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Structure, Bonding, and Dynamics of Thiolates on Copper and Gold Clusters and Surfaces MARTIN KONOPKA, CCMS, Slovak University of Technology (FEI STU), Bratislava, Slovakia, ROGER ROUSSEAU, ISAS/SISSA, 4 Via Beirut, 34014 Trieste, Italy, IVAN STICH, CCMS, Slovak University of Technology (FEI STU), Bratislava, Slovakia, DOMINIK MARX, Ruhr–Universitaet Bochum, 44780 Bochum, Germany — The interaction of alkanethiolates with small Cu and Au clusters and (111) surfaces was studied based DFT modeling with a focus on the metal–thiolate junction. Calculation of fragmentation energies indicate that for Cu_n–thiolate (n = 1,3,...,9) there is a progressive lowering in energy for the fragmentation of the S–C bond in the thiolate from a value of 2.9 eV for $n = 1$ to 1.4 eV for $n = 9$.The electronic origins of this weakening are attributed to a polarization of electron density in the S–C bond as induced by bonding with the Cu_n cluster. For the gold analogues this effect is not observed. On the Cu(111) surface the metal to thiolate charge transfer leads to a non-direction partially ionic bonding with a concurrent flat adsorption energy landscape. As a result, occupation of FCC-hollow,HCP-hollow and FCC-bridge sites is observed during a short finite temperature ab-initio molecular dynamics simulation as opposed to a static model where only the hollow sites are stable minima. Comparison of our results with the available experimental evidence and consequences of the electrostatic profile of the metal-molecule interface are presented. The difference between Cu and Au are discussed in the context of relativistic effects.

Ivan Stich
CCMS, FEI STU

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