Water Monomer and Dimer on Cu(110) Studied Using a Scanning Tunneling Microscope*

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The authors studied the structure and dynamics of water monomer and dimer on Cu(110) by using a scanning tunneling microscope (STM) and density-functional theory (DFT). The monomer adsorbs on top of a Cu atom and thermally hops along the atomic row at 6 K. The hopping motion is also induced via inelastic electron tunneling process. The dimer consists of hydrogen-bond donor and acceptor molecules, that were observed to dynamically exchange their roles via hydrogen-bond rearrangement. The interchange motion was suppressed upon substitution with heavy water, suggesting that the process involves quantum tunneling.

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I. INTRODUCTION

Adsorbed states of water molecules on single-crystalline metallic surfaces have been extensively studied in the last three decades as a model system for understanding water-solid interaction [1, 2]. In particular, copper acts as a catalyst in the water-gas-shift reaction ($\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$) for poison removal and mass hydrogen production [3]. The dynamical properties of individual water molecules on the surfaces, such as diffusion and clustering, are fundamental issues to elucidate the catalysis. Scanning tunneling microscope (STM) has been used to image individual water molecules diffusing over transition and noble metal surfaces [4–8]. Furthermore the migration was induced by STM via the coupling of the vibrational excitation with the lateral motion [6]. The STM also induced formation and fragmentation of water clusters on the surfaces [5, 8].

In this paper, we present a combined STM and density-functional theory (DFT) study of isolated water molecule and its dimer on Cu(110). The Cu(110) surface has an anisotropic structure with the array of atomic rows running along the $[1\bar{1}0]$ direction. The dynamical behaviors of individual water molecules on the surface are visualized with the STM. Water molecules migrate along $[1\bar{1}0]$ either thermally or extrinsically by tunneling electrons. The hopping motion is induced by STM via inelastic electron tunneling process. A water dimer consists of hydrogen-bond donor and acceptor molecules, and their roles are dynamically exchanged via hydrogen-bond rearrangement. The large isotope effect (~ 60) found in the exchange rate

suggests quantum tunneling is involved in the process.

II. METHODS

The experiments were carried out in an ultrahigh-vacuum chamber equipped with an STM (Unisoku, USM-1200). The STM images were acquired in the constant-current mode at 6 K. An electrochemically etched tungsten tip was used as an STM probe. Single-crystalline Cu(110) was cleaned by repeated cycles of sputtering with Ar^+ ions and annealing. The surface was exposed to H_2O or D_2O gases via a tube doser positioned ~ 1 cm from the sample surface at 12 K. The hopping rates of water molecules were determined in two different ways depending on the sample bias voltage (V_s) employed. At $V_s < 40$ mV, the hopping motion was slow enough to be monitored by a tracking routine. The time to catch up a molecule in motion was ~ 1 s. At $V_s > 40$ mV, the hopping motion was monitored by recording tunneling current with the tip fixed over the molecule. The water dimer was produced from two monomers by STM manipulation [8], or by simply increasing the coverage.

The calculations were based on the DFT using plane-wave, pseudopotential code STATE [9]. We calculated the structure of adsorbed water molecules using five-layer Cu slabs and 2×3 surface unit cell with 16 k point sampling, unless otherwise mentioned. The STM simulation based on the Tersoff-Hamann approach [10] was conducted for the dimer with a 3×4 unit cell and finer 64 k points. In the calculation, the sample bias voltage and the tip height were set at 24 mV and 0.5 nm, respectively. We confirmed that the qualitative features were not affected by the tip height. The molecular graphics were produced by the XCRYSDEN graphical package [11].

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FIG. 1: (a) Typical STM image ($53 \times 53 \text{ \AA}^2$) of water monomers on Cu(110). The image was acquired at $V_s = 24 \text{ mV}$ and $I_t = 0.5 \text{ nA}$. Water molecules appear as round protrusions with an apparent height of $0.6 \text{ \AA}$. The tip was scanned horizontally from top to bottom. The inset is a separately taken image that shows relative position of water molecule to coadsorbed CO molecules (24 mV and 0.2 nA). (b) Side view of the calculated structure for water monomer on Cu(110). (c) The same as (b) from top view.

III. RESULTS AND DISCUSSION

A. Water monomer

A water molecule is imaged as a round protrusion [Fig. 1(a)]. The inset shows the relative position of water molecule to coadsorbed carbon monoxide (CO) molecules. The grid lines represent the lattice of the substrate, which is determined by the position of CO that is known to adsorb on top of Cu atoms [12]. Accordingly, the water molecule appears to lie on top of a Cu atom. The DFT calculation shows that water molecule prefers the displaced top site to the other high-symmetry sites with the adsorption energy of 0.34 eV [Figs. 1(b) and 1(c)]. The Cu-O bond length is $2.21 \text{ \AA}$. The hopping barrier to the adjacent top site along the atomic row is 0.12 eV . The azimuthal rotation was found to be facile with the barrier less than 20 meV . The barriers were calculated with three-layer slabs. The structural parameters slightly deviate from those by the recent DFT studies [13, 14]. Tang and Chen proposed laterally displaced position from the top site by $0.88 \text{ \AA}$ [13]. Ren and Meng also proposed the displacement by $0.5 \text{ \AA}$ [14]. In our calculation, the displacement is $0.5 \text{ \AA}$ and the energy difference between these sites and the just top site is within 20 meV . This may reflect the general property of water-metal interac-

FIG. 2: (a) Typical trace of the tip when it tracks a water molecule at 24 mV and 0.5 nA . The red and blue lines indicate the displacements in the $[1\bar{1}0]$ and $[001]$ directions, respectively. (b) Distribution of the time intervals between the hopping events collected from the tracking data. The tunnel conditions are the same as in (a). The fitting to an exponential function gives a hopping rate of 0.13 s^{-1} . The inset shows the hopping rates as a function of I_t at 24 mV . The tip effect is negligible at low I_t , and the residual rate (0.1 s^{-1}) is mainly ascribed to the thermal motion.

tion that the potential energy surface is smooth along the surface in the vicinity of the top site [15].

Water molecules migrate over the surface even at 6 K . A fractional image in the upper right of Fig. 1(a) indicates that the molecule hops along the $[1\bar{1}0]$ direction (atomic row) when the tip scans along the line. The hopping motion is either thermally activated or tip-induced. The contribution of the latter depends on the tunneling condition. A typical trace of the molecule is shown in Fig. 2(a) as a function of time. The tunneling current (I_t) and V_s during the tracking were 0.5 nA and 24 mV , respectively. The traces are represented by the displacement from the original position in the $[1\bar{1}0]$ (red) and $[001]$ (blue) directions. The hopping motion is predominantly along $[1\bar{1}0]$ with a step of one atomic distance ($a_0 = 2.56 \text{ \AA}$). The long-range hoppings are presumably due to short residence time. The time intervals between the hopping events were collected from many cycles of tracking experiments and the distribution is shown in Fig. 2(b). The distribution was fitted by an exponential function whose decay constant is the mean residence time. A hopping rate, the inverse of the mean residence time, was determined to be 0.13 s^{-1} at $V_s = 24 \text{ mV}$. There is a current dependence in the hopping rate [inset of Fig. 2(b)]. The hopping rate is nearly constant at $I_t < \sim 0.5 \text{ nA}$, suggesting that the tip effect is negligible and the motion is thermally activated under this condition. Thus a water molecule thermally migrates along the atomic row with $R_0 = 0.1 \text{ s}^{-1}$ at 6 K . By assuming the pre-exponential factor $\nu_0 \approx 10^{13} \text{ s}^{-1}$, we estimate that $R_0 = \nu_0 \exp(-E_b/k_B T)$ yields the barrier $E_b \approx 15 \text{ meV}$. This barrier is comparable with that on Cu(100) ($\sim 20 \text{ meV}$) [7], but substantially lower than the predicted value of 0.12 eV , indicating that the hopping path should be further optimized in the calculation. The hopping motion becomes tip-induced when I_t exceeds $\sim 0.5 \text{ nA}$ [inset of Fig. 2(b)]. The hopping rate increases with I_t in a similar way, even when V_s is reduced to 5 mV .

The hopping rate varies as a function of V_s . Whereas the tip effect is negligible at $V_s = 24 \text{ mV}$ and $I_t < \sim 0.5 \text{ nA}$, there is a tip-induced hopping at high V_s . The residence time of water molecule was determined as follows: The

FIG. 3: (a) Hopping rates as a function of V_s for H_2O (red circles) and D_2O (blue crosses). The tip height was adjusted to give $I_t = 12 \pm 3$ pA during the voltage pulses. The inset shows typical tunneling current taken with the tip fixed over the molecule at $V_s = 54$ mV. (b) The rate of induced motion as a function of I_t at 54 mV gives a slope of 1.0 ± 0.1 in a logarithmic scale.

tip was positioned over a water molecule and a voltage pulse was applied during which the feedback was turned off. The tunneling current during the pulse shows abrupt decreases that correspond to the motion of the water molecule. Typical result is shown in the inset of Fig. 3(a) ($V_s = 54$ mV). The first and second drops indicate the moments of hopping events to the first- and second-neighbor sites along the atomic row, respectively. The distribution of the times spent by a molecule just below the tip during the pulse, was fitted by a single exponential function in the same way as Fig. 2(b). The hopping rate was obtained as a function of V_s . The tip height was adjusted for each V_s to give $I_t = 12 \pm 3$ pA during the pulse. The results are shown in Fig. 3(a) for H_2O (red circles) and D_2O (blue crosses). Below ~ 40 mV, the observed motion is mainly due to thermal activation. The rates increase by almost two orders of magnitude at ~ 40 – 70 mV for both isotopes. The I_t dependence of the rates was investigated at $V_s = 54$ mV, which is shown in Fig. 3(b) in a logarithmic scale. Here the contribution of thermal motion ($R_0 = 0.1$ s⁻¹) was subtracted to evaluate the rate of the induced motion. The slope of 1.0 ± 0.1 suggests that the motion is induced via inelastic tunneling of single electron with the reaction (hopping) yield of 3×10^{-8} per electron.

The tunneling electron carries a sufficient energy to excite a molecule directly along the reaction (hopping) coordinate. This mechanism is, however, unlikely since the hopping rates increase at ~ 40 – 70 mV, which is far above the estimated value $E_b \approx 15$ meV. On the other hand, it has been argued that molecular motion is induced via anharmonic coupling with the excitation of molecular vibration [16–18]. Ueba and Persson studied the STM-induced hopping motion of a CO molecule on Pd(110) [18]. They showed that it is coupled to the excitation of the C–O stretch mode, and the hopping rate increases almost linearly with V_s above the threshold voltage corresponding to the C–O vibration energy. Accordingly, we fit the rate to a linear function and constant value above and below the threshold, respectively [solid curve in Fig. 3(a)], and obtain the threshold voltage of 43 mV for H_2O . The isotopic difference was not discerned presumably due to large statistic errors in the rates. We calculated the vibrational energy of Cu–O stretch mode (perpendicular-polarized hindered translation) by normal-mode analy-

sis to be 26 meV for H_2O . We tentatively attribute the threshold to the excitation of the Cu–O stretch mode or its overtone, which couples to the lateral motion and excites the molecule to overcome the hopping barrier. An assignment to libration modes, such as wagging mode, is ruled out by the absence of isotope effect. The anharmonic coupling between the translation modes reflects substantial corrugation of the potential energy along the atomic row. The present result contrasts with that for water molecule on Pd(111), where the hopping motion was not induced until the excitation of the scissors mode (~ 200 meV) [6]. This is explained by the difference in the hopping barriers, i.e., $E_b \approx 15$ and 126 meV for Cu(110) and Pd(111), respectively [4].

In addition, the hopping motion is induced even at 24 mV when I_t exceeds ~ 0.5 nA [inset of Fig. 2(b)], although the yield is relatively small ($< 10^{-11}$ hop/electron). At present, the underlying mechanism is not well understood, but it could be ascribed to the close proximity between the tip and the surface at high I_t , which would perturb the potential energy of a water molecule on the surface.

B. Water dimer

Figure 4(a) shows the STM image simultaneously acquired for $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$. The H_2O dimer is characterized by its fractional image, which arises from configurational fluctuation of the molecules. The dynamical property of the water dimer is strongly isotope-dependent. In contrast to the H_2O dimer, the image of the D_2O dimer is static and “egg” shaped with the long axis aligned along the $[1\bar{1}0]$ direction. The D_2O dimer also shows fluctuation, but with much lower rate than the H_2O dimer, thereby enabling the acquisition of the stationary image. The inset shows the registry of the switching $(\text{D}_2\text{O})_2$ with the lattice of the surface. The calculated structure for the water dimer is shown in Figs. 4(b) and 4(c), which are from side and top views, respectively. The dimer consists of hydrogen-bond donor and acceptor molecules. The donor molecule is bound to the top site on Cu(110) while the acceptor is only weakly interacted with the surface. The adsorption energy of the dimer is 0.41 eV per molecule with respect to the gas-phase monomer, which is 0.07 eV larger than that for the adsorbed monomer. The Cu–O bond length is 2.12 and 2.89 Å for the donor and acceptor molecules, respectively. The STM simulation for the dimer [Fig. 4(d)] indicates that the acceptor appears as a higher protrusion than the donor, in agreement with the experimental “egg”-shape image. Thus the bistable fluctuation of the dimer is ascribed to the donor-acceptor interchange motion as shown in Fig. 4(b).

To evaluate the interchange rate, the time intervals of the interchange motion were obtained by recording the tunneling current with the tip fixed over the protrusion of the dimer. Figure 5(a) shows typical current for $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$ at $V_s = 24$ mV. The current shows abrupt jumps between two levels corresponding to the moments of the interchange events. The distribution of time intervals was fitted by an exponential function [Fig. 5(b)], and the interchange rates were determined to be $(6.0 \pm 0.6) \times 10^1$ s⁻¹ and $(1.0 \pm 0.1) \times 10^0$ s⁻¹ for $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$, respectively. The rates were determined at 24

FIG. 4: (a) An STM image ($74 \times 74 \text{ \AA}^2$) for $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$. The inset shows an image of $(\text{D}_2\text{O})_2$ with the lattice of Cu(110) superimposed. The images were obtained at 24 mV and 0.5 nA. (b) The calculated structure of the water dimer (side view). The interchange motion of the H-bond donor and acceptor molecules is shown. (c) The same as (b) but from top view. (d) Simulated STM image for the dimer superimposed by the Cu lattice (white lines).

FIG. 5: (a) Typical current over $(\text{H}_2\text{O})_2$ (top panel) and $(\text{D}_2\text{O})_2$ (lower panel) recorded with $V_s = 24 \text{ mV}$. The tip was fixed over the protrusion with the set point of 24 mV and 0.5 nA. (b) The distribution of time between the interchange events for $(\text{H}_2\text{O})_2$ fitted to an exponential function. The inset shows the result for $(\text{D}_2\text{O})_2$.

mV bias voltage, and show no dependence on the tunneling current from 0.05 to 0.7 nA, indicating that the observed motion is not affected by the tip but is intrinsic to the molecules. The large isotope effect in the rates (~ 60) suggests that the interchange process involves quantum tunneling of hydrogen atom. The barrier for the interchange calculated to be 0.24 eV cannot be overcome thermally at 6 K, thus corroborating the quantum process.

Figures 6(a)-6(d) show a sequence of STM images of two interacting H_2O dimers. The dimers migrate along the surface with comparable mobility to monomers. While the monomers diffuse predominantly along the

FIG. 6: Sequential images of two interacting H_2O dimers ($71 \times 71 \text{ \AA}^2$). (a) Two dimers show dynamical fluctuation. (b) As they migrate and come near each other, one of the two configurations is strongly preferred, indicating that the interchange motion is suppressed due to the interaction. (c) They pass each other and the preference is inverted. (d) The dimers recover their inherent dynamical properties as they diffuse out of the range of the interaction. All images were acquired at 0.5 nA and 24 mV.

$[1\bar{1}0]$ direction, the dimers diffuse rather isotropically. As the two H_2O dimers diffuse and come close to each other, the fluctuation is inhibited temporally with one of the pair strongly preferred [Fig. 6(b)]. When the dimers pass by each other along the $[1\bar{1}0]$ direction, the preference is reversed and another configuration mainly appears [Fig. 6(c)]. Subsequently as they diffuse away from each other, the dimers recover their inherent dynamical properties [Fig. 6(d)]. The distance between the interacting dimers ($\sim 13 \text{ \AA}$) suggests that long-range dipole interaction affects the balance of the double-minimum potential energy for each dimer, highlighting the sensitivity of the tunneling dynamics to the environmental perturbation.

IV. CONCLUSION

Water monomer and dimer on Cu(110) were studied by means of STM in collaboration with DFT. Water monomer, adsorbed on top of Cu atom, migrates along the $[1\bar{1}0]$ direction with a rate of 0.1 s^{-1} at 6 K. The motion is also induced by inelastic electron tunneling that excites the hindered-translation mode of water molecule. Water dimer exhibits characteristic fluctuation, which was ascribed to the H-bond rearrangement within the dimer. The dynamics of the H-bond exchange process was investigated in real time for individual molecules, and we propose that quantum tunneling is involved in the process.

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- [1] P. A. Thiel and T. E. Madey, *Surf. Sci. Rep.* **7**, 211 (1987).
 - [2] M. A. Henderson, *Surf. Sci. Rep.* **46**, 1 (2002).
 - [3] J. Nakamura, J. M. Campbell, and C. T. Campbell, *J. Chem. Soc. Faraday Trans.* **86**, 2725 (1990).
 - [4] T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, *Science* **297**, 1850 (2002).
 - [5] K. Morgenstern and K.-H. Rieder, *J. Chem. Phys.* **116**, 5746 (2002).
 - [6] E. Fomin, M. Tatarkhanov, T. Mitsui, M. Rose, D. F. Ogletree, and M. Salmeron, *Surf. Sci.* **600**, 542 (2006).
 - [7] L. Lauhon and W. Ho, *J. Phys. Chem. B* **105**, 3987 (2001).
 - [8] T. Kumagai, M. Kaizu, S. Hatta, H. Okuyama, T. Aruga, I. Hamada, and Y. Morikawa, *Phys. Rev. Lett.* **100**, 166101 (2008).
 - [9] Y. Morikawa, *Phys. Rev. B* **51**, 14802 (1995).
 - [10] J. Tersoff and D. R. Hamann, *Phys. Rev. Lett.* **50**, 1998 (1983).
 - [11] A. Kokalj, *Comput. Mater. Sci.* **28**, 155 (2003). Code available from <http://www.xcrysden.org/>.
 - [12] M. Doering, J. Buisset, H.-P. Rust, B. G. Briner, and A. M. Bradshaw, *Faraday Discuss.* **105**, 163 (1996).
 - [13] Q.-L. Tang and Z.-X. Chen, *Surf. Sci.* **601**, 954 (2007).
 - [14] J. Ren and S. Meng, *Phys. Rev. B* **77**, 054110 (2008).
 - [15] A. Michaelides, V. A. Ranea, P. L. de Andres, and D. A. King, *Phys. Rev. Lett.* **90**, 216102 (2003).
 - [16] B. C. Stipe, M. A. Rezaei and W. Ho, *Phys. Rev. Lett.* **81**, 1263 (1998).
 - [17] T. Komeda, Y. Kim, M. Kawai, B. N. J. Persson, and H. Ueba, *Science* **295**, 2055 (2002).
 - [18] H. Ueba and B. N. J. Persson, *Phys. Rev. B* **75**, 041403(R) (2007).