

O 3: Metal Substrates: Adsorption and Reaction of Small Molecules I

Time: Monday 10:30–12:15

Location: CHE 91

O 3.1 Mon 10:30 CHE 91

A Nanocar and rotor in a molecule — ●KWAN HO AU-YEUNG¹, SUCHETANA SARKAR¹, TIM KÜHNE¹, OUMAIMA AIBOUDI², DMITRY A. RYNDYK^{3,4}, ROBERTO ROBLES^{5,6}, NICOLAS LORENTE^{5,6}, FRANZISKA LISSEL², CHRISTIAN JOACHIM⁷, and FRANCESCA MORESCO¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — ²Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany, and Faculty of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden, Germany — ³Institute for Materials Science, TU Dresden, 01062 Dresden, Germany — ⁴Theoretical Chemistry, TU Dresden, 01062 Dresden, Germany — ⁵Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 Donostia-San Sebastián, Spain — ⁶Donostia international physics center, 20018 Donostia-San Sebastian, Spain — ⁷GNS & MANA Satellite, CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse, France

Depending on its adsorption conformation on the Au(111) surface, a zwitterionic single molecule machine works in two different ways under STM voltage pulses: It is a unidirectional single molecule-rotor while anchoring on the surface; It is a fast-drivable molecule-vehicle (nanocar) while physisorbed. By tuning the molecular coverage, the conformation of the molecule can be selected as a rotor or a nanocar. The movement triggered by inelastic tunneling excitation is investigated under the same experimental conditions for the unidirectional rotation of the rotor and the directed movement of the nanocar.

O 3.2 Mon 10:45 CHE 91

Controlling the Switching of Azobenzene Derivatives on Graphite-Air Interface — ●THIRUVANCHERIL G. GOPAKUMAR¹, KHUSHBOO YADAV¹, HARIOM BIRLA¹, SHOWKAT H. MIR², THOMAS HALBRITTER³, ALEXANDER HECKEL³, and JAYANT K. SINGH² — ¹Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India — ²Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India — ³Institute for Organic Chemistry and Chemical Biology, Goethe-University Frankfurt, Max-von-Laue-Str. 9, 60438 Frankfurt, Germany

The trans isomer of azobenzene (AB) and its derivatives is the most abundant under equilibrium-thermodynamical conditions and is known to switch between its trans and cis states when triggered by light and electrons/holes on graphite.[1] In this work, we show that AB derivatives are switching between two cis states (cis, cis') when electrons/holes induced switching is performed on a cis dominant non-equilibrium initial condition at HOPG-air interface. The switching efficiency in the cis adlayer is several folds higher than that in the trans adlayer. This is related to the low switching barrier for cis-cis' switching compared to that of trans-cis switching as revealed by density functional theory (DFT) calculations.[2]

1) K. Yadav, S. Mahapatra, T. Halbritter, A. Heckel, T. G. Gopakumar, *J. Phys. Chem. Lett.*, 2018, 9, 6326-6333. 2) K. Yadav, H. Birla, S. H. Mir, T. Halbritter, A. Heckel, J. K. Singh, T. G. Gopakumar, *Appl. Surf. Sci.* 2023, 612, 155747

O 3.3 Mon 11:00 CHE 91

STM-induced ring closure of vinylheptafulvene molecular dipole switches on Au(111) — ●SUCHETANA SARKAR¹, KWAN HO AU-YEUNG¹, TIM KUEHNE¹, OUMAIMA AIBOUDI², DMITRY A. RYNDYK^{3,4}, THOMAS HEINE⁴, FRANZISKA LISSEL^{2,4}, and FRANCESCA MORESCO¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — ²Leibniz Institute of Polymer Research, 01069 Dresden, Germany — ³Institute for Materials Science, TU Dresden, 01062 Dresden, Germany — ⁴Faculty of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden Germany

Dihydroazulene/vinylheptafulvene pairs are known as molecular dipole switches that undergo a ringopening/- closure reaction by UV irradiation or thermal excitation. We show that the ring-closure reaction of a single vinylheptafulvene adsorbed on the Au(111) surface can be induced by voltage pulses from the tip of a scanning tunneling microscope. This cyclization is accompanied by the elimination of HCN, as confirmed by simulations. Post the ring closure reaction, lateral movement induced via voltage pulses from the STM tip shows a different response. This behaviour is discussed by comparing the dipole

moment and the charge distribution of the open and closed forms on the surface.

O 3.4 Mon 11:15 CHE 91

Surface segregation of PdAu(111) in reactive gas environments from ab initio thermodynamics — ●OLGA V VINOGRADOVA, VANESSA J BUKAS, and KARSTEN REUTER — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Catalytic properties of alloys are largely determined by the specific chemical composition at the surface. Differences in composition between surface and bulk regions depend intricately on both the parent metals and surrounding gas-phase environment. While a non-reactive environment is expected to induce surface segregation of the more noble alloy component, a reactive environment such as oxygen often favors the more active component at the surface. Using ab initio thermodynamics, here we explore the structure and composition of the PdAu(111) alloy surface in oxygen, nitrogen, and carbon containing environments. An exhaustive, yet systematic, search of the available phase-space shows the segregation profile in an oxygen atmosphere to follow the anticipated picture described above. Unlike oxygen, however, carbon at low coverages burrows deeper into the alloy substrate without first the adsorbate-induced segregation of Pd at the surface. A nitrogen environment induces an intermediate behavior to oxygen and carbon where the nitrogen atoms first favor either surface or subsurface sites depending on the detailed metallic composition profile.

O 3.5 Mon 11:30 CHE 91

Atomistic investigations on the effect of vibrational excitation on O₂ adsorption on Pt surfaces — ●SIMON HOMANN, BJÖRN KIRCHHOFF, and TMO JACOB — Institute of Electrochemistry, Ulm University, D-89081 Ulm

Platinum is considered an excellent model system for surface studies and is also an important heterogeneous catalyst. Combined with non-thermal plasmas, many studies found an improvement in turn-over frequency compared to thermal catalysis with the non-excited gas phase. One possible contender towards an explanation of this is the interaction of the vibrationally excited molecules in the plasma with the metal surface. As a first proof of concept, we present in this study Born-Oppenheimer molecular dynamics simulations of vibrationally excited Oxygen on low-indexed Platinum surfaces using a reactive force field (ReaxFF). The vibrational density of states simulated this way is in agreement with typical results obtained, *e.g.* from kinetic modeling of the plasma afterglow. The higher vibrational energy leads to an altered adsorption behavior in terms of dissociation and preferred adsorption positions, as well as changes in surface morphology.

O 3.6 Mon 11:45 CHE 91

Fluctuating nature of CO adlayer structures on metal surfaces — ●SUNG SAKONG and AXEL GROSS — Ulm University, Ulm, Germany

The dynamics of atomic and molecular adlayers on surfaces is an critical issue in heterogeneous catalysis and electrocatalysis as it determines how reaction partners can meet on the catalyst surfaces. The adlayer formation influences the performance of catalysts and the structure of the electric double layer. Recently, video scanning tunneling microscope (V-STM) experiments have demonstrated the influence of the CO adlayer dynamics on oxygen diffusion on Ru(0001) [1,2] and the dynamical nature of a CO monolayer on Pt(111) [3]. We will present microscopic pictures of CO adlayer fluctuations on Ru(0001) and Pt(111) based on density functional theory (DFT) calculations and kinetic Monte Carlo (kMC) simulations. The calculations demonstrate how local disorder can lower the adsorption energy of a CO adlayer. We will particularly demonstrate the importance of the so-called door opening mechanism for oxygen diffusion on a CO-covered surface [1,2] and the dynamical nature of CO adlayers [3] by comparing DFT-based simulations with V-STM experiments.

[1] A. Henß *et al.*, *Science* **363**, 715 (2019).

[2] S. Sakong *et al.*, *J. Phys. Chem. C* **124**, 15216 (2020).

[3] J. Wei *et al.*, *Angew. Chemie. Int. Ed.* **59**, 6182 (2020).

O 3.7 Mon 12:00 CHE 91

Self-assembly and dehydrogenation reactions of borazine on

Ag(111) — •TOBIAS WEISS¹, ALEKSANDR BAKLANOV¹, GEORG S. MICHELITSCH², MARTIN SCHWARZ¹, MANUELA GARNICA¹, KARSTEN REUTER³, and WILLI AUWÄRTER¹ — ¹Physics Department E20, Technical University of Munich, Germany — ²Laboratoire des Solides Irradiés, École Polytechnique, France — ³Chair of Theoretical Chemistry, Technical University of Munich, Germany

Borazine ($B_3N_3H_6$), is a prominent precursor for the growth of hexagonal boron nitride (hBN) on metal supports [1]. With monolayer hBN playing an important role in the field of 2D-materials, borazine adsorption, assembly and decomposition on surfaces is a topic of interest. Space-averaging studies revealed flat or tilted adsorption geometries on different substrates depending on their catalytic activity [2,3].

Here, we provide unprecedented real-space insight into adsorbed borazine molecules and their on-surface chemistry in ultra-high vacuum. This scanning tunneling microscopy investigation of the self-assembly of borazine on Ag(111) reveals a highly regular, porous hexagonal phase or a dense packed structure, depending on exposure. Furthermore, tip-induced dehydrogenation reactions of single molecules result in a tilted adsorption geometry. Complementary density functional theory calculations were performed to comprehensively characterize potential reaction products and adsorption configurations.

[1] W. Auwärter, Surf. Sci. Rep., 2019, 74, 1-95

[2] R. Simonson, Surf. Sci., 1991, 254, 29-44

[3] L. Haug, Phys. Chem. Chem. Phys., 2020, 22, 11704