The interaction of thioglycolic acid (HSCH$_2$COOH) with the Au(111) surface is investigated, and it is found that at the low coverage the molecule lies down on the substrate. If the mercaptan-hydrogen atom is eliminated, the resulting SCH$_2$COOH molecule is randomly oriented on the surface. If the carboxylic acid group in the HSCH$_2$COOH molecule is deprotonated instead, the HSCH$_2$COO$^-$ molecule lies down on the surface. However, when the mercaptan-hydrogen atom in the HSCH$_2$COO$^-$ molecule is removed, the resulting SCH$_2$COO$^-$ molecule rises up to a certain level on the substrate. The calculated Raman vibrational spectra decipher which compounds and atomic displacements contribute to the corresponding frequencies. We thus propose a consistent mechanism for the deposition of thioglycolic acid on the Au(111) surface.

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I. INTRODUCTION

Self-assembled monolayers (SAMs) have attracted considerable attention as model systems for many fundamental and technological investigations. The thiol and thiolate-based SAMs have broad applications on supramolecular assembly, wetting, tribology, corrosion inhibition, lithography, chemical and biochemical sensors, optics, and immobilization of DNA, because of both their simplicity and stability. In particular, SAMs can simulate a biological membrane which allows adsorption of proteins to metal surfaces without denaturization. The peptide molecules with some enzymatic activity can be deposited on metal surfaces via the thiol or thiolate linkage monolayer. The deposition of a second monolayer on the top of the first adsorbed thiol or thiolate monolayer yields a bilayer system consisting of two monomolecular films. In other words, a layer of peptide molecules can be bonded to the gold surface via the linkage monolayer formed from the thioglycolic acid (HSCH$_2$COOH).

The chemisorption of the thioglycolic acid on the gold surface was demonstrated using surface-enhanced Raman scattering and ultrafast electron crystallography. It was found when the higher portion of the carboxylic acid groups is deprotonated, the higher portion of the thioglycolic acid molecules adopts a trans conformation. It was also observed that after 2,2'-dithiodiacetic acid is deposited on the Au(111), the SCH$_2$COOH molecules are randomly oriented on the gold surface, that is, the adsorption pattern related to the SCH$_2$COOH is different from that corresponding to the HSCH$_2$COOH. On the other hand, the switchable SAM under the influence of an electrical potential was observed with intentionally created room for conformational changes of the molecules. When the external electrical potential is turned on, the hexadecanoic acid molecules (HS(CH$_2$)$_{15}$COO$^-$) bend their negatively charged COO$^-$ group towards the positively charged gold surface. Simulating this switchable SAM process via the ab initio method requires a prohibitive amount of computer time, so one has to study the simple case: the HSCH$_2$COO$^-$ on the Au(111) surface.

It was recently observed that thiol stays intact when deposited on the regular Au(111) surface, but the S-H bond of the thiol is broken on the defected Au(111) surface. Upon the HSCH$_2$COOH molecules deposit on the Au(111), they can either remain intact, or turn into one of the following substances: 1) SCH$_2$COOH in the presence of the defect on the Au(111); 2) HSCH$_2$COO$^-$ by increasing pH value; 3) SCH$_2$COO$^-$ by the defect and increasing pH value. To get a consistent picture of the thioglycolic acid adsorption on the
Au(111), one has to examine the adsorption patterns of the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$, and SCH$_2$COO$^-$ on the Au(111) separately. Even some theoretical simulations on thiol or thiolate based SAMs have been carried out$^{13-20}$, however, there has been no first-principle calculation which provides an atomic-scale description of the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$, and SCH$_2$COO$^-$ on the Au(111) surface. The electronic properties for this system, such as the projected density of states (PDOS) and the charge density difference, have not been discussed. While a large variety of thiol or thiolate based SAMs has been studied, still little is known about why the SCH$_2$COOH molecules are randomly oriented on the gold surface, and how the HSCH$_2$COOH molecules orient on the Au(111). Thus theory is challenged to propose a consistent model for the thioglycolic acid adsorption process on the Au(111) surface.

In this contribution, we address the adsorption patterns of the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$ and SCH$_2$COO$^-$ molecules on the Au(111) surface from first principle calculation. We present adsorption energies and geometries for these four kinds of molecules on the Au(111) surface at 0.25 ML, and find that they demonstrate different adsorption patterns. We calculate the partial density of states (PDOS) projected on the S and O2 atom (with an attached hydrogen, see Fig. 1) to show their relation to the adsorption patterns, and evaluate the charge-density differences to illustrates the interacting bond between the adsorbates and the Au(111). We also compute the Raman vibrational spectra of these four kinds of molecules adsorbed on the surface to decipher the adsorption mechanism of the thioglycolic acid on the Au(111) substrate. By the comparison of the experimental frequencies with the computational ones, we can identify which compounds and atomic displacements contribute to the corresponding frequencies. We thus reveal how the dissociation of the mercaptan hydrogen atom and the deprotonation of carboxylic acid group play key roles in the adsorption process, and propose a consistent mechanism for the deposition of thioglycolic acid on the Au(111) surface.

II. COMPUTATIONAL METHOD

The calculations were carried out in the slab model with periodic boundary conditions by density functional theory (DFT)$^{21,22}$. The electron-ion interaction has been described using the projector augmented wave (PAW) method$^{23,24}$. All calculations have been performed by
Perdew-Wang 91 (PW91) generalized gradient approximation\textsuperscript{25}. The wave functions were expanded in a plane wave basis with an energy cutoff of 400 eV. The $k$ points were obtained from Monkhorst-Pack scheme\textsuperscript{26}, and $3 \times 3 \times 1$ $k$ point mesh was for the geometry optimization. The optimization of the atomic geometry was performed via conjugate-gradient minimization of the total energy with respect to the atomic coordinates. The supercell consisted of five layers with each layer having 12 Au atoms. The Au atoms in the top three atomic layers are allowed to relax, while those in the bottom two layers are fixed to simulate bulk-like termination\textsuperscript{27}. The vacuum region comprises ten atomic layers, which exceeds substantially the extension of the thioglycolic acid molecule\textsuperscript{21}. For charged systems, a uniform compensating background is incorporated to maintain the charge neutrality of the supercell\textsuperscript{28}. The harmonic approximation was applied to calculate the Hessian matrix and vibrational frequencies. We calculated the gold lattice constant and found it to agree with the experimental value\textsuperscript{29} within 2.1%.

III. RESULTS AND DISCUSSION

In this section, we discuss the adsorption pattern of the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$, and SCH$_2$COO$^-$ on the Au(111) substrate, respectively. The adsorption energy of the system is defined as $E_{\text{ads}} = E_{\text{adsorbate}} + E_{\text{Au(111)}} - E_{\text{adsorbate+Au(111)}}$. The symbol top-fcc (or top-hcp) in the following tables represents the S atom being on the atop site of the gold atom, but leaned toward the fcc (or hcp) hollow center, and analogously for the notations bri-fcc, bri-hcp, etc. The units for the bond length and adsorption energy are Angstrom (Å) and eV.

A. The HSCH$_2$COOH molecule on the Au(111) surface

First, let us begin with our analysis with the geometries and adsorption energies of the optimized structures for the thioglycolic acid on the Au(111) surface at the coverage of 0.25 ML, as displayed in Table I. Here 1.00 ML means one sulfur per three gold atoms, and 0.25ML stands for one thioglycolic acid on a gold surface with twelve gold atoms. In Table I the entries $\theta$, $\textit{tilt direct}$ and $d_{S-Au}$ refer to the polar angle between the normal vector of the surface and the S-C2 direction, the Au(111) surface region towards which the S-C2 is
TABLE I: The geometries and adsorption energies for the structures of thioglycolic acid on Au(111) at 0.25ML. The entries $\theta$, \textit{tilt direct} and $d_{S-Au}$ refer to the polar angle between the normal vector of the surface and the S-C2 direction, the Au(111) surface region towards which the S-C2 is tilted, and the shortest Au-S bond length. The entries \textit{initial} and \textit{optimized site} stand for the S atom attachment site before and after optimization. The maximum adsorption energy is underlined.

| initial site | $\theta$ | $d_{S-Au}$ | optimized site | $\theta$ | tilt | $d_{S-Au}$ | $E_{ads}$ | eV |
|-------------|----------|------------|----------------|----------|------|------------|-----------|-----|
| bri         | 0        | 2.60       | bri            | 2.9      | hcp  | 2.97       | 0.27      |     |
|             | 45       | 2.60       | bri-fcc        | 54.8     | hcp  | 2.89       | 0.45      |     |
|             | 90       | 2.60       | bri            | 86.9     | hcp  | 3.16       | 0.47      |     |
| fcc         | 0        | 2.60       | bri-fcc        | 9.7      | hcp  | 2.98       | 0.32      |     |
|             | 45       | 2.60       | bri-fcc        | 61.0     | hcp  | 3.11       | 0.36      |     |
|             | 90       | 2.60       | top-fcc        | 83.7     | hcp  | 3.18       | 0.50      |     |
| hcp         | 0        | 2.60       | bri-hcp        | 5.8      | fcc  | 2.95       | 0.30      |     |
|             | 45       | 2.60       | bri-hcp        | 54.2     | fcc  | 2.87       | 0.48      |     |
|             | 90       | 2.60       | hcp            | 89.4     | fcc  | 3.58       | 0.44      |     |
| top         | 0        | 2.60       | top            | 8.0      | hcp  | 2.93       | 0.26      |     |
|             | 45       | 2.60       | top            | 54.8     | hcp  | 2.81       | 0.37      |     |
|             | 90       | 2.60       | top            | 74.2     | fcc  | 2.57       | 0.63      |     |

The maximum adsorption energy is underlined.

Table I shows the adsorption energy for the most stable structure of the HSCH$_2$COOH on the Au(111) surface is 0.63 eV, and the adsorption site preferred by the sulfur atom is located at the atop site of the gold atom. This stable configuration is illustrated in Fig. 1a. The polar angle between the normal vector of the surface and the S-C2 direction is 74.2°. Fig. 1b indicates that at the low coverage, the HSCH$_2$COOH tends to lie down.$^8$ The S-Au bond length is 2.57 Å, which suggests that the bonding between the S atom in the
FIG. 1: (a) The thioglycolic acid (HSCH$_2$COOH) on the Au(111) surface. (b) SCH$_2$COOH on the surface. (c) HSCH$_2$COO$^-$ on the surface. (d) SCH$_2$COO$^-$ on the surface.

HSCH$_2$COOH and the gold atom could be described as chemisorption$^{11}$.

B. The SCH$_2$COOH molecule on the gold substrate

Ruan et al. used 2,2'-dithiodiacetic acid to make SAMs on the gold surface$^9$, then the SCH$_2$COOH is deposited on the surface. The SCH$_2$COOH can also be obtained from the HSCH$_2$COOH molecule by taking away the mercaptan hydrogen atom which is initially attached to the sulfur. The adsorption pattern of the SCH$_2$COOH molecule on the Au(111) surface is depicted in Table $^{11}$. The adsorption energy for the most stable configuration of the SCH$_2$COOH on the Au(111) surface in Table $^{11}$ is 2.34 eV, and the favored adsorption site by the sulfur atom is in the hcp hollow center, but leaned to the Au-Au bridge. The corresponding structure is shown in Fig. $^{11}$.b. The sulfur atom forms bonds with two Au atoms, and the S-Au bond length is 2.47 Å. The angle between the normal vector of the surface and the S-C2 direction is 68.0°. However, in Table $^{11}$ there are two configurations marked by # (bri-45° and hcp-45°) with adsorption energies 2.33 eV, which is close to the energy of the most stable one (2.34 eV). The corresponding angles $\theta$ for these two #
TABLE II: The geometries and adsorption energies for the structures of the SCH$_2$COOH molecule on the Au(111) at 0.25ML.

| initial site | θ (deg) | $d_{S-Au}$ (Å) | optimized site | θ (deg) | tilt | $d_{S-Au}$ (Å) | $E_{ads}$ (eV) |
|--------------|---------|----------------|----------------|---------|------|----------------|---------------|
| bri          | 0       | 2.60           | bri-hcp        | 6.5     | fcc  | 2.48           | 2.26          |
| #45          | 2.60    | fcc            | #45            | 46.1    | hcp  | 2.45           | 2.33          |
|              | 90      | 2.60           | #45            | 71.3    | hcp  | 2.42           | 2.17          |
|              | fcc     | 0              | fcc            | 2.60    | hcp  | 2.47           | 2.28          |
|              | 45      | 2.60           | fcc            | 9.8     | hcp  | 2.51           | 2.17          |
|              | 90      | 2.60           | #45            | 71.3    | hcp  | 2.50           | 2.23          |
|              | hcp     | 0              | hcp            | 2.60    | fcc  | 2.47           | 2.22          |
| #45          | 2.60    | hcp            | #45            | 41.6    | fcc  | 2.46           | 2.33          |
|              | 90      | 2.60           | #45            | 68.0    | fcc  | 2.47           | 2.34          |
|              | top     | 0              | top-fcc        | 2.60    | 10.1 | hcp            | 2.40          | 2.01          |
|              | 45      | 2.60           | top-fcc        | 63.0    | hcp  | 2.40           | 1.89          |
|              | 90      | 2.60           | top-fcc        | 70.3    | hcp  | 2.59           | 2.05          |

marked configurations are 46.1° and 41.6°, respectively. This can be interpreted as when the SCH$_2$COOH molecules are deposited on the Au(111) surface, some SCH$_2$COOH molecules lie on the substrate (see Fig. 1b), but some of them rise up to a certain level (corresponding to # marked configurations). Thus in the case of SCH$_2$COOH, the configurations with different tilted angles may admix, and the molecule appears to deposit on the gold substrate randomly.

C. The HSCH$_2$COO$^-$ molecule on the surface

When the thioglycolic acid is adsorbed on the Au(111) surface, its carboxylic acid group (COOH) can be deprotonated and it becomes HSCH$_2$COO$^-$. The optimized adsorption configurations of the HSCH$_2$COO$^-$ molecule on the Au(111) surface are described in Table III. The adsorption energies in Table III demonstrate that the sulfur atom in the
TABLE III: The geometries and adsorption energies for the structures of the HSCH₂COO⁻ molecule on the Au(111) surface at 0.25ML.

| initial site | θ (deg) | d_{S-Au} (Å) | optimized site | tilt θ (deg) | d_{S-Au} (Å) | E_{ads} (eV) |
|--------------|---------|--------------|----------------|-------------|--------------|-------------|
| bri          | 0       | 2.60         | bri            | 1.1         | hcp          | 2.86        | 0.44        |
|              | 45      | 2.60         | bri            | 50.6        | hcp          | 2.66        | 0.67        |
|              | 90      | 2.60         | bri            | 82.8        | hcp          | 2.99        | 0.96        |
| fcc          | 0       | 2.60         | bri-fcc        | 8.0         | fcc          | 2.67        | 0.54        |
|              | 45      | 2.60         | bri-fcc        | 65.4        | fcc          | 2.74        | 0.92        |
|              | 90      | 2.60         | top-fcc        | 77.1        | hcp          | 3.38        | 0.95        |
| hcp          | 0       | 2.60         | hcp            | 1.5         | fcc          | 2.75        | 0.66        |
|              | 45      | 2.60         | top-hcp        | 46.6        | fcc          | 2.57        | 0.81        |
|              | 90      | 2.60         | bri-hcp        | 78.0        | fcc          | 3.62        | 0.83        |
| top          | 0       | 2.60         | top            | 5.7         | hcp          | 2.85        | 0.30        |
|              | 45      | 2.60         | top            | 56.6        | hcp          | 2.65        | 0.94        |
|              | 90      | 2.60         | top            | 82.9        | hcp          | 2.60        | 1.13        |

HSCH₂COO⁻ molecule prefers to stay on the atop site of the gold atom, as indicated in Fig. 1c. The corresponding adsorption energy is 1.13 eV which is larger than that of the thioglycolic acid on the Au(111) surface. The S-Au bond length is around 2.60 Å and the angle θ is 82.9°, which means the HSCH₂COO⁻ molecule is lying down on the gold substrate.

D. The SCH₂COO⁻ molecule on the Au(111) surface

If the mercaptan-H atom in the HSCH₂COO⁻ is detached from the sulfur atom, the resulting compound is the SCH₂COO⁻. Table IV shows that the sulfur atom favors the fcc hollow center with the adsorption energy 2.34 eV. The polar angle between the normal vector of the gold surface and the S-C2 direction is 53.4°; so, after losing mercaptan-H atom, the SCH₂COO⁻ molecules begin to rise, see Fig. 1d. Note that there is a # marked configuration in Table IV whose adsorption energy is 2.33 eV - very closed to 2.34 eV. The
TABLE IV: The geometries and adsorption energies for the structures of the SCH$_2$COO$^-$ molecule on the Au(111) surface at 0.25ML.

| initial site | $\theta$ deg | $d_{S-Au}$ Å | optimized site | $\theta$ tilt deg | $d_{S-Au}$ Å | $E_{ads}$ eV |
|-------------|---------------|--------------|----------------|------------------|--------------|-------------|
| bri         | 0             | 2.60         | bri-hcp        | 9.2              | 2.51         | 2.16        |
|             | 45            | 2.60         | bri            | 44.9             | 2.45         | 2.01        |
|             | 90            | 2.60         | bri-fcc        | 78.6             | 2.43         | 2.21        |
| fcc         | 0             | 2.60         | fcc            | 7.8              | 2.47         | 2.14        |
|             | 45            | 2.60         | bri-fcc        | 53.4             | 2.49         | 2.34        |
|             | 90            | 2.60         | bri-fcc        | 83.2             | 2.49         | 2.28        |
| hcp         | 0             | 2.60         | hcp            | 0.5              | 2.49         | 2.11        |
|             | 45            | 2.60         | bri-hcp        | 39.8             | 2.44         | 2.04        |
|             | 90            | 2.60         | bri-hcp        | 76.4             | 2.45         | 2.27        |
| top         | 0             | 2.60         | bri-top        | 10.1             | 2.54         | 1.88        |
|             | #45           | 2.60         | bri-hcp        | 51.8             | 2.43         | 2.33        |
|             | 90            | 2.60         | top            | 81.8             | 2.38         | 2.08        |

The stable structures in Table IV indicate that when the SCH$_2$COO$^-$ is deposited on the Au(111) surface, the molecule rises up to a certain level (see Fig. 1d).

E. Electronic Structures

To understand how the dissociation of the mercaptan-hydrogen atom and the deprotonation of the carboxylic acid group play roles in the adsorption process, we calculate the partial density of states (PDOS) projected on the S and O2 atoms in the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$, SCH$_2$COO$^-$ molecule deposited on the Au(111) substrate. There are three sharp peaks in the PDOS projected on the S atom in the isolated HSCH$_2$COOH molecule (Fig. 2a). The major contributions of three peaks come from $\pi$, $\sigma$ and $\pi^*$ orbitals in the S-C bond. To calibrate the Fermi level for the isolated molecule,
FIG. 2: (a)-(b) PDOS projected on the S and O2 atom in the isolated HSCH$_2$COOH, (c) DOS for a pure Au(111) surface.

In the calculation we have separated the HSCH$_2$COOH molecule from the gold surface by 8Å so that there is no interaction between the molecule and the substrate. The corresponding PDOS projected on the S atom can be regarded as that in the isolated HSCH$_2$COOH molecule. The density of states for the pure gold surface vanishes above 6eV (Fig. 2c). The π* orbital is located on the right edge of the Au d band, the π orbital is near the left edge of the Au d band, whereas the σ orbital overlaps with the gold d band (Fig. 2a, Fig. 2c).

Upon the HSCH$_2$COOH molecule is deposited on the surface (Fig. 3a), the σ and π* states disperse as a consequence of the mixing with the gold d states, whereas the π orbital remains sharp and shifts toward more negative energy. The adsorption energy of 0.63eV indicates that the major interaction between the sulfur in the HSCH$_2$COOH molecule and the gold surface is not van der Waals force, so Fig. 3a might not have the signature of the weak bond.

If the mercaptan-hydrogen atom is dissociated from the S atom, the π state splits indicating a stronger S-Au bonding interaction originating from the hybridization of the π orbital of the SCH$_2$COOH with the gold d band (Fig. 3b). The PDOS projected on the S atom is insensitive to the deprotonation of the carboxylic acid group, which explains why the profiles of Fig. 3a and Fig. 3b are similar so are Fig. 3b and Fig. 3d. No energy gap in the PDOS projected on the S atom attached to the Au(111) surface (Fig. 3a-3d). This is because the HOMO and LUMO level of the S atom fall into the energy range of the gold d-band with a concomitant hybridization, that is, the PDOS projected on the S atom near the Fermi level is dominated by d-states from the Au(111) surface. The effect of the deprotonation of the carboxylic acid group is demonstrated by the PDOS projected on the O2 atom (Fig. 3d).
FIG. 3: (a)-(d) PDOS on the S in the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$ and SCH$_2$COO$^-$ on the surface, (e)-(h) PDOS on the O2 in the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$ and SCH$_2$COO$^-$ on the surface.

Nine sharp peaks are illustrated in the PDOS projected on the O2 atom in the isolated HSCH$_2$COOH molecule (Fig. 2b). Upon the HSCH$_2$COOH is deposited on the gold surface, some peaks are suppressed (Fig. 3e), however, the PDOS projected on the O2 atom is insensitive to the adsorption and the dissociation of the mercaptan-hydrogen atom (Fig. 3f, Fig. 3g). Fig. 3g and Fig. 3h show that some peaks in Fig. 2b disappear and some others disperse after the carboxylic acid group is deprotonated, which indicates that the deprotonation changes the electronic states around the O2 atom.

To further elucidate the interacting bond between the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$, SCH$_2$COO$^-$ molecule and the Au(111) substrate, we calculate the charge-density difference: $\Delta \rho(\vec{r}) = \rho_{ads/sub}(\vec{r}) - \rho_{sub}(\vec{r})$, where $\rho_{ads/sub}$, $\rho_{sub}$, and $\rho_{ads}$ are the electron charge densities of the relaxed adsorbate-substrate system, of the clean relaxed surface, and of the isolated but adsorption-like deformed adsorbate (without substrate), respectively. The isodensity surfaces of the charge-density difference for the structures of the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$, and SCH$_2$COO$^-$ on the Au(111) substrate are depicted in Figs. 4a-4h. In Fig. 4 we display only the surrounding part of the S-Au bond. As we know, two p-electrons of the sulfur in the HSCH$_2$COOH molecule form a lone pair, and the region around the top of the gold is a charge depletion area. In the configuration
of Fig. 4a, the sulfur atom sits on the top of the gold atom. The lone pair in the sulfur is attracted to this charge depletion region, and 0.3e is transferred from the sulfur lone pair orbital to the gold charge depletion area. Thus when the sulfur atom in the thioglycolic acid is adsorbed on the Au(111) (Fig. 4a), the electrostatic interaction responsible for the bonding comes from the monopole term and the dipole moments in the adsorbate and substrate31. Around the sulfur 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 term31. The sulfur atom stays on the top of the gold atom, that is, the S atom only forms a bond with one gold atom. If the mercaptan-hydrogen atom is detached from the sulfur (Fig. 4b), the S-Au bond is largely covalent with some ionic character32. The sulfur in the SCH₂COOH forms bonds with two gold atoms of the Au(111) surface. The interaction between the HSCH₂COO⁻ and the gold surface is the similar to the thioglycolic acid case (Fig. 4c), except that the O1 atom form an additional bond with the gold atom. There is big depletion of electrons around the gold atom. The $p_x$, $p_y$ orbits in the O1 atom gain extra electrons, but the $p_z$ orbit loses some electrons. Thus, this O1-Au bonding is a convolution between the ionic bond and the covalent bond. Fig. 4d suggests that the S-Au bonds for the SCH₂COO⁻ is a covalent bond with some ionic character.

F. The adsorption mechanism

From the above discussion, we propose the following picture. When the HSCH₂COOH molecule is adsorbed on the gold substrate, it lies down on the surface8 (Fig. 1a). When the 2,2'-dithiodiacetic acid is put on the gold surface, the SCH₂COOH molecules form the SAM on the substrate9. If the thioglycolic acid is deposited on the gold surface with defects, the mercaptan hydrogen atom can be dissociated from the S atom and the HSCH₂COOH molecule becomes SCH₂COO⁻11,12. Some SCH₂COOH molecules lie down on the substrate (see Fig. 1b), but others rise up to a certain level. Thus, in the case of SCH₂COOH, different configurations may admix and the adsorption appears to be randomly oriented9. If the carboxylic acid group in the HSCH₂COOH molecule is deprotonated by increasing the pH value, the resulting HSCH₂COO⁻ lies on the surface (Fig. 1c). However, when the mercaptan hydrogen atom in the HSCH₂COO⁻ molecule is ruptured from the sulfur, the resulting SCH₂COO⁻ molecule rises up to a certain level8 (Fig. 1d).
FIG. 4: The isosurfaces of the charge-density difference for (a) the HSCH$_2$COOH adsorption on the Au(111) surface with blue (accumulation of electrons) and/or red (depletion of electrons) isosurface value, ±0.02e/Å$^3$, (b) SCH$_2$COOH on the surface, (c) HSCH$_2$COO$^-$ on the surface, and (d) SCH$_2$COO$^-$ on the surface. Only three related gold atoms of the Au(111) surface are displayed.

IV. THE RAMAN VIBRATIONAL SPECTRA

To support the above adsorption mechanism, we calculate the Raman vibrational spectra of the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$ and SCH$_2$COO$^-$ adsorbed on the Au(111) substrate, respectively. The Raman vibrational peak frequencies (cm$^{-1}$) for experimental data and computational values for the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$ and SCH$_2$COO$^-$ on the Au(111) surface are listed in Table V. The vibrational frequencies
TABLE V: Raman vibrational peak frequencies (cm\(^{-1}\)): Experimental data and computational values for the HSCH\(_2\)COOH, SCH\(_2\)COOH, HSCH\(_2\)COO\(^-\) and SCH\(_2\)COO\(^-\) on the Au(111) surface. The calculated frequencies which are the closest to the experimental ones are underlined.

| Frequencies | \(\omega_1\) | \(\omega_2\) | \(\omega_3\) | \(\omega_4\) | \(\omega_5\) | \(\omega_6\) | \(\omega_7\) | \(\omega_8\) |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Exp. data\(\&\) | 575 665 763 905 930 1387 1597 1711 | | | | | | | |
| Au-HSCH\(_2\)COOH | 575 653 745 881 | - 1409 | - | 1733 | | | | |
| Au-SCH\(_2\)COOH | 596 670 725 872 | - 1396 | - | 1738 | | | | |
| Au-HSCH\(_2\)COO\(^-\) | 592 619 734 | - 929 | 1369 1627 | - | | | | |
| Au-SCH\(_2\)COO\(^-\) | 598 638 822 | - 838 | 1366 1577 | - | | | | |

were calculated for the most stable configurations at 0.25ML. The calculated frequencies which are the closest to the experimental ones are underlined. The Raman scattering is limited to the center of the Brillouin zone, and the vibrational frequencies are calculated at \(\Gamma\) point.

As shown in Fig. 5a, the frequency \(\omega_1\) (575cm\(^{-1}\), 575cm\(^{-1}\)) (the first number stands for the experimentally measured frequency and the second one is the corresponding theoretical one, which is underlined in Table V) is the vibration of the S-C1 and the C1-C2 stretches (the O1 and O2 atoms displace slightly). The theoretical counterpart suggests that the frequency 575cm\(^{-1}\) comes from the HSCH\(_2\)COOH on the gold surface. Fig. 5b indicates that the mode \(\omega_2\) (665cm\(^{-1}\), 670cm\(^{-1}\)) is attributed to the C1-S vibration of the SCH\(_2\)COOH on the substrate. The frequency \(\omega_3\) (763cm\(^{-1}\), 745cm\(^{-1}\)) corresponds to the C1-S stretch of the HSCH\(_2\)COOH on the surface, where the O1 atom displaces slightly (Fig. 5c). The mode \(\omega_4\) (905cm\(^{-1}\), 881cm\(^{-1}\)) is ascribed to the stretching vibration of the C-COOH in the HSCH\(_2\)COOH molecule on the Au(111) (Fig. 5d). \(\omega_5\) (930cm\(^{-1}\), 929cm\(^{-1}\)) corresponds to the C-COO\(^-\) stretching vibration for the HSCH\(_2\)COO\(^-\) on the gold surface (Fig. 5e). The frequency \(\omega_6\) (1387cm\(^{-1}\), 1396cm\(^{-1}\)) is due to the vibration of the COOH of the SCH\(_2\)COOH on the gold surface (the C1 atom moves slightly, see Fig. 5f). The mode \(\omega_7\) (1597cm\(^{-1}\), 1577cm\(^{-1}\)) can be assigned to this COO\(^-\) stretch in the SCH\(_2\)COO\(^-\) (Fig. 5g), which indicates that after the dissociation of the mercaptan hydrogen atom and the deprotonation of the carboxylic acid group, some original HSCH\(_2\)COOH molecules on the surface have
FIG. 5: (a)-(h) illustrate the calculated atomic displacements for the frequencies $\omega_1 - \omega_8$. The frequency $\omega_8$ (1711 cm$^{-1}$, 1733 cm$^{-1}$) corresponds to the C=O stretching vibration for the HSCH$_2$COOH on the Au(111) substrate (Fig. 5h). Thus the above frequency comparison suggests that after the HSCH$_2$COOH molecules deposited on the Au(111) surface, some stay intact on the surface, the rest have turned into SCH$_2$COOH (via dissociation), HSCH$_2$COO$^-$ (deprotonation) and SCH$_2$COO$^-$ (dissociation and deprotonation).
V. CONCLUSION

We have discussed the adsorption patterns of the HSCH$_2$COOH, SCH$_2$COOH, HSCH$_2$COO$^-$, and SCH$_2$COO$^-$ molecules on the Au(111) substrate by first-principle theoretical calculation. We have computed the partial density of states (PDOS) projected on the S and O2 atoms in the molecules on the Au(111) substrate, which display how the dissociation of the mercaptan hydrogen atom and the deprotonation of the carboxylic acid group affect the deposition and the corresponding electronic configuration. We have calculated the charge-density differences for the molecules on the Au(111) substrate, which illustrates various bonding characteristics. We have also studied the Raman vibrational spectra of the molecules adsorbed on the Au(111) substrate, and by the comparison of the experimental frequencies with the computational ones, we have identified which compounds and atomic displacements contribute to the frequencies. We have found the following adsorption mechanism for the thioglycolic acid on the Au(111) surface. Upon the HSCH$_2$COOH molecules deposit on the Au(111), they can either remain intact, or turn into one of the following substances: 1) SCH$_2$COOH in the presence of the defect on the Au(111); 2) HSCH$_2$COO$^-$ by increasing pH value; 3) SCH$_2$COO$^-$ by the defect and increasing pH value. If the intact HSCH$_2$COOH is adsorbed on the gold substrate, the molecule lies down on the surface. When the SCH$_2$COOH molecules deposited on the Au(111) surface, some SCH$_2$COOH molecules lie on the substrate, but others rise up to a certain level. Thus, in the case of SCH$_2$COOH, different configurations may admix, and the molecules appear to be deposited on the gold substrate in a random fashion. If the carboxylic acid group in the HSCH$_2$COOH is deprotonated, the resulting HSCH$_2$COO$^-$ lies down on the surface. However, when the S-H bond in the HSCH$_2$COO$^-$ is broken and the molecule is turned into SCH$_2$COO$^-$, it rises up to a certain level.
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