

Chemical reactions of water molecules on Ru(0001) induced by selective excitation of vibrational modes

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Abstract: Tunneling electrons in a scanning tunnelling microscope were used to excite specific vibrational quantum states of adsorbed water and hydroxyl molecules on a Ru(0001) surface. The excited molecules relaxed by transfer of energy to lower energy modes, resulting in diffusion, dissociation, desorption, and surface-tip transfer processes. Diffusion of H₂O molecules could be induced by excitation of the O-H stretch vibration mode at 445 meV. Isolated molecules required excitation of one single quantum while molecules bonded to a C atom required at least two quanta. Dissociation of single H₂O molecules into H and OH required electron energies of 1 eV or higher while dissociation of OH required at least 2 eV electrons. In contrast, water molecules forming part of a cluster could be dissociated with electron energies of 0.5 eV.

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1. Introduction

The manipulation of atoms and molecules using the tip of a scanning tunneling microscope (STM) is one of the goals of nanoscience. Exciting internal molecular modes, either vibrational or electronic that deform the molecule along particular reaction coordinates, allows for an unprecedented and detailed study of the different steps involved in a given reaction.¹⁻³ Because of the narrow energy distribution across the Fermi level at liquid helium temperature, the tunneling electrons in an STM are ideally suited to perform vibrational spectroscopy.

The adsorption and dissociation of water on Ru(0001) is a particularly interesting case, as reflected in the vast literature of experimental and theoretical studies.⁴⁻⁸ In this system dissociation is an activated process as water adsorbs molecularly at temperatures below ~140 K. At low temperature dissociation can be activated by energetic electrons, as found in low energy electron diffraction (LEED) or in x-ray photoemission spectroscopy (XPS).^{6,7,9} It can also be promoted by interaction with other adsorbates.^{8,10,11} On Cu(111) and Cu(100), dissociation of water has been observed by using tunneling electrons at energies above ~1.5 eV.^{12,13}

Water monomer diffusion is also an activated process on metal surfaces. Water was observed to diffuse at rates of nm/s below 9 K on Cu(100)¹³ and around 40 K on Pd(111)¹⁴. STM experiments using inelastic electron tunneling have shown that excitation of the H₂O scissor mode at ~200 meV induces the diffusion of water clusters on Cu(111),¹⁵ and of monomers on Pd(111).¹⁶ Excitation of the ~450 mV O-H stretch mode enhances diffusion on Cu(111)¹⁵ and also activates it on surfaces with higher energy barriers, such as Ag(111).¹⁷

In this paper we show how the excitation of vibrational modes by tunneling electrons induces several reactions in water molecules, in hydroxyl groups and in hydrogen atoms on the Ru(0001) surface. Depending on the voltage/current parameters diffusion, desorption, intermolecular bond formation and breaking, and transfer to the tip could be excited.

2. Experimental

The STM experiments were performed using a home-built scanning tunneling microscope in an ultra-high vacuum chamber with a bath cryostat. All data were collected at 6 K at a base pressure below 2×10^{-11} Torr using electrochemically etched W tips. The single crystal Ru(0001) sample was cleaned following a standard procedure reported previously.¹⁸ The resulting surface contained a small amount of C atoms, typically around 0.03 monolayers (ML) relative to the Ru surface, segregated during high temperature annealing.

Milli-Q water in a glass tube, degassed by repeated cycles of freezing, pumping and thawing, was used as the H₂O source. It was introduced in the microscope chamber through a leak valve and a dosing tube directed to the sample. The sample could be annealed in the STM with a resistive heater.

The manipulation experiments were performed by placing the tip over a molecule at selected tunneling parameters, opening the feedback loop, and applying a voltage pulse of controlled duration. The effect of this procedure was monitored by recording the tunneling current and by imaging the local area after the voltage pulse. Reaction dynamics were characterized by the distribution of time intervals from the start of a voltage pulse to the reaction event, indicated by an abrupt change in the tunnel current.

3. Results

3.1. Diffusion, desorption, and tip transfer of single H₂O molecules

After adsorption of small amounts of water at 6 K, isolated molecules are observed which give rise to protrusions (bright spots) in the STM images, as shown in Figure 1a. Some of the molecules are isolated bound to a Ru atom, and some are bound also to a carbon atom. The carbon atoms appear as 35-45 pm deep depressions¹⁸ (dark spots) in the images. The isolated and the C-bonded water molecules give rise to two different types of protrusion, labeled I and II in Figure 1a. The brighter ones (I) with an apparent height of ~55 pm correspond to isolated molecules adsorbed on Ru top sites and with their molecular plane nearly parallel to the surface. The dimmer ones (II), with an apparent height of ~30 pm,

correspond to molecules bound to a C atom at a distance of 0.32 ± 0.03 nm (Figure 1b), as shown by previous STM experiments and DFT calculations.¹⁸ The STM height contrast is mostly electronic in origin, as determined by DFT calculations and STM image simulations. DFT calculations show also a significant covalent interaction between H₂O and C in type II molecules.

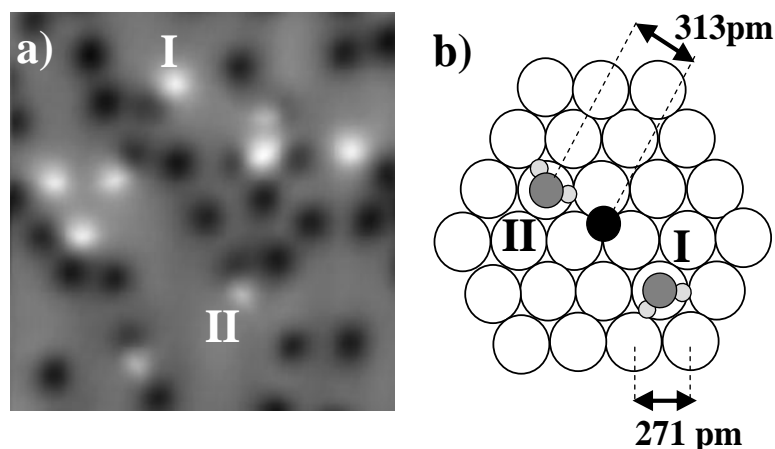


Figure 1. a) STM image (10×10 nm, $V_{\text{sample}} = 50$ mV, $I_t = 0.2$ nA) of a Ru(0001) surface with adsorbed water molecules (bright spots) and with 0.03 ML of C atoms (dark spots). The corrugation of the Ru atoms is too weak (~ 2 -3 pm) to be seen in the image. Type I water molecules are isolated monomers. Type II molecules are bound to C atoms and appear with lower contrast. b) Schematic model showing the geometry of type I and II molecules.

When the tip was positioned over an H₂O molecule (bias 50 mV, current 0.25 to 5 nA), open loop voltage pulses below ± 450 mV produced no noticeable change in most cases. Above this threshold value however, diffusion, desorption, or transfer to the tip could be induced with different probabilities, as revealed by the displacement or the disappearance of the water molecule in subsequent STM images. The energy of the electrons at the voltage onset for these processes is very close to the energy of the O-H stretch mode. Since the process was found to be polarity independent all subsequent measurements were performed using positive voltage pulses (the voltage is applied to the sample, i.e. the electrons flow from tip to sample). A sequence of images from one of these manipulation experiments is shown in Figure 2, where voltage pulses were applied between frames over the water molecules indicated by the arrows. Between (a) and (b) the type I molecule near the bottom was desorbed. A pulse applied to the

type-II molecule in (b) caused cleavage of the C-H₂O bond and the molecule, now of type-I (c), moved 4 lattice sites to the right. Another pulse to the same molecule in (c) moves it one lattice site to the left (d).

Table 1: Relative probabilities of electron induced processes with voltage pulses of 450-550 mV applied for 1 to 3 sec for type I (isolated) and II (C-bonded) water monomers. Initial tunneling conditions: $V_{\text{sample}} = 50$ mV, $I_t = 0.025$ to 0.6 nA for type I and 0.3 to 5 nA for type II. The relative probability of different events did not depend significantly on the initial current setpoint. The C atoms in type II complexes were never observed to move. More than 50 manipulation events are included for each molecule type.

Molecule type	Diffusion	Desorption	Transfer to tip	No observed change
(I) Isolated H ₂ O	79%	6%	10%	5%
(II) C-bonded H ₂ O	51% ^a	33%	0%	16%

^a74% of events dissociate the type II complex

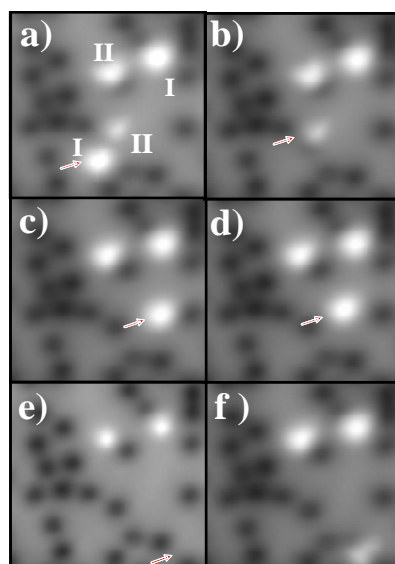


Figure 2. STM images (5×5 nm, $V_{\text{sample}} = 50$ mV, $I_t = 0.2$ nA) showing a sequence of manipulation experiments of water molecules (bright spots) by application of voltage pulses. The arrows point to the location of the tip where a voltage pulse of 3 seconds will be applied. a) Image containing two isolated (I) (brightest spots) and two C-bonded (II) H₂O molecules. b) The type I molecule pointed by the arrow in a) has been desorbed by a 500 mV pulse. c) The type II molecule pointed by the arrow in b) is moved and the complex converted to type I by a 550 mV pulse. The second, more distant type II complex was also dissociated, perhaps by hot electrons scattered at the surface. d) Type I molecule in c) diffused by one Ru lattice site after a 450 mV pulse. e) Type I molecule was transferred to the tip, indicated by its disappearance and by the change in image contrast. f) The water molecule on the tip is transferred back to the surface by a 550 mV pulse, where it bonds with a C atom to form a type II complex. The image contrast has been restored to that of (a-d).

Most diffusion events of water molecules were multisite, single lattice site diffusion such as the example shown in Figure 2c and 2d being less common. Some times a pulse applied at a given location resulted in the diffusion of a molecule located farther away from the tip, an effect not due to a multiple asperity tip as it was observed for many different tips. This type of non-local effect could be mediated by hot surface electrons excited during the pulse. Similar non-local effects have also been observed for

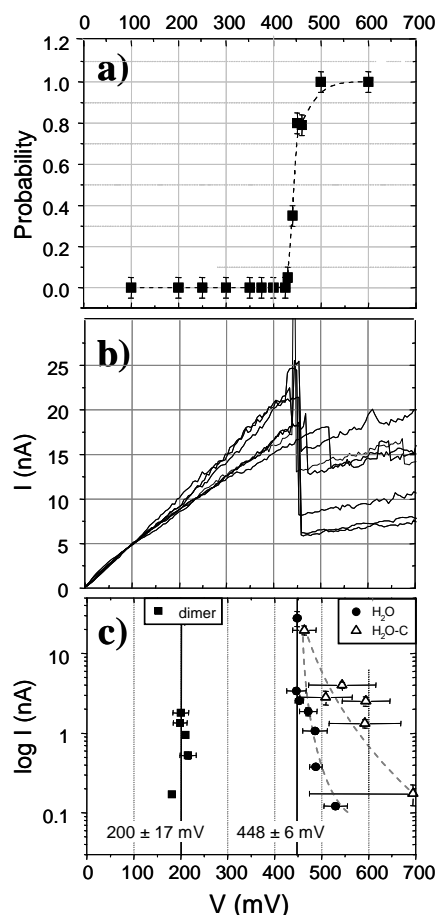


Figure 3 a) Diffusion probability of isolated H₂O (I) monomers as a function of pulse voltage. The initial set-point was $V_{\text{sample}} = 50$ mV, $I_t = 106$ pA, and the pulse duration was varied so as to keep the total electron dose constant at 8×10^8 electrons. Each data point represents 10 individual trials. A sharp onset is observed at 445 ± 6 mV. The error bar for the data point at 435 mV indicates the deviation obtained between two different measurement sets of 10 trials each. b) Open-loop voltage ramps applied to a C-bonded H₂O (II) molecule, starting from tunneling at $V_{\text{sample}} = 100$ mV, $I_t = 5$ nA. The abrupt current jumps are due to the diffusion of the molecule away from the tunneling gap. Each curve was collected on a different C-bonded molecule. c) Current dependence of the voltage pulse inducing diffusion. The higher the current the closer the electron energy is to the vibrational mode energy, 448 ± 6 meV for the OH stretch of isolated or C-bonded H₂O molecules (right panel), and 200 ± 17 mV for the scissors mode in the case of water dimers (left panel)

water on Cu(111).¹⁵ Table 1 summarizes the relative probability for the occurrence of each process for type I and II water molecules.

Figure 3a shows a plot of the electron excited diffusion probability of type I molecules as a function of applied voltage. The pulse duration was adjusted so that each pulse involved a constant dose of 8×10^8 electrons, and the local region was imaged after each pulse to check if the molecule had diffused or not. A clear onset can be observed at 445 ± 6 mV. In another type of experiment the open-loop bias voltage was increased while recording the tunnel current, as in the example in Figure 3b for type II monomers. Loss of the molecule under the tip by diffusion is marked by an abrupt change in the tunneling current. The current dependence was explored by varying the initial closed-loop current set-point before the voltage ramp. At higher initial currents the diffusion occurred closer to the threshold voltage, asymptotically reaching it for high enough currents. Currents of ~ 10 nA were sufficient to diffuse away the molecule at the threshold voltage for type I molecules. Diffusion of type II molecules showed a stronger current dependence and did not converged to the threshold voltage until ~ 100 nA. This is shown in Figure 3c.

As mentioned before these results are independent of voltage polarity and show significant current dependence above the voltage threshold, thus ruling out electric field induced diffusion mechanisms. The energy of the electrons at the voltage onset for monomer diffusion agrees well with the 445 meV energy of the O-H stretching mode observed by electron energy loss spectroscopy (EELS) for H₂O monomers on Ru(0001),¹⁹ indicating that diffusion is induced by excitation of this mode. In multielectron processes, where each electron excites the molecule by an additional quantum, the induced diffusion rate should exhibit a power-law dependence on the tunnel current $R \sim I^N$, the exponent N indicating the number of electrons involved in the excitation process.^{20,21} Figure 4 shows the current dependence of the electron excited diffusion rate at 475 mV, just over the excitation threshold for the O-H stretch. The rate was determined from the average time required to initiate the process, as shown in the inset on top of Figure 4. For isolated H₂O (I), the slope of the log-log plot gives $N = 1.1 \pm 0.2$,

indicating that diffusion is excited by a one-electron process. For C-bonded H₂O (II) we obtain $N = 2.5 \pm 0.1$, therefore diffusion requires at least two electrons. The fractional number could indicate that other excitations in addition to the O-H stretch may play a role in this case. The total yield was also very different for the two cases studied here. At 1 nA the yield was 4×10^{-8} events/e for diffusion of type I, and 3×10^{-11} events/e for dissociation of the C-H₂O bond in type II molecules, 3 orders of magnitude lower than for diffusion of type I.

From the analysis of Ueba and Persson,²¹ inelastic excitation of internal molecular vibrational modes with energies greater than the translational energy barrier can be more efficient at inducing diffusion than multiple excitation of lower energy modes, such as frustrated translations with an energy of ~ 30 meV that are more directly coupled to the reaction coordinates for diffusion. According to this analysis the diffusion energy barrier for isolated water monomers should be larger than 200 meV, corresponding to the scissor mode where a single excitation was shown to induce translation on Pd(111),¹⁶ and lower

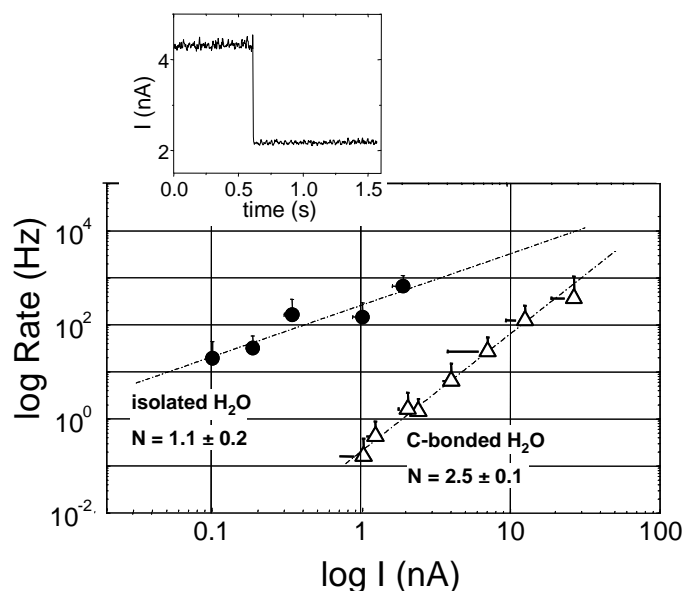


Figure 4. Current dependence of the diffusion rate for isolated (solid circles) and C-bonded (open triangles) water molecules induced by 475 mV pulses. Rates were obtained by averaging the elapsed time until an abrupt change occurred in the tunnel current, as shown in the inset at the top. Images obtained after the current drop verified that each change was due to molecular diffusion. The slope of the linear fit indicates the number of inelastic electrons involved in the process. Whereas the diffusion of an isolated H₂O is a one electron process, the diffusion of C-bonded H₂O, which includes the cleavage of the C-H bond, requires at least two electrons.

than 445 meV, the O-H stretch energy. This is consistent with the calculated 260 meV energy difference between water adsorption on top and bridge sites in Ru(0001) and 190 meV for Pd(111).^{5,22-24} The fact that double or triple excitation of the scissor mode was not observed to induce water diffusion on Ru under the range of tunnel conditions explored in this work places a lower limit on the decay rate for this mode.

For C-bonded H₂O the excitation of a single O-H stretch vibration quantum is not sufficient to induce diffusion. The higher energy barrier in this case is attributed to the cleavage of the C- H₂O bond.

3.2 Water clusters

In addition to monomers, small aggregates of a few water molecules (dimers, trimers, etc.), could also be observed. Although the internal structure of these clusters was not usually resolved in the STM images, the number of constituent molecules in the cluster could be found by disrupting them with voltage pulses. In the case of dimers we could observe the peculiar helicopter-like rotation of the acceptor molecule predicted by Ranea et al.²² In this model one water molecule, the donor molecule, is

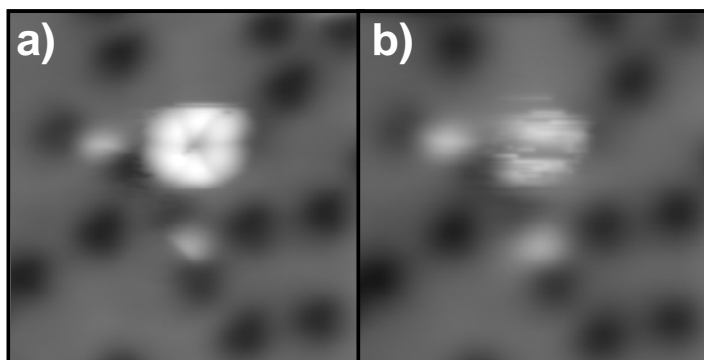


Figure 5. a) Water dimer imaged as a rosette of six maxima due to the rotation of the acceptor molecule around the donor molecule located at the center. The rotation is induced by strong interaction with the tip ($V_{\text{sample}} = 50$ mV; $I_t = 400$ pA). b) At higher gap resistance ($V_{\text{sample}} = 50$ mV; $I_t = 40$ pA) the interaction is weaker and rotation is not clearly observed. Image size: 3.5×3.5 nm.

bound to the surface via the O-lone pair orbital while the other is a H-acceptor molecule weakly interacting with the substrate. In our case, the rotation is enhanced by interaction with the tip at low gap resistance (50 mV, 400 pA), as shown in Figure 5, which moves the molecule to the tip position over

each of the 6 Ru atoms surrounding the donor water molecule bound to the central Ru atom. At higher gap resistance the interaction is weaker and the rotation is not clearly observed.

Excitation of dimers and trimers with electrons of energy less than 200 meV (the scissor mode energy) resulted only in restructuring of the clusters into different configurations. In contrast to the isolated molecules, which required excitation of one OH stretch quantum, translation of water dimers was observed at a threshold voltage of 200 ± 17 mV and currents as low as ~ 0.5 nA in open-loop ramps as the one shown in Figure 3c. This indicates a lower diffusion energy barrier than for monomers which, as we have seen, requires excitation with electrons of energy larger than 445 meV. An easier diffusivity of dimers compared to monomers was also observed on Pd(111)¹⁴, which Ranea et al.²² explained as due to a cooperative mechanism where the donor-acceptor role is successively exchanged when the two molecules bond metastably to the metal atoms. Interestingly a similar experiment performed on rosette-

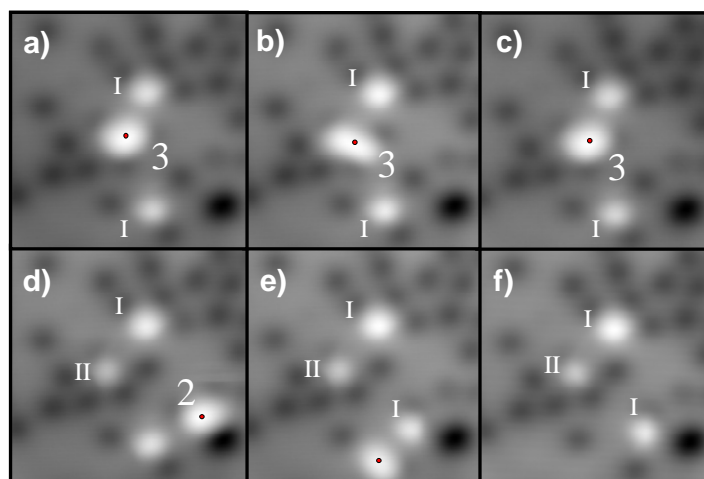


Figure 6. Sequence of 5×5 nm images illustrating the manipulation of a water trimer which produces the unresolved spot near the center marked by 3. Two isolated molecules of type I are also present. Each image was acquired after applying a voltage pulse with the tip at the position marked with a dot. Voltage pulses below 445 meV result only in either translation or internal reorganization of the molecules in the cluster (a-c). Above 200 meV diffusion of the cluster was normally observed. For voltage pulses above 445 meV (O-H stretch) the cluster can be dissociated into monomers or into monomers and dimers. In d) the trimer has dissociated into a monomer bound to a C atom (marked II near the center) and a dimer (marked 2) after a 475 mV pulse. e) Another pulse of the same voltage dissociates the dimer, and the released monomer formed a dimer with the nearby monomer. f) A final pulse of the same voltage diffuses the dimer out of the scanned area.

like rotating dimers on Pt(111) by Motobayashi et al.²⁵, indicates a higher diffusion barrier than for monomers. This could be due to the suppression of the donor-acceptor exchange mechanism on this surface, possibly due to a higher lattice mismatch.

Trimers could be rearranged with voltage pulses below 200 meV and translated with voltage pulses above 200 meV. Excitation of the O-H stretch mode at 450 meV induced intermolecular bond breaking (cluster dissociation). An illustration of several of these events is shown in the images in Figure 6.

3.3 Dissociation of H₂O and OH

Water dissociation on Ru(0001) can be achieved by thermal or by electronic excitations.^{6,8,18} Unlike the quantum state selective excitation of H₂O translation by single or multiple electron processes discussed in the previous section, rupture of the O-H bond could not be achieved with electron energies

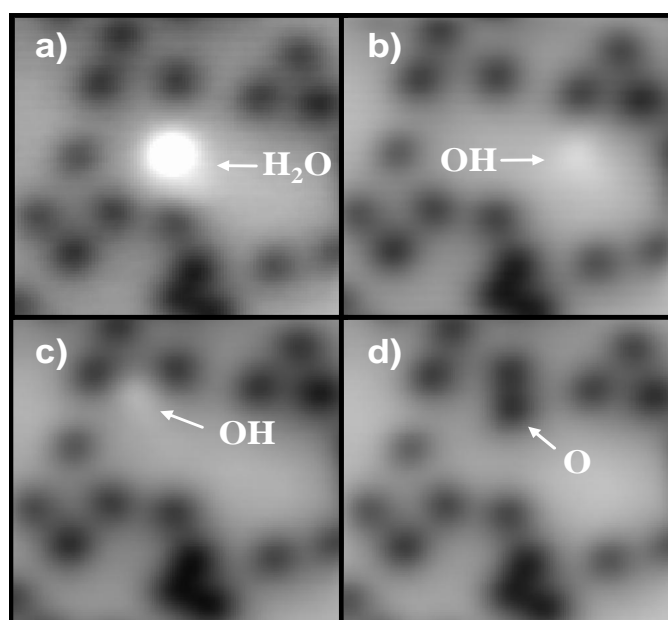


Figure 7. STM images (4×4 nm, $V_{\text{sample}} = 50$ mV, $I_t = 0.2$ nA) of a manipulation experiment showing the sequential dissociation of H₂O into OH and then O. Voltage pulses were applied with the tip located over the molecule (marked by the arrow) after disabling the feedback at the set-point used for imaging. a) Isolated H₂O molecule. b) After a 1.7 V, 50 msec pulse an OH species is formed from the dissociation, and is imaged with a weak contrast spot. The H atom diffused away from the imaging area. c) Pulses above 150 meV are sufficient to cause the diffusion of OH, with no interaction with the surrounding C atoms (dark spots). d) A 2 V, 50 msec pulse over the OH caused its dissociation into O (dark spot marked by an arrow) and H. As in b), the H atom diffused away from the imaging area.

below 1 eV and currents below 30 nA, i.e. by a ladder-type single quanta excitation of the O-H stretch. This is probably due to the very efficient intermodal coupling to the translation modes so that the molecule moves away from the tip region before a multi-electron process can excite a sufficiently high vibrational state to cause O-H bond rupture.

This scenario changes if the voltage pulse is high enough for a single electron to excite multiple quanta of the O-H stretch mode and thus modify the relative yield between diffusion and dissociation. Indeed, by increasing the voltage of the pulse to between 1 and 1.5 V, where two or three quanta of the O-H stretch could be excited per electron, we observed a different behavior. As shown in Figure 7, after a voltage pulse of 1.7 V the appearance of the H₂O molecule changed dramatically. A new species with an apparent height of only 10 pm can now be seen adsorbed at an hcp site displaced from the pulse location by an average of 3 ± 1 Ru lattice sites. Previous work in our group¹⁸ has shown that this species can be identified as OH, confirming the dissociation of the H₂O molecule. The electron energy required for H₂O dissociation is consistent with the barrier of 0.85 eV obtained by DFT for monomers.⁵ The large chemical energy released by the dissociation, together with the low diffusion barrier of OH (shown below), could be the source of the kinetic energy necessary for the large displacement of the products. Both isolated and C-bonded H₂O could be dissociated in this voltage range, but the competition between diffusion and dissociation made it impractical to quantify differences arising from the two initial conditions. Complete dissociation from H₂O to O and 2 H was rarely observed. In all dissociation events, the H atoms either diffuse away from the imaged area (as in Figure 7) or react with a C atom to form CH, as we have shown recently.¹⁸

More significant is the observation that only positive voltage pulses (i.e. electrons tunneling from the tip to empty states of the adsorbate) caused dissociation. This polarity dependence could be due to inelastic scattering promoted by tunneling into an empty orbital states of the molecule¹², or to field-induced effects such as molecule reorientation.²⁶ In the former case, an analysis of the molecular orbital decomposition of the density of states of H₂O on Ru(0001) and their contributions to the tunneling indicates that the HOMO (1B₁) and the LUMO + 1 (2B₂) contribute similarly to the tunneling current at

around -1 and +1 V respectively (the contribution of the LUMO was found to be negligible).¹⁸ The observed polarity dependence could then arise from the bonding and antibonding character of each state respectively.

The OH groups diffused readily even with voltage pulses as low as 150 mV. The onset voltage was polarity-independent, suggesting that diffusion is induced by inelastic excitation of low energy modes, such as frustrated translation and libration modes with energies around 100 meV. Between images (b) and (c) of Figure 7, seven voltage pulses ranging from 0.2 to 1.7 V were applied to the OH that induced only diffusion. It is interesting to note that, although the displacement length on each event was sometimes as large as 6 Ru lattice sites, unlike H₂O, the OH group was never seen to form complexes with C. By increasing the pulse voltage above 2 V, OH could be dissociated into O, as shown in Figure 7(d), with an average displacement of 1 ± 1 Ru lattice site (the appearance of O as a depression in the images is similar to that of C, as shown previously¹⁸). Although the chemical energy released in the OH → O dissociation is similar to the H₂O → OH dissociation, the higher diffusion barrier of O seems to limit its displacement. The O atom was very stable and could not be manipulated by pulses up to 5 V, similar to the case for C atoms. Note that in case of competing reaction channels, diffusion and dissociation in our case, the voltage onset is only an upper limit for the dissociation energy barrier.

The dissociation thresholds for H₂O and OH monomers on Ru(0001) are similar to those obtained by Lauhon et al. on Cu(100), 1.5 V and 4 V respectively.¹³ The diffusion behavior of these two species, however, is completely different. On Ru(0001) it is necessary to excite the high-energy O-H stretch mode to induce H₂O diffusion, while OH diffuses below 150 meV. This is consistent with DFT calculations that find a quasi-degeneracy between fcc, hcp and bridge sites for OH adsorption, leading to low diffusion barriers. In contrast the adsorption site for H₂O is well defined and thus more energetically stable, leading to higher barriers.⁵ In contrast on Cu(100) H₂O already diffuses thermally at 9 K, but OH diffuses only after excitation of the O-H stretching. Thus, the potential landscape is completely different for these two surfaces. Another striking difference is found for the H₂O-C interaction: whereas on

Cu(100) H₂O reacts dissociatively with C-C dimers at 9 K, water forms molecular complexes with C on Ru(0001) and the OH produced by water dissociation seems to be repelled by C.

3.4 Dissociation of water in clusters

In contrast to the behavior of isolated molecules, H₂O incorporated in clusters could be dissociated by electrons of 0.5 eV energy. As shown previously, this could be best observed with clusters larger than dimers or trimers, where diffusion is quenched for internal molecules.^{27,28} In Figure 8 we show an example of a dissociation experiment, where an area containing a cluster of 7 water molecules was scanned at setpoint voltage of 0.5 V. The images were obtained immediately after manipulation at 25 mV and 1 nA tunneling conditions. Scanning at 0.5 V and currents below 300 pA led only to a rearrangement of the cluster molecules into different configurations, as shown in (b). However, after

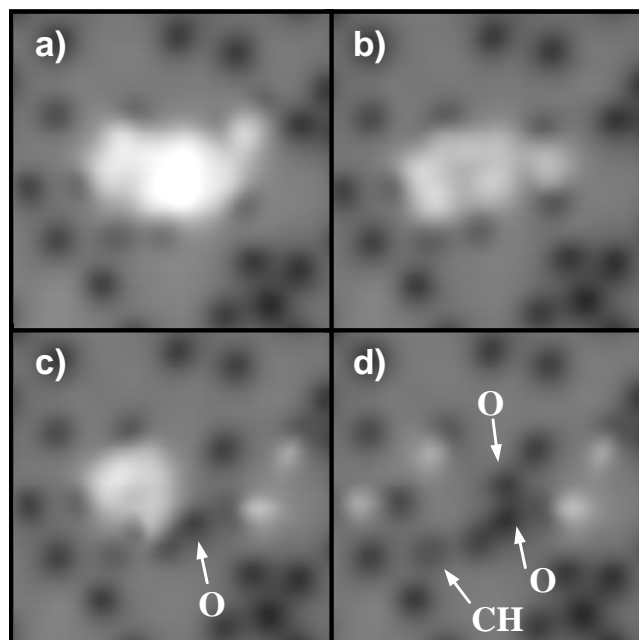


Figure 8. STM images (5×5 nm) acquired at 25 mV and 1 nA tunneling conditions, showing the manipulation of a water cluster. During manipulation the voltage was increased to 0.5 V at increasingly larger tunneling currents. a) Initial intact water cluster containing 7 molecules. b) Scanning at 0.5 V and 300 pA caused restructuring of the cluster into a different configuration. c) and d) After several consecutive scans at 0.5 V and 500 pA three water molecules dissociated to produce O and H. Most of the H atoms produced in the dissociation diffused away from the imaging area, but one was trapped by a C atom to form CH. The 4 remaining intact molecules are bonded with C atoms (type II).

scanning at 500 pA (images c and d) O atoms were produced as a consequence of the complete dissociation of some of the H₂O molecules. CH complexes were also formed from the reaction of H with C (see Figure 7d). The higher probability for observing complete dissociation of H₂O into O + 2H as compared to individual molecules could be a result of quenching of the diffusion channel. Also, the lower dissociation onset voltage is consistent with the lower energy barrier of 0.5 eV calculated for H₂O in a bilayer as compared to 0.85 eV for isolated H₂O.⁵ This experiment represents the first single-molecule, real space evidence, of the autocatalytic behavior of water predicted by theory and observed by other techniques in various metallic and oxide surfaces.^{5,28-35}

4. Summary

The excitation of one or multiple quanta of the O-H stretch mode at 445 meV in H₂O molecules adsorbed on Ru(0001) results in the diffusion, desorption, and dissociation of the molecule. It also leads to the breaking of bonds formed between H₂O and C atoms or with other H₂O molecules. Current-dependent diffusion-rate experiments show that diffusion of isolated H₂O monomers via O-H stretch mode excitation near the threshold is a one-electron process, whereas diffusion of C-bonded H₂O monomers is a two-electron process. On the other hand, diffusion of dimers or trimers could be induced by excitation of the 200 mV scissor mode. Larger clusters could be structurally modified by exciting the scissor mode, or disrupted by exciting the O-H stretch mode.

Isolated H₂O molecules could be dissociated only by single-electron excitations at voltages above 1 V. However, when H₂O is incorporated into clusters it can be dissociated much more easily, requiring only 0.5 V, a result that reflects the autocatalytic behavior of water dissociation, which is due to both a decrease of the reaction barrier and suppression of translation when part of a cluster. The formation of a H₂O-C complex however does not seem to significantly affect the water dissociation voltage onset, although it affects the excitation process now requiring more than one quantum of the O-H stretch vibration.

While oxygen atoms could not be manipulated at voltages as high as 5 V, OH could easily be displaced at voltages as low as 150 mV. Dissociation however required electron energies higher than 1.5 eV. Although the dissociation voltages for H₂O and OH on Ru(0001) are similar to those observed for Cu(100)¹³, the diffusion behavior on these two surfaces is strikingly different. Whereas the diffusion rate of H₂O on Cu(100) via thermal excitations is noticeable at 9 K and OH can only be displaced by exciting the O-H stretch, on Ru(0001) H₂O diffuses only after excitation of the O-H stretch mode and the voltage onset for OH diffusion is 150 mV.

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