Surface vibrations in alkanethiol self-assembled monolayers of varying chain length

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The effect of chain length on the low-energy vibrations of alkanethiol striped phase self-assembled monolayers on Au(111) was studied. We have examined the low-energy vibrational structure of well-ordered, low-density 1-decanethiol (C10), 1-octanethiol (C8), and 1-hexanethiol (C6) to further understand the interaction between adsorbate and substrate. Dispersionless Einstein mode phonons, polarized perpendicularly to the surface, were observed for the striped phases of C10, C8, and C6 at 8.0, 7.3, and 7.3 meV, respectively. An overtone at 12.3 meV was also observed for C6/Au(111). These results, in concert with molecular dynamics simulations, indicate that the forces between the adsorbate and substrate can be described using simple van der Waals forces between the hydrocarbon chains and the Au substrate with the sulfur chemisorbed in the threefold hollow site.

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I. INTRODUCTION

Self-assembled monolayers (SAMs) formed from organic thiols on Au(111) have been studied extensively for over a decade. 1-5 The strong interest in SAMs comes from their robust potential for many chemical, physical, and biological applications. The surface chemistry and structure of a SAM can be tuned by changing functional groups. Tying these powerful properties of self-organization and adaptability together, SAMs have been used for lithography, tribology, nano-electronic and biological sensor applications. 6-8 Alkanethiol SAMs in particular have been studied as a model system for self-assembly. Fundamental studies have focused on the structural phase diagram of alkanethiol SAMs. Two basic phases have been found to be prevalent, a high-density 3 phase formed from large exposures to the alkanethiol, in solution or via vapor deposition, and a low-density 2 phase created with smaller doses. There are a variety of other intermediate and low-density phases, which have varying degrees of overlap between alkanethiol chains. 3,9 The low-density striped phases studied here are all the lowest density phase for that particular chain length.

To better understand the self-assembly process it is necessary to delve deeper into the molecular interactions. Helium atom scattering is a unique tool that can be used to gain insight into the dynamics of monolayers and thin films without damaging the adsorbates. This technique has been used in the past to study thin organic films. For example, Fuhmann et al. have shown it is possible to extract information about friction forces from vibrations of alkane monolayers on Cu(111). 10 Other comparable studies have been used to advance theories on phase transitions, adsorbate diffusion, and energy exchange. 11-14

The majority of these scattering studies have been conducted on physisorbed species, such as alkanes or alkanethiols on Au(111) or Cu(111). 15-18 Of particular interest due to their similarity to SAMs are alkanes/Cu(111) and physisorbed alkanethiols/Cu(100) which have been found to have low-energy FT Ï€ vibrational modes at 7.2 and 6.0 meV, respectively, that are independent of chain length. 19,20 This FT Ï€ vibrational mode has also been found to exist in a chemisorbed 1-decanethiol SAM. 5 In this paper we look at the effects of varying the chain length of chemisorbed alkanethiols on Au(111). By doing this we aim to expand our comprehension of the influence of the chemisorbed sulfur group. This experiment will also help to better characterize the chain–chain and chain–substrate interactions that control the self-assembly process.

II. EXPERIMENT

Experiments were conducted in a high momentum- and energy-resolution helium atom scattering apparatus. Elastic and inelastic scattering events are observed through diffraction and time-of-flight (TOF) measurements, respectively. This instrument has been described in detail elsewhere, and its design will only be summarized here. 21,22 It consists of a cryogenically cooled supersonic helium beam source, an UHV scattering chamber equipped with appropriate surface characterization tools (such as LEED, Auger, etc.), a precession chopper (chopper to sample distance of 1.554 m), and a rotating, long flight path (sample to ionizer distance of 1.005 m) quadrupole mass spectrometer detector. The angular collimation yields a resolution of 0.22° and the Δv/v for most beam energies used is less than 1%. The Au(111) crystal used in these studies was cleaned by repeated cycles of sputtering with 0.5 keV Ne+ ions followed by annealing above 750 K until contaminant levels were below our Auger detection limit and helium reflectivity was maximized. Sur-
TABLE I. A listing of parameters for the VENUS intermolecular potential. The stretch parameters \((k_e, r_0)\) are in mdynÅ and A. The bend parameters \((k_\theta, \theta_0)\) are in kcal/mol and deg. The dihedral parameters \((k_\phi, \phi_0)\) are in kcal/mol Å², kcal/mol Å⁴, kcal/mol, and Å.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C stretch</td>
<td>(k_e=4.86, r_0=1.53)</td>
</tr>
<tr>
<td>C-S Stretch</td>
<td>(k_e=5.70, r_0=1.82)</td>
</tr>
<tr>
<td>C-C-C Bend</td>
<td>(k_\theta=0.862, \theta_0=109.5)</td>
</tr>
<tr>
<td>C-C-S Bend</td>
<td>(k_\phi=0.862, \phi_0=114.0)</td>
</tr>
<tr>
<td>C-C-C and C-S-C-C or S-C-C-C</td>
<td>(k_1=3.705, \phi_1=0, k_2=-0.135), (\phi_2=180, k_3=1.571, \phi_3=0)</td>
</tr>
<tr>
<td>CH₂-CH₃ Lennard-Jones</td>
<td>(a=7204000, b=2032)</td>
</tr>
<tr>
<td>CH₂-CH₃ Lennard-Jones</td>
<td>(a=5915000, b=1668)</td>
</tr>
<tr>
<td>CH₂-S Lennard-Jones</td>
<td>(a=4859000, b=1825)</td>
</tr>
<tr>
<td>CH₂-S Lennard-Jones</td>
<td>(a=5917000, b=2226)</td>
</tr>
<tr>
<td>CH₃ &amp; CH₃-Au Lennard-Jones</td>
<td>(a=3.28, e=0.429)</td>
</tr>
</tbody>
</table>

Alkanethiols (1-decanethiol, 1-octanethiol, and 1-hexanethiol) were purified by repeated freeze–pump–thaw cycles and dosed by backfilling the scattering chamber, from a base pressure of \(10^{-10}\) Torr to pressures of approximately \(10^{-8}\) Torr. High quality striped phase SAMs with domain sizes as large as the underlying gold terraces were prepared by dosing at a surface temperature of 280 K followed by a 10 min anneal below the desorption temperature (\(\sim 400\) K). Diffraction scans from the SAMs were obtained at surface temperatures of 80 K to optimize the signal to noise ratio of the elastic diffraction by minimizing Debye–Waller attenuation. TOF spectra for C10, C8, and C6 were taken at a surface temperature of 100 K to increase the excited vibrational population thereby increasing the probability of an annihilation event. The surface temperature of C6 was varied for Debye–Waller measurements and TOF spectra to probe the dependence of the overtone’s intensity on temperature. All data were recorded with scattering along the \(\langle 110\rangle\) azimuth.

Normal modes analysis of the SAMs was performed using the molecular dynamics code VENUS. The potential energy surface was created using a united atom method and a simple force field potential to account for the harmonic stretches, dihedral angles, and Lennard-Jones interaction:

\[
V = \sum_{\text{stretches}} \frac{k_e}{2} (r-r_0)^2 + \sum_{\text{bends}} \frac{k_\theta}{2} (\theta-\theta_0)^2 \\
+ \sum_{\text{dihedrals}} \sum_{n=1}^3 \frac{k_n}{2} \left[ 1 + \cos(n \phi - \phi_n) \right] \\
+ \sum_{\text{Lennard-Jones}} (a/r^{12} - b/r^6).
\]

The parameters used, shown in Table I, were taken from prior theoretical work on SAMs and alkane films on gold.

The system is modeled with a single thiol chain with the sulfur chemically bound in the threefold hollow site of a Au(111) surface with the chain parallel to the surface and running along the \(\langle 110\rangle\) direction. This adsorption site and chain orientation agree with experimental and theoretical studies of low-density alkanethiols on Au(111). While holding the Au surface atoms rigid, the thiol chain position is energetically minimized. An analysis at a surface temperature of 0 K with no zero point energy was used to extract the vibrational frequencies and modes for the different chain lengths. Since the vibrational modes of interest are low in energy, state populations were assumed to be sufficiently large at temperatures of 100 K to allow for experimental annihilation events and verified via Boltzmann distribution calculations. While experimental data were collected only for C6, C8, and C10, normal modes calculations were performed for 1-butanethiol (C4) and 1-dodecanethiol (C12) along with C6, C8, and C10.

III. RESULTS

The structural characterization of the C10 (11.5\(\times\)\(\sqrt{3}\)) low-density phase on Au(111) is shown in Fig. 1(a). The striped phase was created via vapor deposition of \(-20\) L of C10 onto the reconstructed Au(111) and exhibited domain sizes larger than 400 Å after annealing near the desorption temperature (\(-400\) K). After confirming the quality of the C10 SAM by helium atom diffraction, the sample temperature was raised to 100 K for inelastic scattering. A representative TOF spectrum [Fig. 1(b)] and a dispersion plot [Fig. 1(c)] constructed from the data are also shown. The structure and vibrational modes of C10 have been explored previously. The vibration was identified as an Einstein mode with an energy of 8.0±0.3 meV and assigned as a frustrated translation perpendicular to the surface, \(F_{Tz}\).

Further studies were conducted on the C8 striped phase, (10\(\times\)\(\sqrt{3}\)), on Au(111). The striped phase of C8 also exhibited domains larger than 400 Å. Figure 2 shows a representative diffraction scan from the C8/Au(111) striped phase as well as inelastic data in which a single dispersionless phonon event was observed. The beam energy was varied to optimize the signal to noise ratio of the single phonon scattering. The energy of the creation and annihilation events was \(\Delta E=7.3\pm0.2\) meV and this mode is identified as a \(F_{Tz}\) phonon in agreement with prior work on alkanethiols and alkanes on a variety of substrates.

Data for the C6/Au(111) SAM system are shown in Fig. 3. The diffraction in the \(\langle 110\rangle\) direction matches the 0.275 Å⁻¹ spacing in parallel momentum space established as the low-density striped phase conformation. We believe this to be an (8,3\(\times\)\(\sqrt{3}\)) structure based on the reconstructed (23\(\times\)\(\sqrt{3}\)) Au nearest neighbor spacing as discussed in our prior work. The representative inelastic spectrum in Fig. 3(b) shows two dispersionless modes at \(\Delta E=7.3\pm0.4\) and 12.3±0.4 meV. The lower energy mode we assign to the \(F_{Tz}\) mode found in the longer chain alkanethiol systems. We attribute the higher energy mode, which is also dispersionless [see Fig. 3(c)], to the first overtone of the 7.3 meV \(F_{Tz}\) phonon. This overtone assignment is discussed later.
The Debye–Waller factor, $W(T_s)$, was extracted from the C6 data by measuring the integrated specular peak intensity as function of the surface temperature, which was incrementally increased, at three different incident beam angles. The peak intensity is related to $W(T_s)$ by

$$I = I_0 e^{-2W(T_s)},$$

where $I$ is the reflected peak intensity and $I_0$ is the peak intensity at a surface temperature of 0 K. The Debye–Waller
factor has components from the normal and parallel momentum transfers, $\Delta k_n$ and $\Delta k_z$, and mean square displacements, $\langle U_z^2 \rangle$ and $\langle U_i^2 \rangle$.

$$2W(T_s) = \Delta k_z^2 \langle U_z^2 \rangle + \Delta k_i^2 \langle U_i^2 \rangle.$$  \hfill (3)

The specular diffraction peak has no contribution from $\Delta k_i$, forcing one of the above terms to zero. The expression for $\Delta k_z$ is given by

$$\Delta k_z = k_i \left[ \cos^2 \theta_i + \frac{D}{E} \right]^{1/2} + \left[ \cos^2 \theta_f + \frac{D}{E} \right]^{1/2}.$$  \hfill (4)

The Beeby correction, $D$, accounts for the added attractive potential between the He atom and the surface. $E$ and $\theta$ are the kinetic energy of the He atom and incident or final angle from surface normal. Using the Debye–Waller factor and a Beeby correction of 8 meV taken from prior theoretical work on SAMs,\textsuperscript{15} the mean square displacement perpendicular to the surface can be determined as a function of temperature, $\langle U_z^2 \rangle/dT$. Figure 4(a) shows the normalized natural log of the signal (background contribution subtracted) versus surface temperature plots from which the Debye–Waller factors were extracted. Figure 4(b) shows $W(T_s)$ as a function of incident angle, used to better characterize the $\Delta k_z$ in extracting the mean square displacement. The perpendicular mean square displacement calculated for C6/Au(111) is $0.68 \times 10^{-4}$ Å$^2$ K$^{-1}$, as compared to our value of $2.16 \times 10^{-4}$ Å$^2$ K$^{-1}$ for C10/Au(111). A similar value of $1.40 \times 10^{-4}$ Å$^2$ K$^{-1}$ was reported for C11/Au(111).\textsuperscript{30}
 energies and further explored the Einstein mode by deuterating n-octane. The scaling of the vibrational energy of n-octane to deuterated n-octane showed an excellent agreement with a simple force constant approximation, $E \approx \frac{k}{m}$. The work was then expanded to alkanethiols, 1-heptanethiol and ethanethiol, physisorbed on Cu(111) where a 6 meV FT$_z$ mode was found, again showing no dependence on chain length.

In our study of chemisorbed alkanethiols, the C6 and C8 modes appear, not surprisingly, to be equivalent. For each additional methyl group added to the chain the force constant, $k$, and mass, $m$, will increase in proportion keeping the excitation energy, $E$, constant, with a small perturbation due to the effective mass of the sulfur head group. The equivalence of the C6 and C8 modes implies that the FT$_z$ mode is similar to those in the alkanes on Cu(111) and can be modeled by the simplest of attractions between that of the methyl groups and Au(111).

The difference in vibrational frequency between the physisorbed alkanethiols on Cu and chemisorbed SAMs on Au(111) is likely due to a combination of effects. The chemical bond of the sulfur group to the surface more tightly binds the nearest methyl groups, thereby increasing the overall vibrational energy. The substrates also play a role in the shift due to their different van der Waals radii. Experiments on chemisorbed alkanethiols on vicinal Cu surfaces show no external vibrational modes, though this may be due to a variety of factors, including a larger sulfur substrate binding energy and a $\sim 13^\circ$ tilt angle.

In contrast to the other molecules, C10 does not conform to the expected trend ($E_{C10} = 8.0$ meV, $E_{C8} = 7.3$ meV, $E_{C6} = 7.3$ meV). The C10 mode has a slightly higher energy, enough to provoke further investigation with the VENUS normal modes program. The theoretical study was used to look for any qualitative trend in vibrational energy with respect to chain length. A quantitative agreement was not expected due to the simplicity of the model. Using a single chain removed any constraint to the movement parallel to the surface normally introduced by neighboring or overlapping alkanethiols. The relaxed state of the simulated thiol most likely yielded a lower overall vibrational energy, yet trends in the energy of the sagitally-polarized vibrational modes due to chain length should remain the same. The low-energy modes polarized normal to the surface extracted from VENUS are shown schematically in Fig. 5(a) and include an up–down motion, a scissor, and a bowing motion. These modes, shown in Fig. 5(b) along with a non-$z$-polarized mode, have no discernable trend with respect to chain length.

The increased experimental energy of the C10/Au mode indicates that this striped phase is more tightly bound to the surface. One possible explanation for the increased binding energy is a long-range commensurate structure that adds to the van der Waals forces between the hydrocarbon chains and the Au(111). We have previously demonstrated that 1-decanethiol has a unique unit cell that matches the underlying reconstructed Au(111). The $(23 \times \sqrt{3})$ unit cell of the reconstructed Au(111) coincides with that of twice the C10 repeat spacing, but no commensurate relation exists for the

IV. DISCUSSION

The FT$_z$ modes for C6, C8, and C10 on Au(111) can be modeled by van der Waals forces between the surface and the hydrocarbon chain. The relationship between the FT$_z$ vibrational frequency and chain length in this class of systems agrees in part with prior work on alkanes and physisorbed alkanethiols. Witte et al. showed that alkanes of varying chain length on Cu(111) had essentially the same vibrational

![Sketch showing VENUS generated low-energy normal mode displacements from the equilibrium position for C6. The solid circles represent the equilibrium position; the open circles represent the maximum displacement; the circle with an S is the sulfur.](image)
C6 or C8 unit cells. [The theoretical calculations assumed a deconstructed Au(111) surface and, hence, would not account for the extra binding.] The relatively small shift in the energy of the C10 vibration suggests that the increase in the van der Waals intermolecular forces is due to a commensurate structure.

The higher energy C6 phonon, exhibited in Figs. 3(b) and 3(c), was assigned by comparing its intensity to that of the fundamental excitation as a function of temperature. A simple relationship between the probability of the $m$th phonon transition for oscillators and the surface temperature has been developed,31

$$P_m = \exp(-2W(T_s)) \frac{(2W(T_s))^m}{m!}.$$  

The parameter $m$ is the order of excitation and $W(T_s)$ is the Debye–Waller factor determined for C6/Au(111). This relationship has been used effectively for prior work on noble gases on Ag(111).32 The Debye–Waller factor we derived for specular scattering does not account for the parallel mean square displacement and a fitting parameter was used to account for the parallel displacement in the probability calculations. Figure 6 depicts the experimental dependence of the intensity of the C6/Au phonon modes with respect to surface temperature. The background (linear, multiphonon, and diffuse elastic) has been subtracted to allow for easier comparison. Both the experimental and theoretical ratios of the overtone to the first excitation grow linearly with a slope of $W$ as the surface temperature increases. The agreement between the experiment and predicted probability, shown in Fig. 7, along with prior observations of FT, overtones in alkanes and similar physisorbed systems lead to the assignment of the higher energy C6 phonon as an overtone.19 The discrepancy between the expected energy, i.e., twice that of the first excitation, and the observed energy likely is due to anharmonicity. The lack of an overtone for C8 and C10 is likely due to their larger Debye–Waller factors, which would decrease the overall probability, $P_m$.

V. CONCLUSION

We have performed a series of experimental and simulation studies in order to dissect the forces driving the self-assembly of alkanethiolate monolayers. The striped phases of 1-decanethiol, 1-octanethiol, and 1-hexanethiol exhibit FT$_z$ phonons at 8.0, 7.3, and 7.3 meV, respectively. The 12.3 meV overtone for the C6/Au(111) striped phase is assigned as the excitation of the FT$_z$ mode. Alkanethiols on Au(111) exhibit a distinct single phonon inelastic scattering event with a largely invariant energy. The qualitative molecular dynamics simulations also suggest that the frequencies of the low energy vibrations are relatively constant with respect to chain length. The interactions responsible for these phonons are driven by the van der Waals forces between the methylene/methyl groups and the Au substrate atoms. We also suggest that the modestly increased energy of the C10 mode with respect to C8 and C6 comes from increased binding due to the commensurate structure that C10 has with respect to the Au(111) reconstruction. This work represents a step forward in understanding the forces that govern interfacial self-assembly.

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