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ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · APRIL 2000

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Thiols and Disulfides on the Au(111) Surface: The Headgroup–Gold Interaction

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Received October 8, 1999

Abstract: How thiols and disulfides bind to gold surfaces to form self-assembled monolayers is a long-standing open question. In particular, determining the nature itself of the anchor groups and of their interaction with the metal is a priority issue, which has so far been approached only with oversimplified models. We present ab initio calculations of the adsorption configurations (dissociative and not) of methanethiol and dimethyl disulfide on Au(111) at low coverage, which are based on density functional theory using gradient-corrected exchange-correlation functionals. A complete characterization of their structure, binding energies, and type of bonding is obtained. It is established that dissociation is clearly favored for the disulfide with subsequent formation of strongly bound thiolates, in agreement with experimental evidence, whereas thiolates resulting from S–H bond cleavage in thiols can coexist with the adsorbed “intact” species and become favored if accompanied by the formation of molecular hydrogen.

1. Introduction

Gold surfaces and anchor sulfur organic groups, such as thiols (RSH) and disulfides (RSSR) (where *R* is an alkyl chain), are the prototype components of supramolecular systems using self-assembled monolayers (SAMs)¹ for the functionalization of extended surfaces² and for the preparation of monolayer-protected clusters (MPCs).³ Given the wealth of potential technological applications, including corrosion inhibition, lithography, lubrication, catalysis, and molecular recognition, the interest in the underlying chemistry and physics has been steadily growing during the past decade. However, basic issues are still open, and the need to solve them has become urgent. In particular the chemical processes accompanying the formation of the adsorbed species are largely unknown, the final interface and the nature of the headgroups have not been characterized to satisfaction,⁴ and the existence of dimers versus thiolates in the full-coverage regime of Au surfaces is still under debate.^{5–7}

The adsorption on Au(111) of methanethiol and dimethyl disulfide (*R* = CH₃) at low coverage provides the simplest case, where the influence of van der Waals interactions is minimized. Also in this case a clear understanding is still missing, although experimental investigation of clean single-crystal surfaces under ultrahigh-vacuum conditions dates back to the beginning of the SAM proposal.⁸

Partial attempts^{9,10} to establish the structure and energetics of these complex systems have been previously made which were however based on oversimplified models of the metal surface, consisting of small atomic clusters (with no or limited embedding), and on a limited set of calculations that ignored the possibility of the structural relaxation driven by adsorption processes. To make progress with the aid of computer simulations, we present a state-of-the-art computational approach which relies on a slab as the model of the unreconstructed Au(111) surface, is based on density-functional-theory (DFT), and accounts for all structural modifications caused by adsorption processes. Indeed, Au(111) undergoes a $23 \times \sqrt{3}$ reconstruction in which fcc domains alternate with hcp domains, separated by smaller regions with Au atoms on bridge positions. However, the effects of such a reconstruction on the electronic properties have previously been shown to be negligible.¹¹

We found that dissociation of the disulfide with formation of strongly bound thiolates is favored, in agreement with experimental evidence at low coverage,⁸ whereas thiolates resulting from S–H bond cleavage in thiols can coexist with the adsorbed “intact” species and become favored if accompanied by the formation of molecular hydrogen. Interestingly, dissociation of a dimethyl disulfide molecule has also been predicted to occur on a seven-atom (111) facet of a 38-atom cluster of gold.¹² As expected, however, the final configuration of the thiols on the cluster is very different from that on the surface.

In Section 2, we shall describe the method we follow and compare it with those used in refs 9, 10, and 12. In Section 3, we shall present our results and discuss them in comparison with experimental data and with previous theoretical predictions.

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- (2) See e.g.: Delamarche, E.; Michel, B.; Biebuyck, H. A.; Gerber, Ch. *Adv. Mater.* **1996**, 8, 719.
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2. Method

Our calculations are^{13,14} based on density-functional theory (DFT¹⁵) with exchange-correlation (xc) functionals in the local-density approximation (LDA¹⁶) and including gradient corrections (both BLYP¹⁷ and PBE¹⁸). BLYP is known to provide generally a good description of molecular systems, whereas PBE is expected to account better for systems in which homogeneous and dishomogeneous electron densities coexist.¹⁸ LDA results are also reported but, as we will see, they are of interest only for the sake of comparison.

Norm-conserving, scalar relativistic, *l*-dependent pseudopotentials describe the core-valence interaction for Au, S, and C, which we constructed (for each xc-functional scheme) according to the Troullier–Martins procedure.¹⁹ In particular, for Au 11 electrons (4s and 5d) are considered in the valence. Cutoff radii for Au are 2.35 au for *l* = 0, 1 and 1.5 au for *l* = 2, while for C and S they are 1.2 and 1.5 au, respectively, independent of *l*. Local analytical pseudopotentials are used for H. Valence wave functions are expanded in plane waves up to a kinetic energy cutoff of 50 Ry. Structural and electronic optimizations are made with direct inversion in the iterative space methods.²⁰

Prior to studying the adsorbates, we performed extensive calculations¹⁴ of the structural and electronic properties of bulk Au and of the Au(111) unreconstructed surface. The values calculated²¹ for the (fcc) bulk lattice constant were 4.06, 4.24, and 4.15 Å in the LDA, BLYP, and PBE approaches, respectively, which compare reasonably well with the experimental value of 4.06 Å.²² The cohesive energy is a quantity more difficult to reproduce. We find values of 4.43 (LDA), 2.38 (BLYP), and 3.15 (PBE) eV, as compared to the experimental value of 3.81 eV.²²

Our simulation slabs for the surface consist of four 5 × 5 layers (referred to the unit cell of the truncated bulk) separated by an empty region of ~12 Å along the *z*-direction. In the optimization of the adsorbate–metal complex, the atoms of the layer farther from the adsorption region are kept fixed. We have also verified a posteriori that in the adsorption systems the size of the empty region is sufficient to render the interaction between the adsorption-induced dipoles negligible. In fact, the error in the binding energy caused by this dipole–dipole interaction is at most 0.05 kcal/mol.

To better compare our results with previous work, we briefly recall the methodology adopted. In ref 9 the method used is Hartree–Fock plus correlation treated at the second order of perturbation theory, solved within a localized basis set. Au is treated in an 11e-effective core relativistic potential scheme. The unreconstructed (111) surface is modeled with a two-layer cluster with the atoms fixed in the positions of a truncated bulk. In the calculation of the thiolate in ref 9a, the gold cluster consists of 17 atoms, of which 8 are treated quantum mechanically (7 on the first layer and one on the second) and the others as classical objects. In the calculation of the thiol, ref 9b, the gold cluster consists of 12 atoms (9 + 3), all treated quantum mechanically. The geometry of the molecules is allowed to vary.

In ref 10, the method used is DFT-BLYP, with a relativistic effective-core potential for Au and a localized basis set (6-31G* for S, C, and H). The unreconstructed (111) surface is modeled with a two-layer cluster of 17 atoms (10 + 7), frozen in the positions of a truncated bulk. SCH₃ is kept in the gas-phase geometry of HSCH₃ and calculations

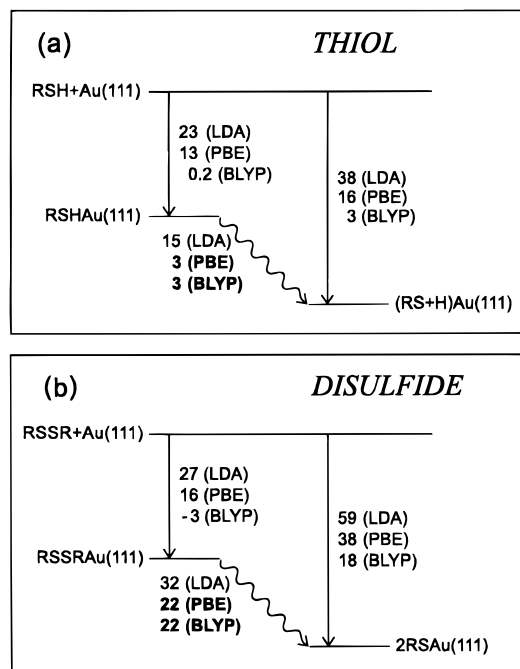


Figure 1. Energies (in kcal/mol) involved in the (a) thiol and (b) disulfide adsorption (*R* = CH₃).

are made for different values of the S–Au distance and of the C–S–Au angle.

In the 38-atom cluster calculation of ref 12, to which we also refer, a plane-wave pseudopotential scheme similar to ours has been adopted. The structure is optimized within LDA, and gradient corrections for the energy are included a posteriori (post-gxc).

3. Results and Discussion

In all xc schemes, optimization of the surface model resulted in a small (~1%) inward relaxation of the outermost layer. We verified that the valence density of states contained key features observed in photoemission,²³ in particular those corresponding to surface states, of which one (of interest here) is close to the Fermi energy (*E*_F).¹⁴ The description of RS–H and RS–SR (*R* = CH₃) bonding could well be compared with experiment, namely the binding energies (BE)²⁴ and the values of the bond lengths (*d*_{SH} and *d*_{SS}).²⁵ For the RS–H bonds, BE = 86 (exp), 100 (LDA), 87 (BLYP), and 91 (PBE) kcal/mol and *d*_{SH} = 1.34 (exp) and 1.35 (LDA, BLYP, PBE) Å. For the RS–SR bond, BE = 65 (exp), 82 (LDA), 56 (BLYP), and 72 (PBE) kcal/mol and *d*_{SS} = 2.03 (exp), 2.02 (LDA), 2.07 (BLYP), 2.04 and (PBE) Å. Although the strong difference of the binding in all cases is reproduced with the three xc functionals, the overbinding of LDA as well as the difficulty in reproducing the weaker bond with all functionals and the better performance of the PBE one are apparent. Such comments will continue to be valid for the description of the adsorption on gold, but again the qualitative discrepancy or similarity of the bonding in different situations will be quite functional independent. We shall rely on the gradient-corrected schemes for a quantitative account of such comparisons. We also note that the outcome of our calculations suggests that LDA may not be appropriate for a quantitative study of the energetics and stability of the SAMs and of the thiol-passivated clusters.

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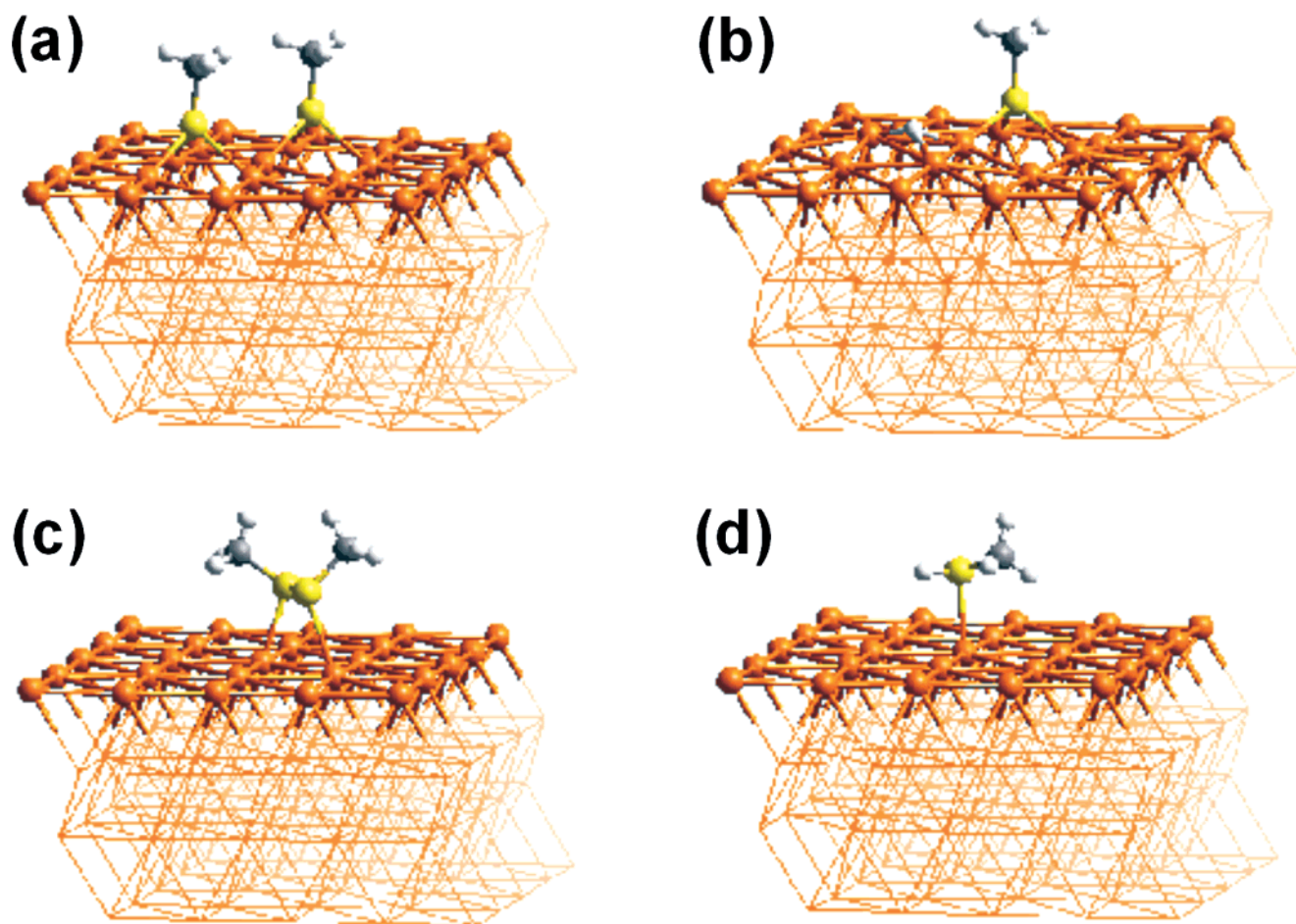


Figure 2. Equilibrium structures for the X-Au(111) systems considered here: (a) $X = 2RS$, (b) $X = RS + H$, (c) $X = RSSR$, and (d) $X = RSH$ (PBE results).

When thiols are used to grow SAMs, it is generally unclear whether thiols remain the final anchor groups or thiolates are formed after cleavage of the (strong) S–H bond. In the latter case, hydrogen could either stick to gold or desorb in the molecular form. No evidence of either process is generally found. Experimental observation of methanethiol adsorption,⁸ using electron-energy-loss spectroscopy (EELS), X-ray photoemission, and temperature-programmed desorption (TPD), is interpreted as supporting the permanence of thiols on the surface. In TPD, however, two adsorbed states are clearly seen ($BE = 12$ and 14 kcal/mol), and some EELS features remain unexplained. In particular, we note that the assignment of a peak at 220 cm^{-1} to the stretch of the weak Au–S bond contradicts that of an EELS peak, only 15 cm^{-1} higher, to the stretch of the strong Au–S bond of thiolates originating from the disulfide adsorption. Our results (see Figure 1) clearly show that the formation of thiolates accompanied by hydrogen chemisorption is thermodynamically favored over thiol adsorption, but only by ~ 3 kcal/mol, so that the two adsorbates may coexist. The appearance of two features in the TPD data ($\Delta BE = 2$ kcal/mol) could reflect this situation. Hydrogen recombination (which could also take place at a subsequent stage of the process and at higher coverage) to form molecular hydrogen helps stabilize the thiolate state (by $1\text{--}3$ kcal/mol) and definitely shifts the equilibrium. This is in qualitative agreement with the conclusions in ref 9b. Despite the similar binding energies, the bonding of RSH and RS on Au(111) is very different: weak chemisorption for RSH and strong for RS. In the latter the two chemisorptive bonds form at the expense of a very strong S–H

bond. The value of ~ 45 kcal/mol estimated from TPD for the S–Au bond strength⁸ compares with our results for the adsorption energy of the RS radical, 37 (BLYP) and 55 (PBE) kcal/mol.

Dimerization upon adsorption has also been proposed for long-chain thiols at high coverage,⁶ hence the suggestion of molecular adsorption of disulfides. On the other hand, when disulfides are used to grow SAMs, experimental evidence exists that the (weak) S–S bond dissociates and results in chemisorption of thiolates.^{1,26} Experimental data for dimethyl disulfide⁸ leave no doubt that dissociation takes place at low coverage. This is supported by our results in Figure 1, where the dimer is only weakly bound to the surface atoms, namely ~ 20 kcal/mol less than the dissociation products. Interestingly, dissociation of a dimethyl disulfide molecule has also been predicted to occur on a seven-atom (111) facet of a 38-atom cluster of gold¹² and to be favored by “at least 1.6 eV ”, namely ~ 38 kcal/mol.

The structure of thiolates adsorbed on Au(111) is difficult to determine experimentally. We find²⁷ that of the few geometrically reasonable positions for S (hcp, fcc, atop, bridge), the fcc 3-fold hollow site [see Figure 2a] is the energetically most favorable one, that binding energies are strongly affected by the modifications induced on the surface, and that in particular the fcc BE is $5\text{--}6$ kcal/mol higher than that of the configuration with S at the hcp site. Around the fcc site the Au–Au distances elongate by $16\text{--}20\%$ upon RS adsorption,

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(27) The optimized geometries are available as Supporting Information.

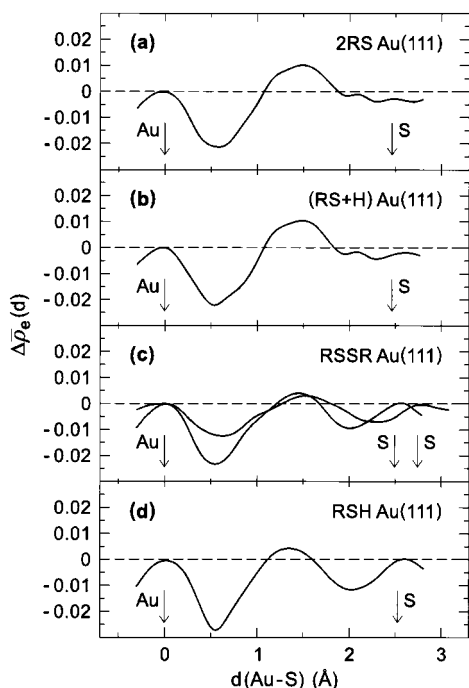


Figure 3. Electron density difference ($\Delta\rho_e(d) = \bar{\rho}_e(d) - \bar{\rho}_{e,Au}(d) - \bar{\rho}_{e,ads}(d)$) averaged and projected on the Au–S bond (s) for the four systems considered here (PBE results). $\bar{\rho}_e$ is the electron density of the metal–adsorbate complex and $\bar{\rho}_{e,Au}$ and $\bar{\rho}_{e,ads}$ are those of the bare surface and of the adsorbate, respectively, kept in the structure of the final state.

and relaxation propagates to the second layer, whereas weaker effects are found in the hcp configuration. Our results contradict the predictions of previous calculations^{9,10} that were used to generate potential energy surfaces for classical molecular dynamics simulations of SAMs.^{10,28} In fact, in ref 9, of the two 3-fold sites only the hcp is explicitly calculated and used to parametrize the Au–S interaction; the two positions are then assumed to be equivalent in the subsequent classical simulation. In ref 10, the fcc, hcp, and bridge sites are described as isoenergetic, i.e., fcc is the minimum, but the energy spread is only 1 kcal/mol. As we have verified, the discrepancy with our calculations is mainly due to the use of cluster models too small to represent the metal surface and to the neglect of surface structural relaxation induced by adsorption.^{9,10} In fact, within our schemes, we have also calculated thiolates adsorbed on a two-layer cluster model (10 atoms (7 + 3)) and on our slab, without allowing relaxation. In the former, fcc and hcp turn out to be isoenergetic; in the latter, fcc is already preferred but by an energy difference of only ~ 2 kcal/mol. We note that in the 38-atom 3D cluster studied in ref 12, the thiolates resulting from dissociation of the disulfide molecule are found to end up on nonadjacent bridge sites. Note, however, that the cluster

(28) See e.g.: Mar, W.; Klein, M. L. *Langmuir* **1994**, *10*, 188. However, for SAMs the situation may well be different, and other configurations may become relevant.

facets are not coplanar: therefore, the environment of a bridge site on the cluster face is very different from that of a bridge site on the surface.

Surface modifications that we determine at the fcc site are the same whether two thiolates [2RSAu(111); Figure 2a] or one and the hydrogens [(RS + H)Au(111); Figure 2b] is adsorbed. For these two systems, Figures 3a and 3b show the distribution of the difference density along one of the three Au–S equivalent bonds, which is indeed strikingly similar, with a clear charge accumulation observed along the bond. Depletion near the Au atom corresponds to depopulation of the surface state near E_F . Mulliken population analysis indicates a net excess charge of $\sim 0.3e$ for the adsorbed RS compared to the free radical. We note that charge transfer from Au to S takes place also in the fully passivated 38-atom cluster of ref 12 but to a much lesser extent (0.08e per S atom).

As expected, the weakly bound species modify the surface to a much lesser extent.²⁷ The RSSR molecule is bonded along an Au–Au bond, i.e., both S atoms are close to an Au atom [Figure 2c]. Note that this conformation is in contrast to the structural model proposed recently for didecanyl disulfide on Au(111),⁷ where only one S is directly bound to Au. RSH is adsorbed on an “atop” site, with the S–C axis nearly parallel to the surface plane [Figure 2d]. This confirms the prediction of ref 9b and also speculations derived from the analysis of the vibrational spectrum in ref 8. Figures 3c and 3d show again a similarity between the two weakly bound adsorbates, and in particular the negligible charge accumulation along the sulfur–metal distance. Correspondingly, we find a minor change of the electronic density of states near E_F .

4. Conclusions

In conclusion, this work has provided the long-needed quantitative ab initio description of the interaction of thiols and disulfides with the Au(111) surface. This constitutes a step forward with respect to previous simple model calculations, which were useful in allowing a first insight into the chemistry of such complex systems, but could only provide a qualitative account of it. On the basis of the results presented here, one can now plan to extend this study to the dynamics of the binding reactions as well as to the stability of monolayer systems on surfaces and clusters, where the role of the chain length must be assessed.

Acknowledgment. The stimulus to this work was born from several discussions with R. L. Whetten, G. Scoles, H. Biebuyck, B. Michel, and E. Delamarche. Most calculations were done on the IBM SP2 at the Center for Parallel Computing, Stockholm, Sweden. H.G. acknowledges a post-doc grant from STINT/NFR and the kind hospitality of the IBM Zurich Research Laboratory.

Supporting Information Available: Listing of coordinates (ASCII). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA993622X