

O 60: Chemistry at Solid/Liquid Interfaces

Time: Wednesday 15:00–18:15

Location: S052

Invited Talk

O 60.1 Wed 15:00 S052

First-principles photo-electrocatalysis beyond the computational hydrogen electrode — ●HARALD OBERHOFER — Technische Universität München, Germany

First-principles based computational modelling assumes an ever increasing role in understanding and partly already optimising catalysts for photo-electrochemical reactions. The success of prevalent approaches like the computational hydrogen electrode (CHE) thereby relies largely on a numerical efficiency sufficiently high as to allow for large-scale screening of catalyst materials. Such efficiency arises out of well chosen descriptors that ideally condense the mechanistic understanding of the ongoing catalytic reactions at the solid-liquid interface.

In recent years, there is increasing evidence that this understanding needs further scrutiny. Critical aspects in this respect are the neglect of solvation effects, the assumption of pathways that exclusively proceed via proton-coupled electron transfer steps, and the neglect of any kinetic limitations in the CHE approach. In this talk I will review our recent activities in addressing these issues with detailed first-principles based multiscale modeling approaches. Thereby, in particular embedding approaches—both on the solid and the liquid side of the interface—have the potential for a refined description without sacrificing computational efficiency.

O 60.2 Wed 15:30 S052

Continuum embedding for photo-electrochemical surface processes — ●MARKUS SINSTEIN¹, HARALD OBERHOFER¹, DANIEL BERGER², VOLKER BLUM³, and KARSTEN REUTER¹ — ¹TU München — ²University of California, Los Angeles — ³Duke University

The problem of global warming has been known for decades and is believed to be linked directly to the exhaust of carbon dioxide and other gases into the atmosphere which are produced in the combustion of fossil fuel. Carbon-neutral energy sources can be obtained by converting abundant sunlight into chemical compounds. Prominent examples for photo-electrochemically driven reactions generating solar-fuel are the water splitting reaction and the carbon dioxide reduction at metal-oxide solid photo-catalysts. A detailed analysis of the involved elementary processes via first-principles calculations is challenging due to the necessity to simultaneously account for the extended semiconductor surface and the liquid electrolyte. Going beyond traditionally assumed proton-coupled electron transfer mechanisms one may furthermore face charged intermediate states where a significant stabilization due to the polar liquid environment is to be expected. This necessitates a method able to capture electrostatic solvent effects whilst being computationally inexpensive in order to allow for efficient catalyst screening. To this end, we implemented an implicit solvation scheme based on the multipole expansion method into the density functional theory package FHI-aims and discuss first investigations on the photo-electro-catalytic oxygen evolution reaction on rutile titanium dioxide surfaces.

O 60.3 Wed 15:45 S052

Molecular dynamics simulations of the libration region of the SFG spectra at the water-air interface. — ●RÉMI KHATIB¹, TAISUKE HASEGAWA², MARIALORE SULPIZI¹, ELLEN H. G. BACKUS³, MISCHA BONN³, and YUKI NAGATA³ — ¹Institute of Physics, Johannes Gutenberg University, Mainz, Germany — ²Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Japan — ³Department for Molecular Spectroscopy, Max Planck Institute for Polymer Research, Mainz, Germany

Sum-frequency generation spectroscopy (SFG) has been used to probe interfacial water structure. Former studies of the stretching and bending modes have evidenced, that non-hydrogen-bonded O-H groups are present at the water-air interface.[1,2] In contrast, the low-frequency librational mode has been much less studied.

In this study, we compute the SFG spectrum at the water-air interface in the libration region by using molecular dynamics simulations. We show that the modelling of the polarizability for the optical response calculation has a drastic effect on the simulated spectra, while force field and dipole models have a minor impact. At the water-air interface, the neighbouring hydrogen-bond partner affects the polarizability in a very heterogeneous way, which cannot be captured with a single point polarizability model per water molecule. In the simulated spectra, the peak of the librational contribution to the imaginary part

of the response is centred at 660 - 750 cm⁻¹.

[1] Du, Q. *et al.*, Phys. Rev. Lett., 1993, 70, 2313-2316. [2] Nagata, Y. *et al.*, J. Phys. Chem. Lett., 2013, 4, 1872-1877

O 60.4 Wed 16:00 S052

Towards First-Principles Modeling of Electrolytic Solvent Effects in Photo-Catalytic Water Splitting — ●STEFAN RINGE¹, HARALD OBERHOFER¹, SEBASTIAN MATERA², and KARSTEN REUTER¹ — ¹Technische Universität München — ²Freie Universität Berlin

Due to the complexity of the physical processes underlying photo-catalytic surface reactions, ab-initio computational approaches have to overcome major challenges concerning accuracy and computational costs. In particular, an efficient description of electrolytic solvent effects - which are crucial for charge driven reactions - is highly necessary. We present an implementation of the modified Poisson-Boltzmann (MPBE) model in the highly parallel and numerically efficient all-electron DFT code FHI-aims.[1] In contrast to most implicit solvent models, this technique combines dielectric solvent response with a mean-field description of solvated finite-sized ions. This has been shown to capture a majority of electrochemical solvent effects appearing in heterogeneous photo-catalysis.[2] We developed a Newton method by linearizing the MPBE and solving the resulting linearized Poisson-Boltzmann Equation (LPBE) by a self-consistent function-space oriented solution scheme which in contrast to common multi-grid solvers is able to exploit the specialized grids and optimized integration schemes of FHI-aims. We demonstrate the approach and its efficiency by investigating hydration and ionic effects on the solvation properties of a wide range of neutral molecules and ions.

[1] Blum, V. *et al.*, Comp. Phys. Comm. 2009, 2175-2196. [2] e.g. Kilić, M.S., Bazant, M.Z., Phys. Rev. E, 2007, 021502.

O 60.5 Wed 16:15 S052

What quantum dynamics tells us about photocatalytic water splitting — ●JAN MITSCHKER and THORSTEN KLÜNER — Carl-von-Ossietzky-Universität, Oldenburg, Germany

Combining quantum chemistry with quantum dynamics is a valuable tool to simulate processes on a femtosecond time scale. In this contribution, the focus is on the photochemistry of water on a rutile (110) surface. Highly accurate potential energy surfaces for the adsorption of water on rutile were calculated on a CASSCF level of theory. The rutile surface is modelled by a cluster embedded in a large point charge field. The electronically excited state resulting from a hole attack on the water molecule was simulated by a positively charged adsorbate. From about 170000 data points for each state the potential energy surfaces were constructed using artificial neural networks for the interpolation.

Two photoreactions were studied: photodesorption and photodissociation. Numerical wave-packet propagation solves the time-dependent Schrödinger equation and accounts for all quantum effects. Our results indicate an MGR mechanism for the desorption due to the repulsive interaction between adsorbate and substrate in the excited state. Describing the photodissociation, however, is much more complicated due to the underlying Hamiltonian. Using a simpler two-dimensional model, the process is dominated by an energy barrier near the Franck-Condon region leading to a splitting of the wave-packet and introducing strong isotope effects.

O 60.6 Wed 16:30 S052

First-principles reaction barriers for the splitting of water on rutile TiO₂ (110) — ●THOMAS STECHER, HARALD OBERHOFER, and KARSTEN REUTER — TU München, Garching, Deutschland

First-principles modelling of electrocatalytic surface reactions is still largely defined by the computational hydrogen approach. This approach evaluates free energy differences between consecutive reaction steps and thereby accounts only for thermodynamic barriers. In order to access additional kinetic barriers in the photocatalytic oxidation of water we present an approach based on *ab initio* molecular dynamics (AIMD) simulations and umbrella sampling. As a first showcase system we consider the initial proton-transfer step during water-splitting on a rutile TiO₂ (110) surface, which was previously studied within the computational hydrogen electrode approach [1]. AIMD on a system of this size is enabled by an electrostatic embedding approach of

both the solid and liquid parts of the reaction site. Furthermore it was found to be imperative that the rearrangement of water, which plays a key role, be considered in the definition of the reaction coordinate. This is achieved by an energy-based reaction coordinate inspired by Marcus theory. Finally, hybrid-level DFT functionals are required for a realistic description particularly of the transition state. Bringing these computational ingredients together allows us to disentangle thermodynamic and kinetic contributions to the reaction barrier. [1] H. Oberhofer and K. Reuter, *J. Chem. Phys.* **139**, 044710 (2013).

O 60.7 Wed 16:45 S052

Structure Sensitivity of the Oxygen Evolution Reaction on Cobalt(II,III) Oxide — ●CRAIG PLAISANCE¹, KARSTEN REUTER¹, and RUTGER VAN SANTEN² — ¹Technische Universität München, Germany — ²Technische Universiteit Eindhoven, The Netherlands

Quantum chemical calculations and kinetic simulations were used to examine the structure sensitivity of the oxygen evolution reaction on several surface terminations of Co₃O₄ [1]. Three characteristically different active sites were identified, all of which carry out O-O bond formation by nucleophilic attack on an oxo coordinated by one to three Co cations. A method was developed to calculate the turnover frequency of oxygen evolution as a function of overpotential, and it was found that three overpotential ranges exist, each with a different active site dominating. At low overpotentials an oxo coordinated to two Co(IV) and one Co(II) at a step edge of the (311) surface is most active. At medium overpotentials, the active site switches to an oxo coordinated to two Co(IV) on the A termination of the (110) surface, and at high overpotentials, to an oxo coordinated to a single Co(V) on the B termination of the (110) surface. The less coordinated oxos are intrinsically more reactive but require a higher overpotential to oxidize to the active state. Analysis of the electronic structure indicates that the intrinsic reactivity is related to the energy to transfer a hole from an oxidized Co cation to the oxo, with the less coordinated sites requiring the least energy.

[1] C.P. Plaisance and R.A. van Santen, *J. Am. Chem. Soc.*, 2015, **137** (46), 14660-72.

O 60.8 Wed 17:00 S052

Improved Chemical and Electrochemical Stability on Perovskite Oxides by Oxidizing Cations at the Surface — QIYANG LU¹, NIKOLAI TSVETKOV¹, LIXIN SUN¹, ETHAN CRUMLIN², and ●BILGE YILDIZ¹ — ¹Massachusetts Institute of Technology, Cambridge MA, USA — ²Lawrence Berkeley National Laboratory, Berkeley CA, USA

Segregation and phase separation of aliovalent dopants on perovskite oxide (ABO₃) surfaces is detrimental to the performance of electrocatalytic energy conversion systems such as solid oxide fuel/electrolysis cells and catalysts for thermochemical H₂O and CO₂ splitting. One key reason behind the instability of perovskite oxide surfaces is the electrostatic attraction of the negatively charged A-site dopants (Sr²⁺ on La³⁺ site) by the positively charged oxygen vacancies enriched at the surface. Here we take La_{0.8}Sr_{0.2}CoO₃ (LSC) as a model perovskite oxide, and modify its surface with additive cations that are more and less oxidizing than Co on the B-site of LSC. We utilized ambient pressure X-ray absorption and photoelectron spectroscopy to prove that the dominant role of the oxidizing surface additives is to suppress the enrichment and phase separation of Sr while reducing the concentration of oxygen vacancies at the surface. Consequently, we found the effect of these oxidizing cations to be significantly improved stability, with up to 30x acceleration of the oxygen exchange kinetics. Finally, the results revealed a *volcano* relation between the oxygen reduction reaction (ORR) kinetics and the oxygen vacancy formation enthalpy of the binary oxides of the additive cations.

O 60.9 Wed 17:15 S052

Enhancement of electrocatalytic activity for oxygen evolution in bimetallic tetrapyrrolyl-porphyrine networks — BENJAMIN WURSTER¹, DORIS GRUMELLI¹, ●DIANA HÖTGER¹, RICO GÜTZLER¹, and KLAUS KERN^{1,2} — ¹Max Planck Institute for Solid State Research, D-70569 Stuttgart — ²Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Hydrogen and oxygen generated by electrochemical water splitting offers a source of clean and renewable energy. The limiting factor is the oxygen evolution reaction (OER) which is a demanding reaction as it involves a four-electron transfer ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$, in alkaline electrolytes). As a result, the reaction has to overcome a large overpotential. Inspired by the reactivity of single metal atom

catalysts and the structure of metallo-proteins, a bimetallic porphyrine catalyst for the OER was fabricated. Tetrapyrrolyl porphyrines provide two different coordination environments for the stabilization of single metal centers: the porphyrine ring and the pyridyl groups. Using this method we intentionally place Co and Fe atoms in either of the two coordination environment within a porphyrine monolayer on Au(111).

Compared to the single metal porphyrines the bimetallic networks show an increase in activity towards oxygen production of approximately two orders of magnitude. The enhancement of the activity is due to a cooperative effect between the metal centers positioned in the two coordination environments. Additionally, the reaction starts with an overpotential of about 300 mV, highlighting the favorable kinetics of the catalyst.

O 60.10 Wed 17:30 S052

Electro-oxidation of methanol from first-principles with an implicit solvation method — ●SUNG SAKONG and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

The methanol electro-oxidation is the central reaction in the direct methanol fuel cell (DMFC). We present a first-principles computational studies addressing the reaction mechanism occurring on the anode of the DMFC based on density functional theory (DFT). The electrode-electrolyte interface is modeled by a Pt(111) slab in an implicit solvent [J. Chem. Phys. **142**, 234107 (2015)]. The electrode potential of the electrochemical cell is parametrized using the computational hydrogen electrode method. Thus DFT calculations yield the energetics of reaction intermediates on the Pt electrode as a function of the electrode potential U . We find that the presence of the implicit solvent leads to subtle changes in the relative energies of the reaction intermediates. Based on calculated activation barriers, a possible reaction scheme is proposed. We will demonstrate that the total oxidation of methanol is possible at electrode potentials of $U > 0.6\text{ V}$ on Pt(111), in agreement with experimental observations. Based on the proposed reaction scheme, we will discuss possible scenarios to improve the performance in the methanol electro-oxidation.

O 60.11 Wed 17:45 S052

Electro-oxidation of methanol and CO on UHV prepared Pt modified Ru(0001) model electrodes — ●JENS KLEIN, FABIAN ARGAST, ALBERT K. ENGSTFELD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm, Germany

Bimetallic platinum-ruthenium catalysts are the state-of-the-art anode electrode materials for direct methanol fuel cells, since they show a much higher activity towards both the methanol (MeOH) oxidation and the CO oxidation compared to the standard anode catalyst Pt. The higher activity has been ascribed to adjacent bimetallic PtRu-sites (‘bifunctional mechanism’). The actual structure of the active sites remained, however, unclear.

For a more detailed understanding of the structure-activity relationship of this system, we investigated these reactions on structurally well-defined nanostructured bimetallic Pt modified Ru(0001) surfaces in a combined ultrahigh vacuum (UHV) – electrochemical (EC) flow cell setup. Different Pt- and PtRu-nanostructures with varying Pt coverage and varying number of adjacent PtRu-sites were prepared by physical vapor deposition of Pt on Ru(0001) at different temperatures and then characterized by scanning tunneling microscopy (STM).

After structural analysis, the model electrodes were transferred to an EC flow cell attached to the UHV system, to investigate their electrocatalytic activity during MeOH oxidation and bulk CO oxidation in H₂SO₄ by cyclic voltammetry. The electrocatalytic activity was correlated with the abundance of key PtRu nanostructures on the surfaces.

O 60.12 Wed 18:00 S052

Equilibrium coverages of ions on metals electrodes — ●FLORIAN GOSSENBERGER, TANGLAW ROMAN, and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Electrocatalytic reactions typically take place close to the surface of the electrode, i.e., in the region of the electrochemical double layer. These reactions might be substantially affect by adsorbates on the electrode which originate from the electrolyte. They can contribute to catalytic steps by directly interacting with the reactants, by changing the work function, or simply by blocking adsorption sites on the surface.

In this study we have addressed the equilibrium coverage of ions on Pt(111) in the presence of electrolytes using density functional the-

ory. By applying the concept of the computational hydrogen electrode, we have derived the stability of structures at the electrode surface at different electrochemical potentials which are a function of electrode potential, pH, ion concentrations and temperature [1].

With this information we are able to draw phase diagrams for several coadsorption systems. Thereby we can address the open ques-

tion whether synergistic effects are present in coadsorption systems of halides (Cl^- , Br^- , I^-) and hydrogen on Pt(111). Our results indicate that the adsorption of these species is competitive, i.e., that either purely hydrogen-covered or purely halide-covered phases are stable.

[1] F. Gossenberger, T. Roman, A. Groß, *Surf. Sci.* **631**, 17 (2015).