Scanning Tunneling Spectroscopy of Molecules on Thin Insulating Films

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Ultrathin insulating films on metal substrates facilitate the use of the scanning tunneling microscope to study the electronic properties of single atoms and molecules, which are electronically decoupled from the metallic substrate.

In the case of molecules on ultrathin NaCl films the electronic decoupling allows the direct imaging of the unperturbed molecular orbitals, as will be shown in the cases of individual pentacene and oligothiophene molecules, as well as of an artificial metallo-organic complex that was formed by STM-based molecular manipulation.

The ionic relaxations in a polar insulator leads to an interesting charge bistability in some atoms and molecules. It is shown that control over the charge-state of individual molecules adsorbed on surfaces can be obtained by choosing a substrate system with an appropriate workfunction. The charge state switching is found to be current induced. The distribution of the additional charge is studied using difference images. These images show marked intramolecular contrast.

The use of Xe as insulating films allows one to also study vibronic properties of ad-molecules that are electronically decoupled from the conductive substrate. In the case of oligothiophene-based molecular wires we observe a non-Born-Oppenheimer regime, for which a coherent coupling of electronic and nuclear motion emerges. This phenomenon should occur in all systems with strong electron-vibration coupling and an electronic level spacing of the order of vibrational energies. The coherent coupling of electronic and nuclear motion could be used to implement mechanical control of electron transport in molecular electronics.