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Vibrational study of water dimers on Pt(1 1 1) using a scanning tunneling microscope

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ABSTRACT

Adsorption and diffusion of isolated water molecules such as monomers and dimers on Pt(1 1 1) surface were directly observed by the scanning tunneling microscopy (STM) at very low coverage and at low temperature. A water dimer appears as a 6-fold symmetric "flower-like" protrusion, which can be explained based on the model that a hydrogen bond acceptor molecule in the dimer is rotating around a donor molecule. We obtained vibrational spectrum of individual water dimers by means of single-molecule vibrational spectroscopic method from the vibrationally-induced lateral hopping motions. Analyzing the spectra suggests a detailed model for adsorption structure of a water dimer where an acceptor molecule of the dimer points toward the surface to form O–H–Pt hydrogen bonding.

1. Introduction

The adsorption and diffusion of water molecules on metal surfaces play an important role in various fields of surface science, such as electrochemistry, heterogeneous catalysis and corrosion. Among the numerous studies on water on well-defined metal surfaces, one of the most intensively investigated topics would be the bilayer structures on metal surfaces [1–6]. Water bilayers consist of both molecule–metal bondings and intermolecular hydrogen bondings, which make the system complicated and make it difficult to understand the influence of each interaction on the structural and chemical properties of the total system. When it comes to isolated monomers and dimers, we can easily consider those interactions separately, because monomers have only a molecule–metal bonding and dimers, the smallest water cluster, have two types of molecule–metal bonding and a hydrogen bonding between each monomer.

Vibrational spectroscopy enables us to get information of bond specific interactions. Variety of vibrational spectroscopic techniques such as infrared adsorption spectroscopy (IRAS) [7–9], high resolution electron energy loss spectroscopy (HREELS) [10–12] and He atom scattering (HAS) [13] have been used as powerful probes of water on metal surfaces. However, the spatial resolution and sensitivity of these methods are not sufficient to detect vibrational signals from individual water monomers and dimers. Conventional vibrational spectroscopy can usually provide only the information of an ensemble of vibrational signals from the water clusters with various sizes including monomers and dimers. It is therefore important to carefully carry out the assignment of vibrational peaks measured on the surfaces especially at very low surface coverage.

Recently, the scanning tunneling microscope (STM) has been used for chemical identification of individual molecules with extremely high spatial resolution [14]. One can obtain vibrational signals of a single molecule by means of vibrational spectroscopy with STM, such as inelastic electron tunneling spectroscopy (STM-IETS) [15] and action spectroscopy [16]. The STM-IETS detects vibrational modes of a single molecule by measuring the total conductance change resulting from the inelastic electron tunneling. However, this method requires high stability of the molecule in the STM junction, and thus is not applicable to some molecules showing mobile character when they are vibrationally excited during measurement. The action spectroscopy measures responses of vibrationally-mediated molecular motion as a function of applied bias voltage. Since the molecular motion is induced by vibrational excitation, action spectrum can reveal which vibrational mode is actually excited and associated with molecular motions [16–20].

In this study, we have investigated adsorption structures and vibrational features of isolated water dimers adsorbed on Pt(1 1 1) surface with an STM at 4.7 K. By means of action spectroscopy, several vibrational signals related to lateral hopping motion

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have been detected, and they are assigned by comparing with previous conventional spectroscopic studies using IRAS and HREELS. Here, we discuss the details of the adsorption structure of individual water dimers on Pt(1 1 1) based on vibrational spectra obtained by action spectroscopy with an STM.

2. Experiments

All experiments were performed with a low-temperature STM (LT-STM, Omicron GmbH) equipped with an ultrahigh vacuum (<3×10^{-11} Torr) chamber. The single crystal surface of Pt(1 1 1) was prepared by cycles of Ar^+ ion sputtering and annealing to 1100 K, exposed to a small amount of water molecules that were injected into the chamber through a dosing tube. During the adsorption, the temperature of the sample surface was kept under 20 K to prevent water molecules from thermal processes such as diffusion, desorption and chemical reaction on the surface, and it was kept at 4.7 K during the STM measurements. An electrochemically etched tungsten tip was used for all STM measurements.

3. Results and discussions

Fig. 1a shows an STM topographic image of water molecules adsorbed on the Pt(1 1 1) surface at a small coverage (<0.005 ML). The topographic images of water isotopomers (H_2O and D_2O) appear the same as each other, but in both case two kinds of protrusions different in size and shape are observed. A closer look at them (Fig. 1b) reveals that the smaller one appears as a round-shaped protrusion and the bigger one looks like a "flower-like" protrusion with 6-fold symmetric lobes. We have assigned each of them as a water monomer and a dimer based on the results of manipulation experiments with STM. The anomalous shape of water dimer can be explained by the model of a "time-averaged" 6-fold shape of a rotating molecule as like the interpretation of similar protrusions observed for CO dimers [21] and CH_3SH monomers [22] on Au(1 1 1) at 5 K, and for 2,5-dichlorothiophenol on Cu(1 1 1) at 15 K [23]. In the case of water dimer, one molecule (hydrogen acceptor) is rotating around the other one (hydrogen donor). It has six equivalent potential minima at the six atop sites for the acceptor, surroundings of fixed atop site for the donor (Fig. 1c), results in longer residence time at these six sites. The assignment of the hydrogen donor molecule as the center of the protrusion is supported by the result of density functional theory (DFT) calculation showing the stronger bonding of the donor with Pt atom than that of the acceptor [24]. No model except one proposed above can explain the fact that only two small molecules show the protrusion occupying one center and six surrounding sites. It is quite natural to consider this way for interpretation of this kind of protrusion in the STM image.

Topographic STM images of the water monomers (Fig. 2a–c) and dimers (Fig. 2d–f) were taken with increasing sample bias. Monomers do not exhibit any diffusion behaviors at a sample bias lower than 100 mV, however they start moving to neighboring sites above 120 mV. Dimers, on the other hand, can diffuse only at a

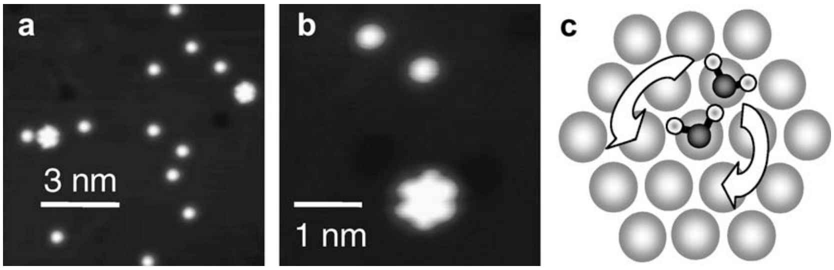

Fig. 1. Topographic STM images of isolated water monomers and dimers on Pt(1 1 1), (a) H_2O, V_{sample} = 20 mV, I_{tunnel} = 0.5 nA (b) D_2O, V_s = 40 mV, I_t = 0.5 nA. (c) A schematic image of presumed adsorption structure of a water dimer on Pt(1 1 1).

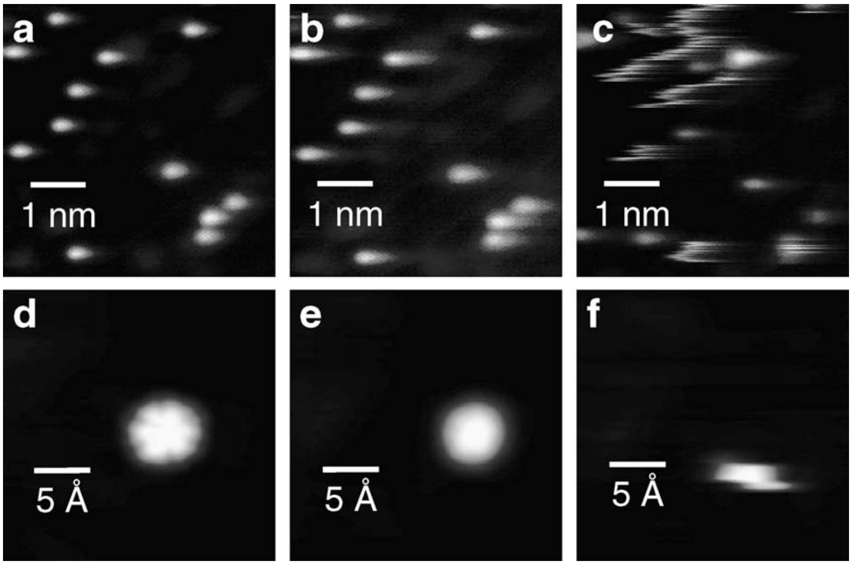

Fig. 2. Topographic STM images of (a–c) H_2O monomers and (d–f) a dimer taken with increasing sample bias. (a) V_s = 30 mV, I_t = 0.6 nA; (b) V_s = 100 mV, I_t = 1.0 nA; (c) V_s = 120 mV, I_t = 1.0 nA; (d) V_s = 40 mV, I_t = 1.0 nA; (e) V_s = 200 mV, I_t = 1.0 nA and (f) V_s = 205 mV, I_t = 1.0 nA.