Electronic excitation of ice monomers on Au(111) by scanning tunneling microscopy

Vibrational spectra and induced processes

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Abstract. Scanning tunneling microscopy, inelastic tunneling spectroscopy, and electron induced manipulation are used to investigate electronic excitation of D_2O monomers and small clusters adsorbed at the elbows of the Au(111) reconstruction. Diffusion of molecules, dissociation of clusters, and rearrangement of the reconstruction is induced by electronic excitation. Threshold energies of between 200 and 250 meV and of 446 meV are explained by combined vibrational modes of D_2O molecules. External vibrational modes of D_2O molecules on Au(111) are identified by inelastic tunneling spectroscopy at $\approx$18, 30, and 41 meV.

PACS. 68.43.-h Chemisorption/physisorption: adsorbates on surfaces – 82.37.Gk STM and AFM manipulations of a single molecule – 68.37.Ef Scanning tunneling microscopy (including chemistry induced with STM) – 68.43.Pq Adsorbate vibrations

1 Introduction

Water is one of the most important and investigated molecules for life. For that reason its properties and behavior have been studied for a long time by chemists, biologists, geologists, and physicists. An overview of its chemical and physical properties is given in reference [1]. A detailed investigation of the dynamic behavior of single water molecules adsorbed on metal surfaces will aid in improving the understanding of chemical and physical properties of water.

In previous experiments by scanning tunneling microscopy (STM) the behavior of water has been investigated on the (111) faces of Pt [2], Pd [3], Cu [4], Ag [5–7], and Au [8]. In particular the adsorption geometry on Pt(111) [2] and Ag(111) [5–7], and electron induced dissociation on Cu(111) [4] were observed. Furthermore, it was shown that it is possible to manipulate the cyclic ice hexamers via its vibrational modes by STM and to identify lower energetic modes by inelastic tunneling spectroscopy (IETS) [9].

So far STM measurements were concerned with H_2O clusters or closed bilayers. The only exception is an article where the diffusion and clustering of water monomers on Pd(111) has been investigated [10].

Of importance for our measurements is a sophisticated study by electron energy loss spectroscopy (EELS) that

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resolved a long discussion about the assignment of vibrational modes and the vibrational characteristics of water on Pt(111) [11].

There is no experimental evidence about the orientation, in which water monomers adsorb on metal surfaces. However, recent ab-initio density functional studies on the adsorption of H_2O on several close-packed transition and noble metal surfaces identified a common binding mechanism, where H_2O binds preferentially in an on-top site with the molecular dipole plane nearly in parallel to the surface [12].

A problem of investigating single water molecules by STM lies in the weak binding of physisorbed molecules. For this reason it is not trivial to perform STM imaging of water monomers adsorbed on weakly corrugated metal surfaces without changing their orientation [8]. Imaging often results in diffusion of the molecules or in picking up a molecule during scanning even at low temperatures and with low tunneling currents and voltages. To circumvent this problem we choose the Au(111) surface as a template. On this reconstructed surface enhanced binding of the monomers on special sites, like the elbows of the herringbone reconstruction, is expected from growth studies [13].

In this article we investigate single D_2O molecules and small clusters adsorbed in the elbow positions of the Au(111) herringbone reconstruction. We induce diffusion of molecules, dissociation of clusters, and reorganization

of the reconstruction lines by exciting the molecules with tunneling electrons at energies above 440 meV. Furthermore, we identify the energies of the frustrated rotation vibrations by IETS at energies of (18 ± 3), (30 ± 5), and (41 ± 7) meV.

2 Experimental

The measurements are performed with a homebuilt low temperature STM that can be cooled with a liquid helium bath cryostat to 5.5 K. The single crystalline Au(111) sample is prepared by cycles of sputtering with Ar^+ at 1.3 keV $(5 \times 10^{-5}$ mbar, $I = 4$ μA) and annealing at 1000 K. The D_2O of a milli-Q quality $(10^7$ Ωcm) has an isotope purity of 98% D_2O as analyzed by nuclear magnetic resonance spectroscopy (NMR). It is purified by freeze-thaw-cycles in UHV to reach a better D_2O cleanness. D_2O is dosed through a leak valve into the load-lock of the preparation chamber. Thereafter the cooled sample (25 K) is placed in front of the valve of the load-lock, which is then opened for the exposition time of 45 s. During deposition the pressure in the preparation chamber rises to 4×10^{-9} mbar. From the pressure ratio (load-lock: preparation chamber) we estimate that the partial water pressure at the position of the sample is about two orders of magnitude larger than the pressure measured in the preparation chamber.

The STM measurements are performed with a PtIr-tip at 5.5 K. Scanning tunneling spectroscopy (STS) spectra are measured in Lock-in technique with a modulation voltage of 10 mV and a modulation frequency of 360.4 Hz. The d^2I/dV^2 plot shown in Figure 7 is the numerical derivative of the measured dI/dV signal averaged over 10 comparable spectra after subtraction of the spectrum taken on the bare surface.

3 Results and discussion

Single D_2O molecules predominately adsorb in the elbows of the reconstruction (Fig. 1). The monomers dominate over a few adsorbed dimers and larger clusters (indicated by the arrows in Fig. 1a). Figure 1b displays a detail-view of the surface. A linescan along the line plotted in Figure 1b is shown in Figure 1c. In this plot the main protrusions are related to the water monomers, the smaller protrusions in between these larger ones are the domain boundaries between hcp and fcc sites of the Au(111) surface. A histogram of the protrusion's heights taken from different images on different places on the sample is shown in Figure 1d. There 40% of the adsorbates appear with a height of (0.13 ± 0.01) nm in the main peak of the histogram. From total statistics we conclude having about 10 times more D_2O monomers than dimers or larger clusters on the surface.

Even in the elbows of the reconstructed Au(111), the water monomers are so weakly bound that they can be easily moved by scanning the surface. While scanning at ± 200 mV does not move the molecules, scanning at
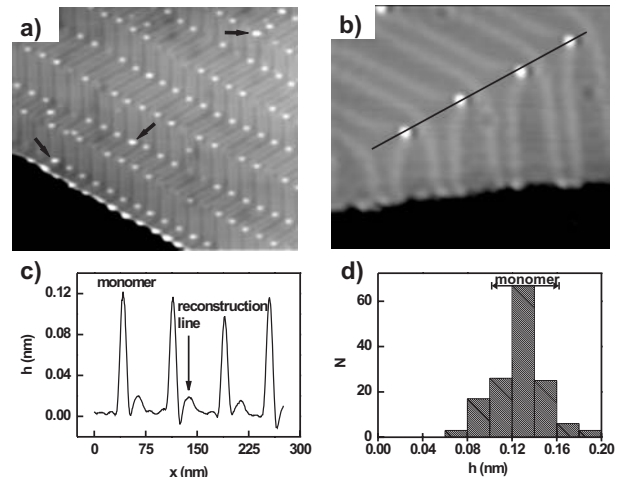
Fig. 1. D_2O-Monomers on Au(111): (a and b) STM images of the Au(111) surface with D_2O monomers at the elbow sites of the herringbone reconstruction, (a) (126×108) nm^2, 214 mV, 21 pA, arrows indicate clusters, (b) (31×27) nm^2, 115 mV, 32 pA. (c) Linescan along the black line marked in (b). (d) Distribution of the apparent height h of the molecules from several images at different sample regions.
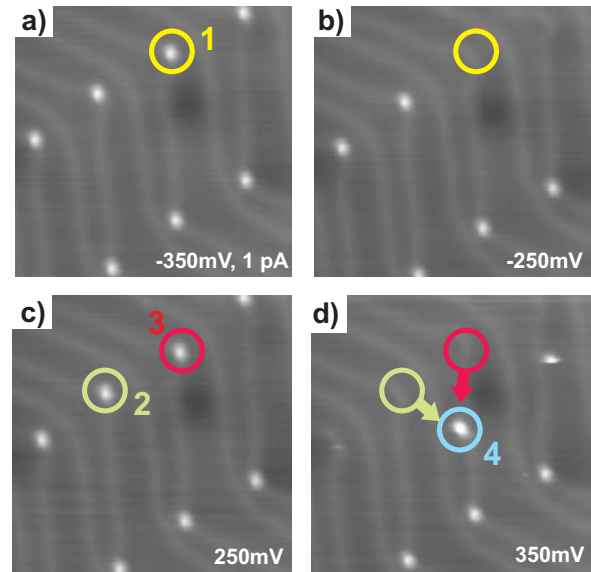
Fig. 2. Induced diffusion: STM topographs $((24 \times 24)$ $nm^2)$ of the Au(111) surface with adsorbed water molecules. The images are taken successively with different bias as indicated at a tunneling current of 1 pA.

± 250 mV and more always move them. Figure 2 shows images taken at different bias voltages at the same spot on the sample. In the images the circled molecules disappear and reappear while repeatedly scanning the same region of the surface, e.g. the monomers labeled as "1" in Figure 2a. This elucidates the weak interaction of adsorbate and substrate of the D_2O/Au(111) system. Between Figures 2b and 2c a monomer labeled as "3" is diffused back to the vacant elbow site. Furthermore, as a result of high scanning voltage a small cluster ("4" in Fig. 2d)

is formed on a nearby hcp region from two monomers ("2" and "3" in Fig. 2c) which were removed from elbow positions. This underlines that single molecules are adsorbed only in the favorite adsorption sites of the elbows and that a molecular gas of monomers is present even at 5.5 K. The threshold energy needed for movement during scanning is related to the excitation energy of a vibrational mode of the D_2O molecule. The scissoring mode was identified before as being responsible for cluster (hydrogen bond) rearrangement through electron injection by STM for H_2O layers on Cu(111) at 205 meV [4]. EELS studies on closed H_2O bilayers on Pt(111) have identified this mode at 201 meV [11]. However, the diffusion we have observed here cannot be due to the excitation of the scissoring mode only, because the isotope effect shifts its energy for D_2O on Au(111) to around 155 meV. We suggest that the diffusion is a result of the combined excitation of the scissoring mode and one of the metal-molecule bending modes. These bending modes were identified at 73 and 92 meV for H_2O monomers on Pt(111) [11]. The isotope shift suggests values of $\sim$58 and $\sim$72 meV for D_2O. This results in total energies of the possible combined modes of $\sim$213 and $\sim$227 meV, which is in the range of the excitation energy of the observed diffusion of the water molecule. This interpretation is corroborated by electron induced excitation of the isomerization of chloronitrobenzene molecules on Cu(111) and Au(111) [15]. Also in this case, a combination of two vibrational modes has to be employed to explain the isomerization.

The difference to the H_2O/Ag(111) case [4], where a single excitation was sufficient might be explained by the diffusion energy of a monomer out of an elbow. The needed energy is likely to be above 155 meV such that a single vibration quantum does not provide enough energy for the diffusion.

The motion out of the elbows and back again can be induced in a more controlled way by exciting the molecules through injecting tunneling electrons directly into them as schematically shown in Figure 3. To perform this manipulation the STM tip is moved above the molecule and the bias voltage is increased by a few hundred mV for a typical time of some hundred ms. The electrons with high enough electron energies may excite vibrations of the molecule and lead subsequently to molecular reactions [16]. The expected I-t-characteristic is shown in Figure 3c. At the beginning of the excitation (t_0) the tunneling current has a value that corresponds to the electronic structure of the adsorbed molecule. In the moment of excitation (t_m), when the molecule moves away from the region under the tip, its disappearance leads to a sharp drop in tunneling current. Induced changes to the molecule-substrate system are verified in STM images taken before and after manipulation with non-manipulative parameters ($U < 250$ mV).

In the following we describe the induced diffusion of water monomers, dissociation of water clusters, and rearrangement of the Au(111) reconstruction. A representative of induced monomer motion with an excitation energy of 420 meV is shown in Figure 4 (the point marks the position of electron injection). The recorded current shows the
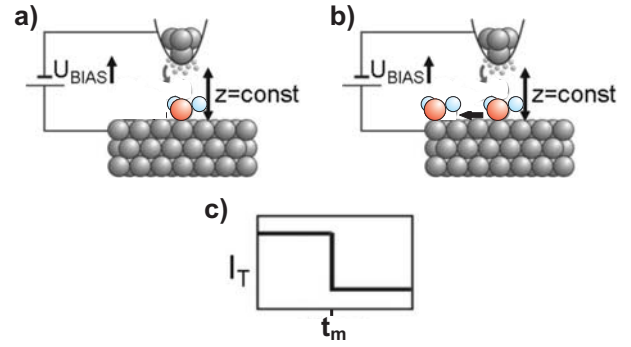

Fig. 3. Schematic view of electron induced manipulation by STM. (a) The STM tip is placed above the target molecule and the bias voltage is increased by a few 100 mV. (b) The molecule moves after a time t_m (typically a few 100 ms). (c) Characteristics of tunneling current as function of time. The current drops at t_m upon motion of the molecule.
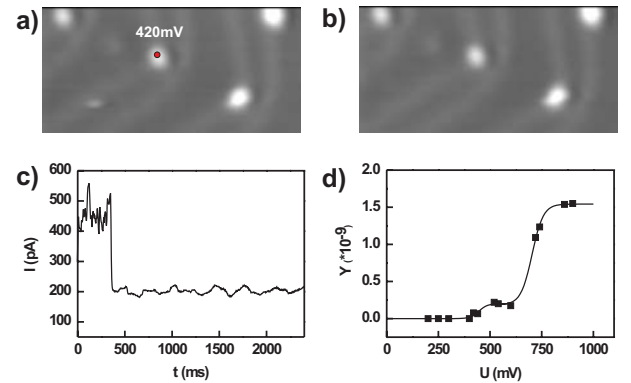
Fig. 4. Diffusion of D_2O: (a and b) (16×7) nm^2 images of D_2O monomers before (a) and after (b) excitation of the monomer with tunneling electrons at a voltage of 420 mV. (c) Recorded I-t-signal during manipulation. (d) Reaction yield Y per electron as a function of bias voltage U showing two steps at threshold voltages of $\approx$446 and $\approx$703 meV.

expected drop (Fig. 4c). Despite the sudden decrease in current, clearly indicating a diffusion event, there is no obvious difference between the images of Figures 4a and 4b. This can be explained by a refilling of the vacant elbow site by (another) D_2O monomer from the molecular gas as discussed above.

The plot in Figure 4d shows the yield per electron for induced diffusion as function of the bias voltage where two steps are obvious at energies of (446 ± 24) and (703 ± 13) meV. It was observed before that the diffusion of H_2O on Cu(111) can be excited by excitation of the OH-stretching mode [4]. For non-hydrogen-bonded H_2O on Pt(111) this mode was measured with EELS at 455 meV [11]. The isotope effect leads to a calculated shift of the excitation energy from 455 meV to $\sim$350 meV. In analogy to the attempted assignment above we suggest the excitation of a combined OD-stretching and metal-molecule bending mode. The total energies of the possible two combined modes are 408 and 422 meV (OD-stretching (350 meV) + bending (58 and 72 meV)). While the second
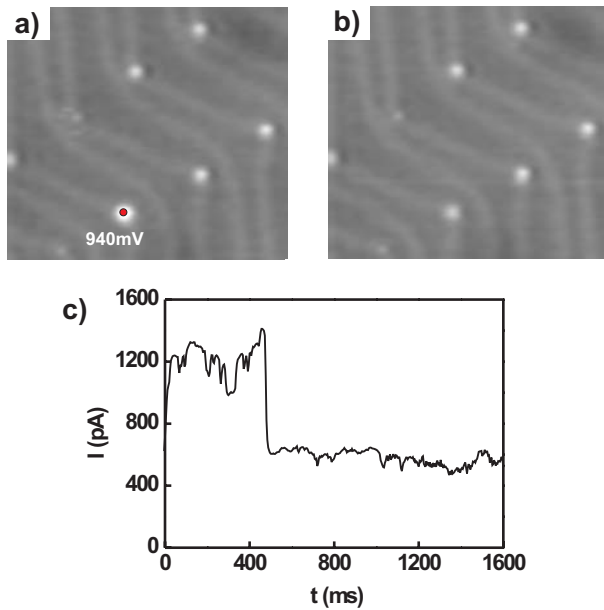
Fig. 5. Abstraction of molecules from a cluster: (a) before excitation D$_2$O cluster is excited at the marked point with the bias increased to 940 mV. In (b) after excitation the cluster is reduced to a monomer ((24 × 22) nm^2). (c) Current I versus time t during manipulation.

threshold energy at 703 ± 13 meV might be a more complicated combination of vibrational modes an assignment without theoretical calculations is not attempted.

Furthermore, molecules can be removed from small clusters, which corresponds to a breaking of hydrogen bonds. In the example shown in Figure 5, molecules are removed by injecting electrons with an energy of 940 meV into a cluster consisting of approximately six molecules (Fig. 5a). The tunneling current (Fig. 5c) shows a similar characteristic as during induced diffusion. After the excitation only a monomer remains (Fig. 5b). As a result of the mobility of single molecules on the surface the detached molecules are not observed in the vicinity of the remaining monomer.

With the same mechanism we induce a permanent reorganization of the surface reconstruction together with the motion of the molecule. Comparison of images before and after manipulation (Figs. 6a and 6b) shows a change of the position of the elbow including the adsorbed monomer. In Figure 6a monomer and elbow lie below the reference line, in Figure 6b they are above it. For this reorganization of the reconstruction the atoms in the domain boundaries have to move only a fraction of the distance between single gold atoms. The transition in Figure 6c is less sharp indicating a multi-atom process. Furthermore, the needed excitation time for reorganization is about a factor 6 longer than for diffusion of a single molecule due to the more complex process of reorganization of the reconstruction (Fig. 6c).

The enhanced binding of the monomers to the elbows of the reconstruction allows for the first time to take IETS spectra on single water molecules. Figure 7a com-
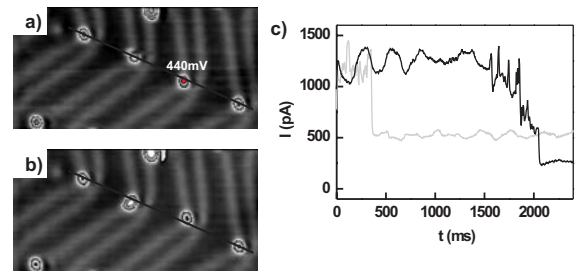
Fig. 6. Rearrangement of herringbone reconstruction: (a) (24 × 10) nm^2 image before and (b) after excitation with 440 mV at the indicated place above the monomer (contrast has been cycled for better visibility of the reconstruction lines). (c) Tunneling current I recorded as a function of time t during reorganization of the reconstruction (dark line), compared to spectrum during direct excitation of motion of a molecule (light line).
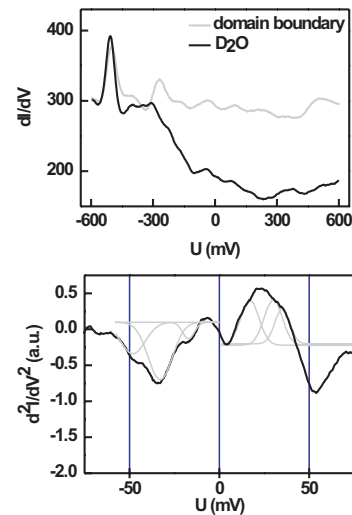
Fig. 7. (a) Comparison of dI/dV spectra taken on the domain boundary and on a monomer adsorbed in an elbow position ($U_{mod} = 10$ mV, $\nu_{mod} = 360.4$ Hz). (b) Differential conductivity (derivative of the measured dI/dV signal after subtraction of surface spectra, averaged over five comparable spectra), three symmetric peaks at ± 18 meV, ± 30 meV, and $-48/+35$ meV are identified by multiple Gaussian fit as the vibrational energy of the frustrated translation, rotations of the monomer.

pares a STS spectrum taken on the domain boundary of the herringbone reconstruction to a spectrum taken above a monomer adsorbed on an elbow of the reconstruction. In the spectra the surface state of Au(111) is located at -507 meV. This peak arises due to an additional tunneling channel that opens at the bottom of the parabolic surface state. The surface state electrons are localized in the surface state because they cannot scatter with the bulk states of the metal without either changing energy or momentum [17]. Figure 7a shows also that the surface state is not suppressed by adsorption of the monomer. The two spectra differ above -300 meV. The spectrum taken over

the domain boundary shows a decrease of the dI/dV signal which is not visible in the molecule spectrum.

The range of the spectra taken above the monomers for identification of vibrational modes is due to the conformational change of water molecules discussed above limited to ± 75 mV, which is the region of the vibrational modes of external molecular vibrations. The d^2I/dV^2 spectra of the monomer show minima/maxima at (18 ± 3) and (30 ± 5) meV in both, the occupied and unoccupied region of the spectrum. At an energy of -48 meV is an additional peak. The related feature in the positive bias range can be localized at $+35$ meV.

We compare these modes to modes measured before with IETS on closed H_2O bilayers on Cu(111) and with EELS for bilayers and sub-bilayer coverages of D_2O on Pt(111) and for H_2O bilayers on Au(111). For H_2O bilayers on Cu(111) a vibrational energy of ≈ 28 meV was identified as frustrated translation mode [9] according to previous EELS measurements on the same surface identifying this mode at 34 meV [18]. The values measured for H_2O-monomers on Pt(111) with EELS are 15 meV for the frustrated translation mode, 28 meV and 36 meV for the frustrated rotation modes (librations) [11]. Based on these values we identify for our measurements of the D_2O monomer on Au(111) the mode at 18 meV and 30 meV as frustrated rotation vibrations (librations). The peaks at -48 and $+35$ meV are also in the range of the frustrated rotation vibration. The difference between the energy values can be explained by a rotation of the water molecules under the tip of the STM as described in reference [19]. The remaining mismatch of the energies is maybe attributed to varying binding energies on different metal surfaces. Also the adsorption site on the elbows of the reconstruction influences the vibrational spectrum of the monomer. As already observed on water molecules adsorbed on step edges the marginal influence of the hydrogen bonds and an additional lateral interaction can result in a shift of the vibrational modes [20].

4 Conclusion

Water monomers deposited at 25 K are mobile and adsorb predominantly in the elbows of the Au(111) reconstruction. Excitation energies between 200 and 250 meV and of (446 ± 24) meV induce diffusion of monomers out of the elbows. These threshold energies can be explained by a combination of an internal mode of the water molecule and a metal-molecule bending mode. At higher excitation energies of 940 meV the detachment of single molecules and therefore the breaking of hydrogen bonds can be induced.

By IETS we identified lower energetic vibrational modes at ≈ 18 and 30 meV as energies of the frustrated rotation modes of the D_2O monomer on Au(111). Two additional non-symmetric peaks at -48 and $+35$ meV are shifted due to a reorientation of the molecules under the STM-tip. The energy values of these peaks are also in the range of the frustrated rotation vibrations.

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