectrum), respectively. The computed values by the B3LYP method at 1298 cm^{-1} for C–O stretching and 1273 cm^{-1} for C–OH stretching shows correlation with our experimental observation. The bands observed at 1790 and 1754 cm^{-1} in FT-IR spectrum and at 1787 and 1752 cm^{-1} in FT-Raman spectrum is assigned to the C=O asymmetric stretching and symmetric stretching vibrations, respectively for benzoyl peroxide. These are in agreement with computed values (1757-1790 cm^{-1}). Generally, C= C stretching vibrations in aromatic compounds from a band in the region of 1430–1650 cm^{-1}.[35,36] Accordingly, in the present study, the C=C stretching vibrations for salicylic acid are observed at 1560-1622 cm^{-1} in FT-IR spectrum and in FT-Raman spectrum at 1560-1620 cm^{-1}. This band observed in FT-IR at 1550-1612 cm^{-1} and 1544-1610 cm^{-1} in FT-Raman for benzoyl peroxide.

The theoretically computed frequencies for C=C stretching vibrations by B3LYP/6-311++G(d,p) method at 1561-1632 cm^{-1} (salicylic acid) and at 1549-1615 cm^{-1} (benzoyl peroxide) shows excellent agreement with recorded spectrum. The ring carbon-carbon stretching vibration occurs in the region 1625–1430 cm^{-1}. In the current study, the band at 1438 cm^{-1} (salicylic acid) and 1452 cm^{-1} (benzoyl peroxide) in FT-IR and at 1430 cm^{-1} (salicylic acid) and 1452 cm^{-1} (benzoyl peroxide) in FT-Raman spectra is assigned

to C–C stretching vibration. This experimental observation exactly correlates with the theoretical calculation by B3LYP/6-311++G(d,p) level at 1434 cm^{-1} and at 1450 cm^{-1} for salicylic acid and benzoyl peroxide, respectively.

Table-3: Experimental FT-IR, FT-Raman frequencies, and assignment for Salicylic acid and for Benzoyl peroxide

FT-IR frequency (cm^{-1})		FT-Raman frequency (cm^{-1})		Assignment
Salicylic acid	Benzoyl peroxide	Salicylic acid	Benzoyl peroxide	
3225	-	3223	-	OH stretching
1334	-	1330	-	OH bend
3000	3062	3010	3060	C-H stretch
700-755	690-712	700-755	690-712	C-H bend
1664-1687	1790	1661-1680	1787	C=O asym stretch
1380	1754	1380	1752	C=O sym stretch
1560-1622	1550-1612	1560-1620	1544-1610	C=C stretch
1438	1452	1430	1452	C-C stretch
1298	1081	1296	1077	C-O stretch
1270	-	1260	-	C-OH stretch
-	833	-	830	O-O stretch

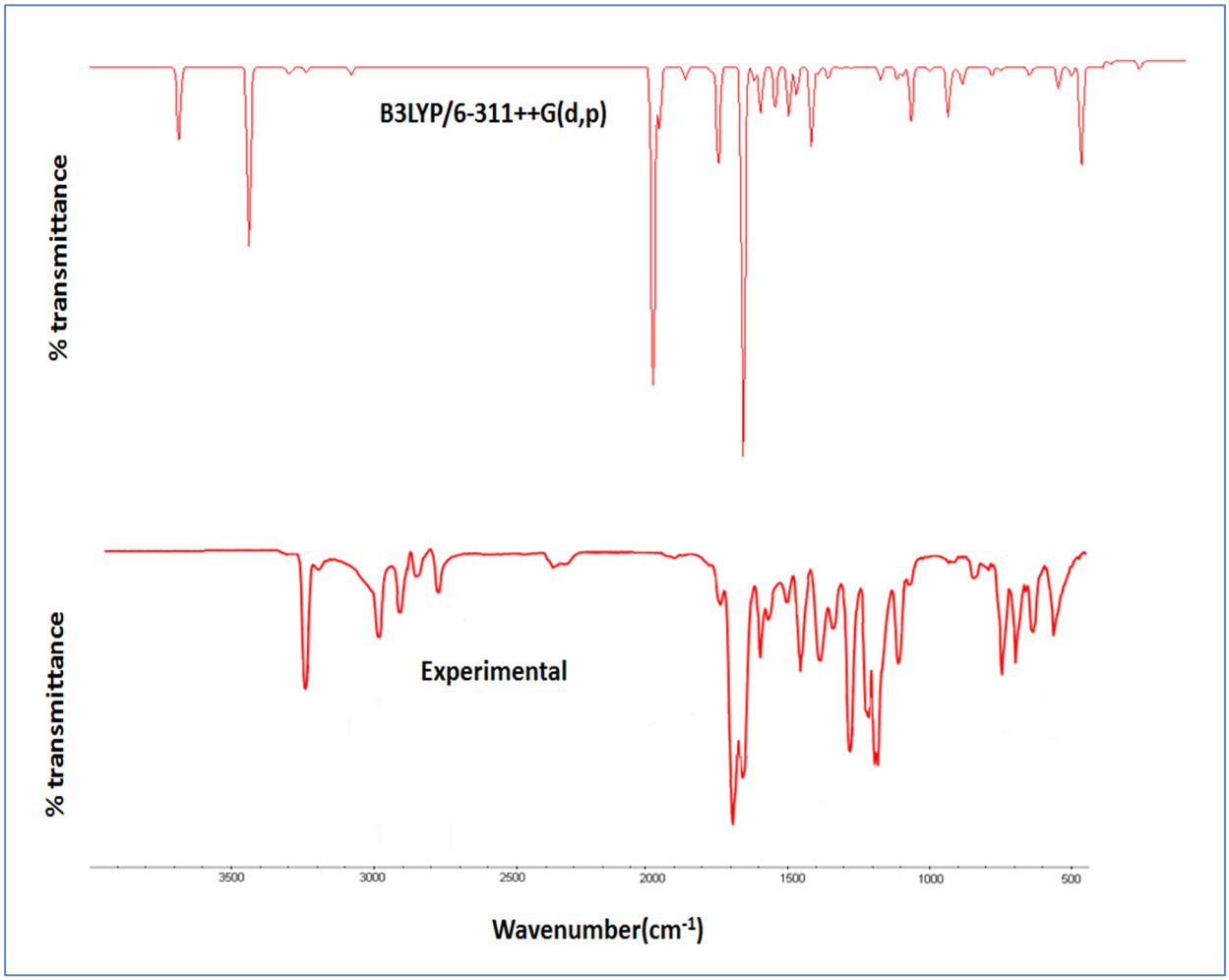

Fig.-2: Experimental and calculated IR spectra of Salicylic acid.

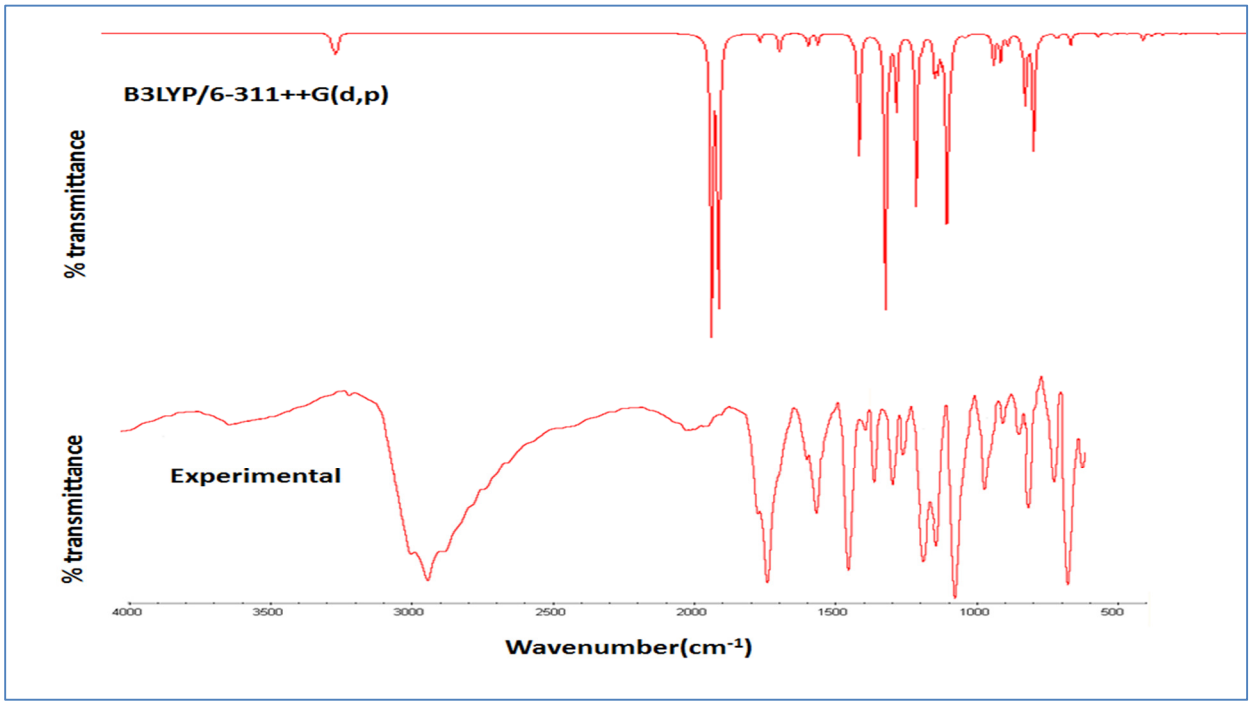

Fig.-3: Experimental and calculated Raman spectra of Salicylic acid.

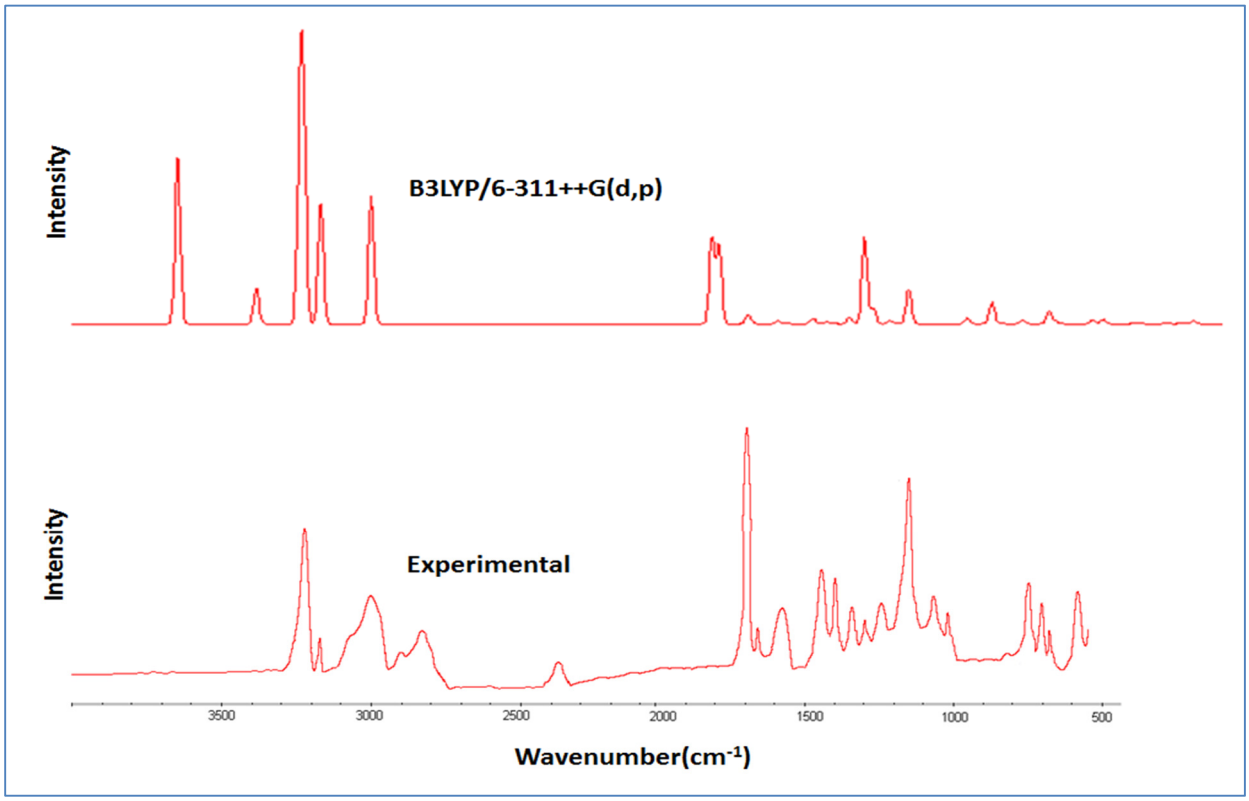

Fig.-4: Experimental and calculated IR spectra of Benzoyl peroxide.

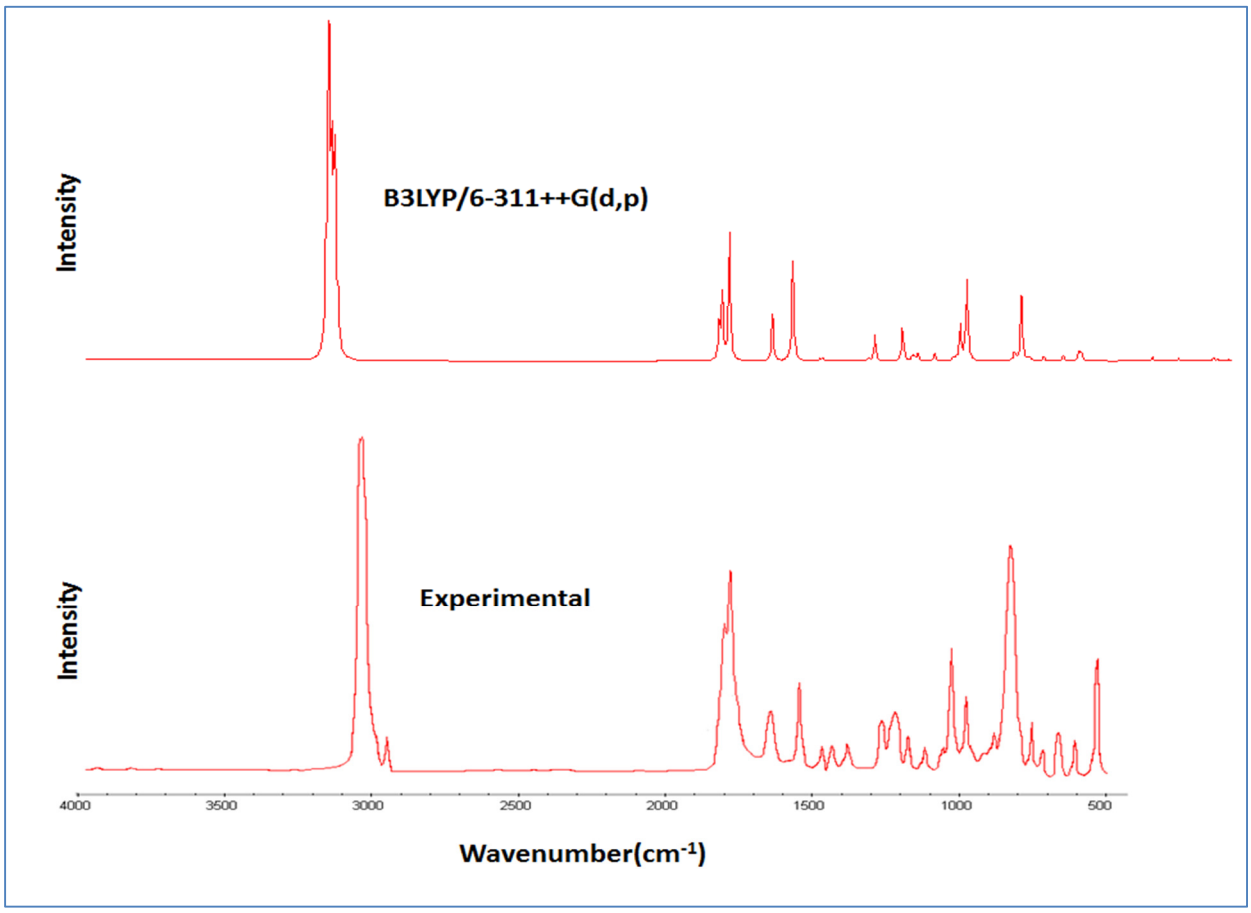

Fig.-5: Experimental and calculated Raman spectra of Benzoyl peroxide.

Table-4:Vibrational wavenumbers obtained for Salicylic acid at B3LYP/6-311++G(d,p) level.

Mode of vibration	Wave number		IR intensity	Raman activity
	Unscaled	Scaled		
1	3639	3494	88.48	118.08
2	3361	3227	219.58	25.85
3	3207	3079	5.28	135.41
4	3194	3066	5.33	129.18
5	3134	3008	6.08	85.55
6	2956	2837	9.25	89.99
7	1753	1683	384.60	60.25
8	1728	1659	74.72	55.17
9	1700	1632	25.03	6.78
10	1626	1561	6.11	2.31
11	1494	1434	118.18	0.69
12	1440	1382	473.12	4.03
13	1395	1339	15.78	1.60
14	1352	1298	55.33	0.67
15	1326	1273	48.20	4.87
16	1269	1218	59.39	61.29
17	1215	1166	25.01	4.18

18	1185	1137	8.63	7.03
19	1183	1135	96.09	2.06
20	1125	1080	8.03	0.62
21	1099	1055	13.28	23.91
22	1059	1016	0.86	0.00
23	1006	965	0.90	0.00
24	966	927	0.05	0.06
25	855	821	14.73	4.29
26	851	817	14.33	0.54
27	785	753	10.30	15.21
28	764	733	65.92	0.22
29	729	700	0.01	0.14
30	664	638	4.64	2.25
31	656	630	59.86	0.24
32	583	560	5.10	8.95
33	564	541	5.31	1.78
34	540	518	19.62	0.15
35	525	504	0.11	0.01
36	428	411	9.61	3.00
37	409	393	3.12	3.28
38	373	358	9.40	0.29
39	245	235	1.55	1.15
40	145	139	26.11	1.11
41	94	90	10.13	0.82
42	54	51	120.29	2.50

Table-5: Vibrational wavenumbers obtained for Benzoyl peroxide at B3LYP/6- 311++G(d,p) level.

Mode of vibration	Wave number		IR intensity	Raman activity
	Unscaled	Scaled		
1	3211	3082	1.51	100.24
2	3202	3074	5.35	119.59
3	3199	3071	5.59	270.63
4	3196	3068	5.70	25.15
5	3190	3062	11.84	156.33
6	3187	3060	7.70	57.59
7	1865	1790	0.32	41.76
8	1854	1780	346.34	72.25
9	1830	1757	312.16	142.16
10	1682	1615	10.47	51.78
11	1614	1549	17.65	107.07
12	1612	1548	3.77	4.57
13	1606	1542	1.82	6.49
14	1523	1462	2.13	0.26
15	1521	1460	0.90	2.20
16	1510	1450	14.66	4.07
17	1478	1418	13.44	0.96
18	1356	1302	2.24	1.14
19	1353	1298	4.10	2.00
20	1339	1285	3.22	1.09
21	1335	1282	1.07	0.22
22	1332	1278	140.78	28.40

23	1237	1187	327.78	36.92
24	1205	1157	6.44	3.90
25	1198	1151	83.96	6.06
26	1186	1138	0.25	3.50
27	1186	1138	1.69	5.74
28	1128	1083	202	8.93
29	1108	1064	7.91	0.21
30	1063	1020	41.02	3.39
31	1053	1011	32.75	2.66
32	1039	998	20.28	39.87
33	1020	979	216.74	11.04
34	1017	977	6.16	79.88
35	1015	975	0.53	3.83
36	1014	973	10.43	0.37
37	1011	970	48.49	2.61
38	1000	960	0.16	0.04
39	997	957	2.86	0.20
40	959	921	0.92	0.52
41	953	915	3.06	0.67
42	917	880	33.48	79.09
43	959	921	0.92	0.52
44	953	915	3.06	0.67
45	911	875	1.20	79.09
46	865	830	33.48	0.75
47	863	828	0.38	0.10
48	853	819	38.22	9.10
49	807	775	4.13	0.94
50	802	770	11.62	3.58
51	755	725	9.49	6.16
52	741	711	84.67	0.24
53	713	685	136.85	0.28
54	703	675	3.34	0.90
55	699	671	1.55	0.23
56	688	660	3.57	6.32
57	633	608	2.45	6.38
58	631	606	0.79	4.29
59	625	600	4.57	7.53
60	580	557	14.84	1.83
61	483	464	4.21	0.76
62	443	425	0.74	0.60
63	437	420	1.96	0.84
64	413	397	0.58	1.48
65	411	395	0.08	0.16
66	382	366	1.20	4.46
67	325	312	9.37	0.50
68	292	281	3.80	3.57
69	254	244	2.47	1.96
70	193	185	1.50	1.00
71	173	166	0.89	3.55
72	161	154	0.58	2.42
73	119	114	0.49	2.02
74	71	68	0.13	2.58

75	58	55	1.85	1.67
76	43	41	0.36	3.42
77	28	27	0.16	6.18
78	23	22	0.44	7.67

Frontier Molecular Orbital Analysis

The HOMO–LUMO energy gap of salicylic acid and benzoyl peroxide was calculated at B3LYP/6-311++G(d,p) level in Table-6. HOMO–LUMO separation, as intramolecular charge transfer from the end-capping electron-donor groups to the efficient electron-acceptor groups through the π-conjugated path.[37] Both HOMO and LUMO sharing in chemical stability.[38] HOMO represents the ability to donate an electron and LUMO represents the ability to obtain an electron. The electronic absorption represents the transition from the ground state to the first excited state describing one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. HOMO and LUMO are directly related to ionization potential and electron affinity respectively. Recently, the energy gap between HOMO and LUMO has been used to prove the bioactivity from intra-molecular charge transfer.[39,40] The plots of HOMO–LUMO for salicylic acid and benzoyl peroxide are shown in Figs.-6 and 7, respectively.

Table-6: Calculated values of HOMO-LUMO energy (a.u) Salicylic acid and Benzoyl peroxide molecules.

	Salicylic Acid	Benzoyl Peroxide
HOMO energy	- 0.32833	- 0.31570
LUMO energy	- 0.18141	- 0.18692
HOMO-LUMO energy gap	0.14692	0.12878

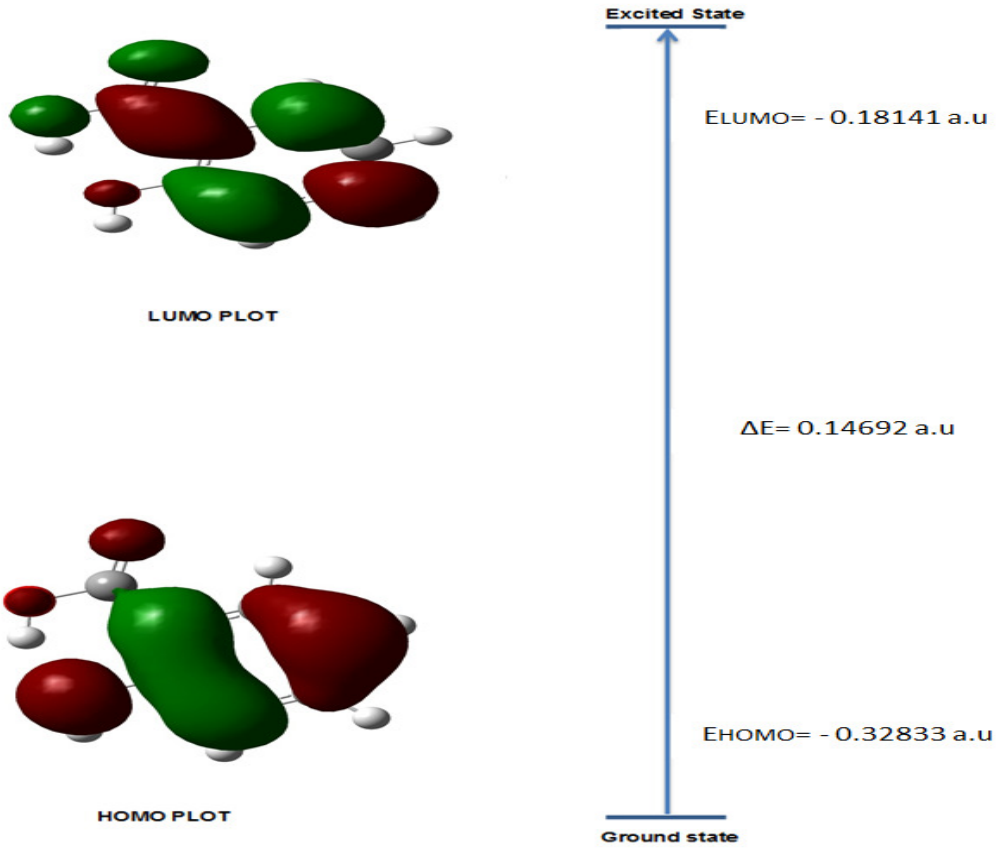

Fig.-6: HOMO and LUMO plots for Salicylic acid.

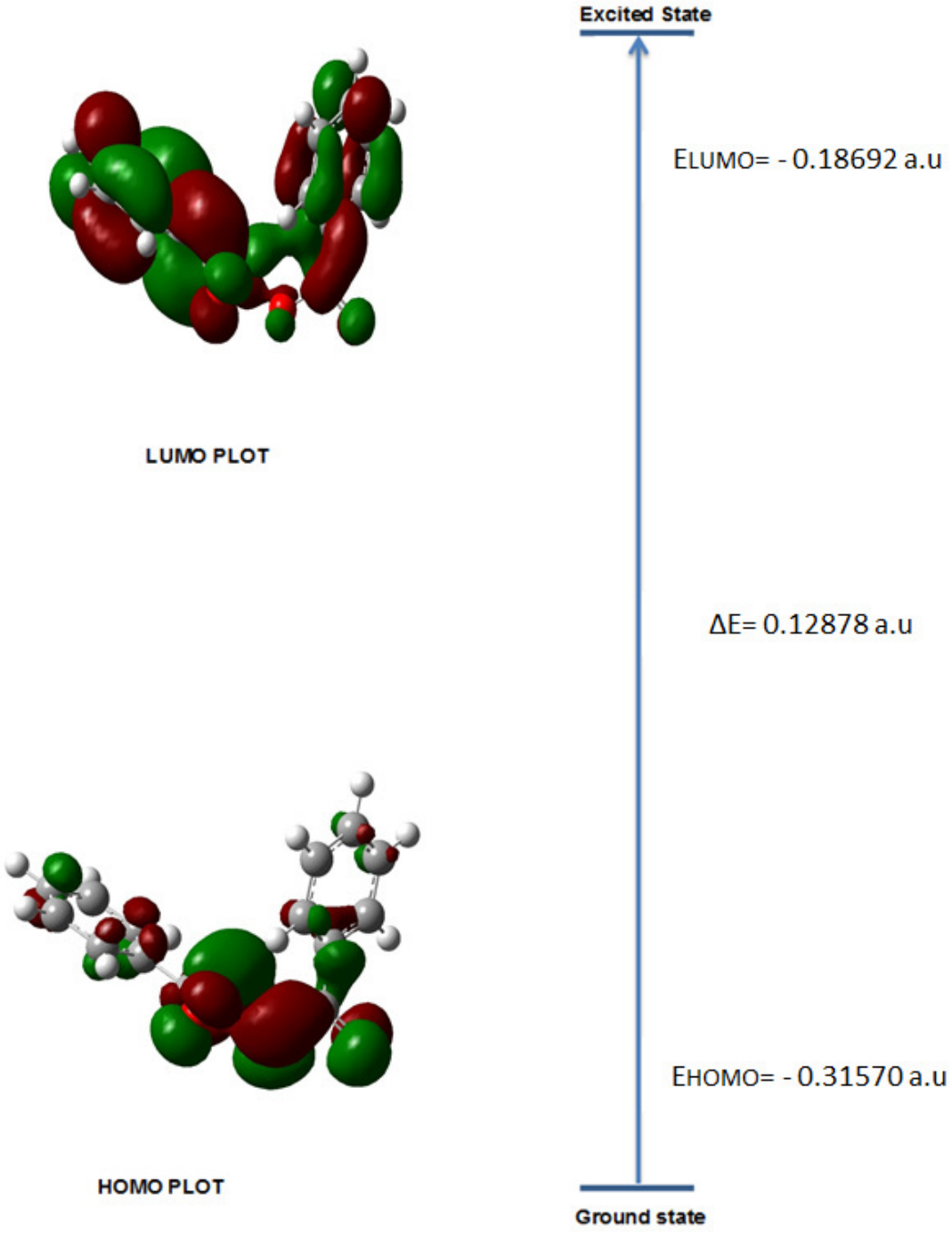

Fig.-7: HOMO and LUMO plots for Benzoyl peroxide

Atomic Charges

Reactive atomic charges are the most important application in quantum mechanical calculations for the molecular system. Mulliken atomic charges of salicylic acid and benzoyl peroxide molecules have been calculated using B3LYP/6-311++G(d,p) are combined in Table-7. The atomic charge of C2 in salicylic acid is 2.053 and C4 in benzoyl peroxide are 0.770. The maximum atomic charge is obtained for C2 in

salicylic acid and C4 in benzoyl peroxide when compare with other atoms molecules. Illustration of atomic charges plotted for B3LYP/6-311++G(d,p) level has been shown in Figs.-8 and 9 for Salicylic acid and Benzoyl peroxide, respectively.

Table-7: Calculated values of Mullikan atomic charges of Salicylic acid and Benzoyl peroxide molecules.

Atoms	Salicylic acid	Atoms	Benzoyl peroxide
C1	-0.048	O1	0.189
C2	2.053	O2	-0.090
C3	-1.729	C3	-0.530
O4	-0.283	C4	0.770
C5	0.592	C5	-0.106
C6	-0.531	C6	-0.318
C7	0.108	C7	-0.189
C8	-0.953	C8	-0.379
O9	-0.293	C9	-0.144
O10	-0.228	C10	-0.181
H11	0.282	C11	-0.248
H12	0.138	C12	0.705
H13	0.173	C13	-0.370
H14	0.175	C14	-0.308
H15	0.200	C15	-0.221
H16	0.343	C16	-0.289
		C17	0.088
		O18	-0.200
		H19	0.195
		H2O	0.179
		H21	0.165
		H22	0.177
		H23	0.212
		H24	0.157
		H25	0.190
		H26	0.162
		H27	0.175
		H28	0.210

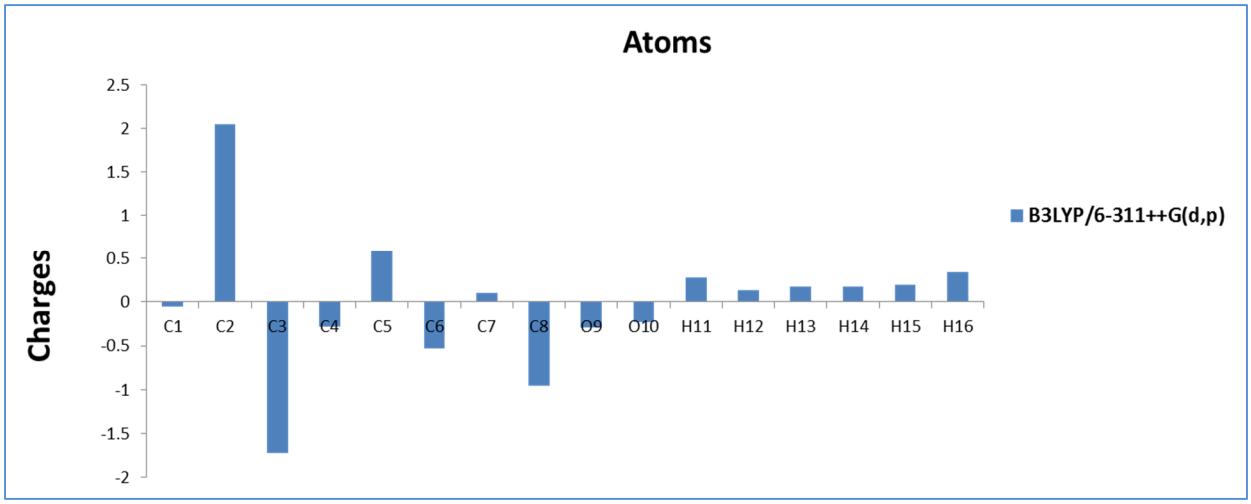

Fig.-8: The atomic Charges for Salicylic Acid.

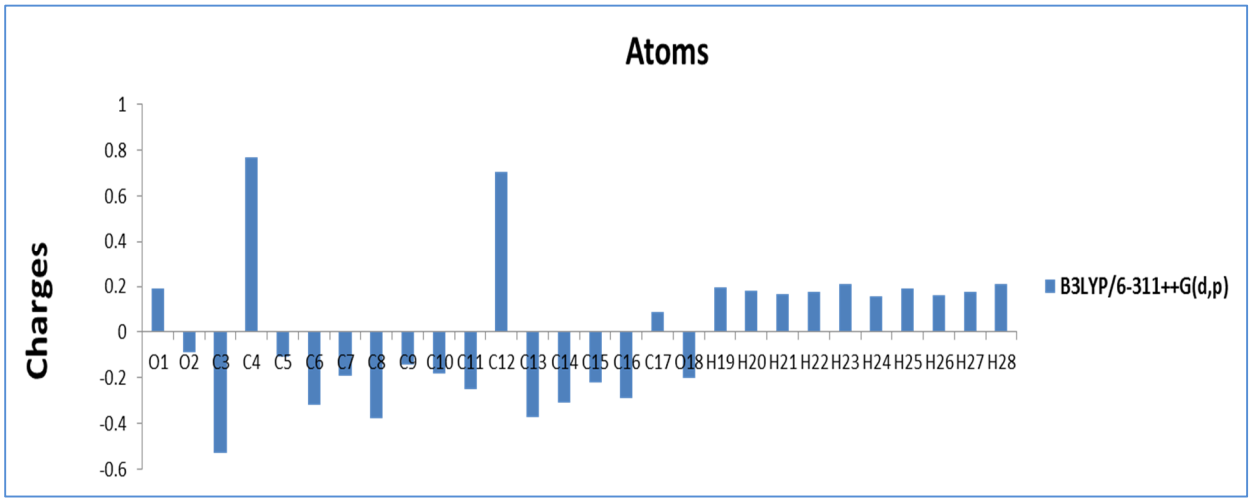

Fig.-9: The Atomic Charges for Benzoyl Peroxide.

CONCLUSION

The proper frequency assignments for salicylic acid and benzoyl peroxide were made from FT-IR and FT-Raman spectra. Both optimized geometry, frequencies, IR and Raman spectra of salicylic acid and benzoyl peroxide were determined and analyzed at B3LYP/6-311++G(d,p) basis set. Both calculated vibrational frequencies and experimental values are in agreement indicating the predict the FT-IR and FT-Raman spectra for these compounds. There is a very small difference between the observed and scaled value of wave number. HOMO and LUMO energy gap of compounds in the ground-state have been calculated by using density functional theory.

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