Water on well-defined platinum surfaces : an ultra high vacuum and electrochemical study

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Water is H_2O, hydrogen two parts, oxygen one, but there is also a third thing, that makes water and nobody knows what that is.

D.H. Lawrence, Pansies
(1885–1930)

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The influence of step geometry on the desorption characteristics of O_2, D_2, and H_2O from stepped Pt surfaces

Abstract *We have compared the desorption characteristics of O_2, D_2, and H_2O from the Pt(533) surface to the Pt(553) surface using temperature programmed desorption. Both surfaces consist of 4 atom wide (111) terraces interrupted by mono atomic steps of the different step geometries: (100) vs. (110), respectively. We find that desorption is influenced significantly by the presence of step sites and the geometry of those sites. In general, molecules and atoms are thought to be bound stronger to step sites than to terrace sites. Our D_2 desorption data from Pt(553) provide an anomalous counterexample to this common belief, since D atoms on this surface appear to be bound stronger by terrace sites. We also show that it is not possible to say* a priori *which step geometry will bind atoms or molecules stronger: recombinatively desorbing O atoms are bound stronger to (100) sites, whereas H_2O molecules are bound stronger to (110) sites. Furthermore, the amount of ad-atoms or molecules that are affected by the presence of steps varies for the different species, as is evident from the various step : terrace ratios of $\sim 1 : 1.3$ for O_2 (O), $\sim 1 : 3$ for D_2 (D), and $\sim 1 : 1$ for H_2O. This indicates that, in contrast to deuterium, more oxygen atoms and water molecules are affected by the presence of steps than would be expected on geometrical arguments alone.*

3.1 Introduction

Platinum is used as the catalyst material for many reactions, in *e.g.* automotive and fuel cell catalysis. In order to find better and cheaper catalysts it is important to understand the interactions between platinum and the reacting species. Often single crystal Pt(111) surfaces are used as a model catalyst. Although this is the least complex system, ultra high vacuum (UHV) studies already show significant complexity in adsorption and desorption phenomena on Pt(111).[11,31,33,40,41,51,55,57,117–120] Real catalytic surfaces, however, have a complex geometry, containing low coordination or defect sites in addition to (111) terraces. These defect sites are often thought to be more active for catalytic reactions involving bond breaking and making.[13] The simplest model for defect sites are regularly stepped single crystal surfaces. In general two different step sites can be distinguished: those with (100) geometry and those with (110) geometry (see figure 1.2c and d), of which the (100) step is the more studied geometry.

Oxygen adsorbs in three different states on Pt(111): physisorbed O_2 molecules are stable below 45 K,[30] chemisorbed O_2 molecules below 100 – 200 K,[11] and atomic oxygen below 575 – 900 K.[11] Oxygen dissociation is activated and atomic oxygen formation occurs via a precursor state of molecularly adsorbed oxygen.[10,31] The maximum O_{ad} coverage that can be reached via background dosing is 0.25 ML. Oxygen atoms bind preferentially in the fcc hollow sites.[38,39] On stepped surfaces some dissociation takes place on the (111) terraces,[45] but dissociation occurs predominantly on step sites.[10,44–49] Oxygen ad-atoms adsorb preferentially on step sites,[37,48] where (100) steps are favored over (110) steps.[44] For (100) steps a twofold edge bridging site is favored, whereas for (110) steps the fcc hollow site behind the step edge is favored.[37] TPD spectra on Pt(533),[10,45,46,50] other surfaces with (100) steps,[49,51,52] and surfaces with (110) steps[9,32,40,53] all show a three peak structure in the molecular oxygen regime (100–250 K) and a two peak structure in the atomic oxygen regime (575–900 K). No recent TPD studies have been performed on (110) steps except for Sano *et al.*,[53] who studied the molecular oxygen regime only.

Molecular hydrogen adsorbs dissociatively on both Pt(111)[55,57] and stepped platinum surfaces.[58–64] On Pt(111), H_{ad} binds preferentially in the threefold hollow sites at all coverages.[57,65] The (100) and (110) surfaces show a more complex TPD spectrum than Pt(111). H_{ad} binds more strongly to the Pt(100) surface than to the Pt(110) surface.[66] However, reactive force field calculations and experiments show that (110) steps are more reactive towards hydrogen dissociation than (100) steps.[60,67,68] Three different binding sites have been proposed for an H-atom on surfaces with (110) steps. Two of these binding sites are associated with the steps, the other one is associated with the (111) terrace.[59] DFT calculations on Pt(211) (Pt$[3(111) \times (100)]$) show a rather deep global minimum for hydrogen adsorption located at the bridge site on top of the step edge. A high barrier hinders motion

from the lower terrace to the step edge.[69] DFT calculations show that the bridge site on the outer atoms is the most stable binding site for a hydrogen atom on (110) sites as well.[70,71] On surfaces with (100) steps TPD spectra show two desorption features: a relatively small feature at 380 K (ascribed to recombinative desorption from step sites) and a large feature below 360 K (ascribed to recombinative desorption from terrace sites and possibly some remaining step sites). The entire Pt(533) surface is saturated at 0.9 ± 0.05 ML.[63] It is not yet clear whether the Pt : H ratio at the step edges is 2 : 1 or larger.[63,69,74] No isotope effect is observed for hydrogen adsorption and desorption.[63]

For water adsorption on Pt(111), the general consensus is that water adsorbs molecularly at all coverages and temperatures (< 180 K). Classically, water adsorbed on metal surfaces is thought to form an ice-like bilayer of hexagonal rings.[6–8] A combined scanning tunneling microscopy (STM) and density functional theory (DFT) study finds that at submonolayer coverages water islands also contain pentagon and heptagon ring structures.[19] Water dosed on Pt(111) at temperatures well below 135 K yields growth of amorphous solid water (ASW).[21] TPD studies show two peaks. The peak at 171 K is associated with monolayer desorption. This peak shows the characteristics of zero-order desorption kinetics,[22] which has been attributed to co-existence of a condensed phase and a 2-dimensional water-gas at sub-monolayer coverages.[21] A second peak, associated with desorption from multilayers, starts at 154 K and increases in temperature with coverage.[23] Only a few studies have been done on the interaction between H_2O and stepped platinum surfaces.[26–28] Water adsorbs preferentially on step sites, forming molecular chains.[28] In TPD spectra on surfaces with (100) steps an extra peak is observed from the lowest coverages onwards at 188 K.[26,27] This peak is associated with desorption from step sites.

When stepped surfaces are investigated usually surfaces with (100) steps are studied. Systematic experimental studies investigating the influence of step geometry on desorption behavior are sparse.[121] In order to validate whether the study of (100) step sites is sufficient to understand the catalytic behavior of platinum, we compare the desorption characteristics of O_2, D_2, and H_2O from the Pt(533) surface to the Pt(553) surface. The surface structures are shown in figure 1.2c and d. Both surfaces consist of 4 atom wide (111) terraces interrupted by mono atomic steps of the different step geometries: (100) vs. (110), respectively. These step geometries are emphasized in figure 1.2c and d by the black markers. It is debatable whether the Pt(553) surface consists of a (110) step with a four atom wide terrace or a (111) step with a five atom wide terrace. However, we believe that the bottom platinum atom of the (111) triangle is too far buried underneath the upper platinum layer (only $\sim 1/3$ of the atom sticks out) to be considered part of the terrace. We use temperature programmed desorption (TPD) and address the influence of step geometry on the binding energy of molecules that adsorb dissociatively with (O_2)

and without (D_2) a chemisorbed molecular precursor state as well as chemisorbed molecules (H_2O).

3.2 Experimental

Experiments on Pt(533) were performed in POTVIS, whereas experiments on Pt(553) were performed in Lionfish. General experimental procedures are described in chapter 2.1.5.

3.3 Results and discussion

3.3.1 Oxygen

In figure 3.1a we show the TPD spectrum of the highest obtained O_{ad} coverage. Following Gee and Hayden[10] we refer to this oxygen coverage as $\theta_O = 0.25$ ML. Oxygen atoms desorb recombinatively from Pt(533) forming O_2. The spectrum has been deconvoluted into two Gaussians centered around 663 and 774 K. The sum of these Gaussians (black line) follows the original data (dots) closely, justifying the use of Gaussian functions to fit the data. For clarity, we do not show lower coverages here, but both peaks show second order desorption behavior, *i.e.* the peak maxima move towards lower temperature with increasing coverage and the peak shapes are symmetrical in all spectra.[10] The integrals of these Gaussians are shown in the upper part of the graph. The low temperature peak at 663 K is associated with desorption from the (111) terraces, whereas the high temperature peak at 774 K is associated with the desorption from step sites.[10] The ratio $O_{ad,step} : O_{ad,ter}$ is approximately 0.11 : 0.14. The oxygen TPD spectra look similar to the ones published previously obtained by background dosing[45] and molecular beam dosing.[10] We do not see signs of the β_0 peak reported by Gee and Hayden,[10] but we have no access to the high kinetic energies available by molecular beam dosing. Multiple peak structures in the TPD spectra for O_{ad} desorbing from Pt(111) were also reported if more than 0.25 ML was present on the surface, but it is not possible to obtain these coverages through mere O_2 background dosing.[33,40–42] Therefore, we conclude that for the β_0 peak to appear, more energy is necessary to dissociate O_2 molecules than is available from a thermal source. The maximum O_{ad} coverage obtained on Pt(111) by background dosing is 0.25 ML.[41] From the fact that the LEED image is a (2×2) structure for both Pt(111) and Pt(533) Gee and Hayden[10] assume the same maximum coverage for Pt(533) for the combination of both peaks visible in the spectrum. We can not confirm this value here. Gee and Hayden report a ratio of $O_{ad,step} : O_{ad,ter}$ of 0.12 : 0.13 ML for the Pt(533) surface, which is slightly different from our ratio. Rar and Matsushima[45] do not report a ratio between the two peaks, but a visual inspection of their TPD spectra suggests that their ratio

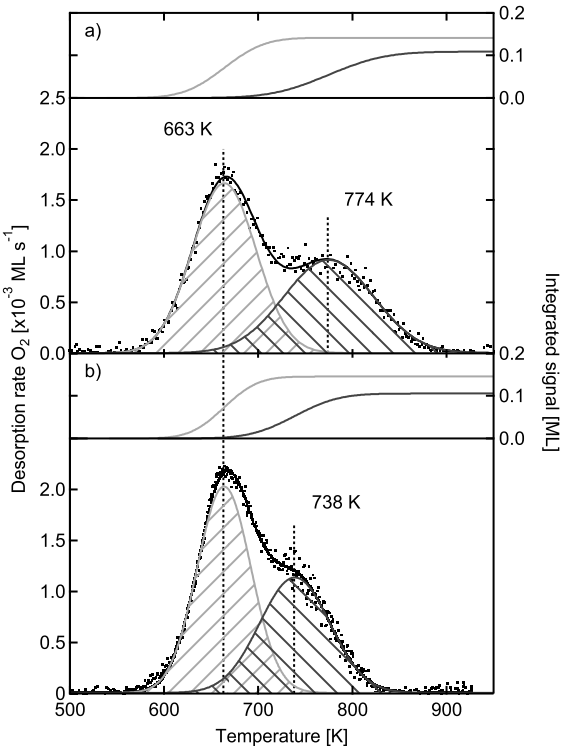

Figure 3.1 TPD spectra of the maximum coverage of O_{ad} (obtained by background dosing of O_2) desorbing from a) Pt(533) and b) Pt(553). The spectra have been deconvoluted by fitting two Gaussians. The top part of the panels shows the integrals of these Gaussians.

approaches ours.

Panel 3.1b shows the same spectra for the Pt(553) surface. Similar to the Pt(533) surface we see two peaks of desorbing oxygen. When these peaks are deconvoluted into Gaussians, the peaks are located at 663 K and 736 K. Since the peak at 663 K is located at exactly the same position as O_{ad} desorbing from (111) terrace sites on Pt(533), we conclude that the oxygen atoms desorbing at this temperature from Pt(553) are desorbing from similar adsorption sites as on the Pt(533) surface. Analogous to the Pt(533) surface we ascribe the 663 K peak to desorption from (111) terrace sites. The remaining adsorption site for the 738 K peak is then due to recombinative desorption from (110) step sites. The desorption temperature from (110) step sites is $\sim$ 36 K lower than from (100) step sites, indicating a significantly lower binding energy on the more open step type. This is in line with DFT calculations at the local-density approximation (LDA) level that predict a higher binding energy

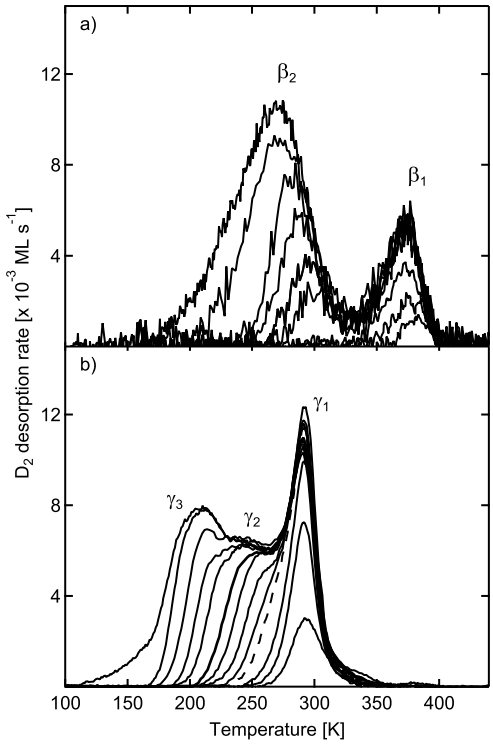

Figure 3.2 TPD spectra of various amounts of D_{ad} desorbing from a) Pt(533) and b) Pt(553).

to (100) type steps than to (110) type steps.[37] The integrals of the individual Gaussians are shown in the upper part of figure 3.1b. The ratio of oxygen desorbing from step to terrace sites is 0.11 : 0.14 ML, which is identical to ratio on the Pt(533) surface. Scanning tunneling microscope (STM) images in combination with DFT calculations show a (2×1) structure for both step types, indicating a similar Pt : O ratio. Therefore, we believe that the similar step to terrace ratios in the oxygen desorption peaks for both surfaces justify considering the Pt(553) surface to be of equal length as the terrace on Pt(533) when it comes to adsorption sites, *i.e.* to have 4 atom wide terraces with a (110) step and not as having a (111) step with a 5 atom wide terrace, at least when O is the adsorbing species.

3.3.2 Deuterium

In figure 3.2a we show data for various amounts of D_2 desorbing from Pt(533). For low coverages a second order desorption peak, β_1, is observed, starting at 383 K

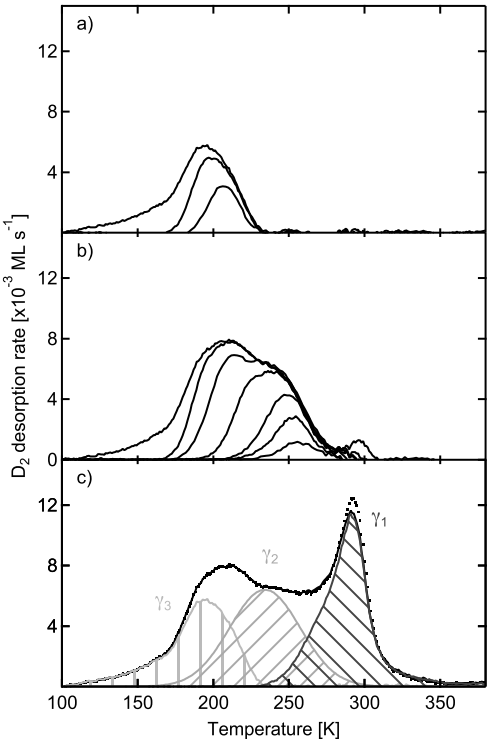

Figure 3.3 Deconvolution of the TPD spectra from figure 3.2b of various amounts of D_{ad} desorbing from Pt(553); a) after removing the γ_1 and γ_2 peaks, b) after removing the γ_1 peak. c) The full deconvolution of the spectrum with the highest obtained coverage.

and saturating at 370 K. At higher coverages a second peak, β_2, (also second order desorption) grows in at 302 K saturating at $\sim$ 260 K. The ratio of $\beta_2 : \beta_1$, as determined from Gaussian fits, at $\theta_D = \theta_{max}$, is 3:1.

Figure 3.2b shows similar measurements but now for the Pt(553) surface. At low coverages a peak, γ_1, is visible at 292 K. This peak shifts slightly to lower temperatures with increasing coverage. The dashed line depicts the spectrum where γ_1 has saturated. At higher coverages a shoulder, γ_2, grows in. The leading edges of the desorption traces with higher coverages are parallel to the dashed desorption trace. Figure 3.3b shows these traces after subtracting γ_1. It can be clearly seen that γ_2 is a second order peak, starting at 256 K and saturating at 235 K. At coverages higher than $\sim$ 63% θ_{max} a second shoulder, γ_3 appears. We have deconvoluted γ_2 and γ_3 by fitting a double Gaussian to the spectrum with the second highest coverage. Figure 3.3a shows the traces after subtracting the Gaussian fitted to γ_2, leaving only γ_3. The γ_3 feature also shows second order desorption kinetics with the peak

Surface	Peak	$\nu(\theta)$ [s^{-1}]	$E_d(\theta)$ [kJ mol^{-1}]
Pt(533)	β_1	$3 \pm 2 \times 10^{11}$	81 ± 5
	β_2	$4 \pm 3 \times 10^{11}$	64 ± 2
Pt(553)	γ_1	$2 \pm 0.4 \times 10^{11}$	65 ± 1
	γ_2	$1.4 \pm 0.9 \times 10^{11}$	53 ± 1
	γ_3	$7 \pm 5 \times 10^{11}$	45 ± 1

Table 3.1 Desorption energies and pre-factors for D_2 desorbing from stepped platinum surfaces.

temperature shifting from 206 K to 196 K. At the largest coverage this peak develops a tail at the low temperature side. The full deconvolution of the TPD from the saturated Pt(553) surface is shown in figure 3.3c. At saturation the ratio γ_3:γ_2:γ_1 is $\sim$ 3:4:4.

Adsorption energies for the different peaks can be obtained using the Polanyi-Wigner equation

$$r_d(\theta) = -\frac{d\theta}{dt} = \nu(\theta)\theta^n e^{\frac{-E_d(\theta)}{RT}} \tag{3.1}$$

where r is the desorption rate, θ the coverage, t the time, $\nu(\theta)$ the pre-exponential factor, n the desorption order, $E_d(\theta)$ the activation energy, R the gas constant, and T the temperature. In the complete analysis method this equation is applied rigorously.[104,105] We performed this analysis for all deconvoluted peaks for various fixed values of θ, obtaining the E_d and ν for each θ. Since the $\ln(r_d)$ vs. $1/T$ plots were relatively noisy, we only kept pairs of E_d and ν with a reasonable pre-factor. The average of the obtained E_d and ν pairs are given in table 3.1. We use these results for qualitative comparison only. It can be seen that β_2 and γ_1 have comparable desorption energies and are thus likely to result from desorption from similar sites.

The Pt(533) surface has been studied previously by Gee and Hayden.[63] In hydrogen desorption from platinum surfaces with (100) steps generally a two peak spectrum is observed.[66] The peaks are ascribed to associative desorption from (111) terraces (β_2) and (100) steps (β_1).[63,66,121] A saturation value of 0.9 ± 0.05 ML has been reported based on TPD results and the pumping speed of the molecular beam chamber;[63] we can neither confirm nor disprove this value here. Desorption of D_2 from Pt(111) peaks at 300 K (shifting to 288 K) with a small shoulder emerging at the highest coverages at 225 K. The shoulder becomes larger when the surface is exposed to D atoms.[122] The similarity between peak temperatures for both the Pt(111) surface and the β_2 peak strongly suggests that the β_2 peak in desorption from Pt(533) is indeed due to desorption from (111) terrace sites.

The TPD spectrum of D_2 desorbing from Pt(553) is significantly different from

that of Pt(533). Most importantly, the spectrum consists of three peaks, not two. Therefore, we can not *a priori* distinguish between γ_1—γ_3 by ascribing one peak to step and another to terrace desorption. It is tempting to treat Pt(553) analogously to Pt(533) and assign the lowest temperature peak to desorption from (111) terraces, as is the case for O_2 desorption. However, when comparing the absolute peak temperatures this assignment appears problematic. The γ_3 peak is not located close to the same temperature as on Pt(111). However, the γ_1 peak is located at this temperature, whereas γ_2 is located at a similar position as the shoulder appearing on Pt(111). The desorption energy corresponding to the γ_1 peak is similar to the desorption energy corresponding to the β_2 peak from Pt(533), which was ascribed to desorption from terrace sites. When the γ_1 and γ_2 peak integrals are summed, a $\gamma_1 + \gamma_2 : \gamma_3$ ratio of 8 : 3 is obtained, which is similar to the $H_{terrace} : H_{step}$ ratio on Pt(533). Therefore, we assign γ_1 and (a part of) γ_2 to recombinative desorption of D atoms from (111) terrace sites. The fact that this happens in two features could be due to different lateral interactions for different D_{ad} coverages. If γ_1 and γ_2 are attributed to desorption from terrace sites, γ_3 would be due to desorption from (110) step sites. This is consistent with qualitative results from Ferrer and Bonzel,[123] who studied hydrogen desorption from both reconstructed Pt(110)–(1×2) as well as from unreconstructed Pt(110)–(1×1). They show that the TPD spectrum of H_2 desorbing from Pt(110) has lower temperature features than Pt(111).[66] Recent calculations show a similar picture: hydrogen adsorption to Pt(110) is energetically more corrugated than to Pt(111) and Pt(110) has more weak binding sites.[71]

To summarize: we attribute peaks labeled γ_1 and γ_2 to desorption from (111) terrace sites on Pt(553), whereas γ_3 is due to a location associated with the presence of (110) step sites. This leads to a terrace : step ratio of roughly 8 : 3, which is similar to the $\beta_2 : \beta_1$ ratio on Pt(533). However, in remarkable contrast to Pt(533), H seems to bind weaker to the step sites on Pt(553) than to the terrace sites. On top of that we note that the different step geometries seem to have a different influence on the desorption of D_2 from terrace sites. In a previous study, where desorption from two $6 \times (111)$ crystals with different step geometries was compared the absence of a three peak structure on the (100) stepped surface was thought to be caused by the less even heating of the thicker Pt(755) crystal.[121] However, the two peak structure for the the (100) step type has now been observed more often[63,74] and the difference in the number of peaks asks for a different explanation. The terraces of Pt(553) exhibit more variation in the binding energy of D_{ad} than the terraces of Pt(533): the former showing two different desorption features vs. only one feature from the latter. Possibly (110) step sites induce different lateral interactions between D ad-atoms on (111) terraces than (100) step sites.

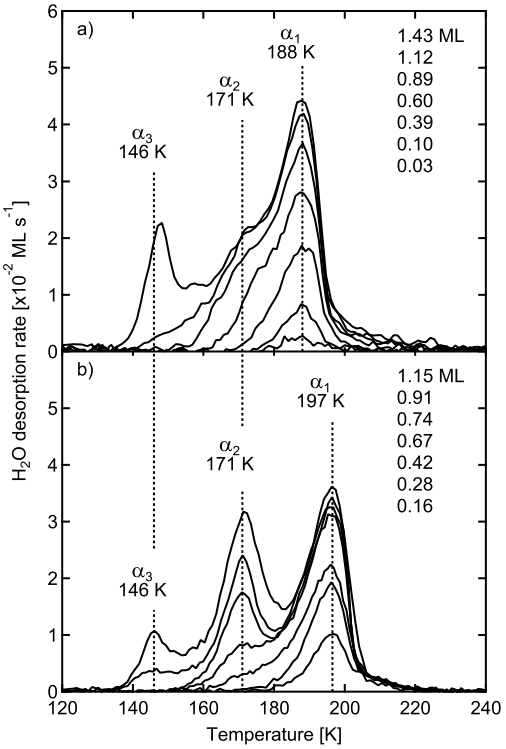

Figure 3.4 TPD spectra of increasing amounts of H_2O desorbing from a) Pt(533) and b) Pt(553).

3.3.3 Water

Figure 3.4a shows traces of varying amounts of water desorbing from the Pt(533) surface. H_2O desorption from the bare Pt(533) surface takes place in three peaks, α_1^{533}, α_2^{533}, and α_3^{533}, with peak temperatures of ~ 188 K, ~ 171 K, and ~ 148 K, respectively. The peak at highest temperature, α_1^{533}, appears at the lowest H_2O coverages. At coverages < 0.25 ML the peak desorption temperature shows a slight increase from 184 K to 188 K with increasing dose. For $\theta_{H_2O} > 0.25$ ML, we observe no shift in desorption temperature up until saturation of the α_1^{533} peak. The second peak, α_2^{533}, is clearly observed prior to saturation of α_1^{533}. The lowest temperature peak, α_3^{533}, is only observed when α_1^{533} and α_2^{533} have saturated. Following Grecea *et al.*,[27] we use the largest combined integral for α_1^{533} and α_2^{533} as a reference for the amount of adsorbed H_2O and refer to this amount as $\theta_{H_2O} = 1$ ML. Dosing larger quantities leads to the appearance of the α_3^{533} peak, which has previously been shown to result from multilayer desorption.[27]

Figure 3.4b shows TPD spectra of various amounts of H_2O desorbing from the

Pt(553) surface. Similar to the Pt(533) surface, we see three peaks in the spectrum, α_1^{553}–α_3^{553}, at, respectively, 197 K, 171 K, and $\sim$ 146 K. At coverages below 0.28 ML we only see the α_1^{553} peak. When the total coverage reaches 0.42 ML, the α_1^{553} peak develops a tail at the low temperature side, which develops into the α_2^{553} peak at higher coverages. The development of the tail takes place before the α_1^{553} peak saturates. The actual peak formation however only happens when the α_1^{553} peak has saturated. Before α_2^{553} saturates a third peak appears at coverages $\geq$ 0.91 ML. Both the α_1^{553} and α_2^{553} peak temperatures do not shift with increasing coverage, suggesting first order desorption kinetics. The α_3^{553} peak shows zero order desorption kinetics starting at 147 K and slowly shifting towards 157 K for a coverage of 4.49 ML (coverages $\geq$ 1.15 ML not shown here).

Our TPD results for desorption of water from the bare Pt(533) surface are very similar to previously published results.[26,27] For example, compared to results of Grecea *et al*. we find accurate agreement regarding the 4 K increase in the α_1^{533} peak desorption temperature for increasing dosages at low H_2O coverages. This increase is likely related to the initiation of molecular chain growth of water molecules along the step edges, as shown in STM studies of imperfect Pt(111) surfaces.[28] We also observe the appearance of the α_2^{533} peak prior to saturation of the α_1^{533} peak. We interpret this observation as proof of limited mobility of H_2O molecules adsorbed onto this surface. A third agreement is the saturation of α_1^{533} and α_2^{533} combined prior to appearance of α_3^{533}. This indicates that the water layer wets the entire surface prior to formation of a water multilayer. The same observation has been made for monolayer growth of ASW on Pt(111) using adsorption and desorption of a noble gas.[120]

In contrast to these similarities, we observe a significant discrepancy in the absolute temperatures reported for the desorption peaks. For α_1^{533}, Grecea *et al*. report 198 K at a TPD rate of 2 K s^{-1} whereas we find 188 K at 1 K s^{-1}. For α_2^{533}, they report 185 K whereas we find 171 K. For the shifting peak temperature of α_3^{533}, they report an initial value of 160 K whereas we find a value of $\sim$ 150 K. Both α_1^{533} and α_2^{533} show first order kinetics, which causes the peak temperature to change with heating rate. We have repeated our experiments with a heating rate of 2 K s^{-1}. In this case we find 192 K for α_1^{533} and 176 K for α_2^{533}. The difference in peak temperature caused by the heating rate is not large enough to explain the discrepancy between the data. Since the off-set seems reasonably constant, we do not expect it to result from impurities or other surface-related origins that would affect mono- and multilayer adsorption differently. Instead, we believe that it is only a matter of accuracy in determining the absolute temperature that causes the difference. Therefore, we also agree that the α_1^{533} peak results from water molecules desorbing from (100) step sites, which provide stronger binding than terrace sites, as was supported by DFT calculations.[27] However, in contrast to the conclusion by Grecea *et al*., we do not consider the higher temperature of α_2^{533} when compared to desorption from the

(111) plane to justify a claim of additional stabilization of water molecules adsorbed onto (111) terraces. The desorption temperature of the α_2^{533} peak in our studies actually agrees very well with a recent desorption study of D/D_2O from Pt(111) by Petrik and Kimmel.[90] Here, desorption from the bare (111) plane is observed at $\sim$ 171 K, which is the same temperature we find for α_2^{533}. Also, our initial value for α_3^{533} corresponds very well to the value reported for multilayer desorption from Pt(111)[21,90] and Pt(533)[26] in several recent TPD studies using low heating rates. We therefore believe that the determination of the absolute temperature by Grecea *et al*. is off-set by $6 - 9$ K, causing an erroneous argument regarding the stabilizing effect of (100) steps on desorption from (111) terraces.

The α_2 desorption peaks are located at 171 K for both surfaces. This agrees very well with a recent desorption study of D/D_2O from Pt(111) by Petrik and Kimmel,[90] who observe desorption from the bare (111) plane at $\sim$ 171 K. This indicates that this peak is due to H_2O desorbing from (111) terrace sites. From our data it is not possible to deduce a desorption order for the α_2^{533} peak, but for the α_2^{553} peak it is clearly first order. This first order desorption is in contrast to H_2O desorbing from Pt(111), where the peak shows zero order desorption kinetics.[22] This has been attributed to the co-existence of a condensed phase and a 2-dimensional water-gas at sub-monolayer coverages.[21] Picolin *et al*. saw a similar effect on a rippled Pt surface. They attributed this to the fact that the smaller (111) terraces on a stepped surface might not allow for the co-existence of these two phases.[124] Our initial temperature values for α_3^{533} and α_3^{553} correspond very well to the value reported for multilayer desorption from Pt(111)[21,90] and Pt(533)[26] in several recent TPD studies using low heating rates. Therefore, we attribute it to multilayer desorption, which is substrate independent.

The α_1 peak contains the most strongly bound water species on both Pt(533) as well as Pt(553). Its position is the only difference between the two: on Pt(533) it is found at 188 K vs. 197 K on Pt(553). Therefore, it is most likely to result from water molecules that are stabilized by the presence of the different step sites. For (100) steps, DFT calculations confirm that H_2O molecules are bound stronger on step than on terrace sites.[27] Morgenstern *et al*.[28] reasoned, based on the Smoluchowski effect and the larger dipole moment of (100) steps, that H_2O molecules were bound stronger to (100) steps than to (110) steps.[125–127] However, we observe the reverse effect: H_2O molecules are bound stronger to (110) steps. We can compare these results to a study by Picolin *et al*.,[124] who observed two extra peaks compared to the Pt(111) surface when the surface was rippled by Ar ion bombardment. The peak positions of their C and D peaks are located at, respectively, 187 and 194 K. This compares quite well to our (100) and (110) step peaks. Our (110) step peak is located at a slightly higher temperature (197 vs. 194 K)). However, Picolin *et al*. observe a lowering of desorption temperature after flashing their sample to 560 K. They attribute this to smoothening of the mounds that were created by the Ar^+

ion bombardment. Our higher desorption temperature for (110) steps compared to their D peak suggests that even before heating the Ar^+ ion bombarded surface has some (100) steps present on the mounds, which influence the desorption temperature from the (110) step sites. In contrast to O_2 and D_2, H_2O binds stronger to (110) steps than to (100) steps. Based on our data we can not exclude a stronger water-metal interaction for the Pt(553) surface, but we are more inclined to use geometrical arguments to explain this difference. The angle between the (111) plane and the (533) plane is 116.6°, whereas it is 125.3° between the (111) and the (553) plane. This gives the Pt(553) surface a more slanting nature than the Pt(533) surface. This could lead to different H_2O adsorption structures for the two surfaces. Adsorbing H_2O molecules form chains on both the upper and lower part of the step.[28,128] One can imagine that it is easier to form hydrogen bonded networks across the more gradual steps of the Pt(553) surface than across the steeper steps of the Pt(533) surface.

On the Pt(533) surface, the α_2^{533} peak appears prior to saturation of α_1^{533}. We have interpreted this as proof of limited mobility of H_2O molecules adsorbed onto this surface. However, the α_2^{553} peak only really develops when α_1^{553} has saturated. This could indicate that H_2O is more mobile on the (110) step edges than on (100) step edges. The more slanting nature of the (110) step might explain this: diffusion across step edges becomes more facile. Another difference between the two surfaces is the dosage at which the multilayer peak starts to appear. On Pt(533), α_1^{533} and α_2^{533} are saturated prior to appearance of α_3^{533}. This is in contrast to the Pt(553) surface, where α_2^{553} has not yet saturated upon the appearance of α_3^{553}. This indicates that while on Pt(533) the water layer wets the entire surface prior to formation of a water multilayer (like on Pt(111)[120]), there are still patches of bare platinum when the multilayer forms on Pt(553). The kinetics of the growth of the second layer of H_2O are different for both surfaces. This could be due to a different structure of the monolayer on the two surfaces, either on the step edges or on the terraces.

Figures 3.5a and b show the deconvolution of the Pt(533) 1.43 ML and Pt(553) 1.15 ML spectra into 3 Gaussians. The top parts of the panels show the integrals of the α_1 and α_2 peaks. The integral of the α_3 peak is not shown, since this is the water multilayer, which can become infinitely large with infinite dosing time, giving no information on the platinum–water interaction. Considering the size of terraces, one may expect a ratio of H_2O bound at step sites versus terrace sites on the order of 1 : 3 or 1 : 4. The ratio of α_1 to α_2 should reflect this. However, on the Pt(533) surface the α_1^{533} peak is considerably larger than the α_2^{533} peak, whereas on the Pt(553) surface the integrals of the two peaks are similar. This indicates that sites which bind water more strongly than the (111) plane are much more abundant on both surfaces than would be expected from geometrical arguments. Considering the results from DFT calculations published for this system,[27] it seems likely that

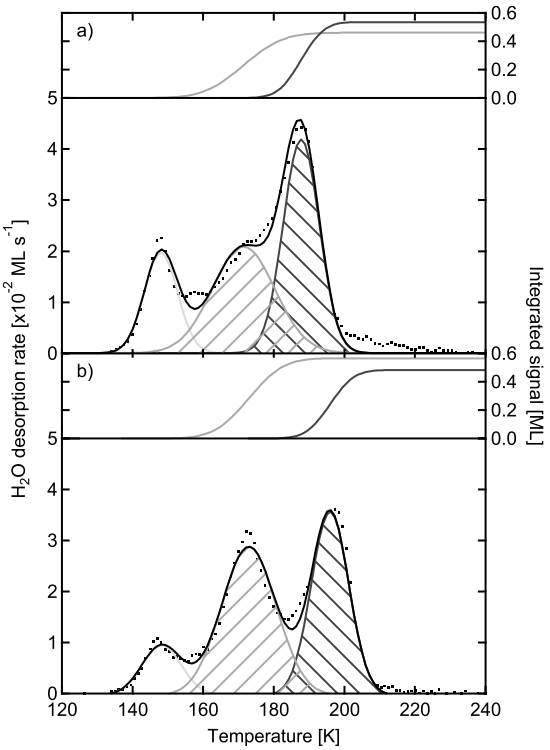

Figure 3.5 Deconvolution of the spectra with the highest H_2O coverage in figure 3.4 into three Gaussians. The top parts of the panels show the integrals of the Gaussian fits to the peaks due to H_2O desorbing from step and terrace sites of a) Pt(533) and b) Pt(553).

molecules desorbing in the α_1^{533} peak originate from both the upper and lower side of the (100) step, and probably also at least in part from the (111) terrace. The DFT study indicates that such locations bind water much more strongly than locations in the middle of the terrace and sites closer to the top side of the step edge. An STM study also indicates water adsorption on both sides of the step edge.[28] Terrace sites further away from step sites seem unaffected. Therefore, we agree with Grecea *et al*. that the (100) steps strengthen binding at (111) terraces on Pt(533) but base our argument on relative quantities rather than on desorption temperatures. Terrace sites further away from step sites are unaffected. H_2O molecules desorbing from the latter sites give rise to the α_2^{533} peak. If we compare the Pt(533) surface to the Pt(553) surface the integrals show a different ratio. For the Pt(533) surface the ratio $\alpha_1 : \alpha_2$ is roughly 5 : 4, whereas it is exactly reversed for the Pt(553) surface, *i.e.* 4 : 5. This shows that even though the effect on the binding energy compared to the

(111) terrace is larger for (110) steps, the amount of H_2O molecules that is affected is smaller than for (100) steps.

3.4 Conclusion

The dependence of molecular desorption on substrate geometry is very complex. Desorption is influenced significantly by the presence of step sites and the geometry of those sites. In general, molecules and atoms are thought to be bound more strongly to step sites than to terrace sites. Our D_2 desorption data from Pt(553) provide an anomalous counterexample to this common belief, since D atoms on this surface appear to be bound stronger by terrace sites. We also show that if an adsorbate binds stronger to step than to terrace sites, it is not possible to say *a priori* which step geometry will have a more pronounced effect. Based on the Smoluchowski effect and the dipole moments of the different step sites, one would expect a stronger binding by (100) step sites than (110) step sites.[125–127] Recombinatively desorbing O atoms indeed show this behavior, but H_2O molecules bind more strongly to the latter step site. This could be due to the unique property of water in forming hydrogen bonds, but it could also be due to other factors. Furthermore, the amount of ad-atoms or molecules that are affected by the presence of steps varies for the different species, as is evident from the various step : terrace ratios of $\sim 1:1.3$ for O_2 (O), $\sim 1:3$ for D_2 (D), and $\sim 1:1$ for H_2O. This indicates that, in contrast to deuterium, more oxygen atoms and water molecules are affected by the presence of steps than would be expected on geometrical arguments alone.

As a final point, we stress the importance of taking into account all step (and terrace) geometries in theoretical and experimental studies. As the accuracy of theoretical calculations increases it is vital to test these theories against new and more accurate experimental data. Nowadays, the better control of sample temperature allows for slower heating rates in TPD and thus for higher resolution and more accurate determination of desorption energies compared to the "older" surface science literature. Moreover, modern computers allow for more facile and better deconvolution of the spectra. We believe that much is still unknown about the interactions of adsorbates with stepped surfaces and research in this field will remain important in understanding structure sensitivity in catalysis.