# Adsorption and dimerisation of thiol molecules on Au(111) using a Z-matrix approach in density functional theory

## (running head: Thiol adsorption on Au(111))

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The adsorption energetics of methanethiolate and benzenethiolate on Au(111) have been calculated using periodic Density Functional Theory (DFT), based on the SIESTA methodology, with an internal coordinates implementation for geometry input and structure optimization. Both molecules are covalently bound with interaction energies of 1.85 eV and 1.43 eV for methanethiolate and benzenethiolate, respectively. The preferred binding site is slightly offset from the bridge site in both cases towards the fcc-hollow. The potential energy surfaces have depths of 0.36 eV and 0.22 eV, the hollow sites are local maxima in both cases, and there is no barrier to diffusion of the molecule at the bridge site. The corresponding dimers are weakly bound for methanethiolate and benzenethiolate, with binding energies of 0.38 eV and 0.16 eV, respectively, and the preferred binding geometry is with the two sulphur atoms close to adjacent atop sites.

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The barrier to dissociation of the dimer dimethyl disulphide is estimated to lie between 0.3 and 0.35 eV.

## 1. Introduction

Computational studies of various kinds have already played a significant role in understanding the energetics and dynamics of thiol based self-assembled monolayers (SAMs) on gold since it is not easy to gain direct experimental evidence at the molecular level for SAMs. The importance of these self-ordering systems and their potential application as platforms for nanoscience and technology are well established. For thorough reviews we refer the reader to Love et. al. 2005 [1]and Ullman [2].

The majority of calculations to date have concentrated on the simplest alkanethiol, methanethiol and its dimer, dimethyl disulphide, as a model system (see for example, [3-10]) It is generally accepted that alkanethiols can chemisorb to the gold surface upon cleavage of the S-H bond, or through dissociation of the corresponding disulphide, with a homolytic bond energy of the order of 1.5 eV. There has been considerable debate over the optimum absorption site, though consensus has now settled upon the near bridge site[5].

The first oxidation product of a sulphur-terminated molecule bound to gold is formation of the disulphide. Gas phase adsorption experiments show that the dimer, dimethyl disulphide, adsorbs dissociatively to give a stable surface bound thiolate

molecule [11], and electrochemical measurements have estimated the barrier to recombinative desorption of the dimer to be less than 1 eV [12]. Some computational studies have already been undertaken to examine the energetics [5, 6] of dimerisation, but not the dynamics. They find that dissociation of the surface bound disulphide is favoured, although agreement with available experimental data is limited.

SAMs based upon aromatic thiol molecules have grown in importance more recently due to their potential application in molecular electronics and similar devices. They can provide a molecular layer that is more rigid than alkyl tailgroups and where $\pi$-conjugation can potentially promote electron transport. Despite these applications, aryl SAMs have received little attention in terms of elucidating the underlying structure and dynamics of the molecular layer. Two recent density functional theory studies investigate the structure and energetics of benzenethiolate adsorption [13, 14]. To our knowledge, the adsorption and formation of the corresponding disulphide has yet to be reported.

The potential energy surface (PES) underlies the behaviour of these molecules on the gold surface and hence the structure and dynamics of SAMs. A detailed knowledge of this surface is therefore extremely useful. However, even for the simplest molecule, methanethiol, this is a difficult task as the number of degrees of freedom is large. The problem is compounded by the fact that the majority of periodic boundary conditions (PBC) codes use Cartesian coordinates to describe the structure and perform optimizations, while potential energy scans are more easily undertaken in internal coordinates. Generally PES maps for thiols on gold have been limited to a small sub-set of degrees of freedom [3, 14], for example sulphur position and molecular tilt, and the maps have been created by scanning a rigid molecule over the gold surface.

In the present work we employ a computational approach similar to our previous work [8, 15] using the SIESTA code [16, 17] that we have modified to allow a mixed Cartesian, Z-matrix description of the molecular geometry [18]. This allows us to map the PES along the atop-bridge-atop path of methanethiolate and benzenethiolate on the gold surface in detail, i.e. the PES is determined by constrained optimization.

We have calculated the adsorption energetics and optimum structures for the corresponding dimers, dimethyl disulphide and diphenyl disulfide, and have mapped the potential energy surface for dissociation of dimethyl disulphide on the gold surface and estimated the corresponding dissociation barrier.


## 2. Methods

The calculations presented in this paper were conducted with the SIESTA software package [16, 17]. This program implements the SIESTA methodology for linear-scaling density functional theory within periodic boundary conditions and is based on the linear combination of atomic orbitals approximation. The valence electrons are described by atom-centred basis sets, and the nucleus/core electrons are represented by norm-conserving pseudopotentials. The key feature of this methodology is that the orbitals are strictly localized in real-space, with a cut-off radius defined by a single energy shift parameter for all atoms that represents the energy increase in the orbitals due to confinement. Exploitation of this locality leads directly to linear-scaling in the construction of the Hamiltonian without the requirement of neglecting integrals based on a threshold value.

The code has been modified to allow coordinate input in a mixed Cartesian internal coordinate format, which is particularly convenient for studying molecules on surfaces. The adsorbate is described by a Z-matrix in the usual manner, while the substrate is described in Cartesian format. More than one Z-matrix is allowed in the input geometry, which makes the description of dimers and their dissociation particularly convenient. The Z-matrix portion of the structure is optimized in internal coordinates. A full description of our Z-matrix implementation is described elsewhere [18].

For the present calculations, the generalized-gradient approximation (GGA) to the exchange-correlation functional due to Perdew, Burke and Ernzerhof (PBE) [19] is used throughout. All calculations are spin restricted and employ a Fermi smearing of 25 meV to aid convergence. A sub-set of spin-unrestricted calculations has been performed to ensure spin restriction does indeed yield the correct ground-state. In all but the dimer dissociation calculations this is the case. We will discuss this dissociation case in more detail in the relevant results section. Norm-conserving pseudopotentials (with a relativistic correction in the case of Au) generated according to the scheme of Troullier and Martins [20] are used. A double-zeta plus single polarisation function is used to represent the 1s electrons in H, 2s and 2p electrons in C, 3s and 3p electrons in S, and 6s and 5d electrons in Au. Transferability of the pseudopotentials has been previously tested by comparison with well-known experimental results and all-electron calculations [8, 15, 21].

For the monomer calculations a 3x3 unit cell, 4 layers deep is used to represent the substrate. This represents a 1/9 monolayer coverage where the interaction between adjacent adsorbates is less than 0.05 eV; in other words we are simulating single molecule

adsorption. Calculations at higher coverage have not been attempted since the present DFT calculations will not reproduce the dispersive tail-tail interactions between the absorbed molecules. A 5x5x1 Monkhurst-Pack [22] grid is used for reciprocal space integration. This relatively coarse grid is sufficient to yield well-converged total and interaction energies for the size of unit cell employed. The orbital energy shift was set to 5mRy and a mesh cutoff of 200 Ry was used for the real space integration of the density and related quantities. The mesh cutoff represents the highest energy plane-wave that can be represented on this grid. We have previously tested these computational parameters extensively and found they yield energies converged, excluding any basis-set effects, to better than 0.05 eV [15]. The force tolerances for geometry optimization were set to 0.04 $eV\text{Å}^{-1}$ for length and 0.0009 $eV\text{deg}^{-1}$ for angles. Although the length tolerance is not particularly tight, the bond lengths and interaction energies are not altered significantly even if this value is decreased to 0.01 $eV\text{Å}^{-1}$.

A larger unit cell is used for the dimer calculations, 4x4 for dimethyl disulphide and 5x5 for diphenyl disulfide, in order to keep the intermolecular interactions below approximately 0.05 eV. The same computational conditions as above are used for geometry optimization and calculation of interaction energies for these two species. For computational efficiency, the potential energy surface for dissociation of dimethyl disulphide was mapped at lower computational conditions, using a 4x4 unit cell 3 layers deep, a 3x3x1 k-grid and 0.01 Ry for the orbital energy shift. These are relatively modest conditions that can only yield an estimate of the dissociation barrier. In any case, as we will discuss below, the dissociation calculations are limited by spin contamination effects as the S-S bond is broken.

Interaction energies are calculated using the standard basis set superposition error (BSSE) correction proposed by Boys and Bernardi [23].

## 3. Results and Discussion

In the following sections we present computational results for the adsorption of the monomers methanethiolate and benzenethiolate, and the corresponding disulphides, on the Au(111) surface. The monomers are shown in Figure 1. For both monomers it has been assumed that the terminal S-H bond has been cleaved and that adsorption occurs through the S atom. Although the final state is generally assumed to be this strongly bound thiolate the mechanisms that lead to this are still unclear. Previous studies suggest that thiols at low coverage and temperature can initially physisorb from the gas-phase with the terminal hydrogen intact and subsequently dissociate to yield the chemisorbed thiolate [see [5] and references therein]. The situation for the most common experimental method of preparation, via solution adsorption, is more complex but again is generally assumed to yield the thiolate species. Dissociative adsorption of the disulphide, or its formation on the surface, further complicates the reaction pathways. As previously pointed out [14], use of the expression 'thiolate' to denote the adsorbed species implies ionic character to the surface bond, as is the case in Au(I)-thiolate complexes. However, the surface species is more likely a covalently bound thiyl. Here we adopt the prevalent nomenclature found in the literature and refer to monomers as thiolates.

[Insert Figure 1 about here]

### 3.1 Monomer adsorption

The potential energy surfaces for methanethiolate and benzenethiolate have been calculated along the atop-bridge-atop path as shown in Figure 2.

[Insert Figure 2 about here]

At each step in the PES a constrained optimization is performed where the sulphur atom is held in fixed registry to the surface while its height above the surface, the remainder of the molecule and surface gold layer are fully relaxed. This is in contrast to previous studies where a rigid molecule is scanned across the surface at varying heights and attitudes. The Z-matrix approach we have implemented in SIESTA thus allows us to map the PES in greater detail than is feasible using more conventional Cartesian coordinates. In addition, geometry optimization in internal coordinates can be a more robust method for finding global minima [18].

The potential energy surfaces for the two monomers are shown in Figures 3 and 4. In both cases the minimum lies close to the bridge site in agreement with previous calculations of the optimum geometry [5, 14]. In both cases a number of points along the PES have been re-calculated in a spin-unrestricted state yielding identical results.

[Insert Figure 3 about here]

[Insert Figure 4 about here]

The shape of the two curves for the different monomers is quite different with a more pronounced potential well centred close to the bridge site for benzenethiolate. Methanethiolate has a deeper well of about 0.36 eV, compared with 0.22 eV for benzenethiolate. Interestingly, the hollow sites are local maxima along this pathway. Cartesian coordinate optimizations can be misleading in this regard and can yield local minima for these sites [5]. We also find local minima if we repeat our calculations using

Cartesian coordinates. We attribute this to the fact that the potential energy surface at this site is relatively flat with respect to tilting of the molecule. Internal coordinate optimizations are found to be more robust because a much tighter force tolerance for the angular optimization can be specified independently of the force tolerance for bond length. Bilic et al. [14] also find the hollow sites to be saddle points for two layer slab calculations, but minima for a four-layer calculation.

There is found to be no barrier to diffusion at the bridge site in contrast to the earlier work of Yourdshahyan et al. [5] and more recently of Cometto et al. [3] where the PES for methanethiolate was estimated by scanning a rigid methanethiolate molecule over the surface. The PES is not only sensitive to the tilt angle of the tail-group with respect to the surface normal but also the orientation of the tail group with respect to the surface atoms. On both sides of the bridge site, the minimum energy is obtained by tilting the tail-group back over the bridge site rather than fixing its orientation.

Table 1 gives the interaction energies, geometries and Mulliken populations obtained from full geometry optimistion of the molecules and surface layer atoms starting from the minima in Figures 3 and 4.

Both molecules form strong bonds to the surface, which, from the Mulliken charges and overlaps of the molecule, are quite covalent in character. As expected the S atom is predominantly two-coordinated to the nearest two surface gold atoms. Interaction energies are relative to the isolated adsorbate and substrate in the adsorbed geometry; they are, in effect, non-adiabatic bond-energies.

[insert Table 1 about here]

Yourdshahyen et al [5], at a similar coverage, calculate an adsorption energy of 1.65 eV for methanethiolate, a tilt angle of 54.3º to the surface normal and displacement of 0.50 Å of the sulphur atom from the bridge site towards the fcc-hollow site. Bilic et al [14], at 1/9 monolayer coverage, find the bridge-fcc site as the minimum for benzenethiolate. This minimum lies 0.09 Å away from the bridge site with a tilt angle of 56º and a binding energy of approximately 1.3 eV. These authors calculate the bridge site to be close in energy to the bridge-fcc site, but with a much larger tilt angle of 68º.

### *3.2 Disulphide adsorption*

The optimum geometries for dimethyl disulphide and diphenyl disulphide adsorption on the Au(111) surface are shown in Figure 5. Only a small portion of the unit cell used to calculate these adsorption geometries are shown in the figure. The entire adsorbate and surface gold layer has been relaxed.

[Insert Figure 5 about here]

In both cases the optimum geometry is with the two sulphur atoms close to atop sites and at equal heights above the gold surface layer. The S atoms are displaced away from the atop sites almost directly along the atop-bridge path for dimethyl disulphide and along the bridge path for diphenyl disulphide. The dimethyl disulphide structure appears to agree with the figure in Gronbeck et al [6], although detailed structural parameters are not given. However, it is at odds with the previous results [5, 24, 25], where the two sulphur atoms are at very different heights above the surface and situated near the bridge site. We have performed a number of optimizations for dimethyl disulphide starting from different initial geometries, to the best of our knowledge the geometry shown in Figure 5

is the global minimum. Using the optimum geometry from Yourdshahyan et al [5] as the starting point still optimizes to the geometry shown in Figure 5. Spin-unrestricted optimizations give exactly the same result. However, if we perform the optimization in Cartesian coordinates the previously reported near-bridge site appears to become a local minimum. This result again illustrates the robustness of internal coordinate optimizations. [Insert Table 2 about here]

The absorption energies and structural parameters for the two disulphides are given in Table 2. The dimers are relatively weakly bound to the surface as can be seen in both the interaction energies and overlap populations with the nearest surface gold atom. There is significant overlap between each S atom and only one gold surface atom, specifically the nearest atop atom. The interaction energy and S-S bondlength for dimethyl disulphide agree well with previous results [5].

Both disulphides adsorbed on the surface are energetically unstable with respect to dissociation into two isolated and adsorbed monomers. The total energy of dimethyl disulphide is 0.41 eV higher than two isolated monomers while this figure for diphenyl disulphide is 0.62 eV. The dissociation energy calculated by Yourdshahyan et al. [5] for dimethyl disulphide is 0.38 eV, whereas Gronbeck et al report a value of nearly 1 eV [6]. Experimental results also show that dimethyl disulphide dissociates on the gold surface at low coverage [11].

Despite the fact that dissociation is energetically feasible, the calculations presented here, and in previous works, find a local minimum for the dimer. In other words, they suggest that there is a barrier to dissociation. To explore this point in more detail we have attempted to calculate this barrier by scanning the PES for dimethyl

disulphide as the S-S bond is broken. Clearly, in the present DFT calculations we can, at best, only estimate this quantity, as it is quite likely the calculations will fail to describe the S-S bond dissociation correctly. This raises another important point with regards to the disulphide optimizations and whether the calculated local minimum is an artefact of using a single-reference calculation, that is during the optimization the S-S bond is prevented from dissociating due to the failure of the method to describe this dissociation correctly.

[Insert Figure 6 about here]

Initially we mapped the PES for the dimer using a spin-restricted calculation in order to gain an approximate idea of its topography and the likely dissociation path on this PES. The results are shown in Figure 6. The PES was obtained by fixing one of the sulphur atoms in its optimum position and scanning the second away from the optimum position while allowing the molecule to relax. For computational expediency, only the tilt angle and orientation of the two tail groups were optimized, while both sulphur atoms were relaxed with respect to height above the surface. The surface gold atoms were fixed in their optimum positions as taken from the initial structure. The calculations were also performed at a lower level of numerical quality on a 3-layer slab. The effects of spin contamination are likely to dominate the reliability of the calculations and hence using very strict computational conditions is an unnecessary expense. The region in which the spin-restricted calculations fail will become evident in the following discussion.

The series of spin-unrestricted calculations shown in Figure 7 were then performed along the two lines shown in Figure 6, passing from the minimum energy site through the saddle point and down to the dissociation products.

[Insert Figure 7 about here]

It is clear from Figure 7 that spin contamination starts to become a problem when the S-S bond is stretched to about 2.5 Å. However, this point is already near the top of the estimated dissociation barrier. For bond lengths shorter than 2.5 Å the total spin is zero and the calculation is presumably reliable. The spin returns to zero at a bondlength of about 2.9 Å, where the S-S bond has now dissociated. Hence, it would appear that it is only the very top of the dissociation barrier where spin contamination renders the calculations unreliable. In addition, we might expect a multi-reference calculation in this region to give lower total energies. From these results we estimate the dissociation barrier to lie between 0.3 and 0.35 eV, and the barrier for formation of dimethyl disulphide from two isolated monomers to be between 0.71 and 0.76 eV. From Figure 7 we can also infer that the spin-restricted mapping of the PES in Figure 6 only becomes unreliable in the region of the saddle point for energy values greater than about 0.3 eV. The majority of the PES is indeed spin zero and unaffected by spin-contamination, hence the use of spin-restricted calculation to map the overall shape of the PES is justified.

Finally, in Figure 8 we plot the overlap populations between the two S atoms, and between the two S atoms and nearest atop surface gold atoms, as the S-S bond is dissociated along the two paths in Figure 6. This is from the same spin-unrestricted calculations as Figure 7.

[Insert Figure 8 about here]

The S-S overlap population varies smoothly from 0.35 to 0.03 as the S-S bond is stretched from equilibrium to about 3.1 Å, that is bond has almost dissociated entirely at 3.1 Å. There is a corresponding increase in the S-Au overlap as the bondlength is

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increased. At equilibrium the S-S bond is strong and the bond to the surface is relatively weak (see Table 2), and as the S-S bond dissociates the S atoms start to form a stronger bond with the gold surface atoms. At the point where the S-S and S-Au overlaps are about the same, the calculations becomes spin contaminated. In this intermediate region the present single-reference calculations cannot describe the competing S-S and S-Au bonds adequately.

## 4. Conclusions

Adsorption of methanethiolate and benzenethiolate and the corresponding dimers on Au(111) have been studied using the density functional code SIESTA. A combination of internal and Cartesian coordinates has been implemented in this code to describe the geometry input and to perform structure optimizations. Internal coordinates are found to be particularly advantageous for this type of surface adsorption calculation. Consequently, we have been able to map the potential energy surfaces for the two monomers in detail along the atop-bridge-atop path. There is no barrier to diffusion at the bridge site and the hcp and fcc hollow sites are saddle points for both molecules. The minimum in the PES is close to the bridge site shifted towards the fcc-hollow site by 0.32 and 0.04 Å for methanethiolate and benzenethiolate, respectively, the depth of the potential wells (between atop and optimum site) are 0.36 and 0.22 eV respectively. Both monomers are relatively strongly bound to the surface, with energies of 1.85 and 1.43 eV, respectively, with the sulphur head-group two-coordinated to the gold surface.

The corresponding dimers, dimethyl disulphide and diphenyl disulphide, are comparatively weakly bound to the gold surface by 0.38 and 0.16 eV, respectively. The

optimum geometry in both cases is with the two sulphur atoms at equal height to the gold surface and positioned near to the atop site. Each sulphur atom in this case is coordinated to a single surface gold atom. Dissociation of the dimers on the surface is energetically favoured by 0.41 and 0.62 eV for dimethyl disulphide and diphenyl disulphide, respectively. Despite the difficulties associated with describing bond dissociation in the present single-reference calculations we have been able to estimate the barrier for dissociation of dimethyl disulphide on the surface to be between 0.3 and 0.35 eV. This result demonstrates the strength of using internal coordinates for investigating surface chemistry. Gas phase reactions between molecules have been studied computationally for many years using this approach. Extending this to reactions on surfaces has, till now, been hampered by the lack of availability of solid-state codes with internal coordinates.

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| Molecule | E (eV) | H (Å) | S-Au (Å) | ΔY (Å) | θ (°) | Q (a.u.) | Overlap (a.u.) |
|---|---|---|---|---|---|---|---|
| Methanethiolate | 1.85 | 2.00 | 2.55<br>2.55<br>3.12 | 0.32 | 55.5 | -0.185 | 0.169<br>0.169<br>0.035 |
| Benzenethiolate | 1.43 | 2.09 | 2.59<br>2.59<br>3.33 | 0.04 | 67.9 | -0.226 | 0.154<br>0.153<br>0.026 |

Table 1. Binding energy (E), adsorption height (H), S-Au bond-lengths, displacement of the S-headgroup from bridge site towards fcc-hollow (ΔY), angle of tail-group with respect to surface normal (θ□), molecule charge (Q) and overlap populations between S and nearest Au surface atoms for the optimized methanethiolate and benzenethiolate adsorbed species.

| Dimer | E (eV) | H (Å) | ΔY (Å) | S-Au (Å) | S-S (Å) | θ (°) | φ (°) | Q (a.u.) | S-S Overlap | S-Au Overlap |
|---|---|---|---|---|---|---|---|---|---|---|
| Dimethyl | 0.38 | 2.62 | 0.51 | 2.73 | 2.14 | 64.6 | -6.2 | 0.146 | 0.342 | 0.093 |
| disulphide | | 2.61 | 0.47 | 2.72 | | 64.7 | -174.2 | | | 0.095 |
| Diphenyl | 0.16 | 2.59 | | 2.77 | 2.16 | 51.4 | 8.8 | 0.024 | 0.329 | 0.083 |
| disulphide | | 2.70 | | 2.85 | | 48.9 | -174.8 | | | 0.073 |

Table 2.  Binding energies (E) and structural parameters for disulphide adsorption. Parameters are: height of S atoms above surface (H) and their offset from the atop site (ΔY), bondlengths between S and atop Au (S-Au), and between S atoms (S-S), tilt of tailgroups with respect to surface normal (θ), orientation of tail group projected onto x-y plane (φ), Mulliken charge of molecule (Q), and Mulliken population overlaps between two S atoms (S-S) and between S atom and atop Au atom (S-Au).

**Figure Captions**

Figure 1.  Benzenethiolate and methanethiolate molecules chemisorbed on the Au(111) surface.  The terminal S-H bond for both molecules has been cleaved prior to adsorption. Sulphur atoms are labelled.

Figure 2. The Au(111) surface showing the path for the potential energy scan.  Second and third layer gold atoms are depicted by successively smaller spheres.

Figure 3.  Potential energy surface for methanethiolate along the atop-bridge-atop path. Energies are relative to the minimum, and the Y-coordinate is relative to the bridge site.

Figure 4.  Potential energy surface for benzenethiolate along the atop-bridge-atop path. Energies are relative to the minimum, and the Y-coordinate is relative to the bridge site.

Figure 5.  Optimum geometries for the thiol dimers, diphenyl disulphide (left) and dimethyl disulphide (right) shown from two different perspectives in (a) and (b). Sulphur atoms are labelled.

Figure 6.  Potential energy surface for dissociation of dimethyl disulphide.  The x- and y-coordinates are relative to the nearest atop gold surface atom, contours are in 0.05 eV intervals and are relative to the optimum energy of the disulphide. The second sulphur atom is fixed at x,y-coordinates of 1.05 and 2.27 Å.

Figure 7. Spin unrestricted calculations for the dissociation of dimethyl disulphide along the two lines shown in Figure 6. Energies are relative to the optimized disulphide and units of spin are number of electrons.

Figure 8. Mulliken overlap populations between the two S atoms and between each S atom and its nearest atop surface gold atom. The total spin of the system is also shown.