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Structure, Bonding, and Dynamics of Alkanethiolates on Copper and Gold Clusters and Surfaces MARTIN KONOPKA, CCMS, FEI STU, ROGER ROUSSEAU, International School for Advanced Studies (ISAS/SISSA), 4 Via Beirut, Trieste, Italy, IVAN STICH, CCMS, FEI STU, DOMINIK MARX, Ruhr-Universitaet Bochum, Bochum, Germany — The interaction of alkanethiolates with small coinage metal clusters and (111) surfaces of copper and gold was studied based on density functional theory with a focus on the metal-thiolate junction. Calculation of fragmentation energies indicate that for Cu cluster-thiolate ($n=1,3,5,7$, and 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 detailed electronic origins of this specific weakening are attributed to a polarization of electron density in the S-C bond as induced by bonding with the Cu cluster. For the gold analogues this effect is not observed and fragmentation at the S-C bond experiences only a slight 10% destabilization as n increases from 3 to 9. On the Cu(111) surface the metal to thiolate charge transfer which 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 the course of 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.

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