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Does the S-H Bond Always Break after Adsorption of an Alkylthiol on Au(111)?

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Abstract

The reaction mechanism for the formation of alkyl thiol SAM on Au(111) is still not clearly understood. Especially, the role of defects on the chemisorption process is an important goal to be addressed. In this work, different minimum energy reaction paths of R-SH dissociation of thiols (with long and short chains and di-thiol species) adsorbed on gold adatom are calculated using periodic density functional theory. Our results show a lower energy barrier for the RS-bond dissociation when two thiols are adsorbed per adatom. In addition, in contrast with the formation of an adatom at the Au(111) which has been shown to depend on the alkyl chain length, the activation energy of the RS-H bond dissociation of thiols adsorbed on an adatom was shown to be independent of the alkyl chain length. The presented results and derived hypothesis support the model that thiols with long alkyl chain thiols mainly adsorb molecularly on Au(111), while for short alkyl chain thiols the S-H bond breaks. This result is explained by the fact that short chain thiols have a lower inter-chain interaction energies and are thus more mobile compared to the long alkyl chain thiols on the Au(111) surface. This feature enables the short chains to reach adequate geometries, driven by entropy, which could deform the Au(111) more drastically and probably pull Au atoms out from surface to form adatoms. With these results a new mechanism is proposed for the formation of alkyl chain thiols on Au(111).

Keywords: SAM, Thiol, S-H bond, Adatoms, Reaction path

Introduction

Due to the vast variety of applications of Self-Assembled Monolayers (SAMs) such as lubrication, electrochemistry, electronic and vibrational spectroscopy, photochemistry, electrical conduction, catalysis, and biological membranes etc., preparation and structural characterization of these interfaces have been of great interest for more than three decades¹.

Alkanethiol/alkanethiolate adsorbates on coinage metal surfaces are widely exploited, particularly the SAMs on Au(111) surface, being the most well-known²⁻⁸. However, the detailed nature of the interface structures starts only now to be revealed by combining experiments and quantum chemical calculations⁹. It is mostly assumed that in the first steps of the formation of SAMs on Au(111), thiolate radicals are involved (after the H-S bond cleavage of the alkanethiol), but how these radicals are formed after releasing an H atom is not yet fully understood.^{10, 11}

First attempts to explain the thiolate radical formation using DFT methods were performed by Busnengo et al.¹⁰ at the molecular level by means of DFT calculations. They showed a reaction pathway for S-H bond breaking of methanethiol on a flat Au(111) surface calculating the associated activation energies. This work, however, only considers the shortest of the alkyl thiols' H-SCH₃ bond cleavage on a clean, defect-free Au(111).

The evidenced role of gold surface defects and particularly Au adatoms may hold the key to the characterization of the thiolate geometry. Indeed, several recent experimental and theoretical studies¹²⁻¹⁷ indicate that thiolate-induced reconstruction may also occur on the Au(111) surface¹⁸⁻²⁴.

Two rather different models of these Au-adatom-thiolate moieties have emerged from different experiments. Low temperature STM imaging conducted at low coverage (only a few % of a monolayer) on the methanethiolate species¹⁵ provides evidence for an Au-dithiolate moiety in which the Au adatom occupies a bridge site relative to the underlying Au(111) surface layer; both S head group atoms are bonded to opposite sides of this adatom such that they occupy near-atop sites relative to the underlying Au surface atoms. Experimental groups observed this Au-dithiolate ordering for propanethiolate²⁵ and butanethiolate¹⁶ at low or intermediate coverage. In DFT studies, thiolate-induced reconstruction of the Au(111) had also been considered^{9, 17, 26, 27}. The preference for an ethanethiolate to adsorb on atop geometry if there is an Au adatom on the surface has also been predicted by calculations by Cometto et al.²⁸⁻³⁰. The total energy of this Au-adatom-thiolate moiety was almost identical at the fcc and hcp hollow sites, and the diffusion barrier between these sites is found to be very low, in agreement with experimental results at room temperature. Using combined experimental measurements and

DFT calculations, Maksymovych et al.¹⁵, have shown that Au-adatom-dithiolate moiety surface structure is energetically favored over the lowest energy structure on the unreconstructed surface. Grönbeck and Häkkinen³¹ have performed calculations on both of the adatom models discussed by others¹⁷, and on a third model in which Au adatoms occupy a mixture of fcc and hcp hollow sites while methanethiolate species bridge these adatoms. This last model has shown the lowest energy. These calculations also indicate an energetic preference for the dithiolate adatom model over the monothiolate adatom moiety. Other results are the work of Mazzarello et al.³² and Cossaro et al.³² that combines DFT-based molecular dynamic (MD) simulations with experimental surface X-ray diffraction data for the $(\sqrt{3} \times \sqrt{3})$ -methanethiolate and $(2\sqrt{3} \times 3)$ rect. hexanethiolate phases, respectively, and photoelectron diffraction data for the methanethiolate phase. The MD simulations favor models with a significant degree of disorder (higher for the methanethiolate species), comprising coexistence of both the Au-adatom-dithiolate species and thiolate species bonding to bridging sites on the underlying surface, together with a significant concentration of surface Au vacancies. It was found, with some modification in the relative coverage, to be consistent with the experimental work (Even some discrepancies in the computed relative coverage were found, these results showed a high concordance with experimental observations). In addition, in a recent work combining DFT calculations and XPS experiments, we have confirmed the spontaneous reconstruction of the surface, by formation of a Au adatom on the surface, shared with two thiol chains, structure that was earlier reported by Mazzarello et al.^{32,33}. Interestingly, the adatom formation was found to be dependent on the thiol chain length where shorter alkyl chains were found to induce a larger reconstruction, and consequently found to be more reactive.⁹ Moreover, the same thiol can form different types of assemblies dependent of the temperature and the coverage, especially for the case of the shortest alkyl chain thiol (methanethiol).³⁴

In a previous study we have investigated the adsorption energies and different geometries of the propanethiol in its molecular and radical states on three different surface unit cells²⁷, and later on we showed that the side chain length is related to the gold surface reconstruction⁹. However, it is not clear yet, a) how the H-S bond cleavage process of adsorbed thiols occurs, b) what is the effect of the alkyl chain length on the H-S bond cleavage, and c) what is the influence of the presence of gold adatoms on the surface. Based on our previous results we investigated the H-S bond cleavage of thiols on gold adatoms as a function of the thiol alkyl chain length. A study in line with our earlier works on thiol self-assembled monolayers on gold surfaces.^{9, 27, 35-38}

Computational Details

Density Functional Theory (DFT) calculations were carried out using the Vienna Ab Initio Simulation Package (VASP)^{39,40}. Electron-electron exchange and correlation interactions were described within the Generalized Gradient Approximation (GGA) by employing the functional of Perdew, Burke and Ernzerhof (PBE)⁴¹. The Projector Augmented Wave (PAW)^{40,42} method was used for the electron-ion interactions. The electronic one-particle wave functions were expanded in a plane wave basis set, up to an energy cut-off of 400 eV. The metal surface was modeled by a slab consisting of five atomic layers that were separated by a vacuum region of 15 Å. The interlayer spacing in the surface was taken from the theoretical lattice parameter calculated for bulk gold (4.17 Å). According to experimental results, the adsorption of thiols forms a $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell. For the surface $5 \times 5 \times 1$, Γ centered k-points were used. As regards the convergence tests of the energy of the model we refer to our previous work^{27,43}.

The adsorption energies (vide ultra) are calculated using as reference the corresponding Au(111) slabs, with or without adatom. The energy of the isolated molecules is obtained after optimization of its start geometry as found in the SAM. No spin polarization nor dipole corrections were considered on this metallic system because of their negligible contributions to the total energy²⁷ and the unproportional needed calculation power. Dispersion corrections were also not included in the NEB calculations, since we consider isolated thiol molecules in our model reactions and it would only slow down the calculations and equally shift the adsorption energy but not the activation energies nor the relative energies²¹. However, in the calculation of the adsorption energies within the SAM the DFT-D3⁴⁴ method was used.

The transition states (TS) of the elementary steps were determined using the Nudged-Elastic-Band (NEB) method.⁴⁵ Reaction pathways were optimized with a set of eight intermediate geometries (sixteen in complex cases), obtained by linear interpolation with a mixed internal and cartesian coordinate system using the string method⁴⁶ as implemented in the Opt'n Path suite.⁴⁷ The obtained approximate transition states were refined by minimizing the residual forces below 10^{-2} eV.Å⁻¹ with the quasi-Newton algorithm implemented in VASP. All potential energy surface (PES) extrema were verified by the calculation of the vibrational frequencies within the harmonic approximation. The Hessian or force constant matrix was computed by finite differences on nuclei forces followed by a diagonalization procedure. The resulting eigenvalues correspond to the harmonic frequencies.

Results and discussion

In order to investigate the effect on the RS-H dissociation reaction mechanism of alkylthiols adsorbed on gold adatom and the effect of the thiol alkyl chain length, three different models are investigated: i) one propanethiol molecule C_3H_7-SH (Fig 1a), ii) two propanethiol molecules $C_6H_{14}-S_2H_2$ (Fig 1b), and iii) one undecanethiol molecule $C_{11}H_{23}-SH$ (Fig 1c). All these species are lying down and adsorbed on a gold adatom positioned on fcc site of Au(111) surface.

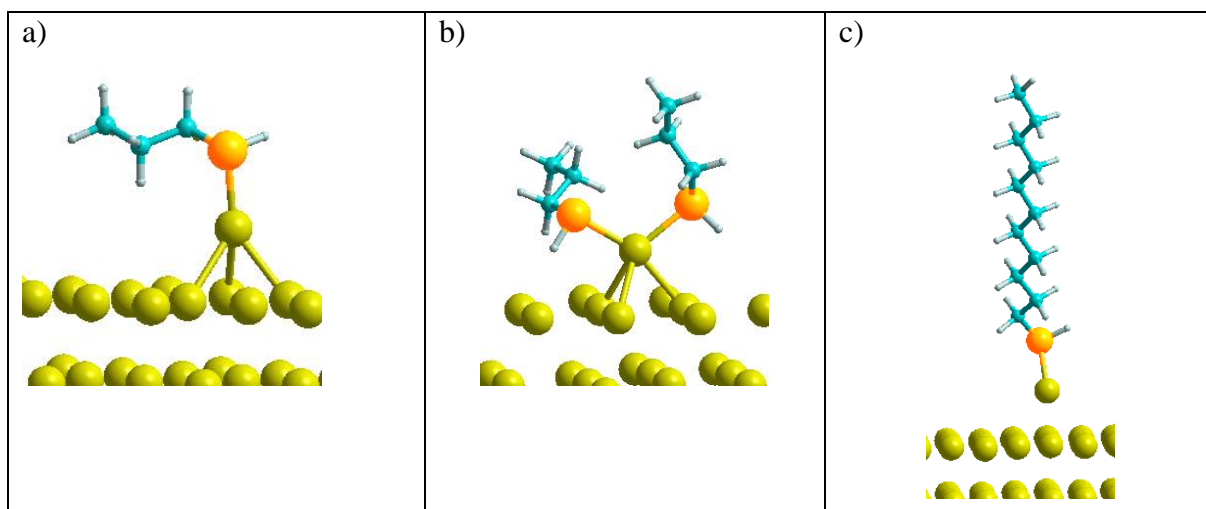


Figure 1: The three different models investigated: a) One propanethiol molecule adsorbed on gold adatom, b) Two propanethiol molecules adsorbed on gold adatom, and c) one undecanethiol molecule adsorbed on gold adatom. (carbon: light blue, gold: yellow, sulfur: orange, hydrogen: white)

Based on these models, three different minimum energy reaction pathways and their corresponding activation energy barriers (ΔE_{act}) for the H-S bond cleavage process on a adatom of Au(111) surface are identified. In the case of the propanethiol pathways, it should be noted that case a) the propanethiol molecule is almost in the lying-down position with an angle of 70° (See Fig. 2) and in case b) a second propanethiol molecule is positioned on a atop-site at 2.40 Å from the Au adatom (See Fig. 3).

Propanethiol (C_3H_7SH) adsorbs molecularly (physisorbed) on an adatom with an adsorption energy of -0.87 eV, being in agreement with our former calculation (-0.84 eV)²⁷. The studied reaction path includes two activation barriers: a first one (TS1) of 1.13 eV (being + 0.27 eV above the reference energy (slab and isolated thiol), and a second one (TS2), which corresponds

to the proton diffusion from Au adatom and Au surface atom (Fig. 2) of 0.30 eV (+0.05 eV above the reference energy value). The calculated activation energy is close to the value of 0.9 – 1.1 eV estimated from experiments (see ref. ⁶) and in agreement with earlier experimental data summarized in the review of Vericat et al.⁷. Interesting to mention is that the ΔE_{act} calculated for the deprotonation of HSCH₃ by Lustemberg et al. and reinterpreted by us is 0.90 eV¹⁰ on Au(111). Nevertheless, it is known that the methanethiol behaves differently compared with the longer alkyl chain thiols, e.g. the SAM organization is less ordered due to the weaker inter-chain interactions.

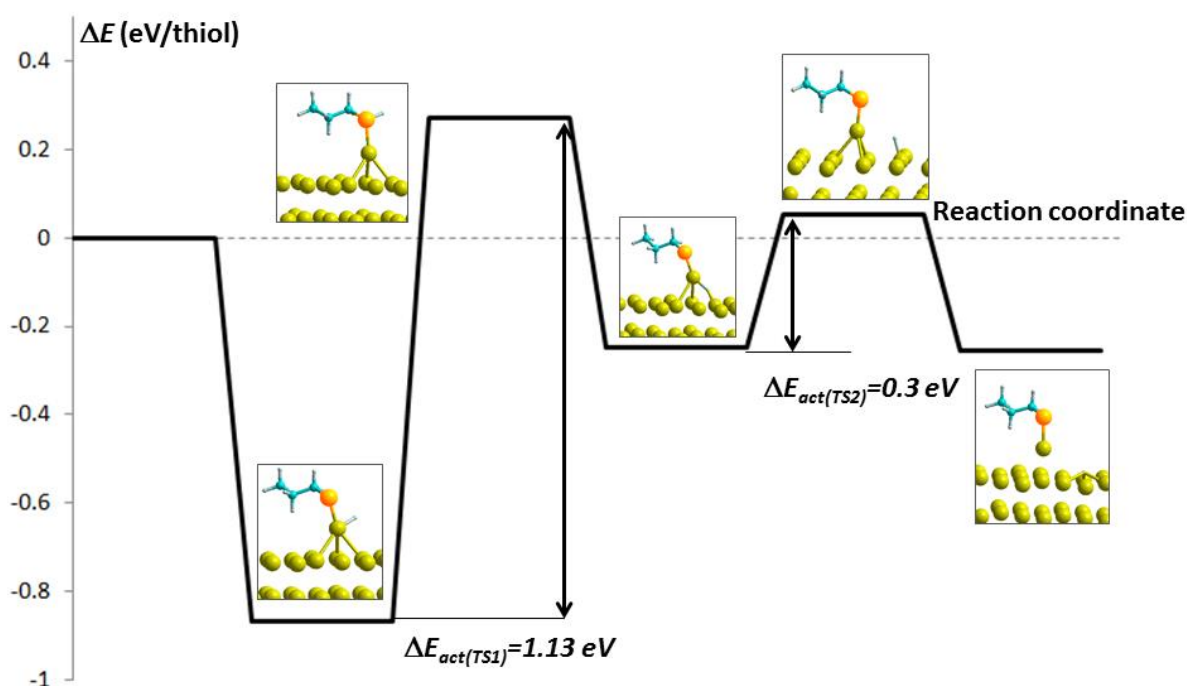


Figure 2. The reaction path for the S-H bond breaking for propanethiol on an adatom/Au(111). The energies reference ($E = 0$ eV/thiol) is calculated as the sum of the energies of bare surface, including Au adatom, and the free propanethiol molecule in gas phase. (Energies in eV, distances in Å, carbon: light blue, gold: yellow, sulfur: orange, hydrogen: white).

In the second considered reaction pathway, the model system contains a Au/Au(111)adatom- on which two thiol molecules are adsorbed. As reported in Figure 3, the overall reaction path includes two successive steps for the deprotonation of two dipropanethiol molecules. The initial reaction step corresponds to the adsorption of a second propanethiol on the Au adatom for which an adsorption energy of -0.4 eV is obtained. This energy is added to the adsorption energy of the first propanethiol, which is lower (less strongly adsorbed) compared with the first thiol

adsorption energy, of -0.87 eV (See Fig. 2). The reaction path includes two activation barriers, a) the breaking of the first RS-H bond (TS1) and b) the second RS-H bond (TS2), respectively.

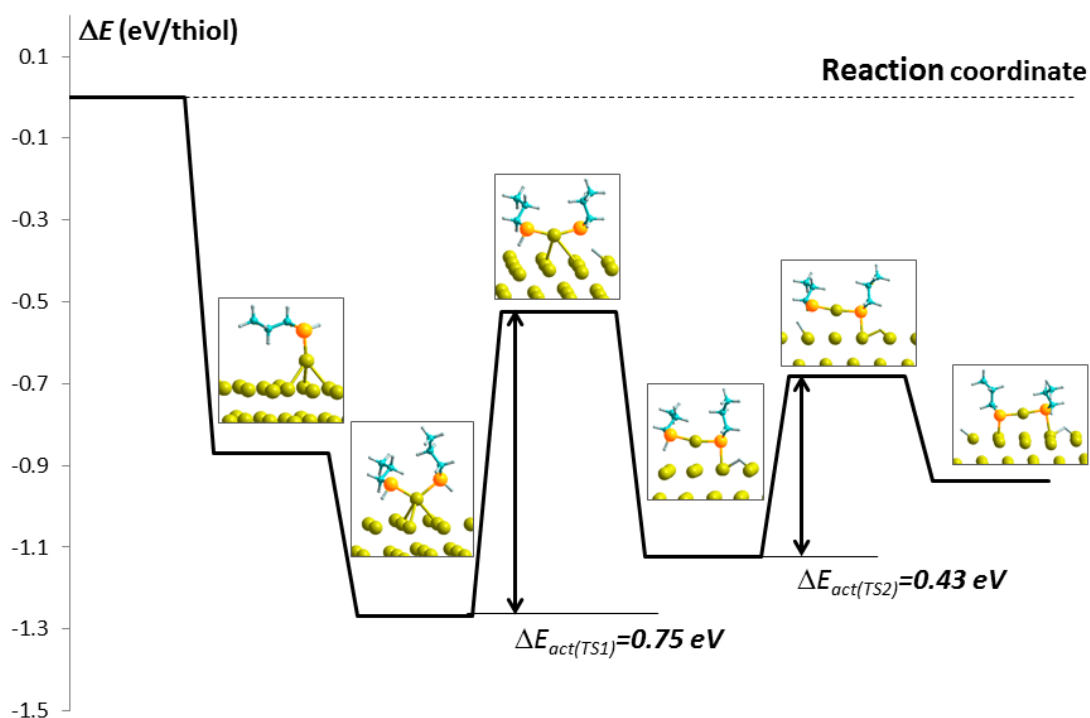


Figure 3. The reaction paths and corresponding geometries studied for the S-H bond breaking for two propanethiol molecules on an adatom/Au(111). The energies reference ($E = 0$ eV/thiol) is calculated as the sum of the energies of bare surface, including Au adatom, and the free propanethiol in gas phase.. (Energies in eV, distances in Å, carbon: light blue, gold: yellow, sulfur: orange, hydrogen: yellow small spheres)

The activation energy corresponding to the first RS-H bond breaking, calculated from TS1 (Fig 3), is equal to 0.75 eV, which is lower than the energy barrier calculated for isolated propanethiol. In addition, the proton transfer process occurring for dipropanethiol is different from the isolated propanethiol case. Indeed, the hydrogen atom does not interact with Au adatom (as for the case of isolated propanethiol) but moves directly to the flat Au(111) surface. The dissociation activation energy of the RS-H bond of the second propanethiol is found to be lower than for the first propanethiol ($\Delta E_{act} = 0.44$ eV; TS2, Fig 3)). This second activation energy is also lower than the activation energy calculated for the RS-H bond breaking in one propanethiol per adatom ($\Delta E_{act} = 1.13$ eV).

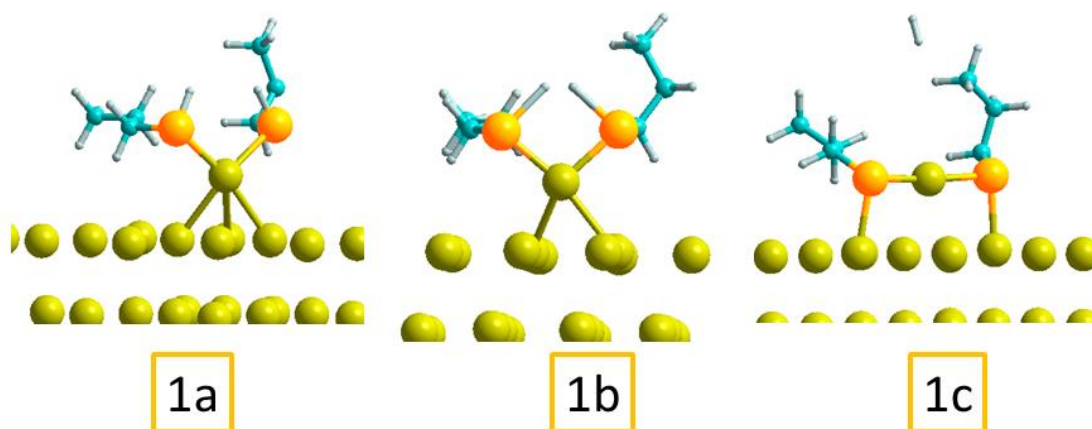


Figure 4: Reaction path with a concerted formation of dihydrogen after the adsorption of two propanethiols on Au adatom. 1a) adsorption of two propanethiols, 1b) transition state, 1c) product. (carbon: light blue, gold: yellow, sulfur: orange, hydrogen: white)

A second reaction mechanism was modeled (not reported reaction path) for the case of two propanethiols per adatom, namely the concerted formation of dihydrogen after the adsorption of two propanethiol molecules (See Fig. 4). This reaction shows a high calculated activation barrier of 1.75 eV, hence excluding this concerted molecular hydrogen formation compared with the single propanethiol molecule adsorption on Au/Au(111) adatom ($\Delta E_{\text{act}} = 1.13$ eV). However, the final chemical state (Figure 4, 1c) is thermodynamically stable by 0.40 eV compared with the two dissociated propanethiols chemisorbed on an adatom and two hydrogen atoms adsorbed on the Au(111) surface. The desorption of H₂ is thermodynamically favored, as expected. So, one can conclude that the formation of a chemisorbed propanethiol monolayer can be formed starting from the adsorption of two propanethiols on an adatom (in vacuum conditions), leading to the formation of H₂.

In the third case the propanethiol molecule in model system (See Fig. 1a) was substituted by an undecanethiol molecule (See Fig. 1c). Undecanethiol adsorbs on an adatom with energy of -1.54 eV. The reaction path for RS-H dissociation (See Fig. 4) is similar to the single propanethiol case (See Fig. 2). The barrier for the S-H bond breaking of undecanethiol is found to be of 1.13 eV, which is equal to the S-H bond breaking of propanethiol. For the hydrogen detachment and diffusion process the system has to overcome a small energy barrier of 0.23 eV which is also similar to the computed value in presence of short chain propanethiol.

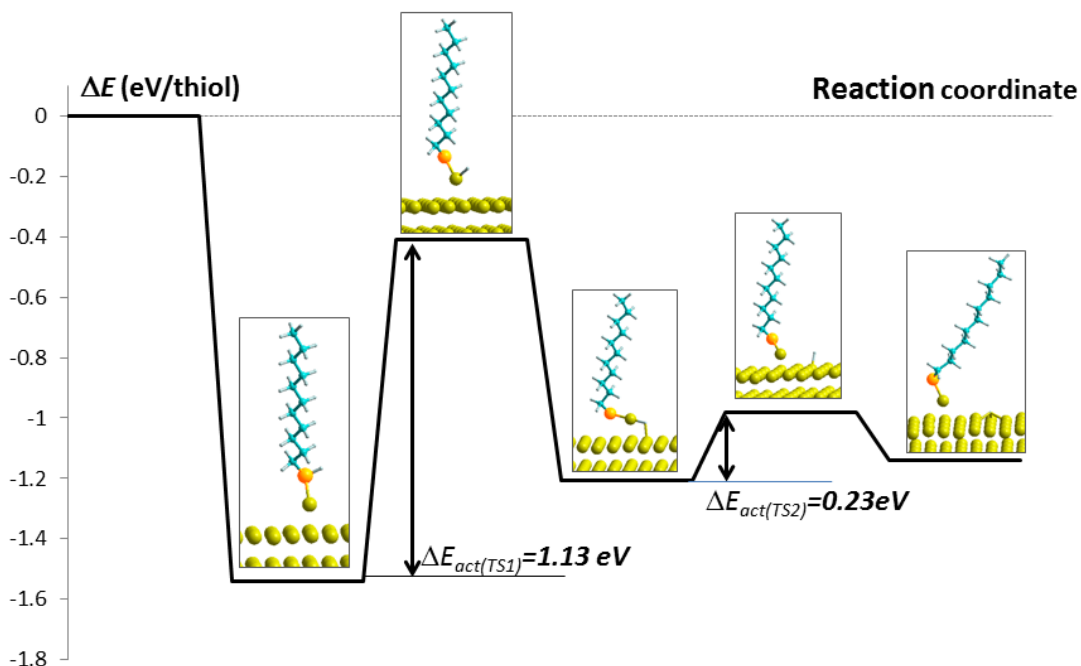


Figure 5. The reaction path for the S-H bond breaking for undecanethiol on an adatom/Au(111). The energies reference ($E = 0$ eV/thiol) is calculated the sum of the energies of bare surface, including Au adatom, and the free undecanethiol in gas phase. (Energies in eV, distances in Å, carbon: light blue, gold: yellow, sulfur: orange, hydrogen: white).

This result indicates at first sight that the activation energy for RS-H dissociation is independent of the alkyl chain length, but dependent on the surface reconstruction, such as the formation/presence of adatoms. This is in line with the fact that the estimated Au-S binding energy (ΔE_{bind}) is the same (≈ -2.6 eV) for both alkyl thiols. The cohesive energy of a Au atom is found to be 3.81 eV⁴⁸. From this value one can approach the energy needed to pull out a Au atom out of the (111) surface, i.e. since Au has coordination 12 in its bulk and 9 at the surface the energy needed to generate an adatom is at maximum $9/12 \cdot 3.81 \text{ eV} = 2.86$ eV, being in the same energy range as the Au-S binding energy.

In the SAM configuration the Au-S binding energy (ΔE_{bind}), is calculated as follows (See Table 1, Fig. 6):

$$\Delta E_{\text{bind}} = \frac{1}{2} \cdot [E(\text{thiol}_A/\text{Au}(111)) - E(\text{thiol}_{A,\text{SAM}}) - E(\text{Au}(111))] \quad (1)$$

with $E(\text{thiol}_{A,\text{SAM}})$ the single point (not geometrically relaxed) total energy of the thiol radicals (2 in the $(2\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell) in the configuration of the SAM but without considering the

Au(111) slab. The SAM unit cell structures are used here, and the energies are referred to the SAM optimized geometry of the isolated thiol molecule.

With this ΔE_{bind} one can obtain an approximation for the inter-chain interaction energy $\Delta E_{\text{int.chain}}$ as following:

$$\Delta E_{\text{int.chain}} = \Delta E_{\text{ads}} - \Delta E_{\text{bind}} \quad (2)$$

$\Delta E_{\text{ads,disp.D3}}$ is calculated according to the following equation:

$$\Delta E_{\text{ads,disp.D3}} = \frac{1}{2} \cdot [E(\text{thiol}_A/\text{Au}(111)) - 2 \cdot E(\text{thiol}_A) - E(\text{Au}(111))] \quad (3)$$

where $E(\text{thiol}_A/\text{Au}(111))$, $E(\text{thiol}_A)$, and $E(\text{Au}(111))$ are the total energies (using the DFT-D3 approach⁴⁴) of the adsorption complex formed by two thiol_A radicals per Au(111) slab, the isolated thiol_A under its radical form, and the Au(111) slab, obtained after separate geometry optimization, respectively. The deformation energy is implicitly included in the calculated energies.

Table 1. Adsorption energy, binding energy, and inter-chain interaction energy for C3 and C11 thiolate on defect free Au(111) surface investigated at the PBE-D3^{49, 50} level. $\Delta E_{\text{ads,disp.D3}}$: the Grimme D3 dispersion corrected adsorption energy, ΔE_{bind} : the estimated Au-S binding energy (Eq. 1), $\Delta E_{\text{int.chain}}$: the estimated inter-chain interaction energy (Eq. 2). Energy values per chain in eV, and distances in Å.

SAMs	$\Delta E_{\text{ads,disp.D3}}$	ΔE_{bind}	$\Delta E_{\text{int.chain}}$
C3	-2.94	-2.63	-0.31
C11	-3.53	-2.60	-0.93

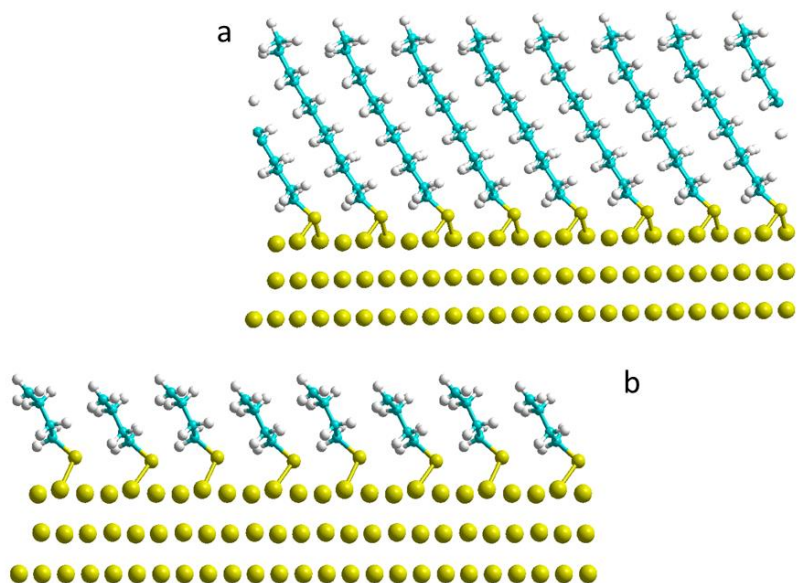


Figure 6. Models for the undecane thiol (a) and propyl thiol (b) SAM on defect free Au(111).

In order to break the S-H bond a surface defect has to be present or has to be formed. In the case the defect has to be formed the short alkyl chains will be privileged in the formation of chemisorbed thiolate species. This result is concluded from our recent results on the self-assembly mechanism of thiol molecules on Au(111), showing a difference depending on the chain length of aminothiols⁹. It was found that short chain aminothiols reconstruct the gold surface more strongly in the self-assembly configuration than long chain aminothiols molecules, probably due to a lower activation barrier for reconstruction. The origin of this lower activation energy might be found in the lower inter-chain interaction energy for the short chains making more mobile on the surface compared with the longer chains. This inter-chain interaction energy was evaluated (See Eq. 2, Table 1).

This observation combined with the present findings unveils a much debated question on the thiol SAM formation: Does the S-H bond break or not?^{9, 27, 38}

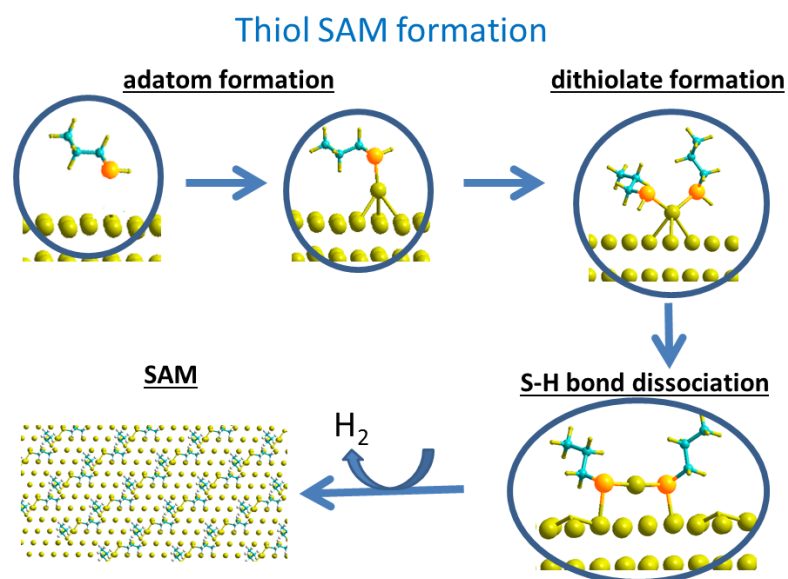


Figure 7. Schematic representation of the proposed short alkyl chain thiol SAM formation.

Taking the above mentioned considerations we propose the following formation pathway for short alkyl chain thiol SAMs (See Fig. 7). A first thiol adsorbs on the surface, and initiates the formation of a protrusion on the Au(111) surface. A second thiol interacts with the adsorption site forming a di-thiol gold species, which subsequently reacts to form a di-thiolate gold species. The organization of these species to a monolayer forms a SAM. SAMs with conformations such as those that have been studied by Ferrighi et al.⁸ For longer alkyl chain thiols the SAM formation might not pass to the formation of an adatom due to the higher interactions between the chains preventing the molecule to relax enough to modify the surface (see higher).

Up to date, it is difficult to ascertain the exact process of the formation of gold adatoms. Are they pulled out from the surface or dragged from an existing step? The real scenario is not yet well established. However, many works agree that the plausible mechanism could be adatoms that are initially taken from the gold surface creating vacancies⁵¹ And to our opinion a dual mechanism should be proposed, combining dragging and pulling gold atoms on/to the surface. Now, concerning the point that it is easier for a shorter chains to pull out a Au atom from the surface, this supposition is based on previous theoretical calculations. For instance, Cometto et al.²⁸ have calculated the adsorption of thiols (CH₃SH and CH₃CH₂SH species) on Au(111) surface as well as on a surface with gold adatoms. Their results suggested that in the presence of surface adatoms, the radical species adsorb on top of the adatom and decrease its barrier for surface diffusion. This barrier is smaller than the barrier for the diffusion of a single gold atom

on Au(111) due to the weakening of the Au-Au bonds as a consequence of the formation of a strong S-Au bond. As a short chain is less sterically hindered than the longer chains its mobility is higher compared to the long chains, the S-Au bond might be stronger than the Au-Au bond (cohesive energy) and by consequence may help to pull out or drag a Au atom more easily. The Au-S bond energy has been shown to be independent of the chain length.

Conclusions

The activation energy for the RS-H dissociation on Au/Au(111) adatoms was investigated using periodic DFT. Three models are investigated based on an adatom containing Au (111) surface: One propanethiol molecule adsorbed on one adatom, two propanethiol molecules adsorbed on one adatom, and one undecanethiol molecule adsorbed on one adatom. It is found that the chain length has no influence of the RS-H bond breaking barrier and that the Au-adatom-dithiol model is a possible reaction pathway for the propanethiol radical formation on Au(111), concluded from the low activation barrier for the reaction (0.75 eV) compared with the single alkanethiol adsorption on a adatom (an activation energy of 1.13 eV was found for propanethiol as well as for undecanethiol).

It was found that the chain length is not determining, it is the formation of the defect on the Au(111) surface. So, this result suggests us to propose a new mechanism for the formation of thiol SAMs on Au surfaces. Combined with our recent finding that short chain aminothiols adsorb chemically on Au(111) and are thus more predisposed to reconstruct the surface compared with the long alkyl chain thiols. This result is explained by the fact that short chain thiols have lower inter-chain interaction energy contributions than long chain alkyl thiols do. Though, the latter being more stabilized by the intermolecular interactions between the alkyl chains. In other words short alkyl chain thiols are expected to restructure the surface more strongly due to their higher mobility and ability to move on the surface to bind with two chains on a surface gold atom, which might become adatoms subsequently. The defects generated will catalyze the RS-H bond breaking more easily. Since there will be more adatoms created when short chain alkyl thiols are adsorbed than long alkyl chain thiols, the long chain alkyl thiols are expected to keep their RS-H bond, at least for a longer time.

Finally, it is not the chain length that will activate the RS-H bond but the defect on Au surface formation energy barrier, and this as a function of the coverage. The next study to confirm this

reaction path would be the study of the reaction mechanism for the Au surface restructuring in the presence of alkyl thiols.

Acknowledgements

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