Theoretical study of charge states in molecular nanostructures on surfaces.

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Abstract

Scanning probe microscopy (SPM) techniques are well known to provide images of molecular structures deposited on surfaces. Equipped with functionalized tips, these techniques have broadly demonstrated to achieve atomic resolution. However, the origin of certain aspects of the obtained images is still under debate.

This thesis investigates the origin of the sharp intermolecular features that frequently appear in the high-resolution SPM images. It is confirmed that the saddle points of the potential energy surface are the origin of the lateral bendings of the probe which are detected as narrow edges in the images. This situation can occur between non-covalently bonded atoms, due to their mere presence. Therefore, they cannot be interpreted as a direct representation of weak intermolecular bonds.

This text also describes the work done to obtain direct images of anisotropic charge distributions, such as σ-holes, using a Kelvin probe force microscope with a properly functionalized tip. The simulations performed using a model developed expressly for this project demonstrate that the images obtained experimentally can reflect both the electrostatics of the tip and the sample.

Additionally, the isomerization of organometallic chains, driven by the strain induced by the substrate on which the chains lie is characterized. To this end, theoretical ab-initio simulations of the molecular dynamics based on density functional theory were performed, which elucidated key aspects of the experimental process.