

O 38: Metal substrates: Adsorption of atoms and inorganic molecules

Time: Tuesday 14:00–15:45

Location: MA 144

O 38.1 Tue 14:00 MA 144

Controlling the competition between Kondo effect and spin-orbit interaction in a single molecule by atomic manipulation — ●EMI MINAMITANI¹, RYOICHI HIRAOKA², RYUICHI ARAFUNE³, NORIYUKI TSUKAHARA², SATOSHI WATANABE¹, MAKI KAWAI², and NORIAKI TAKAGI² — ¹Department of Materials Engineering, The University of Tokyo — ²Department of Advanced Materials Science, The University of Tokyo — ³WPI-MANA, National Institute for Materials Science,

Magnetic molecules on metal surfaces are good playground to investigate and control the magnetic properties of nanostructures. In these systems, the Kondo effect and spin-orbit interaction (SOI) are two major components to determine the magnetism. When the molecule has an integer spin, these components compete each other. If the Kondo effect dominates over the SOI, the Kondo singlet state appears. On the other hand, the zero-field splitting spin state appears in the SOI dominant case. Here we report the control of the transition between these two states in iron phthalocyanine (FePc) on Au(111) by molecular manipulation with scanning tunneling microscope (STM) and elucidate the mechanism by the density functional theory (DFT) and numerical renormalization group (NRG)[1].

[1] R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai, N. Takagi, Nat. Commun 8 16012 (2017).

O 38.2 Tue 14:15 MA 144

First-Principles Compressed-Sensing Study of Oxygen Adsorption at Transition-Metal Surfaces — SOMAYEH FARAJI^{1,2}, ●SERGEY V. LEVCHENKO¹, RUNHAI OUYANG¹, LUCA M. GHIRINGHELLI¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin 14195, Germany — ²Faradayweg 4-6

Understanding the interaction of transition metals (TMs) and alloys with reactive species such as oxygen is important for the design of new catalysts [1]. We use density-functional theory calculations combined with compressed sensing to identify descriptors for adsorption energy of O atom at flat and stepped TM surfaces. The RPBE functional [2] is chosen based on its performance in comparison to available experimental results. Using sparse independence screening with the l_0 sparsifying operator (SISSO) [3], we identify physically interpretable descriptors that predict O adsorption energies based solely on properties of involved species, bulk, and clean surfaces. The maximum absolute error of the prediction is within 0.25 eV. The identified descriptor is built from the following contributions describing the strength of the surface-O interaction: i) surface energy, ii) number of valence electrons in the metal atom, iii) d -band center, iv) difference between the work function and O ionization energy, and v) difference between the d -band center and the s -level of the metal atom.

[1] A. Vojvodic and J. K. Nørskov, National Sci. Rev. **2**, 140 (2015)

[2] B. Hammer *et al.*, Phys. Rev. B **59**, 7413 (1999)

[3] R. Ouyang *et al.*, arXiv:1710.03319 (2017)

O 38.3 Tue 14:30 MA 144

Interaction process of a CO molecule on a copper surface with a metallic tip of a microscope — ●NORIO OKABAYASHI^{1,2}, ANGELO PERONIO², DANIEL MEUER², SONIA MATENCIO², FERDINAND HUBER², MAGNUS PAULSSON³, TOYOKO ARAI¹, and FRANZ J. GIESSIBL² — ¹Kanazawa University, Kanazawa, Japan — ²University of Regensburg, Regensburg, Germany — ³Linnaeus University, Kalmar, Sweden

In order to investigate the vibrational state of a CO molecule put in the force field by a metallic tip, we have developed a method combining atomic force microscopy and inelastic electron tunneling spectroscopy (IETS). In previous, we reported that considering the bond elongation is crucial to reproduce the vibrational energy shift in the force field as well as the linear superposition of the perturbed force. We also reported that the distance dependent IETS intensity can be interpreted by combining the concept of the bond elongation with our previous finding on the IETS intensity [1] that the intensity strongly depends on the fraction of the current passing through the molecule. Here we have improved our method by stabilizing the tip oscillation during the IETS measurements and extended the measurements to the smaller tip molecule distance for the system of a CO molecule on a Cu(111) surface. We demonstrate that the improved data provides the inter-

pretation consistent with our previous conclusion along with the new insight into the tip molecule interaction process. [1] N. Okabayashi, A. Gustafsson, A. Peronio, M. Paulsson, T. Arai, and F. J. Giessibl, Phys. Rev. B **93**, 165415 (2016).

O 38.4 Tue 14:45 MA 144

Control of rotational oscillation by protonation in single triazatruxene molecules — ●ANJA BAUER¹, MARKUS MAIER², WERNER SCHOSSER¹, PHILIPP ERLER¹, FLORIAN SINGER¹, FABIAN PAULY¹, YURIY DEDKOV^{3,1}, RAINER WINTER², and MIKHAIL FONIN¹ — ¹Department of Physics, University Konstanz, D-78457 Konstanz — ²Department of Chemistry, University Konstanz, D-78457 Konstanz — ³Department of Physics, Shanghai University, 200444 Shanghai, China

The opportunity of tuning the electric and magnetic properties [1] as well as the control of molecular motions on surfaces [2], [3], [4] is of great interest since it lays a foundation for the fabrication of molecule-based functional devices. Here we investigate the behavior of single triazatruxene (TAT) molecules on Ag(111) deposited by electrospray ionization method. Low temperature STM measurements reveal three different types of molecular appearance on Ag(111) which we assign to the non-, single- and double-protonated TAT. In non-protonated molecules tunneling current is shown to excite rotational oscillations between two stable adsorption configurations. Protonation, however, leads to an efficient suppression of the rotational oscillation and of the lateral mobility of the molecules. We further show the possibility to switch the oscillation on and off by detaching or attaching hydrogen to the nitrogen atoms of TAT.

[1] B. Borca *et al.*, ACS Nano **9**, 12506 (2015), [2] I. Swart *et al.*, Nano Letters **12**, 1070 (2012), [3] A. Krönlein *et al.*, J. Phys. Chem. **120**, 13843 (2016), [4] H.W. Kim *et al.*, Phys. Rev. Lett. **106**, 146101 (2011)

O 38.5 Tue 15:00 MA 144

Oxidation of Transition-Metal Surfaces: A Cluster-Expansion Study — ●ZHONG-KANG HAN¹, RAY MIYAZAKI³, SOMAYEH FARAJINAFCHI¹, SANTIAGO RIGAMONI², MARIA TROPPEZ², JUN-YA HASEGAWA³, SERGEY V. LEVCHENKO¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin 14195, Germany — ²Humboldt-Universität zu Berlin, Berlin 12489, Germany — ³Hokkaido University, Sapporo 001-0021, Japan

Oxidation of metal surfaces plays a fundamental role when functional devices are in contact with an oxidizing environment. The thermodynamics of oxidation and its dependence on the metal type and surface cut are still not fully understood. We study the adsorption of atomic oxygen at Au, Pt, Ni (110), and Rh (100) surfaces, using a cluster-expansion model, parametrized with RPBE calculations. We find that atomic oxygen randomly adsorbs on the short-bridge site of Au(110) or Pt(110) at low coverages (<25%), forming a $c(2 \times 2)$ pattern as the coverage increases. For coverage >25%, this pattern is destabilized, and a new pattern $c(2 \times \sqrt{2})$ will form with top and hollow sites occupied. Interestingly, although O at short-bridge sites is most stable at low coverages, no short-bridge sites are occupied by oxygen at the coverage of 50%. On the contrary, Ni (110) passes through a variety of ordered adsorbed O phases as the coverage is increased, with a mixed occupation of the short-bridge and other sites. Increasing coverage above 75% for Pt (110) or Ni(110), and above 50% for Au(110) or Rh (100) leads to destabilization of dissociative versus molecular adsorption.

O 38.6 Tue 15:15 MA 144

Effect of polymer coating on H₂ adsorption/desorption on Palladium nanoparticles — ●LUCY CUSINATO and ANDERS HELLMAN — Department of Physics, Chalmers University of Technology, Göteborg, Sweden

Palladium-based materials have been known for their capacity to form hydride phases, making them good candidates for hydrogen storage applications. These applications rely on two fundamental features of metallic palladium: the ability to dissolve hydrogen to form stable hydride and the possibility to easily release the stored hydrogen. Efforts have been made to improve the storage capacity and kinetics, either by modification of the metallic core or by varying the environment of the palladium material. Experimentally, the presence of metal-organic

frameworks or polymers has been shown to improve the kinetics of hydrogen storage. Here, we study this phenomenon from a theoretical (using DFT) point of view in close collaboration with experimentalists. The behavior of palladium and palladium hydride nanoparticles towards H₂ adsorption and desorption, with and without polymer (PTFE, PVDF and PMMA) coating, is studied. A particular focus is set on how to model this kind of nanoparticle/polymers systems for the case of bare and hydride palladium. Stability of palladium hydride nanoparticles is studied, as well as different types of interaction at the Pd-polymer interface. These results are then used to shed light on how the presence of polymers, and the existence of a palladium/polymer interface, can affect the kinetics and thermodynamics of the system in order to facilitate H₂ adsorption and desorption processes.

O 38.7 Tue 15:30 MA 144

Ester formation without any catalyst at the liquid-solid interface — •NGUYEN THI NGOC HA¹, GOPAKUMAR T. G.², YEN N. D. C.¹, CAROLA MENDE³, LARS SMYKALLA¹, ROY BUSCHBECK³, TOBIAS RÜFFER³, HEINRICH LANG³, MAIK SCHLESINGER⁴, MICHAEL MEHRING⁴, and MICHAEL HIETSCHOLD¹ — ¹Solid Surfaces Analysis

Group, Institute of Physics, Technische Universität Chemnitz, Chemnitz, Germany — ²Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India — ³Inorganic Chemistry, Institute of Chemistry, Technische Universität Chemnitz, Chemnitz, Germany, — ⁴Coordination Chemistry, Institute of Chemistry, Technische Universität Chemnitz, Chemnitz, Germany

A chemical reaction (esterification) within a molecular monolayer induced by increasing the molecular packing density of this layer at a liquid-solid interface is studied by ambient scanning tunnelling microscopy (STM). The self-assembled ordered monolayer consisting of trimesic acid and undecanol/decanol with a molecular ratio of both species of 1:1 forms at the interface to the highly oriented pyrolytic graphite (HOPG) out of a solution of TMA in decanol/undecanol. As the packing density is increased at interface, by extended sonication, heating or stirring of the solution the trimesic acid reacts with undecanol/decanol within the monolayer and forms a monoester without the presence of any catalyst. The ester formation at the interface is further confirmed by theoretical calculations and chemical analysis of the solutions using different methods.