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Scanning Tunneling Microscopy Study of Water Molecules on Pd(110) at Cryogenic Temperature

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We show scanning tunneling microscopy (STM) images of water molecules on Pd(110) at a cryogenic temperature of 4.7 K which enables the observation of isolated water molecules. We observe water-induced features in the STM images in a low-coverage region (~ 0.02 ML), which can be classified in terms of height; namely, (A) 0.15 Å, (B) 0.3 Å and (C) 0.55 Å, observed at $V_s = -100$ mV. In a high-coverage region, feature C dominates and forms a local c(2×2) structure. Since the ordered structure is identical with the previously reported superstructure of bilayer water on Pd(110), feature C should correspond to a tetramer of water molecules, a unit of bilayer water. Feature A is located on the Pd(110) row. Since feature A is the smallest one, we consider that this corresponds to the monomer of the water molecule whose existence has been observed previously at temperatures below 10 K by electron energy loss spectroscopy (EELS) measurement. [DOI: 10.1143/JJAP.41.4932]

KEYWORDS: scanning tunneling microscopy (STM), water, Pd(110), gas adsorption, adsorption geometry

1. Introduction

Water adsorption has been investigated using various surface science techniques.[1–11] This is partially due to the rising interest in combining the biological techniques and the processes of metal and semiconductor surfaces. Although a water molecule has a simple structure, its adsorption on metal surfaces has special features that cannot be observed in other adsorption systems. This is mainly due to the strong hydrogen bonding between water molecules that is of the same order as that between the metal and the water molecule and makes the formation of a water cluster easier. Thus, a number of the previous experiments of water adsorption on metal surfaces have been executed on condensed water, where the direct interaction between the metal and the water molecule is masked. However, the interaction between the water molecule and the metal surface is of great interest, since the bonding is formed between a lone pair of a water molecule and metal orbitals whose nature has not been well understood.

In the current report, we show scanning tunneling microscopy (STM) observation of the adsorption of water molecules on the Pd(110) surface at cryogenic temperature. The STM observation at liquid He temperature has recently attracted attention, partially due to the success of measurement of inelastic tunneling spectroscopy (IETS) using STM on a single adsorbate,[12] which enables the direct measurement by vibrational spectroscopy of a single molecule. At the same time, the diffusion of adsorbates is reduced at low temperature, which quenches the motion of the adsorbates before they encounter other adsorbates and form clusters. The images we present in this paper clearly show a water molecule in an isolated form, as well as a locally ordered structure which corresponds to the reported c(2×2) superstructures of bilayer water. To our knowledge, this is the first direct observation of a water molecule in an isolated form.

2. Experimental

All experiments were performed using a low-temperature STM (LT-STM, Omicron GmbH) with an electrochemically etched tungsten tip equipped in an ultrahigh vacuum chamber ($< 3 \times 10^{-11}$ Torr). The Pd(110) surface is kept at 4.7 K during imaging. For the dosing of gas molecules, the sample is detached from the STM cold head and is placed in front of a dosing tube with part of the sample holder being attached to a wobble stick which is pre-cooled with liquid N_2. The dosing process, which starts with the detachment of the sample and ends with returning the sample to the STM head, can be accomplished within 10 s at the fastest. Due to the short time period required for dosing, the increase of the sample temperature is small; the maximum temperature is expected to be below ~ 50 K from the experiment of rare-gas adsorption.

3. Results

A typical topological STM image of the Pd(110) surface is shown in Fig. 1, where a submonolayer coverage of water molecules is dosed on the surface (~ 0.02 ML). The inset image shows a clean Pd(110) surface observed prior to the dosing of water molecules. The Pd row in the $[1\bar{1}0]$ direction, along which Pd atoms are closely packed, follows the diagonal direction from upper left to lower right. Both images are shown in the identical crystallographic direction. The water-induced features are observed as protrusions and bright spots in the image. The variation of these features in the image under a bias voltage and with different conditions of the tip apex, such as that of being coated with a water molecule, is small compared with other simple adsorbates. For example, a CO molecule on Pd(110) is imaged either as a protrusion or as a dip depending on the bias voltage.[13] In addition, CO is observed as a dark feature when the tip has picked up a CO molecule and the surface is imaged with the molecule at the tip apex.[13] In the case of the water molecule observation, such contrast reverse is not observed.

We observe three water-induced features in the image

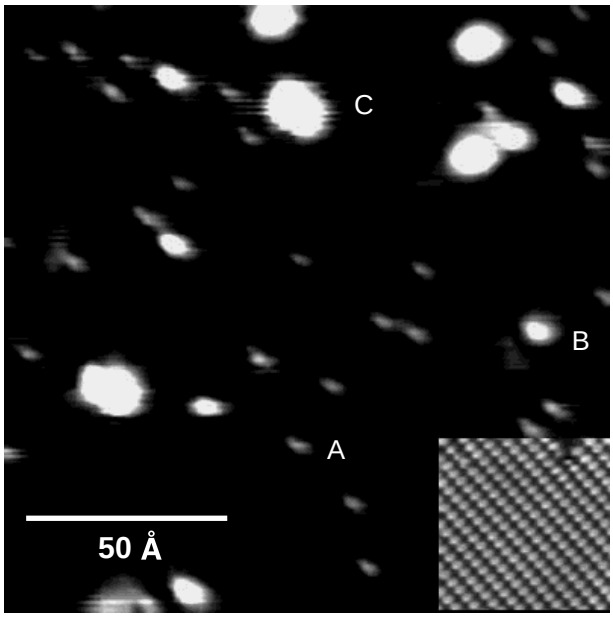

Fig. 1. STM topographic image of submonolayer water molecules adsorbed on Pd(110) surface. Water molecules are dosed at a temperature below 50 K, and STM observation is executed at the sample temperature of 4.7 K. Imaging conditions are $V_{\text{sample}} = -100\,\text{mV}$ and $I_{\text{tunnel}} = 1\,\text{nA}$, and the length-scale is shown in the figure. Inset shows a clean Pd(110) surface obtained prior to dosing of water molecules (area $45 \times 45\,\text{Å}^2$). The crystallographic direction is identical for both images, and the $[1\bar{1}0]$ direction corresponds to the direction from upper left to lower right. Marks A-C correspond to three features induced by the dosing of water molecules, whose typical heights are 0.15 Å, 0.3 Å, and 0.55 Å, respectively.

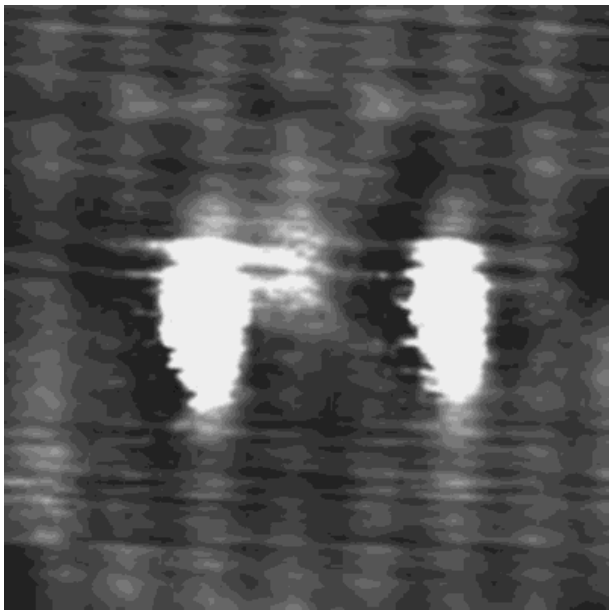

Fig. 2. High-resolution image of feature A which has the characteristic height of 0.15 Å (area $28 \times 28\,\text{Å}^2$, $V_{\text{sample}} = -60\,\text{mV}$ and $I_{\text{tunnel}} = 1\,\text{nA}$). The feature at the Pd row ($[1\bar{1}0]$ direction) is visible in the vertical direction. The elongated water feature is located on the Pd row.

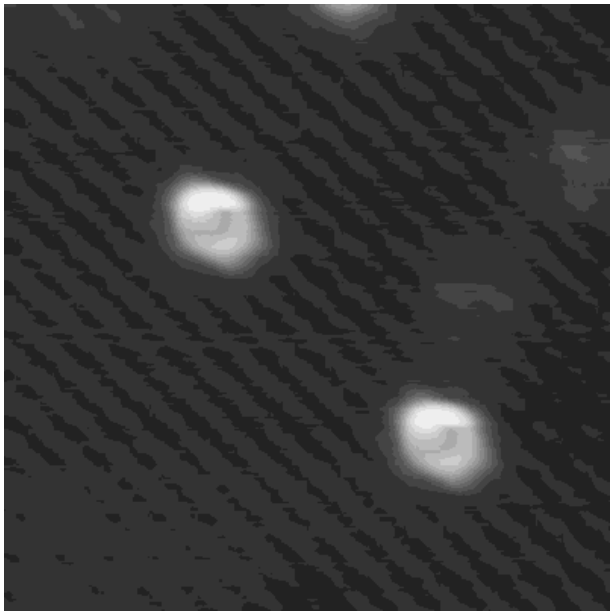

Fig. 3. High-resolution image of feature C with a typical height of 0.55 Å (area $75 \times 75\,\text{Å}^2$, $V_{\text{sample}} = -50\,\text{mV}$ and $I_{\text{tunnel}} = 1\,\text{nA}$). The feature at the Pd row ($[1\bar{1}0]$ direction) is visible in the diagonal direction. The feature induced by the water molecule has a circular shape with a bright and dark contrast in the head and tail of the molecule. The center of the feature is located at the trough of the Pd row.

shown in Fig. 1. They can be classified by height and we refer to them as features A, B, and C with nominal heights of 0.15 Å, 0.3 Å, and 0.55 Å, respectively, observed at $V_{\text{sample}} = -100\,\text{mV}$. The observed heights listed above are too small to be the actual height even for a water monomer regardless of its bonding configuration. The STM tip is basically tracing the contour that gives the same density of states.[13] Since the density of states induced by water adsorption near the Fermi level is expected to be small, the observed height of the water molecule is much smaller than the actual height of the molecule.

The observed height shows a slight bias voltage dependence. Feature B shows a decrease in height with increasing amplitude of the bias voltage; its height is 0.38 Å at $V_{\text{sample}} = -20\,\text{mV}$ and 0.3 Å at $V_{\text{sample}} = -100\,\text{mV}$. On the other hand, feature C shows an increase in height with voltage; it is 0.45 Å at $V_{\text{sample}} = -20\,\text{mV}$, and 0.55 Å at $V_{\text{sample}} = -100\,\text{mV}$. The difference of the bias-dependent height variation should correspond to the difference of the electronic states detected by the STM tip. The height of feature A does not show strong dependence on the bias voltage, which is ~ 0.15 Å.

Next we show a high-resolution image of features A and C. A magnified image of feature A is shown in Fig. 2. Pd(110) rows along the $[1\bar{1}0]$ direction can be seen in the perpendicular direction, where the distance between the rows is 3.9 Å. The water-induced bright area is elongated along the row; the length of the bright area is 7–8 Å along $[1\bar{1}0]$ but its width is less than 3 Å. There are bright spots on the row, but their position along the row cannot be detected with the resolution obtained.

A high-resolution image of feature C is shown in Fig. 3. This particular image is observed with the tip apex coated with water molecules. We intentionally scanned the surface at a reduced gap distance so as to pick up a water molecule. The reasons we consider that the image is obtained with the water molecule on the apex of the tip are as follows. First, the corrugation of the atomic structure of the Pd(110) substrate is significantly higher than that with a bare metal surface. Second, the IETS spectra show distinct features even when measured on a bare metal area.[14,15] The image obtained with

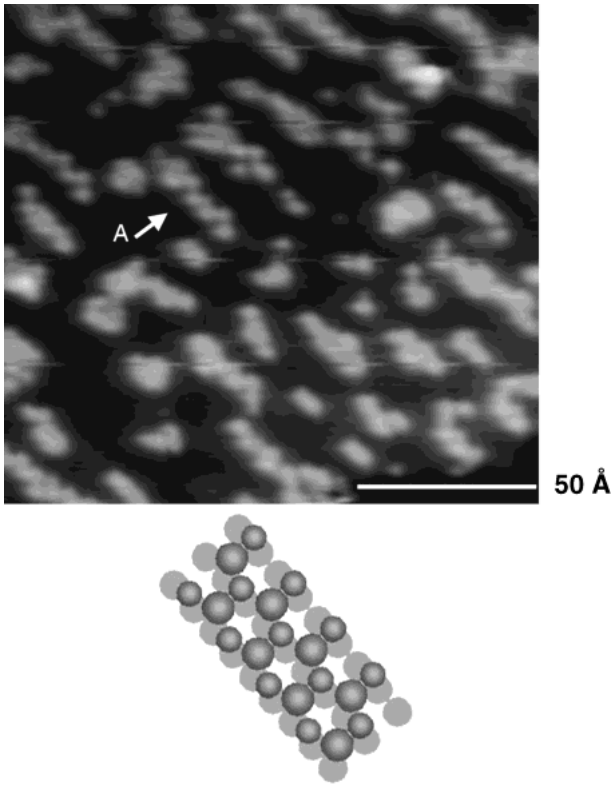

Fig. 4. Topographic image of water molecule on Pd(110) obtained under the conditions of $V_{sample} = -60\,mV$ and $I_{tunnel} = 1\,nA$. Clusters of water molecules on the bare Pd(110) surface with the height of 0.55 Å can be observed. The ordered c(2 × 2) structure of water molecules on Pd(110) proposed in a previous report is shown in the schematic model in the lower panel. The large and small circles with gradation correspond to the oxygen atoms in the top and the second layers of water, respectively (bilayer model). The gray circles correspond to the substrate Pd atoms. The zigzag features observed in the left-panel marked A correspond well with the water molecules in the top layer.

water molecules on the tip apex, however, has an especially high resolution for the determination of the bonding site of the water molecule.[15)]

The image has a characteristic ring shape with bright and dark contrast in the head and the tail of the molecule along the [1$\bar{1}$0] direction. It is evident that the center of the ring is positioned on the trough of the Pd row, although its position along the Pd row is difficult to determine.

When a substantial amount of water molecules are dosed on the surface, water clusters are formed on the surface whose typical image is shown in Fig. 4. The amount of dosed water molecules is larger than that in Fig. 1, but the coverage is still in the submonolayer region, and both clusters and the bare Pd(110) surface are observed. In addition to the increase in the amount of dosed water molecules, the substrate temperature at the time of dosing is higher than that in the case in Fig. 1 due to the increase in the dosing time period. Both conditions promote the collision of the impinging water molecules with each other and thus the formation of clusters of water molecules.

The protrusions have a height of 0.55 Å that agrees with that of feature C in Fig. 1. The crystal direction is the same as that in Fig. 1, and we can identify chain-like water-induced features along the [1$\bar{1}$0] direction. In addition, zigzag-shaped structures can be identified inside the cluster, a clear example of which is marked A in Fig. 4. Although the domain size of the local ordering is small, the superstructure coincides with the reported ordered structure of water on Pd(110) that has the c(2 × 2) structure. In the lower panel, we show a schematic of the c(2 × 2) structure proposed for water molecules on Pd(110).[3,5)] It is based on a model in which a bilayer of water molecules forms a stable bonding configuration. The large and small gray circles with gradation correspond to oxygen atoms of the water molecules in the top and the second layer, respectively. The zigzag-shaped chain of protrusions marked A in Fig. 4 corresponds well with the positions of the water molecules in the top layer.

The correlation of the heights observed for feature C in Fig. 1 and the clusters with the local ordered structure in Fig. 4 suggest that feature C is the unit of the bilayer structure of water molecules.

4. Discussion

We discuss water cluster formation and the origin of the STM features observed for a low-coverage surface. The clusters of water molecules are considered to be formed in a process in which the impinging molecules migrate on the surface before their motion is quenched. Thus we expect more water clusters on the surface if a greater amount of water molecules are dosed at a higher substrate temperature. The difference between the water-induced feature shown in Fig. 1 and that in Fig. 4 could be due to this mechanism; the surface in Fig. 4 appears to contain more water clusters. The chain structure in Fig. 4 is possibly the initial stage of the formation of a wide domain of c(2 × 2) structures which has been reported previously.[3,5)]

The mechanism underlying the initial formation of a one-dimensional chain structure instead of the two-dimensional structure is not clear at this stage. However, the mechanism might be similar to the case of chain structure formation of CO on a Pd(110) surface.[13)] A one-dimensional (1D) CO chain structure along [1$\bar{1}$0] with a two-time periodicity is formed before the formation of a two-dimensional c(2 × 2) structure. For the CO case, we have learned that the hopping of CO is restricted on the Pd row and the inter-row hopping apparently has a higher barrier, which contributes to the formation of the 1D structure. By analogy, the chain structure formation of water molecules might suggest anisotropic hopping of water molecules along the Pd row.

In the structures proposed for a bilayer of water molecules,[3,5,10)] the unit is considered to be a tetramer that is composed of three water molecules in the second layer and one water molecule in the top layer at the hollow position of the second layer. An isolated tetramer corresponds to feature C in Fig. 1 based on the observed height. In addition, the center of the bright spot of feature C is located on the trough of the Pd(110) row. The water molecules at the top layer are located at the trough in the model shown in Fig. 4,[3,5)] which is consistent with the case of feature C.

Both features A and B in Fig. 1 are observed to be lower in height than feature C. Thus, we consider that the number of water molecules contained in features A and B is smaller than that of the tetramer, i.e., four. Since we did not observe any water-induced feature smaller than feature A, it is likely that feature A corresponds to the monomer of the water molecule.

The existence of the water monomer on Cu(100) and Pd(100) surfaces has been reported at the temperature of 10 K.[1)] If we assume that the STM detects the position of the oxygen atom of the molecule, the bonding site proposed for Cu(100) and Pd(100) is consistent with the STM images of feature A shown in Fig. 2 where the bright spots are located on the Pd rows.

Although feature A is most likely the monomer of a water molecule, we cannot reject the possibility that it corresponds to a dimer of water molecules. One of the reasons is the elongated shape of feature A shown in Fig. 2. The protrusion has the length of 7–8 Å along the $[1\bar{1}0]$ direction and the width of ~ 3 Å. As the bonding site is expected to be the on-top position of the Pd atoms, the elongated shape along the $[1\bar{1}0]$ direction can easily be explained if feature A is a dimer in which two water molecules are combined along the Pd row.

However, the question remains why a smaller unit corresponding to a monomer cannot be identified at all in Fig. 1. One possibility is that the impinging water molecules are originally dimers. To confirm this possibility, it is necessary to dose water molecules at an even lower temperature. The modification of the dosing system for this purpose is under way.

5. Summary

We have shown STM images of water molecules on Pd(110) at a cryogenic temperature of 4.7 K. The reduced diffusion length of the adsorbate at low temperature contributes to the quenching of the lateral motion of impinging molecules before the formation of clusters of adsorbates. To our knowledge, an isolated water molecule was imaged by STM for the first time in the current study. We observe three water-induced features in STM images in a low-coverage region (~ 0.02 ML), which can be characterized by their height; namely, (A) 0.15 Å, (B) 0.3 Å and (C) 0.55 Å, observed at $V_s = -100$ mV. In a high-coverage region, feature C dominates and forms a local c(2×2) structure. Since the ordered structure is identical with the previously reported superstructure of bilayer water on Pd(110), feature C is thought to correspond to a tetramer of water molecules, which is a unit of bilayer water. The magnified image of the isolated feature C shows that its center is located on the trough of Pd(110), which is also consistent with the structural model proposed for the bilayer water with a c(2×2) structure. Feature A is located on the Pd(110) row. Since feature A is the smallest feature, we currently consider that this corresponds to the monomer of a water molecule whose existence has been observed previously at a temperature below 10 K by electron energy loss spectroscopy (EELS) measurement. However, the image is elongated along $[1\bar{1}0]$ with a bright area of ~ 7–8 Å; thus the possibility that feature A corresponds to a dimer of water molecules still remains.

Acknowledgments

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