Surface Morphology and Electronic Structure of Methyl-Terminated Alkanethiol Self-Assembled Monolayers and Solid Water Films

by

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ABSTRACT

SURFACE MORPHOLOGY AND ELECTRONIC STRUCTURE OF METHYL-TERMINATED ALKANETHIOL SELF-ASSEMBLED MONOLAYERS AND SOLID WATER FILMS

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This thesis is an investigation of surface morphology and electronic structure of self-assembled monolayers (SAMs) and solid water films deposited on these SAMs using metastable impact electron spectroscopy (MIES) and infrared reflection-absorption spectroscopy (IRRAS). MIES uses electronically excited slow helium atoms which interact exclusively with the outermost surface layer. The results suggested that in the SAMs containing an odd number of carbon atoms the molecular orbitals localized on the terminal methyl groups are more exposed at the surface compared to those with an even number of carbon atoms. It was also established that solid water films are more uniform on a SAM substrate containing an odd number of carbon atoms. Thermal transformation of amorphous solid water to polycrystalline ice was also observed. MIES suggested that the molecular orbital of water attributed to the lone pair on the oxygen atom became less accessible at the surface upon the transformation.
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CHAPTER 1

SAM – Self-assembled monolayer
XPS – X-ray photoelectron spectroscopy
UPS – Ultraviolet photoelectron spectroscopy
IRRAS – Infrared reflection-absorption spectroscopy
AES – Auger electron spectroscopy
STM – Scanning tunneling microscopy
AFM – Atomic force microscopy
MIES – Metastable impact electron spectroscopy
MO – Molecular orbital

CHAPTER 2

SPR – Spin polarized resonance
SERS – Surface enhanced Raman spectroscopy
SFG – Sum frequency generation
\( \alpha \) – Molecular tilt angle of alkanethiols on Au(111)
\( \beta \) – Angle of rotation of the carbon backbone about the molecular axis in alkanethiols on Au(111)
\( \chi \) – Angle of precession which defines the tilt direction in alkanethiols on Au(111)
\( a \) – Lattice parameter of Au(111)
\( \theta \) – Contact angle
\( \gamma_{SV} \) – Solid-vapour interfacial free energy
\( \gamma_{LV} \) – Liquid-vapour interfacial free energy
\( \gamma_{SL} \) – Solid-liquid interfacial free energy
TPD – Temperature programmed desorption
DC – Direct current
RI – Resonance ionization
AN – Auger neutralization
\( He^* \) – Metastable helium atom
\( M \) – Target metal surface
$E_k$ – Kinetic energy of an electron
$E^*$ - Internal energy of a metastable helium atom
$\Phi$ – Work function of a metal surface
PI – Penning ionization
$IP$ – Ionization potential
UV – Ultraviolet
$P_I$ – Probability of Penning ionization
$EED$ – Exterior electron density
$\phi_i$ – Molecular orbital involved in Penning ionization process
$r$ – van der Waals radius of an atom in the molecule
$\Omega$ – Region outside the repulsive molecular surface
$R$ – Ratio of the MIES spectral integral from 5.6 to 6.6 eV to the integral from 3.2 to 5.6 eV
$I_0$ – Incident infrared beam intensity
$k$ – Absorption coefficient
$n$ – Refractive index of a medium
$R_s$ – Reflected intensity of $s$-polarized radiation
$R_p$ – Reflected intensity of $p$-polarized radiation
$d_s$ – Phase shift of $s$-polarized radiation upon reflection
$d_p$ – Phase shift of $p$-polarized radiation upon reflection
$\varphi$ – Angle of incidence
$E_{ip}$ – Electric field due to the incident $p$-polarized light
$E_{is}$ – Electric field due to the incident $s$-polarized light
$E_{rp}$ – Electric field due to the reflected $p$-polarized light
$E_{rs}$ – Electric field due to the reflected $s$-polarized light
$d^+$ – Symmetric CH$_2$ stretching vibration
$d^-$ – Asymmetric CH$_2$ stretching vibration
$r^+$ – Symmetric CH$_3$ stretching vibration
$r^+_F$, FRC – Fermi resonance splitting component of the symmetric CH$_3$ stretching vibration
$r_{a,b}$ – Asymmetric CH$_3$ stretching vibrations
$\parallel$ - Parallel
$\perp$ - Perpendicular
ip – In plane
op – Out of plane

CHAPTER 3

TOA – Time of arrival
UHV – Ultrahigh vacuum
HEA – Hemispherical energy analyzer
$r$ – Radius of the electron-emitting circle at the sample
$r_p$ – Radius of the image at the analyzer entrance slit
$\theta$ – Electron cone semiangle at the sample
$\alpha$ – Electron cone semiangle at the analyzer slit
$E$ – Kinetic energy of electron at the sample
$E_p$ – Kinetic energy of electron at the analyzer slit
$V_{1,2}$ – Potentials applied to the two concentric hemispheres of the HEA
$R_{1,2}$ – Radii of the two concentric hemispheres of the HEA
$R_0$ – Radius at which electrons enter the analyzer
$V_0$ – Potential experienced by electrons at radius $R_0$
$k$ – Spectrometer constant
$\delta \alpha$ – Angle to the tangential direction
$w_1$ – Width of the entrance slit
$w_2$ – Width of the exit slit
CAE – Constant analyzer energy
MCT – Mercury Cadmium Telluride

CHAPTER 4

C16 – Hexadecanethiol
C15 – Pentadecanethiol
C7 – Heptanethiol
C9 – Nonanethiol
C11 – Undecanethiol
C8 – Octanethiol
C10 – Decanethiol
C12 – Dodecanethiol
C14 – Tetradecanethiol

CHAPTER 5

ASW – Amorphous solid water
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CHAPTER 1

INTRODUCTION

1.1 Motivation

The electronic structure and morphology of a surface determine how the surface interacts with the surrounding medium. For example, ligand-receptor interactions in a cell membrane which is a naturally occurring surface regulate transport of molecules across the membrane, sensing, cell growth, division and apoptosis. Man-made biological surfaces are used for drug testing and delivery; as biosensors and materials for contact lenses; artificial tissues and implants. The latter rely on binding of the protein from the surrounding medium to the surface of the synthetic material which in turn depends on the structure and morphology of the surface. Biosensors often contain polymer film materials with unique wetting properties, which are also used as various coatings and lubricants. Understanding how the surface of these polymer films interacts with water allows tailoring their wetting behaviour for various applications.

Direct investigations of the structure and morphology of compositionally complex surfaces are difficult and benefit from having simpler models with more defined and controllable structures. As a result, self-assembled monolayers (SAMs) comprised of small organic molecules, such as alkanethiols, have gained considerable popularity as simpler models for biological interfaces and polymer films. SAMs possess a number of characteristics that make them suitable models for such complex organic surfaces. They are relatively easy to prepare since the molecules spontaneously arrange on the substrate to form a well-ordered structure, and they can be functionalized with various organic groups. SAMs have been extensively analyzed using traditional techniques such as XPS, UPS, IRRAS and AES. However, these techniques have their limitations when it comes to the analysis of the surface structure since photons and
electrons penetrate several atomic distances into the sample, while the outermost surface layer of a SAM is only several Ångströms deep. As a result, it is exceedingly difficult to distinguish between the signal originating from the outermost surface and that from the film bulk. Scanning probe microscopy techniques allow imaging the surface topography, but interpretation of the images can be challenging. In addition, the probing tip used in STM and AFM can also physically damage the SAM. With these concerns in mind, one of the techniques we used in our work was Metastable Impact Electron Spectroscopy (MIES). The principal idea behind MIES was first described by Penning in 1927. It involves a collision between an electronically excited metastable noble gas atom and a target molecule, which leads to emission of an electron. Analysis of the kinetic energy distribution of the ejected electrons can provide information about the electronic structure of the surface. Due to their low kinetic energies which in this work range from 50 to 300 meV, metastable atoms do not penetrate into the bulk of the sample and selectively interact with the electron density of the outermost surface layer which makes them a suitable probe of surface composition and morphology. However, interpretation of MIES data can be very challenging due to the lack of abundant comparative literature since MIES is not commercially available. As a result, MIES is not widely used. For this reason, IRRAS was used as a secondary technique with MIES. The orientational information available from IRRAS and the nature of the outermost exposed MOs from MIES unveil a more complete picture of the SAM surface structure.

This work is comprised of two main independent objectives, both involving the combined approach of IRRAS and MIES. The first objective was to probe the structural differences in the outermost surface layer of SAMs comprised of alkanethiols with even and odd numbers of carbon atoms, as well as how their structure is correlated with temperature. The second objective
was to investigate the interactions of solid water films with SAMs comprised of CH$_3$-terminated alkanethiols with an even and odd number of carbon atoms. Initial deposition of water films at cryogenic temperatures yields an amorphous solid structure which crystallizes upon heating. In this part of the project our objective was to investigate how the nature of the molecular orbitals exposed at the surface may change when the as-deposited amorphous water film undergoes thermally-induced crystallization.

1.2. Scope of the thesis.

This work consists of 7 chapters. Chapter 1 introduces the research topic and the motivation behind it. Chapter 2 opens up with in-depth background information about SAMs, their formation, structure and reviews of the relevant previous work in the literature. Theoretical principles behind MIES and IRRAS are also discussed in this chapter. Chapter 3 provides experimental procedures for the preparation of SAMs and the gold substrates. The description and schematics of the instrumental set-up and all of its components are also given in this chapter. Chapter 4 discusses the results obtained from the MIES and IRRAS investigations of a series of SAMs comprised of alkanethiols with even and odd numbers of carbon atoms. Chapter 5 examines deposition of water on hydrophobic (CH$_3$-terminated) alkanethiol SAMs as probed by MIES and IRRAS. Summaries of most important findings are provided at the end of Chapters 4 and 5. Chapter 6 summarizes the results and conclusions in this work and discusses potential future studies and extensions of this research project. Finally, Chapter 7 provides a listing of all references used in this thesis.
CHAPTER 2
BACKGROUND INFORMATION

2.1 Self-Assembled Monolayers

The term “self-assembly” refers to spontaneous arrangement of molecules on a solid substrate. This phenomenon was first observed by Zisman and Bigelow in 1946 and involved spontaneous formation of alkylamine monolayers on platinum. Improvements in the vacuum technology during the 1960s and 1970s opened up a new chapter in surface science, allowing for investigations of SAM structure and properties using traditional surface analysis techniques. The early research on self-assembled monolayers (1983-1993) focused on the adsorption of organosulfur compounds (alkanethiols RSH, dialkyl sulfides RSR’, dialkyl disulfides RSSR’) from solution or vapour phase onto metal substrates, mainly gold, silver, and to a lesser extent copper, iron, nickel, and platinum. The characteristics of gold that make it the substrate of choice for alkanethiol SAMs include the relatively easy preparation of the highly ordered Au(111) phase, as well as its inertness towards atmospheric oxygen, the latter being important for ambient pressure studies and applications. In addition, alkanethiols form a strong sulfur-gold bond (~210 kJ/mol), displacing any contaminants on the gold surface. From the instrumental point of view, gold substrates are commonly used for such surface analysis techniques as IRRAS, SPR spectroscopy, SERS and ellipsometry. Finally, cells can attach to gold substrates and function without any evidence of toxicity, which is important for applications of SAMs as biological interfaces.
2.1.1 SAM growth from solution phase

Preparation of SAMs from solution phase is experimentally easier and as a result, more common than from the gas phase \(^{24}\). The substrate is typically immersed in alkanethiol solution (10-1000 µM), with solvent choice depending on the nature of thiol molecule. Adsorption times vary, from 2-12 hours being sufficient to form a well-ordered film in the case of longer alkanethiols, and up to 24 hours for shorter chains and certain endgroup functionalities \(^{23,24}\).

It has been found that SAM formation occurs in a stepwise fashion, with each step having a different time scale. During the initial step which is driven by the formation of the gold-thiolate bond and occurs within several minutes, 80-90% of the coverage takes place \(^{25-27}\). STM and AFM studies of SAM growth have also suggested formation of a physisorbed lying-down phase prior to the chemisorptions step \(^{28-30}\). Real-time observation of this phase is normally difficult due to the high rate of the chemisorption events but turned out to be possible in submicromolar solutions. Thus, the initial step in SAM formation has been proposed to consist of physisorption of thiol molecules followed by rapid chemisorption and formation of the gold-thiolate bond which can be represented as \(^{23}\)

\[
CH_3(CH_2)_nSH + Au \rightarrow (CH_3(CH_2)_nSH)_{phys}Au \quad 1(a)
\]

\[
(CH_3(CH_2)_nSH)_{phys}Au \rightarrow CH_3(CH_2)_nS - Au + \frac{1}{2} H_2 \quad 1(b)
\]

It should also be mentioned that the exact mechanism of scission of the S-H bond as well as the fate of the hydrogen atom are not well understood. In terms of the kinetic considerations, the rate of this step decreases with increasing alkanethiol chain length, presumably due to their reduced mobility compared to shorter chains \(^{25,27}\). In a study by Karpovich and Blanchard \(^{31}\) the rate of this step was also found to increase with the solution concentration.
The transition from the lying-down phase to the standing-up dense phase will take place if there are significant lateral van der Waals interactions between the alkanethiol chains which are 4-8 kJ/mol per CH$_2$ unit $^{32}$. In general, the transition between the lying-down and standing up phases is a complex interplay between alkanethiol-gold and alkanethiol-alkanethiol interactions, the latter becoming more dominant with increasing chain length.

The subsequent steps in the self-assembly process occur at much slower rates and involve re-organization of the adsorbed thiol molecules. The self-assembly process of docosanethiol (CH$_3$(CH$_2$)$_{21}$SH) was investigated by Himmelhaus and co-workers using SFG $^{33}$. They found that the initial fast step was associated with chemisorption of the sulfur headgroup to the substrate, progressing with a rate constant of 2500-3000 L mol$^{-1}$ s$^{-1}$. The second step was found to be 3-4 times slower than the first and involved straightening of the alkyl chains. The time scale of the third step was 35-70 times slower than that of the second step, and during this step reorientation of the terminal methyl groups took place.

2.1.2 Structure of alkanethiol SAMs on Au(111)

Alkanethiol SAMs on Au(111) were first prepared by Nuzzo and co-workers in the early 1980s and these initial studies also established major aspects of the SAM structure $^{34,35}$. Orientation of an alkanethiol molecule in a well packed monolayer is illustrated in Figure 2.1, and is defined by three angles: the molecular tilt angle ($\alpha$), the angle of rotation of the carbon backbone about the molecular axis ($\beta$), and the angle of precession ($\chi$) which defines the tilt direction and is derived from the projection of the inclination plane on the substrate plane. The typical values for these three angles for alkanethiols on Au(111) are 30°, 55° and 14°, respectively $^{34,35}$. Structure of alkanethiol SAMs with respect to the Au(111) surface involves formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer in which the distance between the two nearest
alkanethiols is $\sqrt{3}a$, where $a$ is the lattice parameter of Au(111), rotated by $30^\circ$. A secondary $c(4 \times 2)$ superlattice defined by the alternating orientation of the alkanethiol chains has also been observed. The schematics of both of these structures are shown in Figure 2.1(b). It should be noted that despite the common description of SAMs as an ordered surface, various types of defects, such as missing rows, disordered regions and vacancy Au islands may form in the process of self assembly.

**Figure 2.1.** Schematic representation of alkanethiol SAMs on Au(111): (a) side view of a single molecule, (b) top view of the surface showing the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer (solid line) as well as the $c(4 \times 2)$ superlattice (dashed line) and the orientation of the alkanethiol chains (wedges). The dimensions given are expressed in terms of the Au(111) lattice parameter $a$.

### 2.1.3 Even-odd effect in alkanethiol SAMs on Au(111)

The consequence of the $30^\circ$ tilt angle for alkanethiols on Au(111) is the difference in the orientation of the terminal group depending on whether the molecule contains an even or an odd number of carbon atoms. This is known as the odd-even effect and is illustrated in Figure 2.2. SFG investigation by Nishi and co-workers has established that the angle between the
terminal C-C bond and the surface normal is 27° for chains with an even number of carbon atoms and 58° for odd \(^{39}\). The difference in the terminal methyl group orientation between odd and even alkanethiol SAMs was also demonstrated by contact angle measurements for methylene diiodide and nitrobenzene \(^{40}\). Larger contact angles, and therefore, lower wettability, were observed for even chain alkanethiols, since their surface is mainly composed of methyl groups. In contrast, methyl groups in odd alkanethiols are tilted away from the surface normal, exposing more of the underlying methylene groups which have greater attractive dispersive contacts with the area of the droplet, lowering the contact angle \(^{40}\). Interestingly enough, no significant dependence of the contact angle on the alkanethiol chain parity was observed for water, at least on a macroscopic level.

Understanding the odd-even effect in alkanethiol SAMs is crucial for mechanistic studies of formation and properties of various organic films on solid surfaces, since it has implications for the differences in chemical reactivity, electronic properties and physical behaviour, such as wettability and friction \(^{40-43}\).

**Figure 2.2.** The difference in the methyl group orientation between alkanethiols with an even and odd numbers of carbon atoms on Au(111).
2.2 Water films on organic surfaces

Interactions between water molecules and heterogeneous surfaces are complex and are not completely understood \(^{44}\). This is particularly relevant for organic surfaces, which are typically less ordered and more prone to damage than crystalline inorganic surfaces. As a result, organic surfaces often cannot be studied using diffraction and radiation-based techniques. One alternative way of assessing the macroscopic level interactions between the surface and water is measurement of the contact angle of water at the surface \(^{36}\), as shown in Figure 2.3.

![Figure 2.3. Schematic of a droplet on a solid surface, indicating the relationship between the parameters which define the contact angle \(\theta\): \(\gamma_{SV}\) is the solid-vapour interfacial free energy; \(\gamma_{LV}\) is the liquid-vapour interfacial free energy; \(\gamma_{SL}\) is the solid-liquid interfacial free energy.](image)

The contact angle represents the thermodynamic equilibrium between the liquid, vapour and solid phases. As the droplet expands on the surface, the areas of the liquid-vapour and the liquid-solid interfaces increase, while the area of the solid-vapour interface decreases. The changes in the areas are accompanied by changes in the interfacial free energies which eventually equilibrate and the expansion stops. Mathematically, the relationship between the changes in the interfacial free energies is expressed in Young’s equation:

\[
\gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos \theta = 0 \tag{2.2.1}
\]

Contact angles of water are very responsive to the polarity of the outmost terminal surface groups and details of the surface structure \(^{36,45,46}\). As a result, they offer a convenient way of characterizing surfaces as hydrophobic or hydrophilic. For example, the contact angle of water
on the hydrophilic surfaces such as those containing carboxyl or hydroxyl groups, can be less than \(20^\circ\) \(^{45}\), while on hydrophobic surfaces such as those composed of methyl groups, the contact angle can be as large as \(110^\circ\) \(^{45,46}\).

Despite the usefulness of contact angles in describing the interaction between water and a solid surface, they are only applicable to macroscopic droplets. Microscopic-scale interactions of water films at an interface are not well established. This is particularly true for more disordered organic surfaces since most studies focus on well-defined crystalline surfaces, such as metals and metal oxides \(^{47}\). Investigations of water adsorption on organic surfaces are traditionally performed using IRRAS to monitor characteristic water vibrations, as well as TPD for the desorption studies. For example, Dubois and co-workers investigated adsorption of water on alkanethiol SAMs terminated in hydrophobic (-CH\(_3\)) and hydrophilic (-COOH) functionalities \(^{35,48}\). Engquist and co-workers focused on the interactions between D\(_2\)O and CH\(_3\)- and OH-terminated alkanethiol SAM surfaces \(^{49,50}\). Their TPD experiments suggested that the desorption energies for water on the CH\(_3\)- and OH-terminated substrates were 9.8 and 10 kcal/mol, respectively. Based on such small difference in the desorption energies, the authors concluded that adsorbate-adsorbate interactions dominate those between the adsorbate and the substrate. Cluster formation was predicted for water on both CH\(_3\)- and OH-terminated surfaces, with the possible difference of flat two-dimensional water clusters forming on the OH-terminated SAM as opposed to three-dimensional clusters on the CH\(_3\)-terminated SAM. In addition, these types of experiments involve deposition of water films at cryogenic temperatures (< 140 K) which leads to formation of a metastable system that will undergo thermal transformations in order to achieve more thermodynamically stable structure. It was found that water deposited on an alkanethiol SAM at 80 K forms amorphous solid water and will begin transformation to polycrystalline ice.
when heated to 110 K in the case of hydrophobic (CH₃-terminated) surface, while for a hydrophilic (OH-terminated) surface this transformation will not take place until 145-150 K. However, all of the previous investigations of solid water films involve probing of its bulk structure, while the structure of the outermost surface layer remains poorly understood.

2.3 Metastable Impact Electron Spectroscopy

2.3.1 Metastable helium

Helium gas is commonly used as the source of metastable atoms due to the high internal energies of the helium metastables. The two lowest energy excited states of helium are $2^1S_1$ and $2^3S_1$ which have energies of 20.6 and 19.86 eV above the $1^1S_0$ ground state, respectively, as shown in Figure 2.4. The transition from $1^1S_0$ to $2^3S_1$ is spin forbidden but can occur via electron collisions in a discharge, resulting in a long lifetime of the $2^3S_1$ state (7.87×10³ s), while the $2^1S_1$ state has the lifetime of 1.97×10⁻² s. These long lifetimes are the basis of the “metastable” designation.

In gaseous helium excited via a DC discharge which is the type of metastable source used in this work, the fraction of the $2^3S_1$ helium metastable state constitutes approximately 90% of all excited species, while that of the $2^1S_1$ is only 10%. As a result, the more abundant $2^3S_1$ state is typically used in MIES.
2.3.2 Interactions of metastable helium with metal surfaces and molecules

Interaction of metastable helium atoms with a clean metal surface whose Fermi level lies below the 2s helium level occurs via Resonance Ionization (RI) followed by Auger Neutralization (AN)\(^8\), as illustrated in Figures 2.5 (a\(_1\)) and (a\(_2\)). In the process of RI, the 2s helium electron will tunnel into an empty state of the metal, forming a helium ion\(^8\):

\[
He^* + M \rightarrow M^- + He^+ \quad \text{(RI)}
\]

where \(He^*\) is the metastable helium atom, and \(M\) is the target metal surface.
The ion continues to approach the surface, and if energetics allow, an electron from the surface will tunnel into the 1s helium hole, resulting in Auger Neutralization of the cation and ejection of another electron from the metal target:\(^8\):

\[
M^- + He^+ \rightarrow M^+ + He + e^- \quad \text{(AN)}
\]

The kinetic energy of electrons ejected upon the interaction with a metal surface will have a range from 0 eV to the maximum kinetic energy, \(E_{k,\text{max}}\) which is given by:\(^8\):

\[
E_{k,\text{max}} = E^* - 2\Phi \quad (2.3.1)
\]

where \(E^*\) is the internal energy of the metastables (19.86 eV in the case of the helium \(2^3\)S\(_1\) state) and \(\Phi\) is the metal work function. Most metals have work functions of 4-5 eV, such that the electron energy distribution often ranges from 0 to about 10 eV.

In the case when a molecular adsorbate layer is present on the surface, metastable helium atoms will interact with the adsorbed molecules via Penning Ionization (PI) because the access to the metal surface is blocked\(^8\). In this process, shown in Figure 2.5 (b), an electron from one of the molecular orbitals of the adsorbate will tunnel into the He\(^*\) 1s hole, while the electron from the He\(^*\) 2s orbital will be ejected. The kinetic energy of the electrons generated by PI will have the value of:

\[
E_k = E^* - IP \quad (2.3.2)
\]

where \(E^*\) is the energy of the metastable atom, and \(IP\) is the ionization potential of the molecular orbital involved in PI process\(^8\). It should be noted that in MIES, kinetic energy of the ejected electrons is found in the analogous manner to UPS, and furthermore, the two techniques are considered as complementary, especially since UV radiation is also produced in the metastable source and the energy of the photons typically used is 21.2 eV (He(I) line).
Figure 2.5. Schematic depiction of (a₁) Resonance Ionization, (a₂) Auger Neutralization, and (b) Penning Ionization processes.

The probability of PI for a given molecular orbital depends on its overlap with the He* 1s orbital. Thus, the probability of PI, $P_{\text{PI}}$, is proportional to the Exterior Electron Density (EED) which essentially represents the degree of exposure of the molecular orbital $\phi_i$ in the region $\Omega$.
outside the repulsive molecular surface which is defined by the van der Waals radii of the atoms in the molecule $^{8,54}$:

$$P_i \propto (EED)_i = \int_{\Omega} |\phi_i(r)|^2 dr \quad (2.3.3)$$

Consider a molecule with two anisotropic molecular orbitals, A and B that have similar small electron densities. In the gas phase these molecules, schematically illustrated in Figure 2.6 (a), will have random orientations, which will tend to average out the probabilities of PI for the two molecular orbitals $^8$. This in turn leads to comparable intensities of the MIES spectral bands due to the two orbitals in this simplified model. A UPS spectrum of the same species is included for comparison, and as can be seen, in the gas phase, UPS and MIES spectra are very similar, provided similar energies of the UV radiation and metastable atoms.

The situation is different for adsorbed molecules, where the orbital anisotropy is preserved, as shown in Figure 2.6 (b) with orbital B oriented towards the incoming metastable atoms while orbital A is more shielded. The resulting MIES spectrum reflects this orientation, where the intensity of the band due to the ionization of orbital A is now lower than that of orbital B $^{8,54}$. This orientation dependence of the band intensities is not present in the UP spectrum, reflecting the difference in the mechanisms operating in MIES and UPS, that is, greater penetration depth of photons as compared to metastables which selectively interact with the topmost surface layer.
Figure 2.6. Dependence of PI probability on the orientation of the molecules and the resulting MIES and UPS spectral band intensities for (a) gas-phase molecules, and (b) surface species.

2.3.3 MIES of alkanethiol SAMs

The first MIES spectra of alkanethiol SAMs were obtained by Morgner and co-workers\textsuperscript{55,56}. Their work focused on investigation of the standing-up molecular orientation of several alkanethiol chain lengths (C8, C9, C10, C12, C16 and C18) adsorbed on silver and gold substrates, and lying-down orientation of hexadecane on graphite. Table 2.1 summarizes the peak assignments for the MIES spectra of alkanethiols. The authors chose to present the spectra in terms of the electron energies, from which the ionization potentials ($IP$) of the MOs involved in the interaction with metastable helium can be found as

\[ IP = E^* - E_k \]  

(2.3.4)
where $E^*$ is the internal energy of metastable helium (19.86 eV) and $E_k$ is the kinetic energy of the electron ejected upon interaction of metastable helium with the MO. The MO assignment was done on the basis of work by Ozaki and Harada $^{57}$ who investigated Penning ionization of n-alkanes on graphite and correlated the observed spectral features with \textit{ab initio} MO calculations.

\textbf{Table 2.1.} Major peaks observed in the MIES spectra of hexadecane on graphite and nonanethiol on Au(111) and the assignments of their molecular orbital origin $^{55}$.

<table>
<thead>
<tr>
<th>Electron energy (eV)</th>
<th>Orbital assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>$\sigma$ 2s (C-C backbone)</td>
</tr>
<tr>
<td>5</td>
<td>$\pi$ 2p (C-H in the methylene groups)</td>
</tr>
<tr>
<td>9.8</td>
<td>$\pi$ 2p (C-H in the methylene groups)</td>
</tr>
<tr>
<td>Nonanethiol</td>
<td></td>
</tr>
<tr>
<td>6.25</td>
<td>$\sigma$ 2p (C-H in the methyl group)</td>
</tr>
<tr>
<td>10.8</td>
<td>$\sigma$ 2p (C-H in the methyl group)</td>
</tr>
</tbody>
</table>

The major differences in the MIES spectra of hexadecane on graphite and alkanethiols on Au(111) and Ag(111) are due to the different molecular orbitals being exposed in the two cases. For the flat-lying hexadecane molecule, the main peaks observed in the spectrum are due to the interaction of metastable helium atoms with the $\sigma$-type MOs (2.3 eV) which are localized along the C-C backbone and are composed of the 2s C orbitals, as well as the $\pi$-type MOs (5 and 9.8 eV) with mainly C 2p and H 1s character and associated with the C-H bond in the methylene groups. In contrast, for the alkanethiol SAMs in which the molecules are standing upright, the major spectral peaks arise from the interaction of the metastable helium atoms with the $\sigma$-type
MOs (6.25 and 10.8 eV) which are composed of the C 2p and H 1s orbitals of the terminal methyl groups. Due to the surface sensitivity of metastable atoms, the peaks due to the C-C and C-H methylene bands are strongly suppressed because these orbitals are less accessible in the standing-up molecular orientation.

Comparing the MIES spectra of different alkanethiols, the authors observed that with increasing chain length, the position of the peak due to orbitals of the terminal methyl groups at ~6.25 eV shifted to lower energies, and the intensity in the 4.5-5 eV region increased. This was explained on the basis of increasing abundance and less effective shielding of the methylene groups in the case of longer alkanethiols due to the higher number of gauche defects near the chain terminations. Further quantification of the spectral differences between the alkanethiols is expressed as the ratio R which is obtained by dividing the integral from 5.5 to 6.5 eV by the integral from 3.7 to 5.5 eV. As a result, it was found that R reaches its highest value in the case of nonanethiol and decreases with increasing chain length. The authors suggest that the R value may be dependent not only on the chain length but also on the even-odd nature of alkanethiols, however only one odd alkanethiol (nonanethiol) was investigated in that work.

Another MIES study was carried out by Aoki and co-workers and involved methylthiol, ethylthiol and propylthiol adsorbed on Pt(111) in monolayer and multilayer coverage 58. For the monolayer coverage, they observe spectral peaks due to the emission from the orbitals associated with the terminal methyl groups, and to a lesser extent – from the orbitals localized around the methylene groups. Based on this data, the authors concluded that at monolayer coverage the alkanethiol molecules are in a standing-up orientation. When the coverage is increased and multilayers are formed on the surface, emission from the terminal methyl group orbitals is suppressed, while from the methylene orbitals is increased. Two additional peaks are also

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observed in the multilayer spectra which have been assigned to the emission from the $\sigma$ C-C orbital (at ~6.5 eV binding energy), and non-bonding orbital localized on the sulfur atom (at ~4 eV binding energy). The assignments were performed on the basis of \textit{ab initio} calculations.

\textbf{2.4 Infrared Reflection-Absorption Spectroscopy}

Infrared Reflection-Absorption Spectroscopy (IRRAS) is a surface analysis technique, commonly used to determine the structure and composition of organic films. Theoretical principles behind IRRAS are discussed in the section below.

\textit{2.4.1 Infrared spectroscopy from surfaces}

Molecules can become vibrationally excited when their dipole moment interacts with the electric field component of infrared radiation. In the case of molecules adsorbed onto a metal surface, their vibrational excitation will occur via absorption of some fraction of the infrared radiation reflected from the surface. Figure 2.7 depicts the electric fields established at a metal surface for the two components of radiation: the $s$-polarized component (perpendicular to the plane of incidence) and the $p$-polarized component (parallel to the plane of incidence). The $s$-polarized component of radiation undergoes a 180° shift upon reflection at the surface, so the incident and the reflected electric vectors sum up to zero. Since there is essentially no electric field parallel to the surface, vibrational modes of the adsorbed molecule can only interact with the $p$-polarized component. This in turns means that an infrared-active vibrational mode of a molecule adsorbed onto a metal surface must have a component of the transition dipole that is perpendicular to the surface. This is known as the \textit{surface selection rule} \cite{59}. 

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Reflected intensities at the metal surface for the $s$- and $p$-polarized components can be expressed using Fresnel equations, for the complex index of refraction $\tilde{n} = n + ik$, and assuming that $n^2 + k^2 \gg 1$ (valid for frequencies in the infrared region):

\begin{align}
R_s &= \frac{(n - sec\phi)^2 + k^2}{(n + sec\phi)^2 + k^2} \quad (2.4.1) \\
R_p &= \frac{(n - cos\phi)^2 + k^2}{(n + cos\phi)^2 + k^2} \quad (2.4.2)
\end{align}

\[
\tan \Delta = \tan(d_p - d_s) = \frac{2k \tan \phi \sin \phi}{\tan^2 \phi - (n^2 + k^2)} \quad (2.4.3)
\]

where $R_s$ and $R_p$ are the reflected intensities for $s$- and $p$-polarized light, $d_s$ and $d_p$ are the phase shifts upon reflection, $\phi$ is the angle of incidence and $k$ is the absorption coefficient. Thus, such equations are useful for determining the dependence of reflected intensities on the angle of incidence of infrared radiation. While the reflected intensity in the case of the $s$-polarized component is nearly zero for all angles of incidence, the reflected intensity of the $p$-polarized component strongly depends on the angle of incidence and becomes greatly enhanced at grazing incident angles. This relationship has been established by Greenler on the basis of theoretical calculations as well as experimental evidence.

![Figure 2.7](image)

**Figure 2.7.** Reflection of light at a metal surface. Subscripts $s$ and $p$ indicate $s$- and $p$-polarized light while $i$ and $r$ – incident and reflected electric vectors, respectively.
2.4.2 Fourier Transform Infrared Spectrometer

Most modern IRRAS instruments utilize a Fourier Transform, at the heart of which is an interferometer, first described by Michelson in 1851. In an interferometer, the beam produced by the source is split into two components by the means of a mirror known as the beam splitter. The two components travel different path lengths and are reflected towards the beam splitter by two mirrors, a fixed one and a moveable one. The beams are eventually recombined either constructively or destructively at the detector and the sum of all interferences for all wavelengths is known as an interferogram. Constructive interference gives rise to the maximum value of the interferogram and the position of the moveable mirror at which this occurs is defined as $x=0$. The intensity of the interferogram can be represented as

$$I(x) = \frac{1}{2} I(0) + \int_{-\infty}^{+\infty} I(\bar{\nu}) \cos(2\pi x \bar{\nu}) \, d\bar{\nu} \quad (2.4.4)$$

where $I(\bar{\nu})$ is the intensity at a given frequency and $I(0)$ is the intensity at position $x=0$.

Subtraction of the average intensity of the interferogram, $I(\bar{x})$, from Equation 2.4.4, intensity of the interferogram can be expressed as a function of position $x$:

$$F(x) = \int_{-\infty}^{+\infty} I(\bar{\nu}) \cos(2\pi x \bar{\nu}) \, d\bar{\nu} \quad (2.4.5)$$

The mathematical operation which converts signal intensity as a function of time into a spectrum in which intensity varies with frequency is known as Fourier Transform. Performing a Fourier transform on $F(x)$ yields a spectrum:

$$I(\bar{\nu}) = \int_{-\infty}^{+\infty} F(x) \cos(2\pi x \bar{\nu}) \, dx \quad (2.4.6)$$

There are three main advantages associated with using a Fourier Transform spectrometer compared to a dispersive instrument. The first one, known as the Jacquinot’s advantage, refers
to the greater signal-to-noise ratio in the spectra due to the higher signal measured at the detector. The second, Felgett’s advantage, arises from simultaneous detection of all spectral frequencies which results in fast measurements and allows for collection of multiple interferograms which are then averaged to produce spectra of very high signal-to-noise ratio. Finally, Connes advantage is the result of improved photometric accuracy due to an internal calibration standard, usually a HeNe laser \(^6^1\). This triggers the acquisition of \(F(x)\) at accurately known intervals of \(x\).

### 2.4.3 Infrared spectra of alkanethiol SAMs on Au(111)

The most characteristic bands in the IRRAS spectra of alkanethiol SAMs are the C-H stretching vibrations of the methyl and methylene groups. Due to the 30° tilt angle of alkanethiol molecules on Au(111), both methyl and methylene stretches have some component of dipole moment change perpendicular to the surface which according to the surface selection rule can interact with the \(p\)-polarized radiation. The assignments of the vibrational modes of alkanethiol SAMs on gold were initially performed by Parikh and Allara on the basis of semitheoretical analysis of the infrared spectra of SAMs using electromagnetic wave theory \(^6^2\). The most relevant infrared bands for alkanethiol SAMs on Au(111) are summarized in Table 2.2.
Figure 2.8. Transition dipole orientations of CH$_3$ and CH$_2$ stretches of an alkanethiol on Au(111). Solid lines represent orientations directed in the plane of the CCC backbone, dotted lines – out of the CCC plane.

Table 2.2. Description of the most characteristic vibrational modes in densely packed, well-ordered alkanethiol SAMs on Au(111) at 300 K$^6$.  

<table>
<thead>
<tr>
<th>Peak position (cm$^{-1}$)</th>
<th>Mode description</th>
<th>Direction of the dipole moment change</th>
</tr>
</thead>
<tbody>
<tr>
<td>2851</td>
<td>CH$_2$ symm, d$^+$</td>
<td>ip of CCC backbone plane, ip HCH plane</td>
</tr>
<tr>
<td>2878</td>
<td>CH$_3$ symm, r$^+$</td>
<td>$\parallel$ to C-CH$_3$ bond</td>
</tr>
<tr>
<td>2921</td>
<td>CH$_2$ asymm, d$^-$</td>
<td>$\perp$ to CCC backbone plane</td>
</tr>
<tr>
<td>2935</td>
<td>CH$_3$ symm, FRC, r$_F^+$</td>
<td>$\parallel$ to C-CH$_3$ bond</td>
</tr>
<tr>
<td>2952</td>
<td>CH$_3$ asymm, r$^b$</td>
<td>$\perp$ to CCC backbone plane</td>
</tr>
<tr>
<td>2962</td>
<td>CH$_3$ asymm, r$_b$</td>
<td>ip of CCC backbone plane, $\perp$ to C-CH$_3$ bond</td>
</tr>
</tbody>
</table>

Abbreviations: symm = symmetric, antisym = antisymmetric, ip = in plane, op = out of plane, FRC = Fermi resonance splitting component, $\parallel$ = parallel, $\perp$ = perpendicular.
IRRAS spectra of alkanethiol SAMs are known to reflect temperature dependence of the SAM structure. As the temperature is lowered, the molecules re-orient, eliminating gauche defects which causes the intensities of the d⁺ and r⁺ bands to increase by as much as 75% and shift to lower frequencies by 2-3 cm⁻¹.⁶³
3.1 Metastable helium beamline

Schematic diagram of the MIES system is illustrated in Figure 3.1, and is discussed in detail in the sections below. The instrument consists of four stainless steel chambers: the first three chambers constitute the metastable helium beamline, and in the fourth chamber the sample is analyzed using MIES and IRRAS. For the exact operational parameters, refer to Table 3.1 at the end of the chapter.

![Figure 3.1. Schematic top view of the instrument.](image)

The metastable helium beamline consists of the first three vacuum chambers. The primary (source) chamber is evacuated by an oil diffusion pump (Varian VHS-250, 3700 L/s). The chamber contains the metastable source assembly mounted onto an XY motor stage (plane
perpendicular to the beam) as well as a manually operated Z-stage (in the plane of the beam) which allow optimizing the beam position with respect to the sample. The source assembly includes a quartz nozzle with a ~0.3 mm aperture, and a tantalum rod held inside the nozzle. The Ta rod is ~2 mm in diameter and is sharpened to a 45° point. The aperture in the quartz nozzle is at 1 cm distance (Z-direction) from the stainless steel skimmer. Helium gas is introduced into the nozzle and positive high voltage is applied between the tantalum rod and the skimmer (which is at ground), resulting in a glow discharge in which helium $2^1S_1$ and $2^3S_1$ metastables are formed, as well as He(I) UV radiation. The yield of UV photons produced in the beam is about 10% of that of He* metastables. The discharge is very stable and can run for hours without disruptions.

The beam travels through the aperture in the skimmer into the secondary chamber which is also evacuated by an oil diffusion pump (Varian VHS-6, 2400 L/s). In the secondary chamber the molecular beam is modulated by a chopper wheel whose schematic diagram is shown in Figure 3.2. It is designed to have two large “open” sections which allow for the entire beam to pass through, as well as four slits, approximately 0.25 mm wide which only allow the beam through in short duration pulses (~300 μs).

![Diagram of the chopper wheel](image)

**Figure 3.2.** Schematic diagram of the chopper wheel.
Modulation of the beam intensity by the slit design provides a time-of-arrival (TOA) distribution of the beam, in which He* metastables and the UV photons can be distinguished due to their different travel times to reach the detector.

The intensity of the metastable flux is measured in the secondary chamber as electron current by a stainless steel Faraday cup detector. The detector consists of a 0.5” circle behind a rectangular cup with a 3 mm aperture. This detector can be translated into the beam path for diagnostic purposes. When the gate valve following the secondary chamber is open, metastable helium atoms and UV photons travel into the tertiary chamber. The tertiary chamber is pumped by a turbomolecular pump (Edwards STP-451, 480 L/s) to the pressure of mid-10^{-9} Torr. Here, the intensity of the metastable beam can be measured with another Faraday cup and a channeltron detector, both of which are mounted on an arm that can be rotated in and out of the beam path. This Faraday cup detector consists of a stainless steel 0.45” cylinder with a 0.267” circle as the detector surface.

The time-resolved beam profile is obtained using the channeltron detector (Magnum, model #5901, S/N 35308-13) in combination with a pulse detector/amplifier chip (AmpTek A121, S/N 1415) which is mounted on a PC-121 board (AmpTek). A 25 μm aperture was installed at the channeltron entrance in order to prevent detector saturation. 2.5 kV is applied to the channeltron which operates in the multichannel scaler pulse counting mode. The counts from individual metastable atoms and UV photon are presented in the time-of-arrival form, using a timing signal from the chopper controller. A typical time-of-arrival distribution is shown in Figure 3.3.
Figure 3.3. A typical Time-of-Arrival distribution obtained with the channeltron detector in the tertiary chamber.

The velocity distribution of helium metastables can be obtained by dividing the distance they travel to reach the detector (~0.6 m) by the distribution of their times of arrival. This TOA to velocity transformation can be performed for any of the four metastable peaks in Figure 3.3 by setting the time of arrival of the preceding UV photos as “0”. A typical velocity distribution of He* metastables is shown in Figure 3.4. As can be seen from this distribution, velocities of He* metastables range from 1500 to 4000 m/s.
Figure 3.4. Velocity distribution of helium metastables as determined on basis of the TOF distributions and the distance traveled between the chopper and the channeltron detector (0.6 m).

3.2. UHV (analysis) chamber

3.2.1 Load lock and sample transfer

Samples were mounted on a copper sample holder and secured with two copper straps to provide electrical and thermal contact to the gold film. They were then loaded into the load-lock chamber which is evacuated by a turbomolecular pump. When the pressure in the load lock dropped to mid-$10^{-7}$ Torr, the samples were transferred to the analysis chamber via the transfer rod and mounted into the sample support using a wobble stick. The analysis chamber is evacuated by an ion pump (Varian, 400 L/s).

The sample holder is located on the sample manipulator which consists of a copper stage mounted through the top flange. Sample height and rotation are controlled by moving the copper
stage from the supporting feedthrough. Sample tilt is controlled by an inchworm motor (Burleigh UHVL-0.25). A “well” filled with gallium on the sample support provides a rigid contact when the temperature is below the freezing temperature of Ga (29°C).

3.2.2. Temperature control

The temperature of the sample was measured with Omega thermocouples. The sample was heated by a cartridge heater (Watlow) mounted on the sample manipulator and controlled by the Omega Cyc3200 Autotuning Temperature Controller. Cooling of the sample was achieved by liquid nitrogen cold fingers coming down from the liquid nitrogen cryostat attached to the top flange. All cryogenic temperature experiments were performed at ~109 K, the base temperature of the system.

3.2.3. Hemispherical energy analyzer

The metastable helium beam is introduced into the analysis chamber by opening the second gate valve. The beam strikes the sample surface at approximately 45° angle, and the electrons ejected from the sample upon interaction with the beam are measured as a modulated electron current flow to the sample using a Stanford SR-830 lock-in amplifier. Kinetic energy spectra of the ejected electrons were obtained using a hemispherical energy analyzer (VG 100AX) and in-house custom software for data processing. The schematic of the HEA system is shown in Figure 3.5. Electrons are guided by the transfer lens system which focuses them onto the entrance slit to the analyzer. In addition, the transfer lens retards velocity of the electrons so upon passing through the lens it matches the Pass Energy of the analyzer. The relationship between the kinetic energies of an electron at the sample and at the analyzer slit can be expressed as

30
where \( r \) is the radius of the electron emitting circle at the sample, \( r_p \) is the radius of the image at the entrance slit, and \( \theta \) and \( \alpha \) are the electron cone semiangles at the sample and the slit, respectively. Based on the equation, the ratio \( r_p/r \) represents the magnification of the lens, while the ratio \( E/E_p \) is the retardation ratio of the spectrometer.

The HEA itself consists of two concentric shells of different radii with potentials \( V_1 \) and \( V_2 \) applied to them, respectively. When electrons selected by the transfer lens enter the analyzer at the radius \( R_0 \), they experience a potential \( V_0 \) which is found as \(^6\)

\[
V_0 = V_1 \frac{R_1}{2R_2} + V_2 \frac{R_2}{2R_0} \quad (3.1.2)
\]

Electrons with energy \( eV_0 \) at \( R_0 \) will move in a circular orbit of radius \( R_0 \) between the two hemispheres if the potentials applied to the hemispheres are

\[
V_1 = V_0 \left(3 - \frac{2R_0}{R_1}\right) \quad (3.1.3)
\]

\[
V_2 = V_0 \left(3 - \frac{2R_0}{R_2}\right) \quad (3.1.4)
\]

From the above expressions, the potential between the hemispheres can be found as

\[
V_2 - V_1 = V_0 \left(\frac{R_2}{R_1} - \frac{R_1}{R_2}\right) \quad (3.1.5)
\]

This can be rewritten as

\[
V_0 = k(V_2 - V_1) \quad (3.1.6)
\]
where \( k \) is the spectrometer constant \(^{64}\). Electrons of the correct energy, entering the entrance slit, tangentially to the radius, will focus at the exit slit. If electrons have an energy \( \Delta E \) above the correct energy and make an angle \( \delta \alpha \) to the tangential direction, then the shift in the radial position after transversing at 180° is

\[
\Delta R = 2R_0 \left( \frac{\Delta E}{E} \right) - 2R_0 (\delta \alpha)^2 \quad (3.1.7)
\]

The base resolution of the analyzer is given by

\[
\frac{\Delta E_b}{E} = \frac{w_1 + w_2}{2R_0} + (\delta \alpha)^2 \quad (3.1.8)
\]

where \( w_1 \) and \( w_2 \) are the widths of the entrance and exit slits, respectively \(^{64}\).

Finally, after passing between the hemispheres, electrons are detected at the exit slit using a channeltron detector which is operated in the multichannel scaler mode.
Figure 3.5. Schematic diagram of the hemispherical energy analyzer (adapted from Ref. 64)

In our experiments the analyzer was operated in the Constant Analyzer Energy (CAE) mode, in which the pass energy of the analyzer is held constant, and the transfer lens retard velocities of the electrons to a range accepted by the analyzer.

3.2.4. Residual gas analyzer

The analysis chamber contains a quadrupole gas analyzer (HAL 321, Hiden Analytical) whose purpose is to monitor the partial pressures of the gases in the chamber, as well as the
pressures of the compounds to be deposited on the sample surface during experiments involving deposition.

### 3.2.5. FT-IR spectrometer

IRRAS experiments were performed using a Thermo Nicolet 870 spectrometer. The beam exiting the spectrometer was reflected by two adjustable mirrors and guided through a differentially pumped KBr window on the analysis chamber flange onto the sample at a grazing angle (~85°). The reflected beam was focused by an elliptical mirror onto a liquid nitrogen cooled MCT-A detector (Model FT-IR-16-1.0, Infrared Associates Inc.). The detector signal was processed using OMNIC software provided by the manufacturer. Data acquisition, analysis and presentation of the infrared spectra were performed using custom LabView-based software. Typical parameters for all cases except water deposition were 4 cm\(^{-1}\) spectral resolution, 1.89 m/s mirror velocity, 512 scans. The spectra are presented as absorbance spectra, using a clean Au/mica sample as reference. Water deposition was monitored using IRRAS at 4 cm\(^{-1}\) resolution, 1.89 m/s mirror velocity and 128 scans.

### 3.3. Sample preparation

#### 3.3.1. Au (111)/mica preparation

Au(111) surface was prepared by thermal evaporation of gold onto muscovite mica sheets according to the previously published protocol. Freshly cleaved mica (Axim mica, V2 grade) was placed in a stainless steel vacuum chamber pumped by turbomolecular pump. Mica was heated and held at 300°C for 12 hours prior to deposition in order to degass. ~200 nm of gold (ESPI Metals) was evaporated onto mica from a resistively heated molybdenum boat at a rate of ~0.1 nm/min, followed by annealing the newly deposited film at 300°C for 3 hours under vacuum. Au (111)/mica substrates were stored in a desiccator until use.
3.3.2. Preparation of alkanethiol SAMs on Au (111)/mica

Au(111)/mica substrates were cleaned with sulfochromic acid (chromium trioxide in concentrated H$_2$SO$_4$) in order to remove the organic contaminants, then rinsed with copious amounts of ultrapure water (Milli-Q), followed by the final rinse with methanol and dried under a gentle flow of argon.

SAMs were prepared by immersing the cleaned Au(111)/mica substrate into a 1 mM methanolic alkanethiol solution overnight at room temperature followed by rinsing with methanol and drying under argon. The samples were then mounted onto the sample holder and transferred into the load lock immediately.

Alkanethiols were purchased from: 1-hexadecanethiol (97%, Alfa Aesar), 1-pentadecanethiol (98%, Sigma-Aldrich), 1-tetradecanethiol (98%, Sigma-Aldrich), 1-dodecanethiol (98%, Aldrich Atofina), 1-undecanethiol (98%, Sigma-Aldrich), 1-decanethiol (99%, Sigma-Aldrich), 1-nonanethiol (95%, Sigma-Aldrich), 1-octanethiol (98.5%, Aldrich Atofina), 1-heptanethiol (98%, Alfa Aesar).

3.3.3. Deposition of water films on alkanethiol SAMs

Milli-Q water was dosed into the analysis chamber at 1×10$^{-8}$ Torr partial pressure of water, as monitored by the residual gas analyzer. The deposition as well as desorption were monitored by IRRAS.
Table 3.1. Summary of the operational parameters in the MIES system.

<table>
<thead>
<tr>
<th>Parameter description</th>
<th>Numeric value and units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1’ chamber</strong> Chamber pressure</td>
<td>$10^{-7}$ Torr ($10^{-5}$ Torr when operating)</td>
</tr>
<tr>
<td>He gas inlet pressure</td>
<td>60 psi</td>
</tr>
<tr>
<td>Voltage applied to the Ta rod</td>
<td>-2400 V</td>
</tr>
<tr>
<td>Discharge current</td>
<td>8-9 mA</td>
</tr>
<tr>
<td>Current at the skimmer</td>
<td>4-6 mA</td>
</tr>
<tr>
<td><strong>2’ chamber</strong> Chamber pressure</td>
<td>$10^{-8}$ Torr ($10^{-7}$ Torr when operating)</td>
</tr>
<tr>
<td>Chopper rotation frequency</td>
<td>75 Hz</td>
</tr>
<tr>
<td>Faraday cup bias voltage</td>
<td>+30 V</td>
</tr>
<tr>
<td>Current due to the beam</td>
<td>~2 nA</td>
</tr>
<tr>
<td><strong>3’ chamber</strong> Chamber pressure</td>
<td>$10^{-9}$ Torr</td>
</tr>
<tr>
<td>Faraday cup bias voltage</td>
<td>+30 V</td>
</tr>
<tr>
<td>Current due to the beam</td>
<td>~0.4 nA</td>
</tr>
<tr>
<td>Channeltron voltage</td>
<td>+2400 V</td>
</tr>
<tr>
<td><strong>UHV chamber</strong> Chamber pressure</td>
<td>$10^{-9}$ Torr</td>
</tr>
<tr>
<td>Chamber pressure during H$_2$O deposition</td>
<td>$4\times10^{-8}$ Torr</td>
</tr>
<tr>
<td>Sample current</td>
<td>0.08-0.180 nA</td>
</tr>
<tr>
<td>Metastable helium flux</td>
<td>1$\times10^9$ atoms s$^{-1}$</td>
</tr>
<tr>
<td>Sample bias for MIES</td>
<td>-46 V</td>
</tr>
<tr>
<td>HEA channeltron bias</td>
<td>+2400 V</td>
</tr>
<tr>
<td>HEA HV</td>
<td>5 V</td>
</tr>
</tbody>
</table>
CHAPTER 4

EVEN-ODD EFFECTS IN CH\textsubscript{3} TERMINATED ALKANETHIOL SAMS

4.1. Alkanethiol SAM quality assessment

Due to the limited information available in the literature on the MIES spectra and their interpretation for alkanethiol SAMs, one of the main challenges was ensuring that all samples had comparable quality which is important for their structural analysis. For this reason, IRRAS served as the “gateway” technique which allowed us to decide which samples were well-ordered prior to performing MIES analysis, since the infrared signature of alkanethiol SAMs has been extensively investigated. The decision on sample quality was performed on the basis of IRRAS band intensities and positions, which is described in more detail in the section below.

4.1.1. Alkanethiol SAMs with an even number of carbon atoms

Several different C16 SAM samples were analyzed as representative of even alkanethiol SAMs. Our spectra are consistent with the literature\textsuperscript{14,63}, and based on this comparison, Figure 4.1 below illustrates the C-H stretching region of the IRRAS spectrum of a well-ordered C16 SAM at 300 K and 109 K. As was already mentioned in Chapter 1, the most characteristic bands in the IRRAS spectra of alkanethiol SAMs are those due to the C-H stretching vibrations in the CH\textsubscript{2} and CH\textsubscript{3} units. With decreasing temperature, two main effects can be observed in the spectrum. First, the intensities of all bands increase, with the exception of the $r_a^-$ band which is an antisymmetric C-H stretch of the CH\textsubscript{3} unit. It has been previously proposed that for even alkanethiol SAMs the intensities of the $d^+$ (symmetric CH\textsubscript{2} C-H stretch) and $r^+$ (symmetric CH\textsubscript{3} C-H stretch) bands increase with cooling due to straightening of the alkanethiol chains and elimination of gauche defects near the chain terminations. We also observed increase in the intensities of the $d^-$ (asymmetric CH\textsubscript{2} C-H stretch) and $r_b^-$ (asymmetric CH\textsubscript{3} C-H stretch) bands,
presumably due to similar causes. No significant increase in the intensity of the $r_a$ band intensity was observed which can be explained using the surface selection rule: since the transition dipole for this mode is oriented nearly parallel to the surface in the case of even alkanethiols, the intensity of this band will be low even for the most ordered film.

![Absorbance vs Wavenumber Graph](image)

**Figure 4.1.** The C-H stretching region of the IRRAS spectrum of a well-ordered C16 SAM at 300 K (red) and 109 K (blue).

The second effect of temperature decrease is the shift of the C-H stretching bands to lower frequencies which is also attributed to the improved ordering within the film. The observed band positions at 300 K and 109 K are summarized in Table 4.1.
Table 4.1. Band positions in the C-H stretching region of the IRRAS spectrum of a well-ordered C16 SAM at 300 K and 109 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Band position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d⁺</td>
</tr>
<tr>
<td>300</td>
<td>2850</td>
</tr>
<tr>
<td>109</td>
<td>2849</td>
</tr>
</tbody>
</table>

In contrast to the spectrum of a well-ordered film in Figure 4.1, the IRRAS spectrum from a different C16 sample, shown in Figure 4.2, illustrates a greater degree of disorder. First, the intensity of the r⁺ band is very low, which indicates that the terminal methyl groups are not oriented perpendicular to the surface to the same extent as they would in a well-ordered film. Cooling the sample down to 109 K did not introduce significant changes in the band intensities: only a small increase in the intensities if the d⁺ and d⁻ bands can be observed, while those of the r⁺ and r_b⁻ bands remain essentially unchanged. This suggests that the original disorder in the film is present on a large scale and as a result, cannot be eliminated by cooling.
Figure 4.2. The C-H stretching region of the IRRAS spectrum of a poorly-ordered C16 SAM at 300 K (red) and 109 K (blue).

Once the SAM order had been established on the basis of the IRRAS spectra, this information was used for the interpretation of the MIES spectra of the corresponding samples. Thus, Figure 4.3 represents the MIES spectra of the well-ordered C16 SAM discussed in the beginning of this section, while Figure 4.4 is the MIES spectra of the disordered C16 SAM.
Figure 4.3. MIES spectra of a well-ordered C16 SAM at 300 K (red) and 109 K (blue).

The MIES spectra of the well-ordered C16 SAMs agree with the previous work by Morgner and Heinz. The intensity in the low-energy end of the spectrum (0-3.5 eV) is mainly due to the secondary electrons, which are produced when the electrons emitted upon the interaction of metastable helium with the SAM inelastically scatter within the film. A small contribution in this part of the spectrum is also due to the interaction of metastable helium with the $\sigma_{2s}$ orbital of the alkanethiols which is localized along the C-C backbone. The most prominent feature in the spectra after the secondary electron region is the peak at 6 eV which was attributed to the interaction of metastable helium with the molecular orbitals localized around the terminal methyl group ($\sigma_{2p}$ following Morgner’s notation). The electrons emitted upon the interaction of metastable helium with the orbitals localized on the methylene units ($\pi_{2p}$) appear at ~ 5 eV kinetic energy, and since the intensity in this region is low, the MIES spectra reinforce the interpretation that metastable helium atoms interact primarily with the terminal methyl groups, which are highly exposed at the surface in the case of a well-ordered
film. As the temperature is decreased from 300 K to 109 K, the spectral intensity of the peak at 6 eV increases and this peak also shifts towards higher kinetic energies by ~0.3 eV, which corresponds to lower ionization potential of the interacting orbital.

The MIES spectrum of the SAM that indicated disorder in the IRRAS (Figure 4.4), illustrates a different situation in terms of the surface structure. In this case the intensity at 6 eV is lower than for the well-ordered film, and instead two peaks become more prominent, one at ~5.3 eV and the second at ~9.8 eV. Again, following Morgner’s assignments, these two peaks are due to the interaction of metastable helium with the molecular orbitals that have $\pi$ 2p character and are localized on the methylene groups. This observation indicates that in this film the methylene units were more exposed at the surface in comparison with a typical C16 SAM, which also agrees with the conclusion about the disorder in the methyl groups from the IRRAS spectrum in Figure 4.2.

![MIES spectra of a poorly ordered C16 SAM at 300 K (red) and 109 K (blue).](image)

**Figure 4.4.** MIES spectra of a poorly ordered C16 SAM at 300 K (red) and 109 K (blue).
Two more C16 SAM samples were probed first by IRRAS and MIES. As was shown for the well-ordered and disordered C16 SAMs, the intensities of the d\(^+\) and r\(^+\) bands can serve as indicators of the film structure. Figure 4.5 below represents the intensities of these two bands at 300 K and 109 K for the four C16 samples analyzed, with the disordered and well-ordered SAMs discussed above being numbers 1 and 4, respectively.

In order to obtain quantitative information from the MIES spectra, we followed a similar approach to Morgner and Heinz by calculating the ratio (R) of the integral from 5.6 to 6.6 eV (“methyl” region) to the integral from 3.6 to 5.6 eV (energy gap and “methylene” region). In Figure 4.6 we plotted the R values for the four high quality C16 samples in two temperature regimes. Combining the outcomes of the IRRAS and MIES results in the two plots, it is seen that the R value correlates with the relative intensity of the r\(^+\) band. In addition, greater relative increase in the intensity of the r\(^+\) band upon cooling corresponds to the greater increase in the R value. In other words, exposure of the terminal methyl MOs to the incident metastable helium flux increases with increasingly more perpendicular orientation of the terminal methyl groups with respect to the surface and thus, reflects greater film ordering.
Figure 4.5. (a) IRRAS intensities of the r\(^+\) and d\(^+\) bands and (b) R ratios obtained for the four C16 SAM samples at 300 K and 109 K.
4.1.2. Alkanethiol SAMs with an odd number of carbon atoms

A similar approach to the one discussed in the previous section was taken in order to assess the relationship between the IRRAS and MIES spectra of SAMs comprised of alkanethiols with an odd number of carbon atoms, using C15 as a representative sample of the group. Four different C15 SAM samples were first analyzed with IRRAS followed by MIES. A typical IRRAS spectrum of what we consider a well-ordered C15 SAM is shown in Figure 4.6. The major difference in the IRRAS spectrum in Figure 4.6 from the spectrum of the C16 SAM in Figure 4.1 is the relative intensities of the symmetric and asymmetric CH$_3$ C-H stretching bands, r$^+$ and r$^-$, respectively, which is the consequence of the even-odd effect. Unlike the even SAMs, the terminal methyl group for the odd alkanethiols is tilted away from the surface normal so the transition dipole of the r$^+$ mode has a smaller component perpendicular to the surface and therefore, the spectral intensity of the corresponding band is lower than in the case of C16. The opposite occurs for the r$^-$ band whose intensity is greater compared to the C16 spectrum, since now this transition dipole is nearly perpendicular to the surface. Therefore, in the case of a SAM comprised of alkanethiols with an odd number of carbon atoms it is the intensity of the r$^-$ band that reflects the orientation and order within the terminal methyl groups.

Temperature-related spectral changes are similar to those in the C16 spectrum in Figure 4.1: increases in the band intensities and shifts to lower frequencies due to improved ordering within the film are always seen for high quality SAMs. The spectral shifts are summarized in Table 4.2. With regards to the intensity changes, it should be noted that while the intensities of the d$^+$, d, r$^-$, and r$^-$ bands increase significantly for the C15 SAM upon cooling, the change in the r$^+$ band intensity is negligible, if any. The vertical shift in the spectral baseline at 109 K is
due to the slight change in the sample stage position which was found sometimes to occur during cooling.

![Graph](image)

**Figure 4.6.** The C-H stretching region of the IRRAS spectrum of a C15 SAM at 300 K (red) and 109 K (blue).

**Table 4.2.** Band positions in the C-H stretching region of the IRRAS spectrum of a well-ordered C15 SAM at 300 K and 109 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Band position (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>d(^+) 2850  r(^+) 2878  d(^-) 2919  N/A  r(_b)^- 2965</td>
</tr>
<tr>
<td>109</td>
<td>2848  2876  2918  2957  2965</td>
</tr>
</tbody>
</table>

The MIES spectra of the C15 SAM at 300 K and 109 K, illustrated in Figure 4.7, contain very similar features to those in the MIES spectrum of the well-ordered C16 SAM in Figure 4.3.
The peak at 6 eV indicates that in this sample the alkanethiol molecules also expose primarily their methyl terminations at the surface.

![MIES spectra of a well-ordered C15 SAM at 300 K (red) and 109 K (blue).](image)

**Figure 4.7.** MIES spectra of a well-ordered C15 SAM at 300 K (red) and 109 K (blue).

In order to establish the structural effects on the IRRAS and MIES spectra as well as the relationship between the two, we considered the spectral intensities of the $d^+$ and the $r_a$ bands as well as the $R$ values obtained from the MIES spectra for the four C15 samples (numbered 1, 2, 3 and 4) in a similar fashion to the C16 samples in the previous section. The IRRAS intensities obtained for the four samples at 300 K and 109 K are illustrated in Figure 4.8 (a), while the corresponding $R$ values are illustrated in Figure 4.8 (b).

Unlike in the case of the four C16 samples in the previous section, the relationship between the IRRAS intensities and the $R$ values for the four C15 samples is not an obvious one. At 300 K, the $R$ values appear to increase with the increasing ratio between the intensities of the $r_a$ and $d^+$ bands. As was suggested earlier in this chapter, greater relative intensities of the $r_a$ band in the case of SAMs comprised of alkanethiols with an odd number of carbon atoms
indicate better-ordered chain terminations which in turn also leads to greater exposure of the molecular orbitals localized on the methyl terminations at the surface and therefore, greater R values. However, as the samples are cooled down to cryogenic temperatures, the intensities of the $d^+$ and $r_a^-$ bands increase which also leads to changes in their relative intensities. The $R$ values also increase, and as a result, at 109 K the correlation is no longer observed. For example, in the case of sample #3, cooling resulted in the relative intensity of the $d^+$ band being greater than that of the $r_a^-$ band, however this sample also yielded the greatest $R$ value at 109 K. In comparison, sample #4 which at 300 K had the greatest $R$ value, resulted in the smallest increase in it upon cooling among all four samples, although the changes in its IRRAS band intensities were comparable to those from sample #3. On the basis of these observations we conclude that by probing the outermost MOs, MIES is more sensitive to the subtle structural differences between the samples which are not detectable by IRRAS. Nevertheless, the general trend that can be observed from these four samples is the increase in the IRRAS intensities and the MIES $R$ values with cooling. We attribute both of these effects to the improved ordering within the films which takes place with cooling and in the case of the MIES $R$ values specifically, to the higher exposure of the terminal methyl MOs at the surface at lower temperatures.
Figure 4.8. (a) IRRAS intensities of the $r_a$ and $d^+$ bands and (b) $R$ ratios obtained for the four C15 SAM samples at 300 K and 109 K.
4.2. Alkanethiol SAM series

The even-odd effect in SAMs was investigated within a series of eight different alkanethiols: four comprised of alkanethiols with an odd number of carbon atoms (C7, C9, C11 and C15) and four comprised of alkanethiols with an even number of carbon atoms (C8, C10, C12, C14 and C16). As was described in the previous sections, IRRAS was used first in order to determine whether the sample was well-ordered and suitable for comparison, followed by MIES.

4.2.1. IRRAS spectra

The IRRAS spectra of the SAM series are shown in Figure 4.9. The general features of the spectra are similar to those for the C16 and C15 samples described in Section 4.1, where the SAMs comprised of molecules with an even number of carbon atoms follow the trend of the C16 SAM and the ones with an odd number of carbon atoms – that of the C15 SAM in terms of the reversal of the symmetric and asymmetric methyl bands as the result of the methyl group orientation. For shorter chain lengths, such as C7 and C8, the $d^+$ and $d^-$ bands are ~5 and 10 cm$^{-1}$ broader compared to the SAMs comprised of longer alkanethiols which indicates a greater degree of disorder within the film. This can be expected for shorter chains as they do not assemble as well as the longer ones due to the reduced van der Waals interactions between the chains.

As the chain length decreases, resulting in fewer methylene units in the molecule, the intensities of the methylene bands ($d^+$ and $d^-$) also decrease, while those related to the methyl groups remain relatively constant.
Figure 4.9. IRRAS spectra of a series of alkanethiol SAMs at 300 K (red) and 109 K (blue).
4.2.2 MIES spectra

MIES spectra of the alkanethiol SAM series at 300 K and 109 K are illustrated in Figure 4.10. To the best of our knowledge, the temperature effects in the MIES spectra of alkanethiol SAMs have not been previously reported. The relative intensities of the secondary electron peak and the peaks after the energy gap varied between samples, which resulted in somewhat challenging comparison of absolute spectral intensities. As can be observed in Figure 4.10, the key difference between the spectra of SAMs comprised of alkanethiols with even and odd numbers of carbon atoms is the peak around 6 eV which is attributed to the interaction of He* with the MOs localized on the terminal methyl groups. These MOs have primarily σ 2p character and constitute the C-H bond of the methyl group. Spectra of the alkanethiol SAMs with an odd number of carbon atoms exhibit a more pronounced enhancement of the 6 eV peak compared to those with an even number of carbon atoms. The \( R \) values found for the alkanethiols in two temperature regimes are shown in Figure 4.11 and further illustrate the difference between SAMs with an even and odd number of carbon atoms. \( R \) values for alkanethiols SAMs with an odd number of carbon atoms are higher at 300 K and increase more dramatically with cooling than those with an even number of carbon atoms. This indicates that the σ 2p MOs localized around the C-H bond of the terminal methyl groups of the former are more exposed in the interaction with the metastable helium. Analogously to the C15 and C16 SAMs discussed in Section 4.1, we attribute the increase of the \( R \) values with cooling to the effect of re-ordering of the alkanethiol chains and elimination of the defects at the termini which leads to higher exposure of the terminal methyl groups and the resulting shielding of the methylene groups.
Figure 4.10. MIES spectra of a series of alkanethiol SAMs at 300 K (red) and 109 K (blue).
It is also interesting to note that the $R$ value is the highest for mid-length alkanethiols (C10, 11 and 12), and lower for the shorter (C7, C8) and longer chains (C15 and C16). We propose that this is due to the mid-length alkanethiols being long enough to form well-ordered structures but also not too long to have a significant number of gauche defects. In addition to the increase of the intensity in the 6 eV region, this peak shifts to higher energies with cooling for all alkanethiols shorter than C15, as can be also seen from Figure 4.10.

**4.3. Chapter 4 summary**

Even-odd effect in a series of methyl-terminated alkanethiol SAMs on gold were investigated using MIES and IRRAS. IRRAS was used as the “gateway” technique to establish the quality of the films, followed by MIES which determined the nature of the MOs exposed at the SAM surface. It was found that in the case of SAMs comprised of alkanethiols with an odd number of carbon atoms, the electron density located primarily around the C-H bond of the terminal methyl groups was more exposed at the surface compared to those composed of alkanethiols with an even number of carbon atoms, and as a result, had a greater probability of interaction with the incoming metastable helium atoms. It was also determined that within the alkanethiol series, the MOs on the terminal methyl groups indicated greatest exposure at the surface in the case of intermediate length alkanethiol (C9-C12) SAMs. This was attributed to their optimal chain length which allows formation of better ordered films than short chains (C7, C8), yet does not lead to a great number of gauche effects near the chain terminations as in the case of longer alkanethiols (C14-C16).
Figure 4.11. R values obtained for a series of even and odd alkanethiol SAMs at (a) 300 K and (b) 109 K. The points for the C14, C15 and C16 SAMs are averages from three samples in each case.
CHAPTER 5
H₂O FILMS ON C16 AND C15 SAMS

5.1. Deposition at 110 K

5.1.1. IRRAS spectra

Water exhibits several types of vibrations: O-H stretches at 2500-4000 cm⁻¹, H-O-H “scissors” bending at 1500-1650 cm⁻¹, libration modes (wagging, twisting and rocking) at 500-1000 cm⁻¹ and frustrated translations at 200-500 cm⁻¹. The O-H stretching region, comprised of the symmetric (ν₁) and asymmetric (ν₃) stretching modes of isolated water molecules, is diagnostic of changes in the water structure. Amorphous solid water (ASW) which is known to form at temperatures below 130 K, exhibits a single broad peak centered at ~3250 cm⁻¹. This structure of solid water is thermodynamically metastable compared to polycrystalline cubic ice to which it transforms at ~140 K. Hagen and co-workers found that, if heated, ASW deposited on a LiF IR window will transform into polycrystalline hexagonal ice at 150 K. A typical IRRAS spectrum of cubic ice exhibits a sharp band centered around 3290 cm⁻¹ and a strongly pronounced shoulder at 3160 cm⁻¹. Previous studies using X-ray diffraction established that the density of ASW is 0.94 g/cm³, with the nearest O-O neighbor separation of 2.76 Å. Its structure is more disordered and characterized by greater dispersion of the nearest O-O neighbor separations and O-O-O angles compared to cubic ice.
Figure 5.1 illustrates the O-H stretching region in the IRRAS spectra obtained during the deposition of water on the C16 and C15 SAMs, typically observed during our experiments. The spectra in Figure 5.1 were referenced against the pristine C16 and C15 films. It is interesting to note the similarity between the spectra for the two substrates. At low exposure levels the spectra are dominated by a broad peak centered at \( \sim 3250 \) cm\(^{-1} \) which swells over to the higher frequency side and develops a shoulder peak centered at \( \sim 3400 \) cm\(^{-1} \) as the exposure is increased. These spectral features along with the deposition conditions suggest condensation of water vapour onto the substrate in the form of amorphous solid water (ASW).

The differences in the structural order within the two forms of ice lead to the distinct features in the O-H stretching region since this region is comprised of O-H stretches of intermolecularly coupled OH oscillators \(^{69,70}\). An increased disorder in the structure of ASW leads to broadening of the O-H stretching region as well as shifting to higher frequencies \(^{71}\). In addition, the extent of H-bonding formation is also known to affect the band position. Thus, shifting to higher frequencies, as observed for ASW, is characteristic of increased O-O nearest neighbor separation and as a result, weakening of the H-bond which is also consistent with the proposed structure of ASW \(^{67}\).

The C-H stretching region of alkanethiol SAMs (2800-3000 cm\(^{-1} \)) was also responsive to the adsorption of water. The main spectral change observed in this region was the decrease of the \( r^+ \) band intensity in the case of the C16 substrate and the \( r^+ \_a \) band for the C15.
Figure 5.1. O-H stretching region in the IRRAS spectra obtained during the deposition of water on (a) C16 and (b) C15 SAMs.
5.1.2. MIES spectra

The MIES spectra collected after the deposition of each water layer are shown in Figure 5.2 (a) for the C16 and (b) for the C15 SAM. To our knowledge, these are the first reported MIES spectra of water films on organic substrates, with all previous works on MIES of water focusing on metal substrates.\textsuperscript{72,73} Since the spectra obtained on the two organic substrates contain similarities, the following discussion will focus on these aspects first. An observation that stands out in the low energy end of the spectra is the decrease of the secondary electron peak intensity with increasing water exposure. We attribute this effect to charging of the film, which is caused by the insulating nature of water. Charging also leads to shifting of the spectrum to lower kinetic energies was also observed and will be discussed in more detail towards the end of the chapter. Convolution of the shifts due to charging with the depletion of secondary electrons resulted in difficulties with comparison of the spectra since there is no longer a clear constant 0 eV onset observed in the MIES spectra. In order to resolve this issue, we extracted the position of the high-energy cut-off in the UPS spectrum of the SAM which also shifts with charging, and shifted the MIES spectra by the same amounts. Figure 5.2 represents the “corrected” spectra.
Figure 5.2. MIES spectra of water adsorbed on (a) C16 and (b) C15 SAMs obtained at different amounts of water exposure. Electron energies have been adjusted for shifts due to charging of the water film.
The MIES spectra collected prior to water exposure are typical of the C16 and C15 SAMs, as discussed in the previous chapter. As the surface is exposed to water, starting with 0.5 L, new spectral features begin to develop due to the interaction of metastable helium with the MOs of the adsorbed water molecules, schematically represented in Figure 5.3. The first peak due to water appears in the spectrum is centered at ~8.1 eV and corresponds to electron emission from the $1b_1$ orbital, which is localized mainly on the lone electron pair on the oxygen atom and has the lowest ionization potential. The peak attributed to the $3a_1$ MO is expected to appear at ~6-7 eV kinetic energies based on its ionization potential which leads to its at least partial overlap with the SAM peak at ~6 eV. The third water peak at ~2.3 eV kinetic energy is due to the $1b_2$ MO and is initially buried in the secondary electron peak, but as the intensity of this feature decreases, the $1b_2$ peak becomes more pronounced.

A subtle change that takes place in the MIES spectra with increasing water exposure is the initial intensity decrease in the high-energy end, in the ~9-13 eV region. It is reasonable to assume that the main contribution in this region comes from the highest energy peak of the SAM at ~10.8 eV associated with one of the MOs localized on the methyl group. With increasing water exposure, more of the SAM surface is covered, thus leading to a decrease in the intensity originating from the methyl groups. In order to quantify this effect, we integrated the MIES spectra of water films between 9.8 and 12.2 eV and plotted the resulting integrals as a function of
water exposure in Figure 5.4 for both SAMs. The intensity decrease with water exposure is more pronounced in the case of the C15 SAM, decreasing to ~20% of its initial value, while the minimal value for the C16 SAM is ~25%. For both substrates, the minimum values for the intensity between 9.8 and 12.2 eV are achieved between 5 and 10 L of exposure which suggests formation of a monolayer of water. After the initial decrease, the intensity on this region partially recovers. We believe that the intensity increase that occurs after deposition of 10 L of water is due to the tailing of the 1b1 water peak at 8.1 eV. It is interesting that the intensity “recovery” in the 9.8-12.2 eV region after 10 L is more pronounced in the case of the C16 substrate than the C15. Our proposed explanation for this observation is greater extent of clustering of water molecules on the C16 substrate as opposed to more uniform coverage on the C15. Water clusters have greater surface area of water exposed to the metastable helium which would explain greater intensity increase after the deposition of 10 L of water. As the water exposure continues to increase above 10 L, the intensity in the 9.8-12.2 eV region for water on the C16 SAM levels out and approaches similar values to that for the C15 SAM. This suggests that the water film becomes more uniform, resembling that on the C15 substrate. This conclusion suggests that the surface of SAMs comprised of alkanethiols with an odd number of carbon atoms is somewhat more hydrophilic than that of alkanethiolSAMs containing an even number of carbon atoms. This observation is especially interesting since on a macroscopic level the even-odd variation in methyl-terminated alkanethiol SAMs does not affect surface contact angle for water 75. We propose that the surface of the C15 SAM exposes more of the methylene units which are more polarizable and as a result, potentially more hydrophilic than the methyl groups 13. However, more conclusive experimental evidence is required.
Figure 5.4. Integral from 9.8 to 12.2 eV, normalized to the respective values for the bare SAMs, plotted as a function of water exposure for C16 (black) and C15 (red) SAM substrates.

5.2. Thermal transformation of ASW to polycrystalline ice

5.2.1 IRRAS spectra

As was mentioned in the section 5.1, water deposited on a methyl-terminated surface at 110 K forms amorphous solid water, ASW, which is thermodynamically metastable in comparison to polycrystalline cubic ice. Thermal transformation of ASW to polycrystalline ice on CH₃ terminated SAMs was investigated by Engquist and co-workers for D₂O films⁴⁹,⁵⁰. They proposed that partial transformation will begin as early as just above 110 K and will continue until 140 K, at which point water will start desorbing from the surface, reaching complete desorption at 160 K. The authors also proposed formation of three-dimensional water clusters on a hydrophobic surface, such as a methyl-terminated SAM. Formation of the polycrystalline structure involves reorganization of water molecules, and should also affect the nature of the
exposed MOs. To our best knowledge the difference in the surface electronic structure of ASW and cubic ice has not been previously reported, yet it should be detectible with MIES.

In this experiment, we dosed 5 L of water on a C16 SAM substrate at 110 K, monitoring the deposition process with IRRAS, followed by obtaining the MIES spectrum of the film. The sample was then heated to 140 K and held at this temperature for 5 minutes. The O-H stretching region illustrated in Figure 5.5 is the most diagnostic in terms of the observable transformation from ASW to cubic ice. Initially, at 114 K this region contains a broad peak at 3350 cm$^{-1}$ with subsequent formation of the shoulder at ~3400 cm$^{-1}$, analogous to that discussed in Section 5.1 and characteristic of amorphous solid water. As the sample is heated to 140 K, the spectral profile begins to shift to lower frequency, eventually forming a peak at 3240 cm$^{-1}$ and a shoulder peak centered at 3160 cm$^{-1}$. Both features have been attributed to cubic ice in the literature$^{48,66,67}$. Shifting to lower frequencies and sharpening of the spectral band again suggest improved order within the water film associated with reorganization into a polycrystalline framework as well as strengthening of the intermolecular H-bonding. The shoulder at ~3150 cm$^{-1}$ has been assigned due to the contribution from the bonded OH of the surface molecules with a dangling OH bond$^{76}$. 
Figure 5.5. O-H stretching region in the IRRAS spectrum of 5 L water film on a C16 SAM collected during thermal transformation from ASW at 114 K to polycrystalline ice at 140 K.

Two other interesting spectral regions of water, centered at ~1650 and 2250 cm\(^{-1}\) are presented in Figures 5.6 and 5.7. It is also worth noting that the spectral intensities in these two regions are much lower compared to the O-H stretch. The first region has been previously assigned to the bending mode and libration overtone. The most pronounced heating-induced change in this region (Figure 5.5) is the shift to lower frequencies. This observation is consistent with previous literature, although it has been considered as puzzling since both the bend and the librational fundamentals are at higher frequencies in the case of polycrystalline ice as compared to amorphous solid water. In addition, increasing H-bond strength during the transformation is theoretically also expected to cause a shift to higher frequency. Devlin and co-workers had addressed this question and offer the following explanation \(^{76}\). They suggested that the bending vibration which is at higher frequency than the librational overtone becomes increasingly more
mixed with the latter in the process of crystallization which causes the overall absorption in this region to shift to lower frequencies.

![Figure 5.6](image)

**Figure 5.6.** Bending mode/libration overtone region in the IRRAS spectrum of 5 L water film on a C16 SAM collected during thermal transformation from ASW to polycrystalline ice.

The spectral region centered at ~2250 cm\(^{-1}\) also presents a curious case. Upon thermal transformation the position of this band shifts to higher frequencies, as have been previously observed in the literature\(^{67,76}\). It has been previously attributed to the combination of the bending and librational fundamentals\(^{67,77}\), however this assignment is unlikely in the case of ASW and cubic ice because the librational frequency of cubic ice is at 835 cm\(^{-1}\) and the bending mode is at ~1700 cm\(^{-1}\) which places their combination at the frequency of ~2535 cm\(^{-1}\). Devlin and co-workers assign this band to the combination of the librational fundamental frequency (835 cm\(^{-1}\)) and the first overtone (1560 cm\(^{-1}\)), which at 2175 cm\(^{-1}\) provides a better match for the observed band.
**Figure 5.7.** Libration fundamental/first overtone region in the IRRAS spectrum of 5 L water film on a C16 SAM collected during thermal transformation from ASW to polycrystalline cubic ice.

Table 5.1 provides a summary of the most diagnostic bands observed in our IRRAS spectra of ASW and polycrystalline cubic ice, as discussed above.

**Table 5.1.** Bands observed in the IRRAS spectra of ASW and cubic ice.

<table>
<thead>
<tr>
<th>IRRAS region</th>
<th>Position in ASW (cm⁻¹)</th>
<th>Position in cubic ice (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretch ($v_I + v_3$)</td>
<td>3350</td>
<td>3250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3150 (shoulder)</td>
</tr>
<tr>
<td>Libration + first overtone ($v_L + 2v_L$)</td>
<td>2225</td>
<td>2250</td>
</tr>
<tr>
<td>Bending region</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bend ($v_2$)</td>
<td>1660</td>
<td>1625</td>
</tr>
<tr>
<td>First libration overtone ($2v_L$)</td>
<td>N/A</td>
<td>1570</td>
</tr>
</tbody>
</table>
5.2.2 MIES spectra

Figure 5.8 illustrates the MIES spectra of the C16 substrate prior to water deposition, followed by that of the as-deposited, ASW and the transformed polycrystalline cubic ice. Analogously to the previous experiment, the spectra were corrected for the energy shifts due to charging of the water film. The spectrum of ASW exhibits similar features seen for the same exposure on a C16 substrate as discussed in section 5.1, where the most distinct peak at 8.6 eV is attributed to the interaction of metastables with the 1b₁ MO localized on the lone pair of the oxygen atom. In the spectrum of polycrystalline ice, on the other hand, this peak is no longer pronounced, suggesting that the 1b₁ “lone-pair” MO becomes less exposed at the film surface and as a result, does not efficiently interact with the incoming helium metastable atoms. We propose that this observation is due to greater involvement of the 1b₁ orbital in H-bonding which occurs upon the transformation from ASW to polycrystalline ice. Another interesting development is taking place in the high-energy “tail” of the spectrum. As was discussed earlier, the intensity in the region between 9.8 and 12.2 eV is contributed mainly by the SAM substrate. It was found that the integrated intensity in this region decreases to ~20% of its value for the pristine C16 SAM as a result of the formation of ASW. Following the transformation to polycrystalline ice, the intensity in this region increases to ~70% of its initial value. Based on this observation, we propose that water molecules in ASW cover the SAM surface more uniformly and upon thermal transformation, reorganization of water molecules and formation of H-bonds exposes more of the underlying substrate.
Figure 5.8. MIES spectra of pristine C16 SAM substrate (black) at 110 K, ASW formed after exposure to 5 L of water (red) followed by transformation to polycrystalline ice (blue).

5.3. Charging of water films

As was discussed in section 5.1, deposition of water films on the SAM substrates caused shifting of the electron energy spectra to lower values which was attributed to charging of the sample surface due to insulating nature of water. Figure 5.9 illustrates the MIES spectral shifts in the case of the C15 and C16 SAM substrates observed for a given water exposure in the case of layer-by-layer deposition experiments. Spectral shifts for single amounts of exposure for 5, 10 and 20 L were found to be comparable to the corresponding exposures in the layer-by-layer deposition experiments.

Time dependence of the charging effects was also investigated. We found that for a water film formed at 10 L of exposure, the spectral shift was -0.8 eV. After a waiting period of 2.5
hours the shift had increased to -2 eV, suggesting that charging is caused by exposure to the beam and collection of spectra, and is independent of time.

![Graph showing MIES spectral shifts for amorphous water films on C15 and C16 SAM substrates as a function of water exposure.]

**Figure 5.9.** MIES spectral shifts observed for amorphous water films on the C15 and C16 SAM substrates as a function of water exposure during the deposition.

### 5.4. Chapter 5 summary

Electronic structure and morphology of water films formed on methyl-terminated C15 and C16 alkanethiol SAM substrates were investigated using MIES and IRRAS. It was found that water deposited at 110 K forms amorphous solid water based on its infrared signature. The most prominent spectral feature in the MIES spectra of amorphous water films is the peak due to the interaction of metastable helium atoms with the MO localized on the lone pair of the oxygen atom. It was also found that in the case of the C15 substrate, water films were more uniform, covering the underlying substrate to a greater extent than in the case of the C16 SAM.
Thermal transformation of amorphous solid water to polycrystalline cubic ice which occurs at ~140 K was also investigated with IRRAS and MIES. We determined that the MIES peak attributed to the lone pair on the oxygen atom, observed in the spectra of ASW, decreased in intensity upon thermal transformation, suggesting that in polycrystalline cubic ice structure this MO is no longer exposed at the outermost surface later to the same extent as in ASW. We conclude that this is caused by formation of H-bonding network in the polycrystalline ice which involves that oxygen lone pair, making it less accessible to the incoming metastables.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1. Conclusions

As was initially outlined in the research objectives in Chapter 1, this work consists of two main themes. The first one is concerned with the even-odd effect in alkanethiol SAMs on gold, in which the number of carbon atoms in the alkanethiol backbone defines the structure of the outermost surface layer of the SAM. The objective associated with this theme was to investigate the structural differences in the outermost surface layer of even and odd alkanethiol SAMs which consists of the terminal CH$_3$ groups. The second theme was the microscopic scale interactions between water and the surface of CH$_3$-terminated alkanethiol SAMs. The objective in this part of the project was to determine the structure of the as-deposited and thermally transformed water films, as well as the nature of MOs exposed at the film surface before and after the transformation. Both parts of the project used the combined approach of two analytical techniques, IRRAS and MIES. IRRAS is a traditionally used surface analysis technique which allows for determination of the overall orientation of the adsorbed molecules, while MIES probes exclusively the outermost surface layer due to the low kinetic energies of metastable atoms.

Addressing the first research objective, a series of even (C8, C10, C12, C14 and C16) and odd (C7, C9, C11 and C15) alkanethiol SAMs were successfully prepared and analyzed using IRRAS and MIES. One of the main challenges was interpretation of the MIES data due to the lack of comparable available literature, especially when it comes to assessment of the SAM quality. For this reason, IRRAS was used as a “gateway” technique which allowed for determination of the overall structural order within the SAM, followed by MIES analysis. Based on this combined approach, it was found that the exposure of the σ-type MOs localized around
the C-H bond of the terminal methyl groups was correlated with the structural order of the SAMs, as well as the even-odd effect. Thus, these MOs were found to be more exposed at the outermost SAM surface in the case of alkanethiols with an odd number of carbon atoms compared to those with an even. Decreasing the temperature from 300 K to 109 K resulted in improvements in the SAM structure due to elimination of gauche effects, as indicated by the characteristic spectral changes in IRRAS. From MIES it was found that at cryogenic temperatures the exposure of the MOs associated with the methyl groups increased more for odd SAMs than for even.

In order to address the second objective related to water adsorption, MIES and IRRAS were used to investigate the morphology and surface electronic structure of water films deposited on C15 and C16 SAM substrates. It was found that deposition at 110 K leads to formation of amorphous ice, with the $1b_1$ MO localized in the lone pair of the oxygen atom being exposed at the film surface. Amorphous ice films formed on the C15 SAM were found to be more uniform than on the C16 SAM. An increase in the sample temperature from 110 to 140 K caused transformation of amorphous ice to polycrystalline ice. It was also found that the intensity of the MIES peak due to the oxygen lone pair decreased upon thermal transformation, leading us to conclude that in the polycrystalline ice structure fewer $1b_1$ MOs are exposed at the outermost surface layer, most likely due to its greater statistical involvement in the hydrogen-bonding within the polycrystalline structure.

6.2. Future work

The work presented in this thesis has provided important insights into the surface structure of model organic systems - alkanethiol SAMs, in particular can demonstrate the even-odd effect. While we focused on the methyl-terminated surfaces, the potential for future
investigations includes other functionalities, for example –COOH, –OH, –CONH$_2$ and –NH$_2$ terminations which are used to model various biological surfaces. In the case of these functionalities, the backbone chain parity will affect the orientation of the hydrophilic group and as a result, its interactions with adsorbates. Further, the investigations of interfacial interactions of water with functionalized surfaces would be another interesting direction for the IRRAS and MIES work, in particular the surface structure and thermal behaviour of water films which has been previously suggested to form flat 2D clusters on hydrophilic surfaces.

Another desirable aspect of future work with MIES would be improved interpretation and quantification of MIES spectra; presently it is still a rather qualitative technique. Finally, a major part of this work involved instrumental design and development of what is now a complex and sophisticated system for surface analysis, however some components of it need revisiting. For example, the high sample bias required for MIES experiments (-46 V) was most likely the principle reason behind large amounts of secondary electrons being observed in the MIES spectra; ideally this could be decreased by applying a lower sample bias. Another useful adjustment would be the ability to collect MIES spectra while monitoring and controlling the sample temperature which at the moment is not possible. Addition of a sputtering gun to the analysis chamber is a modification planned for the near future, which will allow for in-situ surface cleaning and as a result, enable MIES work with pristine metal surfaces.
CHAPTER 7

REFERENCES


(53) Woestenenk, G. R.; Thomsen, J. W.; van Rijnbach, M.; van der Straten, P.;


156-158, 383.


(61) Skoog, D. A. H., F. J.; Crouch, S. R. Principles of instrumental analysis; 6 ed.;


(64) Seah, M. P. In Methods for surface analysis; Walls, J. M., Ed.; Cambridge


