Deciphering Structural Fingerprints for Hexafluorobenzene with Density Functional Theory

G. Raja[1,*], K. Saravanan[2] and S. Sivakumar[3]

[1]Department of Chemistry, Paavai Engineering College, Namakkal-637 018, India
[2]Department of Chemistry, Thiruvalluvar Government Arts College, Rasipuram-637 401, India
[3]Department of Physics, Government Arts College (Autonomous), Salem-636 007, India

*Corresponding author: E-mail: genuineraja@gmail.com

This work deals with the vibrational spectroscopy of hexafluorobenzene by means of quantum chemical calculations. The FTIR and FT-Raman spectra were measured in the condensed state. The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT) with the standard B3LYP/6-311+G** basis set combinations and was scaled using various scale factors which yields a good agreement between observed and calculated frequencies. The vibrational spectra were interpreted with the aid of normal coordinate analysis based on scaled quantum mechanical force field. The results of the calculations were applied to simulated infrared and Raman spectra of the hexafluorobenzene, which showed excellent agreement with the observed spectra.

Key Words: Vibrational analysis, Hexafluorobenzene, DFT calculations, FTIR, FT-Raman.

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. The modern vibrational spectrometry has proven to be an exceptionally powerful technique for solving many chemistry problems. It has been extensively employed both in the study of chemical kinetics and chemical analysis. The problem of signal assignment as well as understanding the relationship between the observed spectral features and molecular structure and reactivity can be difficult. Even identification of fundamental vibrational wavenumbers often generates controversy.

Harmonic force fields derived from quantum mechanics are widely used for the calculation of wavenumbers and the modes of normal vibrations. Indeed, applying current quantum mechanical methods have opened up the way for calculating the wavenumbers and intensities of spectral bands with a minimum degree of arbitrariness (although the degree depends on the level of the quantum-mechanical treatment) and finding rational explanation for a number of chemical and physical properties of substances[1-5].

However, for a proper understanding of IR and Raman spectra, a reliable assignment of all vibrational bands is essential. Recently, computational methods based on density functional theory are becoming widely used. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the density functional theory (DFT) methods lead to the prediction of more accurate molecular structure and vibrational wavenumbers 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 wavenumbers. 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 wavenumbers, IR intensities and Raman activities.

EXPERIMENTAL

The fine samples of hexafluorobenzene were obtained from Alfa Aesear company and were used as such for the spectral measurements. The Fourier transform infrared spectrum of the title compounds were recorded in the region 4000-400 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 hexafluorobenzene with KBr into pellet form.

The FT Raman spectrum of hexafluorobenzene 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 200 mW power. The reported wave numbers are believed to be accurate within ± 1 cm^{-1}.

Computational details: Quantum chemical density functional calculations were carried out with the 1998 version of the Gaussian suite of program[6] using the Becke3-Lee-Yang-Parr [B3LYP] functional[7-9] supplemented with the standard 6-31G** basis set (referred as DFT calculations). The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming CS 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[10-12].

$$F_{ij}^{Scaled} = (C_i C_j)^{1/2} F_{ij}^{B3LYP}$$

where C_i is the scale factor of coordinate i, F_{ij}^{B3LYP} is the B3LYP/6-31G* force constant in the local internal coordinates and F_{ij}^{B3LYP} is the scaled force constant.

The transformation of force field from Cartesian to internal coordinate, the scaling[13,14], the subsequent normal coordinate analysis, calculation of potential energy distribution (PED) and IR and Raman intensities were done on a PC with the version V7.0 of the Molvib program written by Sundius[15,16]. To achieve a close agreement between the observed and calculated wavenumbers, the least square fit refinement algorithm was used. The force field obtained by this way was then used to recalculate the normal modes PEDs and the corresponding theoretically expected IR and Raman intensities to predict the full IR and Raman spectra. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 10 cm^{-1}.

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities (Si) 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[17-19].

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

where ν_0 is the exciting wavenumber (cm^{-1} units), ν_i is the vibrational wave number of the ith 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 hexafluorobenzene was shown in Fig. 1. The global minimum energy obtained by the DFT structure optimization was presented in Table-1. The optimized geometrical parameters obtained by the large (6-311+G**) basis set calculation were presented in Table-2. The optimized geometrical parameters calculated at B3LYP/6-311+G(d,p) level are slightly larger than those calculated at B3LYP/6-31G(d) level and these calculated values are well
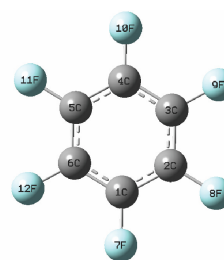

Fig. 1. Optimized molecular structure of hexafluorobenzene

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**	-827.596977

comparable with the available X-ray data on the whole[32]. It is listed Table-3. Hexafluorobenzene belongs to C$_S$ point group symmetry and their 30 normal modes are distributed between two symmetry species as, Γ_{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-4. 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.*[11,13] are summarized in Table-5. The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.

The global minimum energy obtained by the DFT structure optimization for hexafluorobenzene are calculated as -827.596977 KJ/mol. Fluorine is highly electronegative and wishes to obtain additional electron density. The calculated significant alteration of C-C bond lengths is good agreement with experimental structure of hexafluorobenzene. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of hexafluorobenzene are presented in Figs. 2 and 3.
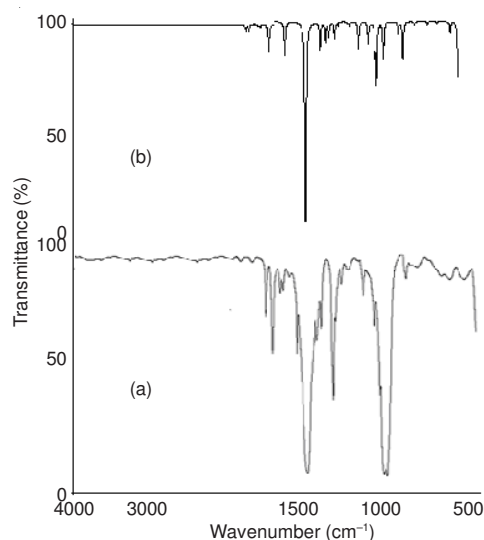

Fig. 2. FT-IR spectra of hexafluorobenzene. (a) Observed (b) calculated with B3LYP/6-311+G**

TABLE-2
OPTIMIZED GEOMETRICAL PARAMETERS OF HEXAFLUOROBENZENE
OBTAINED BY B3LYP/ 6–311+G** DENSITY FUNCTIONAL CALCULATIONS

Bond length	Value (Å)	Bond angle	Value (Å)	Dihedral angle	Value (Å)
C2-C1	1.393715	C3-C2-C1	120.008682	C4-C3-C2-C1	-0.055960
C3-C2	1.393671	C4-C3-C2	119.984347	C5-C4-C3-C2	0.031983
C4-C3	1.393786	C5-C4-C3	120.002683	C6-C1-C2-C3	0.033994
C5-C4	1.393630	C6-C1-C2	120.007819	F7-C1-C6-C5	-179.95800
C6-C1	1.393638	F7-C1-C6	120.025583	F8-C2-C1-C6	-179.98298
F7-C1	1.335638	F8-C2-C1	119.979388	F9-C3-C2-C1	-179.97701
F8-C2	1.335633	F9-C3-C2	119.999072	F10-C4-C3-C2	-179.97600
F9-C3	1.335698	F10-C4-C3	120.019694	F11-C5-C4-C3	179.99004
F10-C4	1.335649	F11-C5-C4	119.985964	F12-C6-C1-C2	-180.00000
F11-C5	1.335624	F12-C6-C1	120.025892	–	–
F12-C6	1.335700	–	–	–	–

*For numbering of atom refer Fig. 1.

TABLE-3
OPTIMIZED GEOMETRICAL AND EXPERIMENTAL
PARAMETERS OF HEXAFLUOROBENZENE

Bond length	Value (Å)	
	Exp[a]	B3LYP[b]
C2-C1	1.39	1.393715
C3-C2	1.39	1.393671
C4-C3	1.39	1.393786
C5-C4	1.39	1.393630
C6-C1	1.39	1.393638
F7-C1	1.33	1.335638
F8-C2	1.33	1.335633
F9-C3	1.33	1.335698
F10-C4	1.33	1.335649
F11-C5	1.33	1.335624
F12-C6	1.33	1.335700

[a]X-Ray. [b]This work.

Fig. 3. FT-Raman spectra of hexafluorobenzene. (a) Observed (b) calculated with B3LYP/6-311+G**

Vibrational force constant: The output files of the quantum-mechanical calculations contain the force constant matrix in Cartesian coordinates and in Hartree/Bohr^2 units. These force constants were transformed to the force fields in the internal local-symmetry coordinates. The local-symmetry coordinates, defined in terms of the internal valence coordinates following the IUPAC recommendations[23-25] are given in Table-5 for hexafluorobenzene. The force fields determined were used to calculate the vibrational potential energy distribution (PED) among the normal coordinates and listed in Table-6.

The bonding properties of hexafluorobenzene were influenced by the rearrangements of electrons during substitutions and addition reactions. The values of the stretching force constants between carbon atoms in hexafluorobenzene are found to be higher. As the atom bonded to carbon increases in mass, the factor µ increases and consequently the wavenumbers
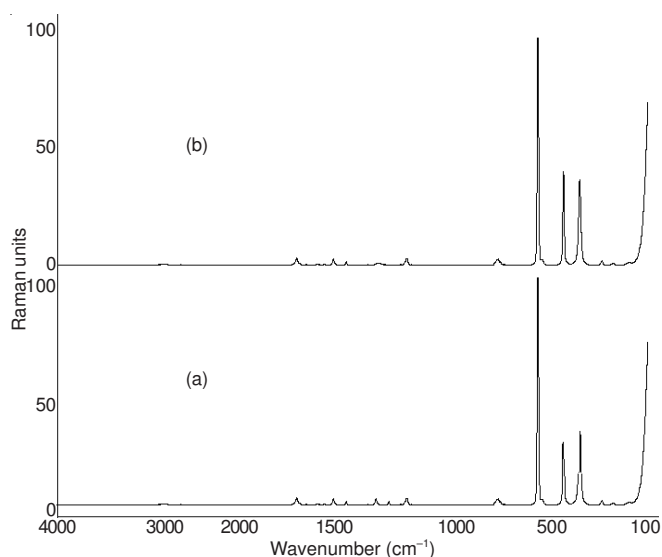
decreases, since fluorine atoms are more electronegative and hence the bonded electrons between the carbon atoms are slightly shifted towards the fluorine atoms of the hexafluoro-benzene. The values of the stretching force constants between carbon and fluorine atoms of hexafluorobenzene were found to be higher than the values of stretching force constant between carbon and hydrogen atoms.

SQM analysis and assignments: The unscaled wavenumbers obtained by B3LYP method are larger than the experimental values of hexafluorobenzene. In order to reproduce the calculated wavenumbers close to the observed wavenumbers, a selective scaling procedure was employed.

TABLE-4
DEFINITION OF INTERNAL COORDINATES OF HEXAFLUOROBENZENE

No(i)	Symbol	Type	Definition
Streching 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 13-24	β_i	C-C-F	C6-C1-F7,C2-C1-F7,C1-C2-F8,C3-C2-F8, C2-C3-F9,C4-C3-F9,C3-C4-F10,C5-C4-F10, C4-C5-F11,C6-C5-F11,C5-C6-F12,C1-C6-F12
25-30	α_i	Bring	C1-C2-C3, C2-C3-C4,C3-C4-C5, C4-C5-C6,C5-C6-C1,C6-C1-C2
Out-of-plane bending 31-36	ω_i	ωC-F	F7-C1-C2-C6,F8-C2-C3-C1,F9-C3-C2-C4,F10-C4-C3-C5,F11-C5-C4-C6,F12-C6-C5-C1
Torison 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

*For numbering of atom refer Fig. 1.

TABLE-5
DEFINITION 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	$(\beta13-\beta14)/\sqrt{2},(\beta15-\beta16)/\sqrt{2},(\beta17-\beta18)/\sqrt{2}$ $(\beta19-\beta20)/\sqrt{2}, (\beta21-\beta22)/\sqrt{2},(\beta23-\beta24)/\sqrt{2}$
19	Bring	$(\alpha25-\alpha26+\alpha27-\alpha28+\alpha29-\alpha30)/\sqrt{6}$
20	Bring	$(2\alpha25-\alpha26-\alpha27+2\alpha28-\alpha29-\alpha30)\sqrt{12}$
21	Bring	$(\alpha26-\alpha27+\alpha28-\alpha29)/2$
22-27	ωC-F	$\omega31, \omega32, \omega33, \omega34, \omega35, \omega36$
28	Tring	$(\tau37-\tau38+\tau39-\tau40+\tau41-\tau42) \sqrt{6}$
29	Tring	$(\tau37-\tau39+\tau40-\tau42)/2$
30	Tring	$(-\tau37+2\tau38-\tau39-\tau40+2\tau41-\tau42) \sqrt{12}$

[a]These symbols are used for description of the normal modes by TED in Table-5. [b]The internal coordinates used here are defined in Table-3.

The calculated wavenumbers were scaled using a set of transferable scale factors recommended by Rauhut and Pulay[14]. The SQM treatment improved the agreement between the experimental and the scaled wavenumbers for the title compound. The calculated vibrational wavenumbers of hexafluorobenzene are listed in Table-6 with the RMS deviations from experimental wavenumbers. Clearly the best agreement with experiment is achieved when the theoretical force field is scaled.

C-C vibrations: There are six equivalent C-C bonds in hexafluorobenzene 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 hexafluorobenzene, many modes of vibrations are infrared inactive. In general the bands around 1700-1400 cm^{-1} in hexafluorobenzene derivatives are assigned to skeletal stretching C-C bands. The bands observed at 1334, 1577, 1683 and 1690 cm^{-1} of hexafluorobenzene 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 1687 cm^{-1} shows excellent agreement with recorded spectral data. The C-C aromatic stretch, known as semicircle stretching, predicted at 1563 cm^{-1} is also in excellent agreement with experimental observations of 1560 cm^{-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 hexafluorobenzene are assigned at 1013 cm^{-1}. The theoretically computed values at 1016 cm^{-1} by B3LYP/6-311++G(d,p) method coincides with experimental observations. The theoretically calculated C-C-C out-of-plane and in-plane bending modes have been found to be consistent with the recorded spectral values.

TABLE-6
DETAILED ASSIGNMENTS OF FUNDAMENTAL VIBRATIONS OF HEXAFLUOROBENZENE BY NORMAL MODE ANALYSIS BASED ON SQM FORCE FIELD CALCULATION

No.	Symmetry species C_S	Observed frequency (cm^{-1})		Calculated frequency (cm^{-1}) with B3LYP/6-311+G** force field				TED (%) among type of internal coordinates[c]
		Infrared	Raman	Unscaled	Scaled	IR[a] A_i	Raman[b] I_i	
1	A'	1690	1688	1701	1687	0.000	7.472	CC(68),bring(13),CF(11),bCF(8)
2	A'	1683	–	1700	1686	0.001	7.472	CC(68),bring(13),CF(11),bCF(8)
3	A'	1577	–	1577	1564	331.454	0.000	CC(50), CF(39), bCF(12)
4	A'	–	1560	1576	1563	331.763	0.000	CC(50), CF(39), bCF(12)
5	A'	1527	–	1542	1530	0.000	1.472	CF(65),CC(35)
6	A'	1364	1350	1370	1359	0.000	0.000	CF(62), bring(38)
7	A'	1334	–	1337	1326	0.000	0.000	CC(96)
8	A'	–	1190	1201	1191	0.000	1.195	CF(79),CC(11),bring(10)
9	A'	1159	–	1201	1150	0.000	1.194	CF(79),CC(11),bring(10)
10	A'	1022	–	1032	1024	221.325	0.000	CF(65),bCF(19),CC(16)
11	A'	1013	–	1028	1016	221.316	0.000	CF(65),bCF(19),CC(16)
12	A'	795	–	826	781	0.000	0.000	bCF(100)
13	A"	–	755	769	750	0.000	0.000	gCF(51),tring(49)
14	A"	–	–	612	605	0.000	0.000	gCF(67),tring(33)
15	A'	587	–	627	593	0.000	0.000	bring(67),CF(33)
16	A'	–	580	600	567	0.000	25.681	CC(66),CF(34)
17	A"	529	–	551	521	0.000	0.000	tring(59),gCF(41)
18	A'	445	–	469	444	0.000	5.046	bring(74),CC(10),CF(8),bCF(8)
19	A'	–	484	469	444	0.000	5.047	bring(74),CC(10),CF(8),bCF(8)
20	A"	–		390	379	0.000	2.808	gCF(100)
21	A"	–	370	–	369	0.000	2.808	gCF(100)
22	A'	–		329	311	1.266	0.000	bCF(72),CC(25)
23	A'	–	310	328	310	1.268	0.000	bCF(72),CC(25)
24	A'	–		280	265	0.000	0.000	bCF(99)
25	A'	–	259	274	259	0.000	0.212	bCF(76),bring(23)
26	A'	–		273	258	0.000	0.211	bCF(76),bring(23)
27	A"	–	214	226	214	4.971	0.000	gCF(100)
28	A"	–	184	194	184	0.000	0.000	tring(100)
29	A"	–		145	137	0.000	0.000	tring(100)
30	A"	–	137	–	135	0.000	0.000	tring(100)

Abbreviations used: b, bending; g, wagging; t, torsion; [a]Relative absorption intensities normalized with highest peak absorption. [b]Relative Raman intensities calculated by Eq.1 and normalized to 100. [c]For the notations used see Table-4.

C-Cl 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 hexafluorobenzene the very strong band at 780 cm^{-1} is assigned to C-F stretching vibration. The theoretical wavenumber of C-F stretching vibration coupled with C-C-C in-plane bending vibration 781 cm^{-1} co-incides very well with the experimental value. The C-F inplane 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[20-25].

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 hexafluorobenzene. 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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