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

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# 6

## A detailed TPD study of H<sub>2</sub>O and pre-adsorbed O on the stepped Pt(553) surface

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**Abstract** Water molecules desorbing from the bare Pt(553) surface desorb in a three peak structure, associated with, respectively, desorption from step and terrace sites and the water multilayer. Upon pre-covering the step sites with O<sub>ad</sub> we likely observe OH formation on step sites. When terrace sites are also pre-covered with O<sub>ad</sub>, OH<sub>terrace</sub> formation is favored over OH<sub>step</sub> formation, presumably because OH formed at terrace sites is more easily incorporated in a hydrogen bonded network of OH/H<sub>2</sub>O. This is a gradual process: with increasing  $\theta_O$  less OH<sub>step</sub> is formed. Thus, in spite of the fact that OH at step sites has a higher binding energy than OH at terrace sites, the possibility of the formation of OH at terrace sites actually inhibits the formation of OH at step sites, leaving O<sub>step</sub> as the most stable water dissociation product on the step.

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## 6.1 Introduction

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The interaction between water and platinum surfaces has been studied extensively because of its importance in electrochemistry, fuel cell catalysis, heterogeneous catalysis, and corrosion chemistry. Three extensive reviews have appeared that summarize the large body of knowledge on water-surface interactions that has been obtained using a variety of surfaces, co-adsorbates, and employed techniques.<sup>6–8</sup> The interaction between H<sub>2</sub>O, O<sub>2</sub> and platinum is especially interesting with regard to fuel cell catalysis, where OH adsorbed at platinum steps sites is considered to be a possible oxygen donor for the oxidation of, *e.g.*, CO, methanol, and ethanol at the anode. The structure sensitivity of these reactions is normally related to water activation,<sup>133,140</sup> which is supposed to occur preferentially at step sites.

Most studies investigating the platinum-water interaction have used the (111) surface as a model. Although this is the least complex system, ultra high vacuum (UHV) studies already show significant complexity in adsorption and desorption phenomena.<sup>118–120</sup> However, a real catalytic surface contains 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.<sup>13</sup> Although some experiments have focused on the influence of steps and defects that are naturally present on a Pt(111) crystal,<sup>28,29</sup> more insight should result from studies employing a better-defined model, such as a regularly stepped surface.<sup>26,27</sup> In addition such studies could provide more insight into the nature of the step-bonded oxygen species that is active in electrocatalysis.<sup>133,140</sup>

The general consensus is that on Pt(111) 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.<sup>6–8</sup> 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.<sup>19</sup> Temperature programmed desorption (TPD) studies show two peaks. One peak at 171 K is associated with monolayer desorption. This peak shows the characteristics of zero-order desorption kinetics<sup>22</sup> and has been attributed to co-existence of a condensed phase and a 2-dimensional water-gas at sub-monolayer coverages.<sup>21</sup> A second peak, associated with desorption from multilayers, starts at 154 K and increases in temperature with coverage.<sup>23</sup> TPD shows a stabilization of the water monolayer by the presence of step sites.<sup>26,27,124</sup> An additional peak is observed at ~ 188 K for (100) steps or at ~ 197 K for (110) steps, which suggests a stronger interaction of water with the (110) step (chapter 3).

TPD studies show that oxygen can adsorb in three different states on Pt(111):<sup>11,31,33,40,41,51,117</sup> physisorbed O<sub>2</sub> is stable below 45 K,<sup>30</sup> chemisorbed O<sub>2</sub> up to 100–250 K,<sup>11</sup> and atomic oxygen up to 575–900 K. Oxygen dissociation is activated and atomic oxygen formation occurs via a precursor state of molecu-

larly adsorbed oxygen.<sup>10,31</sup> The maximum  $O_{ad}$  coverage that can be reached via background dosing is 0.25 ML. Low energy electron diffraction (LEED)<sup>11,32–36</sup> and scanning tunneling microscope (STM)<sup>37</sup> pictures show a  $(2 \times 2)$  pattern. Oxygen atoms bind preferentially in the fcc hollow sites.<sup>38,39</sup> On stepped surfaces a similar  $(2 \times 2)$  LEED-pattern is observed for  $O_{ad}$  as on Pt(111).<sup>9,40</sup> Dissociation takes place at 200 K<sup>45</sup> on the (111) terrace, but occurs predominantly on step sites<sup>10,46–48</sup> between 150 and 230 K.<sup>45,49</sup> Oxygen atoms adsorb preferentially on step sites.<sup>37,48</sup> They are more strongly bound to (100) than (110) step sites.<sup>44</sup> A combined STM and density functional theory (DFT) study<sup>37</sup> shows that for (100) steps a twofold edge bridging site is favored, whereas for (111) steps the fcc hollow site behind the step edge is favored. TPD spectra on Pt(533),<sup>10,45,46,50</sup> other surfaces with (100) steps,<sup>49,51,52</sup> and surfaces with (111) steps<sup>9,32,40,53</sup> all show a three peak structure in the molecular oxygen regime and a two peak structure in the atomic oxygen regime.

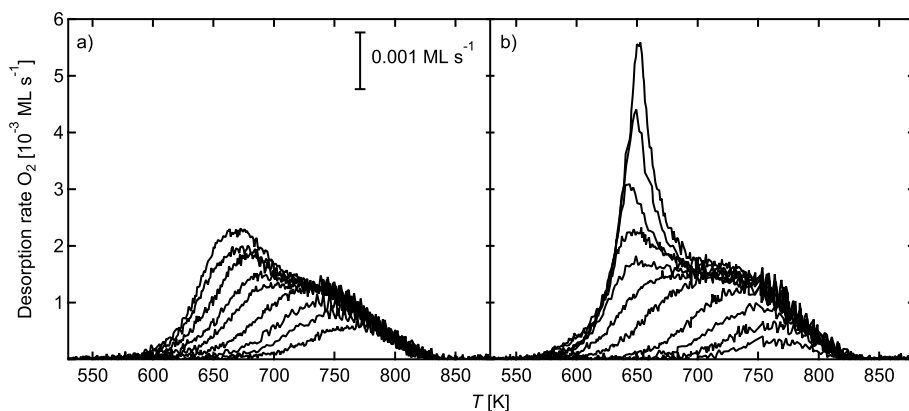
The co-adsorption of  $H_2O$  and  $O_2$  on Pt(111) is known to produce  $OH_{ad}$  for  $150 \leq T \leq 185$  K.<sup>16,75,76</sup> When  $^{18}O_2$  and  $H_2^{16}O$  are co-adsorbed at sub-monolayer coverages and subsequently annealed, the ratio  $^{18}O : ^{16}O$  desorbing in  $H_2O$  is 1 : 2, independent of the initial  $H_2^{16}O$  coverage. Surface OH groups do not readily exchange H with unreacted  $O_{ad}$ .<sup>77</sup>  $OH_{ad}$  is incorporated in a hydrogen bonded network with  $H_2O_{ad}$ <sup>15,79</sup> in a reaction with the following stoichiometry:



All  $O_{ad}$  participates in the OH formation.<sup>16</sup>  $H_2O$  is needed to stabilize the formed OH species.<sup>16,80</sup> All H-groups participate in the hydrogen bonded network and OH is always bonded to the platinum substrate via the oxygen atom. All hydrogen bonds lie parallel to the surface.<sup>76,81</sup> One third of the shared protons is delocalized between two O atoms, making them neither clearly covalently bound nor hydrogen bonded to the oxygen atoms.<sup>82</sup> When  $H_2O$  is removed, the OH groups react to form  $H_2O$  and  $O_{ad}$ .

$H_2O$  adsorbs intact on the reconstructed Pt(110)- $(1 \times 2)$  surface.<sup>86</sup> Interestingly, on this surface  $OH_{ad}$  formed via the co-adsorption of O and  $H_2O$  is not incorporated in a hydrogen bonded network and  $OH_{ad}$  remains stable after water desorption up to  $\sim 205$  K.<sup>87</sup>

We have discussed the main differences between the co-adsorption of  $O_{ad}$  and  $H_2O$  at the Pt(553) surface and the Pt(533) surface in chapter 4. Here, we provide a more in depth study on the influence of the (110) step orientation on oxygen and water (co-)adsorption. Therefore, we (co-)adsorb  $O_{ad}$  and  $H_2O$  with various  $O_{ad}$  and  $H_2O$  coverages on the stepped Pt(553) surface, which consists of 4 atom-wide (111) terraces and a (110) step site. The sample is studied under ultra high vacuum (UHV) conditions using TPD and LEED in combination with isotope exchange.



**Figure 6.1** a) TPD spectra of O<sub>2</sub> desorbing from Pt(553) for varying O<sub>ad</sub> coverages. b) The same spectra, but now without annealing the surface to 1200 K for 3 minutes in between experiments.

## 6.2 Experimental

All experiments were performed in Lion fish. Experimental procedures can be found in chapter 2.1.

## 6.3 Results and discussion

### 6.3.1 O<sub>2</sub> adsorption/desorption

We have discussed the desorption characteristics of the single species (O<sub>2</sub> and H<sub>2</sub>O) in chapter 3 and will only discuss them briefly here. Figure 6.1a shows TPD spectra of various amounts of O<sub>ad</sub> desorbing recombinatively from the Pt(553) surface. At the lowest coverage we observe a single peak at 765 K. With increasing coverage this peak shifts to 736 K, indicating second order desorption kinetics. We attributed this peak to recombinative desorption of O<sub>ad</sub> from step sites. Above 0.11 ML a shoulder appears at 688 K, which also shifts to lower temperature with increasing coverage, indicating second order desorption kinetics, saturating at 663 K for 0.25 ML. We ascribe this peak to desorption from (111) terrace sites. The ratio of oxygen desorbing from step to terrace sites is 0.11 : 0.14 ML. We observed similar behavior on the Pt(533) surface, but the peak associated to desorption from step sites is located  $\sim 36$  K higher on this surface, indicating that oxygen adatoms bind less strongly to (110) steps than to (100) steps as was concluded previously from microcalorimetry.<sup>44</sup>

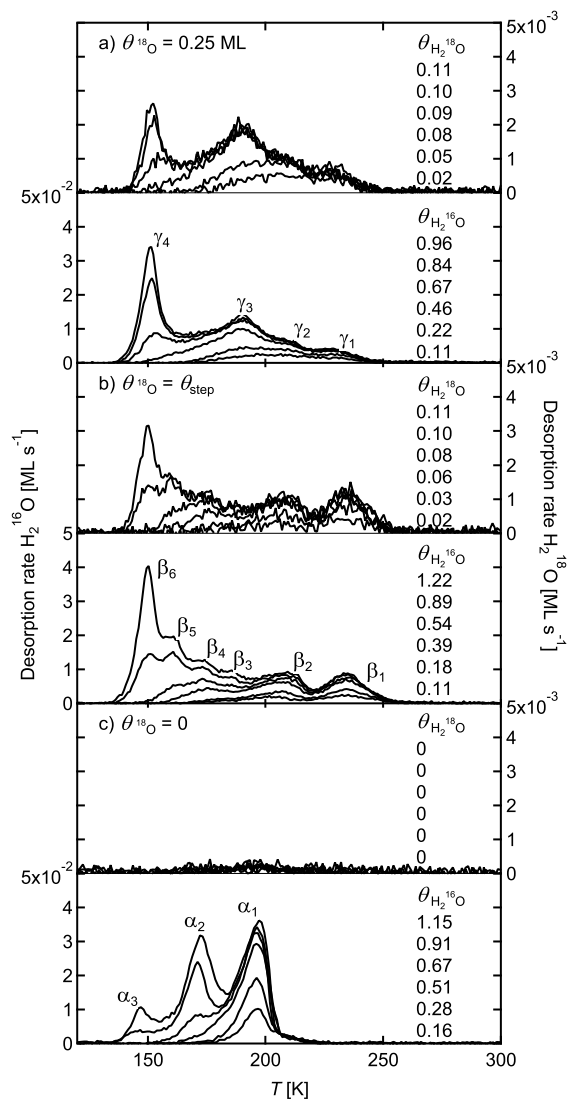
For the isotope exchange experiments we used <sup>18</sup>O<sub>2</sub> instead of <sup>16</sup>O<sub>2</sub>. When dos-

ing  $^{18}\text{O}_2$ , the contamination level of  $^{16}\text{O}$  was maximally 6%. The isotope exchange data are uncorrected for this effect. Figure 6.1b will be discussed in section 6.3.4.

### 6.3.2 $\text{H}_2\text{O}$ desorption from the bare surface

Figure 6.2a shows TPD spectra of  $\text{H}_2^{16}\text{O}$  (lower panel, plotted vs. left axis) and  $\text{H}_2^{18}\text{O}$  (upper panel, plotted vs. right axis) from a Pt(553) surface that has been maximally pre-covered with  $^{18}\text{O}$ . Figure 6.2b shows similar data, but for a surface where only the step sites have been pre-covered with  $^{18}\text{O}$ . Figure 6.2c shows similar data from the bare surface. First, we shall discuss the data from the bare surface. The lower panel (plotted vs. left axis) of figure 6.2c shows TPD spectra of various amounts of  $\text{H}_2^{16}\text{O}$  desorbing from the Pt(553) surface. We see three peaks in the spectrum,  $\alpha_1$ – $\alpha_3$ , at, respectively, 197 K, 171 K, and  $\sim 146$  K. The upper panel of figure 6.2c shows the  $\text{H}_2^{18}\text{O}$  spectra ( $m/e = 20$ ). We observe no significant signals at this  $m/e$  ratio, indicating that our mass to charge ratios between 18 and 20 have a sufficient baseline separation. At coverages below 0.28 ML we observe only the  $\alpha_1$  peak. When the total coverage reaches 0.42 ML, the  $\alpha_1$  peak develops a tail at the low temperature side, which develops into the  $\alpha_2$  peak at higher coverages. The development of the tail takes place before the  $\alpha_1$  peak saturates. The actual peak formation, however, only happens when the  $\alpha_1$  peak has saturated. Before  $\alpha_2$  saturates a third peak appears at coverages  $\gtrsim 0.91$  ML. Both the  $\alpha_1$  and  $\alpha_2$  peak temperatures do not shift with increasing coverage, suggesting first-order desorption kinetics. The  $\alpha_3$  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). The ratio  $\alpha_1 : \alpha_2$  is roughly 4 : 5. We ascribe the  $\alpha_1$  peak to desorption from step sites,  $\alpha_2$  to terrace sites, and  $\alpha_3$  to multilayer water. We define the combined integrals of  $\alpha_1$  and  $\alpha_2$  as a full monolayer water.

The ratio  $\alpha_1 : \alpha_2$  is much larger than would be expected on geometric arguments alone. STM shows that water adsorbs on both sides of the step edge.<sup>28</sup> Therefore, it seems likely that molecules desorbing in the  $\alpha_1$  peak originate from both the upper and lower side of the (110) step, and probably also at least in part from the (111) terrace. Terrace sites further away from step sites seem unaffected. A DFT study on (100) steps indicates that steps bind water much more strongly than locations in the middle of the terrace.<sup>27</sup> The  $\alpha_2$  peak has not yet saturated before the appearance of  $\alpha_3$ . This indicates that there are still patches of bare platinum when the multilayer starts to form on Pt(553).



**Figure 6.2** TPD spectra of H<sub>2</sub><sup>16</sup>O (left axis) and H<sub>2</sub><sup>18</sup>O (right axis) dosed on a) Pt(553) with  $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$ , b)  $\theta_{^{18}\text{O}} = \theta_{\text{step}}$ , and c)  $\theta_{^{18}\text{O}} = 0$ .

### 6.3.3 Co-adsorption of $^{18}\text{O}_{\text{ad}}$ and $\text{H}_2^{16}\text{O}$

$$\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$$

Figure 6.2b shows TPD spectra of various amounts of  $\text{H}_2\text{O}$  desorbing from a Pt(553) surface on which the step sites have been pre-covered with  $^{18}\text{O}_{\text{ad}}$  prior to  $\text{H}_2^{16}\text{O}$  adsorption. First we focus on the  $\text{H}_2^{16}\text{O}$  signal (lower half, plotted vs. left axis). At the lowest coverages we observe a two peak structure,  $\beta_1$  and  $\beta_2$ , shifting from 235 to 233 K and from 204 to 209 K with increasing coverage, respectively. These two peaks grow in simultaneously and have a similar integral. Already at the lowest coverages a small shoulder is visible at  $\sim 185$  K. Above 0.22 ML (before  $\beta_1$  and  $\beta_2$  saturate), this shoulder develops into a two peak structure,  $\beta_3$  and  $\beta_4$ , with peak temperatures of, respectively,  $\sim 185$  K and  $\sim 173$  K. At 0.62 ML another shoulder at the low temperature side starts to develop, eventually resulting in a peak,  $\beta_5$ , at 161 K. At coverages  $\gtrsim 0.86$  ML we reach the maximum number of six peaks with  $\beta_6$  starting at 150 K and shifting to higher temperatures with increasing coverage (higher coverages not shown here). All peaks start to emerge before all higher temperature peaks have saturated. The  $\beta_1$ – $\beta_3$  peaks saturate above  $\sim 1.15$  ML, whereas the other peaks keep increasing in intensity above this coverage. The continuing increase in  $\beta_4$  and  $\beta_5$  is likely to be an optical illusion caused by the increase in  $\beta_6$ , which increases the baseline for the  $\beta_4$  and  $\beta_5$  peaks.

The number of observed peaks makes it difficult to assign each peak separately based on TPD alone. Nonetheless, we will attempt to give a tentative assignment to the peaks. The  $\beta_6$  peak is last to appear and its leading edge is located at the same position as the  $\alpha_3$  peak, which we attributed to desorption from the multilayer on the bare Pt(553) surface. We attribute the  $\beta_6$  peak to multilayer desorption.

On Pt(111), the co-adsorption of O and  $\text{H}_2\text{O}$  is known to cause OH formation. The resulting hydrogen bonded OH/ $\text{H}_2\text{O}$  network has various stable structures, depending the O :  $\text{H}_2\text{O}$  ratio.<sup>14</sup> During a TPD experiment,  $\text{H}_2\text{O}$  molecules are slowly titrated off the surface. This results in a continuously changing O :  $\text{H}_2\text{O}$  ratio. It is likely that, similar to the Pt(111) surface, different ratios have different structures, some of which are more stable than others. Therefore, it seems likely that the  $\beta_1$ – $\beta_5$  peaks observed for  $\text{O}_{\text{step}}/\text{Pt}(553)$  are due to  $\text{H}_2\text{O}$  desorption and re-combinative desorption of  $2\text{OH}_{\text{ad}}$  as  $\text{H}_2\text{O}$  from different stable  $\text{H}_2\text{O}/\text{OH}$  hydrogen bonded networks.

The highest temperature peaks,  $\beta_1$  and  $\beta_2$ , appear simultaneously, indicating that the species can not exist independently. When we sum the  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$  TPD spectra, the combined integral of these two peaks is roughly 0.4 ML, which is slightly less than the integral of the  $\alpha_1$  peak. However, the total integral of the  $\text{H}_2\text{O}$  TPD spectra before the multilayer peak appears has decreased as well, compared to the bare surface, since  $\text{H}_2\text{O}$  and  $\text{O}_{\text{ad}}$  compete for adsorption sites on the steps. Analogous to the bare surface, it is likely that these peaks are the result of desorp-

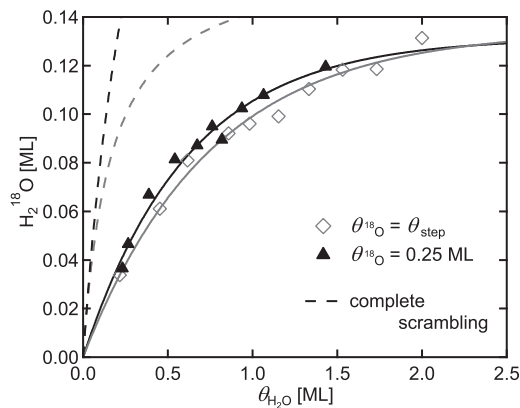
tion from step sites. Both the  $\beta_1$  and  $\beta_2$  peak are strongly stabilized compared to desorption from step sites from the bare surface, *i.e.* they appear at higher desorption temperatures. Similar to oxygen pre-covered Pt(111), this could be due to OH formation. On reconstructed Pt(110)–(1 × 2) OH<sub>ad</sub> is stable up to ~ 205 K without co-adsorbed H<sub>2</sub>O,<sup>87</sup> a similar temperature as the location of the  $\beta_2$  peak.

The  $\beta_3$ – $\beta_5$  peaks have a desorption temperature that is more reminiscent of the terrace desorption peak from the bare surface. These peaks would then be the result of desorption from terrace sites, suggesting that the  $\alpha_2$  peak splits into a three peak structure in the presence of O<sub>ad</sub> on the steps. In spite of the fact that no O, and therefore no OH, is present on terrace sites, the presence of O adatoms on step sites influences H<sub>2</sub>O desorption from terrace sites significantly. The simultaneous appearance of all peaks could be a sign of the limited mobility of H<sub>2</sub>O molecules on this surface.

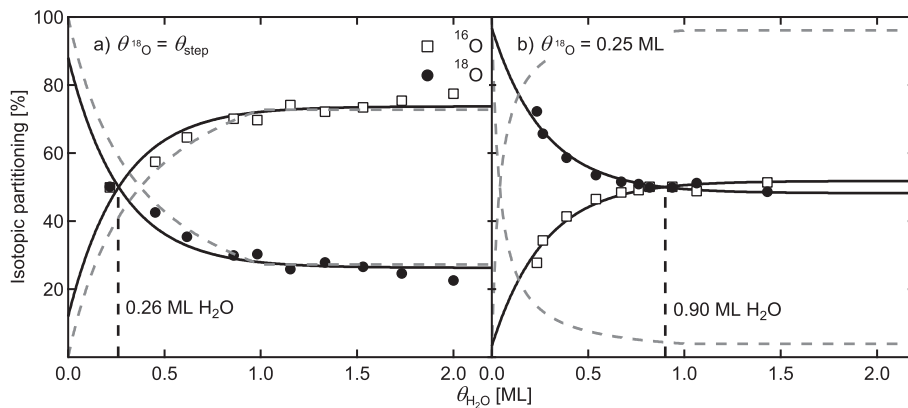
Next, we focus on the H<sub>2</sub><sup>18</sup>O signal (upper half of frame in figure 6.2b, plotted vs. right axis). We observe the same six peak structure as in the H<sub>2</sub><sup>16</sup>O signal. All spectra seem to image their H<sub>2</sub><sup>16</sup>O counterparts. Only  $\beta_1$  is relatively larger than  $\beta_2$  in the two spectra with the lowest amount of water, in contrast to the corresponding H<sub>2</sub><sup>16</sup>O spectra. This could indicate that most OH-recombination via the reverse of reaction (6.1) happens in  $\beta_1$  and that  $\beta_2$  actually contains the H<sub>2</sub>O molecules needed to stabilize the formed OH<sub>ad</sub>. We realize this last explanation is highly speculative, and for instance DFT, Monte Carlo simulations and/or spectroscopy should provide more insight in the nature of the various peaks.

On Pt(553) we observed that the multilayer peak was relatively smaller in the H<sub>2</sub><sup>18</sup>O signal compared to the H<sub>2</sub><sup>16</sup>O signal for  $\theta_{18O} \approx \theta_{step}$  (see chapters 4 and 5). We attributed this to poor coupling between the first and second adsorbed layer. We observe this effect to a much smaller extent on the Pt(553) surface. This indicates that the interaction between the first and second layer is strongly dependent on the structure of the substrate. Apparently the Pt(553) surface facilitates H<sub>2</sub>O exchange between the first and second water layer, whereas Pt(533) is more resilient to exchange.

The gray data in figure 6.3 show the amount of desorbing H<sub>2</sub><sup>18</sup>O, *i.e.* water molecules that have exchanged their oxygen atoms with the pre-adsorbed O<sub>ad</sub>, as a function of the total H<sub>2</sub>O coverage for a Pt(553) surface where only the step sites have been pre-covered with <sup>18</sup>O adatoms. The dashed line shows how much H<sub>2</sub><sup>18</sup>O would desorb if complete isotopic scrambling were to occur, assuming the same 0.25 ML as a maximum coverage for O<sub>ad</sub> on Pt(553) as Gee and Hayden did for Pt(533),<sup>10</sup> and a Pt : H<sub>2</sub>O ratio of 3 : 2 for 1 ML H<sub>2</sub>O. We observe an increase in the amount of desorbing H<sub>2</sub><sup>18</sup>O with increasing  $\theta_{H_2O}$ . This may be expected, since there is simply more H<sub>2</sub>O present to participate in the exchange. The amount of exchange is much smaller than the complete scrambling scenario. We will discuss this data further in the next subsection.



**Figure 6.3** Amount of desorbing  $\text{H}_2^{18}\text{O}$  vs. the amount of adsorbed  $\text{H}_2^{16}\text{O}$  for Pt(553) with  $\theta_{^{18}\text{O}} = \theta_{\text{step}}$  (■) and  $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$  (▲). The dashed lines show the calculated amounts of formed  $\text{H}_2^{18}\text{O}$  for complete isotopic scrambling. The lines fitted through the data are only to guide the eye.



**Figure 6.4** Isotopic partitioning in oxygen TPD spectra for varying amounts of  $\text{H}_2^{16}\text{O}$  dosed on Pt(553) pre-covered with  $\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$  a) or  $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$  b). The dashed lines show the calculated isotopic partitioning assuming complete isotopic scrambling.

Figure 6.4a shows the isotopic partitioning of  $^{16}\text{O}$  and  $^{18}\text{O}$  desorbing as  $\text{O}_2$  for  $\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$ , based on the simultaneously measured  $m/e = 32, 34$ , and  $36$  spectra. We also show the calculated isotopic partitioning if complete isotopic scrambling were to occur. At the lowest  $\text{H}_2\text{O}$  coverages measured ( $0.22 \text{ ML}$ ), we observe that half of all pre-adsorbed  $^{18}\text{O}_{\text{ad}}$  has exchanged with an  $^{16}\text{O}$  from  $\text{H}_2^{16}\text{O}$ . The exchange levels off at coverages  $> 1 \text{ ML}$  at  $\sim 74\%$  of all original  $^{18}\text{O}$  having exchanged with  $^{16}\text{O}$  from water. Apparently, not all water molecules or O atoms have participated in the reversible formation of an  $\text{OH}/\text{H}_2\text{O}$  network. Water adsorbed on terrace sites probably does not interact with the oxygen atoms on step sites and is therefore not likely to participate in the oxygen exchange reaction. STM shows that at low  $\text{H}_2\text{O}$  coverages most molecules are located at step sites.<sup>28</sup> Therefore, below  $0.25 \text{ ML}$  most water is likely located at the steps. An isotopic partitioning of more than  $50\%$   $^{16}\text{O}$  could be caused by more than one  $\text{H}_2\text{O}$  molecule interacting with one  $\text{O}_{\text{ad}}$ . It could also be caused by reaction (6.1) occurring reversibly at low temperatures, moving  $^{18}\text{O}_{\text{ad}}$  as  $\text{H}_2^{18}\text{O}$  to terrace sites or to the multilayer, effectively leaching the  $^{18}\text{O}_{\text{ad}}$ . If the first explanation is true, one  $\text{O}_{\text{ad}}$  atom on step sites interacts with up to three  $\text{H}_2\text{O}$  molecules. This is less than on  $\text{Pt}(111)$ , where up to four  $\text{H}_2\text{O}$  molecules can interact with one O adatom.<sup>14</sup> The difference could be due to the broken symmetry of the (553) surface, introduced by the presence of step sites.

### $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$

Figure 6.2a shows TPD spectra of various amounts of  $\text{H}_2\text{O}$  desorbing from a  $\text{Pt}(553)$  surface which has been maximally pre-covered with  $^{18}\text{O}_{\text{ad}}$  ( $0.25 \text{ ML}$ ) prior to  $\text{H}_2^{16}\text{O}$  adsorption. Again, we focus on the  $\text{H}_2^{16}\text{O}$  spectra first (lower half, plotted vs. left axis). From the lowest coverages onwards we observe a small peak,  $\gamma_1$ , starting at  $232 \text{ K}$  and finally stabilizing at  $228 \text{ K}$  for  $\theta_{\text{H}_2\text{O}} \gtrsim 0.39 \text{ ML}$ . Simultaneous to the appearance of this peak we observe the appearance of a broad feature, centered at  $204 \text{ K}$ . At coverages  $\gtrsim 0.23 \text{ ML}$  this feature splits up into two peaks,  $\gamma_2$  and  $\gamma_3$ , located at  $208$  and  $191 \text{ K}$ . For coverages  $\gtrsim 0.39 \text{ ML}$ , the  $\gamma_3$  peak is the most prominent feature in the spectrum in the monolayer desorption regime. When  $\theta_{\text{H}_2\text{O}}$  becomes larger than  $0.67 \text{ ML}$ , a peak  $\gamma_4$  starts to appear at  $152 \text{ K}$ . Thus, at the largest  $\text{H}_2\text{O}$  coverages we observe a four peak structure. The  $\gamma_1$ – $\gamma_3$  peaks grow in simultaneously, but the  $\gamma_1$  peak saturates at  $\sim 0.33 \text{ ML}$ . The  $\gamma_2$  and  $\gamma_3$  peaks have almost saturated when  $\gamma_4$  starts to appear.

The  $\gamma_4$  peak appears at the same temperature as the  $\alpha_3$  and  $\beta_6$  peaks, which we attributed to desorption from the second water layer. We associate the  $\gamma_4$  peak with the same process. The  $\gamma_1$  and  $\gamma_2$  peaks appear at similar temperatures as, respectively, the  $\beta_1$  and  $\beta_2$  peak. Therefore, it is likely that the  $\gamma_1$  and  $\gamma_2$  peaks originate from recombinative desorption of  $\text{OH}$  and  $\text{H}_2\text{O}$  desorption on step sites. The peak temperature of  $\gamma_1$ , however, has decreased by  $\sim 4 \text{ K}$  compared to  $\beta_1$ .  $\text{OH}$  on step sites is bound less strong on the  $\text{Pt}(553)$  surface when the terrace sites are covered

with  $O_{ad}$  compared to when it has bare (111) terraces. Only one peak appears to be resulting from desorption from terrace sites:  $\gamma_3$ . This shows that the energy differences between various structures of the OH/H<sub>2</sub>O hydrogen bonded network have increased compared to the  $\theta_{18O} \approx \theta_{step}$  case, favoring one structure. TPD spectra of H<sub>2</sub>O molecules desorbing from a Pt(111) surface with an O pre-coverage of 0.25 show a desorption peak from terrace sites around 192 K,<sup>14</sup> which is the same temperature as the  $\gamma_3$  peak. We attribute the  $\gamma_3$  peak to the formation of a hydrogen bonded OH/H<sub>2</sub>O network on the (111) terraces, with a similar stability as the one formed on the Pt(111) surface. The  $\gamma_1$ – $\gamma_3$  peaks start to appear simultaneously. This could indicate that the electronic corrugation of the surface for H<sub>2</sub>O adsorption flattens when O adatoms are adsorbed on terrace sites, reducing the driving force for H<sub>2</sub>O molecules to find an adsorption site where they are bound more strongly, once they are incorporated in the OH/H<sub>2</sub>O hydrogen bonded network. Therefore, diffusion to the steps is more difficult.

Next, we turn to the H<sub>2</sub><sup>18</sup>O signals (upper half of panel, plotted vs. right axis). At the highest H<sub>2</sub>O coverages, we observe a similar four peak structure as in the H<sub>2</sub><sup>16</sup>O spectra. The main difference is that all spectra are a factor of ten less intense compared to the H<sub>2</sub><sup>16</sup>O signals. Another difference is that the  $\gamma_1$  peak saturates earlier, at 0.14 ML, compared to 0.33 ML for the H<sub>2</sub><sup>16</sup>O spectra. The  $\gamma_2$  and  $\gamma_3$  peaks appear to saturate earlier as well. This indicates that after 0.39 ML dosing more H<sub>2</sub>O does not lead to more water molecules interacting with the pre-adsorbed <sup>18</sup>O at step sites. The ratio H<sub>2</sub><sup>18</sup>O : H<sub>2</sub><sup>16</sup>O for the  $\gamma_4$  peak compared to the ratio for the total spectrum has decreased relative to the  $\theta_{18O} \approx \theta_{step}$  case. This shows that the OH/H<sub>2</sub>O layers have a different coupling to the second layer for different  $\theta_{18O}$ .

The black data in figure 6.3 show the amount of desorbing H<sub>2</sub><sup>18</sup>O, *i.e.* the amount of water molecules that have exchanged their oxygen atoms with the pre-adsorbed  $O_{ad}$ , for a Pt(553) surface where the full surface has been covered with oxygen adatoms as a function of the total amount of H<sub>2</sub>O. Similar to the  $\theta_{18O} \approx \theta_{step}$  case, we observe an increase in the amount of desorbing H<sub>2</sub><sup>18</sup>O with increasing  $\theta_{H_2O}$ . The data obtained for the maximum obtained oxygen pre-coverage are remarkably similar to the data obtained when only the step sites were pre-covered with <sup>18</sup>O<sub>ad</sub>. This indicates that an equal amount of H<sub>2</sub>O molecules participates in the interaction with  $O_{ad}$  as in the  $\theta_{18O} \approx \theta_{step}$  case. However, from figure 6.1 we know that there are over twice as many O adatoms present on the surface for H<sub>2</sub><sup>16</sup>O molecules to interact with. An explanation could be that the extra O, *i.e.*  $O_{ad}$  on terrace sites, does not interact with post-dosed water. However, this would not agree with the observation of the  $\gamma_3$  peak in figure 6.2a, which we attributed to recombinative desorption of OH from terrace sites. It also does not agree with the H<sub>2</sub><sup>18</sup>O TPD spectra. They show H<sub>2</sub><sup>18</sup>O desorption from the lowest temperature peak onwards, indicating that the reaction (1.4) occurs reversibly below  $\sim 145$  K. Furthermore, we observed a decrease in the integral of  $\gamma_1$  and  $\gamma_2$  compared to  $\beta_1$  and  $\beta_2$ . Therefore, we think

that on the step sites fewer O adatoms participate in OH formation when the terrace sites are also covered with O adatoms. On terrace sites it is probably easier to incorporate the formed OH in the preferred hydrogen bonded network. Therefore, OH formation on terrace sites competes with OH formation on step sites, even though by itself OH on step sites is more strongly bound. A possible explanation would be that H<sub>2</sub>O molecules participating in the OH/H<sub>2</sub>O network on the terraces are less capable of also interacting with oxygen adatoms on step sites, leading to a decrease in the amount of formed OH on those sites. In any case, it seems that O adatoms are left unreacted at step sites.

Figure 6.4b shows the isotopic partitioning of <sup>16</sup>O and <sup>18</sup>O desorbing as O<sub>2</sub> of  $\theta_{18\text{O}} = 0.25$  ML. At the lowest H<sub>2</sub>O coverages measured, we observe a steep rise in the amount of exchange with the oxygen atom from H<sub>2</sub><sup>16</sup>O. The exchange levels off at coverages > 0.90 ML, where about half of all pre-adsorbed O<sub>ad</sub> has participated in the oxygen exchange reaction. This indicates that one oxygen adatom interacts with up to two H<sub>2</sub>O molecules. This is similar to what we observed on the Pt(533) surface.

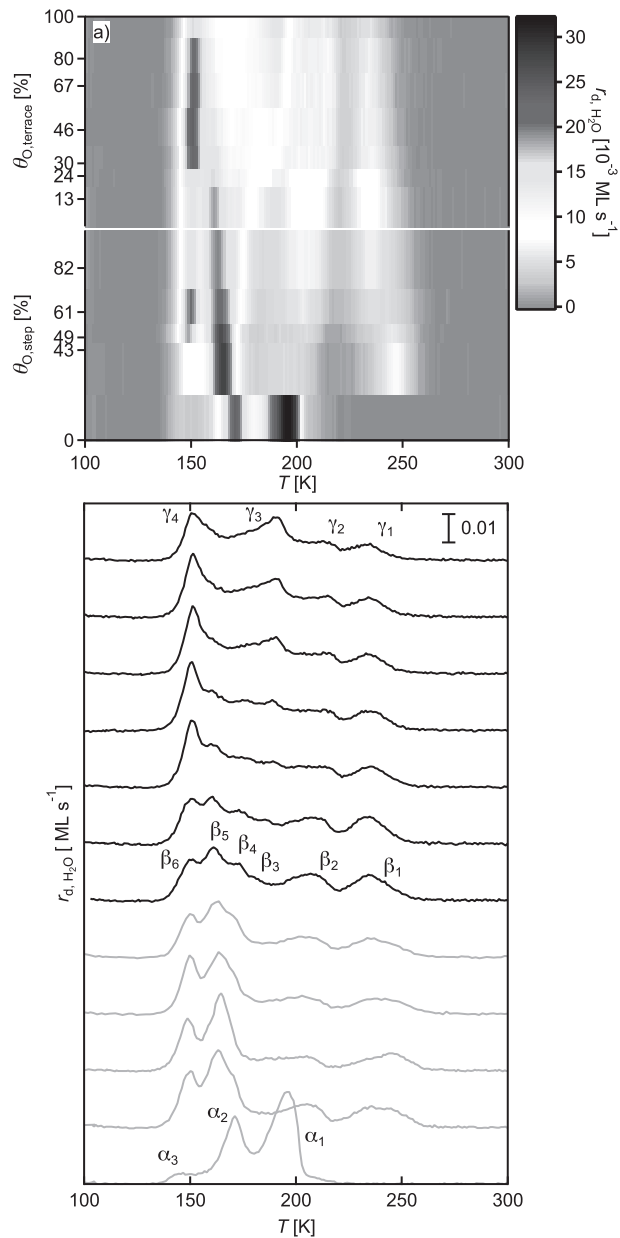
### Varying <sup>18</sup>O pre-coverages

Figure 6.5 shows TPD spectra of ~ 1 ML H<sub>2</sub>O desorbing from a Pt(553) surface that has been pre-covered with varying amounts of O<sub>ad</sub>. The lowest spectrum corresponds to H<sub>2</sub>O desorbing from the bare Pt(553) surface. We observe the three peak structure,  $\alpha_1$ – $\alpha_3$ , with peaks at 197, 171, and 145 K, corresponding to, respectively, H<sub>2</sub>O desorbing from step (stabilized) sites, terrace sites, and other H<sub>2</sub>O molecules. When we start to pre-cover the step sites with O<sub>ad</sub>, the  $\alpha_1$  peak disappears and the  $\beta_1$  and  $\beta_2$  peaks appear instead, both at higher surface temperatures than the original  $\alpha_1$  peak. The  $\alpha_2$  peak at 171 K is reduced to a shoulder to the newly formed  $\beta_5$  peak at 163 K. The  $\beta_1$  peak shifts to lower temperatures and has a decreasing integral with increasing O<sub>ad</sub> pre-coverage, until it ends up being the  $\gamma_1$  peak. The desorption temperature of the  $\beta_2$  peak, increases slightly with increasing O<sub>ad</sub> coverage. However, it is difficult to say whether  $\beta_2$  is actually shifting or if it is an artifact due to the shift of  $\beta_1$ . We attributed mainly  $\beta_1$  to OH at step sites. The decrease in  $\beta_1$  desorption temperature shows that filling more (than half) of the step sites with O destabilizes OH formation on these step sites. The  $\gamma_3$  peak, around 191 K becomes visible when ~ 25% of the terraces sites is pre-covered with O<sub>ad</sub>. The equilibrium of

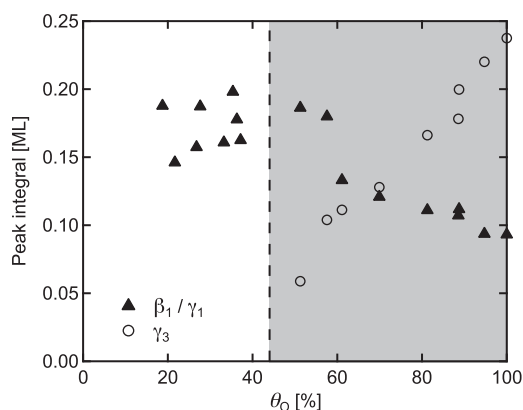


shifts to the left with increasing  $\theta_{\text{O, terrace}}$ . Instead OH is formed on terraces.

The change in  $\alpha_2$  shows that the presence of only a little bit of oxygen (at step sites), influences H<sub>2</sub>O molecules at terrace sites drastically. Around the coverage where all step sites are pre-covered with O<sub>ad</sub> the profile of the TPD is the most



**Figure 6.5** TPD spectra of  $\sim 1$  ML  $\text{H}_2\text{O}$  desorbing from Pt(553) with varying  $\text{O}_{\text{ad}}$  pre-coverages of the steps sites (bottom half) and the full step and part of the terrace sites (top half).

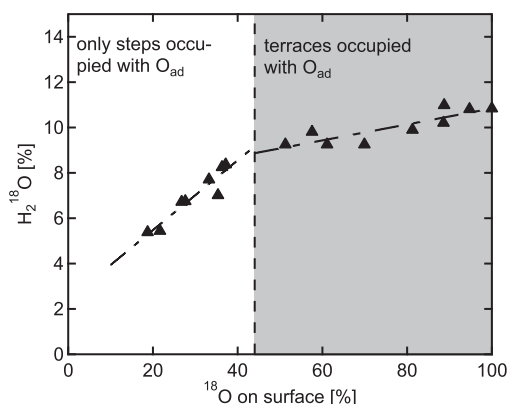


**Figure 6.6** Peak integral of  $\beta_1/\gamma_1$  and  $\gamma_3$  as a function of oxygen pre-coverage

flat, with a high number of relatively small peaks. This could indicate that many stable structures which vary only slightly in adsorption energy exist around this temperature.

When terrace sites become filled with  $O_{ad}$   $\gamma_3$  increases in intensity. In contrast to what is observed on Pt(111),<sup>14,90</sup> the peak temperature of  $\gamma_3$  does not shift with  $O_{ad}$  pre-coverage. The  $\gamma_3$  peak is located at a similar temperature as the peak associated with recombinative desorption of OH from Pt(111) that has been pre-covered with 0.25 ML  $O_{ad}$ . The increase in  $\gamma_3$  indicates that more H<sub>2</sub>O is incorporated in the OH/H<sub>2</sub>O hydrogen bonded network at the (111) terraces at the expense of OH formation on step sites, as we already argued in the previous subsection. To substantiate this statement, we deconvolute the TPD spectra by fitting a total of six Gaussians to all TPD spectra. Gaussians do not describe the peak shape of the data perfectly, but give a reasonable approximation. Moreover, the number of overlapping peaks can make deconvolution of the data difficult, but we find that by keeping some peaks relatively constant, a reasonable fit can be obtained and peak integrals can be quantified. However, we shall only use them for comparison to spectra that have been fit using similar parameters. The resulting peak integrals are shown in figure 6.6. When only the step sites are pre-covered with  $O_{ad}$  the peak integral of  $\beta_1$  is more or less constant. When the terrace sites become pre-covered with  $O_{ad}$   $\gamma_3$  emerges and the integral of  $\beta_1$  decreases. Both figure 6.5 and 6.6 show that this is a gradual process. This situation appears comparable to electrochemistry, where it is possible to control the amount of  $O_{ad}$  or  $OH_{ad}$  on step and terrace sites by varying the electrode potential, *i.e.* the driving force of the reaction. In UHV, however, this is accomplished by varying the particle concentrations,  $\theta_O$  in this particular case.

Figure 6.7 shows the isotopic partitioning in  $\sim 1$  ML H<sub>2</sub>O vs. the amount of pre-



**Figure 6.7** Isotopic partitioning of  $\text{H}_2^{18}\text{O}$  vs. the amount of pre-adsorbed  $^{18}\text{O}_2$  when Pt(553) is covered with  $\sim 1$  ML  $\text{H}_2^{16}\text{O}$ . The dashed line marks the point where the (111) terrace starts to become occupied with  $^{18}\text{O}_{\text{ad}}$ .

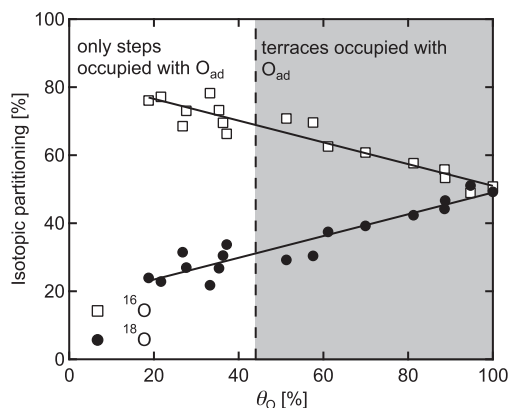
adsorbed  $\text{O}_{\text{ad}}$  on the surface. The white side of the panel shows the  $\theta_{^{18}\text{O}}$  coverages at which only the step sites are (partially) covered with  $\text{O}_{\text{ad}}$ . We observe an increase in the relative amount of water molecules desorbing as  $\text{H}_2^{18}\text{O}$  from 5 to 9%. At coverages larger than 44%  $^{18}\text{O}_{\text{ad}}$ , the terraces start to become occupied with  $\text{O}_{\text{ad}}$  as well. This is shown by the dashed line and the gray area. Here the isotopic partitioning rises much less steeply from 9 to 11%. This indicates that when only step sites are being pre-covered with  $^{18}\text{O}_{\text{ad}}$ , all extra  $^{18}\text{O}_{\text{ad}}$  is likely to participate in the oxygen exchange reaction. When terrace sites become occupied with  $^{18}\text{O}_{\text{ad}}$  as well, not all  $^{18}\text{O}_{\text{ad}}$  atoms participate in the oxygen exchange reaction. The extra O adatoms compete with the  $\text{O}_{\text{ad}}$  on step sites for  $\text{H}_2\text{O}$  molecules.  $\text{H}_2\text{O}$  molecules favor O adatoms on terrace sites, which are more easily incorporated in a hydrogen bonded network, whereas this probably leaves some unreacted  $\text{H}_2\text{O}$  molecules as well.

Figure 6.8 shows the isotopic partitioning of oxygen atoms desorbing as  $\text{O}_2$ . We observe most exchange for the lowest oxygen coverages. A small amount of oxygen is more active in the oxygen exchange reaction. All extra oxygen is less active, though we do not observe a clear discontinuity in the trend when terrace sites start to become filled as well. This is consistent with the observation  $\beta_1$  and  $\beta_2$  decrease with increasing oxygen pre-coverage and that this is a gradual process.

### 6.3.4 Unannealed Pt(553) surface

A final point of consideration is the treatment of the Pt(553) surface, since it is more prone to reconstruction than surfaces with (100) step sites.

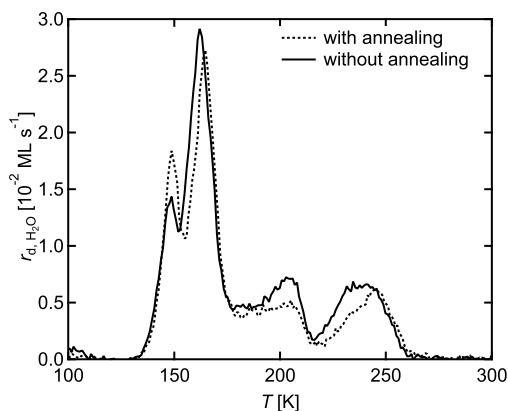
Figure 6.1b shows TPD spectra of varying  $\text{O}_{\text{ad}}$  coverages desorbing from a



**Figure 6.8** Isotopic partitioning of  $^{16}\text{O}$  and  $^{18}\text{O}$  desorbing in  $\text{O}_2$  as function of the amount of pre-adsorbed  $^{18}\text{O}_2$  when Pt(553) is covered with  $\sim 1$  ML  $\text{H}_2^{16}\text{O}$ . The dashed line marks the point where the (111) terrace starts to become occupied with  $^{18}\text{O}_{\text{ad}}$ .

Pt(553) surface, that has not been annealed for 3 minutes at 1200 K following an experiment where oxygen had been adsorbed at the surface. The eight traces with the lowest coverage have been obtained by first saturating the surface and then heating it to 662 – 750 K before cooling down again and subsequently taking the TPD. The three traces with the highest coverage are all from surfaces with the maximum coverage, taken subsequently without any annealing above 1000 K in between. At the lowest coverages we observe one peak. It starts at 767 K and shifts towards lower temperatures (722 K) with increasing coverage, indicating second order desorption kinetics. The behavior of this peak is similar to what we observe with the properly treated surface. At coverages above 0.19 ML a new shoulder appears at 649 K. If we try to obtain the surface with the maximum amount of  $\text{O}_{\text{ad}}$ , this spectrum turns out to be not reproducible. Every subsequent TPD will give more  $\text{O}_{\text{ad}}$  in the peak associated with desorption from terrace sites. This peak shows zero order desorption behavior, which indicates that this peak is no longer due to the recombinative desorption of  $\text{O}_{\text{ad}}$ . Zero order desorption kinetics are typical of concentration independent processes. A conceivable mechanism would be that sub-surface oxygen comes to the surface and reacts immediately with  $\text{O}_{\text{ad}}$ , leaving the O surface coverage constant. Another option would be the formation of oxide clusters which are stable at high temperatures, as is observed on the chiral Pt(531) surface.<sup>141</sup>

Figure 6.9 shows  $\sim 1$  ML  $\text{H}_2\text{O}$ , desorbing from a Pt(553) surface with  $\sim 0.06$  ML oxygen pre-adsorbed, *i.e.* about half of the step filled with  $\text{O}_{\text{ad}}$ . The dashed line shows the spectrum with the properly handled surface. It shows the same structure as we observed in figure 6.5. The solid line shows a spectrum where we did not perform the annealing step in between consecutive experiments. It still shows



**Figure 6.9** TPD spectra of  $\text{H}_2\text{O}$  desorbing from a Pt(553) surface with  $\theta_{\text{O}} = 0.06$  ML with annealing for 3 min at 1200 K between experiments (dashed line) and without annealing (solid line).

a four peak structure, but the integrals of the  $\beta_1$  and  $\beta_2$  peaks have increased by  $\sim 23\%$  compared to the properly treated surface. All peak temperatures, except from the multilayer peak, have shifted slightly towards lower temperatures. The increased integrals of the non-multilayer peaks indicate an increase in effective surface area for the surface without the annealing step. This observation is consistent with the idea that a sub-surface oxide or oxide cluster is formed, that roughens the surface upon desorption.

## 6.4 Conclusion

Water molecules desorbing from the bare Pt(553) surface desorb in a three peak structure. When the step sites are pre-covered with  $\text{O}_{\text{ad}}$  this turns into a six peak structure. On step sites we likely observe OH formation, desorbing in a two peak feature, which has to be stabilized in a hydrogen bonded network of  $\text{H}_2\text{O}$  molecules. The desorption temperature and intensity of these peaks decrease with increasing  $\text{O}_{\text{ad}}$  pre-coverage. Not only  $\text{H}_2\text{O}$  desorption from step sites is influenced, but from terrace sites as well. The many different peaks in the spectrum could be due to different stable structures at different  $\text{O} : \text{H}_2\text{O}$  ratios. When the terrace sites are also covered with  $\text{O}_{\text{ad}}$  we observe a sharp feature at  $\sim 193$  K which we attribute to recombinative desorption of  $\text{OH}_{\text{ad}}$  from terrace sites. At these higher  $^{18}\text{O}_{\text{ad}}$  pre-coverages the amount of exchange is similar to that when only the step sites are pre-covered with  $^{18}\text{O}_{\text{ad}}$ . We attribute this not to inactivity of terrace O adatoms to interact with  $\text{H}_2\text{O}$ , but to the competition between terrace and step O adatoms to react with  $\text{H}_2\text{O}$  molecules. OH formed at terrace sites is more easily incorporated

in a hydrogen bonded network of OH/H<sub>2</sub>O, and is, therefore, favored over the formation of OH on step sites. Thus, in spite of the fact that OH at step sites has a higher binding energy than OH at terrace sites, the possibility of the formation of OH at terrace sites actually inhibits the formation of OH at step sites, leaving O<sub>ad,step</sub> unreacted. This is probably due to the fact that on terrace sites more extensive hydrogen bonded networks can be formed.