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FTIR Spectra, HF and DFT Analysis of o-Chlorophenol and Diphenyl Ether

Shelar Rajendra^{1*}, Patil Arun² and Nirwan Ramesh³

1. Department of Physics, M. S. G. College, Malegaon, Dist. Nashik, Maharashtra, INDIA

2. Department of Physics, A. S. C. College, Surgana, Dist. Nashik, Maharashtra, INDIA

3. Department of Chemistry, M. S. G. College, Malegaon, Dist. Nashik, Maharashtra, INDIA

*rajnshelar@gmail.com

Abstract

The molecular structure and vibrational spectra of o-Chlorophenol (OCP) and Diphenyl ether (DPE) have been investigated by Hartree–Fock (HF) and Density Functional Theory (DFT) using standard B3LYP functional and 6-311G basis set. The results of the calculations are applied to simulate infrared spectra of the title compounds which showed good agreement with the experimentally determined data. It has been found that both methods yield consistent data for the geometric parameters but DFT yielded vibrational frequencies much closer to the experimental data.

Computed values at DFT (B3LYP)/ 6-311G have analyzed and their characterization was made with help of Gauss view visualization program utilizing the data obtained from the Gaussian 03 calculation. A few of the discrepancies observed between the experimental and computed data of vibrational frequencies and their assignments have also been discussed.

Keywords: Infrared spectra, o-Chlorophenol, Ether, Normal mode frequencies, DFT calculation.

Introduction

The most frequently used spectroscopic methods for organic chemists are Ultra-Violet, Infra-Red, Nuclear Magnetic Resonance and Mass-Spectrometry. I.R. measurements through liquid mixtures provide an excellent tool to investigate inter and intramolecular interactions between like and unlike molecules.

Recently, a spectroscopic study of o-Chlorophenol and Diphenyl ether has been made and its various vibrational modes have been assigned using simplified picture of the molecule. Due to existence of many vibrations, it would be difficult to assign the observed frequencies to a particular mode. The density functional theory¹ (DFT) methods have become a powerful tool for the investigation of molecular structure and vibrational spectra.

Supplemented by a visualization program, the assignments can accurately be made. The present work has been performed with viewpoint of getting the vibrational frequencies on an optimized geometry of the titled compound. These frequencies are analyzed and compared

with the experimental data². Attempts have been made to find out an optimum method using a basis set to get a close agreement between the computed and the experimental data. Literature survey shows that no computational studies have been done so far on the titled compound.

This program reports energy, dipole moment, charges, vibrational frequencies, bond angle and bond distance. It is also useful tool for calculations on larger and runs calculations very quickly.

Material and Methods

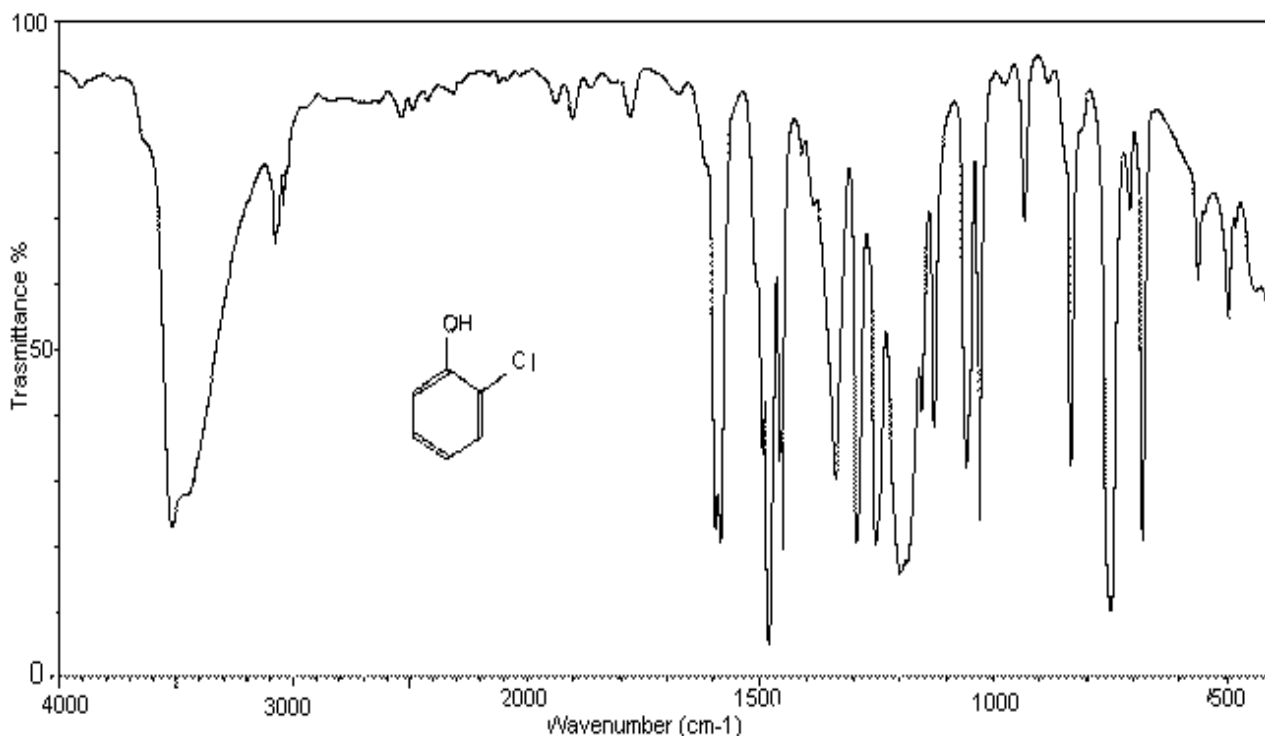
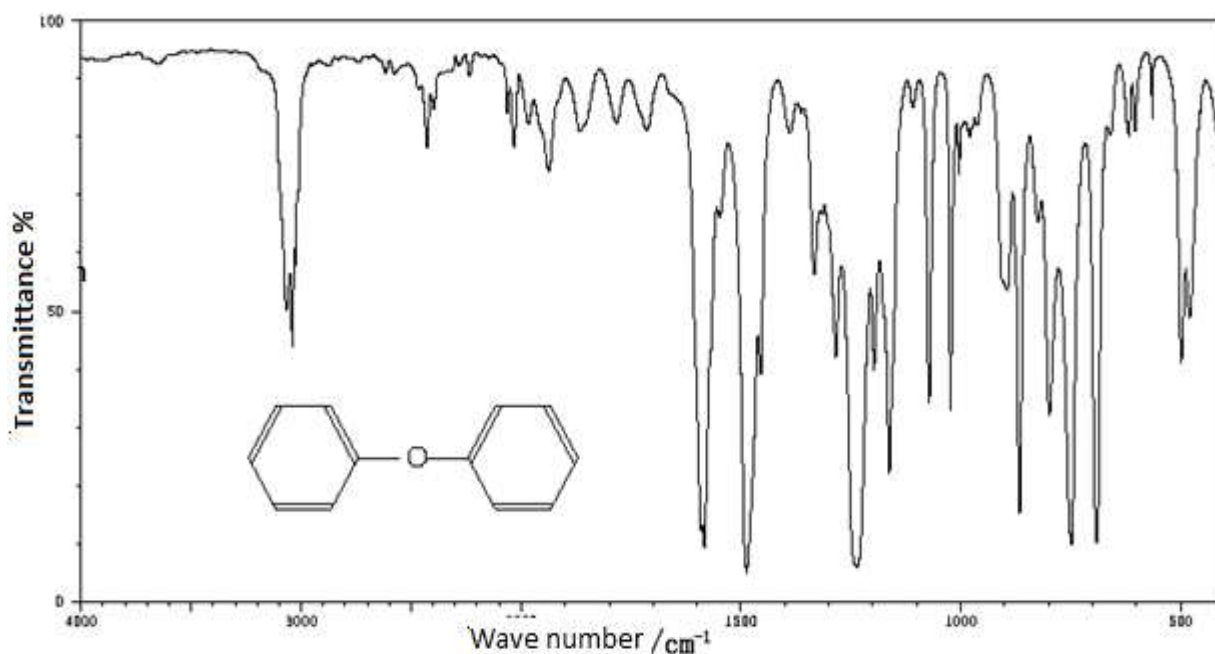
O-Chlorophenol are produced by electrophilic halogenation of phenol with chlorine. Most chlorophenols are solid at room temperature. They have a strong, medicinal taste and smell. Chlorophenols are commonly used as pesticides, herbicides and disinfectants. They are used as bactericides, fungicides and preservatives. The water solubility of chlorophenols is low. Most chlorophenols are commercially applied in the form of a chlorophenol-organic solvent formulation.

Diphenyl ether is an aromatic ether in which the oxygen is attached to two phenyl substituents. It has a role as a plant metabolite. It is found in alcoholic beverages. It is present in muscat grapes, green tea, vanilla, lemon balm, buckwheat, potato chips and grilled beef. It is a flavouring ingredient, starting material in the production of phenoxathiin.

FTIR spectra were recorded on a FTIR spectrometer (Model: SIMADZU 8400S PC) by using KBr pellet in the region 400-4000 cm⁻¹ with 4.0 cm⁻¹ resolution. The transmission values were read in steps of 5%. The spectrometer possesses out to aligned energy optimization and dynamically aligned interferometer. It is fitted with KBr beam splitter, a DLATGS detector. A base line correction was made for the spectra recorded.

Fig. 1 represents the infrared spectra of o-Chlorophenol; we notice the broad and sharp band of O-H stretching at 3621 cm⁻¹, the weak band of aromatic C-H appears at 3078 cm⁻¹. The two C=C stretching at both 1480 cm⁻¹ and 1595 cm⁻¹ are observed. The stretching frequency of C-O and C-Cl are noted at 1190 cm⁻¹ and 748 cm⁻¹ respectively.

Fig. 2 shows the infrared spectra of Diphenyl ether, the two sharp and strong bands are observed at frequencies 1487 cm⁻¹ and 1584 cm⁻¹ corresponding to C=C stretching. A band at 1286 cm⁻¹ is assigned as C-O stretching vibration.

**Fig. 1: FTIR Spectra of o-Chlorophenol****Fig. 2: FTIR Spectra of Diphenyl Ether**

Computational Details: Geometry optimization and vibrational frequencies of titled compounds were calculated at the Hartree-Fock³ and DFT levels with B3LYP (Becke-Lee-Yang-Parr three parameters) hybrid functional with correlation function such as one proposed by Lee, Yang and Parr⁴. B3LYP is most promising in providing reasonable acceptable vibrational wave numbers for organic molecules. Standard 6-311G basis set has been used in the both methods in order to see the effect of correlation. Gaussian 03 software package⁵ has been utilized to accomplish all the calculations.

Results and Discussion

All the theoretical calculations of o-Chlorophenol and diphenyl ether were performed by the use of G03W series of programs. Geometries of optimizations for all of the investigated molecules in this work were carried out using the HF and DFT (B3LYP) method with 6-311G (d, p) basis sets. Computed geometrical parameters are listed in table 1. Results show that both levels predict consistent data. An optimized geometry of titled compounds at DFT (B3LYP)/6-311G (d, p) level is shown in fig. 3.

The detailed analysis of the vibrational frequencies has been performed with computed data obtained at DFT (B3LYP)/6-31G (d, p) and HF and results are presented in tables 2 to 5. The intensities are calculated from the computed data and these are also listed in tables 2 to 5. The computed values have been utilized to simulate IR spectra.

The result shows an agreement with the experimentally observed spectra of titled compounds. A comparison of observed spectra and computational data reveals the agreement. During the present study, visualization of frequencies in 3D has been made by Gassview. With this program, assignments of vibrations can be made with high degree of certainty. Accepted value of scaling factors for DFT is 0.96 and it has been used to correct the frequency values⁷. Scaled frequencies are recorded in tables 2 to 5. The assignment of the computed frequencies is done by

visualizing the vibrations in 3D using Gausview. The values of IR frequencies are compared and the discrepancies observed between experimental and computational data are discussed here.

O-H vibrations

o-Chlorophenol: The non-hydrogen-bonded hydroxyl group of phenols absorbs strongly in the 3584–3700 cm^{-1} region. In the present investigation, the calculations show O-H stretching vibrations at 3621.49 cm^{-1} and these are in close agreement with the experimental values of 3621 cm^{-1} . The OH bending, CH bending and ring deformation in plane are found at 1611.42, 1238.05, 1108.06, 1008.62 cm^{-1} . C-O stretching and ring deformation occur at 817.68. The stretching of C-Cl and ring deformation is found at 661.39 cm^{-1} .

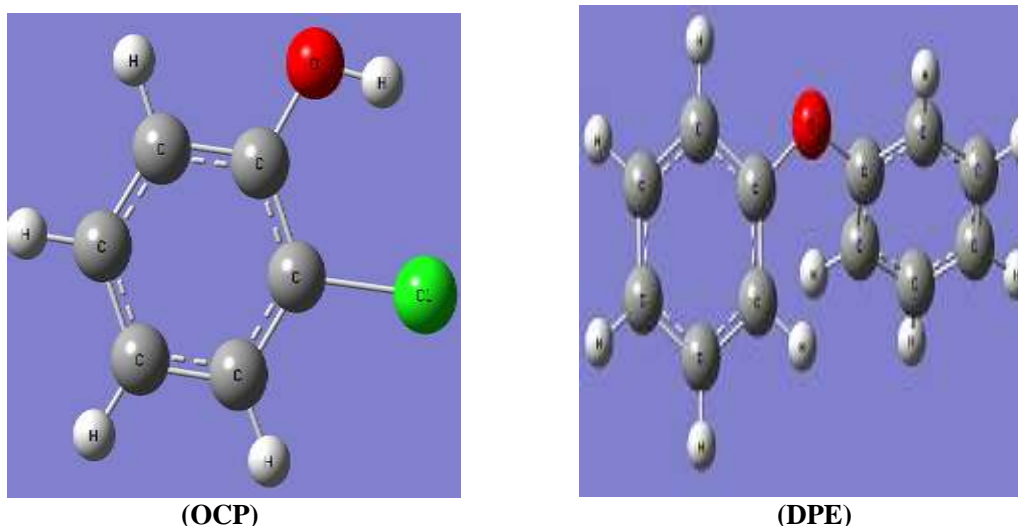


Fig. 3: Optimized geometry of o-Chlorophenol and Diphenyl Ether Obtained at DFT (B3LYP)/6-311G

Table 1

Optimized geometrical parameters of o-Chlorophenol and Diphenyl Ether obtained by HF and DFT calculation

Parameter	o-Chlorophenol		Parameter	Diphenyl Ether	
	HF 6-311 G	DFT 6-311G		Bond length	HF 6-311 G
C1-C2	1.3908	1.4001	C1-C2	1.3868	1.3974
C2-C3	1.3867	1.3924	C2-C3	1.3825	1.3943
C3-C4	1.3881	1.3992	C3-C4	1.3825	1.3943
C4-C5	1.3807	1.3963	C4-C5	1.3868	1.3974
C5-C6	1.3814	1.3887	C5-C6	1.3873	1.3980
C1-C6	1.3826	1.3961	C1-C6	1.3873	1.3980
C1-C7	1.0692	1.0805	C1-H7	1.0705	1.0818
C5-C13	1.8128	1.8375	C2-H8	1.0690	1.0803
C4-O11	1.3658	1.3830	C3-O23	1.3965	1.4199
C2-H8	1.0699	1.0811	C4-H9	1.0690	1.0803
C2-H9	1.0684	1.0800	C5-H10	1.0705	1.0818
C6-H10	1.6836	1.0797	C6-H11	1.0702	1.0814
O11-H12	0.9464	0.9741	C12-O23	1.3964	1.4199

C-H vibrations

o-Chlorophenol: In aromatic compound, C-H stretching vibrations⁸ occur in the region 3000-3100 cm^{-1} which is the characteristics region for the ready identification of C-H stretching vibrations^{9,10}. The calculation shows four C-H stretching vibrations at 3087.18, 3081.29 cm^{-1} by HF method and 3057.36, 3042.29 cm^{-1} by DFT method and these are in close agreement with the experimental value 3078 and 3040 cm^{-1} . The C-H in plane bending vibrations are visualized at 1611.42, 1238.05, 1108.06, 1008.62, 817.68, 786.25 cm^{-1} . Visualization of these frequencies reveals that these vibrations are contaminated by ring deformation, O-H bending, C-C and C-O stretching. The computed value for the C-Cl stretching and ring deformation is 661.39 cm^{-1} . The experimental values is 679 cm^{-1} .

C=C vibrations

o-Chlorophenol: The C=C stretching vibrations occur in the region 1200 - 1680 cm^{-1} . Therefore, in the present study the C=C stretching vibrations of the titled compound is observed at 1224.48 and 1611.42 cm^{-1} along with the CH bending and

CO stretching while the experimental value is at 1261 and 1595 cm^{-1} . The calculated frequencies are on lower side as compared to the experimental values. This may be due to contamination with other coupled vibrations¹¹.

C-O vibrations

o-Chlorophenol: The band due to C-O-C stretching vibrations is observed in the region 800-1300 cm^{-1} . These vibrations are found at 817.68, 806.96 and 1224.48 cm^{-1} along with the ring deformation. Experimental values are observed at 833 cm^{-1} .

C-Cl vibrations

o-Chlorophenol: The C-Cl stretching frequency is generally observed in the region 600-800 cm^{-1} depending on the configuration and conformation of the compound¹². Based on this, in the present investigation C-Cl stretching mode vibrations has been assigned to 661.39 cm^{-1} along with ring deformation while the FTIR band is identified at 679 cm^{-1} presented in table 2 and 3.

Table 2
Fundamental Vibrations of o-Chlorophenol calculated at DFT/B3LYP 6-311 G

Normal mode	Calculated frequency (cm^{-1}) (scaled)	Intensity	Assignments
1	3688.49 (3621)	97.06	OH stretching
2	3057.36 (3078)	10.23	CH stretching asymmetric
3	3042.29 (3040)	14.81	CH stretching symmetric
4	1611.42 (1595)	26.69	CH bending, C=C stretching, CO stretching
5	1238.05 (1261)	16.70	CH bending, OH bending, ring deformation
6	1108.06 (1127)	40.22	OH bending, ring deformation
7	1008.62 (1029)	41.00	CH bending, ring deformation
8	817.68 (833)	16.37	, CO stretching, ring deformation
9	786.25 (748)	99.48	CH bending
10	661.39 (679)	30.67	C-Cl stretching, ring deformation

Table 3
Fundamental Vibrations of o-Chlorophenol calculated at HF 6-311 G

Normal mode	Calculated frequency (cm^{-1}) (scaled)	Intensity	Assignments
1	3516.67	60.44	OH stretching
2	3087.18	7.29	CH stretching symmetric
3	3081.29	8.94	CH stretching asymmetric
4	1571.96	24.54	CH bending, ring deformation
5	1224.48	90.56	C-O stretching, C-H bending, C=C stretching
6	1151.34	21.97	OH bending, CH bending
7	1000.65	193.26	OH bending, ring deformation
8	806.96	51.17	, CO stretching, ring deformation
9	751.54	16.38	CH bending
10	654.72	81.87	ring deformation

Table 4
Fundamental Vibrations of Diphenyl ether calculated at DFT/B3LYP 6-311 G

Normal mode	Calculated frequency (cm ⁻¹) (scaled)	Intensity	Assignments
1	3055.35 (3066)	0.004	CH stretching symmetric
2	3036.78 (3040)	79.53	CH stretching asymmetric
3	1603.04 (1584)	120.65	CH bending, ring deformation
4	1497.70 (1487)	208.51	CH bending, ring deformation
5	1238.92 (1286)	405.58	C-O stretching, C-H bending
6	1067.50 (1072)	16.52	CH bending, ring deformation
7	956.67	2.88	CH bending
8	771.88	21.12	CH bending
9	771.88	32.26	CH bending
10	706.35 (749)	77.00	CH bending

Table 5
Fundamental Vibrations of Diphenyl ether calculated at HF 6-311 G

Normal mode	Calculated frequency (cm ⁻¹) (scaled)	Intensity	Assignments
1	2897.70 (3027)	38.54	CH stretching symmetric
2	2884.89	71.70	CH stretching asymmetric
3	2862.70	1.44	CH stretching asymmetric
4	1471.71	75.97	C=C stretching, CH bending
5	1353.43	5.01	CH bending
6	1111.49	328.25	CH bending, CO stretching
7	997.98	19.67	CH bending
8	857.23	14.04	CH bending
9	740.40	80.60	CH bending
10	651.58	63.73	CH bending

Diphenyl Ether: The molecular structure shows the presence of C-H stretching vibrations in the region 2800-3100 cm⁻¹. In the present study, the C-H vibrations have been found 3066, 3040, 3027 cm⁻¹ by experiment and computed values are 3055.35, 3036.78, 2997.70, 2884.89, 2862.70 cm⁻¹. C-H bending and ring deformation occur at frequencies 1603.04 and 1497.70 cm⁻¹ and are in close agreement with experimental values 1584 and 1457 cm⁻¹. C-O stretching and C-H bending observed at 1238.92 cm⁻¹. Ring deformation is seen at 1067.50 cm⁻¹. C=C stretching occurs at frequency 1471.71 cm⁻¹.

Conclusion

The normal mode frequencies and corresponding vibrational assignment of titled compound are examined theoretically using the Gaussian 03 package. The optimized geometries and complete vibrational analysis of o-Chlorophenol and Diphenyl Ether were performed and analyzed both at HF and DFT levels of theories utilizing 6-311 G(d,p) basis set. The data obtained during the course of present investigation show that a better agreement between the experimental and computed data is obtained by using DFT method.

HF method shows disagreement with experimental data. Some of the assignments were made contradictory to the computed data. However, the assignments made during the

present investigation can put a greater confidence level because these are visualized in three dimensions using a Gaussview program.

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