

Study of adsorption of three N-monosubstituted thioureas on a Au(111) surface: DFT-SIESTA approach

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A study of the adsorption of thiourea and three N-monosubstituted derivatives on Au(111) surface was carried out within the framework of the self-consistent Density Functional Theory (DFT) implemented in SIESTA code [1]. In this regard, three functional groups: formyl, phenyl and 2-furoyl, with different electron-donating/withdrawing effect and different *cis* and *trans* conformations were selected to evaluate its influence.

The analysis of the adsorption geometries and energies allowed us to better characterize the most stable structures, as well as the difference in the strength of the molecule-surface interaction.

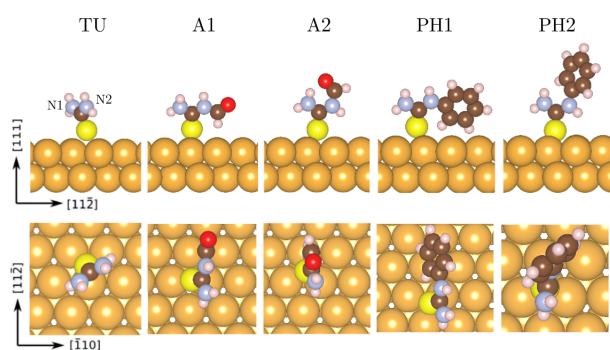


Figure 1: Examples of adsorption geometries of thiourea and *cis/trans* formyl (A1/A2) and phenyl (PH1/PH2) derivatives after full optimizations.

Moreover, the Charge Density Difference (CDD) plots and the Bader charge transfer analysis –reported in our work– implemented in Henkelman code [2], allowed us to delve into the electronic transfer processes that occur during adsorption.

For all cases, the fundamental role of the strong S-Au bond is corroborated, as well as π -Au interactions (red arrows in Figure 2). The latter corresponded predominantly to the *cis* derivatives, due to the orientation and proximity of the functional group with respect to the surface. Only in one of the derivatives (FU3) could the non-covalent interaction $\text{Au} \cdots \text{H} - \text{N}$ be distinguished (black arrow in Figure 2), previously observed in other reports [3].

The final results of our work demonstrate that it is possible to elucidate the interactions between N-

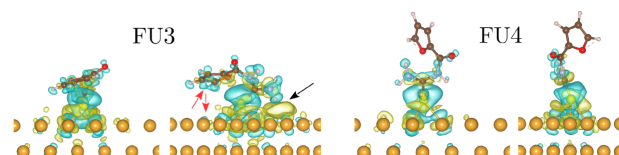


Figure 2: Examples of CDD plots obtained along the directions $[\bar{1}10]$ (left) and $[11\bar{2}]$ (right) for the adsorption of the FU3 (*cis*) and FU4 (*trans*) 2-furoyl derivatives, using an isovalue of 0.001 a.u. The yellow and blue regions represent the loss and gain of electrons, respectively.

monosubstituted thioureas and the Au(111) surface, with mainly covalent nature, employing localized basis sets and pseudopotentials. Crucial long-range dispersive interactions, such as van der Waals forces, were included through a non-local correlation-exchange approximation like the vdW-DF-cx functional [4].

Index Terms: molecule-surface interactions, self-consistent Density Functional Theory, charges transfer analysis, SIESTA code.

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