



KeyWords
Nanonis, IETS,
LT-STM, H₂O

High-resolution imaging and spectroscopy of water on NaCl(001) surface

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Nanonis Modules in Use

Base Package | Internal digital lock-in

System

CreaTec LT-STM/AFM

Introduction

The interaction of water with the surfaces of solid materials is ubiquitous. Many remarkable physical and chemical properties of water/solid interfaces are governed by H-bonding interaction between water molecules. As a result, the atomic-scale description of H-bonding structure and dynamics is one of the most important fundamental issues in water science. Ideally, attacking this problem requires the ability to access the internal degrees of freedom of water molecules, which remains a great challenge due to the light mass and small size of hydrogen.

Experimental details

Using a Nanonis STM control system connected to a CreaTec low-temperature scanning tunneling microscope (STM), we achieved submolecular-resolution imaging of individual water monomers and tetramers adsorbed on a Au-supported

NaCl(001) film at 5 K [1]. We adopted a "decouple and couple" methodology: 1. the water molecule was decoupled electronically from the metal substrate by inserting an insulating NaCl layer; 2. The tip-water coupling was tuned in a controllable way to enhance the molecular density of states of water near the Fermi level. These key steps enabled us to image the frontier molecular orbitals (HOMO and LUMO) (Fig. 1). Notably, we were able to discriminate in real space the orientation of water monomers and the H-bonding directionality of water tetramers based on the submolecular-resolution orbital images.

Accessing the internal degrees of freedom of water molecules allowed us to track the proton transfer along the hydrogen bonds by monitoring in real time the reversible interconversion of the hydrogen-bonding chirality of the water tetramer [2]. We used a chlorine-functionalized STM tip to lower the energy barrier for proton transfer through tip-proton electrostatic coupling such that the proton transfer events can be readily detectable (Fig. 2). It was further revealed that the proton transfer process involved a concerted tunneling of four protons, which were locked and moved in a fully correlated manner as a delocalized quasiparticle. We found that the Cl-terminated tip can either enhance or suppress the concerted tunneling process depending on the details of the coupling symmetry between the Cl and the protons.

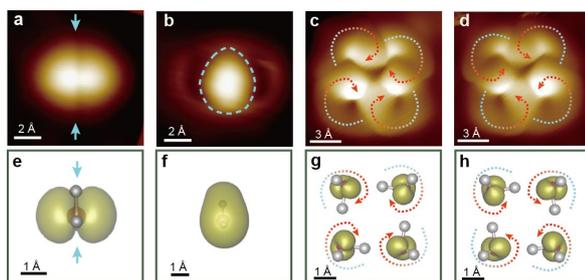


Figure 1. Submolecular-resolution orbital imaging of individual water monomers and tetramers on a NaCl(001) surface. (a) and (b) STM images of the HOMO and LUMO of a water monomer, respectively. Set point: $V = 100\text{mV}$ and $I = 500\text{ pA}$ (a); $V = -100\text{mV}$ and $I = 800\text{ pA}$ (b). (c) and (d) HOMO images of two water tetramers with anticlockwise and clockwise H-bonding loops, respectively. Set point: $V = 10\text{mV}$ and $I = 140\text{ pA}$. (e)-(h) Calculated isosurfaces of HOMO and LUMO orbitals, corresponding to (a)-(d). Adopted from Ref. [1]

In order to access the degree of freedom of hydrogen in energy space, we developed a novel technique called tip-enhanced inelastic electron tunneling spectroscopy (IETS) based on a LT-STM (Fig. 3). The signal-to-noise ratios of the tip-enhanced IETS were amplified by orders of magnitude over the conventional STM-IETS. The relative conductance change can reach about 30%. The conventional IETS signals of water are extraordi-

narily weak since the frontier orbitals of water are located far away from the Fermi level. The key to defeating this limitation is gating the HOMO of water towards the Fermi level with a chlorine-terminated STM tip to resonantly enhance the electron-vibration coupling. With such a tip-enhanced IETS, the hydrogen-bonding energy can be determined with unprecedented accuracy from the redshift in the O-H stretching frequency of water, which allows us to assess the impact of zero-point motion of proton on a single hydrogen bond at the water/NaCl interface [3].

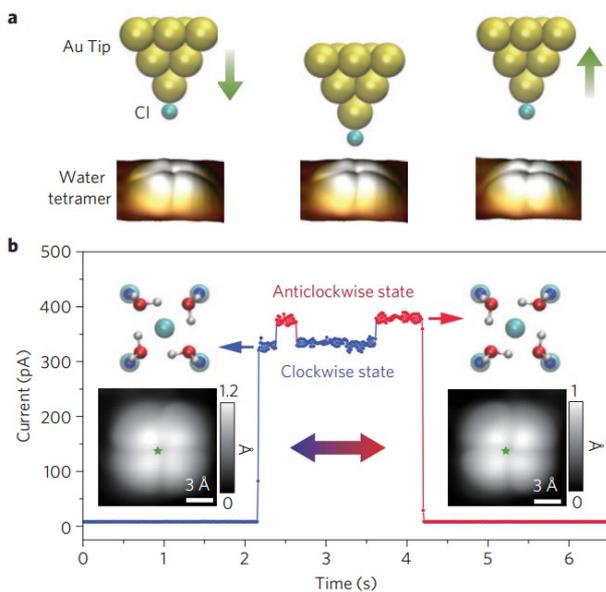


Figure 2. Chirality switching of an H₂O tetramer. (a) Schematic for manipulating chirality of the tetramer by a Cl-terminated tip. Left: the tetramer stays in clockwise state (CS) when the tip is far away from the tetramer (set point: V=5 mV and I= 5 pA). Middle: Reducing the tip height by 230 pm leads to the chirality switching. Right: lifting the tip back to the initial height leaves the tetramer in anticlockwise state (AS). (b) Tunneling current trace recorded during the chirality manipulation shown in (a). Two current levels are clearly distinguished within 300-400 pA, where the low and high current levels correspond to CS and AS, respectively. Adopted from Ref. [2].

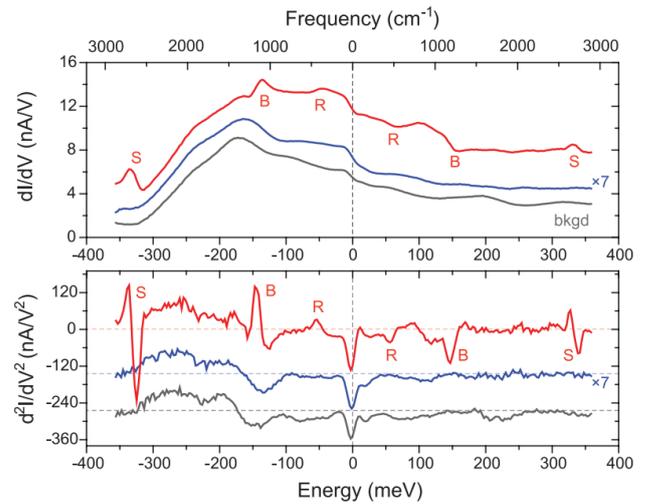


Figure 3. Tip-enhanced IETS of a D₂O monomer. dI/dV and d²I/dV² spectra taken at different tip heights. Red (-1.2 Å) and blue (-0.4 Å) curves were taken on the D₂O monomer. Gray curves (-1.2 Å) were acquired on the NaCl surface (denoted as “bkgd”). The vibrational IET features are denoted as “R” (rotational), “B”(bending), and “S” (stretching) . Dashed horizontal lines represent zero levels of the y axes for each curve. Adopted from Ref. [3]

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