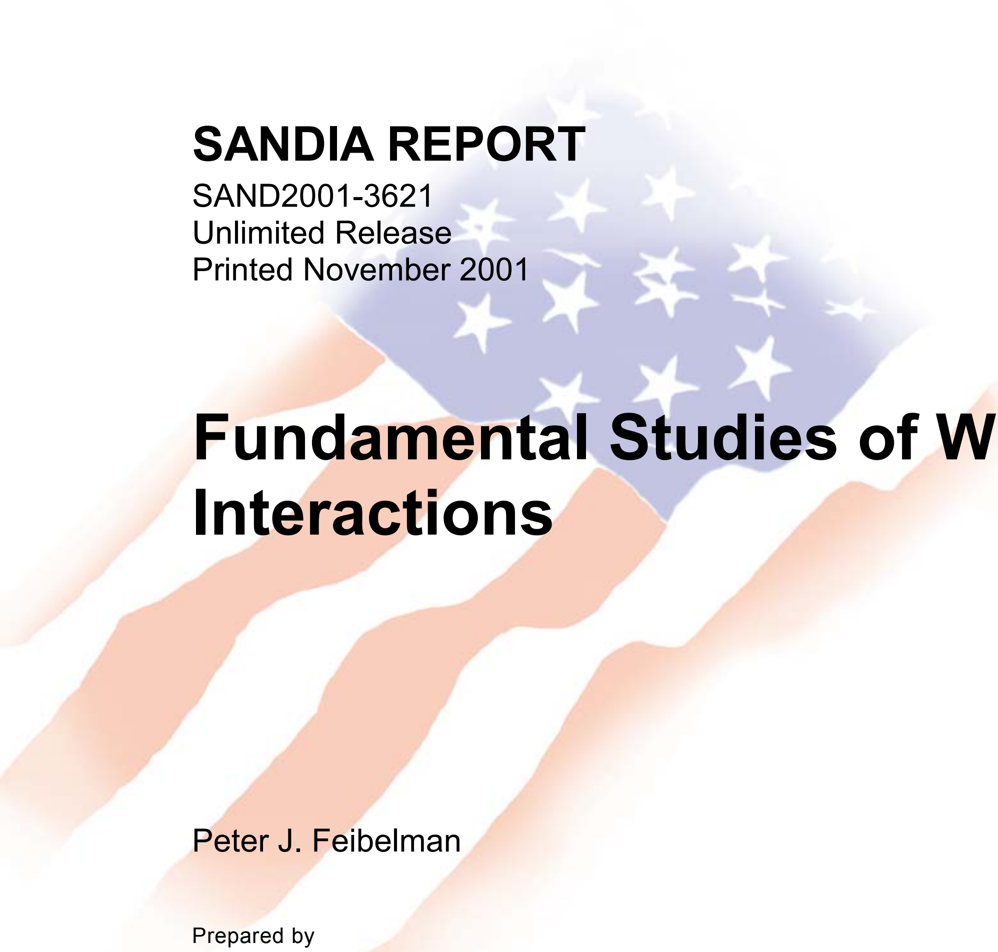

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Fundamental Studies of Water-Surface Interactions

Peter J. Feibelman

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Fundamental Studies of Water-Surface Interactions

Peter J. Feibelman
Surface and Interface Sciences Department
Sandia National Laboratories
P. O. Box 5800
Albuquerque, NM 87185-1413

Abstract

Ab-initio calculations can help to establish the relationship between "hydration forces" (i.e. the hydrophilic or hydrophobic nature of a substrate) and the molecular structure of the water in the immediate vicinity of a surface. As a first step, we have used them to study the structures of ordered arrays of the shortest alkanethiolates on Au(111) and the energetics of water co-adsorption on this surface. Calculated total energies imply that the $\sqrt{3}\times\sqrt{3}$-R30°–CH_3S/Au(111) surface does not support a two-dimensional water wetting layer, despite exposure of substantial Au regions to the vacuum.

Fundamental Studies of Water-Surface Interactions

Introduction

Insight into the factors controlling the hydrophobic-hydrophilic character of surfaces, largely lacking despite intense study of water, is critical to several new thrust areas at Sandia ranging from the development of microfluidic systems to understanding the folding and adhesion behavior of biomolecules such as proteins. I summarize here an initial investigation of near-surface arrangements of water molecules as a function of surface composition and structure. The long-term goal is to learn how a substrate gives rise to observed "hydration forces" (i.e. expresses its hydrophilic or hydrophobic character) by influencing the water structure in its vicinity.

As a first step I have sought to identify a set of model surfaces of varying "hydrophobicity." A commonly studied example of a hydrophobic surface is Au(111) covered by an ordered arrangement of $CH_3(CH_2)_nSH$ or $CH_3(CH_2)_nS$, molecules, strongly bonded through their S atoms to the Au surface. If they are long enough, i.e., if n is roughly 10 or larger, the chains tilt, no Au atoms are exposed to the adjacent medium, and the surface is certainly "hydrophobic." This information suggested the project undertaken here, quantifying how hydrophobic a thiolate-covered surface is as a function of chain length n+1. In work to date, using state-of-the-art, density-functional-theory,[1] total-energy calculations, as embodied in the Vienna ultra-soft pseudopotential code known as VASP,[2-4] I have optimized ordered submonolayer arrangements of CH_3S and CH_3CH_2S on Au(111), and begun investigating the structure and energetics of H_2O co-adsorbed with CH_3S. The main result, so far, is that the $\sqrt{3}\times\sqrt{3}$ - R30°–$CH_3(CH_2)_nS$/Au(111) surface likely does not support a two-dimensional wetting layer, even when n=0 and considerable Au is exposed to the vacuum.

Methods

Results, all theoretical thus far, were obtained with the VASP[2-4] total-energy code, its ultrasoft pseudopotentials (USP's),[5] and the Perdew-Wang '91 Generalized Gradient Approximation (GGA).[6] Au(111) substrates were represented in the calculations by 4- or 6-layer slabs. I optimize atomic geometries by fixing the lower two or three slab layers at bulk relative positions and relaxing the remaining atoms till forces on them are <0.03 eV/Å. Generally this optimization is quite time-consuming because the system under study has stiff and soft bonds. To speed up the optimization, I developed software for VASP that fixes C-H and O-H bond lengths while allowing the other geometric coordinates to relax. I set the slab lattice parameter to 4.18 Å, the bulk GGA value for a 60-**k** sample of the irreducible 1/48th of the Brillouin Zone (BZ) (exp't. = 4.08 Å). To accelerate electronic relaxation, I use Methfessel and Paxton's Fermi-level smearing method (width = 0.2 eV).[7]

Plane-wave calculations involving H and particularly O atoms typically require large basis sets. This requirement is mitigated in VASP by the use of ultrasoft pseudopotentials.[5] To date, I have employed a basis cutoff of only 29.1 Ry. This yields a sublimation energy for Hamann's ice-Ih model[8] roughly 0.05 eV too large, comparing to what Hamann has recently obtained using an independently-written total-energy code, hard, norm-conserving pseudopotentials and a basis cutoff of 130 Ry.[9] Although this error level for pure ice may seem large, it is not when compared to the ~0.2 to 0.3 eV energies by which computed heats of water adsorption in two-dimensional structures differ from the ice sublimation energy. Thus, to determine whether water wets the various surfaces studied, 0.05 eV accuracy has been sufficient. It should be added that errors in the relative energies of the various water phases studied are likely less than 0.05 eV, because of error cancellation. This, at any rate, is the case in my recent studies of water adsorption on Ru(0001).[10]

Results

Water-free, thiolate-covered Au(111) - Preliminary to the study of water adsorption on thiolate-covered Au(111) surfaces it is essential to learn the structure and energetics of thiol adsorption on the metal in the absence of water. This is a more difficult problem than it may appear. There is considerable discussion in the literature on whether adsorbed thiolates dimerize on Au(111).[11] It is also unclear whether thiols actually lose the H originally bonded to the S atom as they adsorb -- and if they do, where the H atoms end up. In the present, first effort, I have not addressed these issues. Instead I assumed that thiols adsorb dissociatively as thiolates plus H atoms, that the H atoms they lose on adsorption recombine and desorb as H_2, and that the remaining thiolates adsorb in a $\sqrt{3}\times\sqrt{3}$ surface arrangement. I then sought the optimal sites and orientations of the adsorbed thiolate radicals. To compute a heat of water adsorption, I subtract the energies of the water-free, and water-covered thiolate-covered surface, and compare the result to the energy of water molecules in gas phase. For comparison with other work on the structure of adsorbed thiolates, I have considered both p(2×2) and $\sqrt{3}\times\sqrt{3}$ surface unit cells.

The question of where thiolate radicals sit on the Au(111) surface has been framed by Yourdashahyan, et al.[12] as a choice among symmetry sites (fcc, hcp, bridge and atop, that is), with the result that the fcc site is preferred. However the calculations reported by this group, for p(2×2) arrangements of CH_3S radicals, appear to have been performed with the C-S direction held fixed along the surface normal. In my own calculations, no such restriction is imposed, and the result (see Fig. 1) is that the C-S direction is optimally tilted by something over 50° to the surface normal. The S-atom resides close to a bridge site, but displaced toward an fcc hollow, such that the C, S and the 2nd neighbor Au to the S atom are virtually colinear. These conclusions hold for both p(2×2) and $\sqrt{3}\times\sqrt{3}$ arrangements of ad-CH_3S. The energy gain from tilting and moving to an off symmetry site is roughly 0.26 eV in the former case and about 0.10 eV in the latter.

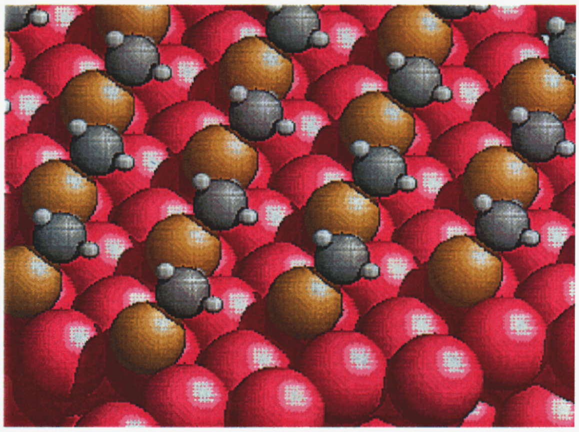

Figure 1. Oblique view of the optimized $\sqrt{3}\times\sqrt{3}$ - R30°-CH_3S/Au(111) structure, with Au atoms colored magenta, S atoms colored gold, C atoms colored grey and H atoms colored white.

These geometric conclusions are confirmed in a recent study by Hayashi et al..[13] They, however, not only performed DFT/GGA calculations of ad-methylthiolate static structure, but also predicted its vibration spectrum and showed that their prediction agrees well with electron energy loss measurements. Thus, the agreement of Hayashi, et al.'s results[13] and mine sets the stage for meaningful studies of water adsorption on the thiolate-covered Au(111) surface.

Water adsorbed on thiolate-covered Au(111) - The initial focus of this work was to learn whether the adsorption of a $\sqrt{3}\times\sqrt{3}$ CH_3S or CH_3CH_2S adlayer on Au(111) leaves enough Au exposed that a water molecule might bind to the substrate. Figs. 2, which are top views of geometry-optimized $\sqrt{3}\times\sqrt{3}$ - R30°–CH_3S/Au(111) and $\sqrt{3}\times\sqrt{3}$ - R30°–[CH_3S +2H_2O]/Au(111) adsorption structures, with atomic radii to scale, suggest that hard-core repulsion by CH_3S does not prevent the hexagonal, H-bonded H_2O layer from approaching the Au substrate.

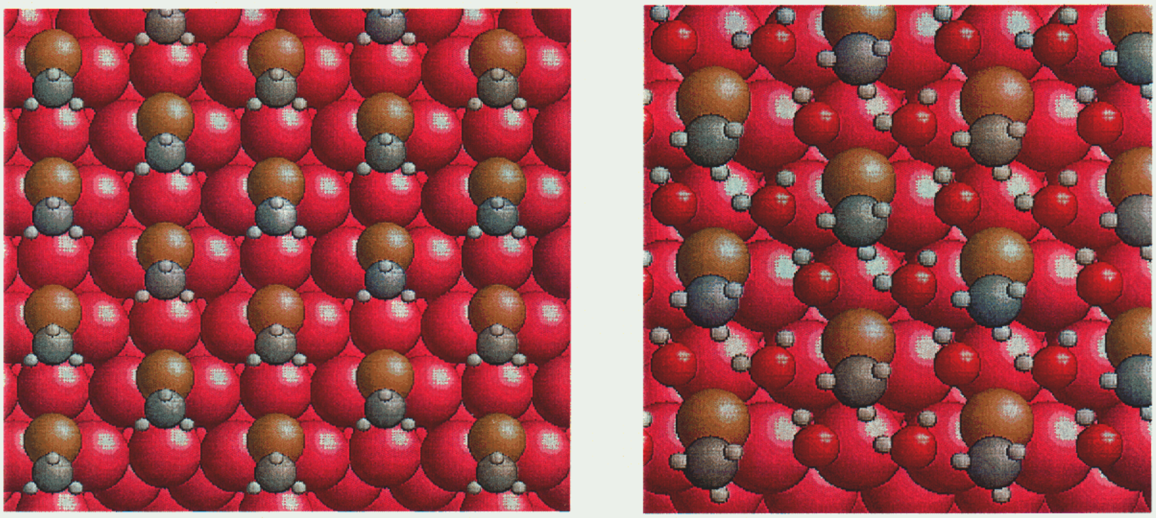

Figure 2. Top views of the optimized $\sqrt{3}\times\sqrt{3}$ - R30°-CH_3S/Au(111) and $\sqrt{3}\times\sqrt{3}$ - R30°–[CH_3S +2H_2O]/Au(111) structures, with Au atoms colored magenta, S atoms colored gold, C atoms grey, oxygen atoms red and H atoms white.

Nevertheless, as the side view shown in Fig. 3 makes plain, the hexagonal H_2O layer does not bind to the metal.

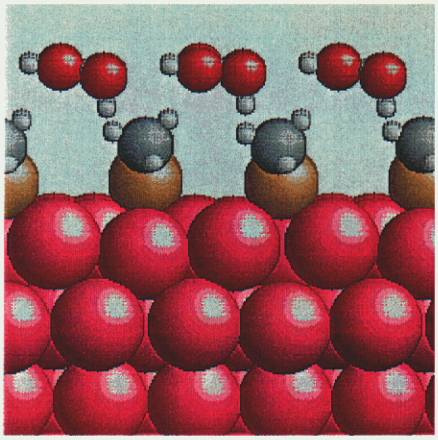

Figure 3. Side view of the optimized $\sqrt{3}\times\sqrt{3}$ - R30°–[CH_3S +2H_2O]/Au(111) structure, with Au atoms colored magenta, S atoms colored gold, C atoms grey, oxygen atoms red and H atoms white.

The heat of adsorption in the optimized water adlayer shown in Figs. 2 and 3 is computed to be 0.48 eV/H_2O-molecule, neglecting corrections for the quantum nature of the proton, i.e., for zero-point vibration. This is considerably smaller than the sublimation energy of ice-Ih computed in the same approximation, namely 0.71eV/H_2O-molecule. Thus, the two-dimensional water overlayer shown in Figs. 2 and 3 is thermodynamically quite unstable relative to three-dimensional ice clusters and unlikely ever to be observed.

It is doubtful that this weak binding stems from having found an unusually shallow relative minimum as a result of positioning the water molecules initially with their O atoms directly above the exposed regions of the Au substrate (though this will soon be tested). After all, finding a deeper minimum corresponding to a different water-substrate registry would mean that water molecules are substantially more strongly bonded to the (hydrophobic) methyl tails of the adsorbed CH_3S radicals than to exposed Au atoms. More likely, weak binding of the water to the thiolate-covered Au is attributable to forming an ad-layer structure in which one of every four H-atoms in the water molecules does not participate in an H-bond.

In summary, evidence till now suggests that even the shortest alkane-thiolate, CH_3S, renders the Au(111) surface hydrophobic.[15] Although, this is a disappointing conclusion from the perspective of trying to identify a suite of surfaces smoothly varying between hydrophilic and hydrophobic, it does imply an opportunity to study a hydrophobic case with a rather small unit cell.

In forthcoming work, I will therefore study more deeply the forces that govern water adsorption on $\sqrt{3}\times\sqrt{3}$ -R30°–CH_3S/Au(111), and will extend results to thicker water overlayers. I will determine by how much displacing the ice-like layer along the thiolate-covered surface lowers its energy and will investigate why non-H-bonding O-H bonds in the adlayer orient with H's down.[14] I will also estimate the strength of the water-methyl interaction by performing calculations of water adsorption on a thiol layer with no Au present.

Calculations for thicker water overlayers will be necessary to compute the water-solid-interface formation energy and thus make contact with the macroscopic concept of a contact angle.[15] This may be a difficult task, since little is known about the near-surface structure of water multilayers. An FY02 LDRD, "The basics of aqueous nanofluidics: "Interphase" structure and surface forces" is expected to help, however. It is aimed at "integrating an accurate classical, molecular-level description of bulk water and ab-initio calculations of the immediate vicinity of the substrate" so as to learn the relationship between the chemical and structural properties of a substrate and the arrangement of adjacent water molecules.

Acknowledgments

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[14] "H-down" means "H between the O and the metal substrate."

[15] Hydrophobicity is a continuously variable surface property, defined in terms of the contact angle between the water and the substrate in question. The bigger the contact angle, the more hydrophobic the surface. A surface that "completely wets" is maximally hydrophilic (i.e., not hydrophobic at all), having a contact angle equal to zero. It is easy to show that this occurs when the adsorption free energy of a one-molecule thick water layer exceeds the sublimation free energy of bulk water. Thus, the result that the water layer of

Figs. 2 and 3 has a heat of adsorption well below the sublimation energy of ice, at 0K, literally implies only that this layer is not a complete wetting structure. It does not say how hydrophobic the thiolate-covered surface is. To determine that, i.e., to predict the contact angle, requires evaluating the surface energy of a water-vapor interface, and the difference between the water-solid interface energy and the solid-vacuum surface energy, according to Young's equation.

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