

The Vibrational Spectra of Trichlorocyclohexylsilane and Formation of Self Assembled Monolayer

M.N.Audline Jini, J.T.T.Kumaran, A.Dickson Benjamin, S.G.Praveen

Department of Physics, N.M.Christian College, Marthandam, Kanyakumari, Tamilnadu, India.

ABSTRACT: The infrared and Raman spectra of trichloro cyclohexylsilane 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 Self Assembled Monolayer of trichloro cyclohexylsilane on Si/SiO₂ substrate was prepared and the resulting surface was studied using Atomic Force Microscopy (AFM).

KEYWORDS: Self assembly, Monolayers, Atomic Force Microscopy

I. INTRODUCTION

Formation of SAM, provides one of the easiest ways to obtain ordered monolayers through strong chemisorption between the substrate and the molecule[1]. Silanes are used as coupling agents to adhere fibres such as glass fibres and carbon fibres to certain polymer matrices, stabilizing the composite material. The silyl derivatives are of growing interest in the field of molecular electronics, for their ability to form well defined self assembled molecular thin films with predefined functions[9]. Hence in this work we have characterized the silyl head group using FTIR and FT Raman Spectroscopy aided by DFT computed molecular parameters.

II. MATERIALS AND METHODS

2.1 Sample preparation and formation of SAM

The AR grade Trichlorocyclo hexyl silane (TCCHS) 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[2]. 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 H₂SO₄/H₂O₂) 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 N₂ gas. The TCCHS was diluted with toluene, [2, 3] to form 0.01 M, 0.05 M, and 0.1 M 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 0.001 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 SiO₂ surface. The substrates were then rinsed in the toluene to remove the multilayer and physically adsorbed materials.

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2.2 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.

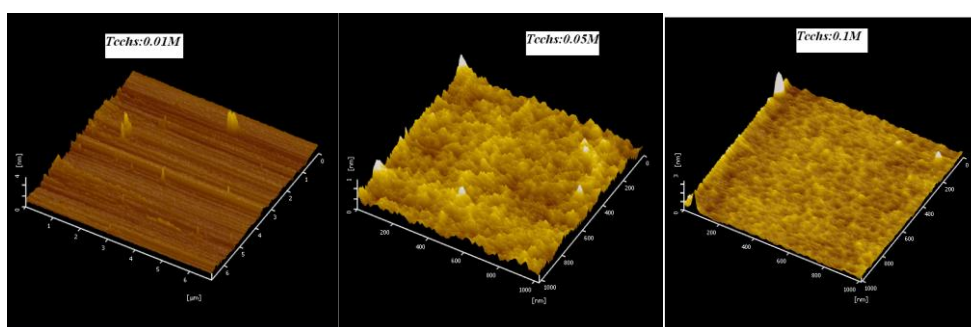


Fig1.AFM micrographs - Formation of SAM of TCCHS on Si/SiO₂ wafers for different concentration

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 .001 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 TCCHS, the surface roughness also decreases, which in turn yields smoother films.

2.3 Quantum chemical calculations

The entire quantum chemical calculations have been performed at DFT (B3LYP) method with 3-21G, 6-31G (d) basis sets and HF method 6-31G (d) basis set using the Gaussian 09 program and 6-31G basis set using TURBOMOLE software. 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 C_s point group symmetry. As a result, the unscaled calculated frequencies, 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.

III. RESULTS AND DISCUSSION

The compound trichloro cyclohexyl silane contains 21 atoms; so there can be 57 (3N-6) normal modes of vibration. The spectral bands of are due to the internal vibrations of methyl group, cyclohexane ring and trichlorosilyl group. The vibrational analysis is based on the FT IR spectrum and FT Raman spectrum as well as the vibrational wave numbers computed at the DFT level with the scaled wave numbers. The optimized geometry of TCCHS from turbomole is candidly shown in figure2.

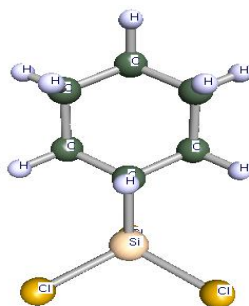


Fig.2.Optimized geometry of TCCHS from turbomole

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3.1 VIBRATIONAL SPECTRA

FT-IR spectra of the present liquid sample TCCHS kept in the liquid window has been recorded using a Agilent Cary 630 spectrophotometer in the wave number range 400–4000 cm^{-1} with the spectral resolution of 2 cm^{-1} .

3.1.1. C-C Vibrations

There are six equivalent C-C bonds and consequently there will be six C-C stretching vibrations in hexane. The C-C stretching vibrations are generally observed at 1200–800 cm^{-1} [9]. The bands are observed at 1108, 1078, 1041, 918, 888, 851, 835 cm^{-1} in IR and 1100, 1075, 1040, 1000, 850, 835 cm^{-1} in Raman are identified as C-C stretching vibrations. The theoretically scaled C-C stretching vibrations by DFT method are at 1113, 1081, 993, 910, 872, 868, 833 cm^{-1} shows excellent agreement with recorded FT-IR spectral data. The theoretically calculated C-C in plane and out-of-plane bending modes have been found to consistent with the recorded spectral values.

3.1.2. SiCl₃ Vibrations

The analysis of vibrational spectral features of SiCl₃ group exposes “silicon hyperconjugation” which is the stabilizing effect of silicon atom observed in organo silicon compounds [4][5]. The effect can be understood in terms of classical hyperconjugation which is the stabilizing overlap between empty p orbital of carbon atom in the ring and the filled r molecular orbital of silicon to chlorine bond, leading to “Beta silicon effect”. The presence of the 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 [5]. The Si-Cl stretching vibration is observed at 791, 743 cm^{-1} in IR and 750, 490, 430, 320, 280, 180 cm^{-1} in Raman respectively. The vibrational frequency obtained from the calculation by DFT method are 783, 705 cm^{-1} in IR and 705, 497, 430, 313, 269, 173 cm^{-1} in Raman. The theoretically scaled value shows excellent agreement with recorded FT-IR, Raman spectral data.

3.1.3. CH₂ Vibrations

The asymmetrical CH₂ stretching vibrations are generally observed at 2972 cm^{-1} [6], 3000–2900 cm^{-1} [7], while the CH₂ symmetric stretch will appear between 2935–2915 cm^{-1} [7]. In this molecule the CH₂ asymmetric stretching are observed at 2950 cm^{-1} as strong band in Raman. The corresponding calculated values are 2981, 2977, 2966 cm^{-1} respectively. And symmetric stretching vibrations are observed at 2933 cm^{-1} as strong band in FT-IR respectively. The corresponding calculated value is 2930 cm^{-1} respectively. The CH₂ scissoring band is generally observed at 1455 cm^{-1} [6], 1480–1440 cm^{-1} [8] while the CH₂ wagging vibration are observed in the region 1307–1304 cm^{-1} [6]. In this molecule the CH₂ scissoring band are observed at 1451 cm^{-1} , 1450 cm^{-1} as strong band in Raman and IR. The corresponding calculated values are 1470 cm^{-1} respectively.

3.2 MULLIKEN AND NATURAL CHARGE DISTRIBUTION

The Mulliken charge is directly related to the vibrational properties of the molecule, and quantifies how the electronic structure changes under atomic displacement; it is therefore, related directly to the chemical bonds present in the molecule. It affects dipole moments, polarizability, electronic structure and more properties of molecular systems.

Table 1: Mulliken and natural charges of the TRCCHS

Atoms	Natural Charge (NBO)	Atomic Charge (Mulliken)(e)
C ₁	-0.47574	-0.243627
C ₂	-0.47163	-0.247541
C ₃	-0.47680	-0.242139
C ₄	-0.47163	-0.247541
C ₅	-0.47574	-0.243626
C ₆	-0.72697	-0.418009
H ₇	0.25161	0.133892
H ₈	0.23692	0.130768
H ₉	0.25516	0.139306

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H ₁₀	0.24777	0.154460
H ₁₁	0.25971	0.159409
H ₁₂	0.23692	0.130768
H ₁₃	0.25516	0.139306
H ₁₄	0.25972	0.159409
H ₁₅	0.24777	0.154456
H ₁₆	0.28451	0.192023
H ₁₇	0.23652	0.129573
Si ₁₈	1.42667	0.748780
Cl ₁₉	-0.36536	-0.243443
Cl ₂₀	-0.36922	-0.242783
Cl ₂₁	-0.36536	-0.243441

The natural population analysis clearly describes the distribution of electrons in various sub-shells of their atomic orbital's [10]. The Mulliken and natural charge distribution of the molecule are calculated for TRCCHS on HF and B3LYP levels with 6-31G basis set in HF and B3LYP methods. The calculated values of the charges of the title molecule are sorted out in table [1].

3.3. HOMO-LUMO ENERGY GAP

Molecular orbital's (HOMO and LUMO) and their properties such as energy are very useful for physicists and chemists and are very important parameters for quantum chemistry. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital's taking part in chemical stability.

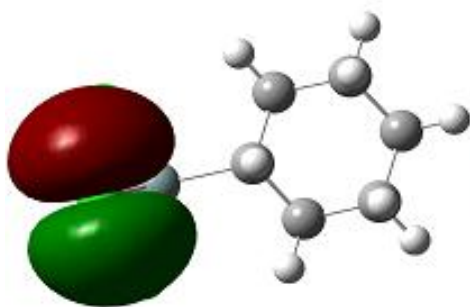


Fig 3a. HOMO of TCCHS

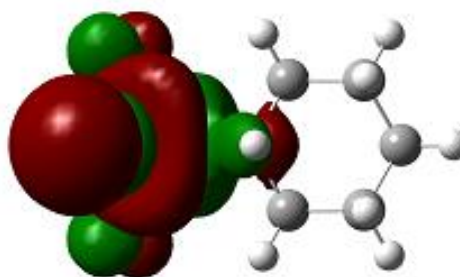


Fig 3b. LUMO of TCCHS

HOMO as an electron donor represents the ability to donate an electron. LUMO as an electron acceptor represents the ability to obtain an electron. The relative energy of the molecular orbital's have been calculated and a graphical representation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of TCCHS are given figures (3a) and (3b). The energy difference between the HOMO and LUMO is about 6.314 eV.

IV. CONCLUSION

The analysis of surface morphology of Trichlorocyclohexyl silane monolayer using AFM indicates the monolayer formation at lower concentration, where the average thickness of the film is around 3nm. The structure of TCCHS was optimized by DFT method, HF method with basis sets 3-21G, 6-31G using Gaussian 09 and Turbo mole Software. The optimized geometry and the vibrational frequencies of the title compound have been calculated and have been found to agree well with experimentally reported values. A plot of the highest occupied molecular (HOMO) and that of the lowest occupied molecular (LUMO) is also made. The HOMO LUMO energy gap is 6.314 eV.

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