

O 103: Focus Session: Molecular Nanostructures on Surfaces: On-Surface Synthesis and Single-Molecule Manipulation IV

Time: Friday 10:30–13:00

Location: HE 101

Topical Talk

O 103.1 Fri 10:30 HE 101
Toward nanofabrication with molecular building blocks — ●CHRISTIAN WAGNER — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany

The control of single-molecule junctions with a scanning probe microscope not only directly benefits molecular electronics and molecular machines, but is also a stepping stone to the more ambitious goal of (supra)molecular nanofabrication. In my talk I will describe key aspects of controlled molecular manipulation. Perhaps the biggest challenge is the lack of information about the atomic configuration of a tip-molecule-surface junction during manipulation. We have developed strategies to monitor this configuration in real time during manipulation or to circumvent the problem using concepts such as reinforcement learning. Precise knowledge of the molecule-surface interactions arising from van der Waals forces and local chemical bonding is central to this endeavor, and I will present our efforts to probe these interactions via molecular manipulation. Appropriate models are another key component in understanding and controlling the manipulation process. I will outline our modeling strategies, ranging from machine-learned models trained on DFT data to models based entirely on experimental observations. Finally, I will discuss scanning quantum dot microscopy, an application enabled by single-molecule manipulation, and report surface potential measurements on atomic chains.

O 103.2 Fri 11:00 HE 101
Faster Single-Molecule Manipulations by STM Tunneling Current Analysis with Neural Networks — ●MICHAEL OBERMAYR, BERNHARD RAMSAUER, and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Scanning tunneling microscopy (STM) allows precise manipulation of single atoms and molecules on surfaces. Recent AI-driven advancements in manipulating arbitrary molecules [1] open the door to automatic assembly of artificial nanostructures. A significant time portion is required for the imaging before and after each manipulation step, which often acts as the speed bottle neck. In this work we train a neural network on the tunneling current to predict the shift in position and orientation of an object, limiting the need for constant imaging.

The challenge in training a neural network lies in obtaining a suitable dataset containing all necessary inputs and outputs. Here we start with a measurement series of single-molecule manipulations paired with the respective precedent and subsequent images of the surface. The action outcome is extracted from these images with machine vision. Thus, a suitable training dataset for neural networks can be generated systematically, while ensuring broad applicability towards arbitrary molecules.

The fully trained network allows to track the manipulated molecule despite skipping a significant fraction of the imaging steps, which leads to an accelerated manipulation process.

[1] B. Ramsauer et al., *J. Phys. Chem. A*, 127, 2041 (2023)

O 103.3 Fri 11:15 HE 101
Tip-induced and thermally activated rotation of bowl-shaped bridged-triphenylamine derivatives on Au(111) — ●SAJJAN MOHAMMAD¹, MILAN KIVALA², MEIKE STÖHR¹, and SABINE MAIER¹ — ¹Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — ²Institute of Organic Chemistry, University of Heidelberg, Germany

We studied the adsorption and rotation under external excitation of bowl-shaped bridged-triphenylamine derivatives on Au(111) using low-temperature scanning probe microscopy. The primarily observed three-lobed structure suggests that individual bridged-triphenylamine molecules adsorb in a bowl-up conformation, with the central atom anchoring to the Au(111) surface and the three benzene rings suspended above it. The onset and mechanism of rotation were examined through STM tip manipulation experiments and thermal activation. Our results demonstrate that the central atom of a bridged triphenylamine acts as an effective axle, ensuring sufficient anchoring to prevent diffusion and facilitating low rotational barriers for single molecule rotors on a metal surface.

O 103.4 Fri 11:30 HE 101
Thermal with electronic excitation for unidirectional rotation of molecule on surface — ●KWAN HO AU-YEUNG^{1,2}, SUCHETANA SARKAR¹, CHRISTIAN JOACHIM³, and FRANCESCA MORESCO¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — ²Physikalisches Institut, Karlsruhe Institute of Technology, 76131Karlsruhe, Germany — ³GNS & MANA Satellite, CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse, France

Exploring the limits of the microscopic reversibility principle, we investigated the interplay between thermal and electron tunneling excitations for the unidirectional rotation of a molecule-rotor on the Au(111) surface. We identified a range of moderate voltages and temperatures where heating the surface enhances the unidirectional rotational rate of a chemisorbed DMNI-P rotor. When manipulated by voltage pulses, the rotational processes are predominantly governed by inelastic tunneling effects. Conversely, at increased temperatures, the rotation adopts a stochastic character. At each electron transfer event during tunneling, the quantum mixing of ground and excited electronic states brings part of the thermal energy in the excited electronic states of the rotor.

O 103.5 Fri 11:45 HE 101
Tuning the planarity of a thianthrene-based molecule on Au(111) — KWAN HO AU-YEUNG¹, SUCHETANA SARKAR¹, SAT-TWICK HALDAR², ●PRANJIT DAS¹, DMITRY A. RYNDYK^{3,4}, ANDREAS SCHNEEMANN², and FRANCESCA MORESCO¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — ²Inorganic Chemistry I, TU Dresden, 01069 Dresden, Germany — ³Institute for Materials Science, TU Dresden, 01062 Dresden, Germany — ⁴Theoretical Chemistry, TU Dresden, 01062 Dresden, Germany

We conducted a comprehensive study on the adsorption geometries of a non-planar aromatic thianthrene-based molecule on the Au(111) surface by scanning tunneling microscopy. The molecules demonstrate two self-assembled structures depending on the orientation of the C-S-C bonds: close-packed islands where they are non-planar and quasi one-dimensional chains where they are planar. Using the STM tip to isolate a molecule from the island, it is observed that the non-planar molecules transform into the planar configuration.

O 103.6 Fri 12:00 HE 101
Flexible Superlubricity Unveiled in Sidewinding Motion of Individual Polymeric Chain — ●J.G. VILHENA^{1,2}, RÉMY PAWLAK², THILO GLATZEL², GIACOMO PRAMPOLINI³, and ERNST MEYER² — ¹University of Basel, Switzerland — ²Universidad Autónoma de Madrid, Spain — ³Consiglio Nazionale delle Ricerche (ICCOM-CNR), Italy

A combination of low temperature atomic force microscopy and molecular dynamic simulations is used to demonstrate that soft designer molecules realize a sidewinding motion when dragged over a gold surface. Exploiting their longitudinal flexibility, pyrenylene chains are indeed able to lower diffusion energy barriers via on-surface directional locking and molecular strain. The resulting ultralow friction reaches values on the order of tens of pN reported so far only for rigid chains sliding on an incommensurate surface. Therefore, we demonstrate how molecular flexibility can be harnessed to realize complex nanomotion while retaining a superlubric character. This is in contrast with the paradigm guiding the design of most superlubric nanocontacts (mismatched rigid contacting surfaces).

O 103.7 Fri 12:15 HE 101
Distance-Dependence of Orbital Density Mapping Using a CO-Functionalized STM Tip — ●FABIAN PASCHKE, LEONARD-ALEXANDER LIESKE, FLORIAN ALBRECHT, and LEO GROSS — IBM Research Europe - Zurich, 8803 Rueschlikon, Switzerland

Knowledge over the tip apex in scanning probe techniques is indispensable to reliably identify the structure and electronic properties of surfaces and adsorbed molecules [1]. In particular, CO-terminated tips are widely used to achieve atomic resolution in atomic force microscopy [2]. In scanning tunneling microscopy (STM) the defined states of a CO tip apex enable high-resolution mapping of ionic resonances, and

resulting orbital density images reflect a mix of *s*- and *p*-wave symmetries of the CO tip states [3-5].

In this work we study the appearance of frontier molecular orbitals of pentacene on a bilayer of NaCl grown on Cu(111) as a function of the tip-sample distance. STM constant-height imaging reveals a transition from *p*- to *s*-wave dominated tunneling. The findings provide an additional control knob to identify molecular electronic and spin states, which often requires STM imaging of orbital densities and careful assignment to calculated molecular orbitals [6].

[1] P. Hapala et al., Phys. Rev. B 90, 085421 (2014). [2] L. Gross et al., Science 325, 1110 (2009). [3] L. Gross et al., Phys. Rev. Lett. 107, 086101 (2011). [4] N. Pavlicek et al., Phys. Rev. Lett. 110, 136101 (2013). [5] A. Gustafsson et al., Phys. Rev. B 93, 115434 (2016). [6] S. Mishra et al., ACS Nano 16, 3264 (2022).

O 103.8 Fri 12:30 HE 101

Visualizing hydrated protons and their interconversion in monolayer water on metal surfaces — •YE TIAN¹, JIANI HONG¹, DUANYUN CAO¹, SIFAN YOU¹, JING GUO², JI CHEN¹, EN-GE WANG¹, and YING JIANG¹ — ¹International Center for Quantum Materials, Peking University, 100871 China — ²College of Chemistry, Beijing Normal University, 100875 China

Hydrated protons are ubiquitous in solutions and involved in a variety of physical, chemical, biological, and energy-related processes. However, imaging and identifying the configuration of Zundel and Eigen cations and hydrated protons within the H bonding network of water remain a great challenge because of the high similarity between the hydronium (H₃O⁺) and the water molecule (H₂O). Recently, we performed the coadsorption of deuterium (D) atoms and D₂O molecules on different metal substrates (Au, Cu, Pt, Ru), where the ionized D⁺ and D₂O molecules can self-assemble into a two-dimensional (2D) hydronium-water overlayer. We have substantially improved the resolution and sensitivity of the qPlus-based atomic force microscopy such that the configuration of Zundel and Eigen cations solvated in the 2D

water network could be directly visualized with an atomic-level resolution. Furthermore, we conducted the tip manipulation experiments to explore the dynamics of hydronium ions at the interface and found a new proton transfer pathway, accompanied with a simultaneous proton transfer from the water layer to the substrate, which is beyond the previously known elementary steps of hydrogen evolution reaction (HER).

O 103.9 Fri 12:45 HE 101

Exploring in-plane interactions beside an adsorbed molecule with lateral force microscopy — SHINJAE NAM¹, ELISABETH RIEGEL¹, LUKAS HÖRMANN^{2,3}, OLIVER T. HOFMANN², OLIVER GRETZ¹, •ALFRED J. WEYMOUTH¹, and FRANZ J. GIESSIBL¹ — ¹Universität Regensburg, Deutschland — ²TU Graz, Österreich — ³University of Warwick, UK

Atomic force microscopy (AFM) with a CO-tip can directly image the internal structure of a planar molecule. However, H-atoms usually cannot be directly observed due to their small size. At the same time, H-atoms are highly important, since they can direct on-surface chemical reactions. Measuring in-plane interactions at the sides of PTCDA molecules with lateral force microscopy allowed us to directly identify hydrogen atoms via their repulsive signature. Additional features in the force data could not be explained by H-bonding of the CO tip with the PTCDA sides. Instead, they are caused by electrostatic interaction of the large dipole of the metal apex. DFT calculations allowed us to estimate the strength of the dipole at the metal tip apex. To confirm that this dipole generally affects measurements on weakly-polarized systems, we investigated the a single CO molecule. We determined the radially-symmetric atomic interaction to be valid over a large solid angle of 5.4 sr, corresponding to 82°. Therefore in both the PTCDA and CO systems, the underlying interaction preventing direct observations of H-bonding and causing a collapse of the radially-symmetric model is the dipole at the metal apex, which plays a significant role when approaching closer than standard imaging heights.