

Imaging Electron Transfer at the Molecular Scale by Atomic Force Microscopy

Laerte L. Patera

Department of Physical Chemistry, University of Innsbruck, Innsbruck, 6020, Austria

Electron transfer is at the heart of many fundamental processes, from photosynthesis to combustion and molecular self-assembly. Yet, its influence on the electronic structure of organic and organometallic molecules remains incompletely understood. In this talk, I will present recent advances in atomic force microscopy (AFM) that allow us to directly visualize and manipulate electron transfer at the single-molecule level.

In the first part of this talk, I will present an AFM-based imaging approach, namely single-electron alternate charging scanning tunneling microscopy (AC-STM), that enables mapping the orbital structure of single molecules upon electron transfer [1]. This method has revealed the effects of electron transfer and polaron formation on the scale of individual molecular orbitals [2,3].

In the second part, I will turn to metal-molecule charge transfer and its role in molecular self-assembly on surfaces. Using a combination of Kelvin Probe Force Microscopy and Scanning Tunneling Spectroscopy, we investigated charge transfer in self-assembled phases of fullerene C₆₀ and a porphyrin derivative. Through detailed analysis of force and tunneling spectra, we reveal that the driving force behind the formation of the row-like structure is the alleviation of repulsive inter-fullerene Coulomb interactions, which in turn promotes a larger degree of charge transfer to the C₆₀ molecules [4]. These findings demonstrate how the delicate balance between substrate-mediated electron transfer and intermolecular interactions can be harnessed to control molecular organization at surfaces.

References

- [1] L. L. Patera, F. Queck, P. Scheuerer, and J. Repp, Mapping orbital changes upon electron transfer with tunnelling microscopy on insulators, *Nature* **566**, 245 (2019).
- [2] L. L. Patera, F. Queck, P. Scheuerer, N. Moll, and J. Repp, Accessing a Charged Intermediate State Involved in the Excitation of Single Molecules, *Physical Review Letters* **123**, 16001 (2019).
- [3] L. L. Patera, F. Queck, and J. Repp, Imaging charge localization in a conjugated oligophenylene, *Physical Review Letters* **125**, 176803 (2020).
- [4] B. Achatz et al., (in preparation).