

# Structure and stability of self-assembled monolayers of organic molecules on metal surfaces

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Self-assembled monolayers (SAMs) are well ordered organic layers spontaneously formed upon adsorption, in solution or in ultra high vacuum, of molecules containing one or more head- groups that present strong affinity to the substrate. Their relatively simple preparation, stability, long-range two-dimensional epitaxy (at the nanometer scale), easy functionalization and the great variety of molecules that can be used as building blocks give SAMs a wide range of potential technological applications [1-3]. Metal surfaces and sulfur-containing molecules have been extensively used during the last 30 years as benchmark systems for the understanding of the growth kinetics and structural properties of SAMs. In spite of the large number of theoretical investigations focused on SAMs of thiols on metal surfaces, various questions on the origin of their structures remain open (see e.g. refs. 4–5 and references therein).

Here, we report on the adsorption geometry and stability of SAMs of alkanethiols ( $\text{SC}_n$ ) on Ag(111), Au(111) and SAMs of aromatic thiols on Ni(111).

For SAMs of  $\text{SC}_n$  on Ag(111), and Au(111), we compare the stability of many possible structures characterized by coverages  $1/3$  and  $3/7$  [6,7]. We find that the different structural properties of the up-right monolayers of  $\text{SC}_n$  on Au(111) and Ag(111) are largely determined by the different (coverage dependent) S-surface binding energies, which in turn, are due to the dissimilar reconstructions induced by the SAMs on both substrates. Thus, our results surprisingly show that the structures of the saturation coverage monolayers of  $\text{SC}_n$  on Au(111) and Ag(111) are barely dictated by the chain-chain interactions in contrast with the usual belief.

In the case of SAMs of aromatic thiols on Ni(111), we present a theoretical-experimental study on the structure and stability of aromatic SAMs with backbone composed of a single phenyl ring and different endgroups, deposited in ultra high vacuum on single crystal surfaces and/or thin films of Ni(111). By means of high-resolution X-ray photoelectron spectroscopy, near-edge X-ray absorption fine structure and thermal desorption spectroscopy in conjunction with density functional theory calculations we get insight into the molecule integrity and bonding configuration and cast some light onto decomposition reactions that may occur at different temperatures and coverages.

## References

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