Scanning Tunneling Microscopic Observation of Adatom-Mediated Motifs on Gold–Thiol Self-Assembled Monolayers at High Coverage

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Self-assembled monolayers (SAMs) formed by chemisorption of a branched-chain alkanethiol, 2-methyl-1-propanethiol, on Au(111) surfaces were studied by in situ scanning tunneling microscopy (STM) under electrochemical potential control and analyzed using extensive density functional theory (DFT) calculations. The SAM forms in the unusual (8 × √3)-4 superlattice, producing a very complex STM image. Seventy possible structures were considered for the SAM, with the calculated lowest-energy configuration in fact predicting the details of the unusual observed STM image. The most stable structure involves two R–S–Au–S–R adatom-mediated motifs per surface cell, with steric-induced variations in the adsorbate alignment inducing the observed STM image contrasts. Observed pits covering 5.6 ± 0.5% of the SAM surface are consistent with this structure. These results provide the missing link from the structural motifs observed on surfaces at low coverage and on gold nanoparticles to the observed spectroscopic properties of high-coverage SAMs formed by methanethiol. However, the significant role attributed to intermolecular steric packing effects suggests a lack of generality for the adatom-mediated motif at high coverage.

1. Introduction

Self-assembled monolayers (SAMs) have been of great interest both experimentally and theoretically as potential applications range from molecular devices to biorecognition to nanotechnology.1 Among all the SAMs studied, alkanethiol monolayers on Au(111) are the most comprehensively investigated due to their strong S–Au interaction and ease of production.2,3 Although numerous studies on thiol–gold SAMs have been performed, some fundamental details of electronic structures and formation processes remain to be clarified, such as the precise atomic-level details of structures adopted at the thiol–gold interface and the factors that control them, factors including both the headgroup interaction and the role of the aliphatic spacer.3

The sulfur–gold (S–Au) junctions that connect the substrate surface to the organic molecules are among the most important aspects of the SAM, with, e.g., the conductance of alkanethiol molecules sandwiched between two gold electrodes depending strongly on the structure.4 While thiol–gold SAMs are usually produced by exposing gold surfaces to alkanethiol or dialkanedisulfide solutions, many studies have demonstrated that the active adsorbates are in fact alkanethiyl radicals formed following loss of the thiol protons or cleavage of disulfide bonds.5–8 The purely physical interactions between alkanethiol molecules and the gold surface are too weak to form stable monolayers,9,10 while the gold surface possesses insufficient reducing power to drive thiol formation.11

Early insight into the nature of the interface between Au(111) and chemisorbed thiol monolayers came from theoretical studies of binding to regular bulk-like (111) surfaces; these suggest that sulfur atoms preferentially locate in the region between the classic fcc and bridge adsorption sites.5,9 However, preferential adsorption to irregular surfaces containing vacancies and/or adatoms has also been predicted.12–17 Much progress has been made experimentally in recent years concerning the structure of SAMs made from alkanethiols. Groundbreaking detailed structural studies on methanethiol SAMs using normal incidence X-ray standing wave (NIXSW) analysis by Roper et al., as well as the scanned-energy and scanned-angle S 2p photoelectron diffraction experiments by Kondoh et al., show that sulfur atoms occupy atop sites,18,19 but insufficient information was obtained to fully identify the interface structure. Some studies proposed that sulfur atoms may be associated with gold adatoms,12–14,20,21 and later this motif was observed in X-ray structures of gold nanoparticles.22 A recent scanning tunneling microscopy (STM) study on thiol–gold SAMs before and after reaction with atomic hydrogen by Kautz et al. also demonstrated that there is additional gold adatom for every two alkanethiol adsorbate molecules,23 consistent with the adatom-mediated model, and it has also been shown that these adatoms can be liberated to form islands.21 The success of these studies raises the possibility that the adatom-mediated motif is produced in general during SAM formation between gold and alkanethiols. A very similar adatom-mediated motif has been observed for SAMs formed from the bidentate ligand 1,10-phenanthroline,24 but small changes in conditions for these SAMs lead to monolayers above the regular flat surface, and the structure is strongly coverage dependent. Direct observation of the adatom-mediated motif within SAMs formed from thiols has been achieved only at low thiol coverage,13 leaving partially answered the important question of the nature of the interface on surfaces at high...
coverage and hence the interconnection between the low-
coverage, high-coverage, and nanoparticle-coverage scenarios.

The gross structural properties at high coverage of gold SAMs
formed using linear alkanethiols are well known, these forming in
the \((3 \times 2 \sqrt{3})\)-4 superlattice (also termed the \((c(4 \times 2)\)
superlattice). The \((3 \times 2 \sqrt{3})\)-4 superlattice means that there
are four adsorbates in each surface cell, with lattice lengths of
3 or \(2\sqrt{3}\) times to the shortest Au–Au distance in bulk,
respectively. Wang et al. proposed that the four adsorbate
molecules in this unit cell attach with two connected in an
adatom-mediated motif while two more attach directly to the
surface gold layer.\(^{16}\) Alternatively, Grönbeck et al. propose that
adatom-bound motifs alone can account for the structure,
possibly with or without local surface gold vacancies.\(^{17}\) Finally,
Cossaro et al. suggested that the structure of the \((c(4 \times 2)\)
superlattice is quite complex involving directly attached adsorb-
ate molecules, local vacancies, and one-dimensional adatom-
mediated \(-\text{(S–Au)}_n\)- zigzag chains.\(^{15}\) In principle, the observed
density of pits on the gold surface\(^1\) provides significant
information that could be used to assess these differing models,
but their concentration is difficult to quantify. Also, while
observed STM images do provide critical information, their
interpretation is not always unambiguous. Many specific ques-
tions thus remain unanswered, and new probes are required.

Progress has been made by considering the analogous
properties of branched-chain alkanethiol monolayers. Indeed,
recent scanning tunnelling microscopy (STM) study found that
a branched alkanethiol chemisorbate on the Au(111) surface
formed quite different structural patterns compared to those for
linear alkanethiols.\(^{25}\) In the report by Chi et al., the self-assembled
monolayer formed from 2-methyl-2-propanethiol is found to adopt the \((2\times7 \times \sqrt{7})\)R19.1 \(^2\) lattice, with two inequivalent radicals in a \((2\times7 \times \sqrt{7})\)R19.1 \(^2\) surface cell.\(^{11,25}\) This structure is strikingly different from the \((3 \times 2 \times 3\)\)-4 and similar
(e.g., \((\sqrt{3} \times \sqrt{3})\)R30\(^o\)) structures found for most SAMs
formed from straight-chain alkanethiols.\(^3\) In particular, there is
no surface pitting involved in the SAM formation, and DFT
calculations indicate that no adatom-mediated motifs are
involved in the binding at all, with the appearance of the unusual
double-occupied surface cell attributed to steric repulsions
between the aliphatic chains.\(^{11}\) Hence, small changes in the steric
interactions between adsorbate molecules can control SAM
structure.

In this work, we employ electrochemical STM technology
(in situ STM) and plane-wave-based density-functional theory
(DFT) to investigate the SAMs formed from a systematically
chosen molecule, 2-methyl-1-propanethiol, on Au(111). This
isomer of 2-methyl-2-propanethiol contains a longer chain
section and a secondary carbon rather than the fully branched
tertiary isomer studied previously and is intermediary with
respect to the well-studied straight-chain alkanethiols. This
modification illustrates the extent to which further interchain
steric interactions could modify the SAM structure.

2. Methods

2.1. Experimental Measurements. 2-Methyl-1-propanethiol
((CH\(_3\))\(_2\)CHCH\(_2\)SH, 98%) was obtained from Sigma. The NH\(_4\)Ac
buffer (5 mM, pH 4.6) was prepared from 5 M stock solution
(Fluka, ultrapure) and solution pH was adjusted by acetic acid
(Aldrich, 99.7%). NaOH (0.1 or 0.5 M) solutions were prepared from
30% stock solution (Merck, ultrapure) and used for voltammetric measurements of reductive desorption. Absolute
ethanol (ultrapure) was from Merck. Milli-Q purified water (18.2
MΩ cm) was used throughout. The Au(111) electrodes used in
both electrochemical and STM measurements were homemade
and pretreated before use as described.\(^{23}\)

The SAMs were prepared by soaking freshly quenched Au(111) electrodes in ethanol solution containing 2-methyl-1-
propanethiol (1–5 mM) overnight, followed by thorough rinsing
with pure ethanol and Milli-Q water before measurements. To
observe the dynamic processes of the SAM formation, 2-methyl-1-
propanethiol was directly added to the electrochemical STM
cell. The details were similar to that for 1-propanethiol.\(^{24}\)

Electrochemical measurements were performed using an Au-
tolab system (Eco Chemie, Netherlands), with a three-electrode
system containing a Pt counter electrode, a reversible hydrogen
electrode (RHE) as the reference electrode, and an Au(111)
working electrode. STM imaging was carried out in the
electrochemical in situ mode using a PicoSPM system (Molec-
ular Imaging Co.) equipped with a bipotentiostat for potential
control of both the substrate and tip. The STM tips were
prepared from Pt/Ir (80:20) wire by electrochemical etching and
covered with Apiezon wax to reduce or eliminate Faradaic
currents.

2.2. Computational Modeling. All the computations were
conducted using periodic density functional theory (DFT)
methods with the Vienna ab initio simulation package (VASP).\(^{26}\)
For the electron–electron exchange and correlation interactions,
the functional of Perdew and Wang (PW91),\(^{27}\) a form of the
general gradient approximation (GGA), was used throughout.
Electron–ion interactions were described using the optimized
relativistic Vanderbilt-type ultrasoft pseudopotentials.\(^{28,29}\) A
plane-wave basis set was employed to expand the smooth part
of the wave functions with a kinetic energy cutoff of 300 eV,
required to properly describe the carbon atoms. VASP utilized
an iterative scheme to solve self-consistently the Kohn–Sham
equations using residuum-minimization techniques. The geo-
metric structure was optimized with the conjugated-gradient
method. The broadening approach proposed by Methfessel and
Paxton with an electronic temperature of 0.2 eV was used for
the calculation of orbital occupancies.

The Au(111) surface was modeled by a supercell consisting of a four-layer slab separated by a vacuum region equivalent to
a six-layer thickness. When the geometry was optimized, the
top two atomic layers and the adsorbates were allowed to relax,
while the lower two layers were fixed at the ideal bulk-like
position (using the lattice constant \(a_0 = 4.18\) Å obtained at the
same level of theory).\(^{30}\) It has been demonstrated that the four-
layer slab is thick enough to obtain reliable results.\(^{11}\) The
methods proposed by Neugebauer and Makov et al. were used
to correct the error for the surface with a large dipole
moment,\(^{31,32}\) when the energy converges slowly with respect to the
\(z\) axis of the supercell. All the calculations of the alkanethiol/Au(111) systems were performed by ignoring spin polarization
as studies on similar systems indicate that the adsorbate–
substrate interaction is strong and the effects of spin polarization
are small. The Brillouin-zone integrations were performed using
Monkhorst–Pack grids of special points, with \((1 \times 6 \times 1)\) and
\((4 \times 4 \times 1)\) \(k\)-points meshes used for the \((8 \times \sqrt{3})\) and \((3 \times
2\sqrt{3})\) surface cells, respectively. These \(k\)-points meshes have
been demonstrated to be sufficient for our purposes.\(^{33}\) STM
images were simulated using the Tersoff–Hamann approxima-
tion\(^{34}\) with a bias voltage of 1.0 V.

While the clean Au(111) surface undergoes a \((22 \times \sqrt{3})\)
reconstruction,\(^{35,36}\) thiol chemisorption lifts the reconstruction,\(^{3,12}\)
and in these equilibrium studies binding only to the unrecon-
structured surface is considered. Even though experimental results
for this system have been obtained in aqueous solution, we
model only monolayers under vacuum conditions. Since the alkanethiol tail groups are hydrophobic, solvent interactions are most likely of only minor importance, in contrast to the SAMs containing ionic tail groups (such as cysteamine) in which solvation of the charged tail groups is critical. The thiol rather than thiolate nature of the headgroup means that the actual surface charge transfer is small, and so once again solvent effects are not of great significance.

3. Results and Discussion

3.1. Experimental Observations. In situ STM images observed over different scanned areas are shown in Figure 1. The surface unit cell is rectangular with dimensions of 23.3 Å × 4.8 Å (Figure 1c). Observation of the reconstruction lines of the bare single-crystal gold surface before addition of the adsorbate allows the absolute orientation of the surface-cell vectors to be determined, indicating that the SAM forms in the \((8 \times \sqrt{3})\) lattice and contains 16 gold atoms per regular surface layer in the unit cell. 

Electrochemical measurements of the surface coverage using reductive desorption (Supporting Information) give a density of \(5.9 \pm 0.4 \times 10^{-10} \text{ mol cm}^{-2}\), indicating a surface coverage (denoted in the number of adsorbate molecules per Au(111) regular-surface gold atom) of \(\Theta = 0.26 \pm 0.02 \sim 1/4\). As expected, this coverage is intermediate between those found for the 2-methyl-2-propanethiol and 1-propanethiol SAMs of 0.14 and 0.33, respectively. Four adsorbate molecules thus occupy each surface unit cell, possibly with four different internal structures. Indeed, four regions in each unit cell are observed in the in situ STM image (Figure 1c) with strongly varying contrast. Some of these features are widely spaced while others are spaced less than the minimum-possible \(S-S\) intra-adsorbate distance, suggesting that each adsorbate can produce more than one STM feature. Hence, very many adsorbate configurations could, in principle, generate this image. The most striking features of the image are two bright spots very close to each other and two dimer spots separated by a large dark region; also, the spots are not collinear.

3.2. Computational Modeling of the Monolayer Structures. Full details of all 70 computed structures for Au(111) SAMs made from 2-methyl-1-propanethiol are provided in the Supporting Information, including calculated STM images for 11 structures. Owing to the multitude of possible structures, we perform systematic investigations, starting with the nature of adsorption of noninteracting or partially interacting molecules on the flat surface (i.e., low to medium coverage). Then we increase the coverage and investigate SAM formation on the regular flat surface Au(111). Structures are then considered in which the gold atoms can rearrange within the unit cell, forming adatoms and vacancies, but transport of gold atoms to or from the unit cell is not allowed. Finally, the number of gold atoms in each surface unit cell is varied, allowing for gold adatoms above regular surfaces and possible associated pit formation. In this way, a range of low-energy structures can be identified and their suitability is further characterized in terms of their relative energy and ensuing STM images.

3.2.1. General Features of Chemisorptions on a Flat Au(111) Surface with Low to Medium Coverage. On a regular Au(111) surface, there are four kinds of high-symmetry adsorption sites: atop, bridge, fcc, and hcp sites. Previous computational studies have demonstrated that sulfur atoms of chemisorbed alkanethiols prefer low-symmetry locations either between the bridge and fcc sites, termed FB, or between the bridge and hcp sites, termed HB. Hence, we calculate the adsorption energy at atop, HB, and FB sites only. Initially we consider adsorbates with similar alkane-chain conformations at sufficiently low coverage, \(\Theta = 1/12 = 0.083\), to avoid intermolecular steric interactions on the \((3 \times 2\sqrt{3})\) supersurface lattice. For comparison we also consider an alternate lattice, \((8 \times \sqrt{3})\), that gives a slightly lower coverage of \(\Theta = 1/16\) but, because of its short unit-cell length in the [112] direction, does actually display significant intermolecular steric interactions.

The energy of adsorption (\(\Delta E\)) is determined from

\[
\Delta E = E_{\text{tot}} - E_{\text{surf}} - E_{\text{ad}}
\]

where \(E_{\text{tot}}\) and \(E_{\text{surf}}\) are the optimized total energies of the systems with and without adsorbate, respectively, and \(E_{\text{ad}}\) represents the energy of the optimized isolated 2-methyl-1-propanethiyl radical calculated allowing for spin polarization.
confirm this analysis, with configurations C and D showing enhanced binding (\(\Delta E = -1.78\) eV per adsorbate molecule for C and \(-1.72\) eV for D) owing to improved substrate relaxation. Configurations A and B are destabilized by steric interactions in the short [112] direction (\(\Delta E = -1.62\) eV per adsorbate molecule for A and \(-1.58\) eV for B). For 2-methyl-1-propanethiol chemisorbates, steric interactions also destabilize the (3 \(\times\) 2\(\sqrt{3}\))-4 and similar lattices in which the SAMs of most straight-chain alkanethiols form, with the calculated energy of adsorption on e.g. the (\(\sqrt{3} \times \sqrt{3}\))R30° lattice being calculated to be just \(-1.32\) eV. These results show the importance of substrate and steric interactions at low to medium coverage, effects that are expected to become more significant when four adsorbate molecules are crammed into the (8 \(\times\) \(\sqrt{3}\)) surface cell at the high coverage (\(\Theta = 0.25\)) actually observed for stable SAMs.

Considering the calculated structural properties in detail (Table 1), we see that those for 2-methyl-1-propanethiol chemisorbed monolayers directly parallel those for related molecules such as methanethiol and 2-methyl-2-propanethiol.\(^{11}\) After adsorption, the Au–Au bond lengths at the adsorption site increase from their optimized bulk value of 2.96 Å to over 3.50 Å while the calculated S–Au bond length of 2.47 Å also indicate a strong metal–molecule interaction. Applying the Bader method which decomposes the space charge density into atomic contributions to our system,\(^{30, 40}\) it is found that only 0.07\(e\) is transferred from the substrate to the adsorbate when 2-methyl-1-propanethiol chemisorbs at the FB site, where \(e\) is the magnitude of the charge on the electron. Changes of ca. 0.2\(e\) have been found in experimental studies\(^{41-43}\) of thiol chemisorption. While in general the significant band lineup error that occurs in DFT for molecular adsorbates on metal surfaces results in an underestimation of calculated charge flows,\(^{23}\) the results again clearly indicate that ionic thiolate states are not involved in the chemisorption. Thus, the adsorbate forms as a thyl species identified as the 2-methyl-1-propanethiyl radical.

### 3.2.2. High-Coverage Adsorption on the Flat Au(111) Surface

Here we consider the possibility that dense SAMs made from 2-methyl-1-propanethiol form on the flat Au(111) surface, as has been observed by STM for related SAMs.\(^{7}\) The most significant aspect of the observed STM images of 2-methyl-1-propanethiol SAMs (Figure 1) is the starkly different separations and contrasts of the features. A similar scenario was also found for chemisorbed monolayers of 2-methyl-2-propanethiol on Au(111), a SAM for which more than one molecule per surface cell was observed to form on the flat Au(111) surface.\(^{25}\) For that molecule, variations in the tilt angles of S–C bonds on the surface were found to account for the STM-image topology,\(^{11}\) our initial computational studies of the high-coverage monolayer test the hypothesis that similar variations also account for the observed STM images for 2-methyl-1-propanethiol SAMs. A wide variety of DFT geometry optimizations were performed starting with conformations similar to C or D from Figure 2, the only conformations shown feasible in the low-density studies on the observed (8 \(\times\) \(\sqrt{3}\)) lattice; full details of the results are provided in the Supporting Information. All of the stable structures found are of similar energy, with \(\Delta E\) varying by less than 0.05 eV. However, the energy of adsorption per radical is \(-1.46\) eV for the most stable case, this being 0.32 eV less stable than that at the lower coverage reported in Table 1. The repulsion between the adsorbates at high coverage is therefore rather strong and could be manifest through either direct steric interactions or significant distortions induced in the substrate lattice.
The simulated STM image of the most stable configuration found is shown in Figure 3; of its four adsorbate molecules, one adopts configuration C while the others adopt configuration D. All the bright spots in the calculated STM image originate from the vertically aligned terminal methyl groups; thermally induced changes in the conformational angles will induce some variation in the calculated image, but the main features are expected to be preserved. Since the tilt angles of the S–C bond are different, the heights of the terminal methyl groups vary (see Figure 3), and therefore, the STM image contrast is modulated. However, the simulated STM image is significantly different from the observed in situ image shown in Figure 1c, with just three resolved features per cell and no large intense closely spaced image pair. Furthermore, owing to the steric interactions associated with the dimensions of the branched chain, no alternate configuration can be envisaged in which vertically aligned chains from two molecules are separated by the observed short distance between the spots of the bright pair. Thus, the hypothesis that four adsorbate molecules assemble on a regular Au(111) surface, akin to the binding observed following chemisorptions of the isomer 2-methyl-2-propanethiol, cannot be supported.

3.2.3. High-Coverage Adsorption with Adatom-Mediated-Bonding Motifs above the Au(111) Surface. Recently, several groups have found, both experimentally and theoretically, that the chemisorption of linear alkanethiols occurs at supersurface gold adatoms\textsuperscript{12–17} that may or may not be associated with surface-layer vacancies; in this binding motif, two adsorbate molecules are always attached to one gold adatom. As four adsorbate chains occupy the unit cell for 2-methyl-1-propanethiol SAMs, either zero, one, or two of these motifs may be formed, and as there exists many sites for each adatom and possible vacancy, a large number of configurations are possible. As a starting point we consider only the structures in which the number of adatoms equals the number of vacancies; for these structures, the number of gold atoms per simulation cell is the same as that for adsorption on the flat Au(111) surface considered previously and so the results may be directly compared. We have examined 18 possible new configurations, optimizing the energy of each structure using DFT; the results for 10 illustrative examples, named configurations a–j, are sketched in Figure 4, while all results are reported in the Supporting Information. Configuration a is the lowest-energy structure found, and the energies for the remaining (8 × $\sqrt{3}$)-4 lattices are expressed relative to its energy. This configuration has two adatom motifs and therefore two vacancies that are found to be located nearly underneath the adatoms. Some variants of this structure are shown in configurations d–i containing different locations for the adatom sites and different arrangements of the vacancies. As some of these configurations are less than 0.3 eV higher in energy than configuration a, the adsorbed molecules and the vacancies may be quite mobile on the surface.

The lowest energy configuration involving no adatoms or vacancies (previously detailed in Figure 3) is also sketched in Figure 4 for comparison with configuration b. Its average energy of adsorption per adsorbed molecule is $-1.46$ eV, much less than the single configuration energies reported in Table 1, owing to the significant steric interactions between the four adsorbate molecules. This unit-cell configuration is $1.33$ eV per cell less stable than configuration a, indicating that adsorption on a flat Au(111) surface will spontaneously induce rearrangement of the surface gold atoms. Much of the strain energy apparent in b is relieved through the formation of just a single adatom-vacancy pair in the surface cell, with configuration c being only 0.24 eV per cell less stable than the double adatom-vacancy structure, configuration a. The possibility that mixed configurations of this type are also important for linear alkanethiol SAMs has been raised by Wang et al.\textsuperscript{16}

Recently, Cossaro et al. proposed that one-dimensional $-S-Au-S-Au-S-$ chains form the SAMs of long-chain linear alkanethiol SAMS on gold with the $(3 \times 2\sqrt{3})$ surface cell.\textsuperscript{15} This precise structure is not feasible on the $(8 \times \sqrt{3})$ surface cell owing to the considerably different unit-cell dimensions of the branched alkanethiol molecules.
motifs in a trans configuration was also observed in the adatom-mediated adsorbate. This configuration involves three adatom/vacancy pairs per unit cell but is 1.44 eV per cell less stable than configuration a and hence should not be favored within 2-methyl-1-propanethiol SAMs.

In general, an important feature of the adatom-bound adsorbate structure is whether the S-C bonds are located cis or trans with respect to each other. In a previous study of this adatom motif within methanethiol SAMs, the cis structure has been found to have the lowest energy. However, in the present case all structures reported in Figure 4 have lower-energy trans configurations; Figure 5 compares the atomic positions and relative energies for the cis and trans variants of configuration a. The alternative result for 2-methyl-1-propanethiol adsorbate could arise from the different interaduct steric interactions; the trans configuration was also observed in the adatom-mediated motifs in a p-mercaptobenzoic acid (p-MBA)-protected gold nanoparticle and hence may in general be preferred for bulkier adsorbate molecules.

The adatom-mediated structures have their Au-S bonds orientated nearly parallel to the surface, with the S-adatom-S angle being 173° for the lowest-energy structure, configuration a. However, the C-S-Au angles show significant variations between 109° and 116° for configuration a. Hence the C-S vectors rise at 52°-62° to the surface normal, quite different to the nearly parallel and nearly vertical orientations apparent in Figure 2 for molecules bound directly to Au(111). The variation in the angles is caused by the steric interactions which force the two adatom-mediated motifs to adopt slightly different structures, giving rise to a variation in height of terminal carbon atoms of 0.25 Å. Figure 6 shows a simulated STM image for this structure where it is compared to an extract of the observed in situ STM image from Figure 1c: all major qualitative features of the experimental image are reproduced. Also shown in Figure 6 are side and top views of configuration a, with the adsorbate chains numbered i–iv. This reveals that all of the bright spots originate from the terminal methyl groups, with the major factor controlling their relative brightness being the height of the carbon atoms above the surface. As each adsorbed molecule orients with two methyl groups upward, a total of eight spots of this type could in principle be found in the simulated STM images. The large central bright region of the computed STM image is assigned to the two methyl groups from molecule (ii), with the close proximity of the two groups emphasizing their significance. Two nearby resolved features arise from methyl groups of molecules (iii) and (i), while a further weak feature arises from molecule (iv). Together, these results account for all of the features in the observed in situ STM image.

In addition, STM images for five alternative configurations have been simulated. Of these only the image for configuration c is in realistic agreement with the observed STM image (see the Supporting Information). Further, as the relative energy of this structure is only 0.24 eV more than that for configuration a, it warrants further consideration. The lowest-energy alternative configuration, configuration f generates a much poorer STM image but is also retained at this stage as a possible option. All the structures considered so far contain the same number of gold atoms in each unit cell as does a flat Au(111) surface. However, Figure 4 indicates that the gold atoms may be quite mobile, requiring further refinements to be made to the optimized structures.

Indeed, the clean gold surface to which the adsorbate molecules initially bind is not flat Au(111) but instead is a reconstructed surface in which 46 surface gold atoms (in two

Figure 5. Atomic structures for two adatom-mediated-bonding motifs adsorbed on flat Au(111) in the configuration a from Figure 4: all-trans isomer; right, all-cis isomer.

Figure 6. DFT-optimized structures (top panels, configuration a plan and elevation) and STM images (lower panels, configurations a, a′, and a′′ and experiment extracted from Figure 1c) for the SAM of 2-methyl-1-propanethiol chemisorbed to the regular and irregular Au(111) surfaces at the observed coverage of Θ = 0.25 in the (8 × √3)-4 substrate lattice. The lines on the plan view indicate interatomic vectors on the clean (111) surface while white circles indicate surface vacancies, gold indicate supersurface gold adatoms, and green indicates the S atoms of the adsorbate molecules. Configurations a′ and a′′ differ from a only in that either one (a′) or two (a″) of the surface gold vacancies are filled from an external atom source.
rows of 23 atoms along the [110] direction) occupy only 44 (rather than 46) bulk-like positions.\textsuperscript{30,44} After formation of the SAM, this reconstruction is lifted, releasing 4.5% of the atoms in a gold layer. These excess gold atoms must either be consumed as adatoms or else merge generating new surface terraces. While terrace growth is difficult to positively identify, the opposing process of pit formation is often observed as a common feature in many thiol–gold SAMs including the present case.\textsuperscript{3} Specifically, the coverage of pits on the surface for the common feature in many thiol–gold STM image.\textsuperscript{37,45} adsorbate coverage measured by electrochemical reductive information offered jointly by in situ STM and electrochemistry. This complementary approach resembles the complementary addition to providing visualization of the SAM at the single-molecule level. 2-methyl-1-propanethiol on the Au(111) surface has been investigated comprehensively both by electrochemical in situ STM and DFT/electrochemical approach used in our previous studies,\textsuperscript{25,35,37,43–47} a highly diverse pattern in both Au–S binding modes and surface packing of short linear and branched similar-size alkanethiols actually emerges. The straight-chain alkanethiol, 1-propanethiol, was shown to bind on a flat Au(111)-electrode surface and pack into a \((\sqrt{3} \times \sqrt{3})R30^\circ\) surface lattice. Extensive Au-atom surface dynamics and pitting accompanies this surface adlayer formation.\textsuperscript{35} The fully branched 2-methyl-2-propanethiol (tert-butanol) instead adopt a strikingly different \((2\sqrt{7} \times \sqrt{7})R19.1^\circ\) surface cell with no surface pitting. Finally, 2-methyl-1-propanethiol (secondary butanethiol) addressed here adopts a third thiol binding and packing mode at high coverage, i.e., a \((8 \times \sqrt{3})\)-4 surface lattice with two gold-atom-mediated surface entities per unit cell as a dominating binding motif. Chemically very similar adsorbates can thus produce strikingly different SAMs.

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Supporting Information Available: Optimized coordinates for 70 SAMs, 4 substrate lattices, the adsorbate radical along with 11 simulated STM images of SMAs, and a linear voltammogram to show reductive desorption of 2-methyl-1-propanethiol. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


