Electron Damage to Supported Ice Investigated by Scanning Tunneling Microscopy and Spectroscopy

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We study the interaction of low-energy electrons with crystalline ice (D_2O) on Cu(111) by low-temperature scanning tunneling microscopy and spectroscopy. Electrons induce dissociation of the molecules with a threshold of ≈ 3 eV. The large dissociation yield of the order of 10^{-8}/electron and the extended area of dissociation are attributed to a shift in conduction band during the dissociation. Voltage dependent differences in imaging of ice and dissociated ice are reflected in the spectroscopic signature.

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The rich physics and chemistry that arise from the complex interactions of electrons with molecules has been investigated in several decades of intense research [1]. However, our knowledge about the local impact of electrons onto supported ice remains surprisingly limited.

Supported ice is well known to be sensitive to electron damage. This sensitivity has made the investigation of supported ice with typical surface science methods particularly difficult and thus even the simplest form of ice on hexagonal surfaces, the so-called bilayer, remains much debated between experiment [2] and theory [3]. The sensitivity to electron damage has consequences not only for the vast field of supported ice research [4], but also to interstellar clouds in astrophysics [5], or rain drop nucleation in atmospheric chemistry [6]. In interstellar space as well as for polar stratospheric clouds and clouds in the tropical tropopause region (typically below 190 K), the water exists predominantly in its solid form and is often nucleated on some support. It is well accepted that in these cases the main effect of radiation damage is usually not produced by the primary interaction of the high-energy quanta, but rather by the action of the secondary species (ions, electrons, or radicals), which are generated along the ionization track. Electrons are the most abundant of these secondary species having an initial energy distribution in the range of a few eV. For a decade the dynamics and products of electron induced dissociation to supported ice was investigated via either the detection of the vibrational spectra of the remaining molecules or an analysis of the desorbed species [7]. The determined energy thresholds could be related to specific dissociative electron detachment resonances.

High-resolution scanning probe studies provide a means for obtaining atomic-scale information about the impact of electrons on supported ice. In the only study reported so far, the crystallization and electron damage of small amorphous ice crystals on Cu(111) was induced by electrons with an energy larger than 3 eV [8]. This qualitative study did not characterize the crystallization or subsequent damage.

In this Letter, we investigate the impact of energetic electrons of a few eV onto thermally crystallized ice on Cu(111) by scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and inelastic electron tunneling spectroscopy (IETS). We show that electrons above ≈ 3 eV initiate dissociation of the molecules within the ice crystal via the conduction band of ice, which is modified during the dissociation thus accelerating the electron damage.

The experiments were performed with a custom-built low-temperature STM [9], which facilitates imaging at 0.5 pA. Low current imaging is important for this study because of the large difference in apparent to real height of up to 1.7 nm for crystalline ice islands [10]. The STM is housed in an UHV chamber with standard facilities for sample cleaning. Its base pressure is below 10^{-10} mbar. The single crystalline Cu(111) and Ag(111) surfaces are cleaned by cycles of Ne^+ sputtering and annealing. The D_2O is degassed in vacuum through freeze-thaw cycles, before it is deposited onto the surface held at 88 K through a molecular tube doser with a rate of 0.3 bilayer/ min. The sample is then annealed to 130 K for 15 min in order to produce well characterized ice islands [10] and transferred into the STM, where measurements are performed at 5 K.

STM imaging of ice is challenging, because the water molecules are easily disturbed by the scanning process due to their large dipole moment and the low energy of a single hydrogen bond [11]. Furthermore, inelastically tunneling electrons starting from approximately 200 mV might easily excite molecular vibrations triggering molecule reorientation [12]. The images presented in this Letter are acquired at parameters that do not influence crystalline ice structures [11,12].

The preparation described above leads to crystalline ice islands [10]. These islands [Fig. 1(a)] consist of two complete bilayers with the same buckling and lattice constant as a nonsupported *Ih* crystal, one partial bilayer, and an additional row of molecules with (2×1) arrangement. The partial bilayer in connection with the additional row of molecules forms facets oriented along the $\langle 112 \rangle$ direction

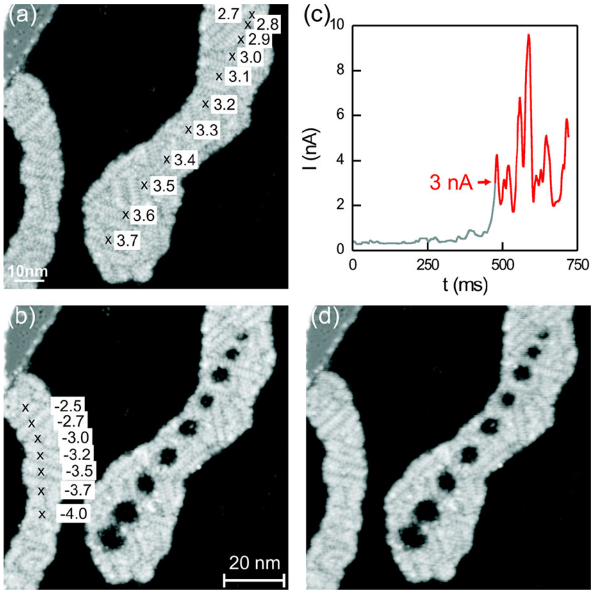

FIG. 1 (color online). Series of IET manipulation of crystalline ice on Cu(111) starting with (0.35 ± 0.05) nA for 0.72 s at crosses with indicated manipulation voltage. (a) STM image of ice islands before manipulation, 2.7 pA, 0.4 V. (b) STM image after series of IET manipulation. (c) I-t characteristics during manipulation with 2.9 V; $I_{\mathrm{thr}} = 3$ nA is marked. (d) STM image after second series of manipulation as indicated in (b).

of the Cu(111) surface. Two opposite facets form ridges that are visible as stripes in the STM image. While the exact arrangement of the molecules is not essential for this study, it is important to note that the reconstruction reduces the number of hydrogen bonds per molecule. This reconstruction is not thought to be specific for ice on Cu(111). For example, a faceting and domains of (2×1) structure were also found in thin ice films on Pt(111) by x-ray absorption spectroscopy [13].

Inelastic electron tunneling (IET) manipulation [14] is performed by placing the tip above a selected point of the ice island, switching off the feedback loop, and then increasing the current within a current range of 0.1–1.6 nA and the voltage within a range of 2.5–4 V at both polarities. At positive bias voltage the electrons tunnel from the tip through the ice into the substrate. The manipulation conditions are maintained for 0.2–0.8 s, while recording the tunneling current. Changes to the structures are verified in subsequent STM images of the same part of the surface.

Figure 1 shows the result of electrons interacting with two elongated crystalline ice islands. In the first manipulation series IET was performed between 2.7 and 3.7 V [Fig. 1(a)]. This manipulation series results in a series of black regions (depressions) above a threshold of 2.9 V around the electron injection point with a diameter up to 4.5 nm [Fig. 1(b)]. Usually, a manipulation leading to a decrease in apparent height of the manipulated species should be accompanied by an I-t characteristic, in which a sudden drop in current indicates the moment of reaction. In contrast, here we find a strong increase in tunneling current followed by rapid changes as exemplified for 2.9 V in Fig. 1(c), where the increase is by more than a factor of 30. Analysis of a multitude of I-t characteristics with and without apparent changes to the STM images at varying manipulation current revealed a threshold $I_{\mathrm{thr}} = 3$ nA. If the current does not rise above I_{thr} during the manipulation no rapid changes are observed in the I-t characteristics and the STM images remain unchanged.

At opposite polarity no changes are observed upon IET manipulation between -2.5 V and -4 V with similar current [Figs. 1(b) and 1(d)]. In fact, we were not able to induce changes by IET at crystalline ice clusters with any negative voltage within the voltage range of tip stability. This strong bias asymmetry in combination with a large threshold of several volts is indicative of a reaction induced by electronic excitation either into an unoccupied molecular orbital or a conduction band rather than a vibrational excitation.

The depression produced by IET might indicate a desorption of the molecules. From energetic reasoning desorption is indeed preferred over dissociation as the former demands breakage of up to three hydrogen bonds, each one of 0.2–0.3 eV only, in contrast to the molecule dissociation energy of 5.1 eV [15]. However, the depth of the depression observed after manipulation is highly voltage dependent as demonstrated in Fig. 2. The three depressions imaged at 0.4 V [Fig. 2(b)] lose apparent depth at 1.4 V [Fig. 2(c)] and are no longer deeper than the surrounding ice at 2.4 V [Fig. 2(d)]. Figure 2(e) quantifies this qualitative observation. In contrast to the quadrupling of the apparent height above the manipulated area, there is no variation in apparent height of the ice crystal up to 2 V and only very slight changes up to 2.5 V. All parts of the manipulated ice appear at least as high as the highest part in the crystalline island at ≈ 2 V. Hence, the apparent depressions observed after manipulation in Fig. 1 do not result from a change in geometric height, but in electronic structure. This excludes that the molecules have been desorbed.

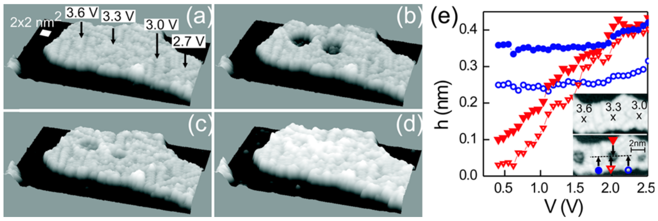

FIG. 2 (color online). Imaging of ice and manipulated ice. (a) STM image before manipulation with 0.4 nA and indicated voltage for 0.72 s. (b)–(d) STM images after manipulation at different bias voltages and with 3 pA: (b) 0.4 V, (c) 1.4 V, (d) 2.4 V. (e) Apparent height h vs V; measurement points are indicated in STM image (bottom): circles, on ice; triangles, on manipulated ice; filled (open) symbols represent highest (least highest) part within the representative structure. STM images are 2D images of (a) and (b). Note that the real height of the ice islands is ≈ 1.4 nm [20].

In order to reveal the change in electronic structure we characterized the manipulated region spectroscopically. For a quantitative comparison of the spectra the tip should be placed at the same height above the different structures, which depends on the set point voltage before the voltage sweep. Based on the apparent height determined in Fig. 2(e) we take a set point of 1.9 V for this comparison. The spectra [Fig. 3(a)] reveal that the current increases linearly when tunneling through the crystalline ice with two distinct changes in slope at ≈ − 0.4 and ≈1.15 V. The first change is indicative of the surface state of Cu(111), which is not completely suppressed by ice adsorption, the second one is of unknown origin. In contrast to this linear increase, the current increases exponentially above the manipulated species. Below 1.9 V the current is thereby higher above the crystalline ice, but the difference reduces with increasing voltage explaining the apparent height changes in Fig. 2(e).

Between the top of the surface state onset and 1.8 V the surface spectrum is in the linear regime as expected . The exponential increase above the manipulated species indicates the onset of its conduction band. This is found at a lower value than the onset of the conduction band of ice [Fig. 3(b)]. A value of approximately 3 V for the latter one is consistent with two-photon photoemission measurements of ice on Cu(111) [17]. For the manipulated species the onset is shifted by approximately 0.4 V closer to the Fermi energy [Fig. 3(b)]. It is this shift of the conduction band during the manipulation that causes the strong increase in current after the dissociation is initiated [cf. Fig. 1(c)].

In order to gather more information about the produced species, we investigate changes to the vibrational spectrum gathered in IETS obtained in lock-in technique. As this technique is not applicable with the low currents needed for imaging of the crystalline islands [10], we analyzed the depression found after a similar manipulation of much smaller clusters (Fig. 4). Electron induced molecule reorientation [11] limits the range in which IETS can be performed on D_2O ice clusters to ±150 meV [8]. We thus investigate these small ice clusters on Ag(111), where the position of the surface state is much closer to the Fermi energy and allows also observation of a change in binding within this limited voltage range.

The spectra taken above the original ice cluster shows three maxima. At $-(69 \pm 3)$ mV the surface state onset (reduced in intensity as compared to the bare surface, not shown) shows that also here the surface state is not quenched completely. The other two maxima have a symmetric form around zero and are in a voltage range characteristic for the librational mode (frustrated translation) [c.f. external vibrations of water molecules measured by IETS on Au(111) [18]]. For the three curves taken at parts of different height of the cluster, the maxima vary from -31 to -46 mV and from 41 to 65 mV. This shift is attributed to the different number of hydrogen bonds (cf. for H_2O on HOPG 63, 75, and 100 meV were measured [19]).

Two differences are observed in the spectra of the manipulated cluster. The surface state is suppressed completely and the external vibration is independent of tip position. The disappearance of the surface state points to a stronger binding of the manipulated molecule than that of ice. The independence of the external vibration on position indicates that the produced species is no longer hydrogen bonded. We conclude that the ice molecules are dissociated to atomic oxygen as OH is dipolar and O_2 is only weakly bound.

We now return to the dissociation threshold. The number of electrons needed for the first dissociation event as indicated by a rise in current above 3 nA in the *I*-*t* curve [c.f. Fig. 1(c)] provides the first indication of the threshold. The fit in Fig. 5(a) gives (2.94 ± 0.04) V.

The area below the *I*-*t* curves corresponds to the number of tunneling electrons, which subsequently dissociate the ice. The number of dissociated molecules is estimated from the real height of the ice islands as determined before [20] and the size of the depression after manipulation. The dissociation rate is voltage and current independent above 3.3 V with 2.5×10^{-8}/electron [Fig. 5(b)]. The threshold of (2.99 ± 0.02) V is consistent with the former value and

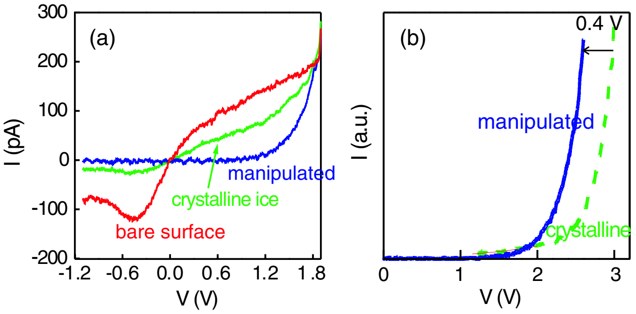

FIG. 3 (color online). *I*-*V* spectra (a) with set point at 1.9 V, average of several spectra (up to 14), and (b) in exponential regime, average of 30 spectra. Spectra are taken with different set points, but renormalized to the value at 1.9 V.

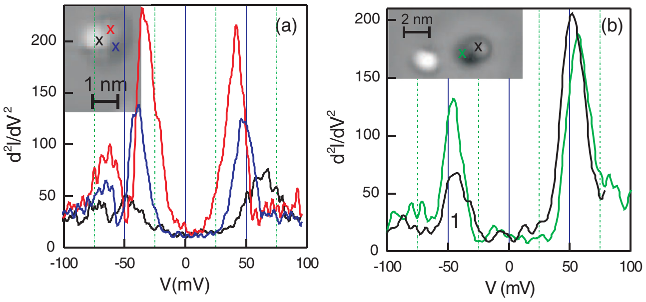

FIG. 4 (color online). *R* signal of IETS spectra (d^2I/dV^2) for small D_2O cluster on Ag(111), average of several spectra measured where indicated on STM images. Parameters: $f_{\mathrm{mod}} = 361.1$ Hz, $U_{\mathrm{mod}} = 8$ mV. (a) Original water cluster, 21 pA, 72 mV, and (b) manipulated cluster, 20 pA, 72 mV.

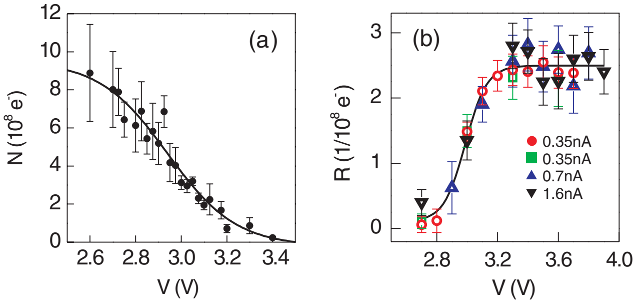

FIG. 5 (color online). Threshold determination for islands on Cu(111), with fits (a) number of electrons N needed for initiation of dissociation event, for $I_{\text{manip}} = (0.65 \pm 0.08)$ nA, and (b) dissociation rate R per molecule for different manipulation currents.

shows that the dissociation is induced by electrons that are injected into the conduction band of ice. It is, however, only about half of the smallest thresholds related to dissociative electron attachment [7].

The conduction band of ice is derived from the antibonding orbitals $4a_1$ and $2b_2$ [21,22]. If the perfect fourfold coordination within the ice is disrupted as in the ridges of the facetted crystalline ice, a localization of antibonding states along the OH bond is recovered [22].

In conclusion, the following picture emerges from our molecular-scale study of the interaction of low-energy electrons with supported ice: Electrons injected into the conduction band of ice are localized in the antibonding states along the OH bond, which opens the possibility of dissociation by electronic excitation. The dissociation shifts the conduction band, thus increasing the electron current and the subsequent electron damage. The shifted conduction band allows the electrons to travel several nanometers to cause damage quite far away (up to 4.5 nm) from the initial injection point. This increases the vulnerability of ice towards low-energy electrons.

Our results give a more quantitative view on possible damage during electron-based structure measurement of supported ice, for which the general belief is that contradictory results reported in literature may stem from electron induced damage during the measurement.

Finally, we believe that our results might be quite general for supported ice. Similar three-dimensional ice grows on other metal supports as already discussed in [9]. Also on these ice structures an injection into the conduction band is possible and similar changes to the conduction band upon first dissociation are likewise expected. The exact site of electron induced dissociation, the cross section, and the distance traveled by the electron might, however, depend on the support.

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[1] R. Balog, J. Langer, S. Gohlke, M. Stano, H. Abdoul-Carime, and E. Illenberger, Int. J. Mass Spectrom. **233**, 267 (2004).

[2] H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Pelmenschikov, L. G. M. Pettersson, and A. Nilsson, Phys. Rev. Lett. **89**, 276102 (2002); K. Andersson, A. Nikitin, L. G. M. Pettersson, A. Nilsson, and H. Ogasawara, Phys. Rev. Lett. **93**, 196101 (2004); J. Weissenrieder, A. Mikkelsen, J. N. Andersen, P. J. Feibelman, and G. Held, Phys. Rev. Lett. **93**, 196102 (2004); S. Haq, C. Clay, G. R. Darling, G. Zimbitas, and A. Hodgson, Phys. Rev. B **73**, 115414 (2006).

[3] P. J. Feibelman, Science **295**, 99 (2002); S. Meng, L. F. Xu, E. G. Wang, and S. Gao, Phys. Rev. Lett. **89**, 176104 (2002); A. Michaelides, A. Alavi, and D. A. King, Phys. Rev. B **69**, 113404 (2004); S. Meng, E. G. Wang, Ch. Frischkorn, M. Wolf, and S. Gao, Chem. Phys. Lett. **402**, 384 (2005); G. Materzanini, G. F. Tantardini, P. J. D. Lindan, and P. Saalfrank, Phys. Rev. B **71**, 155414 (2005).

[4] M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002).

[5] R. Papoular, Mon. Not. R. Astron. Soc. **362**, 489 (2005).

[6] B. J. Murray, D. A. Knopf, and K. Bertram, Nature (London) **434**, 202 (2005).

[7] G. A. Kimmel and T. M. Orlando, Phys. Rev. Lett. **77**, 3983 (1996); M. T. Sieger, W. C. Simpson, and T. M. Orlando, Nature (London) **394**, 554 (1998); Q.-B. Lu, A. D. Bass, and L. Sanche, Phys. Rev. Lett. **88**, 147601 (2002); N. G. Petrik and G. A. Kimmel, Phys. Rev. Lett. **90**, 166102 (2003).

[8] K. Morgenstern and K. H. Rieder, Chem. Phys. Lett. **358**, 250 (2002).

[9] M. Mehlhorn, H. Gawronski, L. Nedelmann, A. Grujic, and K. Morgenstern, Rev. Sci. Instrum. **78**, 033905 (2007).

[10] M. Mehlhorn and K. Morgenstern, Phys. Rev. Lett. **99**, 246101 (2007).

[11] K. Morgenstern and J. Nieminen, J. Chem. Phys. **120**, 10 786 (2004).

[12] K. Morgenstern, H. Gawronski, M. Mehlhorn, and K. H. Rieder, J. Mod. Opt. **51**, 2813 (2004).

[13] D. Nordlund, H. Ogasawara, Ph. Wernet, M. Nyberg, M. Odelius, L. G. M. Pettersson, and A. Nilsson, Chem. Phys. Lett. **395**, 161 (2004).

[14] W. Ho, J. Chem. Phys. **117**, 11 033 (2002).

[15] P. Maksyuterko, T. R. Rizzo, and O. V. Boyarkin, J. Chem. Phys. **125**, 181101 (2006).

[16] The set point above the surface is also chosen at 1.9 V and thus only qualitatively comparable.

[17] C. Gahl, U. Bovensiepen, Ch. Frischkorn, and M. Wolf, Phys. Rev. Lett. **89**, 107402 (2002).

[18] H. Gawronski, K. Morgenstern, and K.-H. Rieder, Eur. Phys. J. D **35**, 349 (2005).

[19] D. Chakarov and B. Kasemo, Phys. Rev. Lett. **81**, 5181 (1998).

[20] J. Stähler, M. Mehlhorn, U. Bovensiepen, M. Meyer, D. O. Kusmierek, K. Morgenstern, and M. Wolf, Phys. Rev. Lett. **98**, 206105 (2007).

[21] A. Nilson, H. Ogasawara, M. Cavalleri, D. Nordlund, M. Nyberg, P. Wernet, and L. G. M. Petterson, J. Chem. Phys. **122**, 154505 (2005); S. Myneni, Y. Luo, A. Näslund, and M. Cavalleri, J. Phys. Condens. Matter **14**, L213 (2002).

[22] M. Cavalleri, H. Ogasawara, L. G. M. Pettersson, and A. Nilson, Chem. Phys. Lett. **364**, 363 (2002).