

Video Article

Probing the Structure and Dynamics of Interfacial Water with Scanning Tunneling Microscopy and Spectroscopy

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Abstract

Water/solid interfaces are ubiquitous and play a key role in many environmental, biophysical, and technological processes. Resolving the internal structure and probing the hydrogen-bond (H-bond) dynamics of the water molecules adsorbed on solid surfaces are fundamental issues of water science, which remains a great challenge owing to the light mass and small size of hydrogen. Scanning tunneling microscopy (STM) is a promising tool for attacking these problems, thanks to its capabilities of sub-Ångström spatial resolution, single-bond vibrational sensitivity, and atomic/molecular manipulation. The designed experimental system consists of a Cl-terminated tip and a sample fabricated by dosing water molecules *in situ* onto the Au(111)-supported NaCl(001) surfaces. The insulating NaCl films electronically decouple the water from the metal substrates, so the intrinsic frontier orbitals of water molecules are preserved. The Cl-tip facilitates the manipulation of the single water molecules, as well as gating the orbitals of water to the proximity of Fermi level (E_F) via tip-water coupling. This paper outlines the detailed methods of submolecular resolution imaging, molecular/atomic manipulation, and single-bond vibrational spectroscopy of interfacial water. These studies open up a new route for investigating the H-bonded systems at the atomic scale.

Video Link

The video component of this article can be found at <https://www.jove.com/video/57193/>

Introduction

The interactions of water with the surfaces of solid materials are involved in various surface reaction processes, such as heterogeneous catalysis, photoconversion, electrochemistry, corrosion and lubrication *et al.*^{1,2,3} In general, to investigate interfacial water, spectroscopic and diffraction techniques are commonly used, such as infrared and Raman spectroscopy, sum-frequency generation (SFG), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), neutron scattering^{4,5,6,7,8}. However, these methods suffer from the limitation of spatial resolution, spectral broadening, and averaging effects.

STM is a promising technique to overcome these limitations, which combines the sub-Ångström spatial resolution, atomic manipulation, and single-bond vibrational sensitivity^{9,10,11,12,13,14}. Since the beginning of this century, STM has been extensively applied to investigate the structure and dynamics of water on solid surfaces^{3,15,16,17,18,19,20}. Additionally, vibrational spectroscopy based on STM could be obtained from the second-derivative differential tunneling conductance (d^2I/dV^2), also known as inelastic electron tunneling spectroscopy (IETS). However, resolving the internal structure, *i.e.* the H-bond directionality, and acquiring reliable vibrational spectroscopy of water are still challenging. The main difficulty lies in that water is a close shell molecule, whose frontier orbitals are far away from the E_F , thus the electrons from the STM tip can hardly tunnel into the molecular resonance states of water, leading to the poor signal-to-noise ratio of molecular imaging and vibrational spectroscopy.

Water adsorbed on the Au-supported NaCl(001) films provides an ideal system for atomic-scale investigation by STM with a Cl-terminated tip (**Figure 1a**), which is performed at 5 K in the ultrahigh-vacuum (UHV) environment with a base pressure better than 8×10^{-11} mbar. On one hand, the insulating NaCl films decouple water molecules electronically from the Au substrate so the native frontier orbitals of water are preserved and the lifetime of the electrons residing in the molecular resonant state is prolonged. On the other hand, the STM tip could effectively tune the frontier orbital of water toward the E_F via tip-water coupling, especially when the tip is functionalized with a Cl atom. These key steps enable high-resolution orbital imaging and vibrational spectroscopy of water monomers and clusters. In addition, water molecules could be manipulated in a well-controlled manner, due to the strong electrostatic interaction between the negatively charged Cl-tip and water.

In this report, the preparation procedures of the sample and the Cl-terminated tip for STM investigation are outlined in detail in section 1 and 2, respectively. In section 3, we describe the orbital imaging technique, by which the O-H directionality of water monomer and tetramer are resolved. The tip-enhanced IETS is introduced in section 4, which allows the detection of vibrational modes of water molecules at single-bond limit, and determination of the H-bonding strength with high accuracy from the red shift in the oxygen-hydrogen stretching frequency of water. In section 5, we show how the water tetramer can be constructed and switched by controlled tip manipulation. Based on the orbital imaging,

spectroscopy, and manipulation techniques, isotopic substitution experiments can be performed to probe the quantum nature of protons in interfacial water, such as quantum tunneling and zero-point motion.

Protocol

NOTE: The experiments are performed on water molecules adsorbed on the Au-supported NaCl(001) film (**Figure 1a**) at 5 K with an ultrahigh-vacuum (UHV) cryogenic STM equipped with Nanonis electronic controller.

1. Fabrication of Experimental Sample

1. Clean the Au(111) single crystal

1. Pump the gas line to the pressure of $\sim 10^{-7}$ mbar and then flush the gas line with Ar gas. Put through the pump/flush cycle for three times.
NOTE: Each pump/flush cycle takes about 30 min.
2. Fill the gas line with Ar gas to the pressure of 2 bar, thus prohibiting the atmosphere to permeate through the gas line.
3. Put the Au(111) crystal on the heater stage, which is mounted on the manipulator in the UHV chamber (base pressure of 1.4×10^{-10} mbar).
4. Clean the Au(111) single crystal by cycles of Ar^+ ion sputtering for 15 min ($p(\text{Ar}) = 5 \times 10^{-5}$ mbar, 1.0 kV, 6 μA) and subsequent annealing at about 900 K for 5 min.
NOTE: The annealing temperature should be decreased slowly, otherwise a high density of step edges will form on the Au surface. 3 - 5 sputtering/annealing cycles are usually used.
5. Transfer the Au(111) sample to the STM scanning stage, and check the cleanliness with STM (Inset of **Figure 1b**).

2. Deposition of NaCl on the Au(111) substrate

1. Degas the NaCl source. Slowly increase the current applied on the Knudsen cell until the temperature of the source reaches 670 K. Degas the NaCl source several times until the pressure of the chamber is below 4×10^{-9} mbar.
NOTE: The increasing rate of the current depends on the outgassing rate of the NaCl source to maintain the pressure of the chamber below 1×10^{-8} mbar.
2. Put the Au(111) sample on the manipulator and adjust the position of the Au sample to make the sample face the shutter of the Knudsen cell.
NOTE: The temperature of the Au(111) substrate could be decreased below room temperature (77-300 K) by cooling down the manipulator head with a continuous flow of liquid nitrogen
3. Increase the current applied on the Knudsen cell until the temperature of the source reaches 640 K, and let the evaporation flux stabilize for 5 min before opening the shutter.
4. Open the shutter and deposit the NaCl onto the Au(111) sample held at 290 K for 2 min.
5. Transfer the Au-supported NaCl sample to the STM scanning stage. Check the coverage and size of the bilayer NaCl(001) islands on the Au(111) substrate with STM (**Figure 1b**).

3. Purify the water under vacuum by freeze-pump-thaw cycles²¹ to remove remaining impurities.

1. Prepare three sealed-off glass-UHV adapters. Place water H_2O , D_2O , and $\text{D}_2\text{O}:\text{HOD}:\text{H}_2\text{O}$ isotopic mixture solutions (2 mL) into three adapters separately, and mount the adapters on the gas line (**Figure 2**).
NOTE: The $\text{D}_2\text{O}:\text{HOD}:\text{H}_2\text{O}$ isotopic mixtures can be obtained by mixing the ultrapure H_2O and D_2O with equal amounts under ultrasonic oscillation for 10 min.
2. Freeze the liquid water with liquid nitrogen. Make sure that the gas line is pumped to the pressure of $\sim 10^{-7}$ mbar before freezing.
3. Open the diaphragm-sealed valve and pump off the atmosphere for 15 min. Then close the diaphragm-sealed valve and thaw the solution.
NOTE: Gas bubbles evolve from the solution when it is thawing.
CAUTION: Let the frozen solvent thaw by itself. Thawing the solution with water bath may cause the glass vessel to break. To freeze and thaw the solution quickly, replace glass-UHV adapters with metal-UHV adapters, though the solution in the metal vessel is invisible.
4. Repeat steps 1.3.2-1.3.3 until no gas bubbles evolve from the solution as the solution thaws. Put through the freeze-pump-thaw cycle at least three times.
5. Close the bellows-sealed valve and leave the gas line in vacuum. Then open the diaphragm-sealed valve, and let the water vapor fill in the gas line.

4. Dose water molecules *in situ* onto the sample surface

1. Decrease the temperature of the sample to 5 K. Open the leak valve slowly to make the pressure of the STM UHV chamber increase to 2×10^{-10} mbar.
NOTE: Water molecules flow into the UHV chamber through the dosing tube, which points to the shutter of the shield. The distance between the shutter and the sample (in the shield) is about 6 cm. The base pressure of STM chamber are better than 7×10^{-11} mbar. The deposition rate is about 0.01 bilayer min^{-1} .
2. Open the shutter. Dose the water molecules onto the Au-supported NaCl surface for 1 min. Then close the shutter and the leak valve.
3. Check the coverage of water molecules on the Au-supported NaCl(001) surface with STM. Isolated water monomers form on the sample surface (**Figure 1c**).

2. Preparation of the Cl-Terminated Tip

1. Fabricate an electrochemically etched tungsten (W) tip.
 1. Place 0.3 mm W wire into a 3 Mol/L NaOH etching solution with an immersion length of about 2 mm.
 2. Apply a 5 V dc potential to the W wire with respect to a platinum ring electrode inserted into the NaOH solution.
 3. Stop the etching process when the suspended W wire fell off. Clean the etched W tip with distilled water and ethanol. Then transfer the W tip into the scanner.

NOTE: The electrochemically etched W tip can be used for one year before exchange.
2. Apply voltage pulses (2-10 V) and controlled crashing procedures (0.25-0.4 nm) on the STM tip until the atomic Cl atoms of the NaCl surface are resolved.

NOTE: The STM tip is poked on a clean region of the Au(111) surface.
3. Position the STM tip over the center of one Cl atom (**Figure 3a**). Bring the bare STM tip close to the NaCl surface in proximity with the set point of $V = 5$ mV and $I = 5$ nA (**Figure 3b**).
4. Retract the tip to original set point (**Figure 3c**) and scan the same area. Check the obtainment of the Cl-tip by improved resolution and a missing Cl atom in the STM image of NaCl (**Figure 3d-e**).

NOTE: Unsuccessful cases may occasionally occur, for example, when the Cl atom doesn't transfer to the STM or multiple Cl/Na atoms adsorb on the tip. If this occurs, repeat the steps 2.2-2.5.

3. Orbital Imaging of Water Monomer

1. Shape the STM tip with voltage pulse (2-10 V) and controlled crashing (0.25-0.4 nm) procedures.
2. Scan the water molecules adsorbed on the NaCl(001) surface with 10 nm by 10 nm frame at 5 K.
3. Focus on one individual water monomer and zoom in. Scan the water monomer in a systematic way as functions of the bias (-400-400 mV) and the tunneling current (50-300 pA).

NOTE: With a bare STM tip, the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of water appear at positive and negative bias, respectively²². Once the tip is Cl-terminated, only HOMO emerges (**Figure 4a**), and the LUMO feature is not observed throughout the accessible bias range (from -400 mV to 400 mV). Even under larger bias voltage, the water molecules will be unstable due to vibrational excitation.

4. Single-Molecule Vibrational Spectroscopy

1. **Setup of the digital lock-in and bias spectroscopy module (Nanonis electronic controller)**
 1. **Setup of bias spectroscopy module:** Select the current, LIX1 (dI/dV spectra signal), and LIX2 (d^2I/dV^2 spectra signal) channels. Set the setting time as 50 ms, and integration time as 300 ms. Increase the integration time and sweep times to obtain smooth spectra. Tune the Z offset to take the bias spectroscopy at different tip heights. Make sure the Z-controller set holds and lock-ins runs during measurement

NOTE: **Setting time** is defined as: the time to wait after changing the bias to the next level and before starting to acquire data to avoid transient effect induced by the bias change. **Integration time** is defined as: the time during which the data are acquired and averaged.
 2. **Setup of lock-in module**

NOTE: The scanning tunneling spectroscopy, dI/dV and d^2I/dV^2 spectra, are acquired simultaneously using a lock-in amplifier by demodulating the first and second harmonics of the tunneling current, respectively.

 1. Modulate the bias and demodulate the current. Set the modulation frequency as a few hundred Hz and modulation amplitude as 5-7 mV. Make sure there is no mechanical and electronic noise at the set point frequency and the corresponding second harmonic frequency.
 2. **Set the first harmonic phase:** Switch to the Z-controller module. Set the tip lift to 10 nm and turn off the feedback. Switch to the lock-in module and turn on the lock-in button (green). Click the first harmonic auto phase and record the phase. Repeat the auto phase at least five times and take the average. Then subtract 90 degrees from the averaged phase to get the phase of the junction.
 3. **Set the second harmonic phase:** Position the STM tip on the Au(111) substrate and start the bias spectroscopy sweep from -1.5 V to 1.5 V. Select the channel LIX 1 and function dY/dX , which together show the derivative of dI/dV spectrum. Find a prominent peak feature in the spectrum and set the corresponding energy as the bias. Turn on the lock-in and keep the STM system in tunneling. Click the second harmonic auto phase at least five times and take the average.

NOTE: Since the second harmonic signals are usually very weak, the phase can fluctuate wildly. When decreasing the tip height to increase the intensity of the signal, the fluctuation of the phase will be much smaller (a few degrees) and the second harmonic phase will be more accurate.
2. **Tip-enhanced IETS of a D₂O monomer**
 1. Scan a water monomer with Cl-tip at the set point of $V=100$ mV and $I=50$ pA.
 2. Position the Cl-tip on the NaCl surface and take the bias spectroscopy as the background signal. Then position the Cl-tip on the water monomer and start the bias spectroscopy sweep.
 3. If the dI/dV and d^2I/dV^2 spectra of water are featureless, simply follow the background NaCl surface (blue curves of **Figure 4c-d**). Decrease the tip height by tuning the Z offset until the vibrational features emerge in the spectra (red curves of **Figure 4c-d**).

NOTE: For the IETS measurement, a long integration time (~1s) and multiple sweeps are needed. For a D₂O water monomer, set the bias range from -360 mV to 360 mV. For H₂O/HOD water monomers, sweep the bias from -475 mV to 475 mV. Comparing with D₂O, H₂O, and HOD, water monomers are more easily disturbed and even swept away during IETS measurement.

3. H-bond strength

1. Repeat steps 4.2.2-4.2.3 and tune the sweep bias range to focus on the stretching mode of water monomers. The IETS of water D₂O, H₂O, and HOD are presented and discussed in ²³.
2. Obtain the H-bonding energy by converting from the redshift of the H-bonded OH stretching frequency (relative to the free OH stretching energy) using this empirical formula:

$$\Delta H = 1.3 \times \sqrt{\Delta \nu} \quad (1)$$

NOTE: ΔH is the H-bonding energy, in kJ/mol; $\Delta \nu$ is the redshift of the OH stretching mode, in cm⁻¹. Convert the unit of H-bonding strength to meV by: 1kJ/mol=10.4 meV/atom. To apply Eq. 1 to the OD stretching mode, the quantity $\Delta \nu$ should be multiplied by a factor: $\nu(\text{OH}) / \nu(\text{OD}) = 1.3612$, where $\nu(\text{OH})$ and $\nu(\text{OD})$ are the OH and OD stretching frequencies of the free HOD molecule, respectively.

5. Molecular Manipulation

1. Construction of a water tetramer (Figure 5a)

1. Scan an area containing four water monomers. Position the Cl-tip on top of a monomer at the set point of V=100 mV and I=50 pA. Decrease the height to the set point of V=10 mV and I=150 pA to enhance the tip-water interaction.
2. Move the Cl-tip along the predesigned trajectories. Then retract the tip to the initial set point (V=100 mV, I=50 pA), and rescan the same area to check that the water dimer is formed.
3. Repeat the steps 5.1.1-5.1.2 to form the water trimer and tetramer.

NOTE: The above manipulation process could be realized by the Nanonis controller (Scan control-Follow me module). Setup of the Scan control-Follow me module:
Bias: 10 mV
Speed: 500 pm/s
Z-ctrl Setpoint: 150 pA
Switch on/off Z-Ctrl: green
Time to wait: 1s
Current Gain: LN 10⁹
Path: Click RECORD button and draw up the designed trajectories on the image, then click the STOP button.
Click the EXECUTE button and the STM tip will move along the predesigned trajectories with the setpoint in the Follow me module. If the water monomer doesn't move, decrease the tip height (smaller bias and bigger current) during manipulation.

2. Chirality switching of a water tetramer (Figure 6)

1. Scan a water tetramer with the Cl-tip. Change the set point to V=5 mV, I=5 pA, and position the tip slightly off the center of the water tetramer.
2. In the Z-controller module, define a distance to lift the tip when the Z-controller is switched off (e.g., Tip Lift: -230 pm). Turn off the Z-controller feedback. Bring the tip close to the water tetramer (~230 pm).
3. Record the current trace, which shows two different levels, indicating that tetramer has undergone reversible interconversion between two H-bonding chirality.
4. Leave the current at the high level and switch on the Z-controller feedback. Retract the tip to the original set point (V=5 mV, I=5 pA). Then scan the water tetramer with the set point of V=10 mV and I=100 pA to check the chiral state of the water tetramer.
5. Repeat steps 5.2.1-5.2.4 at least 10 times to confirm the corresponding chiral state of water tetramer at the high current level.
6. Repeat steps 5.2.1- 5.2.4 at least 10 times, but leave the current at the low level to check the corresponding chiral state of water tetramer.
7. Record the tunneling trace for 20 min, which contains a few hundred switching events
8. Plot the distribution of the times the tetramer spent in the low and high level of the current trace, respectively.
9. Fit the distribution to an exponential decay (Figure 7). Then get the fitted time constant. Inverse the time constant to yield the switching rate.

Representative Results

Figure 1a illustrates the schematic of the STM experimental setup. First, Au(111) substrate is cleaned by sputtering and annealing cycles in the UHV chamber. The clean Au(111) sample shows 22×√3 reconstructed surface, where the atoms of the surface layer occupy both the hcp and the fcc sites forming herringbone structures (Inset of **Figure 1b**). The NaCl is evaporated on the Au(111) substrate, forming bilayer islands (**Figure 1b**). Then water molecules are dosed on the Au-supported NaCl(001) surface through the gas line (**Figure 2**) and isolated water monomers are visualized on the NaCl islands (**Figure 1c**). The Cl-functionalized STM tip is obtained by picking up a Cl atom from the NaCl surface (**Figure 3**), which could gate the HOMO of water to the proximity of E_F via tuning tip-water coupling. **Figure 4a** is the STM image of a D₂O monomer obtained with a Cl-tip, very closely resembling the HOMO of water monomer (Inset of **Figure 4a**). In such a near-resonance case (**Figure 4b**), the HOMO of water couples strongly with the vibration modes, resulting in resonance-enhanced IETS. Considering the key role of tip gating in enhancing the IET signals, this technique is named tip-enhanced IETS. **Figure 4d** is the tip-enhanced IETS of water, in which the frustrated rotational, bending, and stretching modes are all visualized and denoted as "R", "B", and "S", respectively²³. In comparison with conventional IETS, the signal-to-noise ratio of tip-enhanced IETS is dramatically enhanced (up to 30% in relative conductance change), which is crucial for precisely determining the H-bonding strength.

Using the Cl-terminated tip, water molecules could be manipulated in a well-controlled fashion due to the electrostatic interaction between the Cl-tip and water. **Figure 5a** shows the procedure for constructing a water tetramer by dragging four water monomers along the predefined trajectories (green dashed arrows in **Figure 5a**), sequentially. Such a cyclic tetramer structure contains two degenerate chiral states: clockwise and anticlockwise H-bonded loops, which could be discerned from the STM images (**Figure 5b-c**)²². The chirality of the tetramer can be switched once the Cl-tip closely approaches the water tetramer (**Figure 6**), in which region the reaction barrier for proton transfer is effectively suppressed. The reversible interconversion of the H-bonding chirality of the water tetramer can be monitored by recording the tunneling current as a function of time²⁴. The switching rates could be extracted from the current versus time trace. As shown in **Figure 7**, the lifetime distribution of a clockwise tetramer could be fitted by an exponential decay $y = Ae^{-t/\tau}$ (red curve in **Figure 7**), and the inverse of the time constant τ yields the switching rate of CS→AS for a chosen sample bias and tip height.

Based on the orbital imaging, molecular manipulation, and tip-enhanced IETS techniques, the quantum motion of protons of interfacial water could be probed at the atomic-scale. For instance, it is possible to directly visualize the concerted quantum tunneling of protons within the water clusters and quantify the impact of zero-point motion on the strength of a single H bond at a water/solid interface, which are discussed in detail in ²³ and ²⁴, respectively.

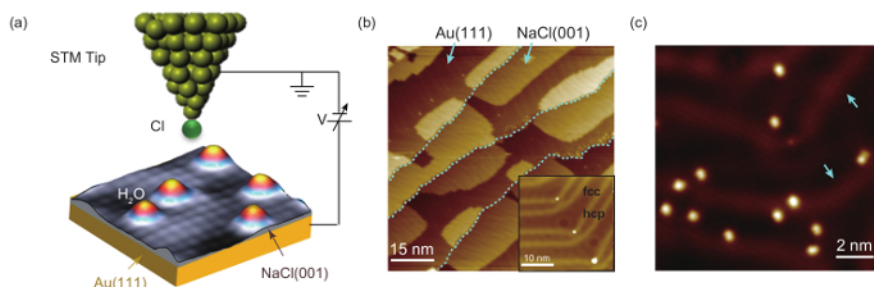


Figure 1: Experimental setup. (a) Schematic of the experimental setup. (b) STM image of bilayer NaCl(001) islands grown on the Au(111) surface. Step edges of the Au(111) surface are denoted by blue dotted lines. The inset shows the STM topography of Au(111) $22 \times \sqrt{3}$ reconstructed surface. (c) STM image of isolated water monomers adsorbed on the NaCl surface. Herringbone structures of the underlying Au(111) substrate are highlighted by blue arrows. Set point: (b) 2V, 9 pA; inset: 100 mV, 50 pA; (c) 100 mV, 50 pA. The STM images in this report were all obtained at 5 K. Adapted with permission from ²², copyright 2014 Nature Publishing Group. [Please click here to view a larger version of this figure.](#)

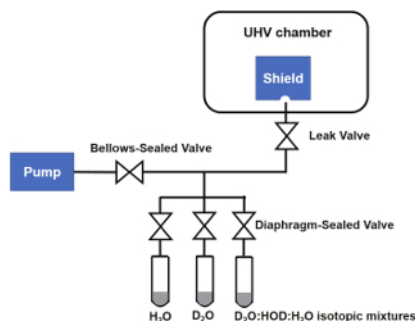


Figure 2: Schematic of the gas line for dosing water molecules on the sample surface. The water was purified under vacuum by freeze-pump-thaw cycles. Then the water molecules were dosed *in situ* onto the sample surface through a dosing tube, which pointed toward the sample with a distance of ~6 cm. [Please click here to view a larger version of this figure.](#)

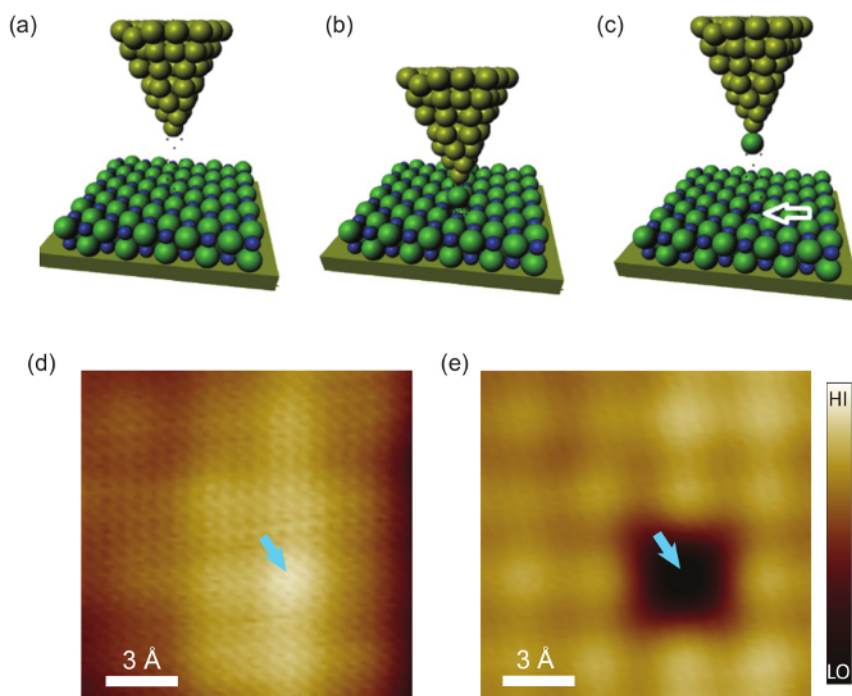


Figure 3: Preparation of a Cl-terminated STM tip. (a-c) Schematic of the procedure to acquire a Cl-terminated tip. The Cl-tip is obtained by bringing a bare STM tip close to the position of the Cl atom of NaCl surface (b), until a Cl atom transfers onto the apex of the STM tip (c). (d,e) STM images of the NaCl(001) surface (same area) acquired before and after the Cl atom adsorbed on the STM tip. The atomic resolution arising from the Cl⁻ anions was resolved. A Cl atom is missing (sky-blue arrow in (e)) and the atomic resolution is improved, indicating that the STM tip is functionalized with a Cl atom. Set point: (d) 50 mV, 100 pA; (e) 50 mV, 50 pA. Adapted with permission from ²⁴, copyright 2015 Nature Publishing Group. [Please click here to view a larger version of this figure.](#)

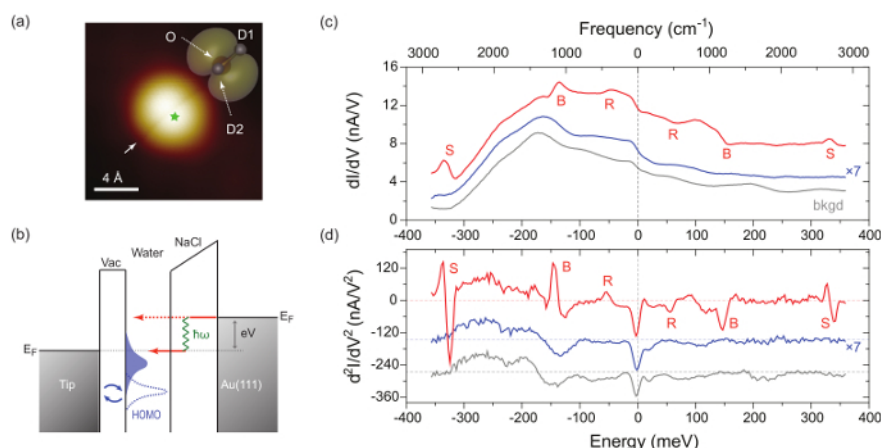


Figure 4: Tip-enhanced IETS of a D₂O monomer. (a) STM image of a D₂O monomer obtained with a Cl-tip ($V = 100$ mV, $I = 50$ pA). The inset shows the calculated isosurface of charge density of the HOMO. (b) Schematic of the tip-enhanced IET process. The Cl-terminated tip "gates", the HOMO to the proximity of E_F , thus resonantly enhancing the cross section of the IET process. (c) dI/dV (d) d^2I/dV^2 spectra obtained at the position of green stars on the water monomer. Red and blue curves are taken on the water monomer with the tip height offset by -120 pm and -40 pm, respectively. The gray curve is the background NaCl signal acquired at the tip height offset of -120 pm. Tip heights are referenced to the gap set with $V = 100$ mV and $I = 50$ pA. "R", "B", and "S" represent frustrated rotational, bending, and stretching vibration mode of water molecule, respectively. These curves are offset, presented in the y axes for clarity, and the zero levels of each curve are denoted by the dashed horizontal lines. Adapted with permission from ²³, copyright 2016 American Association for the Advancement of Science. [Please click here to view a larger version of this figure.](#)

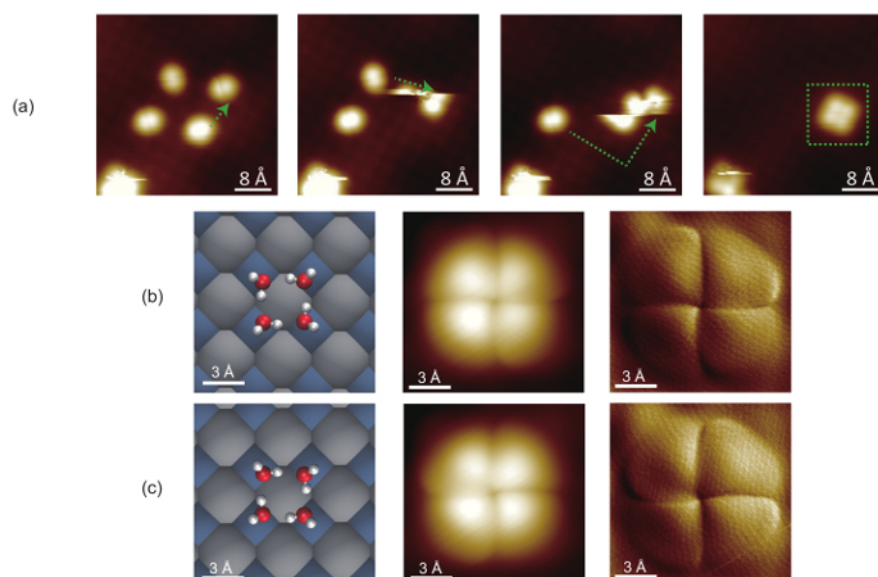


Figure 5: Adsorption configuration and STM topography of water tetramers on NaCl(001)/Au(111). (a) Procedure for constructing a water tetramer. Water monomers are manipulated by the Cl-tip along the predefined trajectories (green dashed arrows) to form a water tetramer. (b,c) Adsorption configuration and STM images of water tetramers with anticlockwise (b) and clockwise (c) H-bonded loops, respectively. The STM images of water tetramer (the second column) show that the boundaries between the four lobes exhibit left-handed (b) or right-handed (c) rotation, which is more evident in the corresponding derivative images (the third column). O, H, Cl⁻, and Na⁺ are denoted by red, white, grey, and dark-cyan spheres, respectively. Set point: (a) 80 mV, 50 pA, (b,c) 10 mV, 80 pA. Adapted with permission from ²², copyright 2014 Nature Publishing Group. [Please click here to view a larger version of this figure.](#)

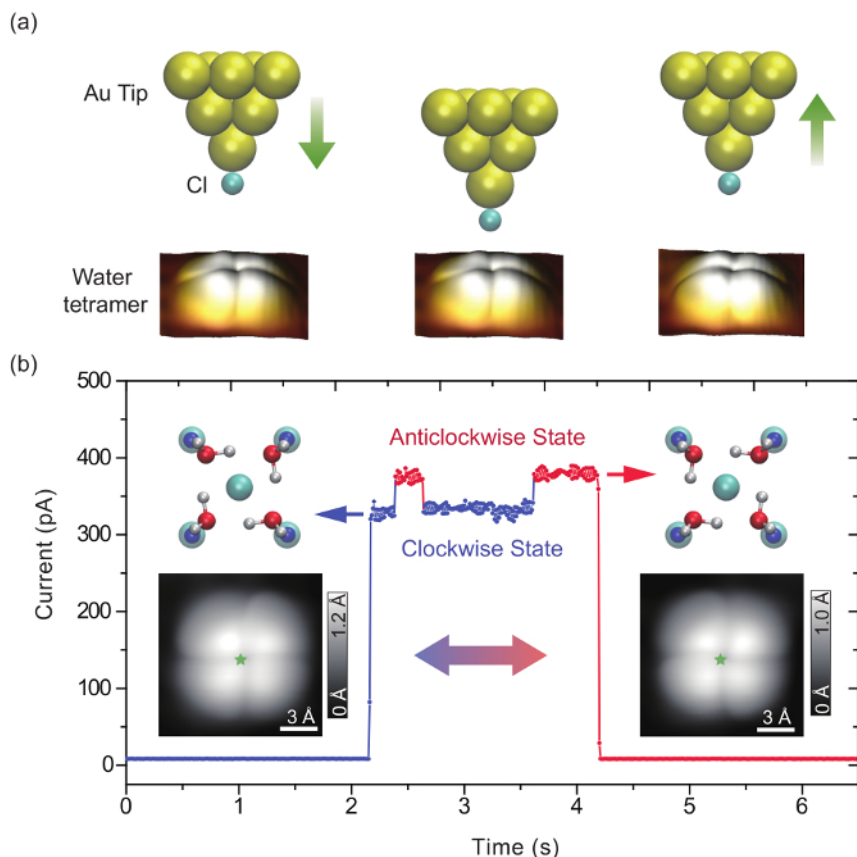


Figure 6: Chirality switching of a water tetramer. (a) Schematic showing the manipulation procedure of chirality switching of a water tetramer with a Cl-functionalized tip. On the left, the tetramer stays in the clockwise state (CS) at large tip height with the set point: $V=5$ mV and $I=5$ pA. In the middle, decreasing the tip height by 230 pm, the tetramer would undergo reversible interconversion between the clockwise and anticlockwise states. On the right, retracing the tip to the original tip height leaves the tetramer in the anticlockwise state (AS). (b) Tunneling current trace during chirality switching recorded at the position of green stars on the water tetramer. The higher and lower level of current correspond to the AS and CS state, respectively. The adsorption configuration and STM images of CS and AS state of tetramer are inserted in (b). O, H, Au, Cl⁻, and Na⁺ are denoted by red, white, golden, cyan and blue spheres, respectively. Adapted with permission from ²⁴, copyright 2015 Nature Publishing Group. [Please click here to view a larger version of this figure.](#)

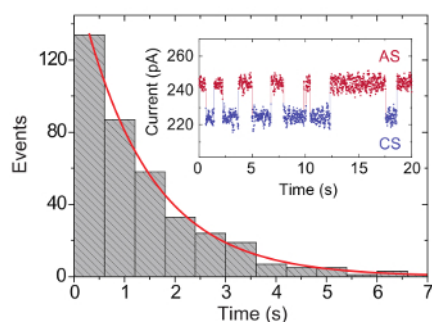


Figure 7: Extraction of the chirality switching rate from the current trace versus time. The lifetime distribution (bin size: 0.6 s) of the clockwise tetramer could be nicely fitted to an exponential decay (red curve) with the time constant of 1.37 s. The switching rate is the inverse of the time constant, 0.73 ± 0.016 s⁻¹. The current trace was acquired at a sample bias of 3 mV and tip height of -295 pm, referenced to the gap set with $V=5$ mV and $I=5$ pA. Adapted with permission from ²⁴, copyright 2015 Nature Publishing Group. [Please click here to view a larger version of this figure.](#)

Discussion

To probe the internal structure, dynamics, and vibrational spectroscopy of water molecules adsorbed on the solid surfaces, paying particular attention to the degrees of freedom of hydrogen, some experimental steps are of crucial importance, which will be discussed in the following paragraphs.

The orbital imaging of water molecules is achieved based on two key steps. First, the insulating NaCl films decouple the water electronically from the Au substrate, second the orbital gating effect of the STM tip via tip-water coupling. To grow bilayer NaCl films on the Au(111) substrate, the temperature of the Au(111) substrate should stay around 290 K. When the temperature of the substrate is much lower, fractal structures form, or the size of NaCl islands are too small. Higher temperatures will lead to the formation of thicker NaCl islands, thus the conducting of the sample will be poor. It is worth mentioning that both HOMO and LUMO could be visualized with a sharp bare tip, while the orbital gating of the Cl-terminated tip is highly selective, such that only HOMO is detectable due to the strong coupling between the HOMO and the P_z orbital of the Cl tip. Since the molecular orbitals are spatially locked together with the geometric structures of molecules, the O-H directionality of water molecules are discerned through submolecular-resolution orbital imaging²².

Compared with real-space imaging, the vibrational spectroscopy of water can offer new insights into H-bonding configurations, dynamics, and H-bonding strength. However, probing reliable vibrational spectroscopy of water with conventional IETS has proven challenging due to the close-shell nature of the water molecule. With a Cl-terminated tip, the IETS signals could be significantly enhanced as the HOMO of water could be tuned to the proximity of E_F via tip-water coupling, resulting in resonant-enhanced IETS²³. As a matter of fact, the IETS of water monomers is very sensitive to the lateral position of the tip. Because the HOMO orbital of water molecules has a node plane in the center, where the molecular DOS is the smallest, this leads to a very small cross section for vibrational excitation. Therefore, the tip is usually positioned slightly away from the nodal plane to maximize the IET signals (green star in **Figure 4a**). Furthermore, tip-enhanced IETS of the water monomer is also sensitive to the tip height. The IET spectra are featureless at large tip-water distance (blue curves in **Figure 4c-d**). With decreasing tip height, the coupling of the tip with the water molecule is enhanced and vibrational features emerge (red curves in **Figure 4c-d**). However, tip-water coupling may have significant influence on the intrinsic energies of the vibrational modes. Indeed, the stretching modes will undergo red shift with decreasing tip height, which can be fitted to inversed exponential decays. To eliminate the tip effect, extrapolate these curves to infinite tip height to obtain the intrinsic vibrational energies²³.

STM is not only an atomic probe for imaging and spectroscopic measurement, but can also manipulate individual atoms and molecules in a well-controlled fashion^{9,10}. In this report, the manipulation of the water molecules on the insulating NaCl films is more controllable when the tip apex is functionalized with Cl because of the long-range electrostatic interaction between the water and the negatively charged Cl atom on the tip. The constructed water tetramer contains two degenerate chiral states: clockwise and anticlockwise H-bonded loops, which can be switched with a Cl-tip. Occasionally, more than two current levels emerge in the current trace during chirality switching arising from the structural relaxation of the Cl atom adsorbed at the tip apex. The chirality switching usually occurs at small tip height, in which region the Cl atom might have multiple metastable adsorption configurations on the tip due to the asymmetry of the tip apex. The hopping of the Cl atom from one configuration to another changes the tunneling current, but does not lead to switching of the tetramer chirality. As a result, no matter how many levels appear, they can be divided into two groups, and each group corresponds to one chiral state of the water tetramer. What's more, the switching rates are sensitive to the tip position in the xyz directions, depending on the coupling of the Cl-tip with the water tetramer. The switching rates will be quenched when the Cl-tip is too close to the water tetramer or positioned off-center relative to the tetramer²⁴. To extract the switching rate from the current trace, the size of the time bin is critical. It is necessary to try several times to select an appropriate time bin to nicely fit the lifetime distribution to an exponential decay. In some cases, the two current levels are so close that the separation is comparable to the noise background, thus the adjacent averaging method is adopted to smooth the current trace to make the two current levels resolvable.

Although STM has been proven to be powerful for characterizing the structure, dynamics, and vibrational spectroscopy of water molecules on solid surfaces at the atomic scale, it suffers from limitations including: (1) conducting substrates are required to obtain the tunneling current, (2) poor temporal-resolution (usually in the order of a few hundred microseconds), (3) perturbation to the water molecules from the STM tip and the high-energy tunneling electrons during the IETS measurement, (4) UHV environment and low-temperature are indispensable. These limitations make STM fall short when compared with conventional methods for investigating water, such as optical spectroscopy, neutron scattering, and NMR. Nevertheless, the short-comings of STM can be overcome by combining other techniques. For instance, qPlus-based noncontact atomic force microscopy (nc-AFM) can be employed to determine the topology of H-bonded networks and even insulating crystal ice^{25,26}. Ultra-fast laser combined STM is a promising tool to achieve both submolecular spatial resolution and femtosecond temporal resolution simultaneously^{27,28}. Furthermore, employing the nitrogen-vacancy (NV) center as the scanning probe (NV-SPM) is expected to be a non-perturbative tool for detecting very weak magnetic signals, such as the spin fluctuations of protons in water and conducting NMR spectroscopy at nanoscale under ambient conditions^{29,30,31}.

Disclosures

Authors have nothing to disclose.

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