The Spectroscopic, HOMO-LUMO, NLO Analyses and Thermodynamical Parameters of Octafluoronaphthalene

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Abstract - *The FTIR and FT-Raman spectra of octafluoronaphthalene (OFN) have been recorded in the region 4000-400 cm^{-1} and 3500-50 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; octafluoronaphthalene; B3LYP; HF; HOMO-LUMO

1. INTRODUCTION

The structure of naphthalene is a benzene like compound, having two six membered rings connected together. Although naphthalene reactions are somewhat less aromatic, they are more reactive than benzene. Naphthalene and its derivatives are biologically, pharmaceutically and industrially useful compounds [1,2]. It is used as a precursor for the synthesis of plastics and dyes, gamma ray detector in photo multiplier tubes and also used in dye stuffs, synthetic resins, coatings, tanning agent and celluloid. Naphthalene is found in both middle and heavy oil fractions at crude oil and is obtained by fractional crystallization. Refined naphthalene is found used in balls, flakes and pellets, largely for use as an insect repellent. [3-5]. Particularly, naphthalene is studied because of its technological applications used in vast number of industrial process. More recently, FT-IR and FT-Raman spectra of

1-methoxynaphthalene, 1-bromo-2-fluoronaphthalene and 1,5-dinitronaphthalene, 6-methoxy-1,2,3,4-tetrahydronaphthalene are reported together with the assignments of the vibrational modes [3,4].

However, the detailed B3LYP/6-311++G(d,p) studies on the complete FT-IR and FT-Raman spectra of octafluoronaphthalene (**OFN**) are not been reported so far. In view of these special properties and uses, the present investigation is undertaken to provide a satisfactorily vibrational analysis of octafluoronaphthalene (OFN). Therefore a through Raman, IR, non-linear optical (NLO) properties, HOMO-LUMO analysis of spectroscopic investigations are reported and complemented by B3LYP theoretical predictions with basis set 6-311++G(d,p) to provide novel insight on vibrational assignments and conformational stability of OFN.

2. EXPERIMENTAL DETAILS

The pure sample of OFN was obtained from Lancaster chemical company, UK and used as such without any further purification to record FT-IR and FT-Raman spectra. The room temperature fourier transform IR spectrum of the title compound was measured in the 4000 – 400 cm^{-1} region at a resolution of ± cm^{-1} using BRUKER IFS-66V Fourier transform spectrometer equipped with an MCT detector, a KBr beam splitter and globar arc source. The FT-Raman spectrum was recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory. The FT-Raman spectrum is recorded in the 3500 – 50 cm^{-1} stokes region using the 1064 nm line of Nd:YAG laser for the excitation operating at 200mW power. The reported wave numbers are expected to be accurate within ± 1 cm^{-1}.

3. COMPUTATIONAL METHODS

The molecular structure of OFN in the ground state is computed using B3LYP with 6-311++G(d,p) basis set. All

the computations are done by adding polarization function and diffuse function on heavy atoms [5,6]. The calculated frequencies are scaled by 0.890 and 0.852 for HF and for B3LYP with 6-311++G(d,p) basis set by 0.934, 0.940, 0.982, 0.952 and 0.969 [7]. The theoretical results enabled us to make the detailed assignments of the experimental IR and Raman spectra of the title compound. The DFT calculations for OFN was performed using GAUSSIAN 09W program without any constraint on the geometry [8].

4. RESULTS AND DISCUSSION

4.1. Geometry optimization

The structural parameters of the optimized molecular structure of the OFN is calculated with B3LYP level using 6-311++G(d,p) basis set. The molecular structure of OFN is shown in Fig.1. The calculated geometrical parameters and definitions of the natural co-ordinates for the title compound are summarized in Table 1. The internal and symmetry co-ordinates of octafluoronaphthalene are given in Tables 2 and 3 respectively.

5. NON-LINEAR OPTICAL EFFECTS

Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [9]. Organic molecules with significant non-linear optical activity generally consist of a pi electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end, forming a 'push–pull' conjugated structure [10]. The total static dipole moment (μ) and the first hyperpolarizability (β) using the x, y, z components are defined as [11].

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \qquad \ldots (1)$$

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

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

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

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

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

The dipole moment (μ) and the first hyperpolarizability (β) are calculated at the B3LYP/6-311++G(d,p) level using Gaussian 09W program package. The first hyperpolarizability (β) for the title molecule is calculated at 0.3144×10^{-30} esu respectively. The calculated values of the title compound are 1.1 times greater than urea (the μ,

and β of urea are 1.3732 debye and 0.37289×10^{-30} esu obtained by B3LYP/6-311++G(d,p) method. These results indicate that OFN is a good non-linear optical material.

6. HOMO-LUMO ANALYSIS

The highest energy occupied molecular orbital (HOMO) of one molecule. The lowest energy unoccupied molecular orbital (LUMO) of the other molecule. These orbitals are the pair that lie closest in energy of any pair of orbitals in two molecules, which allows them to interact most strongly. These orbitals are sometimes called the frontier orbitals, because they lie at the outer most boundaries of the electrons of the molecules.

The HOMO (Highest Occupied Molecular Orbital) - LUMO (Lowest Unoccupied Molecular Orbital) energy gap of OFN is calculated at the B3LYP/6-311++G(d,p). Many organic molecules containing conjugated π electrons are characterized hyperpolarizabilities were analysed by means of vibrational spectroscopy [12,13]. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman Spectrum are weak in the IR spectrum and vice versa. But, the intramolecular charge transfer from the donor to acceptor group, through a single-double bond conjugate path can include large variations of both molecular dipole moments and molecular polarizability by making IR and Raman activity at the same time. The experimental spectroscopic behaviour described above is well accounted for DFT calculations in π conjugated systems that predict exceptionally large Raman and infrared intensities in IR and Raman spectra are comparable, resulting from the electron cloud movement through π conjugated frame work electron donor to electron acceptor groups. The analysis of wave function indicates that the electron absorption corresponds to the transition from the ground to first excited state and is mainly described by one electron excitation from the HOMO to LUMO. The LUMO of π nature, (ie benzene ring) is delocalized over the whole C-C bond. Consequently the HOMO-LUMO transition implies an electron density transfer to almost all the atoms. The atomic orbital compositions of the frontier molecular orbital and few MOS are sketched in Fig.2.

The energy gap reflects the chemical activity of the molecule. LUMO as on electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate the electron.

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HOMO energy   = -0.24651 a.u
LUMO energy   = 0.07788 a.u
Energy gap   = 0.16863 a.u

Moreover, the lower in HOMO-LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule, which influences the biological activity of the molecule.

7. OTHER MOLECULAR PROPERTIES

Several thermodynamic properties like heat capacity, zero point energy, entropy along with global minimum energy of OFN are obtained by HF and density functional methods using 6-311++G(d,p) basis set calculations are presented in Table 4. The difference in the values calculated by both the methods is only marginal. Scale factors are recommended [14] for an accurate prediction in determining the zero point vibrational energy (ZPVE) and the entropy (S_{vib}). The vibration in the ZPVE seems to be insignificant. The total energy and change in the total entropy of OFN at room temperature are also presented in Table 4.

8. VIBRATIONAL ANALYSIS

The vibrational spectral analysis of OFN compound is based on FT-IR (Fig.3) and Raman (Fig.4) spectra. The OFN compound consists of 18 atoms, which has 48 normal modes. The 48 normal modes of OFN are assigned according to the detailed motion of the individual atoms. This compound belongs to C_1 symmetry group. The computed vibrational wave numbers and the atomic displacements corresponding to the different normal modes are used for identifying the vibrational modes unambiguously. The calculated vibrational wave numbers, are measured with infrared and Raman band positions and their assignments are given in Table 5. The total energy distribution (TED) is calculated by using the scaled quantum mechanical program (SQM) and fundamental vibrational modes are characterized by their TED.

Carbon Fluorine vibrations

Aromatic fluorine compounds give stretching bands in the region 1360-1000 cm^{-1} [15]. The vibrations are easily affected by the adjacent atoms or groups. The strong FT-IR and Raman band appeared at 1334, 1204, 1193, 1122 cm^{-1} and 1349, 1290, 1230, 1150 cm^{-1} in OFN is assigned to C-F stretching vibrations respectively. The predicted FTIR and Raman band corresponding to C-F in-plane mode is 870, 801, 787 cm^{-1} and 850, 769, 750, 640, 600 cm^{-1}

respectively. The FT-IR and FT- Raman bands observed at 410 cm^{-1} and 393, 374, 337, 301, 289, 250, 170 cm^{-1} is assigned to C-F out-of-plane vibrations respectively.

Carbon Carbon vibrations

The bands 1430-1650 cm^{-1} in benzene derivatives are assigned to C–C stretching modes [16]. Socrates [17] mentioned that the presence of conjugate substituents such as C=C causes a heavy doublet formation around the region 1625-1575 cm^{-1}. The six ring carbon atoms undergo coupled vibrations, called skeletal vibrations and give a maximum of four bands in the region 1660-1220 cm^{-1}. In this title compound, the FTIR and Raman peaks are observed at 1690, 1662, 1650, 1578, 1557, 1546, 1530, 1513 cm^{-1} and 1624, 1520 cm^{-1} are assigned to C-C stretching vibrations respectively. The in-plane bending and out-of-plane bending vibrations are summarized in Table 5.

CONCLUSION

The molecular structural parameters, thermodynamic properties and vibrational frequencies of the fundamental modes of the optimized geometry of OFN are determined from HF and DFT calculations. The theoretical results were compared with the experimental values. The detailed reliable vibrational assignments and the analysis of the molecule were carried out. The deviation between the experimental and calculated frequencies are reduced with the use of B3LYP/6-311++G(d,p) all levels of calculations and is considered as more reliable method. The NLO property is also observed by predicting the first hyperpolarizability for the OFN due to the substitution in the benzene. A decrease in HOMO and LUMO energy gap, explains the eventual charge transfer within the molecule, which is responsible for the chemical reactivity of the molecule. These calculations are carried out in ground state by using *ab intio* HF and density functional theory methods.

Table - 1: Optimized geometrical parameters (Bond Lengths, Bond Angles and Selected Dihedral Angles) of Octafluoronaphthalene

Bond Length	Value (Å)		Bond Angle	Value (°)		Dihedral Angle	Value (°)	
	6-311++G(d,p)			6-311++G(d,p)			6-311++G(d,p)	
	HF	B3LYP		HF	B3LYP		HF	B3LYP
C1-C2	1.3472	1.3697	C2-C1-C10	121.28	121.5445	C10-C1-C2-C3	0.0028	-1.74551
C1-C10	1.4143	1.418	C2-C1-F11	118.4049	117.9295	C10-C1-C2-F12	-180.0001	179.7355
C1-11F	1.3513	1.3808	C10-C1-F11	120.3152	120.505	F11-C1-C2-C3	180.0011	179.9107
C2-C3	1.3996	1.4042	C1-C2-C3	120.3826	120.2797	C11-C1-C2-F12	-0.0017	1.3916
C2-F12	1.3469	1.375	C1-C2-F12	120.983	120.7107	C2-C1-C10-C8	-179.9987	179.6376
C3-C4	1.3472	1.3697	C3-C2-F12	118.6344	118.9934	C2-C1-C10-C9	-0.0036	2.311
C3-F13	1.3469	1.375	C2-C3-C4	120.3833	120.2796	F11-C1-C10-C8	0.003	-2.0606
C4-C9	1.4143	1.418	C2-C3-F13	118.6338	118.9934	F11-C1-C10-C9	179.9981	-127.3872
C4-F14	1.3513	1.3808	C4-C3-F13	120.9829	120.7107	C1-C2-C3-C4	-0.0023	1.4182
C5-C6	1.3473	1.3697	C3-C4-C9	121.2198	121.5445	C1-C2-C3-F13	-180.0	179.9628
C5-C9	1.4143	1.418	C3-C4-F14	118.4052	117.9296	F12-C2-C3-C4	-179.9995	179.9628
C5-F15	1.3513	1.3808	C9-C4-F14	120.315	120.505	F12-C2-C3-F13	0.0028	-1.4929
C6-C7	1.3955	1.4042	C6-C5-C9	121.279	121.5446	C2-C3-C4-C9	0.0027	-1.7453
C6-F16	1.3469	1.375	C6-C5-F15	118.4039	117.9295	C2-C3-C4-F14	-179.9999	179.9109
C7-C8	1.3473	1.3697	C9-C5-F15	120.317	120.505	F13-C2-C4-C9	-179.9997	179.7354
C7-F17	1.3469	1.375	C5-C6-C7	120.3828	120.2796	F13-C3-C4-F14	-0.0023	1.3916
C8-C10	1.4143	1.418	C5-C6-F16	120.9812	120.7107	C3-C4-C9-C5	-179.9995	179.6376
C8-F18	1.3513	1.3808	C7-C6-F16	118.636	118.9934	C2-C4-C9-C10	-0.0035	2.311
C9-C10	1.4197	1.4473	C6-C7-C8	120.3835	120.2796	F14-C4-C9-C5	0.0032	-2.0608
			C6-C7-F17	118.6357	118.9934	F14-C4-C9-C10	179.9992	-179.3875
			C8-C7-F17	120.9809	120.7107	C9-C5-C6-C7	-0.0024	1.7456
			C7-C8-C10	121.2791	121.5445	C9-C5-C6-F16	180.0002	-179.7354
			C7-C8-F18	118.4033	117.9296	F15-C5-C6-C7	180.003	-179.9104
			C10-C8-F18	120.3176	120.505	F15-C5-C6-F16	0.0029	-1.3915
			C4-C9-C5	123.3248	123.6615	C6-C5-C9-C4	179.9997	-179.6377
			C4-C9-C10	118.3371	118.1468	C6-C5-C9-C10	0.0037	-2.3111
			C5-C9-C10	118.3381	118.1432	F15-C5-C9-C4	-0.003	179.3871
			C1-C10-C8	123.3253	123.6615	F15-C5-C9-C10	-179.999	-1.4184
			C1-C10-C9	118.3371	118.1432	C5-C6-C7-C8	0.0021	-179.9629
			C8-C10-C9	118.3376	118.1433	C5-C6-C7-F17	179.9998	-179.9627
						F16-C6-C7-C8	179.9996	1.4929
						F16-C6-C7-F17	-0.0027	1.7454
						C6-C7-C8-C10	-0.0032	-0.0028
						C6-C7-C8-F18	180.0001	179.9526

For numbering of atoms refer Fig.1.

Table - 2: Definition of internal symmetry co-ordinates for Octofluoronaphthalene

No	Symbol	Type	Definition
Stretching			
1-11	r_i	C-C	C1-C2,C2-C3,C3-C9,C9-C10, C10-C8, C8-C1, C9-C4, C4-C5, C5-C6, C6-C1, C7-C10
12-19	R_i	C-F	C1-F11, C2-F12, C3-F13, C4-F14, C5-F15, C6-F16, C7-F17, C8-F18
In plane Bending			
20-25	α_i	Ring1	C1-C2-C3, C2-C3-C9, C9-C10-C8, C10-C8-C1, C8-C1-C2, C3-C9-C10
26-31	α_i	Ring2	C9-C4-C5, C-C5-C6, C5-C6-C7, C6-C7-C10, C7-C10-C9, C10-C9-C7
32-47	β_i	CCF	C8-C1-F11, C2-C1-F11, C1-C2-F12, C3-C2-F12, C2-C3-F13, C9-C3-F13, C9-C4-F14, C5-C4-F14, C4-C5-F15, C6-C5-F15, C5-C6-F16, C7-C6-F16, C6-C7-F12, C10-C7-F17, C10-C8-F18, C1-C8-F18
Out of plane Bending			
48-55	ω_i	CCCF	F11-C1-C2-C8, F12-C2-C3-C1, F13-C3-C4-C2, F14-C4-C5-C9, F15-C5-C6-C4, F16-C6-C7-C5, F17-C7-C10-C6, F18-C8-C1-C10
Torsion			
56-61	τ_i	Ring1	C1-C2-C3-C9, C2-C3-C9-C10, C3-C9-C10-C8, C9-C10-C8-C1, C10-C8-C1-C2, C8-C1-C2-C3
62-67	τ_i	Ring2	C4-C5-C6-C7, C5-C6-C7-C10-C9, C7-C10-C9-C4, C10-C9-C4-C5, C6-C4-C5-C6
68-69	τ_i	Butterfly	C3-C9-C10-C7, C4-C9-C10-C8

For numbering of atoms refer Fig.1.

Table - 3: Definition of local symmetry co-ordinates for Octafluoronaphthalene

No	Symbol[a]	Definition[b]
1-11	C-H	$r_1, r_2, r_3, r_4, r_5, r_6, r_7, r_8, r_9, r_{10}, r_{11}, r_{12}$
12-19	C-F	$R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}$
20	R1 trigd	$(\alpha_{20} - \alpha_{21} + \alpha_{22} - \alpha_{23} + \alpha_{24} - \alpha_{25}) / \sqrt{6}$
21	R1 symd	$(-\alpha_{20} - \alpha_{21} + 2\alpha_{22} - \alpha_{23} - \alpha_{24} + 2\alpha_{25}) / \sqrt{12}$
22	R1 asymd	$(\alpha_{20} - \alpha_{21} + \alpha_{23} - \alpha_{24}) / \sqrt{2}$
23	R2 trigd	$(\alpha_{26} - \alpha_{27} + \alpha_{28} - \alpha_{29} + \alpha_{30} - \alpha_{31}) / \sqrt{6}$
24	R2 symd	$(-\alpha_{26} - \alpha_{27} + 2\alpha_{28} - \alpha_{29} - \alpha_{30} + 2\alpha_{31}) / \sqrt{12}$
25	R2 asymd	$(\alpha_{26} - \alpha_{27} + \alpha_{29} - \alpha_{30}) / \sqrt{2}$
26-33	bCF	$(\beta_{32} - \beta_{33}) / \sqrt{2}$, $(\beta_{34} - \beta_{35}) / \sqrt{2}$, $(\beta_{36} - \beta_{37}) / \sqrt{2}$, $(\beta_{38} - \beta_{39}) / \sqrt{2}$, $(\beta_{40} - \beta_{41}) / \sqrt{2}$, $(\beta_{42} - \beta_{43}) / \sqrt{2}$, $(\beta_{44} - \beta_{45}) / \sqrt{2}$, $(\beta_{46} - \beta_{47}) / \sqrt{2}$
34-41	ωCF	$\omega_{48}, \omega_{49}, \omega_{50}, \omega_{51}, \omega_{52}, \omega_{53}, \omega_{54}, \omega_{55}$
42	t R1 trigd	$(\tau_{56} - \tau_{57} + \tau_{58} - \tau_{59} + \tau_{60} - \tau_{61}) / \sqrt{6}$
43	t R1symd	$(\tau_{56} - \tau_{58} + \tau_{59} - \tau_{61}) / \sqrt{2}$
44	t R1 asymd	$(-\tau_{56} + 2\tau_{57} - \tau_{58} - \tau_{59} + 2\tau_{60} - \tau_{61}) / \sqrt{12}$
45	t R2 trigd	$(\tau_{62} - \tau_{63} + \tau_{64} - \tau_{65} + \tau_{66} - \tau_{67}) / \sqrt{6}$

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46	t R2symd	$(\tau_{62}-\tau_{64}+\tau_{65}-\tau_{67})/\sqrt{2}$
47	t R2 asymd	$(-\tau_{62}+2\tau_{63}-\tau_{64}-\tau_{65}+2\tau_{66}-\tau_{67})/\sqrt{12}$
48	Butterfly	$(\tau_{68}-\tau_{69})/\sqrt{2}$

[a]These symbol are used for description of normal modes by TED in Table 5

[b]The internal co-ordinate used here are defined in Table 2.

Parameters	Method/Basis set	
	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
Optimized global minimum Energy, (Hartrees)	-1179.80985400	-1179.80985400
Total energy(thermal), E_{total}(kcal mol^{-1})	61.697	58.687
Heat capacity, C_v(kcal mol^{-1}k^{-1})	50.478	54.461
Entropy, S(kcal mol^{-1}k^{-1})		
Total	114.834	119.806
Translational	42.701	42.701
Rotational	33.219	33.280
Vibrational	33.203	43.825
Zero point vibrational energy, (kcal mol^{-1})	53.23299	49.48278
Rotational constants(GHz)		
A	0.60259	0.59054
B	0.34655	0.33845
C	0.22069	0.21515

Table - 4: Thermodynamic parameters of Octafluorornaphthalene

Table - 5: Vibrational assignments of Fundamental modes of Octafluoronapthalene along with calculated IR intensity (Km mol^{-1}), Raman activity (A° amu^{-1}) and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using HF and B3LYP methods.

S. No.	Species C$_1$	Observed fundamentals (cm^{-1})		Calculated values (cm^{-1})								Assignments with TED (%) among types of internal coordinates
		FTIR	FT-Raman	HF/6-311+G(d,p)				B3LYP/6-311++G(d,p)				
				Frequencies				Frequencies				
				Unscaled	Scaled	IR Intensity	Raman Activity	Unscaled	Scaled	IR Intensity	Raman Activity	
		1	2	3	4	5	6	7	8	9	10	11
1.	A	1690	-	1876	1695	0.0009	0.0319	1686	1692	0.0000	4.5212	γCC(90)
2.	A	1662	-	1857	1668	132.3783	0.0000	1672	1665	128.0609	0.000	γCC(98)
3.	A	1650	-	1815	1660	0.0000	48.4715	1636	1655	0.000	43.9141	γCC(88)
4.	A	-	1624	1688	1630	5.9235	0.0001	1544	1620	17.2661	0.000	γCC(87)
5.	A	1578	-	1644	1585	0.0002	65.2931	1495	1580	0.0000	86.6693	γCC(88)
6.	A	1557	-	1635	1563	0.0001	2.4812	1487	1557	0.0000	0.0072	γCC(86)
7.	A	1546	-	1619	1555	486.8813	0.0000	1459	1547	469.0288	0.0000	γCC(85)
8.	A	1530	-	1536	1550	306.0765	0.0000	1398	1532	296.8376	0.0000	γCC(87)
9.	A	-	1520	1470	1530	0.0000	231.0820	1374	1523	0.0000	181.9389	γCC(88)
10.	A	1513	-	1384	1521	0.0000	0.3090	1313	1517	20.7238	0.0000	γCC(85)
11.	A	1480	-	1326	1491	0.0000	7.5392	1243	1483	0.0000	0.3289	R$_1$trigd(60)
12.	A	1431	-	1280	1441	90.6916	0.0000	1199	1438	0.0000	6.7607	R$_1$symd(62)
13.	A	1415	-	1256	1425	20.0237	0.0000	1162	1418	83.4660	0.000	R$_1$asymd(56)
14.	A	-	1349	1195	1356	90.5630	0.0000	1081	1355	61.0783	0.0000	γCF(83)
15.	A	1334	-	1127	1343	0.0000	32.2186	1030	1340	0.0000	19.0042	γCF(84)
16.	A	-	1290	1108	1300	0.0000	1.4636	1005	1295	0.0000	1.8253	γCF(87)
17.	A	-	1230	997	1240	215.9011	0.0000	911	1238	208.7832	0.0000	γCF(85)
18.	A	1204	-	869	1213	0.0049	0.0000	799	1208	0.4484	0.000	γCF(88)
19.	A	1193	-	830	1208	168.9600	0.0000	764	1197	158.9020	0.000	γCF(87)
20.	A	-	1150	801	1160	0.0000	0.0117	730	1155	0.000	0.0000	γCF(85)
21.	A	1122	-	662	1131	0.0000	0.4974	631	1127	0.0000	2.3929	γCF(86)
22.	A	-	1110	644	1120	1.3111	0.0000	629	1113	1.6071	0.0000	R$_2$trigd(65)
23.	A	-	1072	628	1085	0.0000	5.3628	574	1075	0.0000	2.5602	R$_2$symd(68)
24.	A	1050	-	599	1060	1.8813	0.0000	527	1055	1.1930	0.0000	R$_2$asymd(65)
25.	A	962	-	571	972	0.0000	1.7341	524	965	0.0000	2.7377	bCF(76)
26.	A	946	-	534	956	0.0000	29.8016	517	948	0.0000	1.1226	bCF(85)
27.	A	-	920	530	930	0.000	0.0000	505	925	0.000	53.1197	bCF(76)
28.	A	870	-	481	880	0.0047	0.0000	461	873	0.0000	3.2934	R1trigd (54)
29.	A	-	850	450	860	0.0000	0.0000	452	852	0.0244	0.000	R1asymd (54)
30.	A	801	-	445	812	5.6998	0.0000	419	805	0.0156	0.000	R1symd (52)
31.	A	787	-	416	797	0.0000	8.7384	397	790	3.1875	0.000	bCF (77)
32.	A	-	769	397	779	0.0000	1.5383	385	771	0.000	9.4106	bCF (75)
33.	A	-	750	360	760	0.0000	6.2115	353	755	0.000	1.4752	bCF (78)
34.	A	-	640	335	650	6.3576	0.0000	333	643	0.0000	7.6556	bCF (76)
35.	A	-	600	334	610	8.3413	0.0000	308	605	4.0978	0.0000	bCF (78)
36.	A	-	590	319	600	0.0000	2.7565	305	595	3.5107	0.000	R2trigd (56)
37.	A	-	510	302	520	0.0000	2.0492	292	513	0.0000	3.2966	R2symd (52)
38.	A	-	450	301	460	0.0000	1.0826	275	454	0.0000	1.3213	R2asymd (53)
39.	A	410	-	299	420	0.2013	0.0000	273	413	0.0516	0.000	ωCF (71)
40.	A	-	393	295	405	0.0000	0.9602	270	397	1.4804	0.4318	ωCF (63)
41.	A	-	374	205	386	0.1595	0.0000	268	382	2.0553	0.7500	ωCF (66)

S. No.	Species C_1	Observed fundamentals (cm^{-1})		Calculated values (cm^{-1})								Assignments with TED (%) among types of internal coordinates
				HF/6-311+G(d,p)				B3LYP/6-311++G(d,p)				
				Frequencies				Frequencies				
		FTIR	FT-Raman	Unscaled	Scaled	IR Intensity	Raman Activity	Unscaled	Scaled	IR Intensity	Raman Activity	
42.	A	-	337	197	345	16.8424	0.0000	189	342	0.000	1.1098	ωCF (68)
43.	A	-	301	166	318	0.0000	0.2330	177	303	10.6903	0.0000	ωCF(67)
44.	A	-	289	173	301	0.0000	0.0000	162	295	0.0039	0.000	ωCF (64)
45.	A	-	250	124	262	0.0000	0.3731	146	255	0.000	0.0550	ωCF (65)
46.	A	-	170	87	180	0.9266	0.0000	111	176	0.000	0.3851	ωCF (71)
47.	A	-	150	70	160	0.0000	0.0000	79	153	0.5742	0.000	butterfly (76)
48.	A	-	132	45	143	0.0000	3.9928	65	137	0.0005	0.0000	butterfly (76)

Abbreviations: γ – stretching; ss – symmetric stretching; ass – asymmetric stretching; b – bending; ω – out-of-plane bending; R – ring; trigd – trigonal deformation; symd – symmetric deformation; asymd – antisymmetric deformation.
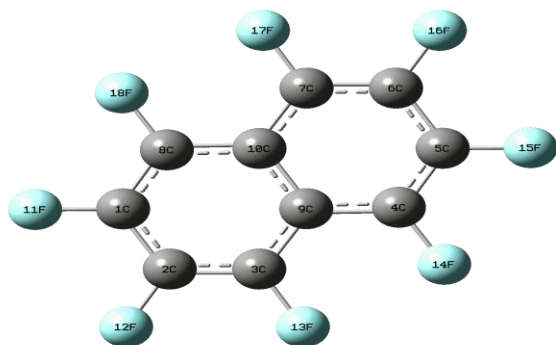

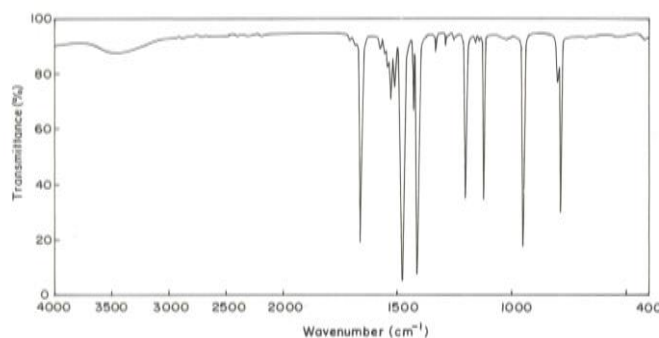**Fig. 1: Molecular structure of Octafluoronaphthalene**

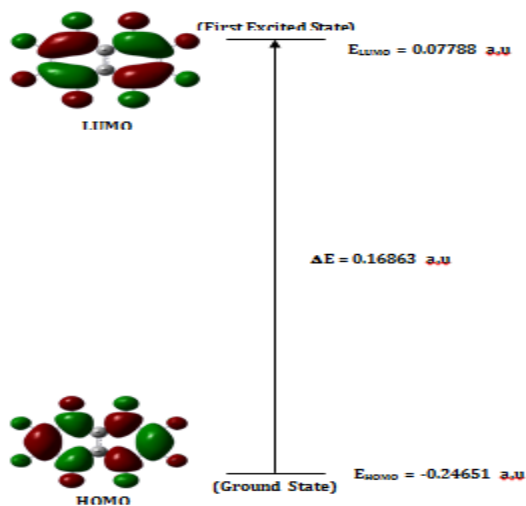**Fig.3:** FTIR spectrum of Octafluoronaphthalene

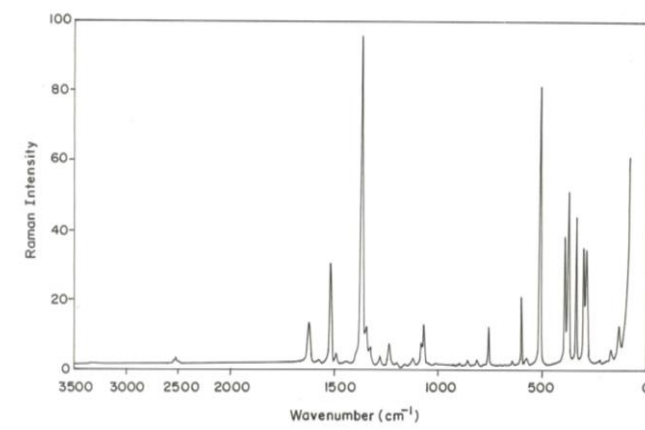**Fig.2: HOMO-LUMO energy of Octafluoronaphthalene**

Fig.4: FT-Raman spectrum of Octafluoronaphthalene

REFERENCES

[1] T. Prabhu, S. Periandy, S. Mohan, *Spectrochim. Acta Part A* 78 (2011) 56

[2] R. John Xavier, V. Balachandran, M. Arivazhagan, G. Ilango, *I. Journal of P. & App. Phy.*, 48, (2010), 245.

[3] M. Arivazhagan, V. Krishnakumar, R. John Xavier, G. Illango and V. Balachandran, *Spectrochim. Acta Part A,* 72 (2009) 941

[4] V. Krishnakumar, N. Prabavathi, S. Muthunatesan, *Spectrochim. Acta Part A* 70 (2008) 991

[5] M.J.Frisch, J.A.Pople, J.S.Binkley, *Journal of Chemical Physics*, 80 (1984) 3265.

[6] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.V.R. Schleyer, *Journal of Computational Chemistry* (1983) 294

[7] N. Sundaraganesan, S. Ilakiamani, H. Saleem, P.M. Wojieehowski, D. Michalska, *Spectrochim. Acta A* 61 (2005) 2995.

[8] M.J. Frisch, G.W. Trucks, H.B. Schlegal, G.E. Scuseria, M.A. Robb, J.R. Cheesman, V.G. Zakrzewski, J.A. Montgomerg, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi,B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J.J. Dannenberg, D.K. Malich, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stetanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 09, Revision A 11.4, *Gaussian, Inc,*Pittsburgh PA, 2009.

[9] Y.X. Sun, Q.L. Hao, W.X. Wei, Z.X. Yu, L.D. Lu, X. Wang, Y.S. Wang, *J. Mol. Struct. THEOCHEM* 904 (2009) 74.

[10] D. Sajan, J. Binoy, I. Hubert Joe, V.S. Jayakumar, J. Zaleski, *J. Raman Spectrosc.* 36 (3) (2005) 221.

[11] H. Tanak, *J. Mol. Struct. THEOCHEM* 950 (2010)5.

[12] M.Arivazhagan, R.Kavitha, V.P.Subhasini, Spectrachimica Acta Part A. Molecular and Biomolecular Spectrascopy 130 (2014) 502.

[13] G. Anandaraju, M. Arivazhagan, N. Rajendran, Elixir Vib.Spec.95 (2016) 41086.

[14] (a) T. Sundius, *J. Mol. Struct.*, 218 (1990) 321. (b) MOLVIB (V.7.0): *Calculation of Hormonic Force Fields and Vibrational Modes of Molecules*, QCPE program No.807 (2002).

[15] S. Manivel, L.F.A. Amirtharaj, M. Arivazhagan, Elixir Vib. Spec. 92 (2016) 38706.

[16] R. Gayathri, M. Arivazhagan, Journal of Molecular Structure 1130 (2017) 876.

[17] Socrates G, *IR and Raman Characteristics Group Frequencies Tables and Charts*, 3rd ed., Wiley, Chichester (2001) 107.