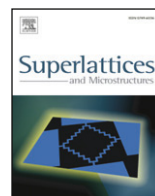




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# Modeling thiols on Au(111): Structural, thermodynamic and magnetic properties of simple thiols and thiol-radicals

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## ABSTRACT

Self-assembled monolayers (SAMs) of functionalized organic/inorganic moieties represent one of the new trends in nanoscience. The most representative models for SAMs are those where saturated and unsaturated thiols on gold surfaces are involved. To give an insight on the site of attack and the reacting species involved in the reactions we have performed mixed gaussian/planewaves periodic DFT calculations on the absorption of simple Me-SX (X = H, <sup>-</sup>, and <sup>•</sup>) species on the Au(111). A bridge-fcc binding site has been confirmed on clear gold surfaces but a more exothermic reaction has been encountered when a reconstructed (adatoms) surface has been considered. Moreover, preliminary and encouraging results on structural and magnetic data on SAMs of the 4-(methylthio)phenyl nitronyl nitroxide and the 4-(methylthio)methyl phenyl nitronyl nitroxide on the Au(111) will be also presented.

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## 1. Introduction

Self-assembled monolayers (SAMs) represent one of the new trends in nanoscience [1,2]. SAMs are those ordered materials (surfactants) which have a shape and a desired chemical composition due to their proper intrinsic characteristics and properly treated surface of the substrate. Atoms or molecules at the surface of a material exhibit different and unprecedented properties from that of the bulk ones [1,2]. In fact, they go from coupling the external environment to the electronic and optical

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properties of the metallic surface to linking molecular-level structures to macroscopic interfacial phenomena. For these reasons the research on their technological applications and the interest in understanding their peculiar properties have been given great impulse in recent years [3]. The most representative models for SAMs are those where saturated and unsaturated thiols on gold surfaces are involved [1,2]. The methylthiols are definitely the precursor of all more complex SAMs based on thiols and that is the reason why they have been widely studied so far. Even if many experimental studies have been carried out on such kind of systems only the periodicity of the high-density full coverage has been widely accepted to be  $(\sqrt{3} \times \sqrt{3})R30^\circ$  [1,4]. Other basic issues are still not well understood or unambiguously defined. For instance, the site of the attack, the nature of the Au–S bond and the reacting species involved in the reaction are still a subject of debate [1,5–7].

Nevertheless, thiols have been widely used to obtain SAMs with particular properties depending on the attached functional group. Recently they have been used in combination with Single Molecule Magnets (SMMs) in a bottom up approach in order to obtain appealing magnetic nano-devices [8]. In this scenario, the theoretical quantum chemical studies can be a valid tool [9,10] to give answers to unanswered basic questions and insights into the formation and properties of precursors of new magnetic SAM nano-devices.

Here we present a computational study performed on thiols on gold with a mixed gaussians and plane waves method. Our results report geometrical data for Me–SX ( $X = \text{H}, ^-, \text{ and } \cdot$ ) species adsorbed onto the gold surface in order to test the method for more complex systems like nitronyl-nitroxides thiols on gold. The energetics of Me–SX species are also reported. The presence of adatoms were also considered. We also present the first periodical study of SAMs of thiol-nitronyl-nitroxide radicals on Au(111). Their interactions with the gold surface, their local structures, and their magnetic properties have also been investigated.

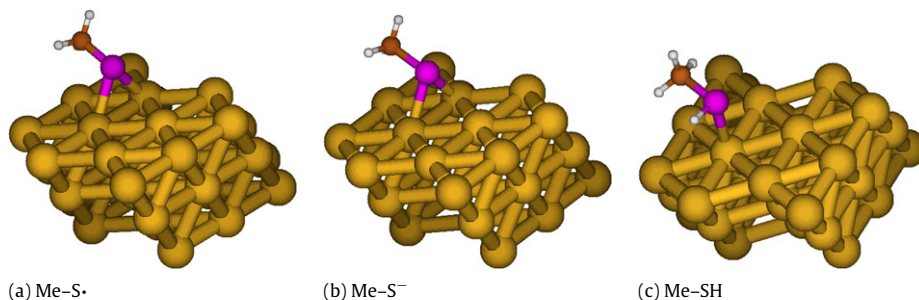
## 2. Computational details

All calculations were performed at DFT level of theory and were carried out with the CP2K program by Parrinello et al. [11] when not explicitly indicated. CP2K is based on the GPW (hybrid Gaussian and Plane Waves wavefunctions) method [12]. The BLYP and the TPSS exchange–correlation functionals were used for the Me–SX systems. Only BLYP was used for the thiol-nitronyl-nitroxide radicals. Double- $\zeta$  GTH basis sets and their relativistic, norm-conserving pseudopotentials [13] were used in addition of a plane basis set with an energy cutoff of 350 Ry. Several unit cells containing a different number of gold atoms ( $\text{Au}_x = 36, 48, \text{ and } 54$ ) were used throughout the calculations. They were properly shaped to obtain a whole three layers gold surface when Periodic Boundary Conditions (PBC) are imposed over an orthorhombic simulation cell. The  $\text{Au}_{37}$  cell was used to mimic a reconstructed cell (one adatoms). The convergence criteria were set to be  $1 \times 10^{-7}$  Hartree for the SCF energy, and  $9 \times 10^{-4}$  hartree/Å (hartree/rad) for the total energy gradient. These parameters are at least as accurate as usually reported in literature for similar systems [14,15]. To define the simulation cell, we took a reference frame where the  $x$  and  $y$  axis are on the surface plane. The cell size along the  $z$  axis was chosen to be 40 Å, compared to an inter-layer distance of 2.35 Å and about 30 Å of empty space. Along the  $x$  and  $y$  axis the cell size varies depending on the number of the gold atoms present in the cell used. Binding energies were computed according to the following expression:

$$\Delta H_f = E(\text{Au}_x\text{-SR}_1\text{R}_2) - [E(\text{Au}_x) + E(\text{R}_1\text{SR}_2)]. \quad (1)$$

Along this definition, positive  $\Delta H_f$  means an endothermic reaction, i.e. no bond formation. No BSSE corrections have been performed.

The studies on the magnetic properties of the 4-(methylthio)phenyl Nitronyl Nitroxide, from here nitPhSMe, and 4-(methylthio)methyl phenyl Nitronyl Nitroxide, from here nitPhCH<sub>2</sub>SMe, have been performed with Jaguar 7.0 [16] suite of programs with a hybrid B3LYP functional together with LACVP basis set (LanL2DZ for Au and 6-31G for the remaining atoms). The magnetic exchange interactions have been computed by performing single point calculations on the CP2K optimized geometry using very tight energy cut-off required for such a type of calculation.



**Fig. 1.** Final geometries for (a) Me-S•, (b) Me-S<sup>−</sup>, and (c) Me-SH unit cells on clean Au(111) surface computed with the TPSS functional.

**Table 1**

A summary of calculated and experimental energetics and geometrical parameters of Me-SH, Me-S<sup>−</sup> and Me-S• on unreconstructed Au(111) surface. *D* is for S–Au(111) distance; Au–S is for the S distances from the closest Au atoms;  $\zeta$  is for the supplementary of C–S–Au(111) angle.

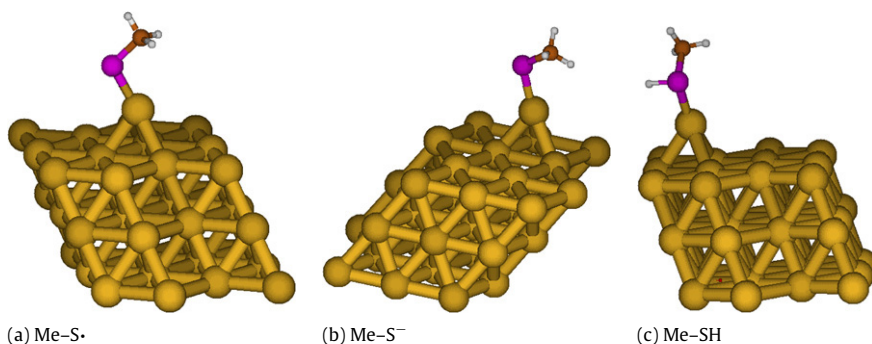
Species	DFT	Position	<i>D</i> (Å)	Au–S (Å)	$\zeta$ (degree)	$\Delta H^f$ (kcal/mol)
Me-S•	BLYP	<i>Fcc-bridge</i>	2.23	2.66	64.70	−26.47
	TPSS	<i>Bridge</i>	2.09	2.54	63.43	−37.2
MeSH	BLYP	<i>physisorbed</i>	3.53	3.97/3.67	81.6	−3.4
	TPSS	<i>Ontop</i>	2.60	2.61	69.1	−12.8
MeS <sup>−</sup>	BLYP	<i>fcc-bridge</i>	2.39	2.84/2.75	64.7	−16.8
	TPSS	<i>fcc-bridge</i>	2.15	2.59/2.61	58.6	−34.1
nitPhSMe	BLYP	<i>physisorbed</i>	3.62	3.92	53.3	+1.6
nitPhS•	BLYP triplet(singlet)	<i>ontop(ontop)</i>	2.63(2.63)	3.35(3.35)	60.0(60.2)	−12.0(−13.3)

### 3. Results and discussion

#### 3.1. Simple thiols

There is a substantial agreement in literature that the most preferred binding site of thiols on a clean gold surface are the atop and the bridge-fcc one, that is, a configuration where the sulphur atom is bound by two gold atoms in a bridge configuration but leaning towards the fcc site. In particular, the majority of theoretical work reported predict bridge-fcc as the preferred site of attack. The initial experimental reports agree with this predictions, however the latest reports contradict and suggest rather an atop configuration. Comparing the results for the Me-SX, we found that the Me-S• species is the most strongly bound species (see Fig. 1 and Table 1). On a flat surface, the geometry optimization always converged on the bridge-fcc configuration (see Table 1). Comparing our data for Me-S• with those found in literature we see that the energy found with TPSS (−37.2 kcal/mol) is in a very good agreement with the recent experimental findings [17] and theoretical works ([6,18] with PBE and [19] with PW91 functionals). In general, the TPSS functional seems to perform better than BLYP and the BLYP functional overestimates the Au–S bond lengths.

Different binding sites other than the bridge or bridge-fcc site are only considered in the earlier reports [20] or those that refer to a reconstructed surface with the presence of adatoms [21]. To check also this possibility, we performed studies on the reconstructed surfaces using Me-S•, Me-SH, and Me-S<sup>−</sup> as test species (Fig. 2). As far as we know, this is the first work comparing different reactivity of these species in the presence of adatoms. Both BLYP and TPSS functionals have been used in the calculations (see Table 2). For Me-S• on the presence of adatom, we found a binding energy of −34.8 kcal/mol for the BLYP and −39.4 kcal/mol for the TPSS functionals. Both results are compatible with the similar result reported by Häkkinen et al. [9]. On the other hand, the most favored species in this case is found to be the Me-S<sup>−</sup> (see Table 2), suggesting a different surface selectivity depending on the presence or the absence of the reconstruction process. A complete table with structural and thermodynamic data together with corresponding references can be find in supplementary material.



**Fig. 2.** Final geometries for (a) Me-S•, (b) Me-S<sup>−</sup>, and (c) Me-SH unit cells on reconstructed Au(111) surface computed with the TPSS functional.

**Table 2**

A summary of calculated and experimental energetics and geometrical parameters of Me-SH, Me-S<sup>−</sup> and Me-S• on reconstructed Au(111). Au-S is for the S distances from the closest Au atoms;  $\lambda$  is for the of C-S-Au(111) angle.  $\tau$  is for the angle between S-Au(adatom) and the normal to the surface.

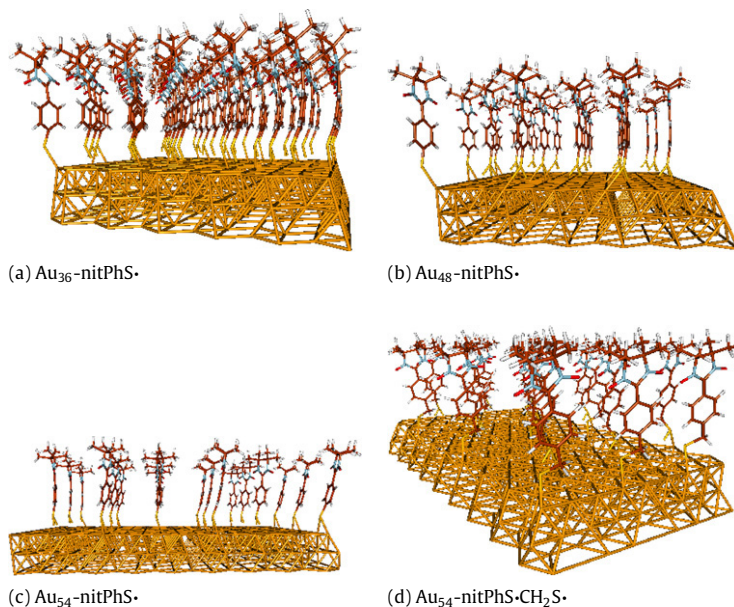
Species	DFT	Position	Au-S (Å)	$\lambda$ (degree)	$\tau$ (degree)	$\Delta H^f$ (kcal/mol)
Me-S•	BLYP	<i>Ontop</i>	2.37	110.9	26.6	−34.8
	TPSS	<i>Ontop</i>	2.32	107.4	28.8	−39.4
MeSH	BLYP	<i>Ontop</i>	2.57	111.4	19.9	−12.5
	TPSS	<i>Ontop</i>	2.45	111.5	24.9	−19.4
MeS <sup>−</sup>	BLYP	<i>Ontop</i>	2.41	105.5	16.7	−35.0
	TPSS	<i>Ontop</i>	1.85	106.8	23.5	−48.8

### 3.2. Thiol-radical

One of the key issues in the studies of SAMs of nitronyl nitroxide radicals on gold is to establish clearly the nature of the adsorbed species (methylated vs. demethylated), thus we have started calculating the enthalpies of formation for the nitPhSMe species on a clear surface of gold with BLYP. Since the spin configuration of the adsorbed molecules is one of the keys to understand the magnetic properties of the resulting monolayer, we have performed our calculations for both the singlet and the triplet spin states. As a first result, we found that the attack of the de-methylated species is strongly energetically favored. In fact, the adsorption of the nitPhSMe on the gold surface was found to be endothermic, with a binding energy of +1.6 kcal/mol. Considering the spin state of adsorption for the nitPhS on gold, we found that the singlet spin state is slightly favored (−13.3 kcal/mol) over the triplet state (−12.0 kcal/mol). The relative energy between singlet and triplet state is especially interesting when one considers the energies of the two states of the molecule in the gaseous phase show an inverse behavior, where the triplet state is found to be the fundamental one, being 2.4 kcal/mol lower than the singlet state. This suggests that the adsorption process significantly influence the magnetic properties of the adsorbed radical.

### 3.3. SAM-Thiol-radicals

Starting from the results in the previous section, we considered the de-methylated species the nitPhS• and the nitPhCH<sub>2</sub>S• and we tried to build monolayers by arranging adsorbed molecules in our simulation cells to form regular superstructures when periodic boundary conditions are imposed (Fig. 3). Our first guess was to consider the ( $\sqrt{3} \times \sqrt{3}$ )R30° arrangement of the nitPhS• molecules in the Au<sub>36</sub> cluster, thus reproducing the superstructure found for methyl-thiol monolayers by functionalizing the thiols with the nitronyl-nitroxide head group. In practical terms, this means considering four molecules per cell. However, this initial guess did not work, since we found a binding energy per radical molecule is highly endothermic: +15.8 kcal/mol. Very close packing of the



**Fig. 3.** Final geometries for  $3 \times 3$  Au<sub>36–48–54</sub>-nitPhS·/Au<sub>54</sub>-nitPhCH<sub>2</sub>S· unit cells on clean Au(111) surface computed with the TPSS functional.

molecules in the unit cell can be a possible explanation for the endothermicity of this reaction. We therefore moved to a model with two radical molecules per simulation cell over the Au<sub>36</sub> cluster. This time, a negative binding energy,  $-1.3$  kcal/mol per adsorbed molecule, was found. Moreover, the two radicals are adsorbed in two non equivalent configurations: one of the radicals still is adsorbed in the bridge position, while the other shifts to an on top configuration. However, this kind of arrangement in the Au<sub>36</sub> cell is not able to reproduce a regular superstructure. Therefore, we introduce the Au<sub>48</sub> and the Au<sub>54</sub> atom unit cells. In the Au<sub>48</sub> cluster with two adsorbed nitPhS· molecules, we found a lower binding energy:  $-2.3$  kcal/mol. This reveals that increasing the inter-molecular distance decreases the repulsive interaction between molecules, thus lowering the total energy. Although the conclusion is not appealing, this bunch of tests allow us to choose the right unit cell model for the calculations, which apart from reproducing the experimental pattern shows a favorable formation energies. Since the calculations so far have been performed with the BLYP functional, which is known to reproduce only the repulsive part of the Van der Waals forces, we expect the inter-molecular repulsive force to be somewhat overestimated in the present work. Another interesting feature of this system is that the adsorbed radicals configuration is now hcp for both the molecules. This suggests that the coverage also influences the configuration of the binding sites. By increasing the inter-molecular distances, the binding energy further increases. For an Au<sub>54</sub> gold atom slab with two molecules per simulation cell, the binding energy per molecule is about  $-3$  kcal/mol where the lattice arrangement is roughly  $(7/4 \times 7/4)$ . Both in the Au<sub>48</sub> and Au<sub>54</sub> systems we can observe a chain-like disposition where the magnetically active nitroxide groups are nearest along a certain direction. An inter-chain interaction for the possible magnetic properties of the monolayer is therefore expected leading to a ladder-like, two dimensional magnetic interactions. Compared to the nitPhS·, the nitPhCH<sub>2</sub>S· seems to form more stable monolayers on gold surface, with an enthalpy of formation of  $-7.0$  kcal/mol per molecule for a system of two molecules in the Au<sub>48</sub> cluster, and  $-7.2$  kcal/mol per molecule for two molecules in the Au<sub>54</sub> cluster. These energies also suggests that the bond strengths of the nitPhCH<sub>2</sub>S· are less sensitive to the coverage than the bond strength of the corresponding nitPhS· system. This different behavior can be explained by a greater flexibility of the nitPhCH<sub>2</sub>S· molecule, granted by the CH<sub>2</sub> group.

To give a preliminary insight into the magnetic properties arising from the ladder-like arrangement, we also performed B3LYP calculations on the optimized Au<sub>54</sub>-nitPhCH<sub>2</sub>S geometry.

In this framework, two magnetic couplings, the intra (within the nitronyl nitroxide molecule) and inter (between two nitronyl nitroxide neighbors)  $J$ 's, were computed. To notice that two different attached species can be found: the main structural difference being the sulphur atom approximately perpendicular to the nitronyl nitroxide ring (**F1**) while the other one being parallel (**F2**) to the ring. Although in both species the interaction is ferromagnetic, the magnitude of  $J$  is strikingly different with  $J$  of  $-311.4$  and  $-32.8 \text{ cm}^{-1}$  for **F1** and **F2**, respectively. However upon grafting on the surface the  $J$ 's reduced to  $-246.7$  and  $-69.1 \text{ cm}^{-1}$  for **F1** and **F2** respectively. The inter  $J$  calculated on a dimeric unit with a closer nitronyl–nitronyl distance of  $4.56 \text{ \AA}$  is antiferromagnetic by  $132.3 \text{ cm}^{-1}$ . However on a different dimeric unit picked with the nitronyl–nitronyl distance of  $8.14 \text{ \AA}$  the interaction becomes ferromagnetic by  $-59.0 \text{ cm}^{-1}$ . A quantitative conclusion about the inter  $J$ 's, however require calculations on larger model complexes which is in progress.

#### 4. Conclusions

In summary, new insights into the reactivity of simple thiols on clean and reconstructed gold surfaces by DFT calculations have been reported. We provided computational evidences for a preferable homolytic cleavage of S–Me or S–H bonds cleavage for clean gold surfaces while no S–Me bond breaking have been observed in the presence of adatoms. Moreover, Me–S• is found to be the favoured species in the clean surface but computations indicates a more complex situation in the reconstructed gold surface case. To obtain a clear cut understanding on the structure and energetics, both kinetic and thermodynamic terms should be considered when the formation of a particular species is of interest. Promising results have also obtained for more complex systems like the nitPhS• and the nitPhCH<sub>2</sub>S• species. A thorough analysis with further calculations on other species and other possible structural models is in progress and will be reported at a later date.

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#### Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.spmi.2008.12.006.

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