

Coverage-Dependent Adsorption of CH₃S and (CH₃S)₂ on Au(111): a Density Functional Theory Study

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The origin of the superlattice present in the commensurate hexagonal structure of self-assembled monolayers of *n*-alkanethiols on gold and the question of whether the thiols are adsorbed onto the surface as dimers (disulfides) or monomers (thiolates) have been under debate for many years. Looking for a better understanding of the structural properties of these systems, we have performed a theoretical study of the molecular and dissociative adsorption of dimethyl disulfide on Au(111) as a function of coverage ($0.25 \leq \Theta \leq 1$), using gradient-corrected density functional (DFT) calculations with a slab geometry. For the dissociated state, our results indicate that the hcp hollow site is much less favorable than the fcc site. For the latter site, we find that, because of surface gold atom relaxation, the adsorption energy depends strongly on Θ , changing from ~ 18 kcal/mol at $\Theta = 0.25$ to ~ 3 kcal/mol at $\Theta = 1$. For the bridge site, instead, the adsorption energy is a weak function of Θ , and for all investigated coverages, this site is by far the most stable. According to our DFT approach, the adsorption of dimethyl disulfide is dissociative with a thermodynamic gain, at $\Theta = 1$, of ~ 13 kcal/mol with respect to the adsorbed molecular state. We also find, however, that the energy of $c(4 \times 2)$ structures containing at least two inequivalent CH₃S groups per unit cell (with a minimum S–S distance of ~ 3.7 Å) is, within the accuracy of our approach, indistinguishable from the pure $(\sqrt{3} \times \sqrt{3})$ hexagonal structure. Our results suggest that the full solution of this thorny problem will require, also for the shortest chains, an estimate of the energetic contribution of dispersion forces that are not included in the DFT calculations.

Introduction

Self-assembled monolayers (SAMs) are ordered molecular assemblies formed by the adsorption of an active surfactant on a solid surface. These systems have been the subject of intense research in recent years, because of both the interest in understanding the origin of their unique behavior, and their technological applications.¹ Among the many varieties of SAMs, special attention has been focused on those involving alkylthiols on gold surfaces, which are generally considered as representative models for this class of systems. Many fundamental issues remain, however, which are poorly understood and/or controversial, such as the mechanism of the formation process, and the nature of the bonding between the adsorbed molecules and the gold substrate.

Several studies have shown that SAMs formed by adsorption of either alkanethiols or di-*n*-alkyl disulfides on the clean Au(111) surface are very similar, and there is evidence that the final chemisorbed state of the molecules is the same in the two cases.² A question of particular relevance is whether the molecules are adsorbed in the form of thiolates or disulfides. For a long time it has been widely accepted that the bonding in these SAMs is in a thiolate-like form, with the sulfur atoms occupying the 3-fold hollow sites of the Au(111) surface. Thus it was assumed that the dialkyl disulfide species, which are observed in temperature-programmed desorption (TPD) studies,³

are formed during the desorption process and are not species that preexist on the surface. This picture, however, was challenged by He and X-ray diffraction and X-ray standing wave results,^{4–6} which showed that the periodicity of the high-density full-coverage monolayers is not $(\sqrt{3} \times \sqrt{3})R30$, but rather a $c(4 \times 2)$ superlattice of the $(\sqrt{3} \times \sqrt{3})R30$ lattice. In this structure, the unit cell contains four thiol residues and two inequivalent sites. From a multiparameter analysis of the X-ray diffraction data⁷ it was also concluded that a better fit of the diffraction intensities could be obtained with use of a model in which the sulfur atoms are located in inequivalent sites at 2.2 Å from each other, rather than with the $(\sqrt{3} \times \sqrt{3})$ thiolate lattice. This, in turn, suggested the existence of S–S bonding, which received further support by the results of several other experiments, involving, among others, sum-frequency generation,⁸ scanning probe microscopy,^{9,10} and high-resolution electron-energy-loss spectroscopy measurements.¹¹

So far relatively few and rather contradictory theoretical quantum chemical studies of alkanethiols on gold surfaces have been reported. With *ab initio* cluster calculations Sellers et al.^{12,13} found that the preferred binding site for the CH₃S radical on the gold surface is the hollow site. A few years later, however, a density functional (DFT) cluster model study by Beardmore et al.¹⁴ indicated that the adsorption energy of CH₃S at the hcp hollow, fcc hollow, and bridge sites is essentially the same. More recently, Häkkinen et al.,¹⁵ in their study of passivated Au₃₈ clusters, considered the stability of a dimethyl disulfide molecule on the seven-atom (111) facet. They found that a molecular adsorption state does exist, but this is energetically unfavorable

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with respect to dissociation and separate adsorption of the two CH_3S fragments on nonadjacent bridge sites. This result, particularly the fact that the bridge site is preferred for the thiolate adsorption, has been confirmed very recently for a slab model of Au(111) by Hayashi et al.¹⁶ Also using DFT slab calculations, however, both Grönbeck et al.,¹⁷ who examined the disulfide and thiolate adsorption in the low-coverage limit, and Yourdshahyan et al.,¹⁸ who used a coverage of 0.75 (one thiolate per periodically repeated 2×2 unit cell), found that CH_3S preferentially adsorbs at the fcc hollow site. Finally, a recent study of the interaction of short-chain alkane thiols with small Au_n ($n \leq 5$) clusters¹⁹ compared many different electronic structure methods. In this cluster size regime, there is no clear preference for single or double coordination of the sulfur to gold, whereas the triple coordination is possible but clearly disfavored.

In this work, we reconsider the issue of the structure and binding in high-density SAMs of alkanethiols on gold by performing a first-principles DFT study of the coverage dependence of the interaction of CH_3S and $(\text{CH}_3\text{S})_2$ with the Au(111) surface. For our calculations we use the Perdew-Wang '91 (PW91) generalized gradient approximation.²⁰ This approximation has performed quite satisfactorily in many studies of strong adsorption on metal surfaces (for a recent review, see ref 21). However, the binding of thiols and disulfides on gold surfaces is in part caused by dispersion interactions,²² which are difficult to capture even when using state-of-the-art gradient-corrected functionals. An indication of such difficulties is, for instance, the fact that two widely used gradient-corrected functionals, PBE²³ and BLYP,²⁴ which are known to give comparable results for strongly (chemically) bound systems,²⁵ have yielded values that differ by as much as 20 kcal/mol for the adsorption energies of the various (molecular and dissociated) species in the low-density limit.¹⁷ An important feature of the results of ref 17, however, is the finding that the *relative* stability of the different adsorbates is independent of the choice of the functional. If we make the reasonable assumption that the same holds also for the high-density systems discussed in the present work, we can expect that the relative energies of the various species should be correctly predicted by our calculations, even if the absolute values of the calculated adsorption energies may ultimately have significant error bars.

Computational Approach and Preliminary Tests

The clean Au(111) surface shows a $(\sqrt{3} \times 23)$ reconstruction,²⁶ but it is known that this structure disappears in the presence of adsorbates. We thus assume that this surface is unreconstructed. To model the surface, we used periodically repeated slabs of four layers,²⁷ separated by a vacuum at least 8 Å wide. Depending on the systems under consideration, different surface cells have been used, as shown in Figure 1. These cells have respectively 1, 3, 6, and 12 Au atoms per layer. The molecular species of interest are adsorbed only on one of the two surfaces of the slab. Their positions, as well as those of the Au atoms in the first three layers, have been fully relaxed until residual forces are found to be less than $0.05 \text{ eV } \text{\AA}^{-1}$ (0.8 pN).

To describe electron–core interactions, we use “ultrasoft” pseudopotentials²⁸ for Au, C, and H, whereas for S a norm-conserving pseudopotential generated according to the procedure of Troullier and Martins²⁹ is used. Valence states include 5*d* and 6*s* shells for Au, 2*s* and 2*p* for C, and 3*s* and 3*p* for S. All pseudopotentials have been generated with the PW91 functional, and those for Au include scalar relativistic effects. The smooth

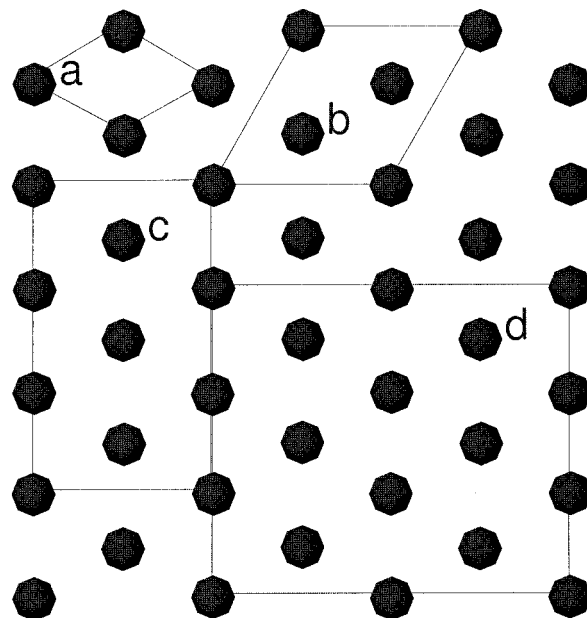


Figure 1. Surface cells used in the calculations. (a) (1×1) ; (b) $(\sqrt{3} \times \sqrt{3})\text{R}30$; (c) $(3 \times \sqrt{3})$; (d) $(3 \times 2\sqrt{3})$. These cells contain 1, 3, 6, and 12 Au atoms per layer, respectively. Cell d corresponds to the $c(4 \times 2)$ superlattice of the $(\sqrt{3} \times \sqrt{3})\text{R}30$ lattice.

part of the wave functions is expanded in plane waves with a kinetic energy cutoff of 20 Ry, whereas the cutoff for the augmented electron density is 160 Ry. To ensure a converged value of the surface energy, the *k*-sampling of the surface Brillouin zone included 96, 48, 16, and 8 *k*-points for the cells of 1, 3, 6, and 12 atoms/layer, respectively.

As a first test on the accuracy of our approach, we have computed the bulk structural properties, i.e., the lattice constant, a_0 , and the bulk modulus, B . Our calculated values, $a_0 = 7.82$ a.u. and $B = 1465$ kbar, compare well with the corresponding experimental values $a_0 = 7.67$ a.u. and $B = 1720$ kbar. The surface energy (γ), instead, is significantly smaller than the experiment: with use of the theoretical lattice constant, we obtain $\gamma = 758 \text{ erg/cm}^2$, to be compared with reported experimental values from 1045 to 1410 erg/cm^2 .³⁰ Such an underestimate is known to be a rather frequent shortcoming of gradient-corrected DFT approaches (see, e.g., refs 31, 32).

To complete our preliminary tests, we have calculated the dissociation energies of (gas phase) methanethiol into $\text{CH}_3\text{S} + \text{H}$ and dimethyl disulfide into $\text{CH}_3\text{S} + \text{CH}_3\text{S}$. We obtained 92 kcal/mol and 70 kcal/mol, respectively, in good agreement with the corresponding experimental values of 86 and 65 kcal/mol.³³

Results

A. $(\text{CH}_3\text{S})_2$ Adsorption: Molecular or Dissociative? Our results for the adsorption energy (E_{ads}) of a $(\text{CH}_3\text{S})_2$ molecule at various coverages are reported in Table 1. The possibility of either molecular or dissociative adsorption is considered. In the former case, to identify the most favorable configuration for the dimethyl disulfide molecules at $\Theta = 1$, several different starting geometries with either one molecule in a $(3 \times \sqrt{3})$ cell, or two molecules at inequivalent sites of a $(3 \times 2\sqrt{3})$ cell [corresponding to the $c(4 \times 2)$ structure] have been optimized (see Figure 2). Included was one of the geometries derived from the analysis of X-ray diffraction data,⁵ as well as other structures in which one sulfur atom per molecule was either in a hcp or fcc hollow site or in a bridge site. The $c(4 \times 2)$ structure proved to be most stable, with an adsorption energy, $E_{\text{ads}} \sim 5.8 \text{ kcal/}$

TABLE 1: Molecular vs Dissociative Adsorption of Dimethyl Disulfide on Au(111) at Various Coverages Θ , Where $\Theta = 1$ Corresponds to One Sulfur Every Three Surface Atoms^a

adsorbed species	Θ	site	Δz	S–M	E_{ads}	cell
(CH ₃ S) ₂	1	~on-top	2.84	3.00	4.4	<i>c</i>
	1	~on-top	2.86	3.00	5.8	<i>d</i>
	0.5	~on-top	2.84	2.98	5.9	<i>d</i>
CH ₃ S+CH ₃ S	1	fcc hollow	1.81	2.59	2.9	<i>b</i>
	0.5	fcc hollow	1.60	2.51	11.5	<i>c</i>
	0.25	fcc hollow	1.59	2.51	18.3	<i>d</i>
	1	hcp hollow	1.90	2.60	−1.1	<i>b</i>
	0.5	hcp hollow	1.70	2.53	4.7	<i>c</i>
	1	bridge	2.09	2.52	18.6	<i>b</i>
	0.5	bridge	2.07	2.50	19.6	<i>c</i>
	0.25	bridge	2.05	2.49	21.8	<i>d</i>

^a The adsorption energy per adsorbed disulfide molecule, E_{ads} (in kcal/mol), is calculated as the difference between the total energy of the interacting surface and adsorbed-molecule system and the sum of the energies of the noninteracting clean Au(111) surface and gas-phase (CH₃S)₂ molecule. Negative values of E_{ads} indicate that the molecule–surface interaction is repulsive. The reported structural information includes the position (site), vertical distance Δz of the (lower) S headgroup from the surface plane (Å), the distance S–M between the S atom and the nearest metal atom, and the surface cell used for the calculations (cells b, c, and d, as shown in Figure 1).

mol, which is ~ 1.4 kcal/mol larger than that for the $\Theta = 1$ structure with all molecules in equivalent sites. In the most favorable configuration both S atoms of each disulfide molecule sit at ~ 2.9 Å above the surface, and the S–S distance is 2.14 Å.

For the dissociative adsorption case, four possible binding sites of the two CH₃S radicals were studied, the on-top site, the fcc and hcp hollows, and the bridge site. The on-top site was verified to be unstable, and only the results for the other three are reported in Table 1. Calculations for these sites were done at three different coverages, $\Theta = 0.25, 0.5$, and 1, with use of one radical per $(3 \times 2\sqrt{3})$, $(3 \times \sqrt{3})$, and $(\sqrt{3} \times \sqrt{3})$ cell, respectively (see Figure 1). To verify the consistency of the calculations with the different unit cells, we compared the adsorption energies obtained with either one thiolate per $(\sqrt{3} \times \sqrt{3})$ cell or four *equivalent* thiolates per $(3 \times 2\sqrt{3})$ cell, and found identical results within a few tenths of kilocalories per mole.

Table 1 shows that for all locations of the CH₃S radical E_{ads} increases with decreasing coverage. This behavior is most pronounced for the thiolates at the fcc hollow sites. In fact, for these sites the decrease in adsorption energy with increasing coverage is so strong that the relative stability of the molecular vs dissociated adsorption states changes with Θ . Thus at low coverage an adsorbed disulfide molecule is less stable than two fcc thiolates, whereas at full monolayer coverage the undissociated state is more favorable (see Figure 3). The large coverage dependence of the CH₃S binding in the fcc site seems to be related to the fact that the surface relaxation/deformation around the adsorbate tends to become increasingly difficult, and therefore smaller, with increasing Θ . As an example, the closest surface atoms around a CH₃S radical at the fcc site are found to relax outward wrt the sulfur headgroup by $\Delta r \sim 0.31$ Å at 0.5 coverage (with $\Delta r_{\parallel} = 0.27$ Å and $\Delta r_{\perp} = 0.14$ Å, parallel and perpendicular to the surface, respectively), and by $\Delta r \sim \Delta r_{\parallel} \sim 0.18$ Å at full coverage. At full coverage, the increased height of the S atom wrt the surface leads to a corresponding decrease in the binding energy.

To confirm the role of surface relaxation in the coverage dependence of the fcc site adsorption, we have recalculated some

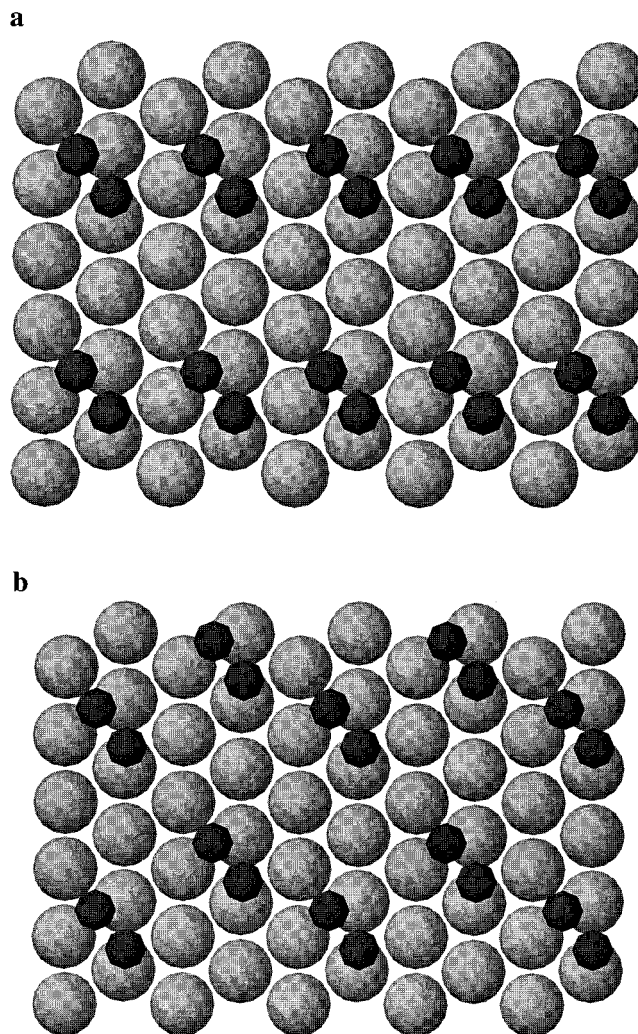


Figure 2. Full coverage monolayer of disulfide molecules on Au(111) (top views). (a) structure with one molecule per $(3 \times \sqrt{3})$ cell; (b) structure with two molecules at inequivalent sites in a $(3 \times \sqrt{3})$ cell. Large gray and small black circles represent Au and S atoms, respectively. Only the sulfur headgroup of the disulfide molecules is shown.

thiolate adsorption energies, keeping the gold substrate frozen in its unrelaxed configuration. For this site we find $E_{\text{ads}} = 1.4$ and -0.4 kcal/mol at $\Theta = 0.5$ and 1, respectively, against the values of 11.5 and 2.9 kcal/mol obtained when the gold substrate is allowed to relax, showing that the dependence of the fcc adsorption energy on coverage is very weak when the gold surface is frozen. These results also explain the lower binding energy and weaker coverage dependence for the adsorption on a hcp site, where the presence of a second layer gold atom located directly under the S atom does not allow the degree of penetration necessary for the lateral displacement of the neighboring Au atoms.

As a further test, because the surface tension of the bare gold surface is not well reproduced by the gradient-corrected PW91 functional, we have repeated a set of representative calculations by using the local density approximation (LDA), which yields a more realistic value for the clean surface $\gamma(\gamma^{\text{LDA}}\text{Au}(111) = 1140 \text{ erg/cm}^2)$, even though it notoriously provides too-high values for binding energies. We found that the difference in the fcc-binding energy between full and 0.5 coverage, which is 4.3 kcal/mol with PW91, is still 3.6 kcal/mol with the LDA. Therefore, our calculated coverage dependence cannot be attributed to the low value obtained for γ .

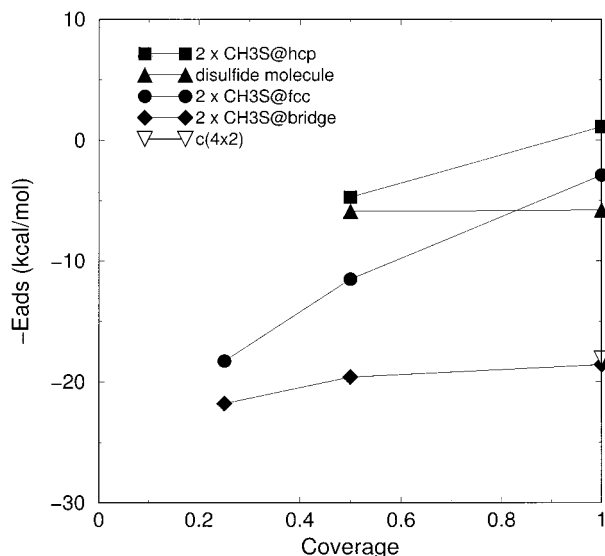


Figure 3. Coverage dependence of the adsorption energy for molecular and dissociative adsorption of $(\text{CH}_3)_2\text{S}$ on Au(111). The value of E_{ads} for the full coverage $c(4 \times 2)$ structure with the thiols at inequivalent bridge sites is also reported (empty down triangle).

In Figure 4a, a top view of the $(\sqrt{3} \times \sqrt{3})\text{R}30$, $\Theta = 1$ monolayer of thiols at the bridge site is displayed. Whereas in the CH_3S adsorbed at the fcc hollow, the S—C bond is almost perpendicular to the surface plane, in the adsorption at the bridge site the S—C bond is strongly tilted, forming an angle of about 58° with the normal to the surface. In addition, the substrate deformation at this site is fairly small at all coverages, as it can be inferred also by the large value of the height Δz of the S headgroup above the surface plane (see Table 1). As a consequence also, the coverage dependence of E_{ads} is much weaker. Thus, although at low coverages the bridge site is only slightly more stable than the fcc site (by ~ 3 kcal/mol per disulfide molecule at $\Theta = 0.25$), it becomes increasingly favored with increasing Θ . At full monolayer coverage, the structure with thiols adsorbed at bridge sites is, by far, more stable than any other configuration, either molecular or dissociated. As shown in Table 1, this may be related to the fact that the bridge site has shorter S—M distances than any other site. Our findings agree well with the results of ref 16, whereas the difference with ref 17 is likely because these authors work at very low Θ , where according to our calculations the difference between bridge and fcc sites tends to vanish.

B. The $c(4 \times 2)$ Structure. Although the full-coverage thiolate structures that we have so far examined have a $(\sqrt{3} \times \sqrt{3})\text{R}30$ periodicity, experimentally the lowest energy structure for *n*-alkanethiol monolayers on Au(111) is a $c(4 \times 2)$ superlattice of the $(\sqrt{3} \times \sqrt{3})\text{R}30$ lattice. This is true also for the very short chains ($n = 1$) considered in this work, as found by very recent He diffraction measurements conducted at Princeton,³⁴ which disagree with earlier observations.^{35,36}

At full coverage, the surface unit cell corresponding to the $c(4 \times 2)$ structure can accommodate four CH_3S radicals, and there should be at least two inequivalent S headgroups. To determine the arrangement of these species, we have optimized the geometries of numerous guessed configurations characterized by either thiols at inequivalent bridge sites, or mixed configurations with two radicals at bridge and two at hollow sites. We found that the mixed fcc-bridge configurations always relaxed to configurations with all the four radicals in Au—Au bridges. In particular, starting from a mixed structure where the distance between the two S headgroups at the fcc and bridge

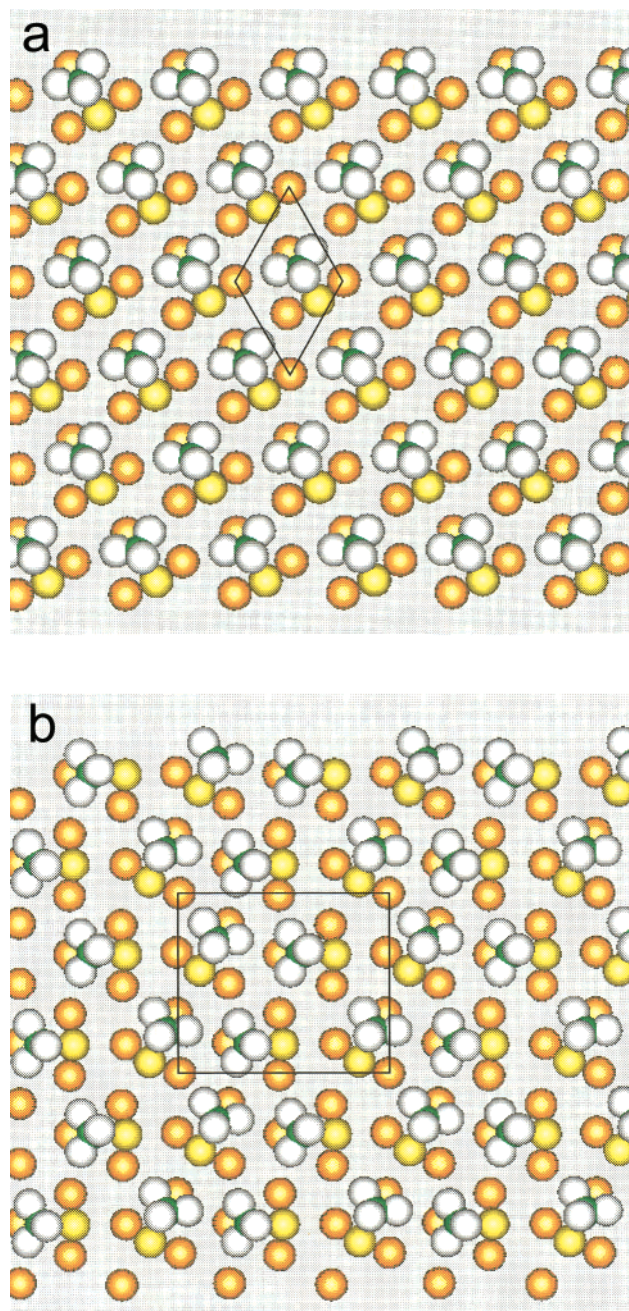


Figure 4. Full coverage monolayer of CH_3S radicals on Au(111) (top views). (a) $(\sqrt{3} \times \sqrt{3})\text{R}30$ structure with all radicals at equivalent bridge sites; (a) $c(4 \times 2)$ structure with radicals at inequivalent bridge sites. For better clarity, only the Au atoms of the first layer are shown. The surface unit cells for the two cases are indicated. Color code: orange = Au, yellow = S, green = C, white = H.

sites was ~ 3 Å [i.e., intermediate between a typical S—S bond length and the S—S distance in the $(\sqrt{3} \times \sqrt{3})\text{R}30$ lattice], the resulting relaxed geometry has the radicals at inequivalent bridges with the shortest S—S distances being ~ 3.7 Å (see Figure 4b). Although the value of E_{ads} for this structure is lower than for the pure $(\sqrt{3} \times \sqrt{3})\text{R}30$ lattice, the difference is extremely small, ~ 0.5 kcal/mol, which is practically within the accuracy of our calculations. However, we stress that our DFT calculations do not include dispersion interactions which, at this point, become necessary to realistically study the microscopic origin of the $c(4 \times 2)$ structure. With the inclusion of these interactions, it is most likely that structures such as those shown in Figure 4b, which exhibit periodic “clustering” of the adsorbed

species, will be stabilized wrt the pure ($\sqrt{3} \times \sqrt{3}$)R30. For completeness we would like to point out here that it is instead unlikely that the addition of van der Waals interactions will fill the ~ 13 kcal/mol gap between the adsorption of the thiolates vs that of the disulfides. This is because the total contribution of dispersion forces is unlikely to be large enough to give rise to differences of the order of 13 kcal/mol.

In conclusion, we have found that although a molecular adsorption state for (CH₃S)₂ on Au(111) does exist, this is thermodynamically unstable wrt dissociation and separate adsorption of the two CH₃S fragments at bridge sites. For all investigated coverages, i.e., $0.25 \leq \Theta \leq 1$, the bridge site is the most stable, as its adsorption energy is a weak function of Θ . This is at variance with the fcc site, for which the adsorption decreases strongly with increasing coverage. The value of E_{ads} that we obtain for the dissociative adsorption at the bridge sites (~ 20 kcal/mol) is somewhat smaller than the disulfide desorption energy of ~ 28 kcal/mol given by TPD experiments.³ This is consistent with the fact that our DFT approach neglects dispersion interactions that are important for these systems.²² Our results also suggest that the experimentally observed $c(4 \times 2)$ superstructure may be explained in terms of thiolates in inequivalent bridge sites, because the energy that we have found for such a structure is, within our approach, almost degenerate with the pure ($\sqrt{3} \times \sqrt{3}$)R30. For a detailed understanding of this structure, however, the tolerance of the various experimental observations to the value of the S–S distance between inequivalent sulfurs and to their relative height over the surface should be assessed, and a theoretical approach that includes dispersion interactions needs to be adopted. Because of its importance in many areas of surface science, the latter challenge is presently being pursued by several groups including ours.

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