Au(111), one has to examine the adsorption patterns of the $HSCH_2COOH$, SCH_2COOH, $HSCH_2COO^-$, and SCH_2COO^- 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 $HSCH_2COOH$, SCH_2COOH, $HSCH_2COO^-$, and SCH_2COO^- 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_2COOH molecules are randomly oriented on the gold surface, and how the $HSCH_2COOH$ 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 $HSCH_2COOH$, SCH_2COOH, $HSCH_2COO^-$ and SCH_2COO^- 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 condtions 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