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Symmetric hydrogen bond in a water-hydroxyl complex on Cu(110)

T. Kumagai, M. Kaizu, and H. Okuyama[*]
Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

S. Hatta and T. Aruga
Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
and JST CREST, Saitama 332-0012, Japan

I. Hamada
WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Y. Morikawa
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

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Water-hydroxyl complexes were produced on Cu(110) and characterized by a scanning tunneling microscope (STM) and first-principles calculations. A water molecule was brought to a fixed hydroxyl (OH) group in a controlled manner with the STM, and two kinds of hydrogen-bonded complexes were produced selectively. A side-on complex, in which a water molecule is bonded to an OH group along the atomic row, is metastable with relatively weak hydrogen bond (0.13 eV). On the other hand, a bridge complex, in which a water molecule is bonded to an OH group across the atomic trough, is most stable and characterized by the strong hydrogen bond (0.44 eV) and the short distance between oxygen atoms (2.5 Å). The distance is in the range of the "low-barrier hydrogen bond," and we show that a symmetric hydrogen bond (HO-H-OH) is formed in the bridge complex, wherein zero-point nuclear motion plays a crucial role.

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I. INTRODUCTION

Proton transfer through a hydrogen bond (O-H···O) is an important process in wide areas of chemistry and biology.[1–4] The strength of a hydrogen bond, which has been correlated with the distance between two oxygen atoms, is a key property that controls the quantum nature of shared proton.[3] In a "normal" hydrogen bond with the O-O distance of ~2.8 Å, proton is attached to one of the oxygen atoms by a covalent bond, giving rise to an asymmetric configuration, as is the case for a water dimer. As two oxygen atoms come close to each other up to ~2.5 Å, proton transfer becomes facile as a result of the barrier reduction. The formation of such a "low-barrier hydrogen bond" to promote proton transfer was postulated to be a key process in enzymic catalysis.[1,2] A singly hydrated hydroxyl anion (H_2O-OH^-), in which a hydrogen atom of the water molecule is bonded to an oxygen atom of the hydroxyl anion, was proposed to be representative of this type of hydrogen bond.[3,5] The shared proton is readily transferred to the hydroxyl anion via the low barrier (0.14 kcal/mol), and thus is centered along the hydrogen bond (HO-H-OH) due to the nuclear zero-point motion.[3] Such a symmetric hydrogen bond was actually observed by x-ray diffraction in compressed ice, wherein the O-O distance reached 2.4 Å under ~60 GPa.[6]

In the previous works, we manipulated individual water molecules on Cu(110) and made a water dimer[7] and a hydroxyl dimer,[8] in which the dynamics of hydrogen-bond exchange reactions were investigated by using a scanning tunneling microscope (STM). In this work, we produced water-hydroxyl complexes in a similar way and studied the properties of the hydrogen bonds with the aid of density-functional theory (DFT) calculations. The image of the complex implies symmetric Zundel-type (HO-H-OH) structure. The calculations showed that while the potential along proton transfer is of double-well type in favor of the asymmetric hydrogen bond, the inclusion of nuclear zero-point energy results in the stabilization of the symmetric configuration.

II. METHODS

The experiments were carried out in an ultrahigh-vacuum chamber equipped with an STM operating at 6 K. The Cu(110) surface was exposed to H_2O or D_2O gases at 12 K to yield very low coverage, where water molecules exist mainly as isolated monomers. The substrate consists of arrays of atomic rows running along the $[1\bar{1}0]$ direction. A hydroxyl (OH) group was produced by dissociating a water molecule with a voltage pulse of 2 V.[8] A water molecule was laterally manipulated along the atomic row and eventually reacted with a fixed OH group in the following way. Typically the bias was reduced to 5 mV while the current was increased to 10 nA over a water molecule (0.5 MΩ gap resistance), and then the tip was laterally moved at 1 Å/s in the $[1\bar{1}0]$ or $[\bar{1}10]$ direction with the feedback maintained. The water molecule follows the tip as it moves, while the gap resistance required for the stable manipulation depends on the tip apex. Under the condition employed, the migration to the next row was never observed even when the tip was moved along [001], probably because the potential barrier over the trough is relatively high.

The calculations are based on DFT (Ref. 9) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation.[10] PBE slightly overestimates the binding energies of H_2O dimer,[11] and slightly underestimates the proton transfer barrier at a short distance (~2.5 Å),[12] but is sufficiently accurate for the present purpose. We utilized the plane-wave pseudopotential method as implemented in the STATE code.[13] The surface was modeled by a five-layer Cu slab with an H_2O-OH complex aligned along the [001] ($[1\bar{1}0]$) direction in a $3\times3(2\times4)$ periodicity, and a 4×4 k-point set was used to sample the Brillouin zone. The adsorbates were put on one side of the slab, and the spurious electrostatic interaction was eliminated by the effective screening medium method.[14] Adsorbates and the topmost two Cu layers were allowed to relax, while remaining Cu atoms are fixed at their respective bulk positions. STM simulations were conducted within the Tersoff-Hamann theory.[15] In the STM simulations, the sample bias voltage was set to 25 mV, and the images were obtained at the constant height of 7 Å from the topmost Cu plane. We confirmed that the qualitative features were not affected by the tip height. Other calculation details can be found in Ref. 8.

III. RESULTS AND DISCUSSIONS

We show sequential images before and after the reaction of a water molecule (H_2O) with an OH group on Cu(110). The water molecule and OH group are bonded to the on-top and short-bridge sites, respectively,[8,16] and they were located along the same row (dashed line) in Fig. 1(a). The OH species favor tilt geometries along [001] or $[00\bar{1}]$.[8,17–19] Its fast switch motion between the two orientations causes the paired depressions in the image.[8] The water molecule was dragged along the atomic row and eventually reacted with the OH group fixed on the same row, giving rise to a pear-shaped product [Fig. 1(b)]. The reaction occurs spontaneously when the reactants come close to each other. The product was never dissociated spontaneously once it was formed, suggesting the formation of a stable hydrogen-bonded complex. The complex was induced to flip between the two equivalent orientations [Figs. 1(c) and 1(d)] at ~60(170) mV for H_2O-OH (D_2O-OD), while they dissociate into water and a hydroxyl group at ~0.18 V. These reactions were observed in the temporal evolution of tunneling current during a voltage pulse recorded with the tip fixed over the complex [Fig. 1(e)]. The thick lines of the higher-current level result from the fast flip motion during the pulse, while the drops indicate the moment of the dissociation. Upon dissociation, the water molecule detached from the fixed OH group along the atomic row, resulting in the same geometry as in Fig. 1(a). Thus we can make and break a hydrogen bond reversibly by manipulating a water molecule against a fixed OH group without interconversion between them.

On the other hand, when a water molecule was reacted with an OH group located on the next row [Fig. 2(a)], a different complex of oval shape was yielded [Fig. 2(b)]. The two dashed lines indicate the atomic rows on which each reactant molecule was located, and the asterisk shows the center position of the original OH group (short-bridge site). From the relative position to nearby water molecules and OH groups, the complex was found to be centered at the hollow site between the rows. The image of the complex is shown in Fig. 2(c) with the substrate lattice superimposed. The line profiles of the image [Fig. 2(d)] suggest that the complex has two mirror planes parallel to the $[1\bar{1}0]$ or [001] axis and is therefore of C_{2v} symmetry.

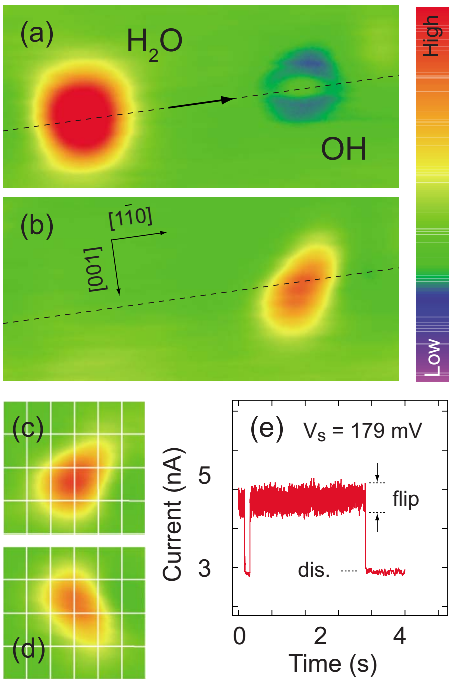

FIG. 1. (Color online) (a) STM images for a water molecule and an OH group located on the same row (dashed line) on Cu(110). (b) A water-OH complex produced by dragging the water molecule to the OH group along the atomic row. The images appear quite large as compared to their actual size, which may arise from extended perturbation of the substrate electronic states due to adsorption. (c) The complex superimposed with the lattice of the substrate. (d) The counterpart of (c). (e) Temporal evolution of tunneling current during a voltage pulse of 179 mV. The tip was fixed over the complex at the height corresponding to 24 mV and 0.5 nA. The thick lines result from the fast flip motion between (c) and (d), and the abrupt decreases correspond to the detachment of the water molecule. Note that the complex was formed again immediately after the first dissociation. The sample bias voltage and tunneling current during the image acquisition were 24 mV and 0.5 nA, respectively, and the size is 47×22 Å^2 for (a) and (b) and 15×14 Å^2 for (c) and (d). The color palette represents the tip height in the constant current mode. Under this high gap resistance (48 MΩ), the adsorbates were observed without perturbation and the substrate Cu atoms were not resolved.

The dissociation of the oval complex into water and an OH group required a voltage pulse higher than 0.5 V, suggesting larger binding energy (E_b) than that for the pear complex. Under lower bias voltage, the oval complex was induced to hop along the trough. By using the tracking routine,[16] the average hopping rates were determined as a function of the sample bias. A typical trace of the complex is shown in Fig. 3(a) as a function of time. 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

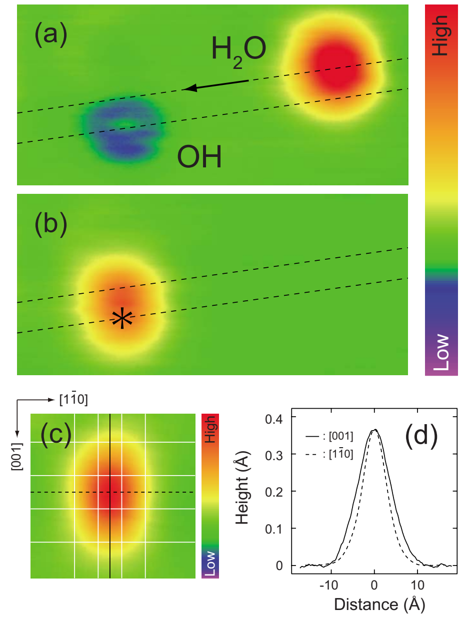

FIG. 2. (Color online) (a) STM images for a water molecule and an OH group located on adjacent rows (dashed lines). (b) The complex produced under this geometry shows an oval shape in contrast to the case of Fig. 1. Thus two kinds of the complexes were produced selectively depending on the reaction geometries. No interconversion between the two complexes was induced by voltage pulses. (c) An STM image of the complex on which the lattice of Cu(110) is superimposed. (d) The height profiles along the solid ([001]) and dashed ([1$\bar{1}$0]) lines in (c). The sample bias voltage and tunneling current during the image acquisition were 24 mV and 0.5 nA, respectively, and the size is 47 × 22 Å^2 for (a) and (b) and 17.5 × 17.5 Å^2 for (c).

distance (a_0=2.56 Å). The time intervals between the hopping events were collected from many cycles of the tracking experiments, and the average hopping rates were determined as a function of the sample bias [Fig. 3(b)]. The threshold voltages are 440 and 330 mV for H_2O-OH and D_2O-OD, respectively, indicating that the excitation of the O-H(D) stretch modes is responsible for the induced hopping motion. It is noted that the deuterated complex was almost immobile at 0.5 nA even at the voltage of 450 mV and required relatively high tunneling current (~20 nA) to be displaced. The current dependence of the hopping rate [Fig. 3(c)] indicates that the motion is induced via single- and double-electron processes for H_2O-OH and D_2O-OD complexes, respectively. The motion is presumably induced via anharmonic coupling of the internal mode to the complex-substrate modes,[20] and the higher reaction order for D_2O-OD suggests that the overtone excitation of O-D stretch (~660 meV) is required to overcome the hopping barrier.

Figure 4 shows the structures of the water-hydroxyl complexes optimized by DFT. The first one consists of H_2O and OH group located along the same row [Figs. 4(a) and 4(b)] and is stabilized by 0.13 eV compared to isolated H_2O and OH group on the surface. The water molecule is displaced from the top site to form optimal hydrogen bond with the OH group through its hydrogen atom. The observed pear complex [Fig. 1(b)] is assigned to this side-on structure. On the other hand, the most stable form of the complex is shown in Figs. 4(c) and 4(d), where the complex bridges the adjacent rows. This bridge complex is stabilized by 0.44 eV with respect to the isolated species on the surface. This hydrogen bond is remarkably strong compared to that for a water dimer on Cu(110) with a normal hydrogen bond (0.14 eV).[7,16] Since the adsorption energy of a water molecule isolated on Cu(110) is 0.34 eV,[16] a water molecule in the complex is stabilized by as large as 0.78 eV with respect to that in gas phase. The oval complex [Figs. 2(b) and 2(c)] may be assigned to this structure. The O-H stretch mode observed in Fig. 3(b) is attributed to the unshared protons. This structure is, however, incompatible with the apparent C_{2v} symmetry of the STM image. Indeed, the STM image simulated for this structure [Fig. 4(e)] has a protrusion over the water molecule and thus away from the top of the hollow site, which is clearly inconsistent with the experiment.

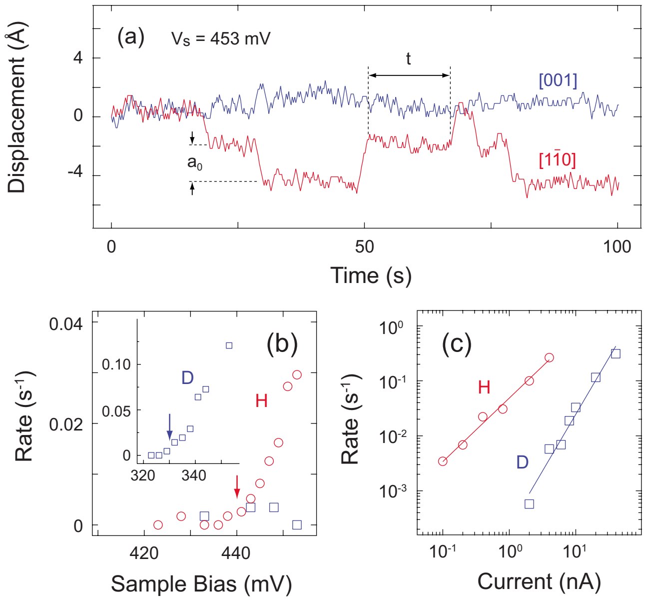

FIG. 3. (Color online) (a) Typical trace of the tip when it tracks an oval complex (H_2O-OH) at 453 mV and 0.5 nA. The red and blue lines indicate the displacements in the [1$\bar{1}$0] and [001] directions, respectively. The hopping rates were determined from the inverse of average residence time *t*. (b) The hopping rates of the oval complexes as a function of bias voltage. The circles and squares represent the rates for H_2O-OH and D_2O-OD, respectively. The tunneling current was kept at 0.5 nA. The inset shows the result for D_2O-OD with the tunneling current of 20 nA. (c) The hopping rates as a function of tunneling current with the bias voltage kept at 443 and 343 mV for H_2O-OH and D_2O-OD, respectively. The corresponding slopes in the logarithmic scale are 1.1 ± 0.1 and 2.0 ± 0.1, indicating single- and double-electron processes, respectively.

To solve this contradiction, we postulate that the shared proton in the bridge complex is delocalized between two oxygen atoms yielding a symmetric configuration [Figs. 4(f) and 4(g)]. The corresponding potential energy is only 16 meV higher than that for the asymmetric configuration. The calculated O-O distance (2.5 Å) and the strong hydrogen bond (0.44 eV) are in line with the low-barrier hydrogen bond. As a matter of fact, the STM image simulated for this

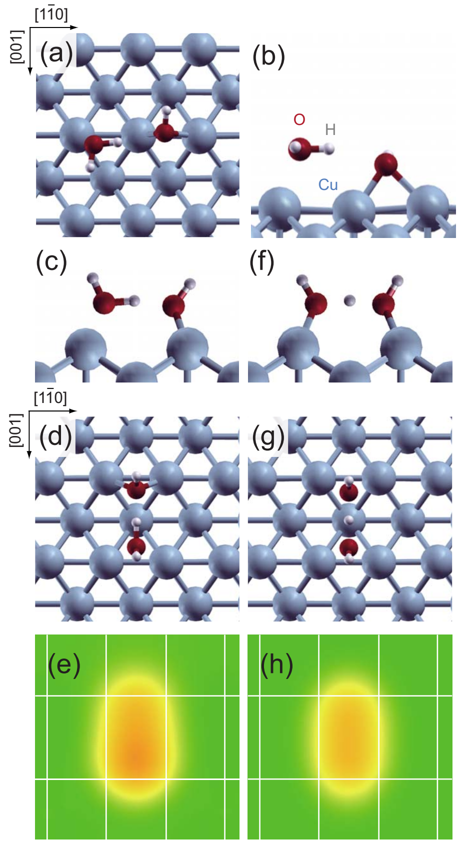

FIG. 4. (Color online) The calculated structures for H_2O-OH complexes. (a) Top and (b) side views of the side-on complex. (c) Side and (d) top views of the bridge complex. (e) The corresponding simulated image with the lattice representing the positions of substrate Cu atoms. The potential energies with respect to water and the OH group isolated on the surface are 0.13 and 0.44 eV for the former (metastable) and latter (stable), respectively. In both cases, the OH groups are slightly negatively charged and water molecules act as hydrogen-bond donors. (f) Side and (g) top views of the bridge complex in the symmetric configuration. The potential energy is 16 meV higher than that for the asymmetric one [(c) and (d)]. (h) The corresponding simulated image. The STM simulations were conducted without considering zero-point effect.

symmetric structure [Fig. 4(h)] is consistent with the experimental STM image.

The adiabatic potential energy for the shared proton in the bridge complex as it is transferred between the two oxygen atoms is shown in Fig. 5 (circles). At each point along the path, the positions of oxygen atoms, residue hydrogen atoms and the topmost two Cu layers were optimized. The potential has a double-well structure with a significantly reduced barrier (16 meV) and small distance (0.2 Å) between the minima. The barrier further decreased to 9 meV, when we used the thicker seven-layer slab with topmost four Cu layers relaxed, using a denser 8×8 k-point set. Therefore the asymmetric configuration is only slightly favored within the accuracy of the present DFT calculation. This implies that the zero-point motion may result in the stabilization of the symmetric configuration. Based on this idea, the zero-point energies (ZPEs) were calculated and the total energies for the asymmetric and symmetric configurations are compared.

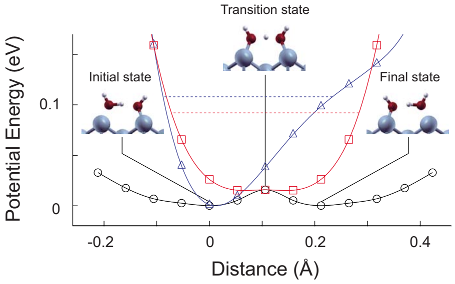

FIG. 5. (Color online) Adiabatic potential energy for the bridge complex along the minimum-energy path of proton transfer between two oxygen atoms (open circles). The two minima and peak correspond to the asymmetric and symmetric configurations, respectively, as shown in the inset. Static potential energies for symmetric (squares) and asymmetric (triangles) configurations were calculated by moving proton along the minimum-energy paths with other degrees of freedom fixed at their optimized geometries. The curves were obtained by a cubic spline fit to the calculated data. Using the obtained potential data, we solved one-dimensional Schrödinger equations numerically. The dashed lines indicate the levels of total energies for each configuration.

Since proton moves much faster than oxygen or Cu atoms, ZPEs associated with the transfer coordinate were calculated by determining the static potential energies with other degrees of freedom frozen and solving one-dimensional Schrödinger equations for the proton motion. The results are shown in Fig. 5 by triangles and squares for the asymmetric and symmetric static potentials, respectively. Calculated ZPEs are 107 and 76 meV for the asymmetric and symmetric configurations, respectively; the delocalized symmetric state has lower kinetic energy by ~30 meV and thus is stabilized in total energies (dashed lines). This suggests barrierless motion of the shared proton and thus formation of a symmetric hydrogen bond. The zero-point motion of the other degrees of freedom should be taken into account, but we assume the effect of their classical treatment is minor and negligible. We note that the D_2O-OD complex appeared almost similar to H_2O-OH in the STM image, suggesting that it is still in the symmetric configuration, although the preference in the kinetic energy is reduced due to the doubled mass.

To make a comparison between the hydrogen bonds in the two complexes, we also calculated the adiabatic potential energy for the side-on complex (Fig. 6). The transfer requires the change in the adsorption sites from the bridge (top) to top (bridge) for the original OH group (water molecule). The potential barrier is relatively high (0.2 eV), suggesting that the side-on complex retains an asymmetric hydrogen bond.

The present result has an implication to the water-OH complexes formed at elevated temperatures and higher coverage.[17,21–28] Water dissociation and OH formation at Cu(110) were investigated mainly by x-ray photoemission spectroscopy.[23–27] The dissociation is only partial and water molecules survive against desorption even at 428 K under near-ambient pressure.[26,27] It was proposed that water molecules are anchored to OH group and stabilized against desorption due to strong H_2O-OH interaction. The STM showed that water-OH chain complex grows along [1$\bar{1}$0] after the water-covered surface was annealed to ~200 K.[28]

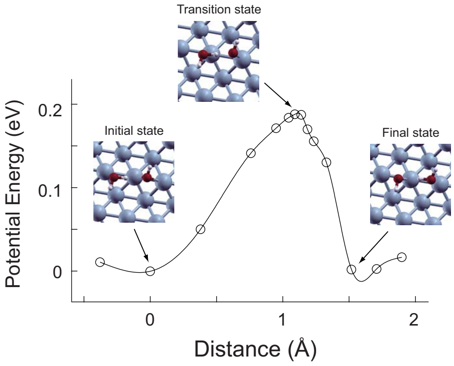

FIG. 6. (Color online) Adiabatic potential energy for the side-on complex along the minimum-energy path of proton transfer between oxygen atoms (open circles). The curve was obtained by a cubic spline fit to the calculated data. As the proton transfers, the binding site of the original OH group changes gradually from the bridge site to the top site, and that of the water molecule in the opposite way. The transition state lies in the off-centered position along the path, resulting in the potential curvature of asymmetric shape.

Since the water molecule is strongly bound in the bridge complex found in the present work ($E_b = 0.78$ eV), it may be a good candidate as a basis that composes the thermal products observed previously.

IV. CONCLUSIONS

We produced two kinds of water-hydroxyl complexes selectively by using STM manipulation of individual water molecules. The corresponding structures and properties of the hydrogen bonds were examined by DFT calculations. The products depend on the position of the two reactants. Upon the reaction between the two on the same row, the side-on complex formed with relatively weak hydrogen bond (0.13 eV). On the other hand, upon the reaction between the two on the adjacent rows, the bridge complex was yielded, which is most stable and characterized by the strong hydrogen bond (0.44 eV). It is proposed that proton centering occurs in the latter as a result of the strong interaction and zero-point nuclear motion.

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*hokuyama@kuchem.kyoto-u.ac.jp

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