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Water-Related Adsorbates on Stepped Platinum Surfaces

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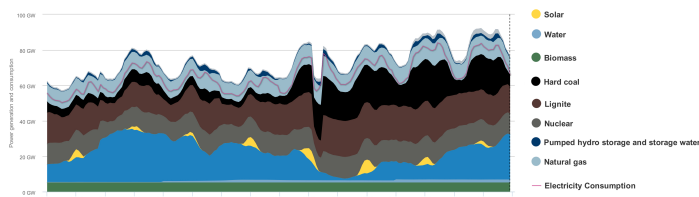
Chapter 1

Introduction

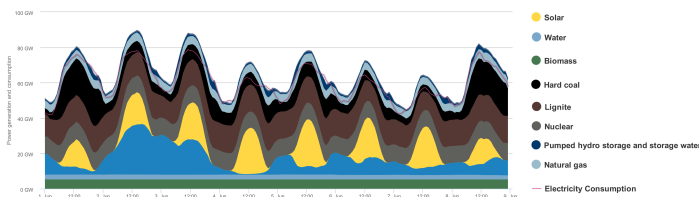
1.1 Fossil fuels, Renewable Energies and Electrochemistry

Fossil fuels are finite. This fact, as un-surprising as it is, will have a large influence on our daily lives already during the lifespan of the current generation. The increase in the cost of energy, be it gas or electricity and the increase in cost of oil-related products will influence our decision-making in the years to come. This makes approaches to reduce our reliance on oil and natural gas for the simple use as energy carriers a key aspect of current scientific research. One of the very few feasible possibilities to overcome this problem is the use of renewable energy sources such as wind, geothermal, solar and water power.

However, many renewable energy sources also currently have massive drawbacks. Germany as one of the most prominent examples for production of renewable energy currently experiences these deficiencies. Figure 1.1 shows the electrical power production of Germany for the first week of January 2015 (Figure 1.1a) and the first week of June 2015 (Figure 1.1b). As can be seen clearly, solar and wind power are, from a technical standpoint, far from ideal candidates for the production of the majority of a country's electricity because of the large variance in their hourly and monthly energy generation rates. An additional challenge is the physical transport of the energy generated, where the energy loss during transmission via power lines increases with geographical distance between the places of production and consumption. Many ideas exist on how to create solutions for the storage problem, one of the oldest being pumped hydro storage powerplants. However, these solutions also have issues, due to their large ecological impact on the environment in which they are built and their limited storage capacities. Also, as discussed above, being able to transport the stored energy



(a) German electrical power production in the first week of January 2015



(b) German electrical power production in the first week of June 2015

Figure 1.1: German electrical power production in the first week of January and June 2015. Data points are given each hour, and separated by different energy sources. Taken from [1]

in a physical medium would help alleviate the transfer problems as well as allow for the use of these energy carriers as mobile fuels for e.g. cars. Electrochemistry offers many approaches for the use of electricity to store energy. The most common of these are the use of batteries and the related supercapacitors for the direct storage of electricity, and the use of electrolysis and fuel cells for the production and conversion of energy carriers. Possible energy carriers are hydrogen via the hydrogen evolution reaction (HER) or also hydrocarbons generated by the reaction of hydrogen with CO_2 , which can then also be transported physically, helping to alleviate the transportation problem. The benchmark catalyst for the HER is the platinum surface. However, platinum is not the metal of choice for large-scale industrial applications due to its high price and low availability. This means that either different catalysts need to be found that can produce similar reaction rates, while still offering a competitive price for the catalyst, or the efficiency of the available platinum must be optimized.

1.2 Linking Surface Science and DFT to Electrochemistry

The search for new catalysts or the desire to make better use of the existing ones requires a detailed understanding of the underlying chemical and physical properties of the platinum surface. Its interaction with the solvent, the electrolyte, the reactant, intermediates and product, and the co-adsorption properties of all of these will influence the reactivity. Additionally, the behavior of water at room temperature, the pH level and the applied voltage will also influence the reaction mechanism. All of these properties must be fully understood to arrive at a complete set of requirements for an improved catalyst. Unfortunately, due to the strong interconnection of all of these properties, elucidating them completely in the real electrochemical environment is not easily feasible. Therefore, approaches that allow for the separation of smaller subsets of these from the electrochemical environment are needed.

Two main approaches are capable of this task: Theoretical approaches, such as density functional theory (DFT) can provide binding energies and models for the interaction of the solvent with the species on the surface, as well as provide information on reaction pathways and onset potentials of the reactions. Unfortunately, these models are limited in their predictive power, both due to their accuracy, as well as due to limitations in the modeling process. Ultra-high-vacuum surface science on the other hand allows for an experimental measurement of physical properties, such as desorption temperatures and sticking probabilities (which are linked to the adsorption energy and barrier), as well as reaction rates for surface-catalyzed reactions. However, also this technique has a downside, which is characterized as the "pressure gap". One of the main differences in this regard, is of course the absence of the full solvent environment under UHV conditions. The solvent can influence the chemical reaction in many ways. First, the solvent molecules can adsorb on the catalyst surface, thereby creating competitive adsorption between the solvent and the reactant. Second, the solvent molecules, when co-adsorbed, can interact favorably or unfavorably with the reactants, intermediates and products which can promote or hinder the chemical reaction. Third, the solvent can act as a reactant itself, by for example acting as a hydrogen donor for an electrochemical hydrogenation step. Consequently, a UHV study is conducted under significantly different environmental conditions than the related electrochemical experiment, which might lead to different behavior of the real system due to the difference in its surroundings.

This means that none of the methods described above by itself can provide a full and meaningful picture of an electrochemical reaction, but by interconnecting

all of the results from all of the techniques there is a good chance to arrive at a more complete picture.

1.3 Defective Surfaces

Due to the difficulty in describing the full chemical reaction in a realistic catalytic system, which generally consists of nano-particles on a support, usually high-symmetry facets of the catalytic metal are chosen as model systems. The well-ordered nature of these facets helps significantly in the elucidation of the chemical processes happening on the surface. The reason for this is that due to the reduced number of distinct adsorption geometries, the identification of the reactive sites and their behavior during the reaction can be deduced from the experimental and theoretical data. Due to the large number of different sites present on nano-particles, this is generally not possible for the real system. Unfortunately, the high-symmetry facets sometimes do not provide a complete picture, since low-coordinated adsorption sites can contribute significantly to the total reaction rates[2, 3].

Due to this, approaches are needed to study low-coordinated lattice sites in the context of surface science and theoretical chemistry[2]. The most common of these approaches is the use of regularly stepped surfaces. These surfaces consist of flat high-symmetry facets that are interrupted by single-atom-high step edges at periodic intervals. The periodicity of the intervals can be chosen very accurately in the experiment by cutting a single-crystal surface slightly outside the chosen high-symmetry plane. The resulting regularly-stepped surface can now be used to identify the experimental behavior of the low-coordinated lattice sites. This is done by separating the results into properties attributed to the high-symmetry terraces and the step-edge sites.

With very few exceptions this experimental approach works very well and has given rise to a general understanding of the reactive behavior of step edges. However, arriving at a detailed microscopic understanding often requires additional data. This can be provided by theoretical approaches, such as density functional theory (DFT).

1.4 Density Functional Theory

The investigation of a multi-atom system at an *ab initio* level requires finding the solution to the Schrödinger equation, which contains a significant number of degrees of freedom. Density Functional Theory makes use of several simplifications to achieve this, which will be briefly discussed in the following [4].

The full Hamiltonian of a system containing atomic cores and electrons is described by:

$$\hat{H} = \hat{T}_e + \hat{T}_c + \hat{V}_{ee} + \hat{V}_{cc} + \hat{V}_{ec} + \hat{V}_{ext}, \quad (1.1)$$

where $\hat{T}_e$ and $\hat{T}_c$ are the kinetic energies of the cores and electrons, $\hat{V}_{ee}$ and $\hat{V}_{cc}$ are the interaction potentials of the particles of the same kind and $\hat{V}_{ec}$ denotes the interaction potential between electrons and cores. $\hat{V}_{ext}$ denotes any external potential acting on the system.

Considering the mass differences between the electrons and cores, it is generally assumed that the electronic part of the Hamiltonian reacts almost instantaneously to changes in the coordinates of the cores. This allows for the separation of the Hamiltonian into an electronic part and a part for the nuclei, which can be treated separately. This separation is called the Born-Oppenheimer approximation:

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ec} + \hat{V}_{ext,e} \quad (1.2)$$

$$\hat{H}_c = \hat{T}_c + \hat{V}_{cc} + \hat{V}_{ext,c} + E_e^0, \quad (1.3)$$

where $\hat{V}_{ext,e}$ and $\hat{V}_{ext,c}$ describe any external potential acting on the electrons or cores and E_e^0 denotes the total energy of the electronic system at a given set of core coordinates. The part containing the cores can now be treated with classical mechanics, while the simplified electronic part needs to be treated with quantum-mechanical methods.

In 1964 Hohenberg and Kohn [5] described a method to calculate the ground state of the wave function of a solid solely based on its electron density $n(\mathbf{r})$, which allows for the reduction of the complexity of the full electronic system with its $3 \cdot N$ coordinates to a system with only 3 coordinates, where N is the number of electrons in the system. Building on this scheme, one year later Kohn and Sham [6] showed that the Hohenberg-Kohn functional can also be written as:

$$\left(\hat{T} + V_H[n] + V_{XC}[n] + V_{ext,e}[n] \right) \phi_i = \epsilon_i \phi_i. \quad (1.4)$$

In this equation, $\hat{T}$ denotes the kinetic energy operator, $V_H[n]$ is the Hartree potential, which describes the electrostatic interaction between the electrons, $V_{XC}[n]$ is the exchange correlation potential and $V_{ext,e}[n]$ describes any external field acting on the electrons. ϕ_i are single-electron wave functions of a auxiliary non-interacting system, where

$$n(\mathbf{r}) = \sum_i^N f_i |\phi_i|^2. \quad (1.5)$$

Unfortunately, this approach cannot reduce the actual complexity inherent in the description of the system, but only shifts it into the exchange-correlation

part of the equation. For this part no closed expression can be calculated for any extended system since this problem has the same complexity as solving the Schrödinger equation for the system itself. However, as it turns out, relatively simple approximations for the exchange correlation energy, such as the local density approximation (LDA) or the generalized gradient approximation (GGA) can provide surprisingly accurate results given their rather simple nature. The GGA approach is built upon the work by Perdew and Wang [7], in which they propose an approximation for the exchange correlation energy that is not only based upon the local density (as is the LDA functional) but also on the gradient of the local density.

$$E_{XC}[n] = \int \epsilon_{XC}(n, |\nabla n|) \cdot n \, d^3r. \quad (1.6)$$

In this work, the PBE functional, proposed by Perdew, Burke and Ernzerhof [8] is used for the approximation of $E_{XC}[n]$. It was chosen for its universally good representation of adsorption energies for all the systems that were considered [9–11]. A more detailed justification for the use of this functional can be found in the relevant sections detailing the theoretical methods for chapters 2 and 3.

1.5 Review of Previous Experimental and Theoretical Results

In this thesis we will discuss the interaction of water-related adsorbates with stepped platinum surfaces, namely the Pt(533) surface and the Pt(553) surface. The choice of adsorbates was made in order to arrive at a more detailed understanding of previously obtained UHV data from our group, as well as to arrive at a better understanding of the interaction of the electrochemical environment with the step edges of platinum surfaces. The two model surfaces consist of a 4-atom-wide terrace and a one-atom-high step for Pt(533) and a 5-atom-wide terrace and a one-atom-high step for Pt(553) and were chosen to mirror the surfaces studied in the experiments. In the following we will discuss the current state of research for the adsorbates that are discussed in this thesis: hydrogen, oxygen, OH and water.

1.5.1 Hydrogen

The adsorption of hydrogen has been the focus of multiple experimental studies due to its link to hydrogenation reactions in heterogenous catalysis, as well as the hydrogen evolution reaction in electrocatalysis. In UHV temperature programmed desorption (TPD) experiments it was found that on Pt(111) hydrogen

displays a single-peak desorption spectrum around ~ 300 K [12]. Introducing a high density of single-atom-high steps gives rise to additional adsorption peaks: for the Pt(211)[13] and Pt(533)[14–16] surface a single high-temperature peak appears at around 370 K on both surfaces. This peak is assigned to the desorption from the (100)-type step edges present on these surfaces, and an increased binding energy is assumed for these sites. The Pt(553)[14] surface shows a significantly more complex spectrum with 2 additional peaks at temperatures below 300 K. This was interpreted by assigning the peak at 300 K to the Pt(111) terrace, while the lowest temperature peak was assigned to the desorption from the (111)-type step edge. Surfaces with increased geometric complexity, such as the Pt(110)-(2x1) missing row reconstruction were also studied with the TPD method and also a spectrum with 3 peaks was identified [17]. The origin of these peaks was however not clear.

DFT simulations of hydrogen adsorption on Pt(111) [18] found a very flat energy landscape for the adsorption wells for low-coverage hydrogen adsorption on the infinite (111) terrace. In a later publication Olsen et al. also discussed the adsorption of low-coverage hydrogen on the regularly stepped Pt(211) surface, which contains (100)-type step edges[19]. It was found that the bridging position at the top of the step edge shows a significantly enhanced binding energy for this step-edge type. In order to elucidate the previously unexplained TPD spectrum of the Pt(110)-(2x1) reconstructed surface Gudmundsdóttir et al. performed high-coverage hydrogen adsorption simulations[20, 21]. It was found that the desorption barriers which are present on this surface significantly alter the order of the desorption pathways compared to what the pure adsorption energies would suggest.

1.5.2 Oxygen

The desorption of oxygen from Pt(111) was studied by Gland et al. [22] using temperature programmed desorption. It was found that oxygen shows two desorption features: a low-temperature feature that was assigned to molecular oxygen trapped in a shallow well above the surface and a high-temperature peak that stems from chemically adsorbed atomic oxygen that associatively desorbs. Adsorption of oxygen at various coverages on the stepped Pt(533) and Pt(553) surfaces was performed in our group [14]. It was found that oxygen exhibits a three peak spectrum for both surfaces: a low temperature peak for the molecular adsorption well, a medium-temperature peak stemming from the (111) terrace and a high-temperature peak originating from the step edges. Note that the desorption temperatures for the step desorption differ between the two surfaces, with Pt(553) exhibiting a lower desorption temperature for the step edge than Pt(533).

Oxygen adsorption on stepped surfaces was also studied using DFT. Feibelman et al. [23] investigated the adsorption of oxygen on the stepped Pt(211) and Pt(221) surfaces. It was found that oxygen prefers the bridged binding site on the Pt(211) surface, while at the (111)-type step oxygen sits in the FCC site adjacent to the upper step edge.

1.5.3 OH

Under UHV conditions water does not split into OH and H [24] on flat or stepped platinum surfaces. This is in contrast to the case in electrochemical conditions, where the presence of OH on the terrace of stepped surfaces is confirmed and the presence of OH on the step edge is strongly suspected[25]. This disparity stems from the differences in the surrounding environment, namely temperature, pressure and the presence of additional water, protons, OH and the applied potential. These factors allow the water to split into OH and H under electrochemical conditions, while under UHV conditions overcoming the energy difference inherent to the reaction is not possible. However, the coadsorption of atomic oxygen with water can allow for the formation of OH on the step and the terrace of Pt(533)[24, 26] under UHV conditions. In both cases it was observed that the OH is preferentially formed at the terraces for full oxygen coverages. OH is more strongly bound at step sites for both surfaces, however it is assumed that the terrace-bound OH inhibits the formation of step-bound OH.

The adsorption of OH has been studied extensively with DFT. On Pt(111) the half-dissociated water layer as it can be encountered in the electrochemical environment was discussed [27, 28] in detail, due to its link to the oxygen reduction reaction (ORR). The half-dissociated water layer consists of a stable $(\sqrt{3} \times \sqrt{3})$ -overlayer, in which every second water molecule is dissociated to form OH. The question whether water will split into OH and H at the step edges that occur on a Pt(111) surface were also a concern for theoretical investigations. The most recent examples are the investigations by Donadio et al. and Peköz et al. for the Pt(221) surface [10, 29], in which they find that the dissociation is not favored for single water molecules. The presence of additional water molecules will facilitate the dissociation by incorporating the formed OH into a hydrogen-bonded network.

1.5.4 H₂O

The interaction of water with the surface of platinum has been the subject of numerous experimental studies [30–35]. On the Pt(111) surface two main adsorption structures have been recorded: a $(\sqrt{37} \times \sqrt{37})$ structure at coverages below one monolayer and a $\sqrt{39} \times \sqrt{39}$ structure that is dominant at coverages

of 1 ML. The structures that are observed do not only contain the hexagonal pattern present in crystalline hexagonal ice I_h , but also pentagons and heptagons. Regularly stepped surfaces were studied with TPD in our group [14], where it was found that water exhibits a two peak spectrum on the Pt(533) and Pt(553) surfaces. The desorption temperatures are very similar for both step-types. The high-temperature peak that only appears on these stepped surfaces is interpreted as strongly bound water adsorbed on the step edges. Additionally, the step edges on defective Pt(111) surfaces were studied using scanning tunneling microscopy (STM) by Morgenstern et al. [32], who observed that the two step edge types present on these surfaces exhibit significantly differing adsorption behavior.

Water adsorption structures have also been discussed in the context of DFT studies. For the Pt(111) surface the $\sqrt{37} \times \sqrt{37}$ and $\sqrt{39} \times \sqrt{39}$ [30] adsorption structures were both verified using DFT calculations. Additional consideration was given to the interaction between the aqueous environment and a fully hydrogen-covered Pt(111) surface, where it was found that the hydrogen layer passivates the surface and leads to a reduced interaction between the water and the surface [36]. Water adsorption on regularly stepped platinum surfaces was first discussed by Meng et al [37], where they proposed the formation of a 1 one-dimensional line structure along the step edge. Additional studies on this topic were performed later by Arnadottir et al. [38, 39].

1.6 Outline of the thesis

The subsequent chapters of the thesis are ordered in the following way:

In chapter 2 we focus on the low-coverage adsorption regime on both model surfaces. We study the adsorption of hydrogen, oxygen, OH and water across the complete surface and arrive at a detailed understanding of the adsorption site preferences. Furthermore, we show that for the Pt(533) surface the low-coverage picture is sufficient to arrive at a clear understanding of the experimental TPD spectra, while for the Pt(553) surface, only water and oxygen can be explained fully by this approach. For the hydrogen desorption from the Pt(553) surface we can only explain the low-coverage part of the spectrum, while a full picture for the the high-coverage part remains elusive. Additionally, we use our data to calculate energetics for the autocatalytic splitting of water at the step-edge sites.

In chapter 3 we model high-coverage water adsorption structures on the (100)-type step edge of Pt(533). We gradually increase the coverage beyond the low-coverage regime and arrive at adsorption geometries of water for medium and high coverage. We find that water forms two lines along the upper and lower step edge, which can be connected in a large number of ways to form different ring

sizes. We find multiple structures with very similar adsorption energies with ring sizes ranging from 4 (tetragons) to 7 (heptagons).

In chapter 4 we present a combined STM and DFT project that investigates the adsorption structures of water around the (111) step edge of Pt(553). We performed a similar DFT analysis for the adsorption geometries as presented on the Pt(533) surface and find that the (111)-type edge present on Pt(553) strongly prefers the formation of double-stranded tetragonally-linked water structures. Our experimental collaborators confirm the formation of these double-stranded water networks on the surfaces using low-temperature scanning tunneling microscopy (STM).

In chapter 5 we discuss high-coverage hydrogen-adsorption calculations on both model surfaces. This is done to help elucidate the previously not well-understood TPD spectrum originating from the Pt(553) surface. On Pt(533) we find that the adsorption energies fall into two main energy ranges, which correspond to the two peaks visible in the TPD spectrum. On Pt(553) we identify the step-edge site as the most favorable adsorption site. Combining this with the experimentally-obtained ratio of the integrals of the different peaks allows us to arrive at a value for the maximum coverage on this surface. It is found that this coverage is significantly lower than on Pt(533). The low-temperature part of the spectrum is found to originate from two energetically different sites on the middle of the terrace of the surface.

The short chapter 6 gives a short summary on the supporting information for each chapter. The subsequent chapter 7 gives a short outlook on possible follow-up projects, while the final chapter 8 gives conclusions based on the obtained results.

References

- (1) Energiewende, A. Agorameter., Retrieved on 26.11.2015, <http://www.agora-energiewende.de/en/topics/-agothem-/Produkt/produkt/76/Agorameter/>.
- (2) Marković, N. M.; Ross, P. N. *Surf. Sci. Rep.* **2002**, *45*, 117–229.
- (3) Koper, M. T. M. *Nanoscale* **2011**, *3*, 2040–3364.
- (4) Dreizler, R. M.; Gross, E. K., *Density Functional Theory: An Approach to the Quantum Many-Body Problem*; Springer: Berlin, Apr. 1996.
- (5) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864–B871.
- (6) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133–A1138.
- (7) Perdew, J. P.; Yue, W. *Phys. Rev. B* **1986**, *33*, 8800–8802.
- (8) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (9) Vasić, D.; Ristanović, Z.; Pašti, I.; Mentus, S. *English Russian Journal of Physical Chemistry A* **2011**, *85*, 2373–2379.
- (10) Peköz, R.; Wörner, S.; Ghiringhelli, L. M.; Donadio, D. *The Journal of Physical Chemistry C* **2014**, *118*, 29990–29998.
- (11) Carrasco, J.; Klimeš, J.; Michaelides, A. *The Journal of Chemical Physics* **2013**, *138*, 024708.
- (12) Christmann, K; Ertl, G; Pignet, T *Surface Science* **1976**, *54*, 365–392.
- (13) Badan, C.; Koper, M. T. M.; Juurlink, L. B. F. *The Journal of Physical Chemistry C* **2015**, *119*, 13551–13560.
- (14) Van der Niet, M. J. T. C.; den Dunnen, A.; Juurlink, L. B. F.; Koper, M. T. M. *J. Chem. Phys.* **2010**, *132*, 174705.
- (15) Gee, A. T.; Hayden, B. E.; Mormiche, C.; Nunney, T. S. *The Journal of Chemical Physics* **2000**, *112*, 7660–7668.
- (16) Gee, A.; Hayden, B.; Mormiche, C; Nunney, T. *Surface Science* **2002**, *512*, 165–172.
- (17) Kirsten, E.; Parschau, G.; Stocker, W.; Rieder, K. *Surface Science* **1990**, *231*, L183–L188.
- (18) Olsen, R. A.; Kroes, G. J.; Baerends, E. J. *The Journal of Chemical Physics* **1999**, *111*.

- (19) Olsen, R.; Badescu, S.; Ying, S.; Baerends, E. *J. Chem. Phys.* **2004**, *120*, 11852–11863.
- (20) Gudmundsdóttir, S.; Skúlason, E.; Jónsson, H. *Phys. Rev. Lett.* **2012**, *108*, 156101.
- (21) Gudmundsdóttir, S.; Skúlason, E.; Weststrate, K.-J.; Juurlink, L.; Jonsson, H. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6323–6332.
- (22) Gland, J. L.; Sexton, B. A.; Fisher, G. B. *Surface Science* **1980**, *95*, 587–602.
- (23) Feibelman, P. J.; Esch, S.; Michely, T. *Phys. Rev. Lett.* **1996**, *77*, 2257–2260.
- (24) Van der Niet, M. J. T. C.; Berg, O. T.; Juurlink, L. B. F.; Koper, M. T. M. *The Journal of Physical Chemistry C* **2010**, *114*, 18953–18960.
- (25) Van der Niet, M. J. T. C.; Garcia-Araez, N.; Hernández, J.; Feliu, J. M.; Koper, M. T. M. *Catalysis Today* **2013**, *202*, 105–113.
- (26) Van der Niet, M. J. T. C.; den Dunnen, A.; Juurlink, L. B. F.; Koper, M. T. M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1629–1638.
- (27) Tripković, V.; Skúlason, E.; Siahrostami, S.; Nørskov, J. K.; Rossmeisl, J. *Electrochimica Acta* **2010**, *55*, 7975–7981.
- (28) Lew, W.; Crowe, M. C.; Campbell, C. T.; Carrasco, J.; Michaelides, A. *The Journal of Physical Chemistry C* **2011**, *115*, 23008–23012.
- (29) Donadio, D.; Ghiringhelli, L. M.; Delle Site, L. *Journal of the American Chemical Society* **2012**, *134*, 19217–19222.
- (30) Feibelman, P. J.; Bartelt, N. C.; Nie, S.; Thürmer, K. *The Journal of Chemical Physics* **2010**, *133*, 154703.
- (31) Fisher, G. B.; Gland, J. L. *Surface Science* **1980**, *94*, 446–455.
- (32) Morgenstern, M.; Michely, T.; Comsa, G. *Phys. Rev. Lett.* **1996**, *77*, 703–706.
- (33) Nie, S.; Feibelman, P. J.; Bartelt, N. C.; Thürmer, K. *Phys. Rev. Lett.* **2010**, *105*, 026102.
- (34) Zimbitas, G.; Haq, S.; Hodgson, A. *The Journal of Chemical Physics* **2005**, *123*, 174701, –.
- (35) Zimbitas, G.; Hodgson, A. *Chemical Physics Letters* **2006**, *417*, 1–5.
- (36) Roman, T.; Groß, A. *Catalysis Today* **2013**, *202*, 183–190.
- (37) Meng, S.; Wang, E. G.; Gao, S. *Phys. Rev. B* **2004**, *69*, 195404.

- (38) Arnadottir, L.; Stuve, E. M.; Jonsson, H. *Surf. Sci.* **2010**, *604*, 1978 –1986.
- (39) Arnadottir, L.; Stuve, E. M.; Jonsson, H. *Surface Science* **2012**, *606*, 233 –238.

Chapter 2

Density Functional Theory Study of Adsorption of H₂O, H, O and OH on Stepped Platinum Surfaces

2.1 Abstract

We report on DFT-GGA-computed adsorption energetics of water and the water-related fragments *OH*, *O* and *H* on stepped Pt surfaces in the low coverage limit. The Pt(100) step edge as encountered on Pt(533) shows increased binding for all species studied, while the Pt(110) step edge, as found on Pt(553) shows only significantly enhanced binding for *O* and *OH*. Comparing these results to ultra-high-vacuum experiments reveals that DFT can explain the main experimental trends semiquantitatively.

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2.2 Introduction

Platinum plays a key role in catalysis, and it is ideally suited as electrocatalyst for low-temperature Polymer Electrolyte Membrane (PEM) fuel cells,¹ water electrolysis and many other electrochemical reactions. Understanding the interaction between platinum surfaces and water molecules at the atomic level is important for the further improvement of its activity and in creating new, cost-effective catalysts that perform similarly to platinum [2, 3]. In order to achieve a complete picture of real catalytic surfaces, which usually consist of small particles on a support, not only the consideration of high-symmetry facets of the surface is required, but also the influence of step and kink sites on adsorption and reactivity [4, 5]. The effect of isolated step sites can be systematically studied using regularly stepped surfaces. These consist of flat terraces of high-symmetry facets interrupted by mono-atomic steps. This setup allows for direct observation of the influence of the step type on the reactivity, thereby providing some insight on the influence of steps on the overall catalytic activity. Traditionally, most experimental and theoretical studies devoted to the interaction of water with platinum surfaces have dealt with either flat Pt(111) surfaces or other facets with rather low surface indices [6, 7]. While this helps to reduce computational efforts, such calculations give limited insight into the adsorption energies of isolated steps due to the influence of step-step interactions and the interactions between all terrace adsorption sites with the step edge on short terraces. However, more recent computational studies [8–10] have considered surfaces with steps of a separation distance similar to the one studied in this paper.

In previous experimental work from our group [11], we studied the desorption of H , O and H_2O from two stepped Pt surfaces, Pt(533) and Pt(553), using the Temperature Programmed Desorption (TPD) technique in ultra-high vacuum (UHV). The Pt(533) surface consists of a 4-atom-long terrace of (111) character and a (100) step edge, whereas the Pt(553) surface has a 5-atom-long (111) terrace and a (111) step edge. A side- and top-view of the surfaces are shown further into the paper as figures 2.1 and 2.2.

It was found that hydrogen desorbs in a two-peak structure from Pt(533) and in a more complicated pattern with two or three peaks from Pt(553). Atomic oxygen was found to desorb in a two-peak structure from both surfaces. The high-temperature peak was found at higher temperatures for Pt(533) compared to Pt(553) [11]. Desorption of H_2O was observed to exhibit a three-peak structure for both Pt(533) and Pt(553). The low-energy peak was assigned to multi-layer desorption. The high-energy peak was attributed to desorption from steps, since it was not observed on the flat Pt(111) surface. The intermediate-temperature peak was located at a temperature comparable to that of Pt(111), therefore it

was assigned to desorption from terraces. The high-temperature peak was detected at comparable temperatures for both surfaces, suggesting that the adsorption energies of water for the two different step geometries are not significantly different. For most adsorbates it was concluded that step sites should bind adsorbates stronger than terrace sites, and for H and O this tendency is stronger for the (100)-type step site. For a more detailed description of the desorption spectra we refer to the original publication.

The aim of this study is to establish a qualitative explanation for the results of the TPD experiments, by computing the adsorption energy of water and its dissociation products H , O and OH on the stepped surfaces Pt(533) and Pt(553) using Density Functional Theory. This will serve as a benchmark for future studies on the interaction of water with adsorbate-covered stepped Pt surfaces and complements other studies on the intrinsic different catalytic activity of (100) and (110) step edges [12].

2.3 Computational

The computations were performed using the ab-initio density functional code VASP [13–16] using the PBE exchange-correlation functional [17] and PAW potentials [18, 19]. The PBE functional was chosen in order to obtain reasonable adsorption energies across the whole range of species studied here to and adequately describe hydrogen bonding among water molecules [20] for future calculations that include solvation. The k-point sampling was done using a Monkhorst - Pack scheme [21] using 9x9x1 sampling for the Pt(111) surface and a 3x9x1 sampling for the stepped Pt(533) and Pt(553) surfaces. A basis set with a cut-off energy of 550 eV was chosen. For all calculations first-order Methfessel-Paxton smearing [22] with a sigma of 0.2 was applied and all energies were extrapolated to an electronic temperature of 0 K. All calculations were performed spin restricted. The replicated images of the cells due to the periodic boundary conditions were separated by about 20 Å of vacuum. Gas phase species were calculated using a 10x10x10 Å unit cell with a 1x1x1 k-point sampling in which the gas phase species were placed.

The Pt(111) surface was a 2x2 replicated surface unit cell with 3 relaxing layers at the top and 2 layers fixed at bulk positions at the bottom. This is beyond what is necessary for convergence on a (111) surface, but proved necessary to achieve consistency with the stepped surfaces. Figures 2.1a) and 2.1b) show a side view of the model stepped surfaces. Fixed layers are black, surface layers are silver, the first subsurface layer is blue and the second subsurface layer is red. Note that when using a 4-layer model to stepped surfaces the atom that forms the lower

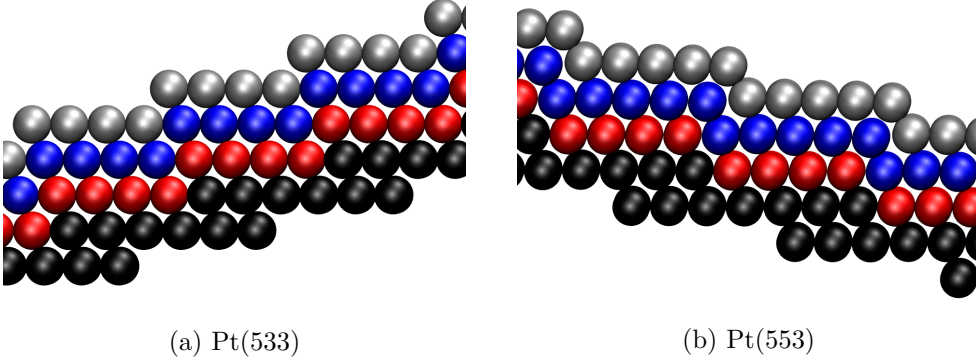


Figure 2.1: Sideview of the two model surfaces

step edge has a nearest neighbor that is fixed in its bulk position, resulting in a distorted step edge. This influences the total energy for that cell and the resulting step geometry. Therefore, we increased the number of layers to 5 to solve this problem. The resulting unit cell was then replicated in the direction parallel to the step edge to achieve similar adsorbate-adsorbate separation as on Pt(111). The free energies of adsorption of H , O , OH and H_2O were calculated as follows:

$$\Delta G_{ads,H} = G_{total,H_{ads}} - G_{clean} - \frac{1}{2}G_{H_2(g)} \quad (2.1)$$

$$\Delta G_{ads,O}^{O_2(g)} = G_{total,O_{ads}} - G_{clean} - \frac{1}{2}G_{O_2(g)} \quad (2.2a)$$

where,

$$G_{O_2(g)} = 2(G_{H_2O(g)} - G_{H_2} - \Delta G_{form,exp}^{H_2O}) \quad (2.2b)$$

and

$$\Delta G_{form,exp}^{H_2O}(g) = -2.37 \text{ eV at } P = 1 \text{ atm and } T = 298.15 \text{ K} \quad (2.2c)$$

$$\Delta G_{ads,O}^{H_2O} = G_{total,O_{ads}} - G_{clean} - G_{H_2O(g)} + G_{H_2(g)} \quad (2.3)$$

$$\Delta G_{ads,OH} = G_{total,OH_{ads}} - G_{clean} - G_{H_2O(g)} + \frac{1}{2}G_{H_2(g)} \quad (2.4)$$

$$\Delta G_{ads,H_2O} = G_{total,H_2O_{ads}} - G_{clean} - G_{H_2O(g)} \quad (2.5)$$

Each individual G was calculated as follows:

$$G_{A_{ads}} = E_{DFT,A} + ZPE(A) - T * S(A)_{vib} \quad (2.6)$$

for adsorbate A and

$$G_{B(g)} = E_{DFT,B} + ZPE(B) - T * S(B) \quad (2.7)$$

for gas-phase species B. Note that $S(B)$ is the total entropy and is taken from reference tables for gas phase species [23].

The free energies of adsorption of oxygen were calculated for two references (Eq. 2.2a and 2.3). One for comparison to gas phase O_2 (Eq. 2.2a) which is the more relevant reference for comparison to TPD experiments, that is calculated based on the experimental formation energy of water (Eq. 2.2b), in order to avoid the inaccuracy of the DFT value for O_2 [24, 25]. The other reference is calculated using water as a reference (Eq. 2.3), which is the relevant reference value for comparison to electrochemistry and for the possible formation of OH on step edges. All adsorption energies below are Gibbs energies and corrected for zero-point energy (ZPE) and vibrational entropy at 298 K, following the methods described by Loffreda [26].

The adsorption sites on Pt(533) and Pt(553) surfaces are illustrated in figures 2.2a and 2.2b. Platinum atoms in the surface layer are colored in silver, those in the subsurface layer are blue and those in the second layer below the surface are red. The adsorption sites are OT for on-top adsorption, B for bridge sites and FCC/HCP for the two three-fold hollow adsorption sites. Bronze bonds represent the direct connection between two surface atoms in the (111) plane, magenta bonds show direct connections in the (100)/(110) steps. A full catalogue of adsorption sites, their associated energies, vibrational frequencies and geometry information is available in the supporting information [27].

2.4 Results and Discussion

2.4.1 The Pt(533) and Pt(553) surfaces

In the absence of adsorbates, the surface relaxation is not extensive, i.e. the displacements of edge atoms are quite small. The total energy gained from relaxing the top three layers of the surface is small (0.0122 and 0.0076 eV per platinum atom in the unit cell for Pt(533) and Pt(553), respectively). In both optimized structures the exposed surface area is minimized by retracting the edge atoms into the deeper layers, as can be seen in figures 2.1a and 2.1b. These relaxation effects on edge atoms lead to a slight tilt of the (111) surface towards the (533)/(553) surface normal.

Adsorption energies on the stepped surfaces are not completely converged with respect to the thickness of the slab. However, tests showed that this leads to a

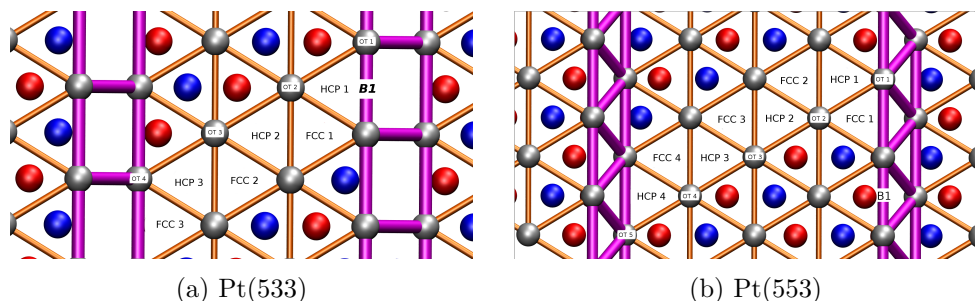


Figure 2.2: Adsorption sites on the stepped surfaces (Surface layer atoms marked silver, second layer atoms blue and third layer atoms red)

uniform shift of the adsorption energies of all sites. The results of these tests can be found in the supporting information. This allows us to look primarily at general trends in adsorption energies. We emphasize that the simultaneous full convergence of all adsorption energies for all species on all surfaces considered here is not within the scope of this paper. In order to observe possible trends in the shift of the d-band center for the step-edge atoms, the LDOS (local density of states) for the surface atoms of the Pt(111) facet and step edge atoms of the two studied surfaces were calculated and can be found in the supporting information. No obvious shift or difference in the d-band center for either surface was observed.

2.4.2 Hydrogen Adsorption

The distinct adsorption sites for hydrogen are the on-top position, the bridge position between two surface platinum atoms and the two three-fold hollow sites, HCP and FCC. These adsorption sites are, from an energetic point of view, almost equivalent, with a slight preference towards the three-fold hollow sites. The results for Pt(111) using our approach can be found in table 2.1. Earlier results obtained by Olsen et al. [28] with two different GGA functionals (BP and PW91) revealed a similar range of adsorption energies as computed here. The functionals in those studies however showed a clear trend towards on-top adsorption, which is not found here. It should be noted that the results of Olsen et al. did not take ZPE and vibrational entropy into account, so they cannot be directly compared to the Gibbs energies of adsorption computed here.

For the stepped surfaces almost all bridge sites on the terrace do not contribute to adsorption, because the two neighboring three-fold hollow sites are, unlike on the flat Pt(111) surface, no longer equivalent in energy. This leads to an energy gradient that moves the hydrogen atom out of the bridge position towards the

Table 2.1: Adsorption energies for hydrogen on Pt(111), Pt(533) and Pt(553)

Adsorption Site	$G_{Pt(111)}[eV]$	$G_{Pt(533)}[eV]^*$	$G_{Pt(553)}[eV]^*$
OT terrace (OT2/OT3)	-0.26	-0.20	-0.18
HCP terrace (HCP2/HCP3)	-0.26	-0.18	-0.15
FCC terrace (FCC2/FCC3)	-0.29	-0.21	-0.21
Bridge terrace	-0.25	—	—
Bridge B1	—	-0.41	-0.26
On-Top OT1	—	-0.26	-0.19
FCC1	—	-0.19	-0.28
HCP1	—	-0.23 **	-0.28
On-Top OT4 / OT5	—	-0.27	-0.16

* Adsorption energy converged to 0.05eV for present layer thickness (see SI)

** Approximate energy, atom fixed at unstable adsorption site

neighboring site with the strongest binding. In table 2.1 we only provide the adsorption sites in the middle of the terrace for comparison to pristine Pt(111). A full overview of all adsorption sites can be found in the supporting information.

On the Pt(533) surface, the strongest binding site is the B1 site on the step edge. The OT1 site, which is also located on the step edge, shows enhanced binding compared to the OT site on the terrace as well. However, the nearby B1 site is significantly more stable, therefore on real surfaces this site will probably not play a role. Another binding site is the OT4, which is located on the lower step edge and also shows slightly enhanced binding compared to Pt(111). It should be noted that this site has a two-fold coordination, despite being identified as an on-top site, since it is also located close to the platinum atom in the upper step edge. The three-fold hollow sites on the step edge, named FCC1 and HCP1, show binding energies comparable to the FCC1 site on the Pt(533) terrace, although the HCP1 site is no longer stable and hydrogen will move to the B1 site with no noticeable barrier. To estimate the energy of this binding site the atom was fixed at the HCP1 site, which then showed slightly enhanced binding compared to the terrace, even in this unrelaxed HCP position. On the Pt(553) surface the situation is significantly different. The most important sites on the surface are again shown in table 2.1. We found that B1 on the step edge of this surface binds hydrogen significantly weaker than the same site on the Pt(533) step edge. The B1 site is therefore no longer the strongest binding site, but is energetically comparable

Table 2.2: Adsorption energies for oxygen on Pt(111), Pt(533) and Pt(553)

Adsorption Site	$G_{O_{ad},Pt(111)}$ [eV] ⁺	$G_{O_{ad},(533)}$ [eV] ^{*,+}	$G_{O_{ad},(553)}$ [eV] ^{*,+}
On-Top, terrace	0.14 / 2.51	0.42 / 2.79	0.43 / 2.79
HCP hollow, terrace	-0.68 / 1.69	-0.62 / 1.75	-0.57 / 1.80
FCC hollow, terrace	-1.14 / 1.23	-0.96 / 1.41	-0.92 / 1.45
Bridge B1	—	-1.43 / 0.94	-1.10 / 1.27
FCC1	—	-1.07 / 1.30	-1.29 / 1.08
OT5	—	—	-0.91 / 1.46

* Adsorption energy converged to within 0.05 eV for present layer thickness (see SI)

⁺ First value for $O_2(g)$ reference, second for H_2O reference

to the FCC1 position. The lower step edge on Pt(553) also binds hydrogen significantly weaker than the comparable geometry on Pt(533). The terrace sites, however, show very similar binding energies as the Pt(533) terraces. This means that the most important difference between the Pt(553) and the Pt(533) surfaces is the stronger stabilization provided by the Pt(533) step edge.

Comparison to Experiment

In the temperature-programmed desorption experiments of van der Niet et al. [11], desorption of deuterium was compared on Pt(111), Pt(533) and Pt(553). They found that the introduction of steps only leads to stabilization of H on the Pt(533) step edge and not on Pt(553). Our DFT findings are in good agreement with those results. Reproducing the details of the TPD spectra requires a more detailed account of lateral interactions and surface diffusion, as presented in [29, 30].

2.4.3 Oxygen Adsorption

In order to ensure consistency with previous results (e.g. [31]), we will briefly discuss the results for oxygen adsorption on Pt(111). We find that the FCC site is the most stable, with an adsorption energy of -1.14 eV with respect to the $O_2(g)$ reference or 1.23 eV on the H_2O -based scale. This is followed by the HCP site and the on-top site. The bridge position is, in contrast to hydrogen, unstable and leads to a shift into one of the hollow sites. It should be noted that our results are all obtained using non-spin-polarized calculations, leading to a slightly

underestimated binding for the on-top site, as can be expected due to an increased net spin of the bonded oxygen when performing spin-polarized calculations.[32]. We find an energy difference between spin-restricted and unrestricted calculations of about 0.1 eV for the on-top site, while no changes are observed for any site with an oxygen atom that is coordinated to more than one platinum atom. None of the affected sites plays a role in the actual adsorption since even their corrected adsorption energies are well above all neighboring sites.

On the stepped Pt(533) surface the situation is similar to the case of hydrogen discussed earlier. The binding energies for the most important sites can be found in table 2.2. The B1 site again shows enhanced binding compared to the Pt(111) surface, although we find no stable binding site on the lower step edge as we did for hydrogen. The FCC1 site on the upper step edge shows an adsorption energy that is comparable to the FCC site on the Pt(111) surface. On the Pt(553) surface the results are again notably different. The strongest adsorption site is now the FCC1 site on the upper step edge, comparable to the case for hydrogen. Additionally, the OT5 site, which actually has three-fold coordination due to its position on the lower edge of the step, is able to bind oxygen.

In conclusion, our calculations for oxygen adsorption on stepped platinum surfaces show that the strongest binding would occur at the B1 position on Pt(533), which binds oxygen significantly stronger than on Pt(111). On Pt(553) we find an increased binding compared to Pt(111) but this increase is less than on Pt(533).

Comparison to Experiment

Van der Niet et al. found in their TPD study that oxygen desorbing from Pt(533) shows a two-peak structure with a peak at 774 K and another one at 663 K[11]. The low-temperature peak was found at a comparable temperature as desorption from Pt(111) and was, therefore, assigned to desorption from terraces. The high-temperature peak was assigned to oxygen desorption from steps. On Pt(553) they found a similar two-peak structure, however the high-energy peak was located at the somewhat lower temperature of 738 K. This suggests that the step edge in Pt(533) binds oxygen stronger than Pt(111) terraces and also stronger than the Pt(553) step edge. This matches satisfactorily our DFT results. The change of the preferred adsorption site from the B1 site on the step edge for Pt(533) to the FCC1 site behind the step edge is in agreement with the results observed by DFT(LDA) and STM in the study by Feibelman et al. [33].

Table 2.3: Adsorption energies for H_2O on Pt(111), Pt(533) and Pt(553), most stable geometries at the given points

Adsorption Site	$G_{Pt(111)}$ [eV]	$G_{Pt(533)}$ [eV] *	$G_{Pt(553)}$ [eV] *
On-Top, terrace, flat	0.28	0.27	0.24
OT1, step edge	—	0.06	0.07

* Adsorption energy converged to within 0.05 eV for present layer thickness (see SI)

2.4.4 H_2O Adsorption

For Pt(111) we find an adsorption energy for water monomers adsorbed in a flat on-top position of 0.28 eV. This value differs significantly from earlier studies, none of which included both ZPE and vibrational entropy. Our raw DFT energy E , -0.23 eV is closer to the literature results of -0.30 eV calculated with PW91 [34, 35]. The Gibbs energy of water adsorption is rather sensitive to the actual observed geometry of adsorption. The actual value for vibrational entropy changes by as much as 30 % when rotating the water molecule at a certain site. Nevertheless, this only changes the adsorption energy by about 0.05 eV at most, and therefore the general trends detailed here are still expected to be valid. For the sake of consistency, in the following we will continue using the same convention as before and provide the Gibbs energies of adsorption at 298K. Due to this convention most adsorption energies will be positive, which is intuitively expected, because water will have desorbed from the surface long before reaching that temperature [11]. We also note that for water the convergence with regard to the number of layers is faster than for oxygen and hydrogen.

The tendency of water to bind preferentially atop platinum atoms is still valid on the stepped surfaces. Table 2.3 contains the adsorption energies for the aforementioned Pt(111) surface and for both stepped surfaces. However, the on-top positions on the step edge bind water with a binding strength of 0.06 eV and 0.07 eV for the Pt(533) and Pt(553) surface respectively, compared to 0.28 eV for Pt(111). This is in qualitative agreement with earlier results for (100) and (110) step edges which showed an increase in binding energy E of ca. 0.15 eV for the step edge compared to flat Pt(111) surfaces [9].

Comparison to Experiment

In the TPD experiments performed by Van der Niet et al, it was found that water desorbs from stepped platinum surfaces in a three-peak structure[11]. The highest-temperature peak was always assigned to desorption from the step edges, since no comparable peak was observed on the Pt(111) surface. The desorption temperature for the step-related peak was found ca. 10K lower on the Pt(533) surface compared to the Pt(553) surface. The intermediate-temperature peak was assigned to desorption from terraces, since it agrees with the peak observed on Pt(111). The lowest-temperature peak was assigned to the desorption of water from multi-layer water structures. The DFT results presented here show qualitative agreement with experiment in that the terrace adsorption energy is lower than the adsorption energy on the step edge. It should be noted that the difference in adsorption energies for Pt(533) and Pt(553) observed experimentally is not explained by the present calculations of the adsorption of single water molecules.

2.4.5 OH Adsorption

As OH is an important water-related intermediate at electrochemical interfaces, we also provide adsorption energies for OH on the three surfaces. Pt(111) shows a large preference to adsorb the OH molecule in either an atop or a bridge position. The FCC and HCP hollows show significantly reduced binding energies. Adsorption energy values for OH on Pt(111) can be found in table 2.4. Our values are in agreement with the results by Nørskov and Campbell et al. [36] for the Pt(111) surface, who reported an adsorption energy of -1.54 eV against a gas-phase OH reference. Using their formation energy for gas-phase OH of 0.32 eV and transforming it to our energy reference yields an adsorption energy of +1.12 eV for the OH adsorption on Pt(111). Our adsorption energy value with ZPE correction but without vibrational entropy for the isolated OH molecule on the Pt(111) surface is 0.91 eV, which is reasonably close given that different functionals were used. Introducing steps into the surface breaks the symmetry of the adsorption sites in one direction of the surface. FCC and HCP hollow sites are not found to be local minima near step edges, suggesting that on Pt(111) they were mainly stabilized into a meta-stable position by the symmetry of the surface. The Pt(533) surface shows an increased binding at the step-edge bridge site, similar as for the other adsorbates. Additionally, we found a difference in the adsorption energy for the terrace bridge sites depending on their orientation. Bridge sites at the terraces of Pt(533) parallel to the step edge were found to be no longer stable near the step edge, while all other bridge sites were stable, although they show decreased binding compared to Pt(111). The binding energy on the step edge of Pt(553) is

Table 2.4: Adsorption energies for OH on Pt(111), Pt(533) and Pt(553)

Adsorption Site	$G_{Pt(111)}[eV]$	$G_{Pt(533)}[eV]^*$	$G_{Pt(553)}[eV]^*$
On-Top, terrace, flat	1.02	1.16	1.18
Bridge, terrace (parallel)	1.02 **	1.08	1.22
Bridge, terrace (other dir.)	1.02 **	1.23	1.16
Bridge B1	—	0.27	0.66
HCP hollow ,terrace	1.54	unstable	unstable
FCC hollow, terrace	1.27	unstable	1.44

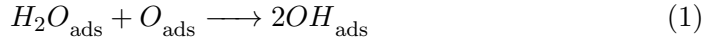
* Adsorption energy converged to within 0.05 eV for present layer thickness (see SI)

** No directional influence on the Pt(111) surface

significantly less favorable compared to the Pt(533) surface. The bridge sites on the Pt(553) terrace show no directional variance with respect to binding energy, and all of them are stable. In conclusion, OH prefers to bind to step edges in the B1 position on both surfaces and is ca. 0.7 eV more stable for Pt(533) and ca. 0.4 eV for Pt(553) compared to Pt(111).

Comparison to Experiment

The adsorption of OH cannot be directly studied in UHV. Typically the generation of OH_{ads} is performed by dosing water onto a Pt surface pre-covered with O_{ads} . This leads to the following net reaction:



Our calculations suggest that this reaction is exothermic on the Pt(100) step, endothermic on the Pt(111) surface and almost thermoneutral for the step edge on Pt(553), with a ΔG of -0.49 eV at 298K for the Pt(533) surface, +0.52 eV for Pt(111) and -0.01 eV for the Pt(553) surface (see table 2.5). These numbers were calculated by considering all adsorbates in isolation on their most stable adsorption sites. No interaction with water was considered, which is certainly important when studying electrochemical reactions [37, 38]. From these results we can conclude that reaction 1 generates more OH_{ads} on the Pt(533) step compared to Pt(553). On Pt(111) this reaction should not take place if stabilizing effects are not accounted for. Surrounding water will play an important role in stabilizing OH adsorbates via hydrogen bonds [39].

Table 2.5: ΔG for reactions (1) and (2) on different surfaces at 298K

	$H_2O_{\text{ads}} + O_{\text{ads}} \longrightarrow 2OH_{\text{ads}}$ (Reaction 1)	$H_2O_{\text{ads}} \longrightarrow OH_{\text{ads}} + H_{\text{ads}}$ (Reaction 2)
Pt(111)	0.52	0.47
Pt(533)	-0.49	-0.23
Pt(553)	-0.01	0.33

Additionally, it is also possible that thermal dissociation of water can result in the formation of OH groups on the surface. For this we considered the following reaction:



This reaction has a ΔG of -0.23 eV on Pt(533), +0.33 eV on Pt(553) and +0.47 eV on Pt(111) at 298K, again with all adsorbates binding to their most stable sites in complete isolation. The results suggest that on the step edge of Pt(553) reaction 2 is endothermic, while for the step edge of Pt(533) water has a thermodynamic tendency to dissociate. On Pt(111) reaction 2 will not take place without further stabilization of OH . In conclusion, it can be assumed that in the low coverage limit on the Pt(533) surface, water will dissociate into H and OH on steps, depending on the barrier of the dissociation reaction, whereas on the Pt(553) surface there is no driving force towards forming OH .

2.5 Conclusions

In this paper, we presented the DFT-GGA adsorption energetics of water and the water-related fragments OH , O and H on stepped Pt surfaces in the low coverage limit for comparison with experimental results on the same surface. The general trend indicates that the (100) step edge present in Pt(533) shows significantly enhanced binding for all studied species, while the (111)/(110) step edge present in Pt(553) shows no significant increase in binding energy for H , noticeable increases for O and OH , although less than the Pt(533) step edge, and similar increases for H_2O when compared to Pt(533). We would ascribe this stronger bonding of the (100) step to its more open character compared to the (111) step, though we note that there is no noticeable change in the local d-band center. Comparison of these results to experimental TPD measurements previously obtained in our group shows that the general trends of the low coverage results of the TPD measurements are matched by the calculations. Nevertheless, for the high coverage limit, as well

as for water and OH , where interactions between the adsorbates play a large role, trends may no longer be explained with the present results. The benchmark study presented here gives confidence that including interactions between adsorbates and water should yield valuable results that will improve the theoretical description of realistic platinum surfaces.

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References

- (1) Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. *Appl. Catal. B: Environmental* **2005**, *56*, 9–35.
- (2) Koper, M. T. M., *Fuel Cell Catalysis: A Surface Science Approach*; Wiley: 2009.
- (3) Rabis, A.; Rodriguez, P.; Schmidt, T. J. *ACS Catalysis* **2012**, *2*, 864–890.
- (4) Marković, N. M.; Ross, P. N. *Surf. Sci. Rep.* **2002**, *45*, 117–229.
- (5) Koper, M. T. M. *Nanoscale* **2011**, *3*, 2040–3364.
- (6) Olsen, R.; Badescu, S.; Ying, S.; Baerends, E. *J. Chem. Phys.* **2004**, *120*, 11852–11863.
- (7) Burch, R.; Daniells, S.; Breen, J.; Hu, P. *J. Catal.* **2004**, *224*, 252–260.
- (8) Rafti, M.; Vicente, J. L.; Albesa, A.; Scheibe, A.; Imbihl, R. *Surf. Sci.* **2012**, *606*, 12–20.
- (9) Arnadottir, L.; Stuve, E. M.; Jonsson, H. *Surf. Sci.* **2010**, *604*, 1978–1986.
- (10) Buso-Rogero, C.; Herrero, E.; Bandalow, J.; Comas-Vives, A.; Jacob, T. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18671–18677.
- (11) Van der Niet, M. J. T. C.; den Dunnen, A.; Juurlink, L. B. F.; Koper, M. T. M. *J. Chem. Phys.* **2010**, *132*, 174705.

- (12) Tison, Y.; Nielsen, K.; Mowbray, D. J.; Bech, L.; Holse, C.; Calle-Vallejo, F.; Andersen, K.; Mortensen, J. J.; Jacobsen, K. W.; Nielsen, J. H. *J. Phys. Chem. C* **2012**, *116*, 14350–14359.
- (13) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561.
- (14) Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251–14269.
- (15) Kresse, G.; Furthmüller, J. *Computational Materials Science* **1996**, *6*, 15 – 50.
- (16) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (17) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (18) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (19) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (20) Hamann, D. R. *Phys. Rev. B* **1997**, *55*, R10157–R10160.
- (21) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (22) Methfessel, M.; Paxton, A. T. *Phys. Rev. B* **1989**, *40*, 3616–3621.
- (23) Ed. Chase, M.; Davies, C.; Downey, J.; Frurip, D.; MacDonald, R.; Syverud, A., *NIST-JANAF Thermodynamical Tables*, Suppl. 1 to Vol 14 of J. Phys. Chem. Ref. Data, 1985; Vol. 14.
- (24) Martínez, J. I.; Hansen, H. A.; Rossmeisl, J.; Nørskov, J. K. *Phys. Rev. B* **2009**, *79*, 045120.
- (25) Calle-Vallejo, F.; Martnez, J. I.; Garca-Lastra, J. M.; Mogensen, M.; Rossmeisl, J. *Angew Chem Int Edit*, *49*.
- (26) Loffreda, D. *Surf. Sci.* **2006**, *600*, 2103 –2112.
- (27) Kolb, M. J.; Calle-Vallejo, F.; Juurlink, L. B. F.; Koper, M. T. M. Supporting Information to : Density functional theory study of adsorption of H₂O, H, O, and OH on stepped platinum surfaces., ftp://ftp.aip.org/epaps/journ_chem_phys/E-JCPSA6-140-043413/, 2014.
- (28) Olsen, R. A.; Kroes, G. J.; Baerends, E. J. *J. Chem. Phys.* **1999**, *111*, 11155–11163.
- (29) Gudmundsdóttir, S.; Skúlason, E.; Jónsson, H. *Phys. Rev. Lett.* **2012**, *108*, 156101.
- (30) Gudmundsdóttir, S.; Skulason, E.; Weststrate, K.-J.; Juurlink, L.; Jonsson, H. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6323–6332.

- (31) Tritsaris, G.; Greeley, J.; Rossmeisl, J.; Nørskov, J. *Catal. Lett.* **2011**, *141*, 909–913.
- (32) Jacob, T.; Muller, R. P.; Goddard, W. A. *J. Phys. Chem. B* **2003**, *107*, 9465–9476.
- (33) Feibelman, P. J.; Esch, S.; Michely, T. *Phys. Rev. Lett.* **1996**, *77*, 2257–2260.
- (34) Meng, S.; Wang, E. G.; Gao, S. *Phys. Rev. B* **2004**, *69*, 195404.
- (35) Vassilev, P.; van Santen, R. A.; Koper, M. T. M. *J. Chem. Phys.* **2005**, *122*, 054701.
- (36) Karp, E. M.; Campbell, C. T.; Studt, F.; Abild-Pedersen, F.; Nørskov, J. K. *J. Phys. Chem. C* **2012**, *116*, 25772–25776.
- (37) Tripković, V.; Skúlason, E.; Siahrostami, S.; Nørskov, J. K.; Rossmeisl, J. *Electrochimica Acta* **2010**, *55*, 7975–7981.
- (38) Van der Niet, M. J. T. C.; Garcia-Araez, N.; Hernández, J.; Feliu, J. M.; Koper, M. T. M. *Catalysis Today* **2013**, *202*, 105–113.
- (39) Lew, W.; Crowe, M. C.; Campbell, C. T.; Carrasco, J.; Michaelides, A. *The Journal of Physical Chemistry C* **2011**, *115*, 23008–23012.

Chapter 3

Initial Stages of Water Solvation of Stepped Platinum Surfaces

3.1 Abstract

Platinum is an active catalyst for a large number of (electro)chemical reactions in aqueous solution. The observed catalytic activities result from an interplay between the intrinsic adsorption properties of platinum surfaces and their interaction with the aqueous environment. Although water networks have been extensively studied on close-packed surfaces, little is known about high-coverage solvation environments around defects. Here, we report DFT calculations on medium- to high-coverage water adsorption structures near the (100) step edge on Pt(533). We find that isolated ring structures adjacent to step edges form hexagons or pentagons. For higher coverages, 6 possible adsorption structures with varying ring sizes along the step edge and almost identical adsorption energies are observed. From our results we conclude that the favorable interaction of the H-down oriented water molecules, adjacent to the step edge, with the step dipole plays an important role in the formation of these structures.

Furthermore, our results explain why water networks on stepped surfaces originate at the step edges, and extend towards the adjacent terraces, in agreement with previous experiments. These results show how step edges act as anchoring points for water adsorption and suggest that solvation of defects might dominate water structures on realistic platinum surfaces.

3.2 Introduction

Platinum is a prominent catalyst for a wide variety of chemical reactions [1–3] in liquid environments. In those environments, the effect of the solvent on the adsorption of reactants, intermediates and products plays a major role in the overall catalytic performance of platinum surfaces [4, 5]. As water is the most frequently used solvent in chemistry, a significant effort has been devoted to water adsorption on Pt(111) surfaces [6–8], leading to several models of catalytic reactions in solvated environments that can be quantitatively compared to experiments [7, 9].

However, in order to model realistic catalytic systems based on nanoparticles with multiple facets, edges and corners, the flat, pristine Pt(111) surface may not provide a comprehensive representation of the entire catalytic system. Defects are known to play a large role in either promoting [10, 11] or hindering [12] (electro)chemical reactions. Moreover, Pt(111) does not always provide the active site for a given catalytic reaction, as, for instance, certain reactions prefer pristine (100) facets [12, 13]. Therefore, it is important to understand how the solvation environment at defects influences the stability of adsorbed intermediates of (electro)catalytic reactions and the associated impact on reactivity. For instance, it is still a matter of debate [14, 15] whether water thermodynamically favors the generation of OH at step edges and why stepped Pt(111) surfaces in acidic media are more active for the oxygen reduction reaction than the Pt(111) itself [16]. Shedding light on these important matters is, however, rather challenging from a computational perspective, in view of the large unit cells needed to describe the surfaces in question and the large number of possible configurations for the adsorbed solvent molecules. This is why, to date, most studies have focused on the treatment of the low-coverage limit of a filled step edge, combined with a clean terrace [17–19], with exception of the recent work of Jinnouchi et al. [5] on Pt. Additionally, extended water structures on stepped gold surfaces were studied by Gross et al. [20]. Since in most experiments the coverages are always above the low-coverage limit, high-coverage computational studies are required to close the "coverage gap".

In this study we approach the real catalytic system from the standpoint of regularly stepped surfaces, particularly the Pt(533) surface, which has a 4-atom-wide (111) terrace and a (100)-type step (see figure S1 in the electronic supporting information (ESI)[21]). Our group has previously carried out experimental work on this model surface in ultra high vacuum (UHV) [14] using temperature programmed desorption (TPD) measurements. It was found that at the highest coverage water exhibits a desorption spectrum with three features: At 188 K there is a distinct peak, attributed to water desorbing from the (100) step edge which, with increasing coverage, grows a shoulder at 171 K, assumed to be related to water

desorbing from a terrace structure. At very high coverages a "multi-layer" peak appears at 146 K, namely the desorption pattern of multiple water layers above the first adsorbed layer. A more recent publication [22] focused on the Pt(755) and Pt(977) surfaces, which have the same step type but an increased terrace width. The wider terraces of these surfaces lead to the presence of a (111)-like desorption peak, which indicates the formation of well-ordered (111)-like water networks. However, on all of the stepped surfaces, the prominence of the step-related desorption peak is higher than expected based on the ratio between step and terrace atoms. This striking observation suggests that the influence of the step edge on the water adsorption structure extends beyond the immediate vicinity of the step itself and hinders the formation of the (111)-like peak observed on pristine surfaces.

Recently, we carried out Density Functional Theory (DFT) calculations on the adsorption of a single water molecule on Pt(533)[23] that showed good qualitative agreement with the trends in the experimental desorption temperatures. However, we were not able to achieve an explanation for the absence of a fully developed (111)-terrace peak on Pt(533). This is a clear indication of the fact that the complexity of water solvation at stepped surfaces cannot be fully captured without accounting for cooperative water-water interaction. Here, we investigate the effect of higher water coverage near the step edge of Pt(533) to observe trends in the adsorption energy of more complex water structures and will attempt to link these trends to the findings previously obtained by TPD experiments.

3.3 Computational Methods

The computations were performed using the *ab initio* density functional code VASP [24–27], the PBE functional [28] and PAW projectors [29, 30]. The PBE functional was chosen in order to obtain reasonable adsorption energies of water, as well as to adequately describe hydrogen bonding among the water molecules [31]. These appropriate features of PBE, combined with the fact that we focus mainly on the trends in adsorption energies, not the absolute values which are important for e.g. wetting behavior, which are described correctly by PBE [17, 32], ensure that no higher levels of DFT, such as van-der-Waals-corrected functionals, are required for our purposes.

The reciprocal space was sampled with the Monkhorst-Pack scheme [33] using 3x9x1 grids for the Pt(533) surface with two atoms per unit cell along the step edge. Larger unit cells were sampled with correspondingly smaller grids, a full list of which can be found in the ESI. For all calculations first-order Methfessel-Paxton smearing [34] with a sigma of 0.2 eV was applied and all energies were

extrapolated to 0 K. A plane-wave basis set with a cut-off energy of 550 eV was chosen. Figure S1 in the ESI shows a side view of the Pt(533) surface, which, as described above, consists of a 4-atom-wide (111)-terrace and a (100)-type step. More information about the surface model used can be found in reference [23].

The average Gibbs energies per molecule for the adsorption of a structure of n H_2O molecules were calculated as follows:

$$\Delta G_{tot,n\cdot H_2O} = \frac{G_{total,n\cdot H_2O_{ads}} - G_{clean} - n \cdot G_{H_2O(g)}}{n} \quad (3.1)$$

Each individual G was approximated as:

$$G_{tot,n\cdot H_2O_{ads}} = E_{DFT,n\cdot H_2O} + ZPE_{n\cdot H_2O_{ads}} - T \cdot S_{(n\cdot H_2O),vib} \quad (3.2)$$

for adsorbed water and

$$G_{tot,H_2O(g)} = E_{DFT,H_2O} + ZPE_{H_2O} - T \cdot S_{H_2O,tot} \quad (3.3)$$

for gas-phase water. The values for $S_{H_2O,tot}$ are taken from tables for gas-phase species in reference [35].

All adsorption energies reported below are Gibbs energies, corrected for zero-point energy (ZPE) and vibrational entropy at 100 K, following the methods described by Loffreda [36]. A reference temperature of 100 K was chosen to facilitate comparison with experimental STM and TPD data. A full set of DFT adsorption energies can also be found in the ESI. It should be noted that the ZPE and entropy do not change significantly between different configurations with the same number of adsorbed molecules.

3.4 Results and Discussion

In presenting our results, the coverage of water will be gradually increased to allow for a more detailed understanding of the consequences of the preferred adsorption structures near the step edge at higher coverages.

3.4.1 Low-coverage Limit

It is well known that on platinum surfaces water adsorbs in a configuration with oxygen on-top of a Pt atom and both hydrogen atoms oriented parallel to the surface plane [23, 37, 38]. Increasing the coverage on Pt(111) leads to interconnected structures, forming $(\sqrt{3} \times \sqrt{3})$ [39, 40], $(\sqrt{37} \times \sqrt{37})$ [41] or $(\sqrt{39} \times \sqrt{39})$ [41] superstructures, depending on environmental conditions, such as the total coverage of water. On the stepped Pt(533) surface, H_2O still prefers to adsorb flat on-top of

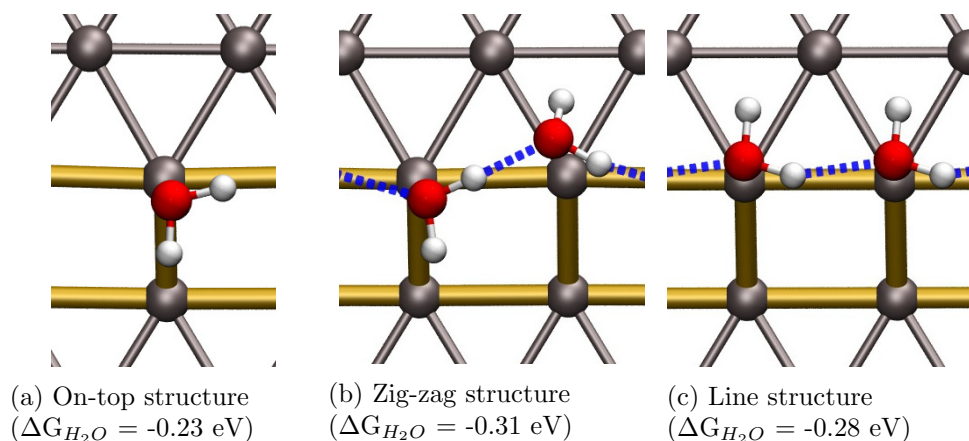


Figure 3.1: Water configurations at the step edge of Pt(533) at low coverage. a) A single water molecule adsorbed at the step edge in on-top position, b)-c) fully covered step-edge configurations. The upper terrace is located at the top of the figure and is separated from the lower terrace by a (100)-like edge, the Pt-Pt bonds of which are marked in gold.

the Pt atoms with a noticeably increased adsorption energy [17–19, 23] on the Pt step-edge atoms as compared to the terrace atoms. Figure 3.1a shows one of the possible orientations of water on the step edge of Pt(533). Rotation around the oxygen has a low energy cost, as long as both hydrogen atoms are still oriented parallel to the terrace plane.

3.4.2 One-Dimensional Chains Along the Step Edge

As reported in earlier publications [17–19] water will form 1-D chain networks on the step edge of Pt(533) and other stepped surfaces due to the higher adsorption energy on the step edge. It is generally accepted that water will assume a “zig-zag” configuration with one water molecule oriented towards the lower terrace and the other one pointing towards the upper terrace, as illustrated in figure 3.1b. It should be noted that both water molecules are not oriented parallel to the terrace plane of the stepped surface, but are slightly tilted. Alternatively, a configuration with all free hydrogen atoms pointing in one direction, as shown in figure 3.1c, was observed, but found to be energetically less favorable by 0.03 eV per H_2O molecule.

Increasing the coverage by adding another water molecule to the upper step edge, as shown in figure 3.2a, or the lower edge, as shown in figure 3.2b, yields a slight improvement of the mean adsorption energy. Since the water next to

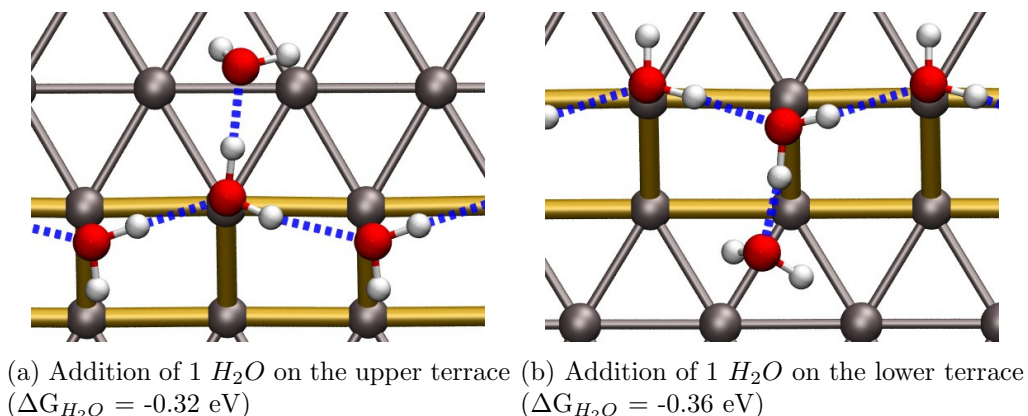


Figure 3.2: Fully covered step edge with one additional water molecule on the Pt(533) step edge.

the step edge always binds in an H-down configuration, which has an unfavorable adsorption energy on the terrace, this would suggest that the hydrogen bond to the step-edge water molecules is significantly stronger than those on the flat Pt(111) terrace. Additionally, we will argue below that this water molecule interacts with the step dipole, enhancing the stability of this adsorption structure. Furthermore, it was observed that the line structure converts back to the zig-zag configuration, after the addition of the water molecule adjacent to the step edge.

3.4.3 Isolated Ring Structures on the Step Edge

The next logical step for increasing the coverage is to assume that water will form closed ring structures, since this will maximize the number of hydrogen bonds per water molecule in the structure. We tested adsorption structures for ring sizes from 4 (tetragon) to 7 (heptagon) to understand the influence of the ring size on the mean adsorption energy. Smaller rings with 3 molecules are not stable due to the large distortion of the hydrogen-bonding angle needed to form a triangle. Structures larger than the heptagon have not been considered due to the limitation in terrace width imposed by the Pt(533) surface. Such a situation would lead to a significant interaction of the structure with the next step edge, resulting in the rupture of the polygons into smaller parts located on both the upper and the lower step edge.

In the following we will only discuss the most favorable structures, which are the isolated pentagon (see figure 3.3b) and the isolated hexagon (see figure 3.3c). The term isolated in this case refers to a water framework in which the

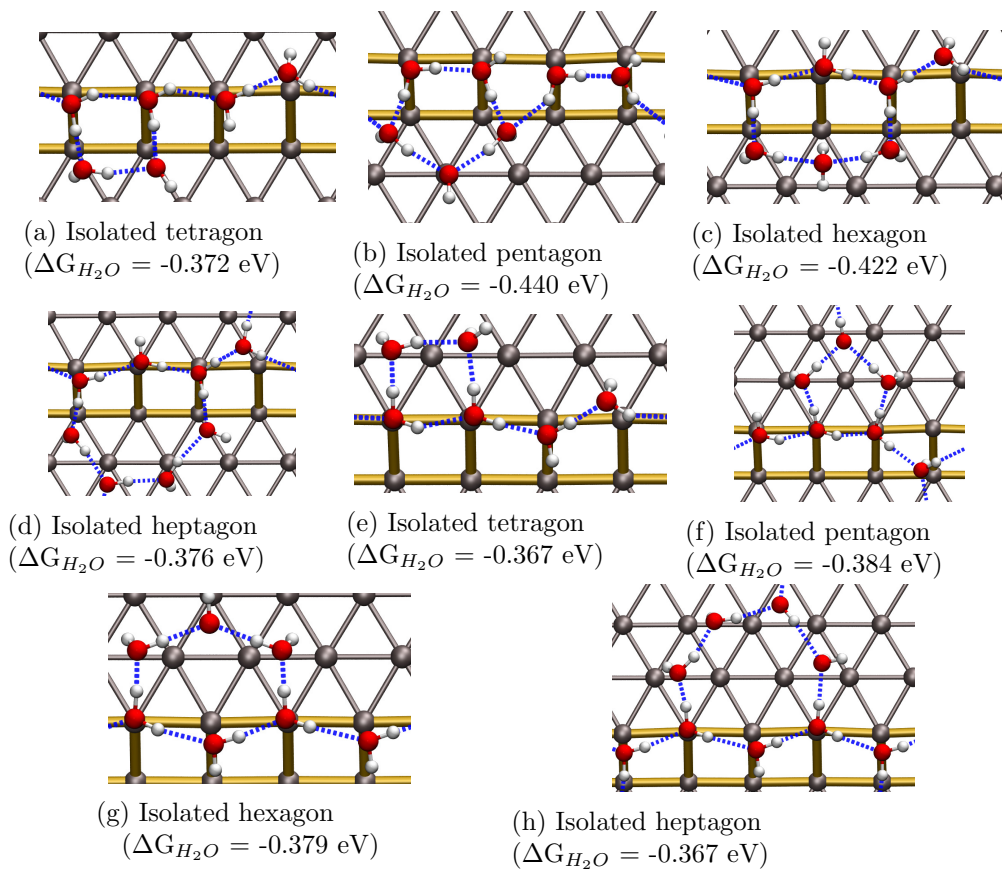


Figure 3.3: Isolated ring structures on the Pt(533) step edge. a)-d) Structures extending towards the lower step edge. e)-h) Structures extending to the upper terrace. The most stable configurations are found for the pentagon in b) and the hexagon in c).

polygons do not share adjacent edges. Adsorption energies for the most favorable configurations of the other two ring-sizes (tetragon and heptagon) can be found in figures 3.3a and 3.3d.

The pentagonal structure prefers adsorbing on the lower step edge as can be seen from the adsorption energy of -0.440 eV in figure 3.3b compared to -0.384 eV in figure 3.3f. The most stable configuration (Figure 3.3b) shows a peculiar structure that breaks the zig-zag arrangement on the step edge completely and replaces it with a hydrogen bonding chain that points down the step edge twice. Given the relatively high stability of the most favorable pentagonal structure on the upper step edge, we conclude that the pentagon itself is quite stable on the (100) step edge, although it is not easily incorporated into the favorable 1-D zig-zag arrangement on the step edge, shown in figure 3.1b.

The next larger ring structure is the hexagon. Again, we find the extension of the water structure to the lower step edge to be more stable with an adsorption energy of -0.422 eV per H_2O molecule leading to a structure with an H_2O molecule that symmetrically accepts two hydrogen bonds, as shown in figure 3.3c. The two sides of the predicted hexagonal structure fit readily into the favorable zig-zag configuration along the step edge that was discussed earlier.

In summary, pentagonal and hexagonal structures adjacent to the step edge are the most favorable isolated ring structures. Furthermore, we observe enhanced binding for adsorption on the lower step edge for pentagons and hexagons compared to the upper step edge configuration. On the other hand, tetragons (see figures 3.3a and 3.3e) and heptagons (see figures 3.3d and 3.3h) show similar energies for both the lower and upper terrace configuration.

3.4.4 Fully-Covered Step Edge

In this section we will discuss our findings on fully covered steps, namely configurations that consist of a 1-D chain and a fully covered lower or upper step edge. It should be clear that the structures presented in the previous section do not directly translate to this higher coverage regime. This is mainly because the most stable low-coverage regime structures cannot be repeated so as to generate fully covered step edges (see figure 3.3). In this section we will only discuss the most favorable adsorption structures, while a full list of all performed calculations can be found in the ESI.

Figure 3.4 shows the most favorable adsorption structures for the studied coverage. We found that there are several different ring sizes with nearly identical binding energies, all extending towards the lower step edge:

- The 4-4-4 structure with an adsorption energy of -0.392 eV consisting of a periodic arrangement of tetragons (see figure 3.4a).

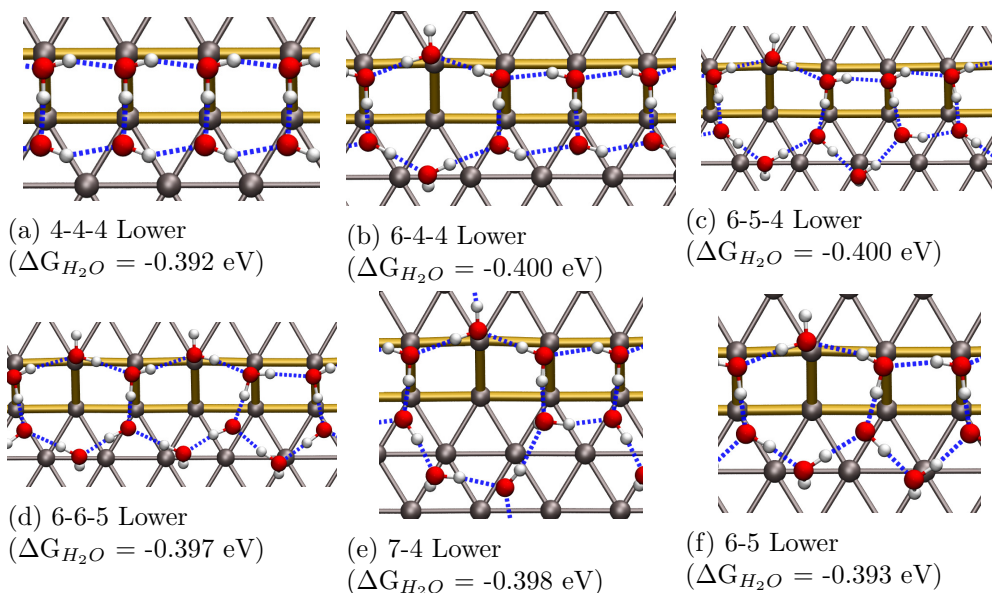


Figure 3.4: Most favorable adsorption structures for fully H_2O -covered step edges on Pt(533). All of these structures have comparable adsorption energetics.

- The 6-4-4 structure with an adsorption energy of -0.400 eV consisting of a hexagon and two tetragons (see figure 3.4b).
- The 6-5-4 structure with an adsorption energy of -0.400 eV which consists of a hexagon followed by a pentagon and a tetragon (see figure 3.4c).
- The 6-6-5 structure shows an adsorption energy with -0.397 eV and consists of two hexagons followed by a pentagon (see figure 3.4d).
- The 7-4 structure, which consists of a heptagon followed by a tetragon, and shows an adsorption energy of -0.398 eV (see figure 3.4e).
- The 6-5 structure, which consists of a hexagon followed by a pentagon, and shows an adsorption energy of -0.393 eV (see figure 3.4f).

The fact that adsorption geometries extending towards the lower terrace are more favorable, as observed for the structures in figure 3.3, is also found for these extended structures and is in accordance to the experimental STM findings of Morgenstern et al. [42]. They found that water on defective Pt(111) surfaces prefers to form clusters located at the bottom of (100) step edges.

The differences in the adsorption energies of all the structures in figure 3.4 are within the intrinsic error associated with the calculated adsorption energies at the DFT-GGA level. This means that we cannot make a clear distinction as to which of these structures, if any, is the most stable. It should be noted that the presence of all observed structures is to be expected in a real system to varying degrees, due to configurational entropy, which is not included in our estimation of the free energies.

The most favorable structures observed for isolated adsorption, namely the hexagon and the pentagon, are not found to be most stable in the high-coverage regime, for two different reasons. Firstly, the most favorable hexagonal structure in the low-coverage regime, as can be seen in figure 3.3c, does not lead to a framework of polygons with adjacent edges, covering the entire step edge. This structure showed a significantly increased adsorption energy compared to those alternatives that were able to fully cover the edge, which makes a full coverage of hexagons energetically less favorable than other possibilities. On the other hand, the pentagon (see figure 3.3b) occupies significantly more space along the lower step edge than along the upper edge, so it experiences compressive strain when forming a structure that is fully occupying the step edge. This compressive strain adversely affects the stability of the entire water framework, making it bind weaker compared to other structures.

We observe that the water molecules adjacent to the step edge prefer to bind in an H-down orientation, as can be seen in figure 3.5a. A similar tendency was observed on the stepped gold surfaces studied by Gross et al [20], however this tendency was not absolute, as upper step edge water could still point H-up, in contrast to our findings here. We ascribe this tendency to the Smoluchowski effect at the step edge[43]. This effect consists of a lack of charge at the top of step edges, which is compensated by an excess charge at the bottom of the step edge. This leads to the generation of a net dipole moment. The component perpendicular to the terrace of this dipole moment interacts favorably with the natural dipole moment of the water molecules that are oriented in an H-down configuration. This situation is illustrated in figure 3.5b, in which we represent the vectors of the dipole moments with the tips pointing from negative to positive charges.

The adsorption height of the step-edge water molecules (for example we observe Pt-O distances of 2.01-2.39 Å for the zig-zag part of the 6-5-4 structure in figure 3.4c) is found to be slightly shorter than the ones encountered for water monomer adsorption on Pt(111) where a Pt-O distance of 2.46 Å for a single water molecule sitting on-top on Pt(111) was found. Note that this is in agreement with the trends in adsorption energies. The height of the adsorbates bordering the lower step edge, with a Pt-O distance of 3.23-3.49 Å for the 6-5-4, are comparable

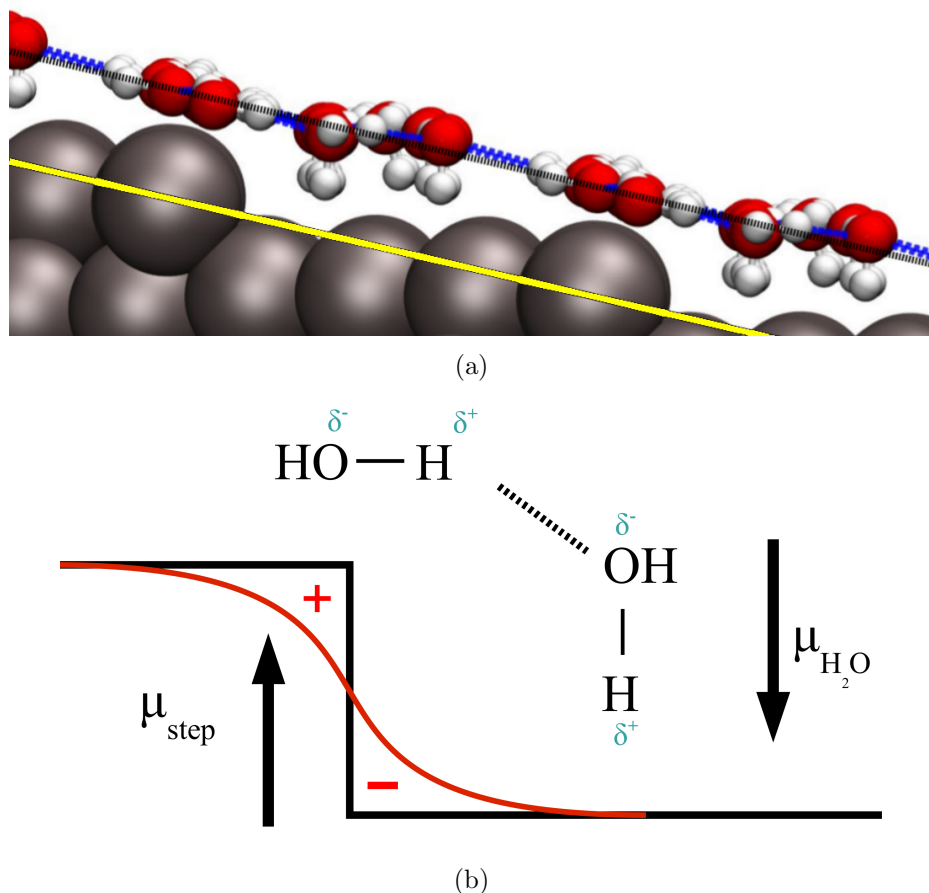


Figure 3.5: a) Illustration of the adsorption heights above the terrace. The surface plane, indicated in solid yellow, and a parallel to the surface plane, indicated in dashed black, are added to guide the eye. b) Schematics of the interaction of water adsorbed near a step edge, with the dipole moment projected perpendicular to the terrace μ_{step} according to the Smoluchowski effect. This effect describes the red electron density line that is following from the sharp drop in atomic potential, indicated in black, with the predicted charge separation marked "+" and "-" in red.

to the adsorption heights measured for the $\sqrt{3} \times \sqrt{3}$ adsorption layer on Pt(111), which shows Pt-O distances of 3.24-3.50 Å.

For larger structures that extend further onto the terrace we observe that the oxygen atoms of the terrace water molecules arrange themselves almost perfectly along the surface plane of the stepped surface, as can be seen in figure 3.5a, where the solid yellow line corresponding to the surface plane is parallel to the dashed black line, on which most of the adsorbates lie. This suggests that the water bilayer in contact with the Pt(533) surface aligns itself as a flat "carpet" regardless of the presence of the (100) defect.

3.4.5 1-D Water Structures at Surface Defects and Implications for Water Networks at Terraces

When small amounts of water are dosed onto a stepped platinum surface, the preferred binding site is the on-top site at the step edge [17–19, 23], rather than the (111)-like terraces. This preference is due to the decreased coordination number of the step-edge Pt atom [38]. The low diffusion barrier for water on flat Pt(111) surfaces [44], combined with this enhanced binding energy at the step edge, leads to a marked tendency to form dimers and larger structures on the step edges.

Intuitively, the water chain on the step edge can be viewed as an extended one-dimensional defect when comparing it to the regular hexagonal arrangement of water on the (111) terrace. However, we find that the step edge water framework is actually the nucleation point for further water adsorption on terraces. This means that the actual influence area of the step edge extends to at least one or two rows of platinum atoms onto the terrace (see figure 3.5a). The effect that the step edge will have on the adsorption geometry is expected to diminish with the distance from the step edge. Hence, the adsorption characteristics of water on a stepped surface with a rather "short" terrace will be dominated by the influence area of the step edge. This explains the absence of a fully developed (111)-like desorption feature observed in TPD experiments for the Pt(533) surface and the appearance of such a peak on the larger Pt(755) and (977) surfaces [22]. This explanation cannot be drawn from a single-molecule or even low-coverage adsorption approach.

It is worth noting that the term "short terrace" depends strongly on the adsorbate in question, its coverage, the step-edge geometry and of course the substrate. For instance, for hydrogen adsorption the Pt(533) surface can be considered to have a "wide" terrace with clear Pt(111)-like features, while for water adsorption the (111) features are absent [22, 45]. Our results indicate that these differences arise due to the existence of long-range cooperative effects in water structures extending beyond the step edge.

3.5 Conclusions

In this study we have performed DFT calculations on the adsorption geometries and energetics of water on and near the step edge of the Pt(533) surface. The coverages that were studied were increased beyond the one-dimensional chain that was previously discussed in the literature. The first stage, beyond the 1-D chain studied before, was the appearance of isolated water ring structures at the step edges. It was found that the (100) step edge prefers to form isolated hexagonal or pentagonal rings in this case. Furthermore, it was observed that the isolated rings preferentially form in the direction towards the lower terrace on the stepped surface. Additionally, water molecules that are not bound to the step edge prefer to adsorb in an H-down configuration.

At higher coverage a full arrangement of periodically ringed structures is formed along the step edge. Multiple structures with similar energies are possible at this coverage. Besides, the observation regarding H-down adsorption and the preference to adsorb towards the lower terrace was also made at these coverages. Our results suggest that the formation of water frameworks on Pt(533) will start at step edges, and extend towards the lower terrace, adjacent to the step edge, in accordance with the observations by Morgenstern et al [42].

Furthermore, the observed structures tend to occupy a large portion of the terrace, as for example the 7-4 structure in figure 3.4e, from which we conclude that the area in which the step edge influences the adsorption geometry extends beyond its immediate vicinity, due to long-range cooperative water-water interactions. This explains the absence of a (111)-like peak in the recorded TPD spectrum of the Pt(533) surface, and suggests a lack of ordered hexagonal water adsorption structures on the terrace of Pt(533). In contrast, stepped surfaces with larger terraces and the same kind of step, such as the Pt(755) and Pt(977) surfaces, allow for an area of hexagonal adsorption structures on them, leading to a (111)-like desorption peak, as observed in TPD [22]. Still, this (111)-like desorption feature is smaller than expected based on the width of the terraces, and we can now ascribe this to the formation of more extended ring-like structures on and near the step edge.

While for (111) surfaces approaches exist to estimate the influence of solvation on adsorption energies [9] by making use of hexagonal water frameworks, very little is known about higher coverage solvation effects at step edges. The periodic structures reported here provide an accurate starting point for such studies. This will ultimately lead to a comprehensive treatment of solvation in aqueous environments that will contribute to a more realistic representation of catalytic processes at electrified solid-liquid interfaces.

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References

- (1) Climent, V.; Feliu, J. M. *Journal of Solid State Electrochemistry* **2011**, *15*, 1297–1315.
- (2) Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. *Appl. Catal. B: Environmental* **2005**, *56*, 9–35.
- (3) Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff, I.; Nørskov, J. K. *Nature Materials* **2006**, *5*, 909–913.
- (4) Fortunelli, A.; Goddard III, W. A.; Sementa, L.; Barcaro, G. *Nanoscale* **2015**, *7*, 4514–4521.
- (5) Jinnouchi, R.; Kodama, K.; Morimoto, Y. *Journal of Electroanalytical Chemistry* **2014**, *716*, 31–44.
- (6) Feibelman, P. J.; Bartelt, N. C.; Nie, S.; Thrmer, K. *The Journal of Chemical Physics* **2010**, *133*, 154703.
- (7) Skúlason, E.; Tripković, V.; Björketun, M. E.; Gudmundsdóttir, S.; Karlberg, G.; Rossmeisl, J.; Bligaard, T.; Jónsson, H.; Nørskov, J. K. *The Journal of Physical Chemistry C* **2010**, *114*, 18182–18197.
- (8) Koper, M. T. *Electrochimica Acta* **2011**, *56*, 10645–10651.
- (9) Tripković, V.; Skúlason, E.; Siahrostami, S.; Nørskov, J. K.; Rossmeisl, J. *Electrochimica Acta* **2010**, *55*, 7975–7981.
- (10) Koper, M. T. M. *Nanoscale* **2011**, *3*, 2054–2073.
- (11) O’Mullane, A. P. *Nanoscale* **2014**, *6*, 4012–4026.

- (12) Li, H.; Calle-Vallejo, F.; Kolb, M. J.; Kwon, Y.; Li, Y.; Koper, M. T. *Journal of the American Chemical Society* **2013**, *135*, 14329–14338.
- (13) Li, H.; Li, Y.; Koper, M. T. M.; Calle-Vallejo, F. *Journal of the American Chemical Society* **2014**, *136*, 15694–15701.
- (14) Van der Niet, M. J. T. C.; den Dunnen, A.; Juurlink, L. B. F.; Koper, M. T. M. *J. Chem. Phys.* **2010**, *132*, 174705.
- (15) Donadio, D.; Ghiringhelli, L. M.; Delle Site, L. *Journal of the American Chemical Society* **2012**, *134*, 19217–19222.
- (16) Bandarenka, A. S.; Hansen, H. A.; Rossmeisl, J.; Stephens, I. E. L. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13625–13629.
- (17) Peköz, R.; Wörner, S.; Ghiringhelli, L. M.; Donadio, D. *The Journal of Physical Chemistry C* **2014**, *118*, 29990–29998.
- (18) Arnadottir, L.; Stuve, E. M.; Jonsson, H. *Surf. Sci.* **2010**, *604*, 1978–1986.
- (19) Meng, S.; Wang, E. G.; Gao, S. *Phys. Rev. B* **2004**, *69*, 195404.
- (20) Lin, X.; Gro, A. *Surface Science* **2012**, *606*, 886–891.
- (21) Kolb, M. J.; Wermink, J.; Calle-Vallejo, F.; Juurlink, L. B. F.; Koper, M. T. M. Supporting Information to : Initial stages of water solvation of stepped platinum surfaces., <http://www.rsc.org/suppdata/c5/cp/c5cp04468e/c5cp04468e1.pdf>, 2015.
- (22) Den Dunnen, A.; van der Niet, M. J. T. C.; Badan, C.; Koper, M. T. M.; Juurlink, L. B. F. *Phys. Chem. Chem. Phys.* **2015**, *17*, 8530–8537.
- (23) Kolb, M. J.; Calle-Vallejo, F.; Juurlink, L. B. F.; Koper, M. T. M. *The Journal of Chemical Physics* **2014**, *140* 134708.
- (24) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561.
- (25) Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251–14269.
- (26) Kresse, G.; Furthmüller, J. *Computational Materials Science* **1996**, *6*, 15 – 50.
- (27) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (28) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (29) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (30) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (31) Hamann, D. R. *Phys. Rev. B* **1997**, *55*, R10157–R10160.

- (32) Carrasco, J.; Klimeš, J.; Michaelides, A. *The Journal of Chemical Physics* **2013**, *138*, 024708.
- (33) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (34) Methfessel, M.; Paxton, A. T. *Phys. Rev. B* **1989**, *40*, 3616–3621.
- (35) Ed. Chase, M.; Davies, C.; Downey, J.; Frurip, D.; MacDonald, R.; Syverud, A., *NIST-JANAF Thermodynamical Tables*, Suppl. 1 to Vol 14 of J. Phys. Chem. Ref. Data, 1985; Vol. 14.
- (36) Loffreda, D. *Surf. Sci.* **2006**, *600*, 2103–2112.
- (37) Michaelides, A. *Applied Physics A* **2006**, *85*, 415–425.
- (38) Calle-Vallejo, F.; Martínez, J. I.; García-Lastra, J. M.; Sautet, P.; Loffreda, D. *Angewandte Chemie International Edition* **2014**, *53*, 8316–8319.
- (39) Roman, T.; Groß, A. *Catalysis Today* **2013**, *202*, 183–190.
- (40) Schnur, S.; Groß, A. *New Journal of Physics* **2009**, *11*, 125003.
- (41) Zimbitas, G.; Haq, S.; Hodgson, A. *The Journal of Chemical Physics* **2005**, *123*, 174701, –.
- (42) Morgenstern, M.; Michely, T.; Comsa, G. *Phys. Rev. Lett.* **1996**, *77*, 703–706.
- (43) Ibach, H., *Physics of Surfaces and Interfaces*; Wiley: 2006.
- (44) Arnadottir, L.; Stuve, E. M.; Jonsson, H. *Surface Science* **2012**, *606*, 233–238.
- (45) Badan, C.; Koper, M. T. M.; Juurlink, L. B. F. *The Journal of Physical Chemistry C* **2015**, *119*, 13551–13560.

Chapter 4

Double-Stranded Water on Stepped Platinum Surfaces

4.1 Abstract

The interaction of platinum with water plays a key role in (electro)catalysis. Herein, we describe a combined theoretical and experimental study that resolves the preferred adsorption structure of water wetting the Pt (111)-step type with adjacent (111) terraces. Double-stranded lines wet the step edge forming water tetragons with dissimilar hydrogen bonds within and between the lines. Our results qualitatively explain experimental observations of water desorption and impact our thinking of solvation at the Pt electrochemical interface.

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4.2 Introduction

For many chemical reactions, metallic platinum is an excellent catalyst due to its moderate adsorption energies of reactants, intermediates, and products[1–4]. In aqueous electrochemical environments, competitive adsorption of the reactant and water, as well as the interaction of water with intermediates, influences reactivity[5]. It is not surprising that the interaction of water with models of Pt catalyst surfaces has attracted considerable interest, in particular Pt(111)[6–10].

The complexity of the interaction of water with the Pt surface is exemplified by the first wetting layer. On Pt(111), water displays unique $\sqrt{37} \times \sqrt{37}$ or $\sqrt{39} \times \sqrt{39}$ networks[7, 11, 12]. However, realistic Pt catalysts are not well described using pristine Pt(111). Theoretical studies indicated that surface defects, e.g. steps, cause significant disruptions of extended water frameworks [13–17].

Experimentally, water has been studied on a wide range of planar metal systems [18–20]. An early scanning tunneling microscopy (STM) study investigated water adsorption on the two step edge types occurring on Pt(111) [21]. It was found that water preferred to form rows along these step edges. The exact nature of the adsorption structure was not resolved. In recent years, multiple theoretical studies have addressed water adsorption and solvation along platinum step edges [13–15, 22]. In these studies, water was found to form one-dimensional (1-D) lines along the step edge.

Recent density functional theory (DFT) studies have explored the generality of 1-D structures on Pt surfaces and how they evolve with water coverage[16, 17]. For Pt(533), which contains 4-atom wide terraces and (100)-type step edges, increasing the number of water molecules within the unit cell, from one water molecule[23] to a higher number of molecules, initially leads to the formation of 1-D lines at the upper edge[17]; this changes as the steps became saturated. Instead of lines, nearly isoenergetic 2-D structures of tetragons, pentagons, hexagons, and heptagons, extending across the step onto the terrace, are favored. These structures qualitatively explain the absence of a distinct water desorption feature from (111) terrace sites on Pt(533)[24]. Only a high-temperature desorption peak with a low temperature shoulder is observed for water coverages up to a monolayer. Alternatively, on the similar Pt(553) surface, with 5-atom wide terraces separated by (111)-steps, two distinct desorption features are observed; a Pt(533)-like high-temperature desorption peak and a desorption peak very similar to that found on Pt(111)[25]. The pronounced differences between such similar surfaces suggest that the structure of adsorbed water depends critically on the atomic geometry of the steps.

In this work, we combined DFT calculations and low-temperature STM to resolve the structure of water adsorbed to the (111)-step type disrupting Pt(111)

planes. In contrast to the (100)-step type, we found a single most favorable structure. It is a new adsorption geometry consisting of two parallel 1-D water strands aligned to form 2-dimensional (2-D) water tetragons. The details of the structure qualitatively explain the distinct desorption of step-bound and terrace-bound water. In addition, this most favorable structure affects our thinking of the solvation environment in Pt electrocatalysis

4.3 Methods

The DFT calculations were performed with the VASP code [26], PAW projectors [27] and the PBE functional [28]. The computational settings used in this study have been described elsewhere [17, 23]. All adsorption energies were calculated as mean Gibbs energies per water molecule at 100 K,

$$\Delta G_{tot,n\cdot H_2O} = \frac{G_{total,n\cdot H_2O} - G_{clean} - n \cdot G_{H_2O(g)}}{n}, \quad (4.1)$$

where the individual G were estimated as:

$$G_{tot,n\cdot H_2O} = E_{DFT,n\cdot H_2O} + ZPE_{n\cdot H_2O} - T \cdot S_{(n\cdot H_2O),vib} \quad (4.2)$$

for the surface-adsorbed species and

$$G_{tot,H_2O(g)} = E_{DFT,H_2O} + ZPE_{H_2O} - T \cdot S_{H_2O,tot} \quad (4.3)$$

for gas phase H_2O . The values for $S_{H_2O,tot}$ appear in reference [29]. The ZPE and vibrational entropy corrections were found to be very similar across all water structures, with a average ZPE per H_2O of 0.666 eV and a standard deviation of 0.0044 eV. The average vibrational entropy correction at 100 K was found to be 0.040 eV per H_2O with a standard deviation of 0.0033 eV. STM simulations based upon the DFT charge densities were performed using the program HIVE by Vanpoucke *et al* [30]. Tip smoothening, as implemented in this software, was used with a tip-size of 0.75 Å [31].

Experiments in Chicago were performed in an ultra high vacuum (UHV) system comprised of a preparatory chamber and STM chamber [32, 33]. The Pt(553) surface (Surface Preparation Laboratory, Zaandam, the Netherlands) was cleaned following published procedures [34]. Surface cleanliness was confirmed via Auger electron spectroscopy and the presence of a sharp low-energy electron diffraction pattern [25]. A directed doser was used to minimize background contamination while exposing the Pt crystal to D_2O . D_2O was used rather than H_2O due to the lower background of D_2O in the UHV chamber. The Pt(553) surface was dosed at

$T_s = 100$ K with the directed doser 1 cm from the crystal face. After exposure, the crystal was annealed at 160 K. TPD spectra were taken with a ramp rate of 1 K s^{-1} . Prior to imaging, the sample was flashed to 175 K. TPD experiments in Leiden were performed on the same Pt sample using a UHV system with a differentially pumped QMS (Baltzers QMA 400). Water was dosed from a directional doser and TPD experiments were performed at a distance between the crystal and the QMS orifice of 2 mm and the same heating rate as in Chicago.

4.4 DFT Prediction of Adsorption Networks along the Step Edge

The formation of tetragonal networks was also preferred at coverages which allow for the formation of fully closed ring structures along the step edge (Fig. 3.4c). The adsorption energy was $-0.441 \text{ eV/H}_2\text{O}$. Any other adsorption structure yielded an energy that was at least $0.013 \text{ eV/H}_2\text{O}$ less favorable. The most likely cause for this exceptional adsorption energy was the underlying geometry of the (111) step edge of Pt(553). In the upper strand, water molecules were adsorbed atop the 7-fold coordinated platinum atoms. In the lower strand, water molecules adsorbed atop the nearest 9-fold coordinated Pt atoms. The rectangular geometry of the involved Pt atoms caused hydrogen bonds to be directed both along and orthogonal to the step edge. The former caused the 1-D lines, whereas the latter caused two lines to form a double-stranded structure. All water molecules making up the lower strand were oriented H-down while all water molecules adsorbed on the upper edge were adsorbed flat atop the edge Pt atoms.

We previously used the Smoluchowski effect to rationalize the geometric configuration of water on Pt(533) [17]. The same holds true for the (111) step edge of Pt(553). This effect consists of a charge separation at steps: a positive partial charge at the upper step edge is balanced by a negative partial charge on the lower edge. Water molecules on the upper edge interact with the positive Pt atoms by adsorbing through the oxygen atom. On the lower edge and the terrace, water orients H-down to maximize the interaction between the negative partial charge of the Pt and the positive charge of the hydrogen atom.

In conclusion, a strong templating effect of the (111)-type step edge on Pt(553) creates the double stranded water structure along the step edge. The geometric orientation can be rationalized by the Smoluchowski effect.

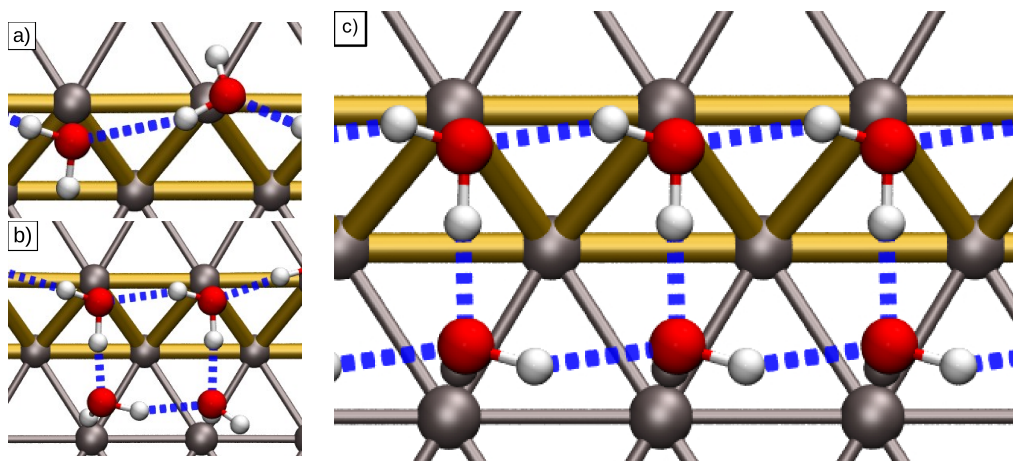


Figure 4.1: Top views of the most favorable adsorption structures for increasing coverage: a) Zig-Zag structure, b) Isolated tetragon and c) Double-stranded, tetragonal 4-4-4 structure extended towards the lower terrace. Platinum atoms appear in silver, oxygen in red, hydrogen in white and the (111) step edge is marked in gold.

4.5 TPD and STM results

4.5.1 TPD Spectra

The TPD spectra in Fig. 4.2 shows three separate peaks for water desorption from Pt(553). In order of increasing desorption temperature, these distinct features correspond to desorption from multilayers, (111) terraces, and step edges. Results from both laboratories were in line with those previously reported on planar and stepped Pt surfaces[25, 35]. Slight differences in peak desorption temperatures ($< 10\text{K}$) were attributed to differences in temperature measurement. Submonolayer water coverages for STM imaging on the Pt(553) sample were obtained by annealing to 175 K after D_2O exposure. This removed multilayer and most of the terrace-bound water. The post-STM TPD trace in Fig. 2 shows that desorption from the step edges was predominant even after prolonged time in the STM (four times longer than necessary to obtain the images), with negligible accumulation of background gases, confirming that water mostly remained on the step edges with some terrace-bound water desorption following imaging. Evidence for the dissociation of water was not observed, which would present itself as a high temperature peak at 270 K [36], associated with $\text{OH}_{ads,step}$ is absent. Furthermore, no isotope scrambling was observed, with the main desorption feature stemming

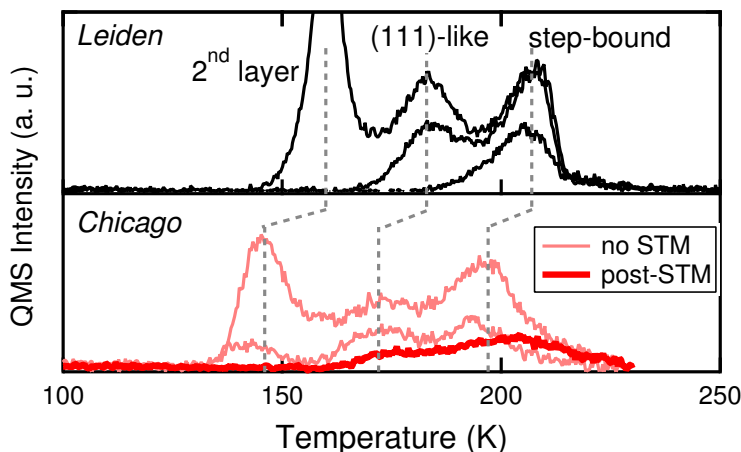


Figure 4.2: TPD spectra of water desorbing from Pt(553)

from $m/z = 20$ (D_2O^+) and its daughter fragment at $m/z = 18$ (OD^+).

4.5.2 STM Imaging

In Fig. 4.3a we show an STM image of clean Pt(553) with the surface composed of regularly sized terraces, about 1.35 nm wide, with crisp step edges. The terraces were mostly 5-atom wide (111) facets separated by one-atom high (111) steps, with around 10% being either 4 or 6-atoms wide. In contrast, after water deposition, the surface corrugation decreased and bright lines were evident along the step edges, as seen in Fig. 4.3b. Imaging conditions were modeled after previous work to limit water perturbation [6, 37]. Tunneling currents below 10 pA revealed that the bright features lie along the step edges (Fig. 4.3b) [37]. The water molecules appeared to arrange in two parallel strands, one line atop the step edge and the second just below, forming the bright step-edge decorations. Some water molecules appeared in between the strands. This was in line with some desorption occurring at ~ 170 K from terrace sites in the TPD spectrum.

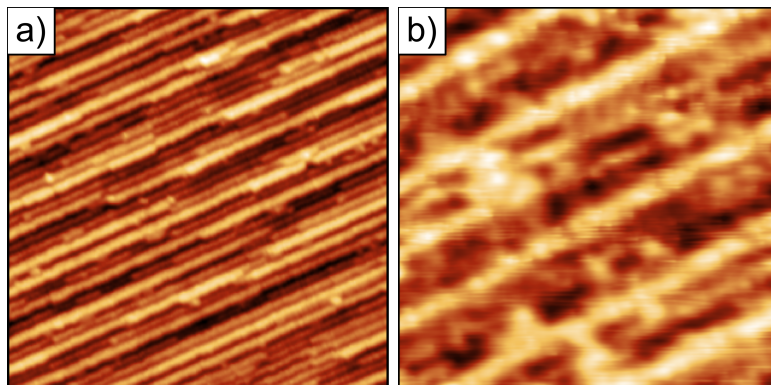


Figure 4.3: a) STM image of the clean Pt(553) surface. $V = 1$ V, $I = 200$ pA, $T_{STM} = 25$ K, $8 \text{ nm} \times 8 \text{ nm}$ b) STM image of the water covered surface. $V = -0.90$ V, $I = -9$ pA, $T_{STM} = 25$ K, $8 \text{ nm} \times 8 \text{ nm}$.

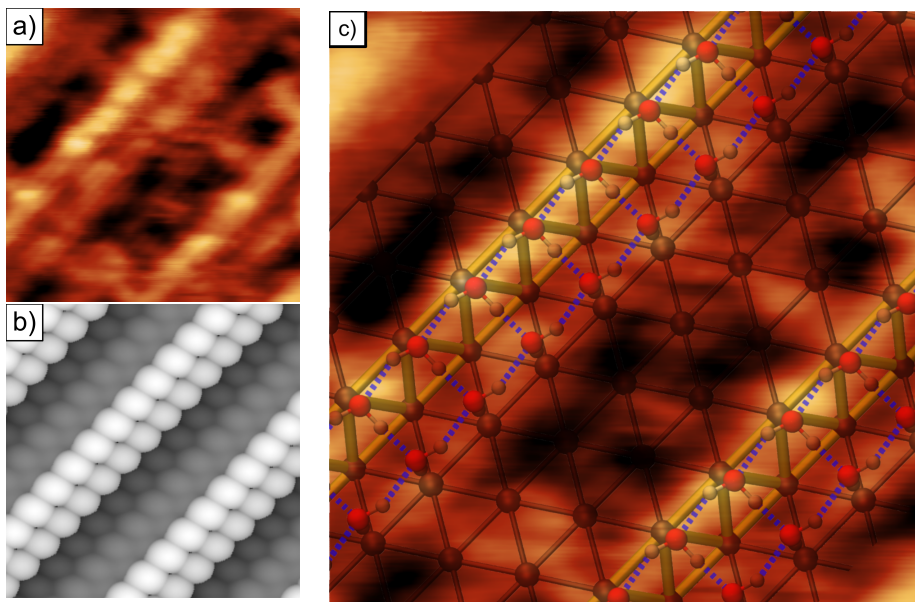


Figure 4.4: a) STM image of D_2O covered step edges on Pt(553). $V = -1$ V, $I = -9$ pA, $T_{STM} = 25$ K, $4.5 \text{ nm} \times 4.5 \text{ nm}$ b) STM simulation of water adsorbed on Pt(553), bright areas are oxygen atoms of water, darker areas are located at Pt terraces, $V = -0.9$ V, c) Overlay of atomic positions of DFT and STM imaging, $V = -1$ V, $I = -9$ pA, $T_{STM} = 25$ K, $4.5 \text{ nm} \times 4.5 \text{ nm}$.

4.6 Comparison of STM and DFT results

Fig. 4.4a shows a representative STM image of adsorbed water on Pt(553). The primary features of this image are the periodic, parallel strands of water molecules described above. Based upon the energetically most favorable double-stranded tetragonal 4-4-4 structure (see Fig. 4.1c), we performed simulations of STM images, which are shown in Fig. 4.4b. The bright stripes in the simulated image, corresponding to the oxygen atoms of water, are in good agreement with the actual STM image. Fig. 4.4c shows the overlay of the calculated periodic double-stranded structure onto the image in Fig. 4.4a. The image based on the DFT geometry was scaled so that the step edge structures in the STM overlap with the periodically repeated step edges in the DFT data. Lattice size and water position on the step edges were consistent across multiple STM images, supporting the double-stranded water structure along the Pt(553) step edges. To exclude possible bias, we considered other possible structures with the next-best adsorption energies per water molecule. We found that these structures did not reproduce the parallel lines observed in the STM images. Additional details on this topic can be found in the supporting information [38].

4.7 Conclusions

In summary, we have demonstrated in this letter a unique water structure that exists along the Pt(553) step edge. DFT calculations predicted the formation of double stranded networks that are connected to form tetragonal structures along the step edge, due to the templating effect of the underlying step geometry. Experimental STM images found two parallel lines of water molecules along the step edge, and verified the templating effect, confirming the formation of double stranded water structures. These results highlight the tremendous effect the electronic corrugation of the stepped Pt surface had on the structures of adsorbed water. Double-stranded configurations of water had neither been theoretically nor experimentally reported until now. Furthermore, our results suggest that the 1-D line is unlikely to be a good representation of a full solvation environment at step edges. Instead, the observed, strongly bound, 2-D structures cover the steps. Accurate assessments of solvation must take these structures into account and are necessary for the determination of surface phase diagrams of actual platinum catalysts.

4.8 Acknowledgments

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References

- (1) Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff, I.; Norskov, J. K. *Nat Mater* **2006**, *5*, 909–913.
- (2) Stephens, I. E. L.; Bondarenko, A. S.; Gronbjerg, U.; Rossmeisl, J.; Chorkendorff, I. *Energy Environ. Sci.* **2012**, *5*, 6744–6762.
- (3) Calle-Vallejo, F.; Tymoczko, J.; Colic, V.; Vu, Q. H.; Pohl, M. D.; Morgenstern, K.; Loffreda, D.; Sautet, P.; Schuhmann, W.; Bandarenka, A. S. **2015**, *350*, 185–189.
- (4) Li, H.; Li, Y.; Koper, M. T. M.; Calle-Vallejo, F. *Journal of the American Chemical Society* **2014**, *136*, 15694–15701.
- (5) Sha, Y.; Yu, T. H.; Liu, Y.; Merinov, B. V.; Goddard, W. A. *J. Phys. Chem. Lett.* **2010**, *1*, 856–861.
- (6) Maier, S.; Stass, I.; Cerdá, J. I.; Salmeron, M. *Phys. Rev. Lett.* **2014**, *112*, 126101.
- (7) Standop, S.; Redinger, A.; Morgenstern, M.; Michely, T.; Busse, C. *Phys. Rev. B* **2010**, *82*, 161412.
- (8) Sakong, S.; Naderian, M.; Mathew, K.; Hennig, R. G.; Gross, A. *The Journal of Chemical Physics* **2015**, *142* 234107.
- (9) Tripković, V.; Skúlason, E.; Siahrostami, S.; Nørskov, J. K.; Rossmeisl, J. *Electrochimica Acta* **2010**, *55*, 7975–7981.
- (10) Skúlason, E.; Karlberg, G. S.; Rossmeisl, J.; Bligaard, T.; Greeley, J.; Jonsson, H.; Norskov, J. K. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3241–3250.
- (11) Feibelman, P. J.; Bartelt, N. C.; Nie, S.; Thrmer, K. *The Journal of Chemical Physics* **2010**, *133* 154703.

- (12) Zimbitas, G.; Haq, S.; Hodgson, A. *The Journal of Chemical Physics* **2005**, *123* 174701, –.
- (13) Meng, S.; Wang, E. G.; Gao, S. *Phys. Rev. B* **2004**, *69*, 195404.
- (14) Arnadottir, L.; Stuve, E. M.; Jonsson, H. *Surf. Sci.* **2010**, *604*, 1978 –1986.
- (15) Peköz, R.; Wörner, S.; Ghiringhelli, L. M.; Donadio, D. *The Journal of Physical Chemistry C* **2014**, *118*, 29990–29998.
- (16) Jinnouchi, R.; Kodama, K.; Morimoto, Y. *Journal of Electroanalytical Chemistry* **2014**, *716*, 31 –44.
- (17) Kolb, M. J.; Wermink, J.; Calle-Vallejo, F.; Juurlink, L. B. F.; Koper, M. T. M. *Phys. Chem. Chem. Phys.* **2016**, *18*, 3416–3422.
- (18) Tatarkhanov, M.; Ogletree, D. F.; Rose, F.; Mitsui, T.; Fomin, E.; Maier, S.; Rose, M.; Cerd, J. I.; Salmeron, M. *Journal of the American Chemical Society* **2009**, *131*, 18425–18434.
- (19) Morgenstern, K.; Rieder, K.-H. *Chemical Physics Letters* **2002**, *358*, 250 –256.
- (20) Mehlhorn, M.; Schnur, S.; Gross, A.; Morgenstern, K. *ChemElectroChem* **2013**, *1*, 431 –435.
- (21) Morgenstern, M.; Michely, T.; Comsa, G. *Phys. Rev. Lett.* **1996**, *77*, 703–706.
- (22) Endo, O.; Nakamura, M.; Sumii, R.; Amemiya, K. *The Journal of Physical Chemistry C*, *116*, 13980 –13984.
- (23) Kolb, M. J.; Calle-Vallejo, F.; Juurlink, L. B. F.; Koper, M. T. M. *The Journal of Chemical Physics* **2014**, *140* 134708.
- (24) Den Dunnen, A.; van der Niet, M. J. T. C.; Badan, C.; Koper, M. T. M.; Juurlink, L. B. F. *Phys. Chem. Chem. Phys.* **2015**, *17*, 8530–8537.
- (25) Van der Niet, M. J. T. C.; den Dunnen, A.; Juurlink, L. B. F.; Koper, M. T. M. *J. Chem. Phys.* **2010**, *132*, 174705.
- (26) Kresse, G.; Furthmüller, J. *Computational Materials Science* **1996**, *6*, 15 –50.
- (27) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (28) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (29) Ed. Chase, M.; Davies, C.; Downey, J.; Frurip, D.; MacDonald, R.; Syverud, A., *NIST-JANAF Thermodynamical Tables*, Suppl. 1 to Vol 14 of J. Phys. Chem. Ref. Data, 1985; Vol. 14.

- (30) Vanpoucke, D. E. P.; Brocks, G. *Phys. Rev. B* **2008**, *77*, 241308.
- (31) Vanpoucke, D. E. P. Ab Initio study of Pt Induced Nanowires on Ge(001)., ISBN: 978-90-365-2873-3, Ph.D. Thesis, University of Twente, 2009.
- (32) Derouin, J.; Farber, R. G.; Heslop, S. L.; Killelea, D. R. *Surface Science* **2015**, *641*, L1 –L4.
- (33) Derouin, J.; Farber, R. G.; Killelea, D. R. *The Journal of Physical Chemistry C* **2015**, *119*, 14748–14755.
- (34) Van der Niet, M. J. T. C.; den Dunnen, A.; Juurlink, L. B. F.; Koper, M. T. M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1629–1638.
- (35) Fisher, G. B.; Gland, J. L. *Surface Science* **1980**, *94*, 446 –455.
- (36) Van der Niet, M. J. T. C.; Berg, O. T.; Juurlink, L. B. F.; Koper, M. T. M. *The Journal of Physical Chemistry C* **2010**, *114*, 18953–18960.
- (37) Nie, S.; Feibelman, P. J.; Bartelt, N. C.; Thürmer, K. *Phys. Rev. Lett.* **2010**, *105*, 026102.
- (38) Kolb, M. J.; Farber, R. G.; Derouin, J.; Badan, C.; Calle-Vallejo, F.; Juurlink, L. B.; Killelea, D. R.; Koper, M. T. Supporting Information to : Double Stranded Water on Stepped Platinum Surfaces., To be submitted, <https://www.dropbox.com/s/ywbpfrm4mo8h0ix/Supplemental-Material.pdf?dl=0>.

Chapter 5

Elucidation of Hydrogen TPD Data from High-coverage DFT Calculations

5.1 Abstract

In this work we discuss high-coverage hydrogen adsorption energies and geometries on the stepped platinum surfaces Pt(533) and Pt(553) and link these results with ultra-high-vacuum temperature programmed desorption (TPD) data to elucidate the origin of the desorption features. We find that for the Pt(533) surface hydrogen exhibits two main adsorption energy regimes. The high-temperature peak is linked to the step edge desorption feature, while the low-temperature feature is connected to the terrace desorption. The ratio between the high-temperature and the low-temperature TPD peaks of 1:3 is reproduced by this interpretation and we arrive at a total Pt:H ratio of 1:1 for the Pt(533) surface. For the Pt(553) surface on the other hand, we find that by combining the results from the deconvolution of the experimental desorption traces with our theoretical results that the high-temperature desorption feature is linked to the step edge desorption. By integration of the TPD spec-

trum, we arrive at a 1:2.25 ratio between step desorption and the remaining two peaks. Therefore, we associate these peaks with the two next-most favorable adsorption sites, which are located on the terrace. This suggests a significantly lower 0.6:1 H:Pt ratio for the Pt(553) surface. From our results we conclude that it is possible to elucidate experimental TPD spectra from simulated adsorption energies for the studied surfaces, due to the low desorption barriers present.

Based on: Manuel J. Kolb, Cansin Badan, Anna Garden, Egill Skulason, Ludo B.F. Juurlink, Hannes Jonsson and Marc T.M. Koper, in preparation

5.2 Introduction

Platinum surfaces are an important catalyst for hydrogenation reactions in heterogeneous catalysis[1]. In these reactions, the interaction between the catalyst and the adsorbed, dissociated hydrogen plays a key role in the catalytic activity. Furthermore, the adsorption of hydrogen also plays an important role in electrocatalysis[2], where it is linked to the hydrogen evolution reaction. Ultra-high-vacuum techniques can help in gaining insight into the adsorption properties of hydrogen and the influence of defect sites for both these fields. Consequently, multiple experimental studies have focused on the interaction of platinum and hydrogen [3–5]. These studies investigated not only the Pt(111) facet, but also regularly stepped surfaces and the influence of step edges on the adsorption properties of hydrogen. From a theoretical standpoint, multiple studies have dealt with hydrogen adsorption on the Pt(111) surface, and its interaction with co-adsorbates [6, 7], however only limited work was done on surfaces containing defects [8].

A suitable experimental technique to obtain information about interaction and adsorption energies is temperature programmed desorption (TPD). However, in this approach there is not always a clear link between the desorption peak and the microscopic process it stems from. Density functional theory (DFT) calculations can help provide this link and can therefore give a better view of the desorption pathways involved. One successful example of using theoretical calculations to elucidate TPD spectra is hydrogen desorption from the Pt(110)-(2x1)-reconstructed surface [9, 10]. In this study, it was found that varying desorption barriers for different coverages can play a large role in determining the desorption pathways. However, to date no studies were performed on surfaces with lower step densities.

Previous work in our group discussed TPD spectra of deuterium desorbing from the Pt(533) and Pt(553) surfaces [5]. It was found that deuterium exhibits a two peak spectrum on Pt(533), which has a (100) step edge. In contrast, the Pt(553) surface, which has a (111)-type step edge, shows a significantly more complex spectrum. Based on these results, we performed DFT calculations on low-coverage hydrogen adsorption on the Pt(533) and Pt(553) surfaces[11]. We found a very good correlation between the adsorption energies and the desorption spectrum for Pt(533). However, the low-coverage adsorption picture was not adequate for explaining the full hydrogen desorption spectrum on the Pt(553) surface.

In this study we perform simulations of high-coverage hydrogen adsorption on Pt(533) and Pt(553). We find that hydrogen on the step edge of Pt(533) shows a slight attractive interaction, while on Pt(553) this attractive interaction is increased noticeably. Interactions on the terrace are found to be short-ranged and repulsive. Based on these results we identify ranges in the differential Gibbs

adsorption energy distribution for the adsorbates on these surfaces which are directly linked to the desorption peaks. These results help explain why the hydrogen desorption spectra from these two seemingly similar surfaces are so distinctly different.

5.3 Computational Methods

We used the *ab initio* density functional code VASP [12–15] and the PBE functional [16] with PAW projectors [17, 18] for our calculations. The Brillouin zone was sampled using a 3x9x1 grid for the super cell which was chosen to be two atoms wide along the step edge. A plane-wave basis set with a cutoff energy of 550 eV was selected. First-order Methfessel-Paxton smearing [19] with a sigma of 0.2 eV was used and all energies were extrapolated to 0 K. Additional information about the model surfaces can be found in reference [11]. Structures were relaxed until the remaining forces were below 0.04 eV/Å.

The adsorption energies are calculated as Gibbs energies and are corrected for zero-point energy (ZPE) and vibrational entropy at 273 K, following the methods described by Loffreda [20]. The total Gibbs energy for each adsorption structure was calculated as:

$$G_{tot,n\cdot H_{ads}} = E_{DFT,n\cdot H} + ZPE_{n\cdot H} - T \cdot S_{n\cdot H,tot}, \quad (5.1)$$

while the gas-phase references were calculated as

$$G_{tot,\frac{n}{2}\cdot H_2(g)} = E_{DFT,\frac{n}{2}\cdot H_2(g)} + ZPE_{\frac{n}{2}\cdot H_2(g)} - T \cdot S_{\frac{n}{2}\cdot H_2,tot(g)}, \quad (5.2)$$

The values for $S_{H_2O,tot}$ are taken from tables for gas-phase species in reference [21]. In order to study the actual energy differences that occur when increasing the coverage, we use the so-called differential (Gibbs) adsorption energies, mirroring previous work on this topic [9, 10]. These are calculated by referencing each energy to the structure with the most favorable energy of all structures with one hydrogen atom less per super cell:

$$G_{diff,n\cdot H_{ads}} = G_{tot,n\cdot H_{ads}} - G_{tot,min,(n-1)\cdot H_{ads}}, \quad (5.3)$$

It should be noted that the ZPE and entropy contributions do not change significantly between different configurations with the same number of adsorbed molecules.

Furthermore, in order to study the influence of barriers on the desorption characteristics of hydrogen from stepped Pt, we performed nudged-elastic-band (NEB) calculations[22]. The barrier calculations were also performed with a cutoff

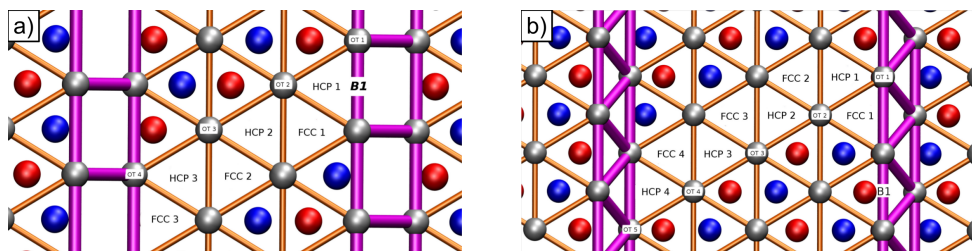


Figure 5.1: Adsorption sites on a) the Pt(533) surface and b) the Pt(553) surface. Surface platinum atoms are marked in silver, first sub-surface layer platinum atoms are represented in blue, while the atoms in the second subsurface layer are shown in red. Figure taken from reference [11]

energy of 550 eV, and were relaxed until the remaining forces orthogonal to the reaction coordinate were below 0.04 eV/Å. The simulations used 7 images along the reaction coordinate. Climbing image NEB calculations [23] for the converged pathways were attempted, but had notable convergence problems even after more than 250 ionic steps. The few calculations that did converge showed no noticeable change in the barrier height compared to the standard NEB calculations.

We use model surfaces for Pt(533) and Pt(553) which are described in more detail in reference [11]. In figure 5.1 we show the naming scheme for the adsorption sites. In this paper the term “coverage” is meant to signify the ratio H:Pt between the number of adsorbed hydrogens per unit cell and the number of surface platinum atoms in the unit cell. We note that it is not always clear what actual H:Pt ratio can be reached under experimental conditions. A clear link to the coverages under experimental conditions will be made in the sections dealing with the elucidation of the TPD spectra. The super cells are identical to the ones in the previous publication [11] and are comprised of two unit cells of the stepped surface replicated along the step edge. This allows for study of isolated hydrogen atoms, as well as for interaction effects at medium to high coverages.

5.4 Results and Discussion

5.4.1 High-Coverage Hydrogen Adsorption on Pt(533) and Desorption Characteristics

In the following we will discuss adsorption structures for increasing coverages of hydrogen on Pt(533). The structures shown are the most favorable configurations for each individual coverage, since we expect that high diffusion rates allow the hydrogen atoms to move to their most favorable positions before the surface

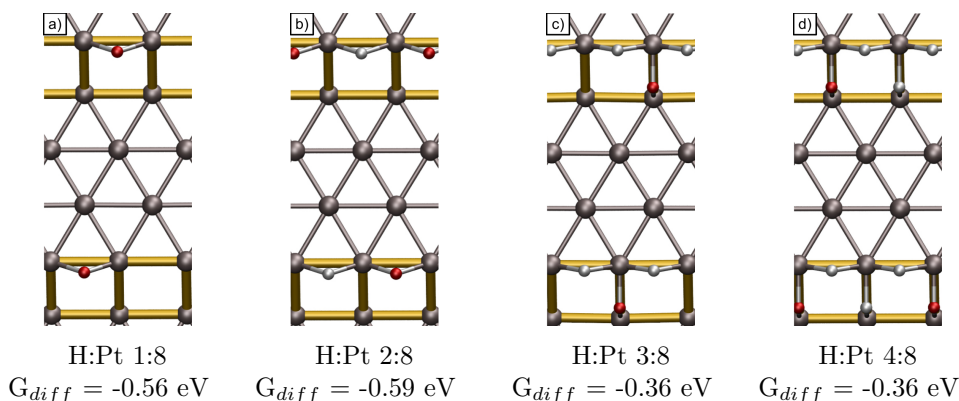


Figure 5.2: Adsorption structures and their respective differential Gibbs adsorption energies for increasing coverages from a) 1 hydrogen to d) 4 hydrogen atoms per super cell. The atom with the lowest differential Gibbs adsorption energy, which is added to increase the coverage, is marked in red.

reaches the desorption temperature of hydrogen.

1-4 Hydrogen atoms (H:Pt = 1:8 - 4:8): Step-edge related adsorption

The most favorable adsorption site on the Pt(533) surface for a single isolated hydrogen atom is the B1 site at the step edge, as shown in Fig. 5.2a, with a (differential) Gibbs adsorption energy of -0.56 eV [11]. We find that the site favored for the adsorption of the second hydrogen atom in the super cell is the other B1 site at the step edge. The differential Gibbs adsorption energy for this site is -0.59 eV and the resulting adsorption geometry can be seen in Fig. 5.2b. The increase in differential Gibbs adsorption energy indicates that there is a slight attractive interaction of ~ 0.015 eV per atom between hydrogen atoms absorbed at the step edge of Pt(533). Further increasing the coverage to include 3 hydrogen atoms per super cell, we find the most favorable site to be the OT4 site with a differential Gibbs adsorption energy of -0.36 eV (see Fig. 5.2c). The OT4 site is located atop the lower step-edge Pt atom but can also be viewed as a bridge site between the upper and lower step-edge platinum atoms. For 4 hydrogen atoms per unit cell we find a preference to occupy the second OT4 site (the resulting adsorption geometry can be found in 5.2d). A differential Gibbs adsorption energy of -0.36 eV was found for this structure. At this point the step edge is completely covered and no further step-related adsorption sites can be occupied without causing strong, unfavorable interactions.

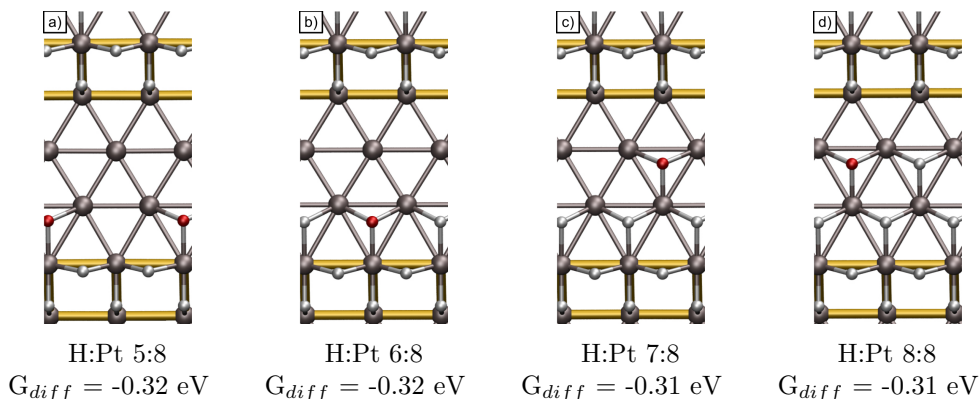


Figure 5.3: Adsorption structures and their respective differential Gibbs adsorption energies for increasing coverages from a) 5 hydrogen to d) 8 hydrogen atoms per super cell. The atom with the lowest differential Gibbs adsorption energy, which is added to increase the coverage, is marked in red.

5-8 Hydrogen atoms (H:Pt = 5:8 - 8:8): Terrace adsorption

Increasing the coverage beyond 4 hydrogen atoms per super cell leads to the occupation of terrace sites. We find that for 5 hydrogen atoms per super cell, the FCC1 site adjacent to the upper step edge is preferred with a differential Gibbs energy of -0.32 eV. The corresponding adsorption geometry can be seen in Fig. 5.3a. The second terrace-bound atom is found to bind preferentially to the second FCC1 site on the terrace with a differential Gibbs energy of -0.32 eV (see Fig. 5.3b). Increasing the occupation of the super cell further, the two FCC2 sites will be filled next. They exhibit differential Gibbs energies of -0.31 eV for the first adsorbate and an identical -0.31 eV for the second adsorbate. The resulting adsorption geometries can be seen in figures 5.3c and 5.3d. Note that the differential Gibbs adsorption energy differences between these 4 sites are very small, independent of the exact order of the filling. This observation, combined with the low diffusion barriers, leads us to conclude that there is no fixed order for filling of, or desorbing from, the terrace. A further increase in coverage was not investigated for the following two reasons. Firstly, a surface with 8 hydrogen atoms per super cell is fully covered (H:Pt = 1:1) and there are no low-barrier adsorption pathways available for further adsorption. Additionally, the experimental TPD spectrum shows a 1:3 ratio between high-temperature and low-temperature peak. This ratio is satisfied for the current 1:1 occupation in the DFT simulation, which indicates that no further hydrogen will be adsorbed.

Table 5.1: Additional reaction barriers for the B1-B1 and lowest energy desorption pathways from Pt(533) for increasing coverages.

Ratio H:Pt in super cell	Pathway 1	E_{barr} [eV]	Pathway 2	E_{barr} [eV]
2:8	B1-B1	0.05	—	—
4:8	B1-B1	0.00	OT4-OT4	—*
6:8	B1-B1	0.00	FCC1-FCC1	0.07**
8:8	B1-B1	0.00	FCC2-FCC2	0.08

* Desorption pathway NEB did not converge at given convergence criteria. Pathway barrier energies were consistently above 0.4 eV.

** Calculation did not converge past 0.1 eV/Å remaining forces

5.4.2 Barriers on the Pt(533) Surface

In order to estimate the influence of possible desorption barriers, we performed NEB calculations for the B1-B1 and lowest-energy desorption pathway at each ratio of H:Pt ranging from 1:4 over 2:4 and 3:4 to 4:4. The results are shown in table 5.1. Note that "additional barrier" in this case refers to any energy barrier on top of the desorption energy (adsorption energy) for the two desorbing hydrogen atoms. We find that at all coverages these additional desorption barriers are below 0.1 eV. The only exception is the desorption from the OT4 sites, which exhibits a complicated pathway due to the unique geometry of the surrounding platinum atoms. Unfortunately, none of our attempts to model this pathway led to a successfully converged NEB calculation. All unconverged results showed barriers in excess of 0.4 eV. However, we are certain that this will not play a large role in the actual physical system, since the diffusion barriers from and to the OT4 site are very small. This means that the pathway can proceed via a diffusion step, followed by desorption from the neighboring FCC2 sites.

5.4.3 Elucidation of TPD Spectra

Figure 5.4a) plots the differential Gibbs energies of adsorption as a function of the coverages described above. Additionally, we introduced general energy ranges that contain the adsorption energies of multiple desorption sites. We observe two general regimes of adsorption energies, namely one regime for the highly favorable B1-bound hydrogen (green area in Fig. 5.4) and one regime for the rest of the adsorption sites, which have less favorable adsorption energy (blue area in Fig. 5.4). The step edge related OT4 sites, also fall into the latter regime,

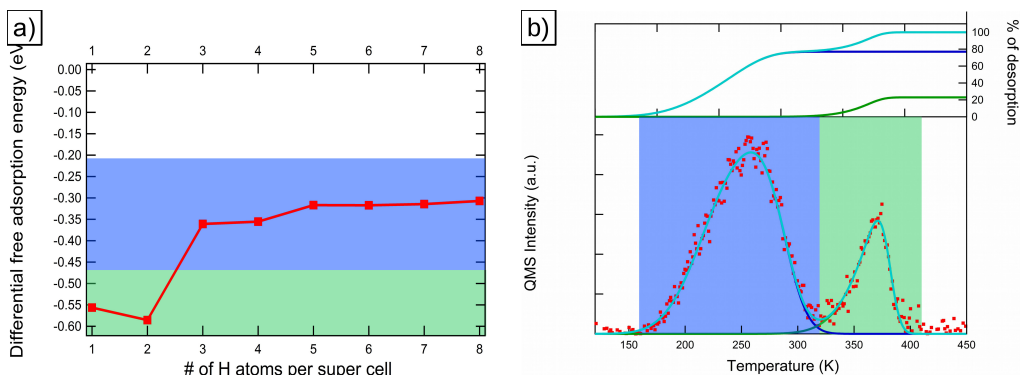


Figure 5.4: a) Differential Gibbs adsorption energies for Pt(533), the two general ranges of adsorption energies discussed below are marked in green (step adsorption) and blue (terrace adsorption), b) TPD spectrum with the colored areas indicating the origin of the peaks in a). Inset in b) shows the integrals of the deconvolution fits (cyan and green) as percentages of the total deconvolution integral (blue)

leading to a 1:3 ratio between the green and the blue areas, which mirrors the experimentally observed ratio of 23:77 or ca. 1:3 [5]. This implies that hydrogen on Pt(533) reaches a ratio of 1H:1Pt and therefore a true 100% coverage. Figure 5.4b) shows the corresponding temperature regions in the experimental TPD spectrum. Furthermore, the attractive interaction between the step-bound hydrogen atoms leads to a slightly sharper peak than the one observed for the terrace, which is reflected in the experimental data.

5.4.4 High-Coverage Hydrogen Adsorption on Pt(553) and Desorption Characteristics

Next we will describe our findings for the Pt(553) surface. We will, as above, only describe the most favorable adsorption geometry for each coverage.

1-2 Hydrogen atoms (H:Pt = 1:10 - 2:10): Step adsorption

In our earlier publication [11], we identified the FCC1 site (see Fig. 5.5a) at the upper step edge with a (differential) Gibbs adsorption energy of -0.24 eV as the most favorable adsorption site for a single hydrogen atom on Pt(553). However, when increasing the occupation to 2 H per super cell, we find that a combination of two B1 sites (see Fig. 5.5b), the same as on Pt(533), is the most favorable adsorption geometry. A differential Gibbs adsorption energy of -0.37 eV

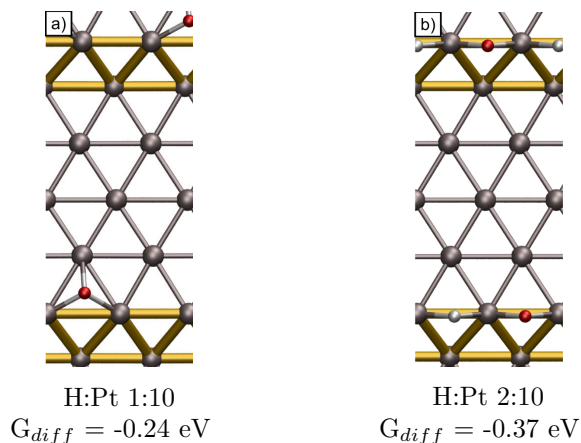


Figure 5.5: Adsorption structures and their respective differential Gibbs adsorption energies for increasing occupations from a) 1 hydrogen to b) 2 hydrogen atoms per super cell. The atom with the lowest differential Gibbs adsorption energy, which is added to increase the occupation, is marked in red.

is observed. Note that this indicates a (for hydrogen) strong attractive interaction of ~ 0.07 eV/H. Apparently, this strong interaction should be associated with the change in preferred binding geometry.

2-6 Hydrogen atoms (H:Pt = 3:10 - 6:10): Terrace adsorption

Increasing the occupation beyond 2 hydrogen atoms per super cell, we find that now the FCC3 site (see Fig 5.6a) in the middle of the terrace is the most favorable site with a differential Gibbs adsorption energy of -0.21 eV. The preference of the sites in the middle of the terrace was also visible for the single-adsorbate picture [11]. Increasing the occupation to 4 hydrogen atoms per super cell, the second FCC3 site (see Fig. 5.6b) is occupied. A differential Gibbs energy of -0.20 eV is calculated for this site. Further increasing the occupation to 5 and 6 hydrogen atoms per super cell leads to the filling of the two FCC2 sites on the terrace. The respective differential Gibbs energies of adsorption are -0.15 eV and an identical -0.15 eV. The adsorption geometries can be seen in figures 5.6c and 5.6d. Note that the step-edge adjacent FCC1 sites are not occupied due to the repulsive interaction with the filled B1 sites.

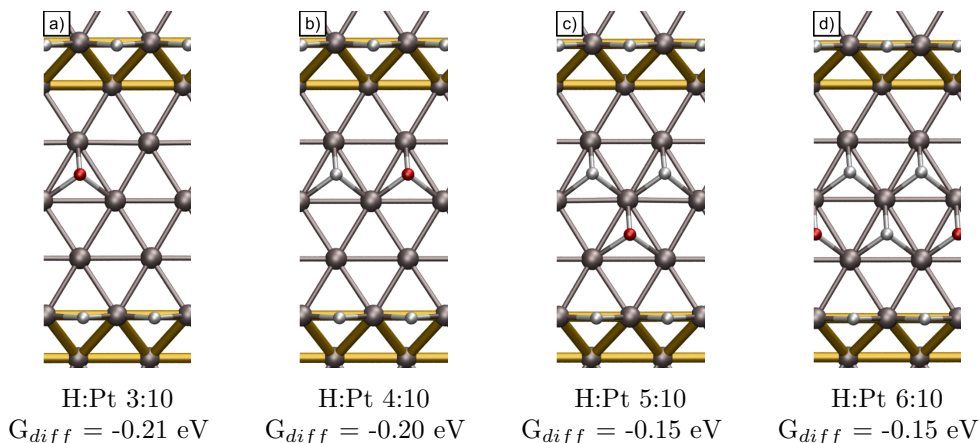


Figure 5.6: Adsorption structures and their respective differential Gibbs adsorption energies for increasing occupations from a) 3 hydrogen to d) 6 hydrogen atoms per super cell. The atom with the lowest differential Gibbs adsorption energy, which is added to increase the occupation, is marked in red.

7-10 Hydrogen atoms: Low Adsorption Energies, Step Adsorption, Complete Restructuring of the Adsorption Geometry

Further increasing the occupation beyond 6 H per cell we observe a drastic decrease in differential Gibbs adsorption energies, to the point that there is little to no energy gain for additional adsorbed H atoms. We will discuss these sites here to arrive at the same 1H:1Pt ratio as for Pt(533), however, we want to point out that it is highly unlikely that these occupations can be reached in the real physical system. This has two main reasons: For any occupation beyond 7 hydrogen atoms per super cell, the adsorption energies are very unfavorable, so adsorption at these sites is energetically possible, but unlikely. Furthermore, for the higher occupations of 9 and 10 hydrogen atoms there are no areas in the unit cell that allow for easy dissociative adsorption of the hydrogen molecule (requiring 2 neighboring, empty FCC sites), leading us to believe that these occupations cannot be reached, at least not in the UHV regime. The first adsorption sites to be filled in this regime are the two weak-binding FCC4 sites at the lower step edge with adsorption energies of -0.05 eV and -0.05 eV, respectively. Their respective adsorption geometries can be seen in figures 5.7a and 5.7b. Increasing the occupation further forces the hydrogen to occupy the OT1 site at the step edge (see Fig. 5.7c), which interacts strongly with the other step-bound hydrogen atoms, especially the B1 site reducing the differential Gibbs adsorption energy to 0.00 eV. Increasing the occupation to 10 H per super cell, we find that shift-

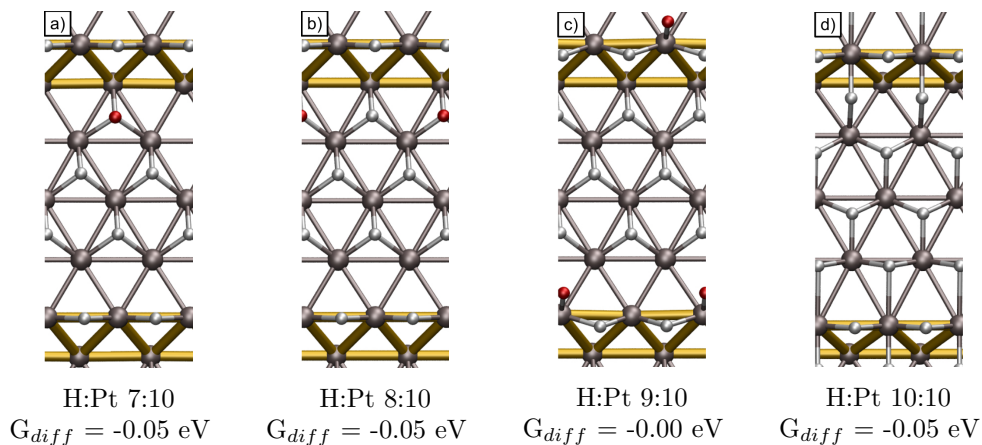


Figure 5.7: Adsorption structures and their respective differential Gibbs adsorption energies for increasing occupations from a) 7 hydrogen to d) 10 hydrogen atoms per super cell. The atom with the lowest differential Gibbs adsorption energy, which is added to increase the occupation, is marked in red. Geometry d) contains no atom marked in red since the complete geometry shifts to HCP adsorption sites

ing the complete adsorption structure to occupy HCP sites instead of FCC sites leads to a small increase in total adsorption energy compared to the FCC-based 10 H structures. Applying the differential Gibbs adsorption energy methodology, which is somewhat ill-defined in this case, we arrive at a value of -0.04 eV for this adsorption geometry. Please specifically note that the HCP-based geometry for 9 hydrogen atoms per super cell is less favorable than the one containing the OT1-adsorbed hydrogen atom. We find it very unlikely that this adsorption geometry will be present in the real system, due to the size of the combined barrier for the shift from the FCC-based adsorption structure to the HCP-based adsorption structure.

5.4.5 Barriers on the Pt(553) Surface

Also for the Pt(553) surface, NEB barrier calculations were performed, the results of which can be found in table 5.2. As described earlier, “barrier” denotes any additional barrier that needs to be overcome beyond the desorption energy differences. We find that without exception all barriers are below 0.1 eV for all adsorption geometries. The B1-B1 pathway generally shows no additional barrier, while the FCC-FCC desorption usually show very low barriers ranging from 0.03 eV to 0.08 eV. In conclusion this means that also on the Pt(553) surface

Table 5.2: Additional reaction barriers for the B1-B1 and lowest-energy desorption pathways from Pt(553) for increasing occupations.

Ratio H:Pt in super cell	Pathway 1	E_{barr} [eV]	Pathway 2	E_{barr} [eV]
2:10	B1-B1	0.00	—	—
4:10	B1-B1	0.00	FCC3-FCC3	0.03
6:10	B1-B1	0.03	FCC2-FCC2	0.05
8:10 *	B1-B1	0.00	FCC2-FCC2	0.08

* Occupations beyond a ratio of 8:10 were not investigated with NEB calculations. The reasons for this are discussed in the section of the text dealing with these occupations.

desorption barriers play no important role.

5.4.6 Elucidation of TPD Spectra

For the Pt(553) surface, inferring the maximum occupation from the pure DFT data is challenging, since it is uncertain if the occupations of 7-10 hydrogen atoms per super cell are present in the experiment. From our theoretical results we conclude that the most favorable adsorption sites (2 B1 sites) must be linked to the highest-temperature desorption feature. Additionally, we find that the highest temperature TPD peak is sharp compared to all other peaks on the Pt(553) surface, indicating (strong) attractive interactions, which mirrors our findings in DFT (though DFT appears to overestimate the attractive interaction). With the high-temperature peak clearly associated with the step edge, we can now obtain an estimate for the full occupation of the surface by comparing the TPD deconvolution integrals for the low-temperature features to this peak. We find a ratio of 1:2.25 for the ratio between the high-temperature peak and the sum of the integrals of the two low-temperature peaks. This suggests a maximum occupation of 6-7 hydrogen atoms per super cell in our calculations. Furthermore, since the remaining two low-temperature features each show similar total integrals as the high-temperature feature, we can assign these peaks to the two next-best pairs of adsorption sites. Therefore, we deduce that the medium-temperature desorption feature is related to the second and third-best adsorption sites (2 FCC3 sites) and the peak low-temperature desorption peak is related to the fourth and fifth-best sites on the surface (2 FCC2 sites). Figure 5.8a) shows the differential Gibbs adsorption energies for 1-10 hydrogen atoms per super cell, with the three

adsorption energy ranges that were discussed above marked in cyan, black and green. Figure 5.8 shows the TPD spectrum with the deconvolution fits and their integrals. Additionally, the temperature ranges associated with the adsorption sites in a) are marked in the corresponding colors.

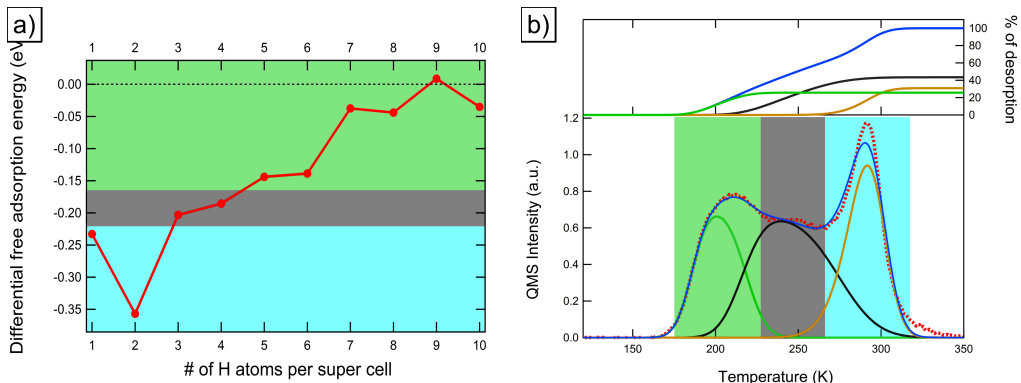


Figure 5.8: a) Differential Gibbs adsorption energies for Pt(553), three general ranges of adsorption energies discussed in the text are marked in cyan (step adsorption), black (terrace adsorption) and blue (low adsorption energy regime), b) TPD spectrum with the colored areas indicating the origin of the peaks in a). Inset in b) shows the integrals of the deconvolution fits (cyan, black and green) as percentages of the total integral (blue)

5.5 Conclusions

From the above DFT results we conclude that the Pt(533) TPD features can be explained by the two main regimes of adsorption energies encountered during the calculations: The high-temperature feature can be linked to the very favorable B1 site at the step edge, while the low-temperature feature can be linked to the 3 occupied terrace sites. The integration of the TPD spectrum supports the observed ratios between step and terrace and suggests a maximum ratio of hydrogen atoms to surface platinum atoms of 1:1. We observe a slight attractive interaction on the step edge of 0.015 eV per hydrogen atom. On the other hand, on the Pt(553) surface we find a more complex adsorption energy landscape. We find that the most favorable adsorption site on the step edge shifts from the FCC1 site, for the lowest occupation studied, to a full occupation of the B1 sites. This is due to a (for hydrogen) remarkably strong attractive interaction of 0.07 eV per hydrogen atom. We combine this knowledge with the integrals obtained from

the deconvolution of the TPD spectra and arrive at a maximum ratio of hydrogen atoms to surface platinum atoms of 0.6:1. This is significantly lower than the value obtained for Pt(533). We assign the two low-temperature features in the TPD to the FCC3 and FCC2 sites, respectively, reproducing the ratio of the integrals of the TPD deconvolution.

5.6 Acknowledgments

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5.7 Bibliography

References

- (1) Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A. *Journal of the American Chemical Society* **1996**, *118*, 2942–2949.
- (2) Conway, B.; Tilak, B. *Electrochimica Acta* **2002**, *47*, 3571–3594.
- (3) Christmann, K.; Ertl, G.; Pignet, T. *Surface Science* **1976**, *54*, 365–392.
- (4) Christmann, K.; Ertl, G. *Surface Science* **1976**, *60*, 365–384.
- (5) Van der Niet, M. J. T. C.; den Dunnen, A.; Juurlink, L. B. F.; Koper, M. T. M. *J. Chem. Phys.* **2010**, *132*, 174705.
- (6) Norskov, J. K.; Bligaard, T.; Logadottir, A.; Kitchin, J. R.; Chen, J. G.; Pandelov, S.; Stimming, U. *Journal of The Electrochemical Society* **2005**, *152*, J23–J26.
- (7) Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff, I.; Norskov, J. K. *Nat Mater* **2006**, *5*, 909–913.
- (8) Olsen, R.; Badescu, S.; Ying, S.; Baerends, E. *J. Chem. Phys.* **2004**, *120*, 11852–11863.
- (9) Gudmundsdóttir, S.; Skúlason, E.; Jónsson, H. *Phys. Rev. Lett.* **2012**, *108*, 156101.

- (10) Gudmundsdottir, S.; Skulason, E.; Weststrate, K.-J.; Juurlink, L.; Jonsson, H. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6323–6332.
- (11) Kolb, M. J.; Calle-Vallejo, F.; Juurlink, L. B. F.; Koper, M. T. M. *The Journal of Chemical Physics* **2014**, *140* 134708.
- (12) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561.
- (13) Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251–14269.
- (14) Kresse, G.; Furthmüller, J. *Computational Materials Science* **1996**, *6*, 15 – 50.
- (15) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (16) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (17) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (18) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (19) Methfessel, M.; Paxton, A. T. *Phys. Rev. B* **1989**, *40*, 3616–3621.
- (20) Loffreda, D. *Surf. Sci.* **2006**, *600*, 2103 –2112.
- (21) Ed. Chase, M.; Davies, C.; Downey, J.; Frurip, D.; MacDonald, R.; Syverud, A., *NIST-JANAF Thermodynamical Tables*, Suppl. 1 to Vol 14 of J. Phys. Chem. Ref. Data, 1985; Vol. 14.
- (22) Henkelman, G.; Uberuaga, B. P.; Jnsson, H. *The Journal of Chemical Physics* **2000**, *113*, 9901–9904.
- (23) Henkelman, G.; Jónsson, H. *The Journal of Chemical Physics* **2000**, *113*, 9978–9985.

Chapter 6

Notes regarding the Supporting Information

- Chapter 2:

The supporting information for chapter 2 contains a full list of adsorption geometry information, adsorption energies and ZPE as well as vibrational entropy correction terms. Furthermore, we give information regarding the convergence of the model surfaces.

The supporting information is available online at the online repository of the Journal of Chemical Physics. ftp://ftp.aip.org/epaps/journ_chem_phys/E-JCPSA6-140-043413/

- Chapter 3:

The supporting information for this chapter contains the full set of adsorption geometries and energies for all tested adsorption structures of water in this study. Additionally, we give account for the calculated ZPE and vibrational entropy terms of each structure.

The supporting information is available online at the repository of the journal Physical Chemistry Chemical Physics at <http://www.rsc.org/suppdata/c5/cp/c5cp04468e/c5cp04468e1.pdf>

- Chapter 4:

The supporting information for chapter 4 contains a set of 5 additional STM images that we analyzed to help elucidate and confirm the adsorption structure present on the surfaces. Additionally, we give a full account of all tested adsorption structures, their adsorption energies as well as the ZPE and vibrational entropy contributions to the free energy.

The supporting information will be available online as part of the publication of the article on which the chapter is based. Until that point in time the supporting material is available online at <https://www.dropbox.com/s/ywbpfrm4mo8h0ix/Supplemental-Material.pdf?dl=0>.

Chapter 7

Outlook

In this final section, we will discuss this research presented in this thesis in context with its relevant fields: water adsorbates at defect sites on platinum surfaces and the field of theoretical and computational electrochemistry.

The work presented here is part of the emerging field of study that deals with the interaction between reactants, intermediates and reaction products at and near low-coordinated or defect sites on heterogeneous catalysts in general, and on platinum surfaces in particular.

About twenty years ago, the study of the catalytic properties of the high-symmetry facets of catalysts from first principles started, due to the appearance of theoretical methods, appropriate density functionals as well as the computational capabilities that enable the description of these multi-atom systems. Since then our understanding of the gas-metal as well as the liquid-metal interface has grown tremendously, due to the interaction between experiment and the new insights created by theoretical calculations. However, the approach described above has typically focused on the aforementioned high-symmetry facets, while any realistic catalytic system contains large amounts of defect sites, which often dominate the overall catalytic activity.

For this reason, theoretical studies have started to appear in the last 5-10 years that deal with extended defect-containing surfaces. In this approach, surfaces with non-trivial Miller indices are used as an approximation for the interaction between adsorbates and defect sites of any possible type. The timing of this development is mainly due to the advancement of computational power, which allows for a study of a reasonably complex stepped surface in the same timeframe as was common for the flat metal surfaces 20 years ago.

The work presented in this thesis has detailed the interaction between the electrochemically relevant adsorbates H, O, OH and H₂O and the simplest defect-

ive platinum surfaces which shows little defect-defect interaction, namely Pt(533) and Pt(553), in relation to experimental UHV work performed in the group of Ludo Juurlink.

Future research in this field of study should focus on extending our understanding of the adsorption properties of adsorbates on any type of defect. Larger terrace sizes can be treated using improved computational capabilities, made available in the last few years. This allows for a better understanding of long-range effects in these systems. In view of this the results shown in chapter 2 should be extended to consider higher coverages of oxygen on facets ranging from Pt(211) to Pt(977). The results obtained in such a future study will help explain UHV TPD results in the group of Ludo Juurlink, in which it was found that the total oxygen coverage present on these stepped surfaces follows an oscillating pattern for increasing terrace length. Furthermore, to better understand the limitations of using smaller terrace widths to model adsorption data, the results obtained in chapter 5 should be extended to include the adsorption on the Pt(211) and Pt(221) surfaces, which will enable a full systematic explanation of the influence of step edge type and terrace width on the desorption behavior of hydrogen from platinum surfaces, as studied experimentally by Cansin Badan in our group.

Step edges, as discussed here, should only form the starting point for these investigations, since kinks and corner sites also have the potential to show high catalytic activity and are also present on real-world catalysts. These model systems however require larger super-cell sizes to be employed, which leads to a great increase in computational cost.

Moore's law predicts a doubling of the number of transistors per square inch, which will lead to a smaller, but still comparable increase in computational capabilities. This development, combined with improved theoretical approaches such as the use of embedding schemes like QM-MM, will enable the treatment of very large systems with reasonable accuracy and computational costs. Furthering this goal, the results obtained in the chapters 3 and 4 are currently being used to test the quality of a REAX-FF empirical force field for the description of water adsorption on step edges as part of a research project in the group of Dr. Jörg Meyer. This will allow for an estimation of the quality of empirical force field data for the description of step-edge bound water, which is crucial for its use in embedded QM-MM approaches. This development may also eventually allow for the treatment of configurational entropy in water adsorption, an aspect that has so far been largely ignored in first-principles computational studies of water at defective surfaces.

In combination, these two factors will allow for the treatment of significantly larger systems, possibly up to the treatment of actual nano-particles in a full

aqueous environment.

Within the field of theoretical electrochemistry, this thesis gives a first idea of the complicated nature of the solvation environments encountered at defect sites. In the current state of the art, theoretical electrochemistry employs the computational hydrogen electrode scheme by Norskov and coworkers to estimate the thermodynamical reaction energies of separate reaction steps. From these, properties of the electrochemical reaction, such as onset potentials, can be calculated.

However, in this scheme usually the actual aqueous electrochemical environment is not considered. If needed, first-order estimates usually model the interaction between the reaction intermediates and a stylized hexagonal water layer which is used to estimate the solvation energy of the intermediates. However, since there is little to no understanding about the solvation environment at defect sites, such as steps, this approach cannot be used to correct electrochemical simulations of reactions on low-coordinated lattice sites.

The results from this thesis have made a first step in remedying this problem by providing an understanding of the structure of the first water layer near step sites, which now allows for the study of the interaction between solvated adsorbates and the solvating water environment. The results obtained in chapters 3 and 4 form a starting point for the calculation of solvation energies of OH situated at the two step edge types.

Chapter 8

Summary

8.1 Summary

This work discusses the adsorption properties of water and the water related adsorbates H, O and OH on the regularly stepped Pt(533) and Pt(553) surfaces. Understanding the influence of defect sites, such as the two types of step edges present on these two surfaces, can help to improve our understanding of the (electro)catalytic properties of platinum surfaces under realistic conditions, where defect sites are abundant.

Most theoretical studies to date have focused on the high-symmetry facets of platinum in order to predict its catalytic properties. While this can certainly help in gaining insight into this subject, real catalytic platinum surfaces will contain defect sites, which are known to exhibit significantly altered catalytic behavior. For this reason, studies were performed that use regularly stepped metal surfaces, on which the step edges are used as model systems for the edges of nano-particles. In this study we present density functional theory calculations on the adsorption properties of the electrocatalytically relevant adsorbates water, OH, O and H in order to gain insight into their adsorption properties on the step edges present on the regularly stepped Pt(533) (4 atom wide (111) terrace and a (100)-type step edge) and Pt(553) (5 atom wide (111) terrace and a (111)-type step edge).

In chapter 2, the discussion starts with an investigation of the adsorption properties of isolated adsorbates on the two model surfaces. We establish a framework for the investigation by choosing the exact parameters of the model surfaces and the computational settings. On this basis we calculate the adsorption properties of the four adsorbate species that are the focus of this thesis. We find that the (100) step edge of the Pt(533) surface binds the adsorbates OH, H and O more strongly than the (111)-edge on Pt(553). For water we find little to no difference

in adsorption energy at the step edge. We use these results for a comparison to previous results of ultra-high-vacuum temperature programmed desorption studies performed in our group, in which we find that, with the exception of the hydrogen desorption on Pt(553), all TPD spectra can be qualitatively explained by our theoretical results. The chapter concludes with an estimation for thermodynamic reaction barrier for the dissociation of water into H and OH and the reaction of water and oxygen to form two OH adsorbates. We find that on the Pt(533) step edge, both reactions are thermodynamically favorable, while on the Pt(553) surface the reaction with oxygen is thermoneutral, and the dissociation reaction is endothermic.

In chapter 3 we propose high-coverage water adsorption structures along the step edge of the Pt(533) surface. We find that if only the step edge is covered with water, the so-called zig-zag configuration is most stable geometry, in accordance to earlier studies. Increasing the coverage to form isolated ring structures leads to a preference of pentagonal and hexagonal ring structures. Increasing the coverage even further to form double-stranded structures, we find 6 almost iso-energetic structures that can cover the step edge. We observe a general trend for a hydrogen-down orientation of the lower-step-edge water molecules, which we rationalize by the Smoluchowski effect. Furthermore, we conclude that the step edge will be a nucleation point for the growth of water structures and will most likely have long-range influences on the adsorption structure for more than 10 Angstrom.

In chapter 4 we present a combined scanning tunneling microscopy and density functional theory study on the adsorption structures on the Pt(553) surface. On this surface we find a very strong preference for tetragonal water structures, both for isolated ring structures, as well as for the double-stranded case. We explain this by a pronounced templating effect of the underlying platinum lattice. The Smoluchowski effect is used to rationalize the orientation of the lower-step-edge water molecules, as was seen on the Pt(533) surface. The results of the theoretical study are confirmed by STM imaging, in which we find double-stranded water structures on the step edges.

Chapter 5 links together with chapter 2 in trying to elucidate the still unexplained hydrogen desorption spectra of the Pt(553) surface by studying the interaction effects present at higher hydrogen coverages. We find that for the Pt(553) surface the interaction effects are limited in range, with a very small attractive interaction for the sites along the step edge and a very weak interaction for the terrace sites. Furthermore, we observe that the adsorption energies fall into two general regimes, one for the step edge adsorption which is more strongly adsorbed and one for all terrace adsorption sites. From these results we conclude the origin of the two peaks in the TPD spectrum for Pt(533) to be the terrace

sites for the low-temperature peak and the step sites for the high-temperature peak. For Pt(553) we find a completely different picture. The adsorption energy for the step edge shows a (for hydrogen) rather large attractive interaction, while the adsorption energy for all sites on the terrace decreases with increasing coverage. For this surface we find four general regimes of adsorption energies, namely the step edge adsorption, which leads to the highest-temperature peak, the two most favorable sites on the terrace, which lead to the second-highest-temperature peak in the spectrum and the two next-most-favorable sites on the terrace which are the origin of the lowest temperature peak. At this coverage we reach the experimentally observed step-to-terrace ratio of 1:2.25, which means that there will be no additional hydrogen atoms adsorbed in the real system. Additionally, the other possible adsorption sites at higher coverages in the DFT calculations also showed a significantly reduced adsorption energy compared to the ones discussed above, which leads us to conclude that these sites will not be occupied.

In summary this thesis has shown that DFT calculations on the GGA level can be used to study water related adsorbates on regularly stepped platinum surfaces. We link our results to experimental observations, which we are able to explain and, in the case of the water structures, even predict. DFT studies can therefore be used to further improve our insight into the solvation of defective platinum surfaces to further our understanding of electrocatalysis.

8.2 Samenvatting

Dit proefschrift gaat over de adsorptie eigenschappen van water en de water gerelateerde adsorbaten H, O en OH aan de regulier gestapte oppervlakken Pt(533) en Pt(553). Begrip van de invloed van defecten, zoals de twee type stapranden aan deze twee oppervlakken, kunnen inzicht geven in de (elektro)katalytische eigenschappen van platina oppervlakken onder realistische condities, waar defecten veel voorkomen.

De meeste theoretische studies leggen de nadruk op hoge symmetrie facetten van platina om katalytische eigenschappen te voorspellen. Al kan dit zeker inzicht geven in dit onderwerp, echte katalytisch actieve platina oppervlakken bevatten defecten, waarvan bekend is dat zij significant andere katalytisch gedrag vertonen. Om deze reden is onderzoek gedaan aan regulier gestapte metaal oppervlakken, waar de stap randen gebruikt worden als model systeem voor de randen van nanodeeltjes. Hier presenteren we dichtheidsfunctionaaltheorie berekeningen aan de adsorptie eigenschappen van elektrokatalytisch relevante adsorbaten water, OH, O en H om begrip te vergaren over de adsorptie eigenschappen aan de aanwezige stapranden in de regulier gestapte Pt(533) (4 atomen breed (111) terras met een (100)-type staprand) en Pt(533) (5 atomen breed (111) terras en een (111)-type staprand).

De discussie wordt begonnen in hoofdstuk 2 met onderzoek naar de adsorptie eigenschappen van gesoleerde adsorbaten aan de twee model oppervlakken. We leggen een fundering voor het onderzoek door de exacte parameters van het model oppervlak en de instellingen van de berekeningen vast te stellen. Op basis hiervan hebben we de adsorptie eigenschappen van de vier adsorbaten waar dit proefschrift op is toegespitst, bestudeerd. We stellen vast dat de (100)-staprand van het Pt(533) oppervlak de adsorbaten OH, H en O sterker bindt dan de (111)-staprand van Pt(553). We vinden weinig tot geen verschil voor de adsorptie energie van water aan stapranden. We vergelijken deze resultaten met eerdere resultaten van ultrahoog vacuum temperatuurgeprogrammeerde desorptie (TPD) metingen in onze groep. Hier vinden we dat, met uitzondering van waterstof desorptie aan Pt(533), alle TPD resultaten kwalitatief verklaard kunnen worden met onze theoretische resultaten. Het hoofdstuk sluit af met een schatting voor de thermodynamische reactie barrières voor de dissociatie van water naar H en OH en de reactie van water en zuurstof om twee OH adsorbaten te vormen. We vinden dat beide reacties thermodynamisch gunstig zijn aan de staprand van Pt(533), maar dat aan Pt(553) de reactie met zuurstof thermoneutraal is, en de dissociatie reactie endotherm is.

In hoofdstuk 3 stellen we water adsorptie structuren voor die langs de staprand van het Pt(533) oppervlak vormen bij hoge bedekkingsgraad. We zien dat wan-

neer alleen de staprand bedekt is met water, de zogenaamde zig-zag configuratie de meest stabiele geometrie is, wat overeenstemt met eerder onderzoek. Wanneer de bedekkingsgraad wordt verhoogd zodat gesoleerde ringstructuren vormen, blijkt dat er een voorkeur is voor pentagonale en hexagonale ringstructuren. Als de bedekkingsgraad ng verder verhoogd wordt zodat dubbelstrengstructuren vormen, zien we 6 nagenoeg iso-energetische structuren die de staprand kunnen bedekken. We vinden een algemene trend voor een orintatie van de water moleculen met de waterstof naar het metaal oppervlak gericht, onderaan de staprand. We rationaliseren deze orintatie van het water middels het Smoluchowski effect. Daarnaast concluderen we dat de staprand een nucleatiepunt is voor de groei van waterstructuren. Dit zal waarschijnlijk een lange afstandsinvloed hebben op adsorptie structuren groter dan 10 ngstrom.

In hoofdstuk 4 presenteren we een gecombineerde rastertunnelmicroscopie en dichtheidsfunctionaaltheorie onderzoek aan water adsorptie structuren aan het Pt(553) oppervlak. Aan dit oppervlak vinden we een sterke voorkeur voor tetragonale structuren aan de staprand, zowel voor gesoleerde ringstructuren als voor de dubbelstrengstructuren. We verklaren dit met een sjabloon effect van het onderliggende platina rooster. Het Smoluchowski effect wordt gebruikt om de orintatie van water aan de lage kant van de staprand te verklaren, zoals ook gezien is bij het Pt(533) oppervlak. De resultaten van dit theoretische onderzoek zijn bevestigd met behulp van STM, waarmee we dubbelstrengs waterstructuren aan de staprand waarnemen.

Hoofdstuk 5 is gekoppeld aan hoofdstuk 2 met het doel de niet verklaarde waterstof desorptie spectra alsnog te verklaren. Dit wordt gedaan door interactie effecten tussen waterstofatomen te bestuderen die aanwezig zijn bij een hogere waterstof bedekkingsgraad. We vinden dat interactie effecten aan het Pt(553) oppervlak plaats vinden op beperkte afstanden, met een erg kleine aantrekkende interactie op plekken langs de staprand en een zeer zwakke interactie voor plekken op het terras. Daarnaast observeren we dat de adsorptie energien in twee algemene gebieden vallen, n voor adsorptie aan de stapranden, welke sterker geadsorbeerd zijn, en n voor alle adsorptie plekken aan het terras. Uit deze resultaten concluderen we dat de oorsprong van de twee pieken in het TPD spectrum voor Pt(533) ligt in terras desorptie bij de lage temperatuurpiek en desorptie van de stapranden bij de hoge temperatuurpiek. Bij Pt(553) zien we iets heel anders. De adsorptie energie voor de staprand geeft aan dat een redelijk grote aantrekkende interactie aanwezig is, terwijl de adsorptie energie van alle plekken aan het terras kleiner wordt met bedekkingsgraad. Voor dit oppervlak vinden we vier algemene gebieden voor de adsorptie energie: namelijk adsorptie aan de staprand welke tot leidt tot de hoogste temperatuurpiek, de twee meest gunstige plekken aan het

terras welke de op n na hoogste temperatuurpiek geeft en tot slot de twee daaropvolgend meest gunstige plekken aan het terras, welke de lage temperatuurpiek tot gevolg hebben. Bij deze bedekkingsgraad bereiken we een experimenteel bepaalde stap-terras verhouding van 1:2.25, wat als gevolg heeft dat er geen additionele waterstof atomen geadsorbeerd zijn in het echte systeem. Daarnaast laten de DFT berekeningen zien dat de andere adsorptie plekken bij hoge bedekkingsgraad een significant kleinere adsorptie energie hebben vergeleken met de adsorptie energien hierboven. Hieruit kunnen wij concluderen dat deze plekken niet bezet worden.

Samenvattend, dit proefschrift toont aan dat DFT berekeningen op het GGA niveau gebruikt kunnen worden om water-gerelateerde adsorbaten aan regulier gestapte oppervlakken te bestuderen. We koppelen onze resultaten aan experimentele waarnemingen, welke we kunnen verklaren en, in het geval van water structuren, zelfs voorspellen. DFT berekeningen kunnen dus gebruikt worden om inzicht te krijgen in de solvatatie van defecten aan platina oppervlakken zodat we meer begrip krijgen over elektrokatalyse.

List of Publications

- Kolb, M.J., Farber, R.; Derouin, J.; Badan, C.; Calle-Vallejo, F.; Juurlink, L.B.F.; Killelea, D.R. and Koper, M.T.M.: *Double Stranded Water on Stepped Platinum Surfaces*, Phys. Rev. Lett., 2016, submitted
- Shen, J.; Kolb, M.J.; Gittle, A.J. and Marc T.M. Koper*: *DFT Study on the Mechanism of the Electrochemical Reduction of CO₂ Catalyzed by Cobalt Porphyrin*, J. Phys. Chem. C, 2016, DOI: 10.1021/acs.jpcc.5b10763
- Bockstedte, M.; Michl, A.; Kolb, M.J.; Mehlhorn, M. and Morgenstern, K.: *The incomplete bilayer termination of the ice (0001) surface*, J. Phys. Chem. C, 2016, 120 (2), pp 10971109
- Kolb, M.J., Wermink, J.; Calle-Vallejo, F.; Juurlink, L.B.F. and Koper, M.T.M.: *Initial stages of water solvation of stepped platinum surfaces*, Phys. Chem. Chem. Phys., The Royal Society of Chemistry, 2016, 18, 3416-3422
- Calle-Vallejo, F.; Díaz-Morales, O.A.; Kolb, M.J. and Koper, M.T.M. : *Why Is Bulk Thermochemistry a Good Descriptor for the Electrocatalytic Activity of Transition Metal Oxides?*, ACS Catalysis, 2015, 5, 869-873
- Kolb, M. J.; Calle-Vallejo, F.; Juurlink, L.B.F. and Koper, M.T.M. : *Density functional theory study of adsorption of H₂O, H, O, and OH on stepped platinum surfaces*, The Journal of Chemical Physics, 140, 134708, 2014

- Li, H.; Calle-Vallejo, F.; Kolb, M.J.; Kwon, Y.; Li, Y. and Koper, M.T.M. : *Why (100) Terraces Break and Make Bonds: Oxidation of Dimethyl Ether on Platinum Single-Crystal Electrodes*, Journal of the American Chemical Society, 2013, 135, 14329-14338

Curriculum Vitae

Manuel Kolb was born on June, 22nd 1986 in Lauf an der Pegnitz, Germany. After finishing *Gymnasium* with the Abitur, he studied Physics at the Friedrich Alexander Universität Erlangen-Nürnberg. His studies finished with a one year Diplomarbeit in the group for theoretical solid state physics of Prof. Dr. Oleg Pankratov and the supervisor Dr. Michel Bockstedte. The title of his diploma thesis was "Surface Vacancies and Low-Coordinated Lattice-Sites on Metal Oxide Surfaces", studying the electronic structure of defect sites on magnesium oxide. He finished his studies with the degree of Diplom-Physiker in September 2012. After this he continued working under the supervision of Michel Bockstedte as a research assistant in the DFG project "Interaction of long living solvated electrons with adsorbates at the surface of ice" until the end of December 2012.

In January 2013 he joined the research group of Marc Koper as a PhD student on the project "Water-Related Adsorbates on Stepped Platinum Surfaces" as part of a TOP grant awarded to Marc Koper and Ludo Juurlink. The aim of this work was to understand the interaction between regularly stepped platinum surfaces and the electrochemically relevant adsorbates H, O, OH and H₂O in the context of earlier UHV experiments. The results of this work are presented here. During the project he spent 3 months as a visiting scientist in the group of Prof. Hannes Jonsson and Dr. Egill Skulason at the University of Iceland. Several parts of this work have been presented at international conferences.

