

Dimerization of methanethiol adsorbates on metal surfaces.

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Self-assembled monolayers (SAMs) are thin organic films that form spontaneously on solid surfaces upon molecular adsorption. Much work has been done specifically on monolayers formed by alkanethiol molecules on a gold substrate [1]. These systems have been studied intensely for their basic interest as prototypical organic interfaces and also for their technological relevance. A wide range of applications has been identified for these layers, for instance in the context of sensor fabrication, but also protective coatings, lubrication, diagnostics or patterned films, and much more.

The most stable structures realized by both methanethiol and methanethiolate on metal substrates are largely determined by the tendency of the adsorbates towards dimerization. In this contribution, computational results on the dimerization behavior of both molecular species on the Au(111) surface are reported. Density Functional theory within periodic boundary conditions has been used to investigate dimerization effects at different levels of coverage. The system CH₃SH on Au(111) was studied at 0.5 and 1.0 ML, and monomer as well as dimer patterns were clearly distinguished, as shown in Figure 1. For both levels of coverage, the dimerized structures were found to be of higher stability than the monomers. In the case of methylthiolate, in contrast, the tendency towards dimerization was found to depend on the level of coverage. At 0.5 ML, a dimerized structure was seen to be favored, at 1.0 ML, however, a monomer configuration was found maximally stable. This latter finding is reflected by experiment [2]. Once a clear distinction is made between thiol and thiolate adsorbates, the respective experimental results for 1.0 monolayer appear consistent.

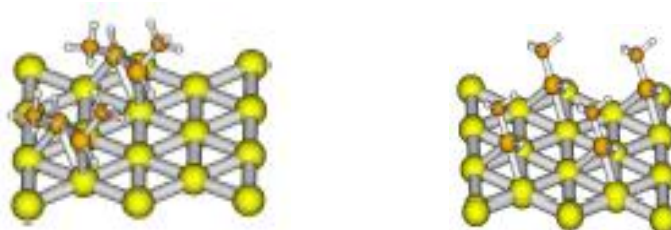


Figure 1: Dimer (left) and monomer (right) configurations of methanethiol on Au(111).

[1] F. Schreiber, *J.Phys.: Condens. Matter* 16, R8881 (2004).

[2] H. Kondoh et al., *Phys. Rev. Lett.* 90, 66102 (2003).

