

# Spectroscopic Examination using Density Functional Theory Calculations on 3-chloro-5-methoxyphenol

Palani Murugan, S. Jeyavijayan, M. S. Revathy, K. Gurushankar

**Abstract:** The complete vibrational assignment of 3-chloro-5-methoxyphenol (CMOP) has been identified by the observed IR and Raman spectral data and vibrational frequencies were calculated by density functional theory method. The ability of the computational method for describing the vibrational modes can be understood by comparing experimental and theoretical spectra. Besides, frontier molecular orbital, Mulliken's charge analyses and molecular electrostatic potential (MEP) surfaces have been computed. The natural bond orbital (NBO) analysis has been studied to analyze the charge delocalization and molecular hyperconjugative interactions.

**Keywords :** DFT calculations, FTIR, FT-Raman, 3-chloro-5-methoxyphenol.

## I. INTRODUCTION

Phenols derivatives are industrially and biologically important compounds. They are versatile originator in the manufacture of pesticides, dyes, plastics, drugs, explosives, etc due to their  $\pi$ -bonding and hydrogen systems. They are also useful in the production of cosmetics, aspirin, sunscreens and hair dyes. Phenols are different from normal alcohols, since they are acidic owing to the influence of OH group with the aromatic ring [1]. Because of their moderate size and resemblance to biological species, Phenol derivatives are interesting molecules for computational studies. The addition of substituents in any system results in the change in charge distribution of molecules and ultimately affects all the molecular properties.

In recent years, phenol derivatives have been the common subjects of both theoretical and experimental effort because of their importance in industry as well as environment. Initially, the vibrational assignments of infrared spectrum of phenol have been studied by Evans [2]. Later, many studies of phenol derivatives have been extended by several researchers [3-5]. Recently, the experimental and DFT studies on many synthesized phenol derivatives have been investigated [6-7]. More recently, Soltani et al. [8] have

**Revised Manuscript Received on December 29, 2019.**

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studied the structural and other molecular properties of 4-bromo-2-(2,5-dichloro-phenylimino)-phenol. During the course of investigation on the phenol compounds, our consideration has been turned towards 3-chloro-5-methoxyphenol (CMOP). Since the superposition of several vibrations, the vibrational assignment of phenol substituents becomes difficult. On the other hand, the spectral comparison with the closely relative molecules provides specific clues regarding the molecular vibrations. In the present investigation, the vibrational spectra of the CMOP have been studied along with theoretical calculations and its various normal modes are identified with greater wave numbers precisely.

## II. EXPERIMENTAL

The Fourier transform infrared spectra of CMOP was recorded in the region  $4000-400\text{ cm}^{-1}$ , using Perkin Elmer FTIR spectrometer and the FT-Raman spectrum of CMOP was recorded on a computer interfaced BRUKER RFS-66V model interferometer in the Stokes region  $4000-50\text{ cm}^{-1}$ . In this study, the DFT-B3LYP functional calculations have been worked out to get the structural and vibrational modes of CMOP. The molecular geometry optimizations, frequencies and other molecular parameters such as electronic, optical, etc were calculated for CMOP with the GAUSSIAN 09W software [9] at DFT level [10,11]. To confirm the vibrational assignment of CMOP, the total energy distribution (TED) were made with the MOLVIB program [12].

## III. RESULTS AND DISCUSSION

The molecular structure of CMOP is shown in Fig. 1. The minimum energy for CMOP calculated by the DFT with 6-31+G(d,p) and 6-311++G(d,p) basis sets are -881.6170699 and -881.7378177 Hartrees, respectively. The optimization geometrical parameters of CMOP are listed in the Table I. From the Table I, the bond length order is  $C2-C3 < C1-C6 < C3-C4 < C5-C6 < C4-C5 < C1-C2$ , which indicates the hexagonal benzene ring structure with little indistinct. This is because of conjugation between the functional groups and the benzene ring. The inclusion of the hydroxy group, chlorine atom and methoxy group substitutions in benzene ring lead to a little distortion. This is evident from the bond angles value of  $C2-C1-C6$ ,  $C2-C3-C4$  and  $C4-C5-C6$  which is found to be  $121.17^\circ$ ,  $122.77^\circ$  and  $120.93^\circ$ , respectively, (B3LYP/6-31+(d,p) method) and are different from typical  $120^\circ$ .

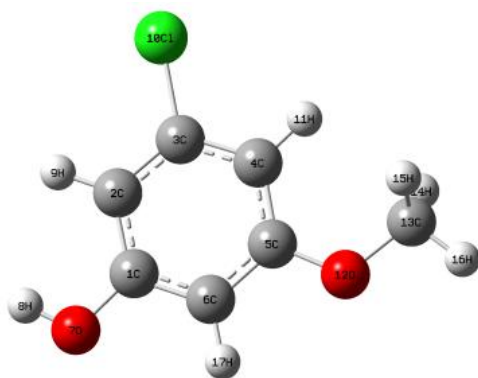


Figure 1. Molecular structure of 3-chloro-5-methoxyphenol

The CMOP contains of 17 atoms that will have 45 vibrational modes in accordance with  $C_s$  point symmetry. The vibrational assignment of CMOP with the calculated frequencies and their intensities are reported in Table II. The experimental and theoretical spectra of CMOP are given in Figs. 2 and 3, respectively.

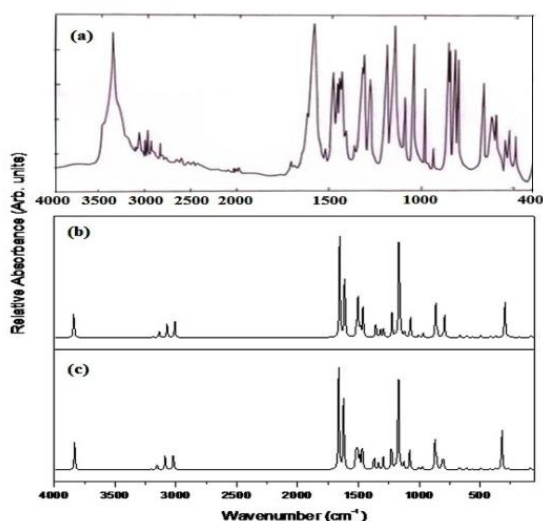


Figure 2. IR spectra of 3-chloro-5-methoxyphenol (a) observed; (b) B3LYP/6-311++G(d,p); (c) B3LYP/6-31+G(d,p).

In the present investigation, the experimental are compared with the calculated frequencies at DFT-B3LYP level using the lower and higher basis sets, which reveals the overestimation of the computed frequencies. This may be due to ignorance of anharmonicity in actual system. From the Table II, the vibrational analysis of CMOP with the unscaled B3LYP force field is generally larger than the experimental frequencies and these discrepancies can be corrected by scaling the calculated frequencies with suitable scale factor [13]. Therefore, a scale factor of 0.9613 is used for B3LYP method and the resultant scaled frequencies are listed in Table II. The frequencies of the stretching and bending vibration can be changed by O-H bonding. The O-H stretching modes appeared in the lesser frequencies range ( $3200-3550\text{ cm}^{-1}$ ) with maximum intensity and peak broadening [14]. In phenol, the O-H in-plane and out-of-plane bending vibrations lies between the frequencies  $1150-1250\text{ cm}^{-1}$  and  $290-320\text{ cm}^{-1}$ , respectively. In CMOP, the IR and Raman peaks found at  $3485$  and  $3482\text{ cm}^{-1}$  are assigned to O-H stretching vibration, respectively, which are further confirmed by the energy distribution of 99%. The in-plane

bending vibrations of hydroxyl group for CMOP have been identified at  $1115$  in both IR, Raman spectra. The out-of-plane bending vibrations of O-H group are assigned at  $160\text{ cm}^{-1}$  in Raman spectrum.

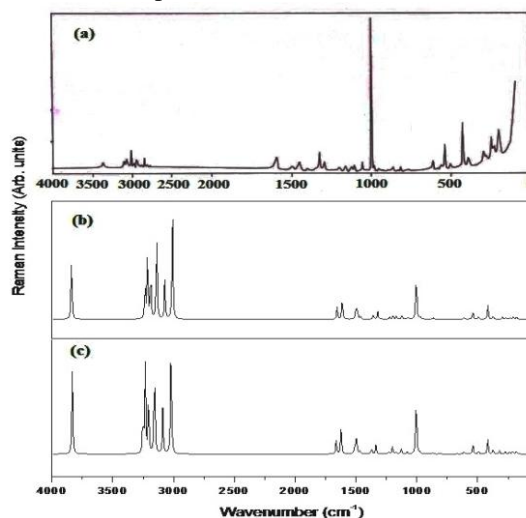


Figure 3. Raman spectra of 3-chloro-5-methoxyphenol (a) observed; (b) B3LYP/6-311++G(d,p); (c) B3LYP/6-31+G(d,p).

The aromatic C-H stretching vibrations usually exhibit various weak bands around  $3100-3000\text{ cm}^{-1}$  [15]. Generally, the C-H in-plane bending and C-C stretching vibrations interact with each other leading to strong bands around  $1300-1000\text{ cm}^{-1}$ . The C-H out-of-plane bending vibrations are powerfully coupled vibrations and their bands lie in the region  $900-667\text{ cm}^{-1}$ . Hence, the IR peaks emerged at  $3102$ ,  $3085$ ,  $3062\text{ cm}^{-1}$  and the Raman bands originated at  $3104$ ,  $3088$ ,  $3060\text{ cm}^{-1}$  in CMOP were assigned to C-H stretching and these normal modes are agreement with their energy distribution percentage.

In the title molecule CMOP, nine normal modes associated to each methyl group. The asymmetric and symmetric C-H stretching modes of methyl group [16] are estimated around  $2980\text{ cm}^{-1}$  and  $2870\text{ cm}^{-1}$ , respectively. The experimental FTIR and FT-Raman spectra of CMOP have  $\text{CH}_3$  out-of-plane stretching bands at  $2945$  and  $2940\text{ cm}^{-1}$ , respectively. The  $\text{CH}_3$  stretching in-plane vibrations are designated at  $3010\text{ cm}^{-1}$  in both vibrational spectra and they are in good agreement with the calculations by B3LYP/6-311++G(d,p) method. The  $\text{CH}_3$  ss modes are recognized at  $2892$  and  $2890\text{ cm}^{-1}$  in the FTIR and Raman spectra, respectively. The symmetrical bend modes  $\text{CH}_3$  sb, is found at  $1352\text{ cm}^{-1}$  in IR and  $1355\text{ cm}^{-1}$  in Raman spectrum. The  $\text{CH}_3$  in-plane bending modes of CMOP are observed at  $1455$  and  $1460\text{ cm}^{-1}$  in the IR and Raman spectra, respectively, and all these modes are also agreed with the literature data [16] as well as TED. The bands at  $1430\text{ cm}^{-1}$  in Raman, is ascribed to  $\text{CH}_3$  out-of-plane bending of CMOP. The bands obtained at  $928\text{ cm}^{-1}$  and  $1120\text{ cm}^{-1}$  in the experimental spectra are consigned to  $\text{CH}_3$  in-plane and out-of-plane rocking modes, respectively, and they prove consistent agreement with the computed values. The halogen atoms appearance in the benzene ring is very important for discussion because the mixing of vibrations is probable in this region [17]. Usually, the C-Cl bands appear in the broad region  $850-550\text{ cm}^{-1}$ .

For CMOP, the band found at 830 cm<sup>-1</sup> in IR and 832 cm<sup>-1</sup> in the Raman have been allotted to C-Cl stretching mode of vibration and the corresponding TED contribution is 74%. In this study, the bands identified at 472 and 175 cm<sup>-1</sup> in the

Raman have been assigned to the C-Cl in-plane and out-of-plane deformations, respectively, and they are in fine concurrence with the previous literature [17].

**Table I. Optimized geometrical parameters of 3-chloro-5-methoxyphenol obtained by DFT-B3LYP method**

Bond length	Value (Å)		Bond angle	Value (°)		Dihedral Angle	Value (°)	
	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)		B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)		B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)
C1-C2	1.404	1.401	C2-C1-C6	121.17	121.07	C6-C1-C2-C3	0.0	0.0
C1-C6	1.392	1.388	C2-C1-O7	121.79	121.80	C6-C1-C2-H9	180.0	180.0
C1-O7	1.368	1.367	C6-C1-O7	117.03	117.14	O7-C1-C2-C3	180.0	180.0
C2-C3	1.391	1.387	C1-C2-C3	117.92	117.94	O7-C1-C2-H9	0.0	0.0
C2-H9	1.085	1.083	C1-C2-H9	121.41	121.37	C2-C1-C6-C5	0.0	0.0
C3-C4	1.396	1.392	C3-C2-H9	120.68	120.69	C2-C1-C6-H17	180.0	180.0
C3-C110	1.760	1.761	C2-C3-C4	122.77	122.80	O7-C1-C6-C5	180.0	180.0
C4-C5	1.403	1.400	C2-C3-C110	118.68	118.68	O7-C1-C6-H17	0.0	0.0
C4-H11	1.081	1.079	C4-C3-C110	118.55	118.52	C2-C1-O7-H8	0.0	0.0
C5-C6	1.400	1.397	C3-C4-C5	117.86	117.90	C6-C1-O7-H8	180.0	180.0
C5-O12	1.363	1.361	C3-C4-H11	119.83	119.81	C1-C2-C3-C4	0.0	0.0
C6-H17	1.083	1.082	C5-C4-H11	122.31	122.29	C1-C2-C3-C110	180.0	180.0
O7-H8	0.966	0.963	C4-C5-C6	120.93	120.80	H9-C2-C3-C4	180.0	180.0
O12-C13	1.424	1.423	C4-C5-O12	123.66	123.73	H9-C2-C3-C110	0.0	0.0
C13-H14	1.097	1.095	C6-C5-O12	115.41	115.48	C2-C3-C4-C5	0.0	0.0
C13-H15	1.097	1.095	C1-C6-C5	119.36	119.50	C2-C3-C4-H11	180.0	180.0
C13-H16	1.091	1.088	C1-C6-H17	120.55	120.47	C110-C3-C4-C5	180.0	180.0
			C5-C6-H17	120.10	120.04	C110-C3-C4-H11	0.0	0.0
			C1-O7-H8	110.18	109.95	C3-C4-C5-C6	0.0	0.0
			C5-O12-C13	118.86	118.88	C3-C4-C5-O12	180.0	180.0
			O12-C13-H14	111.32	111.36	H11-C4-C5-C6	180.0	180.0
			O12-C13-H15	111.32	111.36	H11-C4-C5-O12	0.0	0.0
			O12-C13-H16	105.65	105.71	C4-C5-C6-C1	0.0	0.0
			H14-C13-H15	109.63	109.62	C4-C5-C6-H17	180.0	180.0
			H14-C13-H16	109.41	109.35	O12-C5-C6-C1	180.0	180.0
			H15-C13-H16	109.41	109.35	O12-C5-C6-H17	0.0	0.0
						C4-C5-O12-C13	0.0	0.0
						C6-C5-O12-C13	180.0	180.0
						C5-O12-C13-H14	-61.32	-61.34
						C5-O12-C13-H15	61.32	61.34
						C5-O12-C13-H16	180.0	180.0

**Table II. The observed FTIR, FT-Raman and calculated (unscaled and scaled) frequencies (cm<sup>-1</sup>), IR intensity (km mol<sup>-1</sup>), Raman activity (Å<sup>4</sup> amu<sup>-1</sup>) and probable assignments (characterized by TED) of 3-chloro-5-methoxyphenol using B3LYP method**

Species C <sub>s</sub>	Observed wavenumber (cm <sup>-1</sup> )		Calculated frequencies (cm <sup>-1</sup> )								TED% among types of coordinates
	FTIR	FT Raman	B3LYP/6-31+G(d,p)				B3LYP/6-311++G(d,p)				
			Unscaled	Scaled	IR intensity	Raman activity	Unscaled	Scaled	IR intensity	Raman activity	
A'	3485(vs)	3482(vw)	3831	3683	68.29	116.20	3838	3689	73.58	111.46	vOH(99)
A'	3102(w)	3104(vw)	3252	3126	0.53	51.04	3234	3109	0.60	48.50	vCH(98)
A'	3085(ms)	3088(vw)	3233	3108	0.02	103.94	3214	3090	0.01	100.87	vCH(96)
A'	3062(ms)	3060(ms)	3205	3081	2.70	82.45	3188	3065	2.32	79.41	vCH(94)
A'	3010(ms)	3010(vw)	3156	3034	18.96	129.67	3138	3017	18.99	125.20	CH <sub>3ips</sub> (92)
A'	2892(ms)	2890(w)	3021	2904	51.23	148.31	3010	2894	47.73	159.73	CH <sub>3ss</sub> (90)
A'	1585(vs)	1580(w)	1663	1599	262.48	11.58	1655	1591	255.32	11.65	vCC(88)
A'	1547(ms)		1622	1559	215.52	24.43	1613	1551	214.65	23.20	vCC(86)
A'	1455(s)	1460(vw)	1522	1463	52.86	1.20	1516	1457	47.10	1.09	CH <sub>3ipb</sub> (84)
A'	1438(s)	1435(w)	1508	1450	82.14	6.53	1503	1445	94.82	5.83	vCC(85)
A'	1424(ms)		1489	1431	32.14	2.58	1483	1426	31.95	2.29	vCC(84)
A'	1402(w)	1400(ms)	1468	1411	88.25	3.61	1462	1405	90.76	3.10	vCC(82)
A'	1352(w)	1355(w)	1371	1318	46.94	4.91	1357	1304	50.06	4.86	CH <sub>3sb</sub> (81)
A'	1264(w)		1334	1282	20.89	8.36	1322	1271	22.13	7.88	vCC(80)
A'	1238(s)		1296	1246	30.92	0.26	1293	1243	30.74	0.30	vCO(79)
A'	1175(s)	1172(vw)	1228	1180	87.73	2.07	1223	1176	62.98	1.77	vCO(80)
A'	1148(s)	1150(vw)	1199	1153	6.76	5.16	1196	1150	6.25	4.88	vCO(81)
A'	1115(s)	1115(vw)	1171	1126	317.26	0.35	1165	1120	342.78	0.32	bOH(78)



A'	1080(ms)	1076(w)	1130	1086	21.37	4.39	1124	1081	20.75	4.66	bCH(79)
A'	1031(s)	1030(vs)	1079	1037	52.40	1.63	1074	1032	56.40	1.68	bCH(76)
A'	970(s)	968(vw)	1005	966	8.73	48.56	1005	966	9.98	46.90	bCH(78)
A'	928(ms)	928(vw)	974	936	9.90	1.46	968	931	10.26	1.40	CH <sub>3ipr</sub> (75)
A'	830(s)	832(vw)	869	835	99.00	1.17	866	832	101.33	1.18	vCCI(74)
A'	582(ms)	585(vw)	613	589	3.11	1.43	612	588	3.00	0.99	bCO(74)
A'	576(ms)	575(vw)	606	583	3.52	0.62	607	584	3.46	0.59	bCO(76)
A'	515(ms)	510(w)	539	518	0.28	7.34	539	518	0.39	7.20	bCO(73)
A'	-	472(s)	493	474	6.91	2.18	494	475	7.29	2.17	bCCI(72)
A'	-	398(w)	418	402	3.82	9.82	417	401	3.68	9.71	R symd (72)
A'	-	354(w)	373	359	5.16	3.20	372	358	5.23	3.11	R trigd (70)
A'	-	247(vw)	269	259	4.29	1.38	262	252	1.43	0.20	R asymd (74)
A''	2945(ms)	2940(w)	3087	2968	34.96	52.81	3071	2952	33.67	51.89	CH <sub>3ops</sub> (86)
A''	-	1430(vw)	1498	1440	8.66	13.70	1493	1435	9.75	13.12	CH <sub>3opb</sub> (82)
A''	-	1120(vw)	1171	1126	0.94	1.88	1166	1121	0.59	2.80	CH <sub>3opr</sub> (80)
A''	815(s)	-	855	822	22.69	0.13	850	817	17.61	0.16	ω CH (68)
A''	776(s)	775((w)	818	786	11.42	0.37	810	779	7.34	0.07	ω CH (65)
A''	758(s)	760(vw)	804	773	46.26	0.29	793	762	55.51	0.07	ω CH (63)
A''	635(ms)	634(w)	668	642	9.21	0.13	666	640	7.77	0.03	tR symd (62)
A''	538(ms)	540(ms)	564	542	2.39	0.08	563	541	1.91	0.17	tR trigd (64)
A''	-	290(vw)	322	310	109.28	2.35	298	286	104.95	1.87	tR asymd (66)
A''	-	255(w)	272	261	0.24	0.21	268	258	4.19	1.42	ω CO (61)
A''	-	220(vw)	237	228	0.63	1.45	235	226	0.82	1.16	ω CO (62)
A''	-	205(vw)	212	204	0.01	2.11	207	199	0.00	1.84	ω CO (64)
A'	-	175(w)	181	174	1.83	2.06	180	173	1.78	2.16	ω CCl (62)
A''	-	160(vw)	166	160	0.23	0.11	163	157	0.24	0.08	ω OH (61)
A''	-	-	85	85	6.92	0.29	82	82	6.79	0.28	tOCH <sub>3</sub> (58)

The C-C stretching vibrations bands appear in between 1400 and 1650  $\text{cm}^{-1}$  in benzene derivatives [18]. Hence, the C-C stretching modes of CMOP are established at 1585, 1547, 1438, 1424, 1402, 1264  $\text{cm}^{-1}$  in FTIR and 1580, 1435, 1400  $\text{cm}^{-1}$  in the FT-Raman spectrum. The C-C in-plane and out-of-plane bending modes of CMOP are well identified within their characteristic region in the recorded spectra and the TED % show reliable agreement with the vibrational assignment. For carbonyl contained compounds, the strongest peaks in the region 1260-1000  $\text{cm}^{-1}$  are due to the C-O stretching modes. Therefore, the strongest IR bands at 1238, 1175, 1148  $\text{cm}^{-1}$  and Raman bands at 1172, 1150  $\text{cm}^{-1}$  in CMOP were assigned to the C-O stretching vibration modes and these are supported with the previous assignments [19].

The electronic, optical properties and chemical reactions of the molecules are decided by the highest occupied and lowest unoccupied molecular orbitals (HOMOs and LUMOs) [20]. The atomic orbital compositions for CMOP are shown in Fig. 4. The calculations indicate that the title molecule have 41 occupied MOs. The HOMO is located over OH group, chlorine atom and methoxy group; The LUMO of ring is distributed over the entire C-C bond. The HOMO to LUMO transition explains the transfer of electron density to C-C bond of the benzene ring from OH group, chlorine atom and methoxy group. The energy gap of CMOP reveals the chemical motion and reactivity of the molecule.

The calculation of atomic charges describes a significant task in the application of DFT calculations to molecular structure [21]. Mulliken population analysis has been carried out for the comparison of different choice of the basis sets to illustrate the electron sharing in CMOP. The Fig.5 shows Mulliken's plot of CMOP. The carbon atoms C1, C3 and C5 have the high negative charge since they are attached with

OH, Cl and an O-CH<sub>3</sub> group, respectively, which leads to rearrangement of electron concentration and every hydrogen have a positive charge because they are electron acceptors.

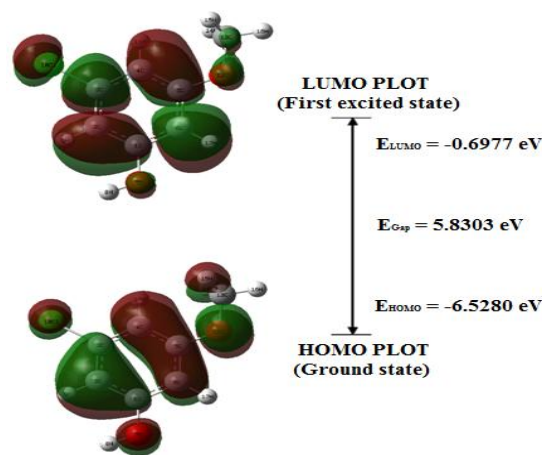


Figure 4. The atomic orbital HOMO and LUMO compositions for 3-chloro-5-methoxyphenol

The electrostatic potential has been utilized to predict sites and relative reactivities in the direction of electrophilic attack [22]. In the present investigation, the molecular electrostatic potential (MEP) map for CMOP is revealed in Fig. 6. The blue (positive) regions of MEP are related to nucleophilic reactivity and the red and yellow (negative) regions to electrophilic reactivity as shown. In the present study, the MEP map shows that the negative potential sites around chlorine and oxygen atoms (Red) and the positive potential sites are on the hydrogen atoms of the benzene ring (Blue).

From these calculated results, the H atoms of the system show the strongest attraction and chlorine and oxygen atoms show the strongest repulsion. These sites provide details regarding the region of intermolecular interactions of CMOP.

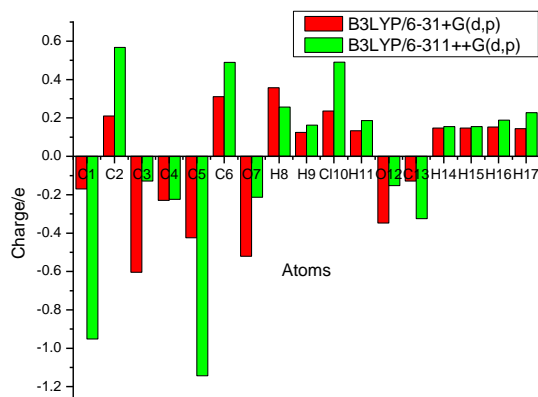


Figure 5. Mulliken's plot for 3-chloro-5-methoxyphenol

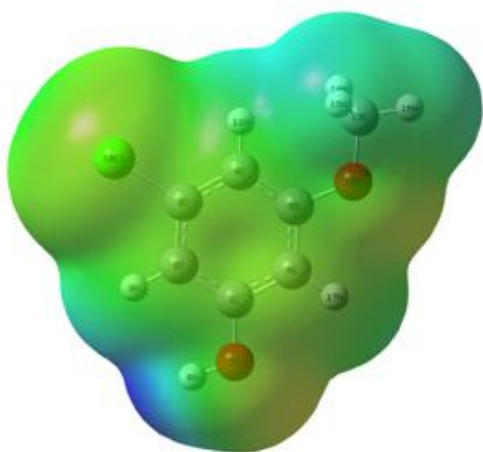


Figure 6. Molecular electrostatic potential (MEP) map for 3-chloro-5-methoxyphenol

Natural Bond Orbital (NBO) analysis is the important tools for localization of the molecular wave functions in optimized electron pairs, equivalent to lone pairs; core pairs on bonding units. In the present study, the change in electron density (ED) of ( $\sigma^*$ ,  $\pi^*$ ) antibonding orbitals and E(2) energies have been calculated using DFT method with the Gaussian 09W package to give clear evidence of stabilization interactions [23]. The NBO basis of CMOP indicates the orbital intramolecular interactions of  $\pi(C1-C6)$  with  $\pi^*(C4-C5)$ , resulting in high electron density (approx. 0.206e) of anti-bonding  $\pi$  orbitals (C-C) which causing stabilization of 12.88 kcal/mol to the system. Similarly, the charge transfer from  $\pi(C2-C3)$  to  $\pi^*(C1-C6)$  amounts to the stabilization of 10.77 kcal/mol and the charge transfer from  $\pi(C4-C5)$  to  $\pi^*(C2-C3)$  leads to the stabilization of 13.15 kcal/mol. Further, the charge transfer from the lone pairs of O7 to anti-bonding C1-C6,  $\pi$  orbital amount to the stabilization of 13.80 kcal/mol, while the lone pairs of chlorine  $n3(Cl10) \rightarrow \pi^*(C2-C3)$  and oxygen  $n2(O12) \rightarrow \pi^*(C4-C5)$ , it is of the order of 6.46 and 15.61 kcal/mol, respectively. Hence, there is a possibility for hyper conjugation between chlorine, oxygen atoms and the benzene ring.

#### IV. CONCLUSION

The geometrical parameters, frequencies and vibrational intensities of 3-chloro-5-methoxyphenol have been carried out using the DFT-B3LYP method. The theoretical and experimental results were compared and provide the most consistent theoretical information on the molecular properties of CMOP. The calculated HOMO and LUMO energies show the occurrence of charge transfer which explains the chemical activity of the molecule. The Mulliken charge analysis explains the rearrangement of electron concentration in the molecule. The MEP surface predicts the relative reactivities towards electrophilic (hydrogen atoms) and nucleophilic (oxygen atoms) attacks. The NBO results imitate the electron transfer mostly because of the lone pair of chlorine  $n3(Cl10) \rightarrow \pi^*(C2-C3)$  and oxygen  $n2(O12) \rightarrow \pi^*(C4-C5)$ .

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