

## O 60: Dielectric and Molecular/Water Interfaces

Time: Wednesday 15:00–18:00

Location: MA 043

O 60.1 Wed 15:00 MA 043

**Towards molecular dynamics simulations of electrolytes in water employing neural network potentials** — ●SINJA KLEES and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

In recent years, artificial neural networks (NNs) have become a promising method to construct reliable and unbiased interatomic potentials for a wide range of systems. By interpolating the energies and forces obtained from first-principles calculations, NN potentials can be constructed systematically and allow to perform large-scale molecular dynamics simulations several orders of magnitude faster than the underlying electronic structure method. Here, we explore the applicability of NN potentials to electrolytes in water. First preliminary results are discussed and compared to density functional theory data.

O 60.2 Wed 15:15 MA 043

**Quantum chemical and quantum dynamical studies of the photocatalytic water splitting on titanium dioxide** — ●JAN MITSCHKER and THORSTEN KLÜNER — Theoretische Chemie, Carl von Ossietzky Universität Oldenburg

We present results from our computer simulations on the photocatalytic water splitting on rutile (110). Our approach consists of a quantum chemical and a quantum dynamical part.

In a first step, we calculated potential energy surfaces (PES) for this system. The surface is made up of a  $\text{Ti}_9\text{O}_{18}$  cluster, saturated by Mg atoms for technical reasons. This cluster is embedded in a large point charge field. This model can describe the adsorption of small molecules successfully on a high level of theory. The bond breaking is a multi-configurational problem. Therefore, CASSCF calculations for the ground state were performed giving a complete (PES) in five dimensions. Furthermore, similar calculations were carried out for an electronically excited state that results from a hole attack on the water. Artificial Neural Networks proved to be very helpful in fitting these potential energy surfaces without the need of an analytical expression. Both PES are necessary for a real quantum dynamical simulation of photoreactions including quantum effects like tunneling. In the second part of our contribution, we present first results for this kind of simulation based on a jumping wave packet approach. For the first time, the motion of hydrogen after the electronic excitation can be elucidated.

[1] J. Mitschker, T. Klüner, *Phys. Chem. Chem. Phys.*, 2014, DOI: 10.1039/C4CP04593A

O 60.3 Wed 15:30 MA 043

**STM and STS of electric and photocatalytic  $\text{H}_2\text{O}$  dissociation on  $\text{TiO}_2$  Anatase (101)** — ●CHRISTIAN DETTE<sup>1</sup>, MIGUEL A. PÉREZ<sup>2</sup>, CHRISTOPHER E. PATRICK<sup>2</sup>, FELICIANO GIUSTINO<sup>2</sup>, SOON J. JUNG<sup>1</sup>, and KLAUS KERN<sup>1,3</sup> — <sup>1</sup>Max-Planck Institute for Solid State Research, D-70569 Stuttgart — <sup>2</sup>University of Oxford, UK-OX1 3PH Oxford — <sup>3</sup>Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Nanosized  $\text{TiO}_2$  photocatalytic water-splitting technology has great potential for low-cost, environmentally friendly solar-hydrogen production to support the future hydrogen economy. However, the reaction mechanism and dynamics of the photocatalytic water dissociation on  $\text{TiO}_2$  anatase (101) have not yet been fully understood. To resolve this ambiguity we first determine fingerprints of O, OH and  $\text{H}_2\text{O}$  on a  $\text{TiO}_2$  anatase surface by using scanning tunneling microscopy (STM) and spectroscopy (STS) in conjunction with first principle density functional theory (DFT). These fingerprints allow us to investigate the changes in the molecular water structure and its dynamics at the interface during and after the photoreaction. Furthermore, the photon induced dissociation will be compared with the electron induced dissociation.

O 60.4 Wed 15:45 MA 043

**Ultrafast Interfacial Reorientational Dynamics of a Leucine Side Chain** — ●MICHAEL DONOVAN, MISCHA BONN, ELLEN BACKUS, and TOBIAS WEIDNER — Max Planck Institute for Polymer Research, Ackermannweg 10 Mainz, Germany 55128

Proteins possess fluctuating structural features which are important for their function. At interfaces, protein motions may be different than in bulk, and this can affect protein function when in contact

with surfaces. We utilize surface specific probes to study the interfacial behavior of protein side chains. As a model system we studied the reorientational dynamics of hydrophobic leucine side chains at the air-water interface. We followed ultrafast reorientational motions of excited methyl groups pointing into the hydrophobic phase using femtosecond SFG pump probe methods. Specifically, orthogonally polarized mid IR pump pulses excite molecular vibrations, and interfacial dynamics are followed by watching the temporal evolution of an interface specific sum frequency generation (SFG) probe pulse until the signal recovers to its steady state value. First, the dynamics of a charged Leucine monolayer are followed through time resolved SFG, and later the dynamics of leucine in an alpha helical and beta sheet peptide are followed. It is shown that these fast reorientational motions can act as probes of the local interfacial environment of the side chain.

O 60.5 Wed 16:00 MA 043

**Molecular Ordering at the Bulk Water/ $\text{TiO}_2$  Rutile (110) Interface** — GIULIA SERRANO<sup>1</sup>, BEATRICE BONANNI<sup>1</sup>, MARCO DI GIOVANNANTONIO<sup>1</sup>, TOMASZ KOSMALA<sup>1,2</sup>, ULRIKE DIEBOLD<sup>3</sup>, ALDO DI CARLO<sup>4</sup>, JUN CHENG<sup>5</sup>, JOOST VANDEVONDELE<sup>6</sup>, KLAUS WANDEL<sup>2</sup>, and ●CLAUDIO GOLETTI<sup>1</sup> — <sup>1</sup>Department of Physics, Università degli Studi di Roma Tor Vergata, Via della Ricerca Scientifica 1, I-00133 Rome, Italy — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Wegeler Str. 12, 53115 Bonn, Germany — <sup>3</sup>Institute of Applied Physics, Vienna University of Technology, Wiedner Hauptstrasse 8-10/134, A-1040 Vienna, Austria — <sup>4</sup>Department of Electronic Engineering and CHOSE, Università degli Studi di Roma "Tor Vergata", Via del Politecnico 1, I-00133 Rome, Italy — <sup>5</sup>The School of Natural and Computing Sciences, Weston Building, Weston Walk, Aberdeen CB24 3UE, UK — <sup>6</sup>Department of Materials, ETH Zürich, Wolfgang-Pauli-Strasse 27, CH-8093 Zürich, Switzerland

Water in direct contact with a solid surface assumes various structures, governed by a delicate relationship between water-surface and water-water interactions. Lateral ordering in the first water monolayer is often observed in UHV, while it is challenging to investigate experimentally if such structures also form when a solid is immersed in the bulk liquid. For the prototypical metal oxide surface  $\text{TiO}_2$  rutile (110) immersed in high-purity water, density-functional theory (DFT) based molecular dynamics (MD) simulations and high-resolved in-situ Scanning Tunneling Microscopy (STM) results show for the first time that neighboring water molecules form dimers in bulk liquid.

O 60.6 Wed 16:15 MA 043

**Water structure at the  $\text{TiO}_2$ /Water interface** — ●SAMAN HOSSEINPOUR<sup>1</sup>, SIMON J. SCHMITT<sup>1</sup>, KIRILL M. BULANIN<sup>2</sup>, and ELLEN H. G. BACKUS<sup>1</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany — <sup>2</sup>Saint-Petersburg State University, Laboratory "Photoactive nanocomposite materials", Saint-Petersburg, Russia

Photocatalytic splitting of water using sun light for production of hydrogen as an environmentally-friendly, storable, transportable, cost efficient and abundant energy source has received much attention in the last decades. Despite the large number of studies focusing on determining and increasing the efficiency of the water splitting process on semiconducting materials especially on  $\text{TiO}_2$ , fundamental questions regarding the exact mechanisms of this process at the molecular level are still not answered. For example, it is unclear what the correlation is between different interfacial structures and the efficiency of the splitting process. The main reason is the absence of an appropriate analytical tool that can specifically probe the electrode/water interface. In this study we utilized sum frequency generation spectroscopy to determine the structure and conformation of interfacial water molecules at the  $\text{TiO}_2$ /bulk water interface. We compared the results with the structure of water molecules adsorbed on the electrode surface from the gas phase. The results showed that there are different water species with different strengths of hydrogen bonding adsorbed to the  $\text{TiO}_2$  surface. We will use these findings to correlate the water structure on different  $\text{TiO}_2$  surfaces to the efficiency of the water splitting process.

O 60.7 Wed 16:30 MA 043

**Solid/water interfaces from theory and experiments: the fluorite/water interface** — ●RÉMI KHATIB<sup>1</sup>, ELLEN H. G. BACKUS<sup>2</sup>,

MARIE-PIERRE GAIGEOT<sup>3</sup>, and MARIALORE SULPIZI<sup>1</sup> — <sup>1</sup>Johannes Gutenberg Universität, 55128 Mainz, Germany — <sup>2</sup>Max Planck Institute for Polymer Research, 55128 Mainz, Germany — <sup>3</sup>Université d'Evry val d'Essonne, 91025 Evry, France

Vibration Sum Frequency Generation (VSFG) spectroscopy is a powerful technique which is able to provide information about surfaces and interfaces selectively excluding the centrosymmetric contribution from bulk. The experimental spectra contain information which is crucial to characterize e.g. solid/liquid interfaces (including hydrogen bond strength, water dipole orientation) but they call for a microscopic/molecular level interpretation.

Here we present a collaborative theoretical/experimental study which provides a new microscopic understanding of the fluorite (CaF<sub>2</sub>)/water interface as function of pH. Our interest is twofold: 1) from the theoretical point of view we develop and test new tools to calculate the VSFG spectra including an ab initio description of the models; 2) from the experimental point of view, we move beyond the current state of the art providing the first Phase-Sensitive VSFG spectra for CaF<sub>2</sub>/water interfaces. The results are encouraging. We provide an atomistic description of the interfaces CaF<sub>2</sub>/water according to a wide range of pH. We can understand the impact of the surface termination on the water orientation and we can show in particular the importance of the electrical field due to ions in solution on the VSFG response.

O 60.8 Wed 16:45 MA 043

**Reduction of the contact resistance of bipolar plates and foils for fuel cells by atmospheric plasma treatment** — •TATIANA FEDOSENKO, NICOLAS WÖHRL, and VOLKER BUCK — University of Duisburg-Essen and CENIDE, Carl-Benz-Str. 199, 47057, Duisburg, Germany

Proton-exchange membrane fuel cells typically consist of two electrodes - bipolar plates, separated by an electrolyte in a form of a proton exchange membrane. In one specific implementation these bipolar plates are made from a graphite/polypropylene composite. Polypropylene (PP) is unintentionally enriched at the surface of the bipolar plates during the manufacturing, thereby significantly increasing the contact resistance between individual plates. In this study bipolar plates were treated in air plasma at atmospheric pressure while the etching time and the distance between the surface and plasma was varied. It is shown how the plasma etching removes the excess polymer matrix at the surface. Furthermore it was measured by Raman Spectroscopy that the plasma is etching the smaller nanostructured carbon from the surface, leaving larger graphitic structures. Since fewer interfaces are between the crystals, the scattering of electrons is reduced and hence the conductivity of the etched samples is higher than the conductivity of the untreated samples. The etching effect on the surface is correlated with the plasma properties as measured by optical emission spectroscopy. Atmospheric plasma treatment is demonstrated to be an efficient and scalable method to improve the properties of bipolar plates.

O 60.9 Wed 17:00 MA 043

**Substrate induced modifications of the electrocatalytic properties of Pt and Pd monolayers on Au: combined electrochemical and periodic DFT study** — •JAN KUČERA<sup>1</sup>, SYLVAIN BRIMAUD<sup>2</sup>, ROLF JÜRGEN BEHM<sup>2</sup>, and AXEL GROSS<sup>1</sup> — <sup>1</sup>Institut für Theoretische Chemie, Universität Ulm — <sup>2</sup>Institut für Oberflächenchemie und Katalyse, Universität Ulm, D-89069 Ulm, Germany

We combine experimental electrochemical approaches with periodic density functional theory (DFT) calculations to elucidate substrate-induced modifications of noble metal electrodes. The systematic utilization of vertical-ligand effects in order to tune electrocatalytic properties of metal electrodes is often hindered by experimental problems in the practical preparation of well defined bimetallic surfaces. As shown recently, smooth and stable Pt monolayer films on Au (Pt-ML) can be realized by using CO as stabilizing agent [1]. Electrocatalytic testing confirmed that the activity of the resulting Pt-ML differs from that of Pt-bulk. Specifically, the electrooxidation of a CO adlayer on Pt-ML is shifted by about 0.2 V to higher potential compared to Pt-bulk. In contrast, comparative examination of Pd-ML and Pd-bulk systems revealed only subtle changes. Theoretical models show that the electronic structure of adsorbed CO remains practically unchanged upon the exchange of the both substrates. However, a variation of the electronic density in the surface metal layer leads to different thermodynamical stabilities of CO adlayers at high-coverages, whose impact on electrocatalytic CO oxidation activity is discussed.

[1] S. Brimaud and R. J. Behm, J. Am. Chem. Soc. **135** (2013) 11716.

O 60.10 Wed 17:15 MA 043

**Nanostructured metal arrays on Si wafers for solar fuel production** — •SIMON FILSER<sup>1</sup>, ROBIN NAGEL<sup>2</sup>, KATRIN BICKEL<sup>1</sup>, QI LI<sup>1</sup>, KONRAD SCHÖNLEBER<sup>1</sup>, GIUSEPPE SCARPA<sup>2</sup>, PAOLO LUGLI<sup>2</sup>, and KATHARINA KRISCHER<sup>1</sup> — <sup>1</sup>TU München, Physik-Department E19a, James-Frank-Str., 85748 Garching, Germany — <sup>2</sup>TU München, Lehrstuhl für Nanoelektronik, Arcisstrasse 21, 80333 München, Germany

One approach for the storage of solar energy is the photoelectrochemical conversion of the climate-wrecking CO<sub>2</sub> into hydrocarbons. It is well-known that bulk metal electrodes, e.g. gold or copper, reduce CO<sub>2</sub> at high overpotentials [1]. The product distributions containing e.g. CO, ethylene and methane sensitively depend on the electrode material and the reaction conditions. Our aim is to integrate such metal catalysts into an electrochemical solar cell to directly transform solar energy into chemical fuels. Conduction band electrons generated by light absorption in the semiconductor are transferred into the metal catalyst where they are used to reduce CO<sub>2</sub> to different products in several reaction steps. We realize such a system by structuring a silicon substrate with chessboard arrays of gold structures which can be electrochemically plated by copper which is the only material known to reduce CO<sub>2</sub> to methane and ethylene. Silicon is chosen as a substrate because its band gap is well-suited to the solar spectrum. In our experiments, we examine the CO<sub>2</sub> reduction efficiency and the product distribution of the CO<sub>2</sub> reduction on goldstructures.

[1] Y. Hori, K. Kikuchi, S. Suzuki, Chem. letters, 1985, 1695-1698.

O 60.11 Wed 17:30 MA 043

**Photoelectrochemical CO<sub>2</sub> reduction on silicon electrodes functionalized with pyridine** — •QI LI<sup>1</sup>, SEBASTIAN LINDNER<sup>1</sup>, ANTON TOSOLINI<sup>1</sup>, MANUEL WINDSCHEID<sup>1</sup>, KATRIN BICKEL<sup>1</sup>, SIMON FILSER<sup>1</sup>, KONRAD SCHÖNLEBER<sup>1</sup>, IGNAZ HÖHLEIN<sup>2</sup>, BERNHARD RIEGER<sup>2</sup>, PATRICK ZELLER<sup>3</sup>, JOOST WINTTERLIN<sup>3</sup> and KATHARINA KRISCHER<sup>1</sup> — <sup>1</sup>Nonequilibrium Chemical Physics, Physics Department, Technical University Munich, Germany — <sup>2</sup>WACKER-Chair for Macromolecular Chemistry, Chemistry Department, Technical University Munich, Germany — <sup>3</sup>AK Wintterlin, Chemistry Department, Ludwig-Maximilians-University Munich, Germany

Solar driven CO<sub>2</sub> reduction to fuels or basic chemicals could provide an exciting new energy conversion pathway. Attempts of creating such a photochemical solar cell have to deal with the large activation barrier of CO<sub>2</sub> reduction which tends to lead to low yields and efficiencies.

Based on the reported catalytic effects of dissolved pyridine on the CO<sub>2</sub> reduction [1,2] we demonstrate that a functionalized p-Si electrode constitutes a promising interface for the photoelectrochemical CO<sub>2</sub> reduction. The interface consists of pyridine molecules which are immobilized on the Si surface via an electrografting process [3]. Modified electrodes have been characterized using electrochemical methods, STM and XPS. The grafted pyridine layer noticeably increases the electrochemical reactivity of the p-Si electrode.

[1] Barton et al., J. Am. Chem. Soc., 2008, 130, 6342-6344 [2] Keets et al., Indian J. Chem., 2012, 51A, 1284-1297 [3] Li et al., Surf. Sci., 2015, 631, 185-189

O 60.12 Wed 17:45 MA 043

**Methanol electrooxidation on UHV prepared Pt modified Ru(0001) model electrodes** — FABIAN ARGAST, •ALBERT K. ENGSTFELD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

The oxidation of methanol (MeOH) on bimetallic PtRu electrodes is described and widely accepted to occur via a bifunctional mechanism, where Pt provides the carbon species and Ru the oxygen species to form CO<sub>2</sub>. Only recently it has been shown in a model catalyst study that bimetallic PtRu structures do not necessarily enhance the catalytic activity. (A.K. Engstfeld et al., *Angewandte Chemie Int. Ed.* **53** (2014) 12936)

We present results on the MeOH electrooxidation on Pt modified Ru(0001) electrodes. The nanostructured electrodes are prepared under ultra high vacuum (UHV) conditions via physical vapour deposition of Pt on Ru(0001) and are characterized by scanning tunnelling microscopy (STM). Subsequently they are transferred to a flow cell system attached to the UHV system for electrocatalytic investigations. We show that PtRu/Ru(0001) surface alloys and Pt island modified Ru(0001) surfaces are essentially inactive for the electrooxidation of MeOH, despite the presence of bimetallic PtRu interfaces. We dis-

Discuss the influence of vertical and lateral ligand effects of the Ru(0001) acting on the Pt structures, preventing the initial dissociation of the MeOH. We also show that electrochemically restructured surfaces show

an enhanced reactivity and we conclude that defect sites on the rough Pt structures are primarily responsible for the increasing activity.