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The Pressure Gap for Thiols: Methanethiol Self-Assembly on Au(111) from Vacuum to 1 bar

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Abstract

Functionalizing noble metal surfaces with (bio-)organic molecules is a vibrant field of research, with key applications in medicine, catalysis and molecular electronics. Control over the molecular self-assembly is essential to create functional devices. Here, we exploit our high-pressure, high-temperature scanning tunneling microscope (STM) to relate the effects of controllable parameters (temperature and pressure) to atomic-scale assembly mechanisms. Using methanethiol self-assembly on Au(111) as a model system, we monitor the formation and assembly of the ubiquitous $(\text{CH}_3\text{S})_2\text{Au}$ “staple” motif into row structures at pressures up to 1 bar. We observe a pressure-induced transition from the usual $1/3$ monolayer (ML) saturation coverage in vacuum to $3/8$ ML at 1 bar, thus providing the first evidence for a pressure gap effect for thiol adsorption. Complementing our experiments, we employed dispersion-corrected density functional theory computations to model the formed surface adlayers, corresponding STM images and the underlying equilibrium thermodynamics.

1 Introduction

Thiol molecules on gold provide a scaffold to attach virtually any organic molecule. While the sulfur head group ensures a firm bonding to the gold substrate, the tail of the molecule can be functionalized with reactive groups that allow bonding to other molecules. In this way, complex structures can be created that specifically target biomolecules in medical science (cf. refs. 17-21 in ref. 1), enhance (chiral) selectivity in catalysis² or provide unique electrical properties for molecular electronics.³ For these applications, control over the thiol surface structure is essential. At first glance, this task appears simple: thiol molecules on gold tend to form crystalline self-assembled monolayers (SAM)s (an overview of acronyms used in this manuscript is provided before the bibliography), even at moderate temperatures.^{1,2,4,5} However, coexistence of multiple phases has proven hard to prevent, particularly for larger thiol molecules.^{4,6,7}

In order to find handles to tune the thiol overlayer structure, intimate knowledge of the bonding behavior and kinetics during self-assembly is required. A wide variety of microscopy,^{4,7-14} spectroscopy,¹⁵⁻²⁰ and scattering²¹ techniques has been applied to these sys-

tems, complemented by theoretical modeling.^{1,19,21–23} It was found that following thiol adsorption, the S-H bond of the head group is broken and H₂ is formed as a byproduct. While formally a thiyl radical is formed in this process, the adsorbate is usually called “thiolate” or thiol, despite having neither a net negative charge nor a hydrogen atom. Thiolates have such affinity for gold that Au atoms are extracted²⁴ from the close-packed terraces to be incorporated in the thiol overlayer structure.^{1,9–11,21} It was established that the Au adatoms are bound by two thiol molecules, forming thiol-Au-thiol “staples”.^{1,4,10,21} In the final step of overlayer formation, the staples self-assemble into crystalline phases.

While the fundamental studies have thus identified the key formation steps and structural elements in self-assembled monolayers, most of them were conducted under vacuum conditions, whereas elevated pressure or liquid phase SAM growth is much more attractive in practical applications. For several metal-adsorbate systems, it was shown that such a "pressure gap" can have significant effect on the behavior of adsorbates.^{25–27} Here, we have studied methanethiol adsorption on Au(111) on both sides of the pressure gap: With our high-pressure, high-temperature scanning tunneling microscope (STM),²⁸ we assess the SAM structures formed at pressures ranging from ultrahigh vacuum to 1 bar, at temperatures up to 523 K. Through the variation of temperature and pressure, we relate control parameters to the kinetic and thermodynamic factors that affect SAM ordering and crystal structure. Our data is compared to extensive density functional theory (DFT) modeling, taking into account the effects of entropy and Van der Waals (VdW) interactions. This methodology allows us to thoroughly characterize SAM formation on the thermodynamic and kinetic level under relevant conditions and characterize the highest ever reported thiol coverage, here achieved at 1 bar and 383 K.

2 Methods

2.1 Experimental Methods

2.1.1 Set-up description

Microscopy at elevated pressure and temperature constitutes a technical challenge. To enable our studies at pressures up to 1 bar, we used the ReactorSTM developed in our group.²⁸ In short, this system allows for preparation and characterization in UHV as well as high pressure STM studies using a 0.5 mL flow cell inside the vacuum system. Gases are introduced into the flow reactor from a dedicated gas supply system, which allows for accurate control over the gas composition, flow and pressure. All components that are in contact with the gas environment are made of corrosion-resistant steel alloys, glass, polyetherimide or Kalrez[®] to prevent degradation upon exposure to reactive gases such as CH₃SH. The use of PtIr STM tips prevents tip degradation during the measurements. Nevertheless, frequent changes in imaging quality due to adsorption/desorption of gas molecules on the tip apex cannot be avoided.

In addition to the scanning tunneling microscope, the system is equipped with a LEED apparatus (Omicron) and an X-ray photoelectron spectrometer (SPECS Phoibos). A quadrupole mass spectrometer was used to verify the purity of the employed gases.

2.1.2 Experimental procedures

The Au(111) sample (Surface Preparation Laboratories)²⁹ was cleaned by cycles of 1 keV Ar⁺ bombardment and annealing at 900 K. For the formation of methanethiolate SAMs under UHV conditions, CH₃SH (N1.8, Westfalen AG, containing approximately 2 Vol% DMDS³⁰) was dosed via capillaries close to the sample surface. All UHV dosing was performed at room temperature.

Prior to high-pressure experiments, all gas lines were flushed with argon for at least 30 minutes. To start the high-pressure exposure, the reactor was slowly pressurized in argon or nitrogen before heating to the desired temperature. In order to minimize the thermal drift in the microscope, the system was allowed an equilibration period of approximately 90

minutes. Whenever expedient, imaging was started before introducing CH_3SH , so that the surface dynamics upon exposure could be monitored.

2.2 Computational Methods

2.2.1 Structure determination

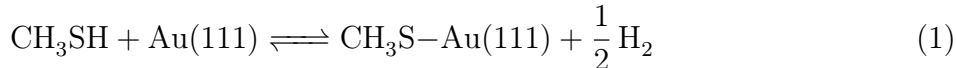
Electronic structure computations were performed using the PAW formalism to account for the ion-electron interaction³¹ as implemented in the VASP 5.4.1.^{32–35} The wave function was expanded in a plane wave basis set characterized by a cut-off energy of 400 eV. The GGA functional PBE^{36,37} was used, in combination with the “dDsC” dispersion correction,³⁸ which has been shown to be accurate for adsorption energies on Pt(111)³⁹ and has been successfully applied to the adsorption of pyridine on Au(111)⁴⁰. A 2nd order Methfessel-Paxton electron smearing (width of 0.2 eV) was applied to metallic surfaces. Ionic relaxations were performed using a Conjugate-Gradient algorithm to a maximum gradient below 0.05 eV/Å, with wave functions converged to 10^{-5} . A Monkhorst-Pack K-point sampling⁴¹ of at least $3 \times 3 \times 1$ was applied for all surfaces in order to converge the adsorption energies. A primitive unit cell parameter of 2.928 Å was specified, corresponding to the optimized Au bulk unit cell of 4.141 Å. A vacuum layer of 10 Å was used to separate the vertical repetitions of the slabs. For the STM simulations, the unit cell was replicated, since our version of the code does not support K-point sampling. We used 5 full metallic layers, of which the three bottom layers were fixed in their bulk positions. Note that the herringbone reconstruction⁴² was neglected in our computations.

STM images were simulated by the approach of Tersoff and Hamann,^{43–45} at a bias voltage of -1 V and a current of 10^{-9} A (unless stated otherwise), based on the PBE band-structure at the Γ point of super cells.

2.2.2 Thermodynamics

Frequency computations were performed to estimate zero-point energies and vibrational entropy corrections within the harmonic oscillator approximation. For these computations,

all gold atoms were kept frozen. All frequencies were real and above 40 cm^{-1} . Adsorption energies for structures with gold adatoms are referenced to the Au(111) surface and Au atoms from the bulk. Adsorption free energies were calculated based on the reaction:



When estimating thermal contributions to the Gibbs energy, we made the usual assumptions of harmonic oscillators for vibrations. For gas-phase molecules we also invoke the rigid-rotor approximation and the Sackur-Tetrode equation for the rotational and translational contributions, respectively. The energy required to bring one Au atom from the bulk onto the Au(111) surface is in the order of 0.7 eV. To allow for a wider comparison of our data to the literature, we also provide data for the calculation of adsorption energies in a DMDS gas atmosphere in Table S1 in the ESI.

3 Results and Discussion

We investigated the effect of pressure on the structure of the methanethiolate overlayer using controlled dosing experiments in vacuum (10^{-6} mbar) and at 1 bar. For the vacuum case, several saturation structures have already been identified in the literature,^{11,46,47} each with $1/3$ monolayer (ML) coverage. In our case, the surface is saturated with a striped phase with a $6 \times \sqrt{3}$ unit cell (see Fig.1) after several hours of 10^{-6} mbar CH_3SH exposure at room temperature (see Fig. S1 in the ESI for the structural evolution during the self-assembly). Similar striped phases have been reported in the literature, although ordering of the stripes into densely packed domains was never observed.^{10,11,46,48} We point out that exchange reactions with strong-binding impurities from the gas feed, such as ethanethiol, can be excluded since the stripe motifs were already observed in the initial stages of self-assembly (90 minutes, see Fig. S1a in the ESI). The stripes have been identified as rows of thiol-Au-thiol “staples,” which can appear in several structural isomers. Our DFT simulations (see ESI section S3.3) of the staple structures indicate that the inclusion of Au adatoms in the SAMs indeed improves the Au-S interaction (~ 0.25 eV per thiol), while the staple packing and isomeric form is determined by the methyl-methyl repulsion (up to ~ 0.4 eV per

thiol). Our computations indicate that several isomers have a very comparable formation energy, explaining why multiple phases have been observed in the literature.^{10,11,46,47} Indeed, depending on the tip's state and its interactions with the surface, the SAM was sometimes observed as a $3 \times \sqrt{3}$ line structure (see Fig. S2 in the ESI).

To identify the experimentally observed structure observed in Figure 1a, we used simulated STM images. The simulated STM image in Fig. 1b (with corresponding ball model in Fig. 1c) shows the best agreement to the experimental image (Fig. 1a), accurately reproducing the alternating brightness in the line structure, in contrast to the simulations of other models (see Fig. S3 in the ESI). Although the fine structure is not fully resolved in the experimental image, the bright protrusions ($\sim 0.1 - 0.2$ Å) originating from half of the methyl groups show the same rectangular pattern in both the experimental and the simulated image. With this good agreement, the structure in Fig. 1c is assigned to the vacuum saturation coverage structure shown in Fig. 1a. Similar to the other phases observed in the literature,^{11,46,47} this structure has a coverage of $1/3$ ML.

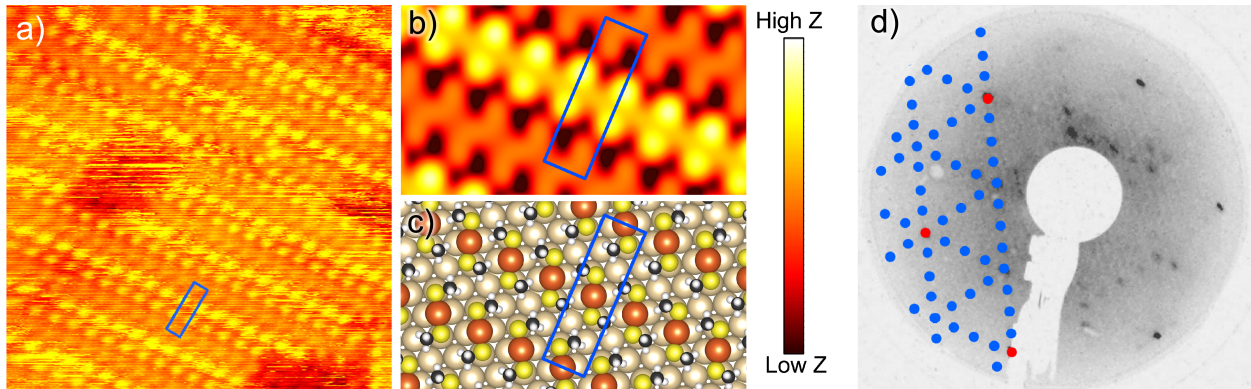


Figure 1: Adsorption structure of methanethiolate on Au(111) after saturation in vacuum. a) $6 \times \sqrt{3}$ methanethiolate SAM obtained after 21 hour dosing ($P_{\text{CH}_3\text{SH}} = 10^{-6}$ mbar, $P_{\text{H}_2} = 10^{-10}$ mbar) at room temperature, 10×10 nm², $U_s = -1.0$ V, $I_t = 150$ pA. Corrugation in SAM structure: 0.05 nm, as determined from line scans perpendicular to the row direction. Note that the corrugation in STM images is strongly affected by the tip apex structure and might therefore change from image to image. b) Simulated STM image (-1V, 500 pA, corrugation: 0.07 nm) for the structure in a), and c) the corresponding ball model. Atoms in orange: Au adatoms, gold: lattice Au atoms, yellow: S, black: C, white: H. d) LEED pattern showing the (1x1) Au lattice (red dots) and the $6 \times \sqrt{3}$ SAM overlayer (blue dots, 3 domain orientations)

To investigate if a coverage higher than $1/3$ ML can be obtained at elevated pressure,

we imaged the Au(111) surface in 1 bar CH_3SH at several temperatures. Fig. 2 shows the structural evolution of the SAM directly after changing the partial pressure of CH_3SH from trace levels to 1 bar at 383 K. The initial vacuum saturation-coverage phase (which appears as a $3 \times \sqrt{3}$ structure in Fig. 2a) is quickly replaced by a new phase with paired lines. The new structure is only stable under high-pressure conditions: when the partial pressure of CH_3SH is brought back down to trace levels, the $3 \times \sqrt{3}$ structure is recovered (Fig. 3). Thus, it is clear that the CH_3SH pressure can be used to drive a reversible phase transition.

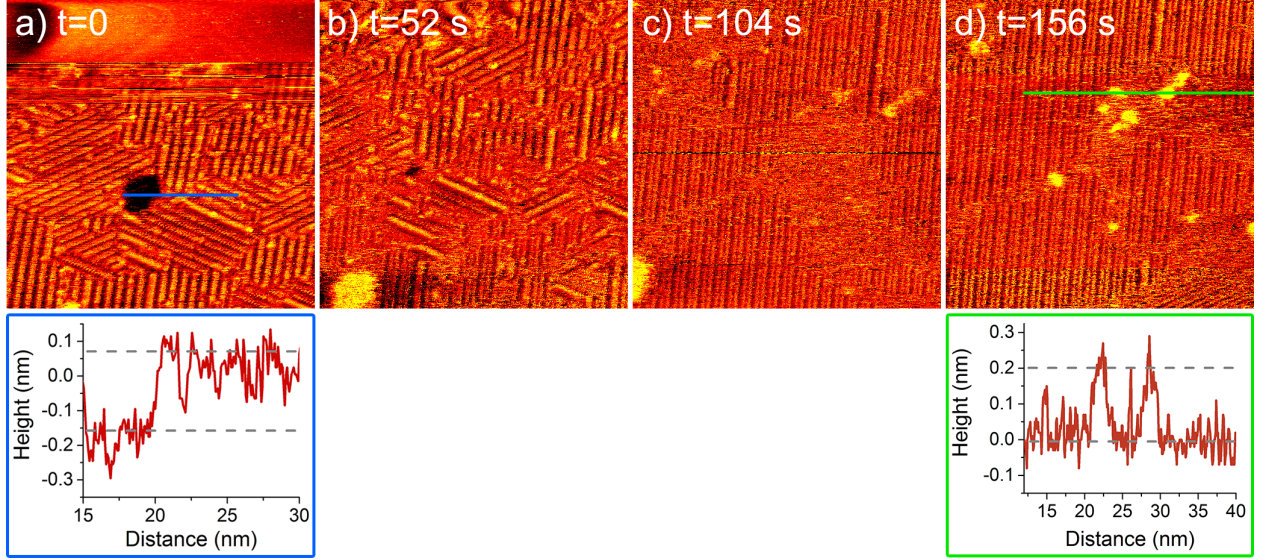


Figure 2: Structural transition from the $1/3$ ML phase to a high-pressure structure after introducing 1 bar CH_3SH at 383 K. Imaging parameters for a-d: $40 \times 40 \text{ nm}^2$, $U_s = -1\text{V}$, $I_t = 150 \text{ pA}$. Height lines identify an Au vacancy island (blue) and Au adatom islands (green).

For such a pressure-driven transition, there is an increase in the adsorbate coverage^{25–27}. To establish which CH_3SH coverage is achieved, we first determined the unit cell shape under high-pressure conditions. This is a challenge, because the drift in the microscope at high pressure and temperature causes some image distortion. Using large-scale images with a high tip speed, we minimized the effect of drift and established that the unit cell has the same orientation as in the $1/3$ ML case. The periodicity perpendicular to the stripes is 4 Au spacings. The periodicity along the stripe direction was determined to be $\sqrt{3}$ Au spacings using Fig. 4c. Thus, we arrive at a $4 \times \sqrt{3}$ unit cell. The highest thiol coverage that allows for reasonable orientation of the methyl groups in this unit cell is $3/8$ ML.

A closer inspection of the images in Fig. 2 reveals that the denser packing of CH_3SH

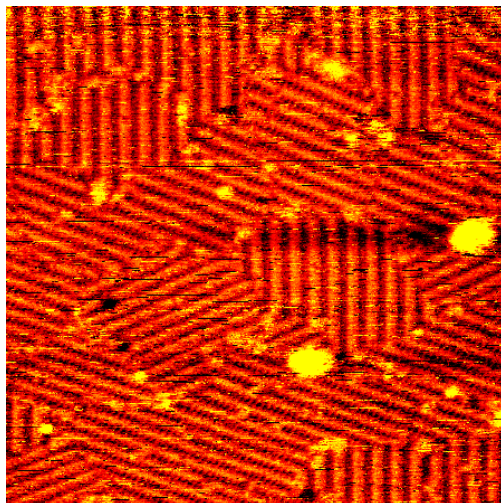


Figure 3: Reversibility of the high-pressure phase transition following decrease of the CH_3SH pressure to trace levels (in 1 bar N_2), 383 K. Imaging parameters: $35 \times 35 \text{ nm}^2$, $U_s = -1\text{V}$, $I_t = 150 \text{ pA}$.

is enabled by the release of Au from the SAM: the vacancy island in Fig. 2a is filled (Fig. 2c) and Au adatom islands (Fig. 2b-d) are formed. We quantified the vacancy island coverage within a few minutes after the transition to high pressure in several fresh areas on wide terraces (see for instance Fig. 4a), thus minimizing the influence of the tip and step edges as sinks for the adatoms. We find that the amount of released Au is large and strongly fluctuating: $0.22 \pm 0.07 \text{ ML}$. This amount is in the same range as the 0.17 ML that is contained in the perfect $1/3 \text{ ML}$ structure. Based on this, one could hypothesize that the high-pressure phase does not contain Au adatoms. However, our DFT computations show that $3/8 \text{ ML}$ structures without Au adatoms are more than 0.2 eV less stable per adsorbed thiol, i.e., more than 0.6 eV for the $3/8 \text{ ML}$ unitcell, than their Au-containing counterparts (see Table S2 in the ESI for the most stable one out of seven tested configurations). Furthermore, the large spread in Au adatom island coverage suggests that there is a second source of Au atoms that shows more fluctuation than a pure crystalline phase. We suggest that the domain boundaries in the SAM are this second source. Indeed, Fig. 3 shows that small Au clusters can be generated at the domain boundaries following dynamical situations such as phase transitions or the initial formation of the SAM.

Based on the discussion above, we considered candidate high-pressure structures with a $4 \times \sqrt{3}$ unit cell, $3/8 \text{ ML}$ CH_3SH coverage and $1/8 \text{ ML}$ Au adatom coverage (see Fig.

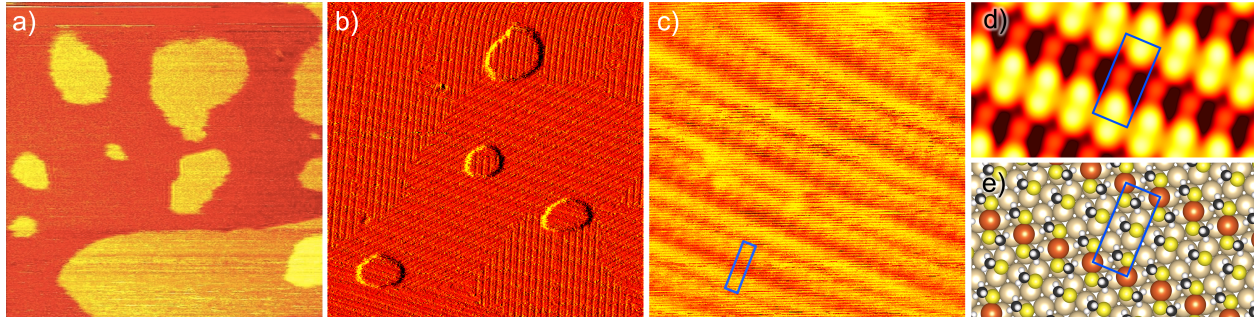


Figure 4: Structure of methanethiolate SAM at 1 bar ($P_{\text{CH}_3\text{SH}} = 1000$ mbar, $P_{\text{H}_2} = 0.35$ mbar), 383 K. a) Au adatom islands shortly after transition to 1 bar (80×80 nm², $U_s = -0.2$ V, $I_t = 120$ pA). b) SAM structure on adatom islands. The STM image was differentiated to visualize the SAM structure on both the terrace and the adatom islands ($80 \text{ nm} \times 80 \text{ nm}$, $U_s = -0.1$ V, $I_t = 800$ pA). c) Details of SAM structure, 10×10 nm², $U_s = -0.1$ V, $I_t = 800$ pA. Corrugation in SAM structure: 0.02 nm. d) Simulated STM image (-1V, 500 pA, corrugation: 0.08 nm) for the structure in c), and e) The corresponding ball model.

S4 in the ESI). Following the structural motifs identified in the literature, these contain a mixture of "staples" and bridge-bonded thiolates.^{10,11,21,46,47,49} Again, we find several isomers with similar formation energy, necessitating further distinction using STM simulations. The simulation in Fig. 4d, based on the structure in Fig. 4e, reproduces the bright paired rows observed in the experiment (Fig. 4c). Note that the row spacing in the experimental image (Fig. 4c) is somewhat stretched due to drift in the microscope under high-pressure, high-temperature conditions. The "bright" row pairs - also clearly observed for the low-pressure case (Figs. 1a, b) - characterize the trans-staple motif for which the methyl groups are equidistant to (1) the Au-adatom to which they are covalently bound through S, and (2) a neighboring Au-adatom. The thiolates between the staples, which are bridge-bonded with a tendency towards the hexagonally close packed (hcp) site, appear dark in both the experimental and the simulated image. The alignment of the bridge-bonded thiolates with respect to the staples is difficult to determine from the experimental image, but the STM-simulations allow differentiation (cf. Fig. S4) between very similar structures. Based on this agreement, we identify the high-pressure structure with the structure shown in Fig. 4e.

With a coverage of $3/8$ ML, this is the most densely packed SAM reported in the literature, evidencing the existence of a pressure gap for thiol adsorption. Note that Mehring *et al.*¹⁴ observed a similar $4 \times \sqrt{3}$ structure after exposure of Au(111) to a 1 mM dimethyldisulfide

(DMDS)/ethanol solution for several hours. They suggested a structure with only $1/4$ ML coverage. While competition between thiol and solvent adsorption might have resulted in such a structure under their conditions, our observation of a pressure-induced transition provides clear evidence for a structure with a coverage higher than that obtained in ultra-high vacuum (UHV).

To relate the observations in Fig.1a and Fig. 4c to equilibrium thermodynamics, we calculated the corresponding adsorption free energies using:

$$\Delta G_{ads} = \Delta E_{ads} + \Delta ZPE_{ads} + \delta H_{ads}^T - T\Delta S_{ads} \quad (2)$$

where E_{ads} is the sum of the electronic energies E_{PBE} and E_{dDsC} , ZPE refers to the zero-point energies, δH^T to the thermal correction to the enthalpy, and S to the entropy. The vibrational contributions of the SAMs were taken into account in the calculation (details in Methods Section 2.2.2) .

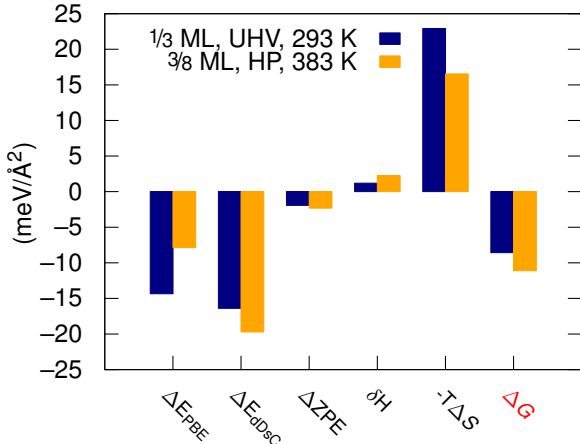


Figure 5: Contributions to the surface free energy according to Eq. 2 for $1/3$ ML under UHV, 293 K and $3/8$ ML under HP, 383 K conditions.

Fig. 5 shows that both the $1/3$ ML and $3/8$ ML structures are predicted to be thermodynamically at least meta-stable at the respective conditions under which they were experimentally observed (see Section 3.4 in the ESI for a discussion on relative stability). Second, the decomposition shows that neither the change in zero point energy (ZPE), nor in

enthalpy corrections, contributes significantly to the adsorption free energy. The adsorption entropy, however, does significantly offset ΔE_{ads} . Since the entropic contribution to the free energy is strongly dependent on temperature and pressure, this shows that the applied conditions strongly influence the stability of the SAM structures. The pressure increase from 10^{-6} mbar to 1 bar lowers the entropic penalty for adsorption according to:

$$\Delta G = k_B T \ln(P/P') \quad (3)$$

Despite the 90 K temperature difference between Fig.1a and Fig. 4c, Fig. 5 shows that the pressure increase dominates and thus lowers the entropy cost, providing a stabilizing force for higher thiol coverage. A further temperature increase should undo this stabilizing effect however, and can even lead to desorption of the SAM. Fig. 6a shows that desorption occurs already at 523 K, where only the (1x1) Au(111) lattice is visible despite the high CH_3SH pressure. Note that the observation of the (1x1) lattice does not imply a completely empty surface, since a small amount of thiulates could be obscured from STM observation due to their fast motion. Indeed, the absence of the herringbone reconstruction indicates that some thiulates remain on the surface. Nonetheless, the coverage decrease demonstrates that the entropy in the gas phase outcompetes both the pressure and the adsorption energy under these conditions.

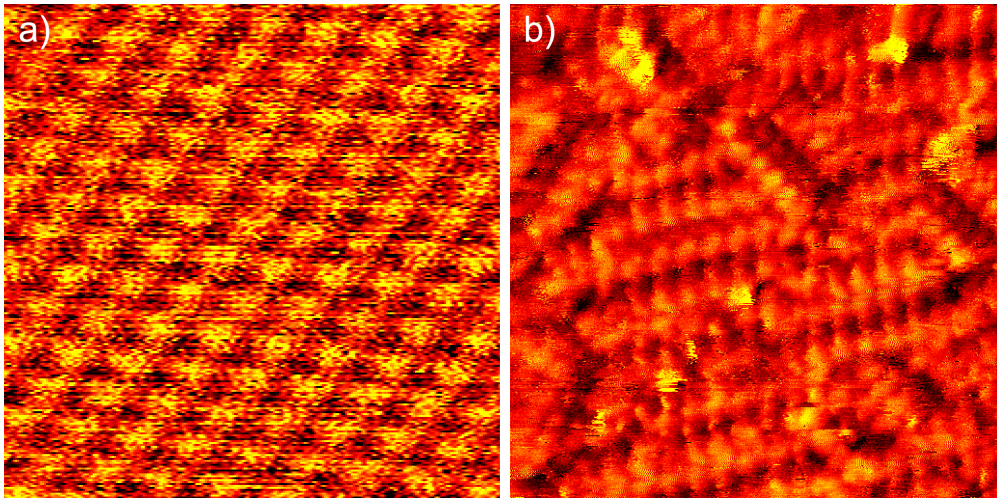


Figure 6: The effect of temperature on CH_3SH adsorption at 1 bar. a) Empty Au(111) surface imaged at 523 K ($2.5 \times 2.5 \text{ nm}^2$, $U_s = -0.3 \text{ V}$, $I_t = 520 \text{ pA}$). b) Kinetically hindered CH_3SH adsorption at room temperature. $10 \times 10 \text{ nm}^2$, $U_s = -0.3 \text{ V}$, $I_t = 520 \text{ pA}$.

At lower temperatures, adsorption kinetics play a dominant role. As can be seen in Fig. 6b, room temperature exposure at 1 bar results in a very poorly ordered structure, containing $3 \times \sqrt{3}$ line structures similar to those observed after UHV exposure. The lack of ordering establishes that thiol adsorption, S-H bond dissociation, and staple formation proceed significantly faster than the ordering process. Note that the SAM structure did not proceed to the $4 \times \sqrt{3}$ phase, even though the thermodynamic driving force is higher than in the experiment at 383 K (Fig. 4c). Clearly, the hampered diffusion at $1/3$ ML coverage prevents the insertion of more thiol molecules into the SAM.

Based on our observations and simulations for various conditions, Fig. 7 shows an overview of the relation between the applied conditions and the observed structure. One distinguishes conditions where the structure is determined by kinetics and others that lead to thermodynamic control. The kinetically controlled region tends toward lower coverage and disorder, and originates from the mismatch between the (fast) staple formation rate and the (slower) staple ordering rate. The rate mismatch is largest for low temperature (Fig. 6b vs. Fig. 4c) and/or high pressure (Fig. 6b vs. Fig. 1a).

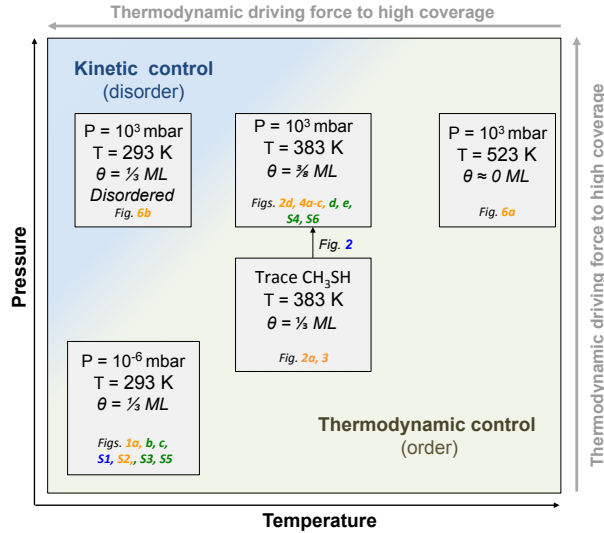


Figure 7: Conceptualization of thermodynamic and kinetic factors determining SAM structures. The different structures and transformations are linked to the Figures in this manuscript. In blue: SAM formation process In green: Theoretical analysis . In orange: equilibrium/kinetically stable SAMs.

At low pressure and/or high temperature, thermodynamic control takes over. Our com-

putations show that the balance of the Au-S interaction, the Van der Waals interactions, and the gas-phase entropy determine the relative stability of the various SAM structures. Through the gas-phase entropy, higher pressure favors higher coverage (Fig. Fig. 4c vs. Fig. 1a), while higher temperature favors lower coverage (Fig. 4c vs. Fig. 6). Note however that our computations show that several structures with the same coverage are energetically very close (see Figs. S3-6 in the ESI). Thus, subtle factors such as the energetic cost of defect formation (impurities, step edges, domain boundaries) may also determine which structure is observed.

4 Conclusion

We have identified the key thermodynamic and kinetic factors that control methanethiolate SAM formation, and have related these factors to the applied temperature and pressure. Most importantly, we have shown that, beside affecting SAM order, the dosing pressure can induce a phase transition to the newly revealed $3/8$ ML phase. Such pressure- or concentration-induced transitions will likely also occur for functionalized SAMs, for which repulsive tail-tail interactions may exist, which are in competition with optimizing the Au-thiol interaction.⁵⁰ We therefore expect that the fundamental insights gained here will apply to a wide range of technologically relevant SAMs, and provide handles for their controlled growth.

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Supporting Information Available

The Supporting Information provides additional STM data and an extensive theoretical analysis based on DFT energetics and simulated STM images. Furthermore, an expression for the equilibrium hydrogen pressure in the reactor is provided. The geometries of all structures are provided in the CONTCAR format. In addition, the energies and entropies computed for the ab initio thermodynamics modeling are provided. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

List of Alphabetically Ordered Acronyms

DFT density functional theory

DMDS dimethyldisulfide

hcp hexagonally close packed

HP high pressure

LEED low-energy electron diffraction

ML monolayer

SAM self-assembled monolayers

STM scanning tunneling microscope

UHV ultra-high vacuum

VdW Van der Waals

ZPE zero point energy

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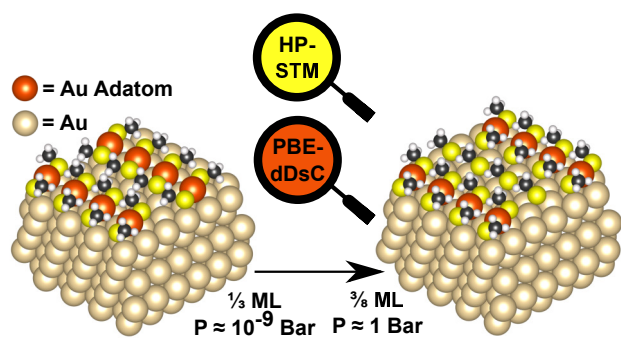
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