INVESTIGACIÓN REVISTA MEXICANA DE FÍSICA **50** (5) 536–540 OCTUBRE 2004

Surface deformations induced by CH_3S adsorption on Au(111) and Cu(111): a DFT study

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Recibido el 6 de mayo de 2004; aceptado el 17 de junio de 2004

Surface deformations induced by methylthiolate adsorption on the (111) faces of Au and Cu are investigated by means of state of the art DFT slab calculations. We find that a significant surface rearrangement takes place when the molecules are adsorbed. Surface deformations are found to be larger for Au than for Cu and the magnitude of the deformations depends on both the coverage and the site of adsorption. Methanethiol adsorption on both Cu(111) and Au(111) [1] is stronger for partial than for full coverage.

Keywords: Density functional calculations; total energy and cohesive energy calculations; chemisorption/physisorption; adsorbates on surfaces; organic self-assembled monolayers.

La adsorción de CH_3S sobre las superficies (111) de Au y Cu induce deformaciones que hemos investigado a través de cálculos cuanto-mecánicos basados en la teoría de funcionales de la densidad (DFT). Hemos encontrado que cuando las moléculas se adsorben, se produce un rearreglo superficial significativo. Nuestros resultados indican que las deformaciones inducidas en la superficie del oro son mayores que las inducidas en la del cobre y que la magnitud de las deformaciones dependen tanto de la fracción de la superficie que es cubierta por las moléculas adsorbidas, como de la posición sobre la cual se establecen dichas moléculas. En ambas superficies, Cu(111) y Au(111) [1], la adsorción es más fuerte para coberturas parciales que para cobertura total.

Descriptores: Cálculos con funcionales de la densidad; cálculos de energía total y de energía de cohesión; quimisorción/fisisorción; adsorbatos sobre superficies; monocapas de moléculas orgánicas autoensambladas.

PACS: 68.43.-h; 68.43.Bc; 68.43.Fg; 71.15.Mb; 71.15.Nc

1. Introduction

Recently, much attention has been focused on the properties of self-assembled monolayers (SAMs) [2,3], particularly of alkanethiols on gold and other noble metal surfaces [4]. Clarifying the structure of these systems is a necessary prerequisite for understanding their behavior, and issues such as the bond distance between the metal surface and the sulphur atom, the preferred site for the S headgroup location, the type of periodicity, and the reconstruction of the surface, have been extensively investigated. In spite of such an intense research, the present understanding of the structure of the monolayer-surface system is still incomplete: for instance, no universal consensus concerning the preferred site for adsorption of the thiolates has been reached yet.

In this work we shall focus on the structure of adsorbed monolayers of methanethiol, the shortest of the alkanethiols, which is the "easiest" from the theoretical point of view. A considerable number of studies have already been performed on the adsorption of methanethiol on the (111) surface of Au [1, 5–17]. Dishner *et al.* [8] carried out a scanning tunneling microscopy (STM) study of the adsorption of CH_3S on Au(111) and observed the influence of the surface reconstruction on the chemisorption. Also by STM, Kondoh *et al.* [10], found that while at room temperature monolayers of CH_3S on Au(111) have a structure with periodicity of $(\sqrt{3} \times \sqrt{3})$R30, at low temperature the structure has a (3×3) periodicity where thiolates are located as tetramers. In a more recent study that included low-energy electron diffraction (LEED), X-ray photoemission spectroscopy (XPS), and density functional theory (DFT) calculations, De Renzi *et al.* [17] suggested a novel phase characterized by the coexistence of the well-known $(\sqrt{3} \times \sqrt{3})$R30 with a new (3×4) superstructure. Studies of methanethiol adsorption on Cu and Ag surfaces are also available [18–23]. Imanishi *et al* [18], performed extended X-ray absorption fine structure (EXAFS) and near-edge X-ray absorption fine structure (NEXAFS) experiments to study the structure of submonolayers alkanethiols $CH_3(CH_2)_{n-1}SH$ adsorbed on Cu(111), and proposed a structure model in which the S atoms are located at a deep three-fold hollow site with significant lateral outward movement of the nearest neighbor Cu atoms. X-ray photoelectron spectroscopy (XPS) investigations by Kariapper *et al.* [19] confirmed earlier results by Prince *et al.* [24] that methylthiolate causes a major reconstruction of the Cu(111) surface. Jackson *et al.* [20], performed normal incidence X-ray standing waves experiments (NIXSW), and concluded that CH_3S is adsorbed on a reconstructed Cu(111) at hollow sites. STM measurements by Driver *et al.* [21] identified three ordered surface phases, one of which presents the S headgroup located at inequivalent bridge sites.

On the theoretical side, after some early quantum chemical cluster calculations by Sellers *et al.* [6,7] and Beardmore *et al.* [9], recently several studies based on Density Functional Theory (DFT) have appeared. Garzón *et al.* [25], performing DFT cluster calculations, found that a methanethiol monolayer causes considerable distortion on the surface of Au$_{38}$. Grönbeck *et al.* [11] performed DFT slab calculations for methanethiol and dimethyl disulfide on Au(111) at low coverage and found the fcc hollow site to be the most favorable position for the S atoms. However, other DFT slab studies [1, 12], reported the bridge site as the most favorable one for CH$_3$S on Au(111) at intermediate and high coverage. Akinaga *et al.* [22], used clusters to model the surface, and found the bridge site to be the most favorable for adsorption on Au(111), and the fcc site for adsorption on Cu(111). A more recent study on alkanethiols on Cu(111) was performed by Ferral *et al.* [23], by means of quantum mechanical calculations on metal clusters where no surface relaxation was allowed.

The aim of the present work is to obtain further information on the structure of SAMS of methanethiol by investigating the deformations that these overlayers induce on the (111) surfaces of Au and Cu. For this purpose, we have performed DFT slab calculations [26] for several possible configurations of the adlayer-metal system at different coverages. We have considered two different metal surfaces, Au(111) and Cu(111), in order to obtain a better grasp on how the stiffness of the surface and its lattice parameter affect the strength of the surface-adlayer interaction and the form of the most stable structure.

For our calculations we use a density functional theory within the Perdew-Wang '91 (PW91) generalized gradient approximation [27]. This approximation has been found to perform quite satisfactorily in many studies of strong adsorption on metal surfaces (for a recent review, see Ref. 28). As in a previous work [1], we assume that the relative energies of the various structures should be correctly predicted by our calculations, even if the absolute values of the calculated adsorption energies may ultimately have significant error bars.

2. Computational approach and preliminary tests

The clean Au(111) surface shows a $(\sqrt{3} \times 23)$ reconstruction [29], but it is known that this structure disappears in the presence of adsorbates. We thus assume that both Cu(111) and Au(111) are initially unreconstructed. To model the surface, we used periodically repeated slabs of four layers, separated by a vacuum at least 8 Å wide. Depending on the coverage (Θ), different surface cells have been used, as shown in Fig. 1. These cells have respectively 3, 6, and 12 metal atoms per layer. One adsorbed molecule per cell corresponds to full coverage $\Theta = 1$, and partial coverages $\Theta = 0.5$ and $\Theta = 0.25$, respectively. The molecular species are adsorbed only on one of the two surfaces of the slab. Their positions, as well as those of the metal atoms in the first three layers, have been fully relaxed until residual forces are less than 0.05 eV Å^{-1} (0.8 pN).

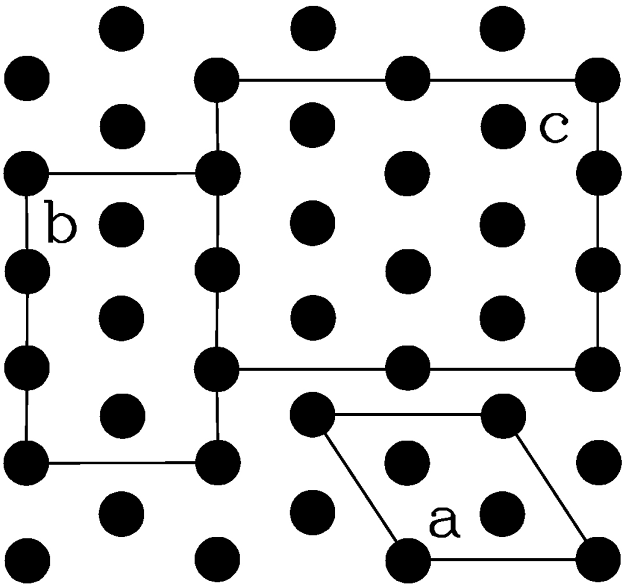

FIGURE 1. Surface cells used in the calculations: (a) $(\sqrt{3}\times\sqrt{3})$R30; (b) $(3 \times \sqrt{3})$; (c) $(3 \times 2\sqrt{3})$ also referred as the c(4×2) superlattice of the $(\sqrt{3} \times \sqrt{3})$R30 lattice.

To describe electron-core interactions, we use "ultra-soft" pseudopotentials [30] in the case of Au, Cu, C, and H, while for S a norm-conserving pseudopotential generated according to the procedure of Troullier and Martins [31] has been used. Valence states include $5d$ $(3d)$ and $6s$ $(4s)$ shells for Au (Cu), $2s$ and $2p$ for C, and $3s$ and $3p$ for S. All pseudopotentials have been generated using the PW91 functional, and those for Au and Cu include scalar relativistic effects. The smooth part of the wavefunctions is expanded in plane waves using a kinetic energy cutoff of 20 Ry, while 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 24, 8 and 4 k-points for the cells of 3, 6 and 12 atoms/layer, respectively.

To test the accuracy of our approach, we calculated the structural properties (lattice constant, a_0, and bulk modulus, B) of bulk Au and Cu, as well as the dissociation energies (DE) of gas phase methanethiol into CH$_3$S+H, and found results in good agreement with the experiment [1].

3. Results

Our results for the adsorption energies (E_{ads}) of the thiol radical and the relaxation of the surface at various coverages are reported in Table I for Cu and Table II for Au. The values of E_{ads} are obtained as the difference between the total energy of the interacting surface-thiolate system and the sum of the energies of the clean surface and the isolated thiolate; the buckling reported refers to the maximum vertical distance between metal atoms in the outermost layer of the surface; the lateral relaxation is presented in percentage, as the maximum elongation in the surface nearest neighbor distance. We have considered three possible adsorption sites: the bridge site

TABLE I. CH_3S on Cu: coverage, Θ, adsorption energy, E_{ads} (in kcal/mol); surface-S distance, Δz, and buckling, B (both in Å); nearest neighbor distance elongation, nne (in percentage).

Θ	site	E_{ads}	Δz	B	nne
1.00	bridge	55.6	1.9	0.05	3
0.50	”	57.0	1.9	0.15	3
0.25	”	57.2	1.9	0.14	4
1.00	fcc	53.0	1.8	0.00	4
0.50	”	55.0	1.7	0.09	6
0.25	”	57.1	1.7	0.10	8
1.00	hcp	52.7	1.8	0.00	3
0.50	”	54.3	1.7	0.09	6

TABLE II. CH_3S on Au: coverage, Θ; adsorption energy, E_{ads} (in kcal/mol); surface-S distance, Δz, and buckling, B (both in Å); nearest neighbor distance elongation, nne (in percentage).

Θ	site	E_{ads}	Δz	B	nne
1.00	bridge	44.3	2.0	0.29	6
0.50	”	44.9	1.9	0.22	9
0.25	”	45.9	1.9	0.23	8
1.00	fcc	36.4	1.8	0.01	9
0.50	”	40.7	1.6	0.17	17
0.25	”	44.1	1.6	0.13	17
1.00	hcp	34.4	1.9	0.03	6
0.50	”	37.3	1.7	0.11	14

which is located above a point between two surface atoms; the fcc hollow site, above a metal atom of the third layer; and the hcp hollow site which is above a metal atom of the second layer.

The results in the tables show several interesting features: The adsorption of the thiol radical on Cu(111) at all coverages is stronger than on Au(111). The site where the radicals are adsorbed more strongly is, for both metals, Au and Cu, what we have called the bridge site, where the sulfur atom is positioned above a point between two metal atoms in the surface, see Fig. 2. At full coverage, the C-S bond is 57 and 44 degrees tilted with respect to the Au and Cu surface normal, respectively, and the C-S vector points towards the fcc hollow site, as shown in Fig. 2. This is in contrast with the results reported by Akinaga *et al.* [22] where the fcc hollow site was found to be the preferred site for adsorption of CH_3S on Cu(111). Most likely this difference is due to the fact that Akinaga *et al.* modelled the Cu surface by using a rather small cluster (two layers and 18 atoms in total) with no relaxations allowed for the bridge site: indeed our calculations indicate that a slab of only 2 layers does not yield converged results. In addition, we have found that surface relaxation is important for both Cu and Au, and the presence of the thiolates causes a considerable rearrangement of the surface, in agreement with experiments [19, 24].

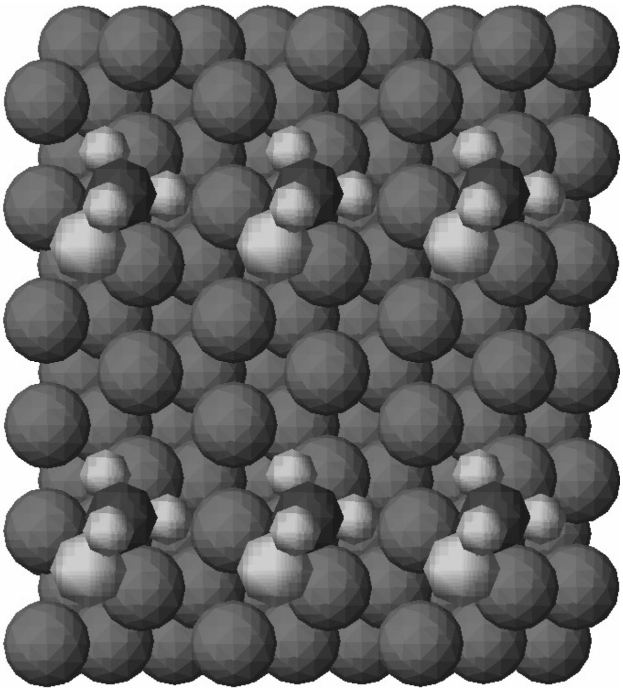

FIGURE 2. Top view of a half coverage monolayer of CH_3S on Cu(111). Adsorption is at the bridge sites, the C-S bond is 44 degrees tilted with respect to the surface normal and the C-S vector points toward a fcc hollow site. The big spheres represent the Cu atoms, the light medium spheres represent the S atoms, the dark medium spheres represent the C atoms, and the small spheres represent the H atoms.

As shown in Fig. 3, there is also a clear coverage dependence of the calculated adsorption energies for the adsorption on Cu, as it was previously found for adsorption on Au [1]: E_{ads} increases with decreasing coverage, with different coverage dependences for the different adsorption sites. Altogether, these variations with coverage are less pronounced for Cu(111) than for Au(111). The coverage dependence of E_{ads} can be related to the surface lateral deformations/relaxations around the adsorbate, which are more pronounced and "easier" for gold than for copper and at low than at high coverages. Also, the coverage dependence is related to the mechanism through which the radical is adsorbed to the surface: For adsorption above hollow sites (fcc or hcp) the sulfur atom is bonded to the three metal atoms around the hollow, these atoms get apart from each other in order for the sulfur atom to get closer to the surface; they can get further apart from each other at low coverage. Also the adsorption above the fcc hollow is stronger than above the hcp hollow, since in the former case the sulfur atom does not feel the repulsion from a metal atom in the second layer of the surface, and can thus get closer to the surface.

For adsorption at a bridge site, the metal surface develops a considerable buckling -the atoms move outwards with respect to the clean surface position- and a bond is established between a S atom and two metal atoms. In this case, since lateral relaxation is not as important as normal relaxation, the coverage dependence of the adsorption energy is not as pro-

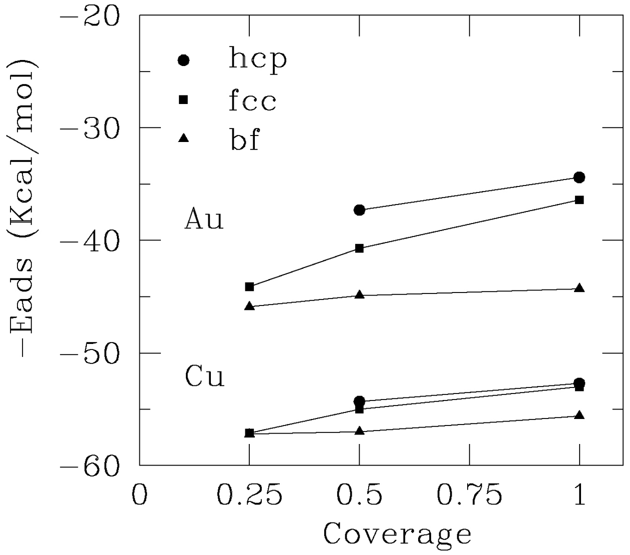

FIGURE 3. Adsorption energy as function of coverage, for CH$_3$S adsorbed on Cu(111) and Au(111).

nounced. We can notice that normal relaxation is important not only for adsorption on Au, but also for adsorption on Cu, specially at partial coverages. The large buckling that the metal surface undergoes when the S atom is adsorbed at the bridge site agrees with the effect observed by Driver and Woodruff [21] (average surface advancing outward), although they do not give a quantitative estimate of the observed relaxation.

At full coverage, the Cu-S bond distance is 2.31 Å for adsorption at the bridge site and 2.33 Å for adsorption at fcc or hcp sites; while at partial coverage, the Cu-S bond distance is the same for the three different sites of adsorption studied, 2.31 Å. Accordingly, Imanishi *et al.* [18] found from EXAFS studies, a Cu-S bond distance of 2.31 Å. These authors assumed that the sulfur atom was adsorbed at a deep three-fold hollow site (fcc), and also detected significant lateral outward movements of the surface. On the gold surface, the Au-S bond distance shows somewhat larger variations with respect to the Cu-S bond: for adsorption at the bridge site, it is 2.52 Å at full coverage and 2.49 Å at partial coverage, while the bond distance for adsorption on other sites is about 0.02 Å larger for similar coverages.

Although it is clear from our calculations that the bridge site is preferred for CH$_3$S on Cu(111), the difference in adsorption energy for adsorption at different sites is not as significant as the difference for CH$_3$S adsorbed at different sites of Au(111) (less than 2.6 kcal/mol vs. 7.9 kcal/mol for full coverage, and 0.1 kcal/mol vs. 1.8 kcal/mol at $\Theta = 0.25$). This result suggests that for adsorption on Cu(111), there may be coexistence of domains where adsorption is at the bridge and at regions where adsorption is at three-fold hollow sites. Interestingly, Kariapper *et al.* [19] interpreted their esperimental results in terms of two different phases of thiolate adsorbed on Cu, and proposed that one phase corresponds to adsorption on a reconstructed region of the surface, and the other to adsorption on an unreconstructed region.

4. Conclusions

Our calculations show that a significant surface deformation takes places when a layer of CH$_3$S$^-$ is adsorbed on the (111) surface of both metals, Au and Cu. We have characterized the surface deformations by estimating the buckling and the nearest neighbor distance elongation around the adsorption site. We have found that surface deformations are larger for Au than for Cu; the magnitude of the deformations depends on both, the coverage and the site of adsorption: the nearest neighbor elongation is larger for adsorption at lower coverages and at less favorable -energetically speaking- sites, while the buckling becomes the largest for adsorption at the most favorable site (bridge), at full coverage for Au and partial coverage for Cu. Over all, we have found that our results agree with experimental studies although they do not quantify the deformations. Besides, our results confirm that adsorption of methanethiol on Cu is stronger at partial coverages than at full coverages, as it was found before for adsorption on Au [1].

Acknowledgments

This work was partially supported by DOE (DE-FG02-93ER45503). The computations have been done mainly on the Cray-T3E of the National Energy Research Scientific Computing Center (NERSC), Berkeley, Ca, and on the IBM-SP3 computer of the Princeton Materials Institute.

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