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# How does an external electrical field affect adsorption patterns of thiol and thiolate on the gold substrate?

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## Abstract

The responsive behavior of methanethiol and methylthiolate molecules on the Au(111) surface with an applied electrical potential is studied, and it is shown how the sulfur adsorption site, the S–H bond orientation and the interacting energy change with an external electric field strength. The electron charge density corresponding to an electric field minus that obtained in zero field, with zero-field optimal geometry, is calculated to explain the responsive behavior. The interacting energy for the intact methanethiol adsorption is larger than that for the dissociative one, showing that an external electric field cannot make the hydrogen dissociate from the sulfur.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Materials and devices that change properties and functions in response to external stimuli are the focus of research in fields of physics, chemistry, biology, material science and engineering [1–6]. Physical effects such as external fields are advantageous in the process of controlling surface adsorption and growth. As we know, the surface morphology can be easily affected by an external electric field. The potential-induced surface morphological changes are observed in metal/electrolyte interface [1]. An excess surface charge can induce a reconstruction on a silver surface [3]. Adsorbates on the surface are stabilized by the presence of the scanning tunneling microscopy (STM) tip [4]. An electric field or surface charging changes the metal bcc(100) surface configurations [5]. The electric field effects on surface diffusion has been studied by the field ion microscopy (FIM) technique, and it was found that an electric field can inhibit or promote surface self-diffusion on Pt(001) surface [6].

On the other hand, alkanethiols form self-assembled monolayers (SAM) on the Au(111) surface, which has wide applications in molecular electronics [7], lubrication [8], lithography [9], and bio-chemical surface functionalization [10]. Its highly ordered structures and chemical stability make these systems ideal for study with a variety of

techniques including atomic-force microscopy [11], infrared spectroscopy [12, 13], high-resolution electron-energy-loss spectroscopy [14], grazing x-ray diffraction [15], scanning probe microscopy [16], low-energy electron diffraction [17], STM [18–22] and others [23–28]. Recently, Maksymovych and co-workers exploited the STM tip to manipulate the formation and decomposition of the methanethiol dimer on the Au(111) surface [29], which shows that an external electric field does affect the adsorption pattern of a thiol molecule. Then, the question of whether an external electrical field induces conformal reorientation of thiol molecule on the Au(111) surface at the low coverage arises. Because of its importance for a wide variety of surface phenomena (i.e., STM, FIM and electrochemical), understanding the influence of an external electric field on surface adsorption is essential for explaining some experimental results. Besides these, the defect on the substrate can catalyze the S–H bond breaking in the process of the methanethiol adsorption on the Au(111) surface [30, 31], however, it is unclear if an external electric field can trigger such a dissociation. Heretofore, the mechanism of the responsive behavior and the dissociation of thiol molecule on the Au(111) surface under an external electrical field is still a mystery.

This prompted us to investigate the interacting behavior of methanethiol and methylthiolate molecules with the Au(111)

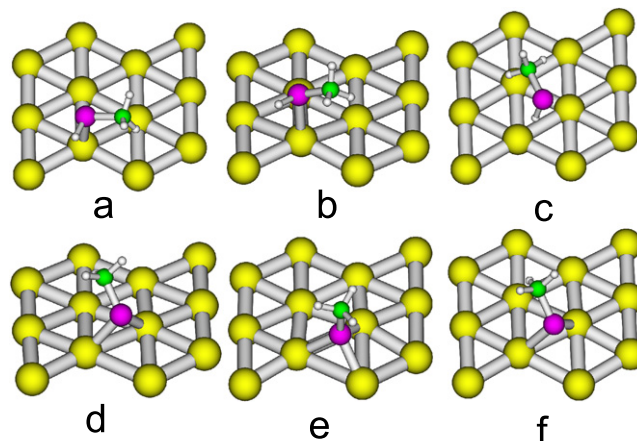
**Table 1.** The geometries and interacting energies for the stable methanethiol configurations on the Au(111) surface (0.25 ML) at various external electric field strengths. The entries  $E_{\text{ext}}$ , S site,  $\theta$ , tilt,  $d_{\text{S-Au}}$  (Å) and  $E_{\text{int}}$  (eV) refer to an external electric field ( $\text{V \AA}^{-1}$ ) perpendicular to the Au(111) surface, the S atom adsorption site, the angle between the S–C bond direction and the normal to the Au(111) surface, the region of the S–C bond tilted, the shortest S–Au bond length and the interacting energy, respectively.

$E_{\text{ext}}$	S site	$\theta$	Tilt	$d_{\text{S-Au}}$	$E_{\text{int}}$
0	top-fcc	73.0	fcc	2.73	0.66
−0.5	top-fcc	72.5	fcc	2.61	0.96
−1.0	top-fcc	65.0	fcc	2.57	1.41
−1.5	top-fcc	54.1	fcc	2.55	1.80
0.5	bri	97.4	hcp	3.95	0.50

surface under an external electrical field by the density functional theory. We will present the interacting energies and geometries for methanethiol and methylthiolate adsorbates on the Au(111) surface in the presence of an external electric field. We show how the sulfur adsorption site, the S–H bond orientation, and the interacting energy of the methanethiol and methylthiolate molecules with the Au(111) substrate are affected by an external electric field applied to the surface. We have calculated the  $z$ -direction electron charge density difference between the charge density obtained with an electric field and that without a field at the zero-field optimized geometry to interpret these responsive behaviors. To see if an external electric field can trigger the dissociation of the S–H bond in the methanethiol adsorbed on the Au(111) surface, we compare the interacting energies between the intact adsorption and dissociative one. We find that the interacting energy for the intact methanethiol adsorption is larger than that for the dissociative adsorption, which shows that even in the presence of an external electric field, the intact adsorption is still stable.

## 2. Theoretical method and surface modeling

The calculations were done in the slab model by density functional theory (DFT) [32]. The electron–ion interaction has been described using the projector augmented wave (PAW) method. All calculations have been performed by Perdew–Wang 91 (PW91) generalized gradient approximation. The wavefunctions are expanded in a plane wave basis with an energy cutoff of 400 eV. The  $k$  points were obtained from Monkhorst–Pack scheme, and  $3 \times 3 \times 1$   $k$  point mesh was for the geometry optimization. The supercell consisted of four layers and each layer with 12 Au atoms. The Au atoms in the top three atomic layers are allowed to relax, while those in the bottom layer are fixed to simulate bulk-like termination [33]. The vacuum region comprises seven atomic layers, which exceeds substantially the extension of the methanethiol molecule. To apply an external electrical field, a planar dipole layer is placed in the middle of the vacuum region [32, 34]. In the presence of an external electrical field, the eight Au layers slab resulted in charge sloshing. We also compared the six layers slab with the four layers slab, and found that the differences of the interacting energy are with 5.3%. However, the computing time for the six layers slab is much longer than that for the



**Figure 1.** (a) The methanethiol ( $\text{CH}_3\text{SH}$ ) on the Au(111) surface without an external electric field. (b)  $\text{CH}_3\text{SH}$  on the surface with a negative external electric field ( $-1.0 \text{ V \AA}^{-1}$ ). (c)  $\text{CH}_3\text{SH}$  on the surface with a positive external electric field ( $0.5 \text{ V \AA}^{-1}$ ). (d) Methylthiolate ( $\text{CH}_3\text{S}$ ) on the Au(111) surface without external electric field. (e)  $\text{CH}_3\text{S}$  on the surface with a negative external electric field ( $-1.0 \text{ V \AA}^{-1}$ ). (f)  $\text{CH}_3\text{S}$  on the surface with a positive external electric field ( $1.0 \text{ V \AA}^{-1}$ ).

four layers slab. In our work, we computed more than 150 configurations, so the best choice for us is the four layers slab. We calculated the gold lattice constant and found it to agree with the experimental value [35] to 2.1%.

## 3. Results and discussion

We begin with the geometries and interacting energies of the optimized structures for the methanethiol ( $\text{CH}_3\text{SH}$ ) on the Au(111) surface at the coverage of 0.25 ML (1.00 ML means 1 sulfur per 3 gold atoms, and 0.25 ML stand for 1 methanethiol on a gold surface with 12 gold atoms) with various external electric field strengths [34], as displayed in table 1 (at each value of the external electric field, 15 different structures have been optimized, the most stable structure is listed on table 1). The interacting energy is defined as  $E_{\text{int}} = E_{\text{CH}_3\text{SH}} + E_{\text{Au(111)+field}} - E_{\text{CH}_3\text{SH}+\text{Au(111)+field}}$ . The symbol top-fcc (or top-hcp) in table 1 represents that the S atom is at the atop site of the gold atom, but leaned toward the fcc (or hcp) hollow center. Some stable configurations on the Au(111) surface in the presence of an external electric field are illustrated in figure 1, where only the methanethiol (or methylthiolate) adsorbate and the top layer of the Au(111) surface are displayed.

Table 1 shows that when the strength of an applied negative electric field increases, the interacting energy  $E_{\text{int}}$  rises, the sulfur adsorption site shows little variation (on the atop site of the gold atom, but leaned to fcc center), the angle between the S–C bond direction and the normal to the Au(111) surface decreases, and the bond length between S atom and substrate  $d_{\text{S-Au}}$  becomes shorter. Thus, when the strength of an applied negative electric field increases, the interaction between the methanethiol adsorbate and gold substrate gets stronger and stronger. If the negative electric

field is in the range of 0 to  $-0.5 \text{ V \AA}^{-1}$ , the geometry changes slightly, which is in accord with the experimental observation [36]<sup>3</sup>. When a positive electric field ( $0.5 \text{ V \AA}^{-1}$ ) applied, the methanethiol molecule starts to desorb from the Au(111) surface. Figure 1(c) depicts this desorption structure in which the distance between S and Au is  $3.95 \text{ \AA}$  (longer than the zero-field S–Au bond length  $2.73 \text{ \AA}$ ). Thus in the low coverage, the orientation of the methanethiol molecule on the Au(111) surface can be tuned by an applied negative electrical field in a certain range ( $-0.5$  to  $-1.5 \text{ V \AA}^{-1}$ ).

To see how an external electric field influences the interaction between the methylthiolate molecule ( $\text{CH}_3\text{S}$ ) and the substrate, we calculated the geometries and interacting energies for the optimized structures of the methylthiolate on the Au(111) surface (0.25 ML) at various external electric field strengths, as shown in table 2. Table 2 displays that if the strength of an applied negative electric field becomes stronger, the interacting energy increases, the sulfur adsorption site is sliding from fcc-bri to fcc, the angle  $\theta$  decreases, but the bond length  $d_{\text{S–Au}}$  shows little variation. When the electric field goes to  $-1.0 \text{ V \AA}^{-1}$ , the previous tilted methylthiolate molecule begins to stand up, i.e., the angle  $\theta$  jumps from  $55^\circ$  to  $1^\circ$ . When the strength of a negative electric field increases, the interaction between the methanethiol adsorbate and gold substrate gets stronger, but the bond length  $d_{\text{S–Au}}$  remains unchanged. When applying a positive electric field, if the field strength increases, the interacting energy first decreases then increases. Unlike the methanethiol case, the S–Au distance in the methylthiolate adsorbate with a positive potential is near to that with zero field. Figure 1(f) reveals that the methylthiolate adsorption structure on the Au(111) surface with a positive external electrical field looks like that without an external electrical field (figure 1(d)). The calculation shows that we cannot adjust the orientation of the methylthiolate on the Au(111) surface continuously. In the range of  $-0.5$  to  $1.5 \text{ V \AA}^{-1}$ , the angle of the S–C bond is around  $55^\circ$ , but within  $-1.0$  to  $-1.5 \text{ V \AA}^{-1}$ , the methylthiolate is nearly vertical to the surface. When the negative electric field is in the range of 0 to  $-0.5 \text{ V \AA}^{-1}$ , even when the interacting energy varies, the orientation of the methylthiolate molecule almost does not change, which is consistent with the experimental results [37].

Let us calculate the electron charge density difference along the surface normal to interpret the responsive behavior. The charge density subtraction is between the charge density obtained with an electric field and that without an electric field at the zero-field optimized geometry. We have plotted the plane-integrated charge density difference as a function of the  $z$ -coordinate (figure 2), which shows how the charges rearrange on application of an external electric field. In the case of the methanethiol adsorption, the positive electric field pulls the electrons back to the gold surface. Troughs 1 and 2 in figure 2(a) indicate the removal of the electrons from the region between the gold surface and sulfur (trough 1)

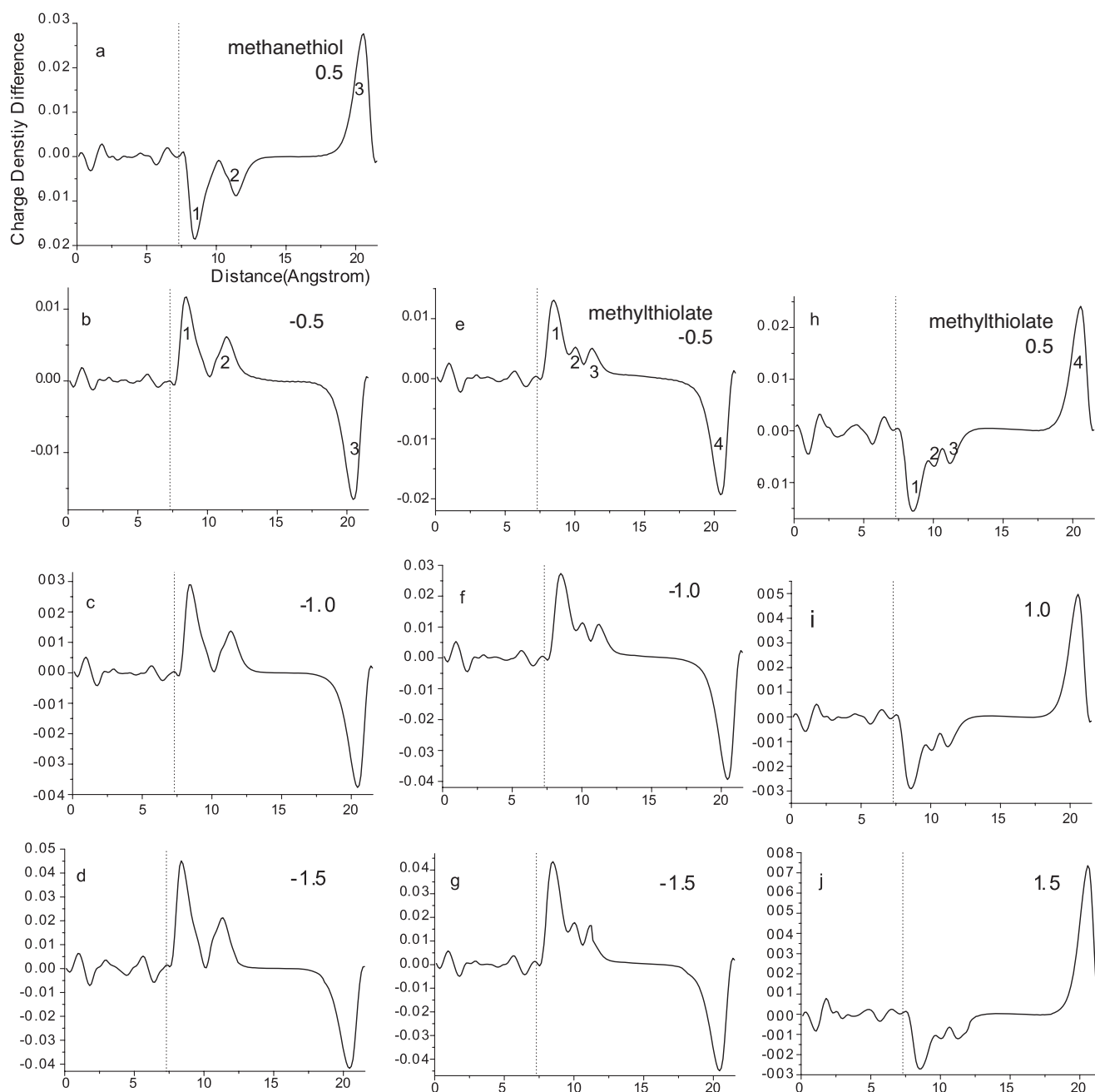
**Table 2.** The geometries and interacting energies for the stable methylthiolate configurations on the Au(111) surface (0.25 ML) at various external electric field strengths.

$E_{\text{ext}}$	S site	$\theta$	Tilt	$d_{\text{S–Au}}$	$E_{\text{int}}$
0	fcc-bri	55.6	hcp	2.45	2.31
$-0.5$	fcc-bri	55.3	hcp	2.45	2.48
$-1.0$	fcc	1.1	hcp	2.46	2.83
$-1.5$	fcc	1.0	hcp	2.45	3.07
0.5	fcc-bri	57.1	hcp	2.48	2.22
1.0	fcc-bri	61.9	hcp	2.52	2.22
1.5	fcc-bri	58.0	hcp	2.50	2.28

and that between sulfur and  $\text{CH}_3$  methyl group (trough 2). The corresponding S–Au bond becomes weaker and more electrons have accumulated on the other side of the slab (peak 3 in figure 2(a)) than in cases without an electric field. The peaks 1 and 2 in figure 2(b) display that the negative field pushes more electrons into the region between S and Au (peak 1) and that around  $\text{CH}_3$  methyl group (peak 2). The S–Au bond gets stronger than that without an electric field. In the presence of a negative electric field, the negatively charged methyl group tends to move away from the surface. However, table 1 shows that the S–C bond length changes slightly in a negative electrical field. Thus, the net effect is that when the strength of an applied negative electrical field increases (figures 2(b)–(d)), the angle between the S–C bond and the surface normal decreases, which explains the responsive behavior of the angle  $\theta$ . The methylthiolate adsorption is similar to the methanethiol case. In an applied negative electrical field, there are more electrons accumulated around the methyl group ( $\text{CH}_3$ ) in the methylthiolate than in the methanethiol (figures 2(b)–(d) and (e)–(g)). When the amount of the electron accumulation exceeds a certain level, the methylthiolate becomes nearly vertical to the surface. In a positive potential, some electrons flow back to the gold surface (figures 2(h)–(j)); the S–Au bond in methylthiolate gets weaker than that without an electric field. Thus, we have shown how the system responds geometrically to the rearrangement of charges in the presence of an applied field.

When the methanethiol is adsorbed on the Au(111) surface, the S–H bond remains intact [30]. If the temperature rises, the methanethiol will desorb from the surface. To see if an applied electric field can break the S–H bond of the methanethiol adsorbate, we calculated the interacting energies for the stable structures of the intact ( $\text{CH}_3\text{SH}$ ) and dissociative adsorption ( $\text{CH}_3\text{S} + \text{H–Au}$ ) on the Au(111) surface. The interacting energies for the intact and dissociative adsorption versus the electric field are plotted in figure 3. Figure 3 reveals that from  $-1.5$  to  $0.5 \text{ V \AA}^{-1}$ , the interacting energy for intact methanethiol adsorption decreases and from  $0.5$  to  $1.0 \text{ V \AA}^{-1}$ , it increases. In the case of dissociative adsorption, from  $-1.5$  to  $0.0 \text{ V \AA}^{-1}$ , the interacting energy decreases; however, above  $0.0 \text{ V \AA}^{-1}$ , the interacting energy increases. Figure 3 displays that in the whole region, the interacting energy for the intact methanethiol adsorption is larger than that for the dissociative one, i.e., the intact adsorption is more stable than the dissociative one. This shows that an external electric field cannot make the hydrogen dissociate from the sulfur.

<sup>3</sup> Upon applying a voltage with respect to a counter electrode, a diffuse layer of ions is formed. However, the interaction between the gold electrode and solvent molecules is small, the model can be regarded as a first-order approximation [2].

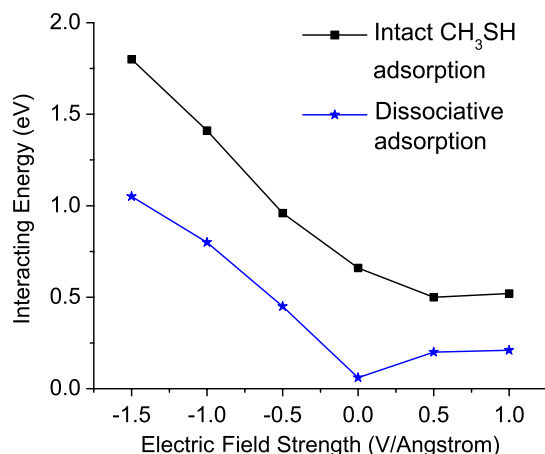


**Figure 2.** The electron charge density difference along the surface normal defined as the charge density corresponding to an electric field minus that obtained in zero field, with zero-field optimal geometry. (a)–(d) methanethiol, (e)–(g) methylthiolate with the negative electric field, and (h)–(j) methylthiolate with the positive electric field. The vertical dotted line represents the position of the gold top layer.

#### 4. Conclusion

Based on *ab initio* calculations, we have shown for the first time how the methanethiol and methanethiolate molecules on the Au(111) surface respond to an applied electrical potential. The sulfur adsorption site, the S–H bond orientation, and the interacting energy vary with the strength of the external electric field. In the low coverage, the orientation of the methanethiol molecule on the Au(111) surface can be tuned by the application of a negative electrical field through a certain range and the methanethiol desorbs from the gold substrate with a positive electrical field. However, the

orientation of the methylthiolate on the Au(111) surface cannot be adjusted continuously. The electron charge density (along the surface normal) corresponding to the external field minus that obtained in zero field, with zero-field optimal geometry, has been calculated to interpret these responsive behaviors. The interacting energies between the intact and dissociative adsorption with an applied electrical potential have been compared. It has been found that the interacting energy for the intact methanethiol adsorption is larger than that for the dissociative adsorption, showing that an external electric field cannot make the hydrogen dissociate from the sulfur.



**Figure 3.** The interacting energies for the intact methanethiol adsorption and dissociative adsorption.

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