Vibrational Spectral Analysis of TCHS used in Self Assembled Monolayer and Formation Dynamics

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Abstract

Infrared and Raman spectra of trichloro hexylsilane has been recorded. Density functional theory, DFT, with the different functional groups was used for the optimization of the ground state geometry and simulation of the Infrared and Raman spectra of this molecule. Calculated geometrical parameters fit very well with the experimental ones. The formation and characterization of Self Assembled Monolayer (SAM) of trichloro hexylsilane helps to understand the mechanism of formation of SAM. The Self Assembled Monolayer of trichloro hexylsilane on Si/SiO2 substrate was prepared and the resulting surface was studied using Atomic Force Microscopy (AFM).

Keywords:AFM,TCHS,SAM

Introduction

In different disciplines of surface engineering Self Assembled (SAM) Monolayer of organic molecules are widely used to modify surface energy, adhesion, friction, surface electrical and electronics properties. In the areas of nanolithography, [1] nanoelectronics,[2] nanophotonics [3] and sensors [4,5],recent advances in microscopy and spectroscopy techniques enables to use SAM and LB monomolecular films for variety of applications. Silane self-assembled monolayers can be used to create a durable protective coating on glass or ceramic surfaces. The covalent bonding between the coating and the surface gives the coating excellent resistance to the damage caused by abrasion and erosion, while the chemistry of the tail group can alter the coating's thermal, ultraviolet and chemical resistance.Chlorosilanes are the most reactive but evolve corrosive hydrogen chloride on hydrolysis. In this work, Trichloro Hexyl Silane is used for the formation of Self-assembled monolayer (SAM). Surface topography and roughness are determined by Atomic Force Microscopy (AFM). We have also characterized the silyl head group using FTIR and FT Raman spectroscopy, with the assistance of DFT computed molecular parameters.

Experimental Work

The compound under investigation namely TCHS is purchased from Sigma–Aldrich chemicals, U.S.A with spectroscopic grade and it was used as such without any further purification. FT-IR spectra of the present liquid sample Trichlorohexylsilane (TCHS) kept in the liquid window has been recorded using an Agilent Cary 630 spectrophotometer in the wave number range 400–4000 cm^{-1} with the spectral resolution of 2 cm^{-1}. FT Raman spectra of Trichlorohexylsilane (TCHS) were recorded using Bruker RFS 27/s spectrometer in the region 4000–450 cm^{-1} with a resolution of 4 cm^{-1}. An Nd : YAG laser of 1064 nm with an output of 100 mW was used as the exciting source.

Sample Preparation and formation of SAM:

The AR grade Trichloro hexyl silane (TCHS) was purchased commercially from Sigma Aldrich and was used as received. The solvent toluene and other inorganic chemicals of GR grade were obtained from Merck. The spin coating technique is used for preparation of SAMs in this experiment, as an interesting alternative to the more common method of submerging the substrate in a silane solution[6],Four inch diameter silicon wafers with a native oxide layer(p-type, h100i orientation, 20–30 X cm resistivity and surface roughness .19 nm) were cut into samples of 1 cm by 1 cm and then, the substrates were first sonicated for 10 min in propanol, acetone and ultrapure water (Millipore Direct-Q,18 MX-cm resistivity). It was then cleaned with piranha solution (3:1 volumetric ratio H_2SO_4/H_2O_2) for few minutes or until the visible reaction stops,taking extreme caution while using very strong oxidant piranha solution, due to its violent reactivity towards organic matter. The silicon wafers were again rinsed with ultrapure water and dried under N_2 gas.The TCHS was diluted with toluene,[7,8] to form 0.01 M, 0.05 M, and 0.1M solutions. It was found that the solution concentration played a vital role in the formation of SAM of silane.since at lower concentrations, it was found to form incomplete island like structures and higher concentrations favored multi layers formation. A smooth monolayer was formed at 0.01 M concentration by spin coating technique. The monolayer formation was optimized with different speeds and a speed of 5000 rpm yielded best result. The spin coating was performed under the anhydrous conditions of a glove box (MBraun M-20). Later, the substrates were exposed to ammonia and hydrochloric acid vapors for a few hours at room temperature to enhance the hydrolysis of silane and to promote the bonding to Sio_2 surface. The substrates were then rinsed in the toluene to remove the multilayer and physically adsorbed materials.

SAM characterization:

Surface topography and roughness were determined by Atomic Force Microscopy (AFM) (Seiko Instruments) using the tapping mode with a single crystal Si tip with a resonant frequency of 300 kHz, with 0.5 kHz scanning speed. Height and phase images were collected simultaneously and analyzed using the manufacturer-provided software.

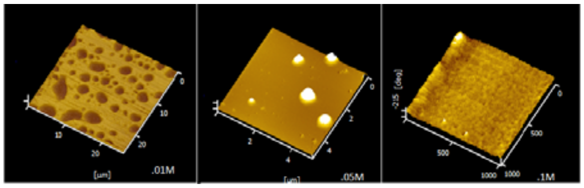

Figure 1: SAM of TCHS for different concentration by using AFM

Fig. 1 shows the morphology of the films obtained from the AFM studies for different concentration along with phase images and its height profiles. It was found that at 0.01 M concentration the films were uniform. An influencing parameter in the formation of SAM is the concentration of the solution, and is related to the amount of aggregate deposited on the substrate. It can be observed from the AFM images that, with lower concentration of TCHS, the surface roughness also decreases, which in turn yields smoother films.

Quantum chemical calculations:

The entire quantum chemical calculations have been performed at DFT (B3LYP) method with 3-21G, 6-311G (d,p) and 6-311++G(d,p)/HF basis sets using the Gaussian 09 program and def sv(p) basis set using Turbomole. The optimized structural parameters have been evaluated for the calculations of vibrational frequencies at different level of theories and a variety of basis sets by assuming Cs point group symmetry. At the optimized geometry for the title molecule no imaginary frequency modes were obtained, therefore a true minimum on the potential energy surface was found. As a result, the un scaled calculated frequencies, reduced masses, force constants, infrared intensities, Raman activities, Raman intensities, and depolarization ratios were obtained. In order to improve the calculated values in agreement with the experimental values, it is necessary to scale down the calculated harmonic frequencies. Hence, the vibrational frequencies calculated at 0.9668 for B3LYP/6-311G(d,p) and the range of wave numbers above 1700 cm^{-1} are scaled as 0.958 and below 1700 cm^{-1} scaled as 0.983 for B3LYP/6 -311++G(d,p) .The assignments of the calculated normal modes have been made on the basis of the corresponding PEDs. The assignments of the calculated normal modes have been made on the basis of the corresponding potential energy distributions (PED). The PEDs are computed from quantum chemically calculated vibrational frequencies using VEDA program [9].Gauss view program has been used to view visual animation and also for the verification of the normal modes assignment. The optimized structure of TCHS is shown in figure 2.

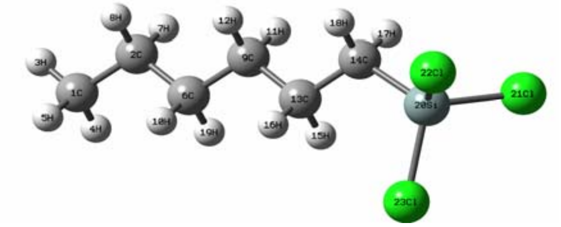

Figure 2.Optimized Structure of TCHS

Results and Discussions

Vibrational Spectral Analysis

The TCHS molecule has 23 atoms, which possess 63 normal modes of vibrations. All vibrations are active both in Raman and infrared spectra.The spectral bands are due to the internal vibrations of trichlorosilyl group,methyl group and methylene group.The vibrational analysis is based on the FT IR spectrum and FT Raman spectrum. Computed FT RAMAN and FT IR spectra of Trichloro Hexylsilane TCHS) are used for the analysis. Detailed vibrational assignments of TCHS have been carried out with the aid of VEDA (Table 2).

CH_2 vibrations

The asymmetrical CH_2 stretching vibrations are generally observed at 3000-2900 cm^{-1},while the CH_2 symmetric stretch will appear between 2935-2915cm^{-1} [10].In this molecule the CH_2 asymmetric stretching are observed at 2933,2962 cm^{-1} and 2931cm^{-1} as strong band in FT-IR and ,FT-Raman. The corresponding calculated value is 2984, 2981,2961,2949,2930 cm^{-1} respectively. And symmetric stretching vibrations are observed at 2862 cm^{-1} and 2891, 2868, 2729 cm^{-1}as strong band in FT-IR and FT-Raman respectively. The corresponding calculated value is 2901, 2906 cm^{-1} respectively. The CH_2 scissoring band is generally observed at 1480-1440cm^{-1} ,while the CH_2 wagging, rocking and twisting vibrations are observed in the region 1430-715 cm^{-1} [11,12]. In this molecule the CH_2 scissoring band are observed at 1469cm^{-1} and 1446 cm^{-1}as strong band in IR and Raman and the calculated values are 1469 cm^{-1} respectively. The CH_2 wagging vibration are observed at 1303cm^{-1} in FT-Raman and the and the assignments are in agreement with the calculated wave numbers 1305 cm^{-1} /6-311G(d,p), respectively. In accordance with the literature, weak bands appearing at 1190 and 1108cm−1 in IR are identified as CH2 asymmetric rocking vibration and found to be in the uncontaminated mode. These assignments are made in conformity with the assignments proposed by Saunders and Smith [13]. The C–H out of plane bending vibrational modes can all be assigned with confidence to the observed wave numbers from the IR and Raman spectra at 896,950 cm^{-1}. The bands at 950 and 784 cm−1 in the Raman are assigned respectively to wagging and twisting mode of methylene group. The calculated values by B3LYP with 6-311G (d,p) and def TZVP (TURBOMOLE) basis sets approximately coincide with the observed values.

C-CH_3 Vibrations

The molecule TCHS contains one methyl group in molecular chain, there are one C–CH_3 stretching vibrations are possible. The C–CH_3 vibrations usually combine with C–H in-plane bending vibration [14,15]. According to which, the active fundamentals appear with very strong to medium intensity at 1383cm−1 in IR and with weak intensity to very weak at 1303 in Raman are identified as C–CH3 stretching vibration. The C–CH3 in-plane bending vibration is found at 1000 and 966 cm−1 and out of- plane bending vibrations are assigned to 335 and 274 cm−1. As reported in to the literature [16], all the above C–CH3 vibrations deviate slightly from the expected range. The assignments also ascribed to methyl modes are in close agreement withthe literature values [17-20]

$SiCl_3$ Vibrations

Vibrational analysis of $SiCl_3$ group is made on the basis of silicon and chlorine group. The analysis of vibrational spectral features of $SiCl_3$ group exposes ‘‘silicon hyper conjugation’’ which is the stabilizing effect of silicon atom observed in organo silicon compounds [21-22]. The presence of the ‘‘Beta silicon effect’’ can be confirmed from the decrease of the partial positive charge in Silicon atom, the decrease of Si–Cl bond strength and consequent shift of vibrational band positions to the lower wave number regions [23].The Si-Cl symmetrical stretching vibration are generally observed in the region 450-535cm-1[24].In TCHS, Si-Cl symmetrical stretching mode is noticed at 481 cm^{-1} as a weak band in Raman which shows a good agreement with the calculated value (471cm^{-1}). The Silicon hyper conjugation is found to cause reduction in Si–Cl bond strength due to ‘no bond resonance’ and changes in partial charges on Si and Cl atoms in addition of electron accepting nature of silyl group leading to intra molecular charge transfer. The comparison of the optimized geometry of TCS with TCHS using DFT has showed that Si–Cl bond length has been increased to 2.16 A°, in TCHS compared to the corresponding value of 2.043 A °in TCS. The decrease of partial positive charge on silicon atom from 0.565 in TCS to 0.50 in TCHS has been found to act as a striving force to the stabilization. The consequent weakening of Si–Cl bond can be observed by comparing the vibrational spectra of TCS and TCHS, as the shift of vibrational band positions to the lower wave number region in TCHS. The overall effect of these behaviors in TCHS is the large polarizability changes for the bending modes of trichlorosilyl group, leading to intensity enhancement in Raman spectrum contrary to computed Raman intensities, which is not observed in other silyl derivatives [25]

NBO Analysis

Natural bond orbital analysis provides an efficient method for studying intra and intermolecular bonding and interaction among the bonds and also provides a convenient for investigating charge transfer or conjugative interaction in the molecular systems [26, 27]. The larger E (2) value, the more intensive in the interaction between electron donors and electron acceptors i.e.the more donating tendency from the electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally correspond to a stabilizing donor-acceptor interaction [28]. The second order Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO basis [29]. For each donor (i) and acceptor (j) the stabilization energy E (2) associated with the delocalization i→j estimated as

$$E_2 = \Delta E_{\bar{y}} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

where qi is the donor orbital occupancy, εi and εj are diagonal elements and F(i,j) is the offdiagonal NBO Fock matrix element. NBO Analysis has been performed on the molecule at the DFT/B3LYP 6-311+ +G (d,p) level in order to elucidate the intramolecular and delocaliztion of electron density within the molecule. The lone pair of n_3 (Cl_{21}) with σ*(Si_{20}-Cl_{22}) is identified as the strongest interaction (30.3758 kJ/mol) while the hyper conjugative interactions of n_3 (Cl_{23}) → σ*(Si_{20}-Cl_{22}) and n_3(Cl_{22}) → σ*(Si_{20}-Cl_{23}) lead to the stabilization of 29.832kJ/mol and 28.451kJ/mol respectively. NBO analysis clearly supports the existence of strong C_{14}-C_{15}· · ·Si_{20} bonding. The interaction between the lone-pair n_2(Cl_{23}) and n_2(Cl_{22}), with the antibonding orbital σ*(C_{15}-Si_{20}) reveals the presence of Cl-Si…C, Cl-Si…Cl intra molecular bonding. The σ(C_{14}-C_{15}) bond is more bent away from the line of centers by 2.9° as a result of lying in the strong charge transfer path towards trichlorosilyl group.

HOMO-LUMO analysis:

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the most important orbital in a molecule. The eigen values of HOMO and LUMO and their energy gap reflect the biological activity of the molecule. A molecule having a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [30, 31]. HOMO, which can be thought the outer orbital containing electrons, tends to give these electrons as an electron donor and hence the ionization potential is directly related to the energy of the HOMO. On the other hand LUMO can accept electrons and the LUMO energy is directly related to electron affinity [32]. Two important molecularorbital (MO) were examined for the title compound, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) which are given in Fig. 3. The properties of TCHS are given in table 1.

Table 1: Properties of TCHS

Properties	Value(eV)
E_{HOMO}	-0.37411au
E_{LUMO}	-0.10886au
Electron affinity,A	2.96eV
Ionization potential, I	1.018eV
Energy gap	7.22eV
chemical potential, μ	-6.57eV
global electrophiliciy ,□	8.14eV

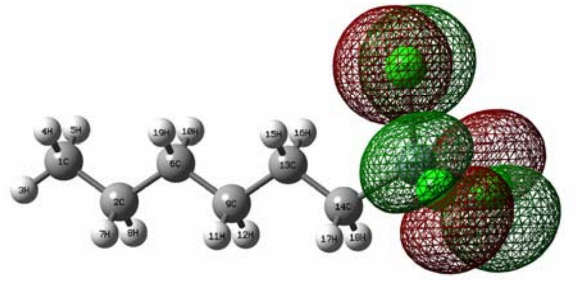

Figure 3.Isodensity plot of TCHS

Conclusion

The analysis of surface morphology of TCHS monolayer using Atomic Force Microscopy (AFM) indicates the monolayer formation at lower concentration, where the average thickness of the film is around 1 nm. The optimized geometric parameters, vibrational harmonic frequencies, PED assignments, molecular orbital energies and other properties (related with HOMO and LUMO energy values) of the compound have been calculated by using DFT/B3LYP and TURBOMOLLE methods with 6-311++G(d,p) basis set.The detailed PED% analysis of the compound showed a good agreement with the experimental data.The calculated HOMO and LUMO along with their plot has been presented for understanding of charge transfer occurring within the molecule.

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