

FT-IR, FT-Raman and SERS Spectral Studies, HOMO-LUMO Analyses, Mulliken Population Analysis and Density Functional Theoretical Analysis of 1-Chloro 4-Fluorobenzene

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Abstract: The FT-IR, FT-Raman and SERS Spectra of 1-Chloro 4-Fluorobenzene (C_6H_4CLF) have been recorded in the range $4000-400cm^{-1}$, the optimized geometry, frequency and intensity of the vibrational bands of C_6H_4CLF have been obtained by DFT levels of theory with complete relaxation in the 6-311**G basis sets. A complete vibrational assignment, aided by the theoretical frequency analysis, has been proposed. The vibrational frequencies calculated are compared with experimental FT-IR and FT-Raman Spectra. The observed and calculated frequencies are found to be in good agreement. A detailed interpretation of the infrared Raman Spectra of C_6H_4CLF is also reported based on mulliken population analysis distribution. The calculated HOMO and LUMO energy gap shows that charge transfer occurs within the molecule.

Keyword: B3LYP, FT-IR, FT-Raman, SERS, 1-Chloro 4-Fluorobenzene

I. Introduction

Surface-Enhanced Raman Scattering (SERS) has recently evolved as an important laser spectroscopic characterization technique applied to biomedically significant molecules to study structural and functional properties. SERS is widely used to elucidate information about the behaviour of biomolecules adsorbed at the metal surfaces, orientation induced by external factors [1-3]. However with different substrates of different characteristics the SERS spectrum of the sample adsorbed will have different characteristics. This causes some difficulty in analysing the SERS spectra. The normal Raman spectral analysis is based on shift in frequency. Enhancing or weakening intensity is related to the adsorption orientation geometry of adsorbates on the surface of the substrates [4-7]. Surface-enhanced Raman Scattering spectroscopy is now a well-established technique where by unusually intense Raman signals are obtained from molecules adsorbed on or placed near rough metal surfaces. Vibrational and SERS spectral investigations of 1-Chloro 4-Fluorobenzene [8,9] supported by density functional theory studies have been reported. The present contribution reports the IR, Raman and SERS spectral studies of 1-chloro 4-Fluorobenzene which can provide information on the adsorption geometry along with the geometry optimization and vibrational calculation using DFT to investigate other molecule bonding features.

II. Experimental

2.1 preparation of Silversol

2.1.1 Creighton Method

Creighton method is one of the best methods for the preparation of silver sol. This method is also called cooling method. First of all 0.024g of sodium borohydride was dissolved in 150ml of deionized water 25ml of this solution was taken and placed in an ice bath and allowed to cool for 15min. 0.021g of silver nitrate ($AgNO_3$) in 100ml of deionized water. The sodium borohydride solution after cooling for 15min, as explained above, was added to this $AgNO_3$ solution, drop by drop, using a burette at the rate of about 1 drop per second. After about 2ml has been added the solution became dark or medium yellow in colour. This yellow colour is stable at room temperature. The UV Absorption spectrum of the silver sol shows a single absorption band at 391nm shown in Fig.1.

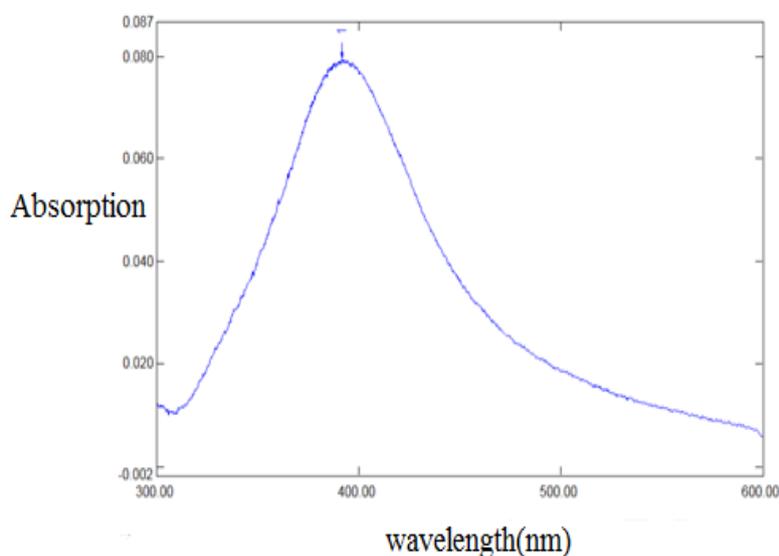


Fig.1 UV-Visible Absorption Spectrum of Silver Sol

The spectroscopic grade sample of 1-Chloro 4-Fluorobenzene(C_6H_4CLF) was obtained from Precision Scientific Company, Coimbatore and used as such for the spectral measurements. The room temperature FTIR Spectrum of the title compound has been recorded in the region $4000-400cm^{-1}$ using BRUKER RFS V model FTIR Spectrometer equipped with a Splitter and global source. FT-Raman Spectrum of C_6H_4CLF was recorded on a computer interfaced BRUKER RFS V model interferometer equipped with FRA-106 FT-Raman accessories the spectrum was measured in the Stokes region $4000-50cm^{-1}$ using Nd:YAG laser operating at 200mW power with 1064nm as the pumping and a liquid nitrogen cooled Ge detector used to record the spectrum. The reported wavenumbers are expected to be accurate within cm^{-1} .

2.2 Preparation Of Samples

1-Chloro 4-Fluorobenzene with Silver sol

A= 0.5 ml (Solution) + 5ml (Silver Sol)

B=0.5 ml (Solution) + 2.5ml (Silver Sol)

The sample solutions of two different concentrations were mixed with the silver sol in the ratio 1:10, thus preparing two sets of solutions. The Raman spectra of the liquid sample, solutions at different concentrations, and solutions mixed with silver sol were recorded using 1064 nm Nd:YAG laser line as the excitation frequency using the Bruker RFS Raman spectrometer. These are shown in Figs. 5- 7.

2.3 Computational Details

The optimized molecular structure of 1-Chloro 4-Fluorobenzene is shown in Fig.2. The optimized geometrical parameters of 1-Chloro 4-Fluorobenzene (bond-lengths and bond-angles) are calculated using B3LYP/ 6-311**G basis sets and presented in Table.1 and Table.2 together with relevant data. Since the exact crystal structure of the title compound is available and also the optimized structure can be compared with other similar systems for which the crystal structure has been solved. Therefore optimized geometrical parameters of 1-Chloro 4-Fluorobenzene are compared to those of title compounds. In order to provide information with regard to the structural characteristics and the normal vibrational modes of C_6H_4CLF the Mulliken and DFT –B3LYP correlation functional calculations have been carried out. The entire calculations have been performed using the GAUSSIAN 09 W software package [10]. Initially the DFT calculations, adopting the 6-311**G basis sets have been carried out and then the DFT employing the BeckeB3LYP keyword, which invokes Becke's three parameter hybrid method and it has been computed using the correlation function of Lee et al [11], implemented with 6-311**G basis set. The DFT representation of the theoretical force constants have been computed at the fully optimized geometry. The symmetry of the molecule was also helpful in making vibrational assignment. By combining the results of the GAUSSVIEW program [12] with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. However, the defined Co-ordinate form completely set and matches quite well with the motions observed using the GAUSSVIEW program. The systematic comparison of the results of experiments have shown that the method using B3LYP functional is the most promising in providing correct vibrational wavenumbers.

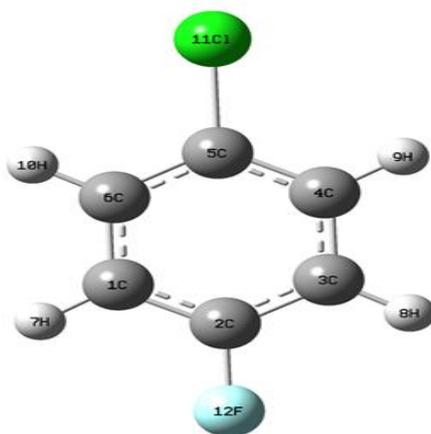


Fig.2 Optimized geometrical parameters of 1-Chloro 4-Fluorobenzene

2.4 Geometrical Parameters

The DFT calculations of the 1-Chloro 4-Fluorobenzene gives the following values for bond-length $C_2-C_1=1.38642\text{\AA}$ and $C_3-C_2=1.39883\text{\AA}$ respectively[13,14]. In the present case of the DFT calculations give C_4-C_3 bond-length as 1.39180\AA and H_1-H_2 bond-length as 1.07961\AA , give the corresponding bond-length of $H_3-H_2=1.07962\text{\AA}$ whereas in the present case the corresponding value is H_4-H_3 bond-length for 1.07930\AA and hydrogen atom H_6-H_5 bond-length as 1.07939\AA , $Cl_5-Cl_4=1.82711\text{\AA}$ and also bond-length as $F_2-F_1=1.40496\text{\AA}$ shown in table.1. For the title compound of the DFT calculations give an around bond-angles 118° . The theoretical value is observed. This must be due to the fact that the theoretical results belong to the gaseous of a single molecule. Whereas in the present case the corresponding bond-angle is $C_3-C_2-C_1=118.3327^\circ$. The $Cl_5-Cl_4-Cl_3$ of bond-angle is 188.9200° and also the $F_2-F_1-F_6=118.3922^\circ$ is slightly longer than $Cl_5-Cl_4-Cl_3$ bond of the ring 188.9200° as shown in Table.2.

1-Chloro 4-Fluorobenzene(B3LYP)	
Parameters	6-311**G
Bond-length(\AA)	
C_2-C_1	1.38642
C_3-C_2	1.39883
C_4-C_3	1.39180
C_5-C_4	1.39180
H_1-H_2	1.07961
H_3-H_2	1.07962
H_4-H_3	1.07930
H_6-H_5	1.07939
Cl_5-Cl_4	1.82711
F_2-F_1	1.40496

Table.1
Optimized geometrical parameters of 1-Chloro 4-Fluorobenzene

1-Chloro 4-Fluorobenzene(B3LYP)	
Parameters	6-311**G
Bond-Angles($^\circ$)	
$C_3-C_2-C_1$	118.3327
$C_4-C_3-C_2$	118.9867
$C_5-C_4-C_3$	122.1477
$H_1-H_2-H_3$	120.2923
$H_3-H_2-H_1$	120.2945
$H_4-H_3-H_2$	120.5128
$H_6-H_5-H_4$	120.4996
$Cl_5-Cl_4-Cl_3$	188.9200
$F_2-F_1-F_6$	118.3927

Table.2

2.5 Homo-Lumo Analysis

Many organic molecules that contain conjugated π electrons are characterized hyperpolarizabilities and have been analyzed by means of vibrational spectroscopy[17'18]. In most of the cases even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and viceversa. But the intra molecular charge transfer from the donor to acceptor group through a single double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability making FTIR and Raman activity strong at the same time. The experimental spectroscopic behaviour described is well accounted for by Mulliken population analysis that predict exceptionally large Raman and infrared intensities for the same normal modes. It is also observed in our title molecule, the bands in FT-IR spectrum have their counterparts in Raman shows that the relative intensities in IR and Raman shows spectra which are comparable resulting in the electron cloud movement through π conjugated frame work from electron donor to electron acceptor groups. The analysis of the wavefunction indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied Molecular orbital (HOMO) to the lowest unoccupied Molecular orbital(LUMO). The LUMO of π nature (i.e:benzene ring) is delocalized over the whole C-C bond by contrasting the HOMO which is

located over methyl groups; consequently the HOMO→LUMO transition implies an electron density transfer to C-C bond of the benzene ring from methyl groups, more over these orbitals significantly overlap in their position for 1-Chloro 4-Fluorobenzene. The atomic orbital compositions of the frontier molecular orbitals are sketched in Fig:3. The HOMO →LUMO energy gap of 1-Chloro 4-Fluorobenzene has been calculated by using B3LYP level. It reveals that the energy gap reflects the chemical activity of the molecule LUMO as an electron acceptor represents the ability to donate an electron the strong charge transfer interaction through π conjugated bridge resulting in substantial ground state donar-acceptor (DA)mixing and the appearance of a charge transfer band in the electron absorption spectrum.

HOMO energy = -0.2704ev

LUMO energy = -0.04839ev

HOMO-LUMO Energy gap = 0.22201ev. The Homo and LUMO energy gap explains the fact that eventual charge transfer interactions is taking place within the molecule.

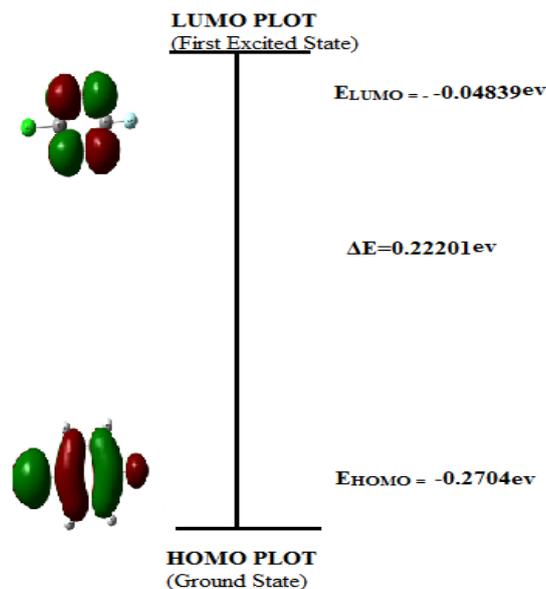


Fig.3 Calculated HOMO-LUMO Plots of 1-Chloro 4-Fluorobenzene and HOMO-LUMO gap

III. Mulliken Population Analysis

2.6.1 Mulliken Atomic Charge

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because atomic charges affect dipole moment polarizability electronic structure and much more properties of molecular systems the total atomic charges of 1-Chloro 4-Fluorobenzene obtained by Mulliken population analysis with 6-311**G basis sets are listed in Table.3 The corresponding Mulliken's plot for title compounds with 6-311**G basis sets are shown in Fig.4. For 1-Chloro 4-Fluorobenzene molecule the atomic charge on C₁,C₂,C₃,C₄,C₆,F₁₂, are negative whereas the remaining atoms are positively charged for basis the Mulliken atomic charge values for all atoms of 1-Chloro 4-Fluorobenzene decreases expect the atomic charge value of C₅ and C₁₁ increases 6-311**G basis set. The Mulliken atomic charge of C₅ in 6-311**G basis of 1-Chloro 4-Fluorobenzene occupies the higher positive value. The basis sets become more negative, while their natural atomic charges show positive value.

Atoms	Atomic charge with (B3LYP)	
	1-Chloro 4-Fluorobenzene	
	6-311**G	
C ₁	-0.026	
C ₂	-0.564	
C ₃	-0.026	
C ₄	-0.938	
C ₅	1.079	
C ₆	-0.938	
H ₇	0.323	
H ₈	0.323	
H ₉	0.292	
H ₁₀	0.292	

Cl ₁₁	0.502
F12	-0.320

Table.3

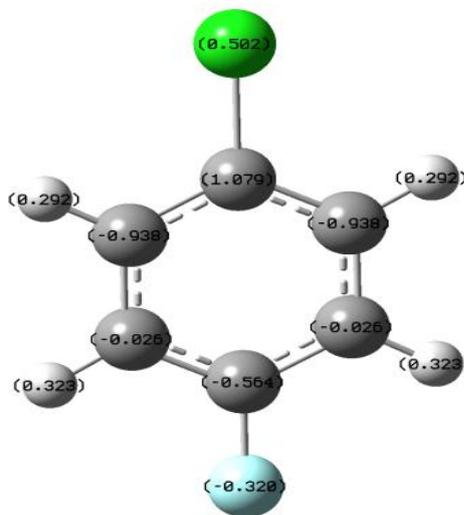


Fig.4The Charge distribution Calculated by the Mulliken method

2.7 Vibrational Analysis

The vibrational spectra analysis of 1-Chloro 4-Fluorobenzene is based on theoretical and experimental FT-IR theoretical and Experimental Raman spectra Fig.5 using Density functional theory at B3LYP/ 6-311**Glevel. The vibrations of 1-Chloro 4-Fluorobenzene phenyl ring modes have been separately analysed. The calculated vibrational wavenumbers measured infrared and Raman band positions and their assignments are given in the Table. 4.

B3LYP/6-311**G		Observed frequency(cm ⁻¹)		SERS(cm ⁻¹)		Assignments(%)
Calculated Frequency(cm ⁻¹)		Raman	FTIR	A	B	
-	239	-	-	-	-	Out of plane bending ring
-	324	328	-	-	-	CO out of plane bending
-	-	383	-	-	-	tOH
349	-	-	-	-	-	CF bending
-	419	-	-	-	-	Out of plane bending phenyl
-	-	-	487	-	-	Out of plane bending phenyl substituent sensitive
-	513	-	-	-	-	ωNH ₂
-	609	-	-	-	-	NH ₂ In plane bending phenyl wagging NH ₂
-	-	-	627	-	-	ν _s S-(OH) ₂
-	-	-	831	-	-	C-H out of plane bending
-	865	-	-	-	-	C-H out of plane bending
652	-	641	-	-	643	C-H Out of plane bending
-	-	803	-	-	-	C-H In plane bending
815	-	-	-	-	816	N-H rocking
-	1045	-	-	-	-	C-H In plane bending
-	-	-	1010	-	-	C-H In plane bending
1086	1092	1088	1087	1077	-	CH bending
1194	1121	1155	-	-	-	C-C Stretching
-	1215	1236	1222	-	-	C-C Stretching
1324	1339	-	-	-	-	ωCH ₂
-	-	-	1490	-	-	CH ₃ symetric bending
-	1538	1588	1587	1595	-	νC=O
1617	1614	-	-	-	-	νC=O
-	-	-	-	1632	-	C=O Stretching
-	1643	-	-	-	-	νsCH ₂

-	-	-	1889	-	-	CH2 asymentric stretch
-	-	-	2856	2886	-	C-H Stretching
-	-	-	2920	-	-	C-H Stretching
-	-	3093	3098	3054	-	C-H Stretching
-	-	-	-	3067	3071	C-H stretching
-	-	-	-	-	3082	νOH(H-bond)
-	-	-	-	-	3093	ν _{as} (N-H)
-	-	-	-	3115	-	ν _{as} (N-H)
3210	3227	-	-	-	-	NH Stretching
3221	-	-	-	-	-	NH Stretching

t, torsional; ω, wagging; ν, stretching; s, symmetric; as, asymmetric; S, strong;

Table.4 Details assignment of fundamental vibrations of 1-Chloro 4-Fluorobenzene

IV. Results And Discussion

2.8.1 FT-IR and Raman Spectrum

The FT-IR and FT-Raman Spectrum of 1-Chloro 4-Fluorobenzene Shows in Fig.5 and Fig.6 the wavenumbers of the observed FTIR and Raman bands their relative frequency calculated values and the assignments are given in Table.4

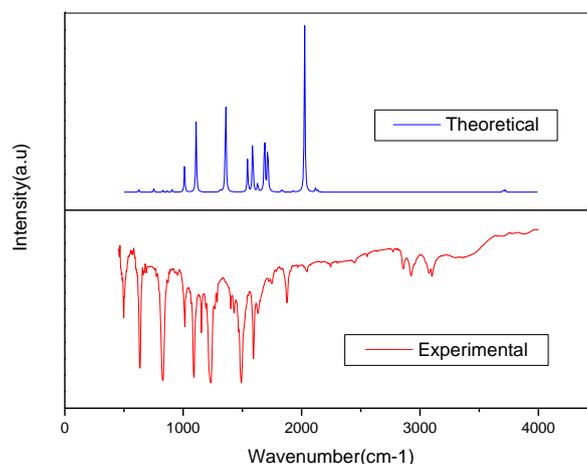


Fig.5 Comparison of observed and calculated FTIR spectra of the title compound

2.8.2 Phenyl Ring Vibrations

The aromatic C-H stretching [19-21] vibrations in mono substituted benzene rings are generally observed in the region 3000-3100 cm^{-1} for 1-Chloro 4-Fluorobenzene ring the strong bands at 2856 cm^{-1} medium bands 2920 cm^{-1} weak bands 2856 cm^{-1} in FT-IR Spectrum corresponds to the ring modes experimentally based on the Eigen vector distribution of the computed vibrational modes while the weak bands in Raman at 3093 cm^{-1} belong to the ring mode respectively

The tangential C-C stretching mode vibrations can be observed [19-21] as a very strong band in Raman at 1236 cm^{-1} as a medium shoulder in FTIR at 1222 cm^{-1} . It is relatively weaker companion can be found as a medium band in the FTIR spectrum at 421 cm^{-1} and 1215 cm^{-1} as a weak band in Raman Spectrum 1194 cm^{-1} and 1155 cm^{-1} and the band positions are supported by computations.

C-H In plane bending modes can be observed in the Raman Spectrum as a medium band at 803 cm^{-1} , the modes are active in FTIR as a strong band 1045 cm^{-1} as a medium band at 1010 cm^{-1} respectively. Normal vibration of phenyl ring is usually referred to as a substituent sensitive vibration. This is confirmed by the strong intense FTIR band and weak intense Raman band. This is supported by computed results.

The absorption bands arising from C-H out of plane bending vibrations are usually observed in the region [21-25] at 1000-675 cm^{-1} . The weak band at 831 cm^{-1} in FTIR spectrum and medium band at 865 cm^{-1} . The computed vibrational modes. The C-H out of plane bending vibrations are observed as a medium band at 652 cm^{-1} weak band at 641 cm^{-1} in Raman spectrum respectively.

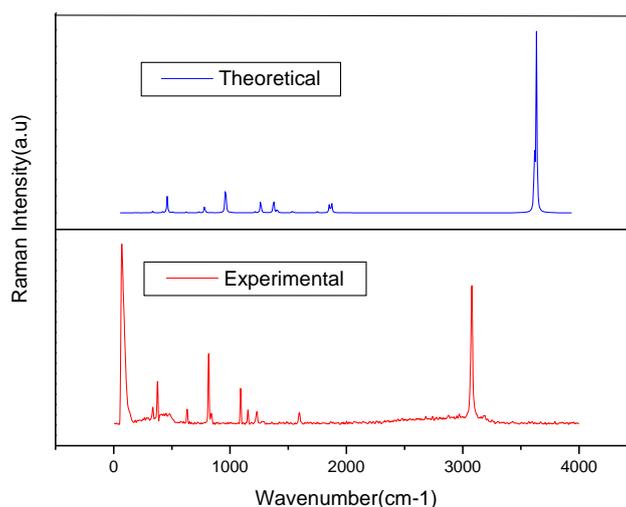


Fig.6 Comparison of observed and calculated Raman spectra of the title compound

2.8.3 Methylene Group Vibrations

The asymmetric CH_2 stretch modes of methylene group is expected in the region [21-23] around 2940cm^{-1} and the symmetric around the region 2860cm^{-1} . In 1-Chloro 4-Fluorobenzene the CH_2 asymmetric stretch mode it is found to be medium intense in FTIR spectrum at 1889cm^{-1} wavenumbers are calculated for methylene CH_2 asymmetric stretch.

The CH_3 Symmetric bending modes can be observed in FTIR spectrum at 1490cm^{-1} medium band respectively. The $\nu\text{C}=\text{O}$ modes can be observed in FTIR band at 1538cm^{-1} weak band and 1587cm^{-1} medium band and 1614cm^{-1} strong band respectively. In the Raman band of $\nu\text{C}=\text{O}$ modes can be observed in Raman band 1588cm^{-1} medium band and 1617cm^{-1} strong band respectively.

The νsCH_2 can be observed in FTIR spectrum at 1643cm^{-1} the wavenumbers are calculated. The C-H bending modes can be observed in FTIR band at 1092cm^{-1} strong band and 1087cm^{-1} medium band. In the Raman band at 1086cm^{-1} strong band and 1088cm^{-1} medium band respectively.

The N-H rocking modes can be observed in Raman spectrum at 815cm^{-1} the wavenumbers are calculated. The $\nu\text{s}(\text{OH})_2$ can be observed in FTIR spectrum at 627cm^{-1} the wavenumbers are calculated. The NH_2 in plane bending phenyl wagging NH_2 can be observed in FTIR spectrum at 609cm^{-1} the wavenumbers are calculated. The out of plane bending phenyl substituent sensitive can be observed in Raman spectrum 487cm^{-1} the wavenumbers are observed.

The CF bending can be observed in Raman spectrum 349cm^{-1} the wavenumbers are calculated. The tOH can be observed in Raman Spectrum 383cm^{-1} the wavenumbers are observed. The CO out of plane bending can be observed in FTIR spectrum spectrum 324cm^{-1} the wavenumbers are calculated. In the Raman spectrum 328cm^{-1} the wavenumbers are observed. The out of plane bending ring can be observed in the FTIR spectrum at 239cm^{-1} the wavenumbers are calculated.

The N-H Stretching modes can be observed as a strong band in FT-IR at 3227cm^{-1} and as a medium band in Raman Spectrum at 3210cm^{-1} and also the strong band in the Raman Spectrum at 3221cm^{-1} the wavenumbers are calculated. The out of plane bending ring modes can be observed as a band in FTIR spectrum at the 239cm^{-1} . The ωNH_2 modes can be observed as a band in FTIR spectrum at 513cm^{-1} . The ωCH_2 modes can be observed as a medium band in the Raman spectrum at 1324cm^{-1} and as a medium band in FTIR spectrum at 1339cm^{-1} . The torsion modes can be observed as a band in FTIR spectrum at 125cm^{-1} the wavenumbers are calculated.

2.9 SERS (Surface Enhanced Raman Scattering) Spectral Analysis

The SERS spectrum of 1-Chloro 4-Fluorobenzene Fig.7 has been recorded by comparing it with the normal Raman Spectrum recorded in the wavenumber range between $500\text{--}400\text{cm}^{-1}$. The relative intensity of the SERS bands are expected to differ significantly from those of the normal Raman Spectrum owing to the specific selection rules [26]. According to the surface selection rules when a molecule is adsorbed flat on the silver surface its out of plane bending modes will be more enhanced and vice versa. When it is adsorbed perpendicular to the surface [27,28]. It is further seen that vibrations involving groups that are close to the silver surface will be more enhanced. It has been suggested that when the wavenumber difference of the normal Raman band and

SERS is less than 5cm-1 the molecular plane will be perpendicular to the silver surface [34]. The orientation of the molecules for 1-Chloro 4-Fluorobenzene can be inferred from C-H stretching vibrations, C-H out of plane bending, C=O Stretching vibration and the SERS surface selection rule [34,35]. It has also been documented in the literature that when a vibration moiety interacts directly with a vibration breathing mode shifted by about 10cm^{-1} along with substantial band broadening in the SERS spectrum.

The C-H Stretching vibrations are observed in the SERS spectrum at $2886, 3054, 3067, 3071\text{cm}^{-1}$. This again supports the possibility of direct interaction between the Fluoro group and the metal surface. This is justifiable because the modes of groups directly interacting with the metal surface will be prominent in SERS spectrum and undergo a wavenumber shift [36,37].

The C-H out of plane bending are present at 643cm^{-1} and N-H rocking are present at 816cm^{-1} in the SERS spectrum from the intensities of the out of plane bending and N-H rocking of vibration of the benzene ring it can be inferred that for 1-Chloro 4-Fluorobenzene adsorbed on benzene ring has a titles orientation.

In the SERS spectrum of 1-Chloro 4-Fluorobenzene the $\nu_{\text{as}}(\text{N-H})$ is strongly enhanced, which indicates NH₂ group interacts more with metal surface [38]. This interaction causes weakening of the N-H bond. Hence more molecules are subjected to absorption and are responsible for strong enhancement of $\nu_{\text{as}}(\text{N-H})$ in the SERS spectrum. Also for 1-chloro 4-Fluorobenzene the enhanced band at 3115cm^{-1} corresponding to $\nu_{\text{as}}(\text{N-H})$ suggests that the interaction between the fluoro group and the metal surface is strong [38]. In the case of $\nu_{\text{C=O}}$ band is present in the SERS spectrum at 1595cm^{-1} and at 1538 and 1587cm^{-1} in the normal Raman spectrum [39]. Such a shift was invoked by Holze [40] to conclude that 1-Chloro 4-Fluorobenzene interacts with the surface via its benzene group in the present case we observed C-H bending in the SERS spectrum at 1770cm^{-1} . Also the $\nu_{\text{as}}(\text{N-H})$ in the SERS spectrum at 3093cm^{-1} as a strong band in the SERS spectrum. The presence of these C=O Stretching modes observed in the SERS spectrum at 1632cm^{-1} . The $\nu_{\text{OH}}(\text{H-bond})$ modes observed in the SERS spectrum at 3082cm^{-1} . The mode corresponds observed as a strong band at 3093cm^{-1} and 3115cm^{-1} in the SERS spectrum respectively corresponding Raman can be observed in the different region. Neither a substantial wavelength shift nor significant band broadening was identified in the SERS spectrum of 1-Chloro 4-Fluorobenzene employing that the probability of a direct band C-H stretching vibration. In the SERS spectrum of 1-Chloro 4-Fluorobenzene Fig:7 the 2886 and 3054cm^{-1} band assigned to the C-H Stretching of benzene are both very strong indicating that the interaction between benzene ring of 1-Chloro 4-Fluorobenzene is strong. But there are no shifts of these two bands compared with the corresponding bands in the Raman Spectrum moreover the medium intense band at 643cm^{-1} in the SERS spectrum. Also the presence of SERS band at 3093cm^{-1} supports that assumption similarly, the enhanced medium intensity SERS band at 3115cm^{-1} is assigned for $\nu_{\text{as}}(\text{N-H})$ the bending modes.

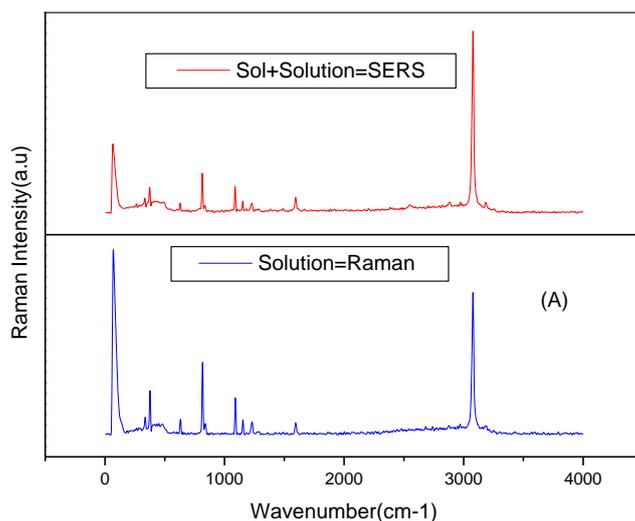


Fig.7 Comparison of Raman and SERS spectra of 1-Fluoro 4-Nitrobenzene(A)

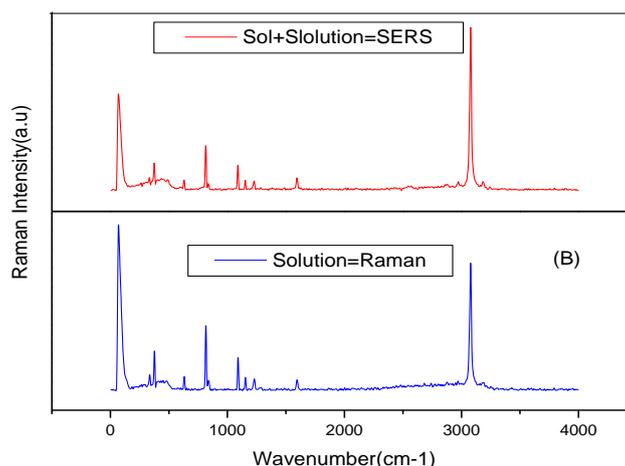


Fig.8 Comparison of Raman and SERS spectra of 1-Fluoro 4-Nitrobenzene(B)

The charge transfer mechanism of SERS can be explained by the resonant Raman mechanism in which charge transfer excitations from the metal to the adsorbed molecule or vice versa occur at the energy of the incident laser wavenumber[41,42]the frontier orbital theory plays a significant role in the understanding of the charge transfer mechanisms of SERS two types of charge transfer mechanisms are predicted. One is molecule to metal and the other is metal to molecule. Molecule to metal charge transfer excitation occurs when an electron is transferred from the highest occupied molecular orbital (HOMO) of the adsorbate to the Fermi level of the metal. Conversely transfer of an electron from the Fermi level of the metal to the lowest unoccupied molecular orbital (LUMO) results in metal to molecule charge transfer the theoretical results shows that HOMO,LUMO energy of the molecule are -0.2704eV , -0.04839eV respectively. Here we conclude that the metal to molecule charge transfer interactions is more preferred in our case. The electron is probably transferred from the metal to the LUMO of the molecule.

Analysing Table.4 we can see that the calculated vibrational wavenumbers have tiny difference. However SERS value are in good enhancement. Raman values compare with SERS spectrum for the SERS spectrum at good enhancement. The calculated vibrational spectra using DFT-B3LYP which are in good agreement with experimental value Fig.6(experiment) A and B the SERS spectrum of good enhancement for most lines.

V. Conclusion

FT-IR,FT-Raman and SERS spectra of 1-Chloro 4-Fluorobenzene were studied the molecular geometry and wavenumbers have been calculated theoretically. The SERS spectrum of the title compound for the two different ratio for the good enhancement. The calculated vibrational wavenumbers obtained by SERS are in the good enhancement with the experimental values obtained for the investigated molecule. 1-Chloro 4-Fluorobenzene of the vibrational spectral analysis was carried out using near FTIR and Raman spectroscopy. The density functional theoretical (DFT) computations were also performed at the B3LYP at 6-311**G basis set to derive the equilibrium geometry, vibrational wavenumbers and intensities vibrational spectral assignments are carried out. The Raman vibrational wavenumbers of the adsorption geometry of 1-Chloro 4-Fluorobenzene on a silver surface has been simulated using DFT-B3LYP and its compared with the experimental spectrum. The calculated vibrational spectra are in good enhancement with experiment value and proved the proposed adsorption configuration. In this study the 1-Chloro 4-Fluorobenzene based on DFT calculations have been carried out. The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

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