

O 49: Oxide and Insulator Surfaces: Adsorption

Time: Tuesday 18:30–20:30

Location: P1A

O 49.1 Tue 18:30 P1A

Synthesis of conjugated organic nanowires on the TiO₂(110) surface — ●JENS BREDE^{1,2}, MIKEL ABADIA¹, MAREK KOLMER³, GUILLAUME VASSEUR^{1,2}, ŁUKASZ ZAJAC³, ALBERTO VERDINI⁴, LUCA FLOREANO⁴, JOSE ENRIQUE ORTEGA^{1,2,5}, and CELIA ROGERO^{1,2} — ¹Centro de Física de Materiales CFM-MPC(CSiC-UPV/EHU), Paseo Manuel Lardizabal 5, E-20018 San Sebastián, Spain — ²Donostia International Physics Center, Paseo Manuel Lardizabal 4, E-20018 San Sebastián, Spain — ³Centre for Nanometer-Scale Science and Advanced Materials, NANOSAM, Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University Łojasiewicza 11, 30-348 Kraków (Poland) — ⁴CNR-IOM, Laboratorio Nazionale TASC, I-34149 Trieste, Italy — ⁵Departamento Física Aplicada I, Universidad del País Vasco, E-20018 San Sebastián, Spain

We have recently demonstrated the synthesis of poly(p-phenylene) nanowires from dibromoterphenyl precursors on the reduced TiO₂(110) surface^a. Here, we summarize our findings and present new data where we used X-ray photoelectron spectroscopy to correlate the behavior of surface anchored hydroxyl groups with changes in the C 1s and Br 3d core levels as a function of annealing temperature. Thus, we obtained clear evidence for the proton-transfer mediated dehalogenation reaction as proposed by Kolmer *et al.*^b In a second experiment we deposited trace amounts of different metals together with the molecular precursors and found highly uniform and ordered arrays of nanowires covering the entire surface. ^a JACS **138**, 5685-5692 (2016) ^b Kolmer *et al.* Angew. Chem. Int. Ed. **52**, 10300-10303 (2013)

O 49.2 Tue 18:30 P1A

On the Photocatalytic Activity of Metal Oxide Surfaces: Adsorption and Decomposition of N₂O on TiO₂(110) — ●MARVIN QUACK, MAX KAUER, and KARINA MORGENSTERN — Chair of Physical Chemistry I, Ruhr-Universität Bochum, Germany

The role of N₂O as a greenhouse gas has been a major issue regarding global warming. In addition, N₂O is known to be responsible for stratospheric ozone depletion. A possible solution to decrease the emission of N₂O is the catalytic decomposition into molecular oxygen and nitrogen using metal oxides. In order to understand the principle of this catalytic process, we investigated adsorption and photocatalytic decomposition of N₂O on a rutile TiO₂(110) single crystal surface by Fourier transform infrared spectroscopy (FTIR) in ultra high vacuum at temperatures from 100 to 150 K. These studies show N₂O adsorbs on the surface in a linear configuration, binding to surface Ti⁴⁺ species via the O-end of the molecule. The effect of UV light irradiation on the catalytic decomposition of the adsorbed molecule has been investigated by *in-situ* infrared spectroscopic measurements. This contribution will discuss the time-resolved depletion of the absorption signals during irradiation in detail.

O 49.3 Tue 18:30 P1A

The acetone/TiO₂ (110) rutile interface: geometry, energetics and vibrational modes — TIM WÜRGER, WOLFGANG HECKEL, ●KAI SELLSCHOPP, STEFAN MÜLLER, and GREGOR FELDBAUER — Hamburg University of Technology, Institute of Advanced Ceramics

Acetone is often present in chemical reactions during the formation of hybrid interfaces, and thus is a potential competitor to coupling agents like carboxylic acids. Therefore, we studied the adsorption geometry and energetics of acetone molecules on the TiO₂ (110) rutile surface with density functional theory (DFT). The focus lies on identifying and quantifying differences between molecular and dissociated adsorption modes. It turns out, that saturation coverage is reached at 0.5 molecules per undercoordinated surface Ti atom. Furthermore, η^1 -acetone binds ≈ 0.23 eV stronger than η^1 -enolate, and 0.70 eV weaker than acetic acid. Corresponding vibrational spectra are presented and compared to IR spectroscopy experiments.^[1]

[1] H. Noei, A. Stierle, DESY Hamburg, private communication.

O 49.4 Tue 18:30 P1A

Micron sized dendritic structures due to water ice on oxide surfaces under ambient conditions — ●KIVANÇ ESAT^{1,2}, ÖZGÜR

BIRER³, and OGUZHAN GÜRLÜ¹ — ¹Istanbul Technical University, Department of Physics, Turkey — ²ETH Zürich, Laboratory of Physical Chemistry, Switzerland — ³Koç University, Chemistry Department, Turkey

Water is one of the most studied yet the least understood molecule at the fundamental level. Its magnificent characteristics can give rise to unexpected phenomena when adsorbed on surfaces. In our work we studied water adsorption on nanoscale chromium oxide particles those had been grown on glass and silicon oxide surfaces. We found out that dendritic structures can form spontaneously on these surfaces due to ambient water. Our systematic studies of dosing such surfaces with humidified air revealed formation of further fractal structures due to water condensation and evaporation. The growth of these structures was observed under an ambient optical microscope in real time. When these samples were transferred to an atomic force microscope (AFM) dendrites due to water ice could still be observed. AFM data showed that these structures could be as high as several hundredths of nanometers, proving them to be three dimensional. Depending on the density of the oxide particles on glass or silicon oxide surfaces, shapes, coverage areas and thicknesses of the dendrites were observed to differ. An explanation could be brought to their formation by use of Electrostatic Force Microscopy measurements.

O 49.5 Tue 18:30 P1A

DFT study of charged O₂⁻ adsorbed on Ca₃Ru₂O₇(001) — WERNFRIED MAYR-SCHMÖLZER, FLORIAN MITTENDORFER, and ●JOSEF REDINGER — Institute of Applied Physics, TU Vienna, Wiedner Hauptstrasse 8-10/134, 1040 Vienna, Austria

An atomic scale knowledge of the surface chemistry of perovskite oxides is surprisingly poor, despite their use in a wide range of important applications, like in sensors, or fuel cells, or even in catalytic processes. Here we present a DFT study of O₂ adsorption on the (001) surface of Ruddelsden-Popper type Ca₃Ru₂O₇. Experimentally Ca₃Ru₂O₇ cleaves nicely, yielding an almost ideally flat rocksalt-like CaO(001) surface. However, due to the tilting and rotation of the RuO₆ octahedra in the bulk different Ca-O distances are present, creating preferred adsorption sites for an O₂ molecule. Upon adsorption O₂ does not dissociate, but rather gets negatively charged. This charging is predicted both for the metallic and the insulating anti-ferromagnetically ordered substrate state, which exists below $T_N < 50$ K. We investigate the origin of the charge transfer using standard PBE, PBE+U and hybrid-functionals and find distinct differences concerning the local magnetic configuration for metallic and insulating states.

O 49.6 Tue 18:30 P1A

Adsorption geometry and infrared absorption of CO₂ molecules on the KCl(100) surface — ●JOCHEN VOGT — Chemisches Institut der Otto-von-Guericke Universität Magdeburg, Germany

The system CO₂/KCl(100) is an example of a physisorption system where a moderate lattice mismatch induces a variety of phases at different coverage, both with and without long-range order. Results of diffraction experiments (LEED, HAS) and infrared spectroscopy have revealed essential adsorbate properties [1]. Simulations of the adsorbate structure on different levels of theory [1,2] are useful to complete the picture by providing suitable structure models as starting points for a LEED structure analysis, and the assignment of observed features in IR spectra. This contribution presents results of plane wave DFT calculations on the structure and infrared absorption of the saturated monolayer phase CO₂-(6 $\sqrt{2}$ \times $\sqrt{2}$)R45°/KCl(100). In accordance with diffraction experiments, the relaxed geometry containing 12 tilted inequivalent molecules exhibits glide-plane symmetry, caused by a modulation of the azimuthal orientation of the molecules. The simulated IR spectrum based on a Γ -point phonon calculation is dominated by a strong red-shifted mode in the region of the CO₂ asymmetric stretch vibration, as observed in IR experiments. However, the DFT result markedly overestimates the experimentally observed excitation band width. [1] F. Traeger *et al.*, J. Phys. Chem. A **115** (2011), 6986 [2] T. Wu *et al.*, Appl. Surf. Sci. **339** (2015), 1