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Scanning Probe Microscopy and Spectroscopy of Molecules on Thin Insulating Films

JASCHA REPP, University Regensburg

Ultrathin insulating films on metal substrates facilitate the use of the scanning tunneling microscope (STM) to study the electronic properties of single atoms and molecules, which are electronically decoupled from the metallic substrate. The ionic relaxations in a polar insulator lead to a charge bi-stability in some adsorbed atoms and molecules. It is shown that control over the charge-state of individual molecules in such systems can be obtained by choosing a substrate system with an appropriate work function. The distribution of the additional charge is studied using difference images. These images show marked intra-molecular contrast [1]. We discuss how atomic-force-microscopy (AFM) in a combined STM/AFM based on the qPlus-sensor [2] reveals additional information that is truly complementary to the STM data set. In the case of a non-planar molecule that shows two different adsorption geometries, only the AFM channel provides reliable information on the conformation of the molecule. In another example of an artificially formed molecule-metal-molecule complex, the AFM channel provides information on the bonding that is important to understand the STM results.

[1] I. Swart, T. Sonleitner, and J. Repp, *Nano Letters* 11, 1580 (2011).

[2] F. J. Giessibl, *Appl. Phys. Lett.* 76, 1470 (2000).