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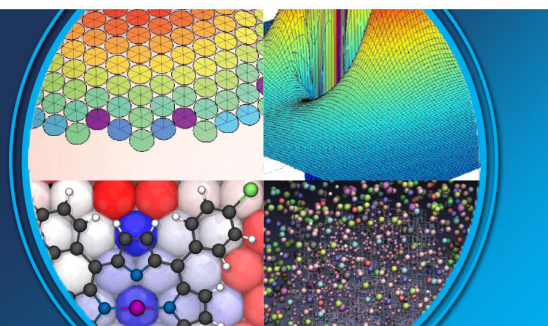
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PERSPECTIVES



Thiol and thiolate bond formation of ferrocene-1,1-dithiol to a Ag(111) surface

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Using density functional calculations, we show that the adsorption of ferrocene dithiol on the Ag(111) surface is remarkably flexible, i.e., a large number of different configurations have binding energies that differ by less than 0.1 eV per molecule. The thiolate bond is slightly favored over the thiol bond (by less than 0.1 eV) but may not be formed due to considerable activation barriers. Electronically, we found that the thiolate bound molecule is conducting, whereas thiol bonds turn it into semiconducting. © 2006 American Institute of Physics. [DOI: [10.1063/1.2387169](https://doi.org/10.1063/1.2387169)]

I. INTRODUCTION

Since the original suggestion by Aviram and Ratner¹ to use single molecules as central elements for controlling electric currents between two electrodes, a large number of experiments and even more simulations have been carried out in order to reach this ultimate goal of molecular electronics. One major problem is the formation of atomic size contacts and the control of their shape on the atomic level. This turns out to be necessary, because a single molecule and the contacts are strongly coupled so that they have to be considered as an entity. As a consequence, all electronic properties depend strongly on the local configurations of both the contacts and the molecule, as demonstrated in several recent simulations (see, e.g., Ref. 2).

A method that has come closest to this goal is the use of molecular break junctions.^{3,4} While conductance through single atoms³ and also through molecules inserted into open break junctions⁵ has been demonstrated, the local configuration cannot be controlled in these junctions, so that only indirect conclusions by comparison with theoretical simulations can be drawn.⁶ Therefore, alternative contacts are currently developed.⁷ While this underlines the importance of simulations, there is also a lack of systematic understanding of molecular binding at such contacts that has to be obtained to a large extent by theoretical calculations.

While different molecules, in particular, alkane chains⁸ have been tested in context with molecular electronics, ferrocene based molecules have only recently attracted interest. In contrast to alkane chains, ferrocene based molecules exhibit a remarkably large conductance^{6,10} without activation thresholds. In addition, the activation barrier for rotation of the two cyclopentadienyl (Cp) rings against each other is very

low¹¹ so that any molecule with a central ferrocene unit can easily adjust its length by this rotation, thus gaining a lot of flexibility in this context.

Alkane thiols and other sulfur containing organic molecules form stable bonds to most metallic surfaces via a thiol end group, in particular, also to gold and silver surfaces.⁹ Therefore, most studies with self-assembled monolayers of organic films or with single molecules have been carried out with thiol end groups. Since gold does not react with air and with most other compounds under ambient conditions, such experiments with gold surfaces can be carried out outside vacuum, which explains the popularity of gold-thiol bonds in context with molecular electronics.^{5,6,10} However, the use of gold electrodes strongly restricts chemical variability of the contacts.

Although thiol end groups are widely used, it is interesting to note that the question whether the S-H group spontaneously dissociates during adsorption is still a matter of debate, at least on noble metals.^{12,13} Only recently, calculations applying density functional theory (DFT) to the adsorption of methanethiol on Au(111) have provided the result that nondissociative adsorption is thermodynamically stable on the perfect Au(111) surface.¹⁴

In terms of electrical conductance, simulations show for Au(111) surfaces that thresholds are strongly affected changing the bond from S to SH (Ref. 15) due to shifts of molecular orbitals.

In this study, we investigate the adsorption of ferrocene-1,1'-dithiol (FDT) on a Ag(111) surface by DFT calculations. In the context outlined above, the adsorption on just a single and also a perfect single crystalline surface is a first step on a defect-free surface. However, as shown by comparing the properties of FDT molecules connected to one and two surfaces, it already yields valuable insights into the bonding between contacts. Apart from the determination of

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the configurations with lowest energies, we also calculated the corresponding electronic structures, which turn out to be more sensitive to local configurations than the thermodynamic properties. Finally, we also address the question of thiol versus thiolate bonding. Possible intermediates between both bonding situations are discussed.

II. TECHNICAL DETAILS

Our calculations were carried out within density functional theory using the projector augmented plane wave method^{16–19} together with the Perdew-Wang generalized gradient approximation (GGA) exchange correlation functional [PW91 (Refs. 20 and 21)] as implemented in the VASP code.

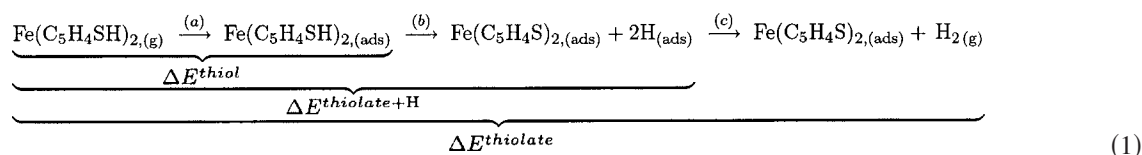
We carried out extended tests for Ag(111) slabs in order to determine optimal convergence at minimal computational cost. For Ag slabs with (1×1) surface structure a cutoff energy of 400 eV and a Monkhorst-Pack k -point grid²² (MP grid) of $(11 \times 11 \times 1)$ turned out to be sufficient for convergence of the total energy to less than 1 meV. With these

parameters the calculated Ag bulk lattice constant is 4.16 Å, slightly larger than the experimental value (4.09 Å).

Because of the size of the FDT molecule, we used for the adsorption of FDT a lateral (4×4) supercell with four Ag layers and a vacuum region of 15 Å. A $(3 \times 3 \times 1)$ MP grid (five irreducible k points) in combination with the smearing scheme proposed by Methfessel and Paxton²³ and a smearing width of 0.2 eV was used for the relaxations. It also turned out to be sufficient for the determination of energetic differences within an accuracy of less than 10 meV for static calculations as an increase of the MP grid to $5 \times 5 \times 1$ has shown. Densities of state (DOS) were obtained using P4VASP.²⁴

The topmost three Ag layers were allowed to relax, whereas the atoms of the fourth layer were kept fixed at their corresponding bulk lattice positions.

Reaction energies ΔE were calculated with the assumption that the following sequence of chemical reactions takes place:



The binding energies are calculated as the differences between the adsorbed species on the surface including the Ag slab after reaction steps (a), (b), and (c), respectively, and the separated FDT molecule plus slab. The reference energy of the FDT molecule was obtained using the same technical parameters, e.g., cutoff energy, and lattice parameters as for the slab calculation.

III. RESULTS

Before starting with calculations of FDT adsorbate geometries we compared the agreement of results for the isolated molecule calculated with GAUSSIAN03 and with VASP, using the same Perdew-Wang correlation functional (PW91) in both cases and the other parameters as given above (optimizations were stopped at gradients smaller than 0.04 eV/Å). This test is not trivial, since the basis sets in these program packages (plane waves in VASP and atomic Gaussian functions in GAUSSIAN03, in the present case 6-31G(d,p) for H, 6-311G(d,p) for C and S, and LANL2DZ for Fe) are completely different. The agreement is remarkably good: Both packages yield the same minimum structure at the configuration with the S atoms bound in plane with the eclipsed Cp rings, but at their maximal possible distance (rotation angle $\phi=144^\circ$) and with the H atoms pointing away from the Cp rings. Further local minima were obtained with both packages by rotating one or both H atoms “inwards” towards the central Fe atom, with energetic differences be-

low 40 meV. A similar almost perfect agreement was obtained for the positions and occupation numbers of the electronic levels, both for the total electron density and its projections onto the individual atoms or atomic groups.

A. Twofold thiolate bond to one Ag(111) surface

We started with the diradical molecule with the two H atoms stripped. In the starting configuration both S atoms were pointing towards the Ag surface. For the starting configurations we tried to systematically sample all possible configurations on the surface. They are schematically shown in Fig. 1 and numbered by 1–9 (see also Table I). The end points of the lines mark the positions of the S atoms. For configurations 1–3 the calculations started with the S atoms 3 Å above the first Ag layer; for the rest this distance was 2 Å. Since the S–S distance in the free radical (3.68 Å, as calculated) is approximately 1.3 times larger than the Ag–Ag nearest neighbor distance, both sulfur atoms cannot be located simultaneously at equivalent positions on the Ag surface without stretching the molecule. The second row of Table I therefore denotes the closest symmetric adsorption sites (ontop, bridging, hcp, and fcc threefold) with the exception of on-top sites, where one of the S atoms was exactly positioned. The third column shows the directions of relaxation (see also right part of Fig. 1). These relaxations are further characterized by the lateral separation between the S atoms after relaxation (S–S), and their individual distances to

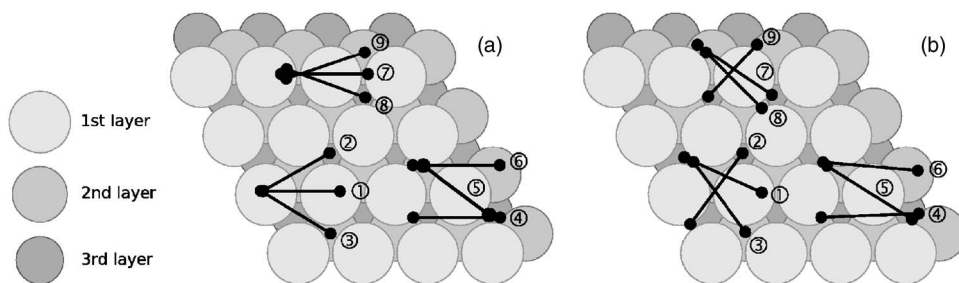


FIG. 1. Schematic of tested configurations for ferrocene dithiolate. (a) Starting configurations. (b) Relaxed configurations. The end points of the lines correspond to the positions of the S atoms. The gray balls represent Ag atoms.

the first Ag layer (Δz_1^S and Δz_2^S). Here the S distances with respect to the averaged position of the first Ag layer are given. They contain partly vertical relaxations of the closest Ag atoms of the first layer, which (e.g., in configuration 1) relax up to 0.2 Å out of the surface plane. Thus the Ag–S bond length variation is smaller than suggested by the values of Δz_1^S and Δz_2^S . For all other Ag atoms the relaxations turned out to be small (below 0.05 Å). An exception is again the Ag atom of the first layer positioned right below the central Fe atom (configurations 5 and 7), which relaxes by a similar amount (0.2 Å) out of the surface plane.

An example of a fully relaxed structure is shown in Fig. 2 for starting configuration 3. In this configuration, the S atoms have reached positions that are intermediate between bridge and threefold coordinated sites. This bonding remains remarkably asymmetric and is accompanied by a considerable tilt of the Cp rings against each other, resulting in an increased separation between the S atoms by 0.6 Å compared to the optimized gas-phase structure. In fact, this configuration has the largest separation between the S atoms that was found in our study. In addition, the Ag–S–C bond angles deviate strongly from 180° so that the FDT molecule appears to be inclined with respect to the surface normal and the S–S axis (see Fig. 2, bottom part). This inclination may be a consequence of the asymmetric S-bonds together with the deformation of the molecule, whereas a direct interaction between H atoms and the Ag surface seems to play no role because of the still too large distances. No inclinations were found for the less asymmetric S-bonding configurations.^{4–9}

As a second example, and in order to demonstrate the variability of the bonding configurations formed, we show in Fig. 3 the relaxed structure resulting from starting configuration 7. Here the rings get rotated in order to reach a better coordinated local environment for the S atoms at the expense

of tilting and rotating the rings. The configurations shown here and in Fig. 2 demonstrate that bonds to the surface are only formed via the sulfur atoms, as expected. Contributions from other atoms, however, are to be expected (see below) and are modified by the deformations of the molecules due to the bonds with the Ag surface.

Surprisingly, a comparison with the last column of Table I, which contains the binding energies E_B of the various configurations with respect to the free FDT radical, demonstrates that the differences in E_B , in spite of the significant differences of local configurations, do not exceed 0.1 eV. Different from ΔE^{thiol} [Eq. (1)], binding energies E_B are defined as energy difference between the Ag(111)/FDT system and the separated systems. This means that the adsorption potential hypersurface for this molecule is remarkably flat, i.e., the internal molecular degrees of freedom are flexible enough to adjust the positions of the S atoms. Only adsorption sites close to on-top positions of Ag atoms seem to be energetically unfavorable. These energetic differences are small enough that a large fraction of them is accessible by thermal excitation at or close to room temperature. These small energetic differences are also reflected in the total density of states (DOS) and in its projections onto individual atoms. The projected DOS of configurations 2 and 7 are shown in Figs. 4 and 5.

Nevertheless, the projected DOS reveals several interesting properties: Compared with the isolated molecule (not shown), the DOS projected onto S and C atoms is considerably broadened and smeared over the whole energy range between 0 and –6.5 eV (all energies are relative to the Fermi level of Ag), an indication that both the molecular orbitals located at the S atoms and (to a lesser extent) at the carbon rings contribute to the bonding with the Ag surface. In the energy range between 0 and –0.5 eV there is a split-off den-

TABLE I. Results of configurations obtained for twofold thiolate bonded ferrocene after starting with the configurations given on the left. The numbers in the leftmost column refer to those in Fig. 1.

	Starting geometry	After relaxation	S–S (Å)	Δz_1^S (Å)	Δz_2^S (Å)	E_B (eV)
1	top, bridge	→fcc, →bridge	4.11	2.44	2.25	2.40
2	top, fcc	→bridge, →fcc	4.37	2.25	2.01	2.49
3	top, hcp	→bridge, →hcp	4.37	2.14	2.00	2.48
4	fcc, fcc	→bridge, →bridge	3.78	1.92	1.89	2.45
5	fcc, hcp	→bridge, →bridge	4.06	1.96	1.87	2.50
6	hcp, hcp	→bridge, →bridge	3.81	1.92	1.90	2.40
7	bridge, bridge	→bridge, →fcc	4.16	1.87	2.03	2.47
8	bridge, fcc	→hcp, →bridge	4.27	1.97	1.87	2.46
9	bridge, hcp	→fcc, →bridge	4.12	1.95	1.85	2.49

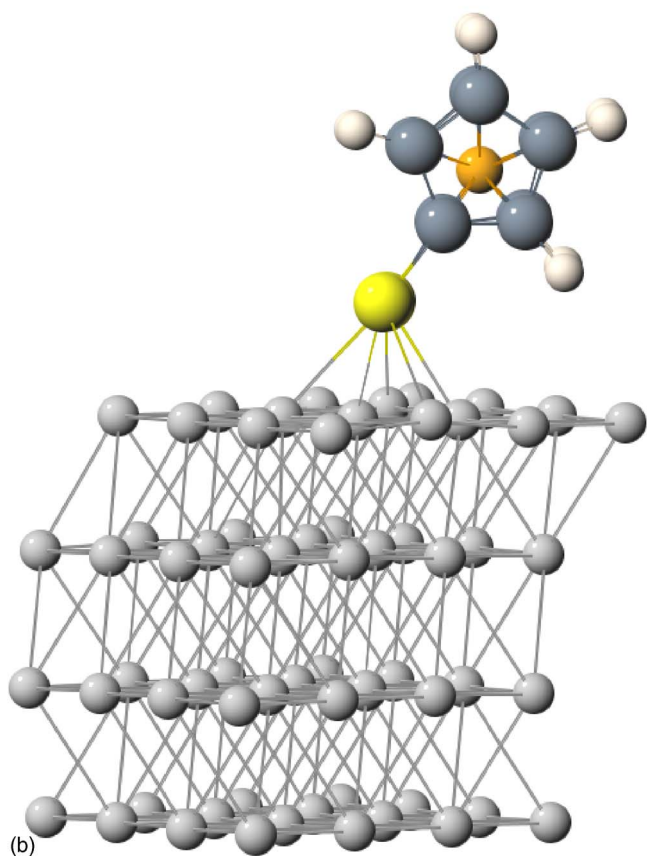
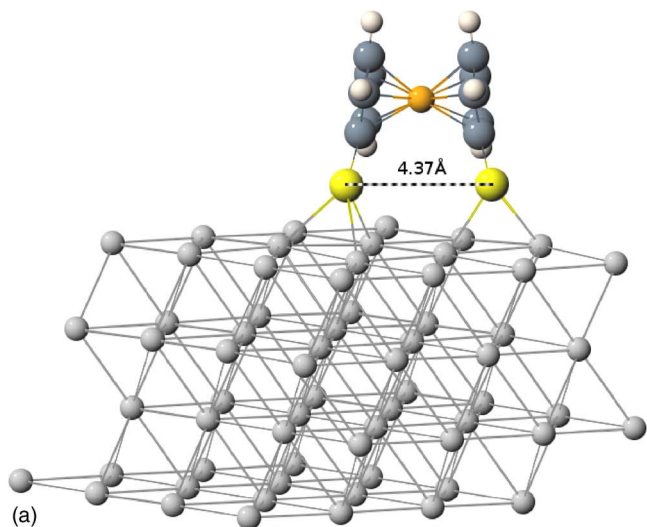


FIG. 2. Relaxed adsorption geometry starting from initial configuration 3 of Fig. 1. The grid represents the Ag crystal. Dark gray balls are C atoms, with the Fe atom in the center. The bonds to the Ag surface are formed by the two S atoms. Two side views of the molecule are shown. Clearly visible is the tilt of the molecular rings against each other (left) and of the molecule as a whole.

sity of states located most pronounced at the central Fe but also in part at the C and the S atoms. This DOS, not found in the isolated molecule, indicates that indeed a delocalized electronic state exists which overlaps with the Fermi level of the Ag substrate. As expected, this part of the DOS is most sensitive to configurational changes, as seen by a comparison of Fig. 4 with Fig. 5. As also seen from these figures, the configurational modifications tested alter the peak splitting

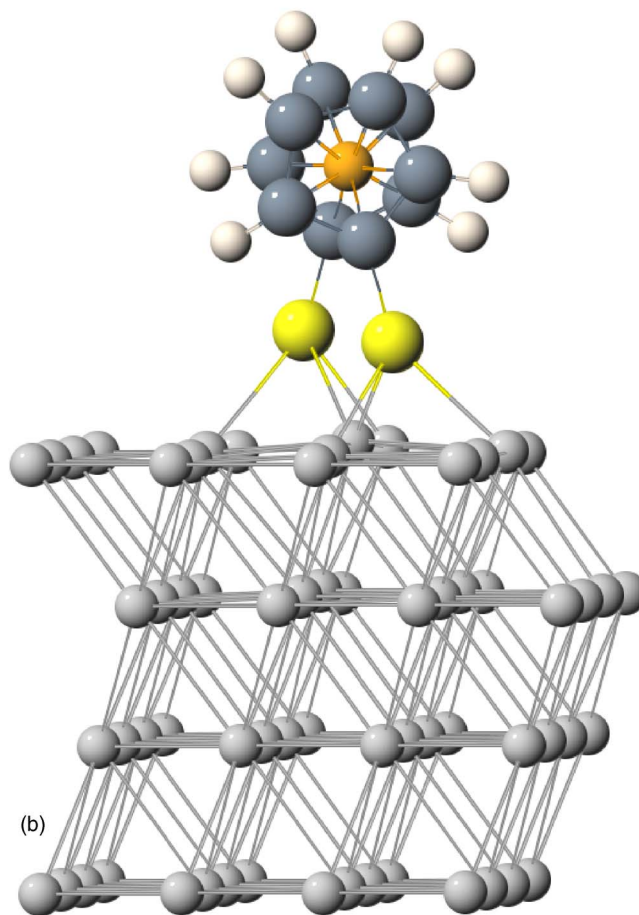
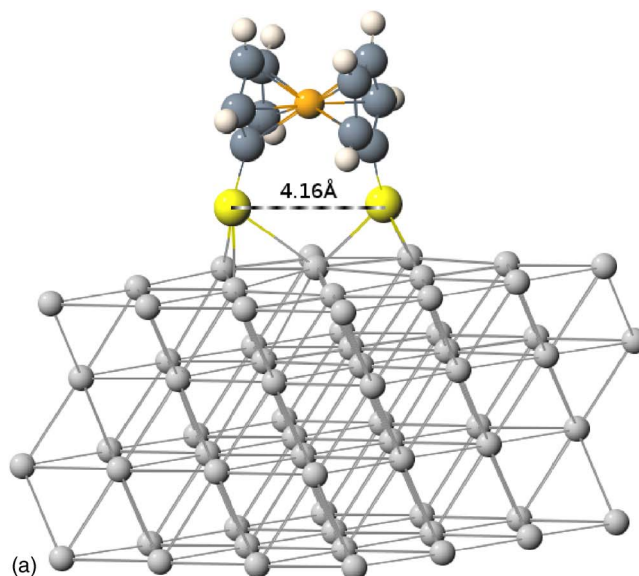


FIG. 3. Relaxed configuration of the FDT radical starting from configuration 7.

and the relative weight of split peaks at E_F , but the delocalized DOS at E_F remains nonzero in all cases tested. In fact, it can account for significant electric conductivity of the adsorbed molecule.

B. Thiol bonding

For comparison, we also investigated the adsorption of intact, undissociated ferrocene-1,1-dithiol molecules starting

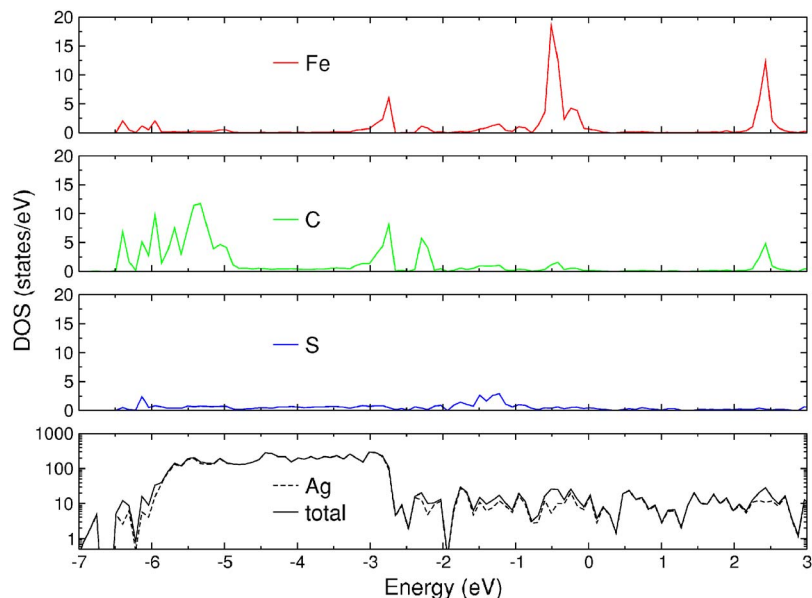


FIG. 4. Total density of state (lowest panel) and DOS projected onto individual atoms or groups of atoms for the relaxed configuration shown in Fig. 2. Energies are given with respect to the Ag Fermi level.

with configurations 1–3 already shown in Fig. 1 using identical technical parameters as in the previous section. The adsorption energies ΔE^{thiol} were obtained from these calculations according to Eq. (1) for thiol. They are listed in the second column of Table II. The energetic differences between the various optimized configurations are similar to those obtained for the thiolate. The bonds, however, are much weaker. The energy gain due to adsorption amounts now to only 0.15 eV/bond. Consequently, the Ag–S distances have increased significantly compared to the thiolate bonds and range now between 3.2 and 3.6 Å.

These bonds are also not strong enough to significantly deform the molecule: The S–S separation is very close to that of the isolated molecule, as seen, e.g., in Fig. 6. This figure also shows that the Ag–S–C bonds are inclined due to the presence of the S–H bond. This makes the molecule sensitive to additional van der Waals-type interactions, which may not be treated correctly by the PW91 functional. Their influence, however, does not change the weak bonding character.

As a consequence, the projected DOS of the thiol-bound FDT molecule shown in Fig. 7 resembles very closely that of the isolated molecule. In particular, the split-off DOS in the range between E_F and $E_F - 0.5$ eV has completely vanished. The delocalized state at $E_F - 0.7$ eV is still present. Thus, according to this calculation, the thiol-bound FDT molecule adsorbed on Ag(111) is semiconducting with an energy gap of 0.5 eV. In contrast, the FDT bound by thiolate is a metallic conductor.

Although the thiol-Ag bond of FDT is weak, there is still the question whether a thiolate bond to the surface can be formed on kinetic grounds because of the high energy of activation in order to split off the hydrogen atom. In order to answer this question, we not only calculated $\Delta E^{\text{thiolate}}$ but also the activation energy on the surface, $\Delta E^{\text{thiolate}+\text{H}}$, necessary to separate a H atom from the rest of the molecule in the adsorbed state (Table II).

$\Delta E^{\text{thiolate}}$ can easily be obtained from the binding energies E_B given in Table I by the following equation:

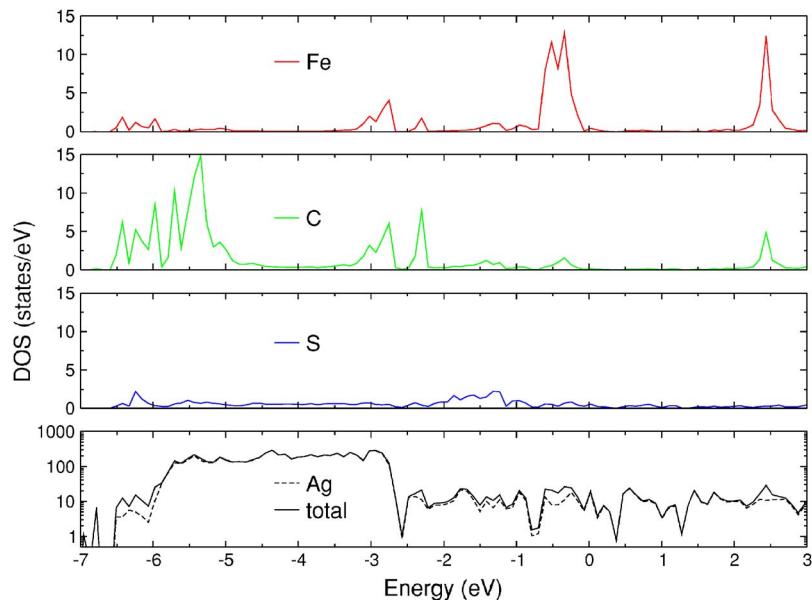


FIG. 5. Total density of state (lowest panel) and DOS projected onto individual atoms or groups of atoms for the relaxed configuration shown in Fig. 3.

TABLE II. Results for the doubly bonded ferrocene-1,1'-dithiol on a Ag(111) surface.

	Starting geometry	ΔE^{thiol} (eV)	$\Delta z_1^{\text{thiol}}$ (Å)	$\Delta z_2^{\text{thiol}}$ (Å)	$\Delta E^{\text{thiolate+H}}$ (eV)	$\Delta E^{\text{thiolate}}$ (eV)
1 ^{thiol}	top, bridge	-0.29	3.20	3.55	+0.38	-0.30
2 ^{thiol}	top, fcc	-0.30	3.17	3.57	+0.20	-0.39
3 ^{thiol}	top, \sim hcp	-0.28	3.24	3.49	+0.24	-0.38

$$\Delta E^{\text{thiolate}} = 2E_B(\text{SH}) - E_B(\text{H}_2) - E_B = 2.10 \text{ eV} - E_B. \quad (2)$$

Equation (2) assumes that the full energy of H_2 recombination can be regained during the dissociation reaction. In separate calculations of the isolated FDT and H_2 molecules, we obtained $E_B(\text{SH})=3.33$ eV for the bond strength of one S–H bond in the FDT molecule and $E_B(\text{H}_2)=4.56$ eV for the H–H bond in the hydrogen molecule. The latter value is in close agreement with the experimental dissociation enthalpy of H_2 , 4.52 eV.²⁵ With these numbers, a net energy gain of at most 0.1 eV can be inferred from Eq. (2) for the thiolate conversion (see Table (2)).

In order to calculate $\Delta E^{\text{thiolate+H}}$, we added to the initial configurations 1–3 for thiolate-bound FDT hydrogen atoms on the closest fcc sites. These sites turned out to be most favorable in a separate calculation with H atoms alone with a binding energy of 2.13 eV. This procedure can be justified by the fact that all geometric parameters of the fully relaxed FDT molecule remained identical to those without adsorbed H close by. The total energy of this combined system, however, is higher than that of the separate systems by values between 0.20 and 0.38 eV for the configurations tested. This approximate activation barrier for S–H dissociation of adsorbed FDT of at least 0.40–0.76 eV is significantly higher than thermal energy close to room temperature. Therefore, spontaneous dissociation on this surface may be questionable for two reasons: One is this activation barrier. The second is whether the dissociation of hydrogen and the formation of a H_2 molecule can be considered as a simultaneous or as a sequential process. Only in the former case is Eq. (2) valid. For the sequential process, the high activation barrier for H split off will strictly prevent thiolate bond formation.

C. Formation of a single bond

In order to obtain an estimate for lateral interactions between the two sulfur bonds, we also calculated adsorption energies for the FDT molecule bound by a single thiolate bond using the same procedures and parameters as for the calculations already described. The results are shown in Table III. For these calculations the second S atom was pointing away from the surface ($\phi=144^\circ$). For data sets 1–3 the Cp rings were initially oriented normal to the surface and remained essentially unchanged in this position after relaxations. Since top sites turned out to be energetically unfavorable in all calculations with two bonds, they were not tested here again. For this configuration of the FDT molecule, fcc and bridge sites turned out to be slightly favored over the hcp site, but the energetic differences are again within 50 meV. This demonstrates that the small selectivity for specific sites

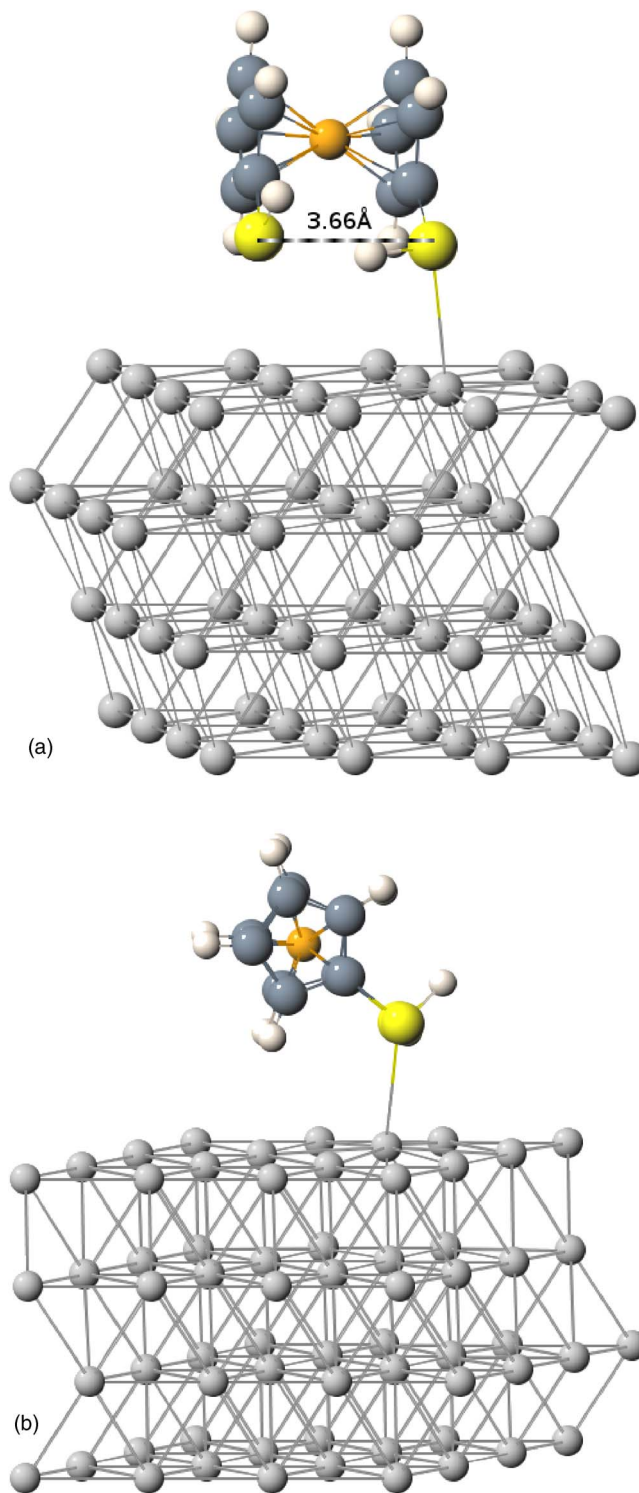


FIG. 6. Exemplary adsorption geometry for a FDT molecule bound to the Ag(111) surface by a S–H bond.

originates directly from the thiolate bond and is not related to compensations by deformations of the molecule in the case of two bonds described in the previous section. Bond distances turn out to be comparable to those obtained with two bonds. The relatively large variation of bond lengths seen in the case of two bonds, however, seems to be a direct consequence of molecular deformations.

The results with the Cp rings normal to the surface can be directly compared with the double thiolate bonds of Table

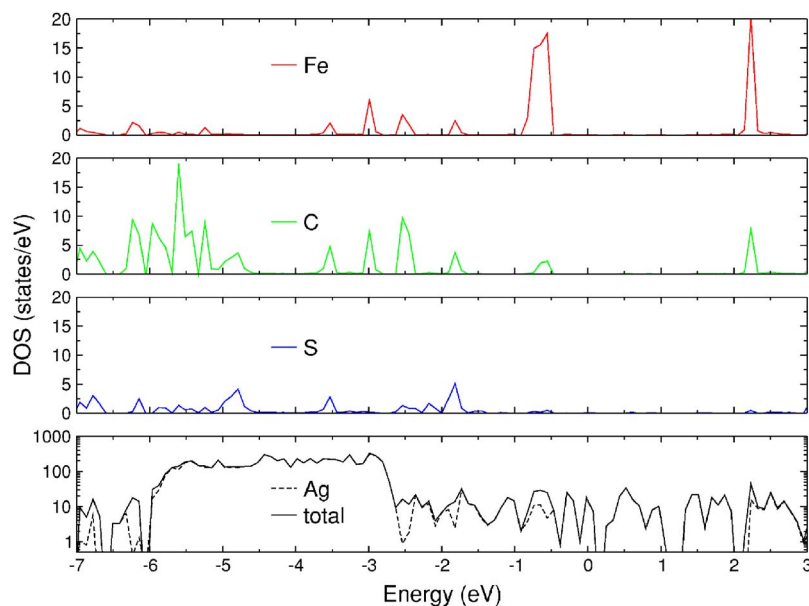


FIG. 7. DOS for ferrocene-1,1-dithiol bound to the Ag(111) surface by a thiol bond.

I. Taking average values for the binding energies per bond, it is obvious that the interaction between the bonds is slightly repulsive with an interaction energy of about 50 meV.

The configurations with the initial ring orientation parallel to the surface (data sets 4 and 5) turned out to be also stable with binding energies very close to those of the other orientation. After relaxation the rings are slightly tilted ($\leq 20^\circ$). This orientation is the preferred orientation found experimentally for pure ferrocene.²⁶ The chemical bond by thiolate is of course much stronger than the van der Waals-type bonding of the pure ferrocene molecule and seems to destroy the preference for the parallel orientation. The initial configuration on the bridge site relaxed to the fcc site and is therefore not listed separately.

For a pure single thiol bond, only the initial configuration on the hcp site ($6, \phi=144^\circ$) was tested. Here no new insights compared to the doubly bound molecule were obtained. The binding energy is within error bars half of that with double bonds.

IV. SUMMARY AND CONCLUSIONS

Using density functional calculations as implemented in the VASP code, we calculated binding energies of various configurations of ferrocene dithiol bound to the Ag(111) surface either by thiolate (S) or by thiol (SH) bonds. For both

TABLE III. Distances and binding energies of ferrocene-1,1'-dithiol bound by a *single* thiolate bond to the Ag(111) surface. Data sets 1–3 and 6 refer to Cp rings oriented perpendicular to the surface; for the others these rings are oriented parallel to the surface.

	Site	Δz^S (Å)	E_B (eV)	ΔE^{thiol} (eV)
1	bridge	2.15	1.31	...
2	fcc	1.95	1.30	...
3	hcp	2.01	1.25	...
4	fcc (Cp)	2.26	1.34	...
5	hcp (Cp)	2.32	1.24	...
6	hcp (thiol)	2.87	...	-0.13

the single and the twofold thiolate bonds, a moderately strong chemical bond is formed. Surprisingly, we found a large number of different molecular configurations with energetic differences of less than 50 meV/bond. Only top site configurations on the Ag surface were found to be energetically unfavorable. This guarantees high flexibility if these molecules are used as single molecular bridges in molecular electronic circuits.

As shown by the DOS projected onto S, C, and the central Fe atoms, the FDT molecule bound by the simple thiolate bond possesses, apart from the lower lying bonding π orbitals, a delocalized electronic orbital that overlaps with the Fermi level of the Ag substrate. Although the total energy is influenced very little by variations of the adsorbate configuration, the molecular contributions to the DOS at the Fermi level depend significantly on the configuration. This contribution to the DOS in the range between E_F and $E_F - 0.5$ eV is missing, if the bonding configuration is changed from S to SH (thiol bond). The surface interaction of the molecule bound by SH is much weaker compared to the S–Ag bond, and the (projected) DOS resembles closely that of the free molecule. In terms of molecular electronics, a change of the bond from S to SH turns the molecule from conducting to semiconducting.

These properties are influenced to a small extent by formation of two bonds to the same surface due to a small repulsion (4% of the binding strength) between the two thiolate bonds on the same molecule. Thus the selectivity introduced by this repulsion in favor of formation of bonds to different surfaces, e.g., in a molecular contact, will be small.

Although in full thermodynamic equilibrium the formation of the thiolate bond is slightly favored, the activation barrier to dissociate the SH bond, as estimated in our calculations, may prevent its formation for kinetic reasons. Since our calculations were carried out on a perfect Ag(111) surface, this prediction may not be valid for a silver surface containing point defects, steps, and kinks, where the energetic situation may be different. This is the task for a future project.

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