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# QUANTUM CHEMICAL INVESTIGATIONS ON BENZENE DERIVATIVE: A DFT STUDY

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**ABSTRACT**

The FT-IR and FT-Raman spectra of Hexaflourobenzene were recorded in the condensed State. Normal co-ordinate calculations were performed with the DFT force field were corrected by a recommended set of scaling factors yielding fairly good agreement between observed and calculated frequencies. The geometry optimization and energy calculations of Hexaflourobenzene were carried out using DFT (B3LYP) methods with 6-31+G* and 6-311+G** basis sets.The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming $C_s$ point group symmetry. The transformation of force field from Cartesian to internal coordinates, the scaling, the subsequent normal coordinate analysis (NCA) including the least-square fit refinement of the scale factors, calculation of potential energy distribution (PED) and prediction of IR and Raman intensities were done on a PC with the version V7.0 of the Molvib program written by Sundius. The total energies obtained for these were found to be -827.59697782 a.u.

**Keywords:** Quantum Chemical Calculations, DFT and Molvib V7.0



## INTRODUCTION

Hexafluorobenzene used in the manufacture of azo dyes, fungicides, rubber chemicals and explosives, and as an algicide in coolant water of air conditioning systems. It is an biological importance exhibiting compound used in tumor studies. So the vibration studies of these molecules would be helpful in understanding the various types of bonding and normal modes of vibration involved in this system. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational wave numbers than the conventional *ab initio* restricted Hartree-Fock (RHF) and Moller-plesset second order perturbation theory (MP2) calculation to understand the structures and the fundamental vibrational wave numbers. In this work DFT calculations are carried out to present a full description of the vibrational spectra of Hexafluorobenzene, especially the assignment of the vibrational modes, using B3LYP/6-31G**, to obtain the geometrics, vibrational wave numbers, IR intensities and Raman activities[1-6].

## EXPERIMENTAL

The fine samples of HFB were obtained from Alfa Aesar company and were used as such for the spectral measurements. The Fourier transform infrared spectrum of the title compounds were recorded in the region 400-4000 $cm^{-1}$ using Perkin-Elmer spectrum RXI spectrophotometer equipped with He-Ne laser source, KBr beam splitter and $LiTaO_3$ detector. The samples were prepared by pressing HFB with KBr into pellet form.

The FT Raman spectrum of HFB were recorded on a BRUCKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory in the stokes region 4000-50 $cm^{-1}$ using 1064 nm line of a Nd: YAG laser for excitation operating at 200mW power. The reported wave numbers are believed to be accurate within $\pm 1 cm^{-1}$.

**Computational Details**

Quantum chemical density functional calculations were carried out with the 1998 version of the Gaussian suite of program using the Becke3-Lee-Yang-Parr [B3LYP] functional supplemented with the standard 6-31G** basis set[7] (referred as DFT calculations). The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming $C_S$ point group symmetry. The theoretical DFT force field was transformed from Cartesian into local internal coordinates and then scaled empirically according to the SQM procedure[8].

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities ($S_i$) calculated by the Gaussian 98 program and adjusted during the scaling procedure with Molvib were converted to relative Raman intensities ($I_i$) using the following relationship derived form the basic theory of Raman scattering.

$$I_i = \frac{f(\upsilon_o - \upsilon_i)^4 S_i}{\upsilon_i \left[1 - \exp\left(\frac{-hc\,\upsilon_i}{KT}\right)\right]}$$

where $\upsilon_0$ is the exciting wave number (in $cm^{-1}$ units), $\upsilon_i$ is the vibrational wave number of the $i^{th}$ normal mode, h, c and k are the universal constants, and f is the suitably chosen common scaling factor for all peak intensities.

## RESULTS AND DISCUSSION

**Molecular geometry and Theoretical spectrum simulation**

The optimized molecular structure of HFB was shown in Fig.-1. The global minimum energy obtained by the DFT structure optimization was presented in Table-1. The title compound belong to $C_S$ point group symmetry and their 30 normal modes are distributed between two symmetry species as, $\Gamma_{3N-6}$= 21 A' (in-plane) + 9 A″ (out-of-plane). Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 42 standard internal coordinates containing 12 redundancies were defined as given in Table-2.

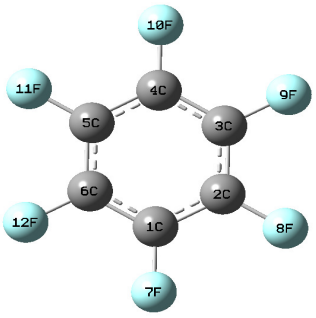


Fig.-1: The optimized molecular structure of Hexafluorobenzene

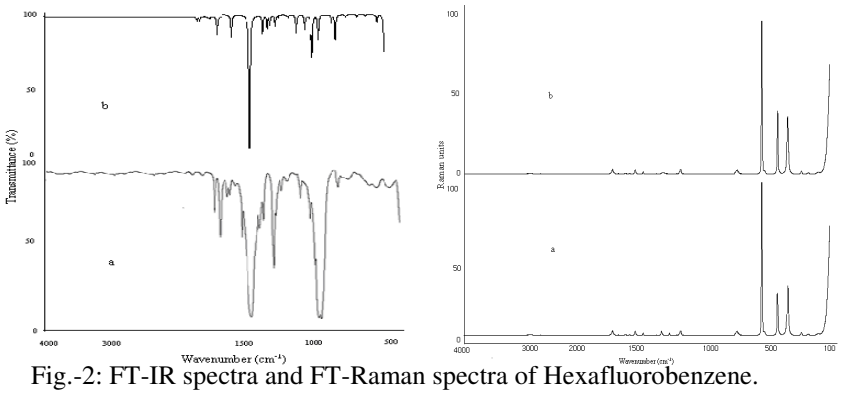


Fig.-2: FT-IR spectra and FT-Raman spectra of Hexafluorobenzene.
(a) Observed (b) Calculated with B3LYP/6-311+G**

From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et. al. are summarized in Table 3. The global minimum energy obtained by the DFT structure optimization for HFB are calculated as -827.596977 KJ/mol.

Fluorine is highly electronegative and wishes to obtain additional electron density[9]. The calculated significant alteration of C-C bond lengths is good agreement with experimental structure of HFB.For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of HFB are presented in Fig.-2 and Fig.-3.

**SQM analysis and assignments**

The unscaled wave numbers obtained by B3LYP method are larger than the experimental values of HFB. In order to reproduce the calculated wave numbers close to the observed wave numbers, a selective scaling procedure was employed. The calculated wave numbers were scaled using a set of transferable scale factors recommended by Rauhut and Pulay. The SQM treatment improved the agreement between the experimental and the scaled wave numbers for the title compound. The calculated vibrational wave numbers of HFB are listed in Table 6 with the RMS deviations from experimental wave numbers. Clearly the best agreement with experiment is achieved when the theoretical force field is scaled[10].

**C-C vibrations**

There are six equivalent C-C bonds in HFB and consequently there will be six C-C stretching vibrations. In addition, there are several in-plane and out-of-plane bending vibrations of the ring carbons. However, due to high symmetry of HFB, many modes of vibrations are infrared inactive. In general the bands around 1400 to 1700cm$^{-1}$ in HFB derivatives are assigned to skeletal stretching C-C bands.

Table-1: Total energies of Hexafluorobenzene, calculated at DFT (B3LYP)/6-31G* and (B3LYP)/6-311+G** level

| Method | Energies (Hartrees) |
|---|---|
| 6-31G* | -827.185639 |
| 6-311+G** | -827.59697782 |

Table-2: Definition of internal coordinates of Hexafluorobenzene

| No(i) | Symbol | Type | Definition |
|---|---|---|---|
| Streching<br>1 - 6 | $r_i$ | C-F | C1-F7,C2-F8,C3-F9,C4-F10,C5-F11,C6-F12 |
| 7 - 12 | $R_i$ | C-C | C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1 |
| Bending<br>13 - 24 | $\beta_i$ | C-C-F | C6-C1-F7,C2-C1-F7,C1-C2-F8,C3-C2-F8,<br>C2-C3-F9,C4-C3-F9,C3-C4-F10,C5-C4-F10,<br>C4-C5-F11,C6-C5-F11,C5-C6-F12,C1-C6-F12. |
| 25 - 30 | $\alpha_i$ | Bring | C1-C2-C3, C2-C3-C4,C3-C4-C5,<br>C4-C5-C6,C5-C6-C1,C6-C1-C2 |
| Out-of-plane bending<br>31 - 36 | $\omega_i$ | ωC-F | F7-C1-C2-C6,F8-C2-C3-C1,F9-C3-C2-C4,<br>F10-C4-C3-C5,F11-C5-C4-C6,F12-C6-C5-C1 |
| Torison<br>37 - 42 | $\tau_i$ | Tring | C1-C2-C3-C4,C2-C3-C4-C5,<br>C3-C4-C5-C6,C4-C5-C6-C1,<br>C5-C6-C1-C2,C6-C1-C2-C3 |

*for numbering of atom refer Fig.-1

The bands observed at 1334,1577,1683 and 1690cm$^{-1}$ of HFB are identified as C-C stretching vibrations. The theoretically scaled C-C stretching vibrations by B3LYP/6-311++G(d,p) are at 1326, 1564,1686 and 1687cm$^{-1}$ shows excellent agreement with recorded spectral data. The C-C aromatic stretch, known as semicircle stretching, predicted at 1563cm$^{-1}$ is also in excellent agreement with experimental observations of 1560cm$^{-1}$ in FT-Raman spectra. As the energies of these vibrations are very close, there is

an appreciable interaction between these vibrations and consequently their energies will be modified. The ring breathing and trigonal bending modes of HFB are assigned at 1013cm$^{-1}$. The theoretically computed values at 1016cm$^{-1}$ by B3LYP/6-311++G (d, p) method coincides with experimental observations.

Table-3: Definiton of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for Hexafluorobenzene

| No.(i) | Symbol[a] | Definition[b] |
|---|---|---|
| 1 - 6 | C-F | r1,r2,r3,r4,r5,r6 |
| 7 - 12 | C-C | R7,R8,R9,R10,R11,R12 |
| 13 - 18 | C-C-F | (β13- β14) /√2,(β15- β16) /√2,(β17- β18) /√2<br>(β19- β20) /√2, (β21- β22) /√2,( β23- β24) /√2 |
| 19 | Bring | (α25-α26+α27-α28+α29-α30)/ √6 |
| 20 | Bring | (2α25-α26-α27+2α28-α29-α30) √12 |
| 21 | Bring | (α26-α27+α28-α29)/2 |
| 22 - 27 | ωC-F | ω31, ω32, ω33, ω34, ω35, ω36 |
| 28 | Tring | (τ37-τ38+τ39-τ40+τ41-τ42) √6 |
| 29 | Tring | (τ37-τ39+τ40-τ42)/2 |
| 30 | Tring | (-τ37+2τ38-τ39-τ40+2τ41-τ42) √12 |

[a]The internal coordinates used here are defined in Table-2.

**C-F vibrations**

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule. Mooney assigned vibrations of C-X group (X = F,Cl, Br, I) in the frequency range of 1129-480 cm$^{-1}$. Compounds with more than one fluorine atom exhibit very strong bands due to asymmetric and symmetric stretching mode. In FT-Raman spectrum of HFB the very strong band at 780 cm$^{-1}$ is assigned to C-F stretching vibration. The theoretical wave number of C-F stretching vibration coupled with C-C-C in-plane bending vibration 781 cm$^{-1}$ coincides very well with the experimental value[11]. The C-F in plane bending and out-of-plane bending vibrations are assigned to the Raman bands at 369 and 259 cm$^{-1}$, respectively. This is in agreement with the literature data.

## CONCLUSION

In this work, the SQM force field method based on DFT calculations at the B3LYP/6-311+G** level have been carried out to analyze the vibrational frequencies of HFB. The various modes of vibrations were unambiguously assigned based on the results of the TED output obtained from normal coordinate analysis. There is a fairly good correlation between the experimental vibrational frequencies and the calculated of harmonic ones. This theoretical information was useful in the assignment of the different fundamentals.

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