

## O 6: Water on Surfaces

Time: Monday 10:30–13:00

Location: H16

O 6.1 Mon 10:30 H16

**Identification of OH groups from water dissociation on  $\text{In}_2\text{O}_3(111)$  with nc-AFM** — ●MARGARETA WAGNER<sup>1</sup>, MARTIN SETVÍN<sup>1</sup>, LYNN A. BOATNER<sup>2</sup>, MICHAEL SCHMID<sup>1</sup>, BERND MEYER<sup>3</sup>, and ULRIKE DIEBOLD<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, TU Wien, Österreich — <sup>2</sup>Materials Science and Technology Division, ORNL, Tennessee, USA — <sup>3</sup>Computer Chemistry Center, FAU Erlangen-Nürnberg, Deutschland

$\text{In}_2\text{O}_3$  is a complex oxide material with a large unit cell where the (111) surface features a total of 12 surface oxygen atoms in four inequivalent sites. Dissociated water molecules result in two hydroxyl groups adsorbed on the surface, but only one type of surface oxygen atoms is involved in the adsorption [1]. With non-contact atomic-force microscopy (nc-AFM) we are able to identify not only the 12 individual topmost oxygen atoms of the  $\text{In}_2\text{O}_3(111)$  surface but also the individual OH groups formed upon water dissociation. Moreover, the hydrogen atom of the surface OH can be manipulated with the STM tip. This can lead to the formation of a new OH group by re-adsorption of the hydrogen atom on one of the inequivalently sited surface oxygen atoms nearby. In this work the individual OH groups are characterized and identified by their force-distance curves.

[1] M. Wagner et al., ACS Nano 11 (2017) 11531-11541.

O 6.2 Mon 10:45 H16

**IR study of  $\text{D}_2\text{O}$  adsorption on K-rich feldspar** — ●WEIJIA WANG<sup>1</sup>, ALEXEI NEFEDOV<sup>1</sup>, ALEXEI KISELEV<sup>2</sup>, THOMAS LEISNER<sup>2</sup>, and CHRISTOF WÖLL<sup>1</sup> — <sup>1</sup>Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany — <sup>2</sup>Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

K-rich feldspar ( $\text{KAlSi}_3\text{O}_8$ ), a widespread component of mineral dust aerosol, plays an important role in Earth's climate and the environmental sciences owing to its high efficiency in heterogeneous ice nucleation, therefore a fundamental understanding of water interaction with feldspar is necessary. Here we presented a systematic UHV infrared spectroscopy study of  $\text{D}_2\text{O}$  adsorption on K-rich feldspar substrate starting from monolayer coverages up to thick water/ice multilayers. Two specific K-rich feldspar samples were used: orthoclase and microcline.  $\text{D}_2\text{O}$  dosing on feldspar samples and IR spectra measurements were performed at low temperatures (118-150 K). IR spectra for  $\text{D}_2\text{O}$  exposing to feldspar surfaces at 118 K unraveled that amorphous solid water is formed because of the limited mobility of water molecules and the more ordered ice structures can be formed on the orthoclase surfaces compared to  $\text{D}_2\text{O}$  growth on the microcline surfaces. The structural transition of the unstable amorphous solid ice towards crystalline ice can be monitored as the sample is annealed. Dosing of  $\text{D}_2\text{O}$  on feldspar surfaces at 150 K caused ice directly into the structure of crystalline. Annealing shows the structures of the crystalline ice are thermal stable till completed water desorption occurs.

**Invited Talk**

O 6.3 Mon 11:00 H16

**Cold water and ice: Insights from computer simulations** — ●ANGELOS MICHAELIDES — University College London, London, UK

Recent work from our research group in which we are trying to understand the intimate molecular level details of water freezing will be discussed. A particular emphasis will be placed on the role the surfaces of foreign materials play in accelerating the nucleation process [1-4] and on the dynamical nature of the nucleation event.

1. M. Fitzner, G. C. Sosso, S. J. Cox and A. Michaelides, J. Am. Chem. Soc. 137, 13658 (2015) 2. G. Sosso et al., J. Phys. Chem. Lett. 7, 2350 (2015) 3. A. Kiselev et al, Science 355, 367 (2017) 4. M. Fitzner et al., Nature Comm. 8, 2257 (2017)

O 6.4 Mon 11:30 H16

**Towards Reality: Interaction of Magnetite  $\text{Fe}_3\text{O}_4(001)$  with Liquid and Ambient Pressure Water** — ●FRANCESCA MIRABELLA, FLORIAN KRAUSHOFER, MATTHIAS MÜLLNER, JIAN XU, JIRI PAVELEC, JAN BALAJKA, MICHAEL SCHMID, ULRIKE DIEBOLD, and GARETH PARKINSON — Technische Universität Wien, Vienna, Austria

Water interaction with iron oxides plays an important role in different fields. The structure of the solid-liquid interface often defines the performance of a material in its applications. As a first step, we studied

the stability of a UHV-prepared  $\text{Fe}_3\text{O}_4(001)-(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$  surface upon interaction with water vapor as well as liquid. We used a new experimental setup that allows to bring a UHV-prepared surface in direct contact with ultrapure liquid water (and vapor) without exposure to air. The effect of water on the surface was then studied with low energy electron diffraction (LEED), X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy (STM). XPS data show that the surface is hydroxylated upon short exposure (seconds) to ultra-pure liquid  $\text{H}_2\text{O}$ . After longer exposure (minutes-hour), STM shows new features, namely rows growing on top of the pristine surface. The growth of these rows is accompanied by a stronger hydroxylation of the surface (XPS) and lifting of the  $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$  reconstruction (LEED). XPS data, several control experiments, and reproducibility in two different UHV chambers let us exclude any contamination. The formation of these rows seems to be restricted to the surface layer. We interpret them as iron-(oxy)-hydroxide species formed by excess iron diffusing out from subsurface layers in a kinetically-limited process.

O 6.5 Mon 11:45 H16

**Nickel doping enhances the reactivity of  $\text{Fe}_3\text{O}_4(001)$  to water** — ●ZDENEK JAKUB, JAN HULVA, FRANCESCA MIRABELLA, FLORIAN KRAUSHOFER, MATTHIAS MÜLLNER, MICHAEL SCHMID, ULRIKE DIEBOLD, and GARETH S. PARKINSON — Institute of Applied Physics, TU Wien, Austria

Spinel ferrites are technologically important materials showing high catalytic activity for oxygen evolution and water gas shift reactions. In our previous work we've described water adsorption on  $\text{Fe}_3\text{O}_4(001)$ , which is also a well-documented model surface for single-atom reactivity studies. In this work we focus on the water adsorption on nickel-enriched  $\text{Fe}_3\text{O}_4(001)$  surface. Using scanning tunneling microscopy, temperature programmed desorption and x-ray photoemission spectroscopy we show nickel adatoms activate the surface for water dissociation and adsorption above room temperature. At the same time, the presence of nickel adatoms on the surface blocks the formation of partially-dissociated water dimers and trimers which are observed on the clean surface. Interestingly, this result does not change when the adatoms get incorporated into the surface by thermal annealing.

O 6.6 Mon 12:00 H16

**Understanding an electrochemical interface from first principles: the case of hematite.** — ●NICOLA SERIANI — The Abdus Salam ICTP, Trieste, Italy

In photocatalytic water splitting, crucial processes take place at the interface between the photocatalyst and the liquid electrolyte, and are influenced by the structure of the interface itself. We have investigated the electrical double layer at the interface between hematite and water at different values of pH, by means of ab-initio simulations based on density functional theory. We show how charging of the surface determines the structure and dielectric properties of the interface, and the interaction of hematite with water. These results help the interpretation of electrochemical measurements, and provide new insight into the kinetics of the water splitting reaction.

O 6.7 Mon 12:15 H16

**Visualizing the atomic edge structure of a two-dimensional ice with atomic force microscopy** — ●RUNZE MA<sup>1</sup>, DUANYUN CAO<sup>1</sup>, CHONGQIN ZHU<sup>2</sup>, YE TIAN<sup>1</sup>, XIAOCHENG ZENG<sup>2</sup>, LIMEI XU<sup>1,3</sup>, ENGE WANG<sup>1,3</sup>, and YING JIANG<sup>1,3</sup> — <sup>1</sup>International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, P. R. China — <sup>2</sup>Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588, United States — <sup>3</sup>Collaborative Innovation Center of Quantum Matter, Beijing 100871, P. R. China

Low-dimensional water is responsible for a broad spectrum of phenomena in materials science, nanoscience, chemistry, biology, and geology. Especially, the edges of ice play key roles in the ice growth/melting, catalytic reaction and molecular adsorption, but atomic-scale structural characterization still remains a big challenge so far due to the fragileness and high reactivity of the ice edges.

Here we report atomic-scale imaging of the edge structures of a two-dimensional bilayer ice grown on Au(111) surface with non-contact atomic force microscopy. We found that the armchair edges coexist with the zigzag ones, with almost comparable population. We were

able to deduce different growth behaviors for the zigzag and armchair edges from the frozen metastable or intermediate structures at the two edges.

This work not only reveals new understanding of the stability and growth of two-dimensional ices, but also opens up new possibility of probing structure and dynamics of "ice at the edge" in real space.

O 6.8 Mon 12:30 H16

**Local Signature of Solvated Electrons** — •CORD BERTRAM<sup>1,2</sup>, PHILIPP AUBURGER<sup>3</sup>, MICHEL BOCKSTEDTE<sup>3,4</sup>, JULIA STÄHLER<sup>5,6</sup>, UWE BOVENSIEPEN<sup>2,6</sup>, and KARINA MORGENSTERN<sup>1</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum — <sup>2</sup>Fakultät für Physik, Universität Duisburg-Essen — <sup>3</sup>Lehrstuhl für Theoretische Festkörperphysik, Friedrich-Alexander Universität Erlangen-Nürnberg — <sup>4</sup>Chemie und Physik der Materialien, Universität Salzburg — <sup>5</sup>Physikalische Chemie, Fritz-Haber-Institut der Max-Planck-Gesellschaft — <sup>6</sup>Fakultät für Physik, Freie Universität Berlin

Electron solvation, like any solvation, induces transient molecular rearrangements of the solvent molecules, which are important for understanding fundamental processes in various scientific fields like surface science and electrochemistry. We investigated the impact of electron solvation on the local, molecular structure at ice surfaces on Cu(111) with low temperature scanning tunneling microscopy, two-photon photoemission, and ab initio theory. UV photons generate excited electrons in Cu(111), which penetrate the conduction band of the ice and solvate at its surface. The electron solvation leads not only to a transient reorientation of water molecules on ice surfaces, but also to permanent structural changes and the motion of individual molecules. These changes occur predominantly close to defect sites because of the defect's abundance of polar dangling OH groups. Our results suggest

that fast energy dissipation during solvation triggers permanent molecular rearrangement via vibrational excitation. This work is supported by the DFG through the cluster of Excellence RESOLV (EXC 2033).

O 6.9 Mon 12:45 H16

**Single ion hydrates under the SPM tip** — •JINBO PENG<sup>1</sup>, DUYANYUN CAO<sup>1</sup>, ZHILI HE<sup>1</sup>, JING GUO<sup>1</sup>, PROKOP HAPALA<sup>2</sup>, RUNZE MA<sup>1</sup>, BOWEI CHENG<sup>1</sup>, JI CHEN<sup>3</sup>, WEN JUN XIE<sup>1</sup>, XIN-ZHENG LI<sup>1</sup>, PAVEL JELÍNEK<sup>2</sup>, LI-MEI XU<sup>1</sup>, YI QIN GAO<sup>1</sup>, EN-GE WANG<sup>1</sup>, and YING JIANG<sup>1</sup> — <sup>1</sup>Peking University — <sup>2</sup>Czech Academy of Sciences — <sup>3</sup>University College London

Ion hydration and transport at interfaces are relevant to a wide range of applied fields and natural processes. To correlate atomic structure with the transport properties of hydrated ions, both the interfacial inhomogeneity and the complex competing interactions among ions, water and surfaces require detailed molecular-level characterization. Here we constructed individual sodium ion (Na<sup>+</sup>) hydrates on a NaCl(001) surface by progressively attaching single water molecules to the Na<sup>+</sup> using a combined scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) system. We found that the Na<sup>+</sup> hydrated with three water molecules diffuses orders of magnitude more quickly than other ion hydrates. Ab initio calculations revealed that such high ion mobility arises from the existence of a metastable state, in which the three water molecules around the Na<sup>+</sup> can rotate collectively with a rather small energy barrier. Our work suggests that anomalously high diffusion rates for specific hydration numbers of ions are generally determined by the degree of symmetry match between the hydrates and the surface lattice. Reference: Peng, J. et al. Nature 557, 701 (2018) Peng, J. et al, Nat. Commun. 9, 122 (2018)