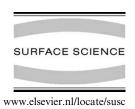


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# Surface vibrations of a highly ordered low-density alkanethiol monolayer measured using inelastic helium atom scattering

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#### Abstract

The low-energy surface vibrational structure of the  $(11.5 \times \sqrt{3})$  striped phase of 1-decanethiol  $(C_{10}H_{21}SH)$  chemisorbed on a reconstructed Au(111) surface has been studied using a high momentum- and energy-resolution helium atom scattering apparatus. Energy-transfer spectra for this system exhibit a dispersionless inelastic feature at 8 meV. We assign this to the frustrated translation of the entire molecule vibrating with polarization perpendicular to the surface. These results are in contrast to the absence of inelastic peaks in the time-of-flight spectra of ordered shorter chain alkanethiols chemisorbed on copper surfaces. Differences in the phonon spectra between these systems are attributed to the longer chain length, the chain orientation, and the weaker S-Au interaction. These results further the understanding of the forces that govern nanoscale self-organization. © 2001 Published by Elsevier Science B.V.

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## 1. Introduction

Self-assembled monolayers (SAMs) have garnered significant interest recently owing to their broad spectrum of potential scientific and technological applications [1–4]. From a scientific standpoint, such monolayers can serve as tunable models for understanding soft materials, such as biological interfaces. Many more applied functions have also been suggested including corrosion resistance, tribology, and nanotechnology, i.e. chemical sensors and molecular electronics.

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The most heavily studied class of SAMs is alkanethiols and, among these, 1-decanethiol ( $C_{10}$ ) adsorbed on gold is the archetype [5–8].

The majority of these studies have focused on structural characteristics utilizing a large ensemble of real- and reciprocal-space surface probe techniques. Taken together, these experiments have mapped out the distinctive phase diagram for ultrathin alkanethiol films. For the purposes of this study, the salient result from these experiments is that there are two principal thermodynamically stable ordered structures for  $C_{10}/Au(1\,1\,1)$ : a lying-down, low-density "striped" phase with  $(11.5\times\sqrt{3})R30^\circ$  symmetry (see Fig. 2 inset) and a high-density "standing" phase with  $c(4\sqrt{3}\times2\sqrt{3})R30^\circ$  symmetry.

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Understanding the internal and external vibrational characteristics of SAMs is a direct route to dissecting the interplay of forces involved in the process of self-assembly. Development of more sophisticated and functional self-organizing structures will only be possible once these subtleties are understood. Only recently, however, have experimentalists begun to probe the low-energy dynamics of these systems, although molecular dynamics simulations have previously suggested an interesting vibrational structure for such systems [9]. Related physisorption systems, such as alkanes, have been similarly characterized [10–12]. Specifically, a wide variety of hydrocarbon monolayers have exhibited a frustrated translation of the whole molecule normal to the surface ( $FT_z$  mode), while studies involving Langmuir-Blodgett films have tended to be dominated by multiphonon scattering [13].

Vollmer et al. have searched extensively for collective vibrations in several shorter chain-length alkanethiols adsorbed on two copper surfaces [14]. Using helium atom scattering (HAS), they observed an  $FT_z$  mode in the disordered, physisorbed monolayers and multilayers but saw no quantized inelastic features for the dense ordered phase of either thiol chemisorbed on either surface. The absence of such soft modes was attributed to two characteristics: the short alkane chain length  $(C_2H_5SH \text{ and } C_7H_{15}SH, \text{ hereafter } C_2 \text{ and } C_7, \text{ re-}$ spectively) and the relatively strong sulfur-copper interaction. By studying  $C_{10}/Au(111)$ , both of these concerns can be addressed. Furthermore, vapor phase preparation and structural characterization of this particular SAM is well documented [8,15,16], but its low-energy vibrational structure is an untapped source of information. HAS is particularly well suited to this study since it can study both structure and dynamics without the threat of probe-induced damage to the SAM integrity [17].

## 2. Experimental

These experiments were carried out in a high momentum- and energy-resolution HAS 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 [18,19], and its design will only be summarized here. It consists of a supersonic helium beam source, an UHV scattering chamber equipped with appropriate surface characterization tools, and a rotating, long flight path (crystal to ionizer distance of 1.005 m) quadrupole mass spectrometer based detector. The angular collimation yields a resolution of 0.22° and the  $\Delta v/v$  for a 32.3 meV beam ( $T_{\text{beam}} = 150 \text{ K}$ ,  $\lambda = 0.80 \text{ A}$ ) is less than 1%. The Au(111) crystal used in these studies was cleaned by repeated cycles of sputtering with 0.5 keV Ne<sup>+</sup> ions followed by annealing above 1000 K until contaminant levels were below our Auger detection limit and helium reflectivity was maximized. Surface crystallinity was confirmed by high quality helium diffraction from the  $(23 \times \sqrt{3})$  "herringbone" reconstruction [20,21] showing an unusually robust full five Bragg orders of diffraction with a concomitant low level of diffuse background (Fig. 1). The average domain size, extracted from the FWHM of the specular diffraction peak with the instrument function deconvoluted, is  $\geq 400 \text{ Å}$ . Relative intensities of the non-specular superlattice peaks are consistent with those observed by Harten et al. [20], suggesting an approximate peakto-peak corrugation of 0.07 A. (This value may be an underestimate due to the "anticorrugation effect" in helium scattering [22].)

The 1-decanethiol (Aldrich, 97%) was purified by repeated freeze-pump-thaw cycles and dosed to scattering chamber backfill pressures of approximately  $10^{-7}$  Torr via a stainless steel tube directed at the gold surface. This directed doser, situated  $\sim 1$  cm from the surface, delivers a higher effective local pressure at the target surface and is employed for vapor phase deposition of organics. High quality 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 ten minute anneal near the desorption temperature ( $T_{\text{anneal}} = 480 \text{ K}$ ). Diffraction from the SAMs was obtained at 70 K to optimize the signalto-noise ratio of the elastic diffraction by minimizing Debye-Waller attenuation. TOF spectra were measured at a surface temperature of 100 K

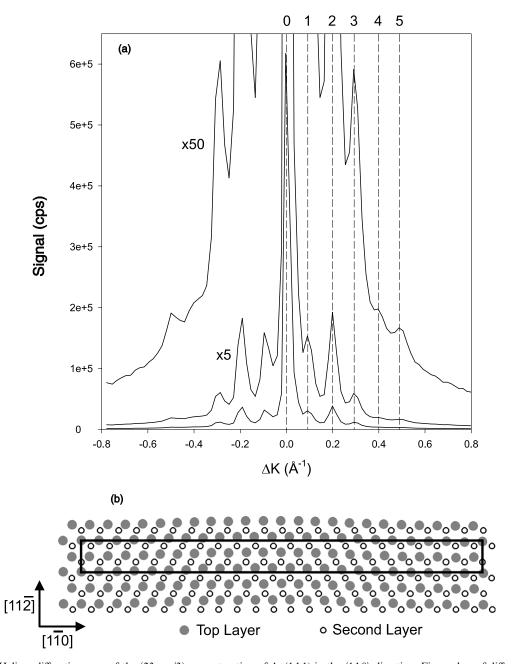


Fig. 1. (a) Helium diffraction scan of the  $(23 \times \sqrt{3})$  reconstruction of Au(111) in the  $\langle 110 \rangle$  direction. Five orders of diffraction are observed on both sides of specular. Kinematic conditions:  $E_i = 19.4$  meV,  $\theta_i = 28.4^\circ$ ,  $T_{crystal} = 200$  K. (b) Top view schematic of the Au(111) reconstruction. Solid circles are the top layer and open circles are the second layer. The topmost layer is compressed by 4.4% along the  $\langle 110 \rangle$  azimuth leading to a smooth and periodic variation in the registry with the second layer from ABC to ABA to ABC stacking. This compression creates an enhanced charge density corrugation easily detected by surface-sensitive helium diffraction.

to allow for sufficient thermal motion of the monolayer while still maintaining a strong signalto-noise ratio. All data were recorded by scattering along the  $\langle 1\,1\,0\rangle$  azimuth.

#### 3. Results

A characteristic diffraction scan of the well-known, chemisorbed, low-density  $(11.5 \times \sqrt{3})$  striped phase of  $C_{10}/Au(1\,1\,1)$  obtained via a  $\sim\!20$  L dose at the target is shown in Fig. 2. An average domain size of at least 400 Å is inferred from the width of the diffraction peaks as there is no broadening added to the substrate specular peak width. After verifying the quality of the SAM, TOF spectra were obtained at incident beam energies of 21.5, 32.3, and 43.1 meV to ascertain the optimal condition for phonon spectroscopy of this system. Representative spectra are displayed in Fig. 3.

At the lowest incident energy studied, approximately the same as that which resulted in an  $FT_z$  mode for  $C_2$  and  $C_7$  on Cu [14], inelastic features were barely perceptible above the background (Fig. 3a). Energy-transfer peaks emerged when the incident energy was increased to 43.1 meV but the multiphonon background intensity was significant (Fig. 3c). With the goal of measuring discrete lowenergy vibrations in mind,  $E_i = 32.3$  meV was selected as a compromise because a clear inelastic peak was observed and the multiphonon intensity was moderate (Fig. 3b). Dispersion measurements performed at this beam energy reveal an Einstein mode at  $\Delta E = \pm 8$  meV, where the creation event is observed for all values of parallel momentum

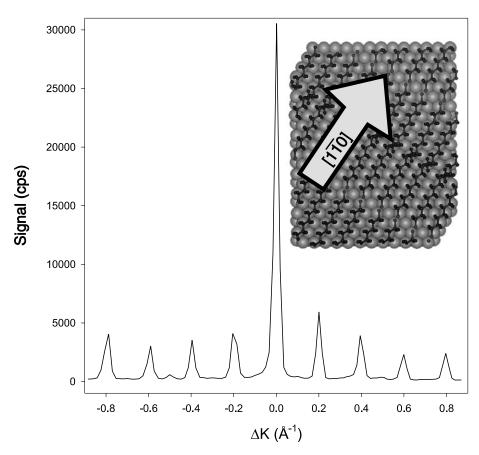


Fig. 2. Helium diffraction scan of one of the three equivalent domains of the  $(11.5 \times \sqrt{3})$  striped phase of 1-decanethiol on Au(1 1 1) in the  $\langle 1\,1\,0\rangle$  direction. The other two domains are structurally identical and rotated  $\pm 120^\circ$  from this domain. Four orders of diffraction are observed on both sides of specular. Kinematic conditions:  $E_i = 5.6$  meV,  $\theta_i = 30.9^\circ$ ,  $T_{crystal} = 70$  K. Inset: Top view schematic of one domain of the striped phase.

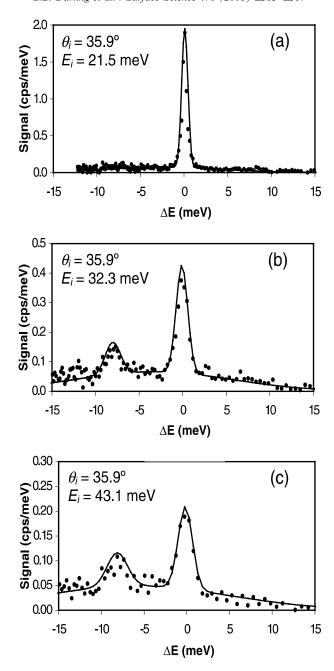


Fig. 3. Representative energy-transfer spectra at (a)  $E_i = 21.5$  meV, (b) 32.3 meV, and (c) 43.1 meV ( $\theta_i = 35.9^{\circ}$ ,  $T_{crystal} = 100$  K) for the striped phase of 1-decanethiol on Au(1 1 1). The principal inelastic feature at  $\Delta E = -8$  meV, seen most clearly in (b), corresponds to the frustrated translation of the entire molecule normal to the surface (FT<sub>z</sub> mode). The broad background in (b) and (c) is a product of multiphonon energy exchange.

transfer, but annihilation events are only seen at sub-specular angles (Fig. 4). We attribute this

feature to the external vibration of the entire molecule with polarization perpendicular to the

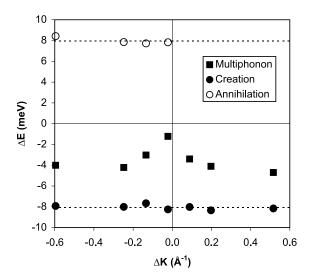


Fig. 4. Dispersion curve summarizing inelastic data  $(\Delta E \equiv \text{energy transfer})$  with respect to the He beam) for the striped phase of 1-decanethiol on Au(111) for  $E_i = 32.3$  meV,  $\theta_i = 35.9^{\circ}$ , and  $T_{\text{crystal}} = 100$  K. The circles denote the FT<sub>z</sub> Einstein mode and the squares represent the most probable multiphonon energy transfer (multiphonon peaks were quite broad:  $\sim 6$  meV FWHM). The multiphonon and creation phonon data points at  $\Delta K = 0.09$  Å<sup>-1</sup> are from the energy-transfer spectrum shown in Fig. 3b.

surface. Such dispersionless features have been seen in atomic [23,24] and molecular systems [10,14]. Moreover, internal modes of the hydrocarbon chain are expected to be somewhat lower in energy [9].

It is not clear that the inelastic features observed in this experiment arise solely from the domain analyzed via diffraction. The structure of this overlayer consists of three equivalent domains of molecules with stripes rotated by 120° with respect to each other. The diffraction data shown in Fig. 2 represent scattering from the domain in which the beam impinges parallel to the molecular axes. Broadside collisions arising from other domains may also participate in inelastic encounters leading to excitation of FTz vibrations. Note, however, that the increased corrugation in this direction dilutes the inelastic scattering. Broadside collisions could be studied directly by scattering 30° away from the diffraction azimuth used here, since in this geometry atoms would hit one of the other striped domains perpendicular to its molecular axes. Studies of this effect will be examined in future experiments.

#### 4. Discussion

Similarity of the frustrated translational mode to that seen for alkanes implies, despite the strong chemisorption of the thiolate end group, that the soft van der Waals interaction between the lying-down hydrocarbon chain and the substrate dominates the observed low-energy phonon mode. Following this assumption and using the harmonic approximation, the ratio of the phonon energies for ordered, chemisorbed  $C_{10}/Au$  and disordered, physisorbed  $C_{7}/Cu$  should compare well with Eq. (1):

$$\sqrt{\frac{n_{\text{CH}_2,C_{10}}m_{C_{10}}}{n_{\text{CH}_2,C_7}m_{C_7}}} = 1.368 \tag{1}$$

where  $n_{CH_2}$  is the number of  $CH_2$  units participating in the van der Waals contact and m is the molecular mass. Indeed, in strong agreement, the ratio of the measured phonon energies is 1.333. The fact that an external vibration is observed at all (whereas none is observed for chemisorbed, standing C<sub>2</sub> or C<sub>7</sub> on copper) suggests that neither chemisorption nor order of the monolayer has a significant impact on the frustrated translational mode. There are two plausible explanations for the slight disagreement of the two ratios. A flat molecule chemisorbed at one end will have a somewhat shorter effective length than its fully physisorbed counterpart. Perhaps more importantly, the minor discrepancy between the two ratios is likely a product of the different substrates, for which one would expect to have different effective force constants.

In fact, the substrate may be the key to understanding why a phonon is observed for  $C_{10}$  chemisorbed on  $Au(1\,1\,1)$  but not for  $C_2$  or  $C_7$  chemisorbed on  $Cu(1\,0\,0)$  and  $Cu(1\,1\,0)$ . The sulfur-substrate interaction is much stronger for copper than for gold, leading to a local relaxation of the substrate atoms in the vicinity of the adsorbate and hence a stiffer bonding contact [25]. Furthermore, there is a qualitative structural dis-

parity between these two systems, namely the orientation of the alkane chain relative to the surface (parallel for this experiment and ~13° from normal for the copper study). Unraveling the contributions from these two effects can be achieved by probing the low-energy dynamics of the  $c(4 \times 2)$ standing phase for decanethiol on gold – a current area of study in our group. These experiments can also serve to empirically assess a recent molecular dynamics investigation of pentadecanethiol chemisorbed on Au(111) in the standing orientation that reported a sizeable density of internal soft modes below 10 meV [9]. It is presumably these soft modes that inhibit helium diffraction from alkanethiol SAMs at surface temperatures above 200 K. The multiphonon background that partially masks the discrete features is a product of scattering from many of these low-energy internal vibrations. Freeing the hydrocarbon chains from substrate interaction by forming the standing phase may allow some of these states to be resolved.

In summary, the dynamics of the well-ordered  $(11.5 \times \sqrt{3})$  striped phase of decanethiol chemisorbed on Au(111) were studied using high-resolution helium atom scattering. In contrast to ethanethiol and heptanethiol chemisorbed on copper, a dispersionless low-energy vibrational mode was observed at 8 meV and was attributed to the frustrated external translation perpendicular to the surface. Further investigations involving the standing phase for this system will assist in identifying the source of this discrepancy. Together, these studies will aid in the understanding of the forces that control the organization of self-assembled structures and contribute to the development of novel nanoscale materials.

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