Ultrafast Molecular Dissociation of Water in Ice

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Using x-ray emission and photoemission spectroscopies to measure the occupied valence levels in a thin crystalline ice film, we resolve the ionization-induced dissociation of water in ice on a femtosecond time scale. Isotope substitution confirms proton transfer during the core-hole lifetime in spite of the nonresonant excitation. Through *ab initio* molecular dynamics on the core-ionized state, the dissociation and spectrum evolution are followed at femtosecond intervals. The theoretical simulations confirm the experimental analysis and allow for a detailed study of the dissociative reaction path.

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Understanding the processes initiated by ionizing radiation in aqueous systems is essential for many diverse fields such as condensed matter physics, biophysics, radiation physics, aqueous chemistry, waste remediation, environmental cleanup, medical diagnosis, and radiation therapy [1]. The initial ionization event produces a molecular water cation and secondary electrons that subsequently cause spurs of excitation, ionization, recombination, and attachment processes. In water, this rich chemistry spans a large temporal range (femtoseconds to microseconds or longer) leading to dissociated water species and hydrated electrons as outcomes. It is a fundamental challenge for the radiation chemistry community to unravel the early time dynamics ($\sim$1 fs) of electronically excited states in water; such short time scales are difficult to access directly with pump-probe measurements [2].

The primary event in radiolysis of aqueous systems—ionization or excitation of a water molecule—governs all the subsequent steps in the radiolytic process. Although much effort has been spent over the past 60 years [1], the dynamics of this electronically excited state has not been resolved. The complexities of water and the ultrafast time scales needed to probe the excited-state dynamics are two major difficulties to overcome. Core excitation in ice and the gas phase offer possibilities to approach these problems through the decay of the core-excited or ionized state. This decay occurs through a number of fluorescent and Auger decay cascades and leads to strongly dissociative valence-ionized final states where the fragmentation products provide indirect information on the dissociation pathways; this has been extensively reported earlier for the gas and condensed phases [3–8].

The dissociation might, however, be important already within the lifetime of the created core hole, i.e., ultrafast dissociation. In this case, the decay process itself can be used to monitor the dissociation dynamics in the core-excited state on a femtosecond time scale ($\sim$3.6 fs for O1s) [9]. Ultrafast dissociation of water has been reported in the gas phase, but only after selective excitation into the strongly antibonding $4a_1$ state [10,11] and not for the (nonresonant) core-ionization case. The crucial question is whether hydrogen bonds between the water molecules could allow for dissociation also in the core-ionized state. Since the effect of a core hole can be described within the $Z + 1$ approximation, a core-ionized H_2O corresponds to an H_2F^+ impurity in an H-bonded network. This is higher in energy than HF + H_3O^+, indicating that the core ionization could initiate proton transfer.

A minor fraction of the core-ionized molecules decays through x-ray emission (XE) leading to a valence-ionized final state. The same final state can also be created using photoemission spectroscopy (PES) in a direct attosecond time scale (10^{-17} s) process without the intermediate core hole. XES and PES thus measure the same electronic structure aspects [2], but on different time scales. (XES probes the O2p part of the electronic structure through the O1s core hole and the dipole selection rule. In PES the different atomic cross sections for the various subshells strongly depend on the photon energy [12]. At, e.g., 75 eV photon energy, the O2p cross section completely dominates, and we should expect to see a similar spectrum compared to XES.) The photon detected in XES results from the decay of the core hole after a typical core-hole lifetime, while the electron detected for the PE spectrum is emitted directly in the initial photon absorption. In this Letter we present a comparison of these two spectroscopies in a well-characterized hydrogen-bonding situation, tetrahedrally coordinated crystalline bulk ice. We show that the electronic structure differences between XES and PES provide evidence for ultrafast dissociation of core-ionized water in ice. Using *ab initio* molecular dynamics, both protons are found to migrate substantial distances along the O-H—O (O-D—O) direction on a femtosecond time scale in the core-ionized state.

The experiments were performed using the surface branch of beam line I511 [13] at the MAX-lab synchrotron radiation laboratory in Lund, Sweden. Using a pulsed gas delivery system, a ten bilayers thick crystalline ice film was epitaxially grown on Pt(111) at a surface temperature of ~140 K. The O1s XE spectra were taken using nonresonant excitation (~540 eV photon energy) [14] and were recorded with a grazing incidence soft x-ray spectrometer [15] at an energy resolution of 0.7 eV. A hemispherical electron spectrometer (SCIENTA) was used for PES with about 100 meV total energy resolution. To avoid beam damage, the sample was scanned during acquisition keeping the number of photons per unit area below an upper limit calibrated using x-ray absorption spectroscopy. The sample temperature was kept at 100 K during the measurements.

We have treated the close-coupled nuclear dynamics and electronic structure using *ab initio* Car-Parrinello molecular dynamics (CPMD) [16,17] simulations rather than as a lifetime-vibrational interference effect. The latter gives a highly accurate description of gas-phase spectra but requires extensive computational effort and is not applicable to complex systems [18]. The simulations were performed using the B-LYP [19,20] functional for a periodic box consisting of 16 water molecules in an ice I_h configuration with zero net dipole moment; the I_h structure was selected for simplicity, but this choice is not expected to affect the conclusions. The creation of the core hole through absorption of an x-ray photon is substantially faster than the atomic motion so that the excitation process can be considered instantaneous [21]. Snapshots from the ground state simulations of the vibrating lattice were used as starting points for the core-ionized simulations, replacing the norm-conserving pseudopotential [22] of one of the oxygens with a specifically developed pseudopotential for the core-hole state with electron occupation $1s^1 2s^2 2p^4$; the cutoff radii of the s and p channels in the pseudopotential generation was set to 1.0 a.u. The subsequent core-ionized dynamics was stopped at regular 1 fs intervals for calculation of XE spectra [23]. The excited-state dynamics is independent of whether we simulate a resonant excitation (putting the former core electron into the lowest unoccupied molecular orbital) or a nonresonant excitation (removing the former core electron). This is in agreement with the extremely rapid electron delocalization rate (<0.5 fs) in bulk ice [24]. The XES energy scale was obtained from comparison with all-electron calculations using the STOBE-DEMON code [25], and the spectra were convoluted with a 0.7 eV Gaussian distribution to account for the broadening in the experiment. Both a normal and a deuterated ice model were equilibrated for 2 ps at the experimental temperature of 100 K before sampling the core-hole excited-state dynamics and the x-ray emission spectra. For each of H_2O and D_2O, 64 trajectories were run at 100 K to generate reliable averages.

Figure 1 contains the experimental valence region PE and XE spectra of the crystalline ice film plotted on a binding energy scale relative to the Pt Fermi level. The peaks are denoted based on the free water molecule: $1b_2$ for the "O2p" lone-pair orbital, $3a_1$ for the mixed "O2s" and O2p O-H bonding orbital, and $1b_1$ for the O-H bonding "O2p-H1s" orbital. The $1b_1$ XE peak is broadened and shifted to lower binding energy relative to the PE spectrum; this is due to the different time scales in the two spectroscopies. The $1b_1$ is the most internally bonding orbital and thus the most sensitive to changes in the internal O-H-bond distance. The shift to lower binding energy indicates that the $1b_1$ orbital has become less bonding, i.e., that the internal O-H bond has been elongated on the time scale of the core-hole lifetime. The effect is demonstrated by a comparison of XE spectra taken for D_2O and H_2O ice (inset of Fig. 1). One would expect D_2O to respond in the same way as H_2O, but with slower dynamics due to the larger mass. As can be seen in the figure, the bonding $1b_1$ peak is less affected in the case of D_2O, supporting our interpretation. Furthermore, we observe no significant differences in the $1b_1$ peak in the PES as a function of excitation energy, although the energy range scanned, 75–560 eV, signifies variations in sampling depth. The near-random ordering of the free O-H groups at the ice surface and the disordered layers in the near-surface region [26] preclude specific angular effects in the PES as well as in the inherently bulk-sensitive XES. The $3a_1$ orbital is strongly affected by the H-bond network formation causing this orbital to split in two and rehybridize, resulting in a loss of p character [27]. As a result, radiative decay from this orbital is weak and makes only a negligible contribution to the XE spectrum.

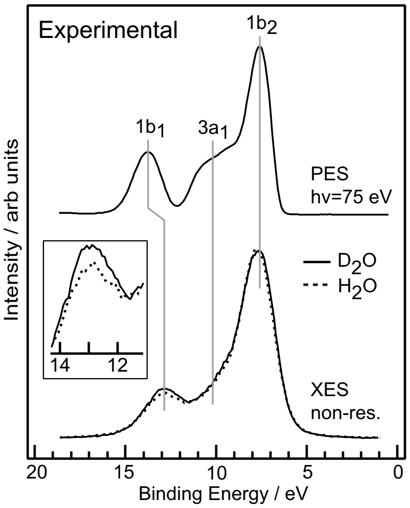

FIG. 1. Experimental valence PE and XE spectra of a crystalline ice film, plotted on a binding energy scale relative to the Pt substrate Fermi level. The three outer-valence orbitals are denoted as for the free molecule. The PE spectrum was taken at 75 eV, and nonresonant excitation (~540 eV) was used for the XE spectra. The latter shows spectra of both H_2O and D_2O ice. An expansion of the XE spectra for the $1b_1$ region is shown in the inset.

In Fig. 2 we present the O1s core-ionized state proton (deuteron) dynamics for a water molecule in a H_2O (D_2O) ice lattice as given by the CPMD simulations. We show the time evolution, averaged over 64 different trajecto-

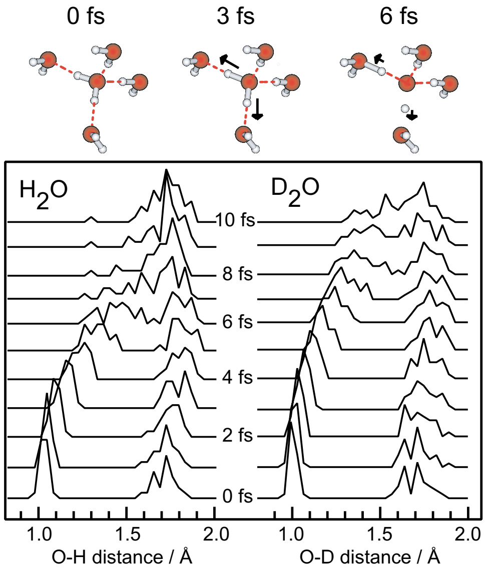

FIG. 2 (color online). Car-Parrinello MD simulations of O1*s* core-ionized state proton (deuterium) dynamics for a water molecule in a H_2O (D_2O) ice I_h lattice, averaged for 64 sampled initial conditions. Shown is the H (D) position along the O-H—O (O-D—O) bond relative to the core-ionized oxygen, measured at 1 fs intervals. At the top of the figure, selected steps in the dynamics are pictured for a core-ionized H_2O and its nearest neighbors.

ries, of the H (D) atoms relative to the core-ionized oxygen. The initial ($t = 0$ fs) positions are given by the ground state simulations with the intramolecular H atoms centered at ~1 Å; the peaks around 1.65 Å correspond to the hydrogen atoms on the neighboring waters donating H bonds to the molecule under study. In the core-ionized state, both of the intramolecular H (D) atoms are found to migrate substantially on a femtosecond time scale. In ice I_h all water molecules are fully coordinated and the differences in the individual core-ionized trajectories are thus only due to the somewhat different initial conditions in terms of vibrational motion. We find that after $\approx$ 6 fs all trajectories for the core-ionized species lead to dissociation of both internal O-H bonds. Comparing H_2O and D_2O we find the expected slower dynamics in the latter case as indicated by experiments (see Fig. 2), and it is only after $\approx$ 8 fs that a similar degree of dissociation has occurred. Here we show the core-ionized state dynamics for 10 fs, but for longer times we observe the reformation of one of the bonds giving the $O1s^{-1}H + H_3O^+$ end product (not shown). With the finite core-hole lifetime in mind (~3.6 fs) [9], we now turn to the question whether this core-ionization-induced dynamics affects the valence structure as probed by XES.

Figure 3 shows the computed and averaged XE spectra as a function of the time step in the radiation-induced dissociation process, convoluted with the experimental 0.7 eV (Gaussian) broadening. The initial spectrum ($t = 0$ fs) corresponds to the photoemission process at the initial geometry, since PES is determined by the

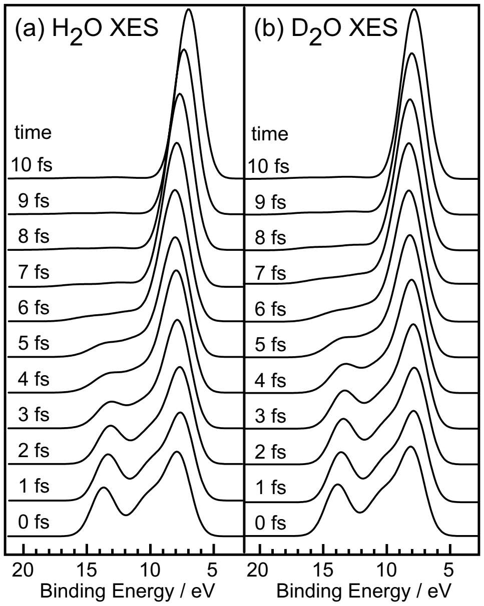

FIG. 3. Computed x-ray emission spectra as function of time (fs) after core ionization for (a) H_2O and (b) D_2O ice I_h plotted on a binding energy scale. The spectra are averaged for 64 trajectories and broadened with 0.7 eV.

initial absorption and is unaffected by subsequent dissociation events (apart from some broadening). During the core-hole lifetime in XES, we see a progressive evolution of the $1b_1$ peak, which loses intensity and moves somewhat to lower binding energy. The $1b_2$ peak—corresponding to the lone-pair state—instead gains intensity and for the fully dissociated species (e.g., $t = 10$ fs), the spectrum shows only this feature as expected for "atomic" oxygen. We again see the slower time-development for the dissociation of the D_2O species expressed in the evolution of the spectra along the reaction path. It is clear that for both H_2O and D_2O, the processes occur on a time scale of the order of the core-hole lifetime.

In order to do a full comparison with the experimental spectrum we must weigh together the different contributions according to the exponential decay associated with the core-hole lifetime. Figure 4 shows the weighted XE spectra for H_2O and D_2O ice compared with the computed PE spectrum (taken as the XES at time $t = 0$ fs). We note the good agreement between the computed and experimental PE spectra lending credibility to the approach taken. Using a lifetime of 3.6 fs [9] for the generation of the theoretical XE spectra, we find that all the salient features in the experimental data are reproduced (compare Fig. 1). In accordance with the experimental observations, the $1b_1$ state moves to lower binding energy and loses intensity with a larger reduction in the case of H_2O than for D_2O. We thus arrive at a very good representation of the experimental spectra and confirm the interpretation of the radiation-induced dissociation in the H-bonded network.

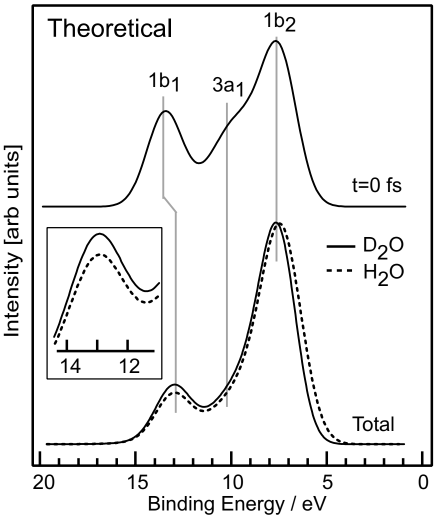

FIG. 4. Computed PE (top) and XE spectra for H_2O (solid line) and D_2O ice I_h (dotted line). The XE spectra are averaged using an exponential decay function (see text).

In summary, we have investigated the dissociation dynamics of core-ionized water in ice using the devised computational scheme as well as experimentally through the comparison between the initial state, as monitored through PES, and the dissociative state, as monitored through XES. Experimental evidence of femtosecond proton migration for the core-ionized state is obtained in the core-hole decay process (via x-ray emission), and the H/D isotope substitution results in an expected slower dynamics. Using *ab initio* molecular dynamics to simulate the excited-state evolution, we can map the nuclear dynamics on a femtosecond time scale. The electronic structure for the dissociative final state following x-ray emission decay is presented in excellent agreement with experiment. It is shown that both protons migrate substantial distances from the core-ionized oxygen to hydrogen-bonded water molecules within the lifetime of the core-hole state—in spite of the excitation being nonresonant—and this is attributed to the connectivity in the hydrogen-bonded network.

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[1] C. D. Jonah, Radiat. Res. **144**, 141 (1995).
[2] U. Keller, Nature (London) **424**, 831 (2003).
[3] G. A. Kimmel and T. M. Orlando, Phys. Rev. Lett. **75**, 2606 (1995).
[4] M.T. Sieger, W.C. Simpson, and T. M. Orlando, Phys. Rev. B **56**, 4925 (1997).
[5] N.G. Petrik and G. A. Kimmel, Phys. Rev. Lett. **90**, 166102 (2003).
[6] R. Romberg *et al.*, Surf. Sci. **451**, 116 (2000).
[7] K. Mase *et al.*, Surf. Sci. **390**, 97 (1997).
[8] W.C. Stolte *et al.*, Phys. Rev. A **68**, 022701 (2003).
[9] M. Neeb, J.-E. Rubensson, M. Biermann, and W. Eberhardt, J. Electron Spectrosc. Relat. Phenom. **67**, 261 (1994).
[10] A.N. de Brito *et al.*, Chem. Phys. Lett. **309**, 377 (1999).
[11] I. Hjelte *et al.*, Chem. Phys. Lett. **334**, 151 (2001).
[12] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).
[13] R. Denecke *et al.*, J. Electron Spectrosc. Relat. Phenom. **101–103**, 971 (1999).
[14] The O1*s* x-ray absorption (XA) spectrum of bulk ice is rather structureless with a strong continuum peak centered at around 540 eV. If electron yield is used to measure the XA spectrum, a considerable amount of intensity in the spectrum is due to surface species. It has recently been shown that the preedge feature in the XA spectra results from species in a broken hydrogen bond situation, e.g., in the present study surface species and possible defects in the ice film. For excitation energies other than this preedge feature, i.e., for excitation of bulk water molecules addressed in this study, we observe no (or very small) dependence in the experimental XE spectra.
[15] J. Nordgren and J. Guo, J. Electron Spectrosc. Relat. Phenom. **110–111**, 1 (2000).
[16] J. Hutter *et al.*, CPMD v. 3.5, MPI fur Festkorperforschung and IBM Zurich Research Laboratory, Rueschlikon, Switzerland, 1999.
[17] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[18] A. Cesar, H. Ågren, and V. Carravetta, Phys. Rev. A **40**, 187 (1989).
[19] C. Lee *et al.*, Phys. Rev. B **47**, 4863 (1993).
[20] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[21] J. Stöhr, *NEXAFS Spectroscopy* (Springer-Verlag, Berlin, 1992).
[22] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[23] M. Nyberg, M. Odelius, A. Nilsson, and L. G. M. Pettersson, J. Chem. Phys. **119**, 12 577 (2003).
[24] D. Nordlund, H. Ogasawara, M. Nagasono, L. G. M. Pettersson, and A. Nilsson (to be published).
[25] K. Hermann *et al.*, STOBE-DEMON, StoBe Software, Stockholm, Berlin, Montreal, 2002.
[26] D. Nordlund, H. Ogasawara, Ph. Wernet, M. Nyberg, M. Odelius, L. G. M. Pettersson, and A. Nilsson, Chem. Phys. Lett. **395**, 161 (2004).
[27] A. Nilsson, H. Ogasawara, M. Cavalleri, D. Nordlund, M. Nyberg, Ph. Wernet, and L. G. M. Pettersson (to be published).