O 31: Focus Session Molecular Nanostructures on Surfaces: On-Surface Synthesis and Single-Molecule Manipulation II

This focus session aims to discuss recent advances in the on-surface synthesis, manipulation, characterization, and understanding of complex molecular architectures on surfaces. The interest in surface-confined molecular nanostructures emerges from their prospective applications in nanoscale (opto-) electronics, spintronics, solar cells, energy storage devices, and other fields. The bottom-up fabrication of surface-supported nanostructures can be based on molecular self-assembly utilizing non-covalent intermolecular interactions, covalent on-surface synthesis, or the direct manipulation of molecules. Molecular self-assembly usually leads to highly ordered nanostructures, controlled by non-covalent interactions, adsorbate-substrate interactions, as well as thermodynamic and kinetic factors. On-surface synthesis by covalent coupling of reactive precursors adsorbed on metallic, semiconducting, or even insulating surfaces has emerged as a powerful method that has opened new possibilities in exploring new routes towards the synthesis of complex low-dimensional nanostructures with unprecedented material properties, often via novel chemical reactions not available in conventional organic chemistry. Finally, the direct manipulation of molecules with the tip of a scanning probe microscope allows for unprecedented chemical transformations or structural modifications, as envisioned by the pioneers of nanotechnology. This focus session is intended to provide a platform for addressing current trends in these closely linked fields from various perspectives in experiment and theory.

Organized by
Sabine Wenzel (University of Marburg) and Christian Wagner (Forschungszentrum Jülich)

Time: Tuesday 10:30–13:00 Location: H24

O 31.1 Tue 10:30 H24

AMAN-SPM: Autonomous Molecular and Atomic Nanofabrication via SPM — •Bernhard Ramsauer[1], Qigang Zhong[2], Bettina Könighofer[3], and Oliver T. Hofmann[1] — [1]Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Graz, 8010, Austria — [2]Institute of Functional Nano & Soft Materials, Soochow University, Suzhou, 215006, China — [3]Institute of Applied Information Processing and Communications, Graz University of Technology, Graz, 8010, Austria

The precise manipulation of individual molecules and atoms using scanning probe microscopy (SPM) offers transformative possibilities for nanofabrication. Yet the inherently stochastic nature at the nanoscale and the labour-intensive process of building nanostructures contains significant challenges. In this contribution, we introduce AMAN-SPM, a tool that integrates reinforcement learning and automation to revolutionize the on-surface synthesis process.

AMAN-SPM employs dedicated reinforcement learning agents to optimize the manipulation parameters, which allows for precise positioning, reorientation, and the controlled breaking and formation of molecular bonds. Coupled with machine vision and path-planning algorithms, this system autonomously constructs nanostructures, eliminating the need for human intervention.

Beyond fabrication, AMAN-SPM enhances real-time data acquisition and analysis, providing detailed physical insights into molecular interactions. This establishes a foundation for scalable nanostructures with tailored properties.

O 31.2 Tue 10:45 H24

Sliding friction over covalent bonds increases with bond order — Shinjae Nam[1], Lukas Hörmann[2,3], Oliver Gretz[1], Oliver T. Hofmann[2], Franz J. Giessibl[1], and •Alfred J. Weymouth[1] — [1]Universität Regensburg, Regensburg, Deutschland — [2]TU Graz, Graz, Österreich — [3]The University of Warwick, Warwick, U.K.

Friction is governed by atomic-scale interactions, yet we lack a complete understanding of its working at this length scale. To address this, we reduce one sliding surface to the limit of a single atom and measure sliding friction with lateral force microscopy over single bonds. We examine islands of PTCDA on Cu(111), which present a rich variety of covalent and hydrogen bonds. There is a large variety in the maximum energy dissipation over different covalent bonds. The maximum energy dissipation over hydrogen bonds has similar values, although energy dissipation over hydrogen bonds is observed at lower heights than over covalent bonds. With DFT-based simulations and a machine-learning model, we determine that larger bond order is correlated to higher sliding friction.

Invited Talk O 31.3 Tue 11:00 H24

Single molecule machines on surface — •Francesca Moresco — TU Dresden. Germany

Scanning tunneling microscopy is a unique experimental technique to control the motion of a single molecule, testing the boundary between classical and quantum movement and making thermodynamics at the scale of a single molecule accessible to experimental investigation. Under the tip of a scanning tunneling microscope, inelastic tunneling electrons or local electric fields can produce controlled rotations or translations of a single adsorbed molecule, while thermal excitation can modify the energy barrier for motion. In this talk, we will discuss the controlled rotation and translation of asymmetric and chiral model structures adsorbed on the Au(111) surface.

O 31.4 Tue 11:30 H24

How to measure cones of reaction for single-molecule collisions — •Matthew J. Timm[1], Stefan Hecht[2], and Leonhard Grill[1] — [1]Institute of Chemistry, University of Graz, Austria — [2]Department of Chemistry & IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Collisions between reagents are necessary for bond formation, and hence fundamental to reaction. The collision outcome depends on the collision energy, which must be enough to overcome the reaction barrier, and on the collision geometry, which modifies the height of this barrier. The collision geometry is defined by the relative orientation of reagents at the point of collision and on the miss-distance between their centers of mass (termed the impact parameter). Selection of impact parameter has been demonstrated for on-surface reactions with a 'surface-molecular-beam' of CF2 'projectiles', formed by dissociation of chemisorbed CF3 molecules with a scanning tunneling microscope tip, aimed along Cu-rows of the Cu(110) surface toward chemisorbed 'targets' [1]. However, control over the relative orientation of the target has remained elusive. Here a singly-debrominated molecular species (BTFyl) is chosen as a target, as it adopts many possible adsorption alignments relative to the incoming CF2 projectile. This allows simultaneous control over both the impact parameter and reagent orientation, thus allowing an unprecedented ability to map how collision geometry contributes to collision outcome.

[1] Anggara, K.; Leung, L.; Timm, M. J.; Hu, Z.; Polanyi, J. C.; Faraday Discuss., 2019, 214, 89-103.

O 31.5 Tue 11:45 H24

Friction Anisotropy in the Sliding Motion of PMMA microsphere on Rippled PVS Surface — •Ebru Cihan[1], Hesam Khaksar[2], Kevin Lubig[3], Stephan Gräf[3], Frank A. Müller[3], and Enrico Gnecco[1,2] — [1]TU Dresden — [2]Jagiellonian University — [3]Friedrich Schiller University Jena

The sliding motion of an elastically driven polymethyl methacrylate

(PMMA) microsphere on a rippled polyvinyl siloxane (PVS) surface (laser-induced periodic surface structures LIPSS) was investigated for different values of normal load, scan velocity and temperature. The morphologies of the PMMA spheres and modified PVS surfaces were observed to be geometrically convoluted in AFM topographies recorded simultaneously with friction measurements. The spheres were rubbed both parallel and perpendicular to the LIPSS, and the resulting friction was found to be nearly constant, exhibiting a stick-slip behavior over time. This result differs from the reverse stick-slip observed in friction characterizations with similar PMMA microspheres on harder periodic surfaces, such as wedge-shaped silicon gratings [Trib. Lett. 67, 2019] and rippled stainless steel [Appl. Mater. Interfaces 15, 2023]. In both scanning cases, the friction force was found to increase linearly with increasing load, consistent with the increase in contact area expected from Persson contact theory. Furthermore, friction was observed to increase logarithmically with velocity, and to decrease with increasing temperature in accordance with Eyring's reaction rate theory. The stability of this sample system suggests its possible application as a basic unit for artificial tactile sensors.

O 31.6 Tue 12:00 H24

Electronic and phononic frictional dissipation in single-molecule dynamics at CO-decorated tips

— •Lukas Hörmann and Reinhard J. Maurer — University of Warwick, Coventry, UK

Friction causes significant energy loss in any moving mechanical device. As the miniaturisation of devices reaches the quantum limit, so do dynamical dissipation processes. Fundamentally quantum mechanical mechanisms govern friction at the nanoscale. We account for all relevant quantum mechanical effects, such as charge transfer, or van der Waals interactions, by employing density functional theory, machine learning, and non-adiabatic molecular dynamics. Using this approach, we investigate friction energy dissipation at the natural limit of singular atoms. This allows us to explore how the local electronic and geometric structure affects the dissipation of mechanical energy, where electron-phonon and phonon-phonon coupling give rise to electronic and phononic excitations. Focusing on the example of CO on various Cu surface geometries, we find that electron-phonon coupling strongly depends on the local electronic density of states, while the geometric structure significantly influences phonon-phonon coupling. Our findings quantitatively agree with experiment. Finally, we present a mechanistic interpretation of our findings that provides insights into the underlying physics of single-molecule dynamics on surfaces.

O 31.7 Tue 12:15 H24

Manipulation of a CO molecule on a copper surface with lateral force microscopy

— •Norio Okabayashi[1], Alfred. J. Weymouth[2], Shinjae Nam[2], Sophia Schweiss[2], Thomas Frederiksen[3,4], and Franz J. Giessibl[2] — [1]School of Mathematics and Physics, Kanazawa University — [2]Institute of Experimental and Applied Physics, University of Regensburg — [3]Donostia International Physics Center — [4]IKERBASQUE, Basque Foundation for Science

The manipulation of a single molecule on a surface by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) has been intensively studied because of its relation to friction research. Recently, we have studied the manipulation process for CO on a Cu(110) surface with AFM, STM and density functional theory [1][2]. We found that at the tip height for the beginning of the manipulation, CO is manipulated from the top to the neighboring top site by transiently using the bridge site, but for lower tip heights, the manipulation occurs from the top to the bridge site and then from the bridge to the neighboring top site. Here, we have extended our experimental technique by incorporating lateral force microscopy, where the tip oscillates laterally [3], to directly observe the energy dissipation during manipulation. Indeed, the observation confirms the validity of our previous claim. This result paves the way for quantitative evaluation of dynamic friction during manipulation. [1] N. Okabayashi, T. Frederiksen, A. Liebig, F. J. Giessibl, Phys. Rev. Lett. 131 (2023) 148001, [2] N. Okabayashi, T. Frederiksen, A. Liebig, F. J. Giessibl, Phys. Rev. B 108 (2023) 165401, [3] A. J. Weymouth, J. Phys.: Condens. Matter 29 (2017).

O 31.8 Tue 12:30 H24

Intermediates, reactions and products of cyclocarbons

— •Leo Gross[1], Fabian Paschke[1], Florian Albrecht[1], Yueze Gao[2], Igor Roncevic[3], and Harry L. Anderson[2] — [1]IBM Research Europe - Zurich, Rüschlikon, Switzerland — [2]Oxford University, Chemistry Research Laboratory, Oxford, UK — [3]University of Manchester, Department of Chemistry, Manchester, UK

Cyclocarbons, molecular allotropes of carbon in which all carbon atoms are two-fold coordinated, have been synthesized on surface using tip-induced chemistry [1-4], and the formation of larger cyclocarbons by dimerization of precursors was shown [4]. This presentation will focus on products, reactions and intermediates of cyclocarbons, generated by tip-induced chemistry on ultrathin NaCl layers and characterized by STM and AFM with CO-functionalized tips.

[1] K. Kaiser et al., Science, 365, 1299-1301 (2019)
[2] L. Sun et al., Nature, 623, 972-976 (2023)
[3] Y. Gao et al. Nature, 623, 977-981 (2023)
[4] F. Albrecht et al. Science, 384, 677-682 (2024)

O 31.9 Tue 12:45 H24

Temperature Induced Ring-Opening Polymerization Reaction for the Synthesis of Carbon Nanoribbons: Strain Influence on the On-surface Synthesis Using [6], [8]-, and [10]Cycloparaphenylenes

— •Miguel Wiche[1], Qigang Zhong[2], Daniel Kohrs[1], Qitang Fan[3], J. Michael Gottfried[4], Daniel Ebeling[1], Hermann A. Wegner[1], and André Schirmeisen[1] — [1]Justus Liebig University Giessen, Germany — [2]Soochow University, Suzhou, China — [3]University of Science and Technology of China, Hefei, China — [4]Philipps University Marburg, Germany

As the on-surface synthesis is an emerging reseach field, there is a lack of general understanding of reaction mechanisms, compared to conventional organic synthesis. Therefore, comprehensive research studies are required to figure out basic principles in the on-surface reaction mechanisms of organic molecules. In this work we investigate the strain influence of a set of Cycloparaphenylenes (CPP) in the temperature induced on-surface synthesis of biphenylene and graphene nanoribbons, using a strain induced ring opening polymerization (ROP) reaction. The decisive step of the polymerization, the ring opening, is found to strongly depend on the ring size and strain of the CPP molecules. Our work suggests that using smaller, highly strained rings, instead of rings with increasing number of phenyl units facilitates the ROP and nanoribbon formation.