CH_3SH molecules deposited on Cu(111) and deprotonation

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We demonstrate that when a methanethiol adsorbed on the regular Cu(111) surface, the dissociative structure is thermodynamically more stable than the intact one. The computational results show that at low temperature, the methanethiol adsorbate prefers the atop site of the regular Cu(111) surface. As the temperature is increased, the S-H bond is broken and the methylthiolate favors the hollow sites. On the defected Cu(111) surface, the dissociative configuration is still thermodynamically more stable than the nondissociative one. The calculation indicates that the hydrogen initially attached to the sulfur would like to form a bond with the copper surface rather than desorb from it. Even though both copper and gold are the noble metals, the stability of the methanethiol adsorption on the Cu(111) substrate is almost the reverse of that on the Au(111).

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I. INTRODUCTION

In recent years, a lot of work has been conducted on the interaction of alkanethiols with gold surface because of their ability to form self-assembled monolayers (SAMs) (see Ref. 1 for a review). These SAM films have wide application on wetting phenomena, tribology, chemical and biological sensing, optics, and nanotechnology. The consistent model for the methanethiol adsorption process on the Au(111) substrate was proposed recently.[2,3] It was revealed that the methanethiols stay intact on the regular Au(111) surface, but the S-H bond ruptures on the defected Au(111) surface. On other noble metals such as copper, the adsorption pattern of the alkanethiols (or alkanethilates) on the Cu(111) is distinct from that on the Au(111) surface.[4–15] Then, one may ask how the S-H bond in the methanethiol on the regular (or defected) Cu(111) surface breaks.

The normal incidence x-ray standing wave measurements show that at the low temperature, the intact methanethiols prefer a local atop site on the Cu(111) surface, but at 140 K, methanethiols turn into methanethiolates depositing on unreconstructed areas of the Cu(111) surface, occupying two nonequivalent hollow sites with similar probability.[4] At room temperature, when methanethiols or dimethyl disulfides adsorbed on the Cu(111), the formation of the pseudosquare reconstruction was observed via scanning tunneling microscopy.[5,6] A grazing incidence surface x-ray study indicates that intact alkanethiols favor hollow sites on Cu(111).[7] However, there has been no experimental proof for hydrogen desorption from such processes. As we know, alkanethiols only stay intact on the regular Au(111) surface, but the S-H bond ruptures on the defected Au(111) surface.[2,3] So far, no theoretical work on the scission of the methanethiol on the Cu(111) surface has been done; thus, it is imperative to study the mechanism of the S-H bond rupture theoretically.

In this paper, we study the adsorption of methanethiol on the Cu(111) surface by the density functional theory.[16] First, we will present adsorption energies and geometries for the nondissociative and dissociative configurations on the regular Cu(111) surface. We demonstrate that the dissociative structure is the most stable one for the regular Cu(111) surface, which is opposite to the case when the methanethiols adsorbed on the regular Au(111).[2,3] The S atom of the intact methanethiol stays on the top of the copper atom of the surface. The energy barrier is about 0.2 eV. This implies that at low temperature, the intact methanethiol prefers a local atop site on the regular Cu(111) surface.[4] As the temperature increased, the energy barrier can be overcome and the hydrogen is detached from the S atom, which is consistent with the experimental observation.[4,6,7] To discuss the stability of configurations for the defected Cu(111) surface, we assume a vacancy in the top layer of the Cu(111) surface. We find that on the defected surface, the dissociative structure is still more stable than nondissociative one. The hydrogen initially attached to the sulfur forms a bond with the Cu(111) substrate instead of desorbing from it.

II. COMPUTATIONAL METHOD

The calculations were performed by the VASP code[16] in two approaches: (1) using the projector augmented wave potential[17,18] and the Perdew-Wang 91 (PW91) generalized gradient approximation to exchange and correlation (XC);[19] (2) the ultrasoft pseudopotential[16] with XC based on the Perdew-Burke-Ernzerhof (PBE) formalism.[20] The wave functions are expanded in a plane wave basis with an energy cutoff of 400 eV. The Brillouin zone integration is performed by use of the Monkhorst-Pack scheme.[21] We utilized a $3\times3\times1$ k point mesh for the geometry optimization. The adopted supercell corresponds to 12 Cu atoms per layer. The Cu atoms in the top three atomic layers are allowed to relax, while those in the bottom layer are fixed to simulate bulklike termination.[22] The vacuum region comprises seven atomic layers, which exceeds substantially the extension of the methanethiol molecule. To examine the accuracy of our approach, we increased the energy cutoff to 500 eV and the number of k points to $8\times8\times1$. In both cases, the difference amounted to less than 1.8%. We further calculated the copper lattice constant and found it to agree with the experimental value[23] within 0.6%.

III. RESULTS AND DISCUSSION

A. Methanethiol molecule deposited on the regular Cu(111) surface

We begin with the geometries and adsorption energies of the optimized structures for the methanethiol on the Cu(111)

TABLE I. The geometries and adsorption energies for the optimized nondissociative and dissociative configurations on the regular and defected Cu(111) at 0.25 ML. The entries S site, θ, tilt, $d_{\text{S-Cu}}$ (Å), and E_{ads} (eV) refer to the S headgroup atom site, the angle between the S-C bond direction and the normal to the Cu(111), the region of th S-C bond tilted, the shortest S-Cu bond length, and the adsorption energy, respectively.

Configuration	S site	θ	tilt	$d_{\text{S-Cu}}$	E_{ads}
	Regular surface				
Intact	Top	65.6	hcp	2.43	0.61
Dissociative	fcc-bri	40.2	hcp	2.26	1.14
Dissociative	hcp-bri	40.6	fcc	2.28	1.11
Methylthiolate (CH_3S)	fcc-bri	46.2	hcp	2.28	2.76
	Defected surface				
Intact	Top	54.0	fcc	2.38	0.74
Dissociative	Two bonds with two Cu atoms	16.6	hcp	2.29	1.64

surface at 0.25 ML, as displayed in Table I. The symbol fcc-bri (or hcp-bri) in Table I represents that the S atom is placed in a fcc (or hcp) hollow region, but leaned toward the bridge. The stable configurations on the Cu(111) surface are shown in Fig. 1.

We calculated 19 nondissociative configurations on the regular Cu(111) surface, which are characterized by the S atom adsorption site (atop, bridge, fcc, and hcp hollow), the angle of the S-C bond, and the direction of the H-S bond. The energy difference among the configurations is around 0.1 eV, i.e., the adsorption energies span 0.30–0.61 eV. However, the adsorption energies weakly depend on the tilting of the alkyl chain, which reveals the ionic nature of the bonding. The first row of Table I displays that the adsorption energy for the most stable nondissociative structure is 0.61 eV [Fig. 1(a)] and the S adsorption site is on the top of the Cu atom. Thus, at low temperature, the intact methanethiol stays on the top site of the regular Cu(111) surface, in keeping with a recent experimental result.[4] The second and third rows of Table I list two most stable dissociative structures on the regular Cu(111) substrate, and their adsorption energies are 1.14 and 1.11 eV. The S atoms for both configurations are in hollow site, i.e., fcc-bri [Fig. 1(b)] and hcp-bri [Fig. 1(c)], which is in favor of the explanation in Ref. 12 (when dynamical effects are considered, only the hollow site occupancy is observed[12]). The first and second rows in Table I reveal that the adsorption energy of the dissociative structure is higher than that of the nondissociative one by 0.53 eV. To further examine this result, we apply the ultrasoft pseudopotential in conjunction with the PBE XC (Ref. 20) to recalculate the above structures and find an adsorption energy difference of 0.51 eV between the cases of cleavage and noncleavage. Thus, we conclude that the dissociative configuration is more stable than the nondissociative one, which is consistent with the experimental observation that at low temperature, the intact methanethiol stays on the regular Cu(111) surface, and when the temperature increased, methanethiolates deposited on unreconstructed areas of the Cu(111) surface, occupying two nonequivalent hollow sites with similar probability.[4]

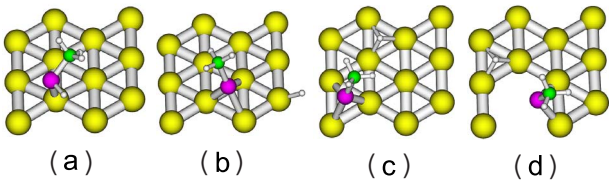

FIG. 1. (Color online) (a) Intact structure on the regular Cu(111). (b) Dissociative structure in the fcc hollow site of the regular Cu(111) (fcc-bri). (c) Dissociative structure in the hcp hollow site (hcp-bri). (d) Dissociative structure on the Cu(111) with a vacancy.

B. Projected density of states

To see why the dissociative structure is more stable than the nondissociative one, we calculated the partial density of states (PDOS) for the H atom initially attached to the sulfur atom [Fig. 2(a)]. The PDOS projected on the S atom adsorbed on the regular Cu(111) surface is illustrated in Fig. 2(b). Figure 2(a) displays that the primary peaks of the hydrogen PDOS for the dissociative structure are at positions of lower energy than those for the nondissociative one. The electronic configuration related to the former case is thus more stable than that corresponding the latter, and the hydrogen atom forms a stronger bond with the Cu(111) surface than with the sulfur atom.

C. Interacting bond

To elucidate the interacting bond between the methanethiol (or methylthiolate) and the Cu(111) substrate, we evaluate the spatially resolved charge-density difference: $\Delta\rho(\vec{r})=\rho_{ads/sub}(\vec{r})-\rho_{sub}(\vec{r})-\rho_{ads}(\vec{r})$, where $\rho_{ads/sub}$, ρ_{sub}, and ρ_{ads} are the electron charge densities of the relaxed adsorbate-substrate system, of the clean relaxed surface, and of the isolated but adsorptionlike deformed adsorbate (without substrate), respectively. The isodensity surfaces of the charge-density difference for the intact and dissociative structure are depicted in Figs. 3(a)–3(c) (to discuss the change of the S-Cu bond before and after dissociation, in Fig. 3, we display only the surrounding part of the S-Cu bond).

The calculated charge transfers from the Cu(111) substrate to the methanethiol for the nondissociative adsorption and to the methylthiolate for the dissociative structure are $0.3e$ and $0.6e$, respectively. Figure 3(a) shows that for the intact adsorption, the electrostatic interaction responsible for the bonding comes from the monopole term (the $0.3e$ charge transfer) and the dipole moments in the adsorbate and substrate.[24] Around the S atom, there is a "ring" of accumulation of electron charge. The electrostatic interaction is dominated by the attractive ionic term modified by a repulsive dipolar term.[24] The sulfur stays on the top of the copper atom, i.e., the sulfur only forms a bond with one Cu atom. The interaction between the methylthiolate and Cu(111) is the ionic bonding.[10,15] The sulfur in the methylthiolate forms

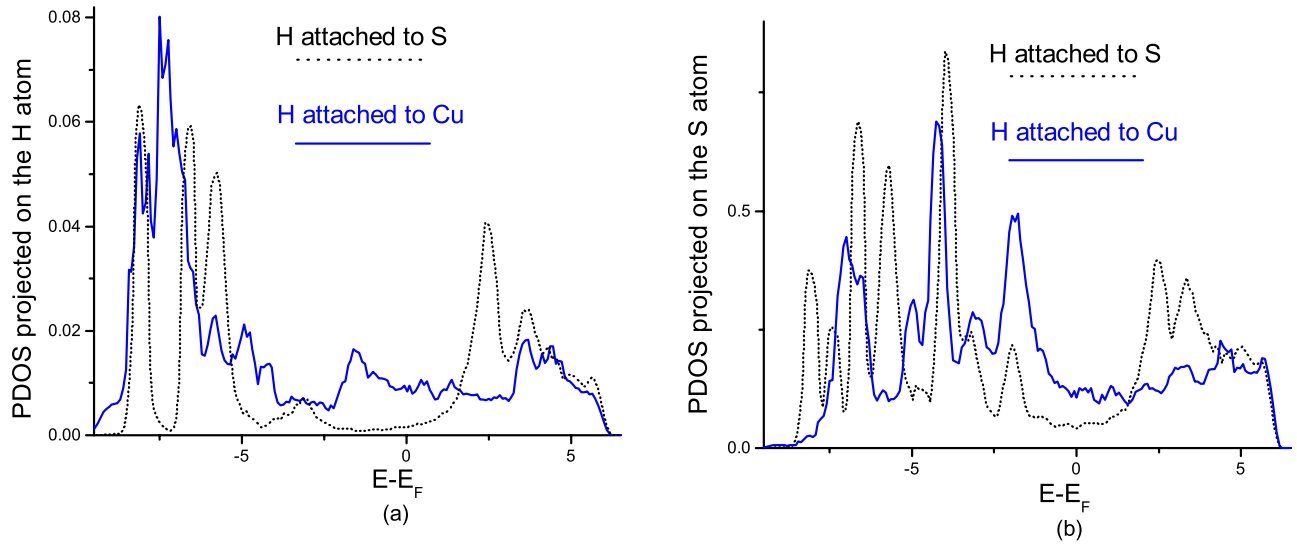

FIG. 2. (Color online) (a) The PDOS projected on the hydrogen atom initially attached to the S atom adsorbed on the regular Cu(111) surface. (b) The PDOS projected on the S atom adsorbed on the regular Cu(111) surface.

bonds with two copper atoms of the Cu(111) surface [see Figs. 3(b) and 3(c)], and its charge transfer ($0.6e$) is two times of that for the nondissociative case ($0.3e$). It indicates that the methylthiolate takes in $0.3e$ electron charge from each copper atom channel ($0.3e \times 2 = 0.6e$), which matches with the fact that the adsorption energy for the dissociative structure (1.14 eV) is about two times of that for intact adsorption (0.61 eV). The charge densities in the $[1-21]$ and $[10-1]$ plane for intact and dissociative adsorptions are shown in Fig. 4, which is consistent with the picture obtained from the isosurfaces of the charge-density difference, charge transfers, and bond structures.

D. Methanethiol molecule deposited on the defected Cu(111) surface

On the regular Cu(111) surface, we found that the dissociative structure is thermodynamically more stable than the nondissociative one. To see if the defects can change the above conclusion, we consider the Cu(111) surface with a vacancy in the top layer of the supercell. The geometries and adsorption energies for the optimized nondissociative and dissociative configurations on the Cu(111) surface with a vacancy are indicated in the fifth and sixth rows of Table I. It shows that the adsorption energy for the dissociative structure [Fig. 1(d)] is 0.9 eV higher than that for the intact one; i.e., the dissociative configuration on the defected Cu(111) surface is thermodynamically more stable than the nondissociative one. For the stable dissociative adsorption, the S atom forms two bonds with two adjacent copper atoms which surround the vacancy.

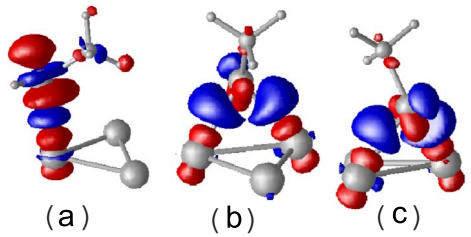

FIG. 3. (Color online) The isosurfaces of the charge-density difference for (a) nondissociative adsorption with blue (accumulation of electrons) and/or red (depletion of electrons) isosurface value, $\pm 0.015e/\text{Å}^3$, (b) dissociative structure (front view), and (c) dissociative structure (back view) with isosurface value, $\pm 0.025e/\text{Å}^3$. Only three related copper atoms of the Cu(111) surface are illustrated.

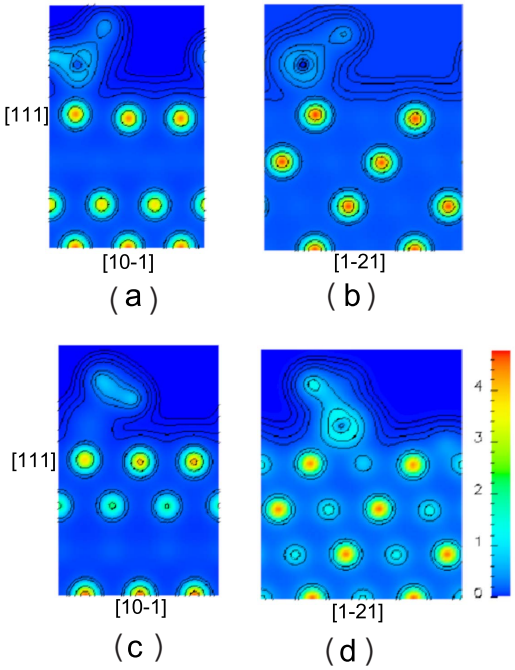

FIG. 4. (Color online) The contour plots of the charge densities. (a) Charge-density plot in $(1-21)$ plane which extends along the $[111]$ and $[10-1]$ directions and (b) in $(10-1)$ plane for the intact adsorption. (c) Charge-density plot in $(1-21)$ plane and (d) in $(10-1)$ plane for the dissociative adsorption.

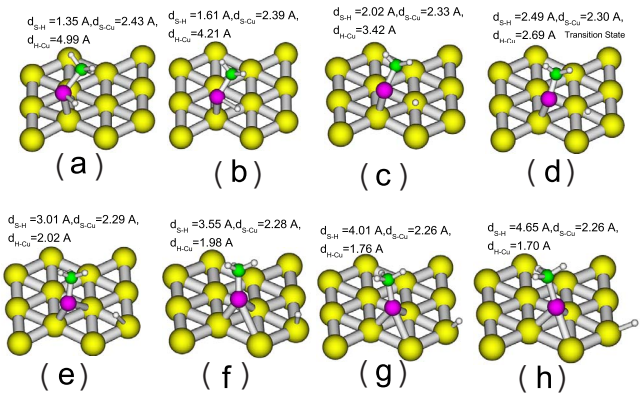

FIG. 5. (Color online) The structures for the initial intact adsorption, the final dissociated one, and the six images.

E. Energy barrier

To explain why at low temperature, the intact methanethiol on the regular surface was observed, and around 140 K, the S-H bond in the methanethiol on the Cu(111) was broken, we calculated the energy barrier for the process that leads from the nondissociative structure [Fig. 1(a)] to the dissociative structure [Fig. 1(b)]. The energy barrier was calculated by the climbing nudged elastic band method,[25–27] where six equidistant images have been used. The atomic configurations for the initial nondissociative adsorption, the six intermediate images, and the final dissociative one are shown in Fig. 5. The structure of the transition state is depicted in Fig. 5(d).

The relative energies along the S-H bond cleavage reaction path are schematically illustrated in Fig. 6. The energy barrier is about 0.2 eV, which is lower than the corresponding energy barrier for the scission of the S-H bond in a single methanethiol molecule. The reason is that when the methanethiol is adsorbed on the Cu(111), the surface plays a role as a catalyst, which can suppress the barrier height. As the temperature is raised, the S-H bond break reaction is activated over the energy barrier, which is consistent with the experimental measurement.[4]

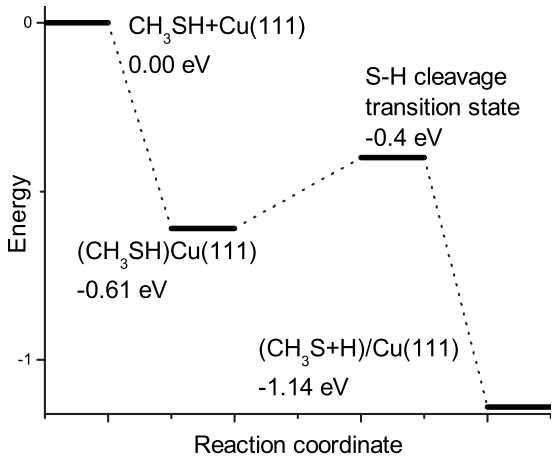

FIG. 6. The relative energy levels along the S-H bond scission reaction paths.

F. Hydrogen atom behavior

We have seen that at low temperature, the intact methanethiol favors the atop site of the Cu(111) surface, and when the temperature increased, the S-H bond in the methanethiol on the Cu(111) surface is ruptured. The hydrogen could either stick to the Cu(111) surface or desorb in molecular form. No experimental evidence of either process has been found. To predict if the hydrogen forms a bond with the Cu(111) surface or desorbs in the hydrogen molecule, we compared the interaction energy for the dissociative structure $E_{(CH_3S+H)/Cu(111)}$ with that for methylthiolate on the Cu(111) and the desorbed hydrogen molecule, i.e., $E_{(CH_3S)/Cu(111)} + \frac{1}{2}E_{H_2}$. We found that $E_{(CH_3S+H)/Cu(111)}$ is lower than $E_{(CH_3S)/Cu(111)} + \frac{1}{2}E_{H_2}$ by 0.24 eV, which implies that the hydrogen would like to form a bond with copper surface rather than desorb from the surface.

To check if the deposited hydrogen modified the methylthiolate adsorption pattern, we calculated 15 methylthiolate structures on the regular Cu(111) surface. The most stable structure is shown in the fourth row of Table I. The second and fourth rows in the table display that the S-Cu bond lengths and the angles θ for the dissociative structure [both the hydrogen and the CH_3S adsorbed on the Cu(111) surface] and for the methylthiolate (only CH_3S) on the Cu(111) are 2.26 Å, 40.2, and 2.28 Å, 46.2°, respectively. The hydrogen adsorbed to Cu(111) modifies the methylthiolate adsorption structure by 6°.

G. Comparison with the methanethiol adsorption on the Au(111) surface

We compare the methanethiol adsorption process on the Cu(111) substrate with that on the other noble metal surface—Au(111). On the regular Cu(111) surface, the methanethiol dissociative adsorption is more stable than the intact one. The corresponding energy barrier is about 0.2 eV. So at low temperature, the methanethiol stays intact on the atop site of the regular Cu(111). When the temperature is raised, this energy barrier is overcome, and the S-H bond breaks. The corresponding hydrogen is adsorbed on the surface. The presence of the defects on the Cu(111) does not change the situation. However, on the regular Au(111) surface, the nondissociative structure is more stable than the dissociative one. At low temperature, the methanethiol favors the atop site of the regular Au(111). As the temperature is increased, the methanethiol molecule desorbs from the regular Au(111). For the defected Au(111), this order of stabilities is reversed. To unveil the origin of the difference between the adsorptions on the Cu and Au surfaces, we calculated the PDOS for the H atom initially attached to the sulfur atom adsorbed on the regular Au(111) surface [see Fig. 7].

Comparing Fig. 7 with Fig. 2(a), we have found that for the Cu surface, the primary peaks of the hydrogen PDOS for the dissociative structure are at positions of lower energy than those for the nondissociative one. However, for the Au surface, the primary peaks of the hydrogen PDOS for the intact structure are at positions of lower energy than those for the dissociative one. Thus, such a comparison explained the

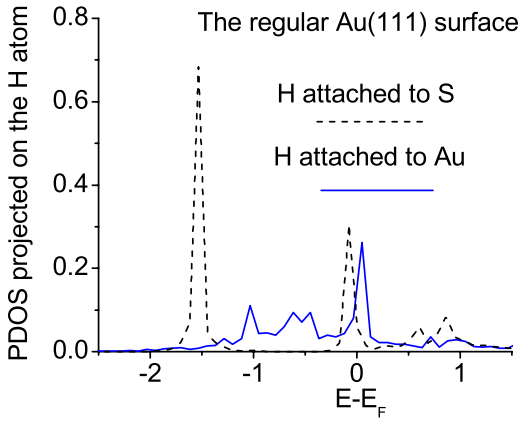

FIG. 7. (Color online) The PDOS projected on the hydrogen atom initially attached to the S atom adsorbed on the regular Au(111) surface.

physical reason of the difference between the Cu and Au surfaces.

IV. SUMMARY

In conclusion, we have demonstrated that when a methanethiol adsorbed on the regular Cu(111) surface, the dissociative structure is thermodynamically more stable than the intact one. The energy barrier for the process that leads from the nondissociative structure to the dissociative one is about 0.2 eV. Thus, at low temperature, the methanethiol adsorbate prefers the atop site of the regular Cu(111) surface.[4] As the temperature rises, the S-H bond is broken, and the methylthiolate favors the hollow sites.[4] On the defected Cu(111) surface, the dissociative configuration is still thermodynamically more stable than the nondissociative one. The calculation shows that the hydrogen initially attached to the sulfur would like to form a bond with copper surface rather than desorb from it. Even though both copper and gold are noble metals, the stability of the methanethiol adsorption on the Cu(111) substrate is almost the reverse of that on the Au(111).

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