Thiolate Adsorption on Au(hkl) and Equilibrium Shape of Large Thiolate-covered Gold Nanoparticles

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Thiolate adsorption on Au( hkl ) and equilibrium shape of large thiolate-covered gold nanoparticles
Georgios D. Barmparis, Karoliina Honkala, and Ioannis N. Remediakis

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I. INTRODUCTION

Understanding the nature of interactions between metals and soft or hard condensed matter systems is a crucial step in the design of new nanocomposite materials. In particular, understanding the factors that affect the shape and size of metal nanoparticles during growth might trigger a new generation of experiments based on the controlled synthesis of nanoparticle-based materials for various applications, including ultra-hard coatings, catalysts of high selectivity, fine-tuned optoelectronic devices, or smart materials for drug delivery and other biomedical applications. During the past two decades, the formation and structure of self-assembled monolayers (SAMs) of alkanethiols molecules adsorbed at noble materials’ surfaces has attracted great interest. Especially gold nanoparticles have been used in a variety of applications in biology, catalysis, and nanotechnology. The interface between alkanethiols and gold is, therefore, a subject of great importance for both basic and applied research. The fundamental question is of course the type and strength of the Au–S bonds at this interface.

There are many theoretical Density-Functional-Theory (DFT) studies on the adsorption of alkanethiols on Au(111). The majority of them investigate the adsorption energy of CH₃S⁻ radical on Au(111). Various groups have studied the dissociative adsorption of dimethyl disulfide (DMDS) on Au(111), both theoretically and experimentally. In particular, Nuzzo et al. suggested, after employing a large variety of experimental methods including X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), and thermal desorption spectroscopy (TDS), that the breaking of the (weak) S–S bond of DMDS leads to the formation of two methanethiolate-surface bonds on Au(111) at low coverage. This cleavage is known to take place even at room temperature. The adsorption of a CH₃S⁻ radical has also been studied on Au(100) and Au(110) surfaces by Masens et al., who found that the adsorption energy of CH₃S⁻ on Au(110) is lower by 0.13 eV than that on (100) and by about 0.43 eV than that of (111). Despite the large number of theoretical studies the nature of a binding site is an open issue. In addition, a systematic study of the adsorption of a CH₃S⁻ radical and the dissociative adsorption of DMDS on high index gold surfaces is missing.

The interaction between alkanethiols and gold has also been studied through several theoretical works on thiolate-protected gold clusters, either using DFT simulations or Molecular Dynamics (MD) simulations to explore the structure and electronic properties of such clusters. In these studies, it was found that the structure and electronic properties of the gold core of ligand-capped gold nanoclusters depend on the chemical nature of the ligand.

For most studies regarding small Au clusters, it has been found that thiolates heavily change the surface structure, by creating Au adatoms. Each Au adatom is bonded to two thiolates, and each terminal S atom makes two bonds, one with the Au adatom and another one with a surface Au atom. This bond has been found to be extremely stable for small Au clusters. The same configuration, including Au adatoms bonded to two RS- groups, has been named the “standard model” for close-packed methylthiolate self-assembled monolayers on Au(111), as it has been found in several experimental and theoretical studies for this system. Such bonds between two S atoms and a Au adatom appear due to low reactivity of Au atoms in the close-packed (111) surface, and are expected to be less likely in stepped or kinked surfaces, where undercoordinated Au atoms form significantly stronger bonds to S. Moreover, the strong steric repulsions...
associated with adsorption of longer molecules will result in
grafting densities of the order of 1 nm$^{-2}$ or less, where it is
unlikely that thiolate groups from two different molecules will
bind to the same Au atom.

Computational studies of thiolate-protected nanoparticles
are usually limited to clusters that generally contain at most a few hundred Au atoms. To investigate the shape of larger thiolate-covered gold nanoparticles, one can use the Wulff construction which has been routinely employed in modern theoretical nanoscience. Examples include Ru nanoparticles for NH$_3$ synthesis, Cu nanoparticles in catalysis, and strained semiconductor quantum dots. Recently, the Wulff construction has been employed to predict the shape of a nanoparticle when interactions between a nanoparticle and its environment are included.

In the present study, we performed DFT calculations to investigate the dissociative adsorption of dimethyl disulfide (CH$_3$S–SCH$_3$) on Au(hkl) surfaces with $h, k, l \leq 3$, and on the kinked Au(421) surface at low-coverage. Furthermore, adsorption energies were employed to calculate interfacial tension between CH$_3$S and Au(hkl) surfaces. Using the Wulff construction method, we predict the equilibrium shape of thiolate-protected gold nanoparticles.

The paper is organized as follows: Section II describes computational details, the definition of the adsorption energy, and introduces the concept of the equilibrium shape. In Sec. III, we discuss the adsorption of CH$_3$S on Au surfaces together with the adsorption energies of various adsorption sites for each surfaces. In Sec. IV, the effects of dimethyl disulfide environment on gold nanoparticles are presented and finally the obtained results are summarized in Sec. V.

II. METHODOLOGY

A. Adsorption

To save computer time, only the simplest possible alkane-thiol radical, methanethiolate (RS- with R=CH$_3$) is considered. Although this excludes steric repulsions between chains, it captures all essential features of the general RS–Au bond. This is a reasonable choice as shown by the recent work of Torres et al. These authors show that the adsorption energy of n-alkanethiols on Au(111) changes by only 2 kcal/mol (0.09 eV/molecule) when the length of chain increases from one to six carbon atoms. Steric interactions between chains have a minor impact on binding energies; for example, Torres et al. find that the binding energies of ethanethiolate and propanethiolate are affected by chain interactions by only 0.1 kcal/mol and 0.7 kcal/mol, respectively.

Our second choice is to focus on low coverage of RS on Au, corresponding to coverages less than 0.2 ML, where the adsorption energy is independent of coverage according to our simulation model. For most cases, the grafting density of adsorbates is of the order of 1 nm$^{-2}$, in accordance with Au nanoparticles dispersed in polymer matrices. In this region, interactions between adsorbates can be neglected and the dissociative adsorption energy of dimethyl disulfide on Au(hkl) per methanethiolate, $E_{ads}$ can be defined as

$$E_{ads} = E_{slab}^{Au(hkl)\text{SCH}_{3}} - E_{slab}^{Au(hkl)} - \frac{1}{2}E_{\text{gas}}^{\text{CH}_{3}\text{SSCH}_{3}},$$

where $E_{slab}^{Au(hkl)\text{SCH}_{3}}$ is the total energy of thiolate-covered slab, $E_{slab}^{Au(hkl)}$ is the total energy of the clean slab, and $E_{\text{gas}}^{\text{CH}_{3}\text{SSCH}_{3}}$ the energy of dimethyl disulfide in gas phase.

B. Computational details

First-principles total energy calculations were performed using DFT as it is implemented in the GPAW/ASE code (https://wiki.fysik.dtu.dk). GPAW uses a projector-augmented wave method to describe core electrons, and it employs real space grids to present electron densities and wave functions. We applied grid spacing of 0.19 Å, and the Brillouin zone of the (111)–(1×1) surface was modelled by a (10×10×1) Monkhorst-Pack grid of $k$-points. $k$-points for all other surfaces are calculated in proportionality to the (111)–(1×1) slab ones. Periodic boundary conditions were applied in all three dimensions. Slabs had thickness of 8 Å or more and they were separated by 12 Å of vacuum. Slab thickness was chosen so that adsorption energy for few characteristic (hkl) orientations was converged within 10 meV. The positions of all adsorbate atoms as well as the first two layers of the slab were fully relaxed. We applied the generalized gradient approximation (GGA) revised Perdew-Burke-Ernzerhof exchange-correlation functional (RPBE). The theoretical lattice constant for Au (4.22 Å) was used, which was found by minimizing the total energy of bulk Au. The slight overestimation of the lattice constant compared to experimental value 4.08 Å is consistent with previous DFT calculations. As we are interested in low thiolate coverage, we make sure that the unit cells are large enough. The minimum distance between an S atom and its periodic image is 5 Å or more in all cases. Thus, it is expected that interaction between adjacent molecules is negligible. Calculations for the gas phase dimethyl disulfide molecule were carried out in a (16×16×16) Å$^3$ unit cell so that interactions between periodically repeated molecules are negligible. Figure 1 displays some typical adsorption overlayer structures investigated in the present study.

C. Equilibrium shape

Under thermodynamic equilibrium, the shape of a given quantity of condensed matter, is that with the minimum total surface energy. In 1901, mineralogist G. Wulff proposed that the closed shape that minimizes the total surface energy is such that the distance of each face from the center (center of mass), $d_{hkl}$ is proportional to the surface tension $\gamma_{hkl}$ of the respective surface, for solids, as a synonym for surface energy per unit area. From this equation, it is easy to show that the distance, $d_{hkl}$, for any
Wulff construction is based on a simple geometrical criterion that the distance of each face is proportional to the surface tension. This favors low-index faces over high-index ones, as high-index faces are steeper. As an example, consider the equation of the \((hkl)\) plane in the Wulff construction,

\[
hx + ky + lz = d_{hlk} \sqrt{h^2 + k^2 + l^2}. \tag{5}
\]

This plane intercepts the \(x\) axis at \(x = d_{hlk} \sqrt{1 + (k/h)^2 + (l/h)^2}\), which clearly increases with increasing \(k\) and \(l\). If two planes have the same surface tension, and hence the same distance, \(d_{hlk}\), from the origin, planes with lower \(k\) and \(l\) indices will be closer to the origin along \(x\) axis and, therefore, will be more prominent in the Wulff construction around the \(x\) direction. Similar arguments apply to other directions, so that planes with high Miller indexes are underrepresented in the equilibrium shape. The Wulff construction method is correct at the thermodynamic limit of very large particles. Nevertheless, Wulff shapes for Au nanoparticles are found to agree with experimental observations even for nanoparticles that contain only a few hundreds of atoms.\textsuperscript{39}

III. DISSOCIATIVE ADSORPTION OF \(\text{CH}_3\text{S–SCH}_3\) ON GOLD SURFACES

The dissociative adsorption energy of dimethyl disulfide was calculated on Au\((hkl)\) surfaces with \(h, k, l \leq 3\) and Au\((421)\). We considered several different adsorption sites and CH\(_3\)S configurations to ensure that the global minimum is found. The Au\((hkl)\) surfaces with \(h, k, l \leq 3\), can grouped into three categories: planar \([100], (110), \text{and} (111)\), stepped \([210], (211), (221), (310), (311), (322), (331), \text{and} (332)\] and kinked \((321)\). Au\((321)\) is the only kinked surface for \(h, k, l \leq 3\). For this reason, we also simulated Au\((421)\) to be sure that our results are applicable to at least two different kinked surfaces. The stepped surfaces can be further divided into subgroups according to the microfacet notation,\textsuperscript{45} depending on the type of the terraces and step edges. In the microfacet notation, a surface with an \(n\)-atom wide \((hkl)\) terrace separated by an \((h'k'l')\) step is denoted by \(n(hkl)\times(h'k'l')\).\textsuperscript{46}

In the following, we discuss briefly the main characteristics of each surface and the adsorption behaviour of methanethiolate on all of them. We consider at least three different adsorption sites for each surface, while more than ten different sites have been tested for the more complex systems. Some characteristic adsorption energies and geometrical details including adsorption site, metal-adsorbate bond lengths, and angles are summarized in Table I.

Au\((100)\), Au\((110)\), and Au\((111)\): On all planar surfaces CH\(_3\)S prefers a bridge site, with exothermic adsorption energies of \(-0.57\), \(-0.71\), and \(-0.15\) eV, respectively. The adsorption energy seems to be invariant under rotations of the methyl group around the S–C bond, since this rotation changes the adsorption energy only by a few meV. We find that \(E_{\text{ads}}\) is roughly inversely proportional to the coordination number, \(z\), of Au atoms bonded to S: 8 for (100), 7 for (110), and 9 for (111). On-top and hollow adsorption sites are highly unfavourable. Adsorption of CH\(_3\)S on these sites is marginally exothermic or even endothermic. The only

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Surface & \(E_{\text{ads}}\) (eV) & \(z\) & Site & Details \\
\hline
Au\((100)\) & \(-0.57\) & 8 & Bridge & \& \(90^\circ\) rotation \textsuperscript{47} \\
\hline
\end{tabular}
\caption{Adsorption energies of CH\(_3\)S on Au surfaces.}
\end{table}
TABLE I. Properties of methanethiolate adsorption on Au surfaces. A is the area per adsorbate in Å\(^2\), and \(z\) is the average coordination number of the Au atoms bonded to S. The adsorption geometry is described by three letters: The first refers to the position of the sulfur atom: (t) for on top, (b) for bridge, and (h) for hollow. The second letter defines the orientation of the methyl group: (t) for planar surfaces, (u) for above the upper terrace, and (l) for above the lower terrace in stepped surfaces. The third letter refers to the direction of one hydrogen atom: (t) for towards the surface, (a) for away from the surface, and (p) when all hydrogen atoms are parallel to the surface. \(E_{\text{ads}}\) is the adsorption energy, \(\phi_{\text{Au-S-Au}}\) the angle between the S and the two Au atoms bonded to S for bridge and hollow site only, \(\theta_{\text{Au-S-C}}\) is the angle between the Au atom bonded to S, the S atom and the carbon. \(d_{\text{Au-S}}\) and \(d_{\text{S-C}}\) are the bond lengths between the Au and S atom and the S and C atom respectively.

<table>
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<th>(z)</th>
<th>Configuration</th>
<th>(E_{\text{ads}}) (eV)</th>
<th>(\phi_{\text{Au-S-Au}}) (deg)</th>
<th>(\theta_{\text{Au-S-C}}) (deg)</th>
<th>(d_{\text{Au-S}}) (Å)</th>
<th>(d_{\text{S-C}}) (Å)</th>
<th>Adsorption sites</th>
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<td>0.81</td>
<td>85.3</td>
<td>107.4</td>
<td>2.45</td>
<td>1.84</td>
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<td><img src="image29.png" alt="Image" /></td>
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<tr>
<td>322</td>
<td>5(111)×(100)</td>
<td>73.43</td>
<td>7.0</td>
<td>b-l-t</td>
<td>0.79</td>
<td>80.9</td>
<td>107.7</td>
<td>2.43</td>
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<td>t-l-t</td>
<td>0.17</td>
<td>...</td>
<td>106.8</td>
<td>2.35</td>
<td>1.84</td>
<td></td>
<td><img src="image31.png" alt="Image" /></td>
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</table>
stable configuration for a hollow site is when the carbon atom resides above the S atom and the hydrogen atoms are placed in a plane parallel to the surface. This configuration is metastable and has the longest bond length between Au–S (>2.60 Å), the smallest angle between Au–S–Au (<71°) and the biggest θ_{Au–S–C} (>125°) angle; values that are far from the average ones, which are 2.46 Å, 79.9°, and 107.6°, respectively. On (110) and on other (hkl) surfaces, a hollow site results in numerical instabilities due to unrealistic charge distribution. To save computational time, we focused on adsorption over bridge sites for the most demanding high-index faces.

These findings agree with other works from the literature. To compare adsorption energies, one has to define the reference state of methanethiolate. Several groups have studied methanethiolate adsorption on Au(111) both experimentally and theoretically. In these studies, the following four reactions are considered:

a. dissociative adsorption of CH₃S–SCH₃,
b. adsorption of CH₃S radical,
c. dissociative adsorption of CH₃S–H, and
d. same as (c), but H is desorbed as H₂.

For Au(111), we find that CH₃S prefers bridge site with adsorption energies of (a) −0.15 eV, (b) −1.26 eV, (c) +0.91 eV, and (d) +0.32 eV. These results agree with the calculations of Molina and Hammer who found −1.13 eV for (b) and +0.40 eV for (d). For (a), Hayashi et al. report a bridge site adsorption with −0.27 eV per CH₃S using the PBE exchange-correlation functional. Although the adsorption energy is different, there is good agreement for adsorption geometry. For example, the bond length between Au and S is 2.50 Å, very close to 2.52 Å found here. Andreoni et al. find −1.60 eV for case (b) and −2.39 eV when PBE was used, confirming that PBE overestimates Au–S binding. They report the Au–S bond at 2.46 Å. Similarly, Maksymovych et al. found a binding energy of −1.77 eV for (b) and a bond length of 2.45 Å for the same adsorption geometry. Masens et al. report an adsorption energy of −1.70 eV for (b) close to −1.73 eV found by Yourdshahyan et al. In case (c), Zhou and Hagelberg report a dissociative adsorption energy of −0.06 eV, but they conclude that the adsorption of the methanethiol is nondissociative since the nondissociative structure of methanethiol displays a higher adsorption energy than the dissociative one by 0.6 eV. They also found the Au–S bond length to be 2.45 Å. The nondissociative adsorption of CH₃S–H has been observed experimentally by Maksymovych et al. using scanning tunneling microscopy (STM).

The difference between adsorption energies for (110) or (100) and (111) is found to be 0.14 eV and 0.42 eV, respectively. These values are in excellent agreement to 0.13 eV and 0.43 eV, respectively, reported by Masens et al. Having established the validity of our method for planar surfaces where several experiments and simulations have been reported, we now proceed to the study of thiolate adsorption on stepped and kinked Au surfaces.

Au(210), Au(310), and Au(320): According to the stereographic triangle of the fcc system, these three stepped surfaces coexist along the same direction, travelling from the (100) to the (110) corner. Hence, (310) can be referred as 3(100)×(110), while (210) is on the so called turning point of the zone, where steps and terraces are indistinguishable, and can be referred to both as 2(100)×(110) and 2(110)×(100). (320) consists of 3-atoms wide (110) terrace and (100)-like step. On (310), CH₃S prefers a bridge site between a step-edge and a step-bottom atom, with coordination number 7 and adsorption energy −0.59 eV. On (210) and (320), the most stable configurations found for two bridge sites, one between
a step-edge and a step-bottom atom and one between a step-edge and a terrace atom, both with average coordination number \( z = 7.5 \). The difference between the adsorption energies is less than 0.05 eV. The adsorption energy for the most stable of them is \(-0.54\) eV for \((210)\) and \(-0.51\) eV for \((320)\). In all cases, the on-top site was found to have less exothermic adsorption energy by about \(0.30\) eV.

\( \text{Au}(211), \text{Au}(311), \text{and Au}(322): \) (311) is a surface on the turning point of the stereographic triangle and thus can be referred to as a 2-atoms wide (100) terrace separated by (111)-like step or 2-atoms wide (111) terrace separated by (100)-like step. It has step-edge atoms with \( z = 7 \) and step-bottom atoms with \( z = 10 \). (211) and (311) are referred to as 3-atoms and 5-atoms wide (111) terrace and (100)-like step, respectively. Au(211) is a typical stepped Au surface, and we commenced our study with this system. We considered about 15 different adsorption configurations to ensure that all low-energy adsorption geometries are taken into account. The preferred one is a bridge site between two step-edge atoms with \( z = 7 \) each, having the methyl group above the lowest terrace and the hydrogen atoms in such a way that one hydrogen is towards the lower terrace and the other two away from it. The adsorption energy for this configuration is \(-0.75\) eV. There are also two metastable states. One with the methyl group rotated along the \( \text{S}−\text{C} \) bond, having two hydrogen atoms towards the lower terrace and one away from it, with \( E_{\text{ads}} = -0.73 \) eV and an other one with the methyl group above the upper terrace with \( E_{\text{ads}} = -0.72 \) eV. The hollow site was found to be highly unfavourable. That it finally relaxed to a step-bridge site. The adsorption energy changes only by 60 meV upon doubling the area of the unit cell, proving that at low-coverage the adsorption energy changes only by 60 meV upon doubling the area of the unit cell.

In all cases, the on-top site was found to have less exothermic adsorption energy by about 0.15 eV. This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.234.75.141 On: Mon, 04 Jan 2016 12:33:08

\( \text{Au}(221), \text{Au}(331), \text{and Au}(332): \) These three surfaces consist of 3-, 4-, and 6-atoms wide (111) terraces, respectively, separated by (111)-like step edge. The step-edge atoms have 7 neighbours, the terrace atoms 9, and the step-bottom ones have 11. The adsorption energy is \(-0.72, -0.68, \) and \(-0.64\) eV, respectively, for a bridge site with the \( \text{S} \) atom between two step-edge atoms and the methyl group above the lower terrace. Bond lengths of \( \text{Au}−\text{S} \) and \( \text{S}−\text{C} \) and the angles \( \phi_{\text{Au}−\text{S}−\text{Au}} \) and \( \theta_{\text{Au}−\text{S}−\text{C}} \) are very close to the average values.

\( \text{Au}(321) \) and \( \text{Au}(421): \) These are kinked surfaces, i.e., contain regular nonlinear steps. The step edge of (321) consists of 2-atoms wide (100) and 2-atoms wide (111). The step-edge atoms have 6 or 8 neighbours alternately. The \( \text{CH}_3\text{S} \) binds on a bridge site between two atoms with 6 and 8 neighbours, with \(-0.75\) eV energy. The step edge of (421) consists of 3-atoms wide (100) [one atom wired than (321)] and 2-atoms wide (111). The step-edge atoms have 6, 7, and 8 neighbours alternately. The \( \text{CH}_3\text{S} \) binds on a bridge site between two atoms with 6 and 7 neighbours, with \( E_{\text{ads}} = -0.79 \) eV. In both cases, the (111) terrace consists of atoms with 9 neighbours terminated by step-bottom atoms with 10 or 11 neighbours. Here, also, bond lengths of \( \text{Au}−\text{S} \) and \( \text{S}−\text{C} \) and the angles \( \phi_{\text{Au}−\text{S}−\text{Au}} \) and \( \theta_{\text{Au}−\text{S}−\text{C}} \) are very close to the total averages.

It is well established that \( E_{\text{ads}} \) for O and CO adsorption on Au is a linear function of the coordination number, \( z \), of Au atoms. 39,49,50 To investigate whether this trend also holds for thiophiotes, we plot in Fig. 2 the adsorption energy as a function of \( z \). Although a general trend for increase of \( E_{\text{ads}} \) with increasing \( z \) can be deduced from Fig. 2, a clear linear dependence was not found. Nevertheless, the average adsorption energies for each \( z \) can be fitted nicely to a straight line. Apparently, the \( \text{CH}_3\text{S}−\text{Au} \) bond depends on many parameters, and not just the coordination number. For example, such a parameter could be the d-band center of the surfaces. However, the \( d \)-band model is not readily applicable to Au surfaces, as Au atoms have filled \( d \) shells. Indeed, our calculations show little correlation between the center of the \( d \)-band and methanethiol adsorption energy. For comparison, a linear dependence between these two quantities has been established for a multitude of other systems. 51 To get a qualitative description of bonding to Au, one needs to apply the more general Newns-Anderson model. Larsen et al. 52 used this general theory to explain calculated adsorption energies of H, O, Li, and F on small Au clusters. However, adsorption of larger molecules, such as thioliates, is more complicated. In this case, electrons can be transferred not only around the adsorbate-metal bond but also in other parts of the molecule. It would have been very difficult to gain insight into this problem without using detailed density-functional theory simulations.

Thiolates prefer bridge sites in all cases. In particular, for \( \text{Au}(111) \) our minimum energy adsorption geometry is identical to that presented by Hayashi et al. 48 and by Maksymovych et al. 47 The on top site was found to be the most unfavourable one, followed by the hollow site. In all stepped surfaces, the methyl part is oriented above steps and in all cases in such a way that one of the hydrogen atoms is directed towards the lower terrace, whereas the other two are pointing away from the surface. The dissociative adsorption energy per thiolate \( E_{\text{ads}} \) ranges from \(-0.15 \) to \(-0.80 \) eV. The bond length \( \text{Au}−\text{S} \) was found to be \((2.46 \pm 0.02) \) Å, in agreement with experimental values \((2.42 \pm 0.03) \) Å from Ref. 14 and \(2.48 \) Å from Ref. 53 and theoretical studies between 2.46 and 2.50 Å. 6,9,11,12,47,48

The angle \( \phi_{\text{Au}−\text{S}−\text{Au}} \) was found to be \((79.9 \pm 2.6)° \) and the angle \( \theta_{\text{Au}−\text{S}−\text{C}} \) \((107.6 \pm 1.7)° \), very close to the tetrahedral structure with \(109.5° \) that dimethyl disulfide prefers and in good agreement with \(109.7° \) found in Ref. 47. In all cases, the distance between the sulfur and carbon atom was found to be about 1.84 Å in excellent agreement with 1.83 Å in Ref. 47 and 1.87 Å found in Ref. 4. The lowest absolute value for the adsorption energy \((0.15 \) eV \) is found for the
close-packed (111) surface. On this surface, we also find the longest Au—S distance (2.52 Å).

IV. THIOLATE-COVERED GOLD NANOPARTICLES

Having calculated the adsorption energies, we now use Eq. (4), together with Au(hkl) surface tension from Ref. 39, to calculate the interfacial tensions of thiolate-covered gold surfaces. Using Eq. (3) with a given distance for the (h′k′l′) surface, we find the distance for the other faces. We choose (h′k′l′) to be the (211) surface which is the one with the minimum interfacial tension. This minimum interfacial tension is a result of the highest absolute value for the adsorption energy combined with a high density of steps. In Table II, we present the ratios of the surface tension of an Au(hkl) surface with respect to the Au(211) surface tension, for covered with CH₃S and clean surfaces.

By increasing the d₂₁₁ distance, we construct nanoparticles of increasing diameter. For each one of them we find all d₃₄₅ and thus construct the Wulff polyhedron. Then we fill it with atoms in the fcc lattice and create an atomistic model of a nanoparticle. Two orthogonal unit cell bases for the fcc lattice of gold are used, one with an atom in the center and an other one without. We constructed more than 30 000 nanoparticles with diameters up to 40 nm. Only a few thousands of them are unique and less than a hundred are in agreement with the continuous Wulff polyhedron.

![FIG. 3. Wulff construction for a thiolate-protected Au nanoparticle. The shape consists almost entirely of (211) faces.](image)

![FIG. 4. Atomistic Wulff construction for thiolate-covered gold nanoparticles at 5.0 and 14.2 nm, respectively. Grey atoms are Au atoms at edges or corners.](image)

![FIG. 5. (Left) Model of a typical Au nanoparticle (d ~ 10 nm, ca. 22750 atoms) in non-interacting environment (sphericity = 89%, 78 μmol of active sites per g). (Right) a same size thiolate-protected gold nanoparticle (sphericity = 95%, 299 μmol of active sites per g). Step and kink atoms are shown in darker color.](image)

<p>| | | |</p>
<table>
<thead>
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<th></th>
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<tbody>
<tr>
<td>γ₂₁₁ (J/m²)</td>
<td>CH₃S</td>
<td>Clean¹</td>
</tr>
<tr>
<td>γ₁₀₀/γ₂₁₁</td>
<td>1.18</td>
<td>1.05</td>
</tr>
<tr>
<td>γ₁₁₀/γ₂₁₁</td>
<td>1.24</td>
<td>1.10</td>
</tr>
<tr>
<td>γ₁₁₁/γ₂₁₁</td>
<td>1.14</td>
<td>0.85</td>
</tr>
<tr>
<td>γ₂₁₀/γ₂₁₁</td>
<td>1.45</td>
<td>1.13</td>
</tr>
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<td>γ₂₁₁/γ₂₁₁</td>
<td>1.39</td>
<td>1.12</td>
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<td>1.25</td>
<td>1.07</td>
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<td>γ₃₂₂/γ₂₁₁</td>
<td>1.16</td>
<td>0.92</td>
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¹Reference 39.

The thus constructed shape might deviate from the thermodynamic limit at small sizes, as some faces might be too small to accommodate a unit cell. At the thermodynamic limit, thiolate-protected gold nanoparticles are almost totally dominated by the (211) surface with a very small amount of (100). In Fig. 3, the equilibrium shape at the thermodynamic limit is shown. This shape is close to a deltoidal icositetrahedron. In Fig. 4, we present atomistic models of the Wulff construction for two different sizes. The nanoparticle with diameter of 14.2 nm is identical to that at the thermodynamic limit. Smaller nanoparticles do not have (100) faces, as this area is smaller than the minimum unit cell of (100). This is the case for all nanoparticles smaller than 14.2 nm. In Table III, we present characteristic values for the nanoparticles in equilibrium, including diameter d in nm, number of the atoms in corners Nₐ, edges Nₑ, surfaces Nₛ, and total Nₜ. We also present the surface area in nm², the volume in nm³, the active site density Nₜ in μmol/g assuming that step-edge atoms are active and the faces appearing for each nanoparticle with the percentages due to the total area for each one face.

Although our method is valid for large nanoparticles and for low coverage, nanoparticles shown in Fig. 4 compare very well to state-of-the-art simulations of the Au₁₀₂(p-MBA)₄₄ cluster by Walter et al.¹⁷ In that work, a very high coverage is considered and Au adatoms bonded to two S atoms are present. When comparing the Au core (Au atoms except the adatoms), as depicted in Fig. 1 of Ref. 17, we find a surprising similarity: In both cases, Au atoms form three-atom-wide (111)-like terraces which are separated by monoatomic steps.

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Comparing the shapes for gold core of thiolate-protected gold nanoparticles with gold nanoparticles in inert gas, we find that the shape changes upon exposure to thiolates towards higher symmetry. An example is shown in Fig. 5. A gold nanoparticle with approximately 10 nm diameter, increases its sphericity from 89% in inert gas to 95%. The sphericity of a nanoparticle equals \( \pi^{1/3}(6V)^{2/3}/A \), where \( V \) is the volume and \( A \) is the area of it; characteristic values are 81% for a cube, 85% for an octahedron, and 100% for a sphere. Such shape change upon exposure to reactive environment is very common for Au nanoparticles.

Thiolate-protected Au nanoparticles might be much more reactive compared to Au nanoparticles in weakly interacting environment. As a rough measure of activity, we consider the density of step-edge atoms. It has been found that undercoordinated Au atoms have increased chemical activity. Of density of step-edge atoms. It has been found that undercoordinated Au atoms have increased chemical activity. Of density of step-edge atoms. It has been found that undercoordinated Au atoms have increased chemical activity.

<table>
<thead>
<tr>
<th>( d ) (nm)</th>
<th>( N_c )</th>
<th>( N_e )</th>
<th>( N_t )</th>
<th>( N_f )</th>
<th>Area (nm²)</th>
<th>Volume (nm³)</th>
<th>( N_{act} ) (μmol/g)</th>
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<td>26</td>
<td>312</td>
<td>456</td>
<td>2461</td>
<td>62</td>
<td>42</td>
<td>644 (211) (100%)</td>
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<tr>
<td>10.45</td>
<td>60</td>
<td>1344</td>
<td>2352</td>
<td>22798</td>
<td>278</td>
<td>404</td>
<td>299 (211) (100%)</td>
<td></td>
</tr>
<tr>
<td>14.21</td>
<td>44</td>
<td>2664</td>
<td>4830</td>
<td>63511</td>
<td>553</td>
<td>1135</td>
<td>221 (211) (99.5%) (100) (0.5%)</td>
<td></td>
</tr>
<tr>
<td>19.23</td>
<td>44</td>
<td>4728</td>
<td>8742</td>
<td>149779</td>
<td>984</td>
<td>2691</td>
<td>159 (211) (99.1%) (100) (0.9%)</td>
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<tr>
<td>24.24</td>
<td>44</td>
<td>7368</td>
<td>13806</td>
<td>291631</td>
<td>1539</td>
<td>5257</td>
<td>127 (211) (99.5%) (100) (0.5%)</td>
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<tr>
<td>29.26</td>
<td>44</td>
<td>10584</td>
<td>20022</td>
<td>502891</td>
<td>2217</td>
<td>9086</td>
<td>106 (211) (99.6%) (100) (0.4%)</td>
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</tr>
<tr>
<td>34.28</td>
<td>44</td>
<td>14376</td>
<td>27390</td>
<td>797383</td>
<td>3018</td>
<td>14428</td>
<td>91 (211) (99.7%) (100) (0.3%)</td>
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V. CONCLUSIONS

Adsorption of thiolates on 14 different Au(\( hkl \)) surfaces at very low coverage is studied as first step towards modelling encapsulated Au nanoparticle. A systematic study of adsorption of CH₃S on Au reveals that bridge sites are preferred in all cases. Several metastable configurations exist for each particular Au(\( hkl \)). Step edges show adsorption energies of \(-0.6\) to \(-0.8\) eV, while terraces have \(-0.5\) eV or higher. Kinked sites do not show significantly stronger binding than step sites. The interface tension between Au(\( hkl \)) and thiolates at very low coverage has a strong dependence on the orientation of Au surface. Large thiolate-protected Au nanoparticles expose mostly (211) faces and are more spherical and more reactive than Au nanoparticles in weakly interacting matrices.

ACKNOWLEDGMENTS

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