

Theory of Nanoscale Atomic Lithography. An ab Initio Study of the Interaction of “cold” Cs Atoms with Organthiols Self-assembled Monolayers on Au(111)

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Received: August 10, 2004; In Final Form: December 1, 2004

This paper deals with the microscopic mechanism of nanolithography of self-assembled monolayers (SAM) of alkanethiol molecules on Au(111) induced by the exposure of the film to a beam of “cold” Cs atoms. Density functional theory calculations have been carried out to elucidate the mechanism of interaction of the Cs atoms with the SAM. We found that the film damage occurs in two steps: the Cs atom penetrates the SAM and at a distance of 10–12 Å from the surface donates one electron to Au, forming a Cs⁺ cation which binds strongly to the surface and interacts with the polar head of the SR molecule. The thermal energy released in this process largely exceeds the energy required to stimulate the desorption of RS–SR disulfide molecules from the Au surface with consequent damage of the film. No chemical interaction occurs between Cs or Cs⁺ and the hydrocarbon chain of the thiol molecule.

1. Introduction

Self-assembled monolayers (SAM) of organic molecules on metal surfaces have attracted a lot of attention because of their potential applications in several fields, from chemical and biochemical sensors to nano-electromechanical systems and molecular electronics.^{1–3} As the size in metal oxide semiconductor systems continues to decrease, the attention has been moved to organic monolayers as alternative active components in microelectronic devices. An essential aspect in the design of new systems for microelectronic applications is represented by the lithographic process. The resolution offered by optical lithography is limited intrinsically by diffraction problems and is directly related to the light wavelength, λ . Atom beams have been proposed some time ago to produce smaller features and finer resolution thanks to the smaller value of the de Broglie wavelength in particle beams.^{4,5} There are basically three categories of atom beams that have been used in this context: metastable noble gas atoms, alkali atoms, and other less explored atoms.⁶ Very recent developments of laser-cooling in atomic physics have demonstrated that atoms can be conveniently and efficiently manipulated through the application of suitable electromagnetic fields.⁷ Laser-cooling technologies make possible to replace the standard mask of optical lithography with an immaterial mask consisting of a particular configuration of standing electromagnetic fields. In practice, the atoms of a beam can be guided and deposited precisely to produce spatially ordered nanostructures or used to impress a particle-sensitive resist.⁸

So far, the mechanism of interaction and damage of the film induced by the atoms is unclear. For metastable rare-gas atoms direct physical damage appears to be the most likely mechanism.^{9–11} Beams of Cs^{6,12–15} and Na¹² atoms have been used to demonstrate that a resist can be patterned. The alkali-metal atoms have a low kinetic energy and no significant internal

energy but they are still able, most likely through a chemical process, to alter the properties of certain resists to allow subsequent etching of the substrate. It has been suggested that open defects of the SAM provide access to the Au–S bonds at the bottom of the monolayer,¹⁴ and it has been found that short-chain thiols are more sensitive than long-chain thiols.¹⁴ However, there are no plausible hypotheses about the microscopic mechanism of the interaction. This can involve the chemical rupture of C–C, C–H, or C–S bonds induced by Cs, or a direct attack to the S–Au interface bonding. It is also unclear if the interacting species is neutral Cs or a Cs⁺ cation formed in the course of the deposition.

To answer these questions we have considered the mechanism of interaction of Cs atoms with organthiols deposited on Au. To the best of our knowledge this is the first ab initio study where the problem is addressed globally. We have considered first the interaction of Cs atoms and Cs⁺ ions with gas-phase organthiol molecules; then we have analyzed the deposition of Cs on Au(111) with and without adsorbed thiol molecules. The calculations have been performed at the density functional theory (DFT) level using the hybrid B3LYP exchange-correlation functionals in combination with cluster models of the Au(111) surface. It should be mentioned at this point that problems exist within DFT theory to describe the Au–SR bond. Different exchange-correlation functionals provide significantly different Au–SR bond strengths.^{16–19} The B3LYP approach used here is in general very accurate for molecular interactions but tends to underestimate the Au–SR interaction. Despite the limitations of DFT in describing this system the results shed some light on the mechanism of chemical modification of the SAM induced by the interaction with Cs.

Before to present the results of our calculations, it is useful to summarize some general features of the alkanethiol films. Self-assembling can be obtained either from vapor phase deposition in ultrahigh vacuum (UHV) or from solution. A question which has stimulated an intense debate is whether the

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molecules are adsorbed in form of thiols, RSH, thiolates, RS^- , or disulfides, RS-SR . The general belief is that the SAM monolayers are adsorbed in thiolate-like form. The reactions are



or



Reaction 1 can be considered formally as an oxidative addition of the S-H bond to the gold surface, followed by reductive elimination of hydrogen, while reaction 2 can be simply regarded as an oxidative addition of the S-S bond to the gold surface. However, TPD experiments have shown that the desorbing species are actually disulfides,²⁰ opening a debate about the real nature of the adsorbate. The hypothesis that disulfides are present on the surface has been corroborated by other experiments pointing to the existence of direct S-S bonds,²¹⁻²³ but recent high quality DFT calculations have shown unambiguously that, while a molecular adsorption state for $(\text{RS})_2$ disulfides exists, this is thermodynamically unstable toward dissociation and formation of adsorbed RS fragments.^{16,24} This is not surprising if we consider that the energy of two Au-SR bonds, $\approx 3-4$ eV,^{1,20,25,26} is not much larger than that of the RS-SR disulfide bond, 2.8–3.2 eV.^{27,28} Also the nature of the adsorbed species, thiol, RSH, or thiolate, RS^- , has been widely discussed. Some early studies²⁰ as well as recent reports²⁹ indicate the existence of undissociated RSH molecules on the surface. In this case however the molecule is physisorbed with typical adsorption energies of 0.6–0.8 eV depending on the chain length (the desorption peak in the TPD spectra is around 300 K).²⁵ A second desorption peak at 500 K is due to a chemisorbed state where the molecule is in thiolate form. In this case the desorption enthalpies are of 1.3 eV and are independent of the chain length.²⁵ In the following, we have considered models of chemisorbed RS units adsorbed on Au, but the conclusions hold in general for every kind of adsorbed thiol molecule.

The preferred adsorption site is controversial. In one of the first *ab initio* studies dedicated to the problem, Sellers et al.^{30,31} found that the three-hollow site is the preferred one. Later, DFT studies showed that adsorption on hollow or bridge sites has essentially the same energy with moderate preference for the three-hollow hcp or fcc sites.^{18,19,32,33} The bonding mode is practically independent of the length of the alkyl chain.³⁴ Other theoretical studies suggest that the bridge site is preferred,^{16,35,36} a conclusion supported experimentally by high-resolution electron energy loss spectra.³⁶ All these results have been contradicted by a recent photoelectron diffraction study which shows that methylthiolate molecules occupy atop sites on Au(111).³⁷ The reason of this apparent confusion is partly due to the small energy differences between the various adsorption sites, partly to a strong coverage-dependence of the adsorption energy, and partly to already mentioned limitations of current formulations of DFT exchange-correlation functionals¹⁶ to describe the Au-SR bond. The general conclusion is that the adsorption site does not play a prominent role in the characteristics of the adsorbed molecule and that the nature of the bond is very similar for adsorption on top, bridge and hollow sites.

Alkanethiols on Au(111) form a well ordered closely packed structure with hexagonal symmetry of the sulfur atoms and an S-S spacing of 4.97 Å.³⁸ The fully extended alkyl chains are tilted with respect to the surface normal by $\approx 30^\circ$.³⁹⁻⁴¹ The large

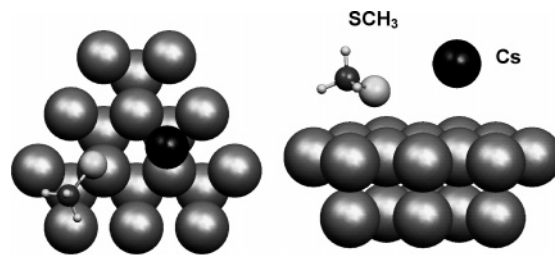


Figure 1. Optimal structure of the $\text{Cs}^+ - \text{SCH}_3\text{Au}_{18}^-$ complex. Left: top view. Right: side view.

change in the tilt value arises from packing requirements that may dictate the final surface-S-C angle. However, the barrier to reorient the chains is quite low,¹ and grain boundaries can form between islands of differently oriented chains. The grain boundaries represent extended defects where the attack of adsorbed species can more easily damage the film.

We conclude this brief account of previous results with a few words on the nature of the Au-thiolate bond. Formally, the bonding arises from a radical species, RS^\bullet , coupled with the electrons of the metal substrate to give a diamagnetic thiolate, RS^- . On a metal substrate the extent of charge transfer is determined by the chemical potential of the two interacting units and the actual nature of the adsorbate is intermediate between neutral RS^\bullet and RS^- . While it is generally accepted that the S-head of the thiol molecule is polar and carries a partial negative charge, the amount of this charge cannot be determined precisely since atomic charges are not quantum-mechanical observables.

2. Computational Details

To calculate the properties of Cs atoms interacting with thiol molecules supported on Au(111) we have used a Au_{18} cluster model with 12 atoms in the first and 6 atoms in the second layer, Figure 1. The Au atomic positions have been taken from bulk gold and kept frozen during the geometry optimization of the adsorbates; the Au-Au interatomic distance is 2.88 Å. In general, finite clusters are not good models of extended metal surfaces. However, the use of periodic slab calculations would pose considerable problems. In fact, in this work we are interested in the study of the interaction of Cs atoms at long distances from a Au surface. This implies that one should use a very large vacuum to separate the Au slabs which represent the Au(111) surface. Furthermore, the ionic nature of adsorbed Cs strongly depends on the coverage. The modeling with periodic calculations of the charge transfer states implies the use of very large supercells in order to screen the surface dipole which results from the interaction.

Density functional theory (DFT) quantum-mechanical calculations have been carried out using the gradient corrected Becke's three parameters hybrid exchange functional⁴² in combination with the correlation functional of Lee, Yang, and Parr⁴³ (B3LYP). This is probably the best functional available for molecular interactions. It is known that DFT does not properly describe dispersion forces which are important in stabilizing self-assembled monolayers on metal substrates.⁴⁴ Furthermore, large oscillations have been encountered in the description of the Au-SR bond with different functionals (see refs 16–19 and 35). This prevents us from quantitative estimates of the energetics of some of the processes investigated in this study.

The Au and Cs atoms have been treated with a small core relativistic effective core potential, ECP. The ECP of three central Au atoms explicitly includes in the valence the $5s^2 5p^6$ -

TABLE 1: Energetics of the Interaction of a Cs Atom or a Cs⁺ Ion with a Gas-Phase Thiolate Species

no.	reaction	ΔE , eV
1	$\text{Cs}^\bullet + \text{H}-\text{CH}_2(\text{CH}_2)_2\text{SH} \rightarrow \text{Cs}-\text{CH}_2(\text{CH}_2)_2\text{SH} + \frac{1}{2}\text{H}_2$	+1.83
2	$\text{Cs}^\bullet + \text{H}-\text{CH}_2(\text{CH}_2)_2\text{SH} \rightarrow \text{Cs}-\text{H} + \frac{1}{2}[-\text{CH}_2(\text{CH}_2)_2\text{SH}]_2$	+1.37
3	$\text{Cs}^\bullet + \text{CH}_3-(\text{CH}_2)_2\text{SH} \rightarrow \text{Cs}-\text{CH}_2\text{CH}_2\text{SH} + \frac{1}{2}[-\text{CH}_3]_2$	+1.23
4	$\text{Cs}^\bullet + \text{CH}_3-(\text{CH}_2)_2\text{SH} \rightarrow \text{Cs}-\text{CH}_3 + \frac{1}{2}[-\text{CH}_2\text{CH}_2\text{SH}]_2$	+1.57
5	$\text{Cs}^\bullet + \text{CH}_3(\text{CH}_2)_2-\text{SH} \rightarrow \text{Cs}-(\text{CH}_2)_2\text{CH}_3 + \frac{1}{2}[-\text{SH}]_2$	+1.61
6	$\text{Cs}^\bullet + \text{CH}_3(\text{CH}_2)_2-\text{SH} \rightarrow \text{Cs}-\text{SH} + \frac{1}{2}[-(\text{CH}_2)_2\text{CH}_3]_2$	-1.25
7	$\text{Cs}^\bullet + \text{CH}_3(\text{CH}_2)_2\text{S}^- \rightarrow (\text{Cs}-\text{S})^- + \frac{1}{2}[-(\text{CH}_2)_2\text{CH}_3]_2$	+0.07
8	$\text{Cs}^\bullet + \text{CH}_3(\text{CH}_2)_2\text{S}^- \rightarrow [\text{CH}_3(\text{CH}_2)_2\text{S}-\text{Cs}]^\bullet$	-0.88
9	$\text{Cs}^\bullet + \text{CH}_3(\text{CH}_2)_2\text{S}^\bullet \rightarrow \text{CH}_3(\text{CH}_2)_2\text{S}-\text{Cs}$	-1.98
10	$\text{Cs}^+ + \text{H}-\text{CH}_2(\text{CH}_2)_2\text{SH} \rightarrow \text{Cs}-\text{CH}_2(\text{CH}_2)_2\text{SH} + \text{H}^+$	+13.90
11	$\text{Cs}^+ + \text{H}-\text{CH}_2(\text{CH}_2)_2\text{SH} \rightarrow \text{Cs}-\text{H} + \text{CH}_2=\text{CH}_2 + [\text{CH}_2\text{SH}]^+$	+7.02 ^a
12	$\text{Cs}^+ + \text{CH}_3-(\text{CH}_2)_2\text{SH} \rightarrow \text{Cs}-(\text{CH}_2)_2\text{SH} + \text{CH}_3^+$	+9.11
13	$\text{Cs}^+ + \text{CH}_3-(\text{CH}_2)_2\text{SH} \rightarrow \text{Cs}-\text{CH}_3 + (\text{CH}_2)_2\text{SH}^+$	+6.18
14	$\text{Cs}^+ + \text{CH}_3(\text{CH}_2)_2-\text{SH} \rightarrow \text{Cs}-(\text{CH}_2)_2\text{CH}_3 + \text{SH}^+$	+11.2
15	$\text{Cs}^+ + \text{CH}_3(\text{CH}_2)_2-\text{SH} \rightarrow \text{Cs}-\text{SH} + \text{CH}_3\text{CH}_2\text{CH}_2^+$	+4.24
16	$\text{Cs}^+ + \text{CH}_3(\text{CH}_2)_2\text{S}^- \rightarrow \text{CH}_3(\text{CH}_2)_2\text{S}-\text{Cs}$	-4.07
17	$\text{Cs}^+ + \text{CH}_3(\text{CH}_2)_2\text{S}^\bullet \rightarrow [\text{CH}_3(\text{CH}_2)_2\text{S}-\text{Cs}]^\bullet$	-0.39
18	$\text{Cs}^+ + \text{CH}_3(\text{CH}_2)_2-\text{S}^- \rightarrow \text{Cs}-\text{S}^\bullet + \frac{1}{2}[\text{CH}_3(\text{CH}_2)_2-]_2$	-3.04

^a In this case the reaction proceeds by formation of $[\text{CH}_2(\text{CH}_2)_2\text{SH}]^+$ which is unstable toward dissociation into $\text{CH}_2=\text{CH}_2 + [\text{CH}_2\text{SH}]^+$.

5d¹⁰6s¹ electrons (19-electrons ECP), while the remaining Au atoms have been treated with a 11-electrons ECP (5d¹⁰6s¹). The ECP of Cs treats as valence the 5s²5p⁶6s¹ electrons. The basis sets used are Lanl2dz with the 19-electrons ECP and Lanl1dz with the 11-electrons ECP for Au⁴⁵ and Lanl2dz for Cs,⁴⁵ respectively. With this approach the electron affinity of the Au₁₈ cluster is 2.69 eV, to be compared with the experimental work function of the Au(111) surface, 5.31 eV.⁴⁶ The ionization potential of the Cs atom, +3.96 eV, is very close to the experimental value, 3.89 eV.⁴⁶ The standard all electron 6-31G basis set^{47,48} was used on H, C, atoms while on S we used an extended 6-311+G* basis set including diffuse and polarization functions. Geometry optimizations have been performed by means of analytical gradients with no symmetry constraints. The calculations have been performed using the Gaussian-98 program package.⁴⁹

3. Results and Discussions

3.1. Interaction of Cs and Cs⁺ with C—C, C—H, and C—S Bonds: Gas-Phase Reactions. We have considered first the gas-phase reaction of a neutral Cs atom with a propanethiol molecule, CH₃(CH₂)₂SH. Since the nature of an adsorbed thiol molecule is intermediate between neutral RS[•] and RS[−], it is useful to consider also the bonding of Cs with CH₃(CH₂)₂S[•] and CH₃(CH₂)₂S[−] fragments. In general, the interaction can involve various parts of the hydrocarbon chain, with rupture of the C—H, C—C, or C—S bonds. The working hypothesis is that the cost for the rupture of one of these covalent bonds is partially or totally compensated by the formation of the corresponding Cs—H, Cs—C, and Cs—S bonds on one side, and by the dimerization of the resulting fragments on the other (formation of H₂ or of longer R—R hydrocarbon chains; see Table 1). The results clearly show that the insertion of Cs into a C—C or C—H covalent bond is always highly endothermic. The rupture of the C—H bond with formation of Cs—R or Cs—H molecules has a net cost of 1.4–1.8 eV (see reactions 1 and 2 in Table 1); replacing a C—C bond with a C—Cs one costs 1.2–1.6 eV (see reactions 3–5 in Table 1). The corresponding barriers can be considerably higher. On this basis, it is possible to exclude any damage on the hydrocarbon chain induced by the deposition of neutral “cold” Cs atoms deposited with virtually no kinetic energy (0.1–0.3 meV).¹⁵

Things are different when we consider the interaction of Cs with the C—S bond. This process, which leads to the formation

of a (Cs—S)[−] or of a Cs—SH fragment on one side and of a R—R hydrocarbon chain on the other, either has a low cost, (Cs—S)[−], or is even exothermic by 1.2 eV, Cs—SH, Table 1, suggesting that a chemical attack of Cs more likely occurs at this point of the chain. This shows that if the adsorbed species is a RSH molecule, and assuming that Cs arrives in the neutral state on the surface, it is likely that this will result in the breaking of the thiol molecule with formation of a hydrocarbon chain.

The last case considered is that of the formation of a direct Cs—SR bond at the expenses of the Au—SR one (the present discussion does not take into account the bonding of the fragments to Au but this will be considered in § 3.3). In principle, one can form a [RS—Cs][−] complex which remains adsorbed on the Au surface or which may desorb depending on the adhesion energy and on the external temperature (see reaction 8 in Table 1). The calculations show that the [RS—Cs][−] complex in gas-phase is bound by 0.9 eV with respect to the isolated fragments. Not surprisingly, the neutral RS—Cs complex is even more stable (2.0 eV) with respect to RS[•] and Cs[•] radicals, see reaction 9 in Table 1. This suggests that when Cs atoms interact with the thiol film, the reaction will take place more likely at sulfur. Of course, this does not take into account problems such as the bond energy of the thiolate to the Au substrate or the mechanism of diffusion of the Cs atom through the film which will be discussed in the following sections.

It is possible that the interacting species is not neutral Cs but rather a Cs⁺ cation. Cs is the most electropositive element, and it has a pronounced tendency to become Cs⁺ when adsorbed on a metal surface (see section 3.2). With Cs⁺ the rupture of the C—H or C—C bonds is no longer radicalic and involves the formation of a proton, H⁺, or of a carbocation, R⁺. The net cost in gas-phase is of several eV; see reactions 10–15 in Table 1. Of course, the binding of the resulting positively charged species to the Au substrate will partly compensate for the large cost, but high barriers are expected for the reaction. Thus, a direct damage of the hydrocarbon chain induced by the Cs⁺ cation is very unlikely on the basis of the results of Table 1.

Things are very different if the interaction involves the detachment of the thiolate from the Au substrate and the formation of a CH₃(CH₂)_xS—Cs complex. This latter species, deriving from the combination of Cs⁺ with a CH₃(CH₂)_xS[−] thiolate anion (reaction 16 in Table 1), is 4.1 eV more stable than the separated charged fragments. This means that if the Cs⁺ cation can directly attack the polar head of the thiol chain

the consequent energy release could be sufficient to induce the desorption of the thiolate from the surface with consequent damage of the SAM film. Another possible reaction is that of Cs^+ with the S atom to form a Cs-S molecule and a hydrocarbon (see reaction 18 in Table 1). In gas-phase this leads to an energy gain of 3 eV. Thus, the working hypothesis of a direct Cs^+-S interaction appears more likely, at least based on purely thermodynamic arguments.

3.2. Formation of Cs^+ . In this section, we analyze the formation of Cs^+ on the Au(111) substrate. The adsorption and the nature of the bond of alkali-metal atoms on metal surfaces have been the subject of a large number of theoretical and experimental studies.^{50–54} A typical signature of the alkali-metal bonding is the change in metal work function Φ . For very low coverage, θ , Φ decreases considerably (by 2–3 eV) until it reaches a minimum for $\theta \approx 0.2$ monolayers. For higher coverages Φ increases until it reaches a plateau in correspondence of the formation of a full monolayer. The classical interpretation is that for low θ the alkali metal atom M donates a full electron to the substrate becoming M^+ .^{55,56} The presence of a cation on the surface induces a polarization of the metal substrate with formation of an image charge and of a surface dipole which reduces the cost to extract electrons from the surface (lowering of Φ). The more cations are present on the surface, the larger is the effect, thus justifying the rapid decrease in work function as θ grows from 0 to ≈ 0.2 . However, as the number of adsorbed cations increases, the build up of positive charge on the surface leads to a Coulomb repulsion among the adsorbates. For $\theta > 0.2$, electrons flow back from the substrate to the alkali cation, with reduction of the surface dipole and increase of Φ . Notice that for this reason the use of periodic supercell approaches to model the charge transfer from an alkali-metal atom to the Au surface is possible only using large supercells, representative of very low coverage. As an alternative one can use cluster models which have been shown to properly describe the bonding of isolated alkali atoms on metal surfaces.^{53,54,56} The work function reaches a stable value after formation of a complete monolayer. Thus, the change in Φ is directly related to the formation of a surface dipole. Here we used this observable property to monitor the Cs/Au interaction.

The analysis of the dipole moment μ as function of the distance of Cs from a Au_{18} cluster model of the Au(111) surface, Figure 2, provides a clear indication of the ionic nature adsorbate.^{56,57} For an adsorbed cation with $q = +1$ and a corresponding image charge $q = -1$ separated by a distance z , $\mu = q \times z$ and $d\mu/dz = +1$; thus the $\mu(z)$ curve is a straight line with slope +1. The Taylor expansion of the dipole moment curve about the equilibrium $z = z_e$ is

$$\mu(z) = \mu_0 + (d\mu/dz)(z - z_e) + (d^2\mu/dz^2)(z - z_e)^2 \quad (3)$$

Figure 2 shows that the $\mu(z)$ curve for Cs-Au_{18} is almost perfectly linear and presents a slope of +1.15, providing strong compelling evidence for the ionic character of the Cs adsorbate. The charge transfer at equilibrium distance is further shown by the net charge of +0.85 on Cs and by a spin population for this atom close to zero (the $\text{Au}_{18}\text{-Cs}$ complex has a doublet ground state).

The Cs-Au_{18} potential energy curve shows a deep minimum at $z = 3.5$ Å; here the $\text{Cs}^+-\text{Au}_{18}^-$ complex is more stable than the corresponding neutral fragments by 1.98 eV. Even for relatively long distances, 10 Å, the $\text{Cs}^+-\text{Au}_{18}^-$ complex is more stable than Cs and Au_{18} by ≈ 0.1 eV. This shows that on a clean Au surface the transfer of one electron and the formation of

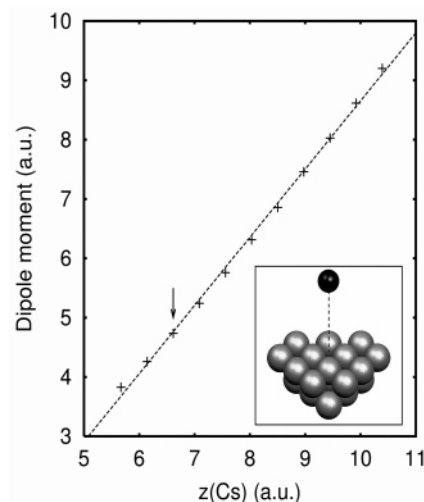


Figure 2. Dipole moment (in au) as a function of the distance (in au) of a Cs atom from a Au_{18} cluster model (inset) of the Au(111) surface. The arrow indicates the equilibrium distance of Cs from the surface.

Cs^+ is energetically favorable even when the atom is far from the surface. Notice that in our calculations the electron affinity (EA) of the Au surface, 2.69 eV, is considerably underestimated with respect to the Au(111) work function, 5.31 eV⁴⁶ (the IP of Cs, 3.9 eV,⁴⁶ is well described). Despite the limited description of the tendency of Au to accept electrons, the charge transfer occurs even for long surface–Cs distances. The next question is if the process is possible also in the presence of an adsorbed alkanethiol molecule.

To this end the following model has been constructed. A S-CH_3 methanethiol has been adsorbed on the Au_{18} cluster. The organic molecule has been placed with the S atom above a 3-fold hollow site and the geometry has been optimized. In the minimum geometry the S atom occupies a bridge site with a distance from the surface plane of 2.29 Å and the methyl group is tilted by 59° from the surface normal. A doublet ground state has been considered for the $\text{Au}_{18}\text{-SCH}_3$ complex. The Cs atom has been moved along the normal to the Au(111) plane directly above the S atom. Thus, the SCH_3 molecule is between Cs and Au_{18} . In this phase no geometry reoptimization of the $\text{Au}_{18}\text{-SCH}_3$ complex has been attempted as the distance of Cs from the surface has been varied. In this respect, the calculations have a purely qualitative purpose.

The interaction of Cs with $\text{Au}_{18}\text{-SCH}_3$ can result in a charge transfer from Cs to Au, as observed in absence of the thiol molecule, or in the formation of a weakly bound complex where the Cs atom is interacting with the methyl group without losing its valence electron. The occurrence of the charge transfer has been monitored by analyzing the charge on Cs. At very long $\text{Au}_{18}\text{-SCH}_3\text{-Cs}$ distances the lowest state corresponds to the neutral fragments (triplet state), with one unpaired electron on $\text{Au}_{18}\text{-SCH}_3$ and the second on the 6s orbital of Cs; the occurrence of a $\text{Cs} \rightarrow \text{Au}$ charge transfer at shorter distances will result in a closed shell ground state with no population of this atomic level.

We have been able to identify two electronic states with different stability. For long Au–Cs distances, $r > 14$ Å, the $\text{Cs-Au}_{18}\text{SCH}_3$ neutral state is preferred but for distances below 14 Å the $\text{Cs}^+(\text{Au}_{18}\text{SCH}_3)^-$ charge transfer state becomes lower in energy. The charge-transfer nature of the interaction is clearly shown by the net charge on Cs, +0.94, for $r(\text{Cs-S}) \approx r_e = 4.4$ Å. Thus, the charge transfer from the alkali metal to Au occurs even in the presence of the methanethiol molecule. With respect

to the clean Au surface the charge transfer takes place at even longer distance, probably because of the electronegative nature of the sulfur atom. Notice once more that this result is obtained using a “limited” description of the Au work function (low EA of Au₁₈). For an extended surface the charge transfer curve will be rigidly shifted by ≈ 2.6 eV to lower energies. Correspondingly, the crossing between the “neutral” and the “charge transfer” curves is expected to move to even longer Au–Cs distances. Of course the present analysis holds for a small film thickness (the methanethiol group extends for about 4–4.5 Å from the surface). To confirm the occurrence of the charge transfer we have considered a longer chain thiol, SCH₂CH₃ and the Cs atom has been moved along the vertical of the C of the terminal CH₃ group. The results show that the charge transfer occurs also in this case, at a distance from the surface of about 10 Å.

To summarize this section, we have shown (a) that at low doses of Cs the interaction with the Au substrate implies an electron transfer and the formation of an adsorbed Cs⁺ cation and (b) that this process occurs also in the presence of an adsorbed thiol molecule. The charge transfer is a nonactivated process and occurs when Cs is far away from the Au surface. This suggests that even “cold” Cs atoms can form Cs⁺ ions. The formation of an electron rich surface on one side and of a Cs⁺ ion on the other side of the SAM provides the driving force for the diffusion of the Cs⁺ ions through the organic chains. The average spacing between the S atoms on Au(111) is ≈ 5 Å,³⁸ and the diameter of the alkane chains ≈ 4.3 Å, i.e., 0.7 Å smaller than the separation between the headgroups. Cs⁺ has an ionic radius of 1.8 ± 0.1 Å.⁴⁶ so that in order to allow the migration along the chains some increase of the distance among the chains is needed. The migration mechanism has not been investigated here but very recent studies have shown that vapor-deposited Cu, Ag and Au neutral atoms penetrate into a SAM film on Au(111) through dynamic formation of diffusion channels in the SAM.⁵⁸ Thus, diffusion through the SAM can occur even for neutral Cs atoms. When this occurs, Cs⁺ ions will form at a distance of about 10 Å from the surface and then will easily migrate to the Au–S interface.

The behavior of alkanethiol molecules on Au(111) under local electric field and tunneling current has been studied in STM experiments with molecular resolution.² Our conclusion that the thiol layer does not prevent Cs from donating one electron to the Au substrate is consistent with the observation that the alkyl molecules do not make a significant contribution to the tunneling current in STM as the electronic density of states of hydrocarbon chains is sufficiently distant from the Fermi level of Au substrate and of the tungsten tip.

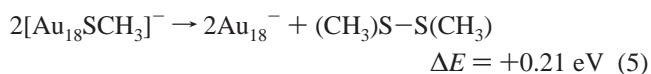
In the STM experiment it has been found that for a positive bias of +2.5 V (sample positive), field induced desorption of decanethiol molecules occurs. The field induced desorption was attributed to a local change in the polarity and weakening of the S–Au bonds.² However, desorption can be induced also by the effect of the tunneling current (tunneling electrons are known to cause the dissociation of chemical bonds). The local electric field in the STM experiments is estimated to be 1.9×10^9 V/m. This is of the same order of magnitude of that generated by a Cs⁺ cation at ≈ 10 Å (20 au) from the metal surface, $\approx 1.2 \times 10^9$ V/m (obtained as the potential energy of two +1/–1 charges at 10 Å, ≈ 1.2 eV, divided by their distance, 10^{-9} m). Although we cannot provide support for the hypothesis that the electron flow from Cs atoms to the Au–SR interface is a mechanism for the film damage, this possibility cannot be excluded a priori.

3.3. Interaction of Cs with Au(111)SCH₃. In this section we consider the direct interaction of a Cs⁺ cation with the polar head of a methylthiol adsorbed on Au. The model used is that of SCH₃ adsorbed on the Au₁₈ cluster. The adsorption energy of the SCH₃ radical to Au₁₈, 0.56 eV, is much too low compared to the experimental estimates of 1.5–2 eV.^{1,20,25,26} The low binding of SCH₃ to Au₁₈ reflects the inadequate description of the Au conduction band by a finite cluster. A considerably stronger bonding is obtained if instead of Au₁₈ we use a Au₁₈[–] cluster to represent the Au(111) surface (since Cs donates one electron to the substrate, this is also the real nature of the substrate in the presence of Cs). In the minimum of the [Au₁₈–SCH₃][–] complex the thiol geometry is similar to that of the neutral cluster, indicating the delocalization of the extra electron on the Au₁₈ substrate, but the bonding is much stronger:



Recent DFT periodic supercell calculations based on the revised version of the Perdew, Burke, and Ernzerhof exchange–correlation functional (RPBE),⁵⁹ rather accurate for chemisorption energies,⁵⁹ give for methanethiol on Au(111) a bond strength of 1.25 eV,¹⁹ almost identical to that obtained here with the B3LYP functional and a Au₁₈[–] cluster. Both values are underestimated compared to the experiment, 1.5–2 eV.^{1,20,25,26} This is due to limitations intrinsic to the DFT method. As it has been shown extensively,^{16,18,19} the Au–SR bond has important dispersion contributions that are not properly described at the DFT level and is strongly dependent on the form of exchange–correlation functional used,¹⁹ going from 1.2 eV with RPBE⁵⁸ to 1.7 eV with Perdew–Wang (PW-91).⁶⁰ The B3LYP functional used here provides very accurate energies for molecular compounds but underestimates the Au–SR bond strength. For this reason, the energetics of the reactions discussed in the following is affected by some errors which, however, do not alter the general conclusions of our study.

On Au₁₈[–], the desorption of the (SCH₃)₂ dimer is endothermic, as found experimentally, with a desorption energy of 0.21 eV, about 1 eV lower than in the experiment, 1–1.3 eV,^{20,25} for the reasons illustrated above:



The optimal structure of a Cs⁺ cation adsorbed on Au₁₈[–] in the presence of SCH₃ is shown in Figure 1 (notice that the whole system is neutral being derived from the interaction of Cs with Au₁₈SCH₃). Cs occupies a three-hollow site while the thiol molecule has been slightly displaced from the position occupied in absence of Cs and binds on-top of a Au atom. The ground state is singlet, and the analysis of the charge distribution clearly shows the cationic nature of Cs. The process is thus



The adsorption of Cs with formation of the Cs⁺–[Au₁₈SCH₃][–] complex releases more than 2.5 eV! This value is an under bound to the real interaction energy because the EA of the Au₁₈ cluster is lower than the work function of Au(111). Thus, in reality the energy gain in reaction 6 can be even higher. The thermal energy released in (6) is dissipated by exciting the phonon modes of both substrate and adsorbate. The energy released largely exceeds that required to desorb a RS–SR dimer

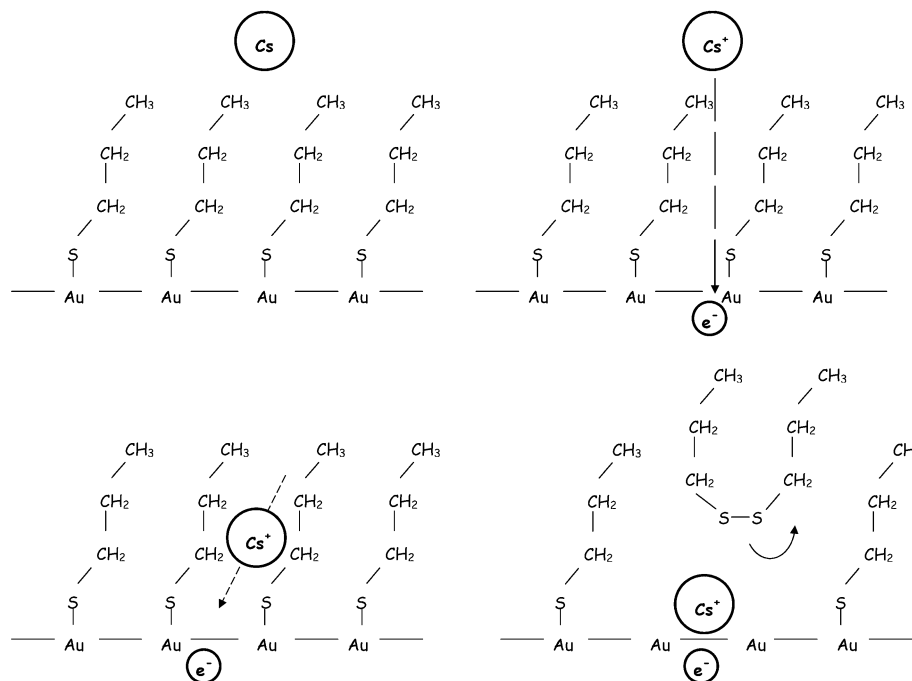
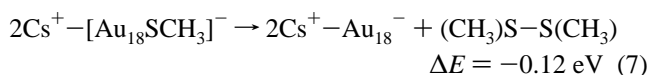


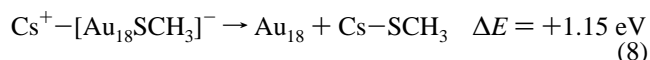
Figure 3. Schematic representation of the interaction of a Cs atom with a SAM of thiol molecules on Au(111): (a) Cs atoms are deposited on the film from the gas-phase with very low kinetic energy; (b) Cs donates one electron to the Au substrate and becomes Cs⁺ at long distance from the surface; (c) the Cs⁺ ion is attracted toward the Au-S interface and diffuses through the film; (d) the energy released in steps a–c promotes the desorption of a dithiol molecule.

even if we consider the experimental value for desorption of disulfide molecules, 1–1.3 eV. Thus, the following step is

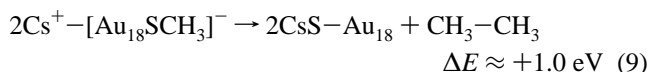


In our approach reaction 7 is slightly exothermic (by 0.12 eV), indicating that the adsorption of Cs⁺ weakens the Au–S bond to such an extent that formation of a gas-phase disulfide molecule is thermodynamically favored in the presence of Cs⁺. This result is partially due to the underestimate of the Au–SR bond strength. If we consider that reaction 5 has an error of ≈ 1 eV, and we apply this correction to reaction 7, the estimated cost for disulfide desorption in the presence of Cs⁺ becomes $\approx +0.9$ eV, to be compared with the energy released in (6), -2.5 eV. Thus, the desorption of disulfide molecules is overcompensated by the energy released in reaction 6.

Before to conclude this discussion, we mention two other reactions that cannot be a priori ruled out as the steps that follow the formation of the Cs⁺–[Au₁₈SCH₃][–] complex. One implies the formation and desorption of a Cs–SCH₃ complex from the combination of Cs⁺ and (SCH₃)[–]. However, the desorption of the Cs–SCH₃ neutral complex from Au₁₈ has a cost of 1.15 eV, and largely exceeds that of desorbing a disulfide molecule:



Another possibility is that the adsorption of Cs results in the breaking of the S–R bond with desorption of a hydrocarbon molecule:



Also in this case the process is endothermic and is less favorable than the desorption of a RS–SR dimer (the energy of the process

was estimated by imposing that the S atom remains on a three-hollow site of the Au(111) surface).

To summarize, neither reaction 8 nor reaction 9 appear to be competitive with respect to disulfide formation, reaction 7. Thus, the conclusion is that the damage in the SAM originates from the desorption of the RS–SR dimers induced by the thermal energy released by Cs adsorption.

4. Conclusions

In this paper, we have considered a possible mechanism to explain the observed damage of self-assembled monolayers of alkanethiols on Au(111) induced by the deposition of “cold” Cs atoms which arrive on the surface with kinetic energies of the order of 0.1–0.3 meV.¹⁵ A number of hypotheses about the interaction mode of Cs with the thiol molecule have been supported or discarded based on accurate quantum-chemical calculation. The working hypothesis is that the damage of the SAM arises from a direct chemical attack of Cs to the Au–thiol bonding. The calculations in fact show unambiguously that a damage of the alkyl chain with rupture of C–C or C–H bonds induced by Cs atoms or Cs⁺ ions is energetically unfavorable and implies high barriers which are totally incompatible with the low-temperature at which the nanolithographic processes are performed. On the other hand, a direct attack of Cs and in particular of Cs⁺ to the Au–S bond seems energetically more feasible.

Using cluster models of the Au–thiol system we have shown that Cs atoms arriving from the gas phase feel the chemical potential of the Au surface even at long distances from it, Figure 3a. This results in a charge transfer with formation of Cs⁺ and an electron rich Au surface, Figure 3b, consistent with the fact that the cost to extract one electron from Cs, 3.96 eV, is smaller than the work function of Au(111), 5.31 eV.⁴⁶ We have shown that the charge transfer occurs even in the presence of an alkanethiol molecule and is a nonactivated process. Of course, long-chain thiols forming a layer of 2–3 nm thickness can

inhibit the electron transfer. However, it has been recently proven that even neutral atoms can diffuse through SAM monolayers.⁵⁸ The fact that short-chain thiols are more sensitive than long-chain thiols¹⁴ is consistent with the proposed mechanism (a direct attack of Cs to the hydrocarbon chain would be independent of the chain length). Once formed, the Cs⁺ ion is attracted by electrostatic forces toward the Au surface, also because of the polar nature of the S-head of the thiolate, and diffuses through the alkyl chains to the interface, Figure 3c. The interaction of the Cs⁺ cation with the Au–thiolate complex releases locally a considerable amount of thermal energy which is sufficient to overcome the barriers involved in the recombination of SR fragments to form RS–SR dimers and in their desorption from the Au(111) surface, Figure 3d.

Notice that the proposed mechanism holds also in the hypothesis that on the surface are present undissociated thiol molecules, RSH, instead of RS thiolate fragments. In fact, the RSH molecules are weakly bound to the surface and desorb around room temperature or below.²⁵ The thermal energy gained in the $\text{Cs} + \text{Au} \rightarrow \text{Cs}^+ + \text{Au}^-$ process exceeds the binding energy of the thiol molecule, so that desorption and consequent film damage are expected also in this case.

Acknowledgment. This work has been supported by the Italian Ministry of Research through a FIRB project on “Manipulation on the nanometer scale by laser-cooling technologies”. We thank Prof. Ennio Arimondo for useful comments and discussions.

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