

O 5: Dynamics of Molecules on Surfaces

Time: Monday 10:30–12:00

Location: S053

O 5.1 Mon 10:30 S053

Electric field driven chemical reaction of single molecules by Scanning Tunneling Microscopy — ●TOMASZ MICHNOWICZ¹, BOGDANA BORCA¹, VERENA SCHENDEL¹, IVAN PENTEGOV¹, ULRIKE KRAFT¹, HAGEN KLAUK¹, PETER WAHL^{1,2}, UTA SCHLICKUM¹, and KLAUS KERN^{1,3} — ¹Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany — ²University of St Andrews, School of Physics and Astronomy, KY16 9SS St Andrews, UK — ³Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Scanning Tunneling Microscopy allows the manipulation of individual organic molecules by various kinds of stimuli, for example tunneling current, electric field or precise mechanical interaction. Here we present a study of chemical bond formation of individual organic molecules, tetraceno-thiophene (TCT), to the copper (111) surface by making use of the electric field present between tip and surface. Ramping the bias voltage, while positioning the tip apex precisely above the thiophene group, results in a change of the molecule's topographic appearance, which we attribute to the breaking of the thiophene group and a chemical bond formation to the copper surface atoms. The threshold voltage, that has to be overcome in order to trigger the reaction, depends linearly on the tip-molecule distance. This is a characteristic behaviour for electric field driven processes. In addition, we measured the single molecule's conductance of about 0.14 G₀ for molecules before reaction and 0.21 G₀ for molecules after reaction (G₀: quantum of conductance).

O 5.2 Mon 10:45 S053

Simultaneous AFM/STM study of chirality and on-surface chemistry of Dibenzo[7]helicene deposited on Ag(111) — ●OLEKSANDER STETSOVYCH¹, MARTIN SVEC¹, JAROSLAV VACEK², JANA VACEK-CHOCHOLOUSOVA², IRENA STARA², ANDREJ JANCARIK², JIRI RYBACEK², PAVEL JELINEK¹, and IVO STARY² — ¹Institute of Physics AS CR, Prague, CZ — ²Institute of Organic Chemistry and Biochemistry AS CR, Prague, CZ

High-resolution AFM images of single molecules brought completely new perspectives in investigation of chemical processes on surfaces. Here we investigated on-surface chemistry of Dibenzo[7]helicene deposited on Ag(111). Annealing above 100°C has induced a [4+2] Diels-Alder cycloaddition reaction, which has initiated complex chemical processes on the surface. We have been able to identify an intermediate step and two final products by means of simultaneous AFM/STM measurements with Xe-tip. The intermediate products form complex chiral structures (dimers, trimers and tetramers). To understand the origin of a chiral orientation, we investigated both the racemic mixture and pure (+)-(P) enantiomer of helicene molecules deposited on the Ag(111) surface. We have found that the chiral orientation of the individual molecules as well as their complexes is driven both by chirality of helicene molecules initially deposited on the surface and annealing conditions. We have demonstrated for the first time a chemical control over the final enantiofacial adsorption of non-chiral molecules on the non-chiral metal surface that has resulted in a global mirror-symmetry breaking.

O 5.3 Mon 11:00 S053

Interaction of a Self-assembled Ionic Liquid Adlayer with Graphite(0001) and Reaction with Coadsorbed Lithium — ●FLORIAN BUCHNER¹, KATRIN FORSTER-TONIGOLD¹, MARAL BOZORGHCHENANI², AXEL GROSS^{1,3}, and R. JÜRGEN BEHM^{1,2} — ¹Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany — ²Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ³Ulm University, Institute of Theoretical Chemistry, D-89069 Ulm, Germany

The ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BMP][TFSA] is a promising solvent/electrolyte for Li-ion batteries. In this model study we investigated the interaction of (sub-)monolayers of [BMP][TFSA] with a frequently used anode material as graphite(0001) under ultrahigh vacuum (UHV) conditions. Scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and dispersion corrected density functional theory (DFT-D) calculations were employed. After vapor deposition at 300 K and subsequent cool-down to 100 K the STM measurements reveal

an ordered (2D) crystalline phase. The row-like adsorption structure is determined by anions and cations which are alternatingly aligned. DFT-D calculations predict that adsorbate-substrate interactions are dispersion interactions, and adsorbate-adsorbate interactions between the ion pairs are equally composed of electrostatic and dispersion interactions. In addition, to mimic an electrolyte, Li was stepwise post-deposited. Subsequent XPS measurements reveal decomposition products of [BMP][TFSA] like LiF, Li₂S, and LiN₃.

O 5.4 Mon 11:15 S053

Direct Observation of Photo-Induced Tautomerization in Single Porphycene Molecules at a Metal Surface — ●HANNES BÖCKMANN¹, SHUYI LIU¹, JOHANNES MIELKE¹, SYLVESTER GAWINKOWSKI³, JACEK WALUK^{3,4}, LEONHARD GRILL^{1,2}, MARTIN WOLF¹, and TAKASHI KUMAGAI¹ — ¹FHI of the MPG, Berlin, Germany — ²University of Graz, Graz, Austria — ³Polish Academy of Sciences, Warsaw, Poland — ⁴Cardinal Stefan Wyszyński University, Warsaw, Poland

Molecular switches are of fundamental importance in nature, and photoexcitation is an important stimulus to selectively drive the switching process. However, the local dynamics of these molecules remain far from being completely understood at the single-molecule level. Here we report the direct observation of photo-induced tautomerization in single porphycene molecules on a Cu(111) surface using a combination of LT STM and laser excitation in the near-IR to UV regime. It is found that the thermodynamically stable trans porphycene is converted to the metastable cis form in a unidirectional fashion by photoirradiation. The wavelength dependence of the tautomerization cross section exhibits a steep onset around 2 eV that corresponds to the energy of the d-band edge of the Cu substrate, indicating a surface mediated excitation mechanism. Additionally, a giant isotope effect (about 100) is observed upon substitution with deuterium. Furthermore, we examined the influence of the local environment on the tautomerization by varying the intermolecular interactions via the molecular density and found a decrease in the cross section at high coverage.

O 5.5 Mon 11:30 S053

Vibrationally induced hydrogen-atom transfer in a single porphycene molecule on Cu(110) — ●SHUYI LIU¹, DELROY BAUGH¹, XUNHUA ZHAO¹, SYLVESTER GAWINKOWSKI², JACEK WALUK², and TAKASHI KUMAGAI¹ — ¹Fritz-Haber Institute, Berlin, Germany — ²Polish Academy of Sciences, Warsaw, Poland

In this talk we present results on the tautomerization of a single porphycene molecules on Cu(110) induced by vibrational excitation via inelastic electron tunneling using an STM. The cis-cis tautomerization was investigated by STS and STM Action Spectroscopy (STM-AS) [1]. STM-AS spectra show steep increases at certain bias voltages, and also exhibits a clear isotope effect when deuterium is substituted for the transferring H-atoms, revealing a vibrationally mediated process. These results indicate excitation of skeletal motion of porphycene plays a crucial role in the reaction. DFT calculations suggest the excited skeletal vibrational mode and N-H(D) stretching transfers energy to the reaction coordinate mode(s) via the anharmonic couplings within the molecule. We also found that the N-H stretching vibration exhibits a noticeable broadening which may be rationalized by strong the anharmonicity of the mode potential that results from the H-bond. Our approach provides a microscopic insight into the electron-vibrational coupling within a single molecule and how it can trigger a chemical reaction. [1] T.K. Prog. Surf. Sci. 90, 239 (2015).

O 5.6 Mon 11:45 S053

Force-induced tautomerization in a single molecule — ●JANINA N. LADENTHIN¹, THOMAS FREDERIKSEN^{2,3}, MATS PERSSON⁴, SYLVESTER GAWINKOWSKI⁵, JACEK WALUK⁵, and TAKASHI KUMAGAI¹ — ¹Department of Physical Chemistry, Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany. — ²Donostia International Physics Center, San Sebastián, Spain. — ³IKERBASQUE, Basque Foundation for Science, Bilbao, Spain. — ⁴Surface Science Research Centre and Department of Chemistry, University of Liverpool, UK. — ⁵Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.

Chemical reactions can be activated by heat, electric or light energy. Force is another way but the fundamental process of mechanical activa-

tion is much less studied. Force-induced bond breaking and formation are the elementary steps in mechanochemical reactions. However, it remains poorly understood at the single-molecule level. In the talk, we present the force-induced intramolecular H-atom transfer (tautomerization) in a single porphycene molecule on the Cu(110) surface at 5 K using nc-AFM. Porphycene is an intriguing model system for studies of tautomerization [1]. Force spectroscopy was employed to quantify the force needed to trigger the cis-cis tautomerization, revealing a few

hundred pN. It was also found that the tautomerization cannot be induced with a Xe-terminated tip, indicating the importance of chemical forces. Furthermore, DFT calculations elucidated the atomistic mechanism behind the force-induced tautomerization.

[1] T. Kumagai et al. PRL 111, 246101 (2013); T. Kumagai et al. Nature Chem. 6, 41 (2014); T. Kumagai, Prog. Surf. Sci. 90, 239 (2015).