

# Modeling Thiols on Au(111): a possible route to the SAM of SMMs. Structural, Thermodynamic, and Magnetic Properties of Simple Radicals

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## 1 Introduction

Thiols have been widely used to obtain SAMs[1] with particular properties depending on the attached functionalised group. Recently they have been used in combination of Single Molecule Magnets in a bottom up approach in order to obtain appealing magnetic nano-devices.

In this scenario, the theoretical quantum chemical studies[2] can be a valid tool to give answers to the unanswered basic questions and insights into the formation and properties of the precursors of new magnetic SAM nano-devices.[3]

Here we present the first computational study performed on the thiols on gold surface with a mixed gaussians and plane waves method. Our results report geometrical data for a series of isolated simple aliphatic and aromatic compounds adsorbed onto the gold surface in order to test the method for more complex systems like nitronyl-nitroxides thiols on gold. We have also attempted to shed some light onto the reaction mechanism takes place between thiols and the gold surface. Energetics for RS-H, R-S•, and RS<sup>-</sup> species are therefore reported (R = CH<sub>3</sub><sup>-</sup> and CH<sub>3</sub>CH<sub>2</sub><sup>-</sup>). The presence of ad-atoms were also considered. Thermodynamics data were also computed for all the chosen compounds.

We also present the first study of SAMs of thiol-nitronyl-nitroxide radicals on Au(111). Their interactions with the surface of gold, their structures, and their magnetic properties have 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.* [4] when not explicitly indicated. CP2K is based on the GPW (hybrid Gaussian and Plane Waves wavefunctions) method. BLYP and TPSS as exchange-correlation functional was used throughout the calculations. Double- $\zeta$  GTH basis sets and their relativistic, norm-conserving pseudopotentials 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 ( $Au_x = 36, 48, \text{ and } 54$ ) 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 (Hexagonal simulation cells are not yet available in CP2K). 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 number of the gold atoms present in the cell used. Binding energies were computed according to the following expression:

$$\Delta H_f = E(Au_x-SR_1R_2) - [E(Au_x) + E(R_1SR_2)] \quad (1)$$

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

The studies on the potential energy surface of the homolytic cleavage of the R<sub>1</sub>S-H and NitS-CH<sub>3</sub> bond have been performed with Jaguar 7.0 suite of programs [5] with a hybrid B3LYP functional together with LACVP basis set (LanL2DZ for Au and 6-31G for the remaining atoms). The transition states have been computed using QST approach implemented in the Jaguar and the nature of the transition states have been analysed by frequency calculations. The magnetic exchange interactions have been computed at B3LYP/LACVP\* level by performing single point calculations on the CP2K optimised geometries using very tight energy cut-off required for such type of calculations.

### 3 Results and Discussion

#### 3.1 Simple Thiols

There is a substantial agreement in literature that the most likely way of binding on a clean gold surface would be a atop one and the bridge-fcc binding modes, that is, a configuration where the sulphur atom is bound to two gold atom like in the bridge configuration, but it is leaning toward the fcc site. In particular, the majority of theoretical works seems to agree about the bridge-fcc as the preferred site. Although the initial experimental results suggest a bridge-fcc binding mode, recent works however have enough evidence to demonstrate a favourable atop binding. Comparing the results for the R-S•, R-SH, and R-S<sup>-</sup> species (where R = Methyl, Ethyl), we found that the R-S• species are the most strongly bound species both for ethyl and methyl thiolates. This trend is followed for the disubstituted radicals as well, where the two chains species are far less bound than the corresponding single-chain molecule. In all our calculations, the geometry optimization always converged in the bridge-fcc configuration which therefore appears to be the preferred one. Comparing our data for Me-S• with those found in the literature we see that the computed binding energy of -37.2 Kcal/mol with TPSS functional is in good agreement to that of the recent experimental and theoretical work. On the other hand, BLYP functional differ by about 22% with that of the recent experimental results. Our BLYP calculations for Et-S• are also in agreement with literature. The TPSS functional seems to perform better than BLYP in the determination of geometries, as the bond length between gold and sulphur are in agreement with the majority of the reported literature values. The bond lengths calculated with BLYP however seems to be somewhat overestimated.

We have also performed studies about the reconstructed surfaces using Me-S•, Me-SH, and Me-S<sup>-</sup> and as test species. As far as we know, this is the first work comparing the different reactivity of these species in presence of ad-atoms. Both BLYP and TPSS functionals have been used in the calculations. For Me-S• on ad-atom, we found a binding energy of 39.4 Kcal/mol for BLYP and of 45.2 Kcal/mol for TPSS functional. Comparing these results to the data of Häkkinen, we found that they are compatible both for BLYP and TPSS potentials (47.3 Kcal/mol). As in the case of unrelaxed surface, the TPSS data seem to better agree with the literature. The sulphur gold atoms distance in the surface is found to be slightly overestimated in BLYP while for TPSS if found have a good agreement.

#### 3.2 Thiols-Radicals

Since one of the key issues in the study of Self Assembled Monolayers of nitronyl nitroxide radicals on gold is to clearly establish if the adsorbed species is the methylated or not methylated one, therefore we started calculating the enthalpies of formation of 4-(methylthio)phenyl Nitronyl Nitroxide (nitPhSMe), and 4-(methylthio)methyl phenyl Nitronyl Nitroxide (nitPhCH<sub>2</sub>SMe), on gold, using the BLYP

functional. Since the spin configuration of the adsorbed molecules is one of the keys to understand the magnetic properties of the resulting monolayer, we performed our calculation by both imposing a singlet and a triplet spin state to the system. As a first result, we found that the attach of the demethylated species is strongly favored. In fact our calculations suggest that the bonding with the nitPhSMe is thermodynamically unfavourable as the computed binding energy is endothermic (1.6 Kcal/mol). Considering the adsorption of nitPhS on gold, we found that the singlet spin state is energetically favored (-13.3 Kcal/mol) over the triplet state (-12.0 Kcal/mol). The relative energy difference between singlet and triplet states are especially interesting when one consider that the energies of the two states of the molecule in the gaseous phase show an inverse behaviour, where the triplet state is the fundamental one (with a margin of 2.4 Kcal/mol). Therefore we can conclude that the adsorption process significantly changes the magnetic properties of the adsorbed radical.

We have also attempted to model the potential energy surface of the S-C homolytic cleavage. The activation barrier leading to the transition state is found to be 15 kcal/mol and the the overall reaction is found to be exothermic with a reaction energy of -30.0 kcal/mol favoring the S-CH<sub>3</sub> cleavage and also supports the calculations performed with CP2K package.

### 3.3 SAM-Thiol-Radicals

Starting from the results in the previous section, we considered the demethylated species nitPhS and 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. Our first guess was to consider the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  arrangement of nitPhS molecules in the Au<sub>36</sub> cluster, thus reproducing the superstructure found for methyl-thiol monolayers by functionalising the thiol with the nitronyl-nitroxide head group. In practical terms, this means considering four molecules per cell. However, this initial guess does not seems to work, because looking at the energetics, we found a binding energy per radical molecules are extremely positive: +63 Kcal/mol. A possible explanation for this behavior, is that in fact, the benzene rings of each of the nitronyl nitroxide radicals are significantly deformed. The packing of the molecules is too close, and inter molecular forces deform the molecules, thus increasing the total energy of the system. We repeated our calculations by placing two radical molecules per simulation cell over the Au<sub>36</sub> cluster. This time a negative binding energy of -2.6 Kcal/mol per adsorbed molecule was found. Also, the two radicals are adsorbed in two non equivalent binding sites one of the radicals still is adsorbed in the bridge position, while the other shifts to an ontop configuration. However, this kind of arrangement in the Au<sub>36</sub> cell does not allows to reproduce a regular superstructure. Therefore, we introduce the Au<sub>48</sub> and Au<sub>54</sub> atoms clusters. In the Au<sub>48</sub> cluster with two adsorbed nitPhS molecules, we found a still lower binding energy: -4.6 Kcal/mol. In conclusion, increasing the inter-molecular distance decreases the repulsive interaction between molecules, thus lowering the total energy. Since the calculations so far have been performed in BLYP, which is known to only reproduce 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 configurations is now hcp for both the molecules. This suggests that the coverage also influences the configuration of the attach 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 is about -6 Kcal/mol. 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 deposition where the magnetically active nitroxide groups are the 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 nitPhS, nitPhCH<sub>2</sub>S seems to form more stable monolayers on gold surface, with an enthalpy of formation of -14.1 Kcal/mol per molecule for a system of two molecules in the Au<sub>48</sub> cluster, and -14.3 Kcal/mol per molecule for two molecules in the Au<sub>54</sub> cluster. These energies also suggest that bond strength of nitPhCH<sub>2</sub>S is less sensitive to the coverage than the bond strengths 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 additional CH<sub>2</sub> spacer group.

We have also performed DFT calculations on the CP2K optimised Au<sub>54</sub>-nitPhCH<sub>2</sub>S geometry with Jaguar to estimate the magnetic coupling for both the intra (within the nitronyl nitroxide molecule) and the inter (between two nitronyl nitroxide neighbours) *J*'s. 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 perpendicular (**F2**) to the ring. Although both the interactions are ferromagnetic, the magnitude of *J* is strikingly different with *J* of -242.6 and -32.8 cm<sup>-1</sup> for **F1** and **F2** respectively. However upon grafting on the surface the *J* reduced to -61.7 and -11.7 cm<sup>-1</sup> for **F1** and **F2** respectively. The inter *J* calculated on a dimeric unit with a closer nitronyl-nitronyl distance of 4.56 Å is antiferromagnetic by 132.3 cm<sup>-1</sup>, however on a different dimeric unit picked with the nitronyl-nitronyl distance of 8.14 Å the interaction is ferromagnetic by -59.0 cm<sup>-1</sup>. A quantitative conclusion about the inter *J*'s, however require calculations on a larger model complexes which is in progress.

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