Water-Metal Surfaces
Insights from core-level spectroscopy and density functional theory

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Abstract

The interaction of water and hydroxyl (OH) species with metal surfaces is central to many surface chemical processes in connection to hydrogen as a clean energy carrier. For instance, OH is considered an essential reaction intermediate in both hydrogen production and fuel cell catalysis. The hydrogen production and fuel cell reaction occur at the triple phase boundary where gas, electrolyte containing water and catalytic metal particles make contact and form both humid and dry regions on the surface of the catalyst, indicating that a successful catalyst will have both hydrophobic and hydrophilic sites. Pt(111) is the most efficient catalyst for the fuel cell reaction, and its performance is enhanced by alloying with other metals, including Cu. The interaction of water with the Cu(110) surface is a particularly interesting case since the energy difference between intact and dissociative adsorption is very small. This may partly be responsible for the preeminence of Cu as the primary catalyst for the water-gas shift reaction (WGSR), which plays an important role in the production of high purity hydrogen for fuel cells. Therefore it is important to understand fundamental factors that affect the ability to form water-metal bonds, the orbital and electrostatic contributions to this bond, as well as the site occupation and orientation of the adsorbed species at active metal surfaces.

To this end, we use experimental and computational techniques to analyze the structure and bonding of water and water plus hydroxyl to metal surfaces, including Pt(111), Cu(111) and Cu(110). Since water has a closed-shell electronic structure, there is Pauli repulsion between water and the metal d- and sp-states. We demonstrate that the ability to form water-metal bonds, or wetting, is controlled by the degree of Pauli repulsion and attractive interactions, which are determined by both the electronic and geometric structure of substrates. On open d-shell Pt(111) the ligand field of water alters the distribution of metal d-electrons to reduce the repulsion. The closed-shell Cu d^{10} configuration, however, does not afford this mechanism for isostructural Cu(111) resulting in three-dimensional cluster formation. In spite of the formal Cu d^{10} configuration, charge depletion at atomic rows on the open Cu(110) surface reduces the repulsion through metal sp-states (Smoluchowski effect), so that formation of two-dimensional ice becomes more favored over three-dimensional clusters. The Smoluchowski effect also leads to an unexpected structure of water at low coverage on Cu(110), and influences the structure of the water monolayer on this surface, which differs from that of close-packed surfaces. We also show that the preferred orientation of the first contact layer of water at metal surfaces, derived in these studies, is directly responsible for macroscopic properties; in particular the wetting property.

With an understanding of the wetting mechanism, we proceed to bridge the pressure gap between our studies of model systems in ultra-high vacuum (UHV) and more realistic conditions for environmental and industrial chemical processes. Specifically, we show how the wettability of a surface can be controlled by the presence of OH groups, acting as anchors for water adsorption, at near ambient conditions. Using in situ photoemission spectroscopy, we find that in the presence of 1 Torr water vapor at 295K, the Cu(110)
surface is covered with a mixed OH and H₂O layer, while the Cu(111) surface remains clean and adsorbate-free. However, with atomic O preadsorbed on Cu(111), the surface reacts with 1 Torr water vapor (H₂O + O → 2OH) to form a mixed OH and H₂O layer. The presence of hydroxyl stabilizes water molecules through strong hydrogen bonds, similar to what we observe on the clean Cu(110) surface. The different wettability on the clean Cu surfaces originates from a lower activation barrier for water dissociation on Cu(110) compared to Cu(111).

Finally, we deduce the structure of water coadsorbed with hydroxyl on Pt(111), a model reaction intermediate in the oxygen reduction reaction (ORR) in fuel cell catalysis. Comparison with the mixed water/hydroxyl layer on Cu(111) and Cu(110) helps to identify a cooperativity effect between surface and hydrogen bonding that drives the stability of this phase. Our findings are relevant to many important natural and technological processes occurring at the water-metal interface, including the fuel cell reaction, which in particular demands understanding of the driving mechanisms behind hydrophobic and hydrophilic sites and the water-metal bond.
To my family
List of Papers

This thesis is based on the following papers, which will be referred to in the text as Papers I-VII:

I. Electronic and structural effects in bonding of water to metals
   *In Manuscript.*

II. Unexpected water structure tailored by a metal surface
   *In Manuscript.*

III. Structure of water adsorbed on the open Cu(110) surface: H-up, H-down, or both?

IV. When water isn’t wet: Origin of the hydrophobic monolayer
    T. Schiros L-Å. Näslund¹, D. Nordlund¹, O. Takahashi², H. Ogasawara¹, L.G.M. Pettersson², and A. Nilsson.
    *In Manuscript.*

V. Hydroxyl induced wetting of metals by water at near ambient conditions

VI. Structure and bonding of water-hydroxyl mixed phase on Pt(111)
VII. Cooperativity effect in surface and hydrogen bonding for the $H_2O+OH$ mixed layer at metal surfaces
In Manuscript.

Papers not included in this thesis:

• **Role of Nitrogen in enhanced stability of III-V Nitride Photocathodes for Solar Hydrogen Production**
  *Manuscript in Preparation.*

• **Molecularly intact and dissociative adsorption of water on clean Cu(110): A comparison with the water/Ru(001) system**
  K. Andersson, A. Gomez, C. Glover, D. Nordlund, H. Öström, T. Schiros,

• **Lithium-7 Nuclear Magnetic Resonance and Ni K-edge X-ray Absorption Spectroscopic Investigation of Electrochemical Lithium Insertion in Li$_x$Ti$_5$O$_{12}$**
  Fabio Ronci, Phillip Stallworth, Theanne Schiros, Xiaodong Guo, Faisal Alamgir, Priscilla Reale, Marten denBoer, and Bruno Scrosati.

• **Defect Physics of CuInSe$_2$ for Photovoltaic Applications using Extended X-ray Absorption Fine Structure (EXAFS).**
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You may say I’m a dreamer, but I’m not the only one.
- John Lennon, *Imagine*
Chapter 1

Introduction

If a picture is worth a thousand words, a surface is worth a thousand pictures.

Since the advent of modern surface science some 30 years ago, water at metal surfaces has been one of the most studied adsorbate systems [1,2] due to its importance in electrolysis, fuel cells, catalysis and corrosion and many other important biological and chemical processes in nature. Yet many open questions remain, and the increasing demand for clean energy technology without greenhouse gas emissions casts a spotlight of renewed interest on the interaction of water with catalyst surfaces. In particular, solar water splitting for the production of hydrogen as a clean energy carrier and fuel cell conversion of hydrogen into heat and electricity, with only water as a byproduct, involve adsorbed water, hydrogen and hydroxyl as key reaction intermediates. In the following a brief introduction to the critical issues in fuel cell catalysis and the relevance of a fundamental understanding of water-metal bonding to these issues is presented. A historical description of the evolution to the current understanding of the interaction of water and water plus hydroxyl with metal surfaces summarizing fundamental aspects is also given.

1.1. Fuel Cell Catalysis

Fuel cells are considered the most promising power generation technology for a sustainable energy infrastructure, particularly when the hydrogen feedstock is produced from renewable resources. While the oxidation of pure hydrogen is not considered a technical hurdle, power loss at the fuel cell cathode remains a problem due to the slow kinetics of the oxygen reduction reaction (ORR), \( \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \). The identification of a catalyst for electroreduction of oxygen with improved efficiency is therefore a major scientific priority. Currently Pt seems to be the only metal that can effectively give a reasonable ORR rate. Two pathways have been considered for the ORR: hydrogenation of oxygen following or preceding O-O bond breaking (direct and peroxide routes, respectively) [3]. The active sites for the ORR on the surface of the catalyst are provided by spatially confined regions called the triple phase boundary, in which both humid and dry regions are present on the surface of the catalyst, as depicted in Fig. 1.1. Our results also show that while water catalyzes the reduction of oxygen, it also poisons the activation of oxygen \((\text{O}_2(\text{g}) + 2\text{Pt} \leftrightarrow 2\text{Pt-O})\), which cannot proceed on a water-covered Pt surface. This dual role of water requires that a successful catalyst will have both hydrophobic and...
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hydrophilic sites. These issues underline the need to understand the factors that influence the wettability of a metal surface as well as details of the water-metal bond, as adsorption sites and binding energy of adsorbed reactants will directly affect catalytic activity. The influence of coadsorbed OH on the water-metal bond, as well as structural details of the OH+H$_2$O layer, is also essential knowledge for details of the reaction mechanism and identifying rate-limiting steps. In a nutshell, these issues span the breadth of this thesis.

Throughout the thesis, the interfacial chemistry at isoelectronic Cu(110) and Cu(111) and isostructural Pt(111) and Cu(111) surfaces are juxtaposed to illuminate electronic and geometric structure effects in the bonding of water and hydroxyl at metal surfaces (see Fig. 1.2 for illustration of the (111) and (110) surface planes). This comparison may also be enlightening since Cu is largely utilized as a catalyst support for the water-gas shift reaction and methanol synthesis, while Pt is the most active catalyst for the fuel cell reaction. Moreover, alloying Pt with Cu, for example, has led to improved catalytic performance in proton exchange membrane (PEM) fuel cells, which may be related to the presence of hydrophilic (Pt(111)) and hydrophobic (Cu(111)) sites (Paper I). The interaction of water with the Cu(110) surface is a particularly interesting case because, although water adsorbs molecularly on this surface, the energy difference between intact and dissociative adsorption is very small [4]. This may be partly responsible for the preeminence of Cu as the primary catalyst for the water-gas shift reaction, which plays an important role in the production of high purity hydrogen for fuel cells [5] as well as industrially important chemicals such as ammonia and methanol [6,7]. Variation in the binding energy of water and hydroxyl with the different metal surface atoms in the alloy, as well as attractive interactions in the adlayer, can lead to compensation effects which facilitate diffusion of OH to neighboring adatoms and provide pathways for proton hopping [8]. Thus, the right choice of catalysts and alloys can coordinate and direct chemical reactions and turn intermediates into products. Yet, despite its importance, the specific nature of water-metal interactions underlying the superiority of the Pt(111) surface for electrocatalysis remains unclear. In this way, a detailed understanding of the structure and bonding of water and hydroxyl at metal surfaces is central to the rational prediction and design of catalysts, especially for the oxygen reduction reaction (ORR) in fuel cell catalysis.

Figure 1.1: Triple phase boundary, characterized by a region where air, electrolyte and catalyst surface meet, at which the ORR reaction proceeds. The direct reaction pathway is shown here.
Figure 1.2: Illustration of the open, corrugated (110), and flat, close-packed (111) surfaces.

1.2. Historical Perspective: Controversies and Challenges

Because of its importance, the interaction of water with metal surfaces has been the center of extended debate due to the multitude of bonding mechanisms and stable overlayer structures water assumes on different metals, as well as the sensitivity of the water adlayer to electron or photon induced damage by the experimental probe. Snapshots of the history of this debate are presented in Fig. 1.2. In 1982, Doering and Madey (DM) [10] proposed an ice-like bilayer structure model for the water monolayer at Ru(0001), consisting of an inner layer of flat-lying water molecules binding to the metal surface through the oxygen lone pair (O lp) orbital and an outer layer of water molecules with one proton engaged in H-bonding in the layer and the other directed toward the vacuum (H-up). Part of the similarity to hexagonal ice (Ih) is the significant vertical displacement between the O atoms of the different water bonding species in the bilayer structure (0.96Å). However, low-energy electron diffraction (LEED) measured for water on Ru(0001) by Held and Menzel in 1994 [11] showed only a small buckling in the 2-D water layer (0.15Å), inconsistent with the DM model. Almost a decade later, Feibelman attributed the planarity of the adlayer to a partial dissociation of water resulting in a nearly flat, hexagonal mixed network of water and hydroxyl [12], based on density functional theory (DFT). Dissociative water adsorption on Ru(0001) was unexpected since water adsorbs molecularly on most close-packed surfaces, including Ni(111), Cu(111), Rh(111), and Pt(111) [13], but the interpretation was supported by two peaks in the O 1s photoemission spectrum at 531.3 and 533.3 eV for water on Ru(0001) [14], corresponding to adsorbed water and hydroxyl. Soon after, in 2002, Andersson et al. showed that while the partially dissociated layer is more stable on Ru(0001), it is kinetically hindered by the competition with desorption and that the OH species observed in the XPS study were likely a result of beam damage to the water layer by the incident x-rays and photoexcited electrons [15]. Molecular adsorption of water on Cu(110) was also demonstrated in a separate report, and previous reports of a partially dissociated layer at this surface were similarly attributed to beam damage of the water layer [16]. Meanwhile, a new "H-down" water structure was identified at the Pt(111) surface using core-level spectroscopy and DFT, with equal amounts of metal-oxygen (O-bonding) and metal hydrogen (M-HO) bonding species [17] forming a nearly flat monolayer.
1.3. **Fundamental Aspects of Water-Metal Bonding**

Solving the structure of the water adlayer, including the proton orientation (H-up or H-down) and hydrogen-bond network, is complicated by the fact that water can form a number of stable configurations on metal surfaces depending on coverage, temperature and growth conditions. For example, different results have been obtained for the dissociation of water on Cu(110) at high temperature depending on heating rate and initial coverage [16,18-22]. The difficulty of growing a perfect water monolayer in UHV, and the sensitivity of the water layer to damage by the x-ray probe further compound the issue. Structural predictions based on theory are also challenging due to a range of issues, including:

- Water-metal and water-water binding energies are relatively weak and comparable in strength [23]
- Stability of H-up and H-down structures at a given surface generally vary by less than 0.1 eV [23,24]
- Energetic barrier for H-up/H-down flipping in the first monolayer is very low [24]
Figure 1.4: Attractive (left) and repulsive (right) contributions to water-metal bonding.
Nonetheless, after extended debate, a general picture has emerged of molecular adsorption for water at metal surfaces, where the dominant part of the adsorption energy comes from the O-bonded water molecules. Adsorbate-substrate interaction, influenced by the geometric and electronic structure of the surface, serves to reduce Pauli repulsion due to orbital overlap of the O $lp$ and metal $d$-states. The attractive and repulsive contributions to water-metal bonding are summarized in Fig. 1.4. In the O-bonding configuration, attraction comes from the electrostatic interaction via the dipole of the water molecule ($\mu=6.2\times10^{-30}$ C-m) and its image dipole in the metal substrate (Fig.1.3, top left). However the dipole-dipole interaction energy is too small – only 0.15 eV for an O-Metal distance of 2.44 Å - to counter the Pauli repulsion alone. Additional channels must be available to increase the attractive interaction and facilitate water-metal bonding. These channels come by way of Coulomb interaction, polarization and charge transfer, and are explored in detail in Paper I.

It is useful to present some background to the interaction in a chemical bonding picture. When water adsorbs on a metal surface, new molecular orbitals are formed with bonding and anti-bonding combinations, as shown in Fig. 1.3 (bottom) for oxygen-bonded (O-bonded) water molecules on Pt and Cu. The bonding orbitals have mostly O 2$p$ character, whereas the anti-bonding orbitals are situated nearer to the metal d-band states and the Fermi level (Fig. 1.3). In general Pauli repulsion is minimized by depopulation of the O $lp$, facilitated by unoccupied water-metal anti-bonding orbitals. The occupied density of s- and p-states of water adsorbed on Cu(110), Cu(111) and Pt(111) and the anti-
bonding character of the water orbitals interacting with the metal $d$-band close to the Fermi level are shown in Fig.1.5. Some transition metal surfaces, like Pt(111), wet, while the interaction of water with noble metals, such as Cu(111), is often too weak to form a uniform overlayer [25,26]. Such electronic structure effects are central to the “$d$-band model” which predicts reactivity of different metals across the periodic table. In Paper I, core-level spectroscopy is combined with density functional theory to study these interactions and the fundamental factors that govern the wettability of metal surfaces.
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The nature of the outer layer has clearly been an issue of controversy for the close-packed surfaces. It is interesting to address how the structure of the water adlayer might change on an open surface in order to identify fundamental driving forces behind water-metal interactions. To this end a detailed picture of the structure and bonding mechanisms for water adsorbed on the open Cu(110), including proton orientation, is derived for sub-monolayer (Paper II) and monolayer coverage and compared to close-packed surfaces (Paper III).

1.4. The OH+H$_2$O Mixed Phase at Metal Surfaces

The myriad of possibilities for the structure and bonding of water at metal surfaces ripple further outward as the interaction with adsorbed hydroxyl (OH) is considered, or in going beyond model UHV systems to atmospheric temperature and pressure ranges. Yet, since most processes of interest in real systems take place at ambient or higher pressures and elevated temperatures, it is important to connect our model studies with more realistic conditions for catalysis. Furthermore, OH plays a central role in surface chemical processes in connection to hydrogen as an energy carrier, as an essential reaction intermediate in both hydrogen production and fuel cell electrocatalysis. It is therefore of great interest to consider the influence of temperature and pressure and coadsorbed OH on water-metal bonding. Related results are discussed in Papers V, VI and VII.

As mentioned, dissociation of water at metal surfaces is an activated process. A well-ordered OH+H$_2$O layer can be systematically prepared by dosing water on an oxygen precovered metal surface, such as Pt(111), as described in detail in Paper VI. Water activates the reduction of atomic oxygen at a Pt(111) surface to generate a mixed OH+H$_2$O phase:

$$\text{Pt-O} + 3\text{H}_2\text{O} \leftrightarrow 2(\text{Pt-OH})(\text{Pt-H}_2\text{O})$$  \hspace{1cm} 1.1

which proceeds via the reaction:

$$3\text{H}_2\text{O} + \text{O}_{\text{ad}} \rightarrow 2\text{OH} + 2\text{H}_2\text{O}.$$  \hspace{1cm} 1.2

This phase has been identified as an important intermediate in the water production reaction over Pt(111) [27] utilized in fuel cell catalysis. This step - the formation of a strongly bound oxygen intermediate and its subsequent reduction to a surface hydroxide - was proposed by Norskov et al as the major cause of overpotential in the cathode ORR [28], itself the major hurdle in fuel cell catalysis. Understanding the origin of the stability of the OH+H$_2$O layer on Pt, and metal surfaces in general, will be key to tuning the adsorption energies to increase the reaction rate.

In a more fundamental sense, comparison of the OH+H$_2$O layer with the pure water layer also provides an opportunity to probe the competitive interplay between water-metal bonding and hydrogen bonding in the adlayer (Paper VII). In contrast to the relatively weak water-metal bonding, with interaction energies confined to a relatively small range, the OH+H$_2$O phase has a significantly higher adsorption energy which varies significantly
between metal surfaces [23]. The origin of this behavior is related to the strong OH-Metal ionic bond, stabilized by charge transfer from the metal substrate to partially occupied \(1\pi\) (lone pair) orbitals of OH [29], as well as the enhanced stability of the H-bond network due to the fact that H\(_2\)O-OH bonds are roughly twice as strong as H\(_2\)O-H\(_2\)O bonds [30]. As a result, water is weaker acceptor and stronger donor of H-bonds in the mixed OH+H\(_2\)O adlayer, leading to an asymmetry in O-O distance similar to the case of OH\(^-\) ions in solution [31]. Fig. 1.5 illustrates the relative bond strengths for H-bonding in the layer and OH+H\(_2\)O-metal interaction. Hydroxyl also pins the structure of the adlayer to the metal lattice, stabilizing water at the metal surface and induces long-range lateral order, which is further enhanced by the strong electrostatic interactions between H\(_2\)O and OH. It is clear that adsorbed hydroxyl (OH\(_{\text{ad}}\)) has a dramatic influence on the structure and bonding of water at a metal surface, which in turn affects reactivity of the surface, however the exact mechanism is unknown. In Section 4.4.3 (Paper VII), we show how a cooperativity effect in surface and hydrogen bonding underpins the stability of the mixed OH+H\(_2\)O layer at metal surfaces.

![Figure 1.5: Relative bond strengths for the different interactions in the water monolayer and mixed OH+H\(_2\)O layer at metal surfaces.](image)

### 1.5. Overview and Goals

The structure of water at metal surfaces results from a complex interplay of a number of effects, including the balance between water-water and water-metal bond strength, electrostatic enhancement and creation of electric fields at the surface through proton orientation and ordering, the degree of lattice match to the metal surface and influence of electronic and geometric structure at a given surface. These factors influence the structure and bonding of water at metals and determine barriers to dissociation, interaction with multilayer ice, and wetting properties. These have enormous implications for a number of environmentally and technologically important reactions, from biology to materials science to electrocatalysis, yet many open questions remain. The somewhat kaleidoscopic nature of the collective theoretical and experimental results for water-metal surfaces, due largely to the complex interplay of interactions at the interface, can obfuscate the connection between fundamental studies and applications to real catalytic systems that can help pave the way to a sustainable energy future. This thesis seeks to tie together some of the disjointed aspects of the general knowledge base relevant for clean energy catalysis with a bow of fundamental understanding. Chapters 2 and 3 provide important details about the experimental methods and theoretical analysis behind the results, which are summarized in Chapter 4. Conclusions and an outlook for future studies are presented in Chapter 5.
Chapter 2

Experimental Methods

*It doesn’t matter how beautiful your theory is, it doesn't matter how smart you are. If it doesn’t agree with experiment, it’s wrong.*

Richard Feynman, American theoretical physicist, 1918-1988

Symbiosis between theory and experiment is key to unveiling fundamental truths about the reactions that sustain us on this planet, from basic life processes to the technology that supports modern society. In this section the experimental details of the surface science measurements behind the results, including synchrotron radiation, experimental set up and techniques used are given.

2.1. **Synchrotron Radiation**

When charged particles, in particular electrons or positrons, are accelerated in a circular orbit, photons are emitted. At relativistic velocities these photons are emitted in a narrow cone in the forward direction, tangent to the orbit. In a high energy electron storage ring the emitted light is called synchrotron radiation and occurs with energies ranging from infra-red to X-rays. Synchrotrons consist of large circular devices where electrons are directed down evacuated pipes by strong magnets positioned around the circumference of the circle. The electrons are produced by an electron gun and circulated and accelerated to relativistic speeds within the storage ring. Synchrotron radiation is produced where the electron path is bent and beamlines are positioned along the bend in order to deliver the photon beam to the experimental instrumentation. This instrumentation is located at endstations where scientists can probe a sample of interest with the highly collimated, high brightness, energy tunable and polarizable beam. The components of a synchrotron radiation facility are shown in Fig. 2.1. Because of the wide range of energies available, and the ability to select wavelengths as short as the distance between atoms in a molecule, synchrotron facilities equip researchers with “x-ray vision” into systems of interest via a plethora of spectroscopic and scattering techniques. Specifically for the work presented in this thesis, synchrotron radiation provides an atom-specific, symmetry-selective probe of the local and chemical environment of a system. Such information is invaluable in understanding the structure, reactivity and/or chemical inertness of a system, and was used here to study the metal-water interface under ultra-high vacuum (UHV) conditions. For further information about synchrotron radiation, the interested reader is directed to Chapter 5 in David Attwood’s comprehensive book, “Soft X-ray and extreme ultraviolet radiation: Principles and Applications” [32].
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Figure 2.1: Typical components of a synchrotron radiation facility: A) Electron gun where electrons are generated from e.g. a heated filament and accelerated into an ultra-high vacuum (UHV) tube. The electron beam is consequently accelerated to near relativistic speeds using e.g. microwaves in a straight section (linear accelerator, LINAC). B) Booster ring where the electrons are circulated, steered by magnets, and further accelerated using a radio frequency cavity (RF cavity) C) Storage ring, in which electrons, deflected by strong magnetic fields, produce synchrotron light in a large range of wavelengths. The circumference of the storage ring range from a few tens of meters to a kilometer or longer depending on the electron energy. D) Beamlines transport the synchrotron light to E) experimental end-stations, with optics to select incoming color (energy) of the light beam. Image adapted from http://en.wikipedia.org/wiki/Synchrotron.

2.1.1 Beamlines

The XPS and XAS experiments were performed at beamline I511 at MAX-lab in Lund, beamline 11.0.2 at the Advanced Light Source (ALS) and beamline 5-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). The measurements presented in the papers were performed in UHV surface science end-stations, except in Paper V, where we compare how things change at higher temperature and pressure using the Ambient Pressure Photoemission (APPES) endstation at beamline 11.0.2 at the ALS.

All three beamlines consist of an undulator, a monochromator, and refocusing optics as exemplified in Figure 2.2 (showing the layout for BL 5.1 at SSRL). An undulator subjects electrons (or positrons) passing through it to a periodically alternating magnetic field to produce a photon beam with different harmonics. Changing the undulator gap, i.e. the distance between the undulator magnets, varies the strength of the magnetic field so that a photon energy of a given harmonic can be selected. At beamline I511, there is a permanent magnet hybrid undulator, which is 52 mm in length and consists of 99 poles (49 periods) with alternating magnetic fields. Beamline 11.0.2 has an elliptically polarizing undulator (EPU) with 37 periods 50 mm in length that can be used in four different polarization modes: circular, elliptical, horizontal and vertical.
Monochromators are used to select a specific photon energy from the x-ray radiation. Bragg diffraction at the monochromator grating (shown in Fig 2.3) spatially separate (disperse) the colors (wavelength) according to the grating equation \( m\lambda = d_0(\sin \alpha + \sin \beta) \), where \( m \) is the diffraction order (typically \( m=-1 \) or \( m=1 \) is used). The dispersed beam is focused onto an exit slit, where the small opening (\(-10–100\mu m\)) effectively selects a small portion \( \Delta \beta \) of the outgoing angle \( \beta \) from the grating, which translates to a narrow bandwidth of the radiation.

As given by the grating equation, the resolution is determined by the line density of the grating and the ability to select a narrow range of incoming angles (\( \Delta \alpha \), defined by entrance slit opening or for entrance-slitless configurations, the electron source) and outgoing angles (\( \Delta \beta \), defined by the exit slit opening). The ultimate resolving power (\(~10'000\)) is often determined by the slope errors of the mirrors and gratings (e.g. error in curvature of a focusing mirror), producing an angle error that translates to an energy error (The slope error multiplies with the number of optical elements in the monochromator setup). With a more complex optical element system like that of I511 at MAX-lab (4 optical elements), a high resolution can be achieved over a large range of energies, but the ease of use comes at the expense of flux due to multiple reflections.

Beamline (BL) I511 is equipped with a modified slit-less SX-700 fixed focus plane
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grating monochromator (PGM), a spherical focusing mirror and movable exit slit with a single grating covering an energy range of 50-1500 eV. At the ALS, BL11.0.2 is equipped with an entrance-slitless, collimated, variable included angle SX-700 PGM with two gratings with different line spacings (d₀) covering low and high energy ranges with different efficiency and resolution in the energy range 95-2000 eV [33-35]. At SSRL, BL 5-1 employs a spherical grating monochromator consisting of an entrance slit, three gratings, and exit slits. The three gratings (300 l/mm (Ni coated), 600 l/mm (Ni coated) and 1100 l/mm (Pt coated)) allow the scanning of energy range from 150 to 1000 eV using the first harmonic radiation from 26-period EPU.

The refocusing optics located downstream between the monochromator and the endstation focus the photon beam horizontally and vertically to a small spot size at the sample. This is preferentially done with grazing incidence mirrors for each direction respectively in a so called Kirckpatrick-Baez (KB) setup and for small spot sizes elliptical shapes are used to reduce spherical abberations. This type of focusing is used at all beamlines used in this thesis, with the exception of SSRL BL 5-1, where the horizontal focusing mirror has a spherical shape. The best measured focal spot sizes are 50x70 um (SSRL), 10x50 um (ALS) and 10x30um (SSRL), but many experiments presented here are performed off focus in order to reduce beam-damage.

2.2. UHV Endstation

For our experiments, UHV conditions are required both to preserve sample cleanliness and due to the short mean free path of electrons which require vacuum for the detectors. The endstation consists of two UHV chambers; a preparation chamber designed for sample preparation and characterization, and an analysis chamber designed for X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS) and X-ray Emission Spectroscopy (XES) on adsorbates, as shown in Fig. 2.4.

The preparation chambers are equipped with an ion gun, LEED optics, and a mass spectrometer. The analysis chambers are equipped with a rotatable Gammadata-Scienta SES-200 (MAX-lab) and SES-100 (ALS and SSRL) electron analyzers for XAS, and partial electron yield detectors for XAS. A horizontally mounted manipulator is provided for experiments with a minimum sample temperature of about 40 K (using liquid He cooling). The manipulator transfers samples between the preparation chamber and the main chamber. Rotation of the analyzer off the E-vector of the linearly polarized beam at I511 allows photoemission signal to be minimized during (polarization-dependent) XAS measurements as well as for (polarization-dependent) symmetry selective XES. At BL 11.0.2 and 5-1, by changing the phase of the undulator magnets, the EPU can rotate the orientation of the E-vector so that rotation of the analyzer is not necessary to access all geometries.
Samples are prepared in situ using a gas inlet system. XPS and XAS spectra were obtained using total energy resolution better than 0.3 eV and 0.1 eV, respectively. A grazing incidence angle of less than 5 degrees for the incoming radiation was used to increase the surface sensitivity and minimize beam damage; particularly crucial for water-metal adsorbate systems in UHV. A base pressure lower than 3 x 10\(^{-11}\) Torr was regularly achieved after bake-out of these systems, and the pressure was kept in the low 10\(^{-10}\) torr range during experiment. For XAS, the direction of the incoming photon beam E-vector was chosen perpendicular to the axis of the electron spectrometer to minimize the photoelectron background. For XPS, the slit size and pass energy of the electron spectrometer together define the resolution and throughput of the analyser; smaller slits and lower pass energy give the highest resolution (lowest flux). The XAS data was measured in partial electron yield mode, in which an electrostatic bias is applied to block photoelectrons and secondary electrons by only allowing electrons with kinetic energy above a given threshold to reach the detector [36]. The metal single-crystals were cleaned by cycles of either Argon or Neon ion sputtering and annealing until a well-ordered low energy electron diffraction (LEED) pattern was obtained and XPS showed no contamination (C, O < 0.1% ML).

2.2.1. Ambient Pressure Photoemission (APPES) Endstation

XPS, and electron spectroscopy in general, is inherently surface sensitive due to the short mean free-path of electrons in a solid, which allows only those photoelectrons excited within the first few atomic layers to escape from the surface and reach the detector. The short mean free path of electrons under atmospheric conditions, due to collisions with molecules in the ambient gas, has traditionally required UHV sample conditions for measurement of an XPS spectrum with acceptable signal to noise ratio. This has been an unfortunate limitation since most interesting interface processes in nature and industry take place at ambient or higher pressures and temperatures. In recent years, advances in instrumentation have overcome this obstacle and made possible in situ XPS measurements at pressures up to 10 Torr.
Experimental Methods

Figure 2.5: Schematic top view of the APPES endstation (left) and water droplet at the sample stage (right). Photo courtesy of the Salmeron Group, ALS, Lawrence Berkeley National Laboratory.

The ambient pressure photoemission chamber at the molecular environmental science (MES) beamline 11.0.2 at the ALS utilizes an electron lens system and differential pumping to extract electrons from a high-pressure cell and transfer them into an electron analyzer, where UHV conditions are maintained. The set-up is shown schematically in Fig. 2.5 (left). Incident x-rays pass through a silicon nitride window and enter the ambient pressure chamber. Photoexcited electrons must be collected as close to the sample as possible to minimize scattering due to the strong interaction of electrons with the surrounding gas and ensure a good signal. Thus, the sample is situated ~0.5 mm from a 0.33 mm diameter aperture, as shown in Fig. 2.5 (right), which serves as the entrance to the differentially pumped system of electrostatic lenses. This is the first of three apertures, 2 mm in diameter, that connect the differentially pumped chambers that systematically reduce the pressure in stages until UHV conditions are reached at the electron analyzer. The total pressure differential is about eight orders of magnitude. In order to control the humidity at the sample to the point of water condensation (Fig. 2.6, right), the sample can be cooled to 100 K by a continuous flow of liquid N₂, or resistively heated with a button heater to 1000 K.

2.3. Core level spectroscopy

Core level spectroscopy, including XPS, XAS, and XES, provides an approach to study the chemical state, local geometric structure, nature of chemical bonding, and dynamics in electron transfer processes centered around one atomic site via the mechanisms of x-ray induced core hole creation and decay. No XES measurements are presented in this work, but the technique is described for completeness, and as background for the theoretical XES.
Figure 2.7: Creation of core holes by photons matched to the binding energy of a core electron, which carries information about its local chemical and electronic environment.

Core holes are created through ionization (XPS) and excitation (XAS) processes stimulated by the absorption of incoming (synchrotron) light with energy matched to the binding energy of a core electron as shown in Fig. 2.7. This absorption causes the core electron to be excited to a bound unoccupied state or to the continuum where it will become a free particle. The core hole decays by radiant and non-radiant processes. After ionization, the absorbing atom is in a highly excited state due to the creation of a core hole. Soon thereafter (A few femtoseconds for light elements) the atom relaxes via core hole decay. Non-radiant de-excitation of core holes forms the basis for Auger Electron Spectroscopy (AES), while radiant decay is studied in XES, both of which provide tools for probing the occupied electronic structure of a model system.

The resulting excitations and relaxations, depicted schematically in Fig. 2.8, form the basis for the various core level spectroscopies. The participating electrons and photons carry important information about the unique chemical and electronic environment of the system to the detectors and displayed to the scientist as a spectral signature.

Figure 2.8: Schematic illustration of the excitation/ionization processes of the core level spectroscopies: XPS, XAS and XES,
2.3.1. X-ray Photoemission

XPS is based on the creation of a core hole via ionization and provides a method to study the geometric, electronic and chemical properties of a sample [39]. In XPS, photons with sufficient energy $h\nu$ are absorbed by a system causing core electrons to be ejected from the sample. If the energy of the photons, $h\nu$, is larger than the binding energy ($E_{BE}$) of the electron, the excess energy is converted to kinetic energy (KE) of the emitted photoelectron. Knowledge of the incoming photon energy ($h\nu$) and the work function ($\phi$) of the sample and measurement of the kinetic energy via an electron analyzer make it possible to calculate the binding energy according to:

$$E_{BE} = h\nu - KE - \phi.$$

2.1

XPS provides information about the chemical, geometric and electronic state of adsorbed species and their coordination to the surface. Changes in an atom’s chemical environment are indicated by binding energy shifts and peak width variations. Since binding energies of core electrons are characteristic for each element and are affected by the chemical environment, XPS allows for a determination of the atomic composition of a sample and the chemical state of a certain element, as well as electronic structure and band structure. In many cases chemical shifts can be used to draw direct conclusions on the local coordination in a system and the electronic change upon adsorption.

The core ionization process in XPS can also be equated to a core-excitation to the Fermi level; in this way the XPS binding energy of an atomic core-level defines the onset of the corresponding XAS edge.

2.3.2. X-ray Absorption

An XAS spectrum reflects the absorption intensity as a function of the incoming photon energy. Near Edge X-ray Absorption Fine Structure (NEXAFS) corresponds to the portion of the absorption spectrum that includes the peaks before the ionization edge and the next 15-20 eV above it in energy, and thus probes bound states and low energy resonances in the continuum. The Extended X-ray Absorption Fine Structure (EXAFS) region encompasses roughly 20 eV to several hundred eV past the x-ray edge and corresponds to an outgoing electron well above the ionization continuum [36]. The particular chemical and local environment of the atom of interest results in a pronounced oscillatory fine structure in the XAS spectrum in this energy range. In this work XAS measurements are confined to the NEXAFS portion of the fine structure which encodes important information about the electronic structure around the atom of interest.

In XAS, a core electron is excited into unoccupied atomic or molecular orbitals at or above the Fermi level, leaving the system in a core-excited final state. An excitation to the Fermi level marks the onset of the XAS spectrum and corresponds in energy position to
the XPS binding energy. The relationship between XAS, XES and XPS binding energy for an O1s core hole is shown Fig. 2.9. The presence of the core-hole, as well as of an excited electron in a previously unoccupied state, provokes a response of the remaining electrons. The core-hole final state modifies the orbital structure, which leads to changes in the total energy and electronic structure of the system. The subsequent changes in energy position and spectral shape can be accurately estimated with the Z+1 (equivalent core) approximation, which considers the effect of a core hole on the valence states as nearly equivalent to placing an extra unit charge on the nucleus. In this picture, a core-ionized atom will have similar chemical properties to the next element in the periodic table [37,38].

Figure 2.9: Relationship between XAS, XES and XPS binding energy for an O1s core hole.

Due to the localization of the core hole created at a certain atomic site, and the dipole selection rule for transitions, excitation of a core s-electron provides a means to project the density of unoccupied p-states (see Fig. 2.9) on the atom of interest. The number of unoccupied energy levels in the initial state gives the total intensity of the spectrum, while the spectral shape reflects the density of states for the core-hole system. In this way XAS provides element-specific information about the density of unoccupied states, local atomic structure including molecular orientation, the nature, orientation, and length of chemical bonds as well as the chemical state of the sample. Due to the dipole selection rule, the absorption cross-sections show a polarization dependent angular anisotropy [36]. Polarization dependent XAS measurements therefore make it possible to determine the orientation of molecular adsorbates, including directionality of hydrogen bonding in an adlayer, information often unattainable by other spectroscopic probes. In paper II this particular feature is exploited to derive a detailed picture of the structure of monolayer water on Cu(110), including the orientation of the hydrogen atoms.
2.3.3. X-ray Emission Spectroscopy

In XES the core hole created by an XA process is filled by the decay of a valence electron into the lower-lying core hole and the energy is conserved by the emission of an x-ray photon of matching energy. This technique can be made surface sensitive through a selective, resonant excitation of a core-electron of a specific atomic site of an adsorbate. Due to the localization of the core-hole, XES provides a detailed element-specific picture of the local electronic structure around a given atomic site with no contribution from the much larger number of atoms in the substrate. The emitted radiation is dominated by the decay of valence electrons from the same atomic center. XES therefore probes the occupied valence states in an atom-specific projection.

In the case of highly oriented adsorbate systems, angular-dependent XES enables the separation of states of different symmetry of the involved orbitals. An important consequence is that one can study states of symmetry which result solely from the chemical bonding. The maximum x-ray emission is generally found in the direction perpendicular to the spatial orientation of the involved atomic p-orbitals. By switching the direction of detection from normal to grazing emission, orbitals of different spatial orientation are probed. For example, for the case of N\(_2\) perpendicularly adsorbed, e.g., on Ni(100) [40], in normal emission geometry, only valence states of \(\pi\)-symmetry contribute to the x-ray emission signal, whereas in grazing emission geometry both \(\pi\)- and \(\sigma\)-orbitals are probed; \(\sigma\)-states can be extracted from the total signal by a simple subtraction procedure.

Together these techniques offer direct information about the structure and bonding in water-metal systems. Here they have helped piece together a consistent picture of the structure of water on Cu(110) (Paper III) and the OH+H\(_2\)O mixed phase on Pt(111) (Paper VI) and, in doing so, illustrated fundamental differences between the interaction of water with open and close-packed metallic surfaces, as well as the influence of adsorbed hydroxyl on water-metal bonding.
Chapter 3

Density Functional Theory

There is an oral legend that P.M. Dirac’s response to Schroedinger’s equation for the electronic wave function $\Psi$ and its validation for simple systems like He and $H_2$ was that, “Chemistry had come to an end – its content was entirely contained in that equation.” Dirac is also said to have added, “Too bad, that in most cases, this equation is far too complex to allow solution.”

The development of density functional theory (DFT), the contribution for which Walter Kohn shared the 1998 Nobel Prize in Chemistry, has opened important and previously unexplored aspects of nature to the researcher which lay testament to the fact that chemistry is, indeed, alive and well. Today, core level x-ray spectra, equilibrium geometry, and other details of chemical interaction including the details of hydrogen bonding in aqueous solutions, can be computed within the framework of density functional theory (DFT). The combination of experimental and theoretical results makes it possible to derive a detailed picture of the molecular orientation and nature of the chemical bonding of an adsorbed layer on a well-defined surface, which is of immense relevance to a number of reactions in heterogeneous catalysis.

The main idea of density functional theory is that a given system of interacting electrons can be completely described via its density instead of its many-body wave function. For N electrons in a solid, which obey the Pauli principle and repel each other via the Coulomb potential, this means that the system depends only on three spatial variables rather than 3*N degrees of freedom. The idea is based on the Hohenberg-Kohn theorems and is realized through the Kohn-Sham equations [41], which are introduced in the following.

3.1. Hohenberg-Kohn theorems

The first Hohenberg-Kohn theorem (1964) states that the electron density $\rho(r)$ of any system determines the external potential $V_{\text{ext}}$ and, consequently, the Hamiltonian of the system since the cusps of the density give nuclear positions and $| \nabla \rho(r) |$ gives the nuclear charge. By knowing $\rho(r)$, all properties can be computed and the ground state energy $E_0$ is furthermore obtained as a functional of $\rho(r)$. The second Hohenberg-Kohn theorem shows that the ground state energy of a system can be expressed uniquely as a functional of the electron density. Based on these theorems, Kohn and Sham [41] introduced a method to minimize the energy functional $E[\rho(r)]$ by varying $\rho(r)$ for N electrons using a variational method. They separated $E[\rho(r)]$ into
Here, $T_0[\rho]$ is the kinetic energy of a non-interacting electron gas with the same density as the real system, moving in an external potential $V_{\text{ext}}$. $U_{\text{cl}}$ represents the pure Coulomb repulsion (electrostatic potential) between electrons and $E_{\text{xc}}$ is the remainder or exchange and correlation term, which contains all of the complicated interactions not accounted for in the other terms. These interactions, which must be approximated since the many-body problem cannot be solved exactly, include: electron exchange, electron correlation between interacting electrons, a correction to $T_0[\rho]$ for a real interacting system to obtain the actual kinetic energy $T_e$, and a self-interaction correction introduced by the Coulomb potential.

The simplest standard expression for the exchange correlation term is the Local Density Approximation (LDA) [41,42], which assumes the exchange-correlation density at each point in the system to be the same as that of a uniform interacting electron gas of the same density. While many ground state properties (lattice constants, bulk moduli, etc.) are well described in the LDA, the dielectric constant is overestimated by 10-40% in LDA compared to experiment. This overestimation stems from the neglect of a polarization-dependent exchange correlation field in LDA. An improvement over LDA comes with the generalized gradient approximation (GGA) which accounts for the variation in the electron density with additional terms that depend not just on the density at $r$, but also the inhomogeneity in the density at $r$. Widely used functionals such as PW96 [43], BLYP [44], B3PW91, etc., are examples of these models.

### 3.2. Spectra Calculations

Calculations of x-ray absorption (XA) spectra and x-ray photoemission (XP) binding energies were performed with gradient-corrected DFT implemented in the StoBe-Demon code [45]. In all calculated x-ray spectra the exchange-correlation contributions were estimated using gradient-corrected exchange and correlation functionals of Becke [46] and Perdew and Wang [47]. The spectra are generated using the transition potential method of Slater [48,49], for which it can be shown that relaxation effects are included to second order. The energy levels and the transition matrix elements between initial and final states are obtained by diagonalizing the Kohn-Sham matrix constructed by orbitals where the core ionized or excited electron has been partly removed [49].

#### 3.2.1. XAS

To generate XA spectra, core and valence relaxation is modeled by removing half a core electron from the core-excited atom. The half-core hole approach accounts for relaxation up to second order and reproduces the core-level excitation energy to within 2 eV of the experimental value (first-row atoms). In the spectrum calculation the normal molecular basis set is augmented by a large diffuse basis (~150 functions) to improve the description of the Rydberg and continuum states [50]. This enables an accurate description of the transitions for a core-excited system with DFT, since the Hohenberg-Kohn theorem
is valid for any state provided it is variationally well defined. The Kohn-Sham matrix is constructed in this extended basis using the optimized half-core-hole density and diagonalized to give the set of unoccupied levels for the excitations. Since the half-core hole approach contains information on both the initial and final state, we can use the same orbitals to describe both. This allows the absorption process to be simplified to a single particle model as in Fig. 2.8, and so that a computationally expensive state-by-state determination of the excited state wave functions and evaluation of the cross sections between non-orthogonal wave functions is not necessary. Instead, the orbitals from the transition potential optimization represent both initial and final states, so the resulting oscillator strengths are obtained as simple orthogonal transition moments with the $1s$ orbital, i.e.

$$I_{1s\rightarrow f} = \frac{2}{3} \frac{\omega_{1s\rightarrow f}}{\langle \varphi_{1s} | \mu | \varphi_{f} \rangle^2}$$

where the one-electron transition is from the initial $1s$ orbital $\varphi_{1s}$ to the final orbital $\varphi_{f}$ with the energy difference $\omega_{1s\rightarrow f}$. The resulting XA spectrum consists of a discrete set of energy levels, each with an associated oscillator strength and line broadening. By convoluting the resulting oscillator strengths, $I_{1s\rightarrow f}$, with Gaussians of linearly increasing full width at half maximum (fwhm), we can simulate the instrumental-, life-time-, and vibrational broadening of an experimental spectrum. For the water metal systems presented here, XA oscillator strengths were broadened with a constant fwhm below the ionization potential (0.7-1.0 eV) and a linearly increasing value up to a maximum (8-14eV) over a 10 eV interval above it, after which the fwhm was kept constant.

The final XAS energy scale for the computed spectra is corrected for relaxation effects through the $\Delta$Kohn-Sham approach [51, 52] and for the relativistic O 1s shift of $+0.33eV$ [53]; in this work the shift in energy is routinely checked against the resonance in the in-plane XA spectrum at 540 eV which is the spectral “fingerprint” of the intermolecular H-bond network of water [54]. The energy of this resonance is constant for water adsorbed molecularly on a range of metal surfaces as well as in solution and for ice [53].

Computed and measured XA spectra were used to derive and quantify the structural details of different coverages of water adsorbed on Cu(110) (Paper II, III) and the mixed OH+H₂O layer on Pt(111) (Paper VI).

### 3.2.2. XES

The theoretical XE spectra were generated based on the oscillator strengths computed from the ground state orbitals, as the square of the matrix element of the dipole transitions from the occupied valence state involved in the decay to the $1s$ core level. As for the computed XAS, the same potential, obtained from the ground state wave function, describes both the initial and sequence of final states [56]. The KS orbital eigenvalues are used as binding energies for the occupied valence states and the highest occupied molecular orbital (HOMO) represents the Fermi level. Due to a fortunate cancellation of errors from neglecting both core and valence relaxation effects [56,57], this ground state picture gives good agreement with experiment [56,58]. Here the resulting spectra are convoluted with Gaussian functions of 1.0 eV full-width-at-half-maximum (fwhm) to
Density Functional Theory
mimic the experimental vibrational broadening.

Due to the dipole selection rule, the XE process for an $O\ 1s$ excitation projects the local $2p$ character onto the spatially localized core orbital, making it a useful tool for population analysis of the $2p$ orbitals [59,60]. While theoretical charge populations are more generally computed using Mulliken population analysis, theoretical XES intensities provide similar results at a reduced dependence on choice of basis set. By integrating each $p$ component ($p_x, p_y, p_z$) of the XES and comparing to the corresponding intensity for the free water molecule or OH ions in solution, we can derive how water and hydroxyl, respectively, change their orbital occupation to bond with a metal surface.

3.2.3. XPS

$O1s$ XPS binding energies were likewise computed in the $\Delta$Kohn-Sham approach [51], as the energy difference between the ground state and core ionized system. Binding energies were corrected for the work function of Cu(110) as well as the relativistic $O\ 1s$ shift [53]. Relative binding energy shifts between water molecules in different geometric configurations were, however, what was used here to verify or reject different possible structure models, rather than absolute values.

3.3. CSOV Analysis

Constrained space orbital variation analysis (CSOV) provides a means of isolating the different channels of orbital interaction and analyzing their contribution to the bonding of water on metal surfaces. This is executed with a step-by-step relaxation of the molecular orbitals (MOs) and combined with an analysis of the changes in occupied orbital structure and total energy of the system at each stage [61,62].

**Figure 3.1:** CSOV steps shown for the case of a water monomer bonding to a metal surface.
The general steps in the CSOV analysis are shown for the case of a water molecule adsorbed at a metal surface in Fig. 3.1. The steps in the ladder represent the interaction energy associated with each CSOV step, with an energy reference defined for the bonding units at long distance in order to obtain separated orbitals. In the first CSOV step, the non-interacting fragments are combined in their nominal bonding geometry but with all their molecular orbitals frozen (FO) as determined for the separated system. This brings out the initial interaction due to exchange and Coulomb interactions (electrostatics) with no orbital rearrangement allowed. In the second step, the units are allowed to polarize; i.e. rotations between occupied and unoccupied orbitals on each unit are allowed. Next, charge transfer between units is turned on systematically by allowing mixing of the occupied orbitals of one unit with the unoccupied orbitals of the other. In the last step, the system is fully relaxed; i.e. polarization and charge transfer are allowed.

In order to isolate the interaction of the center O-bonded water molecule with the metal surface from that of the surrounding water or OH+H\textsubscript{2}O layer, only the center O-bonded H\textsubscript{2}O molecule is separated from the rest of the system (surrounding OH and/or H\textsubscript{2}O and metal substrate) and is frozen in the first step for cases when full adlayers are considered. In this construct, the interaction energy ($\Delta E_{\text{int}}$) associated with the final (relaxed) step includes contributions from H-bonding ($E_{\text{Hb}}$) to the surrounding OH groups and water-metal bonding ($\Delta E_{\text{ads-tot}}$). As a result, and because the reference energy is defined for a system where surrounding OH and H\textsubscript{2}O are already bonded to the metal surface, values of $\Delta E_{\text{ads}}$ cannot be directly compared to the binding energy for water monomers or overlayers on these surfaces. Nonetheless, the relative trends provide important qualitative insight on the influence of adsorbed OH on the balance between H-bonding and water-metal bonding that defines the structure at the interface.

CSOV analysis is carried out for water on Pt(111), Cu(111), and Cu(110) to help understand the basis for the different degree of wettability on these surfaces in Papers I and for water plus hydroxyl in Paper VII to estimate how the different energetic contributions to water-metal bonding are affected by the presence of OH at these surfaces.

### 3.4. Charge Density Differences

For a more detailed picture of electronic charge rearrangement of water adsorbed on different metal surfaces, we can complement the theoretical core level spectra by visualizing how charge moves along different bonding directions with charge density difference (CDD) calculations of the computed wave function. CDD plots were generated by subtracting the sum of the electron density of the isolated water layer and metal cluster from the charge density for the water-metal system. Plots computed for the different CSOV steps (see below), e.g. CDD=(relaxed-frozen) or (relaxed-polarized), are helpful in assigning aspects of the charge rearrangement to different interactions in the bonding mechanism. This was used, for example, in Paper I to illustrate the role of the s–electrons in water-metal bonding for flat (111) and open (110) metal surfaces.
Chapter 4

Summary of Main Results

4.1. Wettability of a metal surface

The wettability of a surface, whether it is hydrophilic or hydrophobic, depends on the physical and chemical properties of the surface. Traditionally, the wetting property of a surface has been characterized by the contact-angle of water droplets at ambient conditions. This gives little microscopic insight into the interaction of water with surfaces, which is essential for predicting the reactivity and behavior of catalyst surfaces. To bridge this gap in understanding, a picture of wettability in terms of the ability to form surface-water bonds and the role of electronic and geometric structure effects is elucidated in Paper I. In particular, the interplay between the repulsive interaction between the oxygen (1b₁) lone pair (lp) and the metal d-shell and attractive electrostatic interactions of the lp with the positive metal core is shown to rule the ability to form water-metal bonds; i.e. the wettability of a surface.

4.1.1. Experimental demonstration of the wetting property

The wettability of a surface can be evaluated experimentally with O1s photoemission spectroscopy (T=135K). For water on Pt(111) the photoemission at 532.2 eV corresponds to water in direct contact with the Pt surface and indicates formation of a 2-D water monolayer (Fig. 4.1). The second water layer, characterized by a peak at 533 eV, begins to form above one monolayer as is identified by a continuous shift in peak position toward the higher binding energy after one monolayer. In contrast, other than a tiny chemical shift, no changes are observed in the Cu(111) XPS as a function of coverage, indicating that a 2-D water layer does not form on this surface. However, the wetting behavior on Cu(110) is radically different from that on Cu(111) but rather similar to that on Pt(111), as seen in XPS. As for Pt(111), formation of a 2-D water layer on Cu(110) is evidenced by a single low binding energy species (533.4 eV) below one monolayer. Likewise, the shift in peak position towards higher binding energy (534.4 eV) corresponds to multilayer growth, which for both Cu(110) and Pt(111) occurs only after completion of the first layer. The increased peak width for these surfaces suggests the presence of more than one type of water molecule adsorbed on the surface in the monolayer phase, as expected from the characteristic picture of the nearly flat two-layer structure of water on metals. It is also important to note that only with extreme care to avoid radiation damage and contamination no OH peak (~530 eV) is observed. This indicates molecular adsorption of water with no dissociation at low temperature for all three surfaces. The structure of the intact overlayer on Cu(110) will be discussed in Section 4.3.
Figure 4.1: O1s XPS spectra measured during water uptake on (A) Pt(111), (B) Cu(111) and (C) Cu(110).

The balance between the strength of the O-bonding channel and the hydrogen-bond network that determines the wetting property of a surface can be directly investigated with x-ray absorption spectroscopy (XAS). Each bonding channel for water (O-bonded, H-bonded, H-up) gives rise to characteristic features in the O1s XAS spectrum, which is decomposed with the help of theory into the respective contributions to the signal in Fig. 4.2. The decomposition highlights the influence of the $d$-band position with respect to the Fermi level on bonding. Since Pt has a partially filled $d$-band, the O $lp$ has a mechanism to depopulate into unoccupied anti-bonding Pt $d$-states to minimize Pauli repulsion. This bonding channel is shown in the molecular orbital diagram in Fig. 1.3 and appears in the experimental and computed O-bonded XAS for Pt at 532.5 eV. In contrast, due to its filled $d$-band, no such feature corresponding to unoccupied anti-bonding states appears in the XAS for either Cu surface. Without the possibility to depopulate charge from the O $lp$ into the empty states of the metal, can water wet a noble metal surface?

For Cu(111) the answer is no. The Cu(111) XAS spectrum is completely isotropic; in- and out-of-plane spectra are identical to each other and to 3-D bulk ice, indicating no interaction with the metal substrate, or non-wetting. In accord with these findings, Mehlhorn and Morgenstern recently used STM to show that bilayer formation is not favored on Cu(111) at any temperature [63]. Nonetheless, water may bond to corrugated metal surfaces even when a flat substrate of the same material does not show a wetting layer [1,2]. Thus it is not surprising that our XPS measurements indicate that the growth mode for water on Cu is very different when the (110) crystal plane is exposed (Fig. 4.1). In the XAS spectra for Cu(110) (Fig. 4.2B), the polarization dependence confirms the well ordered 2-D monolayer indicated by photoemission. The larger intensity of the free OH peak at 535 eV for Cu(110) compared to Pt(111) shows that the less favorable H-bonding channel on Cu leaves a fraction of the OH groups pointing away from the (110) surface [64]. We will come back to this in Section 4.3 (Paper III).
Summary of Main Results

**Figure 4.2:** In- and out-of-plane O1s XAS spectra for ice film (top) and water on: Cu(111), Cu(110), and Pt(111) and computed XA spectra for H-bonded (green line) and O-bonded (blue line) water species on Pt(111) and Cu(110). The computed in-plane spectrum for Cu(110) (black line) corresponds to the low coverage phase. Details are provided in the text.
4.1.2. Surface electrostatics and the “d-band model”

The charge rearrangement accompanying the O-bonding between water and metal is given in Fig. 4.3. The redistribution of electrons in the adsorbed water, which is most significant for Pt(111), is interpreted as depopulation of the lone pair into unoccupied metal states and a corresponding gain of charge in the plane of the metal surface. This polarization of the lone pair to reduce the Pauli repulsion between water and the metal allows for O-bonding. It is clear that the rehybridization is much smaller for the Cu surfaces; we attribute this to the fact that this mechanism is frustrated by a filled d-band, so that both bonding and anti-bonding states become occupied.

Due to the geometric corrugation of the (110) surface, however, electronic smoothing at the interface, i.e. the Smoluchowski effect [65], reduces the abruptness in changes in potential energy along the surface. This leads to a loss of charge on Cu atoms in top sites and a gain of charge for Cu in hollow sites (Fig. 4.3B). This enhances the adsorbate-substrate interaction as the smaller charge density on the rows compared to the bulk serves to reduce the 3d-lp Pauli repulsion and make the O-bonding interaction more favorable. This increases the strength of the attractive interaction on Cu(110) compared to Cu(111).

In addition to charge rearrangement, the Smoluchowski effect causes a change in electron density at the (110) surface; its spatial extent is contracted on the top sites and expanded on hollow sites compared to the flat electron density of the (111) surface, as shown in Fig. 4.4. The waviness of the electron density causes the water to feel an effectively lower electron density at the open surface. Using CSOV analysis, we find this contracted electron density contributes to a smaller initial repulsion of a water monomer on Cu(110) compared to Cu(111), 0.18 vs. 0.51 eV.

We also use CSOV analysis to investigate these effects for the center O-bonded water molecule in the H-down monolayer. Without reorganization of the electronic structure, i.e. in the frozen orbital (FO) configuration, we find the initial repulsion is larger on Pt(111) than on isostructural Cu(111), 1.08 eV and 0.4 eV, respectively, due to the larger extent of the more diffuse Pt 5d-orbitals. However, Pt’s partially filled d-band results in an increased ability to rehybridize these orbitals compared to the spatially more compact and filled Cu 3d\textsuperscript{10} shell, so the relaxation energy is also much greater for water on Pt(111) compared to Cu(111); 2.38 eV and 1.45 eV, respectively. For Cu(110) the initial interaction in the frozen orbital (FO) configuration is actually attractive (-0.04 eV). Due to the charge redistribution with the sp-band caused by the Smoluchowski effect, electrostatic attraction to the positive Cu core compensates for the repulsive contribution from the more rigid d-band such that there is effectively no net initial repulsion for Cu(110).

In fact, when we separate the contributions to the relaxation energy from the metal d-band and s-band using CSOV analysis, we see the latter contributes a significantly larger (nearly double) portion of the relaxation energy than the more rigid d-band for both surfaces of Cu. On the other hand, the depletion of charge on the atomic rows of Cu(110) opens the surface for dative bonding without additional energy costs for polarization.
Summary of Main Results

4.1.3. Digging the s-band hole

We can envision the dative bonding proceeds via the O lp “digging a hole” in the s-electron distribution by a polarization of charge away from the metal in a direction perpendicular to the water-metal bond to expose its positive metal core, shown schematically in Fig. 4.5.
We explore this possibility for s-band polarization by using a free electron Li substrate representing a positive metal core and one s-electron. An outward redistribution of charge in the equatorial plane of the metal bonding atom is observed for both Li surfaces. This charge redistribution exposes the charge of the positive metal core and opens the system for electrostatic dative bonding. The reduced charge along the (110) rows provides an opportunity for charge to be polarized away from the metal bonding atom to the adjacent δ⁺ rows (Fig. 4.6B). This eliminates the cost of significant intra-atomic polarization of the Li atoms so that the initial interaction in the FO electronic structure configuration is attractive (-0.06 eV) (Fig. 4.6C). Here we have a mechanistic explanation for the initial attraction (FO) found for Cu(110), which we expect to be valid for corrugated metal surfaces in general.

However, since this mechanism is unavailable for (111) surfaces, the “digging of the s-band hole”, i.e. redistribution of metal s-electrons, must proceed via a different route. For Li(111) this appears as an internal polarization of charge for the Li atoms (Fig. 4.6A), which, similar to the (111) surfaces of Cu and Pt, has an associated energetic cost (+0.05 eV), see Fig. 4.6C. The movement of s-electrons away from the water-metal bond axis appears only after charge transfer between units in the CSOV analysis is allowed. This confirms that it is not simply a polarization effect but is, in fact, the mechanism that reduces Pauli repulsion and facilitates dative bonding.

![Figure 4.5](image_url)  
**Figure 4.5:** Schematic representation of the s-band polarization that facilitates dative bonding.

![Figure 4.6](image_url)  
**Figure 4.6:** CDD plots for a water monomer adsorbed on A) Li(111) and B)Li(110) (center) and C) CSOV energy values for the frozen orbital (FO) and binding energy (BE) of the relaxed systems.
Summary of Main Results

From this study, it is clear that the affinity of metal to water is ruled by the degree of Pauli repulsion between water lone pair and metal $d$- and $sp$-electrons and the attractive electrostatic interaction, which is determined by both the electronic and geometric structure of the substrate. Three main channels are available to deplete charge along the water-metal bond axis, to lower the repulsion and open for electrostatic dative bonding between the O $lp$ and the charged metal core: (i) A large spatial overlap between the $lp$ and $d$-orbitals results in formation of bonding and anti-bonding orbitals. Partial depopulation of the anti-bonding component polarizes water in a manner that significantly reduces the lone pair occupation. (ii) On open $d$-shell metals, the ligand field effect of water alters the stability of axial and equatorial $d$-orbitals, moving charge away from the water-metal bond axis. Closed $d$-shell metals, however, do not allow for this mechanism. (iii) The electron smoothing effect on rough surfaces causes the mobile $sp$-electrons to occupy the space in between the atomic surface rows resulting in depletion of charge on the bonded metal atoms. This reduces the initial repulsion but also opens for a much stronger attractive electrostatic interaction through dative bonding, which allows bonding even in cases where internal $d$-shell rehybridization is unfavorable.

4.2. Structure of Water on Cu(110)

4.2.1. Unexpected water structure at low coverage

A number of experimental studies, particularly with STM, have revealed complicated variations in the observed or proposed structure of the low coverage phase of water at different metal surfaces, from lacy rosettes to chains to non-hydrogen bonded water molecules [66-72]. For Cu(110), STM measurements show a well-defined water structure for water already at low coverage, which the authors propose consists of flat-lying water molecules arranged into chains that zigzag across the rows, along the [001] direction [66]. Our XAS results show a strong low energy resonance in the in-plane XAS at 533.1 eV for D$_2$O on Cu(110) at low coverage, shown in Fig. 4.7 (top), never before observed for a water-metal system.

The O $1s$ XAS for low coverage D$_2$O on Cu(110) and Ru(0001) along with their STM images are compared in Fig. 4.7. The XAS spectrum for the ice surface is also given to illustrate the characteristic resonances associated with uncoordinated OH in asymmetrically H-bonded molecules at 535 eV and of a H-bonded water network at 540 eV [54, 64, 73]. The XAS signature of intermolecular H-bonding (540 eV) appears in all spectra, indicating immediate clustering of water molecules on the Cu(110) and Ru(0001) surfaces. Intensity is also observed at 535 eV in the in-plane XAS spectrum for Ru(0001) due to uncoordinated OH at the edges of the small isolated clusters that water aggregates into at low coverage on this surface (see Fig. 4.7, XAS and STM image). However, this feature is not discernible in the in-plane XAS on Cu(110). This is due to the fact that water assembles into zigzag chains on the open surface of Cu (Fig. 4.7 STM [66]), as opposed to the isolated clusters observed on flat surfaces such as Cu(111) [70] and Ru(0001) [74].
Figure 4.7: Left: Experimental in-plane XAS for top: 0.3 ML D₂O/Cu(110), center: 0.25 ML D₂O/Ru(0001) [74], and out-of-plane XAS for ice surface (bottom) [54]. Characteristic features associated with A: uncoordinated OH at 535 eV and B: hydrogen-bonding between water molecules at 540 eV are denoted with arrows. A1 (533.1 eV) is assigned to uncoordinated OH in a unique, hitherto unobserved bonding arrangement. Right: STM images showing that water hexamers assemble into chains at low coverage on Cu(110) [66] and remain isolated on Ru(0001) [74].

The most curious aspect of the in-plane XAS of water on Cu(110) is the strong low energy resonance at ~533.1 eV. This low energy feature is seen for OH and atomic oxygen at metal surfaces, but the single XPS peak (not shown, see Paper II) indicates that water adsorbs molecularly at the Cu(110) surface [75]. To the best of our knowledge, the resonance at 533.1 eV has never before been observed for a water-metal system. In fact, in our extensive structural search for a representation of water at low coverage on Cu(110), from dimers and trimers to hexamers anchored over different adsorption sites, no model could reproduce this experimental feature. The best match to experiment corresponds to the (optimized) hexamer structure proposed by Yamada and co-workers based on their STM results [66]. The computed in-plane XAS for a small cluster model of this structure including only one water hexamer are shown in Fig. 4.8A. The lowest energy feature in the computed spectrum appears at 535 eV (Fig. 4.8A) and corresponds to uncoordinated OH parallel to the surface, which is similar to all measured systems with such OH groups [64,73]. While many aspects of the experimental spectrum are well reproduced, the anomalous feature at 533.1 eV is still blaringly absent.
Summary of Main Results

Figure 4.8: Experimental and computed in-plane XAS for (A) low energy hexamer modeled after the structure proposed by Yamada et al. [66] (Fig. 2) and (B) a structure representing the edges of two such adjacent hexamers, shown schematically in the figure.

If this XA resonance is not related to water-Cu bonding, it must be related to water-water interaction. Drawing from the STM observations and based on the spectra corresponding to the structure proposed by Yamada et al. [66], we consider how such hexamers could be arranged in a zigzag pattern, to consider possible unexpected water-water interactions leading to this feature. In order to form extended chains, the uncoordinated hydrogen atoms protruding from a six water ring must face those of the neighboring hexamer. In Figure 4.8B, we see that it is precisely this interaction that produces the low energy resonance in the in-plane XAS. The resonance at 533.1 eV appears in the XAS computed for these water molecules also in the absence of the Cu substrate, confirming that this feature is due exclusively to the unusual bonding arrangement of water molecules.

In Figure 4.9 we see that the large spatial extent of the excited state molecular orbital on the core-excited oxygen (shown in red) involved in the XAS transition leading to the low energy feature clearly encompasses the hydrogen atom protruding from the neighboring hexamer along the [001] direction in this configuration. The bonding arrangements that produce the low energy resonances are also identified in the figure. The polarization dependence of the experimental XAS shows this interaction exists along both the [001] direction and the [110] direction, which along with the STM images provide helpful boundary conditions for how the hexamers arrange themselves along the surface. These conditions are satisfied by parallel rows of identical hexamers oriented along the [001] direction, stabilized by an unusual water environment with hydrogen atoms facing each other over the troughs, separated by a zigzag pattern of clean Cu sites (Fig. 4.9).
Figure 4.9: Low coverage structure of water on Cu(110) (bottom). Cu atoms in the first rows are light grey and second layer atoms are indicated with a darker color and smaller size. Interactions associated with the low energy resonance at 533.1, and orbital contour plots showing the spatial extent of the excited O orbital are indicated in (A) and (B). In the contour plots, the core-excited O is indicated in red, while blue and red lines indicate different phases of the wave function. (C) Illustration of how the Smoluchowski effect provides an attractive electrostatic water-metal interaction to stabilize the unusual structure.

Since the opposing hydrogen atoms are positive, this interaction at the hexamer edges will lower the energy of the excited state. This is similar to the case of solvated electrons, where the hydrogen atoms of water molecules near the cavity containing the electron rotate toward the center of the cavity to interact with and solvate the extra electron [76 and references therein], which lowers the energy of the bonding component of the state. In the present case, the negative troughs of the (110) surface play the role of the solvated electron and electrostatically stabilize this unusual bonding configuration for water, which would otherwise be a high energy defect as, e.g. in the case of Bjerrum defects in ice [77]. This produces a state near the Fermi level in the in-plane XAS, as opposing uncoordinated OH groups protruding from neighboring hexamers hybridize with the “free electron states” of the δ troughs creating an attractive pocket for the electron excited in the XAS. This leads to an energy lowering of the XAS resonance associated with uncoordinated OH from 535 to 533.1 eV. Such low-energy states have also been observed in computed XAS of very asymmetric liquid water structures [78] obtained by partially neglecting charge repulsion when generating water structures from diffraction data [79]; also in this case
Summary of Main Results

pockets with OH groups pointing towards each other were found to lead to computed very low-energy excitations [78].

The stability of the structure can be rationalized based on electrostatic considerations in water-metal and water-water bonding. Due to the Smoluchowski effect, the normally repulsive proton-proton is balanced by the gain of charge on the troughs, which spills over from top sites to smooth the potential energy at the corrugated surface. Further, the water molecules on the edges of neighboring hexamic units within a chain (along the [001]) produce net dipoles in opposite directions. Thus, stabilization of this unusual geometry allows an attractive dipole interaction to enhance the interaction between the neighboring hexamers, which favors propagation of the chain structure. Thus regions of low electron density at the surface (rows) favor water-metal interaction, while dipole-dipole attraction is favored at regions of higher electron density (troughs), which can stabilize atypical proton geometries. Together, these factors provide the electrostatic driving force for water to take an unexpected turn in the low coverage phase, and form an interesting structure hitherto unobserved at a metal surface. On flat surfaces like Ru(0001), in the absence of surface-tailored electrostatics, water hexamers remain isolated at low coverage.

4.2.2. The water monolayer: H-up, H-down or both?

In Paper III we build on some of the clues gained from the wettability study (Sect. 4.1 and Paper I), to build a detailed picture of the structure of water adsorbed on Cu(110) and, by connection to the low coverage phase (Sect. 4.2.1 and Paper II), see how water reorients at higher coverage. To recap: First, the FWHM of the peak in the XPS uptake measurements indicate at least two different bonding species of water exist at monolayer coverage (Fig. 4.1). Second, the d-band model and electron smoothing at the metal surface suggests that this bonding occurs on top sites. Finally, in XAS (Fig. 4.2), we see the free OH peak with significant intensity at 535 eV, which indicates that a fraction of uncoordinated OH groups point away from the substrate. Total energy analysis indicates the H-down hexagonal bilayer is more favorable for water on Pt(111), Cu(111) and Cu(110), and water has been found to adsorb in a H-down configuration on Pt(111) and Ru(0001) [17,80]. However, the barrier for H-up flipping has been found to be very small for water-metal systems [24]. Is the H-down model valid in general for water-metal adsorbate systems, or can the observed variation in water bonding at Cu(110) and Pt(111) result in a different low energy structure for water on an open surface? To put this issue to the test, XAS, XPS, LEED, Infrared Reflection-Absorption Spectroscopy (RAIRS) and DFT were used to study the monolayer water/Cu(110) system in detail.

LEED is a classical surface science tool utilizing the diffraction of low energy electrons from the surface to determine the long-range structure of an adsorbed layer in terms of atomic size, orientation and symmetry of the unit cell [81]. For monolayer water adsorbed on Cu(110), LEED shows an overlayer pattern with a large (7x8) unit cell and indicates possible corrugation of the water layer. The (7x8)-H2O/D2O LEED pattern shows weak spots (relative to water on Pt(111) and Ru(0001)), indicating that the water structure is not pinned into close registry with the substrate but rather likely consists of a hexagonal water network, whose structure is distorted to optimize the water-Cu(110)
interaction. The complex LEED pattern supports a distorted hydrogen-bonded network such as to maximize interaction with the open (110) surface. It also suggests that previous reports of a c(2x2) LEED pattern for water at this surface was caused by beam damage to the sample, producing OH groups that pin the water layer in closer registry with the Cu(110) surface [75].

As with XAS, RAIRS has its own set of selection rules and unique spectral signatures for characteristic bonding channels at surfaces. The observation of vibrational modes of adsorbates on metallic substrates is subject to the surface dipole selection rule: Only vibrational modes with a dipole moment perpendicular to the surface are IR active and produce a measurable absorption band [82]. The fingerprint of non-hydrogen-bonded OH pointing towards the vacuum is an isolated high frequency “free OH” band at 3680 cm⁻¹ [83]. This band is intense for water adsorbed on Cu(110) but negligible on both Pt(111) and Ru(0001), indicating the presence of H-up water molecules for water on Cu(110). However, LEED cannot give information about exact adsorption sites and atomic positions and RAIR cannot quantify the relative amounts of H-up and H-down water in the structure. For such details, we turn to core level spectroscopy.

Out-of-plane XAS where the E-vector is parallel to the surface normal can distinguish the different directionality of O-H bonds in the H-up and H-down configurations [17]. Fitting of computed binding energy peaks to measured XPS and computed XAS to experiment is invaluable for validation, elimination or refinement of a given structure model. Experimental out-of-plane XAS and spectra computed for H-up, H-down and H-up + H-down configurations on Cu(110) are compared in Fig. 4.10. The strong pre-edge feature at 535 eV in the H-up structure model is the spectral fingerprint of dangling OH directed toward the vacuum [54,55]. Due to interaction with the Cu surface, this feature is absent in the H-down computed spectrum. The experimental spectrum has a main strong peak at 537.5 eV with two low energy features at 533.5 eV and 535 eV. The H-down spectrum reproduces the essential features of the experimental XA data but lacks intensity in the feature characteristic of dangling OH at 535 eV; precisely the energy value at which the H-up spectrum has its greatest intensity. It is clear that both species contribute to the experimental spectrum. But by how much?

A best fit between theoretical and measured XAS (Fig. 4.10) indicates a mixed monolayer with 2/3 (±15%) of the outer layer water molecules in an H-down configuration, and 1/3 with hydrogen pointing up toward the vacuum. Thus we find an H-down:H-up ratio of 2:1 for water on Cu(110). By combining XPS peaks representing the O-bonded, H-up and H-down water species to correspond to the H-up, H-down, and mixed (H-up+H-down) monolayer models, we test this fit. The mixed model is constrained to the fit-derived H-down:H-up 2:1 ratio and the 1:1 ratio between number of water molecules in the inner layer with respect to outer layer determined by XAS, and clearly represents the best fit to experiment.

If the water-metal interaction were purely electrostatic, the resulting layer would be likely take the form of a H-up dipole oriented layer. Significantly more hybridization is required in reorientation to the H-down structure, but energy is gained in the H-bonding to the surface. Moreover, an additional attraction arises between the H-up and H-down water
Figure 4.10: Comparison of computed spectra and binding energies for the H-up, H-down and mixed layer structure models to experimental out-of-plane XAS (left) and XPS (right) for monolayer D$_2$O adsorbed on Cu(110). Solid red curve represents the computed XA spectra or fitted XPS peak while black circles denote the measured data; the thin black, small dashed and thicker dashed XPS curves correspond to the O-bonding, H-down and H-up water species, respectively. In the mixed model, XPS peak amplitudes are constrained to the XAS best fit H-down:H-up intensity ratio of 2:1.

molecules, further encouraging a mixed layer, while the energetic barrier for H-up/H-down flipping is very small (0.76 eV for Pt(111) and 0.55 eV for Ru(0001)) [24]. Thus, the H-up/H-down mixed layer on Cu(110) is likely to form not only from the disorder induced and facilitated by the open (110) surface but also from an energetic balance between cost for hybridization, energy gain in bonding to the surface and the dipole interaction. In fact, the energetic cost for hybridization accompanying the final CSOV step, in which charge transfer and Coulomb interaction are allowed, is significantly higher for the H-bonded water compared to the O-bonded water; 0.73 eV compared to 0.4 eV (see Fig. 4.11).
Figure 4.11: Interaction energy for O-Cu and OH-Cu bonded monomers on Cu(110) based on CSOV analysis: A) frozen orbital energy (FO) B) polarization of water, C) polarization of Cu(110) surface, and D) relaxation energy (including charge transfer).

The significant orbital rehybridization required to facilitate bonding indicated by the large interaction step for the charge transfer step of the CSOV is reflected in the charge density difference plot for the H-bonding water species, which is compared to the O-bonding channel in Fig. 4.12. For the O-bonded species, the charge density is decreased along the O-Cu bond in order to minimize Pauli repulsion between the O $lp$ and the Cu $3d$ states. The rearrangement of charge along the Cu-HO bond is more dramatic, in accord with the larger hybridization required for formation of this bond. The bonding involves all three atoms and results in three molecular orbitals that are different in the number of nodes. The lowest orbital is bonding and the highest is anti-bonding between Cu and hydrogen. The gain of charge along the Cu-H bond is caused by charge donation from the Cu substrate to the OH anti-bonding orbital of water. The H-Cu bonding produces a broad band of hybridized anti-bonding states near the Fermi level in the computed O $2p$ XES (not shown). The node between the O and Cu in the middle orbital leads to a non-bonding interaction, which leads to a contraction of charge along the OH bond away from the H and toward the O, so that H-Cu bond formation is accompanied by a weakening of the internal OH bond of water. An increase in charge in the equatorial plane of the Cu atom facilitates the depletion in the axial direction to reduce repulsion from the orbital overlap with the hydrogen. Collectively, these changes are responsible for the larger CSOV energy step to the relaxed state for the H-bonded water compared to the O-bonded water molecule (Fig. 4.11D).

As the water coverage approaches 1 ML, the surface becomes too crowded for all water molecules to remain in the fully O-bonded structure which characterizes the low coverage phase on Cu(110) (Sect. 4.2.1). Above 0.5 ML, the first chemisorbed molecules remain flat but begin to donate 2 H-bonds, while additional water molecules reorient with the OH perpendicular to the surface, forming either 1 (H-up) or 2 chemical bonds (H-down). In total, the stability gained from H-Cu bond comes with an energetic cost for the significant rehybridization required. As the coverage increases and the water density increases, appearance of H-down water provide extra bond energy, while H-up molecules complete the hydrogen bond network with little cost for polarization.
Moreover, lattice mismatch between the (7x8)-water structure and Cu(110) can introduce a significant strain on the H-bonding network which in turn can be relaxed by introducing both H-up and H-down configurations. It is also likely that there are sites in the (7x8)-water structure that directly disfavor a hydrogen-copper interaction, resulting in H-up configurations. In contrast to the behavior of water on close-packed surfaces, open surfaces can provide sites where the energy difference between H-down and H-up is nearly zero, or favors H-up, and both H-down and H-up structures can therefore coexist.

4.3. Hydrophobic water?

Why does determination of whether the hydrogen atoms in interfacial water point up or down deserve so much effort? The reason is that proton orientation in interfacial water has important consequences relevant to a range of atmospheric and biological phenomena as well as electrochemistry. The structure of water at surfaces has important implications for reactivity and multilayer growth of e.g. crystalline ice, which provides a surface for heterogeneous catalysis in interstellar medium and chemical reactions related to ozone depletion in the stratosphere. The ability of water to restructure due to the interaction with additional water layers provides insight to elementary steps for the many reactions in heterogeneous catalysis where H$_2$O, OH, or H act as intermediates, as well as associated barriers. Recently, experiments have revealed a hydrophobic water monolayer on metal surfaces, including Pt(111), Pd(111) and Ru(0001) [83,84,86], where the first monolayer remains exposed to vacuum even at 80 layers of crystalline ice growth. The hydrophobic property of the water layer has been attributed to the H-down water structure at these surfaces. The cathodically ordered layer favoring hydrogen production from water at a metal surface [87] is the H-down configuration, while the H-up layer is favored under anodic polarization. Thus, correlation between the structure and wetting property of a water surface has important implications for the interaction of water with surrounding solution in the electrochemical double layer. In Paper IV we present a chemical bonding picture showing explicitly how the preferential microscopic orientation of the first wetting layer, in fact, defines macroscopic properties, in particular the wetting property.
Figure 4.13: H-bond strength between water layers, in gas phase and adsorbed on Pt(111) (represented with a 7 atom Pt cluster) for: (A) H-up and (B) H-down monolayer, and the mixed OH+H$_2$O layer, for (C) H$_2$O-H$_2$O and (D) H$_2$O-OH bonding. The red and light blue circles indicate H$_2$O and OH, respectively.

To explore the relationship between the structure and the wetting property of the water monolayer, we begin by computing the H-bond strength for a second layer water molecule bonding with the different water molecules in the first monolayer in the H-up, H-down and the H$_2$O/OH coadsorbed layers on Pt(111), with the distance between the adlayer and the Pt surface kept constant. The results and a comparison with the isolated layers in the absence of the Pt substrate are shown in Fig. 4.13.

In the H-up monolayer, the H-up water molecule donates an H-bond of 0.22 eV to a second layer water molecule, both in the isolated layer and when adsorbed on Pt(111) (see Fig. 4.13A). Thus, the hydrophilic interaction between first and second layer water molecules is unhindered by the (weak) interaction of the H-up molecule with the Pt(111)
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Surface. While the ability of the O-bonded water in the H-up layer to accept H-bonds is weakened by its interaction with the Pt surface, it can still bond with second layer water with significant interaction energy (0.13 eV). Consequently, the average H-bond energy to additional water layers is \( \sim (0.22\text{eV}+0.13\text{eV})/2=0.17 \text{ eV} \); comparable to H-bonding between water molecules in an extended network, \( \sim 0.22 \text{ eV} \) computed using the same approach. Thus, continuous formation of thick ice multilayers should proceed on the H-up monolayer in a layer-by-layer fashion. On the contrary, bonding to the Pt surface essentially eliminates the ability of the O-bonded water (and hydroxyl group) to accept a hydrogen bond from second layer water when adsorbed in the H-down layer (\( \sim 0.02 \text{ eV} \)) or the mixed OH+H\(_2\)O adlayer on Pt(111) (0.06 and 0.02 eV for H\(_2\)O and OH, respectively), see Fig. 4.13B. We therefore anticipate experimental evidence for a similarly hydrophobic water/hydroxyl mixed layer on Pt(111), and many other surfaces which favor the flat, fully coordinated bonding geometry.

The origin of the hydrophobic monolayer on Pt(111) has been connected to the lack of uncoordinated OH in the H-down layer that is favored at this surface [24,84]. Yet, we find that the ability of the H-bonded (H-down) water molecule to accept H-bonds from second layer water molecules is unhindered by the presence of the Pt surface (Fig. 4.13B top). Thus, a water molecule coming down towards the water-metal contact layer is insensitive to whether the non-O-bonded waters are H-down or H-up; the H-bond strength to both of them is very similar. The O-bonded water, however, is a very different story. The inability of the O-bonded water in the H-down configuration to accept an H-bond from incoming water limits the average H-bonding between water layers to \( \sim 0.10 \text{ eV} \) (\( (0.18\text{eV}+0.02\text{eV})/2=0.10 \text{ eV} \)), so that H-bonding within ice crystallites is favored over interaction with the first wetting layer.

To facilitate water-metal bonding, Pt d-states polarize charge away from the bond axis while the water lp depopulates to reduce Pauli repulsion [17]. Charge population analysis of the O lp (estimated by integration of the \( p_z \) component of the computed XES, normalized to \( p_z =2 \) for the free water molecule) shows that the ability of the O-bonded water to H-bond to incoming water is also reflected in the electronic structure. The degree of O lp depopulation, which is related to the ability of the water molecule to act as an acceptor, for the O-bonded water in different adlayers is shown in Table 4.1.

In the H-up layer on Pt(111), the O lp depopulation is negligible (\( p_z =1.83 \)) which allows for the hydrophilic interaction with additional water layers (H-bond=0.13 eV). However, at the same O-Pt distance for water in the H-down layer, significant depopulation of the O lp (\( p_z =1.75 \)) due to interaction with the surface limits the ability of the O-bonded water to accept H-bonds from incoming water (H-bond=0.02 eV). The O lp occupation increases with distance from the Pt surface, as drive to polarize charge away from the O-Pt bond decreases with the smaller orbital overlap. By 3.75 Å, the “repopulation” of the O lp saturates, and the H-bond strength to the 2nd layer water computed for the isolated water layer is fully recovered (0.14 eV). These values are very similar to that for the O-bonded water in the H-up layer at close distance (2.35 Å), indicating a cooperativity effect in the bonding, in which the HOH-Pt bond opens a channel enabling a larger O-Pt interaction.
Table 4.1: Population of the O lp pair orbital (obtained by integration of the computed XES spectra projected along the \( p_z \) component) and H-bond energy between first and second layer water molecules as a function of O-Pt distance for the O-bonded H2O in the first monolayer and for OH and H2O in the coadsorbed layer on Pt(111). Orbital occupation is normalized to \( p_z = 2 \) electrons for the free water molecule.

<table>
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</tbody>
</table>

The cooperative effect in the bonding in the H-down case comes from the formation of a closed synergistic loop where additional charge can be removed from the O-down lone-pair as a further help to reduce the repulsion. The charge transfer from the metal surface to the unoccupied OH anti-bonding orbitals of the H-down water (see Fig. 4.12) enables the larger depopulation of charge along the O-metal bond for the O-bonded water. Thus, while the resulting binding energy increase for the H-down water is rather small, the effect on the electronic structure is very large - a balancing effect. This is evident in Fig. 4.14, which shows the difference in charge density for the water molecule O-bonded to Pt(111) in the H-down and H-up configurations. The gain of charge between the O and Pt atom indicates that more charge is centered on the O lp of the O-bonded water in the H-up layer than in the H-down layer, in the larger O lp population in the former (1.83 vs. 1.75).

Thus, the H-down/H-up water molecules act as a switch determining the H-bond strength to the O-down species while their own properties do not change significantly. As the coverage increases, we envision that incoming water molecules bond to the H-down species and do their best to interconnect and create an H-bond network without help from the O-bonded sites. However, due to strain induced by the spacing between protruding H-down waters this effort will likely be rather strained, making formation of 3D crystallites more favorable. However, the energy difference between H-up and H-down layers is tiny (much smaller than the energy that can be gained by forming the additional H-bond) and the barrier for H-down/H-up interconversion is very small. So why don’t the H-down water molecules simply flip?

The answer is very simple: we have been considering the wrong barriers. Since it is only the “switch” molecules that bind to incoming water, pinning them, a totally different barrier for H-up flipping results. While the H-down contact layer is structurally rather flat – it is energetically very corrugated to an incoming H2O. There is no binding to the O-
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bonded species, only to the H-down one. So a water molecule will bind there, pinned in place. The relevant barrier to also bind to the O-down species is the rotation of the H-down water with the connected H-bonded water. This requires breaking that H-bond, and that energy cost is directly added into the barrier. It doesn't happen until enough electrostatic strain is built from having all dipoles more or less in the same direction.

However, despite the non-bonding energetics between the O-bonded water in the H-down layer and incoming water, small changes in the electronic structure of O-bonded water are induced by interaction with second layer water, observed in the computed XES. Therefore, the energetics do not imply there is no interaction between second layer water molecules and the H-down and OH+H2O adlayers, but rather reflect a net cancellation of attractive and repulsive interactions.

We investigate the different contributions to this interaction by computing how charge moves along the H-bond and water-metal bond directions in response to the presence of second layer water molecules, shown in Fig. 4.15. For the H-up layer on Pt(111), the charge redistribution accompanying bonding to the second layer typifies that associated with H-bonding between water molecules [89] and is unperturbed by interaction with the Pt substrate, consistent with the full H-bond strength between layers. This is not the case for the H-down layer on Pt(111). Here, the movement of charge from the axial (water-metal bond) to the equatorial plane of the Pt atom, to reduce Pauli repulsion between the O lp and metal d-states, is less effective when the 2nd layer water is present (Fig. 4.15A). Since the O-bonded water already accepts two bonds, one from the neighboring H-down water molecule and one from the Pt atom beneath it, efforts to accept another from the second layer water should compromise the other two; this appears as a “repopulation” of the O lp. The features support a hydrophobic interaction, though the degree of charge rearrangement along the water-metal bond is small.

In contrast, the rearrangement of charge in the intermolecular hydrogen bonding in the H-down layer Pt(111) is dramatic (Fig. 4.15B). Efforts by the O-bonded water to accept an H-bond from the second layer water molecule compromise its ability to accept H-bonds from its H-bonded (H-down) neighbor. This is manifest as an accumulation of charge on hydrogen of the H-down molecule on the accepting side of the O-bonded water, corresponding to a weakening of this bond, which lowers the interaction energy. Concomitantly, accepting an H-bond from additional water layers drives the O-bonded water to restore the balance between donating and accepting bonds. Accordingly, we observe a major loss of charge on the H atoms on the donating side of the O-bonded water. This makes this same water molecule a much stronger donor and increases interaction energy. The gain and loss of charge accompanying these changes in the electronic structure lead to attractive and repulsive interactions, which cancel in the energy analysis.

Thus, the wetting property of the system is fully determined by the first contact layer of water. Moreover, the hydrogen atom perpendicular to the surface (H-up or H-down) of the non-O-bonded water molecules in the first monolayer acts a switch for the interaction of the O-bonded water and the Pt surface; this interaction plays the decisive role in tipping the balance between hydrophobic and hydrophilic water surfaces. Since the charge population of the O lp of water is influenced by both the electronic and geometric
structure of the substrate as well as by coadsorbed species such as oxygen or hydroxyl, as we will see in Sect. 4.3.3 (Paper VII), these results emphasize the importance of understanding structure of the water monolayer at metal surfaces.

**Figure 4.14:** CDD of the O-bonded water in the H-down and H-up layers on Pt(111), plotted along a slice through the O $lp$ orbital, as shown with a dashed box in the figure.

**Figure 4.15:** CDD plots for bonding of 2nd layer water molecule to the H-down water layer 1) in the gas phase 2) adsorbed on Pt(111) along A) the water-metal bond axis and B) the H-bond network in the water layer. The CDD for B is also plotted on an order of magnitude finer scale to facilitate a more detailed comparison.
4.4. The OH+H₂O mixed phase at metal surfaces

4.4.1. OH-induced wetting of water at metal surfaces

With an understanding of the effect of the geometric and electronic structure of the metal substrate on wetting based largely on UHV measurements, we proceed to bridge the pressure gap and show how the wettability of surface can be controlled by the presence of adsorbed OH groups on the surface, acting as anchors for water adsorption, at near ambient conditions. Using XPS we demonstrated that Cu(111) is hydrophobic while Cu(110) is hydrophilic under UHV conditions (section 4.1 and Paper I). Here we show that while the respective wetting properties of the clean Cu(110) and (111) surfaces are unchanged at near ambient conditions, the hydrophilicity of a surface, i.e. the ability to form water-metal bonds, can be tuned by the presence of adsorbed OH.

Figure 4.16 shows in-situ O 1s XPS spectra measured on Cu(110) and Cu(111) in the presence of 1 Torr water vapor at 295 K, corresponding to a relative humidity (RH) of 5.0 %. On Cu(110), two broad peaks are observed at 530.8 and 532.4 eV binding energy, which are assigned to OH and H₂O, respectively [75, 90, 91]. The partial coverages of OH and H₂O are 0.34 and 0.68 ML, respectively. The Cu(110) surface is thus covered to saturation (i.e., 1 ML) with a mixture of OH and H₂O. In contrast, under identical conditions, the Cu(111) surface remains clean and adsorbate-free. No adsorbate is observed on Cu(111) under 1 Torr H₂O vapor in the temperature range from 333 to 268 K, corresponding to the RH range from 0.67 to 33 %. Thus, as discussed in section 4.1.1 (Paper I), we clearly see that the same metal can exhibit different wetting properties at near ambient conditions by simply changing the orientation of its exposed surface; the Cu(110) surface is hydrophilic while the Cu(111) surface is hydrophobic.

The coverage of water at a metal surface is determined by a balance of adsorption and desorption kinetics in thermodynamic equilibrium. Since the wetting layer on Cu(110) is formed from a mixture of OH and H₂O at near ambient conditions, it is likely that the strong attractive interaction between OH and H₂O dramatically slows down the water desorption kinetics, resulting in the observed large quantities of water adsorbed on Cu(110). In fact, the stabilization of water by OH on metal surfaces has been observed as higher desorption temperatures of water from the mixed OH+H₂O layer than from the molecularly intact water layer under UHV conditions. Likewise, DFT calculations find that a mixed OH+H₂O layer is energetically favored over a pure water layer on Cu(110) [4] and Ru(0001) [12, 92]. The stabilization was largely attributed to the stronger H-bonds in the OH+H₂O layer; found to be almost twice as strong as water-water bonds for the case of OH+H₂O layer [30, 93].

Thus, the enhanced hydrophilicity of Cu(110) compared to Cu(111) is also related to a lower activation barrier for water dissociation (Eₐ diss), i.e., Eₐ diss(110) < Eₐ diss(111) on the open Cu surface. This is demonstrated by the presence of OH species on Cu(110), but not on Cu(111) in the present experiments under near-ambient conditions (see Fig. 4.16). It is also supported by previous UHV studies showing that thermally-induced water
Figure 4.16. O 1s XPS spectra measured in the presence of 1 Torr water vapor on two different clean surfaces of Cu at 295 K (a relative humidity of 5.0 %): Cu(110) and Cu(111), and for a partially oxygen-covered Cu(111) surface ($\Theta = 0.22$ ML) under the same conditions.
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**Figure 4.17:** Temperature dependent O 1s XPS for D$_2$O and OD co-adsorbed on Pt(111) with an excitation energy of 670 eV. Dissociation occurs on Cu(110) [19, 20, 75, 90] but not on Cu(111) [26]. On the other hand, the absence of OH groups on Cu(111) indicates that water dissociation is kinetically hindered on Cu(111) under these conditions ($p$(H$_2$O)= 1 Torr, $T= 268$–333 K). This is supported by the different dissociation barriers for water on Cu(111) and Cu(110) of $\sim$0.87 [95] and $\sim$1.17 eV [96], respectively, obtained from kinetic measurements of the water gas shift (WGS) reaction on these surfaces.

O1s XPS for a partially oxygen covered Cu(111) shows that wetting is indeed controlled by OH groups on the surface (Fig. 4.16, bottom). Preadsorbed atomic O ($\theta= 0.12$) on Cu(111) reacts with 1 Torr water vapor (H$_2$O + O $\rightarrow$ 2OH) to form a mixed OH and H$_2$O layer. The partial coverages of OH and H$_2$O are 0.26 and 0.17 ML, respectively. The hydrophilicity of the Cu(111) surface is thus enhanced by the formation of OH groups that stabilize water molecules through strong hydrogen bonds, similar to what we observe on the clean Cu(110) surface. The different wettability on the clean Cu surfaces originates from a lower activation barrier for water dissociation on Cu(110) compared to Cu(111). It is clear that water chemistry, through the formation of OH groups, plays a decisive role in the wetting of metal surfaces at near ambient conditions.

**4.4.2. Model Reaction Intermediate: OH+H$_2$O/Pt(111)**

The consistency between experimental results under UHV and near-ambient conditions lends credence to the applicability of our model systems to guiding design and prediction of surfaces for real reactions in heterogenous catalysis. The OH+H$_2$O mixed layer adsorbed on a metal surface, in particular, is considered to be identical to the reaction intermediate in the ORR in, e.g. a fuel cell [27,97]. Knowledge of the site occupation and orientation of the adsorbed OH-species and of surrounding water molecules, which we obtain for Pt(111) using core-level spectroscopy under UHV conditions and theoretical simulations in Paper VI, is a fundamental prerequisite to understanding the chemical properties of the interface during the ORR reaction and identifying the origin of the overpotential and rate limiting steps.

Since water adsorbs molecularly on Pt(111), preadsorbed oxygen was utilized to stimulate water chemistry and induce a mixed water/hydroxyl layer. D$_2$O was used instead of H$_2$O to minimize x-ray or electron induced damage to the sample [75]. First, a (2x2)-O layer was prepared at $T<100$ K by an O$_2$-dose and then heated to 350 K [98]. Next, water was dosed at $T<100$ K until a multilayer was achieved, and then heated to 156 K to produce a stable D$_2$O+OD layer. Temperature dependent O 1s XPS measured after dosing multilayer D$_2$O on Pt(111) covered with 0.25 ML of oxygen is shown in Fig. 4.17. Just above 150K, excess water desorbs and the rest begins to react with O; the chemical shifts in the spectra indicate that hydroxyl formation appears in the temperature interval 130-166 K. Further, the temperature dependent XPS also shows that OD co-exists with D$_2$O and that the water-hydroxyl phase is stable over a 30 K temperature range ($\sim$155-185 K) before water starts to desorb. Above 185 K, water desorption makes OD dissociation and
recombinative D₂O formation and desorption favorable, leaving behind atomic oxygen, see lower panel of Fig. 4.17. The very low temperature at which this reaction occurs on Pt(111) compared to the near-atmospheric conditions required for Cu(111) highlights the difference in reactivity of this surface compared to the close-packed surface of the noble Cu metal and alludes to the origin of its preeminence as a catalyst in the water production reaction. The temperature dependent XPS shows that the D₂O+OD on Pt(111) is more stable than the corresponding pure D₂O case, supporting TPD results of a higher water desorption temperature for the mixed layer compared to the pure water layer [98, 99,100].

The O 1s XPS and out-of-plane XAS spectra for atomic oxygen, monolayer D₂O/Pt(111) and the mixed D₂O:OD adsorbed on Pt(111) are shown in Fig. 4.18. Two mixed D₂O:OD phases on Pt(111), with long-range H-bonded order and (√3x√3)R30° and (3x3) units cells, respectively, were observed in the corresponding LEED pattern, in agreement with previous reports and STM [97,99,101]. The O 1s photoelectron peak for 0.25 ML O/Pt(111) is located at a binding energy (E_{BE}) of 529.9 eV, and, by comparison with a previous report, reflects atomic oxygen adsorbed in hollow sites in a (2x2)-O overlayer [102,103]. The O 1s photoelectron peak for D₂O/Pt(111) is located at E_{BE} 532.3 eV and corresponds to 0.7 ML coverage [17]. The XPS spectrum of (D₂O+OD)/Pt(111) consists of two peaks, at 530.1 eV and 531.6 eV, corresponding to OD and D₂O species, respectively. The chemical shifts between the three spectra indicate that all oxygen atoms are in different chemical environments in the D₂O+OD mixed layer compared to the corresponding pure systems and, furthermore, that the majority of pre-adsorbed oxygen atoms are involved in the OD formation. XAS results further indicate that no atomic oxygen remains in the D₂O+OD mixed phase.

**Figure 4.18:** Experimental O1s XAS (out-of plane) and XPS for atomic O, D₂O layer and the D₂O:OD mixed phase.
The out-of-plane spectrum of D₂O/Pt(111) (Fig. 4.18 left) is dominated by intensity around 538.5 eV, corresponding to formation of metal-hydrogen (M-HO) bonds. The absence of this feature, and that corresponded to uncoordinated OH, from the XA spectrum of (D₂O+OD)/Pt(111) indicates that D₂O bonds to the Pt surface solely through its oxygen in the mixed water/hydroxyl layer, in agreement with earlier IR studies [99]. This is reasonable since the stability of the in-plane H-bonding for the mixed water/hydroxyl layer on Pt(111) favors formation of a strong intermolecular H-bond network, whose completion requires all hydroxyl donate their hydrogen to water. The resonance at 532.1 eV in the spectrum for D₂O/Pt(111) is related to depopulation of the water O lp into the Pt(111) d-states, and also appears in the D₂O+OD)/Pt(111) spectrum with even larger intensity. We will see in the following that this is related to the closer D₂O-Pt distance in the coadsorbed layer, which is facilitated by a larger depopulation of the lp orbital. The XA spectrum of (D₂O+OD)/Pt(111) has a second intense energy resonance at slightly lower energy, 530.7 eV, related to depopulation of the oxygen lone pair (O lp) of hydroxyl into the Pt substrate.

To obtain a more detailed picture of the structure of water/hydroxyl adlayer on Pt(111), four structural models were considered and XA spectra and XPS binding energies were computed for each, labeled A-D. The structural parameters and computed spectra are given in Fig. 4.19, left. All models consist of a nearly flat, fully coordinated adlayer with a 1:1 ratio of water and hydroxyl, with OH-Pt and H₂O-Pt distances of 2.1 and 2.2 Å, respectively. Models A and B correspond to phases with (√3x√3)R30° and (3x3) periodicity, respectively, and were generated from high-level DFT optimization. Both have an asymmetry in the lateral O-O distances characterized by long OH-donating and short OH-accepting bonds, though the degree of asymmetry is more pronounced for model A (2.66 and 3.16 Å). Model C represents a symmetric (√3x√3) layer, while model D represents a (3x3) structure with long OH-accepting (2.81 or 3.02 Å) and short OH-donating bonds (2.49 Å); i.e. the opposite asymmetry of models A and B. Model D represents the structure derived by Held and co-workers from a (3x3) LEED pattern [104].

For all four models the computed XAS spectrum reproduces the two sharp peaks in the experimental spectrum around 530 and 532 eV (Fig. 4.19 center), though these peaks are ~1 eV too low in energy in model D. For models A and B, but not for models C and D, the second peak (532 eV) includes contributions from both OH and H₂O. The fact that the second peak in models C and D does not overlap with H₂O contributions and is therefore due to OH transitions alone disagrees with the AES data, which directly shows that resonances from both hydroxyl and water contribute to this peak. Due to the presence of both (√3x√3)R30° and (3x3) phases, it is not only necessary that the combination of features from the different layers successfully reproduces the experimental curve. Therefore, at this point, we can only conclude that a mixture of models C and D is not possible.
Although model A contains a mixture of both OH and H₂O intensities in the second peak, the ratio of the XAS peak heights is too close to unity to fit the experiment. Model B, on the other hand, shows a similar intensity ratio as in the experiment but slightly overestimates the energy separation between the first and second peak. Model C also reproduces the overall spectral shape of the experiment, particularly the resonance at 534.6 eV, but the intensity ratio between the first and second peak is too large. Model D likewise shows a large intensity ratio between the first and second peak and in addition has a mismatch in energy position of the first peak by about -1 eV compared to the experiment. Furthermore, the spectrum of model D has an intensity dip close to 536 eV, which is not observed in the experimental spectrum. We find that a mixture of at least two model structures is necessary to reproduce the experimental XAS spectrum, which is not surprising since the LEED pattern indicates that a mixture of structures is present in the stable phase.

Computed XPS binding energies confirm that a mixture of structures is necessary, and further refine the structural model. Experimental and theoretical XPS peaks for the four models are shown in Fig. 4.19 (right). The too large computed binding energy (ΔBE) shift between OH and H₂O on Pt(111) in model D (3.89 eV) compared to experiment (1.5 eV) eliminates it from consideration. Model C also shows a larger computed ΔBE between OH and H₂O (2.18 eV) compared to experiment, but, due to the broadness in the experimental
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XPS spectrum, this shift is not so large as to conclusively exclude the possibility of contribution from model C in a mixed phase structure. In contrast, $\Delta$BE for model A is too small (1.07 eV) to fit experiment. On the other hand, the $\Delta$BE (1.52 eV) for model B is quite similar that of the experimental XPS spectrum. However, the model B spectrum lacks some of the intensity between the two peaks observed in the experiment. This discrepancy can be relieved by spectral contribution from model A, and this combination is consistent with a mixed ($\sqrt{3} \times \sqrt{3}) R30^\circ$ and (3x3) structure. Likewise, a combination of the large $\Delta$BE in model C combined with contributions from the narrow splitting in model A also offers a reasonable fit with the experiment, as could the XAS spectral features for these two models. We consider such combinations of the ($\sqrt{3} \times \sqrt{3}) R30^\circ$ and (3x3) phases, i.e. model A with model B or model C in different ratios. The computed mixture representing the best fit to the XAS data tends to suffer in its agreement with the corresponding XPS data, and vice versa. As such, it is difficult to unambiguously confirm either model as a precise representation of the ($\sqrt{3} \times \sqrt{3}) R30^\circ$ portion of the mixed phase.

Thus, model A, with the longest OH-donating and shortest OH-accepting bonds, emerges as the most likely structure responsible for the (3x3) phase; model D is ruled out by the poor agreement with experiment. For the ($\sqrt{3} \times \sqrt{3}) R30^\circ$ structure, however, the case is not as clear as both models B and C are in good overall agreement with experimental spectroscopic observations. We envision that the best representation of the ($\sqrt{3} \times \sqrt{3}) R30^\circ$ is a weakly asymmetric adlayer; i.e. a structure with an long donating bond from OH to H$_2$O, with a bond length somewhere in between that of models B and C.

4.4.3. Cooperativity Effect in OH+H$_2$O/Metal Bonding

In contrast to the relatively weak water-metal bonding [3], higher adsorption energies with significant variation among substrates are found for the OH+H$_2$O phase at metal surfaces [3,4-13]. The origin of this variation not fully understood, and is complicated by the fact that the behavior of water at a metal surface, as well as the OH:H$_2$O ratio in the partially dissociated layer varies sensitively with growth conditions and reactivity of the substrate. The stability of the OH+H$_2$O adlayer has, however, been attributed to the large adsorption energy for OH (and O) at metal surfaces. Since large adsorption energies can hinder proton and electron transfer, the stability of the OH+H$_2$O reaction intermediate on Pt has been cited as the major cause of the overpotential in the oxygen reduction reaction (ORR) in fuel cell catalysis [14] which limits the reaction rate. Therefore, understanding the factors that drive the stability of this phase will be key to tuning the adsorption energies to increase the reaction rate. This is addressed in Paper VII, where we use geometric and electronic structure considerations to show that a cooperativity effect between water-metal bonding and hydrogen bonding in the adlayer drives the stability of the OH+H$_2$O layer at metals surfaces.

The detailed structure we derived for OH+H$_2$O/Pt(111) in the previous section (4.4.2, Paper VI), is characterized by top site adsorption, long OH-donating and short OH-accepting bonds to/from water, and is nearly flat due to a shortening (lengthening) of water-metal (OH-metal) bonds compared to pure OH or H$_2$O layers. In this configuration, both OH and H$_2$O interact significantly with the metal surface, which, in conjunction with the stronger H-bond network, results in a higher adsorption energy for the mixed layer.
compared to the pure water layer, and a larger interaction energy between the water molecules and the metal surface obtained from CSOV analysis. In this way, OH groups stabilize water at metal surfaces. However, the presence of water facilitates OH adsorption at surfaces where a pure OH phase is unstable (Pt(111), Cu(111) [99]. Furthermore, the strong H-bonds water donates to OH in the mixed OH+H$_2$O energetically compensate for the electrostatically unfavorable flat, top site adsorption geometry for OH groups, which generally prefer to adsorb upright at higher coordination sites such bridge or three-fold hollow sites [105]. Thus, water also stabilizes OH at metal surfaces.

The stability of the water/hydroxyl layer has roots in both the hydrogen bond network and the interaction through the metal surface. This role of both channels is most evident on Cu(110), where the lateral electrostatic attraction in the layer couples with the favorable electrostatics for adsorption at the charge-depleted rows to easily overwhelm the Pauli repulsion due to orbital overlap between the O lone pair orbitals and the Cu 3-$d$ states. As a result, the interaction between the OH+H$_2$O layer and the Cu(110) surface is already attractive in the FO configuration. In contrast, for the close-packed surfaces, which do not benefit from the favorable electrostatics of the Smoluchowski effect, the enhanced water-metal interaction is not fully realized until polarization and charge transfer between the water and metal atoms are allowed in the CSOV analysis. This indicates that both electrostatics and interaction with the metal substrate are implicated in the balancing act that drives the stability of the OH+H$_2$O layer at metal surfaces; i.e. a cooperativity effect in surface and hydrogen bonding.

Details of the interplay between surface bonding and H-bonding in the layer are illuminated by electronic structure considerations. Since water-metal and OH-metal bonding primarily involves the lone pair orbitals, which are also implicated in accepting of intermolecular H-bonds, the charge occupancy of this orbital is a useful barometer to probe the interaction in the different bonding channels and at different surfaces. The O 2$p$ charge occupation projected along the different bond directions ($p_x$, $p_y$, $p_z$) for OH and H$_2$O in different bonding environments, including the Pt(111), Cu(111) and Cu(110) surfaces are given in Table 4.2. By comparison to the corresponding intensity for the free water molecule or OH$^-$ ions in solution, we can derive how water and hydroxyl, respectively, change their orbital occupation upon interaction with a metal surface. The corresponding movement of charge along different bond directions that accompanies the changes in electronic structure is shown in Fig. 4.20. To isolate the changes in water-metal bonding due to interaction with surrounding OH groups, and following the construction of the CSOV analysis, the CDD plots (Fig. 4.20) reflect the rearrangement of charge when the center O-bonded water is brought in from “infinite” distance to bond with surrounding OH and H$_2$O and the metal surface, which are already relaxed as a unit. As such, charge movement within the neighboring adsorbate molecule or metal atoms is induced solely through interaction with the center water molecule.
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**Table 4.2:** Oxygen charge occupancy for the 2p components of the O-bonded water and OH in different environments, obtained by integration of each component ($p_x$, $p_y$, $p_z$) of the computed XES projected along the different bond directions: $p_x$ is oriented through the plane of the H$_2$O or OH, $p_y$ describes the bond along the H that H$_2$O accepts from H$_2$O or OH, and $p_z$ corresponds to the O $l$p normal to the surface. The numerical 2p populations are normalized to O 2$p_z$ = 2 electrons for the free water monomer. The * indicates whether the orbital occupation corresponds to that of OH or H$_2$O.

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*The high value is due to more contracted 2p orbitals compared to the reference water monomer.
Figure 4.20: *Top:* Charge density difference (CDD) plots for the (1) OH+H₂O mixed adlayer and (2) water monolayer (H-down) on Pt(111) and Cu(111), plotted along (A) the molecular axis of the center water molecule ($p_x$), (B) the OH-H₂O bond on the acceptor side of the center water molecule ($p_y$), and (C) the O-H bond on the donor side of the center water molecule. *Bottom:* schematic of the bonding environment and the density planes.

A number of features indicate that the electronic structure is not a simple mix of pure OH and pure H₂O bonding to the metal surface including, and provide details of a cooperativity effect that drives the structure of the water/hydroxyl adlayer. Specifically, the O 2p orbitals of OH and H₂O undergo the following changes upon adsorption at a metal surface:
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(i) A contraction of charge along the O-H bond of hydroxyl away from the hydrogen atom, which makes adsorbed OH a stronger H-bond donor to water than OH⁻ in solution. This appears as an increase in charge occupation of the p_y orbital for OH (Table 4.2) and a gain of charge in the equatorial plane of the oxygen of OH and a loss of charge on the hydrogen (Fig. 4.20B).

(ii) A gain of charge in the equatorial plane of the water molecules, which aids the depopulation of the O lp of water and H-bonding in the layer (see in p_x in Table 4.2 and Fig. 4.20A).

(iii) A depopulation of the O lp of water to reduce Pauli repulsion with metal d-orbitals (p_z in Table 4.2). The depopulation and corresponding rearrangement of charge is more for water in the mixed OH+H_2O layer as the shorter water-metal distance in the mixed layer requires more O lp electron density to be polarized away from the water-metal bond axis (compare p_z for OH and H_2O in Table 4.2 and Fig. 4.20A1, 2).

(iv) An overall depopulation of the O lp of hydroxyl interacting with the metal surface reflecting the net balance of the loss of charge along the OH-metal bond when OH donates a H-bond to water (Fig. 4.20B) and gain of charge along the OH-metal bond when OH accepts a H-bond from water (Fig. 4.20C).

The gain of charge along the OH-metal bond that accompanies accepting an H-bond from water is reflected by the higher O lp (p_z) population for OH coadsorbed with water compared to a single OH group at a metal surface (Table 4.2). This last feature indicates a versatility of OH to redistribute charge among all constituents in the adsorbate system. Thus, the presence of OH introduces a flexibility in the bonding channels in which charge transfer readily proceeds between water, hydroxyl and metal atoms in a closed loop (see Fig.4.20C).

The influence of the geometric and electronic structure of the substrate on the ability to form water-metal bonds is also apparent in the orbital population analysis and CDD plots. The degree of depopulation of the O lp of water in the pure layer associated with water-metal bonding is similar for hydrophilic Pt(111) and Cu(110), but rather minor for hydrophobic Cu(111) (Table 4.2). Accordingly, the CDD plots show a much larger redistribution of charge along the water-metal bond for Pt(111) compared to Cu(111) (Fig. 4.20A). As discussed in section 4.1 (Paper I) the partially filled d-band of Pt(111) provides a mechanism to redistribute charge to facilitate water-metal bonding that is less available for the isostructural surface of the noble metal, Cu(111) [47,48,49]. Consequently, on Pt(111) the major charge redistribution is accomplished along the water-metal bond, while the rearrangement of charge along the H-bond water donates is comparatively minor (Fig. 4.20C left), and is only mildly enhanced in bonding to OH instead of water. In Section 4.4 we showed how the hydrophilicity of Cu(111) to water can be enhanced by the presence of coadsorbed OH (Paper V). Accordingly, we observe a significantly lower O lp population for water surrounded by OH on Cu(111) compared to the pure water case (Table 4.2), indicative of water-metal bonding. However, the polarization of charge to accommodate the bonding proceeds largely along the H-bond that water donates to
hydroxyl. The charge polarization in the OH+H₂O layer overshadows that along the water-Cu bond, since the filled $d$-band of the noble metal limits the ability of the $3d$ shell to rehybridize charge away from the water-metal bond axis to opening up for dative bond formation. For Cu(110) (not shown), the enhanced electrostatic attraction of the OH+H₂O layer at the corrugated surface, combined with the reduced repulsion through the loss of charge on the (110) ridges, demands less of the H-bond network in stabilizing the interaction. Thus, we see the hydrogen-bond network in the OH+H₂O layer has a very special character; rigid enough to stabilize water at the surface and induce long range order in the adlayer, but flexible enough to accommodate the necessary hybridization for bonding to the surface.

Thus, we find that water-metal bonding is enhanced by the presence of hydroxyl groups through attractive lateral interactions in the layer and charge transfer between OH and the metal. The direction of the charge transfer between OH and metal atoms depends on whether OH is acting as an acceptor or donor of hydrogen bonds. The origin of enhanced stability of the mixed OH+H₂O layer at metal surfaces can therefore be described in terms of a cooperativity effect between water-hydroxyl bonding and interaction with the metal substrate, which is influenced by the geometric and electronic structure of the substrate. Cooperativity between bonding channels can lead to compensation effects which facilitate diffusion of OH to neighboring adatoms and provide pathways for proton hopping \[8,106,107\]. This is central to the right choice of alloy catalysts to coordinate and direct chemical reactions and turn intermediates into products. In this way, a detailed understanding of the bonding mechanism for water and hydroxyl at metal surfaces, including the influence of the electronic and geometric structure of the substrate, is central to the rational prediction and design of catalysts, especially for the ORR in fuel cells.
Chapter 5

Conclusions and Future Work

In summary, we show that the ability to form water-metal bonds is ruled by the balance between counteracting interactions of Pauli repulsion and electrostatic attraction. This balance is influenced by electronic and geometric structure effects, involving the energetic position of the $d$-band center with respect to the Fermi level as well as surface electrostatics. The wettability of a surface can also be tuned with preadsorbed oxygen, which enhances the hydrophilicity of a surface through OH groups which anchor the water molecules at the surface via strong H-bonds. Hydroxyl-induced wetting is related to the higher stability of the mixed water/hydroxyl phase at metal surfaces, which can be described by a cooperativity effect in surface and hydrogen bonding in this system. The different wetting property for Cu(111) (hydrophobic) and Cu(110) (hydrophilic) is attributed to the favorable electrostatics on the open Cu surface due to the Smoluchowski effect. This effect of electron smoothing at a corrugated surface also leads to a unique low coverage water structure on Cu(110), stabilized by electrostatic interactions inaccessible to close-packed surfaces. Likewise, a different low energy structure is found for the water monolayer on Cu(110) characterized by a significant fraction of H-up species, in contrast to the H-down structures found for Ru(111) and Pt(111). The importance of this knowledge is highlighted when we show that the preferential microscopic orientation of the water monolayer determines macroscopic phenomena, such as the wetting property.

This work has identified key relationships related to critical issues for the ORR reaction in fuel cell catalysis. However, for fuel cell to play a part in a sustainable energy economy, the hydrogen feedstock utilized must be produced from renewable resources, such as sunlight and water. With a solid understanding of the water-metal interface, we turn our attention to the “other electrode” in a photoelectrochemical (PEC) cell, at which hydrogen can be produced from sunlight and water. III-V semiconductors, such as GaP, are promising materials for PEC hydrogen production, however, material stability is a serious issue. The addition of dilute amounts of nitrogen to GaP, and surface modifications such as platinization, results in dramatic increases in photocorrosion resistance, but the underlying mechanism is not known. The surface science training behind this thesis will be applied to study fundamental interactions at the interface of water and III-V semiconductor photocatalysts during solar H$_2$ production.

The goal is to apply our suite of experimental and theoretical techniques to study surface reactions of relevance to renewable energy technologies including solar electricity and solar fuels involving hydrogen production and utilization. The forecast is sunny.
Comments on Contribution

The papers presented in this thesis result from extensive collaborative efforts of a number of people, which encompass a number of jobs, some more glamorous than others, including the tightening of flanges on a UHV end station, performing experiments, computing spectra, and rewriting code for the next, more sophisticated calculation. Regarding my part, I played a central role in the experiments in Papers II, V and VI and participated in the data analysis in the other papers. I performed all the theoretical calculations presented here except for the plane-waves based geometry optimizations.
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I dedicate this thesis to family; especially my loving parents, Peter and Angi, my dear husband John, my brother Johnny (Bing!) and my koumbara Alli. Your love is the vehicle that drove this thing over the finish line. This day would mean nothing without you to share it with. Thank you for being here for me today and there for me always.

John, side by side the world is ours. I love you.

Summanfattning

En detaljerad bild av kemisk bindning mellan vatten och metallytor från röntgenspektroskopi och tätthsfunktionalteori.

Växelverkan mellan vatten och metallytor spelar en central roll i en uppsjö av kosmiska, atmosfäriska och biologiska kemiska processer, och även i heterogen katalys, elektrokemi och korrosion. Tack vare betydelsen för yt kemiska reaktioner relaterade till produktion och användande av vätgas som bärare av ren energi står nu många vatten/metallytesystem fokus för förnyat intresse. Speciellt viktigt är ytadsorberat OH vilket förekommer som reaktionsintermediär både i förnyelsebar produktion av vätgas från vatten och solljus, såväl som i bränslec llee selлектrokatalsys.

Bränslec ller anses vara en av de mest lovande teknologierna för en hållbar energiinfrastruktur, särskilt om bränslet i form av vätgas kan fås ur förnyelsebara källor. En djupgående förståelse av mekanism och reaktionsväg för syrereduktionsreaktionen (ORR), innefattande även katalysatorns geometri och elektronstruktur, är nödvändig för utveckling av effektivare bränslec llee skatalysatorer. Denna förståelse hänger i sin tur intimit samman med förståelsen av de grundläggande faktorer som reglerar möjligheten att bilda vatten/metallyte-bindningar, såväl som orientering och placering av ytadsorberade H₂O och OH på aktiva metallytor. Med en kombination av kvantkemiska beräkningsmetoder och synkrotronljusbaserade spektroskopiska tekniker undersöker vi för detta ändamål struktur och bindning av vatten och vatten/hydroxyl på metallytor under ultrahögt vakuum (UHV) och ”near-ambient” (nära atmosfäriska) förhållanden.

Den här avhandlingen belyser nyckelkoncept i förståelsen av ORR-reaktionen i bränslec llee skatalys som kan vara till vägledning för fortsatta studier på området. Identifiering av energi- och kostnadseffektiva material för bränslec llee skatalys är av största vikt för att påskynda förverkligandet av en hållbar framtida vätgasbaserad energiproduktion.
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