

O 63: Focus Session: Functional Molecules at Surfaces III

Time: Wednesday 10:30–13:45

Location: TRE Ma

O 63.1 Wed 10:30 TRE Ma

Molecular Nanotribology: Nanomanipulation & Dynamics of Single-Molecules at Surfaces. — ●J.G. VILHENA¹, REMY PAWLAK¹, PHILIPP D'ASTOLFO¹, SHI-XIA LIU², SILVIO DECURTINS², JUSTIN A. LEMKUL³, GIACOMO PRAMPOLINI⁴, THILO GLATZEL¹, ALEXIS BARATOFF¹, RÚBEN PÉREZ⁵, and ERNST MEYER¹ — ¹University of Basel, Switzerland — ²University of Berne, Switzerland — ³Virginia Tech, USA — ⁴ICCOM-CNR, Italy — ⁵Universidad Autónoma de Madrid, Spain

Understanding the motion/dynamics of a single molecule over a surface is a problem of a paramount importance in designing advanced molecular nanostructures/assemblies. The interest is better realized by the broad spectrum of promising applications including molecular electronic devices, tribology/corrosion inhibition, and 3D nanopatterning. One possible route to achieve a higher control on molecular diffusion along predetermined pathways would be to access the single-molecule mechanics during their on-surface displacements. Twenty years after the first atomic-manipulation it became possible to record the time variations of mechanical forces as we manipulate a molecule over a surface –cryo-force-spectroscopy. In this talk I shall discuss how dedicated all atom molecular dynamics simulations (based in first-principles simulations) coupled with cryo-force-spectroscopy measurements provides a comprehensive understanding of complex on-surface dynamics of the molecules (terpyridine, pyrene chains and ssDNA) over gold surfaces and how dynamic balancing of intra-molecular mechanics and surface comensurability play out in a broad range of conditions.

Invited Talk

O 63.2 Wed 10:45 TRE Ma

The art of molecular manipulation with the scanning tunneling microscope: controlled rotations — ●NICOLAS LORENTE — Centro de Física de Materiales (CSIC-EHU) and DIPC, San Sebastian, Spain

Rotations are key to the functioning of molecular machines. Controlling how to induce and stop the rotation of a molecule about a well defined axle is a difficult task that needs to be mastered. This is an important part of the research undertaken by the EU-H2020 project MEMO (<https://www.memo-project.eu/flatCMS/>). In this talk I will rationalize the ingredients to obtain molecular rotations. Among them, dispersive forces seem to be a must for all molecular systems where rotations can be effected. I will show controlled rotations of two molecular systems. One is a supramolecule formed by aceto-byphenil molecules on Au (111) largely characterized by dispersive interactions [1-3], and the second systems is a radical 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1H-benzoimidazole (o-MeO-DMBI) that binds covalently by a single bond and the rest of the interaction is given by van der Waals forces [4]. We have used density functional theory completed with dispersive forces [3]. We have furthered the study by unraveling the interaction between tunneling electrons and molecular rotations [5].

[1] Anja Nickel et al. ACS Nano 7, 191 (2013)

[2] Vladimir Zobac et al.

[3] Roberto Robles, et al.

[4] Frank Eisenhut et al.

[5] Alexander Croy et al.

O 63.3 Wed 11:15 TRE Ma

Functional molecular arrays constructed through the manipulation of single molecules at room temperature — ●CHAO LI^{1,2}, LI WANG², and RICHARD BERNDT¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — ²Department of Physics, Nanchang University, Nanchang 330031, China

Molecular devices made via the manipulation of single molecules in scanning probe microscopes have usually been assembled at cryogenic temperatures. Only few related manipulation experiments have been demonstrated at ambient temperature, at which application of the molecular devices are more easily conceivable. Here, we present room-temperature intermolecular signal transfer and processing using SnCl₂Pc molecules on a Cu(100) surface. The in-plane orientations of molecules, which were used as information carrier, were effectively coupled through a series of controlled manipulations. The resulting arrays of coupled molecules realize different functions including logical gates, a motor, and a signal transfer circuit. The results highlight a strategy

for building functional molecular devices at room temperature.

O 63.4 Wed 11:30 TRE Ma

LT-STM investigation of transmitting rotation between molecular gears on Au(111) — ●KWAN HO AU YEUNG^{1,2}, TIM KÜHNE^{1,2}, FRANK EISENHUT^{1,2}, MICHAEL KLEINWÄCHTER³, YOHAN GIBBERT³, GIANAURELIO CUNIBERTI², CLAIRE KAMMERER³, GWÉNAËL RAPENNE³, and FRANCESCA MORESCO¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, Germany — ²Institute of Materials Science, TU Dresden, Germany — ³CEMES, Université de Toulouse, CNRS, Toulouse, France

Molecular gear is an essential and elementary component for the construction of planar single-molecule mechanical machines, in which a refined design of molecules, a smart selected surface for anchoring, and a highly controllable rotation are desired. The family of pentaphenyl-cyclopentadiene (PPCP) molecules shows not only the appearance of macroscopic gears, but also the behavior of transmitting rotation from molecule to molecule. Under the investigation of LT-STM on the Au (111) surface, step-by-step, controlled, and transmitting rotations have been examined by lateral manipulation. Further, in order to achieve concentric rotations, and hence, the anchoring properties of molecules, the pristine and radical states of the molecules after tip-induced cleaving at the cyclopentadiene core have been studied.

O 63.5 Wed 11:45 TRE Ma

The role of the dipole moment in electric field induced manipulation of molecules and nanostructures — ●TIM KÜHNE¹, KWAN HO AU YEUNG¹, FRANK EISENHUT¹, OUMAIMA AIBOUDI³, DMITRY RYNDYK², GIANAURELIO CUNIBERTI², BRIGITTE VOIT³, FRANZISKA LISSEL³, and FRANCESCA MORESCO¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, Germany — ²Institute for Materials Science, TU Dresden, Germany — ³Leibniz Institute of Polymer Research, Dresden, Germany

Among the different mechanisms that can be used to drive a molecule on a surface by STM, we used voltage pulses to investigate the movement properties of di-tert-Butyl 2-isocyanoozulen-1,3-dicarboxylate (BCA) molecules. On the Au(111) surface, we observed single molecules and dimers, as well as the formation of metal-organic complexes with gold adatoms. Even if the pure molecule has a strong dipole moment in the gas phase, only metal-organic complexes could be moved by voltage pulses. Measurements at different bias and tip height conditions revealed the electric field effect as main driving force of this motion. In this talk, we discuss the observed movement properties with respect to the molecule dipole moment and the charge distribution of molecules and molecular nanostructures.

O 63.6 Wed 12:00 TRE Ma

Mechanical transmission of rotational motion between molecular-scale gears — ●HUANG-HSIANG LIN^{1,2}, ALEXANDER CROY¹, RAFAEL GUTIÉRREZ¹, CHRISTIAN JOACHIM³, and GIANAURELIO CUNIBERTI^{1,4} — ¹Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01069 Dresden, Germany — ²Max Planck Institute for the Physics of Complex Systems, 01187 Dresden, Germany — ³GNS and MANA Satellite, CEMES-CNRS, 29 rue J. Marvig, 31055 Toulouse Cedex, France — ⁴Dresden Center for Computational Materials Science, TU Dresden, 01062 Dresden, Germany

Manipulating and coupling molecule gears is the first step towards realizing molecular-scale mechanical machines[1]. Here, we theoretically investigate the behavior of such gears using molecular dynamics simulations[2]. Specifically, for a single hexa (4-tert-butylphenyl) benzene molecule, we show that the rotational-angle dynamics corresponds to the one of a Brownian rotor. For two such coupled gears, we extract the effective interaction potential and find that it is strongly dependent on the center of mass distance. Finally, we study the collective motion of a train of gears.

[1]W.-H. Soe, S. Srivastava and C. Joachim, J. Phys. Chem. Lett., 6462 (2019)

[2]H.-H. Lin, A. Croy, R. Gutierrez, C. Joachim and G. Cuniberti, arXiv:1910.06644 (2019)

O 63.7 Wed 12:15 TRE Ma

Rotation and translation of molecular motors on a metallic surface — ●MONIKA SCHIED¹, PETER JACOBSON¹, DONGDONG LIU², JAMES M. TOUR², and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, University of Graz, Austria — ²Department of Chemistry, Rice University, USA

Artificial molecular motors that convert an external energy input into controlled motion have seen great developments in the last decades [1]. While many studies exist in solution, little is known how such functional molecules behave on a surface. Molecules on surfaces have the advantage of a fixed point of reference and confinement in two dimensions making it easier to study the directionality of their motion.

The uni-directional rotation of the motors investigated in this study is based on a combination of double bond isomerisation and helix inversion. This so-called Feringa motor has already been implemented into molecular structures to enable or enhance their lateral translation on metal surfaces [2, 3].

Here, we image and manipulate single motor molecules on metallic surfaces by low-temperature scanning tunnelling microscopy (STM). Rotational and translational movements as well as changes in appearance are observed after voltage pulses with the STM tip.

[1] W. R. Browne and B. L. Feringa, *Nat. Nanotech.* 1, 25 (2006)

[2] T. Kudernac et al., *Nature* 479, 208 (2011)

[3] A. Saywell et al., *ACS Nano* 10, 10945 (2016)

O 63.8 Wed 12:30 TRE Ma

Weakly-bound supramolecular structures: calculations for understanding experiments with the scanning tunneling microscope — ●ROBERTO ROBLES¹, VLADIMÍR ZOBAC¹, KWAN HO AU YEUNG², FRANCESCA MORESCO², DMITRY RYNDYK², CHRISTIAN JOACHIM³, and NICOLÁS LORENTE^{1,4} — ¹Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), San Sebastián, Spain — ²Center for Advancing Electronics Dresden, TU Dresden, Germany — ³Centre d'Elaboration de Matériaux et d'Études Structurales (CEMES), CNRS, Université de Toulouse, Toulouse, France — ⁴Donostia International Physics Center (DIPC), San Sebastián, Spain

4-Acetylbiphenyl is a small aromatic molecule that binds via dispersive forces (van der Waals) with a gold surface. Experiments performed in the group of Dr. Moresco in TU Dresden showed that, under certain conditions of deposition, these molecules formed a 4-molecule superstructure nicknamed the "windmill" because of its cross-shaped structure. These "windmills" are reproducible, directional and resilient to external interactions. Closer inspection of the scanning tunneling microscope images (STM) reveals that the unique seemingly H-bond should take place between a methyl group and the O atoms. This is one of the weakest H bonds if it binds at all. We undertook density functional theory calculations completed by empirical van-der-Waals corrections to study the supramolecular structure. From the simulation of STM images, total energy calculations and Gibbs free-energy estimates, we reach the conclusion that windmills are likely to involve gold adatoms to join the four acetylbiphenyl molecules together.

O 63.9 Wed 12:45 TRE Ma

Bending and twisting of C-C bonds by mechanical lifting of surface-adsorbed polymers — ●PHILIPP D'ASTOLFO¹, GUILHERME DE VILHENA¹, CARL DRECHSEL¹, XUNSHAN LIU², SILVIO DECURTINS², SHI-XIA LIU², RÉMY PAWLAK¹, and ERNST MEYER¹ — ¹Department of Physics, University of Basel, Basel, Switzerland — ²Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland

The torsion and rotation about single carbon-carbon bonds is a natural process that is ever-present in Chemistry- and Surface-Sciences. Due to their small magnitude, measurements of force-induced conformational changes between units of a long polymeric chain have proven difficult until now[1]. To shed light on these processes, we performed lifting experiments using atomic force microscopy (AFM) at 4.8K of different cyclic carbon polymers adsorbed on a gold substrate. In the pulling curves we detected alternating periods related to successive unit detachments of the poly-pyrenylene units vertically lifted from the Au(111) surface. Molecular dynamic (MD) simulations attribute those spacing variations to symmetry-broken bent and rotated conformations of the sliding physisorbed segment and steric hindrance by the just lifted monomer[2]. In a second experiment, we pulled asymmetric cyclopentaacanthrylene-polymers that revealed more complex detaching periods depending on the adsorption motif of the polymer units and the resulting steric hindrance between them.

[1] Kawai et al., *PNAS*, 2014, 11, 111, 3968-3972.

[2] Pawlak et al., *Nano Lett.*, 2019 submitted.

[3] D'Astolfo et al., manuscript in preparation.

O 63.10 Wed 13:00 TRE Ma

DFTB based computational approach to STM imaging, spectroscopy and manipulation of single molecules — SEDDIGHEH NIKIPAR^{1,2}, ●DMITRY RYNDYK¹, SIBYLLE GEMMING², FRANCESCA MORESCO³, THOMAS FRAUENHEIM⁴, and GIANAURELIO CUNIBERTI¹ — ¹IFWW, TU Dresden — ²HZDR, Dresden — ³cfaed, TU Dresden — ⁴BCCMS, University of Bremen

We present a new computational approach and open software realization for STM imaging, spectroscopy, and manipulation. The major motivation of the theoretical modeling is to understand the results of surface chemical reactions and nanoscale mechanical motion stimulated and controlled in the STM experiments on single molecules, polymers, and 2D organic materials at finite voltage bias. In our previous work, we showed that this method gives a good agreement between simulated and experimental STM images. Recently we tested it for STM analysis of polymers [1] and nanocarbons [2]. Especially, in the case of strong interactions between adsorbate (molecular motifs) and substrates, the simulated STM images support the experiment to get insight into the structural deformation of molecular motifs due to substrates. We develop our own open-source DFTB+XT package as a core of the TraNaS OpenSuite - integrated open software suite for nanoscale modeling [3], partially based on the DFTB+ [4] source code.

[1] D. Skidin, et al., *Nanoscale* 10, 17131 (2018).

[2] D. Skidin, et al., *Chem. Commun.* 55, 4731 (2019).

[3] TraNaS OpenSuite, tranas.org/opensuite, [github:tranas-open](https://github.com/tranas-open).

[4] B. Aradi, et al., *J. Phys. Chem. A* 111, 5678 (2007); dftbplus.org.

O 63.11 Wed 13:15 TRE Ma

Controlling orientation, rotation, and translation of a single molecule by STM via an internal electrical dipole — ●GRANT J SIMPSON¹, VÍCTOR GARCÍA-LÓPEZ², A DANIEL BOESE³, JAMES M TOUR², and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria — ²Departments of Chemistry and Material Science and NanoEngineering, and the Smalley-Curl Institute and NanoCarbon Centre, Rice University, Houston, TX 77005, USA — ³Department of Theoretical Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria

Controlling matter at the individual atom and molecule scale gives insight into basic physical and chemical properties which underpin the field of nanoscience. An interesting approach to controlling molecular mobility on a surface is to implement a strong dipole moment in a molecule which can then interact with the electric field of the tunnel junction. We have used a scanning tunnelling microscope (STM) running at low temperatures to induce and probe the motion of molecules adsorbed on a metal surface. Through interaction of the molecule dipole with the electric field of the tip, rotation with 100% directionality is demonstrated. By mapping the rotational behaviour, it was possible to assign a specific pivot point, which is precisely defined by the atomic composition of the molecule and the surface structure, and to visualise the internal dipole of the molecule [1]. Translation of these molecules can also be induced, revealing details about the molecular dynamics by systematic change of the experimental parameters.

[1] G. J. Simpson et al., *Nat. Commun.* 10, 4631 (2019)

O 63.12 Wed 13:30 TRE Ma

Characterizing Tip-Induced Motion and 3D Adsorption Conformations of Terphenyl Derivatives on Metal Surfaces — ●QIGANG ZHONG^{1,2}, DANIEL EBELING¹, JALMAR TSCHAKERT¹, SHIXUAN DU³, DOREEN MOLLENHAUER⁴, HERMANN A. WEGNER⁵, LIFENG CHI², and ANDRE SCHIRMEISEN¹ — ¹Institute of Applied Physics, Justus-Liebig University Giessen, Germany — ²Institute of Functional Nano & Soft Materials, Soochow University, China — ³Institute of Physics, Chinese Academy of Sciences, China — ⁴Institute of Physical Chemistry, Justus Liebig University, Germany — ⁵Institute of Organic Chemistry, Justus Liebig University, Germany

Studying adsorption conformations and motion of single molecules confined on a 2D surface is essential for understanding surface catalysis, molecular reactions, or self-assembly at the atomic level. Due to site-specific molecule-substrate interactions the adsorption conformations are often non-planar, which can lead to characteristic dynamics of the adsorbed molecules. Here, we investigate the non-stationary features of two terphenyl-based molecules (4,4'-diamino-p-terphenyl, DATP and 4-bromo-3'-iodo-p-terphenyl, BrL-TP) on Cu(111) with single-bond resolution using noncontact atomic force microscopy[1,2]. Frustrated translational or rotational movements of the molecules between two

metastable adsorption positions on Cu(111) are observed under the influence of the probe tip. Such non-stationary adsorption states can affect, e.g. the hierarchical dehalogenation of BrI-TP or the local bind-

ing affinity and the self-assembly process of DATP.

[1] Nat. Commun. 9, 3277 (2018). [2] ACS Nano 13, 324 (2019).