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STM OBSERVATION OF SULFUR DIMERIZATION IN ALKANETHIOL MONOLAYERS SELF-ASSEMBLED ON Au{111}

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ABSTRACT

We present for the first time, direct microscopical observation by STM of sulfur dimer formation on alkanethiol self-assembled monolayers (SAM) on sputtered Au substrates. The sulfur dimers are observed when imaging at a bias where the tip-molecule interaction occurs, and are formed by displacement of sulfur atoms from their normal three-fold hollow site residence of the (4 × 2) superlattice to nearest-neighbor bridge-site residence between two Au atoms. The displacement is believed to occur due to defects induced in the alkyl chain of the monolayer due to the proximity of the STM tip. Only one of the sulfur atoms forming the dimer is bound to the surface and they are commensurate with the Au{111} adlattice along its [112] directions.

INTRODUCTION

Self-assembled monolayers (SAMs) of thiol-functionalized molecules on single-crystal Au surfaces have been studied by numerous groups since their discovery. [1,2] Such monolayers self-assemble spontaneously on solid surfaces by cleavage of the S-H bond and subsequent chemisorption to the surface through a covalent Au-S bond. A key issue in the assembly and structure of alkanethiols on Au concerns the formation of disulfide bonds. We have recently verified with atomic-resolution non-contact AFM, [3] that Alkanethiol molecules reside in the three-fold hollow sites of the Au{111} surface with a (3 × 2√3) packing arrangement. Imaging with STM however, shows a slight distortion of this regular hexagonal lattice by rotation of the hydrocarbon chain around its main axis to form a (4 × 2) superlattice. [3] A schematic illustration of the these two packing arrangements commensurate with the Au surface is shown in Fig. 1.

Disulfide bonds are, however, incompatible with the all-three-fold hollow site residence configuration. Grazing incidence X-ray studies [4] suggest that alkanethiol molecules can reside in two distinct sites, but no microscopic evidence for there existence has been reported. Since the measured distance between two successive (nearest-neighbor) different sites on the Au{111} is 2.2 Å, the existence of a S-S bond has been proposed. Adding to the debate are recent reports that SAMs are damaged by exposure to X-rays [5] including changes in sulfur head group bonding that result in the formation of disulfides [6]. The disulfide bond, however, has never been observed on the surface

directly. Indirect observation of S-S dimers in alkanethiol monolayers was presented by Kluth *et al.* [7] using high resolution electron energy loss spectroscopy. They observed the presence of dimers through the S-S stretch vibration in the spectrum of the monolayer, but observed only after annealing to 375 K.

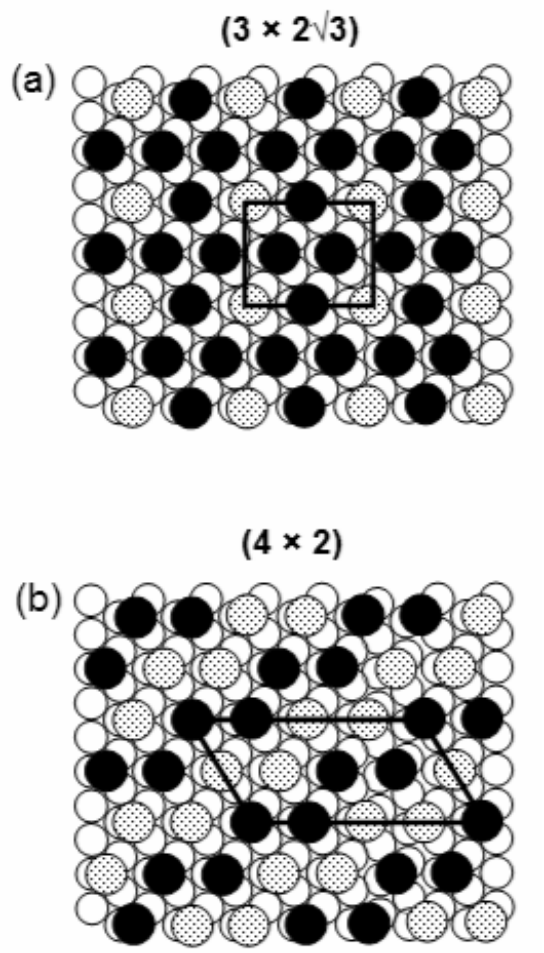


Fig. 1 Schematic representation of the alkanethiol assembly on Au{111}. (a) Schematic illustration of alkanethiol molecules (black circles) on Au{111} (white circles) in a (3 × 2√3) lattice (b) Schematic illustration of alkanethiol molecules in a (4 × 2) superlattice. The dotted circles represent the methyl head rotated ±50° about its main axis.

EXPERIMENTAL

Samples were prepared on annealed sputtered Au films which contained predominantly {111} oriented Au grains and very low *rms* roughness. Details of the Au substrates can be found in Ref. 9. The Au surfaces were then cleaned in ethanol and immersed in a 3:1 mixture of H_2SO_4:H_2O_2 at 398 K for 5 minutes to remove any organic contaminants. After rinsing with deionized water, the Au samples were immediately placed in a 10^{-3} mol dm^{-3} solution of 1-nonanethiol $CH_3(CH_3)_8SH$ (95%, Aldrich) in reagent grade ethanol and then incubated at room temperature for over 24 h. In the 24 h period, a self-assembled monolayer of thickness ~1 nm is formed. Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) characterization was performed with a PicoSPM (Molecular Imaging, Inc.). The STM images were acquired at bias voltages in the range 0 V to +1.50 V in constant height mode. Images were acquired with high gap

impedances to maximize the contribution from the alkanethiol monolayer, [8,9] and in particular, gap impedances of ~7-10 GΩ [10] were required to resolve individual atoms.

RESULTS AND DISCUSSION

1. The Role of Alkyl Chain Defects in Dimer Formation

An observation of the S-S dimer within the monolayer would have significant implications for the formation mechanism of alkanethiol SAMs. In the proposed model for sulfur dimers, a gauche defect exists at the S-C bond. [4] These defects allow for lateral movement of the sulfur head group. For densely packed films, however, a large energy barrier to head-group movement exists because neighboring chains must also be displaced. This barrier was estimated by recent molecular dynamics simulations to be ~11 kcal mol^{-1} in a densely packed hydrocarbon film. [11] Especially relevant to the interpretation of the present experiments is the molecular dynamics work of Mar and Klein. [12] They simulated a system of pentadecanethiol chains, while constraining the sulfur atoms to sit on the threefold hollow sites of the Au{111} surface, and consequently, disulfide bonds were not allowed to form. These authors estimated the density of gauche defects at room temperature to be about 4%; furthermore, these defects are concentrated at the vacuum-monolayer interface. At room temperature there are no defects at the first C-C bond (the one closest to the Au interface), and at 370 K the density of defects at those bonds is still less than 3%. Their density reaches almost 9% at 391 K, signaling that these defects can penetrate into the film with ease at this temperature. [12] Relieving constraints on the position and movement of the sulfur atoms could arguably result in a much larger concentration of defects at the S-C bond.

An STM image of the (4 × 2) superlattice of the SAM at full coverage on Au{111} is shown in Fig. 2(a). The self-assembly process is observed to be kinetically limited, such that immediately following self-assembled monolayer formation, a nonequilibrium structure exists containing many domain boundaries and nonuniformities. Monatomic depressions of the Au lattice, pin-holes in the alkanethiol monolayer, Au{111} monatomic steps and SAM domains and their boundaries are observed. The monolayer is relatively well packed under such conditions and characterized by small (5-25 nm) domains. Typical SAM domain formations are shown in Fig. 2(b). We have observed that such domains can even form on a single crystal surface if nucleation of SAM binding events on a single Au grain is smaller than the terrace size. This nucleation mechanism allows for sulfur binding events to occur independently, resulting in separate domain formation within the SAM.

The formation of gauche defects at the S-C bond in this case is believed to be unfavorable. Annealing to relatively low temperatures (375 K) results in an increase in the domain size as the disorder from the self-assembly process is reduced, coupled with the partial desorption of some of the more weakly bound chains. The only other observations that proposed the existence of sulfur dimers in alkanethiol monolayers suggested that annealing is necessary to remove the disorder in the room-temperature formed monolayer. [7] These changes have effectively reduce steric restraints to gauche defect formation. By using STM tip-sample distances such that the tip scans within the monolayer, rotation of the molecules around their principal axis occurs, effectively simulating the effects induced by a higher density of S-C gauche defects in annealed monolayers. Thus, steric restraints are reduced considerably, releasing the confines on the positions of the sulfur head groups to just one site.

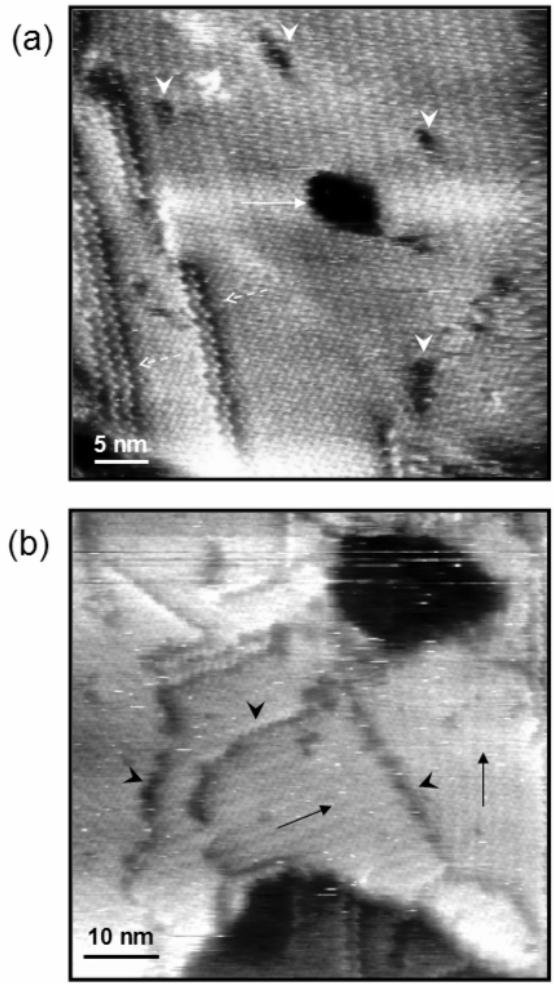


Fig. 2 (a) 35 nm × 35 nm STM image of 1-nonanethiol on Au{111}. The dark spot indicated by an arrow is a single-atom-deep depression in the Au surface. The arrowheads indicate pinholes in the alkanethiol monolayer and the dashed arrows indicate the presence of step edges in the Au{111} lattice. (b) 60 nm × 60 nm molecular resolution STM image of the 1-nonanethiol SAM on the sputtered Au{111} surface showing the mosaic-like domain network. The dark fissures (indicated by arrowheads) are examples of alkanethiol domain walls. Domains of two symmetry-equivalent orientations are indicated by full arrows aligned with the unit cell short-axis.

2. Dimer Formation by Aided Molecular Displacement

One must consider the possibility that the displaced sulfur head group, which dimerizes with an adjacent head group, actually bonds with the Au substrate in a new lattice position. Furthermore, although AFM shows that the three-fold hollow site is the only sulfur residence on the Au{111} lattice at room temperature, it has been unclear until now whether or not two different adsorption sites are possible during self-assembly and whether or not this could be observed microscopically without tip-surface interaction. A difficulty arises in attempting to understand the electronic properties of the insulating alkanethiol monolayer on the Au{111} surface, and in interpreting the patterns in STM images due to the long insulating alkyl chain and near-vertical molecular configuration.

We performed STM imaging of the surface under a range of tip bias (corresponding to tip-surface proximity variation under constant height conditions) to determine, first of all, whether this inequivalence of the sulfur head groups of these two molecules should be described as a perturbation about a single well-defined site leading to the dimer formation, or as two distinct binding sites. Secondly, if so, STM imaging can be used to determine these adsorption sites. A noncontact AFM image of the monolayer is shown in Fig. 3(a) and shows the (3 × 2√3) lattice arrangement of the alkanethiol molecules on the Au{111} surface.

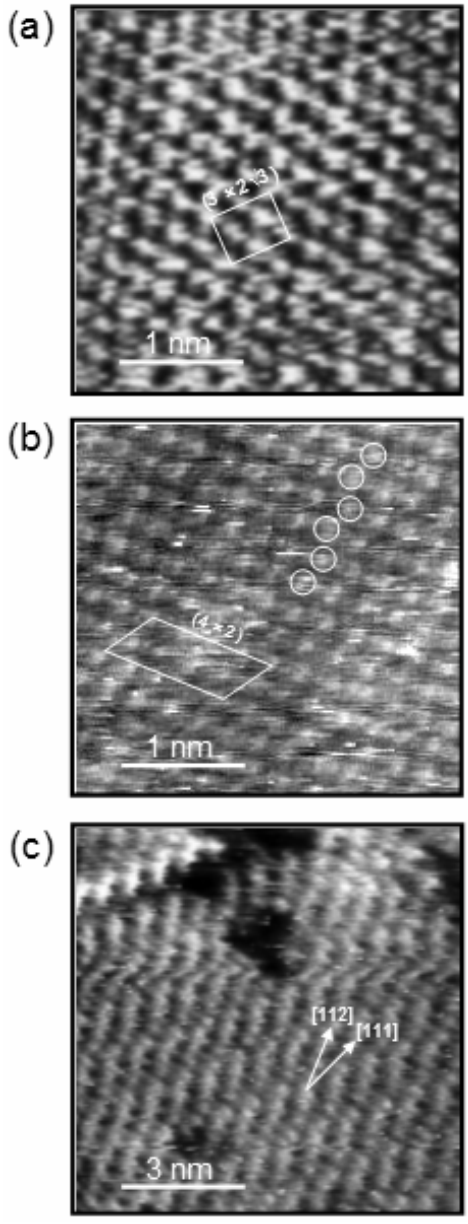


Fig. 3 (a) Non-contact AFM image with molecular resolution of the Au{111} surface, showing the (3 × 2√3) hexagonal lattice of the nonanethiol on the Au. The nearest-neighbor molecules are commensurate with the Au{111} lattice along the [112] directions. (b) STM image of the molecular overlayer in constant height mode with a sample bias of +0.4 V. The characteristic zig-zag pattern of the (4 × 2) superlattice is highlighted by open circles. (c) 9 nm × 9 nm STM image of the same surface as in (a) and (b), but at a potential bias of +1.5 V.

However, STM imaging at a bias potential of +0.4 V results in the observation of the (4 × 2) superlattice of the ($\sqrt{3} \times \sqrt{3}$)R30^o packing arrangement. Figure 3(b) shows this (4 × 2) superlattice, characterized by the zig-zag arrangement of alkanethiol molecules (cf. Fig. 1(b)). We have reported previously that the most likely position for the sulfur atoms is in the three-fold hollow sites of the Au adlattice to which the monolayer is adsorbed, according to the molecular resolution AFM images. In other words, the separation between 1-nonanethiol molecules is similar to the distance between second-neighboring [110] Au rows. However, this can also imply that the molecules are bound either in equivalent three-fold hollow sites on the Au{111} surface or directly on top sites of Au{111} for which the same lattice vectors are expected.

The variation from (3 × 2$\sqrt{3}$) to (4 × 2) arises from twisting of the molecule around its axis of ±50^o and precession around its adsorption site of ±12^o. [3,10] Under such conditions, no S-S bond lengths approaching 2.2 Å, are measured; the nearest neighbor distance being ~3.7 Å. Imaging at +1.5 V, however, shows the presence of sulfur atoms 2.3 Å apart, which is almost equal to the distance between the three-fold Au-hollow site and its nearest Au-bridge site. At this potential, the tip is essentially scanning within the monolayer and detecting the electronic wave function localized at the Au-S bond. However, it is unclear whether the sulfur atoms were adsorbed to two different Au adlattice sites prior to observation or whether the proximity of the tip allowed for sulfur atom movement limited to Au-hollow → Au-bridge sites due to the distance between the two sites being essentially equal to the known S-S bond length. Quantifying the movement induced by the closer proximity STM tip at higher bias is difficult, but the observations are easier explained if one considers that at lower bias, the tip scans above the monolayer and at higher bias, scans in the monolayer.

For imaging where the tip is nearer the vacuum-monolayer interface, the high tunneling gap impedance suggests that the patterns in the STM images reflect the information of the terminal alkyl group. In fact this must be so when topographical effects are taken into account. As previously mentioned, the Au-S bond dominates the density of states detected by the STM tip. However, this density of states decreases markedly with increasing distance from the surface. Therefore, when both the electronic effect (density of states population) and the topographic effect (height above the Au surface) are combined, the dominance of the Au-bound sulfur orbitals in the density of states is reversed, and in the region probed by the tip, the electronic wave function is localized near the terminal part of the hydrocarbon chain. Thus the STM image in Fig. 3(b) shows the (4 × 2) unit mesh where no evidence of S-S dimers is observed. At even higher potential bias, the tip is scanning deep within the monolayer, and only the Au bound sulfur atom is detected, resulting in the image shown in Fig. 3(c). In this case it is observed that the monolayer is still commensurate with the Au{111} lattice as expected, but along its [112] directions. The principal difference between the tip-induced dimerized surface and the (4 × 2) superlattice is that every second sulfur atom along the [112] direction is displaced to the nearest-neighbor Au-bridge site.

Examination of this difference was performed by analysis of the tunneling current. Figure 4(a), shows that in this case the vertical distance between the sulfur atom and the Au-hollow site is greater than that of the sulfur atom bound to the Au-top site. The tunneling current was measured from images such as those in Fig. 3(b) by recording the variation in intensity (and thus distance from the tip) along the [112] direction of the Au lattice, cutting through two successive dimers. Thus, the proximity of the tip causing the change in position of half of the sulfur atoms within the (4 × 2) unit mesh from the Au-hollow site to the Au-top site. This sulfur positioning is illustrated schematically in Fig.

4(b). Furthermore, the dimer is bound to the gold, then, by only one of the sulfur atoms forming the dimer.

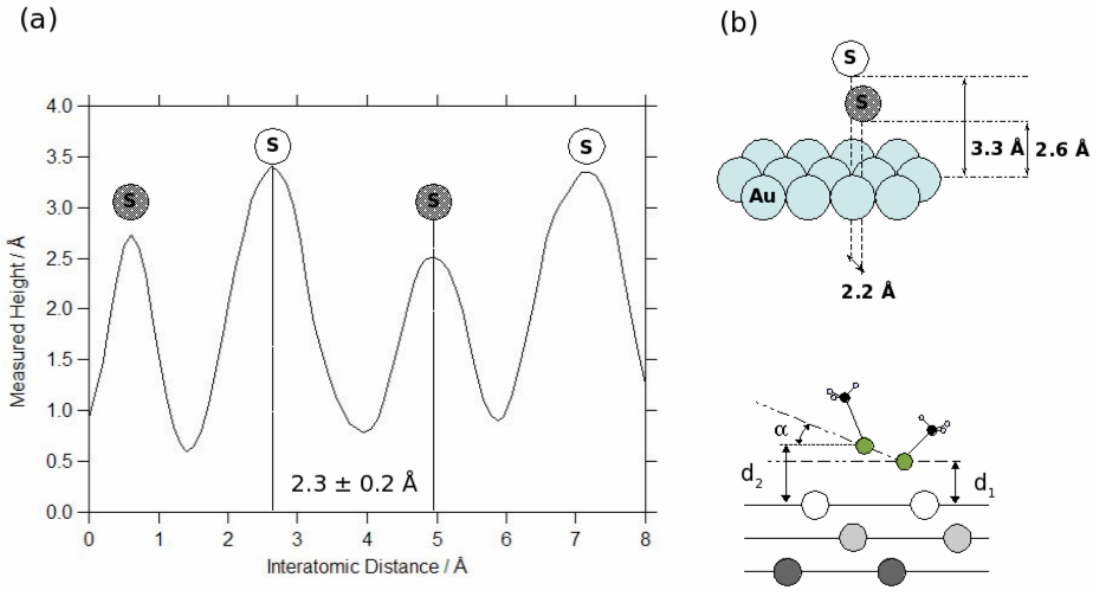


Fig. 4 (a) STM acquired height variation of two sulfur atoms forming a dimer. The data was acquired from the images such as those in Fig. 3(b). (b) Schematic representation of the S-S dimer on the Au{111} surface. The distances shown are measured from the surface plane and only one sulfur atom (Au-bridge site) is bound to the Au lattice. (c) Side-view of (b) showing S-S dimer position on Au{111}. $(d_2 - d_1)$ represents the height displacement of the dimerizing S atom.

These observations show that the measured S-S dimer spacing is ~2.3 Å, and taking into account the positional difference between the Au-hollow site and the Au-top site, a S-S bond angle of $\alpha \sim 20^{o}$ (Fig. 4(b)) is measured with respect to the Au{111} nearest neighbor direction. This measurement corresponds to an angle of ~110^{o} with respect to the Au-S bond (if the sulfur head group is adsorbed on the Au-top site) that is consistent with the tetrahedral bond angle (109.4^{o}). This information suggests that a lone-pair interaction between the two sulfur head groups is a possible explanation for the observed sulfur dimer structure.

3. Molecular Ordering of Dimers on Au{111}

Figure 5 reflects the various possible position of the sulfur atoms on the Au{111} surface in dimerized form. It is possible, theoretically, that independent of the starting adsorption site, the thiol molecules relax to one stable structural ordering, where the molecules form one of two dimers distinguished from one another by the adsorption site and twisting and rotation of the molecular chain. The theoretical adsorption sites for two kinds of sulfur dimers are illustrated in Fig. 5(a) and 5(b).

Figure 5(a) shows the sulfur atoms positioned on both Au-bridge sites. Figure 5(b) depicts a variation where the atoms are positioned at Au-top site (in fact, between the Au-bridge site and Au-top site) and Au-bridge site. Having previously shown that nonanethiol resides in the three-fold hollow site of the Au{111} lattice by imaging with atomic-resolution non-contact AFM and STM [13], imaging with STM at higher tip bias shows

that more than one adsorption site (other than the Au-hollow site) is possible. This second adsorption site is the Au-bridge site between two Au atoms along their [111] directions. Sulfur dimerization, as observed experimentally in Fig. 3(c), occurs when two sulfur atoms are aligned on the three-fold Au-hollow site and the immediate adjacent Au-bridge site, being only ~2.2 Å apart. This dimer is illustrated schematically in Fig. 5(c). Whereas one sulfur head group is laterally located with ~0.5 Å of a Au-top site with a vertical height above the Au{111} lattice plane of ~2.6 Å, the other is found in the annulus surrounding the Au-hollow site with a vertical height of nearly 3.3 Å. In this case only one of the sulfur atoms is bound to the gold surface.

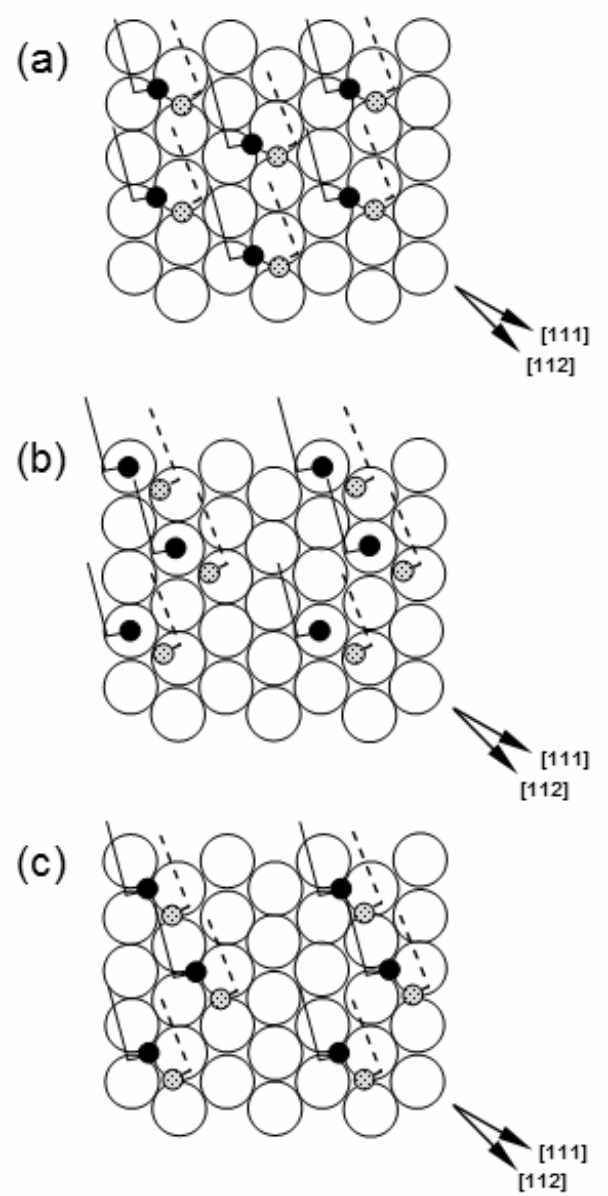


Fig. 5 Schematic illustrations of various different structural models for the (4 × 2) superlattice arrangement of nonanethiol on Au{111}. Each schematic shows the variation of the (4 × 2) structure where dimerization is possible. (a) Au-bridge:Au-bridge dimer structure (b) Au-bridge:Au-top dimer structure (c) Au-hollow:Au-bridge dimer structure. In each schematic, the white circles represent the Au lattice, the black circles represent S atoms in their original position prior to imaging and the dotted circles represent S atoms in dimerized positions.

The theoretical distances have been found [14] to be 2.34 and 3.7 Å, respectively. A comparison between the (4 × 2) structure observed here shows that the 2.3 Å S-S distance, measured by STM, is in favor of dimerized sulfur atoms since the sulfur head group are in nearest neighbor positions along the [112] lattice vectors of the Au{111} lattice. The symmetry of the (4 × 2) unit mesh can, in principle, support a wide range of head group structures. Due to the similarity between this derived S-S spacing and that found for disulfide compounds (~2.0 Å), [15] these results are interpreted in the context of a disulfide adsorption state. Furthermore, this similarity in S-S spacing directly implies that two equivalent sulfur binding states exist in this system. Based on the microscopic evidence, it is natural to think of two sulfur binding sites because the symmetry of the contrast in the STM images clearly demonstrates that two distinct molecules exist within the unit mesh. This biequivalent sulfur positioning is illustrated schematically in Figs. 1(b) and 5(c). The inequivalence of the height of these two molecules above the Au surface and the strictly equal number of each of these molecules within the unit mesh are therefore both defining characteristics of the (4 × 2) unit mesh symmetry. [16] A considerable difference in height of respective sulfur atoms implies that the two sulfur head groups are found in two different lateral adsorption sites.

CONCLUSIONS

In the results presented here, the Au-S distances immediately suggest that although the first sulfur head group is directly bound to the Au{111} surface, no Au-S bond exists for the other sulfur head group. These microscopical results have been interpreted in the context of sulfur dimerization. Such observations are only observed when the tip is essentially scanning within the monolayer, but above the sulfur head groups. Sulfur dimers only form when two sulfur head groups are located on the three-fold Au-hollow site and the immediately adjacent Au-bridge site. It is believed that the motion of the tip within the monolayer allows for the movement of one of the sulfur atoms from a Au-hollow to a Au-bridge site where effective bonding or dimerization can occur. Other wise, the standard (4 × 2) superlattice is observed.

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