SPECTROELECTROCHEMICAL ANALYSIS OF
SELF-ASSEMBLED MONOLAYERS ON GOLD

by

Marilyn Rose Gatin

Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

APPROVED: M.R. Anderson, Chairman

J.D. Graybeal H.M. McNair

J.S. Merola L.T. Taylor

July, 1992
Blacksburg, Virginia
SPECTROELECTROCHEMICAL ANALYSIS OF
SELF-ASSEMBLED MONOLAYERS ON GOLD

by

Marilyn Rose Gatin

Committee Chairman: Mark R. Anderson
Chemistry

(ABSTRACT)

Organic thin films prepared from long-chain organothiols have been self-assembled on gold surfaces and their chemistry and structural properties studied by physical, electrochemical and spectroscopic methods. The mechanism of charge transfer across these organic thin films was of particular interest and was studied by combined spectroscopic and electrochemical methods. The influences of chain length, terminal functional group, and solvent on the electrochemical kinetics were studied. Evidence of a kinetic barrier to charge transfer pointed to a charge-diffusion mechanism across the organic thin films. An Infrared Reflection-Absorption Spectroscopy (IRRAS) method was developed to monitor the titration of acid functionalized films. The method compared favorably with the currently-used goniometry method because the IRRAS method was faster, less prone to operator bias, and provided structural information.
Polarization Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) was used to perform simultaneous electrochemical and spectroscopic characterization of the thin film in the presence of a solvent system. PM-IRRAS results demonstrated that acetonitrile was more disruptive than water to the surface structure of organic thin films. Simultaneous applied potential and PM-IRRAS studies provided evidence for ion penetration into the film in contact with organic solvent which provided a rationale for more facile electron transfer in the organic solvent system.
Acknowledgements

I thank my advisor, Mark Anderson, for setting high standards and encouraging my efforts to meet them. I thank my committee members for their caring and support during my growing and learning processes, especially the difficult chapters: Jack Graybeal, Joe Merola, Harold McNair, and Larry Taylor. Further thanks to Jack Graybeal for the use of his equipment and for always coming up with financial support.

I thank my fellow students for their camaraderie and intellectual discussions: Francis Webster, Susanne Dana, Joannie Chen, and Ray Drumright.

Thanks to Ronna Cadorette for helping wherever she could and for her unfailing support. Thanks to Fred Blair and John Miller in the Physics Shop. I relied upon them for their machining skills and their affection. Special thanks to Heather Hall for both her professional support and friendship.

Most of all I have depended upon the love and support of my family and some very good friends. I am especially grateful for the special care and attention given to me by Mary Chalmers and the confidence I have gained from knowing her. Many thanks to Kevin O'Grady for his love and for giving me strength as I struggled through the many personal changes that came with graduate school. Heartfelt thanks also to my family for their unending patience and support, mostly through the restrictive medium of long distance telephone calls.

iv
# Table of Contents

Chapter 1  Introduction and Literature Review .......................... 1
  1.1 Research Objectives ............................................. 1
  1.2 Introduction .................................................. 1
  1.3 Self-Assembled Monolayer Films ................................. 2
  1.4 Surface Characterization ....................................... 6
    1.4.1 Film Thickness .............................................. 6
    1.4.2 Wettability ................................................ 8
    1.4.3 X-Ray Photoelectron Spectroscopy ........................ 10
    1.4.4 Infrared Spectroscopy .................................... 12
    1.4.5 Electrochemistry .......................................... 13
  1.5 Literature Summary .............................................. 16
  1.6 Theory of PM-IRRAS ............................................. 17

Chapter 2  Experimental ................................................. 21
  2.1 Substrate Material .............................................. 21
  2.2 Substrate Pretreatment ........................................... 21
  2.3 Surface Modification ............................................ 21
  2.4 Optical Ellipsometry ............................................ 22
  2.5 Goniometry ..................................................... 23
  2.6 X-Ray Photoelectron Spectroscopy ................................ 23
  2.7 Cyclic Voltammetry ............................................. 24
  2.8 Infrared Reflection-Absorption Spectroscopy .................... 24
  2.9 Potential Difference Infrared Spectroscopy ..................... 26
  2.10 Polarization Modulation IRRAS ................................ 28

Chapter 3  Alkyl Surfaces .............................................. 32
  3.1 Hexanethiol .................................................... 32
    3.1.1 Film Thickness and Contact Angle ........................ 32
    3.1.2 XPS ....................................................... 34
    3.1.3 Cyclic Voltammetry ...................................... 36
    3.1.4 IRRAS .................................................... 38
    3.1.5 PDIRS .................................................... 40
    3.1.6 PM-IRRAS ................................................ 42
    3.1.7 Summary of Hexanethiol Results ........................... 42
  3.2 Dodecanethiol .................................................. 43
    3.2.1 Film Thickness and Contact Angle ........................ 43
    3.2.2 XPS ....................................................... 43
    3.2.3 Cyclic Voltammetry ...................................... 44
    3.2.4 IRRAS .................................................... 46
    3.2.5 PDIRS .................................................... 46
    3.2.6 PM-IRRAS ................................................ 47
    3.2.7 Summary of Dodecanethiol Results ......................... 47
  3.3 Octadecanethiol ................................................ 48
    3.3.1 Film Thickness and Contact Angle ........................ 48
    3.3.2 XPS ....................................................... 49
    3.3.3 Cyclic Voltammetry ...................................... 50
    3.3.4 IRRAS .................................................... 52
3.3.5 PDIRS ........................................... 52
3.3.6 PM-IRRAS in D₂O ................................. 53
3.3.7 PM-IRRAS in d₅-Acetonitrile ...................... 59
3.3.8 PM-IRRAS under Potential Control .............. 62
   3.3.8.1 D₂O ........................................... 62
   3.3.8.2 d₅-Acetonitrile ................................ 67
3.3.9 Summary of Octadecanethiol Results ............ 73

Chapter 4  Polar Surfaces ............................... 75
4.1 9-Mercaptononanenitrile Surface .................. 75
   4.1.1 Film Thickness and Contact Angle ............ 75
   4.1.2 XPS ............................................ 76
   4.1.3 Cyclic Voltammetry ............................ 77
   4.1.4 IRRAS .......................................... 79
   4.1.5 PDIRS .......................................... 81
   4.1.6 PM-IRRAS ...................................... 81
   4.1.7 Summary ....................................... 82
4.2 11-Mercaptoundecanoic Acid Surface ................ 83
   4.2.1 Film Thickness and Contact Angle ............ 83
   4.2.2 XPS ............................................ 83
   4.2.3 Cyclic Voltammetry ............................ 84
   4.2.4 IRRAS .......................................... 86
   4.2.5 PDIRS .......................................... 88
   4.2.6 Surface Titrations ............................ 89
   4.2.7 PM-IRRAS ...................................... 93
   4.2.8 Summary ....................................... 94

Chapter 5 Summary ..................................... 96

References ............................................... 99

Vita ..................................................... 103
List of Figures

Figure 1. Schematic representation of a monolayer of long-chain thiols on gold .................. 4

Figure 2. Plot of the phase shift of reflected light as a function of angle of incidence .......... 18

Figure 3. Illustration of the effect of the state of polarization on the phase change of p- and s-polarized reflected light ................................. 19

Figure 4. Schematic diagram of a glass electro-chemical cell ........................................ 25

Figure 5. Schematic diagram of a spectroelectro-chemical cell ....................................... 27

Figure 6. Experimental setup for PM-IRRAS ............................................. 29

Figure 7. Cyclic voltammograms of an hexanethiol film and a blank gold electrode .......... 37

Figure 8. IRRAS spectra of octadecanethiol, dodecanethiol and hexanethiol on gold .......... 39

Figure 9. Potential difference infrared spectra for blank and hexadecanethiol-modified gold electrodes .... 41

Figure 10. Cyclic voltammograms of a dodecanethiol film and a blank gold electrode .... 45

Figure 11. Cyclic voltammograms of an octadecanethiol film and a blank gold electrode .... 51

Figure 12. PM-IRRAS spectra of octadecanethiol on gold in D₂O .................................. 54

Figure 13. IRRAS spectra of octadecanethiol on gold ........................................... 55

Figure 14. PM-IRRAS spectra of octadecanethiol on gold in d₃-acetonitrile ...................... 60

Figure 15. PM-IRRAS spectra of octadecanethiol on gold in D₂O at 0.5 Volts vs. SCE .......... 63

Figure 16. PM-IRRAS spectra of octadecanethiol on gold in D₂O at 0.0 Volts vs. SCE .......... 64
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>PM-IRRAS spectra of octadecanethiol on gold in D₂O at - 0.5 Volts vs. SCE</td>
<td>65</td>
</tr>
<tr>
<td>18</td>
<td>PM-IRRAS spectra of octadecanethiol on gold in d₃-acetonitrile at 0.5 Volts vs. SCE</td>
<td>68</td>
</tr>
<tr>
<td>19</td>
<td>PM-IRRAS spectra of octadecanethiol on gold in d₃-acetonitrile at 0.0 Volts vs. SCE</td>
<td>69</td>
</tr>
<tr>
<td>20</td>
<td>PM-IRRAS spectra of octadecanethiol on gold in d₃-acetonitrile at - 0.5 Volts vs. SCE</td>
<td>70</td>
</tr>
<tr>
<td>21</td>
<td>Cyclic voltammograms of a 9-mercaptopnonanenitrile film and a blank gold electrode</td>
<td>78</td>
</tr>
<tr>
<td>22</td>
<td>IRRA spectrum of 9-mercaptopnonanenitrile on gold</td>
<td>80</td>
</tr>
<tr>
<td>23</td>
<td>Cyclic voltammograms of a 11-mercaptopundecanoic acid film and a blank gold electrode</td>
<td>85</td>
</tr>
<tr>
<td>24</td>
<td>IRRA spectrum of 11-mercaptopundecanoic acid on gold</td>
<td>87</td>
</tr>
<tr>
<td>25</td>
<td>Titration of 11-mercaptopundecanoic acid</td>
<td>90</td>
</tr>
</tbody>
</table>
List of Tables

Table 1. Film Thickness and Contact Angles . . . . . . 33
Table 2. XPS Atomic Concentrations . . . . . . . . . . 35
Table 3. Positions of Curve Fitted Peaks for Octadecanethiol on Gold ex situ and in situ . . . . . . 56
Table 4. Positions of Curve Fitted Peaks for Octadecanethiol in D₂O with Applied Potential . . . . . . 66
Table 5. Positions of Curve Fitted Peaks for Octade canethiol in d₆-acetonitrile with Applied Potential . . 71
Table 6. Titration of 11-Mercaptoundecanoic Acid . . . 92
Chapter 1 Introduction and Literature Review

1.1 Research Objectives

The objective of this work was to improve the understanding of the behavior of organic thin films confined to metal surfaces, especially the effect of the environment upon their structure. Polarization Modulation Infrared Reflectance-Absorbance Spectroscopy (PM-IRRAS) enabled the study of organic thin films on metal surfaces in contact with solvents and under potential control. Supporting studies compared physical, chemical, and electrochemical characteristics of various thin films. The films studied were alkanethiols with varying chain length (hexanethiol, dodecanethiol and octadecanethiol), and alkanethiols with polar functional groups at the chain terminus (9-mercaptopenanenitrile and 11-mercaptoundecanoic acid).

1.2 Introduction

Organic thin films have engendered a great deal of research activity in recent years (1). Monolayer films, created by either Langmuir-Blodgett or self-assembly techniques, have generated special interest because of their potential to provide well-defined surfaces. This potential makes them good candidates for application to optical devices, sensors, patternable materials, protective layers,
lubrication, and biological membrane models. Problems such as defects, impurities and lack of mechanical strength have hampered progress with applications but have resulted in extensive efforts to improve the understanding of those factors which affect the preparation and behavior of organic thin films. Interpretations of film behavior during electrochemical experiments indicate that there is a particular need for investigation of the influence of the environment on structure of the monolayer. Our research addresses this need through the application of PM-IRRAS to the study of organic thin films on gold electrodes while in contact with condensed media and during potential control.

1.3 Self-Assembled Monolayer Films

Reports on the spontaneous absorption of various organic monolayers on platinum (2,3), fatty acids and alcohols on oxide surfaces (4,5), and organosulfur compounds on evaporated gold substrates (6) emerged in the early 1980s. The ease of preparation, in contrast with the equipment and cleanliness required for film balance preparation of Langmuir-Blodgett monolayers, made self-assembly techniques attractive to many researchers. By the early 1990's, particular interest in organosulfur monolayers on gold was demonstrated by the wealth of publications appearing in the literature (7-52).
Self-assembled monolayers are prepared by submerging a clean metal surface in a dilute solution of the monolayer-forming species. Surface species and head groups on long chain alkanes, like fatty acids on silver oxide or organothiols on gold, interact to form stable chemisorbed monolayers on the surface with the head group attached to the surface and the rest of the molecule pendant. Cyclic voltammetric investigations of oxidation and reduction of alkanethiol monolayers on gold indicate that, upon adsorption, the thiol hydrogen is lost and the sulfur is oxidized to create a gold thiolate moiety (7). The monolayer formation is spontaneous and may take anywhere from several seconds to several hours depending on the surface, adsorbing species, and solvent conditions.

Monolayers have been prepared from a variety of organosulfur solutions including alkanethiols and disulfides of various chain lengths (8-15), polar-terminated alkanethiols (16-22), phospholipid-terminated disulfides (23), aromatic thiols (24,25), and electroactive thiols (26,27). Monolayers of long chain organosulfur compounds on gold surfaces form stable (28), highly organized, close-packed assemblies which are in an all-trans, fully extended configuration tilted ca. 55° from the surface as illustrated in Figure 1. The size and nature of functional groups involved in the adsorbing compound influence the packing ability of the monolayer. Chain-
Figure 1. Schematic representation of a monolayer of long-chain thiols on gold (29).
terminating groups larger than a methyl group may prevent close packing. Similarly, hydrogen-bonding between chain-terminating groups may prevent close packing.

The chemistry of the terminating group determines the chemical nature of the resulting modified surface, providing a means to tailoring surfaces of various reactivities. Interactions of polar and non-polar molecules of self-assembled monolayers with various chain-terminating groups have been studied by temperature-programmed desorption (29). Non-polar molecules bonded only through very weak dispersive forces to all modified surfaces, while polar molecules bonded much more strongly to polar surfaces (29). These results are consistent with the accepted structure of self-assembled alkanethiol monolayers on gold which places the chain-terminating group at the surface. If the chain-terminating group is polar it would be expected to undergo stronger interactions with polar species and weaker interactions with non-polar species. If the chain-terminating group has no polar character it would be expected to interact only through dispersive forces.

Alkanethiols on gold are shown to undergo structural changes dependant upon temperature similar to changes found for bulk hydrocarbon crystals (30,31). These changes are reversible over the range of 80 to 380 K, degradation of the monolayer structure was observed from 380 to 420 K. The
degradation of structure was interpreted to be a result of the increasing population of gauche conformers in the methylene chain increasing the liquid-like structure of the monolayer. Molecular dynamics simulations of the effect of temperature on monolayers of alkanethiols on gold are consistent with experimentally observed behavior (32).

1.4 Surface Characterization

Organic thin films can be characterized by a variety of physical, electrochemical and spectroscopic techniques. In our work we have depended most heavily upon spectroscopic and electrochemical methods because they are the most informative. However, we have found film thickness data to be valuable in monitoring the quality of samples, and measurement of wettability to be helpful in determining the chemistry of the prepared surfaces. XPS aids in identifying surface species if they are not visible by other means.

1.4.1 Film Thickness

Optical ellipsometry is often used for monitoring film formation (6,9-13,16,18,20-22,28,33-35,36). Optical ellipsometry measures amplitude and phase changes of polarized light from a laser source upon reflection from a surface. Ellipsometric measurement of a clean substrate provides the index of refraction (n) and extinction coefficient (k) for
that solid. Subsequent measurement of a film on that substrate, along with knowledge of \( n \) and \( k \) for the film-forming material, provides a gauge of the film thickness. A recent review (37) describes the theory and instrumentation for this laser-based technique.

Comparison of film thickness for alkanethiol monolayers has shown that ellipsometric results are slightly smaller than values which are estimated by assuming bulk packing densities and full extension of molecules within the monolayers (6,9). This discrepancy between measured and maximum estimated values is likely due to the inability to obtain either clean substrates or perfectly formed monolayers.

Within homologous series of monolayers, increasing film thickness correlates reasonably well with increasing chain length (9,10,12,18,22,34) with notable deviations for short chains (less than 9 methylene units) and long chains (more than 20 methylene units). Several studies show plots of film thickness versus chain length. The slopes of these plots were relatively consistent and indicated an increase in thickness of about 1.5 Angstroms per additional methylene unit. The intercepts of these plots were variable, even negative in some cases. Variability in intercept between studies is likely due to contamination of the gold surface. Films with polar, hydrophilic surfaces appear to be more susceptible to environmental contamination from water than those with non-
polar surfaces (12,20). Because reproduction of environmental conditions is difficult within laboratories, and even less practical between research groups, film thicknesses are best relied upon for only a qualitative assessment of film integrity.

1.4.2 Wettability

The ability of a liquid to spread over a surface, or wettability, is dependant upon interfacial tensions between the liquid and solid phases, the liquid and surrounding vapor phases, and the solid and surrounding vapor phases (38). Wettability is quantified in terms of a contact angle, the angle formed between the liquid and the solid surface. Measurement of contact angles is done by magnification of the three phase region and comparison of the angle between the liquid and solid phases to a graduated scale. The contact angle is extremely sensitive to the macroscopic chemical nature of the surface but provides little information about microscopic features of the surface. However, contact angle measurements are also sensitive to heterogeneity and as such can be used to assess the quality of prepared monolayers.

Contact angle measurements have been used to determine the relative hydrophobicity of terminally-substituted alkanethiol monolayers on gold (6,12,18,23,39). When water is used as the probe liquid, the contact angle increases with
increasing hydrophobicity so that methyl-terminated alkanethiol monolayers have very high contact angles (over 100 degrees) and the water beads up on the surface, while alcohol- and acid-terminated alkanethiol monolayers have very low contact angles and the water spreads over the surface.

Comparison of contact angles has been used to determine the penetration depth of probe liquids into alkyl chains (33,40). Monolayers were prepared with an ester functionality at a fixed distance from the thiol head group and varying length alkyl tail groups appended to the ester oxygen. Contact angles with water changed significantly as the tail group length increased from methyl to butyl but remained constant (and consistent with monolayers with no ether functionality) for groups larger than pentyl. The ester group is effectively screened from hexadecane drops by ethyl groups and is screened from glycerol drops by propyl groups. Hexadecane interacts through dispersive interactions only, water primarily through hydrogen bonding and glycerol through both hydrogen bonding and dispersive interactions. The author proposes that water is able to penetrate further by disordering the terminal alkyl chain but steric hindrance prevents glycerol from penetrating as far as water. Direct experimental evidence on the structure of monolayers in contact with solvents would be of value for these comparisons.
Contact angles can be used to monitor the ionization state of acidic surfaces by probing the surface with aqueous buffers of varying pH (17,33,41). Carboxylic acid-terminated alkanethiol monolayers on gold were found to be less acidic than carboxylic acids in solution (33,41). This difference was attributed to a decrease in the local dielectric constant, compared to bulk solution, at the surface-water interface which would decrease the stability of ions formed by the dissociation of carboxylic acids. Steric effects could also be important in that the adjacent groups may hinder the formation of hydrogen bond between carboxylic acids and water.

Unfortunately, structural information on carboxylic acids in contact with buffered solutions is not available from contact angle measurements. Such structural information would be instrumental in understanding the differences in ionization behavior between bulk carboxylic acids in solution and those affixed to a surface. It is hoped that infrared measurements of these systems will be helpful in understanding the behavior of surface-bound ionizable species.

1.4.3 X-Ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) is based upon the ability of x-rays to have sufficient energy to release electrons from the K shell of an atom. The electron released has a kinetic energy which is dependant upon the energy of the
incident X-ray and the binding energy of the electron. The number of released electrons is plotted versus their kinetic energy to provide an XPS spectrum. Elements are identified by the location of lines in the spectrum with the aid of published tables for each instrument. Individual lines, when examined in detail, provide information on the binding states of the detected elements by analysis of chemical shifts. Shifts within elemental groups result mainly from the electronegativity of the binding partner. Because electrons lose energy as they pass through matter, there is a certain escape depth for photoelectrons. This imposes an analysis depth limit of about 6-10 nm making XPS a surface sensitive technique and well-suited to the study of monolayers.

XPS analysis of alkanethiol monolayers on gold has provided elemental compositions that are consistent with the model of a thiolate moiety at the surface with the substituted alkyl chain intact (8,9,12,18,22,33,34,40,42,43). XPS also shows that so-called "clean" gold substrates are invariably contaminated with carbon- and oxygen-containing substances (12,18). Angular dependant or depth profiling XPS analysis showed that chain-terminating functional groups actually lay at the surface (18,20).
1.4.4 Infrared Spectroscopy

Infrared Reflection-Absorption Spectroscopy (IRRAS) has provided a wealth of structural information on self-assembled monolayers \((6,9,19,12,20,21,30,31,36,40,44)\). Evidence obtained from line shapes and peak positions in the CH stretching region of spectra indicate that long alkyl chains are in a close-packed, crystalline-like assembly \((9,12,21,40)\) in all-trans conformation \((20)\) and are tilted from the surface normal by ca. 30 degrees \((10,20)\). Terminally substituted alkanethiol monolayers have their alkyl chains arranged in similar assemblies with variable orientations of terminal groups \((6,9,12,20,40)\).

Evidence suggests that as the chain length decreases there is a decrease in inter- and intra-chain order and packing density \((10)\). Monolayers with intercalated dipyridinium compounds showed a disruption in the order of the alkyl chains as well as displaying absorptions arising from the intercalated compounds \((36)\). The disordering effect of increasing temperature has been monitored by observing the peak positions and line shapes in infrared spectra until loss of spectral intensity is observed upon desorption \((8,9,30,31)\).

A preliminary study on the application of IRRAS to observation of monolayer films on gold in the presence of deuterated aqueous and non-aqueous solvents suggested a slight increase in conformational disorder near the chain terminus.
(45). A subsequent study using deuterated water and water was consistent with the preliminary study but also described the need for post-collection data manipulation due to the difficulty in providing the same experimental conditions for the sample and the reference (46).

The addition of polarization modulation to IRRAS techniques (PM-IRRAS) has been applied to the study of self-assembled monolayers (43,47). The advantage of PM-IRRAS is that neither an instrumental purge nor a reference sample are required (47). Gas-phase surface reactions, monitored by PM-IRRAS, showed conversion of a carboxylic acid to an acid chloride and further reaction to produce the amine or ester functionality (43). There are no published studies using PM-IRRAS to investigate the interaction of alkanethiol monolayers with solvents.

1.4.5 Electrochemistry

Several electrochemical studies have demonstrated that, in aqueous solution, alkanethiol monolayers on gold act as a barrier to electron transport (10,11,21,22,48). However, in acetonitrile, the monolayer was not a barrier (11). That there was no detectable permanent change in the monolayer detected by ellipsometric or wettability measurements after the electrochemical experiment suggested that acetonitrile caused a "loosening" of the monolayer structure.
It has been suggested that the mechanism of charge transfer across these monolayers is one of electron tunnelling (10,22), while others suggest that a tunnelling mechanism exists but only at defect sites or pinholes in the monolayers (11). Pinholes were not found in one study (10), but found, measured and filled in another (48).

Terminally substituted alkanethiol monolayers provide another area of disagreement among workers in the field. One study shows that alcohol-terminated alkanethiol monolayers do not block electron transfer as well as comparable methyl-terminated films (21), while another shows better blocking properties (22). Both studies show that the monolayers have comparable structural integrity. Carboxylic acid-terminated films allow ion permeation in aqueous solution which suggests a disruption in the packing order in the monolayer (21). This disorder was not found in infrared studies of similar systems (6,20).

Surface potential studies (49) and electrochemical desorption (7) of alkanethiol monolayers on gold give evidence that, upon adsorption of the monolayers, there is a loss of hydrogen from the thiol and oxidation of the sulfur. These studies also observed a relationship between decreasing chain length, surface potential (49), and the potential for reductive desorption (7). Similar results were found in
cyclic voltammetric studies wherein the kinetics of electron transfer slowed with increasing chain length (22,36).

Several groups have worked on the study of monolayers which incorporate electroactive centers, either through intercalation of electroactive species (36,44) or synthesis of alkanethiols with electroactive components (26,27,50-52).

Methylene blue remained at the surface of the alkanethiol monolayer, but its reduced form, leucomethylene blue, partitioned into the monolayer (44). It was also observed that the alkane chains were disordered by the initial incorporation of the electroactive moieties but upon electrochemical oxidation and reduction of methylene blue the alkane chains arranged in a close-packed configuration (44).

Bipyridinium compounds were incorporated into alkanethiol monolayers, were found to exchange electrons with the surface, and they remained in the monolayer after appropriate solvent washes (36). These observations indicated that the redox centers were located close to the electrode. It was further found that ion flux was not hindered, perhaps due to disorder of the alkyl chains. Cyclic voltammetry and electrochemical quartz crystal microbalance studies of viologen-containing alkanethiol monolayers gave evidence that anions and water entered and exited the monolayer during oxidation and reduction, respectively (26).
Ferrocene-terminated alkanethiol monolayers have shown redox reactions whether the monolayers were pure (27) or mixed with methyl-terminated alkanethiols (50,52). Exchange of thiols in the monolayer with thiols in solution was detected but thought to occur easily only at defect sites (50,52).

There are no in situ infrared studies on the effect of applied potential on the structure of monolayers.

1.5 Literature Summary

The literature discussed above has been helpful in understanding the structure and behavior of organothiol monolayers on gold but has left several questions to be answered. The ex situ characteristics have been well described and provide a wealth of information with which to compare our results to ensure that we are able to prepare and measure the same monolayers that are discussed in the literature. It is hoped that the understanding of the pH dependant behavior of ionizable groups at the surface can be improved by using a more structurally informative infrared technique.

The in situ measurements have been with either electrochemistry, which did not provide structural information or with IRRAS, which did not include electrochemical studies. This gap in the body of knowledge is one that we hope to fill by using PM-IRRAS to study the effect of solvent contact and
applied potential on the structure of the monolayer. It is expected that we will be able to gain insight into the mechanism of electron transfer through these films.

1.6 Theory of PM-IRRAS

Polarization modulation IRRAS is a double modulation infrared technique in that it adds switching between p-polarized light (perpendicular to the surface) and s-polarized light (parallel to the surface) at a constant frequency to the mirror modulation of the Fourier transform infrared spectroscopic measurement (43, 47, 53-57). PM-IRRAS takes advantage of the properties of polarized light reflected from surfaces to increase the sensitivity of surface infrared measurement.

Reflected p-polarized light undergoes a phase shift with a change in the angle of incidence as shown in Figure 2. The phase shift is large for p-polarized light as the light approaches glancing angles but there is little phase shift for s-polarized light over the 0° to 90° range. Because s-polarized light is always reflected 180° out of phase, destructive interference occurs at the surface and the contribution of reflected s-polarized light is zero (see Figure 3). Enhancement of reflected p-polarized light occurs because, at the glancing angles used in PM-IRRAS, the reflected light is reflected 90° out of phase and, as Figure
Figure 2. Plot of the phase shift of reflected light as a function of angle of incidence (from M.A. Habib and J.O'M. Bockris, *J. Electroanal. Chem.*, 1984, *180*, 287)
Figure 3. Illustration of the effect of the state of polarization on the phase change of (top) p-polarized and (bottom) s-polarized reflected light (from M.A. Habib and J.O' M. Bockris, J. Electroanal. Chem., 1984, 180, 287)
3 demonstrates, constructive interference increases the amplitude of the p-polarized signal.

Polarization modulation IRRAS experiments use these differences in the properties of reflected s- and p-polarized light to increase the sensitivity of the IRRAS measurement. The surface-bound species absorb only the intensity of p-polarized light because the s-polarized reflected light has zero intensity at the surface. However, the species in the bulk absorb s- and p-polarized light equally.

The signals which are created in the PM-IRRAS experiment are the intensity difference, $I_p - I_s$, and the intensity sum, $I_p + I_s$. The PM-IRRAS spectrum is generated by ratioing the difference to the sum and contains only the infrared reflectance spectrum of the surface species. Ratioing removes the constant intensity attenuation from the bulk absorption, leaving the spectral information from the surface-bound species. Thus, PM-IRRAS is a surface sensitive technique which discriminates against species in the bulk. This advantage of PM-IRRAS makes it possible to investigate in situ structural changes in organic monolayers bound to metallic surfaces upon exposure to solvents and applied potential.
Chapter 2 Experimental

2.1 Substrate Material

The gold substrates used were purchased from Evaporated Metals Films Corp. and consisted of a one inch square glass slide to which a 50 Å thick layer of chromium was applied by evaporation. The chromium layer was used as a bonding agent for the 2000 Å evaporated gold layer. The substrates were purchased in 100 or 200 slide lots; each slide was used once.

2.2 Substrate Pretreatment

The substrates were cleaned immediately prior to use by immersion for 30 seconds to one minute in a hot (90 – 110°C) bath consisting of 1 part 30% hydrogen peroxide and 4 parts concentrated sulfuric acid. Upon removal from the acid/peroxide mixture, the substrate was rinsed with copious amounts of nanopure water (Barnsted/Corning) then rinsed with absolute ethanol for absolute ethanol-based adsorbing solutions, or rinsed with absolute ethanol followed by chloroform for chloroform-based adsorbing solutions.

2.3 Surface Modification

Immediately after the pretreatment above, the substrate was immersed in a 1 – 50 millimolar solution of the thiol in either chloroform or absolute ethanol. The solution was
contained in wide mouth glass jars fitted with PTFE screw-top lids and was reused. The substrate remained in the adsorbing solution for ca. 24 hours. Upon removal from solution, the sample was rinsed well with the adsorbing solvent and dried under a stream of nitrogen. Samples were placed in protective polyethylene slide cases until required. Samples were generally used the day of preparation. Hexanethiol, dodecanethiol, and octadecanethiol were used without further purification as received from Aldrich. The compounds 11-mercaptoundecanoic acid and 9-mercaptor-nonanenitrile were synthesized following published procedures (12,18) and characterized with IR and nmr spectroscopies.

2.4 Optical Ellipsometry

Film thickness measurements were performed on a Gaertner ellipsometer. Optical constants, n and k, for the gold substrate were determined on a substrate which had been cleaned by the pretreatment procedure described above. Several measurements were made at various locations on each blank substrate and the resulting optical constants averaged. The measured optical constants were in agreement with literature values of n (0.23) and k (2.97) (58). Using the optical constants obtained that day, film thickness measurements were obtained from the modified surfaces. Several locations on the surface were sampled and the results
averaged. The measured values were reproducible from day to day.

2.5 Goniometry

Contact angles were measured on a Rame-Hart, Inc. NRL Contact Angle goniometer using the sessile drop method. A 3 microliter drop was delivered to the surface from a flat-tipped microsyringe and the contact angle measured under magnification. The liquid used was either nanopure water or, in the case of titrations, constant ionic strength buffer solutions made up in nanopure water. Sodium phosphate monobasic, dibasic, tribasic, and o-phosphoric acid were used without further purification. Three separate drops were measured, one reading per side, for each sample or pH studied. All measurements were made in the ambient environment.

2.6 X-Ray Photoelectron Spectroscopy

XPS analysis was performed using a Perkin Elmer PHI 5300 spectrometer employing a MgKα(1253.6eV) achromatic X-ray source operated at 15keV with a total power of 400W. After modification with the thiol of interest, a 1/4 x 1/4 inch (approximate) portion was cut with a glass cutter from the 1 x 1 inch sample and secured to the sample holder with double-sided tape. Typical operating pressures were less than 1x10⁻⁷ Torr and the surface area analyzed was a 1 x 3mm rectangle.
The spectrometer was calibrated to the gold 4f$_{7/2}$ photopeak at 83.8eV and all binding energies were referenced to the main CH photopeak at 284.6eV.

2.7 Cyclic Voltammetry

Cyclic voltammetry experiments were conducted using EG&G Princeton Applied Research Potentiostat/Galvanostat model 273 controlled by an IBM model 50Z microcomputer running EG&G Princeton Applied Research model 270 electrochemical software (Version 2.90). The electrochemical cell was constructed to present a 1 cm diameter portion of a gold slide, either a freshly-cleaned blank or the thiol-modified sample, as the working electrode and incorporated a platinum wire secondary electrode and a saturated calomel reference electrode as shown in Figure 4.

Solutions were prepared with either nanopure water or HPLC grade acetonitrile (Baxter or EM Science). Potassium ferrocyanide was recrystallized from water before use. Sodium perchlorate and ferrocene were used without further purification.

2.8 Infrared Reflection-Absorption Spectroscopy

IRRAS measurements were performed using a Nicolet Model 710 FTIR purged with water- and CO$_2$-free air supplied by a Balston Filter Products Type 75-60 system and with p-polarized
Figure 4. Schematic diagram of a glass electrochemical cell.
light incident on the sample via a Cambridge Physical Sciences 
wire-grid polarizer. The sample was presented with the aid of 
a Spectra-Tech™ Model FT-80 Fixed Grazing Angle Specular 
Reflectance sample attachment. Spectra of modified surfaces 
were collected at 8cm⁻¹ resolution using 512 scans and compared 
with a freshly-cleaned gold slide.

Titrations of acid-modified surfaces were monitored by 
IRRAS. The samples were placed in buffer solutions (described 
in Section 2.5) for 30 seconds, removed and dried under a 
stream of dry nitrogen. The majority of the buffer salts were 
removed by the drying procedure. The titrated surfaces were 
compared with blanks treated in the same manner. The carbonyl 
peak areas were calculated by integrating between 1760 and 
1660cm⁻¹ and plotted versus the pH to create a titration curve.

2.9 Potential Difference Infrared Spectroscopy

Potential Difference Infrared Spectroscopy (PDIRS) 
experiments were conducted using a JAS Instrument Systems J-
1600B Potentiostat and a Nicolet 710 FTIR. A sample cell was 
constructed to allow the application of potential during 
infrared reflectance measurements. A schematic diagram of the 
cell is shown in Figure 5. The cell was a 5cm x 5cm x 2cm 
high block of Delrin with a 3ml well machined into it to 
contain liquids. Attached to this base was a spring-loaded 
sample holder controlled by a Newport Corp. micrometer.

26
Figure 5. Schematic diagram of a spectroelectrochemical cell (top) and an expanded view of the working electrode system (bottom).
The sample holder was used to press the gold slide up against a 65 degree trapezoidal calcium fluoride crystal. The slide and crystal bases were in contact with the solution and pressing them together allowed solution to be drawn up between them by capillary action. The calcium fluoride crystal was oriented with one 65° face normal to the incident IR beam, which with solution in the interface, allowed the angle of reflection from the gold surface to be 60° to 65°.

The gold slide was the working electrode, a platinum wire in the bottom of the well was the secondary electrode, and a saturated calomel electrode (SCE) was used as reference. Solutions were prepared with nanopure water. Potassium ferrocyanide was recrystallized from water before use; potassium chloride was used without further purification.

Experiments were conducted by applying a constant potential during which the single beam spectrum of the surface was collected. The single beam spectra at two different potentials were compared to provide the Potential Difference Infrared spectrum.

2.10 Polarization Modulation IRRAS

The optical arrangement used in the in situ PM-IRRAS experiments is illustrated in Figure 6. A wire-grid polarizer (Cambridge Physical Sciences) produces the p-polarized infrared radiation that is directed out of the Nicolet 710
Figure 6. Schematic diagram of the optical components in the experimental setup for PM-IRRAS.
FTIR bench and onto a ZnSe photoelastic modulator (PEM-80, Hinds International, Inc.) which modulated the polarization at 74kHz. The polarization modulated infrared beam was incident on the sample in the holder described in section 2.9. A calcium fluoride window was placed at an angle between the sample and detector in order to null the 74kHz signal. The window compensates for the two polarizations of light being transmitted through the optical path with unequal intensity due to reflections after the photoelastic modulator.

An EG&G Princeton Applied Research model 5204 Lock-In Analyzer was used to demodulate the 74kHz to produce an interferogram whose intensity is proportional to the difference, $I_r - I_s$. This signal is passed through a high-pass filter to remove an associated large dc component and channeled to the A/D converter of the FTIR instrument where it is collected and Fourier transformed by the FTIR workstation to produce a single beam spectrum. The mirror velocity of the interferometer must be slowed to allow the lock-in amplifier time to respond to changes in the amplitude of the interferogram and to allow, at each step in the mirror position, an adequate number of polarization cycles to produce an accurate value of $I_r - I_s$. The sum, $I_r + I_s$, is passed through the normal FTIR signal processing circuits. The modulation efficiency is dependant upon frequency because the birefringence of the photoelastic modulator is chromatic. For
this reason, the photoelastic modulator is tuned to the appropriate region of the spectrum, in our case, the C-H stretch region ca. 3000cm⁻¹ (modulator set at 3.15 microns).

In situ PM-IRRAS experiments were performed by placing a small amount (less than 1ml) of deuterated water or deuterated acetonitrile (Cambridge Isotope Laboratories) between the sample and the trapezoidal calcium fluoride crystal described in Section 2.9. The difference \((I_p - I_s)\) and sum \((I_p + I_s)\) spectra were collected using the appropriate instrumental gain and ratioed to provide the PM-IRRAS spectra.

Simultaneous electrochemical and spectroscopic experiments were performed using the above in situ PM-IRRAS setup and the electrochemical experimental setup described in section 2.9. Fixed potentials were applied during the PM-IRRAS measurement. Solutions were prepared using deuterated water or acetonitrile. Sodium perchlorate was used without further purification. Due to the rapid exchange of atmospheric water with the deuterated solvent water, the aqueous experiments necessitated using a fresh electrolyte solution for each potential investigated. The experiments conducted in acetonitrile solution required periodic replenishing of the solution to replace solvent loss from evaporation.
Chapter 3 Alkyl Surfaces

3.1 Hexanethiol

3.1.1 Film Thickness and Contact Angle

The assembly of hexanethiol on gold had a thickness of 9Å as measured by optical ellipsometry (Table 1), consistent with that found by other workers and is indicative of a liquid-like structure (10). The data on the effect of increasing chain length on the film thickness indicate that chains less than nine methylene groups long form liquid-like structures on gold substrates (10). A liquid-like structure has more gauche kinks in the chains than a crystalline, fully-extended, all-trans structure. The film thickness is, thus, smaller in liquid-like structures than in the corresponding crystalline structures (10).

The contact angle (Table 1) made by water on the surface was 81°. A high angle suggests a hydrophobic surface and is consistent with hexanethiol's insolubility in water. This indicates that an assembly of hexanethiol molecules is present on the gold surface. In keeping with the assembly having a film thickness consistent with a liquid-like structure, the contact angle is not as high as that found for longer chain thiols which form crystalline assemblies on gold (Sections 3.2.1 and 3.3.1). Contact angles have been observed to
Table 1. Film Thickness and Contact Angles for Monolayers on Gold.

<table>
<thead>
<tr>
<th>Monolayer Species</th>
<th>Film Thickness (Angstroms)</th>
<th>Contact Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecanethiol</td>
<td>23</td>
<td>102</td>
</tr>
<tr>
<td>Dodecanethiol</td>
<td>16</td>
<td>94</td>
</tr>
<tr>
<td>Hexanethiol</td>
<td>9</td>
<td>81</td>
</tr>
<tr>
<td>9-Mercaptononane-nitrile</td>
<td>12</td>
<td>49</td>
</tr>
<tr>
<td>11-Mercapto-undecanoic acid</td>
<td>20</td>
<td>41</td>
</tr>
</tbody>
</table>
decrease with decreasing crystallinity in studies of paraffin wax as a function of temperature (59).

3.1.2 XPS

The XPS survey spectrum of a "clean" blank gold substrate was dominated by gold photopeaks 4s, 4p1/2, 4p3/2, 4d3/2, 4d5/2, 4f5/2, 4f7/2, 5s, 5p1/2, and 5p3/2 at 763, 643, 547, 336, 89, 85, 110, 75 and 57eV, respectively. Also present were carbon 1s and oxygen 1s photopeaks. Their presence was due to the ubiquity of these contaminants in the atmosphere and the sensitivity of the XPS method.

The XPS survey spectrum of an assembly of hexanethiol on gold was also dominated by the above-mentioned gold photopeaks. The spectrum contained photopeaks due to carbon 1s and oxygen 1s. The gold 4f7/2, carbon 1s, and oxygen 1s regions were scanned for ca. one, three, and six minutes, respectively and the resulting spectra shifted to the carbon 1s reference photopeak at 285eV. The atomic concentrations listed in Table 2 were normalized to the gold 4f7/2 photopeak. The carbon 1s spectrum displayed a photopeak consistent with those found for hydrocarbons and resulted in an atomic concentration of carbon of 67.6%. The oxygen 1s spectrum contained a photopeak at 532eV indicating significant oxygen contamination (32.4%), consistent with a liquid-like structure which could allow oxidation of the gold surface.

34
Table 2. Atomic Concentrations of Carbon 1s, Oxygen 1s and Nitrogen 1s for Monolayers on Gold (normalized to Au 4f_{7/2}).

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Carbon (%)</th>
<th>Oxygen (%)</th>
<th>Nitrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanethiol</td>
<td>67.6</td>
<td>32.4</td>
<td>--</td>
</tr>
<tr>
<td>Dodecanethiol</td>
<td>94.1</td>
<td>5.9</td>
<td>--</td>
</tr>
<tr>
<td>Octadecanethiol</td>
<td>99.7</td>
<td>0.3</td>
<td>--</td>
</tr>
<tr>
<td>9-Mercapto-nonanenitrile</td>
<td>98.2</td>
<td>--</td>
<td>1.8</td>
</tr>
<tr>
<td>11-Mercapto-undecanoic Acid</td>
<td>73.9</td>
<td>26.1</td>
<td>--</td>
</tr>
</tbody>
</table>
3.1.3 Cyclic Voltammetry

Figure 7a shows cyclic voltammograms for the oxidation of 0.001M Fe(CN)$_6^{3-}$ aqueous solution in the presence of 0.1M NaClO, at an unmodified gold substrate (blank) and at a hexanethiol-modified sample. The hexanethiol sample is partially blocking electron transfer as evidenced by the significantly smaller amount of current passed through it compared to that passed by the blank. Some current, however, is passed which suggests that the hexanethiol structure is not a complete barrier to electron transfer. The anodic peak is absent in the hexanethiol cyclic voltammogram, indicating that the reaction is not reversible at that surface. Because the cathodic peak occurs at a more negative potential at the hexanethiol surface compared with the blank, it appears that the kinetics of the reaction are slower at the hexanethiol surface. These results are consistent with a picture of a liquid-like structure which can be partially penetrated by solvent to allow ions to travel near enough to the gold surface to permit electron transfer. Because the ions must diffuse through a barrier, the reaction is slower and the ions may not travel fast enough to have the reaction be reversible on the time scale of the experiment.

Figure 7b shows cyclic voltammograms for the oxidation of 0.001M ferrocene in acetonitrile solution in the presence of 0.1M NaClO, at a blank and at an hexanethiol-modified sample.
Figure 7. Cyclic voltammograms of an hexanethiol film and a blank gold electrode: (a) 0.001 M ferrocyanide and 0.1 M NaClO, in water, (b) 0.001 M ferrocene and 0.1 M NaClO, in acetonitrile.
Unlike the aqueous system, the current passed by the hexanethiol sample is only slightly less than that passed by the blank, which suggests that the hexanethiol assembly is not a barrier to electron transfer in the acetonitrile system. That the anodic and cathodic peaks' potentials are only slightly more separated at the hexanethiol surface than the separation in the blank suggests that the kinetics of the reaction are only slightly slowed by the hexanethiol assembly. These data indicate that the oxidation of ferrocene in acetonitrile proceeds almost unhindered by the presence of hexanethiol. Acetonitrile appears to penetrate the hexanethiol structure even more than water to allow more and faster electron transfer.

3.1.4 IRRAS

The C-H stretching region of an IRRAS spectrum of hexanethiol on gold is shown in Figure 8c. The spectrum was taken at 8cm⁻¹ resolution using 1024 scans and was ratioed to a blank. The peak at 2966cm⁻¹ is due to the methyl asymmetric in-plane stretch and the peaks at 2937 and 2878cm⁻¹ are assigned to the methyl symmetric stretch which is split by Fermi resonance interactions with the asymmetric methyl deformation mode. Methylene asymmetric and symmetric stretching modes are seen at 2924 and 2954cm⁻¹, respectively, which are consistent with a liquid-like, disordered state.
Figure 8. IRRAS spectra of (a) octadecanethiol, (b) dodecanethiol and (c) hexanethiol on gold.
(10). The infrared results are in agreement with the thickness, contact angle, XPS and cyclic voltammetry results, all of which point to a picture of an assembly of hexanethiol molecules which is structurally disorganized.

3.1.5 PDIRS

Figure 9a shows the potential difference infrared spectrum of 0.005M Fe(CN)$_6^{3-}$ in aqueous solution in the presence of 0.1M KCl for an unmodified surface. The positive peak at 2038cm$^{-1}$ is due to the cyano stretch of the Fe(CN)$_6^{3-}$ species which is present at 0.0V vs. SCE. The negative peak at 2121cm$^{-1}$ is due to the cyano stretch of the Fe(CN)$_6^{3-}$, and its presence indicates that oxidation occurred at the surface of the blank when the applied potential was increased to 0.5V vs. SCE.

Figure 9b shows the PDIRS spectrum of the same solution for the hexanethiol modified surface. The same species are present in this spectrum as were in the spectrum of the blank, indicating that oxidation of Fe(CN)$_6^{3-}$ has occurred at that surface. This oxidation reaction was almost totally blocked in the cyclic voltammetry experiment (see section 3.1.3) but does not appear blocked in the PDIRS experiment. The PDIRS experiment, however, is of a much longer time scale than that used in the cyclic voltammetry. This result provides further evidence for a kinetic rather than physical barrier to
Figure 9. Potential difference infrared spectra in an aqueous solution of 0.001 M ferrocyanide and 0.1 M NaClO₄: (a) unmodified gold electrode, (b) hexadecanethiol-modified gold electrode.
electron transfer and is complementary to the aqueous cyclic voltammetry data which also pointed to hexanethiol providing a slowing effect on electron transfer.

3.1.6 PM-IRRAS

Hexanethiol assemblies on gold were deemed unsuitable for study by Polarization modulation IRRAS because their liquid-like structure on the surface would make structural studies difficult to interpret.

3.1.7 Summary of Hexanethiol Results

The data collected for hexanethiol assemblies on gold suggest that the structure is in a liquid-like, disordered state. The film thickness is too small to be consistent with a fully-extended all-trans monolayer structure, and the contact angle is lower than other, more hydrophobic alkyl monolayers. XPS spectra include oxide peaks and indicate significant oxide presence on the surface which indirectly supports the model of an assembly with a liquid-like structure. Infrared measurements indicated, primarily by the intensity and position of the methylene asymmetric stretch, that the hexanethiol structure was liquid-like.

Electrochemical experiments gave a picture of a hexanethiol surface which is penetrable by ions in water and, to a greater extent, in acetonitrile. The fact that electron
transfer in the aqueous systems was slowed but not prevented by the hexanethiol assembly supports the model of a liquid-like, and, therefore, dynamic structure.

3.2 Dodecanethiol

3.2.1 Film Thickness and Contact Angle

The dodecanethiol monolayer on gold was 16Å thick (Table 1) as measured by optical ellipsometry. That thickness was consistent with that found by other workers and indicated an ordered, crystalline structure (10). Alkanethiols with greater than nine methylene units in the chain were found to self-assemble into nearly perfect all-trans, fully-extended structures on gold surfaces (10).

The contact angle made by water on the surface was 94° (Table 1), which implied that the surface was hydrophobic and was consistent with the insolubility of dodecanethiol in water. This indicated that dodecanethiol had self-assembled into a structure on the surface which prevented water's access to the gold substrate. The contact angle was higher than that found for the shorter chain hexanethiol monolayer and appears to make water less sensitive to the underlying gold surface.

3.2.2 XPS

XPS was used, primarily, as confirmation of the monolayer presence. The XPS survey spectrum from a forty-five second
scan of dodecanethiol monolayer on gold was dominated by gold photopeaks. The gold 4f\(_{7/2}\), carbon 1s, and oxygen 1s regions were scanned for ca. one, three, and six minutes, respectively. The resulting spectra shifted to the carbon 1s reference photopeak at 285eV and the atomic concentrations were calculated and normalized to the gold 4f\(_{7/2}\) photopeak (Table 2). The carbon 1s spectrum had a hydrocarbon-like photopeak and the atomic concentration was 94.1%. The oxygen 1s region contained a photopeak at 532eV with an atomic concentration of 5.9%. This oxygen concentration indicated some minor contamination of the dodecanethiol monolayer.

3.2.3 Cyclic Voltammetry

Figure 10a shows cyclic voltammograms for the oxidation of 0.001M Fe(CN)\(_4^-\) aqueous solution in the presence of 0.1M NaClO, at a blank and at a dodecanethiol-modified surface. The cyclic voltammograms show that very little current flows through the dodecanethiol monolayer compared to that passed by the blank. This means that the dodecanethiol monolayer blocks electron transfer to the gold electrode, effectively passivating it.

Figure 10b shows cyclic voltammograms for the oxidation of 0.001M ferrocene in acetonitrile solution in the presence of 0.1M NaClO, at a blank and at a dodecanethiol monolayer sample. The current passed by the dodecanethiol sample is
Figure 10. Cyclic voltammograms of a dodecanethiol film and a blank gold electrode: (a) 0.001 M ferrocyanide and 0.1 M NaClO, in water, (b) 0.001 M ferrocene and 0.1 M NaClO, in acetonitrile.
almost as large as that passed by the blank, which suggests that, in the acetonitrile system, this monolayer is not a barrier to electron transfer. The anodic and cathodic peaks’ potentials are slightly more separated at the monolayer surface than they are in the blank, suggesting that the kinetics of the reaction are slightly slowed by the monolayer. These results indicate that electron transfer in acetonitrile is affected very little by the presence of the dodecanethiol monolayer.

3.2.4 IRRAS

The C-H stretching region of an IRRAS spectrum of dodecanethiol on gold is shown in Figure 8b. The spectrum was taken at 8cm⁻¹ resolution using 1024 scans and was ratioed to a blank. The peak at 2965cm⁻¹ is due to the methyl asymmetric in-plane stretch, and the peaks at 2937 and 2878cm⁻¹ are assigned to the methyl symmetric stretch which is split by Fermi resonance interactions with the asymmetric methyl deformation mode. Methylene asymmetric and symmetric stretching modes are at 2920 and 2951cm⁻¹, respectively, which are consistent with an ordered crystalline state (10).

3.2.5 PDIRS

The potential difference infrared spectrum of 0.005M Fe(CN)₆³⁻ in aqueous solution in the presence of 0.1M KCl was
obtained at a dodecanethiol surface. The spectrum (not shown) was like those of the unmodified and hexanethiol-modified gold electrodes shown in Figure 9. The positive peak at 2038 cm\(^{-1}\) is due to the cyano stretch of the Fe(CN)\(_{6}^{3-}\) species which is present at 0.0V vs. SCE. The negative peak at 2121 cm\(^{-1}\) is due to the cyano stretch of the Fe(CN)\(_{6}^{3-}\), and its presence indicates that oxidation occurred at the surface of the blank when the applied potential was increased to 0.5V vs. SCE. This result indicates that oxidation of Fe(CN)\(_{6}^{3-}\) has occurred at the modified surface, even though it was blocked in the cyclic voltammetry experiment (see section 3.2.3). This points to a kinetic rather than a physical barrier to electron transfer through the dodecanethiol monolayer: because the PDIRS experiment is much longer than cyclic voltammetry, it appears that there is sufficient time for oxidation to occur.

3.2.6 PM-IRRAS

Polarization modulation IRRAS spectra of dodecanethiol monolayers on gold in the presence of deuterated water and acetonitrile did not have sufficiently high signal-to-noise ratios to be analytically useful.

3.2.7 Summary of Dodecanethiol Results

Results of measurements of dodecanethiol monolayers on gold provide a consistent picture of a close-packed,
crystalline monolayer assembly. The film thickness is almost as large as the thickness calculated for all-trans, full-extended arrays of alkanethiols on gold (10), and the contact angle is essentially as high as a hydrophobic surface can provide. XPS spectra show a surface with little on it except for gold and carbon, which suggests that the gold surface is well-protected from oxidation by the close-packed monolayer structure. The IRRAS spectrum shows a significant methylene asymmetric stretch peak at a position consistent with that found for crystalline hydrocarbon species.

Electrochemical data also support the crystalline structural organization model provided by the other results. In water, electron transfer is slowed by the presence of the monolayer. Electron transfer still occurs which points to a kinetic barrier instead of a physical barrier. Acetonitrile is able to permeate the dodecanethiol monolayer better than water and allows faster electron transfer, probably causing structural disruption in the permeation process.

3.3 Octadecanethiol

3.3.1 Film Thickness and Contact Angle

Octadecanethiol on gold had a thickness of 23Å (Table 1) as measured by optical ellipsometry, consistent with that found by other workers and was indicative of an ordered assembly structure (10). Long chain alkanethiol monolayers,
like those formed from octadecanethiol, have been found to form all-trans, fully-extended arrays of close-packed chains on gold and to have the appropriate film thicknesses (10,45).

The contact angle made by water on the surface was 102° (Table 1). Such a high angle indicates a highly hydrophobic surface and implies that octadecanethiol has effectively self-assembled onto the gold surface. The octadecanethiol surface effectively blocked the gold surface from water and provided a better physical barrier than that formed by either hexanethiol or dodecanethiol, which both had lower contact angles.

3.3.2 XPS

The XPS survey spectrum was dominated by gold photopeaks. The gold 4f$_{7/2}$, carbon 1s, and oxygen 1s regions were scanned for ca. one, three, and six minutes, respectively, and the resulting spectra shifted to the carbon 1s reference photopeak at 285eV. The atomic concentration was calculated and normalized to the gold 4f$_{7/2}$ (Table 2). The carbon 1s spectrum displayed a photopeak consistent with those found for hydrocarbons. The atomic concentration of carbon was 99.7%. The oxygen 1s region contained a weak photopeak at 532eV (atomic concentration 0.3%) indicating very minor oxygen contamination of the octadecanethiol monolayer. XPS results provide confirmation of the monolayer presence on the surface.
and indicate that, essentially, the only two species present are gold and hydrocarbon carbon.

3.3.3 Cyclic Voltammetry

Figure 11a shows cyclic voltammograms for the oxidation of 0.001M Fe(CN)$_6^{3-}$ aqueous solution in the presence of 0.1M NaClO, at an unmodified gold substrate (blank) and at an octadecanethiol monolayer sample. The octadecanethiol monolayer is blocking electron transfer as evidenced by the lack of current flow across it to the gold surface.

Figure 11b shows cyclic voltammograms for the oxidation of 0.001M ferrocene in acetonitrile solution in the presence of 0.1M NaClO, at a blank and at a octadecanethiol monolayer sample. Unlike the aqueous system, octadecanethiol allows some current to pass and indicates that the octadecanethiol monolayer is not a complete barrier to electron transfer in the acetonitrile system. However, the anodic and cathodic peak potentials are more widely separated at the octadecanethiol monolayer surface than at the blank. This demonstrates that the kinetics of the reaction are slowed by the presence of the monolayer. These facts indicate that the oxidation of ferrocene in acetonitrile proceeds in presence of the octadecanethiol monolayer, unlike the oxidation of ferrocyanide in water. Because acetonitrile allows electron transfer, it must allow electrolyte penetration of the
Figure 11. Cyclic voltammograms of an octadecanethiol film and a blank gold electrode: (a) 0.001 M ferrocyanide and 0.1 M NaClO, in water, (b) 0.001 M ferrocene and 0.1 M NaClO, in acetonitrile.
monolayer. In order to allow electrolyte penetration, there must be an accompanying disruption of the close-packed structure. Direct evidence for structural disruption is needed to fully understand the barrier mechanism of monolayers.

3.3.4 IRRAS

The C-H stretching region of an IRRAS spectrum of octadecanethiol on gold is shown in Figure 8a. The spectrum was taken at 8cm⁻¹ resolution using 1024 scans and was ratioed to a blank. The peak at 2964cm⁻¹ is due to the methyl asymmetric in-plane stretch and the peaks at 2936 and 2878cm⁻¹ are assigned to the methyl symmetric stretch which is split by Fermi resonance interactions with the asymmetric methyl deformation mode (10). Methylene asymmetric and symmetric stretching modes are seen at 2918 and 2949cm⁻¹, respectively, which are consistent with a crystalline state of densely packed array of alkyl chains tilted ca. 30° from the surface normal (10).

3.3.5 PDIRS

The PDIRS spectrum of octadecanethiol on gold was obtained under the same conditions as for the blank (Section 3.1.5). The same species were present as were present (spectrum not shown) for the blank (Figure 9), indicating that

52
oxidation of Fe(CN)$_6^{3-}$ has occurred at that surface. This oxidation reaction was blocked in the cyclic voltammetry experiment but is not blocked in the PDIRS experiment. The PDIRS experiment, however, is much longer than that used in the cyclic voltammetry. This result points to a kinetic rather than physical barrier to electron transfer through the octadecanethiol monolayer.

3.3.6 PM-IRRAS in D$_2$O

Figure 12a shows the in situ PM-IRRAS spectrum of a monolayer of octadecanethiol on gold in D$_2$O collected at 8 cm$^{-1}$ resolution using 64 scans. Figure 11a shows the ex situ IRRAS spectrum of an octadecanethiol monolayer on gold for comparison. The spectra were curve fitted and their simulated spectra and the component peaks of the simulated spectra generated. Peak positions are summarized in Table 3.

The simulated spectrum and component peak spectra for the ex situ octadecanethiol monolayer is shown in Figure 13b. The simulated spectrum matches the real spectrum and the component peak positions are in agreement with the literature (10).

The simulated spectrum and component peak spectra for the monolayer in D$_2$O are shown in Figure 12b. The major difference between these spectra and the corresponding spectra for the ex situ monolayer is the apparent broadening of peaks in D$_2$O, which is due to several contributing factors.
Figure 12. PM-IRRAS spectra of octadecanethiol on gold in D$_2$O: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
Figure 13. IRRAS spectra of octadecanethiol on gold: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
Table 3. Peak Positions and Widths of Curve Fitted Peaks for the C-H Stretching Modes of Octadecanethiol on Gold ex situ and in situ.

<table>
<thead>
<tr>
<th>Mode</th>
<th>ex situ</th>
<th>D$_2$O</th>
<th>d$_3$-ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_s$(CH$_3$,ip)</td>
<td>2964 (10)</td>
<td>2962 (16)</td>
<td></td>
</tr>
<tr>
<td>$v_s$(CH$_3$,op)</td>
<td></td>
<td></td>
<td>2956 (11)</td>
</tr>
<tr>
<td>$v_s$(CH$_3$,FR)</td>
<td>2936 (15)</td>
<td>2940 (26)</td>
<td>2932 (17)</td>
</tr>
<tr>
<td>$v_a$(CH$_2$,l)</td>
<td></td>
<td></td>
<td>2924 (10)</td>
</tr>
<tr>
<td>$v_a$(CH$_2$,C)</td>
<td>2918 (16)</td>
<td>2921 (24)</td>
<td>2918 (9)</td>
</tr>
<tr>
<td>$v_a$(CH$_2$,FR)</td>
<td></td>
<td>2896 (7)</td>
<td>2901 (12)</td>
</tr>
<tr>
<td>$v_a$(CH$_3$,FR)</td>
<td>2878 (13)</td>
<td>2871 (1)</td>
<td>2881 (27)</td>
</tr>
<tr>
<td>$v_a$(CH$_2$)</td>
<td>2849 (13)</td>
<td>2852 (6)</td>
<td>2853 (12)</td>
</tr>
</tbody>
</table>

$v_s$ = asymmetric stretch
$v_a$ = symmetric stretch
op = out-of-plane
ip = in-plane
FR = Fermi resonance
l = liquid-like
c = crystalline
The in-plane methyl asymmetric stretch at 2962 cm\(^{-1}\) is slightly broadened, likely by inhomogeneous broadening due to small differences in the local solvent environment (45).

The higher energy component of the methyl symmetric Fermi resonance couplet, which is at 2936 cm\(^{-1}\) in the ex situ spectrum, appears to have shifted to 2940 cm\(^{-1}\) and to have broadened considerably. This peak is likely a composite of two peaks, the methyl symmetric Fermi resonance peak at 2936 cm\(^{-1}\) and an out-of-plane methyl asymmetric stretch.

The low energy component of the methyl symmetric Fermi resonance couplet is shifted from its ex situ position of 2878 cm\(^{-1}\) to 2871 cm\(^{-1}\) and is decreased in intensity; these changes are consistent with exposure of the methyl group to a condensed medium (45). Because changes in one member of the Fermi resonance couplet should be mirrored in the other member, the corresponding high energy component of the Fermi resonance couplet at 2936 cm\(^{-1}\) is probably also shifted to lower energy and decreased in intensity. Furthermore, the out-of-plane methyl asymmetric stretch at 2956 cm\(^{-1}\) is unobserved in the ex situ spectrum (because of the methyl group orientation) but reorientation of the methyl group in situ would increase its absorbance and cause a peak, centered at 2956 cm\(^{-1}\), to appear (45). Two unresolved peaks, due to the increased absorbance at 2956 cm\(^{-1}\) and a high energy methyl asymmetric
Fermi resonance stretch which is red-shifted, could appear as a broad absorbance centered at 2940 cm\(^{-1}\).

The peak at 2896 cm\(^{-1}\) is present in the in situ spectrum but not in the ex situ spectrum. This peak has been assigned to Fermi resonance interaction between the methylene symmetric stretch and overtones of the methylene bending modes (60). The appearance of this peak implies that a perturbation of the methylene chain has occurred in order to bring the symmetric stretch into resonance with the overtones.

Broadening of the methylene asymmetric stretch, observed at 2918 cm\(^{-1}\) in the ex situ spectrum and 2921 cm\(^{-1}\) in situ, is consistent with a slight solvent-induced perturbation as is the decrease in intensity of the methylene symmetric stretch at 2852 cm\(^{-1}\). The slight shift to higher energy by the methylene asymmetric stretch indicates an increase in a liquid-like organization of the alkyl chains (10). Because the shift is slight, the solvent perturbation is probably felt only by those methylene groups near the surface. This is consistent with the hydrophobicity of the octadecanethiol monolayer observed in the contact angle measurements.

The PM-IRRAS spectrum of octadecanethiol on gold in contact with D\(_2\)O suggests that the solvent perturbation of the monolayer structure includes a change in orientation of the methyl group and a slight disordering of the methylene chain, near the surface.
3.3.7 PM-IRRAS in d₅-Acetonitrile

Figure 14a shows the in situ PM-IRRAS spectrum of a monolayer of octadecanethiol on gold in d₅-acetonitrile collected at 8 cm⁻¹ resolution using 64 scans. Curve fitting was done on this spectrum, the simulated spectrum and its component peaks generated and are displayed in Figure 14b. Assignments are summarized in Table 3.

Peaks in the spectrum of octadecanethiol on gold in d₅-acetonitrile are broader than the ex situ spectral peaks (Figure 13a). Again, several factors contribute to this observed broadening.

The in-plane methyl asymmetric stretch that occurs at 2964 cm⁻¹ in the ex situ spectrum is not present in situ. However, the out-of-plane asymmetric stretch, which is missing in the ex situ spectrum, is present in d₅-acetonitrile. The methyl group is oriented in the ex situ monolayer such that there is no component of the out-of-plane methyl asymmetric stretch transition moment perpendicular to the surface and, as such, is not observed in the PM-IRRAS measurement. The in-plane component is observed, however, due to the methyl orientation. When the monolayer comes into contact with d₅-acetonitrile, the methyl group orientation is such that the in-plane and out-of-plane methyl asymmetric stretch intensities are reversed compared with the ex situ spectrum, which suggests a rotation of the methyl group.
Figure 14. PM-IRRAS spectra of octadecanethiol on gold in d$_2$-acetonitrile: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
The two peaks at 2932 and 2881 cm$^{-1}$ are assigned to a Fermi resonance couplet due to the interaction of the in-plane methyl asymmetric stretch with overtones of the methyl bending modes (45). These peaks are somewhat broadened and slightly shifted compared with the ex situ spectrum, which is consistent with contact with a condensed medium.

Most interestingly, two methylene asymmetric peaks are apparent in the in situ spectrum where only one appeared ex situ. The methylene asymmetric peaks, one at 2924 cm$^{-1}$ and one at 2918 cm$^{-1}$, are due to methylene groups in liquid-like and crystalline environments, respectively (10). Further, the methylene symmetric stretch peak position, 2953 cm$^{-1}$ is half-way between the liquid state position of 2856 cm$^{-1}$ and the crystalline position of 2850 cm$^{-1}$ (10) which suggests that it may be two unresolved peaks representative of methylene groups in both liquid-like and crystalline environments.

These results suggest that the monolayer has retained only partial crystallinity upon exposure to d$_2$-acetonitrile and that some part of the structure has been disordered enough to be liquid-like. It appears as though some portion of the chain close to the gold surface has retained its all-trans configuration while the outer portion in contact with the solvent has become disordered.
3.3.8 PM-IRRAS under Potential Control

3.3.8.1 D₂O

PM-IRRAS spectra of an octadecanethiol monolayer on gold in 0.1M NaClO₄, D₂O solution were obtained at 0.5V, 0.0V and, -0.5V (vs. SCE), and are shown in Figures 15a, 16a, and 17a, respectively. The spectra were curve fitted and their simulated and component peak spectra are shown in Figures 15b, 16b and 17b. Peak assignments are summarized in Table 4. Applied potential appears to have little effect on the structural characteristics of the octadecanethiol monolayer as only the peaks ca. 2970 and 2870cm⁻¹ undergo significant change with changing potential. The peak at 2970cm⁻¹ has not been assigned. The peak at 2870cm⁻¹ has been assigned to the low energy component of the methyl symmetric Fermi resonance couplet (45). The high energy component does not appear to be affected by potential changes. The two components of the couplet have been observed to exhibit apparently inconsistent behaviors in another study (45).

The peak decreases in intensity as the potential is made more negative and implies increasing exposure to a condensed medium (45) as the potential is lowered. When the applied potential is positive the predominant species at the surface is solvated ClO₄⁻ and when the applied potential is negative the predominant species at the surface is the solvated Na⁺. The solvated ClO₄⁻ is more bulky than the solvated Na⁺ and
Figure 15. PM-IRRAS spectra of octadecanethiol on gold in 0.1 M NaClO, D₂O at 0.5 Volts vs. SCE: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
Figure 16. PM-IRRAS spectra of octadecanethiol on gold in 0.1 M NaClO₄, D₂O at 0.0 Volts vs. SCE: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
Figure 17. PM-IRRAS spectra of octadecanethiol on gold in 0.1 M NaClO, D_2O at -0.5 Volts vs. SCE: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
Table 4. Peak Positions and Widths of Curve Fitted Peaks for the C-H Stretching Modes of Octadecanethiol on Gold in D₂O as a function of Applied Potential¹.

<table>
<thead>
<tr>
<th>Mode</th>
<th>-0.5 V</th>
<th>0.0 V</th>
<th>0.5 V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Applied</td>
<td>Applied</td>
<td>Applied</td>
</tr>
<tr>
<td>vₓ(CH₃,ip)</td>
<td>2964(31)</td>
<td>2972(8)</td>
<td>2968(13)</td>
</tr>
<tr>
<td></td>
<td>[0.3]</td>
<td>[0.2]</td>
<td>[0.5]</td>
</tr>
<tr>
<td>vₓ(CH₃,FR)</td>
<td>2959(26)</td>
<td>2960(20)</td>
<td>2956(25)</td>
</tr>
<tr>
<td></td>
<td>[2.4]</td>
<td>[1.6]</td>
<td>[2.3]</td>
</tr>
<tr>
<td>vₓ(CH₃)</td>
<td>2931(23)</td>
<td>2937(29)</td>
<td>2932(27)</td>
</tr>
<tr>
<td></td>
<td>[2.8]</td>
<td>[2.6]</td>
<td>[2.7]</td>
</tr>
<tr>
<td>vₓ(CH₂,FR)</td>
<td>2920(22)</td>
<td>2922(20)</td>
<td>2921(21)</td>
</tr>
<tr>
<td></td>
<td>[2.7]</td>
<td>[2.9]</td>
<td>[3.2]</td>
</tr>
<tr>
<td>vₓ(CH₂,FR)</td>
<td>2897(24)</td>
<td>2899(48)</td>
<td>2894(34)</td>
</tr>
<tr>
<td></td>
<td>[0.7]</td>
<td>[1.7]</td>
<td>[1.4]</td>
</tr>
<tr>
<td>vₓ(CH₂,FR)</td>
<td>2873(16)</td>
<td>2871(15)</td>
<td>2867(20)</td>
</tr>
<tr>
<td></td>
<td>[0.5]</td>
<td>[0.3]</td>
<td>[0.4]</td>
</tr>
<tr>
<td>vₓ(CH₂)</td>
<td>2854(10)</td>
<td>2853(8)</td>
<td>2853(10)</td>
</tr>
<tr>
<td></td>
<td>[0.3]</td>
<td>[0.3]</td>
<td>[0.4]</td>
</tr>
</tbody>
</table>

¹ versus SCE.
vₓ = asymmetric stretch
vₛ = symmetric stretch
ip = in-plane
FR = Fermi resonance
allows fewer solvent molecules close to the surface at positive potentials. As the potential is made more negative the concentration of Na\(^+\) increases and, because that species is smaller, it allows more solvent to contact the surface. Thus the surface is increasingly exposed to solvent as the potential is lowered and the intensity of the methyl symmetric Fermi resonance peak decreases.

Because none of the other peaks appear to be sensitive to applied potential changes, it appears that changing the potential has a minor effect on the surface structure in the D\(_2\)O system. This is consistent with the observation that D\(_2\)O does not seriously disrupt the methylene chain structure (Section 3.3.6).

### 3.3.8.2 d\(_5\)-Acetonitrile

PM-IRRAS spectra of an octadecanethiol monolayer on gold in 0.1M NaClO\(_4\), d\(_5\)-acetonitrile solution were obtained at 0.5V, 0.0V and -0.5V (vs. SCE) and are shown in Figures 18a, 19a, and 20a, respectively. The spectra were curve fitted and their simulated and component peak spectra are shown in Figures 18b, 19b and 20b. Peak assignments are summarized in Table 5.

Most noticeable in the applied potential spectra is the absence of the out-of-plane methyl asymmetric stretch and liquid-like methylene asymmetric stretch peaks which were
Figure 18. PM-IRRAS spectra of octadecanethiol on gold in 0.1 M NaClO$_4$, d$_3$-acetonitrile at 0.5 Volts vs. SCE: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
Figure 19. PM-IRRAS spectra of octadecanethiol on gold in 0.1 M NaClO, d$_2$-acetonitrile at 0.0 Volts vs. SCE: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
Figure 20. PM-IRRAS spectra of octadecanethiol on gold in 0.1 M NaClO$_4$ d$_2$-acetonitrile at -0.5 Volts vs. SCE: (a) actual spectrum, (b) simulated spectrum and its curve fitted component peaks.
Table 5. Peak Positions and Widths of Curve Fitted Peaks for the C-H Stretching Modes of Octadecanethiol on Gold in d₈-Acetonitrile as a function of Applied Potential¹.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Peak Position (band width), cm⁻¹</th>
<th>applied</th>
<th>0.0 V Applied</th>
<th>0.5 V Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁(CH₃,ip)</td>
<td>2961(17)</td>
<td>[0.8]</td>
<td>2962(18)</td>
<td>[0.9]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2962(19)</td>
<td>[0.8]</td>
</tr>
<tr>
<td>v₂(CH₃,FR)</td>
<td>2927(22)</td>
<td>[1.1]</td>
<td>2932(19)</td>
<td>[0.7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2933(17)</td>
<td>[0.5]</td>
</tr>
<tr>
<td>v₃(CH₃)</td>
<td>2918(10)</td>
<td>[0.7]</td>
<td>2919(13)</td>
<td>[1.1]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2919(13)</td>
<td>[1.1]</td>
</tr>
<tr>
<td>v₁(CH₃,FR)</td>
<td>2872(7)</td>
<td>[0.1]</td>
<td>2873(8)</td>
<td>[0.1]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2872(6)</td>
<td>[0.1]</td>
</tr>
<tr>
<td>v₃(CH₃)</td>
<td>2850 (10)</td>
<td>[0.3]</td>
<td>2851 (8)</td>
<td>[0.3]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2850 (26)</td>
<td>[0.5]</td>
</tr>
</tbody>
</table>

¹ versus SCE

v₁ = asymmetric stretch
v₂ = symmetric stretch
ip = in-plane
FR = Fermi resonance
present in the d₃-acetonitrile in situ spectrum. This suggests that applied potential increases the crystalline nature of the monolayer when it is in contact with structurally-disruptive d₃-acetonitrile. The presence of solvated ions may force the solvent out of the monolayer and decrease its perturbing effect on the chain structure.

The methylene asymmetric and symmetric stretches at 2918 and 2850 cm⁻¹ appeared to be affected by the changing potential. As the potential became more negative, the intensity of these peaks both decreased. This is consistent with an increase in solvent interaction with the methylene groups. An increase in the concentration of the smaller, solvated sodium cation with decreasing potential would allow the solvent to penetrate further into the monolayer structure which would result in greater disruption of the structure.

The high energy component of the methyl asymmetric Fermi resonance couplet appeared to increase in intensity and breadth and to shift to lower energy as the potential became more negative. However, the low energy component was not affected by changing potential. The intensity increase of the high energy component is inconsistent with the increasing solvent interaction with the surface picture proposed above. The increase in both breadth and intensity of the high energy couplet which is also accompanied by a shift to lower energy is suggestive of a liquid-like asymmetric stretch as the
potential becomes more negative. It is consistent with an increase in intensity of a liquid-like methylene asymmetric stretch at ca. 2924 cm$^{-1}$ because as the solvent interaction with the methylene chain increases, packing of the chains will become disrupted and more disorganized and liquid-like.

3.3.9 Summary of Octadecanethiol Results

The thickness of the octadecanethiol monolayer on gold is consistent with a close-packed, all-trans array of alkyl chains, and the film's hydrophobic nature also points to that picture. The XPS data show that the only species present on the surface are gold and hydrocarbons, indirectly indicative of a highly-ordered film. The IRRAS spectrum, in good agreement with those obtained by other workers, is symptomatic of a close-packed, all-trans array of alkyl chains tilted ca. 30 degrees from the surface normal (10,45).

Electrochemical studies indicated that the octadecanethiol monolayer acts as a kinetic barrier to electron transfer. The time scale of cyclic voltammetry was short enough for the monolayer to prevent electron transfer in an aqueous system but the time scale of the potential difference measurements allowed electron transfer. This points to a kinetic barrier mechanism where the electron transfer is limited by the diffusion time of the electron through the monolayer. The barrier to electron transfer in
acetonitrile was not as great. Acetonitrile allowed more current to pass on the cyclic voltammetry time scale which suggested that acetonitrile might be able to permeate the monolayer structure.

Polarization modulation infrared measurements supported the idea of solvent perturbation of the monolayer structure. D$_2$O was slightly disruptive to the structure, and its effect was probably felt only in the outermost portion of the monolayer. In addition, applied potential appeared to affect only the outer region of the monolayer when in the aqueous system. D$_5$-acetonitrile has a greater disruptive effect on the monolayer structure, causing disordering of the methylene chains at least some of the way into the close-packed array. Evidence for the structural disruption of the monolayer is helpful as it supports a model of acetonitrile permeation into the monolayer.
Chapter 4 Polar Surfaces

4.1 9-Mercaptononanenitrile Surface

4.1.1 Film Thickness and Contact Angle

The monolayer of 9-mercaptopononanenitrile on gold had a thickness of 12Å (Table 1) as measured by optical ellipsometry, indicating that a self-assembled structure was present on the gold surface. If the methylene chains were in a fully-extended, all-trans configuration, the film, with a methyl group in place of the cyano group, should have been nearly 15Å thick (10). The cyano group should take up more space than a methyl group, yet the structure is not even as thick as would be expected for the methyl-terminated model. Thus, the film thickness suggests that the 9-mercaptanonenethiol molecules are not in a crystalline, close-packed array like those found for alkyl-terminated long-chain thiols and are more likely in a liquid-like state, like that found for hexanethiol on gold.

The contact angle made by water on the surface was 49° (Table 1). This low angle suggests a hydrophilic surface and is consistent with a model of an assembly of molecules with the cyano group pendant and the thiol attached to the gold surface.
4.1.2 XPS

The XPS survey spectrum from a forty-five second scan of 9-mercaptononanenitrile on gold (gold photopeaks dominated) was obtained and then the gold 4f$_{7/2}$, carbon 1s, and nitrogen 1s regions were scanned for ca. twelve minutes, twenty-five minutes and one hundred twenty-two minutes, respectively. The resulting spectra were shifted to the carbon 1s reference photopeak at 285eV. The atomic concentrations were calculated and normalized to the gold 4f$_{7/2}$ photopeak, and are summarized in Table 2. The carbon 1s spectrum had a hydrocarbon-like photopeak and the atomic concentration of carbon was 98.2%. The nitrogen 1s region contained a weak photopeak at 399.9eV, indicating the presence of nitrogen in the film. The atomic concentration of nitrogen was 1.8%.

It was expected that the carbon/nitrogen atomic concentration ratio (55/1) would emulate the molecular ratio of 9/1; however, it is likely that a significant portion of the carbon 1s photopeak on any given sample is due to atmospheric contamination. It would appear that, because the oxygen 1s photopeak is relatively large in the survey scan (not shown), contamination by carbon- and oxygen-containing species has occurred. Thus, it is not unexpected that the carbon/nitrogen ratio is larger than would be calculated from their molecular ratio in a surface-bound assembly.
XPS results were conclusive for the presence of nitrogen on the surface which gave evidence for the self-assembly of 9-mercaptanonenitrile on gold.

4.1.3 Cyclic Voltammetry

Figure 21a shows cyclic voltammograms for the oxidation of 0.001M Fe(CN)$_6^{3-}$ aqueous solution in the presence of 0.1M NaClO$_4$, at a blank and at a 9-mercaptanonenitrile-modified surface. The film effectively blocks electron transfer as illustrated by the very small amount of current passed compared to that passed by the blank.

Figure 21b shows cyclic voltammograms for the oxidation of 0.001M ferrocene in acetonitrile solution in the presence of 0.1M NaClO$_4$, at a blank and at a 9-mercaptanonenitrile sample. The current passed through the film is only slightly less than that passed by the blank, which suggests that the surface-bound structure presents little barrier to electron transfer in the acetonitrile system.

Because the peaks are shifted to lower potential at the modified surface compared with the blank, it appears that the kinetics of the reaction are slowed by the surface structure. Acetonitrile appears able to penetrate through the monolayer to allow electron transfer to the gold surface.
Figure 21. Cyclic voltammograms of a 9-mercaptanonanenitrile film and a blank gold electrode: (a) 0.001 M ferrocyanide and 0.1 M NaClO, in water, (b) 0.001 M ferrocene and 0.1 M NaClO, in acetonitrile.
4.1.4 IRRAS

The C-H stretching region of an IRRAS spectrum of 9-mercaptanonanenitrile on gold is shown in Figure 22. The spectrum was taken at 8cm⁻¹ resolution using 1024 scans and was ratioed to a blank. The peaks at 2933 and 2863cm⁻¹ are assigned to the methylene asymmetric and symmetric stretching modes, respectively, and are indicative of a liquid-like surface structure.

The peak due to the cyano stretching mode (occurs at 2245cm⁻¹ in the bulk material) is missing in the spectrum of the surface-bound species. Because IRRAS can only detect vibrational modes which have some component of their transition moment normal to the surface, the cyano group must be oriented parallel to the gold surface. Other workers have reported IRRAS spectra with methylene peak positions indicative of a crystalline assembly and which demonstrated cyano stretch absorbance; however, the 9-mercaptanonanenitrile films in their study were also found to be variable in their wetting and solvent permeation properties (21). Variability in these properties would suggest that 9-mercaptanonanenitrile can form either crystalline or liquid-like structures on gold. The 9-mercaptanonanenitrile assemblies studied in this work demonstrated neither crystalline methylene packing arrangements nor cyano stretch absorbances.
Figure 22. IRRAS spectrum of the CH stretch region of 9-mercaptanonanenitrile on gold.
4.1.5 PDIRS

The potential difference infrared spectrum of 0.005M Fe(CN)₄⁻ in aqueous solution in the presence of 0.1M KCl for a 9-mercaptononanenitrile surface contained the same peaks as shown in the PDIR spectrum of the blank (Figure 9a). The positive peak at 2038cm⁻¹ is due to the cyano stretch of the Fe(CN)₄⁻ species which is present at 0.0V vs. SCE. The negative peak at 2121cm⁻¹ is due to the cyano stretch of the Fe(CN)₃⁻, and its presence indicates that oxidation occurred at the surface when the applied potential was increased to 0.5V vs. SCE. This oxidation reaction was blocked in the time scale of a cyclic voltammetry experiment (see section 4.1.3) but does not appear blocked in the PDIRS experiment where the potential is applied for a much longer time. This difference points to a kinetic barrier to electron transfer through the monolayer in an aqueous environment.

4.1.6 PM-IRRAS

9-mercaptononanenitrile monolayers on gold were unsuitable for investigation by PM-IRRAS because their liquid-like structure would impair the detection and/or interpretation of disruptive changes due to the presence of solvents.
4.1.7 Summary

The low film thickness for the 9-mercaptononanenitrile monolayer suggests a liquid-like packing of the methylene chains in the monolayer. The low contact angle suggests that the cyano group is at the surface causing the monolayer to be hydrophilic. The non-crystalline packing arrangement is supported by IRRAS spectra which show the methylene chains in a liquid-like environment. The IRRAS spectrum of the monolayer on gold does not contain a cyano stretch peak even though it is visible in the bulk spectrum, suggesting that the cyano group is oriented parallel to the gold surface. Because the IRRAS did not show a cyano group on the surface, XPS was used to confirm the presence of nitrogen.

Electrochemical studies of 9-mercaptononanenitrile show that the monolayer acts as a kinetic barrier to electron transfer in water because its ability to allow oxidation of ferrocyanide in aqueous solution depended on the time scale of the experiment. The oxidation occurred in the longer potential difference experiment but was blocked in the shorter cyclic voltammetric experiment. The oxidation of ferrocene in the acetonitrile system was not blocked, suggesting that the solvent allowed charge penetration into the monolayer. The reaction was slowed in the presence of the monolayer but was not reversible, suggesting a kinetic barrier to electron transfer through this monolayer.
4.2 11-Mercaptoundecanoic Acid Surface

4.2.1 Film Thickness and Contact Angle

The self-assembled film of 11-mercaptoundecanoic acid on gold had a thickness of 20Å (Table 1) as measured by optical ellipsometry. This thickness is consistent with a crystalline packing arrangement in the structure because a methyl-terminated, all-trans, fully-extended chain with the same number of carbons should be 18.6Å thick (10).

The contact angle (Table 1) made by water on the surface was 41°. Such a low angle implies that the water is spreading on the surface and is consistent with a model of a close-packed assembly of molecules with the hydrophilic acid group at the surface.

4.2.2 XPS

The XPS survey spectrum from a forty-five second scan of a 11-mercaptoundecanoic acid assembly on gold was dominated by gold photopeaks but also has photopeaks due to carbon 1s and oxygen 1s. The carbon 1s and oxygen 1s regions were scanned for ca. four and seven minutes, respectively, and the resulting spectra shifted to the carbon 1s reference photopeak at 285eV. The atomic concentrations were calculated and normalized to the gold 4f7/2 photopeak (Table 2).

The carbon 1s spectrum displayed a photopeak at 285eV with a shoulder at 289.6eV which is consistent with
carboxylate groups on hydrocarbons (61). The atomic concentration of carbon was found to be 73.0%.

The oxygen 1s region contained a broad photopeak at 533.8eV with an atomic concentration of 26.1%. The photopeak was symptomatic of those found for carboxylic acids in which two peaks are present, one at 534.2eV for the singly bonded oxygen and one at 532.9eV for the doubly bonded oxygen (61).

4.2.3 Cyclic Voltammetry

Figure 23a shows cyclic voltammograms for the oxidation of 0.001M Fe(CN)₆³⁻ aqueous solution in the presence of 0.1M NaClO₄ at a blank and at a 11-mercaptoundecanoic acid-modified surface. The very small amount of current passed compared to that passed by the blank indicates that the film essentially blocks electron transfer to the gold surface.

Figure 23b shows cyclic voltammograms for the oxidation of 0.001M ferrocene in acetonitrile solution in the presence of 0.1M NaClO₄ at a blank and at a 11-mercaptoundecanoic acid sample. Significant current is passed through the film, although less than that passed by the blank, implying that the self-assembled structure presents little barrier to electron transfer in the acetonitrile system.

The cathodic and anodic peaks of the modified electrode are shifted further apart in the cyclic voltammogram than in the blank, indicating that the kinetics of the reaction are
Figure 23. Cyclic voltammograms of a 11-mercaptopoundecanoic acid film and a blank gold electrode: (a) 0.001 M ferrocyanide and 0.1 M NaClO, in water, (b) 0.001 M ferrocene and 0.1 M NaClO, in acetonitrile.
slowed by the surface-bound species. Acetonitrile appears able to penetrate through the structure to allow somewhat retarded electron transfer to the gold surface.

Cyclic voltammetry of 0.001M methyl viologen in a series of aqueous 0.1M phosphate buffers at a 11-mercaptoundecanoic acid surface showed no difference with the differing pH. The ionization state of the surface species is, apparently, not an important factor in the electron transfer mechanism.

4.2.4 IRRAS

The C-H stretching region of an IRRAS spectrum of 11-mercaptoundecanoic acid on gold is shown in Figure 24. The spectrum was taken at 8cm⁻¹ resolution using 1024 scans and was ratioed to a blank. The peaks at 2926 and 2854cm⁻¹ are assigned to the methylene asymmetric and symmetric stretching modes, respectively, and are indicative of a liquid-like surface structure (10).

The broad OH stretch usually dominant in carboxylic acid spectra is missing in the spectrum, but a large carbonyl stretch peak is observed at 1719cm⁻¹. In order to be observed in the IRRAS spectrum the carbonyl vibration must have a component of its transition moment perpendicular to the gold surface. The missing hydroxyl peak suggests that the hydroxyl group is oriented parallel to the surface which would render it invisible to IRRAS.
Figure 24. IRRAS spectrum of 11-mercaptoundecanoic acid on gold in the (top) CH stretch region and the (bottom) carbonyl stretch region (same relative intensity scale).
The carbonyl peak position is consistent with an associated system of hydrogen-bonded acid groups (62). This is consistent with a model of an assembly of highly oriented acid groups at the surface, even though the underlying methylene chain orientation may be more liquid-like than crystalline. The carboxylic acid orientation is, likely, one with the oxygens oriented 45° from the normal. This would allow the carbonyl stretch to be detected and would keep the hydroxyl stretch parallel to the surface and, therefore, undetected in IRRAS.

4.2.5 PDIRS

The potential difference infrared spectrum of 0.005M Fe(CN)₆⁻ in aqueous solution in the presence of 0.1M KCl for a 11-mercaptoundecanoic acid surface (not shown) contained the same species as the spectrum of the blank (Figure 9a). The positive peak at 2038 cm⁻¹ is due to the cyano stretch of the Fe(CN)₆⁻ species which is present at 0.0V vs. SCE. The negative peak at 2121 cm⁻¹ is due to the cyano stretch of the Fe(CN)₃⁻, and its presence indicates that oxidation occurred at the surface when the applied potential was increased to 0.5V vs. SCE. Because the reaction was blocked in the cyclic voltammetry experiment (short time scale) but was not blocked in the PDIRS experiment (longer time scale), a kinetic, rather than a physical, electron transfer barrier is indicated.
4.2.6 Surface Titrations

Figure 25 shows the titration curves of 11-mercapto-undecanoic acid on gold monitored by both goniometry and IRRAS. The curves resulting from both methods of monitoring the ionization of the carboxylic acid group at the surface are in very good agreement. Agreement between the curves indicates that the titration monitored by the IRRAS method can readily be substituted for the titration monitored by the goniometry method. The contact angle titration curve also agree well with similar curves obtained by other workers (17, 33). The contact angle was constant between pH 1 and 6 and decreased as the pH increased from 7 to 13. The carbonyl peak integrated area correlated well with the contact angle behavior in that it also was constant between pH 1 and 6 and decreased as the pH increased from 7 to 13.

Absorbances (not shown) at ca. 1600cm⁻¹ and 1400cm⁻¹ appeared as the carbonyl stretch at 1719cm⁻¹ disappeared. These absorbances are due to carbonyl asymmetric stretch and symmetric stretch, respectively, of the carboxylate which is being formed (62). The IRRAS spectrum of the surface at pH 13 contained no peaks from carbonyl or CH stretches, indicating that the thiol was no longer present on the surface. Spectra of the surfaces at all other pH values contained absorbances in the CH stretch region. Cleavage of the gold thiolate bond is thought to occur at high pH’s (12).
Figure 25. Titration curves of 11-mercaptoundecanoic acid on gold monitored by IRRAS (asterisks) and goniometry (triangles). Error bars indicate standard deviations.
The goniometric method represents an in situ method in that the measurement is made when the solvent is in contact with the surface. The IRRAS method differs in that it represents an ex situ measurement: the surface is not in contact with the solvent at the time of measurement. It is advantageous that the IRRAS method, even though it is ex situ, agrees with the in situ goniometry method. The goniometry experiment is inferior to the IRRAS method for several reasons.

The IRRAS method requires some sample handling prior to the measurement but the measurement itself is performed by the instrument. The goniometry method requires less pretreatment, but the measurement is performed by the operator and is, as such, more prone to measurement error. This is demonstrated by the error bars in Figure 25. The contact angle points (triangles) are the average of seven trials on seven separate days, while the IRRAS points (asterisks) are from one measurement of the integrated areas of IRRAS carbonyl stretch peaks (Table 6). Goniometric measurements which use water as the contacting fluid are sensitive to the temperature and relative humidity of the environment, and special effort must be made to account for differences between measurements made in different laboratories or on different days (59). IRRAS measurements are made in a moisture-purged environment, and no
Table 6. Titration of 11-Mercaptoundecanoic Acid Monitored by Goniometry and IRRAS.

<table>
<thead>
<tr>
<th>pH</th>
<th>Angle Average (degrees)</th>
<th>Angle Std. Dev. (degrees)</th>
<th>Integrated C=O Area (x10⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53</td>
<td>3</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td>56</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>53</td>
<td>2</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>54</td>
<td>2</td>
<td>3.7</td>
</tr>
<tr>
<td>6</td>
<td>54</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>53</td>
<td>1</td>
<td>3.9</td>
</tr>
<tr>
<td>8</td>
<td>49</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>51</td>
<td>3</td>
<td>3.2</td>
</tr>
<tr>
<td>10</td>
<td>44</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>34</td>
<td>4</td>
<td>2.4</td>
</tr>
<tr>
<td>12</td>
<td>30</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>19</td>
<td>3</td>
<td>1.4</td>
</tr>
</tbody>
</table>
special effort is required to assure agreement between measurements taken on different days or in different laboratories.

Goniometric measurements are information-poor when compared to the structural information that is provided by IRRAS data. Goniometry merely provides a measurement of an angle made between a contacting fluid and the surface. The implications of that measurement must be inferred from physical-organic wetting theory (33). Infrared measurement, however, provides direct spectral evidence for the structural changes taking place in the system.

4.2.7 PM-IRRAS

Titration of 11-mercaptoundecanoic acid monolayers on gold with pH adjusted deuterated water gave variable results. The inconsistencies were thought to be due to the low signal to noise ratio and to the difficulty in preparing hydrogen-free pH adjusted solutions.

Given that IRRAS and goniometric titration results agreed so well, it is doubtful whether the PM-IRRAS titration could supply further structural information on the ionization of the carboxylic acid functionality. PM-IRRAS becomes unnecessary because the information is provided by IRRAS. Furthermore, IRRAS is much simpler and easier to perform.
4.2.8 Summary

The film thickness of 11-mercaptoundecanoic acid could be interpreted as consistent with a crystalline packing order of the methylene chains if the carboxylic acid group did not add significantly to the thickness. The low contact angle is indicative of a hydrophilic surface which means that the acid group is very accessible to the contacting solvent. IRRAS information suggests that the methylene chains are not in a crystalline packing arrangement because the methylene stretch modes are indicative of a liquid-like environment. Because a carbonyl stretch peak is observed in the IRRAS spectrum, the carbonyl group must have some component of its carbonyl stretch transition moment perpendicular to the gold surface. The position and intensity of that peak suggest that the carboxylic acid groups are highly associated. Absence of an hydroxyl stretch mode suggests that the hydroxyl group is parallel to the gold surface. The IRRAS spectrum suggests that the carbonyl oxygens are 45° from the normal.

Electrochemical experiments showed that a monolayer of 11-mercaptoundecanoic acid acts as a kinetic, rather than a physical, barrier to electron transfer in aqueous systems. The time scale of the measurement is important; no redox reaction was allowed on the cyclic voltammetry time scale, but electron transfer did occur on the time scale of the potential difference experiment. The fact that changing pH did not
affect the cyclic voltammetry of the aqueous methyl viologen system suggests that the state of ionization of the surface acid species does not play a role in the electron transfer mechanism.

The kinetic barrier to electron transfer in acetonitrile is apparently less than in water because electron transfer occurs on the cyclic voltammetry time scale in the organic system. This suggests that acetonitrile is able to better penetrate the monolayer structure and improve the diffusion of charge through the monolayer.

Titration of the monolayer surface with both contact angle and IRRAS monitoring of the ionization state of the carboxylic acid were in excellent agreement. IRRAS measurements were faster and more structurally informative.
Chapter 5  Summary

The combination of ellipsometry, goniometry, XPS and IRRAS information provided evidence for the liquid-like packing of hexanethiol, 9-mercaptopnonanenitrile, and 11-mercaptoundecanoic acid and for the crystalline packing of dodecanethiol and octadecanethiol on gold. Orientation of chain-terminating groups was also determined by using these methods.

IRRAS and goniometry monitored titrations were in excellent agreement, and the IRRAS method was demonstrated to be faster, less prone to operator bias, and more structurally informative.

Electrochemical studies provided a hypothesis for the mechanism of electron transfer through the monolayers studied. Evidence for a kinetic barrier to electron transfer supports our hypothesis of charge diffusion through the films. Other studies have proposed that electron transfer occurs by electron tunnelling through the methylene chain or occurs primarily at defect sites in monolayers. Our data do not support those interpretations. Electrochemical studies also provided evidence that acetonitrile is more disruptive to the monolayer structure than is water.

PM-IRRAS studies on octadecanethiol monolayers in contact with solvents also support the hypothesis that acetonitrile is more disruptive than water to the surface structure. The
organic solvent had a greater effect on the orientation of the methylene chains than did water. Both solvents affected the orientation of the terminal methyl group.

Simultaneous PM-IRRAS and electrochemical experiments provided an explanation for the more facile electron transfer through the monolayers in acetonitrile. The PM-IRRAS results support a scenario for the penetration of solvated ions into the monolayer structure. PM-IRRAS results for the aqueous system do not provide support for solvated ion penetration in that medium.

The results of these studies, while not conclusive, allow speculation about the mechanism of electron transfer through the alkanethiol films on gold studied here. The mechanism appears to involve charge transport into the monolayer by acetonitrile-solvated ion penetration. Acetonitrile is apparently able to 'solvate' some tail portion of the chain through dispersive interactions and to carry charge-transporting ions closer to the gold surface. Water does not allow significant charge transport through the films studied because it does not penetrate the film's structure to the same extent as acetonitrile. Water cannot, therefore, carry solvated charge-transporting ions close enough to the gold surface to allow electron transfer through the films.

The work presented here does not provide evidence for how many methylene units in long chain monolayers have been
disrupted and, does not, therefore, allow speculation about how close to the gold surface the solvated ions have to penetrate in order for electron transport to occur. Modelling studies, which predict the infrared spectra of monolayers with variously disrupted configurations, would be beneficial in providing a more complete structural picture of the monolayers in different solvent environments. In addition, investigations on the in situ behavior of films with carbonyl or electrochemical functionalities at varying distances from the gold surface would provide further experimental support for the results of this study.
References


Vita

Marilyn Rose Gatin was born on December 18, 1959 and raised in Whitewood, Saskatchewan, Canada. Upon graduation from high school in 1977, Marilyn attended the University of Saskatchewan in Saskatoon, Canada as a psychology major. After a two and a half year formal educational respite, Marilyn returned to the University of Saskatchewan to study chemistry. She received her B.Sc.(Honours) degree in Chemistry as Marilyn O'Grady in 1984 from the University of Saskatchewan in Saskatoon, Canada. Her undergraduate thesis investigated the influence of the solution environment on the fluorescence behavior of proteins. After graduation, Marilyn was employed by Agriculture Canada at the Saskatoon Research Station where she worked on the development of methods for the near infrared analysis of oilseed products.

Marilyn joined the doctoral program at Virginia Polytechnic Institute and State University in November 1987 and was involved in a number of projects during her tenure there. She performed infrared microscopic analysis of petroleum fluid inclusions in geological samples for which she won a Microbeam Analysis Society Distinguished Scholar Award in 1989. Marilyn was involved in research into the nature of molecular interactions at alumina-based liquid chromatographic surfaces through FTIR, ultraviolet and Resonance Raman spectroscopies, and she has studied thin organic films at the
air-water interface through the use of Langmuir film balance and Raman microscope methods. Her doctoral research, under the direction of Mark R. Anderson, involved in situ spectro-electrochemical analysis of thin organic films on gold surfaces. She received the 1991 FACSS Tomas Hirschfeld Student Award for her doctoral research. She completed the requirements for the Ph.D. in July of 1992 as Marilyn Gatin.

Marilyn has accepted employment with Boehringer-Mannheim Corp. in Indianapolis, IN.

104