

O 97: Focus Session: Scanning Probe Microscopy with Quartz Sensors IV

Time: Friday 10:30–12:45

Location: TRE Ma

O 97.1 Fri 10:30 TRE Ma

qPlus-based Lateral Force Microscopy — ●ALFRED J. WEYMOUTH — Universität Regensburg, Regensburg, Deutschland

Lateral force microscopy (LFM) is a branch of AFM in which a component of force perpendicular to the surface normal is measured. Long-range forces have no lateral component over a flat terrace, making LFM ideal to study short-range forces. We have established methods to extract force and potential energy from our observations, and applied these methods to study a number of systems including molecular bending. We have also studied the interaction at the side of a molecular adsorbate, and more recently shown that we can measure the energy dissipation as we pull a molecule at the tip over the surface.

Giessibl et al., Proc. Nat. Acad. Sci. 99, 12006 (2002); Weymouth et al., Science 343, 1120 (2014); Weymouth, J Phys.: Condens. Matter 29, 323001 (2017); Weymouth et al., Phys. Rev. Lett. 124, 196101(2020); Weymouth et al., J. Jap. Appl. Phys. 61, SL0801 (2022)

O 97.2 Fri 10:45 TRE Ma

Exploring in-plane interactions beside an adsorbed molecule — ●SHINJAE NAM¹, ELISABETH RIEGEL¹, LUKAS HÖRMANN², OLIVER T. HOFMANN², OLIVER GRETZ¹, ALFRED J. WEYMOUTH¹, and FRANZ J. GIESSIBL¹ — ¹Institute of Experimental and Applied Physics, University of Regensburg, Germany — ²Institute of Solid State Physics, Graz University of Technology, Austria

In-plane interactions between two molecules on a surface can be used to guide on-surface chemical reactions. Our implementation to study in-plane interactions is Lateral Force Microscopy (LFM), where the tip of an AFM is oscillated laterally to directly measure the lateral forces. We investigate the short-range interactions by approaching the side of an adsorbate with a CO-terminated tip. By obtaining 3D data sets at the sides of PTCDA and CO, we demonstrated the large influence of the metal dipole at the tip apex. While previous work has noted this for strongly polarized materials, including defects in ionic crystals [1] and hBN [2], we showed that the metal tip dipole above CO must be also accounted for when measuring closer to single molecules.

1. M. Ellner et al., Nano Lett. 16, 1974 (2016). 2. F. Schulz et al., ACS Nano 12, 5274 (2018)

O 97.3 Fri 11:00 TRE Ma

Real-space imaging σ -holes and π -holes: a source of electrostatically driven non-covalent interactions — BENJAMIN MALLADA^{1,2}, MARTIN ONDRACEK¹, AURELIO GALLARDO¹, ●BRUNO DE LA TORRE^{1,2}, and PAVEL JELINEK^{1,2} — ¹Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic. — ²Regional Centre of Advanced Technologies and Materials, Palacký University, Olomouc, Czech Republic

Noncovalent interactions between molecules play an important role in supramolecular chemistry, molecular biology, and materials science. For the rational design/tweaking of supramolecular systems, it is helpful to understand the forces that make these systems stick to one another.

In this contribution, I will focus on the real-space visualization of the σ -hole (1) and π -hole (2). By a set of Atomic Force Microscopy (AFM), Kelvin Probe Force Microscopy (KPFM), and Scanning Tunneling Microscopy experiments we discriminate the emergence of both σ -hole and π -hole on a single molecule with unprecedented submolecular resolution. Our findings are fully supported by an atomistic model obtained from DFT calculations which allow us to simulate both AFM and KPFM images. These results may potentially open a new way to characterize biological and chemical systems in which anisotropic charges play a decisive role.

(1) B. Mallada et al. Science 2021, 374, 863 (2) B. Mallada et al. In preparation

Topical Talk

O 97.4 Fri 11:15 TRE Ma

Heteroatom-substituted and three-dimensional nanocarbon materials studied with low temperature STM and qPlus AFM — ●SHIGEKI KAWAI — National Institute for Materials Science, Tsukuba, Japan

Since the first systematic on-surface covalent coupling of bromo-substituted porphyrins,[1] on-surface chemical synthesis has attracted tremendous interest of researchers. Combining with bond-resolved

scanning probe microscopy (SPM) with the qPlus sensor, [2] this field has been rapidly developed. In this contribution, I will present our recent studies on on-surface chemistry with high-resolution SPM operating at low temperature under ultra-high vacuum. We synthesized heteroatom doped [3] and three-dimensional graphene nanoribbons (GNRs) by coupling bromo substituted-propellane molecules on Au(111).[4] In the 3D-GNR, the C-Br bonds distant from the surface remained intact even after the reaction. The radical species were formed by tip-induced debromination and were also stabilized by either Br atom or fullerene molecule. We also developed new on-surface reaction, which can synthesize graphene nanoribbon and covalent organic frameworks with silabenzene units by coupling Si atom and Br-substituted molecule.[5]

Reference: [1] L. Grill, et al., Nat. Nanotechnol. 2, 687. (2007). [2] L. Gross, F. Mohn, N. Moll, P. Lilkeroth, G. Meyer, Science 325, 1110 (2009). [3] S. Kawai, et al Nat. Commun. 6, 8098 (2015) and Sci. Adv. 4, eaar7181 (2018). [4] S. Kawai, et al Sci. Adv. 6, eaay8913 (2020). [5] K. Sun et al, Nat. Chem. (2022) doi:10.1038/s41557-022-01071-3.

O 97.5 Fri 11:45 TRE Ma

Interaction between an artificial and a natural atom — ●FABIAN STILP, MARCO WEISS, and FRANZ GIESSIBL — Institute of Experimental and Applied Physics, University of Regensburg, Universitätsstraße 31, 93053 Regensburg

The surface state of Cu (111), a quasi-2-dimensional electron gas, is trapped to a small surface area of about $15 \times 15 \text{ nm}^2$ by placing 48 CO-molecules in a circular shape on the surface via atomic manipulation. By doing so, one creates a quantum corral with discrete electronic states forming an artificial atom. This structure can be described reasonably well by an infinitely high circular potential well leading to corral states with Bessel-type radial functions and an angular momentum normal to the surface. To investigate the interaction between this artificial atom and a natural atom we bring Fe atoms and CO molecules inside the corral and measure the response of the corral states.

Thanks to the large corral diameter, one can study the structure of the wave functions within that artificial atom by AFM and STM showing an angular dependence of the corral states after placing the perturbations inside the corral. This change of the wave functions leads to an energy shift of a few meV. By investigating the change of the corral states due to the perturbation, one can draw conclusion about the interaction between this artificial atom and a natural atom. Here we expand the interpretation of the adatom acting repulsively on the corral states as stated by Stilp et al. [1].

[1] F. Stilp, A. Bereczuk, J. Berwanger, N. Mundigl, K. Richter, F.J. Giessibl, Science 372, 1196-1200 (2021).

O 97.6 Fri 12:00 TRE Ma

Revelation of an inhomogeneous broadening effect in artificial quantum structures caused by electron-adsorbate scattering — ●MARCO WEISS, FABIAN STILP, and FRANZ GIESSIBL — Institute of Experimental and Applied Physics, University of Regensburg, Universitätsstraße 31, 93053 Regensburg

In 1993 Crommie et al. [1] arranged 48 Fe adatoms on a Cu(111) surface in a circle with a diameter of 14.26 nm. This quantum corral confines surface electrons in a circular potential well. Past investigations with scanning tunneling microscopy revealed energetically discrete eigenstates with radial Bessel functions. These studies on the Fe quantum corral showed unwanted movement of the corral walls during spectroscopic measurements because of the weak bonding of Fe on Cu(111) [1].

We used CO molecules to provide the corral with more stable walls. This permitted us to access a larger voltage window and allowed for a detailed line shape analysis of the corrals eigenenergy levels. Surprisingly, we discovered a dominant Gaussian broadening of the eigenstates.

We find that the spectral width is dependent on the size of the quantum structure. The introduction of a simple model linking the energy dependence of this inhomogeneous broadening with the single particle movement of surface state electrons has shown that the observed behaviour is compatible with an electronic lifetime limitation by interaction with the corral wall.

[1] M. F. Crommie et al., Science 262, 218-220 (1993).

O 97.7 Fri 12:15 TRE Ma

Benchmarking atomically defined probe tips for NC-AFM experiments — DAMLA YESILPINAR¹, BERTRAM SCHULZE LAMMERS¹, ALEXANDER TIMMER¹, ZHIXIN HU², WEI JI³, SAEED AMIRJALAYER¹, HARALD FUCHS¹, and ●HARRY MÖNIG¹ — ¹Westfälische Wilhelms-Universität, Münster, Germany — ²Tianjin University, Tianjin, China — ³Renmin University of China, Beijing, China

Controlling the identity of the tip-terminating atom or molecule in NC-AFM constitutes a milestone in surface science. We consolidate the interpretation of such studies by directly comparing the performance of four atomically defined tips: Cu-, Xe-, CO-, and O-terminated copper (CuOx-) tips. Besides their imaging performances on a metal oxide, we directly compared their capabilities in force mapping during the lateral manipulation of single adsorbed atoms. Expectedly, Cu-tips strongly react with the surface inhibiting stable imaging and picking up the atoms to be manipulated. The chemically inert Xe- and CO-tips, allow entering the repulsive force regime. However, their flexibility leads to dynamic tip bending and pronounced artefacts due to the strongly varying potential above the oxide. Furthermore, tip deflection prevents reaching sufficient threshold forces along manipulation trajectories with high energy barriers. In contrast, the combination of moderate chemical passivation and high stiffness of CuOx-tips turned out decisive for a distinct chemical-specific contrast. Moreover, this results also in a superior performance in the manipulation experiments where their high mechanical stability allows quantitative force measurements also along the trajectories with high energy barriers.

O 97.8 Fri 12:30 TRE Ma

Visualizing electrochemical interfaces with a qPlus sensor-based AFM/STM — ●ANDREA AUER, BERNHARD EDER, and FRANZ GIESSIBL — Institute of Experimental and Applied Physics, University of Regensburg, Germany

Atomic force microscopy (AFM) that can be simultaneously performed with scanning tunneling microscopy (STM) modes using metallic tips attached to self-sensing quartz cantilevers (qPlus sensors) has advanced the field of surface science by allowing for unprecedented high spatial resolution under ultrahigh vacuum conditions. Applying a qPlus sensor, which offers simultaneous STM/AFM and seamless transitions in between, to the field of electrochemistry creates new possibilities to locally image both the 3D layering of the interfacial water and the lateral structure of the electrochemical double layer. In this work, a home-built AFM/STM instrument equipped with a qPlus sensor for operation under precise potential control in an electrochemical liquid cell is presented. The potential-dependent structural interface organization of the electrochemical double layer on both highly oriented pyrolytic graphite (HOPG) and Au(111) electrodes in acidic media is investigated by means of (simultaneous) AFM/STM imaging and force spectroscopy. We observe frequency shift oscillations as a function of the z-piezo distance, which correspond to the layering of the interfacial solvent molecules, where both the number of layers as well as their strength is highly dependent on the applied potential.