Sulfur Adsorbed (Θ=1/2) on Gold (111) Substrate

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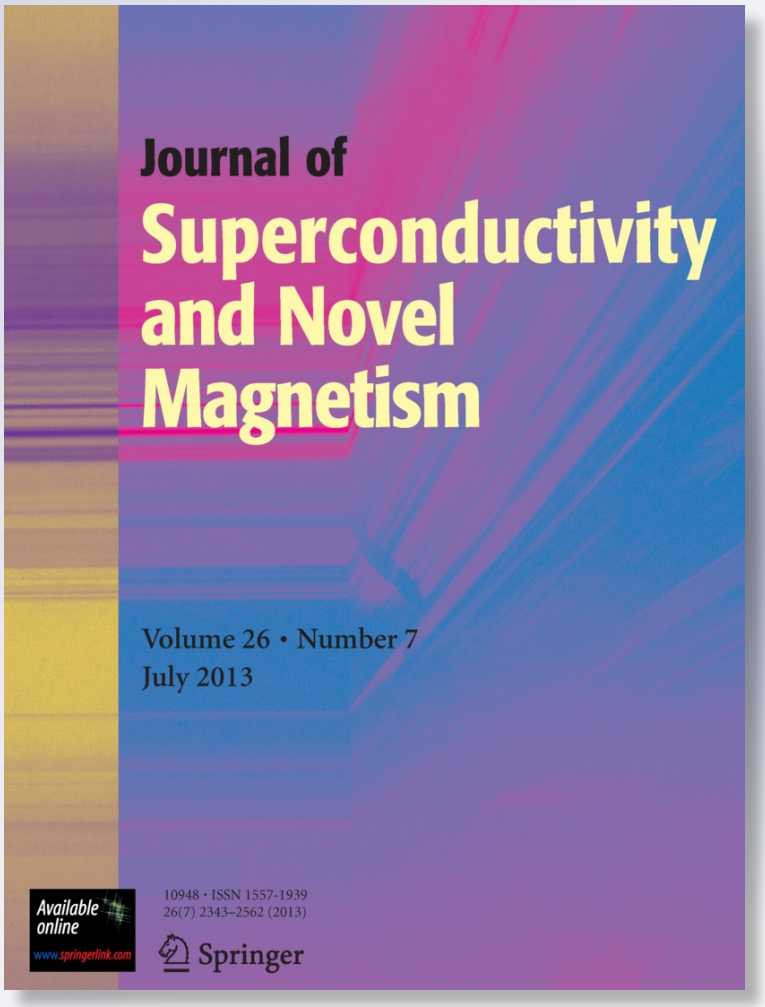

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ORIGINAL PAPER

Sulfur Adsorbed ($\Theta = 1/2$) on Gold (111) Substrate

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Abstract The adsorption of $\Theta = 1/2$ monolayer (ML) of S on Au(111) is calculated. The evolution of the positions of adatoms for 800 K, 500 K, 300 K, 150 K, and 1 K is evaluated by using a density functional theory (DFT)-tight binding approach combined with classical molecular dynamics. For this coverage, there is a controversy about the existence of superficial composite AuS or molecular aggregates. We find a configuration in which sulfur atoms form quasi-S_2 superficial molecules with total energy very close to the monoatomic phase, suggesting the coexistence of both configurations at room temperature. We find that the stability of the dimeric phase is due to the increase of the binding energies between sulfurs. In the other phase, the stabilization occurs due to a formation of AuS dimers. At high temperatures ($T > 300$ K) sulfurs have high mobility which allows the migration among different adsorption sites. At low temperatures the mobility decreases and a thermal activation barrier of 25–30 meV can be estimated.

Keywords Adsorption of S on Au(111) · Ab-intio DFT methods · Molecular dynamics

1 Introduction

The adsorption of sulfur onto gold surfaces is a very interesting problem for different research areas such as catalysis science or the development of new materials for molecular electronics [1–4]. Theoretical and experimental data show that sulfur can form molecular aggregates or superficial structures with long-range order depending on the coverage [5–9].

For Au(111) surfaces and coverages $\Theta \lesssim 1/3$ ML, the adsorption is dominated by the interaction of single sulfur adatoms with superficial gold atoms. On the other hand, for coverages of $\Theta \gtrsim 1/2$ ML, it is suggested that sulfur forms more complex structures [9], AuS compounds [7], or even superficial molecules S_n $(n = 2, \ldots, 8)$ [6, 10]. The diversity of superficial structures is possible because of the high mobility of S on Au for temperatures above 300 K [11].

In this paper we study the adsorption of S with coverage of $\Theta = 1/2$ ML on Au(111) for different temperatures. We find a dimeric phase with energies very close to the monoatomic one, indicating the plausibility of the existence of molecular superstructures.

2 Theoretical and Numerical Methods

We perform the calculations in the framework of the Local Density Approximation (LDA) of DFT applied to systems with translational periodicity. We use the FIREBALL [12–15] code. The interaction with core electrons and nucleus is incorporated through pseudopotentials [16]. The basis set is composed by (numerical) localized wavefunctions, which are strictly equal to zero beyond a cutoff radius, r_i $(i = s, p, d)$. We consider $r_s = 4.3a_0$ and $r_p = 4.7a_0$ for sulfur and $r_d = 4.1a_0$, $r_s = 4.6a_0$, and $r_p = 5.2a_0$ for gold, a_0 being the Bohr radius. The unit cell is composed by four layers of Au, each one with four atoms, and two superficial S atoms so that the coverage is $\Theta = 1/2$ ML as it is shown in Fig. 1. The cell is replicated in the x–y superficial plane,

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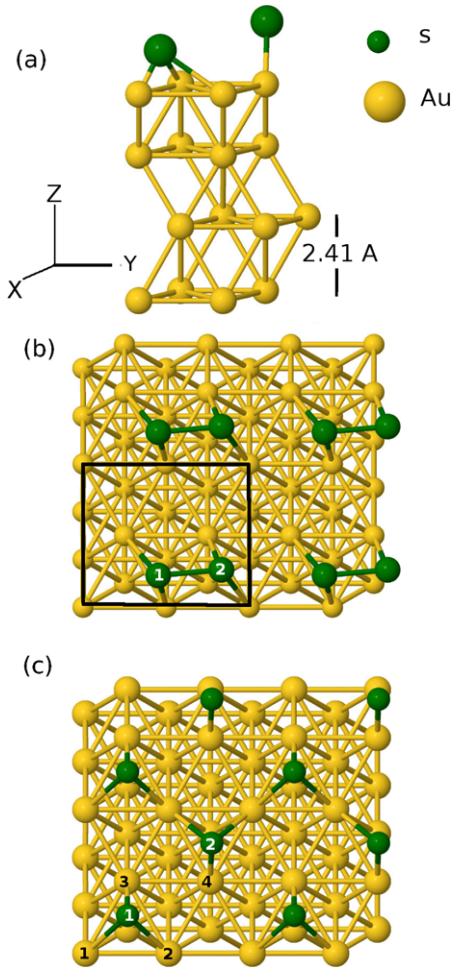

Fig. 1 (**a**) Unit cell used to simulate a coverage of $\Theta = 1/2$ ML. (**b**) and (**c**) Top views of the dimeric and atomic arrangements, respectively. The center of the Au1–Au2–Au3 (Au2–Au3–Au4) triangle is an fcc (hcp) site

and in the z-direction an empty space of 90 Å (equivalent to 37 layers) was added in order to simulate sulfur superficial effects without interaction with the nearest cell along the z-direction. It is not necessary to take into account the herringbone reconstruction of the surface because it is lost when a minimum sulfur coating is added [17, 18].

At temperatures greater than the room temperature, sulfur is expected to have high mobility. So, different geometric configurations can occur depending the sample temperature. To simulate this fact, we calculate the system to 800 K, 500 K, 300 K, 150 K, and 1 K, respectively. The electronic calculation is complemented with classical molecular dynamics. Firstly, atom velocities are randomly assigned following a Maxwell–Boltzmann distribution [13]; then, the atoms move according to LDA forces and the velocities are rescaled in order to assure a constant kinetic energy (or temperature).

The time step for the simulations is 0.2 fs and a maximum of 16000 steps is calculated. The tolerance criteria for convergence is 10^{-4} eV/atom for the total energy and 10^{-2} eV/Å for the forces [11]. In all the cases only the innermost layer of gold is fixed, and the three superficial ones, plus the adatoms, are free to move to optimize the energy. This DFT-MD technique has been successfully used in similar systems exhibiting dynamical fluctuations between two superficial phases [11, 19–21].

Note that the selected time and number of steps do not attempt to reproduce neither an experimental cooling nor a growth situation. The goal of this selection is to facilitate the system to reach low-temperature phases corresponding to local potential energy minima, which are not easily predicted from $T = 0$ K calculations.

3 Results and Discussion

Firstly, different geometric configurations compatible with a temperature of 800 K are explored. The initial positions of the S atoms were hollow-fcc for S1 and top for S2. At this temperature, S can migrate many times among superficial sites, as it is shown in Fig. 2a. As a reference, the boiling temperature of S is 717.8 K. Besides, it is possible to verify along the simulation the formation of dimeric phases and quasi-triangular atomic structures. After 16000 steps, when a dimeric structure is suggested, the system is frozen, and a new calculation for 500 K is started. Subsequent simulations at 300 K, 150 K, and 1 K are performed. For each temperature, the calculation starts with the reached positions at the previous temperature. Figures 2(a1–e1) (left panel) show the results of these calculations. Figures 2(a2–e2) (right panel) resume equivalent results to the previous but with the only difference to allow 9000 steps for 800 K, where a monoatomic phase is reached.

In Fig. 2(a1) the final distance between S atoms is 2.26 Å. This value is quite close to the equilibrium distance of S_2 in gas phase. Figure 3 shows the interaction energy of S–S dimer calculated with FIREBALL, 2.06 Å being the equilibrium distance. For 500 K [Fig. 2(b1)], the sulfur atoms jump from site to site but always remain as dimer with S–S distances oscillating in the range 2.26–2.51 Å. For 300 K, the mobility is much less than in 500 K. The adatoms form a dimer but still can move changing the azimuthal angle [Fig. 2(c1)]. Finally, at 150 K and 1 K, the S atoms do not jump to different sites, and they are stabilized in bridge positions [Fig. 2(d1)]. After simulations the S–S distance is 2.49 Å, close to the equilibrium distance of S_2 molecule. On the right panel, results of another set of simulations are presented. Here the system is stabilized with a superficial structure in which the adatoms are located far enough to resemble a monoatomic arrangement. In any case the adatoms are closer than 3.7 Å (S–S distance is 3.75 Å for 1 K), a distance where the two sulfurs practically do not interact attractively.

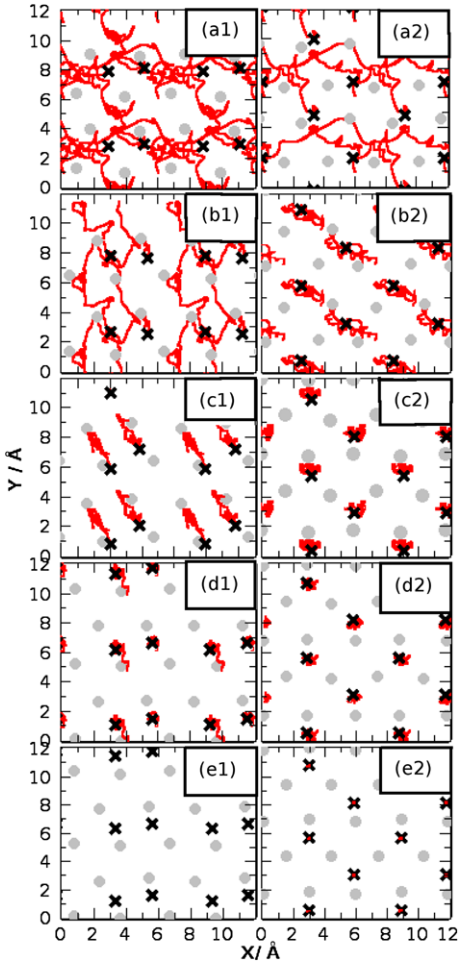

Fig. 2 Superficial phases. *Left panel* corresponds to the dimeric phase, and *right panel* to the atomic one. (**a1**) and (**a2**) $T = 800$ K, (**b1**) and (**b2**) $T = 500$ K, (**c1**) and (**c2**) $T = 300$ K, (**d1**) and (**d2**) $T = 150$ K, (**e1**) and (**e2**) $T = 1$ K. *Thin lines* show the successive positions of S for each simulation step. *Black crosses* indicate the final location of sulfurs after simulation. *Grey points* are the final location of gold atoms of the outermost layer. In all the cases the simulation steps were 16000 except in(**a2**) where 9000 steps were calculated

When the adatoms are stabilized in their final position, they are inside fcc and hcp triangles alternatively but near atop sites. Particularly interesting is to note that the S–Au distances are 2.44 Å, quite similar to the equilibrium distance of the S–Au dimer (2.23 Å). This fact can be interpreted as a slight indicator of a early formation of an AuS superficial composite as it is indicated in Refs. [7, 8], although it is worth mentioning that in our calculations the Au always remain on the (111) surface.

In both sets of simulations it is observed that S atoms are not able to move to different sites at $T \lesssim 300$ K. This result is practically the same as that for coverages of $\Theta = 1/3$ ML. In consequence, a thermal activation barrier of 25–30 meV can be roughly estimated again.

In Fig. 4 the evolution of the total energy for each step of simulation is drawn. For high temperatures, it is impossible

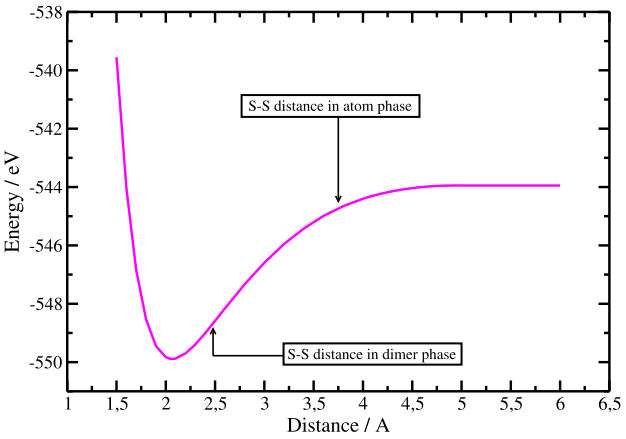

Fig. 3 Interaction energy for the S_2 system calculated with FIREBALL. The final distance in quasi-S_2 dimer phase and atomic phase is indicated with *arrows*

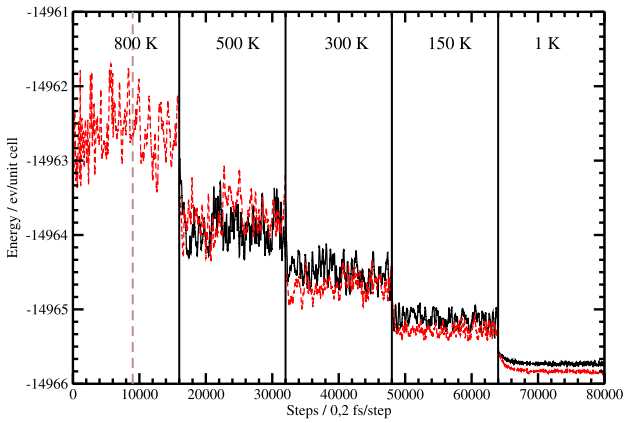

Fig. 4 *Black line*: monoatomic phase. *Red line*: quasi-dimeric phase. *Dashed vertical* indicates the step 9000 from which the simulations drawn in *black* were calculated

to identify a preferred phase, but from $T = 300$ K to lower temperatures, the dimeric phase is more stable, the difference for 1 K being of about 100 meV.

4 Conclusions

The transformation of S to S_2 on Au(111) for S coverages of 1 ML and 0.5 ML is suggested in bibliography data. This coincides with our results which show that a quasi-S_2 phase is energetically more stable. We found that this stability is due to the increase in the binding energies between S–S. The monoatomic phase is stabilized with energies slightly greater than the dimeric phase. In this case the system gain energy because the strong interaction between S and one superficial Au. In both cases the mobility of sulfurs occurring at $T \gtrsim 300$ K allow us to estimate a thermal activation energy of 25–30 meV, in the same way as for coverages of $\Theta = 0.33$ ML.

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