Mapping the electronic resonances of single molecule STM tunnel junction

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A low-temperature scanning tunneling microscope (STM) differential conductance (dI/dV) measurement is a very effective technique to gain access to the low lying electronic states of a molecule weakly coupled to the surface of an STM tunnel junction. By accessing those states, the electron probability distribution of the ground and first excited states of a pentacene molecule had been imaged in real space [1]. Here pentacene was electronically decoupled from the metal substrate by an ultrathin insulating layer and the corresponding STM images are found to be very close to the mono-electronic HOMO and LUMO maps [1]. To have access to more states and therefore to more MO maps, a metal surface where the molecule is physisorbed on the surface of the STM tunnel junction can be used to reduce the energy gap between STM junction tunneling resonances and to get more molecular electronic states inside the STM bias voltage range without destroying the molecule.

First, we show that aside from the two frontier MOs (HOMO and LUMO), the second (HOMO-1) and third (HOMO-2) occupied MOs of a pentacene molecule lying directly on a Au(111) surface can be also imaged [2]. The way to disentangle those MO components from the contribution of higher resonance molecular electronic states will be discussed.

Second, the case of the Cu-phthalocyanine molecule characterized by a double-degenerated LUMO will be presented. An MOs basis set decomposition of the electronic cloud of this molecule does not correspond to

the one provided by the STM dI/dV conductance mapping: during scanning, the tip apex-molecular cloud electronic interactions capture the molecular orbital components of the molecular electronic states located in the dI/dV energy range as a complex mixture of different phases and weight contributions [3].

Finally, the hexabenzocoronene molecule, and some of its oligomers (monomer, dimer, trimer, and tetramer) prepared by an on-surface synthesis on Au(111) were imaged. From the tunneling spectra and the dI/dV maps of these molecules, a given STM dI/dV electronic resonance results from a complex contribution to the local conductance of many molecular states. This makes difficult to reconstruct an apparent molecular orbital electron probability density map in a straightforward manner using the standard quantum superposition of Slater determinants constructed with those mono-electronic molecular orbitals [4].

References:

[1] J Repp et al. Phys. Rev. Lett. 94, 026803 (2005)
[2] W – H Soe et al. Phys. Rev. Lett. 102, 176102 (2009)
[3] W – H Soe et al. J. Phys.: Condens. Matter in press (2012)
[4] W – H Soe et al. ACS Nano 6, 3230 (2012)