Inducing H/D Exchange in Ultrathin Ice Films by Proton Deficiency

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We show that H/D exchange between H_2O and D_2O in ultrathin ice films adsorbed on Cu(100) does not occur through autoionization at temperatures below 140 K. The exchange is, however, facile if a proton deficiency is induced in the ice films by having small amounts of OH preadsorbed on the copper surface. The system was studied using surface infrared vibrational spectroscopy with the aid of density functional theory calculations.

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One of many remarkable properties of water is the efficient transport of H^+ and OH^- ions, in both the liquid and in the different solid phases, compared to other ions. To rationalize the anomalous transport properties interconversion between different hydration complexes surrounding the ion have been evoked in the liquid phase for both ions [1,2]. An important manifestation of the proton transport is the efficient isotopic exchange observed in both water and ice, i.e., $2H_2O + 2D_2O -> H_2O + 2HDO + D_2O$. The Grotthuss mechanism [3] has for more than 100 years provided the basis for the understanding of how the exchange occurs not only in liquid water but also in ice and thin ice layers at surfaces. The isotopic H/D mixing observed in thin ice layers on surfaces has accordingly been proposed to be facilitated by an excess of protons in the ice network, through H_3O^+, much in analogy with the liquid phase [4,5].

In the present work we show conclusive spectroscopic data demonstrating efficient H/D isotopic exchange in a system having a deficiency of protons instead. An ultrathin ice film, consisting of ≥ 2 bilayers (BL) grown as well defined planar structures on a Cu(100) surface, is used for the study. Importantly we show that no H/D exchange occurs in the ice film when the ice layer is chemically uniform and the copper surface is clean. That is, H/D exchange in these ice films does not occur through autoionization ($2H_2O <=> H_3O^+ + OH^-$) below 140 K. Instead, we show that the exchange can be catalyzed by small amounts of OH_{ad} preadsorbed on the surface. While OH_{ad} is readily formed upon water adsorption on many metal [6] and metal oxides surfaces [7] H_3O^+ remains elusive and has not been spectroscopically identified on any metal surfaces so far. As a result the existing model where H/D exchange in thin films at metal surfaces has been assumed to be catalyzed by H_3O^+ [4,5] needs to be revised and refined in accordance with recent theoretical results [8]. The situation for ice is similar to that of liquid water for which the OH^- ion, until recently [2,9,10], has been given much less attention than H_3O^+.

The Cu(100)/water system has been studied using a Fourier transform infrared (FTIR) spectrometer connected to a turbo pumped ultra high vacuum chamber. The Cu(100) crystal has a very low defect concentration indicated by the narrow line width (≤ 1.0 cm^{-1}) of the ν(O-H) mode in OH at low coverages (data not shown). All spectra were recorded below 90 K. The sample temperature was measured using a thermocouple (type E) and controlled using a feedback system (Eurotherm) which allowed for the temperature to be kept both at a constant ($\pm$ 0.5 K) temperature and to be ramped at controlled rate, 4 K/s. Our experimental probe is unique in that the isotopic distribution and the degree of H/D mixing can be monitored at the ice surface as well as in the entire ice layer simultaneously. The mixing at the ice surface is probed by the ν_{free}(O-H) mode of water molecules that have one hydrogen bond protruding out into vacuum at the ice surface, often referred to as the dangling bond. The degree of mixing in the entire ice film is simultaneously probed by the water bending modes, δ(H-O-H), of H_2O, D_2O and HDO. All experimentally observed isotopic shifts of the frequency of the vibrational modes have been confirmed by density functional theory (DFT) calculations (Table I). The integrity of this approach is well documented for surface adsorbates [12] and water complexes [13]. The growth conditions are such that nonporous amorphous solid water is formed [14]. The formation of ice is dominated by a layer by layer growth on the Cu(100) surface as demonstrated by a saturation of the dangling bond mode intensity upon completion of the first bilayer (BL). The intensity stays constant as the coverage is increased up to ≤ 20 bilayers, see inset Fig. 1. This is consistent with a two-dimensional layer by layer growth resulting in large islands with uniform thickness and in agreement with previous scanning tunneling microscopy (STM) studies of water at, e.g., Pt(111) at these temperatures [15]. Also, water has been shown to be highly mobile on the Cu(100) surface already at 20 K [16].

The layer by layer growth allows for the preparation of isotopically distinct sandwiched layers of ice. This is

TABLE I. Vibrational shifts induced by isotopes as determined by DFT calculations compared to experimental data. The calculated dangling bond frequencies are scaled by 0.9679 to account for anharmonicity [11].

Cu(100) B3LYP	Dangling bond stretch mode [cm^{-1}]				Bending mode of dangling bond water [cm^{-1}]	
$6-311++g(3fd,3pd)$						
Isotopic mix	Scaled Calc. Cu(100)	Exp.	Shift Calc.	Shift Exp.	Calc. Norml[a]	Exp.
H-OH + $3H_2O$	3717	3697	...	...	1651[a]	1651[a]
H-OD + $3H_2O$	3715	3694	−2	−3	1402	1404
H-O^{18}H + $3H_2O$	3704	3687	−13	−10	...	...
H-OH + $3D_2O$	3716	3697	−1	...	1646	...
D-OD + $3D_2O$	2706	2726	...	...	1204	1207
D-OH + $3H_2O$	2698	2713	−9	−13	1487	1506
D-OH + $3D_2O$	2697	2713	−10	−13	1489	...

[a] The bending mode region is normalized with respect to the $\delta(H\text{-}O\text{-}H)$ mode frequency, at 1651 cm^{-1}, in the isotopically uniform film.

experimentally confirmed and summarized in Figs. 1(a) and 1(b) and Table I. Initially a 0.9 BL of D_2O is adsorbed on a clean Cu(100) surface, at 90 K, Fig. 1(a). The ice layer does not wet (or only partially wets) the Cu(100) as apparent by the ν_{free}(O-D) mode at 2728 cm^{-1}, giving rise to a hydrophilic first layer of ice, as observed for, e.g., Cu(111) [17]. On top of this ice layer H_2O (0.9 BL) is adsorbed at 84 K, Fig. 1(b). Characteristic of layer by layer growth, the ν_{free}(O-D) mode disappears and is replaced by the corresponding ν_{free}(O-H) mode at 3697 cm^{-1}. In the bending mode region, 1000–1800 cm^{-1}, both δ(D-O-D) at 1207 cm^{-1} and δ(H-O-H) at 1651 cm^{-1} are readily observed (small amounts of HDO originating from H/D exchange at the chamber walls are always present). After heating, at 140 K for 240 s, a 1:1 mix of H_2O and D_2O is obtained at the ice surface which is evident by the appearance of both ν_{free}(O-H) and ν_{free}(O-D) dangling bond modes with similar intensity, Fig. 1(c). Importantly both the bending mode and the ν_{free}(O-D) mode regions show that there is no H/D exchange in the film. That is, no increase of intensity of bending modes corresponding to HDO (1400–1500 cm^{-1}) is observed and no low energy shoulder develops, on the ν_{free}(O-D) band at 2726 cm^{-1}, to be associated with DHO.

The result is dramatically different when the experiment is repeated with small amounts of hydroxyl preadsorbed on the copper surface. In short, hydroxyl is produced by exposing the surface to oxygen at 470 K where O_{ad} is formed. At 90 K, >1 BL of H_2O is adsorbed. Hydroxyl, $\leq$ 0.07 monolayers [18], is formed by the reaction: $O_{ad} + H_2O_{ad} - > 2OH_{ad}$ at 170 K, where excess water desorbs. The surface is then recooled to $\leq$ 90 K before exposure to D_2O and then H_2O following the exact procedure as above. Accordingly, the spectrum of the first layer of D_2O is clearly indistinguishable from the one obtained on the clean metal surface, compare Figs. 1(a) and 1(a′). When the second layer of water H_2O is added the presence of OH_{ad} still does not influence the vibrational spectrum. Figures 1(b) and 1(b′) are indistinguishable as long as the sample is kept below 90 K. After heating, at 140 K for 240 s, the two water isotopologues are completely mixed, i.e., 25% H_2O, 50% HDO and 25% D_2O is observed, Fig. 1(c′). As above all spectra are recorded after the sample temperature has returned to $\leq$ 90 K. The mixing is clearly observed in the bending region, Fig. 1(c′), demonstrating that the proton diffusion in the thin ice layer is very efficient at 140 K. Importantly, H/D mixing facilitated by autoionization, through ($2H_2O <=> H_3O^+ + OH^-$), is clearly negligible at these temperatures (and times $\leq$50 min data not shown.) (For comparison copies of the spectra for the heated ice layer, Figs. 1(c) and 1(c′), are put on top of the spectra for the unheated layer as grey spectra, as indicated by the arrows.) The complete isotopic scrambling is confirmed by the reference spectrum, Fig. 1 ref, recorded for a 1:1 premixed H_2O/D_2O sample.

The mode assignments and the isotopic shifts were supported by density functional theory (DFT) calculations performed within the GAUSSIAN 09 package [19] and the B3LYP functional. Four water molecules adsorbed on a Cu(100) surface were used as a model for the dangling bond water molecule, Fig. 2. For the initial geometry optimization the $6-311+g(d,p)$ basis set was used with all 13 copper atoms frozen at the FCC bulk positions, one hydrogen atom was added to close the electronic shell. For the frequency calculations this geometry was frozen, with exception of the dangling bond H_2O molecule (dashed circle in Fig. 2), and reoptimized using the $6-311++g(3df,3pd)$ basis set. A small but consistent improvement has been observed for isotopic vibrational shifts in water dimers by increasing the size of the basis set [13]. The aim of the frequency calculations is to model vibrational shifts of the dangling bond water molecule when HDO is formed. All other vibrational modes in the cluster are accordingly ignored. In Fig. 1 only the calculated shifts, black vertical lines, upon formation of HDO are shown. That is, for ν_{free}(O-H) and ν_{free}(O-D) the calculated frequencies are normalized with respect to the experimental value of the unmixed isotopologue. All the

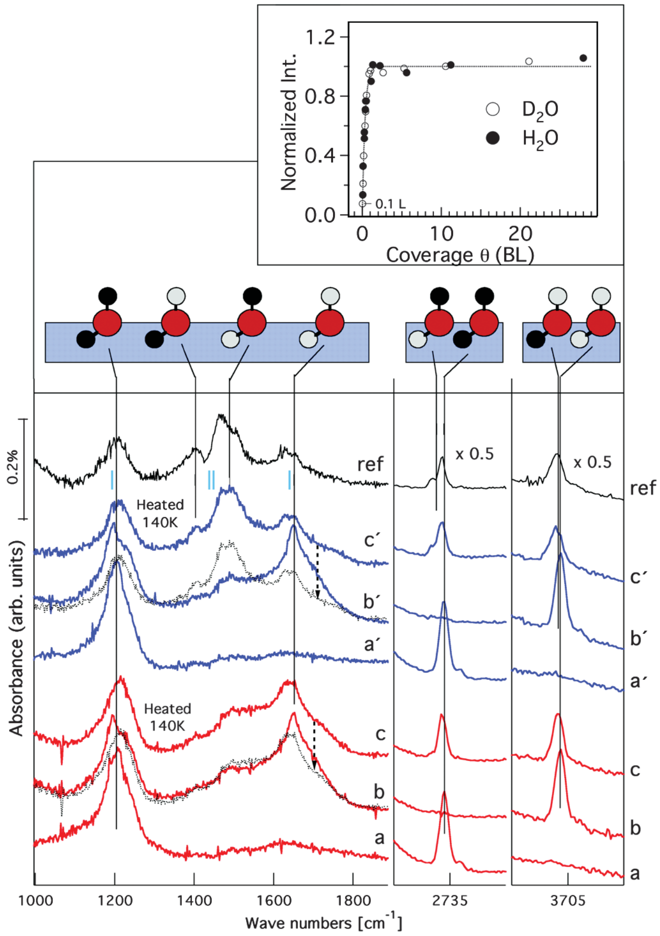

FIG. 1 (color). Infrared vibrational spectra of water adsorbed on a clean Cu(100), recorded below 84 K. (a) 0.9 BL D_2O, (b) +0.9 BL H_2O, (c) Heated to 140 K for 240 s. Infrared vibrational spectra of water adsorbed on Cu(100) pretreated with OH_{ad}. (a') 0.9 BL D_2O, (b') +0.9 BL H_2O, (c') Heated to 140 K for 240 s. (ref) adsorption of a 1:1 H_2O/D_2O premixed sample adsorbed on the clean Cu(100) surface. In cases where the sample was heated just before, (a),(c) and (a'),(c') recording of the spectra started at ≤ 90 K. The vertical black lines show the calculated frequency shifts for the different isotopologues. The corresponding blue short lines in (c') indicates the shift induced when dangling bond is coordinated to an additional water molecule. Inset shows normalized intensities of ν_{free}(O-H) and ν_{free}(O-D) modes in two different isotopically distinct ice films as a function of water coverage.

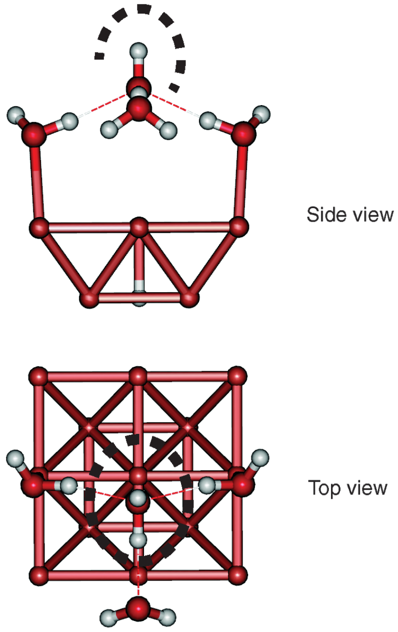

FIG. 2 (color). Model of dangling bond molecule, inside dashed line, as optimized by the density functional theory calculations.

frequencies of the modes in the bending mode region, 1000–1800 cm^{-1}, are normalized with respect to the experimental value of the δ(H-O-H) mode in dangling bond H_2O (1651 cm^{-1}). As seen in Table I the calculations allow for a clear and consistent description of all isotopic shifts in both spectral regions shown in Fig. 1. The formation of HDO results in a downshift of the ν_{free}(O-H) mode by 3 cm^{-1} and a downshift of the ν_{free}(O-D) mode by 13 cm^{-1}, as confirmed by the DFT calculations, Table I. While the size of the shifts is counterintuitive it follows from the fact that the dangling bond vibrational mode in H_2O is essentially decoupled from the rest of the water molecule whereas in D_2O this is not the case. The ν_{free}(O-D) mode is therefore more strongly influenced by the formation of the mixed species. In the water bending mode region, 1000–1800 cm^{-1}, discrimination between H_2O, HDO, D_2O and DHO can clearly be made for dangling bond molecules. To get a qualitative description of the bending modes shifts, that occur upon addition of the second BL, an additional water molecule, adsorbed oxygen down, was placed on the dangling bond hydrogen in Fig. 2. The calculated shifts of the embedded water molecule are shown as blue vertical lines in Fig. 1(c$'$) and reproduce the experimental shifts qualitatively.

As a reference a conventional hexagonal ice structure on a Cu(111) surface was also explored in the same manner. On this surface the frequencies of the dangling bond molecule were only modified slightly, ≤ 10 cm^{-1}, the isotopic shifts even less, ≤ 2 cm^{-1}, as compared to the Cu(100) surface. These results are consistent with water's high ability to adapt to various surface structures [20].

Isotopic scrambling or complete mixing requires, in addition to proton transfer in the network, that there is either an efficient self diffusion of the water molecules in the ice or a combination of water rotational motion and rapid proton transfer, making diffusion of water molecules unnecessary [4]. In the latter case, oxygen stays relatively immobile in the network while the protons only are transferred and the scrambling is facilitated through the combination of proton transfer and rotation of water molecules [4]. In the light of recent theoretica [8] and experimental [15] work it seems plausible that both of these processes are activated at 140 K, but that the proton diffusion may start at a much lower temperature. Interestingly an increased translational diffusion in amorphous solid water has previously been observed in the region above the glass transition temperature at 136 K and before crystallization [21,22].

The phase transition of amorphous ice to cubic ice below 150 K [23] could potentially influence the present experiments. For these ultrathin layers it appears likely, however, that the structure is different from bulk ice as the presence of the surface enforces a one-dimensional ordering, perpendicular to the surface. Accordingly, no difference could be experimentally observed if the first BL of water was preheated to 140 K before the adsorption of the second BL.

H/D exchange in water adsorbed on the surface of rutile $TiO_2(110)$ has been observed previously [24]. The presence of OH on these surfaces [25] is well documented and we propose that the exchange is facilitated by OH in the $TiO_2(110)/H_2O$ system as well. Proton transfer between H_2O and OH has also been proposed to facilitate macroscopic diffusion of OH into regions of H_2O on Pt(111) [26]. In the latter experiment a region ≥ 0.4 mm broad, consisted of H_2O only and on each side of it a mixed $H_2O + OH$ layer. The regions were monitored using X-ray photo electron spectroscopy (XPS) with respect to OH diffusion into the H_2O region. That experimental data do not, however, allow for discrimination between OH diffusion and proton transfer, making the proposed mechanism tentative. A mechanism involving formation of H_3O^+ was also necessary to account for the measured diffusion kinetics while spectroscopically not observed.

OH is readily formed, and has been identified spectroscopically, when water adsorbs on a large number of different surfaces, e.g., mineral [27], metal oxide [25], and metal [28,29] surfaces. In contrast H_3O^+ remains to be spectroscopically identified on a metal surface. The mechanism demonstrated here will therefore be of importance for the proton diffusion and kinetics of ice nucleated on many different type of particles at low temperatures, particles to be found in, e.g., the atmosphere and in outer space. The results presented here is the first conclusive spectroscopic demonstration of efficient proton transfer in a solid quasi two-dimensional water network having a deficiency of protons.

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[1] D. Marx *et al.*, Nature (London) **397**, 601 (1999).
[2] M. E. Tuckerman, D. Marx, and M. Parrinello, Nature (London) **417**, 925 (2002).
[3] C. J. T. d. Grotthuss, Ann. Chim. (Paris) **LVIII**, 54 (1806).
[4] C. W. Lee, P. R. Lee, and H. Kang, Angew. Chem., Int. Ed. **45**, 5529 (2006).
[5] S. C. Park, K. H. Jung, and H. Kang, J. Chem. Phys. **121**, 2765 (2004).
[6] M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002).
[7] U. Diebold, S. C. Li, and M. Schmid, in *Annual Review of Physical Chemistry* (Annual Reviews, Palo Alto, 2010), Vol. 61, p. 129.
[8] X.-Z. Li *et al.*, Phys. Rev. Lett. **104**, 066102 (2010).
[9] R. Ludwig, Angew. Chem., Int. Ed. Engl. **42**, 258 (2003).
[10] E. F. Aziz *et al.*, Nature (London) **455**, 89 (2008).
[11] M. P. Andersson and P. Uvdal, J. Phys. Chem. A **109**, 2937 (2005).
[12] P. Uvdal, R. Asmundsson, and A. D. MacKerell, Jr., Phys. Rev. Lett. **82**, 125 (1999).
[13] J. Ceponkus, P. Uvdal, and B. Nelander, J. Chem. Phys. **129**, 194306 (2008).
[14] K. P. Stevenson *et al.*, Science **283**, 1505 (1999).
[15] S. Nie, N. C. Bartelt, and K. Thurmer, Phys. Rev. Lett. **102**, 136101 (2009).
[16] S. Andersson, C. Nyberg, and C. G. Tengstål, Chem. Phys. Lett. **104**, 305 (1984).
[17] A. Michaelides and K. Morgenstern, Nature Mater. **6**, 597 (2007).
[18] The OH coverage was estimated based on the oxygen atom coverage, determined from oxygen exposure and the molecular beam sticking data in; J. Hall, O. Saksager, and I. Chorkendorff, Chem. Phys. Lett. **216**, 413 (1993) assuming a complete conversion of atomic oxygen to OH_{ad}; 0.07 monolayers of OH_{ad} is therefore an upper limit.
[19] M. J. Frisch *et al.* (Gaussian, Inc., Wallingford CT, USA, 2009).
[20] J. Carrasco *et al.*, Nature Mater. **8**, 427 (2009).
[21] R. S. Smith, C. Huang, and B. D. Kay, J. Phys. Chem. B **101**, 6123 (1997).
[22] R. S. Smith and B. D. Kay, Nature (London) **398**, 302 (1999).
[23] V. F. Petrenko and W. R. Whitwoeth, *Physics of Ice* (Oxford University Press, Oxford, 1999).
[24] N. G. Petrik and G. A. Kimmel, Phys. Rev. Lett. **99**, 196103 (2007).
[25] L. E. Walle *et al.*, Phys. Rev. B **80** (2009).
[26] M. Nagasaka *et al.*, Phys. Rev. Lett. **100**, 106101 (2008).
[27] S. L. Stipp and M. F. Hochella, Geochim. Cosmochim. Acta **55**, 1723 (1991).
[28] G. B. Fisher and B. A. Sexton, Phys. Rev. Lett. **44**, 683 (1980).
[29] P. J. Feibelman, Science **295**, 99 (2002).