Absorption geometry and interfacial properties for CH3SH self assembled on Cu(110)

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Introduction

With the aim to characterize the real nature of the S-Cu bond and to shed light on the interfacial electrostatics for a copper surface, an ab initio study has been carried out for CH$_3$SH self-assembled on a Cu(110) substrate. Theoretical results suggest that the adsorption of the substrate is rather weak and that the molecular structure assembled on a Cu(110) substrate. Theoretical results suggest that the binding of the adsorbate to the substrate is rather weak and that the molecular structure assembled on a Cu(110) substrate. Therefore for a p(2x2) and a c(2x2) CH$_3$S coverage, a detailed analysis on the adsorbed geometries has been necessary to elucidate the electronic properties at the interface. By studying the partial density of states (PDOS) and the electronic distributions in the real space, a strong hybridization among p-orbitals of sulfur and d-states from the metal substrate is noticed. Work function variations of CH$_3$S/Cu(110) were also monitored when the coverage changes between 0 ML and 0.5 ML.

Theory and Computational Details

Calculations were executed in the framework of Density Functional Theory using the Generalized Gradient Approximation (GGA) in the Perdew-Burke-Ernzerhof parameterization. Atoms were described by Ultrasoft Pseudopotentials with a kinetic energy cutoff of 35 Ryd. The Fermi energy was calculated using the Gaussian Broadening technique, with a smearing parameter of 0.05 Ryd. To study the molecule-substrate interaction, the cubic lattice constant (3.67 Å) was optimized by minimizing the total energy of the bulk Cu and the Cu(110) surface was modeled by a 7 Cu-layers and 10 vacuum layers (2 Å) supercell with a 2x2 surface unit cell. (Fig. 1). The Brillouin-zone (BZ) integration was executed with a 8x8x1 Monkhorst-Pack mesh, corresponding to 16 k-points in the irreducible SBZ. All calculations were performed with the PWSCF code and all the figures were realized by the XCRYSDEN graphical package.

Relaxed Geometries

Section I: Dissociation of the molecule

It is experimental known that the adsorption of methanethiol on the clean Cu(110) surface is characterized by the formation, through the S-H bond cleavage, of an adsorbed mercaptan.

The same result has been obtained by relaxing the CH$_3$SH-system structure. What we noticed was that if for methanethiol the binding to the surface is rather weak (physisorption), larger adsorption energies and smaller bond lengths appear (chemisorption) when the molecule dissociates (as in Fig. 1), yielding H and CH$_3$S.

Section II: Adsorption geometries for methanethiolate

For the methanethiolate a wide study of adsorption configurations has been performed. For the CH$_3$S/Cu(110) system, both p(2x2) and c(2x2) configurations have been analyzed: energies and structural parameters obtained for the most stable configurations ("shortbridge" site in Fig. 2-3) for the two coverages (with an initial S-surface distance of 1.2 Å) are here reported in Tables I and II. The binding energy, in the irreducible BZ, was calculated by using the PW91 functional and norm-conserving pseudopotentials.

Electronical properties

For the analysis of the electronic properties of the most stable configurations found for both chemisorption and physisorption, we used the electronic charge density difference. If for methanethiol an electrostatic interaction, rising from a mutual polarization, appears, for methanethiolate an electron accumulation is clearly present among S atoms and the substrate (Fig. 4).

To highlight the real nature of the bond, then, we studied the modification induced on the p-PDOS of the Cu surface atoms (black line by the CH$_3$S adsorption. Results show that, in respect to the clean Cu(110) (red dashed line in Fig. 5), new states appear at the upper edge of the d-Cu band, at -1 eV, and the density of states increases at ~3-4 eV and decreases around ~2 eV. Comparing this analysis with the density of states associated to sulfur and carbon atoms (respectively the red line and the blue dashed line in Fig. 6) we can attribute the observed variations in the copper properties to the presence of sulfur p-states (both at -1 eV and also at ~3-4 eV).

References