The interaction of solid water with methyl-terminated self-assembled monolayers of alkanethiols containing odd and even numbers of carbon atoms

by

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ABSTRACT

THE INTERACTION OF SOLID WATER WITH METHYL-TERMINATED SELF-ASSEMBLED MONOLAYERS OF ALKANETHIOLS CONTAINING ODD AND EVEN NUMBER OF CARBON ATOMS

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The odd – even effect in the wetting of methyl-terminated self-assembled monolayers (SAMs) have been previously observed on a microscopic level and in ambient conditions. However, fundamental understanding of the interaction of a water adsorbate with the surface remains inconclusive. Using infrared reflection-absorption spectroscopy (IRRAS), the average structural orientations of water molecules deposited on SAMs with even and odd number of carbon atoms, were diagnosed under cryogenic and UHV conditions. A peak deconvolution method was developed in this work to unambiguously monitor changes in the broad O-H stretch band of solid water as the system was manipulated. This analysis confirmed that the geometry of the methyl terminal groups at the interface influences the as-deposited water molecules’ interactions with the substrate, and more specifically, the peak positions. After the transition from amorphous solid water (ASW) to crystalline ice (CI), molecular orientations of water adsorbed on the surface were not affected by the interaction with the even and odd SAMs. Moreover, the peak analysis revealed a transformation of the dominant width broadening component from Gaussian (heterogeneous broadening factors) to Lorentzian (homogeneous broadening factors) during crystallization of water deposited on all SAMs.
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LIST OF ABBREVIATIONS AND SYMBOLS

C12  1-dodecanethiol SAM
C16  1-hexadecanethiol SAM
C15  1-pentadecanethiol SAM
C11  1-undecanethiol SAM
AIC  Akaike Information Criterion
ASW  Amorphous Solid Water
Å    Ångström = 10^{-10} meter
AFM  Atomic Force Microscopy
AN   Auger Neutralization
CI   Crystalline Ice (A combination of $I_c$ and $I_h$ crystalline ice forms, as opposed to amorphous form)
$I_c$  Cubic Ice
DFT  Density Functional Theory
FTIR Fourier Transform Infrared Spectroscopy
FWHM Full Width at Half Maximum
HEA  Hemispherical Energy Analyzer
$I_h$ Hexagonal Ice
IRRAS Infrared Reflection-Absorption Spectroscopy
IP   Ionization Potential
L    Langmuir (L) = 10^{-6} Torr·s, unit of exposure of a surface to gas at 10^{-6} Torr during 1 second
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<td>LO</td>
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<td>SFG</td>
<td>Sum Frequency Generation Spectroscopy</td>
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<td>Ultrahigh Vacuum</td>
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**TERMINOLOGY**

**Even SAMs** – methyl-terminated self-assembled monolayers (SAMs) with even number of carbon atoms (C16 and C12) in the alkyl chain

**Odd SAMs** – methyl-terminated self-assembled monolayers (SAMs) with odd number of carbon atoms (C15 and C11) in the alkyl chain
CHAPTER 1

Introduction

The wetting behavior of adsorbates on surfaces found in nature has many useful practical applications. Self-cleaning window glasses, paints and textiles have been designed to mimic the way lotus and rice leaves repel water from the surface.\(^3\) Similarly, antifogging and antireflection coatings have been developed from the way mosquito and moth eyes decrease fog and glare.\(^4\) Fundamental understanding of how water interacts with a variety of surfaces under specific environmental conditions allows the development of surfaces with distinct physical and chemical properties tailored to the desired application.\(^5\)

One of the well-studied methods to model and construct surfaces that can be manipulated at the molecular level involves self-assembled monolayers (SAMs). These are organic chains that have functional head groups with strong affinity to a specific solid substrate. When those functional groups are chemisorbed on the substrate uniformly, the organic chains arrange, through van der Waals interactions, to form a highly ordered monolayer. The thickness of the monolayer is determined by the organic chain length.\(^6,7\) SAMs can be easily functionalized by changing the terminal group to produce surfaces with various properties, such as, hydrophobic or hydrophilic, pH sensitive\(^8\), photosensitive\(^9\), conductive, and selective for biosensing applications.\(^10\) However, it has been shown that even without changing the terminal groups, surface properties can be altered by the orientation of the terminal group at the
interface, which is determined by the number of organic units in the chains. Fluctuations in surface properties due to odd or even number of units in the SAM’s chain are generally termed “odd – even effects”.\textsuperscript{11,12}

Even though the structure of methyl-terminated alkanethiol SAMs is well studied and their properties are thought to be well-understood, the wetting of these SAMs have been debated for over 25 years.\textsuperscript{11,13,14} The existence of odd - even effect in the wettability of methyl-terminated alkanethiol SAMs is believed to be due to differences in the structural orientations of the methyl terminal groups and/or dipole interactions at the surface. SAMs chemisorbed on Au(111) substrate with even number of carbon atoms (even SAMs) have terminal –CH\textsubscript{2}CH\textsubscript{3} bond oriented along the surface normal. SAMs with odd number of carbon atoms (odd SAMs) have terminal –CH\textsubscript{2}CH\textsubscript{3} bond tilted away from the surface normal, and thus exposing underlying methylene groups. These exposed methylene groups are thought to be more polarizable than methyl groups, thus, causing water adsorbates to have a stronger interaction with the odd SAMs than with the even SAMs.\textsuperscript{12,15,16} Most groups sought to study these wetting properties using macroscopic techniques such as contact angle measurements, and achieved conflicting results.\textsuperscript{11} Our approach to understand adsorbate – surface interactions lies at the molecular level. Two surface sensitive techniques, Infrared Reflection-Absorption Spectroscopy (IRRAS) and Metastable Impact Electron Spectroscopy (MIES), were used in this study to analyze the orientations of solid water molecules adsorbed on methyl-terminated alkanethiol SAMs with odd and even number of carbon atoms, under cryogenic and high vacuum conditions.
Metastable Impact Electron Spectroscopy (MIES) is a highly surface sensitive analysis technique that measures the kinetic energy of the electrons ejected upon the collision of metastable atoms with the surface molecules. Due to their low kinetic energy (60 – 100 meV), the metastable atoms do not penetrate the solid surface, and thus, provide information about the energy states of the outermost exposed atoms and molecules at the surface.\textsuperscript{17,18} Because MIES is a relatively new technique, and is not commercially available, comparison of the obtained spectra to those found in literature is not always possible. As a result, Infrared Reflection-Absorption Spectroscopy (IRRAS), with a large surface chemistry data-base, is advantageous to provide information about the integrity of the sample being analyzed, as well as the averaged orientations of water adsorbate and its crystalline order on the surface.

It has been previously shown that water molecules adsorb on alkanethiol SAMs in the form of amorphous solid water (ASW) at temperatures below \(~130\) K, and transform to crystalline ice (CI) as the temperature increases to approximately 140 K.\textsuperscript{19} This irreversible transformation was monitored using the O-H stretch band in the infrared spectra of solid water adsorbed on these films. The shape and intensity of the O-H stretch (3000 - 3600 cm\textsuperscript{-1}) is strongly influenced by the strength of hydrogen bonding between the water molecules, and thus, highly informative of average molecular orientations on a surface.\textsuperscript{20,21} It was hypothesized that the different geometry of the methyl terminal groups in alkanethiol SAMs with odd and even number of carbon atoms, could lead to the formation of water networks that exhibit an O-H stretch band with different position and shape.
In light of this information, the objective of this study was to answer the following questions:

(1) How do adsorbate – surface interactions and odd – even geometry of SAMs influence the orientations of amorphous solid water (ASW)?

(2) How do adsorbate – surface interactions and odd – even geometry of SAMs influence the transition of amorphous solid water (ASW) to crystalline ice (CI)?

Work on the subject has already begun in our group by Lyagusha\textsuperscript{19}, whose main focus was to analyze the spectral differences between methyl-terminated alkanethiol SAMs with odd and even number of carbon atoms, at room and cryogenic temperatures. Lyagusha also presented preliminary MIES and IRRAS results of water adsorbed on C16 (1-hexadecanethiol) and C15 (1-pentadecanethiol) SAMs. However, she focused on trends above a monolayer of water (1 – 5 monolayers).\textsuperscript{19} In this work, the focus was shifted to a submonolayer deposition of water on even (C16 and C12) and odd (C15 and C11) SAMs. A qualitative difference was detected between the O-H stretch bands of water adsorbed on odd and even SAMs in the IRRAS spectra, and so a quantitative statistical method was developed to study these differences.
CHAPTER 2

Background Information

2.1. Self-Assembled Monolayers (SAMs)

As the name suggests, self-assembled monolayers (SAMs) are organic constituents that spontaneously assemble from the solution or gas phase on to solid substrates to form a uniform monolayer. Generally SAMs consists of three parts: (1) the head group, which anchors the molecule to a substrate by a covalent bond, (2) the spacer, often an alkyl chain (of variable length) which provides a physical barrier between the substrate and the surface and helps stabilize the structure through lateral van der Waals interactions, and (3) the terminal group, which can be functionalized according to the desired application of the surface. This elegant molecular system allows the investigation of fundamental concepts in competing intermolecular forces and their implications in technological applications.

Coinage metals are frequently used as substrates for SAMs due to their preferred (111) surface construction, however, gold is the most suitable for the application since it does not oxidize and maintains minimal surface roughness under ambient conditions. In 1983, Nuzzo and Allara reported first the self assembly of disulfides on Au(111) thin film, and alkanethiols on gold SAMs have been extensively studied and used to model simple molecular surfaces. The formation of such highly ordered uniform monolayer is driven by the bond energy of S – Au (209 kJ/mol) and the van der Waal interactions between the spacer hydrocarbon chains (4 – 8
kJ/mol per methylene).\(^7\) Due to the high stability and reproducible preparation method, methyl-terminated SAMs on Au(111) are the focus of this review.

The favoured method of preparing SAM films is by adsorption of the organic molecules from solution. This is a simpler and much easier to control method than deposition from gas phase.\(^7,24\) It is accomplished by immersing a substrate such as Au(111) thin film in a several millimolar alkanethiol solutions in an organic solvent of choice. Due to the strong thiol affinity to gold, any adventitiously physisorbed molecules are displaced from the gold surface.\(^7\) The adsorption times of the alkanethiol to the substrate depends on the chain length of the alkanethiols. Long alkanethiols chains (chain length of 10 – 22 carbons) take between 2 to 12 hours to adsorb and rearrange to a well ordered structure, while short chains (2 – 9 carbons) take approximately 24 hours. One might attribute this effect to the increase in van der Waals interactions in longer hydrocarbon chains however longer hydrocarbon chains also have lower mobility and might have the opposite effect.\(^24\)

Kinetic studies using Scanning Tunneling Microscopy (STM) imaging at low temperatures and low alkanethiol coverage\(^25\), show that the adsorption process of the alkanethiol molecules on Au(111) can be separated into three steps. The first step is the physisorption of alkanethiols on the gold substrate through van der Waals interactions. Over the duration of this step, the substrate is 80–90% covered by alkanethiol molecules in a lying-down configuration. The physisorption step can be represented as.\(^26\)

\[
\text{CH}_3(\text{CH}_2)_n\text{SH} + \text{Au} \rightarrow (\text{CH}_3(\text{CH}_2)_n\text{SH})_{\text{physAu}}
\] (eq. 2.1)
The second step is the chemisorption, which is driven by the formation of the S-Au covalent bond. The exact mechanism of this reaction is not well established with regards to the adsorption site of the sulfur head group to the gold or the fate of the mercaptan hydrogen. For the former issue, recent DFT calculations seem to agree on a combination of 2-fold bridge sites and 3-fold hollow adsorption sites, where the sulfur head is bonded to two gold atoms but positioned in a gap between three gold atoms in the (111) plane, however conclusive experimental proof is yet to be discovered.\(^7\) As for the later issue, Kankate et al.\(^{27}\) found evidence that H$_2$ gas is generated and can partially reduce nitro terminal groups on the SAMs to amino groups. Thus, the chemisorption of alkanethiols to gold can be written as follows:

\[
(CH_3(CH_2)_nSH)_{physAu} \rightarrow CH_3(CH_2)_nS - Au + \frac{1}{2} H_2 \quad \text{(eq. 2.2)}
\]

The final step of the self-assembly process is the transitioning of the alkyl chains from a lying-down to an all-trans (standing-up) configuration. Hara et al.\(^{28}\) showed that this step is a nucleation type processes and starts at step edges defective sites on the gold surfaces. Also, it has been shown that this transition is 3 to 4 times slower than the chemisorption step due to van der Waals interactions between the alkyl chains.\(^{29}\) Figure 2.1 represents the three steps in the adsorption of alkanethiols to the Au(111) surface. Note that the nucleation process is shown without the defective sites on the surface. Studies employing AFM and STM show that these step sequences occur in both gas phase and liquid phase alkanethiol adsorption.\(^{30}\)
Figure 2.1: Steps of the adsorption of alkanethiol on Au(111) substrate: a. physisorption of alkanethiols on the gold substrate, b. formation of the S-Au covalent bond, and c. transitioning from a lying-down to an all-trans (standing-up) configuration.
2.2. Structure of alkanethiol SAMs and “odd – even effects”

As previously mentioned, the final step in the SAMs formation process is the rearrangement of the alkyl chain from a lying-down to an all-trans configuration to form a high density layer on a substrate. For methyl-terminated alkanethiol SAMs on Au(111), the average chain density was measured to be 21.62 Å²/chain with 4.99 Å spacing between adjacent methylene unit.\(^{14}\) This all-trans configuration allows SAMs to be characterized according to three angles (Figure 2.2a): \((\alpha)\) tilt angle - the angle between the C-C backbone and the surface normal, \((\beta)\) twist angle - the rotation angle of the plane containing the C-C backbone about the axis along the alkyl chain (\(\beta = 0^\circ\) when the C-C backbone plane is parallel to the page as shown in Figure 2.2a), and \((\theta)\) the angle between the terminal C-C bond and the surface normal.\(^{6,22}\) FTIR studies of methyl-terminated alkanethiol SAMs on Au(111) show tilt angle \((\alpha)\) of \(~30^\circ\) and twist angle \((\beta)\) of \(~50^\circ\)\(^{12,31}\) resulting from \(sp^3\) hybridization of the sulfur atom. The \(\theta\) angle depends on the number of methylene units in the spacer group (or the number of carbons in the methyl-terminated alkanethiol SAMs). Through sum frequency generation (SFG) studies, \(\theta\) was found to be \(27^\circ\) from the surface normal for methyl terminated SAMs with even number of carbons and \(58^\circ\) for those with odd number of carbons (Figure 2.2b).\(^{32,33}\) The \(\theta\) angle determines the structural orientation of the terminal group at the surface and influence interactions with adsorbate molecules. In general, changes in surface properties that are due to the number of units in a molecule, without changing the chemical composition of the material, are described as “odd – even effects.”\(^{12}\)
Figure 2.2: a. Schematic diagrams of methyl-terminated alkanethiol SAMs chemisorbed on Au(111) substrate, showing the three characteristic angles: tilt angle ($\alpha$), twist angle ($\beta$), and the angle between the terminal C-C bond and the surface normal ($\theta$). b. Measured $\theta$ angles for methyl-terminated alkanethiols SAMs with odd and even number of carbon atoms.
Patterson et al.\textsuperscript{34} probed the orientation of the methyl terminal groups of alkanethiol SAMs with odd and even number of carbon atoms by compressing each film with femtosecond shock waves. It was found that the compression caused the $\theta$ angle in pentadecanethiol (C15) SAM to increase and then recover during decompression. However, compressing the octadecanethiol (C18) SAM resulted in terminal gauche defects without recovery of the all-$trans$ configuration of the SAM during decompression.\textsuperscript{34} Porter et al.\textsuperscript{15} used frictional force microscopy to analyze the surface friction of $\text{CH}_3(\text{CH}_2)_n\text{SH}$ SAMs on Au(111) films consisting of odd and even number of carbon atoms in the alkyl chain ($12 \leq n \leq 16$). They found that odd SAMs yield higher friction coefficients than even SAMs. The group attributed the higher friction coefficients of the odd SAMs to the exposure of an underlying methylene unit and thus causing the surface to be slightly polarizable in comparison to the even SAMs.\textsuperscript{15} More recently, Ramin and Jabbarzadeh\textsuperscript{35,36} conducted molecular dynamics simulations of alkanethiol SAMs on Au(111) to study the frictional properties differences due to the odd – even effect, and achieved the same results as obtained by Porter et al.\textsuperscript{15} In addition, they simulated the surface friction of alkanethiol SAMs with odd and even number of carbon atoms in the presence of water at low pressure. They still found that the friction coefficients of hydrated odd SAMs were higher than hydrated even SAMs, but the unexpected result was the larger drop in the friction coefficient upon the introduction of water to the pristine odd SAM versus the even SAM counterpart. They attributed this result to the ability of the water molecules to interact with the slightly more polarizable surface of the odd SAMs and thus lubricate the surface more effectively than with even SAMs.\textsuperscript{37}
2.3. Odd – even effect in the wettability of alkanethiol SAMs

Depending on the polarity of the surface, water molecules are structurally oriented on the surface to increase attractive interactions either between the water molecules themselves, or between the water molecules and the surface. Such wetting behavior of a surface is commonly probed by measuring the contact angle of a drop of liquid water on the surface. Contact angle (\(\theta_C\)) is defined as the angle between the drop’s tangent and the solid surface at the three-phase interface of solid, liquid and vapour (Figure 2.3).\(^{38}\) Using equation 2.3, Young\(^{39}\) correlated the contact angle to the equilibrium between the free energies (J/m\(^2\)) at the solid-vapor (\(\gamma_{SV}\)), solid-liquid (\(\gamma_{SL}\)), and liquid-vapor (\(\gamma_{LV}\)) interfaces. For surfaces with a high solid-liquid (\(\gamma_{SL}\)) interfacial energies, such as hydrophobic surfaces, the contact angle ranges between 90° to 120°. For hydrophilic surfaces with low \(\gamma_{SL}\), the contact angle usually varies between 0° to 90°.

\[
\cos \theta_C = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]  
(eq. 2.3)

Figure 2.3: Schematic diagram of a liquid water drop on a solid surface, showing the three-phase interface of solid, water and vapour.
The existence of odd–even effects in contact angles of water on methyl-terminated alkanethiol SAMs has been the topic of debate for over 25 years. The Porter group\(^{13}\) observed fluctuation in contact angles of water on a series of 11–17 carbon atoms chain length SAMs adsorbed on silver thin films instead of gold substrate. A difference in contact angles of 3–5° was detected between odd and even SAMs, while the even SAMs yielded greater contact angles. However, this oscillation in contact angles is in reverse to those predicted for alkanethiol SAMs adsorbed on silver. Due to the sulfur atom sp hybridization upon binding to silver, the θ angles (the angle between the terminal C-C bond and surface normal) of the odd and even SAMs are in reverse to those on gold. On Ag(111) substrate, the terminal methyl group of the even SAMs are tilted away from the surface normal and expose an underlying methylene groups.\(^{11,40}\) Since it was hypothesized that the exposed methylene groups are causing the surface to be more polarizable, even SAMs on Ag(111) should have yield lower contact angles.\(^{12,15,16}\)

On the other hand, the Whitesides group\(^{14}\) performed contact angle measurements of water drops on a series of methyl-terminated alkanethiol SAMs with 3–21 carbon atoms adsorbed on gold and silver thin films, and observed no odd–even effect in wettability. Other groups also show no evidence of odd–even effect with water on SAMs.\(^{41–43}\) In 2014, Thuo et al.\(^{40,44}\) sought to explain the discrepancy between these two groups by focusing on the gold and silver substrate roughness. They argued that the lack of odd–even effect is due to the substrate morphology and repeated the water contact angle measurement with smooth Au(111) and Ag(111) thin films prepared by template stripping method. Thuo et al. observed an odd–even oscillation in their contact angle measurements that follows the hypothesis
mentioned above. Even SAMs adsorbed on Au(111) yielded 2 – 4° higher contact angles (with maximum standard error of 0.9°) than odd SAMs, while on Ag(111), odd SAMs yielded 2 – 3° higher contact angles (with maximum standard error of 1.3°) than even SAMs. As can be seen from these contact angles and their standard errors, the difference between the contact angles of water on alkanethiol SAMs with odd and even number of carbon atoms is small and approaching the theoretical limit of the technique.\textsuperscript{15,40}

Measuring the contact angle of a liquid on a surface is a macroscopic technique to determine molecular interactions in the liquid/solid interface and thus very sensitive to the metal substrate type, morphology, and SAMs ordering. Therefore, there is a need for a more sensitive technique to investigate surface interactions at the molecular level. In this study, Infrared Reflection-Absorption Spectroscopy (IRRAS) was used to determine how the geometry of the methyl terminal groups influences the average molecular orientations of water molecules adsorbed on alkanethiol SAMs with odd and even number of carbon atoms. Due to technical difficulties with the instrument used in this study, Metastable Impact Electron Spectroscopy (MIES) was only used to qualitatively determine the coverage of water adsorbate on the alkanethiol SAMs during transition from amorphous solid water (ASW) to crystalline ice (CI). Detailed description and background information of both techniques are provided in Chapter 3.
2.4. Infrared spectra of solid water and peaks assignment

The shape and intensity of the O-H stretch (3000 – 3600 cm\(^{-1}\)) of water in the infrared spectra is strongly influenced by the strength of hydrogen bonding between the molecules and thus is highly informative of their averaged orientations in the sample.\(^{45}\) Since early 1930s the shape of the O-H stretch has been used as a probe to identify the crystallinity of solid water and the interpretation of its features has been of the utmost importance.\(^{1,46-49}\) Two or three peaks are commonly observed in the O-H stretch band of solid water adsorbed on a cold substrate (as can be seen in Figure 2.4). The Peaks’ positions and absorbance intensities are strongly depended on the temperature, pressure and in some cases on the rate of deposition on a substrate.\(^{50}\) It has been shown that at temperatures below \(~130\) K water vapour condenses on a substrate and exhibits no crystalline character and thus called amorphous solid water (ASW). Upon annealing at 140 – 160 K, ASW transforms irreversibly into cubic ice (I\(_c\)) and upon further annealing (160 – 240 K), I\(_c\) undergoes another irreversible transition to hexagonal ice (I\(_h\)).\(^{51-53}\)

Based on a wide collection of IR and Raman spectra of solid water from various studies prior to 1977, Whalley\(^1\) proposed an assignment of the O-H stretch of bulk ice and ASW. Because the reported IR and Raman spectra of ice I\(_c\) and I\(_h\) were identical and their structural features are close to each other, Whalley\(^1\) assigned ice I\(_h\) by analogy to ice I\(_c\) (together labeled as crystalline ice (CI) in this work). He assumed a simple ordered model of tetrahedral hydrogen bonding network with collective symmetric (\(v_1\)) and asymmetric (\(v_3\)) stretches. Then he added to the model intermolecular coupling and transverse optical (TO)/longitudinal optical (LO) splitting. Intermolecular coupling most strongly influenced the symmetric stretch, while the transverse optical (TO)/longitudinal optical (LO) splitting was larger for the asymmetric stretch.
Figure 2.4: The measured O-H stretch band in transition mode infrared spectra of: a. amorphous solid water (ASW) at 80 K (bottom) and crystalline ice (CI) at 100 K (top) as reported by Whalley¹, and b. i. Crystalline ice particles with 60 nm diameter at 38 K and ii. 100 nm crystalline ice film at 20 K as reported by Buch and Devlin². [Graphs are reprinted with permission from a. Canadian Journal of Chemistry and b. Journal of Chemical Physics]
The transverse optical (TO) vibration includes transition dipole moments moving in the direction perpendicular to the propagation of the light, while the longitudinal optical (LO) vibration includes transition dipole moments moving in the direction parallel to the propagation of light.\(^1\) In the IR spectra of bulk crystalline ice (CI) held at 100 K (Figure 2.4a top spectrum), Whalley assigned the high intensity central peak at 3220 cm\(^{-1}\) as the asymmetric stretch with mostly vibrations at the TO mode (\(v_3\) TO), the low-frequency shoulder at 3150 cm\(^{-1}\) as symmetric with “in-phase” intermolecular coupling (\(v_1\) in-phase), and the high-frequency feature at 3380 cm\(^{-1}\) as a combination of asymmetric stretch with LO vibrations (\(v_3\) LO) and symmetric stretch with “out-of-phase” intermolecular coupling (\(v_1\) out-of-phase).\(^1\)

The assignment of the spectral features of ASW was similar to that of CI under the assumption that ASW is a disordered form of the CI tetrahedral model. In the spectra of bulk ASW at 80 K (Figure 2.4a bottom spectrum), the central peak (assigned as \(v_3\) TO) is now at 3253 cm\(^{-1}\), the low-frequency shoulder (\(v_1\) in-phase) is at 3191 cm\(^{-1}\), and the high-frequency shoulder (\(v_3\) LO and \(v_1\) out-of-phase) is at 3367 cm\(^{-1}\). With the exception of the high-frequency shoulder, the peaks of ASW are at a higher wavenumber and the low-frequency shoulder is less pronounced than in the spectrum of CI. This was attributed to the distortion of hydrogen bonding network in ASW.\(^1\)

In 1999, Buch and Devlin\(^2\) published a new interpretation to the peaks assignment of CI made by Whalley.\(^1\) They defined the spectral features in the O-H stretch band in terms of four oscillating dipole moments surrounding an oxygen atom in a nearly tetrahedral formation. In the IR spectrum of CI (Figure 2.4b.I), the central peak at 3220 cm\(^{-1}\) was interpreted by them as
two dipoles moving toward the oxygen center while the other two dipoles moving away. This is similar to asymmetric stretch of a single water molecule with TO and LO modes (ν₃ TO and ν₃ LO). The low-frequency peak at 3150 cm⁻¹ was attributed to a transverse mode which is subjected to a strong coupling between neighbouring dipole moments (ν₁ in-phase TO). The high-frequency peak at 3350 cm⁻¹ was attributed to dipole moments in a longitudinal asymmetric mode in a combination with symmetric intermediate state in which there is no coupling with neighboring dipole moments (ν₃ LO and ν₁ out-of-phase).²

The O-H stretch peak assignments cited so far in this section were obtained in transmission IR mode (0° incidence angle or normal incidence), while IRRAS is operated at grazing angle (~85° incidence angle in this work). The reflection geometry, and thus surface selection rule, plays a significant role in determining the shape (peak's intensity and position) of the O-H stretch of solid water adsorbate. Jenniskens et. al.⁵⁴ compared the transmission O-H stretch spectra of 200 nm thick ASW (80 K) and Cl (160 K) to those obtained in IRRAS mode (87° incidence angle on thin gold substrate). In the IRRAS spectra of both ASW and Cl the peaks are at higher wavenumbers relative to the transmittance spectra. Also, the high-frequency peak intensity is enhanced while the low-frequency peak intensity is weakened in comparison to those observed in the transmittance spectra. More recently, Mitlin and Leung⁵³ simulated the O-H stretch spectra of 1 nm thick Cl film adsorbed on copper substrate (at 163 K) using Fresnel equations at varying incidence angles. Their calculated O-H stretch peak positions in transmission mode are in good agreement with the experimental spectrum of Cl nanoparticles (60 nm diameter) reported by Buch and Devlin² (Figure 2.4b.I). Mitlin and Leung⁵³ noticed similar effects in shifting of peak positions and intensities from 0° to 86° incidence angle as
reported by Jenniskens et. al.\textsuperscript{54} Table 2.1 summarizes the assigned peak positions in the O-H stretch bands of bulk ASW and CI as reported by Whalley\textsuperscript{1}, Buch and Devlin\textsuperscript{2} in transmission mode, and by Mitlin and Leung\textsuperscript{53} in IRRAS mode. Also shown are the approximate peak positions observed by Lyagusha\textsuperscript{19} for ASW and CI adsorbed on C16 SAM.

Table 2.1: O-H stretch band peak assignments and positions in transmission and IRRAS modes of amorphous solid water (ASW) and crystalline ice (CI)

<table>
<thead>
<tr>
<th>IR mode:</th>
<th>Reference:</th>
<th>Peak position (cm\textsuperscript{-1}) in transmission mode</th>
<th>Peak positions (cm\textsuperscript{-1}) in IRRAS mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Whalley\textsuperscript{1}</td>
<td>Mitlin and Leung\textsuperscript{53}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Buch and Devlin\textsuperscript{2}</td>
<td>Lyagusha\textsuperscript{19}</td>
</tr>
<tr>
<td></td>
<td>ASW</td>
<td>CI</td>
<td>ASW (40 L\textsuperscript{\star})</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td></td>
<td>CI (5 L\textsuperscript{\star})</td>
</tr>
<tr>
<td>$\nu_1$ in-phase</td>
<td>ASW</td>
<td>3191</td>
<td>3150</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>3150</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3160</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 3160</td>
</tr>
<tr>
<td>$\nu_1$ TO</td>
<td>ASW</td>
<td>3253</td>
<td>3220</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>3220</td>
<td>3325</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 3250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3240</td>
</tr>
<tr>
<td>$\nu_1$ LO</td>
<td>ASW</td>
<td>3367</td>
<td>3380</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>3350</td>
<td>3395</td>
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<td></td>
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<td>3355</td>
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<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~ 3360</td>
</tr>
<tr>
<td>$\nu_1$ out-of-phase</td>
<td>ASW</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 Langmuir (L) = 10\textsuperscript{-6} Torr-s, unit of exposure of a surface to gas at 10\textsuperscript{-6} Torr during 1 second

Since Buch and Devlin published their interpretation of the O-H stretch band, it is common to find theirs as well as Whalley’s peak assignment used in literature.\textsuperscript{50,53–55} These assignments were based on theoretical models of the O-H stretch vibrational modes, and were only qualitatively fitted to the broad peaks and shoulders observed in the IR spectra of ASW and CI (Figure 2.4). In addition, both studies justify the use of the same peak assignment for ASW and CI by indicating that the ASW is a disordered form to the tetrahedral structure of CI. This implies that upon the irreversible transition from ASW to CI, the three peaks observed in the IR spectrum of ASW shift to produce the three peaks observed in the CI spectrum. However,
in this work, an additional peak was observed during this thermal transition, which conflicts with the interpretations presented in these studies.

The aim of this project was to determine how the surface geometry of the methyl terminal groups of alkanethiol SAMs with even and odd number of carbon atoms affects the orientation of as-deposited water molecules, and the transition from ASW to CI. Based on the literature review provided in the previous section, it was hypothesized that on the surface of odd SAMs, the as-deposited water molecules would form a more uniform monolayer due to the increased affinity of the water molecules to the exposed methylene groups at the interface. While on the surface of even SAMs, water molecules would adsorb as clusters to minimize interactions with the substrate. In order to test this hypothesis, a peak deconvolution method was used in this work, to determine how many peaks lie under the broad O-H stretch band, and to unambiguously monitor changes in peak parameters as the system is manipulated (described in Section 3.8).
CHAPTER 3

Experimental Methods

3.1. Infrared Reflection – Absorption Spectroscopy (IRRAS)

Infrared Reflection – Absorption Spectroscopy (IRRAS) is a surface analysis technique that measures the intensity of the IR radiation absorbed by a molecule on a reflective surface as a function of the corresponding wavenumber (cm$^{-1}$). For optical absorption to occur, the molecule must undergo a change in its dipole moment as it is vibrationally excited, and the orientation of this transition dipole moment must align with the electric field vector of the radiated light. The later condition becomes more significant when analyzing systems, such as self assembled monolayers (SAMs), with fixed orientations with respect to the IR beam.$^{56,57}$ The radiated light has two electric field components: the s-polarized light (Es) has an electric field vector in the direction perpendicular to the plane of incidence (which is defined by the incident and the net reflected light propagation), while the p-polarized light (Ep) component has an electric field vector in the plane of incidence. Upon reflection from the metal surface, the electric field of the incident light undergoes a phase shift (Figure 3.1). The s-polarized component of the electric field vector undergoes a 180° phase shift but maintains the same magnitude, which causes the net s-polarized electric field component to approach zero. Going back to the absorption condition mentioned above, molecules with a component of transition
dipole moment aligned with the s-polarized electric field vector will not absorb the radiation and therefore are not observed with IRRAS. On the other hand, the p-polarized component of the electric field vector phase shifts by nearly 90° and maintains its magnitude upon reflection, which causes the p-polarized components of the incident and reflected light to add constructively in the direction of the surface normal. \textsuperscript{57} Hence, molecules with a component of transition dipole moment aligned with the p-polarized electric field vector will absorb the radiated light and will be enhanced in the IRRAS spectrum. It was shown by R. Greenler\textsuperscript{57} that this enhancement is at maximum at near grazing angle (85 – 88° from the surface normal) of the incident light. The process described here is called the surface selection rule.\textsuperscript{56}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.1.png}
\caption{Geometry of the incident and reflected vectors of s-polarized (Es – perpendicular to the plane of incidence where the vector direction is out $\bigcirc$ and into $\bigotimes$ the page) and p-polarized (Ep – in the plane of incidence) light upon reflection from the metal surface.}
\end{figure}
The surface selection rule is often combined with group theory analysis of the vibrational transitions in surface molecules to interpret IRRAS spectra. This is useful in determining how well a SAM film is ordered, how temperature affects the packing order of the film, as well as, observing the differences between alkanethiol SAMs with odd and even number of carbon atoms. Parikh and Allara\textsuperscript{58} assigned the C-H stretching bands of methyl terminated alkanethiol SAMs as shown in Table 3.1.

Table 3.1: Characteristic C-H stretch bands in the IRRAS spectra of methyl-terminated alkanethiol SAMs adsorbed on Au(111) substrate and band positions at 300 K\textsuperscript{59}

<table>
<thead>
<tr>
<th>Stretch band</th>
<th>Description of the transition dipole orientation</th>
<th>Band position (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric CH\textsubscript{2} (d\textsuperscript{1})</td>
<td>In C-C backbone plane and in H-C-H plane</td>
<td>2851</td>
</tr>
<tr>
<td>Symmetric CH\textsubscript{3} (r\textsuperscript{1})</td>
<td>In C-C backbone plane and parallel to C-CH\textsubscript{3} bond</td>
<td>2878</td>
</tr>
<tr>
<td>Asymmetric CH\textsubscript{2} (d\textsuperscript{1})</td>
<td>Perpendicular to C-C-C backbone plane</td>
<td>2921</td>
</tr>
<tr>
<td>Asymmetric CH\textsubscript{3} (r\textsuperscript{b})</td>
<td>Perpendicular to C-C-C backbone plane and perpendicular to C-CH\textsubscript{3} bond</td>
<td>2957</td>
</tr>
<tr>
<td>Asymmetric CH\textsubscript{3} (r\textsuperscript{a})</td>
<td>In C-C-C backbone plane and perpendicular to C-CH\textsubscript{3} bond</td>
<td>2962</td>
</tr>
</tbody>
</table>

Using this assignment, Garand et al. measured the dependence of the C-H stretches on temperature.\textsuperscript{59} They found that absorbance intensities of the symmetric CH\textsubscript{3} (r\textsuperscript{1}) and CH\textsubscript{2} (d\textsuperscript{1}) bands increased by 75% as the temperature decreased from room temperature (300 K) to 25 K and all peaks shifted by 2 – 3 cm\textsuperscript{-1} to lower wavenumbers. These effects were attributed to an increase in the packing order and reduction of gauche defects in the alkanethiol chains as the temperature decreases.\textsuperscript{58} Lyagusha\textsuperscript{19} obtained IRRAS spectra of a series of methyl-terminated
alkanethiol SAMs with chains varying from 7 to 16 carbon atoms. She compared the C-H stretch bands of odd and even SAMs and observed spectral changes due to temperature (comparable IRRAS spectra of even (C16 and C12) and odd (C15 and C11) SAMs are shown in Figure 3.3). The major differences in the spectra of odd and even SAMs are the intensities of the symmetric and asymmetric CH$_3$ peaks. In the C-H stretch band of odd SAMs, the symmetric CH$_3$ (r$^+$) peak is less pronounced than in the C-H stretch band of even SAMs and it is the only stretch vibration band that does not increase in intensity with decreasing temperature. However, in the case of even SAMs, the asymmetric CH$_3$ (r$^-$) peak is lower in intensity than in the C-H stretch band of odd SAMs and does not increase in intensity with decreasing temperature. These results are correlated to the surface selection rule and the terminal methyl group orientations in even and odd SAMs (Figure 3.2). In even SAMs, the symmetric CH$_3$ (r$^+$) transition dipole moment has a greater component along the surface normal (27° from the surface normal) and therefore is more intense than in odd SAMs (58° from the surface normal). The situation is reversed in the case of asymmetric CH$_3$ (r$^-$) where its transition dipole component along the surface normal is greater in odd SAMs (32° from the surface normal) than in even SAMs (63° from the surface normal). Figure 3.3 shows C-H stretch band in the IRRAS spectra of even and odd SAMs, adsorbed on Au(111) substrate at room (black – 300 K) and cryogenic (red – 120 K) temperatures.
Figure 3.2: Schematic diagram of the transition dipole moments of methyl (CH$_3$) and methylene (CH$_2$) stretch vibrational modes in methyl-terminated alkanethiol SAMs with odd and even number of carbon atoms. Solid lines represent transition dipole moments in the plane of the C-C backbone plane. Dashed lines represent transition dipole moments perpendicular to the C-C backbone plane.
Figure 3.3: C-H stretch in the IRRAS spectra of methyl-terminated alkanethiol SAMs with even (C16 and C12) and odd (C15 and C11) number of carbon atoms, adsorbed on Au(111) substrate, at room (black – 300 K) and cryogenic (red – 120 K) temperatures.
3.2. Metastable Impact Electron Spectroscopy (MIES)

Metastable Impact Electron Spectroscopy (MIES) is a surface analysis technique that measures the kinetic energy distribution of electrons ejected upon the collision of metastable atom (an atom with a long-lived excited state) with the outermost atoms and molecules at the surface.\(^{17,18}\) It is a highly sensitive and nondestructive technique due to the use of noble gas atoms with low kinetic energies (60 – 100 meV) to probe the surface. The ionization process due to a collision between a metastable atom (\(M^*\)) and a target atom or molecule (\(T\)) was first observed by F. M. Penning in 1927 while investigating discharge phenomena of noble gases.\(^{60,61}\) Penning\(^{60}\) represented this process as follows:

Penning Ionization (PI): \[ T + M^* \rightarrow T^+ + M + e^- \] (eq. 3.1)

Helium’s long excited state lifetime in the triplet state (7870 seconds)\(^{62}\), \(He^* (2^3S_1)\) with 19.8 eV, leads to its frequently use in MIES as the metastable atom. While the singlet excited state of helium, \(He^* (2^1S_1)\), with 20.6 eV, has lifetime of 0.0197 seconds.\(^{61}\) According to quantum mechanics selection rules, optical transitions from \(He^* (2^3S_1)\) triplet state to ground state (\(1^1S_0\)) and vice versa are doubly forbidden. First, the triplet excited state shares the same angular momentum quantum number (\(S, l = 0\)) as the ground state and second, the two electrons in the metastable state have parallel spins while the ground state has anti-parallel spin configuration.\(^{62}\) Approximately 90% of the long-lived excited helium atoms produced in the \(He^*\) source are in the triplet (\(2^3S_1\)) state and the rest are in the singlet (\(2^1S_1\)) excited state.\(^{63}\) This is due to the high kinetic energy of electron collisions with the helium atoms in the DC discharge that allows the transition from ground state to triplet state. Afterwards, the excited...
He\(* (2^3S_1)\) are removed from the source and the forbidden direct photon decay from He\(* (2^3S_1)\) to ground state (1^1S_0) is the cause to the metastable state.\(^{61}\)

There are two probable mechanisms in which the metastable atoms de-excite through their interaction with the surface. The first mechanism corresponds to most transition metal surfaces, of which the Fermi level is below the energy of the 2s orbital of the incident metastable atom; de-excitation has been shown to proceed by Resonance Ionization (RI) followed by Auger Neutralization (AN).\(^{61}\) Figure 3.4a shows the energy level diagrams of these two steps. Upon collision of the excited helium atom with the metal surface, the electron from the 2s orbital of He\(*\) tunnels into the empty valence energy band of the metal, and thus ionizes the metal target molecule (T).\(^{62}\)

Resonance Ionization (RI):
\[
\text{He}\,* + T \rightarrow T^- + \text{He}^+ \tag{eq. 3.2}
\]

Next, an electron at the Fermi level of the metal target ion (T\(^-\)) drops down in energy to fill the 1s orbital of He\(^+\) while another electron gains this energy and is ejected from the surface to an energy above the vacuum level:

Auger Neutralization (AN):
\[
T^- + \text{He}^+ \rightarrow T^+ + \text{He} + e^- \tag{eq. 3.3}
\]

The electron is ejected with kinetic energies that range from 0 eV to the maximum kinetic energy (\(E_{K max}\)) of:

\[
E_{K max} = E_i^{eff} - 2\Phi \tag{eq. 3.4}
\]
where $E_{i}^{\text{eff}}$ is the effective ionization energy of the metastable atom (in this case, He*(2\(^3\)S\(_1\)) with 19.8 eV) and $\Phi$ is the work function of the target metal, which is 4-6 eV for noble metals.\(^{62}\)

\[ \text{Figure 3.4: Energy level diagrams of a. Resonance Ionization + Auger Neutralization, and b. Auger Deexcitation.} \]

The second de-excitation mechanism is Penning Ionization (PI) (also called Auger Deexcitation AD) and it is usually applied to surfaces covered by adsorbates (Figure 3.4b). In this case, the valence energy states of the metal cannot overlap with those of the incident He* because of the presence of the adsorbate molecules. As a result, the valence electron of the adsorbate molecule transfers to the 1s orbital of He* while the electron from the 2s orbital is ejected.
The electron ejected by this process has a kinetic energy \( E_K \) of:

\[
E_K = E_i^{\text{eff}} - IP
\]  
(eq. 3.5)

where \( E_i^{\text{eff}} \) is the effective ionization energy of the metastable atom (He*(2\(^3\)S\(_1\)) 19.8 eV ) and \( IP \) is the ionization potential of the molecular orbital of adsorbate molecule. Following equation 3.5, the ionization potential of the molecular orbital (MO) involved in the de-excitation process can be calculated by measuring the kinetic energy of the electron ejected from the surface. The probability of a certain molecular orbital on the surface of the adsorbate to interact with the He* atom depends on the degree of exposure of the molecular orbital. In the MIES technique, the number of electrons ejected from the surface, i.e. peak intensity, is plotted against their corresponding kinetic energy, the outmost molecular orbital of the exposed molecule will have greater intensity in the spectrum than those that are less exposed.

Figure 3.5 represents the MIES spectra of C16 and C15 SAMs at 300 K. Also shown are the outermost MOs of methyl-terminated alkanethiol SAMs that interact with the He* atoms through Auger Deexcitation. The large peak between 0 and 3.5 eV was attributed to low energy secondary electrons produced by inelastic scattering of the electrons within the SAM. Following Morgner and Heinz’s assignment\(^ {64} \), the peak at 6 eV corresponds to the \( \sigma(2p) \) MOs localized around the methyl terminal groups, while the peak between 4 and 5 eV was assigned to the \( \pi(2p) \) MOs of the methylene unit. Obscured by the large secondary electrons is the peak that corresponds to the interaction of He* atoms with the \( \sigma(2s) \) MOs of C-C bond of the alkanethiols.\(^ {19,64} \)
In the case of water adsorbates, there are three occupied MOs in the valence band of water which can interact with the incoming He* atoms: 1b₁, 3a₁ and 1b₂. The peak at 1.5 eV was assigned to 1b₂ MO, which has a bonding character in the interaction of H and O atoms. It is asymmetric with respect to a mirror plane normal to the molecular plane (the molecular plane contains the O and the two H atoms). The peak between 5 and 6 eV corresponds to 3a₁ MO which also has bonding character in the interaction between H and O atoms. However, it is symmetric with respect to the molecular plane. Lastly, the peak at 8 eV, which was assigned to 1b₁ MO, has a nonbonding character corresponding to the oxygen’s lone pairs of electrons and it is asymmetric with respect to the mirror plane normal to the molecular plane. Figure 3.6 shows the three highest occupied MOs of water in the MIES spectra of C16 exposed to 70 L (1 Langmuir (L) = 10⁻⁶ Torr·s) water at 110 K. In this project, MIES spectra were obtained to
qualitatively determine the coverage of water adsorbate on the alkanethiol SAMs during transition from amorphous solid water (ASW) to crystalline ice (CI) (see Figure 7.27 in the Appendix).

**Figure 3.6:** MIES spectra of C16 SAM exposed to 70 L of water at 110 K.
3.3. Instrumentation

Figure 3.7 shows schematic diagram of the in-lab built instrument used in this research which combines the two surface analysis techniques: metastable impact electron spectroscopy (MIES) and infrared reflection-absorption spectroscopy (IRRAS). For MIES experiments, helium atoms are excited to a metastable state \((\text{He}^*)\) by electron-atom collisions in the DC discharge in the primary chamber. The \(\text{He}^*\) beam (vertical red line in Figure 3.7) travels through a chopper wheel in the secondary chamber which can modulate the beam flux. Faraday cups and channel electron multiplier (CEM) detectors are installed on a rotatable arm in the secondary and tertiary chambers to measure the \(\text{He}^*\) beam flux when needed, and can be moved out of the beam path to pass into the analysis chamber. \(\text{He}^*\) atoms collide with the sample mounted in
the center of the analysis chamber, causing the ejection of electrons according to the mechanisms described above. The kinetic energies of the emitted electrons are measured using the hemispherical energy analyzer (HEA). As shown in Figure 3.7, the sample can be rotated about the vertical central axis of the spherical chamber to allow IRRAS spectra to be obtained.

3.3.1. Metastable helium (He*) beam line

Starting from the primary chamber which is leftmost in Figure 3.7, the primary chamber contains the DC discharge set-up to excite He atoms from ground state \(1^1S_0\) to triplet \(2^3S_1\) and singlet \(2^1S_1\) states. It was determined that approximately 90% of the excited species produced in the discharge are in the triplet \(2^3S_1\) state and 10% are in the singlet \(2^1S_1\) state. In addition to these two species, He(I) UV radiation is also produced with 21.2 eV.\(^{61}\)

He gas (Linde Gases, 99.999% pure) flows at 60 psi through stainless steel capillary tube into a quartz nozzle in the source chamber (6 mm diameter and approximately 0.3 mm aperture). A tantalum rod of 2 mm diameter is held inside the quartz nozzle at 10 mm distance between its sharpened tip and the nozzle's aperture. The quartz nozzle aperture is also 10 mm away (Z-direction) from the stainless steel skimmer. The position of the nozzle/Ta rod assembly can be aligned with the stationary skimmer using stepping motor driver moving in the XY planes (perpendicular to the molecular beam axis) and a manually operated Z-stage (along the axis of the beam). Under normal operating conditions, the voltage applied to the Ta rod is 2500 V (by a Vacuum Generators high voltage power supply) with respect to the grounded skimmer, which results in discharge current of 8 – 9 mA and a pinkish-white plasma.
Two oil diffusion pumps, a Varian VHS-250 (He pumping speed: 4600 L/s) and a Varian VHS-6 (He pumping speed: 3000 L/s), are used to reduced the pressure in the primary and the secondary chambers, respectively, to pressures in the range of $10^{-6} - 10^{-7}$ Torr during operation (backed with a rotary vane mechanical pump Leybold Trivac D8B). The tertiary chamber is evacuated by an oil-free turbomolecular pump (Edwards STP-451, 480 L/s) to a pressure of low-$10^{-8}$ Torr, and it is backed by a dry scroll pump (Varian SH-100).

The molecular beam travels from the nozzle through a cone shaped stainless steel skimmer (2 cm diameter at the base, 6 cm long, and 1 mm opening) into the secondary chamber, in which it is modulated by a chopper wheel and the beam current is measured with a Faraday cup detector. The chopper wheel is made of a 1 mm thick aluminum disc mounted on a brushless DC electric motor. Attached to the wheel is a plastic transparent disk patterned with black lines which, along with an optical isolator, allows controlling the rotational frequency of the chopper wheel (75 Hz) and coupling the frequency with beam currents detected with a lock-in amplifier (SR-830, SRS Instruments). A multi-channel scalar program is used to divide electron emission counts into fixed time interval (bins) relative to a set point on the chopper wheel. The addition of signal from several time bins allows the signal-to-noise ratio of the electron counts to increase. The two open sections on the chopper wheel allow all beam components to pass through while the four slits (0.25 mm wide) allow the beam to pass in short pulses of approximately 300 μs. Thus, the separation of the He(I) UV photons and He* atoms can be achieved and seen in a time-of-flight profile of the beam components (Figure 3.8). This profile was obtained using a channel electron multiplier (CEM) detector in the tertiary chamber coupled with the time signal sent from the chopper to the lock-in-amplifier. By setting the He(I)
UV peak as a reference (at 0 μs), the relative velocity distribution of He* atoms can be calculated by dividing the distance travelled from the source to the CEM detector (0.6 m) by the time of flight. Under 60 psi He inlet pressure and 8.8 mA discharge current, the velocity distribution of He* atoms was found to range from 1500 to 4000 m/s with maximum at 2500 m/s and 0.05 – 0.30 eV kinetic energy range. It is important to note that the kinetic energy of the He* atoms is much smaller than their internal energy ($2^3S_1$ 19.8 eV).

**Figure 3.8:** Schematic diagram of the chopper wheel and the corresponding Time-of-Flight profile of the beam components.
3.3.2. Analysis chamber

He* atoms enter the analysis chamber via the gate valve between the tertiary and analysis chambers. The analysis chamber is evacuated by an ion pump (Varian V400 Triode, 400 L/s) with typical pressure of low $10^{-9}$ Torr. Here the metastable atoms collide with the sample at approximately 45° angle from the surface, and the resulting electron emission process is detected with a hemispherical energy analyzer (HEA, VG 100AX). By simply rotating the sample about the vertical axis, IRRAS experiments can be conducted at incidence angle of 85° relative to the surface normal.

Sample holders with freshly prepared surfaces are introduced into the ultra high vacuum chamber through a pressure isolated load lock chamber. The load lock is vented to atmospheric pressure with nitrogen gas to reduce atmospheric water molecules sticking to the walls of the chamber. Sample holders are loaded through an O-ring sealed access hatch at the top of the chamber onto aluminum transfer stage that can hold up to 3 samples. The chamber is pumped down to low $10^{-7}$ Torr by a turbomolecular pump (Pfieffer TMU-065) backed with dry scroll pump (Varian SH-100). Using a magnetic transfer rod, the aluminum stage can be pushed into and withdrawn from the analysis chamber where a wobble stick is used to lift the sample holder from the aluminum stage and mounted on the sample manipulator.

In order to maintain ultra-high vacuum conditions, the analysis chamber and HEA are wrapped with braided heating wires (OMEGA) and heated to 120° C to desorb gases (mainly water molecules) from the chamber walls. Aluminum foil is also wrapped around the heating wires to distribute the heat more evenly across the chamber walls. This bake-out process is monitored with a quadrupole gas analyzer (Hiden Analytical LTD 321) and is conducted when
the partial pressure of water exceeds $10^{-10}$ Torr, and stopped when the partial pressure of water reach its base pressure of $2\times10^{-11}$ Torr. The quadrupole gas analyzer is also used to monitor the partial pressures and purity of gases dosed into the chamber using a high-precision leak valve (VG) for deposition experiments.

### 3.3.3. Sample manipulator

Figure 3.9 shows a schematic diagram of the sample manipulator and the copper sample holder. The sample holder is mounted onto the rotatable sample manipulator inside a gallium well that is heated above the gallium melting point (29.8° C) while exchanging samples and then cooled down to solidify the sample onto a copper block. The use of Ga not only secures the sample holder in its place, but also provides thermal and electrical conductivity to the sample itself. The copper block is suspended between two stainless steel support beams using two glass beads set into 2 mm bearings. The sample suspension assemble allows to electrically and thermally isolate the sample holder and copper block from the grounded chamber during MIES experiments (where -30 V bias is applied to the sample) as well as to adjust the sample horizontal tilt using an inchworm motor (Burleigh UHVL).

A cartridge 25 W heater is inserted into the copper block while a K-type thermocouple is attached to it in order to heat and monitor the surface temperature using an Omega (Cyc 3200) cryogenic temperature controller. A liquid nitrogen reservoir is used to cool the sample to cryogenic temperatures (down to 120 K after 4 hours). This is done by a thermally conductive copper plate attached to liquid nitrogen tank and a sapphire disc to conduct heat but electrically isolate the copper clamps plates from the tank. Six oxygen-free high thermal
conductivity copper braids (OFHC, 1/4” Flat, Lesker) are attached to the sapphire disc and copper sample block to conduct heat from the sample to the liquid nitrogen reservoir. A Vespel bushing and O-rings (Dupont) allow the electrical isolation of this assembly from the central stainless steel rod and the two support beams. The rotatable stainless steel rod allows the sample to be rotated by approximately 270°.
Figure 3.9: a. Schematic diagram of the sample manipulator and b. picture of a sample holder with gold substrate.
3.3.4. Hemispherical Electron Analyzer (HEA)

The kinetic energies of electrons ejected through collisions of metastable helium atoms with the surface molecular orbitals are measured using a VG 100 AX hemispherical electron analyzer (Figure 3.10) which consists of a transfer lens system, a concentric hemispherical sector analyzer and an electron multiplier detector (Channeltron 7010, Photonis). The transfer lens system focuses the emitted electrons to the entrance slit (4 mm wide) of the analyzer and scales their kinetic energies to match the pass energy range accepted by the analyzer. The two hemispherical stainless steel surfaces of the analyzer (with $R_1$ and $R_2$ radii) are negatively charged ($-V_1$ and $-V_2$ potentials) so that they create a radial electrostatic field through which only electrons with energy $E_0 = eV_0$ (also called pass energy) and trajectory radius $R_0$ can move across the field without colliding with the walls of the analyzer. The sector plate potentials can be defined in terms of their individual radius and mean radius ($R_0$) as follows:

\[ V_1 = V_0 \left( 3 - 2 \frac{R_0}{R_1} \right) \]  \hspace{1cm} (eq. 3.6)

\[ V_2 = V_0 \left( 3 - 2 \frac{R_0}{R_2} \right) \]  \hspace{1cm} (eq. 3.7)

The potential of the selected electron is given by:

\[ V_0 = V_1 \frac{R_1}{2R_0} + V_2 \frac{R_2}{2R_0} \]  \hspace{1cm} (eq. 3.8)
Although the electrons passing through the entrance slit are said to be monoenergetic, the energy resolution of the analyzer is given as:

$$\Delta E = \frac{E_0(W_{in}R_1+W_{out}R_2)}{2R_0} + (\delta \alpha)^2 \quad \text{(eq. 3.9)}$$

Where $\delta \alpha$ is the angle between the actual electron tangential direction with energy $E_0 \pm \Delta E$ and the ideal tangential direction with energy $E_0$, $W_{in}$ and $W_{out}$ are the entrance and exit slit widths respectively.

Once the energy selected electrons reach the exit slit, they are detected by the channeltron and the counts per second (intensity signal) are recorded. This system is operated at a Constant Analyzer Energy (CAE) mode which means that the hemispherical elements are held at constant potentials and pass energy, while the transfer lens system alone selects and focuses the electrons at the entrance slit. In this research the pass energy was set to 5 eV and the transfer lens system scanned over a range of 0 – 23 eV kinetic energy relative to the sample bias (-30 V) with 100 meV steps and channeltron bias of +2800 V. The channeltron signal was also coupled to the chopper rotational frequency through the multi-channel scalar program. All MIES experiments were conducted by adding the electron counts of 5000 bins of 2.6 μs time interval and averaged over 100 cycles at 75 Hz chopper frequency. The presented MIES spectra are obtained by integrating the bins signal corresponding to the open sections of the chopper versus the electron kinetic energy.
Figure 3.10: Schematic diagram of hemispherical electron analyzer (HEA)
3.4. Sample preparation

3.4.1. Au(111) thin films

The first step to achieve a highly ordered alkanethiol self-assembled monolayer (SAM) films is to prepare and maintain closed-packed Au(111) surfaces. This was reproducibly done by thermally evaporating gold (purchased from The Royal Canadian Mint, 99.99% pure) onto muscovite (mica) slides in a custom-built stainless steel high vacuum instrument (“Midas”). The 1 × 3 inch mica slides (0.15 - 0.18 mm thickness, Grade V1, Ted Pella Inc.) were first cleaved to expose a fresh laminar layer using scalpel and several drops of methanol to facilitate the separation of two adjacent layers. These were then secured with the fresh side exposed, to a copper plate that can hold 8 mica slides. The copper plate was face down inside a bell-shaped stainless steel evaporation chamber with a 0.2 g gold pellet in a molybdenum heating boat (K. Lesker) at the base of the chamber. The chamber is evacuated to 10⁻⁷ Torr using a Varian TV301 turbomolecular pump and after degassing the mica slides for 12 hours at 300°C, the pressure drops to 5×10⁻⁸ Torr. A Quartz crystal microbalance was used to monitor the rate of deposition of 1 Å/s while evaporating gold onto the mica slides to achieve thickness of 200 nm. After deposition, the gold coated mica slides were left to anneal for an additional 3 hours at 300°C and to promote larger Au(111) grain sizes. After the annealing process, the gold coated mica slides were removed from the chamber and stored in a desiccator until further use.

Before immersing the gold substrates in the desired alkanethiol solution, the gold coated mica slides were cleaned by following the procedure published by Kang and Rowntree⁶⁹. Gold surfaces were acid washed with sulphochromic acid (2.25 mL of chromium trioxide in 200 mL of concentrated sulphuric acid) for 45s to remove organic contaminants from the
surface, washed repeatedly with ultrapure water following with methanol to wash away the acid, and dried under a stream of argon gas. Finally, the acid washed substrates were placed in a UV-Ozone cleaner (Jelight 342) for 30 min. The ozone produced by the dissociation of molecular oxygen (using UV radiation), reacts with trace organic contaminants on the surface to provide a uniform SAM.

3.4.2. Alkanethiol SAMs on Au(111) films

SAM films were prepared by immersing the freshly cleaned Au(111) surfaces in 1 mM solution of the desired alkanethiol in methanol and left in a warm water bath for 24 hours. Afterwards, the films were rinsed with methanol, gently dried with argon, and then cut to size and mounted on the sample holder to be inserted into the load lock chamber.

The following alkanethiols were used as received: 1-hexadecanethiol (C16 97%, Alfa Aesar), 1-pentadecanethiol (C15 98%, Sigma-Aldrich), 1-dodecanethiol (C12 98%, Aldrich Atofina), and 1-undecanethiol (C11 98%, Sigma-Aldrich).

3.5. IRRAS Measurements

Infrared reflection – absorption spectra were obtained using a Nicolet iS50 FT-IR spectrometer and an external MCT/A detector (FT-IR-16-1.0, Infrared Associates Inc.). The collimated infrared beam is directed from the spectrometer and focused on the sample using two gold coated adjustable mirrors. To avoid interference of atmospheric water and CO₂ peaks in the spectra, the mirrors leading the beam into the chamber and out of the chamber to the detector are enclosed in acrylic boxes purged with dry, CO₂ free air. The beam passes through a
differentially pumped KBr window into the analysis chamber, reflects from the sample surface at a ~85° incidence angle, and passes through another differentially pumped KBr window out of the chamber. Next, it is focused on the liquid nitrogen cooled MCT/A detector using an ellipsoidal gold coated mirror (Nicolet).

Spectra were collected using OMNIC software which controls spectrometer parameters, however, the raw data is relayed to a custom-built Lab-VIEW program which allows series collection of spectra at set time or temperature intervals. Table 3.2 lists the spectrometer parameters used to collected spectra.

**Table 3.2: IRRAS Acquisition Parameters**

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<th>Value</th>
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<tr>
<td>- SAM films</td>
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3.6. MIES Measurements

Metastable impact electron spectra were obtained using metastable He* (~90% $^3S_1$ 19.8 eV) atoms produced in the DC discharge in the primary chamber. The He* source is operated at a 60 psi inlet pressure, 2500 V applied to the Ta needle, and 8 – 9 mA discharge current. Beam current is monitored using Faraday cup detectors in the secondary and tertiary chambers, with optimal emission currents of ~2 nA and ~0.4 nA, respectively. The sample is positioned in a 15° angle away from the hemispherical energy analyzer (HEA) toward the He* beam. A bias of -30 V (relative to ground) is applied to the sample. The pass energy of the HEA is set to 5 eV and the transfer lens system scans over a range of 0 – 23 eV kinetic energy relative to the sample bias (-30 V) with 100 meV steps and channeltron bias of +2800 V. Electron counts are collected by the multi-channel scalar in 5000 bins of 2.6 µs time interval averaged over 100 cycles with 75 Hz chopper frequency. Spectra are extracted by integrating the bins signal and plotting against kinetic energy. Table 3.3 lists the instrumentation parameters used to collect MIES scans.
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<tr>
<td>Analysis chamber pressures</td>
<td>low $10^{-9}$ Torr</td>
</tr>
<tr>
<td>Pressure while dosing water</td>
<td>low $10^{-8}$ Torr</td>
</tr>
<tr>
<td>Partial pressure of water</td>
<td>$1\times10^{-8}$ Torr</td>
</tr>
<tr>
<td>Sample current</td>
<td>0.08 – 0.180 nA</td>
</tr>
<tr>
<td>Sample bias for MIES</td>
<td>-30 V</td>
</tr>
<tr>
<td>HEA channeltron bias</td>
<td>+2800 V</td>
</tr>
<tr>
<td>HEA pass energy</td>
<td>5 eV</td>
</tr>
</tbody>
</table>
3.7. Water dosing experiments

Ultrapure (Milli-Q) water was dosed into the analysis chamber through a custom-built dosing board that allows the degassing of liquids before they are introduced to the sample. One drop of ultraclean water was placed in a quartz dosing tube and subjected to a series of freeze-pump-thaw cycles until the base pressure in the dosing board is established (~30 mTorr). The pressure is measured using a capacitance manometer (MKS Baratron 622B) and the dosing board is pumped using a scroll pump (Varian SH-100). Once the sample was cooled to 120K, water was dosed into the chamber at partial pressure of $1 \times 10^{-8}$ Torr for the desired time period (unit of exposure: 1 Langmuir = $10^{-6}$ Torr·s), while ensuring that only the partial pressure of water is rising in the chamber and not of other atmospheric gasses (using a quadrupole gas analyzer).

Two types of water dosing experiments were conducted in this research on each alkanethiol SAM surface. The first observed the changes in water adsorbate’s orientations and interactions with the surface as the water molecules are deposited on the surface at temperature of 120 K. IRRAS and MIES scans were taken after each deposition starting with 0.5 L and gradually increasing water exposure up to 20 L. The second experiment observes the transition of amorphous solid water (ASW) to crystalline ice (CI) on each surface, by exposing the sample to 5 L of water at 120 K and heating the surface to 150 K. The Omega temperature controller was used to ramp up the sample temperature at rate of 0.5 K/min and IRRAS scans were taken at approximately 2 minute interval (64 – 128 average scans were taken between 1 K temperature variations).
3.8. Multiple peaks – fit analysis

Previous studies concerning the wide O-H stretch band of ice in the IR spectra have been able to only qualitatively monitor changes in the broad peak and shoulders of the band. Commonly, this was done using the peak assignments described by Whalley\(^1\) or Devlin and Buch\(^2\). In this work, a peak deconvolution method was developed to measure the spectral differences in the O-H stretch band of water adsorbed on methyl-terminated alkanethiol SAMs with odd and even number of carbon atoms, as well as, to monitor changes during the transition from amorphous solid water (ASW) to crystalline ice (CI).

The scientific graphing and data analysis software, OriginPro 2015\(^7\), was used to fit multiple peaks to the O-H stretch band in the IRRAS spectra of water adsorbed on alkanethiol SAMs. Using Levenberg-Marquardt iteration algorithms for non-linear regression, 400 iterations of a chosen model parameters were used to minimize the reduced chi-square (\(\chi^2_{\text{Red}}\)) value during the regression process. The reduced chi-square is the mean deviation from the experimental curve and can be calculated from the residual sum squares (RSS) as follows:

\[
\chi^2_{\text{Red}} = \frac{RSS}{\text{Variance} \times DF} = \frac{1}{DF} \sum \frac{(y_{\text{exp}} - y_{\text{theo}})^2}{\sigma^2}
\]  

(eq. 3.10)

where \(y_{\text{exp}}\) is the experimental data point, \(y_{\text{theo}}\) is the theoretical data point, \(\sigma\) is the variance (square of the standard deviation which is on average \(1.4 \times 10^{-4}\) in this work), and DF is the degrees of freedom which is equal to the total number of data points (N) minus the number of adjustable parameters of the chosen model (k). When the difference between the \(\chi^2_{\text{Red}}\) values of two successive iterations is less than a certain tolerance value, the curve-fit is
said to be successfully converged. An unsuccessful convergence means that the tolerance value was not reached within 400 iterations.\textsuperscript{71,72}

The two line shape profiles used in this work are Gaussian and Voigt. The normal distribution function of Gaussian (eq. 3.11) was used to simulate peaks subjected to heterogeneous broadening mechanism. Heterogeneous broadening describes the increase in the linewidth of an atomic transition caused by local effects that influence the absorbance of atoms or molecules differently.\textsuperscript{73,74} A common cause to heterogeneous broadening in a solid medium is the location of the atom or molecule in a crystal lattice which can lead to absorption at slightly shifted wavenumber. A Gaussian has three adjustable parameters per peak in addition to the baseline offset ($y_0$): peak center ($x_c$), area ($A$), and width ($w$).

$$y = y_0 + \frac{A}{w\left(\frac{\pi}{2}\right)} e^{-\frac{2(x-x_c)^2}{w^2}}$$

(eq. 3.11)

The Voigt function (eq. 3.12) is a convolution of two distribution functions: Gaussian (eq. 3.13) and Lorentzian (eq. 3.14). While a Gaussian is used to simulate peaks with heterogeneous broadening, the Lorentzian is used to simulate peak broadened by homogeneous factors. Homogeneous broadening describes the increase in the linewidth of an atomic transition caused by effects that equally influence the absorbance of different atoms or molecules in the sample.\textsuperscript{73,74} Assuming each spectral line broadening effect is independent; the Voigt profile provides a way of measuring the width component of each fitted peak influenced by Gaussian or Lorentzian broadening mechanism.
The Voigt profile has four adjustable parameters per peak in addition to the baseline offset ($y_0$): peak center ($x_c$), area ($A$), Gaussian full width at half maximum ($w_G$), and Lorentzian full width at half maximum ($w_L$). The convoluted full width at half maximum (FWHM) of each peak can be estimated as follows:

$$FWHM \approx 0.5346 \, w_L + \sqrt{0.2166 \, w_L^2 + w_G^2}$$  \hspace{1cm} (eq. 3.15)

The next step is to statistically determine which model best fit the experimental data. F-test is commonly used to compare the fitting quality of two models however it can only be applied in cases where one model is a simpler form of the other model (“nested models”). For example, Gaussian with 3 peaks fitted to the experimental curve and Gaussian model with 4 peaks. Provided that the model with the greater number of parameters will always fit the experimental curve better (lower RSS) or just as well as the model with a fewer parameters, F-test can be used to determine whether the difference is significant within a given confidence.
level. In order to compare the fitting quality of multiple models which are not necessarily nested, such as Gaussian and Voigt models, Akaike Information Criterion (AIC)\textsuperscript{76,77} was calculated following eq. 3.17. The AIC value represents a trade-off between the goodness of fit of the model (the first term of the equation) and the number of parameters included in the model (second and third terms of eq. 3.16). The model with the lowest (most negative) value represents the best fitted model.\textsuperscript{75,77}

\[
AIC = \begin{cases} 
N \ln \left( \frac{RSS}{N} \right) + 2k & \text{when } \frac{N}{k} \geq 40 \\
N \ln \left( \frac{RSS}{N} \right) + 2k + \frac{2k(k+1)}{N-k-1} & \text{when } \frac{N}{k} < 40 
\end{cases} 
\text{(eq. 3.16)}
\]

Once the best-fit model was identified, model parameters (peak centre, area, and FWHM) were averaged over the temperature ranges of 120 – 135 K and 145 – 150 K for each sample (Tables 7.1 – 7.5 in the Appendix). A two-tailed t-test (95% confidence level) was used in order to determine whether the averaged peak parameters of even SAMs are significantly different than odd SAMs. The t-value was calculated as follows:\textsuperscript{78}

\[
t - \text{value} = \frac{|\bar{x}_{\text{odd}} - \bar{x}_{\text{even}}|}{\sqrt{\frac{s_{\text{odd}}^2 (n_{\text{odd}} - 1) + s_{\text{even}}^2 (n_{\text{even}} - 1)}{n_{\text{odd}} + n_{\text{even}} - 2}}} \sqrt{\frac{n_{\text{odd}} n_{\text{even}}}{n_{\text{odd}} + n_{\text{even}}}} 
\text{(eq. 3.17)}
\]

Where \(\bar{x}_{\text{odd}}\) and \(\bar{x}_{\text{even}}\) are the means of the model parameters of odd and even SAMs, \(s_{\text{odd}}\) and \(s_{\text{even}}\) are the corresponding standard deviations, and \(n_{\text{odd}}\) and \(n_{\text{even}}\) are the number of measurements. If the calculated t-value is greater than t-critical (2.4469 for two-tailed test with
6 degrees of freedom) at the 95% confidence level, the two means are considered to be different. However, if the t-value is smaller than t-critical, the two means are the same and there is no difference between odd and even SAMs.\(^78\)
CHAPTER 4

Results and Discussion

4.1. Water deposition on alkanethiol SAMs with an odd and even number of carbon atoms

4.1.1. O-H bond stretch during water deposition

In order to investigate how the geometry of the methyl terminal group influences the orientations of amorphous solid water (ASW) molecules at the interface, it was crucial to start the analysis at submonolayer exposure levels and temperature range below the transition temperature to crystalline ice (CI). A former group member, Lyagusha\textsuperscript{19}, performed preliminary experiments of water deposition on C16 and C15 SAMs and found that in the instrumentation used in this work, 5 L exposure (1 Langmuir = $10^{-6}$ Torr·s) leads to the adsorption of approximately a monolayer of water molecules on each SAM’s surface. She also showed that water adsorbed on both SAMs transitioned from ASW to CI at approximately 140 K.\textsuperscript{19} In light of this information, pristine C16 and C15 SAMs were initially exposed to 0.5 L water at 110 K. After obtaining IRRAS spectrum of the adsorbed water molecules, the exposure was gradually increased to produce a monolayer of water molecules (~ 5 L) on each SAM, while obtaining IRRAS spectra after each deposition. This procedure was repeated to achieve approximately four monolayers (20 L) of water adsorbate, while maintaining deposition temperature of 110 K (Figure 4.1a). Comparison of the O-H stretch band of water adsorbed on
Figure 4.1: a. O-H stretch in the IRRAS spectra of C16 and C15 methyl-terminated alkanethiol SAMs exposed to 0.5 – 30 L water at 110 K. b. Comparing the O-H stretch of water adsorbed on C16 (black) and C15 (red) in the submonolayer (0.5 – 5 L) water exposure.
C16 (black) and C15 (red) SAMs after 0.5, 1, 2 and 5 L water exposures are shown in the four plots in Figure 4.1b.

The O-H stretch bands in the IRRAS spectra shown in Figure 4.1 are dominated by two peaks at 3280 cm\(^{-1}\) and \(~3380\) cm\(^{-1}\) which can be assigned, following Whalley’s\(^1\) O-H stretch peak assignment (Table 2.1), to asymmetric transverse optical vibration (\(\nu_3\) TO), and a combination of asymmetric longitudinal optical vibration (\(\nu_3\) LO) with symmetric out-of-phase (\(\nu_1\) out-of-phase) vibration stretch. At submonolayer water deposition (Figure 4.1b), the \(\nu_3\) LO + \(\nu_1\) out-of-phase (\(~3380\) cm\(^{-1}\)) peak is more intense in the C16 spectra than in C15. With increasing water exposure (0.5 to 5 L), the \(\nu_3\) TO peak (3280 cm\(^{-1}\)) is shifted by \(~20\) cm\(^{-1}\) to lower wavenumber in the C15 spectra while it is shifted slightly to higher wavenumber in the case of C16 spectra. The shoulder at \(~3150\) cm\(^{-1}\) is assigned to the symmetric in-phase vibration stretch (\(\nu_1\) in-phase) and is more pronounced in the C15 spectra than in C16. At water exposures above a monolayer (5 – 20 L), \(\nu_3\) LO + \(\nu_1\) out-of-phase peak (\(~3380\) cm\(^{-1}\)) becomes as intense as the \(\nu_3\) TO in the C16 spectra, whereas, in the C15 spectra the \(\nu_3\) TO remains dominant.

The prominent \(\nu_1\) in-phase peak and shifting of the \(\nu_3\) TO peak to lower wavenumber have been associated with strengthening of hydrogen bonds between the water molecules in the sample.\(^{47,79,80}\) Comparing these O-H stretch bands to those found in literature, the overall line shape of 10 – 20 L water adsorbed on C16 SAM matches the IRRAS spectral features of bulk ASW\(^53\), and the corresponding O-H stretch band of water adsorbed on C15 resembles the spectral features of a transformed ASW film to Cl.\(^53\) These results imply that on the surface of C15 SAM, water molecules are deposited to form aggregates with stronger hydrogen bonds.
than on the surface of C16 SAM. As water exposure is increased above a monolayer on the surface of C15 SAM, there is a strengthening of the hydrogen bonds between the water molecules as the clusters grow to form an ice film. In the case of water adsorbate on C16 SAM, the slight shift to higher wavenumber and the increase intensity of the $\nu_3 \text{LO} + \nu_1 \text{out-of-phase}$ peak indicates a weakening of hydrogen bonds and an increased disorder in the ice film. These results contradict the hypothesis which indicates that on the surface of C15 SAM, the as-deposited water molecules would form a more uniform monolayer due to the increased affinity of the water molecules to the exposed methylene groups at the interface.

Unfortunately, due to a technical difficulty with the cryogenic instrument used in this project, the water deposition experiments shown in Figure 4.1 were conducted only once at 110 K, and repeated at 120 K deposition temperature. Figure 4.2 shows the O-H stretch in the IRRAS spectra of C16, C15 and C11 SAMs initially exposed to 0.5 L and gradually exposed to 20 L water, at deposition temperature of 120 K. The procedure was repeated with C12 SAM but at 122 K deposition temperature.
Figure 4.2: O-H stretch band in the IRRAS spectra of C16, C15 and C11 SAMs exposed to 0.5 – 20 L water at 120 K and C12 SAM at 122 K.
There was no significant difference between the O-H stretch bands of water adsorbed on C16, C15 and C11 SAMs. The lack of odd – even effect in the spectra at 120 K in comparison to those at 110 K can be explained by the higher temperature of the surface – adsorbate interface. At 120 K, the water molecules are able to diffuse and/or re-orient on the SAM’s surface, and so any spectral difference in the O-H stretch due to the geometry of the terminal-methyl groups in the odd/even SAMs is lost. The overall band shape of 20 L water deposited on C16, C15 and C11 SAMs (Figure 4.2), is in agreement with that of bulk ASW film deposited on copper substrate at 131 K, published by Mitlin and Leung. In all the spectral profiles in Figure 4.2, there is a strengthening of the high-frequency peak (ν₃, LO + ν₁, out-of-phase vibrational modes) and shifting to higher wavenumbers (~3380 to 3410 cm⁻¹), with increasing water exposures from 0.5 L to 20 L. A similar trend was observed in water deposition experiments in other studies, and is associated with weakening of the hydrogen bonds between the water molecules in the film.

In the O-H stretch spectra of water deposition on C12 at 122 K, the peak at ~3245 cm⁻¹ is more distinct than in the corresponding spectra of water on C16, C15 and C11 SAMs at 120 K. This peak was not assigned by Whalley, or Buch and Devlin, since it was not detected in their spectra. But it was observed by Mitlin and Leung, in their O-H stretch spectra during the transition of thick ASW film (240 L) to Cl. This spectral feature also appears in this work; in the IRRAS spectra of 5 L water deposited on SAMs (see Section 4.2). The appearance of this peak at ~3245 cm⁻¹ was associated with thermal effects and not odd/even effect. Figure 7.1 (in the Appendix), shows the O-H stretch spectra of two C11 SAMs exposed to 0.5 – 20 L water, at 120 K and 122 K deposition temperature. The peak at ~3245 cm⁻¹ is more intense in the O-H stretch
spectra of water deposited on the C11 film at 122 K than at 120 K. These spectral differences further support the explanation to the lack of odd – even effect in the O-H stretch spectra of water adsorbed on SAMs at 120 K. As the deposition temperature increases, water molecules have more thermal energy to overcome diffusion barrier on the surfaces of odd SAMs. This leads to the elimination of odd – even effect in the wetting of the SAMs.
4.1.2. Dangling O-H bond stretch during water deposition

The peak at 3680 – 3700 cm\(^{-1}\) corresponds to O-H stretch of water molecules with hydrogen atoms that are not involved in the hydrogen-bond network (incomplete coordinated O-H bonds) and thus called dangling bonds. Where the O-H stretch at 3000 – 3600 cm\(^{-1}\) provides information on the hydrogen bonding in the whole film, the dangling O-H stretch is representative of the surface features of water film. Figure 4.3a shows the dangling O-H stretch in the IRRAS spectra of C16 SAM exposed to 0.5 – 20 L water at 120 K. Figure 4.3b plots the maximum absorbance intensity (black line) of the dangling bonds peak and the wavenumber (red line) at which the maximum occurs, with respect to the corresponding water exposure. The dangling bonds spectra of C12, C15 and C11 exposed to 0.5 – 20 L water are shown in the Appendix (Figure 7.8). The dangling O-H stretch intensity is much lower than that of O-H stretch and susceptible to spectral noise, thus only general trends can be inferred from this surface feature. When comparing the line shapes of the dangling O-H stretch of water adsorbate on all films, there are no specific observable differences that are due to the geometry of the terminal methyl groups. At 0.5 L, the maximum absorption point is at \(~3697\text{ cm}^{-1}\) which is in agreement with the peak position of dangling O-H stretch of ASW found in literature.\(^1\) This peak was assigned by Buch and Devlin to the dangling hydrogen atom of 3-coordinate water molecule.\(^2,3\) The absence of a peak at 3720 cm\(^{-1}\), which corresponds to dangling O-H stretch of 2-coordinate water molecule\(^4\), suggests that at 120 K, as-deposited water molecules have sufficient energy to re-orient and form hydrogen bonds with neighbouring water molecules, thus becoming 3-coordinate water molecules. The slight shift (approximately 4 cm\(^{-1}\)) of the observed dangling O-H feature to lower wavenumbers with increasing exposure implies that
the newly adsorbed 3-coordinated water molecules are able to form slightly stronger hydrogen bonds with underlying water molecules than those in the preceding deposition (peak position of dangling O-H stretch in Cl film is 3690 cm\(^{-1}\)). The general increase in the absorbance intensity with increasing exposure is consistent with experimental and simulated dangling O-H stretch changes during film growth specifically for ASW. The model proposed in literature which corresponds to this spectral feature growth is one in which internal dangling bonds in pores inside the water clusters are minimized by the ability of the water molecules to reconstruct and the observed dangling O-H feature solely represents the external dangling bonds at the water cluster surface. At the submonolayer region, the number of dangling bonds increases with water exposure as the water clusters increase in size but once a monolayer is reached, there is a saturation of the number of dangling bonds on the surface. The surface selection rule of the IRRAS technique indicates that only dangling O-H bond stretch with a transition dipole moment component perpendicular to the surface can be observed. This means that the peak intensity of the dangling bonds stretch might not be proportional to the actual number of dangling 3-coordinated O-H bonds on the surface. However, since there is a clear trend in the peak intensity and its dependence on water exposure in all SAMs, it can be concluded that newly-adsorbed dangling bonds are randomly oriented on the water cluster surface.
Figure 4.3: a. Dangling O-H stretch in the IRRAS spectra of C16 SAM exposed to 0.5 – 20 L water at 120 K. b. Maximum absorbance intensity (black line) and the wavenumber (red line) of the dangling bonds peak versus water exposure.
4.2. Transition from amorphous solid water (ASW) to crystalline ice (CI)

4.2.1. O-H bond stretch during crystallization

In this section, the goal is to understand how the geometry of the terminal methyl groups, in alkanethiol SAMs with odd and even number of carbon atoms, influence the orientations of water adsorbates on the surface, as amorphous solid water (ASW) and during transition to crystalline ice (CI). Figures 4.4 and 4.5 shows the spectral evolution of the O-H stretch of even (C16 and C12) and odd (C15 and C11) SAMs exposed to 5 L (1 Langmuir = $10^{-6}$ Torr·s) water vapour, as the substrate temperature increases from 120 K to 150 K. Focusing on C16 1 + 5L plot (Figure 4.4), as water molecules adsorb on the surface at 120 K, two peaks at 3320 and 3390 cm$^{-1}$ are visible in the spectrum with a small shoulder between 3150 and 3180 cm$^{-1}$. Analogous to the ASW spectra shown in Section 4.1, the peaks at 3320 and 3390 cm$^{-1}$ were assigned as asymmetric transverse optical vibration ($\nu_3$TO), and a combination of asymmetric longitudinal optical vibration with symmetric out-of-phase vibration ($\nu_3$LO + $\nu_1$ out-of-phase), respectively. The shoulder between 3150 and 3180 cm$^{-1}$ was assigned as symmetric in-phase vibration stretch ($\nu_1$ in-phase). These peak positions and relative intensities are in agreement ($\pm 5$ cm$^{-1}$) with those reported by Mitlin and Leung$^{53}$, for 40 L ASW deposited directly on copper substrate at 131 K.
Figure 4.4: O-H stretch region in the IRRAS spectra of 5 L water deposited on methyl-terminated alkanethiol SAMs with even number of carbon atoms, C16 and C12 (two samples each, labeled as 1 and 2). Spectra were obtained after exposing each SAM to 5 L water at 120 K (black line), and during transition from ASW to CI (120 – 150 K). Spectra were obtained at approximately 1 K temperature interval and referenced with the corresponding pristine SAM film.
Figure 4.5: O-H stretch region in the IRRAS spectra of 5 L water deposited on methyl-terminated alkanethiol SAMs with odd number of carbon atoms, C15 and C11 (two samples each, labeled as 1 and 2). Spectra were obtained after exposing each SAM to 5 L water at 120 K (black line), and during transition from ASW to CI (120 – 150 K). Spectra were obtained at approximately 1 K temperature interval and referenced with the corresponding pristine SAM film.
As the substrate temperature increases to 144 K (in C16 1 + 5L plot, the O-H stretch at this temperature is marked with a bold red line), several changes are taking place in the O-H stretch band. The low frequency shoulder between 3150 and 3180 cm\(^{-1}\) becomes more prominent, the middle peak at 3320 cm\(^{-1}\) doubles in intensity and shifts to 3245 cm\(^{-1}\), and the high-frequency peak decreases in intensity while shifting to \(\sim 3360\) cm\(^{-1}\).

Wojcik et al.\(^8\) considered the rapid increase in intensity of the \(\nu_3\) TO peak and overall shifting to lower wavenumber as the onset of crystallization and strengthening of the hydrogen bonding network. With further annealing (144 – 150 K), the three visible peaks maintain their relative positions however decrease in intensity, probably due to desorption of water molecules from the surface. These peak positions and the general shape of the O-H stretch band are also in agreement with crystalline ice spectrum of copper substrate exposed to 5 L water at 160 K, reported by Mitlin and Leung.\(^{53,55}\) Following Whalley’s peak assignment \(^1\), the three major peaks in the spectra of CI are assigned to be similar to ASW. The low-frequency shoulder, 3150 – 3180 cm\(^{-1}\), was assigned as in-phase \(\nu_1\) vibration mode, the central peak at 3245 cm\(^{-1}\) corresponds to \(\nu_3\) LO mode, and the high-frequency shoulder corresponds to out-of-phase \(\nu_1\).

Similar trends are observed in spectra of 5 L water deposited on odd and even SAMs, upon the transition from ASW to CI. In all the plots in Figures 4.4 and 4.5, there is a rapid increase in intensity of the \(\nu_3\) TO peak and overall peak shifting to lower wavenumber. However, there are noticeable differences between the O-H stretch band shapes of ASW adsorbed on odd and even SAMs. Figure 4.6 compares the O-H stretch bands of 5 L water deposited on odd (dotted lines) and even (solid lines) SAMs at 120 K, and the corresponding O-H stretch bands.
after crystallization (at 150 K). Since there is no significant difference between the transformed O-H stretch bands (Figure 4.6b) of water on odd and even SAMs, it can be concluded that the cause to the odd – even effect in the ASW spectra is eliminated as the interface temperature increases. In the ASW spectra (Figure 4.6a), the intensity ratios of the $\nu_3$TO peak (~3320 cm$^{-1}$) to the $\nu_3$LO + $\nu_1$ out-of-phase peak (~3400 cm$^{-1}$), are in the range of 1.00 - 1.03 for even SAMs, and 1.07 – 1.25 for odd SAMs. This indicates that a larger population of water molecules on odd SAMs has a dominant $\nu_3$ TO vibration relative to $\nu_3$LO + $\nu_1$ out-of-phase vibration modes, in comparison to that on even SAMs. These results imply a greater intermolecular coupling (stronger hydrogen bonds) between the as-deposited water molecules on odd SAMs, relative to those on even SAMs.
**Figure 4.6**: Comparison of the O-H stretch bands of water adsorbates in the IRRAS spectra of alkanethiol SAMs with odd (C15 and C11) and even (C16 and C12) number of carbon atoms (two samples each, labeled as 1 and 2) exposed to 5 L water. **a.** Obtained after deposition at 120 K. **b.** Obtained after annealing to 150 K.

In the previous section, odd – even effect was not detected in the O-H stretch spectra of 0.5 – 20 L ASW deposited on SAMs at 120 K. The reason why odd – even effect was observed in this section might be due to the experimental design. During the water deposition experiments (Section 4.1), the SAMs films were gradually exposed to water, starting with 0.5 L and up to a monolayer (5 L). In between depositions, water adsorbates have time to overcome surface corrugation and/or electronic dipole interactions barriers on each surface. When exposing
SAMs to 5 L directly, the water molecules adsorb to the surface have less time to reorient on the SAM surface before a monolayer of water is deposited.

Whalley, Buch and Devlin provided assignments only to the three apparent peaks in the O-H stretch spectra of ASW and Cl, which seems to suggest that the same three peaks in the ASW spectra are shifting during crystallization to produce the three peaks observed in the Cl spectra. However, looking closely at the spectra (in all the plots in Figures 4.4 and 4.5) during crystallization, an additional peak is present between 3245 and 3250 cm⁻¹. This peak becomes more prominent at ~130 K, and as the surface is heated to ~145 K, it merges into the central peak at 3250 cm⁻¹. Mitlin and Leung observed similar transitional peak and at 3245 cm⁻¹ in the O-H stretch spectral evolution of 240 L water deposited on copper substrate, but they did not provide an explanation. Jenniskens et al. also reported the appearance of a fourth peak during the crystallization of 20 nm thick ASW film (at 80 K) to Cl (160 K). In their spectra, the transitional peak remained visible after the water film transformed to Cl and cooled down to 80 K. Figure 7.9 (in the Appendix), compares the changes in the absorption of this additional peak (3245 – 3250 cm⁻¹) shown in the spectral evolution of the O-H stretch bands (in Figures 4.4 and 4.5) of 5 L water on odd and even SAMs, as the temperature is raised from 120 to 150 K. There is no visible distinction between the onset temperature (in which the absorption starts to rapidly increase) of water transition from ASW to Cl, on the surface of odd and even SAMs. These results further support our previous conclusion that the cause the odd – even effect in the ASW spectra is eliminated as the sample temperature increases. Since this transitional peak merges into the high-intensity peak at 3250 cm⁻¹ during crystallization, it is qualitatively
impossible to separate the two peaks and monitor variations, due to temperature or odd–
even effects, in only one peak at a time.

A statistical method was used in this study to systematically analyze the spectral
features observed in the O-H stretch bands of 5 L water adsorbed on odd and even SAMs, and
their changes during crystallization. As mentioned above, there are three or four visible peaks
in the O-H stretch spectra shown in Figures 4.4 and 4.5, and only three of these peaks were
assigned by Whalley¹, or Buch and Devlin². The second purpose of this statistical analysis was to
resolve the number of peaks composing the O-H stretch bands of ASW and CI. To find a
common model that best fit the O-H stretch spectra in Figures 4.4 and 4.5, and can be used to
quantitatively compare the deconvoluted peak parameters of the O-H stretch of 5 L water
adsorbed on odd and even SAMs.
4.2.2. O-H stretch peak deconvolution results

Keeping in mind that the analysis discussed so far is solely based on qualitative observation of the O-H stretch bands (peak positions and relative intensities) of water adsorbed on odd and even SAMs. Following the statistical procedure described in Section 3.8, the goal was to establish which model, Gaussian or Voigt, best describes the experimental data, how many peaks lie under each spectral line in the O-H stretch plots in Figures 4.4 and 4.5, and how temperature influences the deconvoluted peaks parameters. The first model considered was Gaussian (the simpler model) with three peaks included in the fitting. Starting with C16 1 + 5L plot, each spectral line at the temperature range 120 – 150 K was fitted with three Gaussian peaks as shown in Figure 4.7 for 120 K and 142 K spectra. Next, the Gaussian peak parameters (peak center ($x_c$), area ($A$) and width ($w$)) along with the calculated AIC values were plotted versus the corresponding temperature as shown in Figure 4.8. The error bars shown in the plots of parameters versus temperature are the standard error associated with each value during the iteration process and are generated by OriginPro 2015 software. According to the Gaussian 3-peaks model, the peak positions of ASW are 3217, 3298, and 3394 cm$^{-1}$ (averaged across the temperature range 120 – 135 K) and of CI are 3160, 3245, and 3316 cm$^{-1}$ (averaged across the temperature range 145 – 150 K). Beside the high frequency peak at 3316 cm$^{-1}$ and the unreported low frequency peak in the ASW spectra, these peak positions are in agreement with those reported by Mitlin and Leung$^{53}$ and Lyagusha$^{19}$ (Table 2.1). Looking at the AIC versus temperature plot in Figure 4.8, the AIC is fairly constant before the transition to CI (120 – 135 K), rapidly increases to a maximum at 144 K during the crystallization, and then decrease again during the desorption of water molecules from the surface (144 – 150 K).
a. O-H stretch of as-deposited water at 120 K

b. O-H stretch of water adsorbate at 142 K

**Figure 4.7**: O-H stretch spectra of C16 1 exposed to 5 L water at a. 120 K and b. 142 K, fitted with 3 Gaussian peaks.
Figure 4.8: Model parameters of 3 Gaussian peaks (a. peak centre, b. area and c. width), fitted to O-H stretch bands of C16 1 + 5L (shown in Figure 4.4), and d. the model AIC value plotted with respect to the corresponding temperature.
This procedure was repeated on the same set of data (C16 1 + 5L) but fitted with three Voigt peaks instead of Gaussian. Figure 4.9 shows the fitted spectra lines at 120 and 142 K, and Figure 4.10 shows the change in parameters and AIC as the temperature increased. This model has a lower AIC curve than the Gaussian model, indicating a better fit. Similar to the Gaussian model, the AIC is fairly constant between the temperatures 120 – 135 K, at the maximum 144 K and then decreases as the surface is further annealed to 150 K. The averaged peak positions for ASW (120 – 135 K) are: 3195, 3307, and 3408 cm\(^{-1}\), and for CI (145 – 150 K): 3151, 3244, and 3350 cm\(^{-1}\). These peak positions are in the range of those reported by Mitlin and Leung\(^{53}\), and Lyagusha\(^{19}\). With the Voigt model, it is possible to separate the Gaussian (heterogeneous broadening) and Lorentzian (homogeneous broadening) contribution to the FWHM of each fitted peak. Figure 4.10 shows the change in Gaussian and Lorentzian FWHM as well as the convoluted FWHM as the surface temperature increase. Peak 1 has contribution from both broadening mechanisms as ASW but during the transition into CI, the Lorentzian contribution drops to zero while the Gaussian remains relatively the same as before the transition. Peak 2 starts with a major Gaussian contribution and switched to Lorentzian after crystallization, while peak 3 has contribution from both Gaussian and Lorentzian before and after crystallization.
Figure 4.9: O-H stretch spectra of C16 1 exposed to 5 L water at a. 120 K and b. 142 K, fitted with 3 Voigt peaks.

a. Changes in peak centre (cm\(^{-1}\)) with Temperature (K)

b. Changes in peak area with Temperature (K)
c. Changes in Gaussian FWHM (cm\(^{-1}\)) with Temperature (K)

d. Changes in Lorentzian FWHM (cm\(^{-1}\)) with Temperature (K)

Figure 4.10: Model parameters of 3 Voigt peaks (a. peak centre, b. area, c. Gaussian and d. Lorentzian FWHM, and e. convoluted FWHM), fitted to O-H stretch bands of C16 \(1 + 5L\) (shown in Figure 4.4), and f. the model AIC value plotted with respect to the corresponding temperature.
Since four peaks were identified in the O-H stretch transition spectra from ASW to CI in the odd and even plots in Figures 4.4 and 4.5, Gaussian and Voigt models with 4 peaks were next considered. Figure 7.10 (in the Appendix) shows the change in parameters and AIC versus temperature for the Gaussian-4 peaks model and Figure 7.11 for the Voigt-4 model. According to the AIC, Voigt-4 model provides a better description of the experimental data than Gaussian-4 model. The standard error bars in Figure 7.11 are large before and during crystallization (especially for peak 3) but are small for the spectra of CI. This implies that during iteration process, there is a difficulty to position the added peak in the ASW spectra but not in the CI spectra. Comparing Voigt-4 to Voigt-3 peaks model, the positions of peaks 1, 2 and 4 are the same for ASW spectra with an added peak (peak 3) at 3371 cm\(^{-1}\). In the case of CI, the low frequency peak is now at 3160 cm\(^{-1}\), peak 2 is at relatively the same position as in Voigt-3 model, but peak 3 in the Voigt-4 model is now at a lower wavenumber (3274 cm\(^{-1}\)) while peak 4 is shifted to higher wavenumber (3369 cm\(^{-1}\)) relative to peak 3 in Voigt-3 model. Looking at the Gaussian/Lorentzian FWHM contributions in Figure 7.11, peaks 1, 2 and 4 are relatively the same as was described for the three peaks in Voigt-3 model, while peak 3 in the Voigt-4 model has a major Gaussian contribution before and after crystallization.

As mentioned above, Voigt-4 model has the lowest AIC curve between the models discussed so far, however, in order to know if this model provides the absolute minimum AIC values that can be achieved for the O-H stretch spectra of C16 1 + 5L, Gaussian and Voigt models with 3 – 6 peaks and possibly 7 peaks were also considered. Figure 4.11 shows the AIC values for Gaussian and Voigt models with 3 to 7 peaks as a function of temperature for C16 1 + 5L plot (Gaussian-7 peaks model is not shown since it did not successfully converge). This
procedure was repeated for the O-H stretch spectra of 5 L water on C12 1, C15 1, and C11 1 in Figures 4.1 and 4.2. Gaussian-6, Voigt-6 and 7 peaks models (labeled as G6, V6 and V7 in Figure 4.11) produced the lowest AIC values in all films. However, Gaussian-6 show drastic fluctuation in AIC values between 140 – 150 K for C16 + 5L plot and did not successfully converge for the CI spectra (135 – 150 K) in the other plots in Figure 4.11. The 7 peaks fitted into the spectra using the Voigt-7 model were not consistent between successive O-H stretch spectra in the temperature range 120 – 135 K and also did not converge in the spectra above 143 K. Voigt-6 peaks model provided low AIC values and consistently fitted 6 peaks into the O-H stretch spectra without difficulty.
Figure 4.11: AIC values of Gaussian (G) and Voigt (V) models with 3 to 7 peaks as a function of temperature fitted to the O-H stretch spectra of C16 1, C15 1, C12 1, and C11 1 + 5L in Figures 4.4 and 4.5.
4.2.3. Voigt – 6 peaks model

To this date, the most common O-H stretch assignment used in literature is that made by Whalley in 1977\(^1\) and he assigned the three visible peaks in the O-H stretch spectra of amorphous solid water (ASW) and crystalline ice (CI) using four vibrational modes: the low-frequency shoulder as \(v_1\) in-phase, the central peak as \(v_3\) TO, and the high-frequency peak as \(v_3\) LO and \(v_1\) out-of-phase. Now that the best model to describe the O-H stretch spectral evolution spectra in Figures 4.4 and 4.5 has been shown to be Voigt with 6 peaks, assigning these peaks using four vibrational modes is not ideal. However, a systematic comparison of peak parameters of 5 L water adsorbed on even and odd SAMs and as ASW transitions to CI, can be done using this model. Figure 4.12 shows six Voigt peaks fitted into the O-H stretch spectra of C16 1 + 5L at 120 and 145 K, and Figure 4.13 shows the change in parameters as the film was annealed. The standard error bars associated with the iteration process are omitted from the spectra for clarity. In the temperature ranges 120 – 135 K of ASW and 145 – 150 K of CI, the peak positions are stable and there are no significant changes in areas and widths. While all six peaks shift to lower wavenumbers during the transition from ASW to CI, peak 5 shifts the most (by 88 cm\(^{-1}\)). At the low-frequency region, peaks 1 and 2 do not change as drastically as the other peaks; Peak 1 area slightly increases but the FWHM of both peaks decrease and have mostly Gaussian contribution before and after the transition. Peak 3 shifts by 65 cm\(^{-1}\) and the major width contribution is switched from Gaussian to Lorentzian during the transition. Only peak 5 increases in area and FWHM during the transition, while peaks 4 and 6 areas increases but their FWHM decreases. The major width contribution of peaks 4, 5, and 6 at ASW is
Gaussian but during the transition to CI, the Gaussian contribution of peak 4 decreases slightly and the Lorentzian contribution increases for 5 and 6 increases drastically.

**a. O-H stretch of as-deposited water at 120 K**  
**b. O-H stretch of water adsorbate at 145 K**

![Graph showing O-H stretch spectra of C16 1 exposed to 5 L water at 120 K and 145 K, fitted with 6 Voigt peaks.]

**Figure 4.12:** O-H stretch spectra of C16 1 exposed to 5 L water at **a.** 120 and **b.** 145 K, fitted with **6 Voigt peaks.**
**a.** Changes in peak centre (cm$^{-1}$) with Temperature (K)

**b.** Changes in peak area with Temperature (K)

**c.** Changes in Gaussian FWHM (cm$^{-1}$) with Temperature (K)

**d.** Changes in Lorentzian FWHM (cm$^{-1}$) with Temperature (K)
**Figure 4.13: Model parameters of 6 Voigt peaks (a. peak centre, b. area, c. Gaussian and d. Lorentzian FWHM, and e. convoluted FWHM), fitted to O-H stretch bands of C16 1 + 5L (shown in Figure 4.4), and plotted with respect to the corresponding temperature.**

The O-H stretch spectra of 5 L water exposure at 120 and 145 K fitted with six Voigt peaks, on even and odd SAMs are shown in the appendix along with the changes in Voigt profile’s parameters as the temperature increases. Because there are no drastic changes in peak parameters in the temperature ranges of 120 – 135 K and 145 – 150 K. The averages and standard errors of the peak parameters over these temperature ranges were calculated (listed in Tables 7.1 – 7.5 in the appendix) and summarized in Figures 4.14 – 4.18 for two films of each even (C16 and C12) and odd (C15 and C11) SAMs. A two-tailed t-test was used to determine if the average peak parameters for even and odd SAMs are significantly different from each other at 95% confidence level.
**Figure 4.14:** Comparing the average peak centers (cm\(^{-1}\)) of 6 Voigt peaks fitted to ASW (120 – 135 K) and Cl (145 – 150 K) O-H stretch spectra of even (grey area: C16 and C12) and odd (white area: C15 and C11) SAMs exposed to 5 L water.

**Figure 4.15:** Comparing the average peak areas of 6 Voigt peaks fitted to the ASW (120 – 135 K) and Cl (145 – 150 K) O-H stretch spectra of even (grey area: C16 and C12) and odd (white area: C15 and C11) SAMs exposed to 5 L water.
Figure 4.16: Comparing the average Gaussian FWHM (cm$^{-1}$) of 6 Voigt peaks fitted to the ASW (120 – 135 K) and CI (145 – 150 K) O-H stretch spectra of even (grey area: C16 and C12) and odd (white area: C15 and C11) SAMs exposed to 5 L water.

Figure 4.17: Comparing the average Lorentzian FWHM (cm$^{-1}$) of six Voigt peaks fitted to the ASW (120 – 135 K) and CI (145 – 150 K) O-H stretch spectra of even (grey area: C16 and C12) and odd (white area: C15 and C11) SAMs exposed to 5 L water.
Figure 4.18: Comparing the average FWHM (cm\(^{-1}\)) of 6 Voigt peaks fitted to the ASW (120 – 135 K) and CI (145 – 150 K) O-H stretch spectra of even (grey area: C16 and C12) and odd (white area: C15 and C11) SAMs exposed to 5 L water.

As seen in the case of C16 1 + 5L, all peaks shift to lower wavenumbers during the transition from ASW to CI. Despite the visual growth of the low-frequency shoulder in the O-H stretch thermal evolution, peak 1 changes the least between all peaks during the transition from ASW and CI. It shifts by 13 – 17 cm\(^{-1}\) to lower wavenumbers (beside C16 1 – 34 cm\(^{-1}\) and C15 1 – 24 cm\(^{-1}\) shift), the area increased by 0.8 – 1.6 for even SAMs but has no change (within the standard error) in the odd films (except in C11 2 where the area increased by 1.0), the FWHM decreases by 19 – 28 cm\(^{-1}\) (beside C16 1 – decreases by 48 cm\(^{-1}\)), and the main width broadening mechanism in peak 1 at ASW and CI is Gaussian. Peak 2 shift to lower wavenumbers by 20 – 37 cm\(^{-1}\) during the transition from ASW to CI. Its area decreases by 0.6 – 1.2 for even
films but for odd film the decrease in area is different between C15 and C11 films. In the two C11 films peak 2 area remains the same, but for C15 1 and 2 the area decreased by 1.8 and 2.2, respectively. While the major width contribution of peak 2 is Gaussian in both ASW and Cl for even SAMs, the major peak width broadening contribution for C15 SAM is Lorentzian in ASW and transitions to Gaussian in Cl. For peaks 3, 4, and 5, the ASW peak positions are at lower wavenumbers in odd SAMs than in even SAMs, while the Cl peak positions are about the same for all films. T-test also shows a significant difference between odd and even SAMs (t-value is greater than the t-critical) in the ASW spectra but not in the Cl spectra. Peak 3 areas and FWHM values decrease slightly during the transition from ASW to Cl with no discrepancy between odd and even SAMs. On the other hand, peak 3 width in ASW is dominated by the Gaussian component but it is lower in the odd SAMs than in the even SAMs (as indicated by the t-test), and vice versa for the Lorentzian component. Peak 4 is also dominated by Gaussian component in the ASW spectra but there is no discrepancy between odd and even SAMs. Peak 5 positions shift the most, consistently in all SAMs, but the shift is greater in even SAMs (by 79 – 88 cm\(^{-1}\)) than in odd SAMs (by 53 – 73 cm\(^{-1}\)). Its peak area and FWHM increases during the transition into Cl, where the Gaussian component remains fairly constant for ASW and Cl. The Lorentzian component of peak 5 is increasing after the transition for all SAMs. This increase in the Lorentzian component in peak 5 might be influenced by the drastic conversion in the dominant width broadening component from Gaussian to Lorentzian in peak 6 as the water films transition to Cl.

The above statistical analysis of the peak parameters of O-H stretch band of ASW and Cl have led to several conclusions. First, the major difference between water adsorbed on even
and odd SAMs is in the positions of peaks 3, 4, and 5 in the ASW spectra, but not in the CI spectra. Table 4.1 lists the peak centres (cm\(^{-1}\)) of the six Voigt peaks fitted into the O-H stretch bands of 5 L ASW deposited on odd and even SAMs. This analysis confirms that the geometry of the methyl terminal groups at the surface influence the as-deposited water molecules’ interactions with the substrate. After crystallization, the geometry of the methyl terminal groups no longer influenced the orientations of water molecules on the surface. Second, the transformation of the dominant width broadening component from Gaussian to Lorentzian during crystallization in peaks 4, 5, and 6, indicates a reduction of heterogeneous broadening factors and an increase in the homogeneous broadening factors in the water films. To the extent of our literature search, these results are the first to show such transition of the peak broadening mechanism from Gaussian to Lorentzian during water crystallization.

**Table 4.1:** Average peak positions and corresponding standard error values of the six Voigt peaks fitted to the O-H stretch bands of even and odd SAMs exposed to 5 L amorphous solid water (ASW).

<table>
<thead>
<tr>
<th>Peak</th>
<th>Average peak positions of ASW adsorbed on even SAMs (cm(^{-1}))</th>
<th>Average peak positions of ASW adsorbed on odd SAMs (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3171.66 ±0.69</td>
<td>3166.85 ±0.61</td>
</tr>
<tr>
<td>2</td>
<td>3253.08 ±1.49</td>
<td>3242.32 ±0.99</td>
</tr>
<tr>
<td>3</td>
<td>3301.36 ±1.20</td>
<td>3291.53 ±0.87</td>
</tr>
<tr>
<td>4</td>
<td>3351.87 ±0.88</td>
<td>3337.34 ±1.44</td>
</tr>
<tr>
<td>5</td>
<td>3411.01 ±0.73</td>
<td>3397.41 ±1.84</td>
</tr>
<tr>
<td>6</td>
<td>3428.72 ±1.40</td>
<td>3424.26 ±1.40</td>
</tr>
</tbody>
</table>
4.2.4. Dangling O-H bond stretch during crystallization

Figure 4.19a shows the dangling O-H stretch in the IRRAS spectra of 5 L water on C16 2 SAM film in the temperature range of 120 – 150 K. Figure 4.19b shows the maximum absorbance intensity (black line) of the dangling bonds peak and the wavenumber (red line) in which the maximum occurs with respect to the corresponding temperature. Following the spectral evolution of the dangling O-H stretch peak with temperature, there are two major peaks in the spectra at 3696 cm\(^{-1}\) and \(~3689\) cm\(^{-1}\). Initially, the 3696 cm\(^{-1}\) peak has higher intensity than the peak at \(~3689\) cm\(^{-1}\). It starts to decline at 122 K while the \(~3689\) cm\(^{-1}\) peak gains intensity after 137 K. These peak positions of the dangling O-H stretch are in agreement with those found in literature for amorphous solid water (ASW) and crystalline ice (CI)\(^{81,82,84}\), respectively, and were assigned by Buch and Devlin to dangling hydrogen atoms of 3-coordinate water molecule.\(^{82,83,87}\) In the O-H stretch spectra of C16 2 + 5L (Figure 4.4), the transition from ASW to CI occurred at the temperature range of 135 – 145 K. Yet, the dangling bond stretch corresponding to CI (3689 cm\(^{-1}\)) starts to develop at 122 K. This indicates a higher sensitivity of the dangling bond stretch to temperature changes, in comparison to the O-H stretch. Monitoring the recovery of the symmetric (r\(^{s}\)) and asymmetric (r\(^{a}\)- and r\(^{b}\)-) CH\(_3\) stretches (2800 – 3000 cm\(^{-1}\)) during the transition from ASW to CI can provide information on surface coverage by the water adsorbate. For C16 2 + 5L, all C-H stretch bands start to increase at 135 K and fully recover by 150 K. This early sign of recovery (at 135 K), before water starts to desorb from the SAM’s surface (145 – 150 K), suggests that the water molecules cluster on the surface during the transition from ASW to CI, to expose the underlying SAM. This result was also
observed in the MIES spectra obtained during the transition of ASW to Cl on the surface of C11
(see Figure 7.27 in the Appendix).

Figure 4.19: a. IRRAS spectra of the dangling O-H stretch of 5 L water adsorbate on C16 at the
temperature range between 120 K (bold black line) and 150 K (bold red line). Each spectral line
is referenced with its corresponding pristine C16 SAM film. b. The black line represents the
maximum absorbance intensity of the dangling O-H stretch in the IRRAS spectra of 5 Langmuir
water on two C11 films and the red line shows the wavelength in which the maximum
absorbance occurs versus the corresponding temperature.

Similar trends in the dangling O-H stretch, where two peaks are observed during the
transition from ASW to Cl, are also seen in the spectral evolution of C11 1 + 5L (Figure 4.20a)
but not in the rest of the SAMs films exposed to 5 L water. Figure 4.20 compares the spectral
evolution of the dangling O-H stretch on the surface of two C11 films. Similar plots of C15 and C12 are shown in the Appendix (Figure 7.26). In the C11 1 + 5L spectra (Figure 4.20a) the shift to lower wavenumber (~3695 to 3689 cm\(^{-1}\)) occurs drastically at 135 K (blue bolded line). The overall peak intensity remains mostly unchanged in the temperature range of 120 – 140 K, and upon further heating, the intensity decreases. Similar to the C-H stretch recovery of C16 2 during the transition of 5 L from ASW to CI, the methyl C-H stretch bands intensities start to increase at 130 K, and are fully recovered by 140 K (besides \(r_s^-\) which recovers 96% of its initial intensity).

In contrast to C11 1 + 5L (Figure 4.20a), the dangling O-H stretch spectral evolution on C11 2 is significantly different. During the water transformation from ASW to CI, the peak position is relatively constant (1 – 2 cm\(^{-1}\) fluctuations are considered as noise since the spectrometer resolution is 2 cm\(^{-1}\)). The peak intensity remains constant in the temperature range of 120 – 135 K and decrease with further heating. According to the corresponding O-H stretch band, desorption of water molecules from the C11 2 SAM surface starts at 145 K. The methyl C-H stretch intensities of C11 2 start to increase at 130 K but do not recover fully by 150 K; \(r_s^+, r_6^-, \) and \(r_5^-\) recover 75%, 90% and 79% of their initial intensity. The drop in dangling bond stretch intensity prior to desorption and the incomplete recovery of the methyl C-H stretch bands suggest that the peak intensity is not proportional to the actual number of dangling bonds on the water clusters. The surface selection rule of the IRRAS technique indicates that only dangling O-H bond stretch with a transition dipole moment component perpendicular to the surface can be observed. As the solid water adsorbed on the surface of C11 2 undergoes crystallization and cluster formation, the dangling bonds on the water cluster external surface
might reconstruct in a specific orientation which causes the dipole moment component perpendicular to the surface to decrease. The disproportionality between the number of dangling bonds and the peak intensity was also observed by Mitlin and Leung in thin crystalline ice films on copper, where there was no change in the peak intensity with increasing film thickness.\textsuperscript{52,55}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_20.png}
\caption{IRRAS spectra of the dangling O-H stretch of 5 L water adsorbate on two C11 SAMs at the temperature range between 120 K (bold black line) and 150 K (bold red line). Each spectral line is referenced with its corresponding pristine C11 SAM film.}
\end{figure}
Figure 4.21: The black line represents the maximum absorbance intensity of the dangling O-H stretch in the IRRAS spectra of 5 L water adsorbate on two C11 films (Figure 4.20) and the red line shows the wavenumber in which the maximum absorbance occurs versus the corresponding temperature.
CHAPTER 5

Conclusions

The objective of this project was twofold: (1) to determine how the surface geometry of the methyl-terminal groups of alkanethiol SAMs with an odd and even number of carbon atoms affected the orientation of as-deposited water molecules, and (2) to determine how the methyl-terminal group’s geometry influenced the transition of amorphous solid water (ASW) to crystalline ice (CI). The first part of the objective was investigated (in Section 4.1) by depositing 0.5 L on pristine odd and even SAMs, and then gradually increasing the exposure to 20 L. According to the water deposition experiments conducted at 110 K deposition temperature (Figure 4.1), water molecules adsorbed on the surface of C15 SAM formed aggregates with stronger hydrogen-bonds (have “like-crystalline” character) in comparison to water adsorbed on the surface of C16 SAM. With increasing water exposure above a monolayer, there was a strengthening of the hydrogen-bonds on the surface of C15 SAM, as the water clusters grow to form an ice film. However, on the surface of C16 SAM, there was a weakening of the hydrogen bonds and increased disorder in the ASW film. This result contradicted the hypothesis provided in literature (see Section 2.3) which implies that water molecules interact with the slightly polarized surface of C15 SAM to form a more uniform monolayer, thus weaker hydrogen bonds between water adsorbates, than on the surface of C16 SAM. This even-odd discrepancy was not
observed in the water deposition experiments conducted at 120 K (Figure 4.2). It was suggested that at 120 K deposition temperature, the as-deposited solid water molecules had sufficient thermal energy to rearrange on the SAMs' surfaces. Thus, any spectral differences in the O-H stretch due to the geometry of the terminal - methyl groups in odd and even SAMs was lost. As was observed in the O-H stretch spectra of water deposited on odd and even SAMS in Figure 4.2, there was a weakening of the hydrogen bonds between the water adsorbates as the exposure was increased from 0.5 to 20 L.

The dangling O-H stretch of water deposited on even and odd SAMs (Section 4.1.2) also showed no spectral difference due to the orientation of the methyl terminal groups. Combining the information obtained from the O-H stretch and dangling O-H stretch vibrational bands of water deposited on even and odd SAMs at 120 K, a model of ASW deposition can be proposed. At submonolayer exposure levels of the SAMs films to water, newly-adsorbed water molecules were able to re-orient to form hydrogen bonds with neighbouring water molecules, and minimize 2-coordinate dangling bonds. With increasing exposure, water molecules with incomplete coordination on the cluster surface were able to form slightly stronger hydrogen bonds with neighbouring molecules (~4 cm⁻¹ shift in the dangling O-H stretch to lower wavenumber). However, beyond a monolayer of water adsorbate on the SAMs films, there was an increase in disorder in the bulk of the water film.

The second part of the objective mentioned above was investigated (in Section 4.2) by depositing approximately a monolayer of water molecules (5 L water exposure) on even and odd SAM at 120 K, and subsequently annealing the surface to 150 K to induce crystallization. As
can be seen in Figure 4.6, there was an observable difference in the O-H stretch spectra of 5 L ASW on even and odd SAMs, but not in the transformed spectra to crystalline ice.

In Section 4.2.2, a statistical method was developed to unambiguously monitor changes in the O-H stretch bands of 5 L water deposited on even and odd SAMs during crystallization. It was revealed that Voigt with six peaks model best fit the O-H stretch bands of ASW and CI of water adsorbate on all SAMs (Section 4.2.3). This analysis confirmed that the geometry of the methyl terminal groups at the surface influences the as-deposited water molecules’ interactions with the substrate, and more specifically, the peak positions. After the transition from ASW to CI, water orientations on the surface were not affected by the interaction with the even and odd SAMs. Moreover, the peak analysis revealed the transformation of the dominant width broadening component from Gaussian to Lorentzian during crystallization. This indicated a reduction of heterogeneous broadening factors and an increase in the homogeneous broadening factors as the water molecules reorganized to form a stronger hydrogen-bonding network. Since O-H stretch band’s interpretations found in literature\textsuperscript{1,2} only assign three observable peaks using four vibrational modes (see Section 2.4), there is a chance that these interpretations present an oversimplified model to the vibrational modes of solid water. The peak deconvolution analysis presented in this work, provides the basis for further studies of the O-H stretch peak assignment, as well as, the interaction of solid water with various surfaces.
CHAPTER 6

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Appendix

7.1. Water deposition on alkanethiol SAMs with an odd and even number of carbon atoms

Figure 7.1: O-H stretch in the IRRAS spectra of two C11 SAMs exposed to 0.5 – 20 L water at 120 K and 122 K.

Following the deconvolution procedure described in Section 3.8, Gaussian and Voigt models with 6 and 7 peaks were fitted into the IRRAS spectra shown in Figure 4.2. Gaussian-6, Voigt-6 and 7 peaks models (labeled as G6, V6 and V7, respectively, in Figure 7.2) produced the
lowest AIC values for C16 and C15 SAMs. Gaussian-6 did not successfully converge for spectra of SAMs exposed to 0.5 and 1 L in Figure 4.2. The 7 peaks fitted to the spectra, using the Voigt-7 model, showed no improvement in the AIC values (more negative values) in comparison to Voigt-6 model. Voigt-6 peaks model provided low AIC values and consistently fitted 6 peaks into the O-H stretch spectra without difficulty. Figures 7.3 – 7.7 compares the parameters (peak center, area, Gaussian FWHM, Lorentzian FWHM, and convoluted FWHM) of six Voigt peaks fitted to the IRRAS spectra of water adsorbate on even (C16 and C12) and odd (C15 and C11) SAMs, and plotted against the water exposure (0.5 – 20 L).

**Figure 7.2**: AIC values of Gaussian (G) and Voigt (V) models with 6 and 7 peaks as a function of temperature fitted to the O-H stretch spectra of C16 and C15 exposed to 0.5 – 20 L water at 120 K as shown in Figures 4.2.
Figure 7.3: Comparing the peak centers (cm$^{-1}$) of 6 Voigt peaks fitted to the O-H stretch band in the IRRAS spectra of SAMs with even (C16 and C12) and odd (C15 and C11) number of carbon atoms, exposed to 0.5 – 20 L water at 120 K deposition temperature (except C12 at 122 K).
**Figure 7.4:** Comparing the peak areas of 6 Voigt peaks fitted to the O-H stretch band in the IRRAS spectra of SAMs with even (C16 and C12) and odd (C15 and C11) number of carbon atoms, exposed to 0.5 – 20 L water at 120 K deposition temperature (except C12 at 122 K).
Figure 7.5: Comparing the Gaussian FWHM (cm$^{-1}$) of 6 Voigt peaks fitted to the O-H stretch band in the IRRAS spectra of SAMs with even (C16 and C12) and odd (C15 and C11) number of carbon atoms, exposed to 0.5 – 20 L water at 120 K deposition temperature (except C12 at 122 K).
Figure 7.6: Comparing the Lorentzian FWHM (cm$^{-1}$) of 6 Voigt peaks fitted to the O-H stretch band in the IRRAS spectra of SAMs with even (C16 and C12) and odd (C15 and C11) number of carbon atoms, exposed to 0.5 – 20 L water at 120 K deposition temperature (except C12 at 122 K).
Figure 7.7: Comparing the FWHM (cm$^{-1}$) of 6 Voigt peaks fitted to the O-H stretch band in the IRRAS spectra of SAMs with even (C16 and C12) and odd (C15 and C11) number of carbon atoms, exposed to 0.5 – 20 L water at 120 K deposition temperature (except C12 at 122 K).
7.2. Water deposition on alkanethiol SAMs with an odd and even number of carbon atoms:

dangling O-H stretch

a.

b.
Figure 7.8: Left: Dangling O-H bond stretch in the IRRAS spectra of a. C12, b. C11 and c. C15 SAMs exposed to 0.5 - 20 L water. Right: The black line represents the maximum absorbance intensity of the dangling O-H stretch in the IRRAS spectra, and the red line shows the wavenumber in which the maximum absorbance occurs, versus the corresponding water exposure.
7.3. Transition from amorphous solid water (ASW) to crystalline ice (CI)

**Figure 7.9:** Absorbance intensity (mAbs unit) of the peak at 3245 cm$^{-1}$, observed in the O-H stretch spectral evolution of 5 L water deposited on odd (C15 and C11) and even (C16 and C12) SAMs (in Figures 4.4 and 4.5), with respect to the corresponding temperature.
7.4. O-H stretch peak – fit analysis

Figure 7.10: Model parameters of 4 Gaussian peaks (peak centre, area and width), fitted to O-H stretch bands of C16 1 + 5L (shown in Figure 4.4), and the model AIC value plotted with respect to the corresponding temperature.
Figure 7.11: Model parameters of 4 Voigt peaks (peak centre, area, Gaussian and Lorentzian FWHM, and convoluted FWHM), fitted to O-H stretch bands of C16 1 + 5L (shown in Figure 4.4), and the model AIC value plotted with respect to the corresponding temperature.
7.5. Voigt – 6 peaks model

![Graphs showing O-H stretch spectra of C16 2 + 5L water at 120 and 145 K, fitted with 6 Voigt peaks.](image)

**Figure 7.12:** O-H stretch spectra of C16 2 + 5L water at 120 and 145 K, fitted with 6 Voigt peaks.
**Figure 7.13:** Model parameters of 6 Voigt peaks (peak centre, area, Gaussian and Lorentzian FWHM, and convoluted FWHM), fitted to O-H stretch bands of **C16 2 + 5L** (shown in Figure 4.4), and the model AIC value plotted with respect to the corresponding temperature.
Figure 7.14: O-H stretch spectra of C12 1 + 5L water at 120 and 145 K, fitted with 6 Voigt peaks.
Figure 7.15: Model parameters of 6 Voigt peaks (peak centre, area, Gaussian and Lorentzian FWHM, and convoluted FWHM), fitted to O-H stretch bands of $\text{C}_{12} \ 1 + 5L$ (shown in Figure 4.4), and the model AIC value plotted with respect to the corresponding temperature.
Figure 7.16: O-H stretch spectra of C12 2 + 5L water at 120 and 145 K, fitted with 6 Voigt peaks.
**Figure 7.17:** Model parameters of 6 Voigt peaks (peak centre, area, Gaussian and Lorentzian FWHM, and convoluted FWHM), fitted to O-H stretch bands of C12 2 + 5L (shown in Figure 4.4), and the model AIC value plotted with respect to the corresponding temperature.
Figure 7.18: O-H stretch spectra of C15 1 + 5L water at 120 and 145 K, fitted with 6 Voigt peaks.
Figure 7.19: Model parameters of 6 Voigt peaks (peak centre, area, Gaussian and Lorentzian FWHM, and convoluted FWHM), fitted to O-H stretch bands of C15 1 + 5L (shown in Figure 4.5), and the model AIC value plotted with respect to the corresponding temperature.
Figure 7.20: O-H stretch spectra of C15 2 + 5L water at 120 and 145 K, fitted with 6 Voigt peaks.
Figure 7.21: Model parameters of 6 Voigt peaks (peak centre, area, Gaussian and Lorentzian FWHM, and convoluted FWHM), fitted to O-H stretch bands of C15 2 + 5L (shown in Figure 4.5), and the model AIC value plotted with respect to the corresponding temperature.
Figure 7.22: O-H stretch spectra of C11 1 + 5L water at 120 and 145 K, fitted with 6 Voigt peaks.
Figure 7.23: Model parameters of 6 Voigt peaks (peak centre, area, Gaussian and Lorentzian FWHM, and convoluted FWHM), fitted to O-H stretch bands of C11 1 + 5L (shown in Figure 4.5), and the model AIC value plotted with respect to the corresponding temperature.
**Figure 7.24:** O-H stretch spectra of C11 2 + 5L water at 120 and 145 K, fitted with 6 Voigt peaks.
Figure 7.25: Model parameters of 6 Voigt peaks (peak centre, area, Gaussian and Lorentzian FWHM, and convoluted FWHM), fitted to O-H stretch bands of C11 2 + 5L (shown in Figure 4.5), and the model AIC value plotted with respect to the corresponding temperature.
Table 7.1: Average peak centers (cm\(^{-1}\)) and corresponding standard errors of six Voigt peaks fitted to ASW (120 – 135 K) and Cl (145 – 150 K) O-H stretch spectra of even (C16 and C12) and odd (C15 and C11) SAMs exposed to 5 L water (in Figures 4.4 and 4.5).

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- t-values were calculated according to equation 3.17, using four values for each population of even and odd (two samples of each SAM).
- For two-tailed test with 6 degrees of freedom (DF = (n\(_{odd} - 1\)) + (n\(_{even} - 1\))) and at 95% confidence level, t-critical is equal to 2.4469.
- The t-values are bolded in Tables 7.1 – 7.5, in cases where the t-value is greater than t-critical, and thus, the two population of even and odd are considered to be different.
Table 7.2: Average peak areas and corresponding standard errors of six Voigt peaks fitted to ASW (120 – 135 K) and Cl (145 – 150 K) O-H stretch spectra of even (C16 and C12) and odd (C15 and C11) SAMs exposed to 5 L water (in Figures 4.4 and 4.5).

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| C16 2 | 4.9829          | 0.2646 | 2.9121          | 0.3362 | 3.7068          | 0.3136 | 4.1454          | 0.1026 | 5.4962          | 0.2313 | 6.7312          | 0.3458 |
| C12 1 | 3.6090          | 0.1148 | 2.3322          | 0.2205 | 2.8029          | 0.2158 | 3.1354          | 0.2809 | 3.3298          | 0.1934 | 4.7873          | 0.1645 |
| C12 2 | 4.2162          | 0.9662 | 3.7568          | 1.0534 | 2.5248          | 0.3184 | 3.9039          | 1.1034 | 4.1124          | 0.5732 | 4.9982          | 0.5039 |
| C15 1 | 1.7180          | 0.1989 | 1.5098          | 0.2507 | 2.5785          | 0.1223 | 1.6278          | 0.1754 | 1.6456          | 0.2805 | 2.3945          | 0.3169 |
| C15 2 | 3.0897          | 0.2622 | 2.7827          | 0.2806 | 2.6911          | 0.1811 | 3.1790          | 0.2909 | 3.7570          | 0.2697 | 4.2438          | 0.2317 |
| C11 1 | 3.9057          | 0.0914 | 3.0272          | 0.1598 | 2.7889          | 0.4059 | 3.4911          | 0.3634 | 4.2331          | 0.3256 | 4.9809          | 0.1610 |
| C11 2 | 4.6296          | 0.1767 | 4.3523          | 0.1945 | 4.7689          | 0.2948 | 4.4991          | 0.2431 | 5.3951          | 0.2471 | 5.9673          | 0.2082 |
| t-value | 1.0258       | 0.1171 | -0.3937         | 0.5052 | 0.5171          | 0.9815 |
Table 7.3: Average Gaussian FWHM (cm$^{-1}$) values and corresponding standard errors of six Voigt peaks fitted to ASW (120 – 135 K) and Cl (145 – 150 K) O-H stretch spectra of even (C16 and C12) and odd (C15 and C11) SAMs exposed to 5 L water (in Figures 4.4 and 4.5).

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Table 7.4: Average Lorentzian FWHM (cm\(^{-1}\)) values and corresponding standard errors of six Voigt peaks fitted to ASW (120 – 135 K) and CI (145 – 150 K) O-H stretch spectra of even (C16 and C12) and odd (C15 and C11) SAMs exposed to 5 L water (in Figures 4.4 and 4.5).

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Table 7.5: Average FWHM (cm\(^{-1}\)) values and corresponding standard errors of six Voigt peaks fitted to ASW (120 – 135 K) and CI (145 – 150 K) O-H stretch spectra of even (C16 and C12) and odd (C15 and C11) SAMs exposed to 5 L water (in Figures 4.4 and 4.5).

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7.6. Dangling O-H bond stretch during transition from ASW to CI

a.

![Graph showing absorbance and wavenumber for C15 2 + 5L](image)

b.

![Graph showing absorbance and wavenumber for C12 1 + 5L](image)
Figure 7.26: Left: Dangling O-H bond stretch bands in the IRRAS spectra of 5 L deposited on a. C15 2, b. C12 1 and c. C12 2 SAMs, at temperatures 120 - 150 K. Right: The black line represents the maximum absorbance intensity of the dangling O-H stretch in the IRRAS spectra, and the red line shows the wavenumber in which the maximum absorbance occurs, versus the corresponding water exposure.
7.7. MIES results during the transition from ASW to CI

Figure 7.27 presents the MIES results obtained before (black line) and after (red line) exposing a C11 SAM to 5 L water held at 120 K, and the spectral changes resulting from the annealing of the surface to 150 K. It has been estimated that exposing the film to 5 L (1 Langmuir (L) = 10⁻⁶ Torr·s) water leads to the deposition of a monolayer of water molecules on the surface.¹⁹ As was described in Section 3.2, the peak at ~6 eV of the pristine C11 spectrum (black line) was assigned to the kinetic energy of electrons ejected through the interaction of metastable helium (He*) atoms with the σ(2p) molecular orbitals (MOs) of the methyl terminal groups. Upon the deposition of a monolayer of water on the surface, the He* atoms interact with the highest occupied molecular orbitals of water, instead with those of the alkanethiol SAM. The peak at ~6 eV in the C11 + 5L spectrum (red line) corresponds to the 3a₁ MO of water. Most prominent in this spectrum is the peak at 8.1 eV, which was assigned to the 1b₁ MO localized on the lone electron pair of the oxygen atom. While annealing the surface from 120 to 150 K, the intensity of the 1b₁ peak decreases. This observation implies that the 1b₁ MO is less exposed at the interface to incoming He* atoms, and most likely involved in hydrogen bonding with neighbouring water molecules. This result is also indicative of a transition from amorphous solid water (ASW) to crystalline ice (CI).

As mentioned above, the σ(2p) peak of the methyl terminal group is obscured by the 3a₁ peak of the water adsorbate in the C11 + 5L spectrum (red line). The σ(2p) peak recovers its intensity in the MIES spectra obtained after 135 K (purple line). It has been shown in the IRRAS spectra in Figures 4.4 and 4.5 that water molecules starts to desorb from the SAM’s surface at 145 – 150 K temperature range. This early sign of recovery (at 135 K) suggests that the water
molecules cluster on the surface during the transition from ASW to Cl, to expose the underlying SAM. Similar trend was observed in the MIES spectra of water adsorbate on C16 and C15 SAMs during crystallization.

Figure 7.27: MIES spectra of pristine C11 SAM (black) at 120 K, C11 SAM exposed to 5 L water (red) at 120 K and during crystallization to 150 K.