Quartz Crystal Gravimetry as a Technique for Studying the Stability of Self-Assembled Monolayers

by

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Self-assembled monolayers (SAMs) adsorbed to gold substrates have a wide variety of actual and potential industrial and biotechnological applications (e.g., corrosion prevention, biosensors, molecular scaffolds). To employ SAMs in a setting outside of the laboratory, their stability and physical behavior in a variety of conditions must be understood. In this study, quartz crystal gravimetry (QCM) is used to examine the stability of alkanethiols on gold when exposed to extreme temperatures and to solvents. It is found that QCM provides a useful real-time method for studying the behavior of SAMs when exposed to solvents, but is not an acceptable technique in examining the stability of SAMs when conducting thermal studies.

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CHAPTER I

INTRODUCTION

Background

Surface science has been a extensive subject of research interest for decades, encompassing the chemistry and physics occurring at many types of surfaces, such as human cell membranes, glass, silicon, and various metals. Over the past twenty years, science and technology have been enriched by the development of a particular subset of surface science: self-assembled monolayers (SAMs).

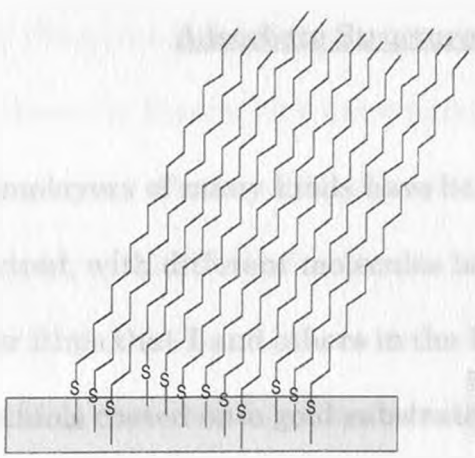

Figure 1A: A model of octadecanethiol adsorbed onto a gold substrate. This is the simplest alkanethiol studied and characterized, as it has no internal functional groups. In both figures, the angled chains represent linked carbon atoms.

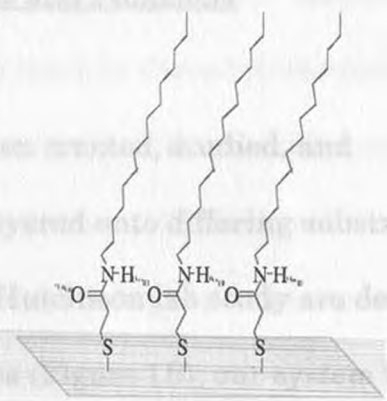

Figure 1B: An alkanethiol that contains only one amide group. It is similar to octadecanethiol, but contains internal amide bonds. Amide bonds are molecular connections between a carbonyl group of one molecule and an amine residue of another.

The chemical nature of SAMs is exactly as the name implies: a quantity of similar molecules will arrange themselves onto a particular surface (or "adsorb"), without the assistance or direction of the investigator, in a particular configuration with aggregation of molecules occurring in essentially two dimensions (Figure 1). These "monolayer films," as they are often called, can extend to macroscopic dimensions in length and width, but are restricted in the dimension of height. As a monolayer, the film is one molecular layer thick. The size of the monolayer system is one of its most extraordinary properties. The adsorbate (or molecule layering onto the substrate) is approximately one-billionth of a meter thick, or about a thousandth of a wavelength of light. Monolayers, in keeping with anything else that small, cannot be detected by the human eye.

Adsorbate Structures and Functions

Monolayers of many kinds have been created, studied, and characterized, with different molecules layered onto differing substrates. The monolayer films that I and others in the Hutchison lab study are derivatives of alkanethiols coated onto gold substrates (Figure 1B); our system is a modification of the well-investigated alkanethiol-gold system.[1] In Figure 1A, there are two regions within the adsorbate molecule: the alkane region and the thiol region. An alkane is a chemical group with carbon atoms saturated

with hydrogen atoms (also called "hydrocarbon"), and a thiol is a group in which a sulfur and hydrogen are attached to the remainder of the molecule. This particular sulfur-containing group is capable of *chemisorption* (chemical binding to a surface) and thus strongly adheres to gold and other metals.[1d]

The principal chemical difference between the molecules in Figures 1A and 1B is the presence of amide groups in the hydrocarbon chain of Figure 1B. Amide bonds are vital to the existence of proteins; they connect amino acids, molecules in our bodies that constitute proteins when they are connected in series. Figure 1B depicts a unique capability of amides: *hydrogen bonding*.[2] Hydrogen bonds are directional, attractive forces (with an enthalpy of 3-5 kcal/mol, meaning that 3-5 kilocalories of energy are required to break this bond) that occur between the carbonyl oxygen and a neighboring nitrogen-hydrogen group. Essentially, the hydrogen atom is shared by the oxygen and nitrogen atoms, bridging the two. Molecules such as those shown in Figure 1A cannot participate in these interactions as they do not have amide bonds, so they do not have the added stability provided by these attractive forces. The key similarity between the molecules in the figure is that they all have long carbon tails. Interactions between these carbon "tails" (often called *hydrophobic interactions*, short van der Waals interactions with an enthalpy of about 0.5 kcal/mol)[3] assist the self-assembly process. In the laboratory, we can synthesize molecules with different

numbers of amide bonds and/or different numbers of carbon atoms in the hydrocarbon tail.

Figure 1B shows that the molecule adsorbed as a monolayer has an amide bond in it. Amide bonds are the building blocks of proteins; long, saturated hydrocarbon tails like those in Figure 2 are also the building blocks of cellular membranes. Thus, this particular material (the adsorbate) is constructed from materials found in biology, as it contains an amino acid (or two or three, depending on the specific molecule we make) and a long, saturated hydrocarbon tail.

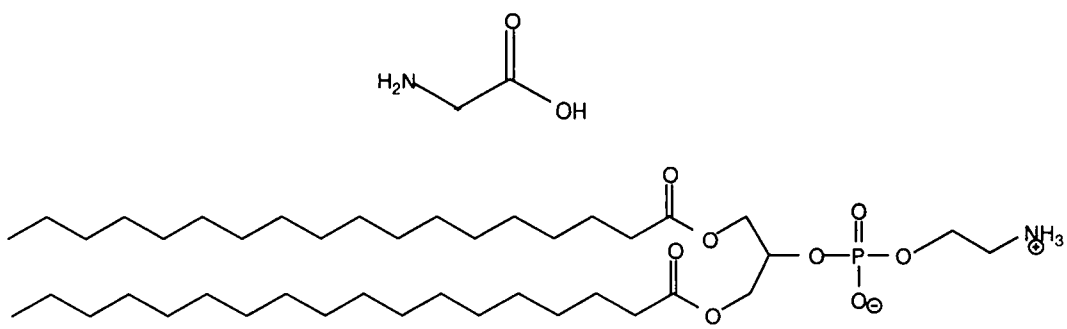

Figure 2: On the top half of the figure is the amino acid glycine. The free amine and the acid groups condense with their respective counterparts (i.e., amine binds with acid) to form an amide bond , which are functional groups in the adsorbates. A typical phospholipid encountered in cellular membranes is depicted on the bottom half; a characteristic feature is the long, saturated hydrocarbon chain, another functionality of the alkanethiol.

This conclusion is extremely meaningful when placed in context of the technological importance of self-assembled monolayers.

Applications

Synthetic monolayer materials can be used for an abundance of applications. For example, they can be employed as biosensors,[4] in which the binding of a passing molecule in the body can trigger a signal through the SAM which may in turn be connected to a microcomputer, evoking an electronically directed response. A practical example of this would be an internal glucose monitor, used to monitor the blood sugar level for diabetics. Out of necessity, it would have to be extremely small, a criterion which a self-assembled monolayer clearly satisfies. The carbon atom at the surface opposite the gold could be functionalized in such a manner that a passing sugar molecule like glucose would bind to it and release, sending electrical signals to the gold surface. The number of these binding reactions could be tallied to give an indication of the representative blood sugar level. Signals that the computer perceives as low sugar levels could then be directed to an internal dispenser of glucose, such as an artificial pancreas. This is an example of one of numerous biological applications for which self-assembled monolayers are capable.

In a more industrial setting, SAMs can be used as lubricants, or corrosion prevention devices. The long hydrocarbon matrix facing away from the metal might be exposed to the air, oxygen, and water when placed in a functional setting. All of the above can lead to the corrosion (or rusting) of

metal surfaces. The interaction of oxygen or water with the hydrocarbon surface is analogous to a drop of water trying to pass through an oil (oils are made up of long carbon chains such as these). The close packing of the carbons stacked together will block the penetration of water to the metal surface.

Hypotheses

If devices such as these monolayers are to be used in any sort of practical fashion, they must be stable in a variety of conditions to which they might be exposed. A known problem with alkanethiols is that they become rapidly disordered at approximately 115 °C and then desorb at 175 °C.[1e] *My hypothesis is that replacing the hydrophobic interactions with hydrogen bonds will enhance the stability of the monolayers.* As stated earlier, the hydrogen bonds are strong attractive forces; it takes 3-5 kilocalories (kcal) of energy per mole to break these associations between the molecules.[2] On the other hand, it only takes 0.5 kilocalories of enthalpy per mole to disrupt the hydrophobic interactions,[3] which are very weak and take little energy to break. I will test my hypothesis by synthesizing and studying monolayers where the methylene groups are replaced with hydrogen bonding amide groups. I expect that molecules with amide groups will be much more stable when exposed to extreme heat and a variety of different solvents than a molecule that has no amide groups. I would expect that a molecule with no capability

to hydrogen bond, such as the first shown in Figure 3, would present the least amount of resistance to high temperatures. It is proposed that the additional hydrogen bonding will have a synergistic effect on SAM resistance to heat and nonpolar solvents. I will study four different molecules as seen in Figure 3.

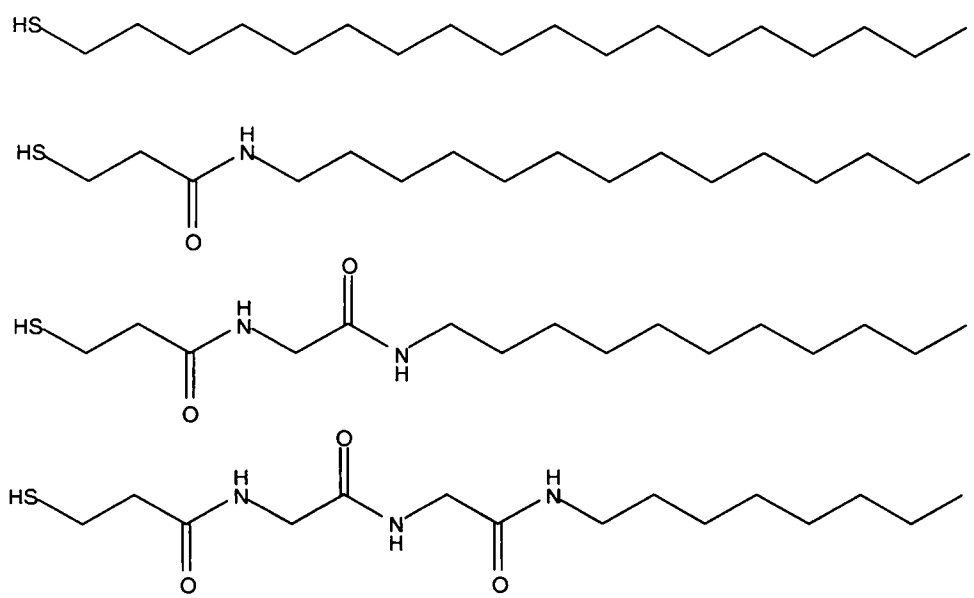

Figure 3. Molecules synthesized for stability studies. From top to bottom: octadecanethiol, 1-amide-14 carbon tail (denoted 1AT-C14), 2AT-C11, and 3AT-C8. All of these molecules are the same length from end to end, but vary by amide to carbon tail composition.

I will determine their stability when exposed to extreme temperatures and solvents such as alcohol, or *n*-hexane (a six-carbon hydrocarbon) (see below).

There is precedence and preliminary support for this hypothesis through previous work done in our lab; tests have been performed to monitor SAM desorption in solvent as measured by contact angle goniometry (CAG),[5]

as well as thermal desorption experiments as measured by X-ray photoelectron spectroscopy[6] (XPS) (to be discussed below). However, we look to a quartz crystal microbalance to study further the *real-time* stabilities of these SAMs when exposed to high temperatures and a variety of different solvents.

Quartz Crystals as Ultrasensitive Weighing Devices

A quartz crystal microbalance (QCM) (Figure 4), will be used to study the stability of these monolayer films. A QCM is in essence a crystal that is a mass determination device, detecting almost infinitesimal changes in mass (hence a *micro*balance). We choose to use quartz crystals because the microbalance design is the most effective and sensitive tool to measure the adsorption and desorption of these molecules because it can detect the addition and loss of mass (molecules desorbing from the gold surface).[7] This property of microbalances is critical upon recalling the size of the self-assembled monolayer. Plated with gold electrical contacts, the quartz crystal is especially suitable for this experiment, as the thiol head group of the adsorbate will bind to the surface of the gold electrode.

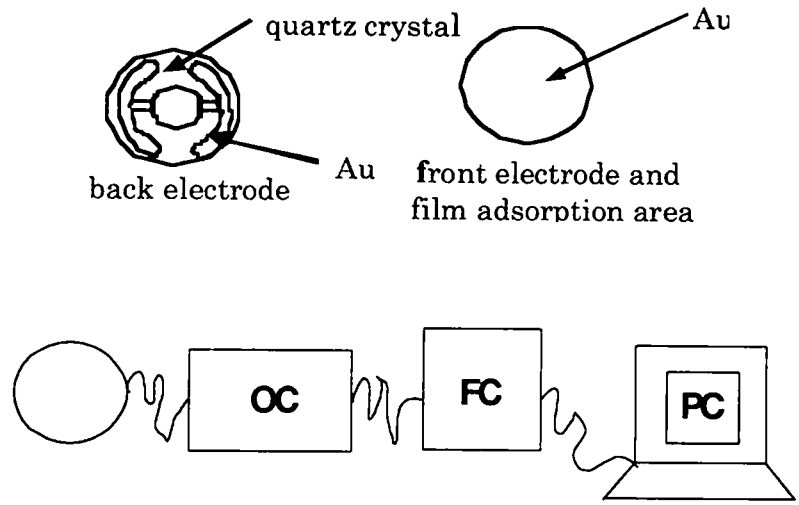

Figure 4. The top half of the illustration depicts the front and back sides of a quartz crystal, showing the deposited gold metal electrodes. The lower half of the figure shows the electronics circuit necessary for the collection of the experimental data. Wires are drawn between electronic connections to symbolize electronic connections. Figure is not to scale.
Legend: OC = oscillator circuit; FC = frequency counter; PC = personal computer

QCM Theory

It is important to understand the fundamental properties of quartz crystals when applying them to microbalance settings. Quartz crystals are *piezoelectric*. Piezoelectricity was discovered in 1880 by the Curies when they discovered that a pressure exerted onto a small piece of quartz effected an electric potential; conversely, they also observed that applying an electric potential across a quartz surface resulted in its physical deformation. This internal mechanical stress can be induced upon affixing electrodes to a quartz crystal unit and connecting it to a periodic voltage source (i.e., an oscillator circuit); then, the quartz can be made to vibrate at the frequency (or rate) of the driving voltage.[7e] If this frequency of oscillation is close to one of the

mechanical resonances of the quartz itself, then the amplitude of the physical deformation will be maximal. The quartz crystal is coated with gold electrical contacts on both sides, which provide locations for applying the potential and connecting it into a circuit. The crystal oscillates with standing waves of minute amplitude.

The quartz can vibrate along all three of its axes. The crystal can oscillate in a longitudinal mode (where the crystal extends and compresses – imagine pulling and pushing an accordion); it can also oscillate laterally, moving from side to side (the shear mode, as it is called). Finally, it can oscillate torsionally, where the crystal is actually twisting in space (imagine wringing out a washcloth). The quartz crystal can be cut in the proper orientation so that only one mode of resonance is highlighted and so that the others are silenced. This is often done by cutting the crystal so that the shear mode of resonance is completely dominant, and that the vibrations of the crystal stay completely one-dimensional. This is desirable, as it is well known that the shear vibrational mode is the most sensitive to the addition or removal of mass.[7e] These oscillations are subject to considerable distortion due to thermal and mechanical stress. Crystals can be cut in a specific, crystallographic orientation so that the pressures inflicted upon the crystal by stresses such as temperature are minimal; nonetheless, quartz crystal oscillators operate best at ambient temperature, and optimally when the temperature is tightly regulated. The crystal has its own intrinsic oscillation

frequency; when coupled to a driving frequency supplied by an electrical oscillating circuit, the amplitude of its vibration is maximal.[7e] These vibrations are not detectable to the human eye; we certainly cannot count them manually, so we must attach a frequency counter within the circuitry to monitor the change in the crystal's oscillation frequency.

There is known to be a relationship between the change in a crystal's oscillation frequency as a function of temperature.[7e] Lu, in his chapter on the theory and practice of QCM, illustrates a dependency relationship of the two; it appears to be a cubic relationship, i.e., the change in frequency is a function of the temperature to the third power. However, this relationship is not directly modeled, and there is no literature discussing this mathematical relation further; all that can be said with certainty from this article and by personal observation is that there is a nonlinear dependence of the frequency as a function of temperature. Elucidating the mathematical relationship empirically was not pursued.

The crystal's oscillation frequency will vary, directly and proportionally (for small mass loading such in the case of a SAM), with the amount of mass added to or desorbed from the crystal:[8]

$$\Delta f = - C_f \Delta m \qquad (1)$$

where Δf is the change in the crystal's oscillation frequency and Δm is the change in the film's areal density (density is the weight per unit volume of what is being added onto the quartz, so the *change* in areal density is

therefore the change of the density over the area of the gold electrode).[7e] The product of the film's areal density change and the area of gold that had film deposited onto it yields an approximate change in mass. This mathematical relationship is the Sauerbrey equation (named after the scientist who pioneered the microbalance field), and describes the direct dependency of the two variables.[9]

The quartz crystal microbalance is not precisely quantitative with respect to absolute mass change (i.e., it cannot indicate with certainty that a mass addition of a billionth of a gram has occurred), but rather it can give an indication of a relative mass change and also evidence of how fast the process of adding or losing mass has occurred. Achieving a picture of a *change* in the molecules per unit area is more effective, as the area of available adsorption sites on the gold face of the quartz crystal is arduous to calculate. Therefore, we are satisfied with relative changes in mass. We are also satisfied with a representation of a real-time view of how fast the process occurs, as kinetic data (or information on the rates and equilibria of the respective processes) is more useful information to have in the overall experimental scheme; we want to see how the addition of hydrogen bonding functionalities (such as amide groups) would affect the overall stability of SAMs changing as a function of time, which the QCM would be able to detect.

Theory of Experiments

The stoichiometric chemical reaction that we are monitoring is the addition of thiol to elemental gold in order to form the chemisorbed thiol. The hydrogen that terminates the thiol group is released during the reaction by an unclear mechanism.[1d] The current hypothesis is that the thiol hydrogen is released as a radical, two of which recombine to form molecular H_2.

$$Au + RSH \rightleftharpoons Au\text{-}SR + (1/2)H_2$$

The 'RSH' for this experiment is any of the four molecules illustrated in Figure 3. Au represents gold metal, and the H_2 is the molecular hydrogen that is released during the chemisorption process. In these types of adsorption processes, the Langmuir adsorption isotherm is used to closely approximate the molecular processes of the experiment. The Langmuir adsorption isotherm has three primary postulates:[7a-c]

1. The total adsorption that occurs in this system is limited to one monolayer. This assumes that there are no interactions from adventitious adsorption, stacking, etc.
2. The surface sites designated for adsorption are all deemed to be equivalent; that is, all of the gold atoms that are destined to interact with the thiol headgroup of the adsorbate are chemically and physically the same.

3. The adsorption of thiol to one gold site is chemically and physically independent of whether or not the gold site adjacent to it already has (or does not have) thiol bound to it.

These postulates are used to approximate adsorption conditions and to provide a framework in which to study these systems. These postulates are indeed approximations; we know that the first postulate holds true because of the chemical nature of the alkanethiol, and because we have extensively characterized it to be so.[10] With an unreactive methyl surface, it would be an impossibility to covalently form more than one monolayer. While it is true that some residual alkanethiol may lie on the surface of the monolayer, we know that it is not chemically bound in any way and can thus be removed with copious rinsing.

We know that the second postulate is not entirely true. It has long been known that alkanethiols adsorb onto gold crystallites with the Miller indices of (111) and (100).[11] Depending upon the crystal face presented to the alkanethiol [whether Au(111) or Au(100)], the thiols will order in a certain manner across the surface, giving characteristic electron diffraction patterns and infrared spectra. The lattice plane of the thin gold layer on the crystal, whether (111) or any other, is unknown. Additionally, the gold layer appears to be macroscopically rough in appearance, indicating that there may be large defect domains in which the gold atoms are spaced at different heights relative to one another, or missing entirely.

The third postulate states that the occupancy of one alkanethiol molecule on the gold substrate is independent of the state of occupancy of an adjacent gold site, where an additional alkanethiol adsorbate may (or may not) be present. This postulate is used as an approximation, as there may be either favorable or unfavorable interchanges between the adsorbate, another adsorbate, and the gold substrate. For example, it may be difficult for an adsorbate molecule to reach an available gold atom if there are many other surrounding adsorbate molecules that are already bound to the gold (steric difficulties); also, there are slightly favorable dispersive forces between adjacent adsorbates. As discussed previously, there are van der Waals interactions (0.5 kilocalories per mole) between the alkyl tails, and, depending on whether or not there is an amide domain near the gold surface, there may be strong, directional hydrogen bonding interactions (~3-5 kcal/mol). The formation of a network of hydrogen bonds, driven by the enhanced enthalpic contributions, would greatly favor the rapid assembly of a monolayer film. In spite of all of these inconsistencies, it is generally accepted throughout the scientific community that all of these corrections are reasonably small in comparison to the overall energetic picture and thus the Langmuir isotherm approximation is maintained.[7a-c]

Mathematical Parameters of Experiments

In this section, we strive to calculate the free energy of adsorption ΔG_{ads} of SAMs of these particular adsorbates (Figure 3), to know how energetically favorable SAM formation is. As mentioned earlier, the gold surface of the crystal appears to be macroscopically rough, qualitatively indicating that there may be defective adsorption sites within the gold. Karpovich and Blanchard, who perform microbalance experiments within the field of SAMs, claim that surface roughness is irrelevant because surface coverage (or the fraction of a monolayer) is generally expressed as a dimensionless quantity, Θ.[7a] According to the Langmuir adsorption isotherm, the rate of the surface reaction is:

$$\frac{d\Theta}{dt} = (k_a C)(1 - \Theta) - k_d\Theta \qquad \textbf{(2)}$$

where Θ is the fraction of surface covered, $(1-\Theta)$ is the fraction of surface yet to be covered (available for adsorption), C is the concentration of alkanethiol (usually expressed in moles thiol/liter of solvent), k_a is the rate constant for adsorption, and k_d is the rate constant for desorption.[7a]

The above equation gives us the rate of change of surface coverage as a function of time, so integration of this equation would give us the fraction of surface covered Θ, at any instant of time, t. Integration of **(2)** with respect to time gives:

$$\Theta(t) = [C/(C + [k_d/k_a])](1 - e^{-(k_a C + k_d)t}) \quad \textbf{(3)}$$

As the observed rate constant for the process will be a convolution of both the associative and dissociative rate constants, we may substitute k_{obs} for $k_a C + k_d$. Similarly, we can substitute a constant, K', for $C/(C + [k_d/k_a])$. The equation becomes much more simplified:

$$\Theta(t) = K'(1 - e^{-(kobs)t}) \quad \textbf{(4)}$$

As stated previously, the data collected is raw crystal frequency at periodic time points. Assuming that $-\Delta f(t)$ is directly proportional to $\Theta(t)$ as implied by **(1)**, a plot of $-\Delta f(t)$ as a function of t can be fitted to **(4)**. An exponential growth constant, k_{obs}, will be elucidated. The observed rate constants can be plotted for several experiments using different alkanethiol concentrations – these rate constants can then be plotted against their respective concentrations to yield a straight line of the form:

$$k_{obs} = k_a C + k_d \quad \textbf{(5)}$$

where k_a is the slope of the line and k_d is its y-intercept. It is well known that the equilibrium constant, K_{eq}, for any equilibrium process is the ratio of the rate of the forward reaction over the rate of the reverse reaction; here, the equilibrium constant for the formation of a SAM is the ratio of the rate of thiol adsorption (k_a) over the rate of alkanethiol desorption (k_d). Using the relation of the free energy of formation of a SAM to the equilibrium constant of the process,

$$\Delta G_{ads} = -RT \ln K_{eq} \quad \textbf{(6)}$$

ΔG_{ads} can then be calculated. If the free energy is a negative value, then we can know that overall, SAM formation is an energetically favorable process; conversely, if the free energy of SAM formation is a positive value, then we would know that this process is unfavorable.[12]

Background of Solvent Experiments

Earlier in the introduction, a variety of practical applications for monolayer films were discussed. In order for these laboratory projects to come to the industrial arena, their stabilities must be characterized for a variety of conditions to which they might be exposed. I plan to ascertain the stability of the monolayer films in two different experimental conditions: when the monolayers are exposed to higher temperatures (non-ambient) and when they are exposed to a variety of solvents. The principles of the experiments are the following: a monolayer film (of any of the adsorbate molecules illustrated in Figure 3) is adsorbed onto a quartz crystal (appropriate microbalance experiments and other characterizations would be utilized to determine the monolayer's presence on the crystal).

For experiments that test the film's stability upon exposure to solvent, solvent is flowed across the SAM on the crystal face and the resonant frequency is monitored to observe any change in the crystal's oscillation. We expect the solvent molecules to penetrate the alkyl matrix and, depending

upon the type of solvent used, permeate the amide domain as well. The solvent molecules may or may not contribute to the desorption of the alkanethiol by contributing a favorable energy and entropy of solvation, in which it is more energetically favorable for the alkanethiol to be dissolved in the solvent rather than adsorbed to the gold substrate. As predicted from the Sauerbrey equation, we expect that an increase in the oscillation frequency would correspond to the desorption of the alkanethiol from the gold surface. I expect molecules with low amide content to be more soluble (or to more readily dissolve) in solvents such as hexane, because they are most similar in chemical composition and together have favorable hydrophobic interactions. As oil and water do not mix, I expect such films to be very stable in water, because it would be an energetically unfavorable situation for the molecule to desorb from, or come off of, the gold. Conversely, I expect molecules with a large amide region to be more soluble in water (or have a lesser degree of stability or ability to desorb from the gold when exposed to water) and very stable when exposed to hexane. An aspect of this experiment that is less than straightforward is that the microbalance also "weighs" the solvent molecules that are present in addition to the SAM; the mass offset of the desorption of an adsorbate is convoluted by the quartz crystal contacting and weighing solvent molecules present both outside of and partitioned into the SAMs. Algorithms have been published for the deconvolution of the solvent loading effect from the monolayer formation effect.[13]

Background of Temperature Experiments

Upon deviation from ambient temperatures, the oscillation frequencies of quartz crystals cease to be stable, meaning that it will not remain steadily at one resonance frequency. Although it is well known that crystals cut in various crystallographic orientations have frequencies that behave in a nonlinear manner at temperatures well above and well below room temperature, we postulated that *they may be behave reproducibly* when exposed to identical stresses. For example, exposing a bare crystal to extreme temperatures would cause the crystal to deviate from its fundamental frequency in a characteristic pattern. After adsorbing a SAM onto the crystal, the adsorbed crystal could be exposed to extreme temperatures in a manner identical to that of the bare crystal. The two curves could theoretically be subtracted, the only difference between them being an effect of the monolayer's behavior or desorption.

For experiments that would examine the stability of the film upon exposure to non-ambient temperatures, the crystal is exposed to high temperatures and we watch for a change in the crystal's oscillation frequency. We expect that the monolayer undergoes a "melting" of sorts, where the alkyl chains lose their semi-crystalline form and become fluidlike and disordered.[1e] As the chains become disordered, they lose the van der Waals interactions

that play the large part in holding the alkyl chains together. After the melting transition and resulting disorder of the adsorbates' alkyl chains, we expect that the desorption of the adsorbate from the gold would involve the breaking of the gold-sulfur bond, as that is the only force remaining that links the alkanethiol to the surface. This chemical bond, upon exposure to high temperature, would be given an excess of thermal energy, in effect causing its breakage (the vibration of the bond would be so great as to separate the two atoms). I would predict that a molecule that has many hydrogen bonds (as in the one containing three successive amide bonds) will be the most stable of the series when exposed to the highest temperature, because the stabilizing forces of the hydrogen bonds will keep the molecule stable when it is exposed to high temperatures. Similarly, I would expect octadecanethiol, which contains no amide bonds and thus has no ability to hydrogen bond, to possess the least amount of temperature-related stability and will desorb from the gold surface first.

Hydrogen bonds are vital to the existence of proteins, and to many other molecules found in nature such as deoxyribonucleic acid (DNA), due to the added strength that they confer between adjacent molecules. It is exciting to apply this same concept to self-assembled monolayers, in which we can capitalize upon these stabilizing forces (considered primarily in biological applications) and apply them to uses in materials science (for technological applications). It is useful to examine the stability of amide-

containing SAMs as compared to alkanethiol SAMs of the same overall length (where the hydrophobic interactions have been replaced with hydrogen bonding ones) in order to study their comparative behaviors when they are exposed to high thermal stress and to a variety of solvents. Most importantly, the use of a quartz crystal microbalance allows for studying the stability of these SAMs in *real-time*, where the behavior of the monolayer films can be monitored as a function of time.

CHAPTER II

MATERIALS AND METHODS

Supplies

All chemicals were used as received from Aldrich, Bachem, or Fisher Scientific with the exception of CH_2Cl_2 which was distilled over CaH_2. Quartz crystals for the initial thermal desorption studies were purchased from Leybold Inficon at a fundamental resonance frequency of approximately 6 MHz and with gold-plated electrodes and a chromium adhesion layer. An adhesion layer is used because gold metal itself will not adhere to the quartz. Chromium will, however, stick firmly to quartz and the gold in turn adheres strongly to the chromium. All quartz crystals used in the advanced thermal investigations in the argon tube furnace were purchased from International Crystal Manufacturing (ICM, http://www.icmfg.com/labmic). Quartz crystals (#131229) were ordered at a fundamental resonance frequency of approximately 6 MHz, unbonded, unpolished, and with Au-plated electrodes (diameter = 0.268"). The crystals had a chromium underlayer evaporated directly onto the quartz to serve as an adhesion layer; subsequently, approximately one micron of gold was evaporated on top of the chromium.

The oscillator circuit used in this experiment, with shielded housing, a transformer power supply, and a connector for coaxial cable (to electronically connect it to the frequency counter), was purchased from ICM as well (#35360). The frequency counter used to collect data was a Tektronix Frequency Counter (model DC5010), borrowed from the Wybourne Laboratory, and data was assimilated on a Hewlett Packard PC computer borrowed from the Donnelly Laboratory. A computer program had to be created in order to record the data being emitted from the frequency counter. For kinetic accuracy, data needed to be collected every two seconds. Due to the lengthy nature of the experiment and the fact that one person could not do every task manually associated with these experiments, an electronic bridge was needed to connect the data output of the frequency counter to the computer (Appendix A: RKSCOUNT). "C" programming language was chosen because the computer was equipped to create, compile, and execute "C" programs.

Crystals were always cleaned by a UV-ozonolysis instrument (Boekel Industries) and dried in a stream of argon. The ultraviolet light makes ozone molecules, which are powerful oxidizers. The ozone molecules will oxidize adventitiously adsorbed material (normally water-insoluble) to fragments that are soluble in water. Copious rinsing with nanopure water (Barnstead E-pure) will remove the majority of such impurities. Both gold-plated sides of the crystals were UV-cleaned for 5-7 minutes on both sides, rinsed well with

nanopure water, and then argon-dried. Crystals were either exposed to piranha solution (1:5 30% H_2O_2 : conc. H_2SO_4 only when noted – CAUTION: strongly oxidizing, will react violently with organic materials), or rinsed with a variety of solvents depending upon the specific experiment performed.

Experimental Descriptions

Initial thermal investigations were performed in the Edwards Evaporator, a machine commonly utilized to deposit thin films upon many different types of substrates. A quartz crystal is located within the deposition chamber (part of the instrument that can be put under high vacuum), and its function is to monitor the thickness of films deposited by computing the amount of mass added to the quartz. The quartz crystal, in its arm-like housing, is oriented close to the substrate awaiting deposition, thus providing an accurate measurement of how much material has been deposited onto the substrate – the theory is that the quartz crystal is receiving as much evaporated material as the substrate, and thus provides an accurate measure of thickness. The quartz crystal housing is water-cooled; metallic tubing encircles the arm and contains continuously flowing, ambient-temperature water (from an outside source) that keeps the quartz crystal thermally regulated, and thus stable in frequency. In order to expose the crystal to heat, water at a temperature of 93 (± 1) °C was introduced into the quartz

crystal housing by blocking the flow of ambient water and inserting alternate tubing which was connected to the recirculating reservoir of hot water.

For the evaporator, the only frequency measurement gauge available was an electronic device that output the frequency of the quartz crystal. Unfortunately, there was no available way to interface the output box to either a computer or a chart recorder so as to tabulate the data, so measurements (frequency per time) were taken by hand. The chamber housing the quartz crystal was put under vacuum (pressure of approximately 1.0 E-6 mbar) so as to free the crystal from the weights of solvents after cleaning and air.

The experimental setup for the advanced thermal investigations (those higher than 93 °C) is depicted below as Figure 5.

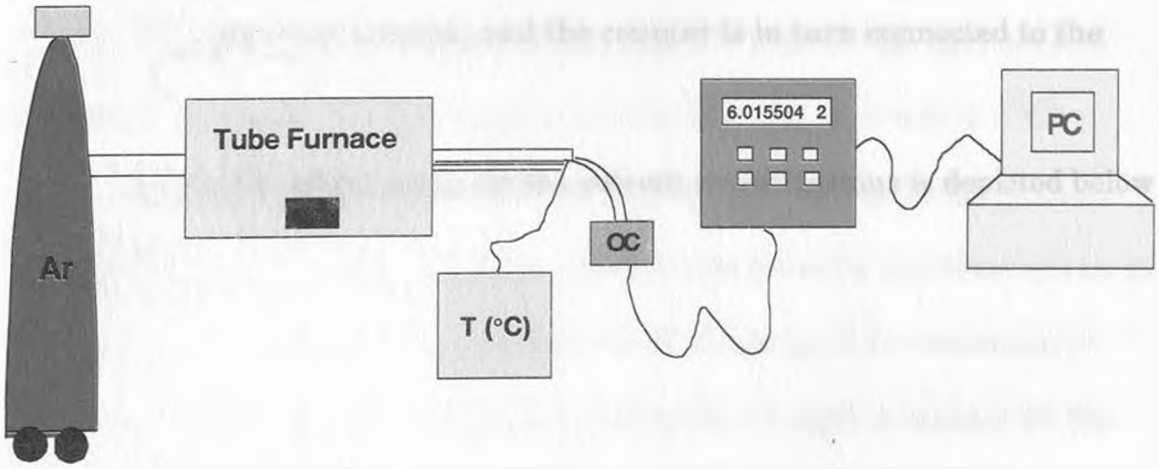

Figure 5: Experimental setup for the tube furnace thermal investigations. Legend: Ar = tank of argon gas that is connected to the tube furnace in order to keep the device under an inert environment; T(°C) = thermocouple probe that has an extension inside the glass tube; OC = oscillator circuit; FC = frequency counter; PC = personal computer. Figure not drawn to scale.

A flow of argon from the argon tank provides an inert environment within the tube furnace. The tube furnace consists of a cylindrical, glass tube that rests on a ceramic, nonconductive support. Heating coils are underneath and above the glass tube and buried within the ceramic; they are controlled by a programmable, digital thermostat on the outside of the apparatus. The crystal rests within the glass tube, and is connected to the oscillator circuit by ceramically insulated wire leads exiting the glass tube through a small aperture that is sealed with epoxy. Additionally, a thermocouple lead is inserted into the tube furnace along with the crystal in order to achieve an independent measurement of the ambient temperature within the glass tube. This serves to corroborate the reading of the thermometer of the tube furnace temperature controller. The oscillator circuit is then connected via a coaxial cable to the frequency counter, and the counter is in turn connected to the computer.

The experimental setup for the solvent investigations is depicted below as Figure 6.

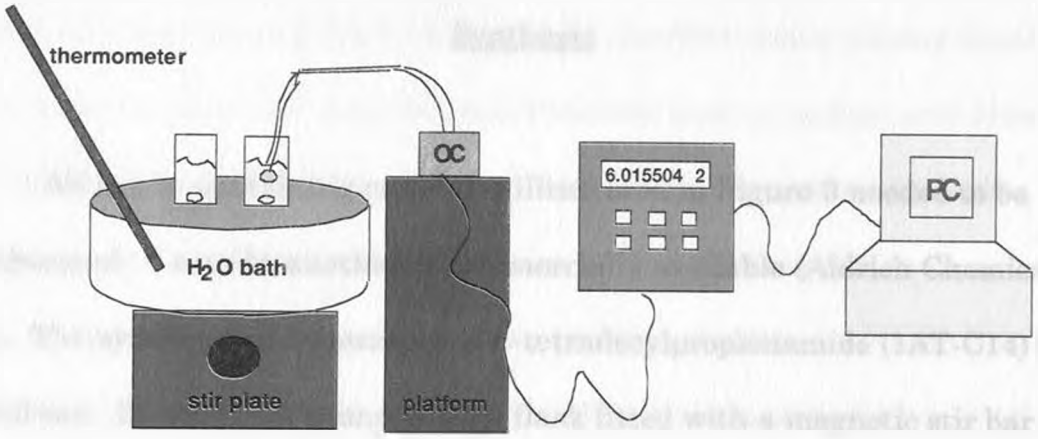

Figure 6: Experimental setup for the solvent studies. The oscillator circuit, frequency counter, and personal computer are shown.

Two beakers of solvent, fitted with magnetic spin bars, are sitting partially submerged in a room-temperature water bath, which is elevated upon a magnetic stir plate. Although not depicted in the above figure, the water bath itself is actually elevated off of the stir plate via rubber stoppers in order to avoid heating the environment of the quartz crystal by the heat emitted from the stir plate motor (an analog mercury thermometer with 0.1 °C increments is employed to monitor any temperature change of the system). The quartz crystal is suspended into the solution from the oscillator circuit by short, connecting wires. The oscillator circuit rests upon a nonconductive platform in order to have the optimal position and height necessary for the crystal's proper suspension; the circuit is connected to the frequency counter and personal computer as described previously.

Synthesis

All amide-containing molecules illustrated in Figure 3 needed to be synthesized. 1-octadecanethiol is commercially available (Aldrich Chemical Co.). The synthesis of 3-mercapto-*N*-*n*-tetradecylpropionamide (1AT-C14) is as follows. In a 250 mL round-bottom flask fitted with a magnetic stir bar, 0.5518 g (3.730 mmol) *S*-acetyl-3-mercaptopropionic acid, 0.7011 g (3.964 mmol) 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide•HCl (EDCI), and 0.0477 g (0.369 mmol) 4-dimethylaminopyridine were dissolved in 100 mL dichloromethane at room temperature, Upon addition of *n*-tetradecylamine, the solution remained clear and colorless, but cooled slowly. After stirring under nitrogen for 2-4 h, the organic solution was washed with 3 x 100 mL saturated sodium bicarbonate, 3 x 100 mL 0.01 M hydrochloric acid solution (adding brine as needed to resolve emulsions), and 1 x 100 mL distilled water. The organic portion was separated, dried over sodium sulfate, and filtered. The solvent was removed in vacuo to yield a white solid. In an Erlenmeyer flask, 1.24 g sodium hydroxide was dissolved in 125 mL absolute methanol. This was added all at once to the white solid in a 250 mL round bottom flask. After stirring under nitrogen for 0.5 to 1 h, 40 mL 5% hydrochloric acid was added all at once. A white precipitate immediately formed, and stirring was continued for 0.5 h. After addition of 25-50 mL brine, the product was extracted with 3 x 80 mL of dichloromethane. The

organic portion was washed with 3 x 100 mL distilled water (adding 25 mL brine as needed to resolve emulsions), dried over sodium sulfate, and filtered. The solvent was removed in vacuo to yield a white microcrystalline solid which was recrystallized from 95% ethanol. Yield (with respect to *n*-tetradecylamine starting material) 78%. mp 68.1-69.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.75 (broad, 1H), 3.26 (m, 2H), 2.82 (m, 2H), 2.47 (t, J = 6.7 Hz, 2H), 1.62 (t, J = 8.3 Hz, 1H), 1.51 (m, 2H). 1.36-1.22 (broad, overlapping resonance, 22H), 0.88 (t, J = 6.5 Hz, 3H).

The synthesis of ((3-thioaceto)*N*-propionyl)glycine, the precursor to forming the alkanethiol with two amide groups is as follows. To a 250 mL, sparged round bottom flask fitted with a stir bar, 3.3550 g (22.64 mmol) of *S*-acetyl-3-mercaptopropionic acid, 3.00 g *t*-butyl ester glycine • HCl (22.87 mmol), and 0.2739 g 4-dimethylaminopyridine (2.24 mmol) were dissolved in 150 mL freshly distilled dichloromethane. 4.69 mL triethylamine (33.63 mmol) was added via syringe, followed by the addition over 5 min of 4.2974 g 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide · HCl (22.42 mmol). All molecules dissolved, yielding a clear, yellow solution. The reaction stirred for 6 hours under nitrogen. The organic phase was washed with distilled water (2 x 50 mL), 1 M HCl solution (2 x 50 mL), and 1 M $NaHCO_3$ solution (1 x 50 mL). The organic portion was dried over sodium sulfate, and the solvent was removed in vacuo to yield a clear oil. Yield 84%. The *t*-butyl ester protecting group of the coupled product was then deprotected by heating the coupled

product directly (neat) at 240-250 °C for 15-20 minutes. The *t*-butyl functionality cleaves and is liberated as isobutylene gas, yielding the free acid. To the flask, distilled water and chloroform are added; the acid is extracted into the water layer and the water is pipetted off. The water is removed in vacuo to yield a red viscous oil that crystallizes upon standing. ^{1}H NMR (300 MHz, D_2O): δ 3.962 (s, 2H), 3.12 (t, 2H), 2.63 (t, 2H), 2.36 (s, 3H).

The synthesis of 3-thioaceto-*N*-(*N'*-*n*-undecylacetamido)propionamide, the precursor to forming the alkanethiol with two amide groups, is as follows. This molecule was synthesized up to the point where the last synthetic step was to hydrolyze the thioester under basic conditions. The molecule was left in its thioacetate-protected form (air- and moisture-stable) until ready to adsorb to gold, as the thiol will form disulfide when exposed to air.

75 mL of freshly distilled dichloromethane was added to a sparged, round-bottom flask. 0.3816 g (1.70 mmol) of 1-amide, precursor acid was added, followed by 0.3037 g (1.77 mmol, 0.3815 mL) undecylamine. The acid was insoluble until the addition of the amine, and a clear yellow solution resulted. 0.0212 g (0.174 mmol) 4-dimethylaminopyridine was added to the mixture, 0.3332 g EDCI (1.74 mmol, (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide • HCl) was added incrementally. The reaction mixture was allowed to stir overnight at room temperature under inert atmosphere. The organic phase containing the final product was washed with 1 M HCl (3 x 50

mL), 1 M $NaHCO_3$ (2 x 50 mL), and distilled water (3 x 50 mL). The organic phase was concentrated in vacuo to yield a yellow solid. ^1H NMR (300 MHz, $CDCl_3$ with 5% CD_3OD): δ 6.61 (broad, 1H), 6.30 (broad, 1H), 3.86 (d, 2H), 3.23 (q, 2H), 3.12 (t, 2H), 2.54 (t, 2H), 2.32 (s, 3H), 1.49 (broad, 2H), 1.29-1.24 (broad overlapping resonance, 16H), 0.87 (t, 3H).

The molecule containing three amide bonds and an alkyl tail of eight carbons (name, 3AT-C8) was not synthesized because it was not needed at this stage of experiments. All molecules are synthesized in an analogous manner to that of the previous, by adding as many amide groups as desired through successive coupling and deprotecting of the glycine residues, and through varying the alkyl tail length in the amine (through an alternate, commercially available amine).

Self-assembled monolayers on the quartz crystals designed for the thermal experiments were formed by making a .001 M solution of adsorbate molecule in absolute ethanol and exposing one side of the gold substrate to that solution for approximately 24 hours in a soaking cell. Soaking cells were made by fusing together two pieces of glass tubing; one piece had on the end an O-ring seal joint (ID = 5 mm, OD = 8 mm, O-ring = 110, Chemglass #CG-124-01), and the other had on the end a threaded joint (#CG-351-10) in order to seal off the tubing via a screw cap (#CG-353-10). One side of the quartz crystal was placed facing the O-ring seal, and was clamped tightly via a stainless steel pinch clamp (#CG-150-01) against the joint while being

sandwiched between a Viton® O-ring (110) and a glass slide. Adsorbate solution was filled from the top, and the device was leakproof.

Characterization

Additionally, X-ray photoelectron spectroscopy (XPS) was used as a characterization technique to verify that the alkanethiol was bound to the gold, and also to tell the different types of atoms adsorbed onto the gold surface. The principle behind photoelectron spectroscopy is to measure the binding energy of electrons from various atoms contained in molecules on surfaces. The binding energy depends on both atomic identity and shell origin. When an incident X-ray bombards an atom (as part of a molecule) confined to a surface, an electron from that atom is emitted. This electron is funneled up into a detector and analyzer, which calculate the electron's binding energy. A photoelectron will have a unique binding energy that is characteristic of its chemical environment (including atomic identity and shell origin). Thus for example, one could tell on the basis of binding energy measurement the type of atoms that are being hit by the X-rays, and approximately the ratios of atoms based upon the intensity of electrons with certain binding energies. XPS was performed on a Kratos HSi Analytical Spectrometer using a monochromatic Al Kα source (13.5 kV, 15 mA), pass energy of 20.0 eV, 0.1 eV data spacing, and with binding energies referenced to Au($4f_{7/2}$) at 84.0 eV.

CHAPTER III

RESULTS AND DISCUSSION

Low Temperature Thermal Investigations

Initial low temperature experiments (<100 °C) were performed in the Edwards evaporation machine. The crystals were exposed to a temperature of 93 °C in the first experiments. This was a reasonable temperature at which to perform experiments because we have previously done partial desorption of an ODT SAM at about 50 °C under argon for approximately 80 minutes (as previously discussed in the introduction).[6] However, the two major experiments performed were not successful. It was recommended by the Edwards company that the mechanical and electrical components within the evaporation machine should not be exposed to temperatures greater than 95-100 °C;[14] thus, 93 °C was the highest temperature at which we chose to perform experiments in this system. Figure 7 shows the background run and desorption run for a monolayer of 1-octadecanethiol adsorbed onto a quartz crystal. The top half of the graph (the blue run) shows the frequency change of the crystal as a function of temperature. We can see that the frequency decreases upon exposure to the 93 °C water flowing through the metallic

coils, which is extremely confusing as it does not correspond to the characteristic increase in frequency upon increasing temperature as predicted by Lu.[7e] This may be an artifact of the "frequency counter" that is connected to the quartz crystal housing, so experiments proceeded. Once an ODT monolayer film was adsorbed onto the crystal, we see that the initial frequency of the crystal is now 85 Hz *less* than in its bare state (the pink run), indicative of the fact that something has adsorbed onto the crystal. Upon exposing the crystal with a monolayer on it to the hot water, we can see no obvious difference throughout the run other than the vertical offset from the presence of the SAM, which remains constant.

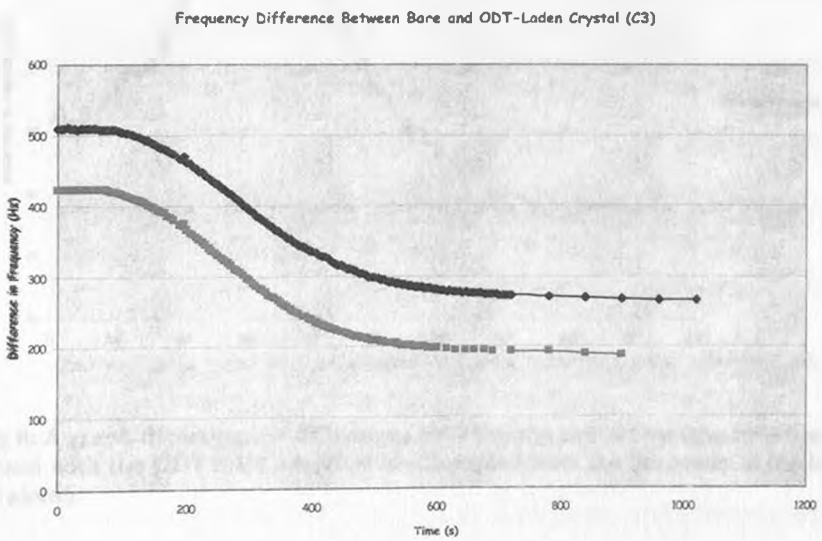

Figure 7: A graph of crystal frequency shift upon exposure to 93 °C water. The blue section of the graph is the bare crystal, whereas the pink section of the graph is a quartz crystal with a monolayer of 1-octadecanethiol adsorbed onto it.

We see no large *offset* so as to indicate that the monolayer film is desorbing. If the pink curve came up to match that of the blue curve, that would imply

that the film had desorbed from the crystal and that the crystal with the monolayer would now be clean and identical to the bare crystal. Figure 8 shows a subtraction of the two curves; there is no obvious desorption occurring. Theoretically, we would expect that if there were no desorption occurring that the difference between the two curves would be constant. This constant difference is not, in fact, observed. We see an increase of about 15 Hz in the crystal's oscillation frequency, followed by a gradual decrease down to about 8 Hz less than the original difference of the two frequencies.

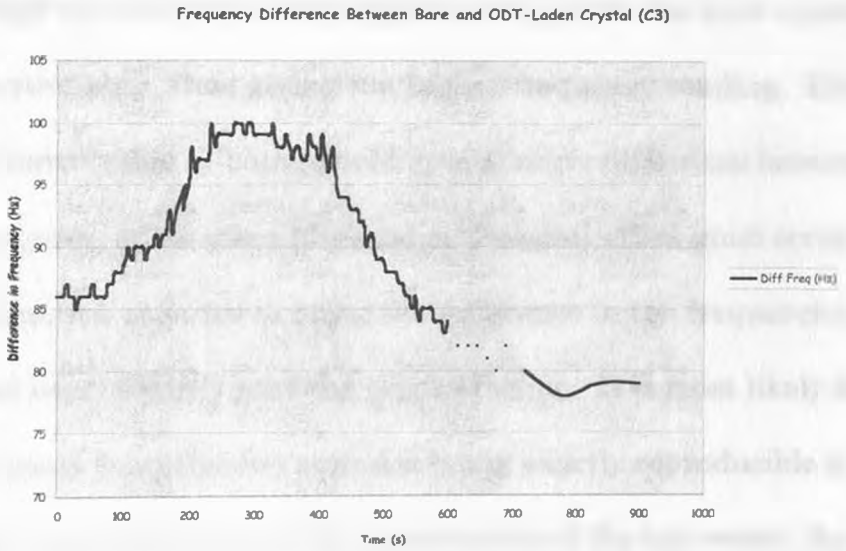

Figure 8: A graph depicting the differences between the two curves (the frequency of the crystal with the ODT SAM adsorbed is subtracted from the frequency of the bare crystal alone).

There are several reasons why the shape of the difference curve is not constant. We know that the monolayer is not beginning to desorb because the change does not stay at one end permanently. Rather, it increases and decreases, thus suggesting that adventitious material (i.e., extra ethanol from

the soaking jar that was not entirely dried off, other contaminants, etc.) may be settling on the crystal and then being pulled off by vacuum. The curve is set up so as to have a positive difference; therefore, the frequency of the crystal *with* the monolayer film is subtracted from the frequency of the bare crystal alone (it has a higher frequency value). Thus, an increase in the difference between the runs of the two crystals means that either something is settling on the crystal with the film adsorbed onto it (thus it is "weighing" more and thus has a lower frequency), or that perhaps the combination of heat and high vacuum was removing something from the bare crystal (ethanol, water, etc.), thus giving it a higher frequency reading. Either of these, or a convolution of both, would give a larger difference between the two curves. However, some other physical or chemical effect must occur in the opposing direction in order to bring the difference in the frequencies back down to and even slightly past the original value. It is most likely that the difference arises from the two runs not being exactly reproducible (i.e., there was a slight time difference in the introduction of the hot water, the crystal had some adventitiously adsorbed material on it while it was exposed to air that was not present in the other run, etc.). Even so, the magnitude of the variations in the graph of frequency differences (Figure 8) are only a fraction of the 85 Hz that we see as the "signal," and we can consider the bump an insignificant change.

To pursue the line of experiments and see how another crystal would respond with a different SAM, a monolayer of 1AT-C14 was adsorbed onto a new quartz crystal. Even though exposure to 93 °C heat for about 15 minutes had no effect on an ODT monolayer (in our hypothesis, an ODT monolayer was expected to be the *least* resistant to heat), it would be doubtful that similar exposure to a film containing hydrogen bonding would be any less stable. This idea was supported by running a frequency-temperature background run, followed by adsorption of a 1AT-C14 SAM and then exposure to the 93 °C water (Figure 9):

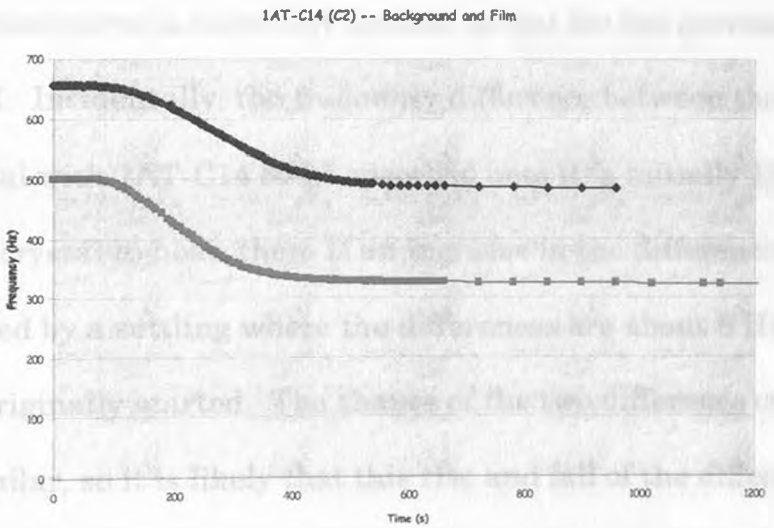

Figure 9: A graph of crystal frequency shift upon exposure to 93 °C water. The blue section of the graph is the bare crystal, whereas the pink section of the graph is a quartz crystal with a monolayer of 1AT-C14 adsorbed onto it.

Again, it is not apparent that the SAM is beginning to desorb off of the quartz crystal. A subsequent graph of the subtraction of the two curves shows (Figure 10):

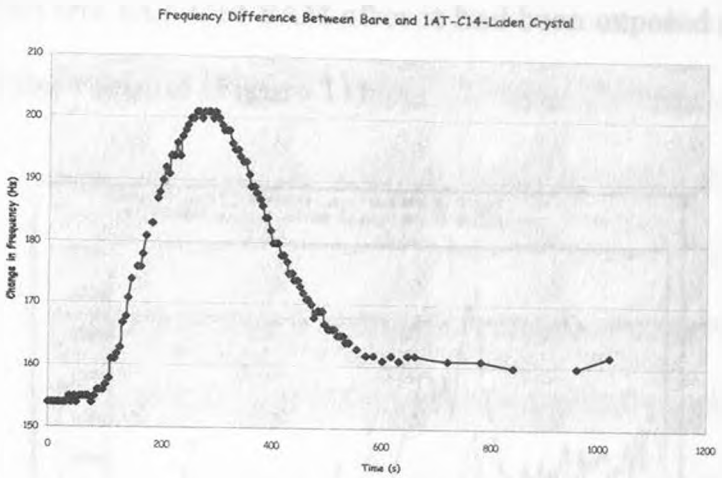

Figure 10: A graph of frequency difference between a bare quartz crystal and the same crystal with a 1AT-C14 SAM adsorbed onto it. There is still the same type of rise and fall behavior as observed in Figure 8.

This subtraction curve is extremely similar to that for the previous case with an ODT SAM. Incidentally, the frequency difference between the bare crystal and the crystal with 1AT-C14 SAM adsorbed onto it is initially 155 Hz. Upon exposing the crystal to heat, there is an increase in the differences of about 45 Hz, followed by a settling where the differences are about 8 Hz *more* than where they originally started. The shapes of the two difference curves are relatively similar, so it is likely that this rise and fall of the difference values is an artifact of the system.

In order to verify that no desorption was occurring on the 1AT-C14 film, X-ray photoelectron spectroscopy (XPS) was performed on the gold quartz crystal that had a monolayer film adsorbed onto it. XPS was done to verify that the SAM had actually formed in the first place and would not come off of the gold by exposure to high vacuum. A second XPS experiment

was performed on the 1AT-C14 SAM after it had been exposed to the heated, metal coils and the vacuum (Figure 11):

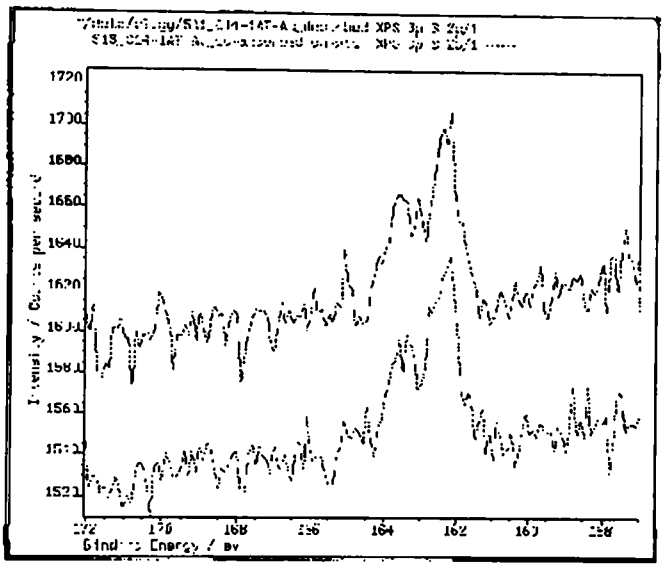

Figure 11: X-ray photoelectron spectroscopy (XPS) performed on the quartz crystal with a 1AT-C14 SAM both before (top) and after (bottom) exposure to the heated, metal coils. The spectra shown are the multiplexes of the S 2p doublet. There is no significant difference between the two spectra. This supports the hypothesis that no desorption occurred during the exposure to heat.

These XPS spectra shows that sulfur is present both before and after the film's exposure to heat. Sulfur was chosen as the representative element to analyze, assuming that if the sulfur atoms were present and bound to the gold, then so would be all of the rest of the adsorbate. The S 2p peak (or the photoelectrons emitted from the 2p orbital of the sulfur atom) forms a doublet. In sulfur bound to gold, the 2p(1/2) peak appears at about 162.1 eV, while the 2p(3/2) peak appears at about 162.3 eV (1 eV = 1.602E-19 J).

These initial thermal desorption experiments in the Edwards evaporation machine were concluded upon realizing that exposure to 93 °C or less would not initiate SAM desorption from the gold in vacuum. Considering the difficulty of modifying the evaporator to achieve temperatures higher than approximately 95 °C, it was decided to pursue a new microbalance technique that could accommodate increased temperatures, perhaps up to 300 °C.

High Temperature Thermal Investigations

In order to expose the crystal to temperatures higher than 93 °C, new efforts had to be made to design a device that could expose the crystal to high temperatures with no detriment to the device itself. An argon tube furnace was used to house the quartz crystal; the crystal was be placed inside a cylindrical, glass tube that is surrounded by a furnace that could heat to 600 °C or so higher than 93 °C (see Chapter 2 for a more detailed diagram and description of experimental setup). The furnace tube has its own digital, programmable thermometer that measures the temperature of the glass (the glass is resting directly on top of partially covered heating coils). However, it is prudent to note that the temperature of the glass is not necessarily the temperature inside the glass tube's cylindrical hollow (especially since the argon that is flowing in from the tank is cool). Thus, an independent

thermocouple was epoxied into the glass tube; it was positioned to be as close as possible to the quartz crystal, and its probe was always suspended in the argon environment, and not the glass, as was the crystal. This discrepancy in temperatures of the glass tube and the argon-filled hollow of the glass tube was illustrated when performing experiments and raising the temperature of the furnace tube in two ways: upon slowly programming the thermometer of the furnace tube to increase 2 °C per minute, the independent thermocouple lagged behind the thermometer of the furnace tube by 1 to 5 degrees; however, when the temperature was programmed to ramp immediately up to 150 °C, the independent thermometer lagged usually by 50 °C until it caught up minutes after the temperature equilibration of the tube and its inside hollow filled with argon.

These new experiments required the purchase of an oscillator circuit from ICM (see Chapter 2 for details), considering how for the initial thermal investigations the Edwards evaporator already had an oscillator circuit as part of its mechanics -- experiments were performed on preexisting equipment. New quartz crystals were purchased from ICM as well, as they were designed to fit the oscillator circuit. XPS was performed initially on one quartz crystal, after proper cleansing, as representative of the entire shipment. The only XPS peak frequencies found were characteristic elements of the quartz crystal and residual contamination; all peaks could be assigned and accounted. The majority of photoelectrons detected were from the gold

atoms that were evaporated on top of the quartz. However, minute amounts of carbon, oxygen, and chromium were found as well. The oxygen and carbon most likely settled onto the crystal during the transfer from cleansing to the ultra-high vacuum XPS. The amount of carbon and oxygen contaminant is consistent with the level of such contamination we have previously observed on gold substrates made in our lab, upon which we were subsequently able to form well-ordered SAMs. The chromium signal would be from the chromium adhesion layer that is sandwiched between the gold and the quartz itself; apparently it is migrating (or has migrated) nearer the air-gold surface. The result of this XPS study was to show that the crystals can indeed be satisfactorily cleaned by UV-ozonolysis, and that whatever material the crystals may encounter en route from factory to experiment can be removed with ease.

In the high temperature experiments, argon gas was allowed to flow through the glass tube and around the quartz crystal so that the crystal would be in an environment with the least amount of air present as possible. The argon flowed through at a rate that was arbitrary, but constant throughout all of the experiments. Usually, the system was purged with argon flowing for approximately five minutes.

The first few experiments consisted of exposing a bare quartz crystal to a large heat stress, in order to see how it would respond (Figures 12 and 13). The crystal was placed in the tube housing (which had been previously

purged of air with argon), and the temperature was increased up to 248 °C at the rate of 2 °C per minute.

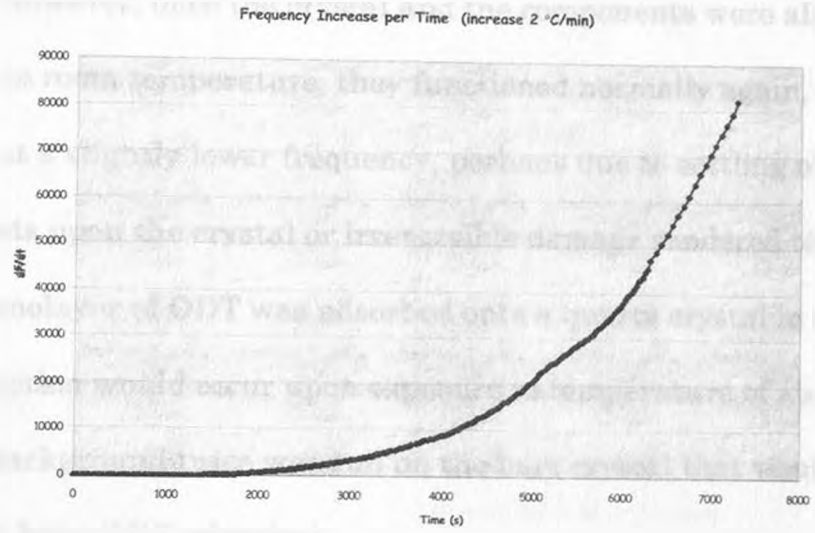

Figure 12: First frequency-temperature experiment in the high temperature investigations and using the new setup, illustrating frequency increase per time upon raising the temperature 2 °C/min. The temperature was raised to 248 °C.

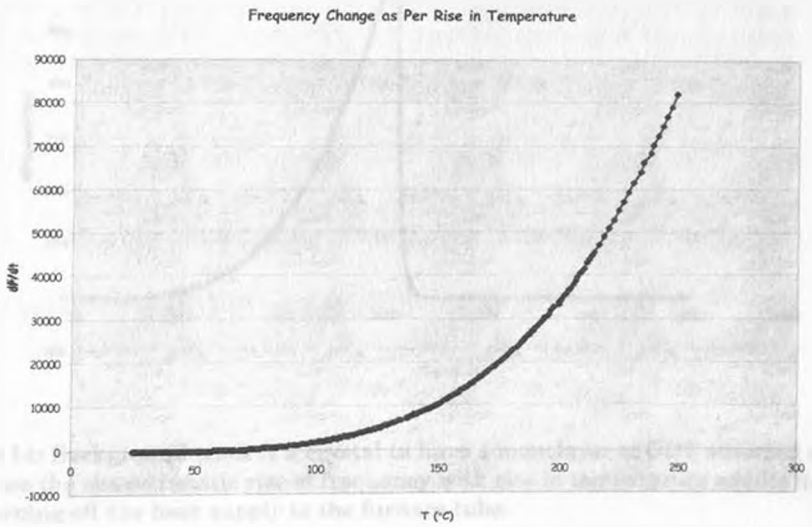

Figure 13: First frequency temperature experiment. In this graph, the change in frequency was plotted as a function of change in temperature (the temperature was raised approximately 2 °C/min). We can see that there is a nonlinear increase as per direct change in temperature, as predicted by Lu.[7]

The crystal was only raised to the temperature of 248 °C on this and all subsequent runs because the crystal failed in the circuit (it ceased to oscillate). However, once the crystal and the components were allowed to cool back down to room temperature, they functioned normally again, although oscillating at a slightly lower frequency, perhaps due to settling of contaminants upon the crystal or irreversible damage rendered to the crystal.

A monolayer of ODT was adsorbed onto a quartz crystal in order to see if any desorption would occur upon exposure to temperature of about 230 to 240 °C. A background trace was run on the bare crystal that would successively have ODT adsorbed.

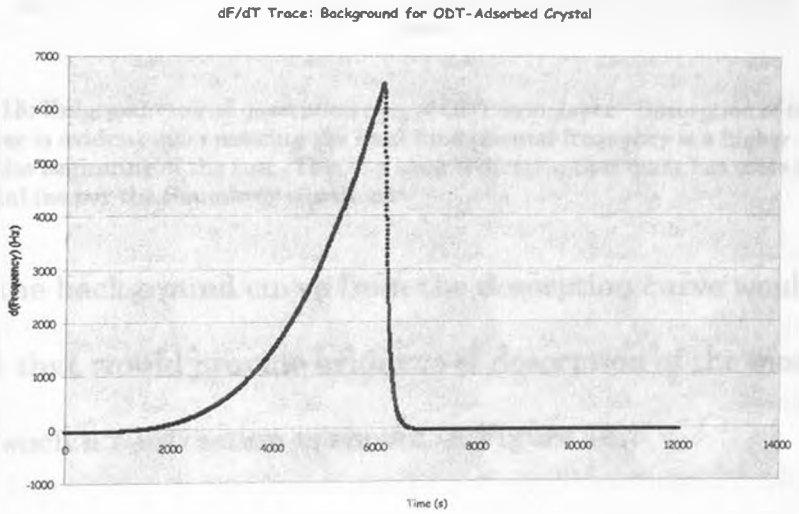

Figure 14: Background trace of a crystal to have a monolayer of ODT adsorbed onto it. We see the characteristic rise of frequency with rise in temperature and its fall upon turning off the heat supply to the furnace tube.

After adsorbing a monolayer onto this same quartz crystal and exposing it to temperatures up to approximately 230 °C for approximately 6000 seconds, we can clearly see that the monolayer has desorbed from the crystal (Figure 15);

we see the increase of approximately 43 Hz in the fundamental frequency (Karpovich *et al.* report[7a-c] observing frequency shifts due to alkanethiol SAMs in solution of about 45-50 Hz).

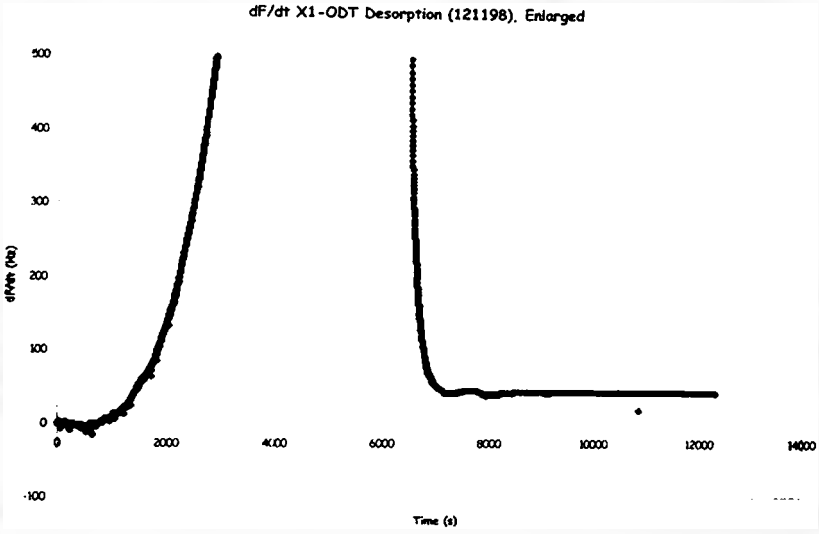

Figure 15: Enlarged view of desorption run of ODT monolayer. Desorption of the monolayer is evident upon noticing the final fundamental frequency is a higher value than at the beginning of the run. This is a clear indication that mass has come off of the crystal (as per the Sauerbrey equation).

Subtracting the background curve from the desorption curve would ideally yield a graph that would provide evidence of desorption of the monolayer. The curve of such a subtraction is shown in Figure 16.

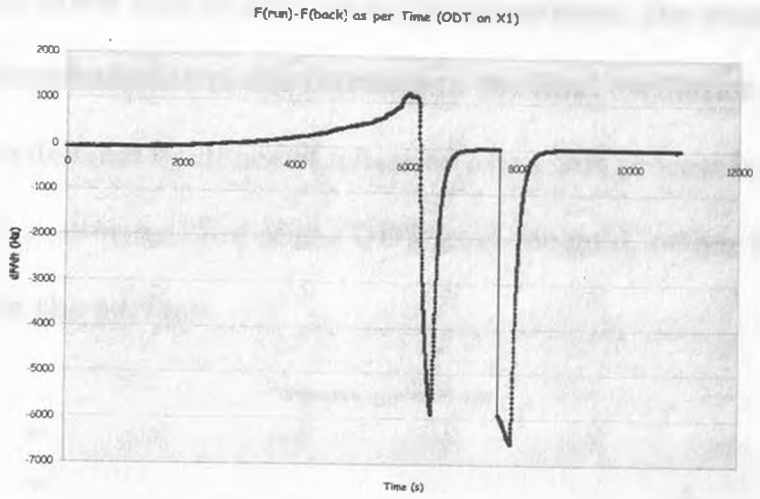

Figure 16: A subtraction of the background trace (Figure 14) from the desorption run of ODT (Figure 15) plotted against time. The plot does not depict a recognizable desorption pattern. At the end of the experiment, there is in fact a 43 Hz difference, presumably due to the desorption of the monolayer. However, this 43 Hz change is invisible due to the axis scaling and the width of the data point plotted.

It is clear that there is no physical principle that would predict a real desorption curve such as this. Upon graphing the change in frequency as a function of the change in temperature for the desorption of ODT (Figure 17), we see a curve extremely similar to Figure 13, which illustrates the frequency shift for exposing a bare crystal to changing temperatures. We can see that the magnitude of the *difference* increases as a function of the temperature; therefore, this refutes the original hypothesis of maintaining a constant value for the subtraction of the curves and seeing a desorption "curve" or "pattern" a region on the graph where desorption of the monolayer is obviously occurring. We can see through analysis of the data that there is no such sector of the graph that clearly illustrates the phenomenon. We know that at the beginning of the experiment, an ODT monolayer is adsorbed onto the

crystal, and we know that at the end of the experiment, the monolayer has presumably desorbed (due to the increase in the final oscillation frequency), but there is no distinct evidence of *where* or *when* this process is occurring. It could easily be a slow melting of the ODT from the gold, rather than a sudden departure from the surface.

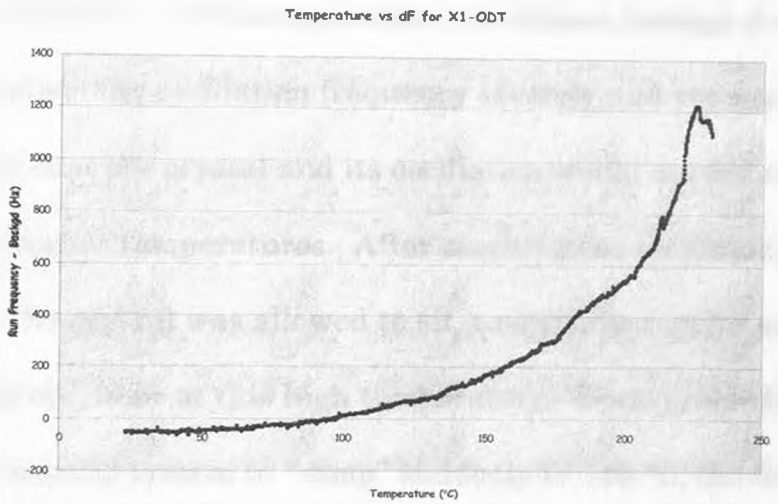

Figure 17: The difference of the background run from the run attempting to desorb the monolayer plotted against increasing temperature. The magnitude of the difference increases nonlinearly as a function of temperature.

A disturbing characteristic of all of the experiments described up to this point was the lack of reproducibility between trial to trial. All of these experiments certainly did not come easily or smoothly. The few experiments that are presented are those that proceeded to completion relatively free of disturbances (or with correctable deviations). During many experiments, it was noticed that identical experiments performed on apparently identical crystals behaved differently, although experimental conditions were being reproduced as closely as possible. In order to verify these observations that

apparently similar experiments were behaving differently, a series of three experiments were performed with this behavior as its focus.

A bare crystal was cleaned thoroughly and placed in the argon tube furnace; the tube furnace was allowed to purge with argon gas in order to expel air. The tube furnace thermostat was increased abruptly to a temperature of 150 °C – this temperature was chosen because it was high enough to displace the oscillation frequency severely and yet was low enough a temperature that the crystal and its oscillation would not fail as it had done previously at higher temperatures. After reaching the maximum temperature, the crystal was allowed to sit, undisturbed under argon, for approximately one hour at this high temperature. Upon programming the tube furnace heating system to "ramp" suddenly to 150 °C, the frequency increased drastically (as expected). Consequent to sitting for an hour at 150 °C, the frequency, upon reaching a maximum, began to decay in a nonlinear manner. Upon sitting for an hour, the power of the tube furnace was shut off and the crystal was allowed to cool, and eventually return to its original oscillation frequency within a few Hertz (Figure 18).

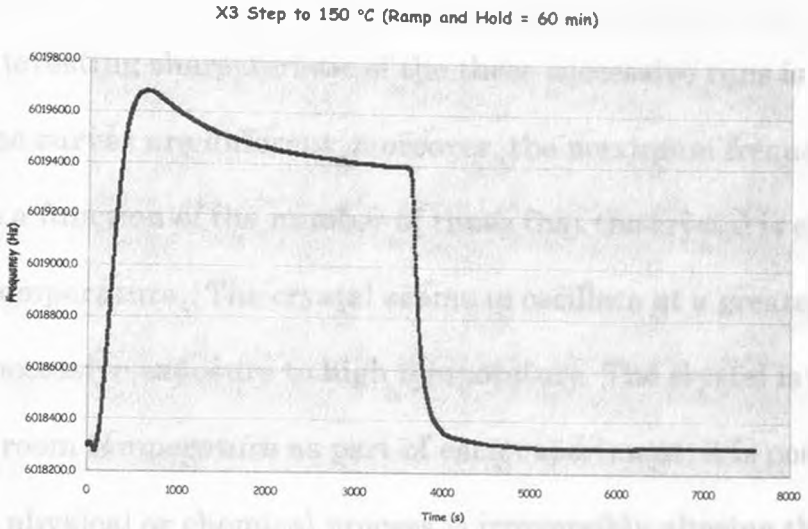

Figure 18: First step experiment to 150 °C. The crystal housed in the furnace tube is exposed to an abrupt temperature change, followed by sitting undisturbed at 150 °C for approximately 60 minutes. A nonlinear decay can clearly be seen.

The experiment was repeated two more times (Figure 19); it was found that although the runs were identical with regard to experimental conditions, the individual frequency-temperature traces of each of the runs were different between all three experiments.

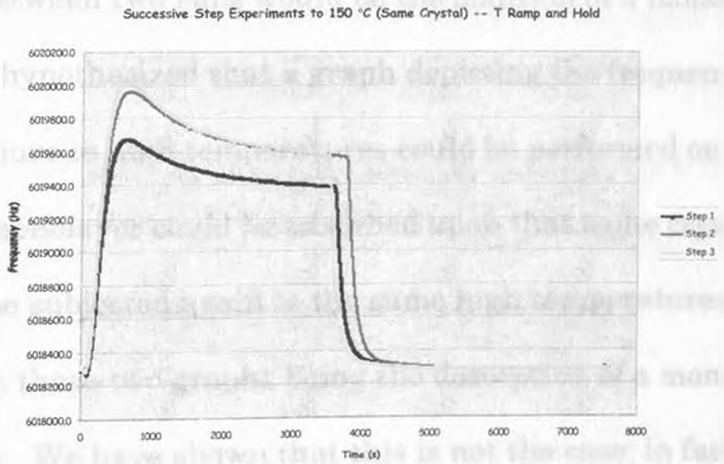

Figure 19: Three successive experiments, in which the quartz crystal was exposed suddenly to 150 °C, allowed to sit for approximately one hour, and then allowed to cool to room temperature. It is clear to see that the traces are not identical between all three experiments.

An interesting characteristic of the three successive runs is that the heights of the curves are different; moreover, the maximum frequency increases as a function of the number of times that the crystal is exposed to the 150 °C temperature. The crystal seems to oscillate at a greater frequency with each successive exposure to high temperature. The crystal is allowed to cool back to room temperature as part of each experiment; it is possible that some sort of physical or chemical process is irreversibly altering the oscillation pattern of the quartz crystal as time progresses. It is important to notice that the crystal starts and ends on essentially the same frequency for each experiment; the end results are the same, but it is the middle process, the time in which a monolayer would be desorbing, that is not reproducible from run to run. Therefore, as the oscillation pattern is changing with the number of exposures to high temperature changes, it is not reasonable that the only change between two runs would be the addition of a monolayer. Originally, it was hypothesized that a graph depicting the frequency shift as a function of exposure to high temperatures could be performed on a bare quartz crystal; a monolayer could be adsorbed upon that same crystal, and the crystal could be subjected again to the same high temperatures, the only difference between these two graphs being the desorption of a monolayer at a given temperature. We have shown that this is not the case; in fact, the difference graph (Figure 17) is a convolution of the desorption of the monolayer and other physical processes which are unknown at this point,

such as reversible and irreversible changes in the quartz at high temperatures.

A hypothesis was considered that the nonlinear decay in frequency could be a response from the crystal being contaminated. Although the crystal is in an airfree environment under argon, it is possible that there could be contamination in the argon tank, pressure-reducing valve, or Tygon tubing leading to the tube furnace, and that the contaminant (i.e., contaminants, grease) could be blowing across and settling on the crystal. If contaminants were indeed settling on the crystal, then the apparent frequency would decrease. This would be a possible explanation for the decrease in frequency.

To test this hypothesis, the crystal was placed in the argon-purged tube, and the argon flow was cut off at the beginning of the temperature ramp so that there would be no continuous contamination blowing across the crystal, provided there is some contamination source in the argon delivery system. The furnace tube was purged with argon. The quartz crystal was promptly inserted, and the furnace tube temperature was raised up to 150 °C. The result is no different than those with the argon flowing (Figure 20).

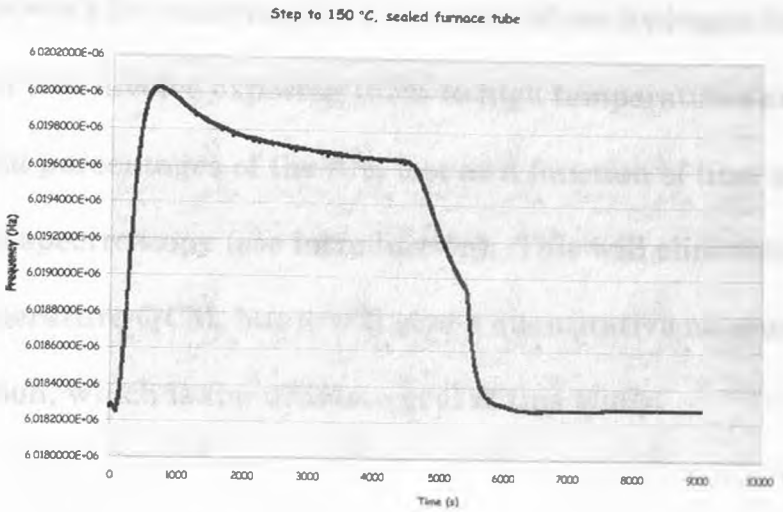

Figure 20: Ramp experiment up to 150 °C without a flow of argon, and holding the crystal at that temperature for 60 minutes. We can see that there is still the nonlinear decay in frequency as seen in the previous experiments. The bump in the right hand side of the graph is simply an increased rate of cooling due to opening the ceramic lid of the tube furnace, and does not affect the overall experiment.

After performing many quartz crystal microbalance experiments that involve significant deviations from room temperature, it is clear that this is not an optimal way to study the desorption of self-assembled monolayers on gold. Although the experiments are extremely difficult to reproduce, that is not the most significant problem. The most difficult part of the experiment to overcome is the lack of knowledge about the physical behavior of the crystal. There is no literature reporting similar thermal desorption of any type of SAMs. When discussing these experiments with those knowledgeable about the general operation of quartz crystals,[15] it is a "rule of thumb" that no experiments are carried out at temperatures that deviate significantly from room temperature.

Future work for studying the desorption of our hydrogen bonding SAMs on gold will involve exposing them to high temperatures and then to analyze *ex situ* percentages of the film lost as a function of time as per X-ray photoelectron spectroscopy (see introduction). This will eliminate the need for high-temperature QCM, but it will give a quantitative measurement of SAM desorption, which is the ultimate goal of this study.

Solvent Investigations

As mentioned in the introduction, there were two studies that were designed to study the stability of SAMs on gold – exposure of SAMs to temperatures that were far above room temperature, and exposure of SAMs to different types of solvents. After determining that exposing the quartz crystal (along with the SAM) to high temperatures was not experimentally feasible, it was decided to pursue experiments monitoring the adsorption of monolayers in solution and watching them desorb, if possible. The experiments to this end were designed to model those described by Karpovich and Blanchard in *J. Chem. Ed.*[7a] Essentially, they suspended a quartz crystal in clean solution, let the crystal's oscillation equilibrate while stirring, and then injected a small, precise amount (an aliquot) of alkanethiol. It was evident that monolayers had formed by the damping of the oscillation of the quartz crystal. They report frequency offsets of 45-50 Hz for their alkanethiol

monolayer adsorbing onto the gold.[7b] They performed these experiments with a variety of alkanethiols (what changed from molecule to molecule was the length of the alkyl tail), a variety of alkanethiol concentrations, and at a variety of temperatures (but all close to room temperature and at a constant temperature around ambient to avoid perturbing the quartz crystal). The point of these experiments is to obtain *in situ* kinetic measurements that describe how fast adsorptions occur as a function of the various conditions (i.e., concentration, temperature, etc.) and allow determination of the equilibrium properties of the system (i.e., equilibrium constant, the free energy of adsorption). The reason for reproducing these experiments with octadecanethiol (see Figure 3) is to illustrate to ourselves that the experiments that we want to perform are sound and practical. If Blanchard's work is reproducible, then our experiments should proceed without too many problems.

The first few experiments were not successful. In the literature, it is recommended that the quartz crystals should be cleaned with a piranha solution (1:3 30% H_2O_2 : conc. H_2SO_4) for five minutes. Exposing the crystal to piranha for any length of time (30 seconds, for example), rendered the crystal useless, as the piranha attacked the chromium underlayer or gold itself, causing the metal(s) to drift off of the crystal. With the mass coming off of the crystal, the response of the frequency was to drift steadily upwards. Although this steady upward drift could be accounted for in the background

frequency of the crystal, it is not experimentally sound to perform measurements on damaged crystals. After continued failed experiments using piranha, this particular cleansing technique was abandoned altogether.

One of the first few experiments performed was a test run, to see if it was possible to duplicate Blanchard's experiment, or even approximate it. A crystal was UV-cleaned and rinsed well. It was allowed to sit at room temperature in a beaker stirring with 99.0 mL of *n*-hexane. 1.00 ml of a 0.010 M stock solution of ODT was injected as far away from the crystal as possible, resulting in a net concentration of 0.1 mM ODT in *n*-hexane. The frequency counter was collecting data for frequency before, during, and after SAM adsorption. The resulting graph is shown in Figure 21 (raw data); a graph showing the rate of change of mass added is shown in Figure 22.

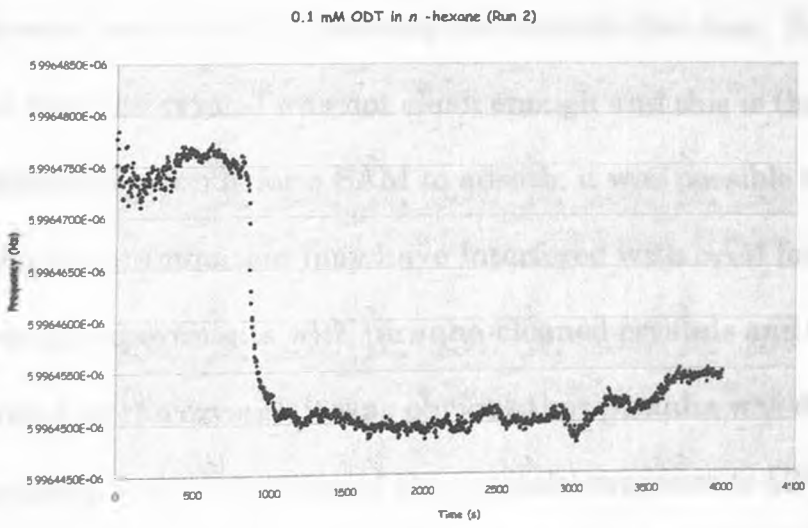

Figure 21: A graph illustrating the adsorption of ODT onto a quartz crystal. This crystal in particular was not cleaned with piranha solution. The 1 ml aliquot of thiol was injected at time = 700 s. There is an offset of about 30 Hz, and it takes on the order of 10 minutes for adsorption to come to completion. The offset of frequency is on the order of what Blanchard reported (45-50 Hz), but the time needed for a SAM to completely form is off by a factor of 10.

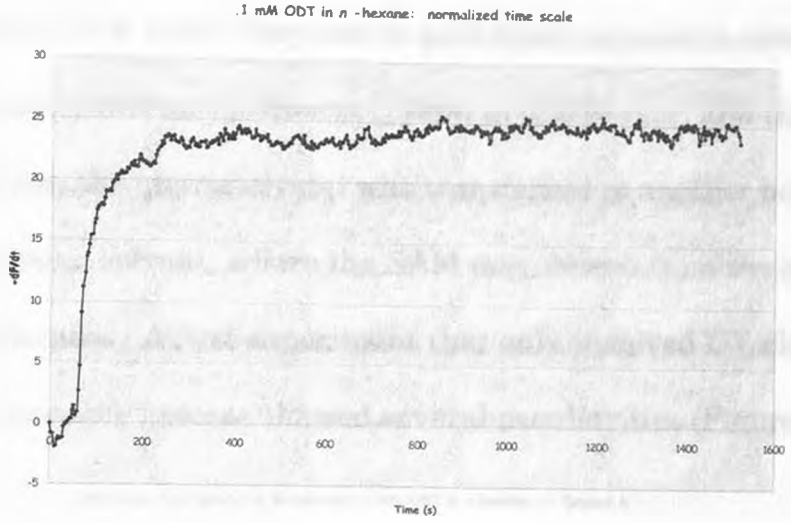

Figure 22: The negative change in frequency as a function of time. Where the curve increases dramatically is the injection of the thiol aliquot. Graphing the frequency this way allows a view of how mass is adding to the crystal as a function of time ($-\Delta f \propto \Delta m$).

At this point, because it was a preliminary experiment, we did not know that the piranha would damage the crystals to such an extent, so these experiments were performed by cleaning the crystals this way. It was hypothesized that the crystal was not clean enough and this is the reason why it took 500-600 seconds for a SAM to adsorb; it was possible that some residual surface contamination may have interfered with SAM formation. Upon performing experiments with piranha-cleaned crystals and noting the damage incurred to the crystal, it was obvious that piranha was doing more damage than good, and so the time of the crystals' exposure to UV-ozonation was increased to 7 minutes. (This was enough to get all contaminants off for subsequent adsorptions.)

In addition to wanting to observe the kinetics of SAM formation, we also desire to know how stable they are on gold when exposed to solvents. Thus, a SAM was formed on the quartz crystal in one beaker, and then to attempt desorption, the quartz crystal was transferred to another beaker containing only clean solvent, where the SAM may desorb from the gold if its equilibrium so dictates. A first experiment that only involved UV-cleaning for the crystal cleansing process showed several peculiarities (Figure 23).

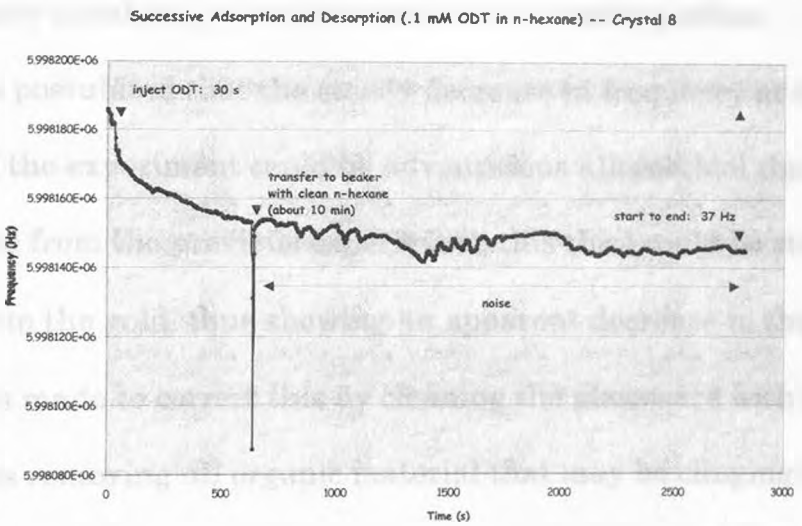

Figure 23: Graph showing a SAM adsorption and then a successive desorption attempt via transferring the quartz crystal with the newly formed SAM upon it to a clean beaker filled with clean solvent (*n*-hexane, the same solvent that was used for adsorbing the SAM).

The two major aberrant parts of this graph are the downward trend of the frequency before the injection of the alkanethiol (time 0 to 300 seconds) and the erratic frequency of the crystal after it had been transferred to the beaker filled with clean *n*-hexane. The crystal is supposed to be equilibrating with the solvent during the time 0 to 300 seconds, and this should be ample

time for the crystal to adjust its oscillation after coming into contact with the solvent.[7a] Second, it is unusual to have the wild oscillation when the crystal is in the clean beaker; it is expected that this would be flat, or that it would be increasing (linearly) by a few Hertz to show the desorption of the SAM off of the gold. Although appearing to be an oddity, the large downward spike is merely the artifact of moving the crystal to the second beaker. The spike is downwards due to the force with which the crystal is experiencing the solvent; loosely speaking, it can be ascribed to a dunking effect.

It was postulated that the steady decrease in frequency at the very beginning of the experiment could be adventitious alkanethiol that resides in the glassware from the previous experiment; this thiol could be steadily adsorbing onto the gold, thus showing an apparent decrease in the frequency. An effort was made to correct this by cleaning the glassware with piranha solution, thus removing *all* organic material that may be clinging to the glassware. A set of three experiments was set up to run under identical experimental conditions and see how the runs and adsorption curves changed as a function of time. The glassware was cleaned thoroughly with piranha every time an experiment was performed (and right before the experiment, as well, so the glassware would not become recontaminated with organic material in the air). The crystals were UV-cleaned for seven minutes on each side, followed by extensive rinsing. Nanopure water was used first, to remove all oxidized and water-soluble impurities; a rinse of freshly distilled

THF followed, to remove any water that may have still been clinging to the crystal. The THF rinse was followed by rinsing with *n*-hexane, which would be the solvent for the experiment. After the rinses, the crystal was dried in a stream of argon, and was immediately clipped into the oscillator circuit and immersed into a beaker of 99 mL of clean *n*-hexane. The beakers of solvent along with the supply of 0.01 M stock solution were placed in a water bath, and solution and solvents were allowed to equilibrate with the water to reach room temperature (see diagram in Chapter II for complete experimental setup). This measure was taken to prevent any oscillation fluctuations due to the crystal sensing changes in temperature. The results of the experiments are all graphed on the same scale (Figure 24.

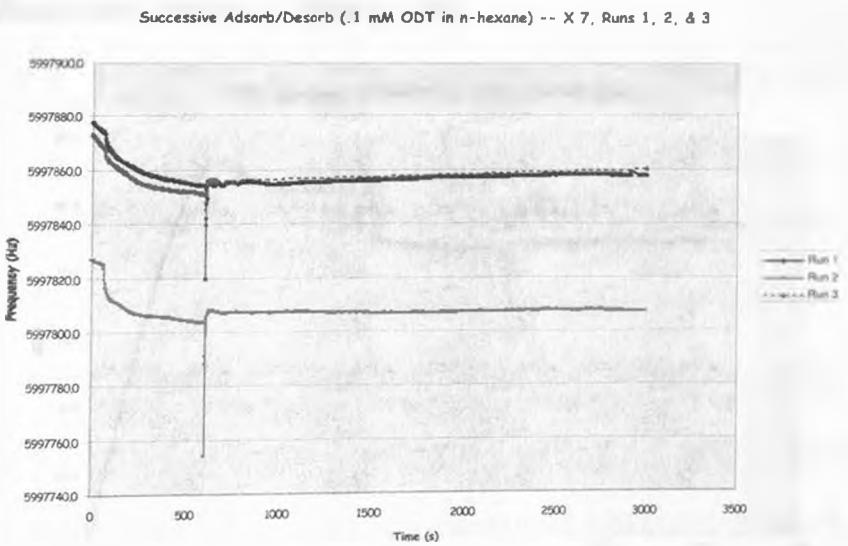

Figure 24: Successive adsorption and desorption of ODT (0.1 mM solution) on the same quartz crystal three times, using as optimal conditions as possible. The noise upon transferring the quartz crystal to a new beaker is now gone, but the initial decrease in frequency remains in all three cases, although the rates of decrease are not identical. The injection of the thiol aliquot is shown on the left of the graph (where the downward plunge begins). The transfer to the second beaker is at about 10 minutes, where the spike is shown.

Overall, the noise that was originally seen upon transferring the crystal to a new beaker is gone. However, the combination of all of these optimal techniques did not eliminate the issues of greatest concern (those seen in the beginning of the experiment): the downward drift of frequency, and the length of time that it takes to adsorb a SAM onto the gold.

The stirring had been at the lowest possible level to avoid fluctuation of the oscillation frequency; however, upon personally communicating with Blanchard,[15] it appears that the slow stirring is what was causing the time for SAM adsorption to be so long. Upon performing the experiment again with a new crystal, this time stirring at the highest possible speed, the adsorption time is 50-60 seconds, identical (within experimental error) to the time that Blanchard reported (Figure 25).

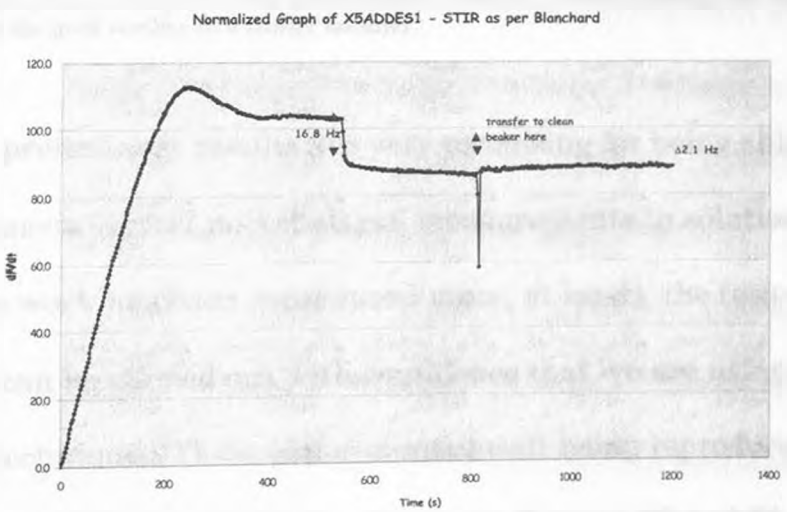

Figure 25: An adsorption experiment followed by a successive desorption experiment in a second beaker of *n*-hexane. The difference between this experiment and the previous one is the rate at which the solution is stirred. Here, the stir motor is set at the top speed. The time at which it takes the ODT SAM forms is between 50-60 seconds.

Expanding the region of adsorption on this graph and plotting it in a way to illustrate the relative amount of thiol adding on the crystal, we can more easily see that the adsorption time is down to values seen by Karpovich and Blanchard (Figure 26):

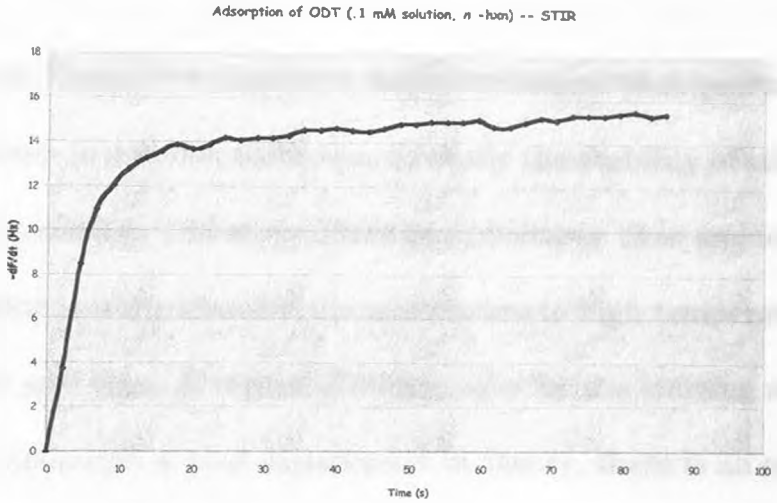

Figure 26: Adsorption curve of an ODT SAM forming on the quartz crystal. In this experiment, the stirring rate was dramatically increased, hence allowing the thiol access to the gold surface in a timely manner.

These preliminary results are very promising for being able to accomplish quartz crystal microbalance measurements in solution. Now that the literature work has been reproduced (once, at least), the future experiments can be carried out with confidence that we are using an appropriate technique. These experiments await being reproduced, to give us confidence that results such as those shown in Figures 25 and 26 are reliable.

CHAPTER IV

CONCLUSIONS AND FUTURE WORK

Through these investigations, we have learned that quartz crystal microgravimetry is a viable technique to study the stability of self-assembled monolayers *in solution* and at constant temperatures near ambient. The crystal behavior is unpredictable upon exposure to high temperatures and does not show any signs of reproducibility, save for the starting and ending frequencies. Although a good experiment in theory, there is an excess of unknown variables in the thermal experiments (i.e., reversible and irreversible crystal damages, crystal failure at temperatures of about 250 °C, etc.) that make it difficult if not impossible to extract information from the experiments, especially when the majority of the physical processes underlying the experiment (i.e., the quartz) are unknown.

My most important conclusion is that quartz crystal microgravimetry is a useful process for the experiments performed in solution. Now that results have been obtained consistent with those in the literature (Figure 27), it is important that further experiments be performed (in solution) in order to obtain kinetic parameters and stability information on amide-containing self-

assembled monolayers. With regards to the successful experiments, several important factors should be noted.

1. It was found that keeping everything scrupulously clean (i.e., piranha-clean all glassware, stir bars, etc.) was important as it reduces bringing contaminants into the microbalance system.

2. A fast stirring rate (to the point of cavitation) is desired when performing experiments in solution; in the case of adsorbing SAMs onto the gold, a fast stirring rate keeps the mixing time faster than the rate of adsorption kinetics. In other words, fast stirring enables a true picture of adsorption to be achieved, rather than having the adsorption rate be slowed by mixing because the adsorbate is not initially in the physical location necessary for adsorption.

3. It is important to keep the stock solutions of thiol (the 0.01 M reservoir of which a 1 mL aliquot is added to the 99 mL of solvent stirring) fresh, as the adsorption kinetics for alkyldisulfides will be different from those of alkanethiols.

4. It is important to thermally equilibrate all solutions and solvents well before use to ensure that the quartz crystal will not be perturbed by changes and fluctuations in temperature. Similarly, it is important that experiments be done at constant temperature near room temperature.

Thermal desorption experiments will be continued, but using other techniques (such as XPS) rather than QCM. The SAMs on gold slides (there

would be no particular need for gold-evaporated quartz crystals) can be subjected to hot temperatures under a known flow rate of argon; then XPS experiments can be performed *ex situ* at various temperature exposures to calculate the percentages of SAM desorption. Once the temperature window for desorption is known, desorption as a function of *time* can be studied. At the very least, the overall data will support a qualitative comparison of the thermal resistance of the various amide-containing SAMs, providing a test of our original hypothesis whether or not the addition of hydrogen bonds will increase the thermal resistance of a SAM.

There are further solution experiments that need to be performed. First and foremost, experiments identical to that for Figures 26 and 27, where Blanchard's work was being reproduced, need to be completed in order to verify that this is a reproducible set of data. After this has been established, the kinetic parameters of adsorption can be elucidated by finding the observed rate constants at various temperatures and at various concentrations of ODT. Once these ODT experiments have been performed as a control and kinetic parameters extracted from the experiments, the same experiments can be performed on the amide-containing series to see how the kinetic parameters change as a function of amide content (and as a simultaneous loss of methylene content).

Up to this point, it has been difficult to extract desorption data from the experiments in which the SAMs were transferred to the second beaker;

the drift upwards in frequency, although expected, is on the order of the drift/noise of the frequency counter. One hypothesis for seeing no obvious (or minimal) desorption is that the crystal is carrying with it into the other beaker droplets of a 0.1 mM thiol solution. These droplets of thiol solution may contain enough alkanethiol to form tens or even hundreds of monolayers, thus altering the equilibrium for SAM desorption (disrupting how the desorption process would normally occur). The next reasonable experiment would be to alternate drying the crystal with argon after rinsing it with ethanol with successive dunks in clean *n*-hexane.

To study the stability of SAMs when exposed to different solvents, we have also designed and constructed a small flow cell has been constructed that exposes one side of a quartz crystal to a solvent chamber. The flow cell is made out of Teflon, which is resistant to most solvents; there is a pathway of Teflon tubing designed for the flow of solvent across the crystal. A SAM could be adsorbed on one face of a quartz crystal, clamped into the holder, and solvent flowed across the SAM surface. The crystal is connected to the oscillator circuit, and thus the desorbing SAM can be detected in the usual manner. A sacrifice that this flow cell system makes is that there is a loss of equilibrium parameters. As the thiol is desorbing, it is being flushed on through continuously with fresh, clean solvent, and no new equilibrium is established, so the opportunity for the alkanethiol to adsorb back on the crystal is difficult to model. It is also important to see how these SAMs resist

a variety of solvents; it would be of technological relevance to test a series of solvents of increasing polarity. Unfortunately, if the solvent used is too polar (i.e., water, ethanol), the solvent will interfere with the quartz crystal circuitry due to its high dielectric constant.

Quartz crystal microgravimetry is an outstanding technique that can be used to detect mass from a wide variety of sources; it is certainly not limited to alkanethiols. Throughout the experiments, it is imperative that experimental conditions are reproduced as identically as possible, in order to avoid the introduction of extra variables that would convolute experiments. Of all of the experiments described herein, it is critical to design reproducible conditions for best results. Only now that the introductory concepts and idiosyncrasies have been learned can we expand and fully utilize the applications of quartz crystal gravimetry.

APPENDIX A

'C' COMPUTER PROGRAM TO AUTOMATE DATA COLLECTION

```
//RKSCOUNT.C

#include<time.h>
#include <qchpib.h>
#include<stdio.h>
#define ISC
7L
#define SOURCE 721L

main()
{
FILE*fp;
int cnt, stsize, cont;
float freq, tyme,
delaysec, span;
double
value2;

clock_t
ticks0;
char strg[80], freqst[80], freqst2[80], value[80];

printf("Total length of the
experiment (s):  ");
scanf("%f", &span);
printf("Save the experiment as
filename: ");
scanf("%s", strg);
fp=fopen(strg, "w");
printf("Measurement interval (s):  ");
scanf("%f", &delaysec);


freqst=="CHA A; SLO POS; TERM HI; COU DC;
ATT 1; AUTO;";
IOOUTPUTS(SOURCE,freqst,strlen(
```

```
freqst));
ticks0 =
clock();

while (((float)clock() -
ticks0)/CLK_TCK < span)
{
        IOTRIGGER(SOURCE);
        freqst2=="AVE-1 FREQ;
        SEND;";
        IOOUTPUTS(SOURCE,freqst2,strle
        n(freqst2));
        IOENTERS(SOURCE, value,
        &stsize);
        printf("%s\n", value);
        tyme = ((float)clock() -
        ticks0)/CLK_TCK;
        fprintf(fp, "%f %s\n", tyme, value);
        value2 = kbhit();
        if (value2 !=
        0)
        {
                cont = 0;
        }
        delay(delay
        sec);

}
fclose(fp);
}

delay(delay_time)
float delay_time;
{
clock_t ticks2, tick_org,
clock();
float sec;
ticks2 =
clock();
while((sec = (float)(clock() -
ticks2)/CLK_TCK)<delay_time);
}
```

References

1. (a) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558-569. (b) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437-463. (c) Karpovich, D. S.; Schessler, H. M.; Blanchard, G. J. *Thin Films* **1998**, *24*, 44-81. (d) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533-1554. (e) Fenter, P. *Thin Films* **1998**, *24*, 112-149.

2. Tam-Chang, S.-W.; Biebuyck, H. A.; Whitesides, G. M.; Jeon, N.; Nuzzo, R. G. *Langmuir* **1995**, *11*, 4371-4382.

3. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J. Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321-335.

4. (a) *Clinically Useful Biosensor Membrane Development.* McCaffrey *et al.* In Biofunctional Membranes. (Ed. D. A. Butterfield). Plenum Press: New York, 1996. (b) Clegg, R. S., and Hutchison, J. E. *Langmuir* 1996, *12*, 5239-5243. (c) Sigal, G. B.; Bamdad, C.; Barberis, A.; Strominger, J.; Whitesides, G. M. *Anal. Chem.* **1996**, *68*, 490-7. (d) Cass *et al. Anal. Chem.* **1984**, *56*, 667-671.

5. Clegg, R. S., and Hutchison, J. E. *J. Am. Chem. Soc.* **1998**, *120*, 2486.

6. Contact angle goniometry (CAG) is a screening technique used in our laboratory that gives an indication as to the order of the methyl surface of a SAM. A tiny droplet of water is placed directly on top a SAM-coated gold slide, and one measures (with a protractor printed on a microscope piece) how "beaded up" the water droplet is. The more hydrophobic the surface is (as if the gold were coated with a layer of grease), the more the water will bead up into a ball in order to avoid contact with the oil. If the surface presented to the air is slightly less hydrophobic (or more hydrophilic), then the bead of water will spread out more across the surface. The "angle" in CAG is the measure of the angle from the gold/droplet interface to the tangent of the water drop at its intersection with the gold. Ordered methyl surfaces usually present contact angles ranging from 110° to 120°. Disordered methyl surfaces usually give contact angles below 110°. See Reference 3.

7. (a) Karpovich, D. S., and Blanchard, G. J. *J. Chem. Ed.* **1995**, *70*, 466-470. (b) Karpovich, D. S., and Blanchard, G. J. *Langmuir* **1994**, *10*, 3315-3322. (c) Schessler, H. M.; Karpovich, D. S.; and Blanchard, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 9645-9651. (d) Okahata, Y.; Kawase, M.; Niikura, K.; Ohtake, F.; Furusawa, H.; Ebara, Y. *Anal. Chem.* **1998**, *70*, 1288-1296. (e) Lu, C. "Theory and Practice of the Quartz Crystal Microbalance." In: Lu, C., Czanderna, A. W. (Eds.) *Applications of Piezoelectric Quartz Crystal Microbalances*. New York: Elsevier, 1984.

8. Equation **(1)** illustrates that a loss in mass (or a negative Δm) will correspond to an increase in the crystal's frequency of oscillation.

9. C_f is merely a crystal-dependent constant. In this case of mass loading, C_f is: $(2f_q^2)(\rho_q \upsilon_q)^{-1}$. The subscript '$q$' denotes that the features refer specifically to the quartz: f refers specifically to the intrinsic oscillation of the quartz crystal (which depends upon the crystal cut); ρ refers to the density of the quartz crystal (usually 2650 kg/m^3); and υ is the shear wave velocity (how fast the standing wave travels during the oscillations, about 3340 m/s). For example, for a crystal with an intrinsic oscillation frequency of 6 MHz (or six million oscillations per second), the C_f would be equal to approximately 8.135 MHz m^2/kg. Therefore, if the areal density of the film being adsorbed onto the gold is known, the approximate mass necessary to effect a desired change in the crystal's oscillation frequency can be calculated (which can ultimately be detected on a frequency counter).

10. In our laboratory, we have characterized these monolayers by XPS, external reflective-FTIR, CAG, and double-layer capacitance electrochemical studies. See Clegg, R. S.; Reed, S. M.; Smith, R. K.; Barron, B.; Rear, J. A.; Hutchison, J. E. *submitted to J. Am. Chem. Soc.*

11. Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Chem. Phys.* **1993**, *98*, 678.

12. As an aside, we are predisposed to believe that SAM formation is indeed an energetically favorable process; as described in the beginning of the

introduction, SAM formation occurs via a spontaneous creation of an ordered assembly of adsorbate molecules without the assistance of the investigator. Therefore, as a hypothesis, we would expect that the equilibrium constant for this process is positive, while the free energy of SAM formation would be a negative value.

13. Martin, S. J.; Granstaff, V. E.; Frye, G. C. *Anal. Chem.* **1991**, *63*, 2272-2281.

14. Edwards customer service, personal communication

15. (a) O. H. Griffith, personal communication. (b) G. J. Blanchard, personal communication.