Scanning Probe Spectroscopy of Individual Molecules on Thin Insulating Films

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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. This setup enables to perform spatially resolved vibronic spectroscopy in a double barrier tunnelling junction geometry. We show that the spatial position of the electron injection as well as the local wave function symmetry dramatically affect the electron-vibron coupling. We observe that the energy dissipation associated with the electron attachment, the so-called reorganization energy, spatially varies by more than a factor of two. We investigated $C_{20}S_2H_{12}$ molecules adsorbed on ultrathin layers of NaCl by means of atomic force-microscopy (AFM) in a combined STM/AFM based on the qPlus-sensor. These non-planar molecules exist in two stable conformations. By means of excitations from inelastic tunneling electrons we can switch between both conformations. We present atomic force microscopy (AFM) measurements with submolecular resolution directly revealing the conformational changes. From AFM data and taking the chirality of the molecules into account, we could unambiguously determine the pathway of the conformational change. Hence, the AFM channel reveals additional information that is truly complementary to the STM data set. Finally, we formed artificial metal-organic complexes on the same substrate by means of inelastic excitations. The electronic decoupling of the ultrathin NaCl films enabled the study of the molecular electronic structure of the constituents and the complex by means of scanning tunnelling spectroscopy. The actual bonding geometry was determined from AFM images with submolecular resolution. Exploiting the symmetry of the complex its electronic structure can be rationalized from considering the linear combinations of the constituents' orbitals.