

O 73: Surface dynamics: Reactions, elementary processes and phase transitions II

Time: Wednesday 16:45–18:00

Location: MA 043

O 73.1 Wed 16:45 MA 043

Near-Field Enhanced Photochemistry of Single Molecules in an STM Junction — ●HANNES BÖCKMANN¹, SYLWESTER GAWINKOWSKI², JACEK WALUK², MARKUS B. RASCHKE³, MARTIN WOLF¹, and TAKASHI KUMAGAI¹ — ¹Department of Physical Chemistry, FHI Berlin, Germany — ²Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland — ³Department of Physics, Department of Chemistry, University of Colorado, Boulder, USA

Optical near-field excitation of metallic nanostructures can be used to enhance photochemistry and promote photocatalysis. However, few studies have yet addressed near-field induced chemistry at the single-molecule level. Here we report the near-field enhanced tautomerization of porphycene on a Cu(111) surface in a scanning tunneling microscope (STM) junction. The light-induced tautomerization is mediated by photogenerated carriers in the Cu substrate. It is revealed that the reaction cross section is significantly enhanced in the presence of a Au tip compared to the far-field induced process. The strong enhancement occurs in the red and near-infrared spectral range for Au tips, whereas a W tip shows a much weaker enhancement, suggesting that excitation of the localized plasmon resonance contributes to the process. Additionally, the near-field enhanced tautomerization is examined in and out of the tunneling regime. Our results suggest that the enhancement is attributed to the increased carrier generation rate via decay of the excited near-field in the STM junction. Additionally, optically excited tunneling electrons also contribute to the process in the tunneling regime.

O 73.2 Wed 17:00 MA 043

Semiconductor surface chemistry induced by electronic excitation – tip-induced ether cleavage on Si(001) — GERSON METTE¹, ALEXA ADAMKIEWICZ¹, TAMAM BOHAMUD¹, MARCEL REUTZEL¹, ●MICHAEL DÜRR², and ULRICH HÖFER¹ — ¹Philipps-Universität, 35037 Marburg — ²Justus-Liebig-Universität Giessen, 35392 Giessen

Reactions of organic molecules on silicon typically proceed via an intermediate state and the conversion barrier between intermediate and final state determines the final products. Electronic excitation, e.g., by tunneling electrons from an STM tip, can open additional reaction channels which are not accessible by means of thermal activation.

Here we show that tip-induced cleavage of the datively bonded intermediate of THF on Si(001)[1] leads to covalently bound final configurations which are not observed for the thermally activated reaction. We find one single threshold in the dependence of the conversion rate on applied bias for all final configurations. Below the threshold, the conversion rate depends nonlinearly on the tunneling current, indicating a reaction induced via multiple excitations of vibrational modes. Above the threshold, this dependence is linear, indicating direct excitation by electron transfer into the antibonding C-O orbital of THF. In the latter case, the molecules on the excited PES are not subject to the strong restrictions which control the transition state on the ground state PES, thus leading to the observed larger variety of final products. [1] G. Mette, et al., ChemPhysChem 15, 3725 (2014).

O 73.3 Wed 17:15 MA 043

Rotation and Translation of a Single Molecular Dipole — ●GRANT J. SIMPSON¹, VÍCTOR GARCÍA-LÓPEZ², JAMES M. TOUR², and LEONHARD GRILL¹ — ¹University of Graz, Graz, Austria — ²Rice University, Texas, USA

Controlling matter on the atomic scale using the tip of a scanning tunneling microscope (STM) is now a well-established field. The *pushing* and *pulling* STM manipulations employ rather close-range interactions and can be used to position single atoms and molecules on a surface with exquisite precision. Furthermore, a number of molecular

processes such as rotation and conformational switching can be induced through inelastic electron tunneling or through interaction with the electric field in the STM junction. Gaining control over the direction of rotation and translation of single molecules is more challenging though. In the current work it is shown that an in-built permanent molecular dipole can be used to achieve a high degree of control over the motion of a single molecule. Through interaction of this dipole with the electric field of the tip, unidirectional rotation and translation is demonstrated [1]. Additionally, by mapping the behavior of this motion, it is possible to visualize the internal electric dipole in a single molecule.

[1] G. J. Simpson, V. García-López, P. Petermeier, L. Grill, and J. M. Tour, Nat. Nanotechnol. 12 (2017) 604.

O 73.4 Wed 17:30 MA 043

O adatom diffusion in a dense CO matrix on Ru(0001) with video-rate variable temperature STM — ●ANN-KATHRIN HENSS¹, PHILIPP MESSER¹, DON C. LAMB¹, ROLF SCHUSTER², and JOOST WINTTERLIN¹ — ¹Chemie Department, Ludwig-Maximilians Universität München — ²Institut für Physikalische Chemie, Karlsruher Institut für Technologie

To obtain reliable kinetic parameters of surface processes it is necessary to collect data over a wide range of temperatures. For scanning tunneling microscopes (STM) this range is usually limited by the slow imaging rates. We improved a home-built beetle-type STM by modifying the scan control unit and the data acquisition system to enable video-rate STM imaging with up to 50 images per second. The STM is also equipped with a liquid helium cryostat and heating facilities, giving access to temperatures between 50 and 500 K. The combination of temperature variability and video-rate imaging allows us to monitor surface diffusion of single atoms over a much broader temperature range than before. First experiments were performed on the diffusion of oxygen adatoms in a dense layer of CO molecules on Ru(0001). Videos of the moving oxygen atoms, obtained between -50 °C and room temperature and analyzed by particle tracking, show a surprisingly complex dynamic behavior. The data provide microscopic insight into atomic transport processes on "crowded surfaces", the typical situation in heterogeneous catalytic reactions.

O 73.5 Wed 17:45 MA 043

Phase Diagrams of Titanium Clusters in a Reactive Oxygen Atmosphere: a Replica-Exchange Grand-Canonical *ab initio* Molecular-Dynamics study — ●YUANYUAN ZHOU, MATTHIAS SCHEFFLER, and LUCA M. GHIRINGHELLI — Fritz-Haber-Institut der Max-Planck-Gesellschaft

TiO₂ has widespread applications such as photocatalysis, photovoltaics, and oxide electronics. To help elucidate the microscopic details of the catalytic processes, experimental and theoretical works have been performed on titanium-oxide clusters in the past decade (e.g., S. Bhattacharya *et al.*, PRB **91**, 241115 (2015)). Here, the replica-exchange (RE) grand-canonical (GC) molecular-dynamics method, recently developed by us, is used to explore Ti_{4/8} cluster in contact with a reacting atmosphere of O₂ molecules. The method enables the unbiased, efficient calculation of complete $p - T$ phase diagrams. The system is modeled via DFT, at the PBE level. The GC ensemble is adopted to describe clusters in a reactive atmosphere. RE allows for an efficient sampling by shuttling configurations from regions of low T or high chemical potential (μ) to regions of high T or low μ . This massively parallel method requires no prior knowledge of the phase diagram and takes only the potential energy function together with the desired μ and T ranges as inputs. We identify the thermodynamically most stable phases of Ti_{4/8}O_x at realistic T/p_{O_2} conditions, as a first step towards an understanding of the complex titanium-oxide surfaces at the atomistic level.