

FTIR, FT-Raman Spectra, First-Order Hyperpolarizability, HOMO-LUMO, NBO, and Mulliken Charge Analyses of p-Chlorofluorobenzene

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ABSTRACT

The FTIR and FT-Raman spectra of p-chlorofluorobenzene (P-CFB) have been recorded in the region $4000-400\text{ cm}^{-1}$ and $3500-50\text{ cm}^{-1}$, respectively. The structural and spectroscopic data of the molecule in the ground state were calculated by using density functional theory (DFT) employing B3LYP and *ab initio* Hartree Fock (HF) method with 6-311++G(d,p) basis set. The geometry of the molecule was fully optimized, vibrational spectra were calculated and fundamental vibration were assigned on the basis of potential energy distribution (TED) of the vibrational modes calculated with scaled quantum mechanical (SQM) method. The optimized structure of the title compound was interpreted and compared with the reported experimental values. The calculated HOMO-LUMO energy gap reveals that the charge transfer occurs within the molecule. Thermodynamic properties like entropy, thermal energy, zero point vibrational energy have been calculated for the molecule.

Keywords: FTIR; FT-Raman; p-chlorofluorobenzene; DFT; *ab initio*; HOMO-LUMO

I. INTRODUCTION

Benzene is mainly used as an intermediate compound to make other chemicals, its mostly produced derivatives include styrene, which is used to make polymers and plastics. Benzene is a clear, colourless, no corrosive and highly flammable liquid with a sweet odour. It evaporates into the air very quickly and dissolves slightly in water. Benzene is also used to some type of rubbers, lubricant, dyes, detergents, drugs, and pesticides. Benzene is also a natural part of crude oil, gasoline [1]. Chlorobenzene is an important industrial solvent and widely used intermediate in production of commodities such as herbicides, dyestuffs, and rubber [2]. Fluorine is the most abundant halogen in the earth's crust. However, only a dozen fluorinated organic compounds have been identified in nature. The incorporation of fluorine-containing groups into an organic molecule often drastically perturbs the chemical, physical and biological properties of the parent compound. The fluorinated compounds are widely used to medicinal, pharmaceutical, agricultural, and material sciences [3].

For proper understanding of IR and Raman spectra, several theoretical methods, ranging from semi

empirical to DFT approaches, are invaluable tools [4,5] and each method is having its own advantages. The Hartree-Fock *ab initio* method have to give good results provided a reasonable basis set, and an appropriate correlation treatment is taken into account. On the other hand, a powerful quantum chemical tool is used to give the electronic structure of the molecule has been evolved by B3LYP method [6]. The DFT method includes an electron correlation, in an alternative way to perform vibrational analysis of moderately large organic molecules. In the frame work of DFT approach, different from exchange and correlation functions are routinely used. Among these, the B3LYP combination is the most used, since it proved its ability in reproducing various molecular properties, including vibrational spectra.

Literature survey reveals that the *ab initio* HF and DFT/B3LYP frequency calculations of P-CFB have not been carried out so far. As a continuation of recent studies on structural and theoretical investigations of some substituted benzene derivatives, the main aspects of this investigation are structural analysis, molecular geometries and vibrational spectra of p-chlorofluorobenzene (P-CFB) are calculated by applying density functional theory (DFT) and *ab initio*

(HF) and HOMO-LUMO, NBO analyses have been used to give more information regarding charge transfer within the molecules.

II. METHODS AND MATERIAL

1. Experimental Details

The pure sample of p-chlorofluorobenzene was obtained from Lancaster chemical company, UK and used such as for spectral measurements. The FT-IR spectrum of the compound was recorded in the region 4000-400 cm^{-1} using the BRUKER IFS-66V FT-IR spectrometer equipped with an MCT detector, a KBr beam splitter and globar arc source. The spectral resolution is $\pm 1 \text{ cm}^{-1}$.

The FT-Raman spectrum of the sample was recorded between 3500-100 cm^{-1} using the BRUKER FRA 106 FT-Raman instrument using 1064 nm excitation from an Nd: YAG laser. The reported wave numbers are expected to be accurate within $\pm 1 \text{ cm}^{-1}$.

2. Computational details

In order to provide information with regard to the structural characteristics and the normal vibrational modes of P-CFB, the Hartree-Fock and DFT-B3LYP correlation functional calculations have been carried out. The entire calculations were performed using the GAUSSIAN 09W software package [7].

Initially, the HF level calculations, adopting the 6-311++G(d,p) basis set were carried out and then the DFT employing the Becke-3-Lee-Yang-Parr (B3LYP) supplemented with the standard basis set 6-311++G(d,p). The B3LYP is the most popular and efficient exchange correlation functional for calculating functional for calculating energies and geometries, it has been proven to be able to yield reliable results for small molecules [8]. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants has been computed at optimized geometry by assuming C_s point group symmetry. Scaling of the force field was performed according to SQM procedure [9,10] using selective scaling in the natural internal coordinate representation [11,12]. Normal coordinate analysis was

performed to obtain full description of the molecular motion pertaining to the normal modes using MOLVIB program version 7.0 written by sundius [13,14].

3. Prediction of Raman intensities

The Raman activities (S_i) calculated with GAUSSIAN 09W program are subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [15,16].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i \left[1 - \exp\left(\frac{-hc \nu_i}{kT}\right) \right]} \dots \dots \dots (1)$$

Where ν_0 is the exciting frequency in cm^{-1} , ν_i is the vibrational wave number of i^{th} normal mode; h , c and k are fundamental constants and f is a suitably chosen common normalization factor for all peak intensities.

III. RESULTS AND DISCUSSION

3.1. Molecular geometry

The optimized molecular structure of p-chlorofluorobenzene is shown in Fig.1. The optimized geometrical parameters of p-chlorofluorobenzene obtained by the HF and B3LYP with 6-311++G(d,p) as basis set are shown in Table 1. The structural data provided in Table 1 indicate that various bond lengths are found to be almost same at HF/B3LYP/6-311++G(d,p) level. However, the bond length and bond angle by HF method is smaller than by B3LYP method. Detailed description of vibrational modes can be given by means of normal coordinate analysis. The internal coordinates describe the position of the atoms in terms of distance, angle and dihedral angle with respect to origin of the atom. The symmetry coordinates are constructed using the set of internal coordinates. In this study, the full sets of 42 standard internal coordinates (containing 12 redundancies) for p-chlorofluorobenzene were defined as given in Table 2. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combination of internal coordinates following the recommendations of Fogarasi et al., [17,18] and is summarized in Table 3.

3.2. Vibrational assignments

The molecule P-CFB belongs to C_s point group symmetry, and it consists of 12 atoms its leads to 30 fundamental normal modes of vibrations are distributed among the symmetry species as:

$$\Gamma_{3N-6} = 21A'(\text{in-plane}) + 9A''(\text{out-of-plane})$$

The detailed vibrational assignments of fundamentals often made on the basis of the unscaled frequencies by assuming the observed frequencies, so that they are in the same order as the calculated ones. Then for an easier comparison of the observed values, the calculated frequencies are scaled by the scale to less than 1, to minimize the overall deviation. Therefore, we have used the different scaling factor values for HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods. The result indicates that the B3LYP calculations approximate the observed fundamental frequencies much better than the HF results. The detailed vibrational assignment of fundamental modes of P-CFB along with the calculated IR and Raman frequencies and normal mode descriptions are reported in Table 4. The observed FTIR and FT-Raman spectra are shown in Fig. 2 and 3 respectively.

3.2.1. C-H Vibrations

The aromatic C-H stretching vibrations are normally found between 3100-3000 cm^{-1} [19]. The C-H stretching vibrations of P-CFB are observed at 3100, 3071, 3050 cm^{-1} in IR spectrum and 3076 cm^{-1} in Raman spectrum. The assigned values of C-H stretching vibrations are showed good agreement with the available literature data [20]. The C-H in plane bending vibrations are coupled with ring C-C stretching modes. The C-H in plane bending vibration of P-CFB appears at 1285, 1230, 1152 cm^{-1} in IR spectrum and 1287, 1236, 1153 cm^{-1} in Raman spectrum and C-H out of plane bending vibrations are observed at 635 cm^{-1} in IR spectrum and 813, 627, 370 cm^{-1} in Raman spectrum.

3.2.2. C-Cl Vibrations

The vibration belonging to bond between the ring and the halogen atom was discussed here, since mixing of vibrations are possible due to lowering of molecular symmetry and the presence of heavy atoms on the periphery of molecule. The C-Cl absorption is obtained

normally between 850 and 550 cm^{-1} [21]. The C-Cl stretching mode vibration is found at 687 cm^{-1} in Raman spectrum. The in-plane bending vibration is observed at 460 cm^{-1} in Raman spectrum. The C-Cl out of plane bending vibration is observed at 320 cm^{-1} in Raman spectrum. These are good agreement with the literature data [22].

3.2.3. C-F Vibrations

The C-F stretching mode vibrations are normally found between 1400-1000 cm^{-1} [23]. In the title molecule C-F stretching vibration found at 1405 cm^{-1} in IR spectrum. The C-F in-plane bending vibration mode for the mono fluorinated benzene normally assigned at 250-350 cm^{-1} [24]. The C-F in-plane bending vibration of P-CFB is appeared at 502 cm^{-1} in IR spectrum and 505 cm^{-1} in Raman spectrum. The C-F out of plane bending vibration observed at 272 cm^{-1} in Raman spectrum. The reported values are good agreement with literature data [25].

3.2.4. C-C Vibrations

The bands between 1430 and 1650 cm^{-1} in the aromatic and the heteroaromatic compounds are assigned to C-C stretching vibrations [26]. Accordingly, In the present investigation, the C-C stretching vibrations of P-CFB is observed at 1637, 1596, 1485 cm^{-1} in FT-IR and at 1590, 1490, 1380 cm^{-1} in FT-Raman spectrum. The C-C in plane bending vibrations are observed at 1430, 1085, 1020 cm^{-1} in IR spectrum and 1087 cm^{-1} in Raman spectrum. The C-C out of plane bending vibrations is observed at 830 cm^{-1} in IR spectrum and 1010, 838 cm^{-1} in Raman spectrum.

4. HOMO-LUMO Analysis

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital energy (LUMO) are very important parameters for quantum chemistry. The frontier molecular orbital can provide a reasonable qualitative interaction of the exciting properties and the ability of the electron or hole-transport [27]. HOMO, which can be thought the outermost orbital containing electrons, tends to act as electron donor. On the other hand, LUMO can be thought the innermost orbital containing free places to accept electrons [28].

The HOMO and LUMO energy calculated by HF method with 6-311++G(d,p) basis set. The calculated values are shown in Table 5. This electronic transition absorption corresponds to the transition from the ground to the first excited state and is mainly described by an electron excitation from the HOMO to the LUMO. The atomic compositions of the frontier molecular orbital are shown in Fig 4.

An electronic system with a larger HOMO-LUMO gap should be less reactive than one having a smaller gap [29]. The HOMO-LUMO gap value of the title compound is 0.22185 a.u. The electron movement between these orbitals could easily occur so that we observe a peak value around in the UV-VIS spectrum, which is shown in Table 6. The calculated absorption spectrum of the title compound showed a high energy band gap, with a peak at 208.08 nm and a low energy band at 206.05 nm. The excited state lies at 5.1642 eV (240.08 nm). Electronic transition from the HOMO-LUMO are mainly derived from the electronic transition of $\pi \rightarrow \pi^*$. This is also confirmed by analysing the UV-Visible spectrum. The UV-Visible spectrum is shown in Fig 5. The computed excitation energies, oscillator strength and electronic transition configuration are shown in Table 6.

5. First Hyperpolarizability

The first hyperpolarizability (β_0) of this novel molecular system and related properties (β_0, α_0 , and $\Delta\alpha$) of P-CFB are calculated using B3LYP/6-311++G(d,p) basis set, based on finite field approach. First hyperpolarizability is third rank that can be described by 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [30]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3x3x3 matrices in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous of the expansion becomes

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \dots \quad (2)$$

Where E^0 is the energy of unperturbed molecules, F_α is the field at the origin μ_α , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the

components of dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moment μ , the mean polarizability α_0 , the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyperpolarizability β_0 using the x, y, z components they are defined as:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}}$$

$$\alpha_0 = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta\alpha = \frac{1}{2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2 \right]^{\frac{1}{2}}$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \text{ And}$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{zzx}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yyz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Since the value of mean polarizabilities and hyperpolarizability of the GAUSSIAN 09W output are reported in atomic units (a.u) and therefore, the calculated values have been converted into electrostatic units (esu) ($1 \text{ a.u} = 8.3693 \times 10^{-33} \text{ esu}$) [31]. Theoretically calculated values of first hyperpolarizability and dipole moment are $0.171332 \times 10^{-30} \text{ esu}$ and -0.0365101 Debye . The reference value of urea is $0.37289 \times 10^{-33} \text{ esu}$. The first hyperpolarizability of the title compound is 0.45 times greater than that of urea.

6. Atomic charges

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation [32] to molecular system, because atomic charge affect dipole moment, polarizability, electronic structure and much more properties of molecular systems. The charge distributions calculated by Mulliken method for the equilibrium geometry of P-CFB are listed in Table 7. The corresponding, Mulliken plots are shown in Fig 6. Mulliken atomic charges p-chlorofluorobenzene have been calculated using B3LYP and HF method at 6-311++G(d,p) basis set. The calculated charges by HF are relatively lesser than B3LYP method. The atomic charge of C_4 in p-chlorofluorobenzene is 0.641693 and 0.606013 using 6-311++G(d,p) level of B3LYP and HF

methods respectively. The maximum atomic charge is obtained for C₄ when compare with other atoms.

6. NBO analysis

The natural bond orbital (NBO) calculations were performed using NBO 5.0 [33] program as implemented in the Gaussian 09 package at the DFT/6-311++G(d,p) level in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the delocalization or hyper conjugation.

The hyper conjugative interaction energy was deduced from the second order perturbation approach [34].

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i} \dots\dots\dots (3)$$

Where q_i is the donor orbital occupancy i and j are diagonal elements orbital energies and $F(i,j)$ is the off diagonal NBO fock matrix element. The larger $E^{(2)}$ value the more intensive is the interaction between electron donors and acceptors, i.e., the more donation tendency from electron donors to electron acceptor and the greater extent of conjugation of the whole system [35].

Delocalization of electron density between occupied lewis type (bond or lone pair) NBO orbital and formally unoccupied (antibond or Rydberg) non-lewis NBO orbital corresponds to a stabilizing donor-acceptor interaction.

The second-order perturbation theory analysis of fock matrix in NBO basis of P-CFB shows that strong intramolecular hyperconjugative interactions of π - electrons, which are depicted in the Table 8. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro-disturbance theory are reported.

The intramolecular interactions due to the orbital overlap of π (C₁-C₆) with π^* (C₄-C₅), resulting in high stabilization energy of 21.92 kcal/mol in P-CFB. The charge transfer from the lone pair of F₇ to anti-bonding C₁-C₆ amounts to stabilization energy of 19.00 kcal/mol in p-chlorofluorobenzene. The strong stabilization energy occurs 259.96 kcal/mol due to π^* (C₄-C₅) \rightarrow π^* (C₂-C₃) interaction. This highest

interaction around the ring can induce the large bioactivity of the molecule.

7. Other molecular properties

Several thermodynamic properties like zero point vibrational energy, rotational constants, rotational temperature, thermal energy, entropy, molar capacity at constant volume have been obtained by B3LYP and HF methods using 6-311++G(d,p) basis set. The obtained values are presented in Table 9.

IV. CONCLUSION

The optimized geometries, harmonic vibrational wavenumbers and intensities of vibrational bands of p-chlorofluorobenzene have been carried out using the HF and B3LYP methods using the standard 6-311++G(d,p) basis set. This DFT based quantum mechanical approach provides the most reliable, theoretical information on the vibrational properties of p-chlorofluorobenzene. The difference between the observed and scaled wavenumber 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. Therefore, the assignments made at higher levels of theory with only reasonable deviations from the experimental values seem to be correct. The TED calculation regarding the normal modes of vibration provides a strong support for the frequency assignment. The lowering of HOMO-LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The thermodynamic, first-order hyperpolarizabilities and total dipole moment properties of the molecule have been calculated. The NBO analysis reveals that hyper conjugative interaction and stabilization of the molecule.

V. REFERENCES

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Table 1

Optimized geometrical parameters of p-chlorofluorobenzene computed at HF and B3LYP method with 6-311++G(d,p) basis set.

	HF	B3LYP	Experimental values ^a
Bond Length (Å)			
C1-C2	1.3749	1.3864	1.406
C1-C6	1.3749	1.3864	1.390
C1-F7	1.3731	1.405	
C2-C3	1.3877	1.3988	1.399
C2-H8	1.0689	1.0796	
C3-C4	1.3805	1.3918	1.399
C3-H9	1.0685	1.0794	
C4-C5	1.3804	1.3918	1.392
C4-Cl10	1.8058	1.8271	
C5-C6	1.3877	1.3988	1.398
C5-H11	1.0685	1.0794	
C6-H12	1.0689	1.0796	
Bond Angle (°)			
C2-C1-C6	123.017	123.2134	120.1
C2-C1-F7	118.4903	118.3923	
C6-C1-F7	118.4928	118.3942	
C1-C2-C3	118.4301	118.3329	118.6
C1-C2-H8	120.1618	120.2928	
C3-C2-H8	121.4081	121.3743	
C2-C3-C4	119.1034	118.9866	124.5
C2-C3-H9	120.4828	120.5138	
C4-C3-H9	120.4138	120.4996	
C3-C4-C5	121.9163	122.1478	122.3
C3-C4-Cl10	119.0411	118.926	
C5-C4-Cl10	119.0427	118.9262	
C4-C5-C6	119.1036	118.9865	118.3
C4-C5-H11	120.4157	120.5009	
C6-C5-H11	120.4807	120.5126	
C1-C6-C5	118.4297	118.3328	120.1
C1-C6-H12	120.1644	120.2946	
C5-C6-H12	121.4059	121.3726	

For numbering of atoms refer Fig.1

^aFor Ref. No.38.

Table 2:

Definition of internal coordinates of p-chlorofluorobenzene.

No (i)	Symbol	Type	Definition ^a
<i>Stretching</i>			
1 – 4	r_i	C – H	C2-H8, C3-H9, C5-H11, C6-H12
5	R_i	C – F	C1-F7
6	q_i	C – Cl	C4-Cl10
7 – 12	Q_i	C – C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1
<i>In - plane bending</i>			
13 – 18	α_i	Ring	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
19 – 26	β_i	CCH	C1-C2-H8, C3-C2-H8, C2-C3-H9, C4-C3-H9, C4-C5-H11, C6-C5-H11, C5-C6-H12, C1-C6-H12
27 – 28	δ_i	CCl	C3-C4-Cl10, C5-C4-Cl10
29 – 30	ρ_i	CCF	C2-C1-F7, C6-C1-F7
<i>Out - of - plane bending</i>			
31 – 34	ω_i	C – H	H8-C2-C1-C3, H9-C3-C2-C4, H11-C5-C4-C6, H12-C6-C1-C5
35	ψ_i	C – Cl	Cl10-C4-C3-C5
36	σ_i	C – F	F7-C1-C2-C6
<i>Torsion</i>			
37 – 42	τ_i	tring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3

^aFor numbering of atoms refer Fig.1

Table 3 : Definition of local symmetry coordinates of p-chlorofluorobenzene.

No (i)	Type ^a	Definition ^b
1 – 4	CH	r_1, r_2, r_3, r_4
5	CF	R_5
6	CCl	q_6
7 – 12	CC	$Q_7, Q_8, Q_9, Q_{10}, Q_{11}, Q_{12}$
13	R trigd	$(\alpha_{13} - \alpha_{14} + \alpha_{15} - \alpha_{16} + \alpha_{17} - \alpha_{18})/\sqrt{6}$
14	R symd	$(-\alpha_{13} - \alpha_{14} + 2\alpha_{15} - \alpha_{16} - \alpha_{17} + 2\alpha_{18})/\sqrt{12}$
15	R asymd	$(\alpha_{13} - \alpha_{14} + \alpha_{16} - \alpha_{17})/\sqrt{2}$
16 – 19	b CH	$(\beta_{19} - \beta_{20})/\sqrt{2}, (\beta_{21} - \beta_{22})/\sqrt{2}, (\beta_{23} - \beta_{24})/\sqrt{2},$ $(\beta_{25} - \beta_{26})/\sqrt{2}$
20	b Cl	$(\delta_{27} - \delta_{28})/\sqrt{2}$
21	b CF	$(\rho_{29} - \rho_{30})/\sqrt{2}$
22 – 25	ω CH	$\omega_{31}, \omega_{32}, \omega_{33}, \omega_{34}$
26	ψ CCl	ψ_{35}
27	σ CF	σ_{36}
28	tR trigd	$(\tau_{37} - \tau_{38} + \tau_{39} - \tau_{40} + \tau_{41} - \tau_{42})/\sqrt{6}$
29	tR symd	$(\tau_{37} - \tau_{39} + \tau_{40} - \tau_{42})/\sqrt{2}$
30	tR asymd	$(-\tau_{37} + 2\tau_{38} - \tau_{39} - \tau_{40} + 2\tau_{41} - \tau_{42})/\sqrt{12}$

^aThese symbol are used for description of normal modes by TED in Table 4.

^bThe internal coordinates used here are defined in Table 2.

Table 4

The observed (FTIR and FT-Raman) and calculated (Unscaled and Scaled) frequencies, IR intensity, Raman intensity and probable assignments (Characterized by TED) of p-chlorofluorobenzene using B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) methods and basis set.

Abbreviations: v – stretching; b – bending; g – out-of-plane bending; t – torsion; R – ring; trigd – trigonal deformation; symd – symmetric deformation; asymd – antisymmetric deformation.

S. No.	Symmetry Species C.	Observed Frequency (cm ⁻¹)		B3LYP/6-311++G(d,p)					HF/6-311++G(d,p)				Assignment (TED %)	
		FTIR	FT-Raman	Calculated Frequency (cm ⁻¹)		Force constant	IR intensity	Raman intensity	Calculated Frequency (cm ⁻¹)		Force constant	IR intensity		Raman intensity
				Unscaled	Scaled				Unscaled	Scaled				
1	A	3100	-	3220	3104	6.7039	0.5520	274.3160	3385	3109	7.4204	0.8048	249.0203	vCH(99)
2	A	-	3076	3218	3081	6.6877	1.5290	8.2238	3383	3083	7.4048	2.2223	4.8833	vCH(98)
3	A	3071	-	3204	3075	6.5912	0.1669	93.4003	3367	3082	7.2972	0.0768	88.2800	vCH(99)
4	A	3050	-	3202	3054	6.5875	2.0296	2.4472	3366	3060	7.2870	1.7827	3.1538	vCH(99)
5	A	1750	-	1636	1755	11.6767	1.7182	11.2527	1776	1762	13.3752	3.3699	15.7221	vCC(79), bCH(11)
6	A	1637	-	1618	1642	8.5309	3.7961	9.4183	1774	1648	10.1830	7.8932	8.2672	vCC(51), bCH(10), Rsymd(8)
7	A	1596	-	1525	1600	2.9997	135.3574	1.3012	1656	1607	3.6586	152.8987	2.0018	vCC(50), bCH(21)
8	A	-	1590	1430	1595	3.3222	1.2144	0.1213	1542	1598	3.6883	2.1126	0.1087	vCC(52), bCH(15), Rsymd(9)
9	A	1485	1490	1341	1494	1.3556	1.5165	0.8989	1447	1499	1.5626	1.6197	0.4503	vCC(85), bCH(12)
10	A	-	1380	1329	1383	10.5158	1.5676	1.2097	1325	1389	3.9257	105.2779	10.9314	vCC(49), bCH(13), Rtrigd(8)
11	A	1430	-	1214	1436	1.6882	48.8388	3.7540	1303	1442	6.6034	4.2218	2.2300	Rtrigd(65), vCF(24)
12	A	1405	-	1187	1410	1.4706	58.5936	15.7328	1285	1417	1.1761	15.5649	6.5856	vCF(78)
13	A	1285	1287	1129	1295	1.0246	8.2625	0.0978	1199	1298	1.2964	3.9021	0.6327	b CH (76), v CC (14)
14	A	-	1236	1087	1243	2.2377	50.2493	13.3504	1174	1250	2.7400	46.6349	12.9628	b CH (78), v CCl (12)
15	A	1230	-	1043	1238	2.2302	26.7624	1.0689	1126	1243	1.0332	0.0000	0.0018	b CH (72), v CC (13)
16	A	1152	1153	994	1160	0.7943	0.0000	0.0176	1121	1165	2.4786	26.9145	1.2664	b CH (60)
17	A	1085	1087	961	1094	0.7012	0.1367	0.1154	1085	1099	0.9513	0.2480	0.0257	Rsymd (62), v CCl (14)
18	A	1020	-	858	1028	0.6638	90.1218	0.5066	967	1034	0.8504	106.0430	0.5175	Rsymd (59), v CC (19)
19	A	-	1010	843	1017	0.5204	0.0000	0.0244	954	1024	0.6670	0.0000	0.0206	tRtrigd (57), g CCl (10)
20	A	-	838	815	847	2.6962	2.1410	30.5419	879	853	3.0665	1.7363	36.2842	tRsymd (59), g CF (12)
21	A	830	-	706	838	1.2873	0.1615	0.1521	790	844	1.3737	1.4339	0.2057	tRsymd (58), g CH (15)
22	A	-	813	653	824	1.8119	0.0477	6.4457	704	829	2.1033	0.0707	6.9775	g CH (48), b CCl (12)
23	A	-	687	609	699	1.8837	56.7709	0.7780	660	704	2.1597	56.1195	2.3692	v CCl (85)
24	A	635	-	511	646	0.4178	20.5276	0.7174	572	653	0.5087	23.5192	0.8238	g CH (50), tRsymd (12)
25	A	-	627	436	637	0.3284	0.0000	0.0012	480	646	0.3871	0.0000	0.0001	g CH (54), tRsymd (10)
26	A	502	505	407	516	0.5200	2.4047	0.7532	445	523	0.6224	3.5869	0.4080	b CF (55), Rsymd (11)
27	A	-	460	363	472	1.5149	0.9459	13.1395	392	478	1.7515	0.7172	15.3650	b CCl (58), Rsymd (14)
28	A	-	370	328	381	0.4749	1.6101	0.8642	366	386	0.5757	2.3649	0.9144	g CH (50), tRtrigd (11)
29	A	-	320	251	332	0.3704	2.7641	1.1769	272	338	0.4307	3.7852	1.2447	g CCl (54), b CH (17)
30	A	-	272	124	283	0.1067	1.9523	0.0785	139	290	0.1337	2.5136	0.1455	g CF (55), b CH (14)

Table 5:

HOMO-LUMO energy gap of p-chlorofluorobenzene using B3LYP/6-311++G(d,p) method and basis set.

Parameter	Values (a.u)
HOMO energy	-0.27024
LUMO energy	-0.04839
HOMO – LUMO energy gap ΔE	0.22185

Table 6:

The computed excitation energies, oscillator strength and electronic transition configuration of p-chlorofluorobenzene.

Excited state	EE (eV)/ wavelength (nm)	F	Configuration	CI expansion coefficient
1	5.1642/240.08	0.0161	32 → 35 33 → 34	-0.33575 0.62153
2	5.9359/208.87	0.1003	32 → 34 33 → 35	0.30096 0.63377
3	6.0172/206.05	0.0006	33 → 36 33 → 38	0.67755 -0.15901

Table 7:

Atom number	Atomic charges	
	B3LYP	HF
C1	-0.455701	-0.554014
C2	-0.133070	-0.071075
C3	-0.687802	-0.780802
C4	0.641693	0.606013
C5	-0.687096	-0.779788
C6	-0.132314	-0.070248
F7	-0.331552	-0.399434
H8	0.314996	0.397856
H9	0.304304	0.388725
Cl10	0.547316	0.476274
H11	0.304245	0.388663
H12	0.314980	0.397831

Table 8

Second order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intramolecular bonds of p-chlorofluorobenzene.

Donor (<i>i</i>)	type	ED/e	Acceptor (<i>j</i>)	Type	ED/e	E ⁽²⁾ (kJ mol ⁻¹) ^a	E(<i>j</i>) – E(<i>i</i>) (a.u) ^b	F(<i>i,j</i>) (a.u) ^c
C ₁ -C ₆	π	1.65978	C ₂ -C ₃	π^*	0.33519	19.88	0.29	0.068
C ₁ -C ₆	π	1.65978	C ₄ -C ₅	π^*	0.39572	21.92	0.28	0.071
C ₂ -C ₃	π	1.68225	C ₁ -C ₆	π^*	0.37805	21.26	0.27	0.068
C ₂ -C ₃	π	1.68225	C ₄ -C ₅	π^*	0.39572	19.19	0.27	0.065
C ₄ -C ₅	π	1.68373	C ₁ -C ₆	π^*	0.37805	18.48	0.28	0.065
C ₄ -C ₅	π	1.68373	C ₂ -C ₃	π^*	0.33519	20.99	0.29	0.070
F ₇	LP(3)	1.92658	C ₁ -C ₆	π^*	0.37805	19.00	0.42	0.086
Cl ₁₀	LP(3)	1.93189	C ₄ -C ₅	π^*	0.39572	12.48	0.31	0.061
C ₄ -C ₅	π^*	0.39572	C ₂ -C ₃	π^*	0.33519	259.96	0.01	0.080

^a E⁽²⁾ means energy of hyper conjugative interaction (stabilization energy).

^b Energy difference between donor and acceptor *i* and *j* NBO orbitals.

^c F(*i,j*) is the Fock matrix element between *i* and *j* NBO orbitals.

Table 9:

Thermodynamic properties for p-chlorofluorobenzene obtained by HF and B3LYP method with 311++G(d,p) basis set.

6-

Values

Parameters	B3LYP	HF
Zero-point vibrational energy (kcal mol ⁻¹)	51.82891	55.68314
Rotational Constants (GHz)		
A	5.62413	5.73056
B	0.91812	0.93815
C	0.78928	0.80617
Rotational Temperature (kelvin)		
D	0.26992	0.27502
E	0.04406	0.04502
F	0.03788	0.03869
Thermal Energy (kcal mol⁻¹)		
Total	55.821	59.394
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	54.044	57.617
Entropy (cal mol⁻¹ kelvin)		
Total	80.990	79.317
Translational	40.500	40.500
Rotational	28.758	28.696
Vibrational	11.733	10.121
Molar capacity at constant volume (cal mol⁻¹ k⁻¹)		
Total	24.018	22.078
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	18.056	16.117

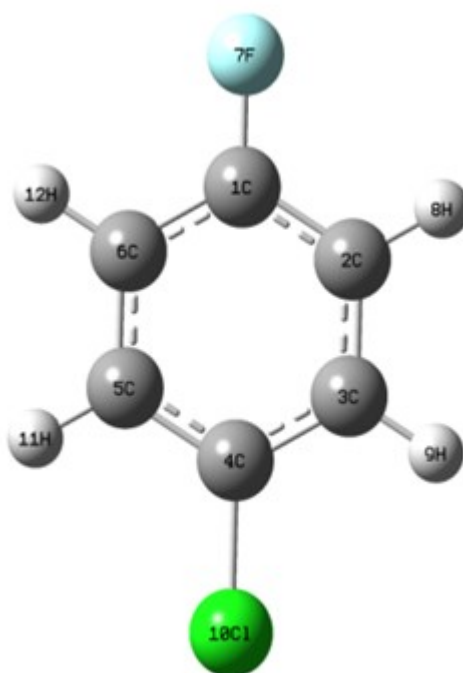


Figure 1. Optimized molecular structure of p-chlorofluorobenzene

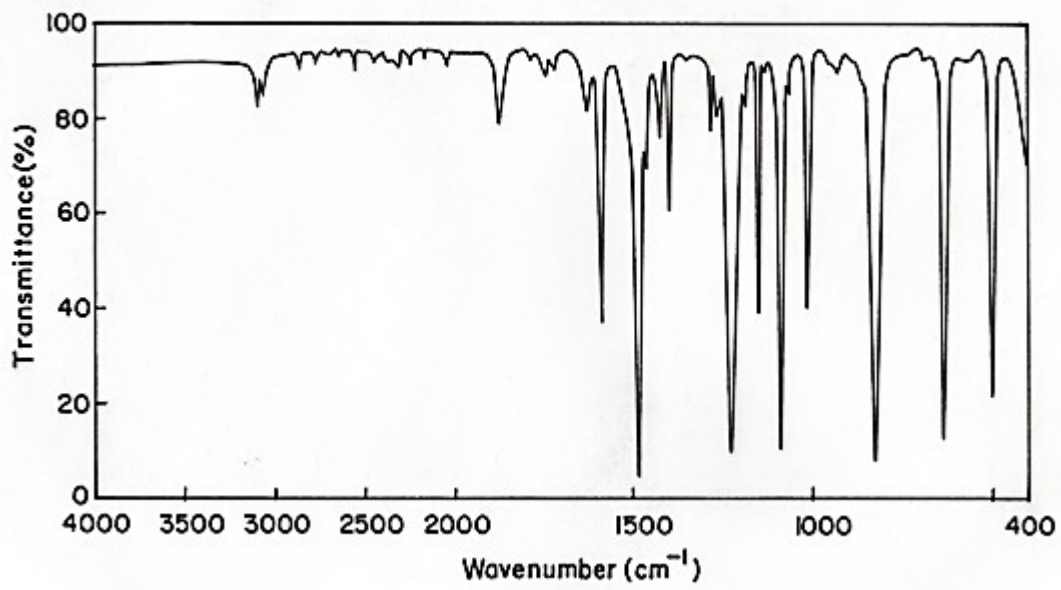


Figure 2. FTIR Spectrum of p-chlorofluorobenzene

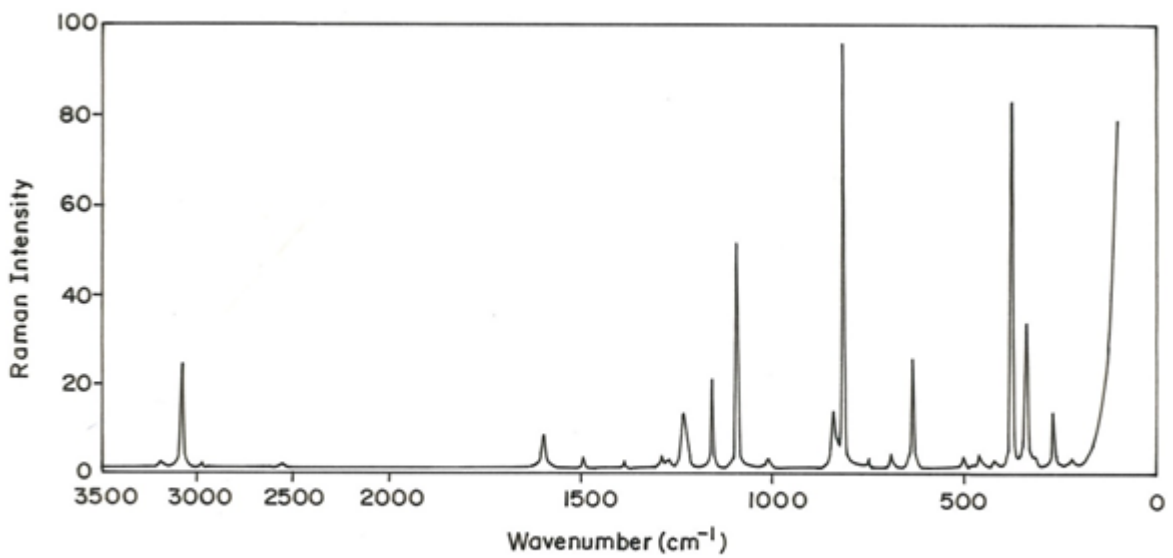


Figure 3. FT-Raman Spectrum of p-chlorofluorobenzene

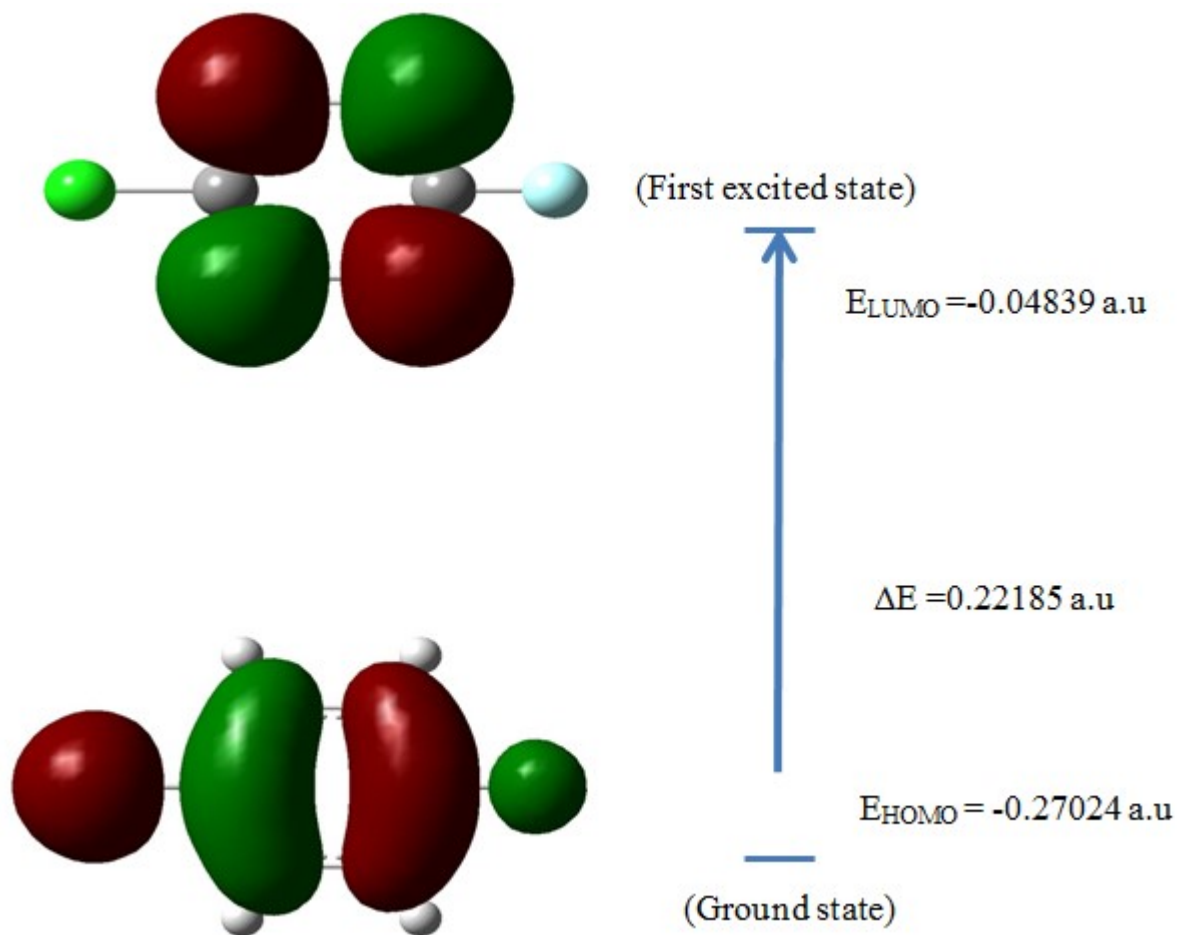


Figure 4. The frontier molecular orbitals for p-chlorofluorobenzene

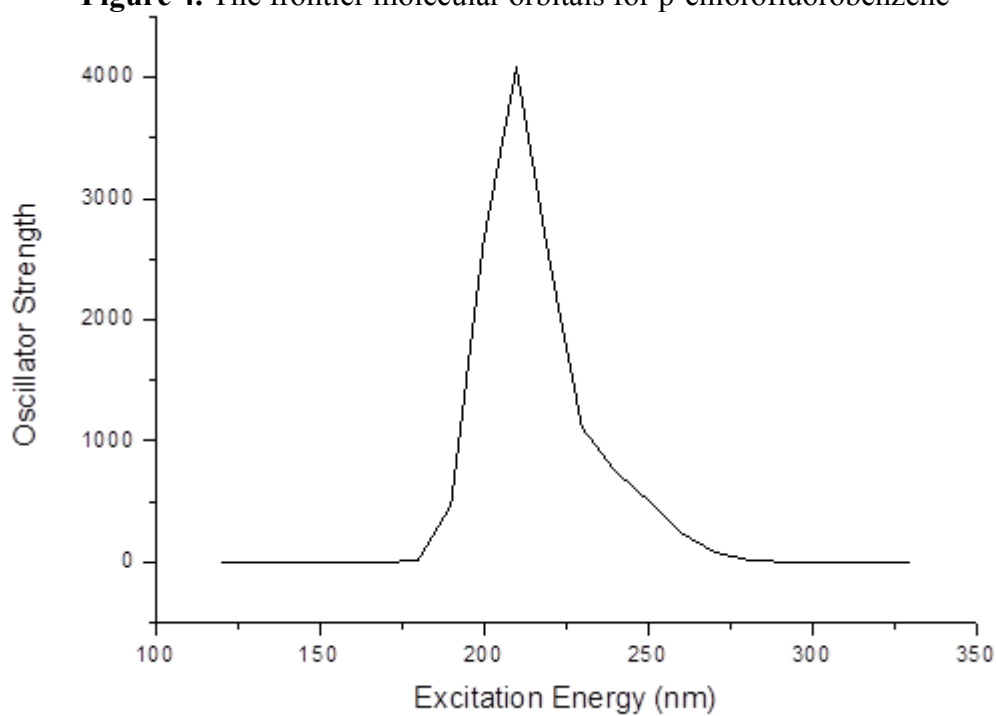


Figure 5. UV-VIS Spectrum of p-chlorofluorobenzene

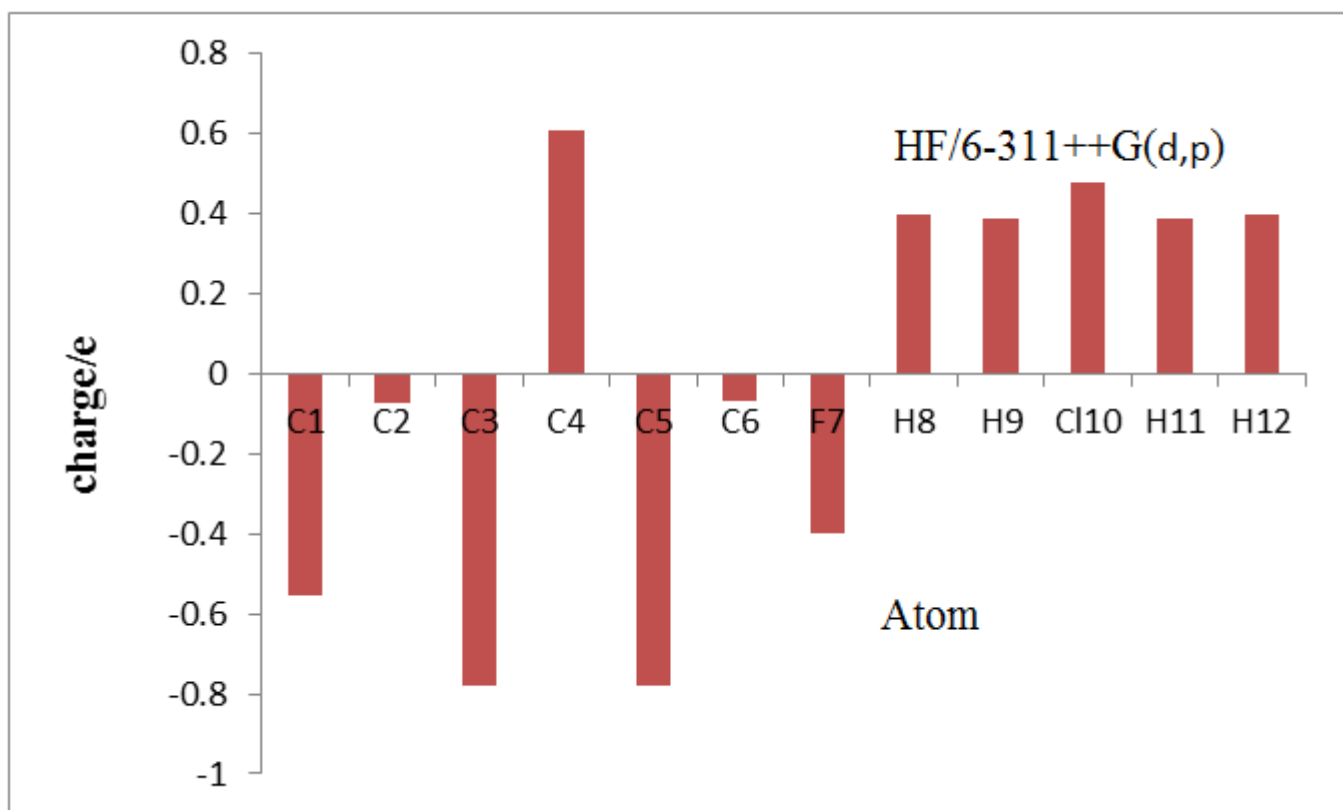
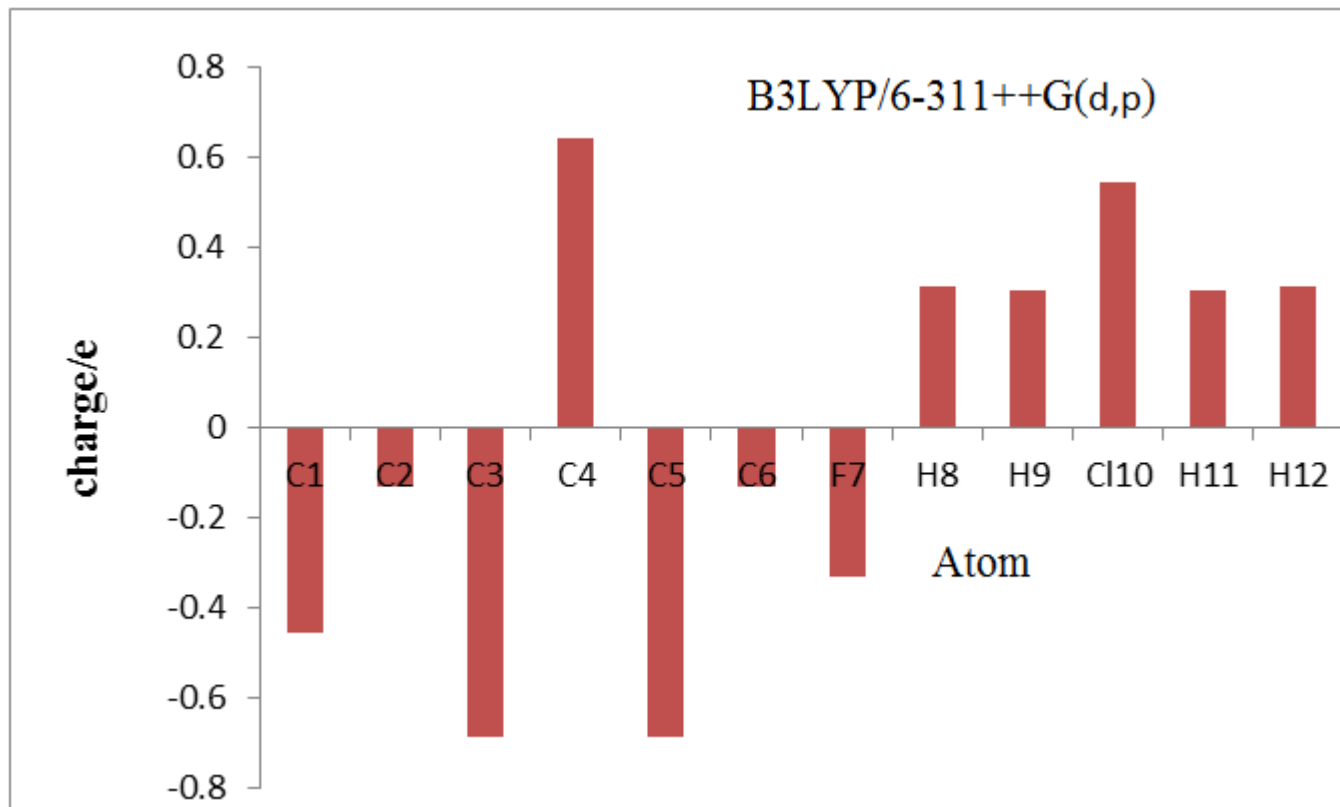


Figure 6. Mulliken charges of p-chlorofluorobenzene