Imaging molecular processes at surfaces: from single-electron transfer to dihydrogen bonding

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Electron transfer plays a crucial role in many chemical processes, from photosynthesis to combustion and corrosion. However, the effect of electron transfer on the electronic structure of organic molecules remains largely unclear. Unveiling these fundamental aspects requires the development of experimental tools allowing the observation of electron transfer down to the single molecule level. In the first part of this talk, I will present an imaging approach, namely single-electron alternate charging scanning tunneling microscopy (AC-STM), allowing mapping the orbital structure of single molecules upon electron transfer [1-3]. In this way, we unveiled the effects of electron transfer and polaron formation on the single-orbital scale.
In the second part of the talk, I will focus on the characterization of dihydrogen bonding (DHB). This represents a peculiar intermolecular interaction, arising from hydrogen atoms acting as both proton acceptors and donors. Despite its significance, the manifestation of DHB in molecular assemblies on surfaces has remained elusive. Here, I will present evidence of DHB within borazine assemblies on Au(111) surfaces [4]. By means low-temperature scanning tunneling microscopy (LT-STM), distinct configurations have been unveiled, exhibiting single and double DHB motifs. Complementary density functional theory (DFT) calculations shed light on the delicate interplay between substrate adsorption and intermolecular interactions, elucidating the stabilization mechanisms driving the formation of borazine clusters on Au(111).

[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] M. Zeilerbauer, et al. in preparation.