n-Alkyl Thiol Head Group Interactions with the Au(111) Surface

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Abstract

State-of-the-art first principles calculations based on density functional theory were performed on CH$_3$(CH$_2$)$_{n-1}$S-Au(111) systems. We show that the adsorption site of methylthiolate at low coverage on the Au(111) surface is the fcc site, not the hcp site as has been recently reported. Further, we report results for chain length dependency and the electronic structure of the system.

The interaction between organic materials and solid surfaces has been extensively studied because of the broad range of industrial applications.$^1$–$^4$ Self-assembled monolayers (SAMs) hold special interest, because the presence of the thiol group greatly strengthens the molecule-surface interactions, inducing order in the layer. SAMs have important potential applications in industry, such as sensors, transducers, detectors, packaging and insulating layers for integrated circuits, functionalization of surfaces, thin coatings for electrodes, and corrosion inhibition.

The long-chain alkane thiols [CH$_3$(CH$_2$)$_{n-1}$SH, or C$_n$] form SAMs on the Au(111) surface. Their simplicity, highly ordered structures, and chemical stability make these systems ideal for study with a variety of techniques including atomic force microscopy,$^5$–$^7$ infrared spectroscopy,$^7$–$^9$ high-resolution electron-energy-loss spectroscopy,$^7$ grazing X-ray diffraction,$^1$–$^3$ scanning tunneling microscopy (STM),$^1$–$^3$ scanning probe microscopy,$^1$–$3$ low-energy electron diffraction (LEED),$^1$–$^3$ He atom diffraction,$^1$–$^3$ and theory.$^1$–$^3$ Despite
extensive studies of this system, there are many controversies regarding its structure.

Two competing structural models, the “standard model” and the “sulfur-pairing model”, have considerable support. In the standard model, alkanethiol molecules exhibit a hexagonal \((\sqrt{3} \times \sqrt{3})R30^\circ\) lattice. Alkanethiolates occupy three-fold hollow sites of the Au (111) surface with S-S spacings of 4.99 Å, and the molecular axes are tilted by 30°-35° with respect to the surface normal.\(^{13-23,30-35}\) The sulfur-pairing model involves a \(c(4 \times 2)\) superlattice of the hexagonal lattice, where alkanethiolates form sulfur head group dimers with S-S spacings of 2.2 Å.\(^{9-12,24-26}\) Furthermore, other structural models have been reported, including \(n \times \sqrt{3}\) unit cells \((8 \leq n \leq 10)\).\(^{36-39}\) There is even controversy among proponents of the sulfur pairing model, with some researchers suggesting top and hollow-bridge positions for the sulfurs, while others propose a hollow and hollow-bridge dimer.

In order to understand the structure fully one must include the effect of coverage, chain length, and temperature. However, because the differences between these structures center around the thiol head-group locations, theoretical investigation of the thiol-gold chemisorption bond is vital. Since interactions with the metal surface appear to dominate the molecular arrangement of SAM systems, the interaction of a methylthiolate \((\text{CH}_3\text{S})\) with the Au (111) surface presents a prototype system to study this entire class of systems.

Both LEED\(^2\) and ultrahigh-vacuum cryogenic STM\(^1\) studies show a \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern of \(\text{CH}_3\text{S}\) monolayers at room temperature, with head-groups at three-fold hollow sites, while at 110 K a disordered hexagonal \((3 \times 4)\) lattice has been reported.\(^4\) The S-S distances in the latter study (3.3 Å) are much longer than the 2.2 Å and much shorter than 4.99 Å from the sulfur-pairing and standard models. Two theoretical studies have concluded that the adsorption site for a single thiol molecule on the gold (111) surface is the hcp hollow site.\(^{30,31}\) These results also support the standard model. However, despite the overall agreement of the results, there are discrepancies regarding the S-Au distance and the tilt of the molecule in these two independent studies.

The main objective of our study is to identify the adsorption site for thiols on gold (111), and to explain the structural properties. We have performed first-principles calculations
based on density-functional theory (DFT) to study the adsorption of methylthiolate on the Au (111) surface. Our results show that a single CH$_3$S molecule adsorbed on the Au (111) surface chemisorbs on the fcc site. We also find that further increase of the hydrocarbon chain does not affect the adsorption site. All of the first-principles calculations have been performed with the plane-wave pseudopotential code “dacapo”.

In our DFT calculations, the wave functions are expanded in a plane-wave basis set, the electron-ion interactions are described by ultra-soft pseudopotentials (USPP), and the generalized gradient approximation (GGA) for the exchange-correlation functional has been used. The Kohn-Sham equations are solved self-consistently, using a Pulay density-mixing scheme to update the electronic density between iterations. The occupation numbers are updated using a recently developed technique based on minimization of the free-energy functional. A finite electronic temperature is used, in order to reduce the number of $k$-points needed, and all total energies are then extrapolated to zero electronic temperature. For the optimization of atomic structure, a damped molecular-dynamics (DMD) method has been used.

When using the slab geometry in the plane wave pseudopotential method, errors most often arise from the pseudopotential or from lack of convergence with respect to the number of $k$-points, the cutoff energy, and the system size. When generating pseudopotentials it is of great importance to preserve the eigenvalues for all relevant atomic configurations, not just in the reference configuration. However, in order to have correct lattice constants for metals it is also of importance to preserve the charge density in the tail region for all relevant atomic configurations. For H (1s$^1$), C (2s$^2$2p$^2$), S (3s$^2$3p$^3$3d$^{0.5}$), and Au (5d$^{9.5}$6s$^{1}$6p$^{0.5}$) the USPPs were generated using cutoff radii ($r_c$) of 0.60, 1.24, 1.45, and 2.00 bohr, respectively, and the maximum transferability errors were less than 2 mRy. All potentials are tested and compared to experiment and to all-electron calculation.

We find that although the 3$d$ orbitals of S are nearly unpopulated in simple molecules, such as S$_2$, the $d$ channel has great impact on the behavior of the pseudopotential. The 3$d$ orbitals give S enhanced polarizability and enable a great variety of bonding configurations.
through hybridization. A comparison between two USPPs for S with and without the $d$-projector (transferability errors less than 2 mRy in both potentials) show binding energies ($E_b$ of $S_2$) of 2.51 and 3.08 eV/atom (all-electron and experimental values are 2.49 eV/atom and 2.37 eV/atom), respectively.

In order to reduce calculation errors due to finite slab thickness, different slab geometries (3-8 layers thick) have been tested using different numbers of $k$-points and vacuum layers (see Fig. 1). A slab consisting of 6+7 Au+vacuum layers, a cutoff energy of 30 Ry, and a $4 \times 4 \times 1$ grid of special $k$-points is found to give converged results (convergence within a few meV). Table I shows the equilibrium parameters for the clean Au (111) surface and the free CH$_3$S and CH$_3$SH molecules compared to experiment and other calculations.

The first step toward a detailed understanding of the SAM structure is to investigate the adsorption site of the simplest C$_n$ (CH$_3$S) on the surface. Therefore, we calculated the total energy of a single CH$_3$S molecule in a ($2 \times 2$) surface unit cell, for a coverage of 0.25. As shown in Fig. 3a, the thiolate was moved from top to fcc, then over the bridge site to the hcp site using different molecular orientations. The supercell consisted of 6 Au(111) layers and 7 layers of vacuum. The three topmost Au layers and the molecule were optimized using the DMD method until the total force for the system was less than 0.01 eV/Å. Figure 4 shows calculated potential energy surfaces for two different molecular orientations along the diffusion path. The dashed curve is for the orientation used in Ref. 30 and the solid line is the minimum-energy path. Our results show that the staggered configuration is preferred over the configuration used in previous studies. The results of surface buckling and other optimization effects for the preferred orientation (solid line) are summarized in Table II and shown schematically in Fig. 3b.

The calculated chemisorption energy difference between fcc and hcp, $\Delta E_{\text{hcp-fcc}} = 0.10$ eV, shows that a single CH$_3$S molecule adsorbed on the gold surface prefers the fcc site over hcp. This is in contrast with results of Refs. 30 and 31, which are based on cluster calculations and classical MD. In the cluster calculations, only two gold layers were used. As a result, the surface energy is far from converged, and the effect of gold atoms in the third
layer is not included. As can be seen from Fig. 1, the gold (111) surface energy is converged only when six or more gold layers are used. Furthermore, the energy difference between having the molecule at the fcc or hcp sites, \( \Delta E_{\text{hcp-fcc}} \), increases from 0.04 to 0.10 eV as the slab thickness is increased from four to six gold layers. This indicates the importance of slab size and suggests that the use of a two-layer gold slab is insufficient for accurate results.

Regarding the effect of hydrocarbon chain length, we performed calculations using two and three carbons in the chain. The results show no changes in the preferred adsorption site (fcc), and \( \Delta E_{\text{hcp-fcc}} \) is 0.15 eV and 0.18 eV for two- and three-carbon thiols, respectively. These calculations indicate that the preference for fcc becomes stronger with increasing number of carbons in the chain.

The induced charge density (Fig. 4) shows an increase of charge between the Au and S atoms, when a thiol molecule is adsorbed on the fcc site. The metallic electrons (via Pauli repulsion) shift this region of enhancement, so that it is farther from the surface than expected.

In summary, we have presented state of the art DFT calculations of thiol molecules adsorbed on the Au (111) surface at low coverage. This study demonstrates that the fcc site is the preferred location for a single thiol, and the electronic changes which accompany chemisorption are elucidated. Furthermore, the importance of having a minimum of six gold layers in the model, and of including \( d \) orbitals in the sulfur pseudopotential were highlighted.

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TABLE I. Structural and energetic results for the clean gold (111) surface (slab consists of 6 Au and 7 vacuum layers) and the CH$_3$S and CH$_3$SH molecules. Comparison of calculated results for the interlayer relaxations $\Delta d_{12}$, $\Delta d_{23}$, and $\Delta d_{34}$ (1 = top layer) of the Au(111) surface. The presented distances are in Å, and the surface energy ($E_s$) is given in eV/Å$^2$.

|                  | $\Delta d_{12}$ (%) | $\Delta d_{23}$ (%) | $\Delta d_{34}$ (%) | $E_s$ |
|------------------|---------------------|---------------------|---------------------|-------|
| Clean Au (111) surface: |                     |                     |                     |       |
| This work        | 0.97                | -0.48               | 0.07                | 0.101 |
| Calc.            | -0.24               | 0.05                | 0.04                | 0.084 |
| Expt.            | 0.00                |                     |                     | 0.096 |
| Optimized parameters for CH$_3$S: |                     |                     |                     |       |
| r(CS)            | 1.789               | r(CH$_a$)           | r(CH$_b$)           | r(CH$_c$) |
| This work        |                     | 1.070               | 1.068               | 1.068  |
| Calc.            |                     | 1.799               | 1.095               | 1.091  |
| $\theta$(SCH$_a$) |                     | $\theta$(SCH$_b$)  | $\theta$(SCH$_c$)  | $\phi$(H$_a$SCH$_b$) |
| This work        | 109.8°              | 110.7°              | 110.7°              | 116.3° |
| Calc.            | 107.0°              | 111.6°              | 111.6°              | 118.0° |
| Optimized parameters for CH$_3$SH: |                     |                     |                     |       |
| r(CS)            | 1.827               | r(CH)               | r(SH$_d$)           | $\theta$(CSH$_d$) |
| This work        |                     | 1.08                | 1.36                | 97.2°  |
| Expt.            | 1.819               | 1.09                | 1.34                | 96.5°  |
TABLE II. Calculated parameters for CH$_3$S interaction with the Au (111) surface. The parameters $d_{C-S}$, $d_{S-Au}$, and $d_{x,y}$ are the distances between the C and S atoms, between the S and the center of mass (CM) of the topmost Au layer, and the interlayer separation between the CMs of two adjacent layers. $\delta_{xa}$, $\delta_{xb}$, and $\delta_{xc}$ give the surface buckling.

|                  | fcc   | hcp   | bri   | top   |
|------------------|-------|-------|-------|-------|
| $\Delta E_{chem}$ (eV) | 0.00  | 0.10  | 0.40  | 0.95  |
| $d_{S-Au}$ (Å)    | 1.788 | 1.831 | 1.990 | 2.493 |
| $d_{12}$ (Å)      | 2.399 | 2.398 | 2.430 | 2.410 |
| $d_{23}$ (Å)      | 2.386 | 2.382 | 2.398 | 2.379 |
| $d_{34}$ (Å)      | 2.393 | 2.389 | 2.401 | 2.398 |
| $\delta_{1a}$ (Å) | 0.001 | 0.005 | 0.008 | 0.015 |
| $\delta_{1b}$ (Å) | 0.004 | 0.006 | 0.007 | 0.011 |
| $\delta_{1c}$ (Å) | -0.003| -0.007| -0.008| -0.021|
| $\delta_{2a}$ (Å) | 0.000 | 0.000 | 0.004 | 0.010 |
| $\delta_{2b}$ (Å) | 0.002 | 0.002 | 0.005 | 0.009 |
| $\delta_{2c}$ (Å) | -0.003| -0.003| -0.004| -0.003|
| $r_{(CS)}$ (deg.) | 1.848 | 1.846 | 1.840 | 1.835 |
| $r_{(CH_a)}$ (deg.) | 1.105 | 1.105 | 1.106 | 1.106 |
| $r_{(CH_{b,c})}$ (deg.) | 1.104 | 1.104 | 1.105 | 1.106 |
| $\theta_{(SCH_a)}$ (deg.) | 108.6 | 108.7 | 108.9 | 109.1 |
| $\theta_{(SCH_{b,c})}$ (deg.) | 108.5 | 108.5 | 108.8 | 108.9 |
FIGURES

FIG. 1. The Au(111) surface energy in eV/Å² as a function of Au layers for different numbers of k-points and vacuum thickness. All calculations are performed using a 30 Ry cutoff energy.

FIG. 2. The adsorption energy for a CH₃S molecule on the Au(111) surface along the diffusion path shown in Figure 3. Small figures show top views for molecular orientation at each site. Solid and dashed lines represent energies for orientations shown below and above the curve, respectively.

FIG. 3. Schematic presentation of the interaction of CH₃S with the Au(111) surface. T, H, B, and F denote top, hcp, bridge, and fcc sites, respectively. dₓᵧ is the interlayer distances between layers x and y, where the top layer is denoted 1. δₓa and δₓb represent buckling for nearest and δₓc for the next-nearest neighbors of the S atom.

FIG. 4. Calculated induced and total charge density when the methylthiolate is adsorbed on the fcc site. 3-D isosurface (a) and a slice parallel to the surface between S and Au (c) of the induced charge density, and a slice of the total charge density (b) are presented.
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