Anisotropy in the Adsorption of H_2O at Low Coordination Sites on Pt(111)

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The H_2O adsorption on Pt(111) at 140 K is investigated by temperature-variable scanning tunneling microscopy. H_2O adsorbs preferentially at the upper side of step edges. At these low coordination sites the adsorbates are bound stable as quasi-one-dimensional chains up to 160 K. In contrast, the desorption from the two-dimensional H_2O islands on the terrace has already started at 145 K. The occupancy of the sites at the upper side of step edges is different at the two types of dense packed steps. This adsorption anisotropy is correlated with the different dipole moment of the two types of steps. [S0031-9007(96)00492-9]

The adsorption of H_2O on metal surfaces was intensively studied in the past [1]. Different investigations of the system H_2O/Pt(111) [2–6] show that water adsorbs via island formation [3,5]. The desorption peak temperatures in thermal desorption spectroscopy (TDS) experiments were determined to be 165 and 175 K for the multilayer and the so-called bilayer, respectively [3,4]. First principle calculations of the interaction of single H_2O molecules with a Pt_{10} cluster have shown that the binding between Pt and H_2O is mainly caused by the mixing of unoccupied Pt $5d$ states with the occupied lone pair orbitals of the H_2O molecule. This results in an energy gain of about 0.5 eV. The adsorption site was found to be on top. The reason is that the Pt charge density on top is lower, which reduces the repulsive part of the interaction [7].

In this work we present the first scanning tunneling microscopy (STM) study of water adsorption on a metal surface, which shows that H_2O adsorbs preferentially at the low coordination sites at the upper side of step edges. This appears to be the adsorption site of highest thermal stability. Surprisingly, the H_2O occupancy of these sites is different for the two types of dense packed steps.

The experiments were performed in an UHV-STM apparatus described elsewhere [8]. The background pressure was below 1×10^{-10} mbar. The sample was prepared by repeated cycles of Ar^+ bombardment, oxygen exposure, and subsequent flashing to 1000 °C. This procedure results in a clean, well-ordered surface as checked by low energy electron diffraction Auger electron spectroscopy and the STM. Water of milli-Q quality with an electrical resistivity of 10^7 Ω cm was used for the exposure. Just before water exposure the sample was flashed to 500 °C to desorb all adsorbates from the surface. The water adsorption has been performed by filling the chamber with a H_2O pressure of 5×10^{-9}–1.1×10^{-8} mbar and keeping the sample temperature at 140 K. The gas inlet was routinely checked by a mass spectrometer with automatic background subtraction. The only peak not related to H_2O, which has an intensity of more than 0.1% of the H_2O peak, was $M = 28$ with an intensity corresponding to somewhat

less than 1% of H_2O. We assume that this is due to residual N_2 solved in the water reservoir. However, N_2 does not adsorb on Pt(111) down to 80 K [9]. The H_2O pressure during the experiment was checked by a hot filament gauge located outside the line of sight of the sample only at the beginning and at the end of the exposure. The STM tip has to be removed from the sample during water exposure to avoid shadowing effects, which were found to be relevant if imaging and exposure were performed simultaneously. Moreover, the tunneling voltage was switched off during the exposure to avoid possible field induced dissociation of the water molecules at the tip. After exposure the pressure was reduced below 2×10^{-10} mbar within 2–5 min. The tunneling conditions were generally chosen to be $|U| \leq 1$ V and $I \leq 0.3$ nA. The presented images were recorded in the differential mode giving rise to images appearing as illuminated from the left. All images show the same crystallographic orientation within $\pm 5°$.

In order to study a possible effect of steps on the adsorption behavior of H_2O, we pretreated the surface by ion bombardment at 760 K. This results in vacancy islands having a near to equilibrium shape [10]. As indicated in Fig. 1(a) the hexagonal monolayer deep islands have boundary steps in the close packed $\langle 110 \rangle$ directions. The three shorter and three longer steps are called $\langle 110 \rangle / \{100\}$ and $\langle 110 \rangle / \{111\}$ steps, or A and B steps, respectively. Both types of steps are not completely straight indicating that a few kinks are frozen in at the step edges. Figure 1(a) shows the surface after a H_2O exposure with $(3 \pm 1) \times 10^{14}$ molecules/cm² [11] at 140 K. The STM image, recorded also at 140 K, shows the resulting ice submonolayer as an elevation [12]. The adsorbed H_2O appears to aggregate in two types of structures. At the lower side of the step edges two-dimensional patches of ice are found, while at the upper side of step edges the H_2O molecules form quasi-one-dimensional chains (less than 10 Å wide in the STM images). The H_2O density in the chains is different above the two different types of step edges [13]. This can be seen in more detail in Fig. 1(b). The H_2O exposure in Fig. 1(b) is twice that in Fig. 1(a).
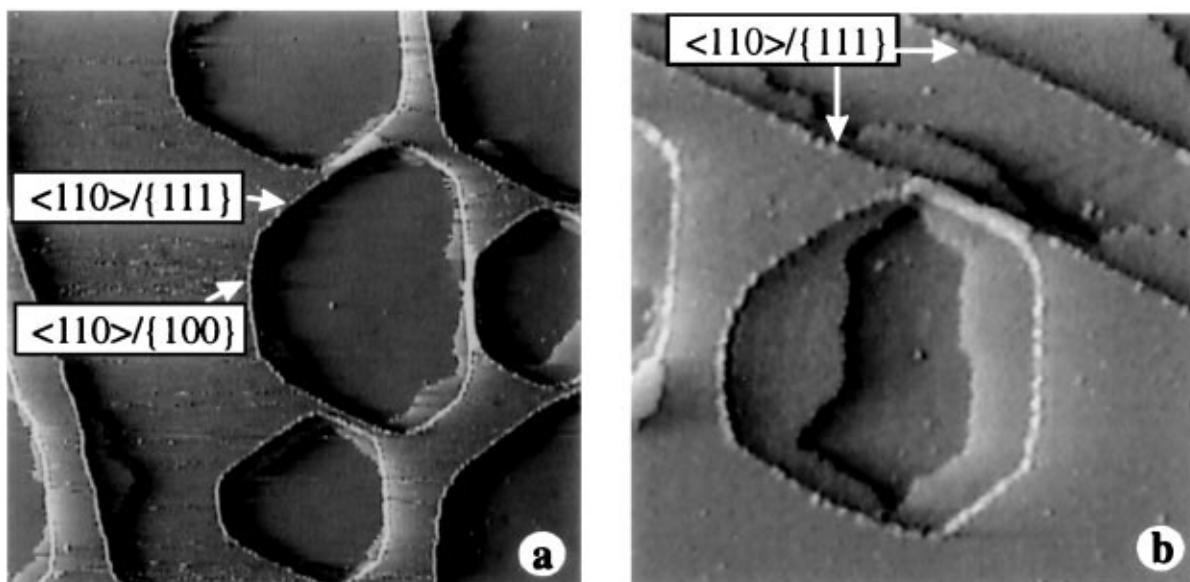
FIG. 1. Adsorption of H_2O on a Pt(111) surface: (a) H_2O exposure with 3×10^{14} molecules/cm^2, $p = 8 \times 10^{-9}$ mbar, $T = 140$ K, 1830 Å $\times$ 1830 Å, $U = -1$ V, $I = 0.2$ nA. (b) H_2O exposure with 6×10^{14} molecules/cm^2, $p = 8 \times 10^{-9}$ mbar, $T = 140$ K, 1090 Å $\times$ 1090 Å, $U = -1$ V, $I = 0.2$ nA. The orientation of the monatomic Pt steps bounding the hexagonal vacancy islands as well as those crossing the image are labeled in (a) and (b), respectively.

At the lower side of the step edges the ice growth in two dimensions continues and it is evident that this growth is not different at the two types of step edges. In contrast, the width of the one-dimensional chains at the upper side of step edges is unchanged. Moreover, the H_2O density above the two different types of steps stays different. Above the short $\langle 110 \rangle / \{111\}$ step H_2O forms a quasicontinuous chain, which occassionally widens on the upper terrace, while the chain at the upper side of the $\langle 110 \rangle / \{111\}$ step consists of isolated segments separated by 20 to 80 Å. The last type of step decoration can also be recognized by looking at the steps crossing Fig. 1(b), which both are of the $\langle 110 \rangle / \{111\}$ type. The distance of 20 to 80 Å between isolated segments is of the order of the typical interkink distance found at the nearly straight steps after the standard preparation cycle. This suggests that the decoration of the $\langle 110 \rangle / \{111\}$ step, in contrast to that of the $\langle 110 \rangle / \{100\}$ step, is due rather to kink decoration than to real step decoration.

As shown above, the adsorption of H_2O on Pt(111) at 140 K starts at the upper and the lower side of step edges. Since the adsorption at the upper side of step edges is more surprising, we will discuss this adsorption in more detail. To compare the binding energy of the H_2O molecules adsorbed at the upper side of step edges with binding energies at other sites, it is necessary to discuss the sticking coefficient and the activation temperatures of different processes. The sticking coefficient of H_2O on the Pt(111) surface at 100 K is 0.7 and coverage independent [14]. We can estimate the sticking coefficient at 140 K from the apparent coverage in the STM images. The coverage in Fig. 1(a) after an exposure with $D = (3 \pm 1) \times 10^{14}$ molecules/cm^2 is $\Theta =$

$(5.5 \pm 1)\%$. Since an ice bilayer on the Pt(111) surface has a density of 1.0×10^{15} molecules/cm^2 [2], the sticking coefficient is $s = 0.18 \pm 0.07$. The sticking coefficient increases with coverage. For the experiment shown in Fig. 1(b) the corresponding values are $D = (6 \pm 2) \times 10^{14}$ molecules/cm^2, $\Theta = (20 \pm 1)\%$, and $s = 0.33 \pm 0.1$. The fact that the sticking coefficient at 140 K is lower than at 100 K and increases with coverage (in contrast to 100 K) suggests that some molecules desorb from the surface *before* they are incorporated into the ice layer. Indeed, we have checked that at 140 K size and shape of the ice layer islands do not change on a time scale of 25 min. This excludes, for this temperature, considerable detachment and desorption of H_2O molecules from the steps of the ice bilayer.

Both processes, detachment from the steps of the ice bilayer and desorption, become observable at 145 K. Figure 2(a) shows an experiment where the Pt surface was first covered with a complete ice bilayer as checked by imaging at 120 K. Then the surface was heated to 145 K. After 6 min Fig. 2(a) was recorded. Partial desorption has taken place and irregular formed ice layer vacancy islands (e.g., I and I_b) appear. As can be seen in Fig. 2(b) the ice layer shows a corrugation due to a superstructure [15], while the regions where H_2O is desorbed is imaged flat similar to the clean Pt(111) surface. In Fig. 2(a) the step edges of the ice layer vacancy islands (I and I_b) appear frizzy. This is in contrast to the step edges of the ice covered Pt vacancy islands (e.g., II). Frizzy steps indicate motion of step edges [16]. The smaller ice layer vacancy island (I_b) has a typical shape of an island, which moves as a whole during the scanning procedure. Such

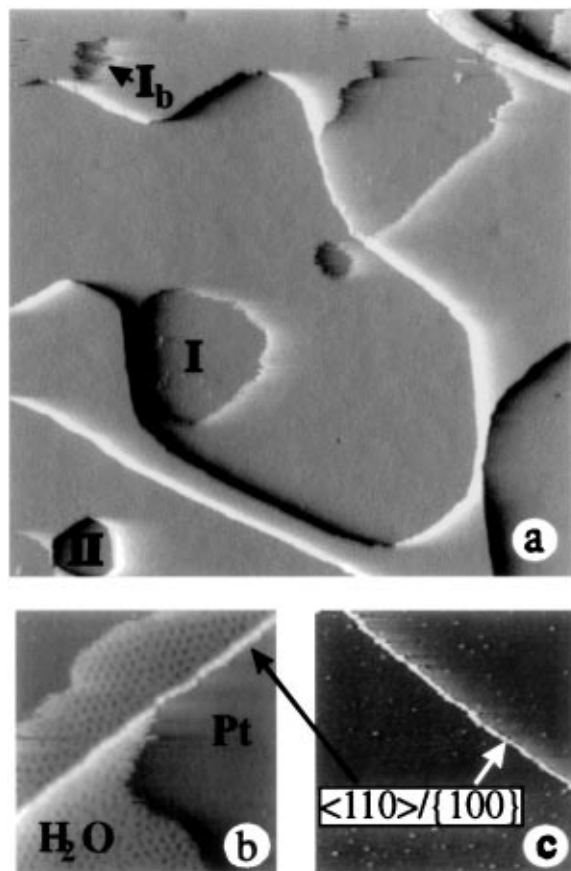FIG. 2. Desorption of H_2O from a Pt(111) surface covered with a full bilayer of H_2O: (a) Bilayer prepared by H_2O exposure with 4×10^{15} molecules/cm^2, $p = 1.1 \times 10^{-8}$ mbar, $T = 140$ K, heated to 145 K and imaged after 6 min at this temperature, 2100 Å $\times$ 2100 Å, $U = -1$ V, $I = 0.2$ nA; I and I_b: vacancy island in the ice layer due to desorption, II: fully ice covered Pt-vacancy island. (b) Bilayer prepared as in (a) but heated to 145 K for 15 min and imaged at 140 K, 390 Å $\times$ 390 Å, $U = -1$ V, $I = 0.2$ nA. (c) Bilayer prepared as in (a) but heated to 160 K for 2 min and imaged at 20 K, 1060 Å $\times$ 1060 Å, $U = -1$ V, $I = 0.2$ nA.

shapes were demonstrated to result from the movement of vacancy islands at speeds comparable to the image scanning [see [17] for the case of Ag(111)]. We have thus observed two apparently different processes which start to take place between 140 and 145 K. One is the desorption of H_2O molecules from the ice covered surface, the other is the change of shape and position of the vacancy islands of the ice bilayer. It is reasonable to assume that a *unique* atomic process is responsible for both: the detachment of H_2O from the edges of the ice bilayer. This would obviously explain the frizzy steps and the moving vacancy islands [17]. On the other hand, since isolated molecules can desorb from the Pt surface even at 140 K, the H_2O molecules detached from the edges of the ice bilayer can easily desorb from the surface at 145 K. The detachment

from edges of the ice bilayer is thus the rate limiting step for desorption.

To desorb the complete bilayer from the Pt terraces, the sample must be heated for more than 20 min to 145 K or for 2 min to 155 K. Such a desorption behavior is compatible with the TDS-bilayer peak between 170 and 180 K measured with a heating rate of 10 K/s [3,4]. In contrast, the ice chain at the upper side of the step edge stays stable after these annealings and even after a 2-min anneal to 160 K. This is demonstrated in Fig. 2(c). The complete bilayer was removed except for the molecules decorating the upper step edge.

We conclude: The H_2O molecules adsorbed at the upper side of step edges are bound thermally more stable than the molecules incorporated in ice islands on the terrace. It is tempting to correlate the desorption from the chains to the TDS peak at 200 K, which was ascribed to water monomers in the IRAS study of Ogasawara, Yoshinobu, and Kawai [6]. However, the high temperature peak reported in Ref. [6] corresponds to about 10% of the bilayer. It seems unlikely that such a large amount of molecules would decorate the upper steps unless the step density has been exceedingly high in the reported experiments.

The preferential adsorption at the upper side of step edges has previously been observed for Xe adsorption on the Pt(111) surface [18]. One might be surprised that H_2O behaves similarly. On the other hand, calculations by Müller [7,19] have shown that the binding mechanisms for H_2O and Xe on Pt(111) are comparable. Both systems have a full sp shell and the attractive interaction with the metal is due to the mixing of these closed shell states with unoccupied Pt $5d$ states. The unoccupied states of the adsorbates lie far above the vacuum level and their interaction with the occupied Pt states is of minor importance. Moreover, it was shown that the dipole moment of the H_2O molecule is not important in the H_2O metal interaction [20].

At the upper side of the Pt-step edges the charge density is reduced due to the Smoluchowski effect. Theoretical considerations show that this is correlated with a d-electron charge transfer from the step atom to the surrounding atoms [21]. The resulting higher density of unoccupied Pt $5d$ states at the upper side of step edges explains that the H_2O molecule and the Xe atom will be more strongly bound at these sites. In addition, the lower charge density above the step edges reduces the repulsive part in the Pt-H_2O interaction and allows the H_2O molecule to get closer to the Pt atom, leading to stronger bonding. This qualitative argument is supported by calculations of Müller, who found that the adsorption energy increases by around 100 meV, when the H_2O molecule is moved from the center of a Pt$_{10}$ cluster representing the (111) surface to the edges of the cluster [22].

The different behavior of the two different steps may be understood in the same way. Besocke, Krahl-Urban, and Wagner [23] have found that the two different steps have different dipole moments. The dipole moment of the $\langle 110 \rangle / \{100\}$ step is 20% higher. Since the dipole moment correlates with a reduced charge density above the step atom, it is understandable that the higher dipole moment of the $\langle 110 \rangle / \{100\}$ step might give rise to a higher binding energy and a preferential occupation of sites at the upper side of this type of close packed step [24]. Of course such a qualitative argument has to be checked by detailed calculations.

In summary, we have shown that H_2O on Pt(111) adsorbs preferentially at the upper side of step edges. The adsorption density above the $\langle 110 \rangle / \{100\}$ step (A) is higher than above the $\langle 110 \rangle / \{100\}$ step (B). This adsorption behavior is consistent with a binding model, which describes the interaction of the unoccupied Pt $5d$ states with occupied H_2O states as the main attractive part of the H_2O binding energy.

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[12] The image in Fig. 1(a) is disturbed by some (bright and dark) stripes in the scanning direction. They are probably due to an interaction of the tip with H_2O molecules. One may speculate that the tip picks up a H_2O molecule and looses it after a certain scanning path.

[13] The steps on the right side of the vacancy islands in Fig. 1(a) are imaged too bright to observe the discontinuity of the ice chains. This is a consequence of the differential imaging mode.

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[24] We can exclude that the electrostatic dipole-dipole interaction between the steps and the H_2O molecule explains the different behavior. We estimated an upper limit of this interaction by assuming that (a) the H_2O molecule is directed parallel to the step dipole, (b) the H_2O molecule keeps its gas phase dipole moment, and (c) the dipole-dipole distance (3.2 Å) is less than the dipole-dipole distance from the calculations [7] (3.5 Å). According to the step dipole moments determined in [24] we find a contribution to the binding energy of 40 and 34 meV for the $\langle 110 \rangle / \{100\}$ and $\langle 110 \rangle / \{111\}$ steps, respectively. Assuming an identical chemical bond the difference between the binding energy at the two steps would be 6 meV, which is too low to explain the experimental observed differences.