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

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Some scientists claim that hydrogen, because it is so plentiful, is the basic building block of the universe. I dispute that. I say that there is more stupidity than hydrogen, and that is the basic building block of the universe

Frank Zappa (1940–1993)

9

The interaction between H₂O and pre-adsorbed D on the stepped Pt(553) surface

Abstract *We have studied the interaction of Pt(553) with varying coverages of pre-adsorbed deuterium and water under ultra high vacuum conditions and compare these results to Pt(533). We use temperature programmed desorption spectroscopy and isotopic labeling to study how pre-adsorbed D influences the adsorption of H₂O and the exchange between H₂O and D. Water still wets a completely deuterium pre-covered Pt(553) surface, in contrast to Pt(533) where the surface becomes hydrophobic, though pre-adsorbed deuterium does cause a destabilization of the water. For high water coverages, the mobility of the water islands is limited and the coupling between the first water layer and second water layer is poor. The exchange between the H and D atoms mainly takes place at the D/Pt(553) surface and not in the multilayer. For 1.3 ML of water on top of different amounts of deuterium, the exchange mainly takes place when deuterium covers most of the (111) terraces. When deuterium also occupies sites around the steps, the exchange is inhibited.*

9.1 Introduction

The interaction between platinum surfaces and water is essential for our understanding of electrochemistry, heterogeneous catalysis, corrosion chemistry, and fuel cell catalysis. Therefore, the interaction of water with a variety of single-crystal transition-metal surfaces and co-adsorbates has been studied frequently.^{6,7} Pt(111) is considered to be the least complex system to study, although this system already shows significant complexity in adsorption and desorption phenomena.^{118–120} The interaction of water with Pt(111) has been studied in detail under ultra high vacuum (UHV) conditions with a large variety of techniques.^{20,22,23,28,29,34,157–160}

However, real catalysts have low coordination and defect sites, which are thought to be more active for catalytic reactions involving bond breaking and making.¹³ Stepped single crystal surfaces allow for the introduction of such defects in a controlled manner in surface science studies. However, few experimental studies have focused on the interaction of water with platinum surfaces containing defects.^{26–28,44} Scanning tunneling microscopy (STM) shows that water adsorbs preferentially at the upper side of step edges, forming molecular chains.²⁸ Two different step orientations can be distinguished: (100) steps and (110) steps. Temperature programmed desorption (TPD) spectra of water desorption from the stepped Pt(533) surface (Pt[4(111) × (100)]) reveal two sub-monolayer states and one multilayer phase. The presence of step sites causes an additional stabilization of water for sub-monolayer coverages in comparison to Pt(111). A peak around 188 K (low water coverages) is attributed to water desorption from (100) step sites and a peak around 171 K to water desorption from (111) terrace sites. A third peak (water coverage > 1 ML), located around 148 K, is due to the desorption from the water multilayer. Step geometry can strongly influence desorption behavior. Water molecules bind more strongly to the (110) step sites of the Pt(553) (Pt[4(111) × (110)]) surface than to the (100) step sites of the Pt(533) surface, with a desorption temperature of 197 K on (100) steps vs. 188 K on (100) steps. The peak temperatures of water desorption from terraces (171 K) and from the multilayer (~ 150 K) are not affected by the step geometry (chapter 3).

The interaction between hydrogen and transition metal surfaces like platinum is often studied in relation to hydrogenation reactions.^{55,56,59,61,63,72–74,161–167} Molecular hydrogen adsorbs dissociatively on both Pt(111)^{55,65} and stepped platinum surfaces.^{59,63,64} TPD spectra of deuterium desorbing from Pt(533) show two peaks: at 380 K, associated with recombinative desorption of D_{ad} from (100) steps, and below 300 K, mainly associated with recombinative desorption of D_{ad} from (111) terraces.⁶³ The TPD spectra of deuterium desorption from Pt(553) are significantly different. Instead of two peaks, three peaks are observed, located at 292 K, 256–235 K, and 206–196 K. The two high-temperature peaks are associated with deuterium desorption from (111) terrace sites, whereas the low temperature peak is

associated with desorption from sites related to (110) steps. This is remarkable, as it implies a weaker adsorption of H to the (110) step site compared to the (111) terrace site (chapter 3).

In electrochemical environments (*e.g.* hydrogen fuel cells and the reversible hydrogen electrode) water and hydrogen are both present on a platinum surface, making co-adsorption studies of relevance.⁸⁸⁻⁹¹ On deuterium pre-covered Pt(111), D₂O desorption in the monolayer regime occurs at higher temperatures (175 K, compared to 170 K for D₂O desorption from the bare Pt(111) surface), indicating that D₂O on Pt(111) is stabilized by co-adsorption with deuterium. For higher deuterium coverages the stabilization becomes weaker and the D₂O desorption peak shifts back to lower temperatures (172 K).⁹⁰ Co-adsorption TPD experiments with different hydrogen isotopes (H₂O on top of D_{ad}) show exchange between deuterium atoms and water molecules.⁸⁹ It remains unclear what the intermediate species is, but mixtures of hydrated species such as H₅O₂⁺, H₇O₃⁺, and H₉O₄⁺ have been suggested as the most likely candidates.⁹³

In contrast to the stabilization observed on Pt(111), the stepped Pt(533) surface shows only one peak in the TPD spectrum when the surface has been totally pre-covered with D_{ad}. This peak is located around 150 K and, therefore, ascribed to desorption from the water multilayer. Experiments in which the deuterium pre-coverage is varied show that the peak of water desorption from step sites (188 K) disappears when deuterium saturates the step sites. When deuterium is also pre-covering part of the terraces, the water desorption peak shifts gradually to lower temperatures. This is attributed to the formation of 3-dimensional amorphous solid water (ASW) clusters at the steps (see chapter 3).

As step geometry can have a significant effect on adsorption and desorption phenomena (chapters 3 and 4), we investigate here this influence for the co-adsorption of D and H₂O on the stepped Pt(553) surface, which has (110) steps, for comparison with the results obtained for Pt(533), which has (100) steps (chapter 8). We use TPD in combination with isotopic labeling to investigate how pre-adsorbed D influences adsorption of H₂O, and the exchange between deuterium and water in both experiments.

9.2 Experimental

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

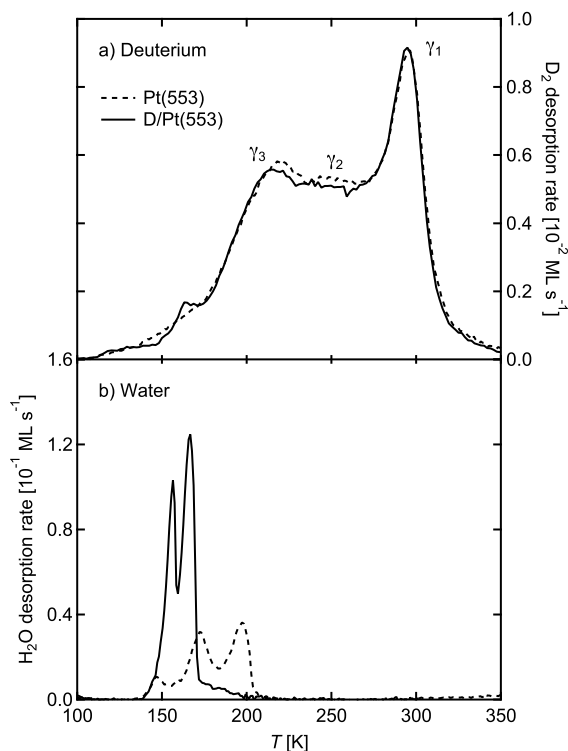


Figure 9.1 TPD spectra of a) deuterium and b) water in co-adsorption experiments (solid lines; $\theta_D = 1$; $\theta_{H_2O} = 1.92$ ML) and of both species desorbing in separate experiments from bare Pt(553) (dashed lines; $\theta_{H_2O} = 1.15$ ML).

9.3 Results

9.3.1 H₂O and D₂ desorption from Pt(553) and D/Pt(553)

The solid lines in figure 9.1 show TPD spectra of deuterium (a) and 1.9 ML H₂O (b) desorbing from a Pt(553) surface fully pre-covered with D_{ad}. For the deuterium signal $m/e = 3$ and 4 were added, whereas $m/e = 18, 19$, and 20 were added for the water signal, in order to show the total amount of the species desorbing from the surface. For reference we also show both species desorbing from the bare surface (dashed lines).

We have discussed the TPD spectra from the bare surface in chapter 3. Briefly, the TPD spectrum of D₂ can be deconvoluted into three peaks: γ_1 , γ_2 , and γ_3 (deconvolution not shown here). We refer to this spectrum as 1 ML D₂, without implying a D_{ad} : Pt ratio of 1 : 1. Water desorbing from bare Pt(553) shows three peaks,

located at 197 K (desorption from step sites), 171 K (desorption from terrace sites), and ~ 146 K (desorption from the water multilayer). Following Grecea *et al.*,²⁷ we use the largest combined integral for the two high temperature peaks as a reference for the amount of adsorbed H_2O and refer to this amount as $\theta_{\text{H}_2\text{O}} = 1$ ML.

When H_2O and D_{ad} are co-adsorbed on Pt(553), the D_2 TPD spectrum (solid line) is very similar to that on bare Pt(553). The only significant difference between the spectra is that deuterium desorption from the H_2O post-covered surface starts a little later and subsequently gives a small additional peak at 163 K. At higher temperatures, the spectra are identical within our margin of error. For $\theta_{\text{H}_2\text{O}} \leq 1.92$ ML the additional peak at 163 K becomes less pronounced and shifts to higher temperatures with decreasing water coverage. At $\theta_{\text{H}_2\text{O}} \leq 1.28$ ML the onset of deuterium desorption is no longer delayed, but the small peak is still discernible. The corresponding water TPD spectrum shows only two peaks at 156 and 167 K. The start of the water desorption in the second peak coincides with the onset of deuterium desorption.

9.3.2 $\theta_{\text{D}} = 1$ ML; $0 < \theta_{\text{H}_2\text{O}} < 2.28$ ML

Figure 9.2 shows $m/e = 19$ (HOD) (a) and 18 (H_2O) (b) TPD spectra after dosing varying amounts of H_2O onto a Pt(553) surface fully pre-covered with D_{ad} .

First, we focus on the H_2O spectra (figure 9.2b). For $\theta_{\text{H}_2\text{O}} = 0.13$ ML, a broad peak is observed at 162 K. For the lowest water coverages the peaks' leading edges overlap and the peak shifts with increasing water coverage to 167 K for $\theta_{\text{H}_2\text{O}} = 0.87$ ML, suggesting zero order desorption kinetics. For higher coverages, the peak no longer shifts with increasing coverage, suggesting first order desorption kinetics. The maximum integral of this peak is 0.89 ML. Before saturation of the high temperature peak, for $\theta_{\text{H}_2\text{O}} \geq 0.62$ ML, a second peak appears at the low temperature side. This peak shows the characteristics of zero order desorption kinetics with its peak desorption temperature shifting from 151 K (0.87 ML) to 158 K (2.14 ML).

Next, we focus on the HOD signal (figure 9.2a), measured simultaneously. Here, we also observe a two peak structure. The high temperature peak shifts from 165 K ($\theta_{\text{HOD}} = 0.05$ ML) to 169 K ($\theta_{\text{HOD}} = 0.14$ ML), with increasing H_2O coverage. The peak temperature in the HOD spectrum is ~ 3 K higher than the corresponding temperature in the the H_2O spectrum. In contrast to the H_2O signal, the high temperature peak saturates prior to the appearance of the low temperature peak ($\theta_{\text{HOD}} = 0.12$ ML). This is at a slightly higher water coverage than in the corresponding H_2O spectra. The low temperature peak appears at coverages > 0.13 ML HOD. Unlike the high temperature peak, this peak appears at the same temperature as in the H_2O spectra. The peak temperature shifts to higher desorption temperatures, from 154 K (0.13 ML HOD) to 158 K (0.14 ML HOD), with increasing H_2O coverage, showing the same zero order desorption kinetics as the H_2O spectra. The

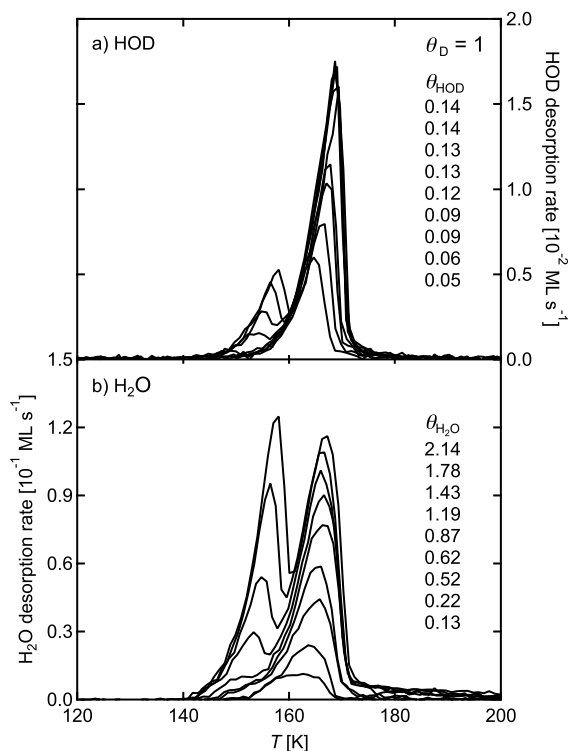


Figure 9.2 TPD spectra of water dosed onto a Pt(553) surface fully pre-covered with D_{ad} : a) HOD and b) H₂O.

low temperature peak is relatively small in the HOD spectra compared to the high temperature peak.

The D₂O signal is $\sim 1\%$ of the HOD signal (not shown). It shows only one peak, with identical behavior as the high temperature peak in the HOD spectrum, shifting from 165 K to 169 K with increasing H₂O coverage. The intensity of the signal does not vary significantly with water dosage.

In figure 9.3 we compare water desorption spectra from D/Pt(553) to those from D/Pt(111)⁹⁰ and D/Pt(533) (chapter 8). The solid spectrum shows the water desorption spectrum from figure 9.2 with the second largest amount of water (1.92 ML) desorbing from a fully deuterated Pt(553) crystal. The dotted spectrum shows ~ 2 ML D₂O desorbing from D/Pt(111) (taken from ref.⁹⁰). The spectrum without filling shows 1.34 ML water desorbing from D/Pt(533) (taken from chapter 8). We first note that the multilayer desorption peak appears ~ 1 K earlier on the D/Pt(111) surface than on the stepped surfaces. However, the Pt(111) experiments were performed in a different laboratory. Therefore, we attribute this dis-

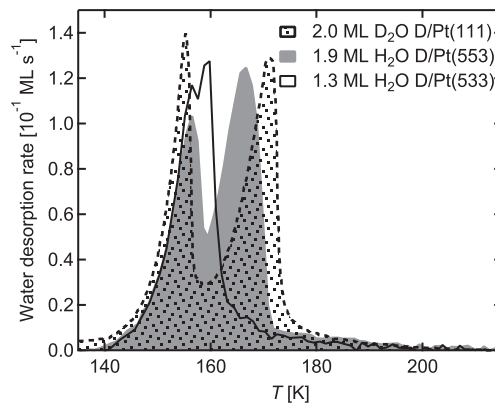


Figure 9.3 TPD spectra of co-adsorption experiments with water dosed onto a fully pre-covered deuterium surface: ~ 2 ML D_2O on $D/Pt(111)^{90}$ (dotted), 1.92 ML H_2O on $D/Pt(553)$ (solid), and 1.34 ML H_2O on $D/Pt(533)$ (chapter 8) (no fill).

crepancy to a difference in absolute temperature calibration between the two labs. Both $D/Pt(553)$ and $D/Pt(111)$ show a clear two peak structure. We shall not discuss the multilayer peak further, since this peak is similar for all surfaces. For the $Pt(553)$ surface, the high temperature peak shows a destabilization of 4 K (167 vs. 171 K) compared to the middle peak in figure 9.1b (dashed line), associated with desorption from (111) terrace sites on the bare surface. On $Pt(111)$, however, the presence of D stabilizes the same peak by 1 K (171 vs. 170 K). Note that this stabilizing effect is reported to be stronger for lower θ_D , with a maximum shift to 176 K for what is referred to as a relative dose of 100.⁹⁰ (The dose shown here is a relative dose of 4800, which is the largest dose reported in ref.⁹⁰)

In contrast to the two peak structure observed on $D/Pt(111)$ and $D/Pt(553)$, we only observe one peak on $D/Pt(533)$. At first glance the $D/Pt(533)$ spectrum might be considered as two close peaks around 157 and 159 K. However, we have shown earlier that this feature is in fact one peak with a deflection due to the crystallization of ASW to crystalline ice (CI). In chapter 8, we have shown that from the lowest coverages onwards a zeroth-order peak grows in with desorption starting from 140 K. This shows that the feature observed on $D/Pt(533)$ should be interpreted as only one peak.

Figure 9.4a shows the dependence of the extent of isotopic partitioning towards HOD and D_2O for varying amounts of water dosed after saturating the $Pt(553)$ surface with deuterium. The remaining isotopic fraction (H_2O) is much larger and not shown in order to focus on the isotopic fractions of HOD and D_2O . When we dose a small amount of water (0.18 ML) on the deuterated $Pt(553)$ surface, we observe that 27% of all water desorbs as HOD. The isotopic fraction HOD decreases with in-

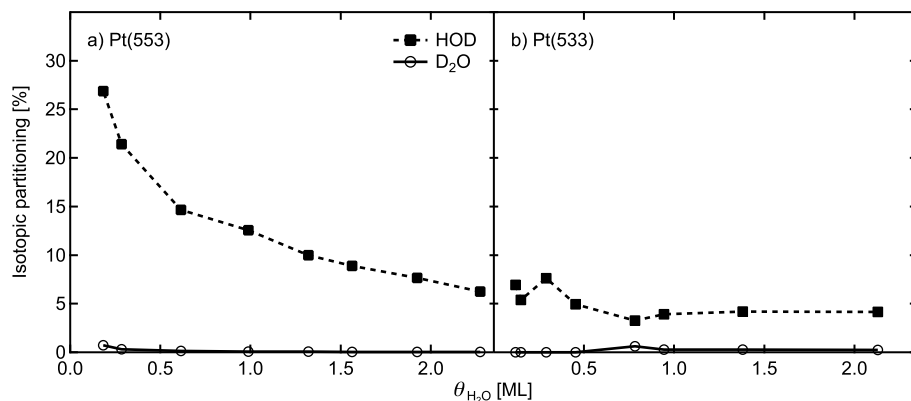


Figure 9.4 Isotopic partitioning of HOD and D₂O desorbing from deuterium pre-covered a) Pt(553) and b) Pt(533) with different amounts of dosed H₂O.

creasing H₂O coverage. At 1 ML of water, the fraction of water desorbing as HOD has decreased to 12.5%. At 2.28 ML of water, an isotopic partitioning of 6.2% remains, but it is still decreasing. Note that this implies that the total amount of HOD desorbing increases with increasing water coverages. The isotopic partitioning for D₂O is much smaller, but follows a similar trend as HOD, with a slightly higher isotopic partitioning for low water coverages. The isotopic fractions of D₂ and HD show a trend consistent with the data for H₂O, HOD, and D₂O, with a decreasing D₂ signal and an increasing HD signal with increasing water coverage. Unlike what we observed for Pt(533), we observe little difference in the relative peak heights between the $m/e = 3$ and 4 spectra other than a scaling factor. The γ_3 peak is slightly smaller in the HD spectra compared to the D₂ spectra.

Figure 9.4b shows similar data for Pt(533). The relative yield of HOD is slightly larger at lower H₂O coverages (7.6 vs. 4.2% at the highest coverage), but compared to the Pt(553) surface the isotopic partitioning is relatively constant and significantly lower. The total amount of HOD increases linearly with increasing $\theta_{\text{H}_2\text{O}}$ and is also much smaller than on Pt(553). The relative yield of D₂O is even lower, around 0.6%.

9.3.3 $\theta_{\text{H}_2\text{O}} \approx 1.3 \text{ ML}; 0 < \theta_{\text{D}} < 1$

Figure 9.5 shows TPD spectra of $\sim 1.3 \text{ ML}$ water dosed onto a Pt(553) surface with varying D pre-coverage, ranging from 0 to 1 ML. More than 1 ML of water was dosed in order to ensure that the high temperature peak(s) are saturated. Therefore, the multilayer desorption peak, around 148 K, is observed in all spectra. Water desorption from bare Pt(553) shows three peaks at 197 K, 171 K, and $\sim 148 \text{ K}$. With a small amount of deuterium, the highest temperature peak decreases and shifts

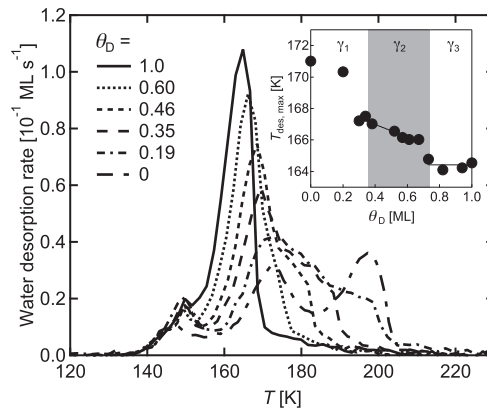


Figure 9.5 TPD spectra of ~ 1.3 ML of water dosed on a Pt(553) surface with a varying deuterium pre-coverage (0–1 ML). The inset shows the temperature of maximal desorption rate of the middle peak as a function of deuterium pre-coverage. The γ_1 , γ_2 , and γ_3 areas show which peaks are visible in the corresponding D_2 TPD spectra, and thus which sites are pre-covered with D.

to lower temperatures. However, it remains visible as a shoulder until 73% of the surface is pre-covered with deuterium (not all spectra are shown here). The middle peak shifts to lower temperatures with increasing θ_D . The inset of figure 9.5 shows the temperature of maximal desorption rate of water for this peak with varying deuterium pre-coverages. The γ_1 , γ_2 , and γ_3 areas show which peaks are visible in the corresponding D_2 TPD spectra, and thus which sites are pre-covered with D. Simultaneously to the shift of the high temperature peak, the middle peak broadens, making it difficult to determine its exact temperature. The peak sharpens for $\theta_D \geq 0.3$. From this point on we observe two regimes, which coincide with different adsorption sites for D being filled. Initially the peak temperature decreases linearly for $0.3 \geq \theta_D \geq 0.73$, in the regime where the γ_2 peak in the D_2 TPD spectra gets filled. For $\theta_D \geq 0.73$, where the D_2 γ_3 peak becomes occupied, the peak temperature remains constant at 164 K within our margin of error.

Figure 9.6 quantifies the isotopic partitioning corresponding to the TPD spectra shown in figure 9.5. For the bare surface, the ratio between deuterium desorption from (111) sites and (110)-type sites is $\sim 8 : 3$ at saturation (chapter 3). Therefore, we can divide the graph into two regimes, *i.e.* a regime where deuterium occupies (111) sites and a regime where deuterium also occupies (110)-type sites. The isotopic partitioning of HOD increases linearly from 8% to 18% in the first regime. When the (110) sites become occupied by deuterium as well, the isotopic partitioning of HOD decreases drastically from 18% to 9.5%. The isotopic partitioning of D_2O follows the same trend as HOD with a maximum around a deuterium coverage of 74% with an isotopic partitioning of 2.8% D_2O .

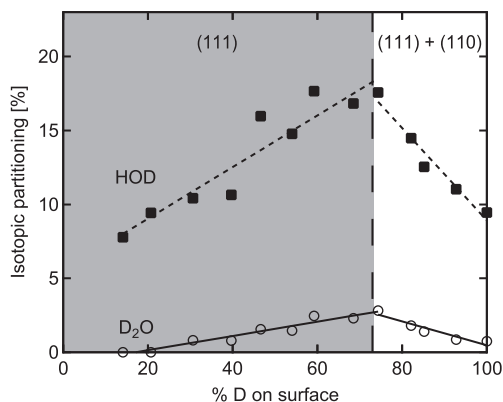


Figure 9.6 Isotopic partitioning of HOD and D₂O desorbing from a Pt(553) surface pre-covered with different amounts of deuterium and ~ 1.3 ML H₂O. The amount of D on the surface can be divided into two regimes, *i.e.* a regime where D_{ad} only occupies (111) sites and a regime where D_{ad} occupies (110)-type sites as well.

9.4 Discussion

9.4.1 H₂O and D₂ desorption from Pt(553) and D/Pt(553)

Deuterium desorption from bare Pt(553) can be divided into three peaks associated with desorption of deuterium from the (111) terrace sites (γ_1 and γ_2) and sites at the (110) steps (γ_3) (chapter 3). Upon co-adsorption of 1 ML deuterium and 1.92 ML water on Pt(553) the main features of the TPD spectrum, and therefore the assignment, remain unchanged. The additional peak in the co-adsorption experiment is located at the same temperature as the start of the water desorption in the high temperature peak. This behavior is reminiscent of the ‘molecular volcano’ observed for water adsorbed on top of CCl₄ on Au(111), where CCl₄ desorption is blocked by the water overlayer and occurs abruptly when holes are formed in the overlayer by water desorption.¹⁴⁷ We also observe a delay in the onset of deuterium desorption, indicating that the water overlayer temporarily blocks deuterium desorption. Once the water from this overlayer starts to desorb, the underlying D_{ad} can desorb recombinatively as well, causing a temporarily higher D₂ desorption rate compared to the bare surface.

We have previously assigned the three peaks of water desorption from bare Pt(553) to water desorption from (110) step sites (197 K), (111) terraces sites (171 K), and the water multilayer (~ 146 K) (chapter 3). We ascribe the two peak structure in co-adsorption experiment to desorption from the water multilayer (low temperature peak) and water still in contact with the platinum surface. This will be discussed in more detail in the next subsection. Deuterium desorption is blocked until

the second peak, *i.e.* H₂O interacting with the deuterium-covered platinum starts to desorb. This indicates that the water monolayer fully covers the surface. This is in stark contrast to the similar Pt(533) surface where pre-adsorption of D induces hydrophobicity (chapter 8).

However, the delay in deuterium desorption is no longer observed at $\theta_{\text{H}_2\text{O}}$ as high as 1.28 ML, indicating that below this coverage we do not have a fully developed monolayer, but probably some multilayer formation as well. The growth of the monolayer is non-uniform. Perhaps this is due to a limitation in the water mobility. The effect diminishes with decreasing H₂O coverage. When less of the D/Pt(553) surface is post-covered with H₂O, uncovered patches of D adatoms can desorb uninhibited.

The high temperature peak in the water spectra shows zero order desorption kinetics (figure 9.2). This is also reflected in the shift towards higher temperatures of the additional peak in the deuterium spectra. The additional peak remains visible for the lowest water coverages, implying that water has to be adsorbed at the sites from where the first D_{ad} starts to desorb recombinatively, which are (110) sites.

9.4.2 $\theta_{\text{D}} = 1 \text{ ML}; 0 < \theta_{\text{H}_2\text{O}} < 2.28 \text{ ML}$

Upon pre-covering the Pt(553) surface with 1 ML D_{ad} the three peak structure of water gets converted into a two peak structure. The peak at 151 K shows zero order desorption kinetics and is located at the same temperature at which water multilayer desorption from bare Pt(553) starts. Therefore, we ascribe this peak to water multilayer desorption. The two high temperature peaks merge into one peak, which we ascribe to desorption of water still interacting with D/Pt(553). The step induced stabilization of water on bare Pt(553) is removed by the pre-adsorbed deuterium. On Pt(533) we also observed a destabilization of H₂O by pre-covering the surface with D_{ad}, which we attributed to an electronic effect (chapter 8). On Pt(553), however, the maximum integral of the peak at 167 K is $< 1 \text{ ML}$. Therefore, D_{ad} actively blocks water adsorption sites on this surface, showing that a geometric effect may be at play as well.

The high temperature peak shows zero order desorption kinetics at low $\theta_{\text{H}_2\text{O}}$, but for $\theta_{\text{H}_2\text{O}} \geq 0.87 \text{ ML}$ this shifts to apparent first order desorption kinetics. Zero order desorption kinetics of H₂O on Pt(111) have been interpreted as the result of the co-existence of water islands with a 2-dimensional lattice gas at equilibrium.²¹ We expect the same to be the case for D/Pt(553) at low H₂O coverages. At higher water coverages we observe an increasing peak height at a fixed desorption temperature. Although this may be interpreted as being due to a baseline lift of the high temperature peak with an increasing multilayer, implying that the peak does not actually increase in intensity, we believe that we observe a shift to first order desorption kinetics. High water coverages no longer allow for a co-existing two phase system. Figure 9.1 suggests that the monolayer does not grow in uniformly. There-

fore, we believe that the increase in intensity we observe for the high temperature peak is due to more water desorbing that was directly in contact with D/Pt(553).

The multilayer peak appears well before saturation of the high temperature peak in the H₂O desorption spectrum. For higher water coverages, more adsorption sites on top of water are available to form water multilayers, but there are still some vacant sites left for water adsorption that have a direct interaction with the D/Pt(553) surface. This indicates that water mobility is limited and that water tends to stick to the place where it hits the surface.

Relatively little water desorbs in the multilayer peak for the HOD spectra compared to the H₂O spectra. Therefore, the exchange between H and D atoms to form HOD mainly takes place at the Pt(553) surface, but not between water layers. This is also reflected in the HOD signal; the high temperature peak shifts towards higher temperatures, but the multilayer peak does not. The water mobility between the first and second layer is limited, indicating that the coupling between them is poor. We did not observe this effect on Pt(533), where at least the partially deuterated surface shows a similar amount of exchange to the monolayer as to the multilayer, indicating that the morphology of the first water layer for both surfaces is completely different, with as a consequence that the reactivity is completely different.

On Pt(111) the presence of D_{ad} stabilizes H₂O on the surface. The origin of this effect is not well understood.⁹⁰ We do not observe this stabilization for both stepped surfaces in figure 9.3. In fact, the co-adsorption with D_{ad} destabilizes H₂O on stepped surfaces. Water forms large hydrogen bonded networks on the flat Pt(111) surface.⁷ Apparently, these networks are stabilized by the presence of a small amount of D_{ad}, but adding more D_{ad} annuls the extra stabilization.⁹⁰ On stepped surfaces the (111) terraces are interrupted by mono-atomic steps, limiting the maximum size of the "perfect" water islands. Water forms hexagonal ring structures on surfaces.^{6,7} Since the hexagons are more confined on stepped surfaces, the relative amount of D per H₂O hexagon may be relatively high compared to Pt(111). On the latter surface it was shown that at too high D_{ad} : H₂O ratios the stabilization diminishes, though it does not disappear completely, in contrast to the stepped surfaces.

The two step geometries show completely different behavior in the water TPD spectra from the deuterated surface. Both surfaces show a destabilization of the water by pre-adsorbed D, but the D/Pt(533) surface shows only one desorption peak, whereas D/Pt(553) shows two desorption peaks. The one peak structure on D/Pt(533) was attributed to the growth of ASW "snowballs" on step sites (chapter 8). On the D/Pt(553) surface, on the other hand, the first layer of water still wets the surface. This is also reflected in the fact that we observe the deflection at 163 K in the deuterium TPD spectra, which show that H₂O wets the entire surface. The $m/e = 3$ and 4 spectra show only a small bias towards exchange in the γ_1 and γ_2 peaks in the Pt(553) co-adsorption experiments. We will argue in the next

subsection that D atoms adsorbed at (110)-type sites have little interaction with the water overlayer. We believe this does not imply that water is primarily adsorbed at terraces, but rather that it has no preferential adsorption site. This is in contrast to D/Pt(533) where the deuterium spectra show a clear bias towards exchange (and therefore water localization) at steps. The Pt(553) surface has a more slanting nature than the Pt(533) surface, which could make it possible for hydrogen bonded networks to form over the (110) steps.

The absolute amount of HOD increases with increasing amounts of water, indicating that exchange of H and D atoms between water and deuterium continues to increase. On D/Pt(553), the isotopic fraction of HOD (and D₂O) is larger for smaller $\theta_{\text{H}_2\text{O}}$. For low water coverages a two phase system of water islands and a 2-dimensional lattice gas co-exist on the surface, similar to the situation on Pt(111).²¹ Probably, at low $\theta_{\text{H}_2\text{O}}$ a relatively high amount of water is in this lattice gas phase on D/Pt(553), and therefore very mobile. When more water is dosed, relatively more water islands are formed, decreasing the water mobility. This may lead to the observed relative decrease in the amount of exchange. The isotopic fractions of HOD and D₂O on Pt(533) are much lower than on the Pt(553) surface. This can be explained by the fact that the exchange of H and D to form HOD mainly takes place in the first layer of water, where the water still interacts with the platinum surface. Because of the hydrophobic character of the D/Pt(533) surface there is little direct interaction between water and the D/Pt(533) surface, causing only a small amount of exchange between H and D atoms.

9.4.3 $\theta_{\text{H}_2\text{O}} \approx 1.3 \text{ ML}; 0 < \theta_{\text{D}} < 1$

The temperature of water desorption from (110) steps and (111) terraces shifts gradually to lower temperatures with increasing deuterium pre-coverage (figure 9.5). This indicates that the binding energy for water with the D/Pt(553) surface gradually decreases with increasing deuterium concentration. This is qualitatively similar to what we observed on Pt(533) (chapter 8). On Pt(553), however, the presence of only a small amount of D_{ad} influences the entire water TPD spectrum: both the high and middle temperature peaks are influenced. At Pt(533) the processes corresponding to the two peak temperatures are more separated, *i.e.* first the high temperature peak disappears completely, when step sites become covered with D_{ad} ,¹⁶⁸ while the middle peak is not yet influenced. Only when $\sim 1/4$ of all terrace sites on Pt(533) are covered with D_{ad} does the middle peak gradually shift to lower temperatures (chapter 8). Since deuterium prefers the (111) terraces over the (110) steps on Pt(553) (chapter 3, the deuterium affects the entire hydrogen-bonded network on the (111) terraces at the lowest D_{ad} coverages. We do not observe a decoupling of the two peaks as on Pt(533), but the entire network is affected. Initially, the peak temperature of water desorption decreases with increasing deuterium pre-coverage. In the regime where (110) sites become covered with D no change is observed in the TPD

spectra, indicating that the additional D atoms at these sites do not interact with the water overlayer. Possibly this is due to a "buried" nature of the D atoms, *e.g.* by adsorption in the through of the (110) step.

The HOD and D₂O isotopic partitionings show a maximum when deuterium is covering most of the terraces. For low deuterium coverages a small amount of deuterium is available to form HOD and D₂O, which leads to relatively small isotopic fractions for these species. With increasing deuterium coverage more deuterium becomes available for the exchange, resulting in more HOD and D₂O formation. When the deuterium starts to occupy the steps as well, the isotopic fractions of HOD and H₂O suddenly decrease. Apparently, contact of water with bare platinum sites of (110) geometry is beneficial for the exchange reaction. Deuterium adsorption at these sites has a poisoning effect on the exchange. On Pt(533) we also observed that contact with bare platinum is beneficial to the exchange, but this was not associated with a particular site.

9.5 Conclusion

Let us summarize the various effects of the interaction of Pt(553) with water when deuterium is pre-adsorbed. The TPD spectra of deuterium desorbing from bare Pt(553) are comparable to the spectra of deuterium desorbing in co-adsorption experiments with water. The only difference is an additional small feature for the spectrum of 1 ML of deuterium in the co-adsorption experiment, caused by the water overlayer, which temporarily blocks the deuterium desorption. The spectra of water desorption from bare Pt(553) differ from the spectra of water desorption in the co-adsorption experiments. The three peak structure of water desorption from bare Pt(553) changes into a two peak structure. Pre-adsorbing deuterium onto the surface leads to a destabilization of the water. For high deuterium coverages, water still wets the entire D/Pt(553) surface. Deuterium does not create a hydrophobic surface for the water, in contrast to D/Pt(533) on which surface water has a tendency to cluster (chapter 8). For 1 ML of deuterium with different amounts of water the exchange between H and D atoms is mainly taking place directly at the Pt(553) surface and not in the multilayer. Coupling between the first and second water layer is poor in this system and water mobility is limited for high water and deuterium coverages. The hydrogen-bonded network for ~ 1.3 ML of water on different amounts of pre-adsorbed deuterium on the (111) terraces is immediately affected by the presence of a small amount of deuterium, since deuterium prefers the (111) terraces over the (110) steps. The (110) step sites still cause some stabilization for water adsorbed there for $\theta_D < 0.46$ ML. The exchange between H and D atoms is mainly taking place when deuterium is only pre-adsorbed at the terraces. When deuterium is also pre-covering the low coordination sites around the steps, the exchange becomes less. Contact of water with bare (110) platinum sites

is, therefore, beneficial for the exchange reaction.

The structure of the platinum surface is very important for the mobility of the water and the size of the water islands that can be formed on the surface. Not only the absence or presence of step sites influence the stabilization of the water islands, but also the step geometry is very important in the water stabilization. We suggest that due to the more slanting nature of the Pt(553) surface compared to the Pt(533) surface, the hydrogen-bonded network can reach over the (110) step sites, making the surface non-hydrophobic, in contrast to the Pt(533) surface with (100) steps. As a general conclusion, we can not *a priori* predict what the effect of the step (and terrace) geometries will be in different experiments. It is important to take into account the differences between different step geometries, to obtain a better understanding of structure sensitivity in catalysis.

