

Structures and Processes at metal-liquid Interfaces

The water-metal interface is of significant interest not only from a fundamental but also from an applied point of view, as in the context of corrosion and catalysis. This is particularly true in electrochemistry, which has attracted a lot of attention recently due to its relevance in hydrogen production and energy storage and conversion, as realized for example in fuel cells. At the same time, modern electrochemistry is becoming increasingly concerned with the development of an atomistic understanding of electrochemical processes. In spite of the complexity of electrochemical interfaces, theoretical studies can contribute significantly to the progress in this field in a similar way this has already happened in the related field of surface science. In particular, electronic structure calculations based on density functional theory (DFT) calculations can nowadays describe in considerable detail the structures of complex interfaces.

While it is of course important to determine the energetically most stable structure of water on metal substrates, in most applications, the metal-water interface under ambient conditions is of interest, i.e. at temperatures around room temperature. For a reasonably good treatment of water-metal interaction, it is advantageous to use ab initio molecular dynamics (AIMD) simulations, wherein the forces necessary to integrate the classical equations of motion are determined 'on the fly' through DFT.

In spite of the numerous studies on the subject of metal-liquid interfaces, there is still a number of gaps that need to be filled. For example, up until now, little attention has been paid to the fact that under electrochemical conditions and low potentials, the platinum electrode is covered by hydrogen. In the following section we discuss how this fact changes our perception of how water behaves near a platinum electrode, as well as some recent results on understanding water structure on metal surfaces with step defects, bringing us closer to real electrochemical environments.

Water Structure on hydrogen-covered Electrodes

There is still some disagreement between experiment and theory regarding the hydrogen equilibrium coverage: whereas experiments indicate that at 0 V relative to the normal hydrogen electrode the hydrogen coverage should be about 0.66 monolayer (ML), density functional theory calculations yield a hydrogen coverage of 1 ML. Still, there is a qualitative agreement that there is significant hydrogen coverage, and it is very likely that the presence of these adsorbed species has a profound influence on the structure of the electrode-electrolyte interfaces and on the processes occurring at these interfaces.

We have performed ab initio molecular dynamics simulations to study the structure of water layers on clean and hydrogen-covered Pt(111) electrodes

at room temperature. In addition to Pt(111) covered with one monolayer of hydrogen, also hydrogen-covered Pt(111) with a hydrogen vacancy and with one additional hydrogen atom per surface unit cell were considered. The typical structure of a water/H/Pt system is shown in Figure 1. A quick inspection shows clear signs of disorder in the water bilayers. In order to make a more quantitative description of the disorder in these systems, we have calculated distribution func-

tions of some relevant structural parameters of the first water bilayer in order to more clearly see the extent to which the water bilayer is disordered, through the following parameters:

(1) Planar deviation. The distances of oxygen atoms of the ordered water structure are practically the same all throughout the bilayer. Thermal disorder is measured here as the extent to which oxygen atoms deviate from this planar arrangement.

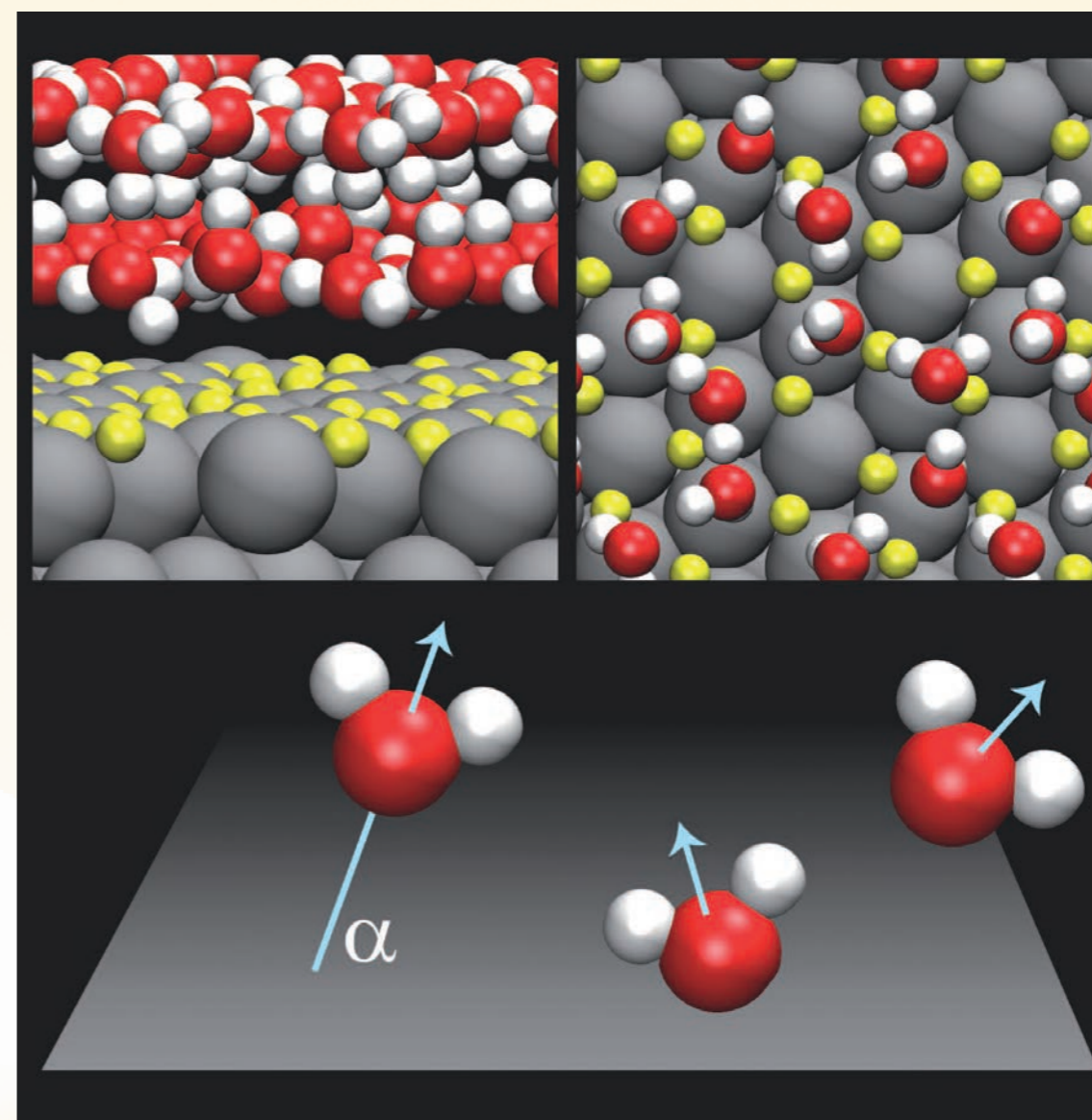


Figure 1: Analyzing the structure of water at the metal-water interface. Clockwise, from top-left: planar deviation, hexagonal structure deviation, orientational inhomogeneity. Surface-adsorbed hydrogen is drawn in yellow.

(2) Hexagonal structure deviation. The angle formed by any three adjacent oxygen atoms in the ordered water structure is almost exactly 120° , and so a honeycomb network of perfect hexagons is one of the most obvious characteristics of the ordered water bilayer. Disorder is measured here as the extent to which O-O-O angles deviate from 120° .

(3) Orientational inhomogeneity. The two criteria mentioned above refer to disorder observable through the relative positions of water molecules in three-dimensional space. Here, disorder is measured by the orientations of water molecules with respect to the surface and with respect to each other.

(4) O-H bonding. It is interesting to examine what effect the hydrogen cover has on the OH bonds on the nearest water layer. In particular, proton transfer events at the metal-water interface and within the water molecule network are examined.

We find that in the presence of a hydrogen layer on Pt(111), the distance of the water molecules from the metal atoms is increased by more than 1 \AA compared to clean Pt(111) indicative of a weakened water-electrode interaction [1]. All considered water bilayers on clean and hydrogen-covered Pt(111) are more disordered than ice, although far from the liquid state.

Surprisingly, a stronger order in the water bilayer on hydrogen-covered Pt(111) in terms of maintaining the honeycomb structure and orientational homogeneity has been found. At room temperature, one would expect less strongly-bound water layers on the metal surface to be more liquid-like, i.e., to have greater disorder, because the water molecules are free to move beyond the periodic constraints of the surface.

It is thus surprising to find more order for the case of water on hydrogen-covered Pt(111). One may argue that the stronger order in the water layer is attributable to the coordination of

the water bilayer with the hydrogen cover through long-range hydrogen bonds, given the fact that the hydrogen atoms of the full monolayer do not leave the fcc hollow sites. This explanation is however unapt given that the creation of hydrogen bonds does not lead to greater separation between bonding species, not to mention the fact that the surface-bound hydrogen atoms are not static and do vibrate within the immediate vicinity of the fcc hollow site. The opposite result is attributed to the fact that the presence of the hydrogen layer weakens the interaction of the water with the surface, and the resulting stronger water-water interaction promotes the unexpected order in the water bilayer. This is consistent with the fact that hydrogen bonding is highly orientational.

Proton transfer events were observed only in the molecular dynamics run with a 13/12 ML hydrogen cover in between platinum and water (see Fig. 2). In panel (b) we can see that the top-site adsorbed hydrogen atom moves up to the water layer, as the receiving

water molecule prepares to transfer one of its hydrogen atoms to a neighboring water molecule. A series of transfers of hydrogen atoms within the water bilayer is observed, jumpstarted by the initial transfer of hydrogen from the platinum surface.

The weakly bound hydrogen adatom is found to be transferred to the water layer during the 11 ps run time of the AIMD simulations, leading to the formation of hydronium complexes. This suggests that the opd hydrogen on Pt(111) is in a dynamical equilibrium with protons in the water. Aside from the close proximity of the top-site adsorbed opd hydrogen to the water layers, it is also less strongly bound to the platinum surface. In contrast to this loosely bound hydrogen, the rest of the hydrogen cover is relatively intact. Within the limited run time of the molecular dynamics performed, no fcc-bound hydrogen atom was observed to hop out of the fcc three-fold-hollow sites.

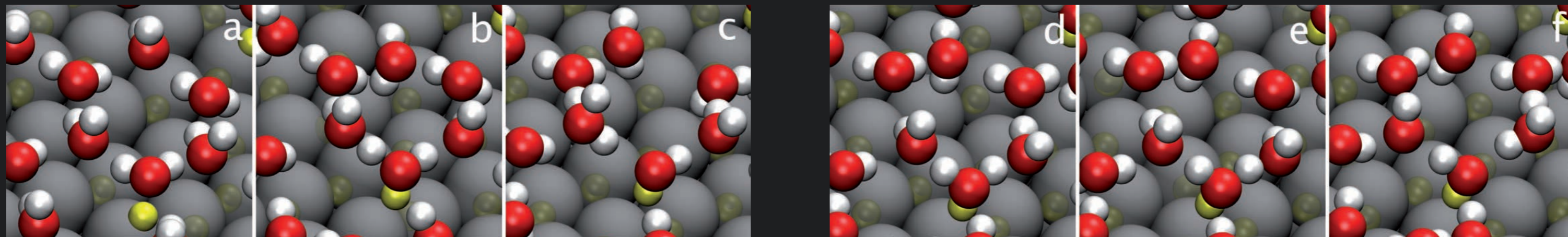


Figure 2: Snapshots showing proton transfer. The weakly-adsorbed hydrogen atom is shown in brilliant yellow in order to distinguish it from the rest of the hydrogen atoms covering the platinum surface. (a)-(b) transfer from the Pt surface to the interface water; (c)-(f) proton transfer within water molecules.

Proton transfer, while shown to occur, is found to be a relatively rare event if one is to look at all O-H bonds in the water layer. Our results also suggest that proton transfer/exchange in the Pt-water interface is not very likely to occur for hydrogen coverages ≤ 1 ML.

Water Structure on stepped Surfaces

Stepped surfaces are particularly interesting as these are present in any realistic surface and often exhibit specific electronic and chemical properties. Recently, vibrational spectra of water adsorbed on Au(100), Au(511) and Au(11 11) were measured at low temperatures (140K) using electron energy loss spectrometry (EELS) by H. Ibach [2]. This work was motivated by the observed large reduction in the Helmholtz capacitance or inner-layer

capacitance on stepped gold and silver surfaces. Three different structural models for a water layer on Au(511) were proposed, but a final assessment of the true water structure solely based on the vibrational spectra could not be made.

The structural, electronic and vibrational properties of a water layer on Au(100) and Au(511) were studied by first principles total-energy calculations and ab initio molecular dynamics simulations [3]. On Au(100), it was found that a structural model based on a (2x2) surface unit cell is not realistic.

The most stable structures on Au(100) and Au(511) surface were obtained. From the vibrational spectra of the simulation, several fundamental aspects have been observed. On the Au(100) surface, the OH stretching mode

can be found at 3,500 cm^{-1} and the non-hydrogen-bonded (NHB) hydrogen stretching mode disappeared, which was caused by the weak reaction between water layers and the Au(100) surface. On the Au(511) surface, three peaks can be found around 3,500 cm^{-1} (3,300 cm^{-1} , 3,500 cm^{-1} and 3,600 cm^{-1}), in which the division of two hydrogen-bonded (HB) hydrogen stretching modes might be caused by the influence of the step edge. The simulation results, both the positions and the relative intensity of the peaks agree with the experimental data quite well. AIMD results show that at 141 K on Au(100) the rectangular structure is thermodynamically not stable and on Au(511) the structure we obtained is quite stable. And the charge density difference shows a rather localized and strong polarization at the step edge on Au(511). All of the phenomena indicate a strong reaction between the step edge and the water layer, and rather different electronic properties compared with the flat gold surface.

Ongoing Research / Outlook

The surface of metal electrodes often contain specifically adsorbed ions such as chlorine coming from the electrolyte environment, and these adsorbed species substantially modify the work function of the metal surface. We show that this phenomenon is not just due to charge transfer alone, but also largely due to the polarization on the adsorbed species. More importantly, we are interested in how the presence

of these adsorbed ions affects the water structure at the interface, and on its implications on the electrode potential. Along these lines we are also looking at processes at the solid/electrolyte interface under potential control, particularly on describing the electrocatalytic oxidation of methanol.

References

- [1] Roman, T., Groß, A.
Catal. Today, submitted
- [2] Ibach, H.
Surf. Sci., 604 (2010) 377
- [3] Lin, X., Groß, A.
Surf. Sci., in press
- [4] <http://www.uni-ulm.de/en/nawi/institute-of-theoretical-chemistry.html>

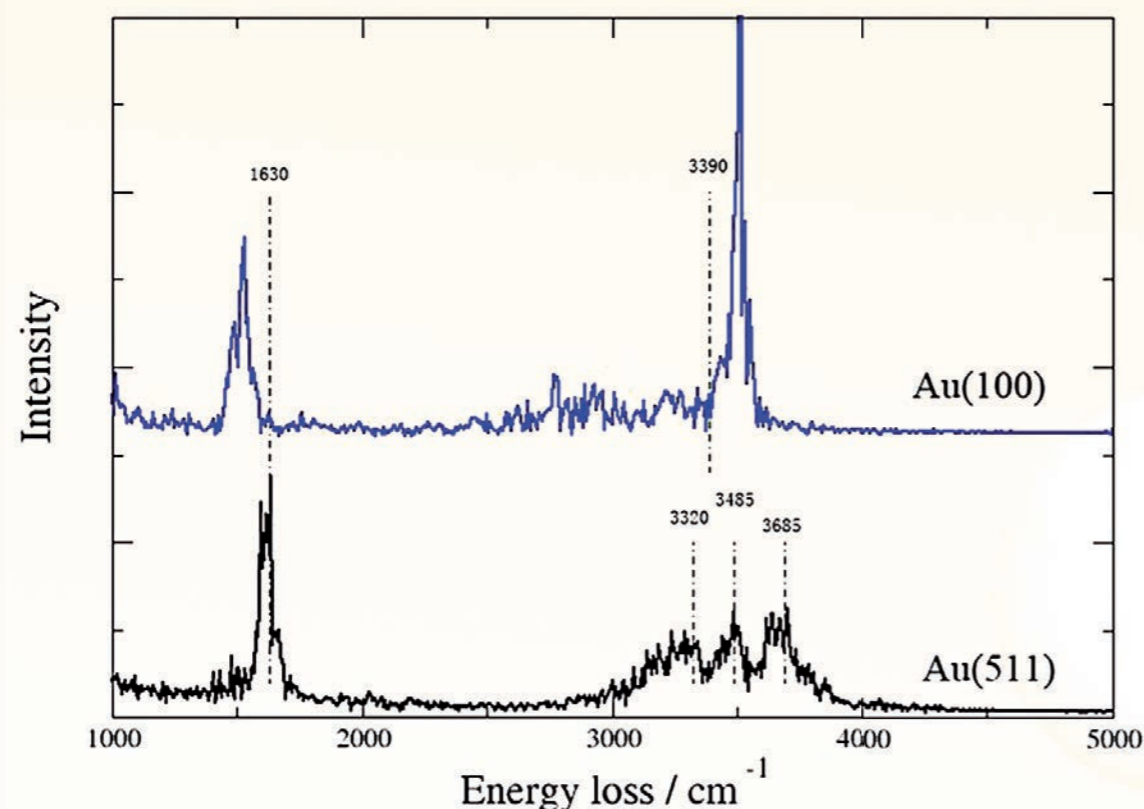


Figure 3: Calculated vibrational spectra of the water layer on Au(100) and Au(511). Experimentally observed modes are indicated by dashed lines.

- Tanglaw Roman
- Jan Kucera
- Katrin Tonigold
- Xiaohang Lin
- Daniela Künzel
- Axel Groß

Institute of
Theoretical
Chemistry,
Ulm University