

Water clusters on Cu(110): Chain versus cyclic structures

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Water clusters are assembled and imaged on Cu(110) by using a scanning tunneling microscope. Water molecules are arranged along the Cu row to form “ferroelectric” zigzag chains of trimer to hexamer. The trimer prefers the chain form to a cyclic one in spite of the reduced number of hydrogen bonds, highlighting the crucial role of the water–substrate interaction in the clustering of adsorbed water molecules. On the other hand, the cyclic form with maximal hydrogen bonds becomes more favorable for the tetramer, indicating the crossover from chain to cyclic configurations as the constituent number increases. © 2011 American Institute of Physics. [doi:10.1063/1.3525645]

I. INTRODUCTION

Water clusters and overlayers on metal surfaces have been extensively studied with relevance to various chemical processes, such as corrosion and heterogeneous catalysis.^{1–4} It has been found that the structures are critically dependent on the substrates because they are determined by an interplay between the intermolecular and water–substrate interactions. The latter is well studied for individual water molecules isolated on the surfaces at low coverage and low temperature, while the interplay is less understood because of the presence of several metastable configurations even for small water clusters. Therefore, it is essential to investigate the structures and energetics of individual water clusters to understand the interplay and also the mechanism of extended overlayer growth in a systematic way.

Recently, the advancement of scanning tunneling microscopy (STM) enables us to observe and characterize individual water clusters on metallic surfaces in a single-molecule limit. Successive aggregation of water molecules to form dimer to pentamer was observed while they diffuse thermally over Pd(111).⁵ The dimer was found to be composed of H-bond donor and acceptor molecules, wherein the former is directly bonded to the surface while the latter interacts weakly with the substrate.⁶ The donor–acceptor interchange motion via H-bond rearrangement was observed in the water dimer adsorbed on Cu(110).^{7,8} A cyclic form of water hexamer, which is believed to be the most stable, was imaged on Cu(111) (Ref. 9) and Ag(111) (Ref. 10). Cyclic hexamers were sequentially decorated by additional water molecules to yield heptamer to nonamer.¹¹ It was proposed that the competition between the ability of water molecules to bond to the substrate and to accept hydrogen bonds from other molecules can rationalize the structure of the small water clusters on these surfaces. However, the structural characterization of

adsorbed water clusters of intermediate size, such as trimer and tetramer, remains lacking.

Water clusters of various configurations have been proposed on metal surfaces involving cyclic, chain, and double-donor types.^{12–14} Among these, the one-dimensional (1D) water chain is of particular interest because it provides an ideal 1D model system composed of water molecules. The water islands grown along the Pt steps¹⁵ were predicted to form a zigzag H-bond chain, where one OH bond of each molecule contributes to the H-bond chain, while the other remains intact pointing outward.¹² Such 1D water is known to exist in biological systems, mediating proton translocation across the transmembrane proteins.¹⁶ Water molecules confined in carbon nanotubes were intensively studied as a model system to investigate the structure and dynamical properties of 1D water chains.^{17,18}

In this work, we observe and characterize several isomers of small water clusters on Cu(110) by STM in conjunction with density-functional theory (DFT) calculations. Water chain clusters are assembled by adding water molecules one by one with the STM, thus making the constituent number unambiguously defined. Water molecules are arranged along the Cu atomic row, forming (meta)stable hydrogen-bonded chains of trimer to hexamer. The clear dependence of the images on the even/odd constituent numbers reveals the zigzag arrangement of water molecules along the chains, which is analogous to those postulated to exist inside biological channels. The chains are found to be “ferroelectric,” where the OH bond of each water molecule contributing to the hydrogen bonds is oriented in one direction. A DFT calculation is employed to investigate the stability of the chains against the cyclic structure. The trimer prefers the chain form to the cyclic form on Cu(110), while the latter is the most stable for the gas-phase counterpart. For the tetramer, on the other hand, the cyclic form was found to be the most favorable. The preference is also different from that predicted for the clusters on other surfaces.^{12–14} These results indicate that the structure of small water clusters is crucially dependent on the underlying substrate.

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II. METHODS

The experiments were carried out in an ultrahigh-vacuum chamber equipped with an STM operating at 6 K. An electrochemically etched tungsten tip was used as an STM probe. The STM images were acquired in constant current mode with the bias voltage applied to the sample. A single crystalline Cu(110) was cleaned by repeated cycles of argon ion sputtering and annealing. The surface consists of arrays of atomic rows running along the $[1\bar{1}0]$ direction. The clean Cu(110) surface was exposed to a small amount of H_2O gas at 12–20 K to yield very low coverage. While isolated monomers were dominant on the surface after the exposure at 12 K due to its limited mobility, water clusters of various sizes and shape emerged after the exposure at 20 K. The water clusters were also assembled by STM manipulation of individual water molecules in the following way:^{19,20} First, the tip was positioned over the water molecule and the gap resistance was decreased to 0.5 M Ω to reduce the tip-molecule distance. Then the tip was laterally moved at 1 $\text{\AA}/\text{s}$ along the Cu row to the desired position. The molecule followed the tip typically in the “pulling” mode,²⁰ and, thus, was brought to the vicinity of another water cluster. Finally, the molecule could spontaneously coalesce with the cluster after diffusing slowly ($\sim 0.1 \text{ s}^{-1}$) along the Cu row.⁸ If a water molecule was brought directly to the cluster, it would be broken by the approaching tip with such a low gap resistance. The location of the clusters on the surface was determined from the relative position to the monomers which are known to be centered on top of Cu atoms.⁸ While the monomers prefer the deviated top site,^{8,21–23} it is imaged on the exact top site, presumably because it is dynamically rotating around the top site with a small barrier (less than 20 meV).⁸

DFT calculations²⁴ were performed using the STATE (Ref. 25) code, within the Perdew–Burke–Ernzerhof (PBE) (Ref. 26) generalized gradient approximation (GGA). Wave functions and argumentation charge were expanded in a plane-wave basis set, and electron–ion interactions were described by pseudopotentials.²⁷ Water trimers and tetramers were put on one side of five-layer slabs with (3×4) and (4×6) periodicities, respectively, and artificial electrostatic interaction was eliminated by the effective screening medium method.²⁸ Brillouin zone sampling was done using 4×4 and 2×2 Monkhorst–Pack²⁹ k -point sets for (3×4) and (4×6) cells, respectively. Other computational details can be found in Ref. 30.

In the interaction of water with a metal surface, the van der Waals (vdW) interaction plays an important role.³¹ We used the van der Waals density functional (vdW-DF) of Dion *et al.*³² for a correct account of the vdW interaction. We also estimated zero-point energy (ZPE) by calculating harmonic vibrational frequencies. It turned out that inclusion of the vdW interaction and the ZPE correction does not alter our conclusion with PBE–GGA. Therefore, in the following we report the adsorption energies and geometries obtained using PBE–GGA, and details of vdW-DF and ZPE calculations are reported in the supplementary material.³³

III. RESULTS AND DISCUSSION

A water trimer was produced from a monomer and a dimer located on the same Cu row (dashed line) [Figs. 1(a)–1(c)]. The dimer is bonded along the Cu row as depicted in the inset of Fig. 1(a) and characterized by the fluctuation as a result of its continuous H-bond exchange motion.^{7,8} The monomer (a round protrusion) diffused along the Cu row and encountered with the dimer. The reaction is illustrated in the inset. The yielded trimer, imaged as an asymmetric triangle, was never ruptured or transformed spontaneously. The structure of the trimer was optimized by using DFT [Fig. 1(d)]. It

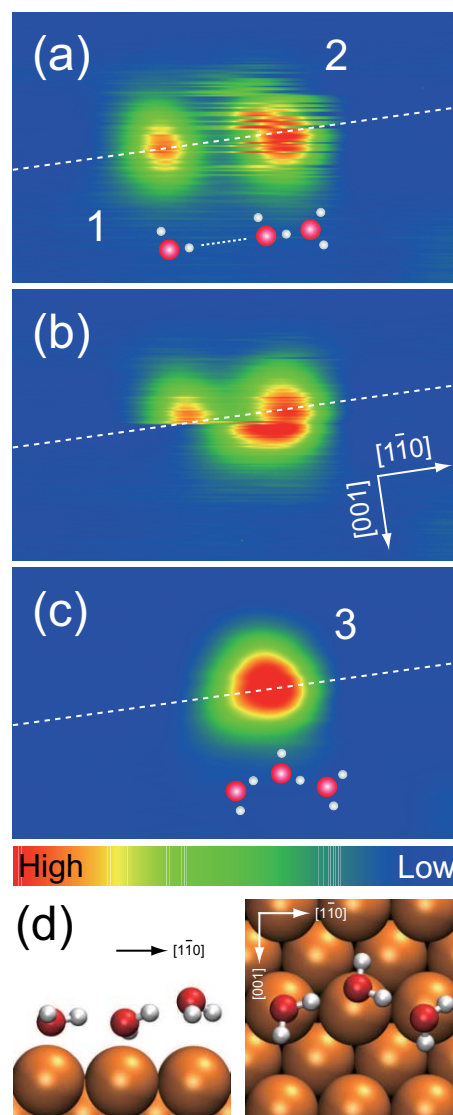


FIG. 1. Sequential STM images showing the reaction between a monomer and a dimer. (a) A monomer (labeled with 1) and a dimer (labeled with 2) are located in proximity along the Cu row (dashed line). The dimer shows two-state fluctuation corresponding to the H-bond interchange motion. The fluctuation is not equal due to the interaction with the monomer. The structures are depicted in the inset. (b) Diffusing along the Cu row, the monomer encountered with the dimer to yield a trimer. (c) The trimer (labeled with 3) is imaged as a distorted triangle. The apparent height of the trimer is typically 0.8 \AA , while that of the monomer is 0.6 \AA . All images were obtained at 24 mV sample bias and 0.5 nA tunneling current. Scan area is $50\times 30 \text{ \AA}^2$. (d) The structure of the $[1\bar{1}0]$ -chain trimer optimized by DFT.

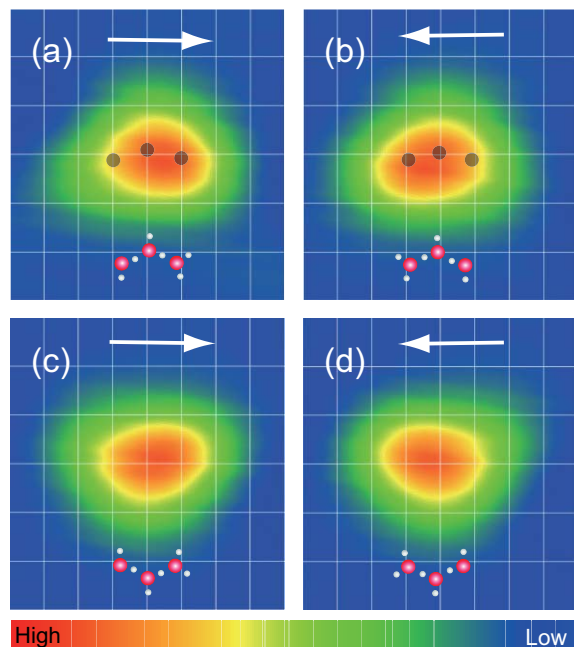


FIG. 2. (a)–(d) STM images of the $[1\bar{1}0]$ -chain trimer in four equivalent orientations. The inset illustrates the corresponding structures. The grid lines represent the lattice of Cu(110) that is depicted through nearby monomers centered on top of Cu atoms. The three dots in (a) and (b) depict the positions of water molecules, and the arrows indicate the directions of hydrogen bonds (dipole moment). The trimer interconverts between the four orientations by applying 0.12 V voltage. The conversion is associated with H-bonds rearrangements within the chain. The images were acquired at 24 mV and 0.5 nA. Scan area is $20 \times 22 \text{ \AA}^2$.

is arranged in a chain along the Cu row ($[1\bar{1}0]$ -chain trimer). Calculated binding energy (E_b) is 0.458 eV/ H_2O with respect to monomers isolated in the gas phase. The H-bond acceptor [right end of Fig. 1(d)] is 0.73 Å higher than the donor (left end) from the surface. Therefore, the acceptor side is presumably imaged as higher protrusion,⁷ which results in the distorted triangle image. Accordingly, the image in Fig. 1(c) is assigned to the orientation in Fig. 1(d). The four equivalent orientations of the $[1\bar{1}0]$ -chain trimer are shown in Figs. 2(a)–2(b), which can be mutually transformed by a voltage pulse of 0.12 V. The corresponding structures and the directions of the hydrogen bonds (dipole moments) are depicted in the inset.

Another type of trimer (labeled with 3') is shown in Fig. 3(a), in comparison with the $[1\bar{1}0]$ -chain trimer (labeled with 3) described above. No other structure than these two species was observed for the trimer. The second type arose from the reaction between a dimer and a monomer on different Cu rows and has four equivalent orientations [Figs. 3(b)–3(e)]. The orientation flips between Figs. 3(b) and 3(c) or Figs. 3(d) and 3(e) spontaneously with the time scale of ~ 1 s. The second trimer eventually transforms to the $[1\bar{1}0]$ -chain trimer, suggesting that it is metastable. Considering the registry and shape of its image, we propose the structure of the second trimer by using DFT [Fig. 3(f)]. Two water molecules are bonded across the trough along $[001]$ and another one is attached to the end as an acceptor ($[001]$ -chain trimer). The calculated E_b is 0.457 eV/ H_2O with respect to monomers isolated in the gas phase. The cyclic form, which is the most stable in the gas phase³⁴ and was predicted to exist on Pt(111),¹²

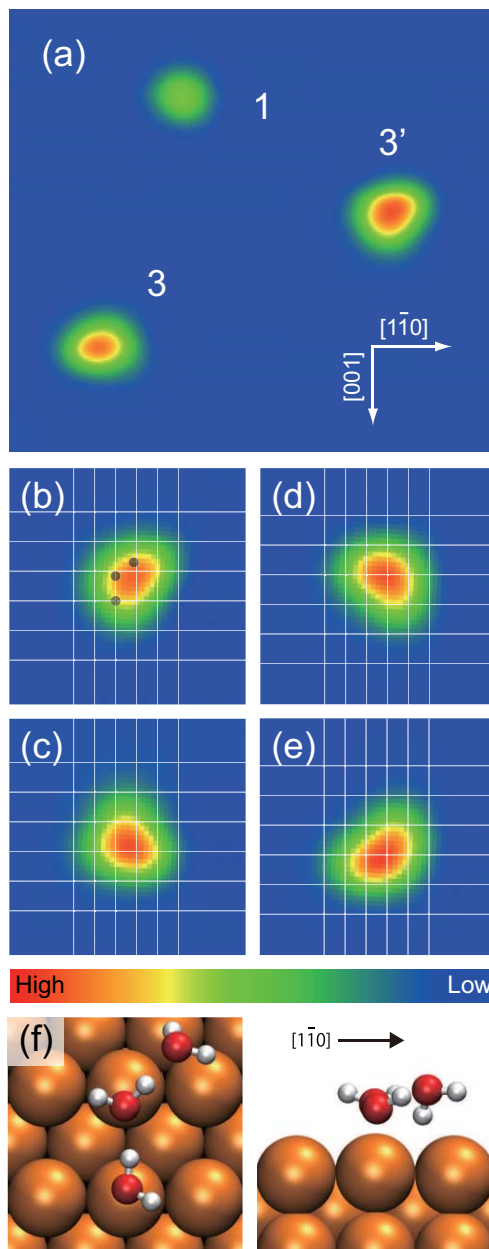


FIG. 3. (a) In addition to the $[1\bar{1}0]$ -chain type (left, labeled with 3), we observed another type of the trimer (right, labeled with 3'). The latter transforms spontaneously between (b) and (c) or (d) and (e) with the time scale of ~ 1 s and eventually converts to the $[1\bar{1}0]$ -chain type. The monomer (top, labeled with 1) is shown for comparison. The apparent height is typically 0.9 Å for the second trimer. (f) The optimized structure for the second trimer, in which two water molecules are bonded along $[001]$ and another one is attached to the end forming a chainlike structure ($[001]$ -chain trimer). The positions of water molecules are depicted in (b) with three dots. The images were obtained at 24 mV and 2 nA for (a) and 24 mV and 0.5 nA for (b)–(e). Scan area is $75 \times 68 \text{ \AA}^2$ for (a) and $28 \times 28 \text{ \AA}^2$ for (b)–(e).

was not observed and therefore is unfavorable when adsorbed on Cu(110) in spite of its maximized number of H bonds. Adsorption of a water cluster requires optimum adsorption sites wherein the energy gain both from water–water and water–substrate interactions is maximized; the adsorption geometry is determined by a delicate balance of these interactions. The cyclic form cannot find an optimum site, presumably because of the geometrical constraint of the quasi-1D Cu(110) surface.

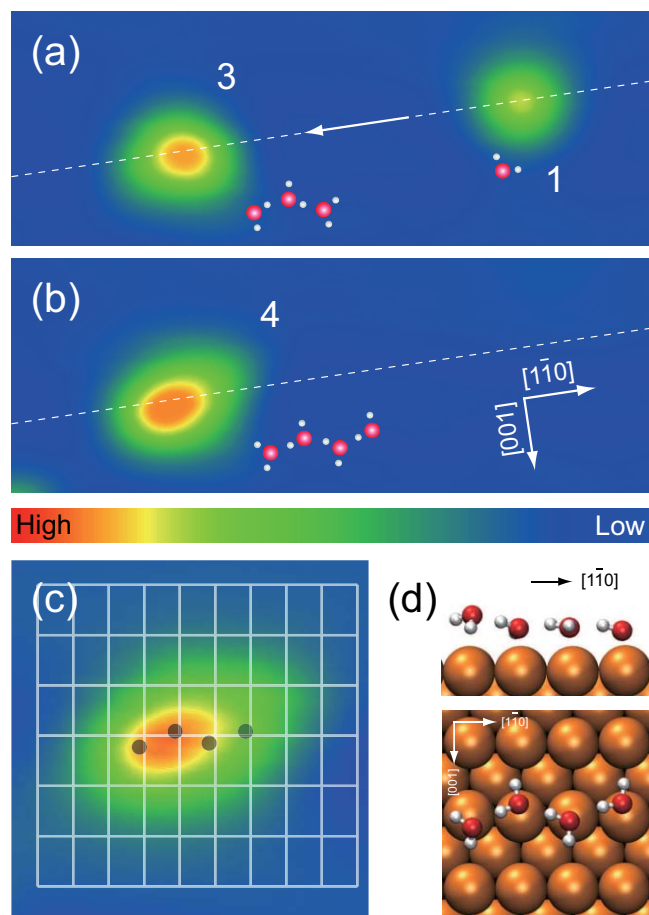


FIG. 4. Sequential STM images before and after the production of a tetramer. (a) A monomer (labeled with 1) was attached to the end of a $[1\bar{1}0]$ -chain trimer (labeled with 3) along the Cu row (dashed line). (b) The yielded tetramer is imaged as a distorted parallelogram (labeled with 4). The orientation was flipped during the reaction. (c) The registry of the tetramer. The dots depict the positions of water molecules. (d) The structure of the tetramer optimized by DFT. The end molecule of single acceptor is most protruded from the surface, thus contributing to the brightest feature in the image. The apparent height of the chain tetramer is typically 0.9 \AA . The images were obtained at 24 mV and 0.5 nA for (a) and (b) and 24 mV and 2 nA for (c). Scan area is $69 \times 25 \text{ \AA}^2$ for (a) and (b) and $25 \times 25 \text{ \AA}^2$ for (c).

Likewise, the one-donor–two-acceptor configuration proposed on Cu(111) (Refs. 11 and 13) and Ni(111) (Ref. 14) is unfavorable on Cu(110). These findings highlight the decisive role of the underlying substrate in the clustering of small number of water molecules. A chain tetramer was produced along the Cu row by attaching a water molecule to one end of the $[1\bar{1}0]$ -chain trimer [Figs. 4(a) and 4(b)]. The reaction is illustrated in the inset. The tetramer appears as a distorted-parallelogram protrusion, which is again rationalized by the end molecules bonding as a single donor or an acceptor. The registry of the tetramer and its optimized structure are shown in Figs. 4(c) and 4(d), respectively. It is analogous to the $[1\bar{1}0]$ -chain trimer, in which the single acceptor molecule is relatively high from the surface contributing to the highest protrusion in the image. The vertical displacement between the H-bond acceptor [left end of Fig. 4(d)] and the donor [right end of Fig. 4(d)] is 0.74 \AA with E_b of $0.484 \text{ eV/H}_2\text{O}$.

In a similar way, it was feasible to assemble longer chains along the Cu row. The pentamers in a distorted “trapezoidal”

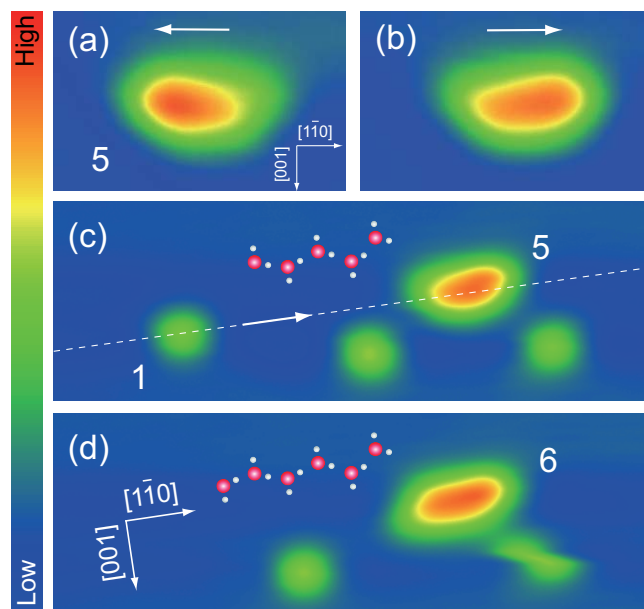


FIG. 5. (a) A chain pentamer assembled along the Cu row. (b) The counterpart of (a) in which the sequential hydrogen bonds point in the opposite direction. The arrows indicate the directions of hydrogen bonds. The end acceptor molecule in the chain appeared most protruded, and thus we can distinguish between the two directions. (c) A monomer (labeled with 1) and a chain pentamer (labeled with 5) are located on the same Cu row (dashed line). (d) The monomer was attached to one end of the pentamer to yield a chain hexamer (labeled with 6). The inset illustrates the structure of the chains. All images were obtained at 24 mV and 0.5 nA . Scan area is $31 \times 19 \text{ \AA}^2$ for (a) and (b) and $99 \times 33 \text{ \AA}^2$ for (c) and (d).

shape oriented in two opposite directions are shown in Figs. 5(a) and 5(b). The pentamer was further extended to a chain hexamer as shown in Figs. 5(c) and 5(d). A clear dependence of the image shapes on the even/odd constituent numbers indicates the zigzag arrangement of water molecules along the chains. Furthermore, the orientation of the hydrogen bonds in the chains is apparent in the image as shown in Figs. 5(a) and 5(b), suggesting that the chains are ferroelectric, where one OH bond of each molecule contributing to the hydrogen bonds points in one direction. Analogous 1D water chains were proposed to grow along the step edges of the Pt surface.^{12,15,35,36} The zigzag arrangement of water molecules was suggested by x-ray diffraction,³⁶ whereas the H-bond configuration remained unclear since hydrogen atoms were invisible with this method.

By applying a voltage pulse to the chain tetramer, we observed its conversion to two different isomers which were imaged as a triangular [Fig. 6(a)] or a round [Fig. 6(b)] protrusion. The three isomers convert to each other by applying voltage pulses with the STM. The threshold voltage for the conversion from the chain to the others is 0.12 V , while that from the round (triangle) species to the others is $0.18 (0.14) \text{ V}$,³⁷ implying that the round isomer is relatively stable. The round tetramer is featureless and centered on the hollow site, while the triangular one appears to be of C_s symmetry with its mirror plane along $[001]$.

Several structures of the tetramer were examined by DFT calculations, and some candidates were found for the observed three isomers. Among these, we propose the

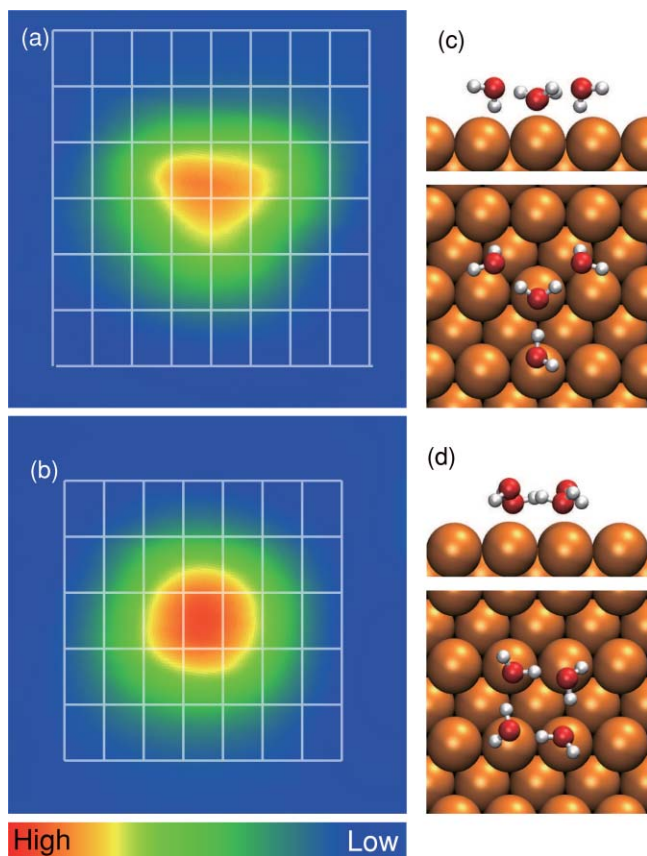


FIG. 6. STM images of two isomers of the tetramer. The structures proposed by DFT calculation are also presented. (a) The triangular species is assigned to the tetrahedral configuration with the center molecule acting as a double donor and single acceptor [(c)]. (b) The round species is centered on the hollow site and is assigned to the cyclic configuration [(d)]. The apparent height is typically 1.0 and 1.2 Å for the triangular and round tetramers, respectively. All images were obtained at 24 mV and 2 nA. Scan area is $25 \times 25 \text{ \AA}^2$.

corresponding structures based on the symmetry and registry of their images. The triangular isomer is assigned to the structure in Fig. 6(c), wherein the center molecule simultaneously acts as double donor and single acceptor, the same configuration as proposed for the tetramer on Cu(111).¹³ The chain and triangular isomers are almost degenerated in energy ($E_b = 0.489 \text{ eV/H}_2\text{O}$ for the triangular one). The round tetramer is assigned to the cyclic form [Fig. 6(b)], wherein each molecule acts as H-bond donor and acceptor at the same time. The cyclic structure is predicted to be the most stable ($E_b = 0.504 \text{ eV/H}_2\text{O}$) among all structures considered, as is for the gas-phase counterpart.³⁸ The cyclic tetramer is buckled with a vertical displacement of 0.66 Å and has two O–O bond lengths of 2.61 and 2.79 Å along and perpendicular to the Cu row, respectively. From the calculated charge density difference, we found that there are strong and weak H-bonds which correspond to the short and long O–O distances, respectively. Such an asymmetric structure was proposed for the cyclic hexamers on Cu(111),^{11,13} which is a result of the competition between the ability of water molecules to bond to the substrate and to accept H-bonds from other molecules. It is notable that whereas the vertical displacement is apparent in the STM images for the chain tetramer, the similar

displacement of the cyclic tetramer is not observed. The absence of the expected corrugation was also reported for the cyclic hexamer on Cu(111),¹¹ which was attributed either to the tip-induced reorientation of water molecules in the cluster as they were imaged or alternatively to the dynamical fluctuation between several configurations which is much faster than the time scale of STM measurement.⁴ Likewise, the featureless image in Fig. 6(b) might result from the tip induced and/or intrinsic fluctuation of the molecular height in the cluster that accompanies with no H-bond cleavage, and thus requires minimal activation.

As the temperature increases, water molecules readily diffuse and aggregate spontaneously to form a variety of clusters. Typical image of the surface prepared at 20 K and acquired at 6 K is shown in Fig. 7. Based on the knowledge obtained here, many of them are identified and labeled with their constituent numbers. The trimer and tetramer were observed mainly in the $[1\bar{1}0]$ -chain and cyclic forms, respectively, indicating that they are thermodynamically favorable among several isomeric structures. The longer chains as well as unidentified larger clusters were also observed. When water molecules are adsorbed at higher temperature ($\sim 80 \text{ K}$), they aggregate into the unique 1D island of $\sim 10 \text{ \AA}$ width that grows exclusively along $[001]$,³⁹ which was recently proposed to consist of interlinked water pentagons.⁴⁰ While individual water molecules are inherently unresolved in the water island as well as in the clusters by STM,⁴ assembling the 1D island from well-defined parts of clusters may provide new insight into its internal structure.

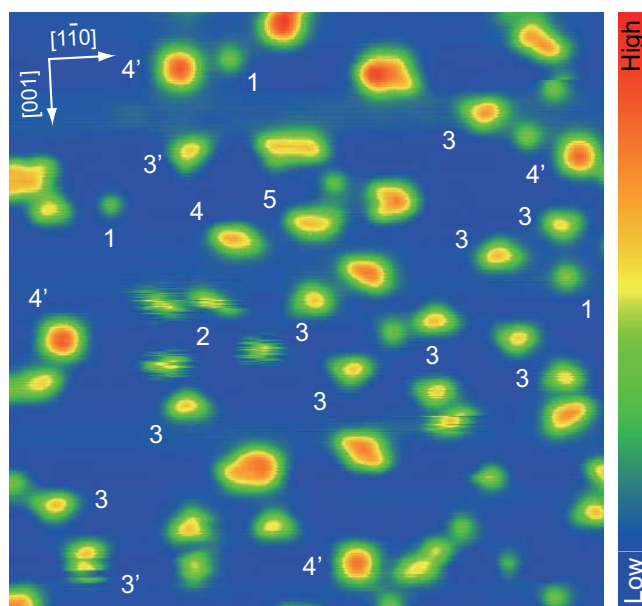


FIG. 7. STM images of various clusters spontaneously formed at 20 K. The identified clusters are labeled with their constituent numbers. The majority of the trimer was the $[1\bar{1}0]$ -chain type (labeled with 3). The $[001]$ -chain trimer (labeled with 3') in the bottom left is mobile and thus appears fractional. The tetramer was most likely observed in the cyclic form (labeled with 4'). The range of the height shown in the color bar is from -0.2 to 1.3 \AA . The image was obtained at 24 mV and 0.5 nA and the scan area is $170 \times 170 \text{ \AA}^2$.

IV. CONCLUSION

We assembled and characterized small water clusters on Cu(110) by using STM and DFT. Water molecules were arranged along the Cu row forming (meta)stable zigzag chains of trimer to hexamer. The trimer prefers chain forms to a cyclic form probably due to the geometrical constraint of the quasi-1D Cu(110) surface. For the tetramer, on the other hand, the cyclic form is the most favorable among the three isomers observed. These inclinations are quite different from those of gas-phase counterparts and on other surfaces, demonstrating the impact of the substrate on the clustering behavior of adsorbed water molecules.

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- ¹P. A. Thiel and T. E. Madey, *Surf. Sci. Rep.* **7**, 211 (1987).
- ²M. A. Henderson, *Surf. Sci. Rep.* **46**, 1 (2002).
- ³A. Verdaguer, G. M. Sacha, H. Bluhm, and M. Salmeron, *Chem. Rev.* **106**, 1478 (2006).
- ⁴A. Hodgson and S. Haq, *Surf. Sci. Rep.* **64**, 381 (2009).
- ⁵T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, *Science* **297**, 1850 (2002).
- ⁶V. A. Ranea, A. Michaelides, R. Ramirez, P. L. de Andres, J. A. Verges, and D. A. King, *Phys. Rev. Lett.* **92**, 136104 (2004).
- ⁷T. Kumagai, M. Kaizu, S. Hatta, H. Okuyama, T. Aruga, I. Hamada, and Y. Morikawa, *Phys. Rev. Lett.* **100**, 166101 (2008).
- ⁸T. Kumagai, M. Kaizu, H. Okuyama, S. Hatta, T. Aruga, I. Hamada, and Y. Morikawa, *e-J. Surf. Sci. Nanotechnol.* **6**, 296 (2008).
- ⁹K. Morgenstern and K.-H. Rieder, *J. Chem. Phys.* **116**, 5746 (2002).
- ¹⁰K. Morgenstern and J. Nieminen, *Phys. Rev. Lett.* **88**, 066102 (2002).
- ¹¹A. Michaelides and K. Morgenstern, *Nature Mater.* **6**, 597 (2007).
- ¹²S. Meng, E. G. Wang, and S. Gao, *Phys. Rev. B* **69**, 195404 (2004).
- ¹³A. Michaelides, *Faraday Discuss.* **136**, 287 (2007).
- ¹⁴D. Sebastiani and L. Delle Site, *J. Chem. Theory Comput.* **1**, 78 (2005).
- ¹⁵M. Morgenstern, T. Michely, and G. Comsa, *Phys. Rev. Lett.* **77**, 703 (1996).
- ¹⁶M. H. B. Stowell, T. M. McPhillips, D. C. Rees, S. M. Soltis, E. Abresch, and G. Feher, *Science* **276**, 812 (1997).
- ¹⁷G. Hummer, J. C. Rasaiah, and J. P. Noworyta, *Nature* **414**, 188 (2001).
- ¹⁸D. L. Mann and M. D. Halls, *Phys. Rev. Lett.* **90**, 195503 (2003).
- ¹⁹T. Kumagai, M. Kaizu, S. Hatta, H. Okuyama, T. Aruga, I. Hamada, and Y. Morikawa, *Phys. Rev. B* **81**, 045402 (2010).
- ²⁰L. Bartels, G. Meyer, and K.-H. Rieder, *Phys. Rev. Lett.* **79**, 697 (1997).
- ²¹Q.-L. Tang and Z.-X. Chen, *J. Chem. Phys.* **127**, 104707 (2007).
- ²²Q.-L. Tang and Z.-X. Chen, *Surf. Sci.* **601**, 954 (2007).
- ²³J. Ren and S. Meng, *Phys. Rev. B* **77**, 054110 (2008).
- ²⁴P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
- ²⁵Y. Morikawa, H. Ishii, and K. Seki, *Phys. Rev. B* **69**, 041403 (2004).
- ²⁶J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²⁷N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991); D. Vanderbilt, *ibid.* **41**, 7892 (1990).
- ²⁸M. Otani and O. Sugino, *Phys. Rev. B* **73**, 115407 (2006); I. Hamada, M. Otani, O. Sugino, and Y. Morikawa, *ibid.* **80**, 165411 (2009).
- ²⁹H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ³⁰T. Kumagai, M. Kaizu, H. Okuyama, S. Hatta, T. Aruga, I. Hamada, and Y. Morikawa, *Phys. Rev. B* **79**, 035423 (2009).
- ³¹I. Hamada, K. Lee, and Y. Morikawa, *Phys. Rev. B* **81**, 115452 (2010).
- ³²M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* **92**, 246401 (2004).
- ³³See supplementary materials at [<http://dx.doi.org/10.1063/1.3525645>] for details of vdW-DF and ZPE calculations.
- ³⁴N. Pugliano and R. J. Saykally, *Science* **257**, 1937 (1992).
- ³⁵M. L. Grecea, E. H. G. Backus, B. Riedmüller, A. Eichler, A. W. Kleyn, and M. Bonn, *J. Phys. Chem. B* **108**, 12575 (2004).
- ³⁶M. Nakamura, N. Sato, N. Hoshi, J. M. Soon, and O. Sakata, *J. Phys. Chem. C* **113**, 4538 (2009).
- ³⁷The threshold voltages were determined as follows: The tip was fixed over the protrusion of the clusters at 24 mV and 0.5 nA, and then a voltage pulse was applied. We defined the threshold as the minimum voltage that induces a reaction within 10 s.
- ³⁸J. D. Cruzan, L. B. Braly, K. Liu, M. G. Brown, J. G. Loeser, and R. J. Saykally, *Science* **271**, 59 (1996).
- ³⁹T. Yamada, S. Tamamori, H. Okuyama, and T. Aruga, *Phys. Rev. Lett.* **96**, 036105 (2006).
- ⁴⁰J. Carrasco, A. Michaelides, M. Forster, S. Haq, R. Raval, and A. Hodgson, *Nature Mater.* **8**, 427 (2009).