CHARACTERIZATION OF SELF-ASSEMBLED MONOLAYERS BY SUM

FREQUENCY GENERATION SPECTROSCOPY AND IMAGING

MICROSCOPY

A Dissertation Presented to

the Faculty of the Department of Chemistry

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

By

Jack Deodato C. Jacob

August 2013

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ABSTRACT

This dissertation reports the characterization of self-assembled monolayers utilizing sum frequency generation (SFG) vibrational spectroscopy and imaging microscopy. Several variables were studied for their effect on the conformational order of the formed monolayers. In the analysis of octadecanoxy-phenylethanethiolate monolayers on gold, it was determined that the presence of an aromatic ring near the gold substrate caused no significant loss of the conformational order of the monolayer. Gauche and kink defects were observed by SFG spectroscopy, caused by the cross-sectional difference of the alkoxy chains and the aromatic ring, forcing the chains to tilt and kink until the methylene groups further above the chains can align to form the all-trans conformation. Additional octadecyl chains attached to the aromatic ring led to an increase in gauche defects, implying the decrease of conformational order is also due to steric effects. SFG imaging microscopy was used to determine the effect of the grain size of the gold substrate on the quality of monolayers produced. Analysis of the resulting images revealed that dodecanethiolate monolayers grown on surfaces with a large average grain size have fewer gauche defects within the alkyl chain assembly and thus are more conformationally ordered than those deposited on smaller-grained substrates. This variance between surfaces was not observed with octadecanethiolate monolayers, possibly due to the increased conformational ordering associated with their longer chain length enables the these thiolates to reduce any chain disordering induced by the grain size of the substrate. Finally, the *in situ* SFG spectroscopy was used to monitor selfassembled monolayers as they reductively desorb in alkaline solution.

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Chapter 1: Introduction

1.1. Self-assembled Monolayers

Molecular self-assembly is the spontaneous process by which molecules organize into structurally ordered arrangements without guidance from an outside source. These molecules are held together by non-covalent bonds, such as hydrogen bonds, van der Waals interactions, and π - π interactions.¹ Self-assembly can be classified into two categories: static and dynamic. Static self-assembly occurs in systems at equilibrium and do not require energy, while in dynamic self-assembly, energy in necessary for the process to proceed. Examples of molecular self-assembly are abundant in nature, such as the lipid bilayers of cells,² and the quaternary structures of proteins.³

A self-assembled monolayer (SAM) is an organized layer of organic molecules adsorbed on a surface and its formation involves static two-dimensional self-assembly. Compounds that form SAMs have functional groups called "headgroups" that have a strong chemical affinity for the surface substrate (Figure 1.1). For alkanethiolate-gold SAMs, the headgroup-surface affinity is so robust that even other adventitious organic materials already present on the surface can be displaced. The parts of the molecule that are oriented away from the surface are called "tailgroups" and they provide the exposed SAM interface with its fundamental character. In between the headgroups and the tailgroups often are alkyl chain "spacers", which are also essential because they provide the van der Waals interactions that drive the self-assembly process. These molecules can be tailored by varying headgroups,⁴⁻⁸ endgroups,⁹⁻¹⁶ and spacers¹⁷ to change the wetting and interfacial properties of the monolayer for different applications.¹⁸ which can act as a thin protective barrier on metals against corrosive agents. Due to their strong chemical affinity to metal surfaces, self-assembled monolayers production is uncomplicated and can be done in various solvents and conditions. Because of this, these nanoscale films have been used in a variety of applications such as lubricants for micromechanical systems,¹⁹ and sacrificial coatings for nanolithography,²⁰ and corrosion inhibition studies.²¹⁻²⁷



Figure 1.1. Diagram of a self-assembled monolayer.

1.2. The Au(111) Substrate

Of the several different types of SAM systems based on various combinations of headgroups and substrates,²⁸ the most studied are alkanethiols adsorbed on metal surfaces including the coinage metals gold, silver, and copper.²⁹ Additionally, SAM research has extended to surfaces such as stainless steel,³⁰ zinc,²⁷ and several others. Most investigations have concentrated on gold as the substrate of choice because of its inertness to the formation of oxides, its resistance to atmospheric contamination and its strong chemical affinity to the sulfur headgroups.²⁸

The most common method of preparing gold surfaces for SAM formation is by growing thin films onto silicon wafers, glass, or mica, usually by physical vapor deposition under high vacuum conditions (<10⁻⁵Torr). For silicon wafers and glass slides, a prelayer of titanium or chromium is required to improve the adhesion between gold and the substrate.²⁸ Thermal deposition of gold on Si (111) typically produces films with small grains of 45-60 nm in diameter, while grains of 600 nm and above can be achieved by flame annealing gold evaporated on mica.^{28,31} Grain size can also be increased with different methods such as treatment with strong acids,^{32,33} template stripping,³⁴ and electrochemistry.³³ After annealing, gold surfaces will have large flat grains with (111) orientation separated by monoatomic height steps.

1.3. Preparation of SAMs on Metals

The formation of SAMs reflects the favorable structural dynamics whereby the adsorbed film reduces the interfacial energy of the surface's interface. SAMs derived from alkanethiols are formed by the chemisorption of hydrophilic headgroups onto a substrate from either the vapor or liquid phase followed by a slow two-dimensional organization of the hydrophobic alkyl chains.³⁵ For alkanethiols, the sulfur atoms have generally been described as chemically bonding to the three-fold hollow sites of the gold surface.³⁶ This reaction is highly exothermic, with an enthalpy of ~-150 kJ mol⁻¹, and provides the energy to drive self-assembly. At low coverage, it is believed that the alkyl chains assume a flat-lying monolayer. As surface coverage increases, and the alkyl chains are forced together, the monolayer adopts an upright configuration.

Chemisorption of the alkanethiols can occur in a matter of seconds. The alkanethiols then undergo a slow two-dimensional rearrangement to reduce chain to chain separation and to optimize the van der Waals interactions between the chains. This rearrangement step can take a matter of hours to days to form a fully ordered monolayer. After these organizational steps, long chain alkanethiols assume a well ordered and densely packed monolayer with a hexagonal ($\sqrt{3}x\sqrt{3}$)R30° lattice.³⁷ Many factors influence the self–assembly of these monolayers such as temperature, solvent, nature of the adsorbate, and the substrate.^{28,38,39} Surface topography also plays an important role in the formation of a well-ordered monolayer.^{40,41}

1.3.1. Solution Deposition

SAMs are usually prepared by immersing a metal film in a dilute solution of the alkanethiol for 18-48 hours. Ethanol is the most commonly used solvent, due to several reasons: most thiols are slightly soluble in it, it is relatively inexpensive even at its highest purity, and it is non-toxic. The low solubility of the thiols in ethanol may also help in the formation of SAMs by driving these thiols onto the metal surfaces by aggregation, speeding up the self-assembly process.^{8,42} The presence of molecular oxygen might inhibit the formation of SAMs by oxidizing the thiols into disulfides and this is prevented by purging the system with nitrogen. Assembly occurs at room temperature, but some studies have found that increasing the initial temperature of the solution to 50°C and allowing the system to cool to room temperature can produce better SAMs. This

might be partly due to desorption of any existing adsorbates on the gold surface due to the high temperature.

1.3.2. Patterning SAMs

The ability of SAMs to acts as etch resists makes them very important in lithography. Using SAM patterns to protect certain parts of a metal surface from an etchant, nanostructures can be produced with relative ease. There are several methods to produce well-defined patterns of SAMs.

Microcontact printing (μ CP) is done by drop-casting an ethanolic solution of SAMs on an elastomeric stamp formed from materials such as polydimethylsiloxane (PDMS), and then pressing the stamp on a metal surface such as gold, silver, copper, or mild steel.³⁷ Typical stamps use PDMS because its elastomeric properties, E = 1.8 MPa, allows them to fit the contour of surfaces in applications where intimate contact is needed, and owing to its low surface energy, $\gamma = 21.6 \text{ dyn/cm}^2$.⁴³

After the transfer of the pattern to the metal, the resulting patterned SAM can be used in several different applications or backfilling can be used to add a different type of adsorbate in the unstamped area of the metal, producing a patterned film in the form of a mixed monolayer. Previous studies have shown that microprinted SAMs are not as wellordered as those made by immersion when formed by printing for 1-10 s (time against the surface) with stamps inked with 1-10 mM solutions of thiol.^{44,45 46}



Figure 1.2. Schematic diagram of microcontact printing using a PDMS stamp on gold. (a) Thiols diffuse from the stamp onto the gold surface. (b) The red arrow shows thiol transfer at areas of non-contact while the green arrow shows the diffusion of thiols from areas of contact to the blank areas.

Microcontact printing is a very important technique as it can be used to design surfaces with specific chemical properties at the micrometer scale level. The process is, however, beset with problems, one of which is the diffusion of non-covalently bound molecules which can occur after printing, as illustrated in Figure 1.2. Also, when a gold surface microprinted with one SAM is immersed in a solution of another alkanethiol, adsorbate backfilling or displacement has been noted on the stamped patterned surface.⁴⁷⁻

Other patterning techniques include ink-jet printing,⁵⁰ photolithography,⁵¹ and scanning probe lithography.⁵²

1.4. Methods of Analyzing Self-assembled Monolayers

Understanding the fundamental structure and properties of a SAM is essential for determining how ongoing SAM research can be directed to practical applications. There

are many methods available for the chemical analysis of SAMs, each of which has advantages and disadvantages.⁵³ X-ray photoelectron spectroscopy (XPS) can probe the chemical composition and oxidation state, SAM coverage and thickness by measuring the kinetic energy of electrons emitted up on x-ray irradiation.^{54,55} However, this technique requires an ultra-high vacuum condition so it is limited to studying solid surfaces and low vapor pressure liquids. Infrared absorption and Raman scattering are used to study the molecular moieties, molecular orientation, and SAM crystallinity in atmospheric and vacuum condition.⁵⁶⁻⁵⁸ These linear spectroscopic techniques, however, are not surface specific because atmospheric gas and interfacial liquid molecules in the beam path can interfere with the analysis. The penetration of the beam to bulk sample is another disadvantage which dilutes the surface specific signal to the bulk signal. Scanning probe microscopy techniques, like atomic force microscopy (AFM) and scanning tunneling microscopy (STM), are used to determine the 2D structure of SAMs in UHV, liquids and ambient conditions. These techniques can only show the strictures of the monolayers and still require other techniques to determine the surface chemical composition.

Non-linear spectroscopic technique such as second-harmonic generation (SHG) and sum frequency generation (SFG) are used for probing surface molecules.^{59,60} SFG can determine molecular orientation and the monolayers' conformational order while SHG can determine surface coverage, surface symmetry and interfacial electric field strength.⁶¹

1.4.1. Sum Frequency Generation Spectroscopy

Sum frequency generation (SFG) spectroscopy is a second-order, non-linear process that provides vibrational spectra of the molecules at the interface. This technique is surface sensitive, as SFG can only occur in asymmetric environments such as the interface. The bulk phase of most materials is centrosymmetric at the macroscopic scale, and thus does not contribute to the spectra. SFG have been used to monitor molecular surface interactions, to determine the nature of chemical bonding, and to probe the structures of interfaces.

In 1986, the first SFG spectrum from surface molecules was obtained by Shen and co-workers by scanning a monolayer of coumarin dye on fused silica.⁶⁰ Since then SFG has been used to study surface molecular orientation, dynamics, and imaging.^{60,62-67}

Sum frequency generation studies of self-assembled monolayers have been performed previously.^{22,68-71} One application for SFG has been the use of the spectra in the determination of the density of a monolayer. In a well-packed monolayer, the alkyl chains form an all-*trans* configuration, and the methylene groups are in a centrosymmetric system, and thus do not exhibit SFG resonances. In less ideal monolayers, gauche defects occur, and at these defects the methylene groups are non-centrosymmetric and become SFG-active. Thus, the presence of methylene resonances in the SFG spectra has been used to evaluate the orderliness of alkyl monolayers.

Several groups have conducted orientational studies of alkyl chains on surfaces using SFG, making it possible to estimate the average methyl tilts of alkanethiols from the results obtained from this data. By comparing the ratio between the intensities of the symmetric and antisymmetric methyl C-H stretches (r^+/r^-) of the ppp spectra with a theoretical orientation curve, Wang⁷¹ and Hirose^{70,72} have approximated the tilt angle of the terminal methyl groups of monolayers. It has been particularly useful in characterizing methyl terminated alkanethiols on different metals, on the basis of conformational order.

1.4.2. Sum Frequency Generation Imaging Microscopy

SFG spectroscopy is very useful in providing information about the interfacial structure of a surface. However, it can only provide the average information of a given area and does not show local characteristics due to the surface topography. Metal surfaces are inherently heterogeneous, consisting flat terraces surrounded by steps and defects. Thus, in a system consisting of self-assembled monolayers on a metal, the regions with the highest order would give the greatest contribution to the signal. However, in chemical imaging, the area can be divided into smaller regions which can be individually analyzed. This would give a better picture of what is really occurring at the surface.

A recent technique, sum frequency generation imaging microscopy (SFGIM) provides chemical images of the surface.⁷³⁻⁷⁶ Contrast is based on the vibrational frequencies of the adsorbed molecules on the surface.⁴⁷ The microscope is capable of characterizing the spatial and chemical nature of molecules on a surface and is an excellent technique in chemical imaging, to supplement the SFG spectroscopy technique by providing structural and orientational details. In addition, distribution analysis of the SFG images can provide information on conformational order of the SAMs.

The first SFG imaging was performed in 1999 by Mathias Flörsheimer and coworkers.^{77,78} The experiment proved that SFG imaging could be done, but the configuration that was used limited the system to transparent samples. Kern and coworkers built a SFG imaging microscope in Germany, and produced chemical images of patterned monolayers on gold.^{45,79} Cimatu and Baldelli improved upon the design and built a SFG microscope with a spatial resolution of 2 µm which has been used to image several surface systems.^{49,80-84} SFGIM has been used to probe various surfaces such as corrosion on metal surface, chemical imaging of patterned surface, orientational and conformational distribution of surface molecules, and local electron-hole dynamics.^{82,85-87}

1.4.3. Electrochemistry

SAMs have potential use as nanoscale insulators or capacitors;⁸⁸ however, studies have found that electrolytes can degrade these monolayers.⁸⁹ Two aspects of SAMs play very important roles in producing a rigorous barrier: the stability of the thiol-metal bond against both oxidative and reductive desorption, and the ability of the monolayer to repel ions.⁸⁹ One route to such analysis is via voltammetry, which has been used to characterize the sulfur-metal bond of alkanethiolate monolayers.

Cyclic voltammetry is a technique where the potential is swept linearly versus time from two potentials, E1 and E2 and then reversed. During the potential sweep, current is measured. Using cyclic voltammetry, alkanethiols can be desorbed either by oxidation or reduction.²⁷

Determining the ionic permeability of a SAM is also a useful approach to analyzing the insulating properties of a monolayer. SAMs on metals exposed to an electrolytic solution can be viewed as a Helmholtz ideal capacitor, with the metal and the solution acting as the capacitor plates, and the monolayer acting as the dielectric material. Previous studies using electrochemical impedance spectroscopy have shown that as the alkyl chain length increases, SAMs become better insulators.⁹⁰

1.5. Dissertation Contents

The goal of this study is to characterize several self-assembled monolayers utilizing SFG spectroscopy and SFGIM. In **Chapter 2**, the theories and instrumentation used in the succeeding chapters will be presented.

Chapter 3 describes the SFG spectroscopy of alkoxy-phenylethanethiolate SAMs on gold. Their SFG spectra were used to determine the order and the orientation of the adsorbates on the surface of gold. Model phenylethanethiols were synthesized and analyzed to determine the effect of these factors on the SFG intensity of the aromatic C-H stretching modes: (1) the symmetry along the benzene ring and (2) the presence of long alkoxy chains on the ring.

Chapter 4 presents the study of the effect of grain size of gold substrate on conformational order of monolayers derived from dodecanethiol (DDT) and octadecanethiol (ODT) prepared on two gold surfaces with different grains sizes: atomically flat gold (gold deposited on mica) which has a large average grain size, and gold deposited on silica, which has small average grain size. These SAMS were probed with sum frequency generation imaging microscopy (SFGIM) to determine the effect of grain size of the surface on the conformational order and the methyl tilt of the monolayers' alkyl chains.

Chapter 5 describes the *in situ* SFG monitoring of self-assembled monolayers being desorbed from gold in an electrochemical cell. SFG spectra were taken at different electric potentials to study the effect of chain length on desorption.

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Chapter 2: Theory and Instrumentation

2.1. Sum Frequency Generation

2.1.1. Theory

When molecules interact with the weak electric field, the molecular vibrational response is linear and has an induced dipole of

$$\mu = \mu^o + \alpha E \qquad \qquad \text{Equation } 2.1$$

where μ^{o} is the permanent dipole of the molecule due to the localized electron distribution around an atom or a functional group and α is the polarizability of the molecule. More intense electric fields, such as those produced by a pulsed laser beam, produce a molecular response that becomes non-linear as higher-order polarizabilities contribute significantly to the induced dipole.^{1,2} These additional contributions can be incorporated in Equation 2.1 to produce

$$\mu = \mu^{o} + \alpha E + \beta : EE + \gamma : EEE + \dots$$
 Equation 2.2

where β and γ are the second- and third-order hyperpolarizabilities. The polarization of the system, *P* can be written as:

$$P = P^{(0)} + \varepsilon_0 (\chi^{(1)} \cdot E + \chi^{(2)} : EE + \chi^{(2)} : EEE...)$$
 Equation 2.3

 $P^{(0)}$ is the static polarization, ε_0 is the vacuum permittivity, and $\chi^{(i)}$ is the ith-order susceptibility. SFG is an example of a second-order non-linear optical process.

Sum frequency generation occurs when two laser beams of frequency ω_1 and ω_2 visible laser interact to generate an output beam at the sum frequency, ω_{SF} . Surface SFG uses a tunable infrared laser and a fixed visible frequency beam which are pulsed simultaneously on a surface.^{3,4} When the IR beam is tuned through a vibrational resonance of the adsorbate, it induces a vibrational transition from the ground state to an excited state. The visible beam simultaneously induces a transition to a higher energy non-stationary state similar to an anti-stokes Raman process to produce the coherent SFG beam. The spatial and temporal overlap of the two beams is essential to produce SFG. The SFG beam is generated at an angle which can be calculated

$$\omega_{SFG} n_{SFG} \sin \theta_{SFG} = \omega_{IR} n_{IR} \sin \theta_{IR} + \omega_{vis} n_{vis} \sin \theta_{vis}$$
 Equation 2.4

n is the refractive index of the medium through which the beams pass through, and θ is the angle of the beams to the surface normal.



Figure 2.1. Schematic diagram of a typical SFG configuration. Two incident beams of visible (green) and IR (red) are overlapped on the surface and generate a coherent SF beam at an angle, θ_{SFG} , defined by conservation of momentum and energy.

The intensity of the SFG beam, I_{SFG} , is directly proportional to intensities of the two input beams and the square of the sum frequency susceptibility, $\chi_{ijk}^{(2)}$.

$$I_{SFG} \propto \left| \sum \left[F_i \chi_{ijk}^{(2)} \left[F_j E_j \right] F_k E_k \right]^2 \right|$$
 Equation 2.5

Local field effects, F_i , F_j , and F_k correlate the SFG intensity with the second-order susceptibility. The second order nonlinear susceptibility, $\chi_{ijk}^{(2)}$, has two components: $\chi_{NR}^{(2)}$ is the non-resonant susceptibility arising from the gold substrate, while $\chi_R^{(2)}$ contains the vibrational information of the molecules on the surface. On dielectric surfaces, nonresonant component is small and real, but metal and semiconductor surfaces can be large and complex.²

$$I_{SFG} \propto \left|\chi_R^{(2)} + \chi_{NR}^{(2)}\right|^2 = \left|\sum \frac{A_q}{\omega_{IR} - \omega_q - i\Gamma} + \chi_{NR}^{(2)}\right|^2 \qquad \text{Equation 2.6}$$

A_q is the amplitude of the resonance, ω_q is the frequency of the qth vibrational mode, and Γ is the damping constant. Notably, $\chi_R^{(2)}$ is a macroscopic quantity that can be related to microscopic quantities by Equation 2.7. $\chi_R^{(2)}$ is proportional to average hyperpolarizability of the adsorbate, $\beta^{(2)}$, which in turn is proportional to the product of the IR and Raman transition moments.

$$\chi_R^{(2)} \propto N \langle \beta^{(2)} \rangle$$
 Equation 2.7

Thus, molecular vibrations will only be SFG-active if they are IR-active and Ramanactive. In the electric dipole approximation, SFG only occurs in non-centrosymmetric crystals or at the interface, since Raman and IR transitions are exclusive in centrosymmetric media.

2.1.1.1. Surface Selectivity

In a centrosymmetric environment, all directions are equivalent and the value of $\chi_{iik}^{(2)}$ for all directions must be equal.

$$\chi_{ijk}^{(2)} = \chi_{-i-j-k}^{(2)}$$
 Equation 2.8

As a third-rank tensor, changing the three subscripts of $\chi_{ijk}^{(2)}$ would be equivalent to reversing the axis system and changing the sign under the inversion operation.

$$\chi_{ijk}^{(2)} = -\chi_{-i-j-k}^{(2)}$$
 Equation 2.9

Thus, under the electric dipole approximation, SFG is forbidden in centrosymmetric environments, as $\chi_{ijk}^{(2)}$ must be zero to satisfy both Equations 2.8 and 2,9.^{1,2,5} This makes SFG surface specific as the bulk of most materials are centrosymmetric and thus SFG is not allowed. At the interface, the inversion symmetry is broken and SFG can occur.
2.1.1.2. Orientational Analysis Using SFG Spectroscopy

Because SFG is coherent and can probe different tensors of the surface susceptibility, it can be used to analyze the polar ordering of molecular groups on the surface. Orientational analysis is performed by comparing the ratios of peak intensities with a calculated theoretical orientation curve. By using the ratios of peak intensities, several parameters such as incident electric fields and the number of molecules can be factored out.

Fresnel coefficients are used to correct for local field effects at a specific frequency and coordinate axis and calculated from refractive index of the incident medium (n_1) , monolayer (n_m) and substrate (n_2) . The local field correction factors are as follows.⁶

$$F_{x} = \frac{2n_{1}\cos\theta_{t}\cos\theta_{i}}{n_{1}\cos\theta_{t} + n_{2}\cos\theta_{i}}$$

$$F_{y} = \frac{2n_{1}\cos\theta_{i}}{n_{1}\cos\theta_{i} + n_{2}\cos\theta_{i}}$$
Equation 2.10
$$F_{z} = \frac{2n_{2}\cos\theta_{i}\sin\theta_{i}}{n_{1}\cos\theta_{t} + n_{2}\cos\theta_{i}} \frac{n_{1}^{2}}{n_{m}^{2}}$$

2.1.1.3. Macroscopic Susceptibility

The magnitude of $\chi_{ijk}^{(2)}$ depends on the polar orientation of the molecule on the surface. By varying the polarizations of the input and output beams, the Cartesian components of $\chi_{ijk}^{(2)}$ can be determined, which in turn allows the orientation of the surface molecules to be deduced.

 $\chi_{ijk}^{(2)}$ is composed of 27 tensor elements, though due to symmetry constraints, there are only 7 non-zero components.^{2,5,7} Since the x and y axes are equivalent for an isotropic surface, there are only four combinations of polarizations that allow sum frequency emission: $\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)}, \ \chi_{xzx}^{(2)} = \chi_{yzy}^{(2)}, \ \chi_{xxz}^{(2)} = \chi_{yyz}^{(2)}, \ and \ \chi_{zzz}^{(2)}$.

On the isotropic surface, the SFG effective susceptibility is as follows:

$$\chi_{eff}^{(2)} = -F_{xxz}\chi_{xxz}^{(2)} + F_{yyz}\chi_{yyz}^{(2)} - F_{xzx}\chi_{xzx}^{(2)} + F_{yzy}\chi_{yzy}^{(2)} + F_{zxx}\chi_{zxx}^{(2)} + F_{zyy}\chi_{zyy}^{(2)} + F_{zzz}\chi_{zzz}^{(2)}$$
Equation 2.11
$$F_{ijk} = F_iF_jF_k$$

Table 2.1. The 27 Tensor Elements of $\chi_{ijk}^{(2)}$. Non-zero Components are in Bold.

XXX	хух	XZX	yxx	уух	yzx	ZXX	zyx	ZZX
xxy	хуу	xzy	уху	ууу	yzy	zxy	zyy	zzy
XXZ	xyz	XZZ	yxz	yyz	yzz	ZXZ	zyz	ZZZ



Figure 2.2. Reflection of a plane wave from a surface normal to the page. The p-components of the wave parallel to the page, while the s-components are perpendicular to it.

The contribution of each component depends on the polarization of the input and output beams. On the surface, light can be expressed as a combination of two linear polarizations, *s* and *p*. The *s*- and *p*-polarized beams have electric field vectors perpendicular and parallel to the plane of incidence, respectively. As a result, *s*-polarized light contains the *y*-component and *p*-polarized light contains the *x*- and *z*- components of the electric field. Each polarization combinations probe a different tensor element of $\chi_{ijk}^{(2)}$:

$$\chi_{eff,SSP}^{(2)} = F_{yyz} \chi_{yyz}^{(2)}$$

$$\chi_{eff,SPS}^{(2)} = F_{yzy} \chi_{yzy}^{(2)}$$

$$\chi_{eff,PSS}^{(2)} = F_{zyy} \chi_{zyy}^{(2)}$$

$$\chi_{eff,PPP}^{(2)} = -F_{xxz} \chi_{xxz}^{(2)} - F_{xzx} \chi_{xzx}^{(2)} + F_{zxx} \chi_{zxx}^{(2)} + F_{zzz} \chi_{zzz}^{(2)}$$
Equation 2.12

For example, the combination of the *s*-polarized visible beam (y component) and a *p*-polarized IR beam (z component) would induce the $\chi^{(2)}_{yyz}$ component to produce an *s*-polarized SFG beam (x component) or ssp. For monolayers on metal surfaces such as gold, copper, or silver, the Fresnel coefficients of the *z*-component of the IR electric field at the surface are much larger than the *x*- and *y*-components (Table 2.2). Thus, on gold, sum frequency emission is dominated by polarization combinations with a *z*-component of the IR electric field namely *ssp* and *ppp*.⁸

	F_x	F_y	F_z
IR (2980 cm ⁻¹)	0.017 -0.091 <i>i</i>	0.006 -0.0462 <i>i</i>	0.793 +0.0731 <i>i</i>
Visible (532 nm)	0.432-0.487 <i>i</i>	0.185 -0.430 <i>i</i>	0.474 +0.270 <i>i</i>
SFG (459 nm)	0.493 -0.278 <i>i</i>	0.322 -0.320i	0.440 +0.161 <i>i</i>

 Table 2.2.
 Fresnel Coefficients for Gold/Air Interface

2.1.1.4. Hyperpolarizability

When the frequency of the input IR beam is near a vibrational resonance of the molecules on a surface, the second-order hyperpolarizability, β_{abc} , is given by^{1,9}

$$\beta_{abc}(\omega_{SFG}) \propto \left\{ \frac{\langle g | \mu_a | s \rangle \langle s | \mu_b | v \rangle}{\omega_{sg} - \omega_{SFG}} - \frac{\langle g | \mu_b | s \rangle \langle s | \mu_{la} | v \rangle}{\omega_{sg} - \omega_{Vis}} \right\} \times \frac{\langle v | \mu_c | g \rangle}{\omega_q - \omega_{IR} - i\Gamma_q} \qquad \text{Equation 2.13}$$

where μ is the electric dipole operator, $|g\rangle$ is the ground state, $|v\rangle$ is the excited vibrational state, and $|s\rangle$ is the non-stationary state of the molecules, and Γ_q is the relaxation time of the qth vibrational resonance. The first term and second term corresponds to Raman and IR transition moments. This leads to the SF selection rule which states that the vibrational mode must be active on both Raman and IR transitions in order to be SFG active. With this rule, the non-zero molecular hyperpolarizability tensor elements among of β_{abc} could be determined for a given molecular symmetry using the character table for the assigned point group.

For example, the methyl group C-H stretching mode is assigned as having a $C_{3\nu}$ symmetry.

C_{3v}	E	2C ₃	$3\sigma_{\rm v}$	IR	Raman
A1	1	1	1	Z	xx+yy, zz
A2	1	1	-1		
Е	2	-1	0	(x,y)	(xx-yy,xy), (xz,yz)

From the character table, 11 non-vanishing components of the methyl group C-H stretching resonance can be deduced:

$$\beta_{aac} = \beta_{bbc}, \beta_{ccc}$$

$$\beta_{aaa} = -\beta_{bba} = -\beta_{abb} = -\beta_{bab}$$

$$\beta_{aca} = \beta_{caa} = \beta_{bcb} = -\beta_{cbb}$$

$$Anti-symmetric$$
Equation 2.14

2.1.1.5. Coordinate Transformation

 $\chi_{ijk}^{(2)}$ is the macroscopic average of the microscopic hyperpolarizability, β_{abc} . $\chi_{ijk}^{(2)}$ is described in the surface fixed coordinate system (x,y,z) while β_{abc} is described at the molecular fixed coordinate system (a,b,c). To relate the values (V) from one axis system to another, a Euler rotation is used.

$$\begin{bmatrix} V_x \\ V_y \\ V_z \end{bmatrix} = R_z(\psi) R_y(\theta) R_z(\phi) \begin{bmatrix} V_a \\ V_b \\ V_c \end{bmatrix}$$
Equation 2.15

The Euler angles (ψ, θ, ϕ) define the mutual orientation of the two coordinate systems. The twist angle, ψ is formed by rotating the molecular coordinates along the c-axis. The tilt angle, θ is the angle between the xy- and ab-plane formed by tilting the molecular coordinates while the a-axis is in the xy-plane. The rotation angle, ϕ is formed by rotating the molecular coordinates along the z-axis on the xy-plane.



Figure 2.3. Diagram of surface coordinates (x, y, z) and molecular coordinates (a, b, c). The *z*-axis is the surface normal in surface coordinates and the *c*-axis is the rotation axis of molecule.

The transformation matrices are:

$$R_{z}(\psi) = \begin{bmatrix} \cos\psi & \sin\psi & 0\\ -\sin\psi & \cos\psi & 0\\ 0 & 0 & 1 \end{bmatrix}$$

$$R_{y}(\theta) = \begin{bmatrix} \cos\theta & 0 & -\sin\theta\\ 0 & 1 & 0\\ \sin\theta & 0 & \cos\theta \end{bmatrix}$$
Equation 2.16
$$Rx(\phi) = \begin{bmatrix} \cos\phi & \sin\phi & 0\\ -\sin\phi & \cos\phi & 0\\ 0 & 0 & 1 \end{bmatrix}$$

The SFG susceptibility may then be written as follows:

$$\chi_{ijk}^{(2)} = \frac{N}{\varepsilon_0} \sum \left\langle R_z(\psi) R_y(\theta) R_z(\phi) \beta_{abc} \right\rangle$$
 Equation 2.17

Accordingly, the symmetric stretching component of $\chi_{ijk}^{(2)}$ on an isotropic surface can be expressed using the combination of hyperpolarizability components of a C_{3v} symmetry molecule.

$$\chi_{xxz}^{(2)} = \chi_{yyz}^{(2)} = \frac{1}{2} N \beta_{ccc} ((1+R) < \cos \theta > -(1-R) < \cos^{3} \theta >)$$

$$\chi_{xzx}^{(2)} = \chi_{yzy}^{(2)} = \frac{1}{2} N \beta_{ccc} (1-R) (<\cos \theta > -<\cos^{3} \theta >)$$

$$\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)} = \frac{1}{2} N \beta_{ccc} (1-R) (<\cos \theta > -<\cos^{3} \theta >)$$

$$\chi_{zzz}^{(2)} = N \beta_{ccc} (R < \cos \theta > +(1-R) < \cos^{3} \theta >)$$

Equation 2.18

R is the ratio of β_{aac} and β_{ccc} which is obtained from the Raman depolarization ratio, and $\langle \rangle$ indicates the average of the molecular orientation and θ is the orientation tilt angle.^{10,11} With an assumption that the molecules on a surface possess identical orientation, the magnitude of susceptibility is estimated to a delta-function distribution. The SFG effective susceptibility in each polarization combination for the symmetric stretching mode of the C_{3v} symmetry molecules on an isotropic C_{∞v} surface is as follows.

$$\begin{split} \chi_{eff,SSP}^{(2)} &= F_{yyz} \frac{1}{2} N \beta_{ccc} \left((1+R) \cos \theta - (1-R) \cos^3 \theta \right) \\ \chi_{eff,SPS}^{(2)} &= F_{yzy} \frac{1}{2} N \beta_{ccc} \left(1-R \right) (\cos \theta - \cos^3 \theta) \\ \chi_{eff,PSS}^{(2)} &= F_{zyy} \frac{1}{2} N \beta_{ccc} \left(1-R \right) (\cos \theta - \cos^3 \theta) \\ \chi_{eff,PPP}^{(2)} &= -F_{xxz} \frac{1}{2} N \beta_{ccc} \left((1+R) \cos \theta - (1-R) \cos^3 \theta \right) \\ &\quad - F_{xzx} \frac{1}{2} N \beta_{ccc} \left(1-R \right) (\cos \theta - \cos^3 \theta) \\ &\quad + F_{zxx} \frac{1}{2} N \beta_{ccc} \left(1-R \right) (\cos \theta - \cos^3 \theta) \\ &\quad + F_{zxx} \frac{1}{2} N \beta_{ccc} \left(1-R \right) (\cos \theta - \cos^3 \theta) \\ &\quad + F_{zzz} N \beta_{ccc} \left(R \cos \theta + (1-R) \cos^3 \theta \right) \end{split}$$

2.1.1.6. Methyl Group Tilt Orientational Analysis

Because SFG is coherent and capable of probing different tensors of the surface susceptibility, it is possible to estimate the orientation of molecules on the surface. Orientational Analysis involves fitting the line shape of the SFG spectra using Equation 2.6 and acquiring the experimental values for the amplitude A_q , the vibrational frequency ω_q , and the line width Γ_q , of the peaks. Mathematica 9, a computational software program, was used to perform these tasks.

For a methyl terminated alkanethiol, the assignment of the observed modes at 2750-3050 cm⁻¹ range are: the methyl symmetric C-H stretch (r^+) and its Fermi resonance

 (r^{FR}) at 2870 cm⁻¹ and 2935 cm⁻¹, respectively, and the methyl antisymmetric in-plane (r^{-1}) and out of plane (r_b^{-1}) C-H stretching modes at 2965 and 2955 cm⁻¹, respectively. Also included in the fitting are the methylene symmetric C-H stretching $(d^+, 2850 \text{ cm}^{-1})$ and its Fermi resonance stretching $(d^{FR}, 2915 \text{ cm}^{-1})$ modes.

The tilt angle of the final carbon-carbon bond associated with the terminal methyl group (or the methyl group's surface orientation) of an alkanethiols-based monolayer can be estimated by deriving the ratio of the intensities of the symmetric and anti-symmetric C-H vibrational stretching modes (r^+/r^-) for the methyl C-H bonds. The symmetric and anti-symmetric stretching modes of the methyl group are orthogonal, such that as the terminal methyl group tilts away from the surface normal, the intensity of the r^- mode increases while the r^+ mode decreases. By comparing the ratio between the intensities of the methyl symmetric and antisymmetric C-H stretches (r^+/r^-) of the ppp spectra with a theoretical orientation curve, the tilt angle of the terminal methyl group can be approximated using the bond polarizability model and calculations done by Wang and co-workers¹² and by Hirose and co-workers.^{13,14}

To accurately compare the (r^+/r^-) ratios, the amplitudes of the resonances are divided by their linewidths:

$$I = \left(\frac{A}{\Gamma}\right)^2$$
 Equation 2.20

The ratios on the methyl C-H stretching resonances are computed as follows:

$$\left(\frac{r^{+}}{r^{-}}\right) = 1.33 \frac{I_{r^{+}}}{I_{r^{-}}}$$
 Equation 2.21

The intensity of the symmetric methyl C-H stretching resonance I_{r^+} is multiplied with 1.33 to estimate the contribution of the Fermi resonance.^{13,14}

Adopting the C_{3V} symmetry for the methyl terminal group of an alkanethiolate monolayer, the methyl group tilt angle can be approximated by the ratio of the effective susceptibilities of the methyl symmetric and antisymmetric C-H stretching modes taken at the PPP polarization ($|\chi_{PPP,SS}^{(2)}/\chi_{PPP,AS}^{(2)}|^2$).

The susceptibility of the methyl symmetric stretch is computed as:

$$\chi_{PPP,SS}^{(2)} = -F_{xxz} \frac{1}{2} ((1+R) < \cos\theta > -(1-R) < \cos^3\theta >)\beta_{ccc}$$

$$-F_{xzx} \frac{1}{2} (1-R) (<\cos\theta > -<\cos^3\theta >)\beta_{ccc}$$

$$+F_{zxx} \frac{1}{2} (1-R) (<\cos\theta > -<\cos^3\theta >)\beta_{ccc}$$

$$+F_{zzz} (R < \cos\theta > +(1-R) < \cos^3\theta >)\beta_{ccc}$$

While the susceptibility of methyl in-plane antisymmetric stretch is:

$$\chi_{PPP,AS}^{(2)} = -F_{xxz} (\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle) \beta_{aca}$$

- $F_{xzx} \langle \cos^3 \theta \rangle \beta_{aca}$
+ $F_{zxx} \langle \cos^3 \theta \rangle \beta_{aca}$
+ $F_{zzz} 2(\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle) \beta_{aca}$
Equation 2.23

The (r^+/r^-) ratio can then be plotted against the theoretical curve of $|\chi_{PPP,SS}^{(2)}/\chi_{PPP,AS}^{(2)}|^2$ to estimate the methyl group tilt angle.



Figure 2.4. (Left) Intensity of r^+ and r^- vs. methyl group tilt angle (ppp polarization). (Right) r^+/r^- intensity ratio vs. methyl group tilt angle.

2.1.2. SFG Instrumental Set-up

The SFG instrumental system can be divided into six types of components that contribute to laser data production, collection and recording: the Nd:YAG laser, the optical parametric generator/amplifier (OPG/OPA) assembly, the waveplates/polarizers the sample stage, the monochromator/detector, and the computer which processes the data. However, simply outlining the role of these components would not provide a clear picture of the operation of the SFG instrumentation.

A second approach is to follow the laser beam through the SFG assembly. The laser system is comprised of a laser which generates a stable 1064 nm fundamental beam that goes through an optical parametric generation/amplification (OPG/OPA) system that can convert the beam into a 532 nm beam and a tunable infrared beam. After the OPG/OPA system, the resulting beams can be directed to produce specific experimental results. For the sum frequency generation set-up used in this study, the beams can be used either to collect SFG spectroscopy spectra or SFG imaging microscopy (SFGIM) images. For SFG spectroscopy, the 532 nm and IR beams are used while for SFGIM, the 1064 nm and IR beams are utilized. For both procedures, the beams pass through several optics until they finally overlap on a surface to generate the SFG signal.

2.1.2.1. Nd:YAG Laser Beam Generation

The laser used in the SFG instrumental system is an Ekspla PL2251A-20-G-X, a 20Hz picosecond-pulsed laser. This laser system has been describe in full elsewhere.^{15,16} Briefly, the system is comprised of the laser head which generates the laser beam which is amplified by the main cavity and amplifier. The cooling system utilizes circulating water from an external chilled water supply to remove heat from the laser head. The laser is designed to have a fundamental output of 1064 nm with an ~ 20 picosecond pulse duration. The maximum pulse energy of the fundamental laser output is 50 mJ with less than 1.5% stability. Initially the beam diameter is set to ~ 8 mm, but it has been modified to a larger diameter for pumping OPG/OPA crystals without damaging the crystals. The divergence of the fundamental beam is less than 0.5 mrad.

2.1.2.2. OPG/OPA Laser Beam Processing

The 532 nm and tunable IR beams are generated from the 1064 nm beam in the OPG/OPA as shown in Figure 2.5. The 1064 nm beam is split in two by beamsplitter BS2. One beam is directed to a delay for the second process through mirror M4 while the residual beam is converted to 532 nm using a potassium titanyl phosphate crystal (KTP),

then further split in two by beamsplitter BS3. One beam is used as the visible component of the SFG analysis while the other beam undergoes a "seeding process".



Figure 2.5. Illustration of the optical layout of the OPG/OPA component.¹⁵

The 532 nm beam is split by beamsplitter BS4 where one beam is sent through two potassium titanyl phosphate crystals (1 and 2) to generate the signal and the idler beams, and the other beam goes through a delay. The idler beam is sent to mirror M9 and both the signal and idler beams are directed to mirror M6 and reflected back. The delayed 532 nm beam coalesces with the idler beam on M9 on the second pass of the idler beam from M6. M6 is mounted on a translation stage to accurately adjust the overlap of the two beams. The generated signal and idler beams are then phase-matched with the delayed 1064 nm beam from M4 using a type II phase matching condition. By rotating and turning the nonlinear birefringent crystals, KTA 3 and 4 the polarizations of the generated beams can be set to extraordinary (e) and ordinary (o). The second set of crystals generates an e-polarized signal beam and an o-polarized idler beam. The horizontally polarized e-beam changes direction since it is oriented along the rotational plane but the vertically polarized o-beam is not affected. Since the pump beam is vertically polarized, eoo phase matching occurs, and the combination of a horizontal signal, vertical idler, and vertical pump beam occurs. The crystals are rotated to the optimal positions using motors controlled by a version of Laservision Motor Control Software.

2.1.2.3. SFG Spectroscopy Set-up

The vertically polarized tunable IR and 532 nm beams are sent from the OPG/OPA through a series of optics to the sample stage, as shown in Figure 2.6. The IR beam passes through a halfwave plate (HWP1) to allow polarization control. Mirror M24 directs the beam via lens L3 which reflects off mirrors M27 and M28 towards the sample stage. A HeNe laser is used as an optical guide in aligning the invisible IR beam.



Figure 2.6. Illustration of the SFG system optical layout after the beams exit the OPG/OPA component, detailing the SFG spectroscopy layout.

The 532 nm beam is reflected off mirrors M19 and M20, which are on a translation stage to provide fine tuning of the temporal overlap of the IR and 532 nm beams. Beamsplitter BS1 redirects a portion of the green beam to the reference channel. The green beam passes through polarizer PL2 and halfwave plate HWP3, which is coated with a 532 non-reflection coating. A waveplate HWP2 is used to adjust the intensity of the green beam. Mirror M21 sends the beam to mirror M22 to the sample stage.

The IR beam from M28 is reflected off M30 towards the sample while the 532 nm reflects from M22 and M31. The angles of the IR and 532 beams are 60° and 50°, respectively, from the surface normal of the sample. The SFG beam that is generated follows a path that is ~51° from the surface normal and is kept aligned using pinholes Polarizer QWP1 controls the beam's polarization. A focusing lens directs the SFG beam to the monochromator.



Figure 2.7. Illustration of the SFG spectroscopy sample stage.

The monochromator improves the signal to noise ratio by blocking stray light from the detector. An R3788 Hamamatsu photomultiplier tube detects and amplifies the SFG photons and converts the data to an electrical signal that is processed by a Stanford Research SR250 gated integrator and box car averager. A gate of 10ns wide is activated by the trigger in the boxcar to minimize interference from stray light. A Standard Research SR245 computer interface sends the signal from the boxcar to the computer and a LABVIEW program records the spectra at a scan rate of 1 cm⁻¹ and 20 shots/point. The sample stage is replaced by a pinhole, and the 532 nm, the IR, and the SFG beams are made to overlap though this pinhole and pinholes P1, P2, and P3 by adjusting their respective mirrors. Another HeNe laser is used as an optical guide for the invisible SFG beam. The sample stage is then put back and a clean gold slide is used as a reference for SFG analysis. The 532 nm beam coming off the slide is aligned through guide pinholes by adjusting the height of the sample stage. The SFG guide beam is then aligned though two pinholes to insure that the beam is completely entering the monochromator (Figure 2.7.).

2.1.2.4. SFG Imaging Microscopy Set-up

The setup of SFGIM is shown in Figure 2.8. The design of the microscope is discussed in detail elsewhere.¹⁷ The tunable mid-IR beam is overlapped with the 1064 nm beam to generate the SFG beam at around 800 nm. The incident angles of the 1064 nm and mid-IR beams are set to 60° and 70° from the surface normal, respectively. The SFG output beam follows a path that is at an angle of 62.1° from the surface normal, and is subsequently directed through a 1:1 telescope to maintain the size of the beam as it goes along the optical path. The telescope contains a short pass filter to filter out the 1064 nm beam. The SFG signal is then reflected on a diffraction grating which has 1200 grooves/mm, a blaze angle of 26.9° and a blaze wavelength of 776 nm. The grating is used to provide an intermediate image without producing any distortion aberration. Using the combination of the telescope and the grating, the objective lens, the CCD camera can capture an image that is similar to having the camera placed along the surface normal.¹⁷



Figure 2.8. Illustration of the SFGIM optics at the sample stage.

The SFG beam is passed through a 10X infinity-corrected long working distance (30.5 mm) objective lens and reflected off a series of gold mirrors. A tube lens is used to collimate the light before going to the CCD camera. A 1024 x 1024 pixel array CCD camera is used to capture the SFG image. The camera is an intensified camera (i-CCD) and contains a Gen III intensifier (Roper Scientific, USA). Maintaining the detector temperature at -20 °C reduces errors caused by dark current.

The two input beams are overlapped using a pinhole in place of the sample stage. The sample stage is then placed back. A clean gold film is used to align the SFG guide beam (HeNe laser). The grating is removed to allow the beam to pass through two pinholes right after the telescope. Fine-tuning the beam alignment involves recording the intensity of the SFG signal while adjusting the IR and 1064 beam mirrors. SFG analysis is performed by continuously collecting images from the SFG beam while tuning the frequency of the IR beam. An image is captured every 5 cm⁻¹ by adjusting the speed of the IR tuning motors to the number of collections needed by the CCD camera.

2.2. Electrochemistry

2.2.1. Theory

Electrochemistry is a useful tool in characterizing monolayers due to its surface specificity, since all reactions occur at the interface between the electrode and the solution. Electrochemical studies can vary the electrode potential to control the different processes such as surface charge density, and the adsorption and desorption of ions on the surface.¹⁸

Most electrochemical reactions follow Nernst equation, which describes the relationship between the potential of an electrode and the concentrations of the oxidized (O) and reduced (R) species.

$$O + ne^{-} \rightleftharpoons R$$

 $E = E^{0} - \frac{RT}{nF} \ln \left(\frac{C_{R}}{C_{O}} \right)$ Equation 2.24

 E^0 is the redox potential for the reaction involving O and R, R is the gas constant, T is the temperature of the system, n is the number of electrons involved in the reaction and F is the Faraday's constant.

Reductive desorpting of alkanethiols on gold in alkaline solutions is a oneelectron process:

$$RS-Au + e^{-} \rightleftharpoons RS^{-}_{(surface)} + Au(0)$$
$$RS^{-}_{(surface)} \rightarrow RS^{-}_{solution}$$

Cyclic voltammetry (CV) experiments require at least 3 electrodes for the precise control of the external potential being applied: a working electrode where the potential is being varied in relation to the reference electrode and a counter electrode that completes the current measuring circuit. In CV, a potential is applied to the system and the Faradaic current response is measured.¹⁹ The potential is linearly ramped across a range of potentials or potential window while measuring the current response, and then the potential window is swept in the opposite direction. This inversion can be done multiple times during a single experiment (Figure 2.7).

This experiment allows monitoring of reversible reactions on the surface. For example alkanethiols can be reversibly adsorbed at the oxidation scan and desorbed at the reductive scan. In a CV plot, peaks would appear which represents the quantity of charge that is associated with the reaction occurring at that potential.

The current measured from a CV experiment can be classified into two. The Faradaic current is the electron transfer due to redox reactions while the non-Faradiac current is due to double layer charging (capacitive charging).

2.2.2. Electrochemistry Set-up

Cyclic voltammetry experiments were performed in a custom electrochemical cell shown in Figure 2.9.



Figure 2.9. Plot of potential in a cyclic voltammetry experiment.



Figure 2.10. Schematic of the electrochemical cell.

Teflon fittings and glass were used in all electrochemical experiments to prevent contamination. Glassware was cleaned via soaking in $HNO_3 + H_2SO_4$ overnight and washing with Millipore filtered water. A platinum wire and a Ag/AgCl in saturated KCl solution electrode were used a the counter electrode and reference electrode, respectively. The working electrode is an evaporated gold film on silica. The electrolyte solutions were bubbled with nitrogen gas for 15 minutes and the headspace was kept filled with the inert gas to remove oxygen from the system. Cyclic voltammetry was performed with a 263A Princeton Applied Research (PAR) potentiostat, controlled by the supplied software, Powersuite. The potential scan rate used to record the CV was 50 mV/s. All measurements were done in 0.1N KOH (Sigma-Aldrich, 85%).



Figure 2.11. Illustration of SFG electrochemical cell.

For the *in situ* monitoring of alkanethiol desorption by SFG, the SAM coated gold slide was immersed in a deaerated 0.1M NaOH-D₂O solution and then covered with a CaF₂ window (diameter = 2.54 cm, thickness = 0.4 cm). Deuterium oxide (D, 99.9%) was purchase from Cambridge Isotopes Laboratories Inc. A custom Ag/AgCl in saturated KCl electrode was used as the reference electrode,²⁰ and a clean platinum wire was used as the counter electrode. To complete the connection, a thin gold wire was placed between to gold slide and the window. The cell was fully deaerated by bubbling with nitrogen gas and was kept under nitrogen atmosphere. A 263A Princeton Applied Research Potentiostat/Galvanostat manually controlled the potential of the cell. The sample was allowed to equilibrate for 5 minutes after each change in potential before analyzing with SFG.

2.2.2.1. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy is a useful non-destructive technique in characterizing the quality of a monolayer, as it can provide information about the interface, its structure and the reactions currently taking place. EIS measures the response of an electrochemical cell to a small AC potential perturbation around its equilibrium point at different frequencies.²¹ The voltage probe is usually kept small (1-10mV) to produce a pseudo-linear response.

The response of the system to this perturbation is measured in terms of impedance, Z. Impedance is expressed as a complex sum where the real part relates to the resistance (Z) and the imaginary part to the capacitance (Z^{22}). The impedance can be

represented by a vector diagram displaying the in-phase (Z') and out-of-phase (Z'') called the Nyquist plot. It is the most used in literature as it allows easier prediction of the equivalent circuit but does not show frequency dependence. The Bode plot complements the Nyquist Plot by displaying the impedance or phase angle against the frequency. The Bode plot allows the determination of the absolute value of the impedance Z and the phase angle, φ .

The total impedance of a system is determined by the impedance of the different components in the electrochemical cell. The total contribution varies at different frequencies; electron transfer kinetics dominates the high frequencies while diffusion dominates the lower frequencies.

EIS analysis provides information about the interface, its structure and the reactions that are occurring. It can compute the resistance and capacitance of a coating on a metal such as a SAM. Ideally, a well-ordered SAM should have a phase angle of 90° in a Bode phase plot at the low frequency range $(1-10^3 \text{ Hz})$ where diffusion dominates. A φ > 88 is considered a good capacitor while lower phase angles suggest current leakage due to defects in the monolayer.

2.2.2.2. Impedance Measurements

Electrochemical impedance spectroscopy (EIS) measurements were conducted using a three-electrode configuration, with a SAM-coated film used as the working electrode, an Ag/AgCl (3 M NaCl) as the reference electrode, and a platinum rod as the counter electrode. The measurement utilized an aqueous solution of 0.1 N KOH (85% ,Aldrich) as the electrolyte.

The impedance data were collected using a 263A Princeton Applied research potentiostat/Galvanostat in combination with a PAR M5210 lock-in amplifier. A sinusoidal potential modulation of 10 mV amplitude was superimposed on a constant dc potential during impedance measurements. The amplitude and the phase shift of the resulting current were recorded at each frequency from 100 kHz to 1 Hz.

2.3. References

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Chapter 3: Characterization of Self-assembled Monolayers Derived from Octadecyloxyphenylethanethiols by Sum Frequency Generation

3.1. Introduction

Self-assembled monolayers (SAMs) are organized layers of organic molecules spontaneously adsorbed onto the surface of solids. These molecules can be tailored by varying headgroups,¹⁻⁵ endgroups,⁶⁻¹³ and spacers¹⁴ to change the wetting and interfacial properties of the resultant monolayer for various applications.¹⁵ Many SAMs systems have been studied, and most investigations have concentrated on gold as the substrate because of its inertness to form oxides, its resistance to atmospheric contamination, and its strong chemical affinity to sulfur headgroups.¹⁶

Alkanethiolate SAMs are created by the chemisorption of hydrophilic "headgroups" onto a substrate from either the vapor or liquid phase, followed by a slow two-dimensional organization of the hydrophobic "tail groups".¹⁷ After the organizational step, long chain alkanethiols assume a well-ordered and densely packed monolayer¹⁸ that can act as a nanoscale protective barrier on metals against corrosive agents. Given their dense packing and their ease of preparation, SAMs are attractive for use in corrosion inhibition.

One drawback of SAMs is their instability; in particular, they can be removed by exposure to elevated temperature, displacement by other molecules, and mechanical stress. One strategy to enhance stability is to establish multiple anchor points between the substrate and the molecules of the monolayer. Multidentate thiols,^{3,19} having multiple thiol moieties within a headgroup, show promise with their increased thermal stability but exhibit decreased conformational order due to steric hindrances. In recent efforts to Reprinted with permission from *J. Phys. Chem. C*, **2013**, *117* (18), pp 9355–9365. Copyright 2013 American Chemical Society.

address this shortcoming, a family of alkyoxyphenylethanethiols (Figure 3.1) having terminal mono-(**R1ArMT**), di-(**R2ArMT**), and tri- (**R3ArMT**) octadecyloxy chains was developed and their self-assembly on gold, examined.²⁰ Based on previous investigations,²¹ it was hypothesized that the octadecyl components of these thiols would form well-ordered monolayers similar to long chain alkanethiols, while the aromatic ring in future analogs could provide several points of attachment for multidentate binding.



Figure 3.1. Thiols analyzed in this chapter. From left to right: 2-(4-(octadecyloxy) phenylethanethiol (**R1ArMT**), 2-(3,5-bis(octadecyloxy)phenylethanethiol (**R2ArMT**), and 2-(3,4,5-tris (octadecyloxy)phenylethanethiol (**R3ArMT**).

In this chapter, SAMs derived from these alkoxy-phenylethanethiols were probed using sum frequency generation spectroscopy (SFG), and their SFG spectra were used to determine the order and the orientation of the adsorbates on the surface of gold. Model phenylethanethiols were synthesized and analyzed to determine the effect of these factors on the SFG intensity of the aromatic C-H stretching modes: (1) the symmetry along the benzene ring and (2) the presence of long alkoxy chains on the ring.

3.2. Experimental Section

3.2.1. Materials

Octadecanethiol (**ODT**, Sigma), heptadecanethiol (**C17**, Sigma), and 2phenylethanethiol (**PET**, Sigma) were used as received without further purification. The synthesis of **R1ArMT**, **R2ArMT**, and **R3ArMT** are described elsewhere.²⁰ The compounds 2-(4-methoxyphenyl)ethanethiol (**MET**), 2-*p*-tolylethanethiol (**TET**), 2-(3,4dimethoxyphenyl)ethanethiol (**3,4-DMP**), and 2-(3,5-dimethoxyphenyl)ethanethiol (**3,5-DMP**) were synthesized from their bromide precursors (Sigma) via thioacetate substitution and then deprotection using lithium aluminum hydride (LiAlH₄).

3.2.2. Preparation of SAMs

Gold substrates were prepared by the thermal evaporation of gold onto chromiumprimed silicon wafers at a rate of 1 Å/s in a chamber equipped with a diffusion pump at high vacuum pressure of 10^{-6} torr. After the deposition of 1000 Å of gold, the chamber was cooled to room temperature and flushed with ultra-pure nitrogen gas. The gold slides were immersed in 1 mM thiol solutions (THF) and allowed to equilibrate for a period of 72 hours. The resultant SAMs were thoroughly rinsed with THF and ethanol, and then blown dry with ultra-pure nitrogen before characterization in air.

3.2.3. Analysis and Treatment of Data: SFG Spectroscopy

The SFG spectrometer used in the experiments has been described in Chapter 2. An EKSPLA PL-2251A Nd: YAG laser at 1064 nm with a 19 ps long pulse and a 20 Hz repetition rate was used as the pump source. The optical parametric generation/optical parametric amplification (OPG/OPA) (LaserVision) system generates a tunable infrared (IR) beam from 2000 to 4000 cm⁻¹. The visible 532 nm beam was produced by doubling the frequency of the 1064 nm beam via a KTP crystal. The visible and IR beams, adopting a co-propagating configuration in which incidence angles of the visible and IR beams are 50° and 60° , respectively, were spatially and temporally overlapped at the surface to produce an SFG signal. The SFG beam was passed through an interference filter and a monochromator to eliminate scattered light and collected with a photomultiplier tube (PMT). Two polarization combinations, ssp (s-polarized SFG, spolarized visible beam, and p-polarized IR beam) and ppp, were acquired in the C-H stretching region from 2750 to 3150 cm⁻¹ for each sample. The scan rate was 1 cm⁻¹/s with an average of 20 laser shots per data point. Each spectrum is an average of 5 or more scans.

3.2.4. SFG Imaging Microscopy (SFGIM)

The SFG imaging microscope uses the same laser source as the system described above but utilizes the 1064 nm fundamental and the tunable IR beam at incident angles of 60° and 70° from the surface normal, respectively, to produce the SFG signal. The SFGIM uses a ppp polarization configuration and offers a spatial resolution of 2 μ m.²³

Data were collected by tuning the IR beam at a constant rate and averaging the SFG signal in 5 cm⁻¹ intervals with 3000 shots per data point.²⁴ A 400x400 μ m² pixel area image of the surface was divided into 10x10 squares, producing 1600 regions. The spectra of these regions were individually extracted with ImageJ²⁵ and fitted using Mathematica 8.

For tilt-angle analysis, the ratios of the methyl symmetric and anti-symmetric modes (r^+/r^-) were compared with the bond polarizability model.²⁶⁻²⁸ The ratios of the CH₂/CH₃ were used analyze gauche defects. The results were then remapped into contour plots to show the spatial distribution of the ratios.

3.3. Results and Discussion

3.3.1. SFG Spectra

Due to the co-linear configuration of the SFG instrument, the non-resonant signal of the gold substrate has a phase opposite that of the monolayer. When the molecules are in resonance, a destructive interference occurs, producing dips instead of peaks. Given this background, the SFG spectra of SAMs derived from **ODT** and **C17** are shown in Figure 3.2. The observed resonances can be assigned to the vibrations of the alkane chain of the alkanethiols: the CH₂ symmetric stretch (d+) at 2850 cm⁻¹ and its Fermi resonance (d^{FR}) at 2915 cm⁻¹, the symmetric stretch of the CH₃ group (r⁺) at 2870 cm⁻¹

and its Fermi resonance (r^{FR}) at 2935 cm⁻¹, and the CH₃ antisymmetric out-of-plane and in-plane stretches $(r^{op} \text{ and } r^{-})$ at 2950 and 2965 cm⁻¹, respectively.²⁹⁻³²



Figure 3.2. SFG spectra of SAMs derived from $CH_3(CH_2)_{17}SH$ (**ODT**) and $CH_3(CH_2)_{16}SH$ (**C17**) on gold in the CH region (**a**) ppp and (**b**) ssp polarization configuration. The **ODT** spectra are offset by 0.8 for clarity.

The SFG spectra of **ODT** and **C17** are characteristic of densely packed and wellordered monolayers on gold. Both spectra are dominated by strong dips attributed to the C-H stretching modes of the terminal methyl group. The near absence of methylene C-H stretching modes at 2850 and 2915 cm⁻¹ indicates that both monolayers are well ordered. In well-packed monolayers such as those formed by long chain alkanethiols on gold, the alkyl chains assume an all-trans configuration. In this environment, the methylene modes have local centers of inversion and are therefore SFG-inactive.^{29,33}

Figure 3.3 shows the ppp and ssp spectra of the phenylethylthiol SAMs on gold in air. Specifically, Figure 3.3.a shows the ppp spectrum of **R1ArMT**, which exhibits

strong resonances at 2878, 2938, 2950, and 2966 cm⁻¹ assigned as r⁺, r^{FR}, r^{op}, and r⁻ modes of the terminal methyl group, respectively. Weak methylene modes d⁺ and d^{FR} appear at 2850 and 2915 cm⁻¹. Tbroad dip at 3061 cm⁻¹ was assigned as the v2 aromatic C-H stretch using Wilson's nomenclature³⁴ (vide infra). The ssp spectrum of **R1ArMT** in Figure 3.3.b features the methyl symmetric C-H stretch (2881 cm-1) with its Fermi resonance (2939 cm-1), and the v2 aromatic C-H stretch as a dip at 3068 cm-1. The resonance at 3037 cm-1 was assigned as an aromatic C-H stretching mode v7b.39



Figure 3.3. SFG spectra of **R1ArMT**, **R2ArMT** and **R3ArMT** SAMs on gold in the CH region (a) ppp and (b) ssp polarization configuration. Spectrum was offset by 0.3 for clarity. $R = CH_3(CH_2)_{17}$

The ppp spectrum in Figure 3.3.a of SAMs derived from **R2ArMT** shows dips at attributed to the methyl group at 2877, 2936, 2950, and 2965 cm⁻¹ assigned as r^+ , r^{FR} , r^{op} , and r^- , respectively. Methylene modes d⁺ and d^{FR} appear at 2850 and 2915 cm⁻¹. It is similar to the **R1ArMT** spectrum, with the notable absence of the aromatic stretching mode at 3060cm⁻¹. Further, the ssp spectrum in Figure 3.3.b has dips at 2881, 2940, and

2966 cm⁻¹ assigned as r⁺, r^{FR}, and r⁻, respectively. Similarly, the ppp spectrum in Figure 3.3.a of SAMs derived from **R3ArMT** show similar resonances as **R2ArMT** at 2881, 2940, 2950, and 2967 cm⁻¹, assigned as r⁺, r^{FR}, r^{op}, and r⁻, respectively. The ssp spectrum in Figure 3B has dips at 2878, 2935, and 2961cm⁻¹ assigned as r⁺, r^{FR}, and r⁻, respectively.

SAMs derived from **R1ArMT**, **R2ArMT**, and **R3ARMT** all exhibit SFG spectra similar to **ODT** and **C17**, with the methyl stretching modes in dominance, suggesting that these thiols form well-ordered monolayers on gold. However, weak methylene resonances for all of these new SAMs suggest the presence of some degree of disorder. Methylene CH stretching modes at 2848 and 2916 cm⁻¹ usually suggest minor gauche defects on the chains in the monolayers (e.g., from either pinhole defects or collapse sites).³⁵ However, in the case of these SAMs, the methylene modes might stem from kinks caused by having alkoxy groups attached to the phenyl ring.

The mismatch in the cross-sectional areas between the aromatic and the alkyl portions of these thiol adsorbates introduces a 10-25% void space in the monolayer, causing the methylene groups attached to the aromatic ring (up to five carbons) to compensate by kinking and bending until the methylene groups further up the chain align to form an all-trans configuration.³⁶ These kink defects introduce a non-centrosymmetric environment, causing the methylene groups to be SFG-active. However, the alkoxy chains of these adsorbates are of sufficient length to compensate for this void space such that the interface of the SAMs exhibit characteristics similar to a well-ordered monolayer as shown in previous analyses.²⁰

3.3.2. Methyl Group Tilt Angle

The methyl group tilt angle can be estimated by deriving the r^+/r^- ratio. The symmetric and anti-symmetric stretching modes of the methyl group are orthogonal, such that as the methyl group tilts away from the surface normal, the intensity of the r⁻ mode increases while the r⁺ mode decreases (Figure 3.4). This relationship can be qualitatively observed in both ppp and ssp spectra of **ODT** and **C17** (Figure 3.2). **ODT** possesses an even chain length, and SAMs derived from it exhibit a methyl tilt of ~35°.³⁷ Its r⁺ intensity is considerably greater than its r⁻ intensity. On the other hand, the adsorbate **C17**, having an odd chain length, exhibits a methyl tilt of ~55°, and its r⁺/r⁻ ratio is greater than that of **ODT**.

By comparing the ratio between the intensities of the symmetric and antisymmetric methyl stretches (r^+/r^-) of the ppp spectra with a theoretical orientation curve (Figure 3.4), the tilt angle of the terminal methyl group can approximated using the bond polarizability model and calculations done by Wang and co-workers²⁸ and by Hirose and co-workers.^{26,27} Alternatively, the positions where the alkoxy chains are attached to the ring might also contribute to the methyl group tilt. The alkoxy chain of **R1ArMT** is connected to the para position of the ring, while the **R2ArMT** alkoxy chains are anchored at the meta positions. These two positions on the ring have dissimilar heights and angles in relation to the surface normal, and might affect the tilt of the terminal methyl groups. It is also important to note that the measured methyl tilt angles are the average of all the methyl groups on the surface.



Figure 3.4. (Top) Intensity of r^+ and r^- vs. methyl group tilt angle (ppp polarization). (Bottom) r^+/r^- intensity ratio vs. methyl group tilt angle.
	<i>r</i> ⁺	r	<i>r</i> ⁺ / <i>r</i> ⁻	Methyl Group Tilt Angle (deg)	Range
ODT	2.9 ± 0.1	1.03 ± 0.1	2.85 ± 0.1	33.8	0.8
C17	2.5 ±0.1	2.03 ± 0.1	1.25 ± 0.1	55.9	4.9
R1ArMT	1.8 ± 0.1	0.68 ± 0.1	2.69 ± 0.1	34.8	1.0
R2ArMT	1.8 ±0.1	0.83 ± 0.1	2.16 ± 0.1	39.2	1.5
R3ArMT	1.8 ± 0.1	1.14 ± 0.1	1.58 ± 0.1	47.2	2.7

 Table 3.1. Methyl Group Tilt Angles of Analyzed Phenylalkanethiols

3.3.3. Chemical Imaging and Distribution Analysis

To gain an even better understanding of the chemical morphology of the surface, SFGIM was used to scan the monolayers. SFG spectroscopy, though a surface-sensitive process, shows only the average spectra of the SAMs of a 1 mm area of the substrate, the typical laser spot size. Because only the average spectra is analyzed, there is a bias for the regions of high order, since their SFG signal would be much greater than those of disordered areas. SFGIM can provide additional information on the spatial distribution of the methyl group orientations and the conformational order of the monolayers by accounting for the regions of lower orientation and conformational order. Each 10 x 10 pixel ROI is analyzed independently and assigned a methyl group tilt angle based on the r^+/r^- ratio curve presented in Figure 3.5. This curve assumes a delta-function distribution for the methyl tilt angles, where all the alkyl chains in given ROI assume the same tilt angle. The conformational order is estimated from the ratio of the methylene symmetric

and the methyl symmetric C-H (d^+/r^+) stretching modes. Furthermore, the distributions of methyl group tilt angles and d^+/r^+ can be used to estimate the magnitude of the monolayer disorder by comparing the standard deviations of the distributions.



Figure 3.5. SFGIM intensity (r^+/r^-) ratio vs tilt angle. Each curve represents a different distribution width (σ , deg) where $\sigma = 0^\circ$ is the δ function distribution (black curve). The estimated tilt angles of the studied SAMs are also shown.

The calculated methyl tilt angles of each were remapped onto two-dimensional contour plots along with the histograms showing the number of times the tilt angles occurred (Figure 3.6). A Gaussian distribution function was used to approximate the average and standard deviation of the tilt angles (Table 3.2). The methyl group tilt angles of the SAMs agree with the trend derived from SFG spectroscopy: **R1ArMT** < **R2ArMT** < **R3ArMT**. The contour plots and the histograms show that the methyl tilt angles of the SAMs are homogenous with a standard deviation of less than 6°, suggesting that their conformational order is similar to SAMs derived from alkanethiols such as **ODT**.²³



Figure 3.6. Contour plots of (r^+/r) ratio of SAMs derived from (a) **R1ArMT**, (b) R2rMT, and (c) **R3ArMT** with their corresponding histogram plots (d, e, f, respectively)

Molecule	Methyl Group Tilt Angle (deg)	Range (deg)	CH ₂ /CH ₃ Ratio	Range
R1ArMT	33	4	0.13	0.09
R2ArMT	39	6	0.24	0.14
R3ArMT	43	6	0.41	0.16

Table 3.2. Methyl Group Tilt Angles and CH₂/CH₃ Ratio of Phenylalkanethiols on Gold

It is also interesting to compare the methyl group tilt angle distributions derived from SFGIM with those obtained from the average spectra of a 400 x 400 sample spot. In Figure 3.5, each curve shows a different distribution width and tilt angle range based of the Gaussian distribution function. At $\sigma = 0^{\circ}$, the delta function assumes that all the alkyl chains will have the same tilt angles, which is not a reasonable assumption. For **R1ArMT**, which has an average $(r^+/r)^2$ of 2.0, is estimated to have tilt angles/distribution width pairs: (33°, $\sigma = 0^{\circ}$), (28°, $\sigma = 10^{\circ}$) and (24°, $\sigma = 20^{\circ}$). Similarly, at distribution widths ranging from 0° to 20°, **R2ArMT** has a methyl group tilt angle ranging from 37° to 41° and **R3ArMT**, from 42° to 50°. However, these methyl group tilt angles and distribution widths do not necessarily reflect actual values. A previous SFGIM study has shown that distributions obtained from large ROIs tend to favor tilt angles of 40-60°. ^{23,38} Methyl tilt angles outside this range have lower SFG intensities and thus are not detected.²³ The advantage of SFGIM is that it can experimentally determine the distribution by extracting the methyl group tilts angles from small ROIs independently, thus accounting for the less-favorable molecular arrangements and provide a better interpretation of the surface.

The chain density of the **R1ArMT** SAM is lower than that of SAMs derived from alkanethiols such as **ODT** due to the void space created by the volume dissimilarity between the alkoxy chain and the benzene ring. The diminished van der Waals interactions lead to diminished conformational order. For **R2ArMT**, the two alkoxy chains on the meta carbons of the aromatic ring might force the alkoxy chains to twist and kink until the methylene groups nearer the surface are able to form all-trans conformations. The **R3ArMT** SAM experiences additional disorder from the three alkoxy chains on the benzene ring. The para alkoxy chain is significantly different with the ones connected to the meta carbons in terms of height and tilt angle. All these factors can introduce defects in the monolayer and decrease its conformational order. However, the standard deviation of the methyl group tilts (Table 3.2) show no significant increase in conformational order, implying the methylene groups near the aromatic ring might kink and twist, but nearer the surface, the chains align to form all-trans conformations.

Gauche defects near the monolayer-air interface can be indirectly measured using contact angle experiments. Previous studies have reported that gauche defects that expose the methylene groups at the interface can cause a methyl-terminated SAM to become more wettable.^{2,3} Rittikulsittichai et al. reported the trend of the hexadecane and decalin contact angles of the studied SAMs to be as follows: **ODT** ~ **R1ArMT** > **R3ArMT** >> **R2ArMT**,²⁰ which implies that the **R1ArMT** monolayer has a similar conformational order as **ODT**, followed closely by **R3ArMT**, while the SAM derived from **R2ArMT** proved to be the least ordered of the monolayers.



Figure 3.7. Contour plots of (d+/r+) ratio of SAMs derived from (a) R1ArMT, (b) R2ArMT, and (c) R3ArMT with their corresponding histogram plots (d, e, f, respectively).

Comparing the degree of film order of these SAMs based on the relative intensity of d^+/r^+ , Figure 3.7 shows that the **R1ArMT** SAM has weak methylene resonances, and the methylene resonances of the **R2ArMT** and **R3ArMT** SAMs are significantly stronger. For **R2ArMT**, the two alkoxy chains are attached to the meta positions of the aromatic ring, leaving the para position unoccupied. The kinking and twisting of the alkoxy chains might be insufficient to overcome the disorder caused by this void space. This conformational disorder leads to gauche defects in the **R2ArMT** SAM, which are detectable in both SFG and contact angle measurements.

For the **R3ArMT** SAM, however, the methylene gauche defects observed by SFG were undetectable in contact angle measurements using non-polar probe liquids (e.g., hexadecane). Contact angles are particularly sensitive to gauche defects near the surface, such as those commonly found in loosely packed monolayers. The methylene resonances from the **R3ArMT** SAM might arise from kink defects where the alkoxy chains are attached to the phenyl ring, undetectable by contact angle measurements but visible to SFG spectroscopy. Tillman and co-workers³⁶ studied the incorporation of a phenoxy group into long chain alkyltrichlorosilane SAMs and found that chains having eight or more carbon units above the ring would produce monolayers having contact angles similar to normal alkylsilane SAMs, suggesting that the addition of the third alkoxy chain at the para carbon reduces gauche defects near the surface by filling the void space and allowing the chains to align to form all-trans configurations. Table 3.2 shows that surface heterogeneity of the d⁺/d⁻ increases as follows: **R1ArMT** < **R2ArMT** < **R3ARMT**,

which also suggests that the conformational order decreases when additional alkoxy chains are attached to the benzene ring.

3.3.4. Aromatic CH Stretch

The resonance appearing at 3070 cm⁻¹ in both the ppp and ssp spectra of **R1ArMT** can be assigned as an aromatic in-phase C-H stretch v2.³⁴ The identity of the resonance was in question because the SAMs derived from **R2ArMT** and **R3ArMT** exhibit no aromatic C-H resonances, and all three thiols possess a C_{2v} symmetry along the aromatic ring that allows phenyl C-H stretching modes to be SFG-active. However, only the **R1ArMT** SAMs exhibit this dip. Nishi and co-workers when analyzing *o*-, *p*-, and *m*-methyl phenylmethanethiol SAMs on gold, observed no resonances in this region.³⁹ Bell et al., in their analysis of phenyltosylates found that the *p*-disubstituted aromatic compounds having C_{2v} symmetry had a resonance at 3057 cm⁻¹, which they assigned as the combination of the *v2* modes and *v2*0b, and a dip at 3021 cm⁻¹ assigned as *v2*0a.⁴⁰ Figure 3.8 shows these normal mode assignments.

It is plausible that the aromatic C-H modes of **R1ArMT** are SFG-active due to local C_{2v} symmetry at the aromatic ring. To test this hypothesis, several SAMs were prepared from 2-phenylethanethiol (**PET**), 2-(4-methoxy-phenyl)ethanethiol (**MET**), and 2-*p*-tolyl-ethanethiol (**TET**) and analyzed by SFG spectroscopy. **PET** was chosen because when it forms a monolayer, its aromatic ring has local C_{2v} symmetry (Figure 3.9) due to the different substituents attached to carbons 1 and 4. For **TET**, on the other hand,

the methyl and ethyl groups attached to the 1^{st} and 4^{th} carbons, respectively, of the aromatic ring are sufficiently similar that its local symmetry would approximately be D_{2h} .



Figure 3.8. Aromatic stretching C-H modes



Figure 3.9. Proposed symmetries of the model phenylalkanethiols

Since **TET** has a local center of inversion, its aromatic C-H modes would be SFG-inactive. **MET** should either have a C_{2v} or D_{2h} symmetry. If the methoxy group is sufficiently different from the ethyl group at the para position, the **MET** molecule should possess C_{2v} symmetry and will exhibit an aromatic C-H stretching resonance. Otherwise, **MET** would have D_{2h} symmetry.



Figure 3.10. SFG spectra of SAMs derived from MET, PET, and TET on gold in the CH region

Figure 3.10 shows that the SFG spectrum of the SAMs derived from **PET** exhibits a dip at 3070 cm⁻¹, which is assigned to v2, the aromatic ring C-H stretching mode. In contrast, SAMs derived from **TET** exhibit the r⁺ and r^{FR} modes (Fermi resonance with the CH₃ deformation overtone), but the r⁻ mode is noticeably absent due to its low IR intensity and low Raman cross-section.^{39,41} The spectrum of the SAMs derived from **MET** exhibits aromatic C-H stretches modes at 3013 and 3077 cm⁻¹. The results agree with the hypothesis that **PET** having a C_{2v} symmetry, would have SFG-active aromatic C-H modes, while **TET**, having D_{2h} symmetry would not. **MET** and consequently **R1ArMT**, also have C_{2v} symmetries since their aromatic stretching modes are SFG-active.

Compound	Wavenumber	Vibrational Assignment
DET	(<i>cm</i>)	
	3070	aromatic v2 C-H stretch
	2835	methoxy out of plane CH stretch $v_s CH_{2(out)}^{42,43}$
MET	2904	CH_3 bending mode overtone ⁴³
HS	2936	v _{as} CH _{2(out)} stretch ⁴³
	2999	$vCH_{(in)}^{43}$
	3058	aromatic v2 CH stretch
ТЕТ	2871	In phase methyl symmetric stretch
- HS	2927	methyl symmetric stretch Fermi resonance
	3003	methyl asymmetric stretch

Table 3.3. Vibrational Assignments of SAMs Derived from PET, MET, and TET

Thus, the C_{2v} symmetry of **R1ArMT** allows its aromatic C-H stretches, which have A₁ symmetry, to be SFG-active. Also, the presence of this aromatic stretching mode shows that the aromatic ring is oriented nearly perpendicular to the surface. It can then be inferred that the aromatic ring of the **R1ArMT** monolayer is oriented along the surface normal. In contrast, the **R2ArMT** and **R3ArMT** monolayers exhibit no aromatic C-H stretching modes in their SFG spectra. It is possible that the long alkoxy chains affect the orientation of the benzene rings, decreasing the aromatic stretching mode intensities. If this phenomenon is at play, short methoxy groups attached to the benzene ring should not significantly affect its orientation, and aromatic stretching modes

should appear the SFG spectra. То this hypothesis, 2 - (3, 4 in test dimethoxyphenyl)ethanethiol (3,4-DMP) was synthesized and analyzed. 2-(3,5dimethoxyphenyl)ethanethiol (3,5-DMP) was also synthesized and analyzed because it has no plane of symmetry perpendicular to ring plane, and its aromatic C-H stretching modes should be SFG-active. As shown by Figure 3.11, both thiols show methoxy resonances but no aromatic stretching modes, which suggests that the long alkoxy chains did not cause the SFG inactivity of the aromatic C-H stretching modes by altering the orientation of the benzene ring. The lack of aromatic C-H resonances in 3,5-DMP spectra also suggests that the symmetry of **R2ArMT** and **R3ArMT** was not the reason why these two thiol adsorbates exhibit no aromatic resonances in SFG.



Figure 3.11. SFG spectra of SAMs derived from **3,5-DMP** (top) and **3,4-DMP** (bottom) SAMs in the CH region on gold slides immersed in 1 mM solution of thiols.

Further information could be gleaned from Raman spectroscopy studies of the phenylalkanethiols (Figure 3.12). As shown in the Raman spectra, only **R1ArMT** has a peak in the aromatic CH region, whereas **R2ArMT** and **R3ArMT** have Raman contributions only from aliphatic CH stretching modes. It has been observed that electron-donating groups (EDGs), such as alkoxy groups, reduce the aromatic C-H Raman intensities significantly.⁴⁴ The addition of 2 or more EDGs on the aromatic rings might cause the **R2ArMT** and **R3ArMT** aromatic rings to exhibit weak Raman intensities, which might rationalize why both corresponding monolayers exhibit no aromatic stretching modes in SFG.



Figure 3.12. Raman spectra of R1ArMT, R2ArMT, and R3ArMT.

Compound	Wavenumber	Vibrational Assignment
	(cm^{-1})	
3,4-DMP	2835	methoxy out of plane CH stretch
SH		$v_s CH_{2(out)}^{42,43}$
°	2907	CH ₃ bending mode overtone ⁴³
	2936	v _{as} CH _{2(out)} stretch ⁴³
/	3000	$vCH_{(in)}^{43}$
3,5-DMP	2837	methoxy out of plane CH stretch
HS	2014	$v_{s}CH_{2(out)}$
	2914	CH_3 bending mode overtone
	2936	$v_{as} CH_{2(out)} stretch^{45}$
-	3002	$vCH_{(in)}^{43}$

Table 3.4. Vibrational Assignments of SAMs Derived from 3,4-DMP and 3,5-DMP

3.4. Conclusions

SAMs formed by the alkoxyphenylethanethiols, **R1ArMT**, **R2ArMT** and **R3ArMT** were found to be well ordered with gauche and kink defects. These defects were caused by the cross-sectional difference of the alkoxy chains and the aromatic ring, forcing the chains to tilt and kink until the methylene groups further above the chains can align to form the all-trans conformation. Orientation analyses show that methyl group tilt increases as the number alkoxy chains attached to the aromatic ring is increased, implying conformational order is reduced due to steric effects. By analyzing several model phenylethylthiols with different symmetries along the aromatic ring, it was confirmed that **R1ArMT** exhibits an aromatic C-H stretch. The SFG spectra of SAMs of **PET**, **MET**, and **TET** suggests that phenylethanethiols form closely packed monolayers with the benzene rings oriented along the surface normal. Analysis of **3,4-DMP** and **3,5-DMP** suggest that the **R2ArMT**'s and **R3ArMT**'s lack of SFG-active aromatic

resonances was not due to changes in the orientation caused by long alkoxy chains nor it was due to symmetry. Raman data suggest that the electron withdrawing alkoxy groups decreased the Raman cross section which in turn weakened the SFG intensity of the aromatic C-H stretching resonances.

3.5 References

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Chapter 4: Effect of the Grain Size of the Gold Substrate on the Conformational Order of Self-assembled Monolayers as Determined by Sum Frequency Generation Imaging Microscopy

4.1. Introduction

Alkanethiolate self-assembled monolayers (SAMs) on Au(111) have been one of the most studied systems due to their ease of formation, high conformational order, stability, and versatility.¹ Because of the specific interaction between the thiol headgroup and the metal substrate, these SAMs can be formed in several types of solvents, resulting in robust films. Since the monolayer's tailgroups can be readily altered,²⁻⁹ the interfacial properties of the surface can be tailored for various applications.¹⁰ SAMs are also widely used as building blocks for the bottom-up production of different types of devices.^{11,12}

Monolayer self-assembly consists of several structural phase transitions.^{13,14} Earlier sum frequency generation (SFG) studies have found that a SAM undergoes at least three phases during its formation: the assembly process where the thiol-gold bonds are formed; the reordering of the alkyl chains from a highly kinked state into an all*-trans* conformation; and, finally, the alignment of the methyl groups.¹⁵⁻¹⁷ Many factors influence the self–assembly of these monolayers such as temperature, solvent, nature of the adsorbate, and the substrate.^{1,18,19} Surface topography also plays an important role in the formation of a well-ordered monolayer.^{20,21}

Different methods and conditions yield thin gold films with very different topographies. Thermal deposition of gold on Si(111) typically produces films with small grains of 45-60 nm in diameter, while the flame annealing of gold evaporated on mica generates grains of 600 nm and above .¹ Grain size can also be increased using different

methods such as treatment with strong acids,²² template stripping,²³ and electrochemistry.²⁴ Surface stress measurements indicate that the kinetics of SAM assembly and the monolayer structure are dependent on the grain size.²⁵ Reductive desorption studies have shown that alkanethiols grown on large gold grains were more ordered and less susceptible to desorption than those formed on smaller gold grains,^{20,26} making these substrates essential in applications where SAMs are used as insulation barriers. Gold substrates with small grains, on the other hand, have shown to be better substrates for microcontact printing, as the small grains minimize the roughness of the edges of the microstructures.^{1,27}

Several works have proven that SFG spectroscopy is a useful tool in the study of SAMs.²⁸⁻³² It is surface sensitive and does not require ultra-high vacuum conditions, external labeling or subtractive techniques to achieve sensitivity. A more recent SFG method, SFG imaging microscopy (SFGIM), is capable of characterizing the spatial and chemical nature of molecules on a surface and is a good technique for chemical imaging. Although SFGIM does not offer the same lateral resolution of scanning probe microscopy (SPM) techniques such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM), it supplements these techniques by providing both structural and orientational details for the monolayer. In addition, statistical distribution analysis of the SFGIM images can provide information regarding the conformational order of the SAMs. Hernandez and co-workers studied the effect of multidentate SAMs using SFGIM and found that multiple headgroups decreased the monolayer's conformational order.³³

SFG is a second-order non-linear process that occurs when two laser beams are spatially and temporally overlapped on a surface, generating a third beam at the sum of the two input frequencies.^{34,35} In the case of the SFGIM set up, the microscope utilizes a fixed wavelength 1064 nm beam and a frequency-tunable infrared (IR) laser beam. When the IR beam is tuned to a vibrational resonance of an adsorbate, the nonlinear susceptibility increases, which also causes the intensity of the SFG beam, I_{SFG} to increase proportionally (Equations 4.1 and 4.2).

$$I_{SFG} \propto \left|\chi^{(2)}\right|^2 I_{IR} I_{1064}$$
 Equation 4.1

$$\chi^{(2)} \propto \left|\chi_{R}^{(2)} + \chi_{NR}^{(2)}\right|^{2} = \left|\sum \frac{A_{q}}{\omega_{IR} - \omega_{q} - i\Gamma} + \chi_{NR}^{(2)}\right|^{2}$$
 Equation 4.2

$$\chi^{(2)} = \left|\chi_{R}^{(2)} + \chi_{NR}^{(2)}\right|^{2} = \left|\chi_{R}^{(2)}\right|^{2} + \left|\chi_{NR}^{(2)}\right|^{2} + 2\left|\chi_{R}^{(2)}\right| \left|\chi_{NR}^{(2)}\right| \cos[\varepsilon - \delta(\omega_{IR})] \quad \text{Equation 4.3}$$

 $\chi_{RR}^{(2)}$ is the near-resonant susceptibility arising from the gold substrate, while $\chi_{R}^{(2)}$ contains the average vibrational information of the molecules on the surface. $\chi_{R}^{(2)}$ is proportional to the number of molecules generating the signal multiplied by the average hyperpolarizability of the adsorbate, $\beta^{(2)}$, which in turn is proportional to the product of the IR and Raman transition moments.

The SFG spectra generated in this study were normalized to the frequency with the highest intensity and were fitted using Equation 4.2, where A_q , ω_{IR} , ω_q , and Γ are the amplitude, IR laser frequency, vibrational transition frequency, and the damping constant, respectively. A comparison of the peak intensities for the various vibrational modes determined the orientation of the molecules at the surface.^{36,37}

This study describes the results of the SFGIM analysis of dodecanethiol (**DDT**) and octadecanethiol (**ODT**) on two different types of gold surfaces: annealed gold on mica (**LG**), which has a large average grain size, and evaporated gold on a chromium-primed silicon wafer (**SG**) which has a small average grain size.

4.2. Experimental Section

4.2.1. Materials

Octadecanethiol (>98%, Sigma-Aldrich), dodecanethiol (>98%, Sigma-Aldrich) and ethanol (100%, Aaper) were used as received without further purification. Tetrahydrofuran (>99%, Sigma-Aldrich) was distilled before use to remove the butylated hydroxytoluene (BHT) stabilizer.

4.2.2. Gold Film Preparation

Small-grained (**SG**) gold was prepared by the thermal evaporation and deposition of chromium (~100 Å) and gold (~1000 Å) onto silicon (100) wafers at a rate of 1 Å/s in a chamber equipped with a diffusion pump. The diffusion pump operated at a high vacuum pressure of 10^{-6} Torr. After the deposition, the chamber was cooled to room temperature and flushed with ultrapure nitrogen gas.

Large-grained (LG) gold was in the form of atomically smooth gold on mica sheets, which were purchased from Agilent Technologies, and were annealed using a

hydrogen/air flame before SAM formation. The gold on mica was placed on a preheated quartz plate and a small hydrogen/air flame was quickly swept back and forth across the surface.

Topography characterization of the gold samples were performed with an Agilent 5500 atomic force microscope using Sharp Nitride Lever (SNL) tips from Bruker. All scans were done in contact mode. Grain size was determined using the grain SPM software (Gwyddion).³⁸

4.2.3. Preparation of SAMs

The gold substrates were immersed in 1 mM ethanolic thiol solutions for 48 hours. The resultant SAMs were thoroughly rinsed with tetrahydrofuran and ethanol, and then blown dry with ultra-pure nitrogen gas before characterization in air.

4.2.4. Laser System and SFGIM Set-up

The SFG imaging microscope used in the experiments has been described in Chapter 2. An EKSPLA PL-2251A Nd:YAG laser at 1064 nm with a 19 ps long pulse and a 20 Hz repetition rate was used as the pump source. The optical parametric generation/optical parametric amplification (OPG/OPA) (LaserVision) system generates a tunable infrared (IR) beam from 2000 to 4000 cm⁻¹. The 1064 nm fundamental and the tunable IR beam are used to probe the surface at the incident angles of 60° and 70° from the surface normal, respectively, to produce the SFG signal. The SFGIM uses a ppp

polarization configuration and offers a spatial resolution of 2 μ m.⁴⁰ A Roper 1024×1024 pixel array camera was used as the detector.

Data were collected by tuning the IR beam at a constant rate and averaging the SFG signal in 5 cm⁻¹ intervals with 5000 shots per data point.⁴¹ A 700×700 μ m² pixel area image of the surface was divided into 10×10 squares, producing 4900 regions of interest (ROI). The spectra of these regions were individually extracted with ImageJ⁴² and fitted using Mathematica 8.

For tilt-angle analysis, the ratios of the methyl symmetric stretching mode (r^+) and anti-symmetric mode (r^-) were compared with the bond polarizability model.^{37,43,44} The ratios of the SFG intensities of the methylene symmetric stretching mode (d^+) and methyl symmetric stretching mode (r^+) were used to analyze the collected data for gauche defects. The results were then remapped into contour plots to show the spatial distribution of the ratios.

4.3. Results

4.3.1. Chemical Imaging and Distribution Analysis

The AFM images of the two substrates used in this study are shown in Figure 4.1. Using an SPM software by Gwyddion,³⁸ it was determined that annealed gold on mica (**LG**) has a grain size ranging from 400-600 nm in diameter and a root-mean-square (rms) roughness of ~8Å, while vapor-deposited gold on a chromium-primed silicon wafer (**SG**) has a grain size ranging from 40-60 nm and an rms of 15Å.



Figure 4.1. Contact AFM images of SG gold (left) and LG gold (right) acquired in air.

The average SFG spectra with a 700×700 pixel area for **DDT** and **ODT** on **SG** gold and **LG** gold in the 2750-3050 cm⁻¹ region are shown in Figure 4.2. The spectra are from well-ordered SAMs as these are dominated by the resonances for the methyl symmetric stretching mode, r^+ , and its Fermi resonance, r^{FR} , 2880 and 2930 cm⁻¹, respectively, and the signal associated with the resonance of the methyl antisymmetric inplane and out-of-plane stretches (r^- and r_b^-) at 2960 and 2950cm⁻¹, respectively. Less obvious are the methylene stretching modes (symmetric, d^+) and Fermi resonance, d^{FR} at 2850 and 2925 cm⁻¹, respectively.



Figure 4.2. Average SFG spectra of SAMs derived from DDT on (a) SG gold and on (b) LG gold, and ODT grown on (c) SG gold and on (d) LG gold.

4.3.2. General Analysis

The SFGIM process consists of taking a series of images at the 2750-3050 cm⁻¹ range, stacking them, and then dividing the compiled image into 10×10 pixel ROIs. The normalized SFG spectra are extracted from each ROI and independently fitted to Equation 4.2. From these data, the following information can be inferred: gauche defects can be deduced from the ratios of the intensities of the methylene and methyl symmetric

stretching resonances (d^+/r^+) and the tilt angles of the terminal methyl groups can be derived from the r^+/r^- ratio.

4.3.3. Chain Defect Analysis

The presence of d⁺ and d^{FR} modes could be used as an indicator of defects located within a SAM.⁴⁵ A dense, well-ordered SAM will have minimal methylene C-H stretching modes in its SFG spectra due to the high conformational order of its alkyl chains. After the chemisorption of the thiols, the alkyl chains realign into an all-*trans* configuration. This arrangement places the methylene moieties in a centrosymmetric environment, rendering them SFG-inactive. Kinks and gauche defects arising from pinholes, domain boundaries, structural steps, and intergrain boundaries of the substrate introduce an inversion center on the alkyl chain and cause the methylene stretching resonances to be SFG-active.

Molecule	Substrate	Methyl Group Tilt Angle (deg)	Range (+/-)	d^+/r^+	Range (+/-)
DDT	SG gold	32	4	0.2	0.10
	LG gold	22	3	0.1	0.08
ODT	SG gold	34	5	0.05	0.08
	LG gold	23	5	0.05	0.08

Table 4.1. Methyl Group Tilt Angles and d^+/r^+ Ratios for DDT and ODT on LG and SG Gold

The d^+/r^+ ratios of **DDT** shown in Figures 4.3 and 4.4 indicate that **DDT** monolayers grown on **LG** gold have fewer gauche defects than those grown on **SG** gold. The average d^+/r^+ ratio of **DDT** on **LG** gold is 0.1 while **DDT** on **SG** gold has a ratio of 0.2 (Table 4.1). This suggests that **DDT** monolayers on **LG** gold have a higher degree of conformational order than those on **SG** gold. The contour plot in Figure 4.4 shows the conformational disorder of **DDT** on **LG** gold.

As shown in Figure 4.3, the d^+/r^+ ratios of **ODT** on both **SG** gold and **LG** gold are less than those of **DDT**, which implies that **ODT** forms more ordered monolayers than those of **DDT**. The results also suggest that the substrate does not affect the conformational order of the SAMs formed from **ODT** as both have very low d^+/r^+ ratios.



Figure 4.3. Histogram plots of d^+/r^+ ratios for derived from **DDT** on (a) **SG** gold and (b) **LG** gold, and **ODT** on (c) **SG** gold, and (d) **LG** gold



Figure 4.4. Contour plots of d'/r' ratios for SAMs derived from DDT on (a) LG gold and (b) SG gold, and ODT on (c) LG gold, and (d) SG gold

4.3.4 Tilt Angle Analysis

Figure 4.5 shows the histograms of the r^+/r^- ratios of **DDT** and **ODT** monolayers on **LG** gold and **SG** gold. The range of the ratios of the SAMs formed on **LG** gold is larger than those grown on **SG** gold. In previous SFGIM experiments,^{40,51} a wide $r^+/r^$ range (> 2) would indicate a heterogeneous surface. The ranges of the SAMs of **DDT** and **ODT** on both **SG** and **LG** gold suggest that these monolayers are very homogenous. The results also indicate that SAMs formed on SG gold have a narrower range of r^+/r^- ratios suggesting they are slightly more homogenous than those grown on LG gold.



Figure 4.5. Histogram plots of r^{+}/r^{-} ratios for SAMs derived from DDT on (a) SG gold and (b) LG gold, and ODT on (c) SG gold, and (d) LG gold.

For the tilt angle analysis of the terminal methyl group, the ratio of the peak intensities of the methyl symmetric and antisymmetric stretching modes (r^+/r^-) of each 10 square pixel ROI were derived and plotted against the r^+/r^- ratio curve presented in Figure 4.6. The calculated methyl tilt angles of each ROI were then remapped onto two-dimensional contour plots. These plots, along with the histograms showing the number of times the tilt angles occurred, are shown in Figures 4.7 and 4.8. A Gaussian

distribution function was used to approximate the average and standard deviation of the tilt angles. This data can be found in Table 4.1.



Figure 4.6. Intensity of r^+ and r^- vs methyl group tilt angle (ppp polarization) (**a**). SFGIM intensity (r^+/r^-) ratio vs tilt angle (**b**). Each curve represents a different distribution width (σ, deg) where $\sigma = 0^\circ$ is the δ function distribution (black curve).

The average methyl group tilt angles from the surface normal of the **DDT** monolayers deposited on **LG** gold and **SG** gold are 22° and 32°, respectively, as shown in Figure 4.7. **DDT** on **LG** gold has an insignificantly narrower tilt range than **DDT** on **SG** gold. The tilt angle distributions of these SAMs do not reflect the wider distribution of r^+/r^- ratios found in Figure 4.5. This is due to the steepening of the r^+/r^- ratio vs tilt angle (Figure 4.6b) curve at angles less than 30°. This suggests that r^+/r^- ratio would be a more accurate gauge in the homogeneity of the monolayers.

An SPM study has shown that for **DDT** on **SG** gold, most domains remain in the lying down phase,²⁵ with a few domains achieving the upright phase. However, this was not observed in SFGIM. Such domains are only tens of nanometers in size - many orders of magnitude less than the 100 square micron ROIs that SFGIM can resolve.

As seen in Figure 4.6a, when the methyl group tilt angles are higher than 60°, both r^+ and r^- intensities weaken. Consequently, signals from "lying down" domains are overwhelmed by domains with methyl group tilt angles lower than 55°. The **ODT** monolayers follow the same trend. **ODT** on **LG** gold has a methyl tilt angle of 23° while **ODT** on **SG** gold has a tilt angle of 34°, as shown in Figure 4.6.



Figure 4.7. Histogram plots of methyl group tilt angles for SAMs derived from DDT on (a) LG gold and (b) SG gold, and ODT on (c) LG gold, and (d) SG gold.



Figure 4.8. Contour plots of methyl group tilt angles for SAMs derived from DDT on (a) LG gold and (b) SG gold, and ODT on (c) LG gold, and (d) SG gold.

The contour plot of **ODT** on **LG** gold in Figure 4.8c features a defect site in the upper left corner: a defect which would not be detected in non-imaging SFG. Standard SFG techniques can only provide the average spectra of the sample, producing data similar to that shown in Figure 4.2. This underscores the usefulness of SFGIM in studying surfaces in combination with non-imaging SFG. By breaking the sample spot

into smaller regions and analyzing each region separately, SFGIM provides surface structure information that was previously unavailable by non-imaging surface spectroscopic techniques.

4.3.5. Standard Deviation Versus Gaussian Distribution Width Analysis

Figure 4.6b shows the r^+/r^- ratio versus the methyl group tilt angle curve at different Gaussian width distributions. The different curves all intersect at the r^+/r^- ratio of 1.2 which corresponds to an angle of 34°. This suggests that when methyl group tilt angles are near this value, all Gaussian width distributions could be valid.



Figure 4.9. Standard deviation versus distribution width of DDT on (a) LG gold and (b) SG gold, and ODT on (c) LG gold, and (d) SG gold.

The methyl group tilt angle of each SAM was calculated from the r^+/r^- ratio using the curves with increasing Gaussian distribution widths ($\sigma = 5$, 10, 15, 20, 25, 30, 35, and 40) as presented in Figure 4.3b. The standard deviation from each analysis is then plotted against the distribution width and fitted with an interpolation function in Mathematica 8. The value where the standard deviation and the Gaussian distribution intersect was then determined. As seen in Figure 4.9, the intersection of the derived standard deviation and Gaussian distribution widths is near the delta function distribution. This suggests that with homogenous monolayers such as **DDT** and **ODT** on gold, the delta function distribution is a good estimate for the distribution of the methyl group tilt angles.

4.4. Discussion

4.4.1. Effect of Substrate

The results presented in this study suggest that the grain size of the gold substrate has a significant effect on the conformational order and the homogeneity of the monolayers than can form on its surface. The monolayer formed by the chemisorption of **DDT** on **SG** gold had more gauche defects than the one formed on **LG** gold. The r^+/r^- ratios also indicate that SAMs on **SG** gold have a narrower orientation distribution than those grown on **LG** gold. It is hypothesized that these results are due to the monolayer domains that form on different locations on the gold grain.

SAMs form domains via the homogenous nucleation and aggregation of the alkanethiols on a gold terrace. Each domain has a different chain tilt orientation based on its nucleation site. As the coverage increases, mismatches occur at the boundaries of

differently oriented domains, causing disorder and gauche defects in the monolayer. The typical domain size is 5-15 nm,⁴⁶ and the maximum area a domain can grow is determined by the topography of the substrate.²⁶

Assuming that the average domain size is 10 nm,²⁶ the number of alkanethiol domains that can form on a large gold grain (~600 nm in diameter) would be ~ 3500. It can be then be inferred that there is a significant difference with the domains that form on the center of the grain and at the boundary. At the center of a gold terrace, the domains are more-densely packed and assume a tilt ~30⁰ from the surface normal. The domains that form at the grain boundaries are less packed and consequently more tilted and more disordered than those formed at the domain's center. Because of the difference in conformational order between domains at the center and at the edge of a gold grain, there is a wider distribution of chain orientations which may cause the minor heterogeneity of r^{+}/r^{-} ratios found in SAMs on LG gold. Since there are less grain boundaries in large grained gold, gauche defects are minimal.

In contrast only ~25 domains can form on SG gold where the average grain size is ~50 nm in diameter. Thus, the domains on the center of the small grain would have the almost the same conformational order as those formed at the grain boundaries. The monolayer would be uniformly disordered across the grain which leads to more gauche defects that are detected as d^+ resonances in the SFG spectra, but also this leads to a more uniform orientation distribution as where all the angles are more tilted from the surface normal.
4.4.2. Effect of Chain Length

As shown in Figure 4.3, the d⁺/r⁺ ratios of **ODT** are low on both **SG** gold and **LG** gold, suggesting that for long chain alkanethiols, the substrate plays a minimal role on conformational order. Additional methylene spacers in the **ODT** alkyl chains increase the interchain van der Waals interactions which in turn increases the stability and order of the monolayer.⁴⁸ Long chain alkanethiols can form larger domains with fewer vacancy islands than short chain alkanethiols, which decreases the number of boundaries that produce gauche defects.⁴⁹

Frictional studies have found that alkanethiols having greater than 15 carbons chains can act as "boundary lubricants" by dampening the frictional responses that arise from topological changes at grain boundaries for a scanning AFM tip.⁵⁰ This suggests that the conformational order brought about by the increased chain length allows **ODT** to reduce the disorder introduced by domain boundaries. All these factors inhibit the formation of gauche defects in **ODT** SAMs.

4.5. Conclusions

SFGIM was used to evaluate dodecanethiolate and octadecanethiolate selfassembled monolayers formed both on gold with large, flat grains formed directly on mica and gold with small irregular grains formed by vapor-deposition of gold on a chromium-primed silicon wafer. Both thiols formed homogenous monolayers on both types of gold, with LG gold producing relatively less homogenous films than SG gold. DDT on small-grained gold was found to have more gauche defects than DDT on largegrained gold, while **ODT** can form conformationally ordered films irrespective of the grain size of the gold substrate.

The grain size of the gold substrate is an important factor on the conformational order and the homogeneity of the monolayers that form on it. Domains that grow near the grain boundaries would be less dense and thus less ordered. On large-grained gold, there is a significant difference in conformational order between grains on the center of a grain and those that form at the edges. Thus, there is a wide distribution of chain tilt angles ranging from the least tilted at the center of the grain to the most tilted at the grain boundaries. On small grains, however, the difference between these two types of domains would be minimal, as the distance between the center and the grain edge is only \sim 30 nm. Therefore, the domains on a small grain would have uniformly low conformational order across the grain and the overall monolayer will have a narrower tilt distribution than those formed on **LG** gold.

Chain length also plays an important role on the conformational order of the monolayers formed. **DDT** monolayers on **SG** gold have more domains that grow on the grain boundaries than **DDT** monolayers on **LG** gold, and thus, exhibit more gauche defects. **ODT**, on the other hand, forms low defect monolayers, independent of the grain size of the gold substrate. This indicates that the increased conformational ordering associated with the increased chain length of **ODT** enables the **ODT** SAMs to reduce any chain disordering.

4.6. References

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Chapter 5: *In Situ* Vibrational Study of the Reductive Desorption of Alkanethiol Monolayers on Gold by Sum Frequency Generation Spectroscopy

5.1. Introduction

Long chain alkanethiols produce a well-ordered and densely packed monolayer on metals¹⁻³ which can act as a protective barrier against corrosive agents such as water, oxygen and aggressive ions.⁴⁻⁹ The process for producing these SAMs is uncomplicated and can be done in a variety of solvents and under various conditions, due to their strong chemical affinity to metal surfaces. Because of these characteristics, these nanoscale films have been used in a variety of applications such as lubricants for micromechanical systems¹⁰ and sacrificial coatings for nanolithography.¹¹

The electrochemistry of alkanethiolates on gold surfaces has been extensively studied.¹²⁻²⁰ Alkanethiols can be desorbed by the application of sufficient negative potential by a one-electron process:

$$RS-Au + e^{-} \rightleftharpoons RS^{-}_{(surface)} + Au(0)$$
$$RS^{-}_{(surface)} \rightarrow RS^{-}_{solution}$$

After desorption, the desorbed thiolates dissolve into the bulk solution and diffuse away from the surface, depending on their solubility in that particular liquid. The electrochemical desorption of SAMs have found several potential uses in surface chemistry,²¹ such as modifying the wettability of the surface,²² producing phasesegregated binary SAMs, producing SAM microstructures,²³ controlled released of cells¹⁹ or nanoparticles,²⁴ and recycling electrodes in biosensors.²⁵ Several studies have used the reductive desorption of SAMs to characterize the metal substrate¹² and monolayer coverage.²⁰ The reductive potential of alkanethiol SAMs in alkaline solutions were found to depend on several factors such as the pH of the electrolyte solution, the nature of electrolytes, the surface of the substrate, and the length of the alkyl chain. As pH is decreased from 13.7 to 5.9, the reductive peak was observed to broaden and shift to the positive direction. It was found that using three different bases, the reductive peak shifts $\text{LiOH} < \text{NaOH} < \text{KOH.}^{12}$ Furthermore, the reductive peaks shifted to the negative direction as the chain length increases.¹²

The readsorption of these alkanethiol monolayers was also dependent on the chain length of the alkyl chains. Previous studies reveal that, depending on the solubility of the desorbed molecules, these thiolates may either readsorb to the surface or diffuse into the solution. Butanethiol, having solubility in water of 0.6 g/L, was shown to be desorbed without readsorbing. Hexadecanethiol, on the other hand, was almost insoluble in the solvent used in a study by Yang and co-workers and was shown to readsorb during the oxidative stage of the cyclic voltammetry (CV) experiment.¹³

Several authors have offered explanations for the mechanism for monolayer desorption. One theory is that once desorbed, alkanethiolates form bilayers¹¹ or micelles^{26,27} and that these structures either provide a means for the surfactants to readsorb on the surface or to diffuse into the solution, while another theory is that SAMs retain the two-dimensional monolayer structure which readily enables the surfactants to either readsorb or slowly diffuse away from the surface.²⁸ STM measurements taken

during electrochemical desorption have found aggregates on the gold surface, which were assumed to be desorbed thiolates.²⁹

In situ infrared (IR) vibrational measurements of the reductive desorption and readsorption of SAMs on gold have found that these monolayers become more disordered after desorption.^{14,30} *Ex situ* sum frequency generation (SFG) spectroscopic studies of alkanethiolate SAMs before and after desorption have found that SAMs formed from short chain alkanethiols can desorb after 30 CV scans while those formed from long chain alkanethiols retain their crystalline structure.³¹ The goal of this chapter is to utilize sum frequency generation to monitor alkanethiol adsorbates as they desorb from a gold surface *in situ* in order to further improve the understanding of the desorption process. Additional information such as orientation and order during the desorption process were also obtained.³²

5.2. Experimental Section

5.2.1. Materials

Octadecanethiol (**ODT**) (>98%, Sigma-Aldrich), decanethiol (**DT**) (>98%, Sigma-Aldrich) potassium hydroxide (Sigma-Aldrich, 85%) and ethanol (100%, Aaper) were used as received without further purification. Tetrahydrofuran (>99%, Sigma) was distilled to remove the butylated hydroxytoluene (BHT) stabilizer before use. Deuterium oxide (D, 99.9%) was purchase from Cambridge Isotopes Laboratories Inc.

5.2.2. Gold Film Preparation

Chromium (100 Å) and gold (1000 Å) were thermally evaporated onto silicon(100) wafers at a rate of 1 Å/s in a chamber equipped with a diffusion pump at high vacuum pressure of $\sim 10^{-6}$ Torr. After the deposition, the chamber was cooled to room temperature and flushed with ultrapure nitrogen gas. The gold-coated wafers were cut into slides (~ 1 cm \times 3 cm) and rinsed with ethanol before use.

5.2.3. Preparation of SAMs

The gold slides were immersed in 1 mM thiol ethanolic solutions and allowed to equilibrate for 48 hours. The resultant SAMs that formed on the gold surfaces were thoroughly rinsed with THF and ethanol, and then blown dry with ultra-pure nitrogen gas before characterization in air.

5.2.4. Laser System and SFG Set-up

The SFG imaging microscope used in the experiments has been described elsewhere.³³ An EKSPLA PL-2251A Nd:YAG laser at 1064 nm with a 19 ps long pulse and a 20 Hz repetition rate was used as the pump source. The optical parametric generation/optical parametric amplification (OPG/OPA) (LaserVision) system generates a tunable infrared (IR) beam from 2000 to 4000 cm⁻¹.

For tilt-angle analysis, the ratios of the intensities of the methyl symmetric and anti-symmetric C-H stretching $modes(r^+/r^-)$ were compared with the bond polarizability model devised by Hirose^{34,35} and Wang.³⁶ The ratios of the peak intensities of the

methylene and methyl symmetric C-H stretching modes (d^+/r^+) obtained by SFG were used to analyze the SAM films for the relative presence of gauche defects.

Cyclic voltammograms were taken using a 263A Princeton Applied Research Potentiostat/Galvanostat which is controlled by PowerSuite software. A platinum wire was used as the counter electrode and the reference electrode was Ag/AgCl in saturated KCl.³⁷ Cyclic voltammetric measurements were conducted from -0.3 to -1.35 V at a scan rate of 50 mV s⁻¹. The potential was initially swept towards the negative to reduce the SAMs and then reversed to reoxidize the desorbed thiolates. The gold substrate was mounted at the bottom of the cell using an O-ring and a clamp. The solution of the cell was deaerated by bubbling N₂ gas for 30 min before analysis, and the electrochemical cell was placed under a nitrogen atmosphere during all electrochemical measurements. The area of the working electrode was determined by the area of the exposed surface, which in turn was equal to the area within the O-ring, 1.69 cm².

For the *in situ* monitoring of alkanethiol desorption by SFG, the SAM-coated gold slide was immersed in a deaerated 0.1M NaOH-D₂O solution and then covered with a CaF₂ window (Figure 5.1). A custom made Ag/AgCl in saturated KCl electrode was used as the reference electrode,³⁷ and a hydrogen flame-annealed platinum wire was used as the counter electrode. To complete the connection, a thin gold wire was placed between the gold slide and the window. The cell was fully deaerated by bubbling with nitrogen gas for 30 min and was kept under a nitrogen atmosphere. A 263A Princeton Applied Research Potentiostat/Galvanostat controlled the potential of the cell during operation.





Figure 5.1. (Top) Illustration of an SFG electrochemical cell. (Bottom) The cell in placed in an enclosure filled with nitrogen gas.

5.3. Results and Discussion

5.3.1. Electrochemistry

The cyclic voltammograms of **DT** and **ODT** monolayers on gold are shown in Figure 5.2. For **DT** SAMs, two broad current peaks are seen for the first cathodic sweep. The first peak at -1050 mV was assigned at the reductive peak and the peak at -1250 mV is assumed to be from hydrogen evolution. The peak at small and broad anodic peak can be seen at the return sweep, which is attributed to the partial readsorption of the thiolates on the gold surface. The second cathodic sweep features a weaker reductive peak at -1050 mV, suggesting that only a fraction of the decanethiolates reoxidized on the surface. For the third cycle, the reductive peak is even weaker, suggesting that even more of the thiolates have diffused away from the surface.



Figure 5.2. Cyclic voltammogram of a **DT** (a) and **ODT** (b) on gold in 0.1 M KOH aqueous solution.

ODT SAMs, on the other hand, exhibited two reductive waves at -1100 and -1250 mV on the first cathodic sweep. The reductive potential of the **ODT** adsorbates occurs at a much lower potential than for **DT** owing to either the decreased ion permeability of the monolayers due to the increased intermolecular interaction between the alkyl chains,¹³ or to a decrease in the fractional drop of the applied potential across the monolayer as the alkyl chain increases.¹² For the anodic sweep, a small and broad peak is assumed to be caused by the reoxidation of the thiolates. The second and all subsequent cycles shows one reductive wave at -1100 mV, and a small readsorption peak at -950 mV, suggesting that the monolayer desorbs and partially readsorb on the gold surface. The decreasing magnitude of the succeeding reductive peaks again suggests that not all of molecules undergo reoxidation.

5.3.2. Sum Frequency Generation

All SFG spectra in this study were taken with both input beams and the SFG signal set to p-polarization or ppp. The assignment of the observed modes are: the methyl symmetric C-H stretch (r^+) and its Fermi resonance (r^{FR}) at 2870 cm⁻¹ and 2935 cm⁻¹, respectively, and the methyl antisymmetric in-plane (r^-) and out of plane (r_b^-) C-H stretching modes at 2965 and 2955 cm⁻¹, respectively. Also included in the fitting are the methylene symmetric C-H stretching (d^+ , 2850 cm⁻¹) and its Fermi resonance stretching (d^{FR} , 2915 cm⁻¹) modes.

Long chain alkanethiols such as **DT** and **ODT** form well-ordered monolayers with the alkyl chains aligning to an all-trans configuration, where there is a local inversion at the middle of each C-C bond. Thus, methylene stretching modes are not observed in crystalline monolayers. Gauche defects break up the symmetry in the chain, allowing the methylene modes to be SFG-active. The presence of methylene stretching modes are qualitative indicators of defects and the d^+/r^+ ratio is a useful indicator of conformational disorder.

The ratio of the symmetric and antisymmetric methyl C-H stretch (r^+/r^-) on the other hand, can be used to estimate the average tilt of the terminal methyl group. Orientation analysis was done by deriving the intensity ratios of the symmetric and antisymmetric stretching modes of the terminal methyl groups from the curve fitting. These ratios were then compared to theoretical orientational curve and the methyl group tilt was approximated using the bond polarizability model and calculations.^{34-36,38} The analysis assumes that the monolayer surface is rotationally isotropic about the surface normal and the local symmetry of the methyl group is C_{3v}.

5.3.2.1. Reduction of DT SAM

The SFG spectra of the **DT** chains on gold during the first reductive reduction cycle are shown in Figure 5.3. The spectrum acquired before reductive desorption, as shown in the topmost plot, reveals that the spectrum is dominated by peaks associated with the r^+ and r^- modes. At -400 mV, the r^+/r^- ratio of the **DT** SAM on gold is estimated to correlate with a methyl group tilt angle of ~37°, which is consistent with tilt angles associated with densely packed SAMs derived from even-numbered alkanethiols.

Methylene C-H stretching modes (d^+ and d^-) at 2850 and 2915 cm⁻¹ are not evident, suggesting that the monolayer is well-ordered and crystalline.



Figure 5.3. Normalized SFG spectra of **DT** SAMs on gold obtained during the first reductive desorption cycle, proceeding from the top down as labeled.

At -800 mV, the peak for the methylene symmetric C-H stretching vibration (d⁺) appears suggesting that at this potential, the monolayer is becoming more disordered. At -1050 mV, all resonant signals disappears, indicating that the monolayer has been desorbed and has started to diffuse away from the surface. The current density at this potential is estimated from the CV analysis to be 68 μ A/cm² (Table 5.1). Upon returning

the potential to -800 mV, the peaks associated with the methyl C-H stretching vibrations start to reappear, but are weaker in intensity than the previous spectrum at -800 mV. When the potential was set back to -400 mV, more of the thiolate chains readsorb and reform the monolayer, as seen from the increase in the intensity of the band associated with r⁺. However, the intensity of this band after the cycle is much lower than that of the initial monolayer, likely because the monolayer is now less compact and the alkyl chains are more disordered. The presence of the methylene C-H stretching modes at 2850 and 2915 cm⁻¹, verifies that the monolayer has more gauche defects due to this disordering. These results are in agreement with that of the CV experiment, that the **DT** SAM desorbs and a fraction of the monolayer reabsorbs to the surface.

	Potential (mV)	Methyl Group Tilt Angle (deg)	d^+/r^+	Current Density (µA/cm ²)
	-400	37	0.1	0
	-800	43	0.3	3
1 st cycle	-1050	NA	NA	68
·	-800	62	0	7
	-400	42	0.1	0
2 nd cycle	-400	50	0	0
3r ^a cycle	-400	49	0	0
4 th cycle	-400	69	0	0

Table 5.1. Methyl Group Tilt Angles and d^+/r^+ Values for a DT SAM at Different Potentials

5.3.2.2. Reduction of an ODT SAM

Figure 5.4 shows the SFG spectra of **ODT** on gold during the first desorption cycle. At -400 mV, only the methyl C-H stretching modes are evident, with no methylene resonances, indicating that the monolayer is well-ordered. The initial methyl group tilt angle is calculated to be 29°. At potentials of -800 and -1200 mV, the methyl group tilt angle did not significantly change (~30°), but methylene resonances at 2850 and 2915 cm⁻¹ appear in the spectra, suggesting that there is a disruption in the order of the alkyl chains.



Figure 5.4. Normalized sum-frequency spectra of **ODT** on gold obtained during the first reductive desorption cycle, proceeding from the top down as labeled.

At -1350 mV, the methyl group tilt angle changes slightly (41°). From the CV experiment in Figure 5.2., the current density at this potential is estimated to be 156 μ A/cm² (Table 5.2), which indicates that reduction is taking place at this potential. However, the **ODT** monolayer remains intact. At more negative potentials, bubbles began to form on the gold surface, probably due to hydrogen evolution. Setting the potential back to -800 mV, the methylene symmetric stretch disappears, suggesting that the conformational disorder observed at negative potential is reversible.

	Potential (mV)	Methyl Group Tilt Angle (deg)	d^{+}/r^{+}	Current Density (µA/cm ²)
1 st cycle	-400	29	0.1	0
	-800	31	0.2	8
	-1200	30	0.3	101
	-1350	29	0.1	156
	-1200	30	0.3	46
	-800	30	0.2	5
	-400	32	0.1	0
2 nd cycle 3r ^d cycle 4 th cycle	-400	35	0.1	
	-400	35	0.1	
	-400	36	0.1	

Table 5.2. Methyl Group Tilt Angles and d^+/r^+ Values for an ODT SAM at Different Potentials

5.3.2.3. Multiple Reduction Cycles

Additional reductive desorption cycles on the **DT** monolayer were performed and are shown in Tables 5.1 and 5.2. For clarity, only the first and fourth desorption cycles are presented in Figure 5.5. The two spectra on top show no discernible resonances, implying that at the reductive potential (-1050 mV), the monolayer desorbs and diffuses away from the surface. As shown in Figure 5.3, a fraction of the thiolates can still readsorb. After four cycles, the intensities of the methyl resonances have drastically been reduced, and the methyl tilt angle is estimated to be ~70°. This is an indication that the monolayer is disordered and the alkanethiolates are nearly flat on the surface in a low-density phase.⁹ In contrast, **ODT** monolayers still retain the original crystalline structure after 4 desorption cycles (Figure 5.5).



Figure 5.5. Normalized sum frequency spectra of (a) DT and (b) ODT monolayer on gold during four reductive desorption cycles. The spectra taken at desorption potential were offset by +0.1 for clarity.

5.3.3. Discussion

5.3.3.1. Cyclic Voltammetry

The CV scans of both **DT** and **ODT** show multiple reductive waves. The presence of multiple voltammetric desorption waves have been observed by other investigators and reported in numerous studies,^{20,39-43} and have been attributed, in general, to the difference in the strength of the surface bonds of alkanethiolates on gold on terrace sites and step sites. Evaporated gold on silica is predominantly composed of Au(111) but also present are steps and kinks, which can be viewed as equivalent to Au(110), Au(100), and Au(210).^{12,39} Surface roughness plays two competing roles in the desorption potential. More atomically rough surfaces such as Au(110) have lower potential of zero charge (PZC) than those of Au(111), making their reductive potentials more negative.⁴⁰ However, rougher surfaces also produce less ordered monolayers with higher ionic permeability, which make their reductive potential more positive.

Fluorescence microscopy has been used to observe that thiols on regions with (111) orientation desorb at more positive potentials than for other lattice structures.⁴⁴ Other authors attribute these multiple waves to the difference in ionic permeability between the center of a domain and its boundaries.^{45,46} Previous studies have proposed a shrinkage mechanism in the desorption of **ODT** on gold.⁴⁷⁻⁴⁹ This theory proposes that thiols at domain boundaries are the first to be desorbed and as reducing potential is continued, the domains shrink. Other factors such as alkanethiol chain length^{40,41} and solution pH¹³ have shown to affect the presence of multiple desorption waves.

For octadecanethiolates on SAMs, the first peak at -1100 mV is assumed to be from thiolates on regions where gold has a (111) crystallinity. The reductive peak at -1250 mV might come from the desorption of thiols on the steps and defect sites of the gold substrate or from hydrogen evolution.

The small oxidative wave for SAMs formed from **DT** and **ODT** on gold attributed to the readsorption of the alkanethiolates is very different from studies that used Au(111) single crystals as substrates, which gave very strong reductive and oxidative peaks.^{10,21,28} The substrates for the present study are evaporated gold on silica, which is polycrystalline in nature. Previous research using polycrystalline gold could only detect a weak double-layer current, or multiple reductive peaks and a very weak oxidative peak.^{41,45,50} Thiolates desorb and readsorb on sites with different crystallographic orientations at different potentials.³⁹

On polycrystalline gold, thiolate desorption overlaps the hydrogen evolution current, making the oxidative current unreliable in quantifying the readsorption of the alkanethiols. Morin and co-workers have observed that hexadecanethiol deposited on polycrystalline gold on quartz have a small oxidative peak that disappears after several cycles. They also found that flame-annealing the gold substrate produced SAMs with voltammograms comparable to those of single crystal gold.¹³ Evaporated gold on silica however, is not compatible with flame annealing due to the formation of gold silicides.⁵¹

5.3.3.2. Surface Coverage Estimation by Cyclic Voltammetry

Integrating the desorption peak at -1050 mV, the reductive charge of **DT** at the first sweep was estimated to be 140 μ C/cm², far larger than those reported in other studies.^{12,13,52} **ODT** shows a similar reductive charge of 170 μ C/cm². These values are higher than the theoretical reductive charge of 70 μ C/cm², which corresponds to the 7.2 x

 10^{-10} mol/cm² coverage for a fully formed monolayer ($\sqrt{3} \times \sqrt{3}$)R30° on gold.⁵³ This difference may be due to surface roughness of the gold substrate⁵⁴ which increases the actual surface area¹² and the non-Faradaic contribution due to capacitive charging.^{12,13,41,55} The overlap between the reductive peak and the hydrogen evolution also complicates the computation of the desorption charge.

SAM Molecule	Cycle	Reductive Charge (µC/cm ²)	Percent Reoxidized Previous Cycle
	1^{st}	140	
DT	2^{nd}	99	70
	$3^{\rm rd}$	61	62
	4^{th}	22	35
	1 st	170	
ODT	2^{nd}	105	62
	3 rd	62	59
	4^{th}	34	55

Table 5.3. Reductive Charge of DT and ODTSAMs on Gold at ConsecutiveVoltammetric Cycles

Because reductive desorption is a one-electron process, the reductive charge can be used to estimate the surface coverage. Taking the ratios of the reductive charges would give a rough estimate on how much of the monolayer is reduced and oxidized at each cycle. At the second reductive sweep of **DT** SAM, a value of 99 μ C/cm² was obtained, suggesting that only 70% of the monolayer reoxidized on the gold surface (Table 5.3). After the second cycle, 61% of the thiolate reoxidized, as shown by the reductive peak at the third sweep. The reductive charges obtained from **ODT** SAM at different consecutive sweeps, suggest that only 60% of the monolayer are reoxidized after every sweep. The incomplete reoxidation of both SAMs may be due to the thiols diffusing away from the surface into the bulk of the solution or the formation of disulfides.³¹

5.3.3.3. Conformational Disorder at Non-reductive Potentials

At potentials more positive than the reductive potential, methylene C-H stretching modes appear in the SFG spectra of both monolayers, suggesting the chains have become more disordered. It has been observed in EIS measurements that alkanethiol monolayers produce defects and become more permeable to ions and water at reductive potentials more positive than the reductive potential.⁵⁶⁻⁵⁹ The cause of these defects are still unknown, but it has been hypothesized that at negative potentials, the electric field exerts a torque on headgroups, causing conformational disorder on alkyl chains located at the domain boundaries, which are less dense and have more conformational degrees of freedom than the chains at the center of the domain.⁶⁰ It is also possible that the defects are caused by the desorption of thiolates from domains near the grain boundaries.⁴⁷⁻⁴⁹ This conformational disorder could be the source of the methylene resonances observed in the SFG spectra.

5.3.3.4. Reduction of DT and ODT SAMs on Gold

SAMs formed from **DT** and **ODT** behave differently at their reductive potentials as observed from their SFG spectra. The methyl C-H stretching resonances disappear in the spectra of **DT** on gold at -1050 mV suggesting that the thiolates have diffused away from the gold surface. **ODT** on the other hand, still shows strong methyl symmetric C-H modes, indicating that though desorbed, the monolayer is still intact and near the gold surface. This difference is ascribed to the difference in the solubilities of the desorbed thiolates in the 0.1N KOH solution. **DT** is slightly soluble in alkaline solutions (~ 1.2 mg/L),²⁸ or 6.9 x 10⁻⁶ mol/L while the solubility of **ODT** in water is less than 5 x 10⁻⁴ mg/L or 1.7 x 10⁻⁹ mol/L.⁶¹ Assuming the space between the gold film and the CaF₂ window is 50 microns, the volume of liquid under the CaF_2 window (2.54 cm diameter) can be estimated as 2.2×10^{-5} L. At full coverage, the surface concentration of **DT** and **ODT** on gold is estimated to be 7.2×10^{-7} mol/cm². Once desorbed, the concentration of **DT** and **ODT** in the liquid would both be ~1.7 x 10^{-4} mol/L. Thus, a fraction of the decanethiolates desorbed from the surface could slowly dissolve and diffuse away from the gold surface to the bulk of the solution outside the space between the window and the gold substrate. This conclusion is supported by *in situ* fluorescent microscopy studies by Bizzoto and co-workers which showed that at negative potentials the thiols they studied desorbed as thiolates and diffused away from the surface.⁶² The thiol in their study had an 11 carbon chain and thus its solubility should be closer to that of **DT** than **ODT**. Because of these thiolates are more soluble in alkaline solutions than **ODT**, they are free to diffuse away into the bulk solution.

On the other hand, octadecanethiolates' low solubility and diffusion rate cause it to be locked into a crystalline formation that can be readsorbed to the surface. This agrees with previous studies that observed a SAM formed from **DT** desorbed completely from gold while 75 - 90% of a SAM formed from **ODT** readsorbed on the surface.²⁸

5.3.3.5. Surface Density Versus Potential

Since the peak amplitude is proportional to the number of vibrational modes on the surface (Equation 2.7), the amplitude of r^+ can be used to estimate the density of the monolayers at different potentials in the desorption process, assuming that the molecules on the surface have a narrow orientation distribution. As shown in Figure 5.6, the normalized r^+ amplitudes of **DT** SAMs drop to zero at the reductive potentials. **ODT** monolayers, however, still retain a strong r^+ amplitude at reductive potentials, in spite of the large current running through the surface. It can also be observed that the r^+ amplitude of **DT** decreases at subsequent cycles, suggesting that a portion of the decanethiolates is slowly diffusing away from the surface during the reduction. The **ODT** monolayer on the other hand is still a dense monolayer after four redox cycles.



Figure 5.6. Normalized r^+ amplitudes and current densities of (top) **DT** and (bottom) **ODT** SAMs at different cathodic potentials.

5.3.3.6. Nature of Desorbed Alkanethiolates

There is still much debate about the exact nature of a reductively desorbed monolayer. In addition to possibly forming bilayers or micelles, desorbed octadecanethiolates are also believed to form disulfides.^{31,61,63} Templeton and co-workers, studying thiols adsorbed on gold nanoparticles, found that the monolayer desorbs as disulfides when liberated by I_2 or NaCN.⁶⁴ Gold powder in ethanol has also

been found to oxidize 4-aminobenzenethiol to its disulfide.⁶⁵ Thermal desorption studies have also found that alkanethiolates desorb differently depending upon whether they are assembled in a well-packed domain or a diffused one. Dense domains desorb as disulfides while low-density domains desorb as thiolates.⁶³ However, another study found that when 2-napthalenethiolate on gold undergoes in-place exchange by **DT**, it desorbs as a thiol.⁶⁶

The electrochemical impedance spectroscopy (EIS) Bode phase plot shown in Figure 5.7 provides additional information on the nature of the ODT monolayer after desorption. An XPS study showed that **ODT** completely desorbs at potentials lower than -1200 m V.⁵² Ten CV sweeps were thus performed on **ODT** SAM on gold in 0.1 M NaOH solution from -400 to -1350mV. The SAM was analyzed by EIS from 100 kHz to 1 Hz before and after the CV experiment. Ideally, a well-ordered SAM should have a phase angle of 90° in a Bode phase plot at the low frequency range (1-1000 Hz) where diffusion dominates. After 10 cycles, the phase angle of the monolayer at the low frequency range dropped from 84 to 81°, suggesting the SAM retains its low ion permeability. After a thorough washing of ethanol, the phase angle decreased to 66°. This implies that the monolayer is composed of physisorbed molecules, held in place by the insoluble octadecanethiolates that are still attached and unable to diffuse in water during reductive desorption. These thiolates are more soluble in ethanol, and thus a portion is removed after the subsequent washing, decreasing the monolayer density and causing the monolayer to be more permeable. Figure 5.7b shows the SFG spectra of the monolayer before and after CV. Even after 10 CV cycles and a thorough washing with ethanol, the SFG spectra is still that of a well-ordered monolayer. A method to characterize the desorbed molecules is still needed to fully understand the nature of the desorbed monolayer.



Figure 5.7. (Left) EIS Bode phase of an **ODT** SAM on gold (**a**) before and (**b**) after 10 CV cycles and (**c**) after washing with ethanol. (Right) SFG spectra of **ODT** on gold (**A**) before and (**B**) after 10 CV cycles and washing with ethanol.

Based on the results shown in Figure 5.4, reduced octadecanethiolates do not form micelles or bilayers. Micelles or bilayers would cause a rearrangement of the alkanethiolate chains, which should be observed in the SFG spectra as the disappearance of the methyl C-H stretching modes at reductive potentials. That the SFG can still detect the methyl C-H stretching modes from **ODT** at desorption potentials suggests that even though the monolayer has fully desorbed, the van der Waals interactions of its alkyl chains and its low solubility in water allow it to retain its crystalline structure. This supports the model that octadecanethiolates are present as a two-dimensional layer on the surface and do not form micelles.³¹

5.4. Conclusions

Reductive desorption of **DT** and **ODT** SAMs grown on evaporated gold on silica were monitored using *in situ* sum frequency generation. Negative potentials caused disordering in the monolayer's alkyl chains, as evidenced by the appearance of d⁺ modes in the collected spectra. At reductive potentials, **DT** thiolate molecules diffuse away from the surface, while **ODT** thiolate molecules retain their two-dimensional structure near the gold layer. After 4 cycles, a large portion of the **DT** SAM has fully desorbed, as evidenced by its methyl group tilt angle while a majority of an **ODT** monolayer existed as a physisorbed layer on the gold surface, held in place by the interactions between the alkyl chains by molecules still chemisorbed on the surface.

5.5. References

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Chapter 6: Concluding Remarks

This dissertation has endeavored to demonstrate a complete presentation of how sum frequency generation spectroscopy have been applied to the study of self-assembled monolayers, starting from a comprehensive overview of the fundamental theory and scientific understanding of these subjects, as outlined in Chapter 1 and Chapter 2. The results presented in the preceding chapters established the utility of sum frequency generation in determining chemical information on self-assembled monolayers.

In Chapter 3, sum frequency generation (SFG) vibrational spectroscopy analyses were performed on self-assembled monolayers (SAMs) formed via the adsorption of 2-(4-(octadecyloxy)phenylethanethiol (**R1ArMT**), 2-(3,5-bis(octadecyloxy)-phenylethanethiol (**R2ArMT**), and 2-(3,4,5-tris(octadecyloxy)phenylethanethiol (**R3ArMT**) on gold. The SFG spectra showed that the monolayers formed were closely packed and well ordered. Through the use of orientational analysis, it was determined that as additional octadecyloxy chains were attached to the aromatic ring, the apparent methyl group tilt angle increased and conformational order decreased. Aromatic C-H stretching modes exhibited in the SFG spectra suggest that the aromatic rings have a C₂ axis along the surface normal. In order to enable a more complete interpretation of the data, model phenylethanethiols with different symmetries along the benzene ring were synthesized and used to identify vibrational modes and to help determine the surface orientation of the alkoxyphenylethanethiols. From this analysis, we concluded that SAMs derived from **R1ArMT** exhibit aromatic C-H stretching modes due to the C_{2v} symmetry at the ring. In contrast, SAMs derived from **R2ArMT** and **R3ArMT** exhibit no aromatic C-H stretching modes due to their low Raman cross section.

Chapter 4 presented the results of sum frequency generation imaging microscopy (SFGIM) of SAMs derived from dodecanethiol (DDT) and octadecanethiol (ODT). These monolayers were prepared on two gold surfaces possessing different grain sizes: atomically flat gold (gold deposited and annealed on a mica substrate) which has a large average grain size (~600 nm), and gold vapor deposited on a chromium-primed silicon wafer without subsequent annealing, which has small average grain size (~50 nm). These SAMS were probed to determine the effect of the gold surface's grain size on the conformational order of the alkyl chains in the film and the tilt angle of the monolayers' methyl tailgroup. CH_2/CH_3 ratios suggest that monolayers derived from **DDT** on surfaces with a large average grain size have fewer gauche defects within the alkyl chain assembly and thus are more ordered than those deposited on smaller-grained substrates. It is hypothesized that this is due to the fact that smaller grains have more alkanethiol domains at the grain boundaries and thus form monolayers with more defects. The data collected for this study also indicates that ODT produces monolayers of similar conformational order on both types of gold surfaces. Methyl group tilt angle analyses suggest that **DDT** and **ODT** monolayers grown on smaller-grained gold are slightly more homogenous than on annealed gold on mica. It is hypothesized that there is a disparity of conformational order between domains at the center of the grain and those at the grain boundaries leading to a wider gradient in methyl group tilt angles starting with those that are almost parallel to the surface normal at the center of the domain to those that are more
tilted at the domain boundaries. Smaller-grained gold, such as evaporated gold on silica, produces uniformly less ordered domains across the grain, producing a narrower distribution of tilt angles.

Chapter 5 presented the *in situ* monitoring of the reductive desorption of decanethiolate (**DT**) and octadecanethiolate (**ODT**) SAMs on gold in aqueous alkaline solution using sum frequency generation. At desorption potentials, **DT** thiolates diffuse away from the surface as seen from the disappearance of the SFG signals for the methyl C-H stretching modes. The presence of a strong SFG resonant signal throughout the desorption cycle suggests that SAMs formed from **ODT** retain their two-dimensional structure near the gold layer. After four cycles, a major portion of the **DT** SAM has fully desorbed while the **ODT** SAM exists as a physisorbed layer, anchored by molecules still chemisorbed on the gold surface.

It can be concluded from the experiments presented in this manuscript that SFG analysis is truly a useful tool to characterize self-assembled monolayers. It is recommended that further study of the effect of grain size on the conformational order of SAMs be done by studying thiolates on ultra-flat gold.¹ The *in situ* monitoring of surface reactions such as copper oxidation and reduction,² and electrochemical lithography³ via SFG spectroscopy or SFGIM is also suggested.

6.1. References

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