

One-Dimensional Zigzag Chain of Water Formed on a Stepped Surface

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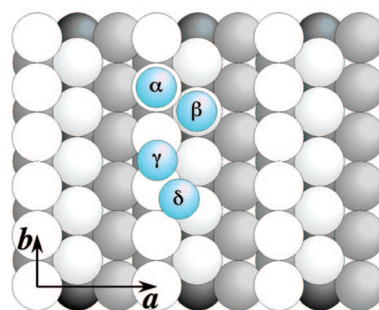
We determined the structure of water at step edges on the stepped Pt(211) = 3(111)–(100) surface using surface X-ray diffraction. Adsorbed water molecules form a chain with a zigzag configuration along the step line through hydrogen bonds. The chain comprises two types of water molecules. One is adsorbed on the top of the step atom and has a shorter Pt–O distance than that adsorbed on terrace sites, which indicates stronger adsorption at step edges. The other is displaced from the precise on-top sites and has an elongated Pt–O distance. The hydrogen-bonding configuration of the water chain is different from the tetrahedral arrangement of ice. The interaction of the water molecules with the surface distorts the hydrogen bonds in the water chain.

Introduction

Small clusters of water and low-dimensional water on surfaces are of crucial importance, not only for chemical processes such as corrosion and heterogeneous catalysis, but also for physiological processes. The structural determination of low-dimensional water is necessary to elucidate the complex hydrogen-bonding configuration and ice-nucleation mechanism. However, it is difficult to preferentially construct the structure of a water cluster with well-defined size on a surface, because the low hopping barrier of adsorbed water induces the formation of inhomogeneously sized clusters and extensive hydrogen-bonding network structure. The structure of water is affected by interaction with other materials. The structures of monomer water and small water clusters adsorbed on surfaces depend on the structure, temperature, and electronic states of the surface.^{1–6} Recently, many studies have focused on the detailed structure of the 2-D (two-dimensional) icelike layer, where water is molecularly or dissociatively adsorbed and the orientation of water is H-up or H-down.^{7–10}

Differences in the interactions between water and the surface may be available for the structural control of low-dimensional water on a surface. The adsorption energies of water at steps and kinks are higher than those at terraces. Scanning tunneling microscopy (STM) has revealed that water molecules are preferably gathered at the upper side of the step on Pt(111).¹¹ The desorption temperature of water adsorbed on a step is higher than that on a terrace, according to a temperature-programmed desorption (TPD) study,¹² which indicates that the adsorption sites of water can be controlled by temperature. Density functional theory (DFT) calculations have predicted that a one-dimensional (1-D) water chain is formed along the step edge by OH...O hydrogen bonding.^{12,13} These calculations of the zigzag water chain predicted different structural models and adsorption energies.

Top view



Side view

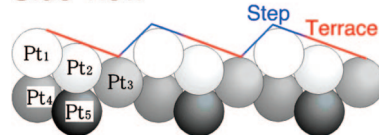


Figure 1. Schematic model of Pt(211). The blue circles indicate the adsorption sites of water: (α) atop site on the step, (β) atop site on the terrace, (γ) bridge site on the step, and (δ) bridge site on the terrace. The Pt(211) surface has three atomic rows: the step (Pt₁), the terrace (Pt₂), and the corner (Pt₃).

In this investigation, the structure of water adsorbed on a stepped surface was determined using surface X-ray diffraction (SXD). In order to elucidate the structure of 1-D water, the Pt(211) surface was used as a template substrate. Pt(211) has well-defined step lines with high density, as shown in Figure 1. X-ray diffraction of a high-index plane has been used to successfully determine the detailed structure of regularly arranged molecules on a step. Although water at surface defect sites, such as steps, has been thought to play an important role in catalytic reactions, the detailed adsorption structures have not been studied experimentally. The present study shows that the specific behavior of water adsorbed on a step is different from that of icelike water on a terrace.

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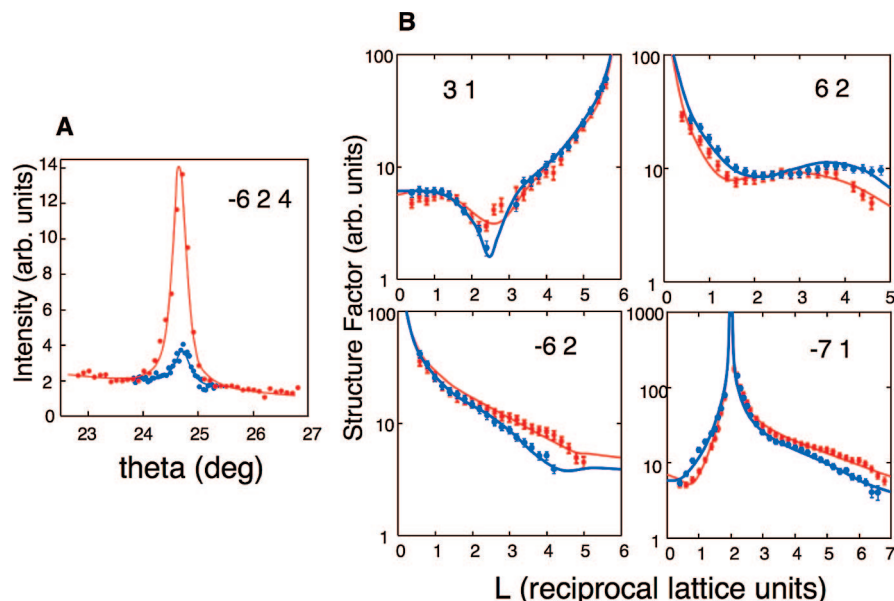


Figure 2. (A) X-ray diffraction profiles measured by rocking scan around the axis normal to the surface at $(HKL) = (-6\ 2\ 4)$ for clean (red circles) and water-adsorbed Pt(211) (blue circles). (B) Structure factors from the $(HK) = (3\ 1)$, $(6\ 2)$, $(-6\ 2)$, and $(-7\ 1)$ CTRs of clean (red crosses) and water-adsorbed Pt(211) (blue circles). Solid lines are calculated structure factors from the optimized model.

Experimental Section

The Pt(211) sample (Surface Preparation Laboratory, The Netherlands) was prepared by repeated cycles of Ar^+ bombardment and annealing at 1100 K, until a sharp (1×1) low-energy electron diffraction (LEED) pattern was obtained. We have reported that Pt(211) is reconstructed into a (2×1) structure after annealing above 1200 K, whereas the surface has a (1×1) structure with annealing below 1150 K.¹⁴ Deuterium oxide (D_2O) was used in order to reduce beam damage. D_2O was purified under vacuum by freeze–thaw cycles to remove remaining impurities. Surface X-ray diffraction measurements were performed with an ultrahigh vacuum (UHV) chamber mounted on a $(2 + 2)$ -circle diffractometer at BL13XU (SPring-8) for surface and interface structure determination.¹⁵ The X-ray wavelength used was 0.061 nm. The incident angle was fixed at 0.7° (α fixed mode). A scintillation counter was used as the detector, and Soller slits with an angular resolution of 0.4° were used. The slits in front of the detector were fully opened. Integrated intensities were corrected for Lorentz and polarization factors. A rectangular surface coordinate system was used for the Pt(211) crystal in which the reciprocal wave vector was $Q = Ha^* + Kb^* + Lc^*$, where $a^* = 2\pi/a$, $b^* = 2\pi/b$, $c^* = 2\pi/c$, $a = 679.7$, $b = 277.5$, $c = 961.3$ pm, and L is along the direction normal to the surface.¹⁶ Structure refinements were conducted using the least-squares method with the ANA-ROD program.¹⁷ Optimization of structural parameters, scale factors, surface fraction factor, occupancy factor, and roughness factor were performed. All parameters were refined simultaneously using crystal truncation rods (CTRs).

Results and Discussion

Surface X-ray diffraction analysis of a clean Pt(211) surface without adsorbed water was conducted first. The integrated intensity of 506 reflections along 21 CTRs was collected by rocking scans around the axis normal to the surface, as shown in Figure 2A. The structure factors were averaged assuming the Pm space group and yielded 305 independent reflections with a reproducibility of 8.9%. Structural analysis was performed by optimization of the atomic coordination from the

topmost (Pt_1) to the fifth (Pt_5) layer, in order to minimize the least-squares residual between the observed and calculated structure factors. The total number of free parameters was 17. One Pt atom is contained in the unit cell of each layer, which has two degrees of freedom in the x and z directions, based on the assumption of the Pm space group. The optimized structure provides a good fitness of $\chi^2 = 2.48$. Figure 2B shows typical profiles of the observed and calculated structure factors along the rods. The atomic positions of the refined structure of clean Pt(211) are listed in Table 1A.

Figure 3A shows the optimized model of the clean Pt(211) surface. Surface relaxation was observed: the atoms in the first and the second layer are shifted downward by 24(1) and 9(1) pm, respectively, compared with the ideal bulk terminated positions. The interlayer spacings of the first and second layers are 61(2) and 77(1) pm, respectively. A similar contraction was observed for reconstructed Pt(211).¹⁴ Displacement of the atoms below the third layer is within 4(1) pm.

Water was dosed on clean Pt(211) at a surface temperature of 25 K using a pulse doser, and the sample was then heated to 155 K for 5 min for the desorption of water on the (111) terrace. It was confirmed that water is adsorbed on the step using TPD. TPD from 1 ML (monolayer) of water revealed two desorption peaks at 170 and 190 K, which correspond to water desorption from the terrace and the step, respectively. After the sample was heated to 155 K for 5 min, the desorption peak at 170 K disappeared, indicating that water adsorbed on the terrace can be removed by heating to 155 K, which is consistent with previous STM and TPD results.^{11,12} A single desorption peak at 190 K remained after the X-ray measurements. A total of 587 reflections were collected along 21 CTRs at 25 K. After each rod measurement, the sample was annealed to 1100 K and adsorbed water was once again prepared. The CTR profiles after annealing are identical to those of the clean surface. Averaged structure factors, assuming the Pm space group, yielded 328 independent reflections with a reproducibility of 7.6%. The CTR profiles of Pt(211) with adsorbed water are obviously different from those for the clean surface, as shown in Figure 2. For the structure determination of adsorbed water, five initial models

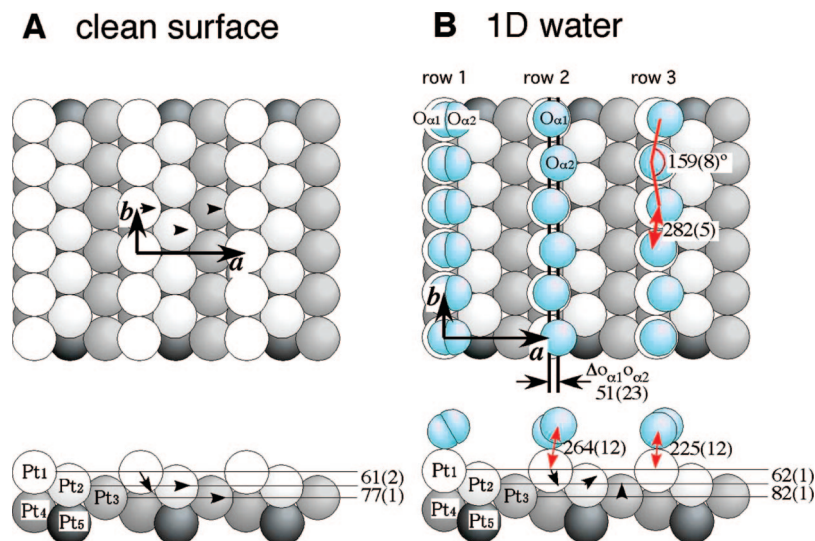


Figure 3. Schematic model of clean Pt(211) (A) and water adsorbed on Pt(211) (B). Arrows indicate the direction of atomic shift from the bulk position. Row 1 indicates the model obtained using crystallographic data and assuming the Pm space group. Rows 2 and 3 indicate the final structure models.

TABLE 1: Atomic Coordinates, Roughness Factor, and Surface Fraction for the Optimum Geometry of a Clean Pt(211) Surface (A) and Water Adsorbed on a Pt(211) Surface (B)^a

	(A) clean Pt(211)			(B) water adsorbed on Pt(211)		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
O _{α1}				0.0613(80)	0.0000	0.7176(108)
O _{α2}				0.1216(71)	0.0000	0.7487(106)
Pt ₁	0.0173(6)	0.0000	0.4788(10)	0.0078(4)	0.0000	0.4865(5)
Pt ₂	0.3462(5)	0.5000	0.4152(8)	0.3446(4)	0.5000	0.4224(9)
Pt ₃	0.6719(4)	0.0000	0.3348(6)	0.6673(5)	0.0000	0.3370(5)
Pt ₄	−0.0009(4)	0.5000	0.2481(5)	−0.0032(3)	0.5000	0.2490(4)
Pt ₅	0.3340(3)	0.0000	0.1663(4)	0.3358(4)	0.0000	0.1695(4)
Pt ₆	0.6667	0.5000	0.0833	0.66667	0.5000	0.0833
roughness factor		0.00(3)			0.146(37)	
surface fraction		1.00(2)			0.994(8)	
χ^2		2.48			1.91	

^a The coordinate system is rectangular. $a = 679.7$, $b = 277.5$, $c = 961.3$ pm, and $\alpha = \beta = \gamma = 90^\circ$. The z position of the seventh platinum layer (Pt₇) is defined as $z = 0$.

were considered for the water adsorption site: an atop site on the step (α), an atop site on the terrace (β), a bridge site on the step (γ), a bridge site on the terrace (δ), and two atop sites on both the step and terrace ($\alpha + \beta$), as illustrated in Figure 1. The models α – δ contain one oxygen in the unit cell. The total number of free parameters is 19. We also used the model without water. The atomic positions of Pt and water oxygen were optimized, because the position of hydrogen atoms could not be determined due to the small scattering cross section. Structural refinements show that model α (adsorption at an atop step site) is in good agreement with the experimental data obtained with a χ^2 value of 1.94. Model β and the clean surface gave χ^2 of 2.15 and 2.24, respectively. However, for models γ , δ , and $\alpha + \beta$, the atomic parameters of oxygen diverged, and these models did not yield appropriate structures. The χ^2 for model α was improved by more than 10% compared with that of model β . The X-ray scattering cross section of oxygen is significantly smaller than that of platinum ($Z_{\text{Pt}}^2/Z_{\text{O}}^2 = 95$). The improvement of χ^2 implies a significant structural difference between models α and β . It was determined that water oxygen prefers the atop site of a step (α) to that of a terrace site (β). The Pt–O bond lengths in models α and β were 243(8) and 224(8) pm, respectively.

If all the oxygen atoms of water are located at the same position of the step, a straight chain structure would be formed

by OH...O hydrogen bonding with neighboring water molecules. However, previous DFT calculations suggest that zigzag chains created by hydrogen bonding are stable.^{12,13} The model was then optimized by the incorporation of two oxygen atoms at the same step site in the unit cell, in order to determine whether the water arrangement is straight or a zigzag chain. After structural refinement with 22 free parameters, two different oxygen atoms (O_{α1} and O_{α2}) separated by $\Delta_{\text{O}_{\alpha1}\text{O}_{\alpha2}} = 51(23)$ pm were found, which provided a final χ^2 of 1.91. The goodness of χ^2 was slightly improved by using the model with two different oxygen atoms. Row 1 in Figure 3B shows the optimized model assuming the Pm space group. The atomic coordinates and structural parameters are listed in Tables 1B and 2, respectively.

The positions of the two oxygen atoms (O_{α1} and O_{α2}) are very close to each other (51(23) pm); therefore, they cannot occupy the same site at the same time. The occupancy factor of each oxygen is equally 47(6)%. This means that one Pt atom of the step site can be occupied by either one of two different oxygen, because water has a statistically disordered structure. Water O_{α1} is located nearer from the surface (225(12) pm) than water O_{α2} (264(12) pm). The different Pt–O distances can be explained by water O_{α2} forming hydrogen bonds with water O_{α1} at neighboring atop sites. Two waters (O_{α1} and O_{α2}) can be alternately adsorbed at the atop sites, forming a zigzag chain

TABLE 2: Structural Parameters of the Zigzag Water Chain Adsorbed on Pt(211) at 25 K

parameter	length (pm) or angle (deg)
Pt–O _{α1}	225(12)
Pt–O _{α2}	264(12)
O _{α1} H–O _{α2} or O _{α2} H–O _{α1}	282(5)
ΔO _{α1} O _{α2}	51(23)
∠O _{α1} O _{α2} O _{α1} or ∠O _{α2} O _{α1} O _{α2}	159(8)

as shown by rows 2 and 3 in Figure 3B. The occupancy factors of the first and second Pt layers are 92(4)% and 93(1)%, respectively, whereas that of Pt atoms below the third layer is 99(1)%. Adsorbed water is saturated at the step, according to the coverage estimated by $47(6) \times 2/92(4) = 1.0$. Water molecules are not isolated as a monomer species, but instead form a 1-D chain by hydrogen bonding to neighboring water molecules. A small part (<8%) of the surface may be reconstructed to form a complicated structure even at 1100 K. The Pt(211) surface is reconstructed to a more stable (2×1) structure by thermal annealing, and the fractional order reflection of the reconstructed surface is clearly observed above 1200 K.¹⁴

The SXD data does not reveal the position of hydrogen atom; therefore, the detailed configuration of the OH...O hydrogen bonding is uncertain. Vibrational and X-ray spectroscopic studies are necessary for the elucidation of the hydrogen-bonding structure; however, many theoretical studies for 1-D zigzag water suggest that one hydrogen atom of each water participates in hydrogen bonding, i.e., single hydrogen-bond donor and acceptor.^{12,13,18} From infrared reflection absorption spectroscopy (IRAS) study on Pt(533), only the hydrogen-bonded OH stretching band was observed, and the absence of a free OH band indicated that free OH is parallel to the surface, because of the surface selection rule.¹² Final structure results in a 159(8)° angle for adjacent O_{α1}–O_{α2} axes. It is well-known that the structural arrangement of water in bulk ice (*Ih* or *Ic*) obeys the Bernal–Fowler–Pauling (BFP) rules.^{19,20} According to the BFP rules, water oxygen in ice is tetrahedrally bonded to four other oxygen atoms and there is only one hydrogen atom on each O–O axis. The angle between the neighboring O–O axis is 109°. The 1-D arrangement of water induces distortion to form the typical hydrogen-bonding configuration. The water (O_{α2}) is unable to approach the surface, due to the distortion of the hydrogen-bonding geometry with neighboring water molecules. If the 1-D chain obeys the BFP rules, then ΔO_{α1}O_{α2} is 160 pm. The interaction of a second water molecule with the surface reduces the separation of the zigzag chain. The averaged OH...O length is 282(5) pm, which is comparable to a typical hydrogen-bonding distance.

The OH bond of the water is dissociated, producing an adsorbed hydroxyl group (OH_{ad}) and oxygen (O_{ad}) on many transition metal surfaces.¹ The formation of a mixed layer of OH and water has also been reported on Ru(001) and oxygen-precovered Pt(111).^{7–9,21} The oxygen atoms of OH_{ad} and water form a coplanar layer on these surfaces. However, the formation of OH_{ad}, O_{ad}, and a mixed layer of OH and water can be excluded from the following reasons. According to Figure 3 and Table 2, the two oxygens are not planar, but the Pt–O bond lengths of O_{α1} and O_{α2} at the step edge are 225(12) and 264(12) pm, respectively. It has been reported that the Pt–O bond length of OH_{ad} is below 210 pm.²² The Pt–O bond lengths of adsorbed oxygen are much shorter than those of water and OH_{ad}, and the favored adsorption site is the hollow site rather than the atop site.²³ Although a large number of theoretical studies have been carried out to determine the adsorption structure of water on

metal surfaces, there are few reports that have experimentally determined the bond lengths between metal and water oxygen. We have determined the adsorption structure of monomer water on Ni(111).²⁴ The Ni–O distance is 224 pm, which is comparable to that of Pt–O in this study. However, the atomic radius of Ni is smaller than that of Pt. The Pt–O bond length of adsorbed water is 0.23–0.24 nm on Pt(111).⁸ The Pt–O_{α1} distance (225(12) pm) on Pt(211) is shorter than that on Pt(111), which may imply stronger adsorption energy of a water molecule at the step site. DFT calculations of the zigzag water chain predicted different structure models: the water (O_{α2}) is far from the surface (317 pm) in one model,¹² whereas it binds directly to the step site (245 pm) in the other.¹³ The water (O_{α2}) obtained from experimental result is located between the two models. At this time, we cannot explain why our experimental result differs from those of DFT calculations. In the case of adsorbed water on transition metal surfaces, there are some contradictions between theoretical calculations and experimental results. Water oxygen binds strongly to step Pt atoms via the oxygen lone pair. This explanation is rationalized by the fact that the upper site of the step edge is positively charged due to the Smoluchowski effect. A positively charged step atom may induce the donation of electrons from the lone pair.²⁵ The oxygen lone pair of water then acts as an electron donor and the substrate acts as an electron acceptor.

The layer distance between Pt₁ and Pt₂ of water adsorbed on Pt(211) are also contracted similar to those of clean Pt(211). However, the vertical positions of Pt₁ and Pt₂ are shifted upward by 7 pm compared with the clean surface. This displacement is due to attractive forces between surface atoms and water, and Pt–O bond formation weakens the internal bonds of the substrate atoms. The upward shift of surface atoms caused by water adsorption has also been reported on Ru(0001) and Ni(111).^{24,26} Water adsorption reduces surface relaxation, which has been observed in other adsorption systems.

Conclusion

The formation of a 1-D zigzag water chain was observed along the step line on the stepped platinum surface using SXD. The water molecule is preferably adsorbed at the step site. Two types of adsorbed water are found at the step site. One type is strongly adsorbed on the step atom, and the other binds to the neighboring adsorbed water via hydrogen bonding. The Pt–O bond lengths of the two waters imply that both molecules interact with Pt atoms. The structural arrangement of the water chain is governed by the strong interaction with Pt step atoms as well as intermolecular hydrogen-bonding interactions.

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Supporting Information Available: Other CTR profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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