Intermolecular Bond Length of Ice on Ag(111)

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Water adsorbed in submonolayer coverage on Ag(111) at 70 K forms hydrogen-bonded networks. High resolution images in combination with calculation reveal that single protrusions represent a cyclic water hexamer with the intermolecular bond stretched to the silver lattice constant of 0.29 nm. Scanning tunneling spectroscopy indicates that the bond length within the two-dimensional hydrogen-bonded water layer is shortened. The spectra contain further information about the vibrational modes of water molecules.

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Water is one of the most important molecules for life. It has consequently aroused research interest throughout the centuries [1]. As its uniqueness leaves many mysteries unsolved [2], water is still studied in a spectrum of fields including meteorology, geology, and physical chemistry [3,4]. The importance of the properties and the dynamic behavior of water adsorbed at metal surfaces in electrochemistry, catalysis, and corrosion science resulted in many experimental studies (cf. the review of Thiel and Madey [5]). These have demonstrated that H_2O monomers remain molecularly intact on most metal surfaces held at low temperatures, because the thermodynamically favorable dissociation of a single water molecule is a highly activated process. Furthermore, internal bond angle and bond length of the molecule are only slightly perturbed from the gas phase values. The lateral interaction between the molecules is comparable to the H_2O-metal interaction favoring the formation of hydrogen-bonded networks. On hexagonal metal surfaces, intermolecular hydrogen bonding leads to the formation of a hexagonal two-dimensional lattice known as "bilayer ice." The resulting structure consists of water molecules within a bilayer which are hydrogen bonded into hexagonal rings such that alternating molecules are raised or lowered by 0.048 nm relative to the central plane to give the proper tetrahedral bonding angles. This structure persists even for incomplete layers [6]. The cyclic water hexamer is the smallest possible entity of this bilayer, and its detailed study should provide important insights into the properties of bulk ice. Molecular dynamic studies show that this cyclic basic unit is also important in liquid water [7,8].

Only each second water molecule in the water bilayer is bound directly to the surface via an oxygen lone pair orbital while the other molecules are held by hydrogen bonds to these first layer molecules. The misfit between the naturally occurring hexagonal I_h ice lattice and the hexagonal surface lattice determines the bond strength of water on such a surface and therefore the desorption temperature in thermal desorption spectroscopy (TDS) [5]. As the intermolecular bond strength is similar to the bond strength of the molecule to the surface, it is not obvious which of the two bonds is weakened, i.e., whether the original bond length is sacrificed for a commensurate overlayer or the bond length is preserved and the bond to the surface is weakened.

From all ice bilayers investigated by TDS, the one on Ag(111) has the lowest desorption temperature [5]. A 10% mismatch exists between the Ag(111) surface lattice [$a = 0.289$ nm, next-nearest-neighbor distance (NNN): 0.5 nm] and the triangular unit of crystalline I_h ice (oxygen-oxygen: 0.274 nm at 90 K; NNN: 0.446 nm). H_2O adsorbs on Ag(111) molecularly below $T = 155-170$ K [5]. Calculations show that on Ag(111) the on-top site corresponds to the energetically most stable position [9].

In this paper, we investigate the O-H $\cdots$ O bond length within hydrogen-bonded ice formed at 70 K on Ag(111). For an isolated hexamer on the terrace, we find that the bond length is stretched from the naturally occurring I_h ice to fit the lattice constant of silver. In contrast, for larger hydrogen-bonded structures we find indications that the bond length is compressed by a similar amount. To this means, we use scanning tunneling microscopy (STM) and inelastic electron tunneling spectroscopy (IETS). For the ice hexamer, we utilize high resolution imaging in combination with model calculations of STM images. For the two-dimensional structures, we utilize tunneling spectroscopy and interpret peaks in the spectrum as vibrational frequencies whose energy depends on the intramolecular bond length.

The experiments were performed in a low temperature STM-UHV chamber with standard facilities for sample preparation and characterization. The single crystalline Ag(111) is prepared by sputtering with 1 keV Ar^+ ions (3×10^{-5} mbar, $I = 25$ μA) for 30 min and annealing to 800 K for 15 to 30 min. Its suitability for the experiment is checked by Auger electron spectroscopy, by low-energy electron diffraction, and by direct inspection with the STM. The H_2O of milli-Q quality is further purified under vacuum by freeze-thaw cycles to remove remaining impurities. Quadrupole mass spectrometry is used to monitor gas purity. The largest peak not related to H_2O is $M = 28$ (N_2 or CO), which is only 1% of the $M = 18$ (H_2O) peak.

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Prior to deposition, the water is frozen by pumping and held below −5 °C during deposition. Water is dosed onto the crystal at around 70 K by backfilling the entire vacuum chamber through a leak valve (10^{-8} to 10^{-9} mbar) for 2 to 20 min. The crystal remains within the cold shields of the cryostat during deposition. Because of this indirect geometry, the pressure at the sample is more than 3 orders of magnitude lower than this background pressure. Deposited amounts are therefore estimated from the STM images. STM images are taken at 7 K with PtIr tips. For scanning tunneling spectroscopy, a lock-in technique is used with a modulation voltage of 20 mV and a modulation frequency of approximately 230 Hz. Tips are considered to be suitable for the investigation, if, on the bare surface, the spectra show only the onset of the silver surface state at around −70 mV.

Figure 1 shows that water molecules are sufficiently mobile to form clusters at 70 K. On small terraces and at the ascending step edge of larger terraces a closed packed layer has formed. On the two-dimensional network the second layer has heterogeneously nucleated discernible as protrusions on a continuous background [10]. On larger terraces, we find a discontinuous line of molecules at the descending step edge and occasionally single protrusions.

In order to reveal the origin of the isolated protrusions on the terraces, high resolution images are taken at low voltage [Fig. 2(a)]. These reveal a threefold structure with a distance between the protrusions of 0.5 nm. This compares well with the NNN distance on Ag(111). In hexagonal bilayers on Pt(111), only each second molecule (the one bound to the surface) in the buckled structure is imaged [11]. Therefore, each protrusion might represent a basic unit of the ice bilayer: a cyclic hexamer [Fig. 2(c)].

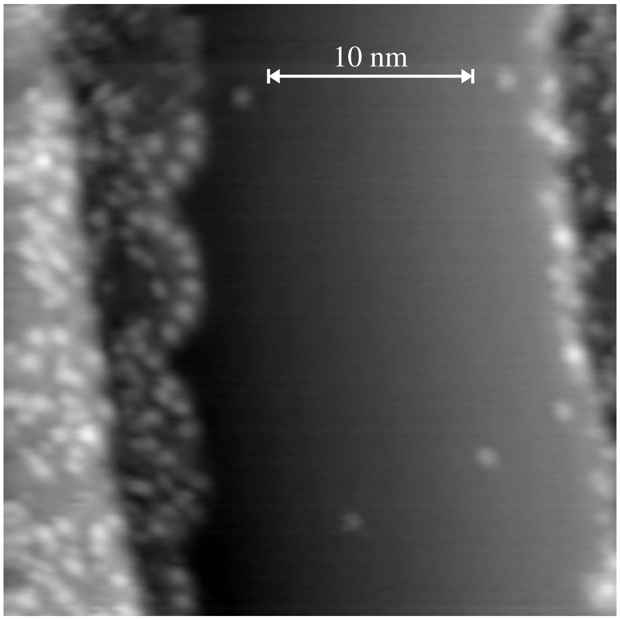

FIG. 1. Water on Ag(111): STM image of about half a bilayer. $U = 2$ V, $I = 0.21$ nA.

To corroborate this interpretation, we calculated STM images. To this end, the electronic structure of the tip-adsorbate-substrate system is calculated in tight-binding basis. Denoting the orbitals of the silver tip with index t and the orbitals of the substrate with index s, we obtain a formula for the tunneling current [12]:

$$j = \frac{2\pi e}{\hbar}\int [f(E) - f(E + eV_b)] \times \mathrm{Tr}[\rho^0_{s's}(E)T_{st}(E)\rho^0_{tt'}(E)T^\dagger_{ts'}(E)]\,dE\,, \qquad (1)$$

where ρ^0 is the density of states matrix for the noninteracting system (without adsorbate), and T is the transition matrix between the eigenstates of the tip and the eigenstates of the substrate. The presence of the adsorbate is taken into account in the transition matrix:

$$T_{st}(E) = \Delta_{st} + \Delta_{sa}G^+_{ab}(E)\Delta_{bt}\,, \qquad (2)$$

where Δ is the matrix for hopping integrals of tip-adsorbate-substrate interactions, and $G^+_{ab}(E)$ is the matrix element of the Green function between two orbitals of

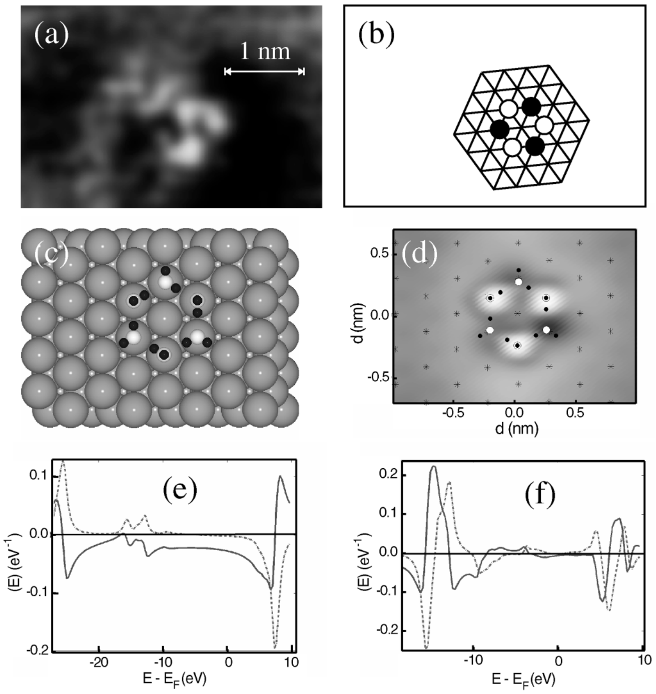

FIG. 2. (a) High resolution image of single protrusion: $U = 19$ mV; $I = 0.8$ nA. (b) Structural model for water hexamer; white circles represent imaged molecules (not bound to the surface), black circles represent not-imaged molecules; grid is taken from atomic resolution image and is to scale with STM image in (a). (c) Ball model of cyclic water hexamer. (d) Calculated STM image of water hexamer at −460 mV; stars indicate the position of the Ag atoms, white circles of the oxygen atoms, and black circles of the hydrogen atoms. Imaginary (dashed line) and real (solid line) parts of two cases of the intramolecular elements of the Green function, $\Gamma(E) = -\frac{1}{\pi}G_{\alpha\beta}(E)$: (e) α is the s orbital of the upward hydrogen of the upper layer molecule and β is the p_z orbital of the adjoining oxygen; (f) α is the same s orbital and β is the p_z of the oxygen of the neighboring lower layer molecule.

the adsorbate system. This formulation of the T matrix allows us to analyze tunneling channels for possibly insulating adsorbate molecules. The density of states matrix for the substrate and the STM tip are calculated to the fourth moment using the recursion method as described in Ref. [13] and the Green function for the interacting systems is calculated by solving Dyson's equation for a coupled system as in Ref. [14].

Our calculations reveal that the STM image of a hexagonal ring of H_2O molecules strongly depends on the bias voltage. This is interesting, since there is a wide gap between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) even in the adsorbed form. Thus, one would expect that the molecules act as small insulating entities. Within this gap the *imaginary part* of the Green function is practically zero [15]. However, the Green function in the T matrix of Eq. (2) may have a nonzero *real part* within the gap. A simple interpretation for the contribution of the imaginary and real parts of the Green function can be given: If the imaginary part is zero, tunneling through the molecule does not take place through an eigenstate of the system. Rather, a nonzero real part means that the molecule can be seen effectively as a finite potential barrier which causes damping of the wave function and a possible phase shift with respect to a through-space wave [16]. Thus, there may be complicated interference effects on the total current due to phase differences between different tunneling channels.

The calculated STM image [Fig. 2(d)] for a cyclic hexamer with the molecules adsorbed in on-top positions indeed shows only three protrusions. However, it is the molecules *not* bound directly to the surface that give rise to the bright contrast. The *upper layer molecules* can be seen as bright spots at some bias voltages [Fig. 2(d)], because the s orbital of the upward hydrogen of the upper layer molecules and the p_z orbital of the adjoining oxygen have a large real part of the interorbital Green function close to Fermi level [Fig. 2(e)]. The overlap between the STM tip and this hydrogen and, on the other hand, between the p_z orbital and the substrate is relatively large. These two factors give a significant contribution to the tunneling current. On the other hand, the correlation between the orbitals of the upper layer molecule and, e.g, the p_z orbital of the lower layer molecule is very small [Fig. 2(f)], and thus tunneling through both molecules at the same time is rather improbable. Because of the hybridization and the directionality of the bonds, the *lower* layer molecules do not have such an upward orbital overlapping with the STM tip. Also, the vertical distance between the upper and the lower water layers makes this overlap significantly smaller as compared to that of the upper layer and the tip. Therefore, the image of the lower layer easily vanishes to the background.

Furthermore, in the calculated image the distance between the protrusions indeed corresponds to the distance between the molecules. Therefore, the intermolecular hydrogen bonds within the ring are stretched from the ice I_h values to accommodate to the silver surface lattice [17].

To our knowledge, Fig. 2 represents the first real-space image of the isolated ice hexamer [18]. The importance of this observation can be appreciated by noting that the cyclic hexamer is one of the prominent morphologies found in computer simulations of liquid water and is the structural motif for ice I_h [7,8].

Although we regularly achieved atomic resolution on the silver surface, we have been unable to resolve any structure within the first layer of the structure grown from the step edge. Instead, we analyze IETS data taken on the close packed layer (Fig. 3). Peaks in d^2I/dV^2 spectra are related to vibrational modes of the molecules, because, whenever the bias overcomes the energy of a vibrational mode of the molecule, an inelastic channel opens. This produces a sudden increase in the slope of the IV curve and therefore a peak in the d^2I/dV^2 spectra [19]. A typical spectrum taken on the first layer is depicted in Fig. 3. The differentiated spectrum (d^2I/dV^2) shows three features above the noise level already discernible in the nondifferentiated spectrum: A multiple peak around 100 mV extending from 70 and 125 mV and two single peaks at $\approx$250 mV and at $\approx$360 mV with FWHM of 18 and 15 mV, respectively [20].

Vibrational data for water adsorption on Ag(111) has not yet been published. Therefore, we compare these peaks to *multilayer* adsorption of H_2O on Ag(110) at 130 K [21]. This is justified, because the qualitative feature of this spectrum is not very sensitive on the substrate [5]. The peak positions measured in electron energy loss spectroscopy are indicated in Fig. 3(b). Values for other metals and faces are given in brackets. The peak at 29 meV (25 to 33 meV on other metals) has been attributed to the frustrated translation of the molecules, the broad peak at 100 meV (66 to 102 meV) to the three frustrated rotations, the peak at

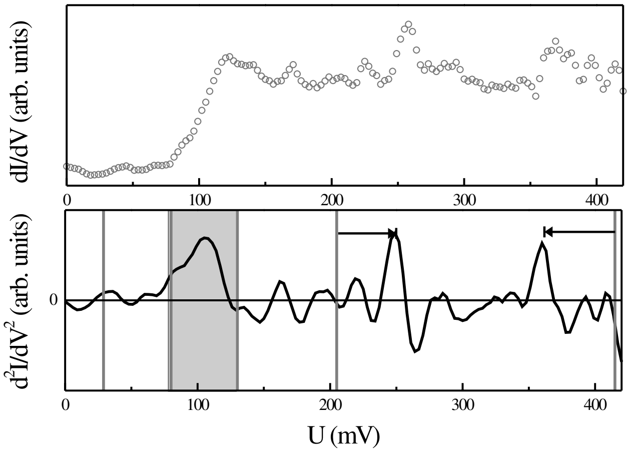

FIG. 3. (a) Differential conductance (dI/dV) on a water bilayer; (b) differentiated spectra (d^2I/dV^2); gray lines indicate vibrational modes for multilayer adsorption of H_2O on Ag(110) [21].

205 meV (189 to 206 meV) to the intramolecular deformation (scissoring mode), and the one at 415 meV (401 to 429 meV) to the OH-stretching mode. In addition, the metal-molecule stretching mode was found between 40 and 82 meV. The gas phase values for the scissoring and for the OH-stretching mode are 198 and 453 meV, respectively [22]. Thus adsorption and hydrogen bonding lead to a redshift of the O-H stretch frequency. It leads to a blueshift of the scissoring mode as long as bonding to the surface is weak [5].

Based on this, we attribute the peak at higher voltages of the multiple peak around 100 meV to the frustrated rotations. The broadness of the peak is in accordance with the existence of three rotations. The peak at lower voltage of the multiple peak, we attribute to the metal-molecule stretching mode. We point out that IETS seems not to be sensitive to the frustrated translation of the molecule at around 30 meV.

The vibrational energies for the intramolecular bond stretching vibrations are known to have an energy dependence on the hydrogen bond length O-H $\cdots$ O in crystalline phases of ice [23]. Thus, the position of the stretching mode could be used to determine the O-O bond length. We attribute the peak at 360 meV to the O-H stretch, although the shift is anomalously large compared to the surfaces (with smaller misfits) investigated. The observed peak at 360 meV corresponds to a O-H $\cdots$ O bond length of $\approx$0.25 nm [5]. This is small even compared to the lattice constant of I_h ice. A bond length of 0.25 nm in solid ice requires a (unreasonable) pressure of 23 GPa [24]. However, for free water clusters consisting of n molecules, the OH-stretch has been calculated to be 397 meV for $n = 5$ and 385 meV for $n = 8$, and in these clusters the O-O distance is reduced, for instance, for $n = 6$ to 0.265 nm and for $n = 8$ to 0.262 nm [25].

We cannot unevocally attribute the mode at 230 meV, because it is rather improbable that it is the blueshifted scissoring mode. More likely, it is a combination of several modes, e.g., a combination of the bending and librational modes has been reported at 280 meV in I_h ice [26].

In conclusion, we show the first scanning tunneling spectra for water molecules in a water bilayer and interpret them in terms of vibrational modes in the molecule. The latter method shows how the pioneering work on IETS with the STM of Stipe, Rezaei, and Ho [19] can be extended to determine bond lengths within molecular superstructures.

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