On the nature and origin of di-cationic, charge-separated species formed in liquid water upon X-ray irradiation

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Identifying the initial products of the interaction of high-energy radiation with liquid water is essential for understanding the yield and patterns of damage in aqueous condensed matter, including biological systems. Up until now several fast reactions induced by energetic particles in water could not be observed on their characteristic timescales, and hence some of the reaction intermediates involved, particularly those requiring nuclear motion, have not been considered in describing radiation chemistry. Here, through a combined experimental and theoretical study, we elucidate the ultrafast proton dynamics in the first few femtoseconds after X-ray core-level ionization of liquid water. We show through isotope analysis of the Auger-spectra that proton-transfer dynamics occurs on the same timescale as electron autoionization. Proton transfer leads to formation of a Zundel-type intermediate [HO*··H··OH$_2$]$^+$, which further ionizes, forming a so-far unnoticed type of di-cationic, charge-separated species with high internal energy. We call the process proton-transfer mediated charge separation.

The primary processes in water initiated by X-radiation are poorly understood despite their paramount importance in different fields. Understanding the energy and charge re-distribution in water upon X-ray photon absorption is vital for a design of more efficient radio-oncology schemes,[1-2] for disentangling the physical basis of genotoxic effects on living tissues,[3-5] for minimizing the damage of biological samples during X-ray diffraction

experiments,[6] as well as for controlling the performance of nuclear reactors under operating conditions.[7] Current understanding of electron-initiated processes in aqueous systems, following energy deposition, and the subsequent radical chemistry have been recently reviewed.[8] An explicit consideration of radicals and molecular species formed via multiple ionization processes of water, involving for instance atomic oxygen and hydrogen peroxide, can be found in the radiolysis literature, *e.g.* in refs.[7,9] However, the knowledge of the ultrafast processes and mechanisms in water radiolysis remains to large extent unexplored.

In the present work we focus on the processes following O1s core-level ionization of water. The highly excited species formed by the core ionization relaxes primarily via Auger-electron decay. As shown in Figure 1b, Auger decay of a water molecule involves refilling the water core-hole by one of the valence electrons, and the simultaneous emission of another valence electron, the Auger electron, from the same water molecule. The resulting highly reactive doubly ionized H_2O^{2+}(aq) molecule, with both vacancies (holes) located at the same site (denoted here as 2h state), then undergoes ultrafast Coulomb explosion, forming dominantly $O + 2H^+$.[10-11]

In recent years a set of novel non-local autoionization processes has been identified to play an important role in weakly bonded atomic and molecular systems.[12-14] One such relaxation process is Intermolecular Coulombic Decay (ICD), initially observed upon inner-valence ionization of van der Waals-bonded clusters,[12,15-17] and later also (hydrogen bonded) water clusters.[18] In the ICD process, the energy provided by an outer valence electron upon filling the vacancy is used to expel a second electron from an atom or molecule neighboring the initially ionized site. Throughout the process the two units (two water molecules in our case) can be considered as being electronically distinct; see scheme Figure 1c. The final product is a doubly charged species, but with the two positive charges located on different water units, *i.e.*, a $[H_2O^+ \cdot \cdot H_2O^+]$(aq) complex is formed. Computational work suggests that the ICD process is a rather general mechanism for electronic deactivation in hydrogen-bonded molecules in water such as hydrated biomolecules,[19] ammonia,[20-21] or water molecules interacting with a protein residue.[21] More recently ICD-like processes have also been observed for core-ionization and core-excitation of aqueous solutions.[20,22-26] The core-ionization induced processes of ICD type have been also observed and thoroughly discussed for water [27-28] and ammonia clusters.[29] An important difference between relaxation of core-holes and inner-valence holes is that single core-ionization energies are greater than the

lowest valence double-ionization energies; thus the Auger channel is always open upon core-ionization whereas it might be energetically forbidden upon inner-valence ionization.[14]

Here we explore yet another alternative relaxation route of core-ionized liquid water which is mediated by the ultrafast motion of a proton in the intermediate core-hole state (summarized in Figure 1d). The term 'mediated' and the corresponding acronym PTM account for the fact that some of the processes considered here are possible only if proton transfer had taken place. These processes occur on the timescale of the oxygen 1s core-hole lifetime (approximately 4 femtoseconds),[30] which is comparable to the 9 fs period of a full O–H vibration in water. Experimentally, we perform a so-called core-hole-clock measurement,[31-33] which is based on detecting electron energies emitted by autoionization, occurring continuously from the geometrically evolving manifold of core-ionized structures. The relaxation into two-hole final states is taken to be mono-exponential; the time constant is the core-hole lifetime. The Auger spectra of water thus contain temporal information about changes in the electronic structure induced by ultrafast proton transfer in the core-ionized state.

At some point during the proton transfer, the two initially interacting water units form a Zundel-type cationic species, $[HO^*{\cdot\cdot}H{\cdot\cdot}OH_2]^+$(aq) (step 1 in Figure 1d). Relaxation by autoionization of the core-hole state can therefore take place from a continuum of non-equilibrium structures, even at this short timescale. In the proton-transfer mediated Auger (PTM-Auger) process core-excited HO* emits an Auger electron (*2*-branch in Figure 1d). In the proton-transfer mediated ICD process (PTM-ICD) energy released in the core-refill of HO* is instead used to ionize the H_2O of the Zundel-type species (*3*-branch in Figure 1d). Both mechanisms are explicitly written in Figure 1d, steps 2', 2'' and steps 3', 3'' for the Auger and ICD case, respectively. Here, internal conversion, IC, may occur because the states formed in the upper process have somewhat larger energy as we show below.

We denote the final electronic states of these charge separated di-cationic complexes, $[HO^+{\cdot\cdot}H_3O^+]$(aq) and $[H_2O^+{\cdot\cdot}H_2O^+]$(aq), 1h•1h (as opposed to 2h for normal Auger, occurring in the ground-state geometry). We further distinguish the 1h•1h states depending on whether charge delocalization occurs through normal ICD, *i.e.*, in the ground-state structure ((1h•1h)$_{ICD;}$ Figure 1c), via ICD in the distorted geometry ((1h•1h)$_{ICD*}$ through PTM-ICD; Figure 1d, step 3'), or via local de-excitation in the distorted geometry ((1h•1h)$_{Auger}$ through PTM-Auger; Figure 1d, step 2'). The 1h•1h states can be experimentally distinguished from the 2h states by their different Auger electron spectra. The actual occurrence of PTM-CS

effects is reflected in the larger intensities of the 1h•1h signature in the Auger spectra from $H_2O(aq)$ than for $D_2O(aq)$, as soon will be demonstrated. The importance of nuclear dynamics for core-ionized liquid water and for water excited into the antibonding $4a_1$ state has also been invoked to the explain X-ray emission spectra from liquid water.[34-39] With Auger-electron spectroscopy we now explicitly address the electronic structure of the excited intermediates and the character of the 2-hole final states by specifically measuring the kinetic energy of electrons emitted during nuclear relaxation. The charge separation mechanisms (Figure 1d) will be interpreted with the help of *ab initio* calculations.

Results and Discussion

Core-level ionization induced autoionization spectra: $H_2O(aq)$ *vs.* $D_2O(aq)$

Experimental electron energy spectra for autoionization of light and heavy liquid water are shown in Figure 2 for three different photon energies. In Figure 2a the photon energy is 600 eV, *i.e.*, sufficient to cause direct core-ionization, being more than 60 eV above the O1s ionization threshold of liquid water.[40] The spectrum in Figure 2a is dominated by normal Auger electron emission (Figure 1b). For normal water, similar ionization-autoionization spectra have been obtained earlier.[27,41-42] Peak *1*, near 505 eV kinetic energy (KE), identifies the leading (normal) Auger transition. The feature relevant for the present study, however, is the shoulder *2*, near 510 eV KE. For core-level ionization (Figure 2a), but not for excitation (see below), this peak has no gas-phase analogue,[27] and is the unambiguous electronic-structure signature of 1h•1h final states, whose energies are lower than for the 2h states, thus leading to higher KE of the outgoing electron in the autoionization event. Our interpretation of the shoulder at 510 eV KE is further supported by our constrained DFT calculations on small water clusters presented below and in the Supplementary Information (SI), Figures S1 and S2.

The crucial observation to be made from Figure 2a is, however, the much stronger intensity observed for 1h•1h states of $H_2O(aq)$, as compared to $D_2O(aq)$. Such large isotope effect cannot be due to the subtle ground-state structural differences between light and heavy water.[43] This agrees with the fact that the direct photoionization spectra of liquid water[44-45] and water clusters[46] exhibit a very small isotope effect, which is also consistent with our simulated Auger spectra being essentially identical for small water clusters formed by H_2O and D_2O when nuclear dynamic effects are not included (see SI, Figures S1 and S2). We therefore conclude that the difference spectrum of Figure 2a reflects the effect of nuclear

dynamics in the ionized state. The situation is different for excitation, when the extra electron must be taken into account. Absolute strengths of decay into 1h•1h states cannot be determined here because of the small intensity of peak *2* on top of a larger peak from local Auger decay, peak *1*, the exact spectral shape of which is unknown.

Core-level excitation induced autoionization spectra: H₂O(aq) *vs.* D₂O(aq)

For comparison we also present the analogous spectra for resonant excitations at the O1s absorption main-edge (537.5 eV photon energy, Figure 2b) and at the O1s absorption pre-edge (535 eV, Figure 2c). This case will be only briefly considered here. In the excitation spectra, peak *1* appears at somewhat larger KEs due to spectator energy shifts, an effect which previously has been discussed for water in great detail.[41-42] For core-level ionization and excitation the spectral changes between normal and deuterated water are fairly similar; compare the respective differential spectra. Proton dynamics thus seems to be of importance for decays from all intermediate states reached throughout the O1s near-edge absorption fine structure of liquid water (here the delocalized two-hole final state contains an additional excited electron; 1e1h•1h). This has also been concluded from previous X-ray emission studies.[34-36,39] In the present study, we use Auger spectroscopy for the experimental identification of nuclear dynamics upon ionization, which is mediated by the solvent; gas-phase water does not dissociate upon O1s ionization, but it does upon excitation.[30] The dynamics of molecular water upon core-level ionization and excitation has been followed in detail by classical simulations.[47] These authors corroborate the importance of O–H bond lengthening for explaining the part of the spectrum designated as peak *2*.

Nuclear motion in the core-ionized state

We now turn to a discussion concerning the nature of the 1h•1h states (peak *2* in Figure 2a) in terms of PTM-CS processes (*i.e.*, steps 2' and 3' in Figure 1d). To quantify the effects of nuclear dynamics we have carried out calculations of proton dynamics in core-ionized water clusters.

Our results for the water dimer are shown in Figure 3. The dimer geometry corresponds to the structure of condensed-phase water; here we use the I$_h$-ice structure with the O··O distance set to 2.7 Å. Figure 3a shows the lowest potential-energy curve along the O–H bonding direction of the core-ionized water molecule. This mode is identified as the most important proton-transfer coordinate since the O–H bond vibrates rather fast, as does the free O–H bond which however does not dissociate upon core ionization. Potential energy curves

for other relevant modes of the quasi-tetrahedral water pentamer are presented in the SI, Figure S3. In agreement with previous computations[39] we observe that for water clusters the O–H bond dissociation is energetically feasible, unlike for gas-phase water ionization as we have already mentioned. The electron deficient core-ionized water molecule releases a proton to an accepting neighboring water molecule (Figure 1d, step 1). Since the potential energy surface is rather flat, the driving force for this reaction is not strong. However, the energy content of the vibrational O–H wave packet is large, and as a consequence the wave-packet dispersion is considerable even within the 4 fs core-hole lifetime. This is seen when comparing the calculated wave packets of the ionized water dimer in the ground-state geometry and the structure evolving after 4 fs, when the average O–H distance has increased (Figure 3a). Although the center of the wave packet moves only slightly, there is a considerable change in shape, and the high-energy tail of the distribution quickly penetrates into the neighboring molecule. Effects are smaller for heavy water with the distributions for D_2O staying much more compact. Note that the hydrogen-transfer process is barrierless for the O··O distances in liquid water, but a barrier does appear at larger distances.[48-49]

These findings are in agreement with previous calculations.[38-39] Recent density functional theory based simulations of core-ionized liquid water have shown that about 27% of water molecules have the O–H bond distance larger than 1.3 Å within the O1s lifetime.[34,50] At these elongated bond lengths, however, a proper distinction between the subunits in the $[HO^*··H··OH_2]^+$ hydrogen-bonded species is no longer possible (Figure 1d).

The nature of the 1h•1h states

Figure 3b presents the singlet final-state energies of the doubly ionized water dimer along the hydrogen-transfer coordinate. These di-cationic states are the final states of the autoionization process. The analysis of the electronic wave functions reveals that the nine lowest energies correspond to delocalized 1h•1h states. Near the ground-state geometry (*i.e.*, near 1 Å O–H distance), the delocalized states are the normal ICD states, denoted here as $(1h•1h)_{ICD}$; their electronic structure can be expressed as $H_2O^+··H_2O^+$. The rates for decay into these states are probably rather small though, as suggested by calculations for ammonia clusters,[29] and normal ICD is unlikely to make a strong contribution to the 1h•1h peak in the spectrum. The first doubly ionized local state corresponding to a $H_2O^{2+}··H_2O$ charge distribution has, at the water equilibrium distance, an energy approximately 10 eV higher than the lowest delocalized state in the singlet manifold. This state, indicated by orange dots, has essentially 2h character, *i.e.*, the two positive charges can still considered being localized on

the initial water molecule. The large energy difference implies that 2h and $(1h \bullet 1h)_{ICD}$ states can readily be distinguished by electron spectroscopy. For larger O–H/D distances, however, 2h-state energies drop quickly. The electronic structure gradually changes from $H_2O^{2+} \cdot\cdot H_2O$ into $OH^+ \cdot\cdot H^+ \cdot\cdot OH_2$, denoted here as $(1h \bullet 1h)_{Auger}$ state.

The important conclusion from Figure 3b is that proton-transfer mediated Auger processes represent a viable route to populate the low-energy final di-cationic states found in the experiment. For instance, at the O–H distance of 1.4 Å, the lowest-lying $(1h \bullet 1h)_{Auger}$ final-state (which has gone from a pure 2h state to approach a $(1h \bullet 1h)_{Auger}$ state) is as much as 5 eV below the corresponding 2h energy in the ground-state geometry. We can only speculate about the probability for the creation of 1h•1h states within an ICD-type transition (final state denoted as $(1h \bullet 1h)_{ICD*}$ with electronic structure described best as $OH \cdot\cdot H^+ \cdot\cdot OH_2^+$). Arguably these processes are favorable for larger O–H distance when the two water units interact more strongly. The energy difference between $(1h \bullet 1h)_{Auger}$ and $(1h \bullet 1h)_{ICD*}$ states is however not large enough to distinguish these two types of PTM processes in the experiment. Internal conversion between $(1h \bullet 1h)_{Auger}$ and $(1h \bullet 1h)_{ICD*}$ states, as indicated in Figure 2d, is possible. Eventually the system will undergo further relaxation to the lowest level, but on a much slower time scale; a similar point was made in ref.[39] The different PTM processes leading to different charge-separated complexes are likely to affect solution chemistry, though, but the details remain to be explored. Below we briefly speculate what happens after the autoionization event.

To make a more direct connection between the calculated energies of 2h and (1h•1h) states in Figure 3b and measured kinetic energies, we present in the figure inset the projection of the wave packets from Figure 3a on the energy axis, obtained by the reflection principle.[46] Results are shown only for the first singlet state (the singlet contribution typically dominates the overall spectral signal; triplet states are given in SI, Figure S4), with the two holes localized on the hydrogen donor molecule. We also restrict our analysis to $(1h \bullet 1h)_{Auger}$ final states correlating with the 2h state as these final states are formed within an essentially local autoionization process. The diabatic state corresponding to the doubly charged donor water molecule has been approximated by a linear function in the region spanned by the wave packet. The graphs thus represent the high-energy onsets of the Auger signal for the local Auger processes, blue for $H_2O(aq)$ and red for $D_2O(aq)$. Solid curves correspond to electron emission spectra from the initially populated structures, *i.e.*, for a wave packet at $t = 0$. The curve thus can be associated with the normal Auger signal of H_2O^{2+}. The dashed curves,

shifted toward higher kinetic energies, represent electron emission corresponding to a distribution of geometries the system would assume at 4 fs if no autoionization process had taken place. The final states then correspond to the $(1h \bullet 1h)_{Auger}$ states. A further shift in energy will be caused by populating $(1h \bullet 1h)_{ICD*}$ states but is not considered in the simulations of Figure 3. Since this shift is small, it is not resolved in the present experiment, and thus an experimental distinction between the two PTM-CS autoionization routes is not possible here. Regarding the decay probabilities, it would seem reasonable that the probability of Auger decay of the core-excited Zundel-like cation is similar to Auger decay of core-ionized single water molecule. Whether the PTM-ICD process becomes more likely than normal ICD is clearly one of the interesting questions that remain to be answered.

Analysis of the electronic structure in the core-ionized state indeed supports the proton-transfer mechanism suggested above, whereas the transfer of a neutral hydrogen atom is less likely (*e.g.*, partial charge on transferred hydrogen at the O–H distance of 1.4 Å is 0.7e). The Mulliken population analysis and inspection of the electronic wave function also indicates that the electronic structure of the $(1h \bullet 1h)_{Auger}$ and $(1h \bullet 1h)_{ICD*}$ final states can be indeed associated with $OH^+ \cdot \cdot H^+ \cdot \cdot H_2O$ and $OH \cdot \cdot H^+ \cdot \cdot H_2O^+$. Such a description is however only approximate due to the strong interaction between the moieties. While the above structures represent the dominant 'resonance structures', one can also expect a certain degree of covalency.

Implications for radiation chemistry

It follows from our arguments that the core ionization of liquid water leads to formation of not only the doubly charged H_2O^{2+} molecule but also to charge-separated $[OH^+ \cdot \cdot H_3O^+](aq)$ and $[H_2O^+ \cdot \cdot H_2O^+](aq)$ complexes formed in highly excited vibrational states. The possible role of the $[H_2O^+ \cdot \cdot H_2O^+](aq)$ complex formed within regular ICD for biomolecular damage has been discussed recently.[21,51] But neither the proton-transfer mediated ICD-type nor the Auger-type charge separated states were considered so far. We can only speculate on the reactions following the autoionization process, and we argue that even the relatively subtle differences in energy and structure for ICD *vs.* PTM-ICD will have an effect on the subsequent chemical reactions. Following the formation of the doubly charged system, the two positive charges created in close proximity will be forced to separate because of the strong Coulomb repulsion. Very likely the charge separation proceeds via release of protons towards neighboring water molecules; proton transfer between H_2O^+ and H_2O is very fast for valence ionized water molecule ($\approx$20 fs),[52] and the gas-phase rate constant for the reaction of

OH$^+$ with water is almost as large as for the H$_2$O$^+$ + H$_2$O reaction.[53] Thus, two OH radicals and two H$_3$O$^+$ cations will probably be immediately formed starting from [H$_2$O$^+$··H$_2$O$^+$](aq), while an oxygen atom and two H$_3$O$^+$ cations or an OH radical and another H$_2$O$^+$ will result from [OH$^+$··H$_3$O$^+$](aq) species.[53] On a longer (sub-picosecond) scale, the overall result of the core ionization is the formation of various reactive oxygen species, particularly OH radicals, O(^{3}P) atoms and H$_2$O$_2$; similar processes are considered for multiple ionization in water radiolysis.[9] The relative yield, spatial distribution and energy state of these reactive particles are controlled by the early processes described in the present contribution.

Summary

We have experimentally identified a novel type of non-radiative relaxation process upon core ionization in a hydrogen bonded system. These processes lead to new type of di-cationic, charged separated species, [OH$^+$··H$_3$O$^+$](aq) and [H$_2$O$^+$··H$_2$O$^+$](aq), forming upon core ionization of liquid water involving ultrafast dissociative nuclear motion. Up until now these species have not been accounted for in the radiation chemistry of water, which usually assumes H$_2$O^{2+}(aq) as the only initially created doubly charged species. In particular Auger processes other than the local one have not yet been considered in water radiation chemistry and physics. [2,54-55]

Figure 4 graphically summarizes our main findings. Core-ionization of liquid water leads to a time-evolving cationic Zundel-type structure within a few femtoseconds, containing a bridging proton and a core-excited HO* radical, which then autoionizes. Energies of this transient cationic structure are shown at the top of the figure, and the two PTM-CS autoionization channels, one local (PTM-Auger) and one non-local (PTM-ICD) are depicted. The final charge-separated reactive di-cationic products of the PTM routes have much lower energies than the doubly charged water molecule, H$_2$O^{2+}, and hence the charge-delocalized complexes will likely play different roles in radiation-induced processes in water. The two charge-separated forms, [OH$^+$··H$_3$O$^+$](aq) (from PTM-Auger) and [H$_2$O$^+$··H$_2$O$^+$](aq) (from PTM-ICD), engaging in different immediate fragmentation, will likely lead to different spatial and internal energy distribution of the primary products, and thus in turn make different contributions to overall radical yields going onto the diffusive phase of the radiation chemistry. In contrast to valence ionization, PTM processes tend to lead to more radical centers, and the damage yield is thus higher. Analogous relaxation processes, involving proton transfer and autoionization, seem so far to be exclusive for processes initiated by core

ionization. The autoionization processes are closed energetically upon outer valence ionization. For inner-valence ionization of the water dimer, the ICD channel is open but sequential double ionization by PTM autoionization has not been identified.[56]

We argue that simulations of radiation chemistry processes at the molecular level need to include the mechanisms identified here. Furthermore, we expect that the PTM-Auger and PTM-ICD processes represent a generic feature for hydrogen bonded systems. Recent advances in X-ray science, such as the advent of ultra-short pulses from free electron lasers and high harmonics sources, may allow to further detail the findings in this work by time-resolved experiments.

Methods

Experimental

Photoelectron-spectroscopy measurements were performed from a 15 μm-sized vacuum liquid-water jet [57-58] at the soft-X-ray U41-PGM undulator beamline of BESSY II, Berlin. The jet velocity was ~ 80 ms^{-1}, and the jet temperature was 6°C. Electrons were detected with a hemispherical electron analyzer, separated by a 100-μm diameter orifice from the liquid jet at a distance of approximately 0.3 mm. Details regarding jet preparation, experimental resolution, and spectra acquisition have been described earlier. [57,59]

Computational

The calculations of dynamical events following the core ionization were performed on water dimer model with geometrical parameters taken from hexagonal ice, setting the O⋯O distance exactly to 2.7 Å. The core-ionized states were calculated using the CASSCF method with frozen core orbitals. We used an active space consisting of 19 electrons in 10 molecular orbitals. The doubly ionized states were calculated with CASSCF method, with an active space of 10 electrons in 7 orbitals. States with singlet multiplicity were considered (triplet states shown in the SI, Figure S4). The character of the final states (localized or delocalized positive charge) was analyzed by expressing the configuration state functions in a basis of localized molecular orbitals. The energies of Auger electrons for a given structure were calculated as a difference between the water dimer of the core-ionized species and the doubly charged species. The probability of an Auger-type transition was considered to be independent on the O–H distance, considering the final states with localized charge on the

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initial core-hole atom only. The aug-cc-pCVDZ basis was used for oxygen and aug-cc-pVDZ basis for hydrogen atom. All calculations were done with MOLPRO 2009 suites of codes.[60]

The nuclear wave function was propagated on the core-ionized potential energy surface using a split operator (SO) technique. The wave packet was discretized on 1024 grid points on a grid ranging from 0.6 to 2.2 Å with imaginary absorption potential applied on the boundaries. A time step of 1 a.u. was used in the propagation. The initial wave function was obtained by wave packet propagation in imaginary time.

Acknowledgments

Author contributions

S. T. and B. W. conceived, designed, and performed the experiments, and analyzed the data. P. S. and M. O. conducted the calculations and contributed in data interpretation. N. O. and R. S. contributed materials and/or analysis tools. B. W., P. S., S. T., U. H., and S. E. B. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

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Figure Captions

Figure 1   Schematic of the three autoionization mechanisms of core-ionized liquid water considered in this study: normal Auger decay **(b)**, intermolecular Coulombic decay, ICD **(c)**, and proton-transfer mediated charge separation, PTM-CS (with the two autoionization routes of the Zundel-like intermediate) **(d)**. For **(b)** and **(c)** the relevant energy levels are shown. Starting point is the creation of a hole in the water core-level by photoionization **(a)**. Energy levels for **(d)** depend on the nuclear geometry, which varies in time during the proton-transfer process.

Figure 2   Auger-electron spectra from normal (blue) and heavy (red) liquid water together with the absolute intensity difference between the two spectra (in black). **(a)**, **(b)**, and **(c)** correspond to water O1s ionization, main-edge, and pre-edge excitation, respectively, with photon energies as indicated. All spectra are displayed as measured, and corrected only for photon flux. For ionization **(a)**, the positive difference signal (blue shaded) identifies non-local final states (charge delocalization), 1h•1h. This signal is compensated by loss of signal from normal Auger final states, 2h (corresponding to red-shaded area in the difference spectrum). For core-level excitation **(b)**, **(c)** such a clear distinction between local and non-local states is not possible due to additional signal at similar kinetic energies, partially arising from participator Auger electrons (see text for details).

Figure 3   Potential energy curves of ionized water dimers. **(a)** Potential energy curve (in green) along the hydrogen-transfer coordinate for the lowest core-ionized state of water dimer from quantum dynamical calculations. Also shown are the respective wave packets (squared wave function) at times $t = 0$ fs (corresponding to ground-state molecular structure) and $t = 4$ fs (corresponding to Zundel-type intermediate). Wave packets for H_2O are presented in blue; solid line for $t = 0$ fs, and dashed line for $t = 4$ fs. Red color shows the analogous data for D_2O. At the large O–H distances at the far right proton transfer is complete. **(b)** Calculated energy curves of the doubly charged final states resulting from autoionization of the cationic structures (of Figure 3a) evolving along the hydrogen-transfer coordinate. Orange dots mark the lowest-energy 2h states corresponding to doubly charged donor water unit ($H_2O^{2+}\cdot\cdot OH_2$ turning gradually into $HO^+\cdot\cdot H^+\cdot\cdot OH_2$); all other states are of 1h•1h character ($H_2O^+\cdot\cdot OH_2^+$ turning gradually into $HO\cdot\cdot H^+\cdot\cdot [OH_2]^+$). Only singlet electronic states are presented (triplet states are given in SI, Figure S4). **Inset:** Kinetic energies of electrons originating from local

Auger process for light and heavy water for two different times; the position of all peaks was shifted to match the experimental maximum of the local Auger peak of normal water.

Figure 4   The main findings of this work summarized in a graphical form. The potential energy curves of the ground state (black), core ionized state (orange) and final states (green) are sketched. Photoionization projects the ground-state wave packets of normal and deuterated water (solid blue and red lines) onto the intermediate core-ionized state surface (thick orange arrow), which is repulsive along the proton transfer coordinate (independent axis). Within 4 fs, the wave packets evolve, more so for normal water (dotted blue and red lines). Within this time interval, autoionization occurs continuously (thin arrows, orange to green), and populates local two-hole (2h) states, and charge separated states of the two different types discussed in the text $(1h \bullet 1h)_{ICD}$, $(1h \bullet 1h)_{Auger}$. The vertical Gaussians illustrate the distribution of energies of the doubly ionized states which are associated with autoionization of an evolving distribution of Zundel-like geometries.

References

1   Seiwert, T. Y., Salama, J. K. & Vokes, E. E. The concurrent chemoradiation paradigm - general principles. *Nat. Clin. Pract. Oncol.* **4**, 86-100, (2007).

2   Howell, R. W. Auger processes in the 21st century. *Int. J. Radiat. Biol.* **84**, 959-975, (2008).

3   Eschenbrenner, A. *et al.* Strand breaks induced in plasmid DNA by ultrasoft X-rays: Influence of hydration and packing. *Int. J. Radiat. Biol.* **83**, 687-697, (2007).

4   Wang, C. R., Nguyen, J. & Lu, Q. B. Bond Breaks of Nucleotides by Dissociative Electron Transfer of Nonequilibrium Prehydrated Electrons: A New Molecular Mechanism for Reductive DNA Damage. *J. Am. Chem. Soc.* **131**, 11320-11322, (2009).

5   Alizadeh, E. & Sanche, L. Precursors of Solvated Electrons in Radiobiological Physics and Chemistry. *Chem. Rev.* **112**, 5578-5602, (2012).

6   Weik, M. *et al.* Specific chemical and structural damage to proteins produced by synchrotron radiation. *Proc. Natl. Acad. Sci. U. S. A.* **97**, 623-628, (2000).

7   in *Recent Advances, Applications, and Interfaces* (eds Y. Hatano, Y. Katsumura, & A. Mozumder) (CRC Press 2010, 2010).

8   Garrett, B. C. *et al.* Role of water in electron-initiated processes and radical chemistry: Issues and scientific advances. *Chem. Rev.* **105**, 355-389, (2005).

9   Meesungnoen, J. *et al.* Multiple ionization effects on the yields of HO_2/O_2^- and H_2O_2 produced in the radiolysis of liquid water with high-LET $^{12}C^{6+}$ions: a Monte-Carlo simulation study. *Chem. Phys. Lett.* **377**, 419-425, (2003).

10   Tavernelli, I. *et al.* Time-dependent density functional theory molecular dynamics simulations of liquid water radiolysis. *Chem. Phys. Chem.* **9**, 2099-2103, (2008).

11 Gaigeot, M. P. *et al.* A multi-scale ab initio theoretical study of the production of free radicals in swift ion tracks in liquid water. *J. Phys. B-At. Mol. Opt. Phys.* **40**, 1-12, (2007).

12 Cederbaum, L. S., Zobeley, J. & Tarantelli, F. Giant intermolecular decay and fragmentation of clusters. *Phys. Rev. Lett.* **79**, 4778-4781, (1997).

13 Müller, I. B. & Cederbaum, L. S. Electronic decay following ionization of aqueous Li$^+$ microsolvation clusters. *J. Chem. Phys.* **122**, 194305, (2005).

14 Hergenhahn, U. Interatomic and intermolecular coulombic decay: The early years. *J. Electron Spectrosc. Relat. Phenom.* **184**, 78-90, (2011).

15 Marburger, S., Kugeler, O., Hergenhahn, U. & Möller, T. Experimental evidence for interatomic Coulombic decay in Ne clusters. *Phys. Rev. Lett.* **90**, 203401, (2003).

16 Jahnke, T. *et al.* Experimental observation of interatomic Coulombic decay in neon dimers. *Phys. Rev. Lett.* **93**, 163401, (2004).

17 Hergenhahn, U. Production of low kinetic energy electrons and energetic ion pairs by Intermolecular Coulombic Decay. *Int. J. Radiat. Biol.* **88**, 871-883, (2012).

18 Mucke, M. *et al.* A hitherto unrecognized source of low-energy electrons in water. *Nat. Phys.* **6**, 78-81, (2010).

19 Schwartz, C. P., Fatehi, S., Saykally, R. J. & Prendergast, D. Importance of electronic relaxation for inter-Coulombic decay in aqueous systems. *Phys. Rev. Lett.* **105**, 198102, (2010).

20 Lindblad, A. *et al.* Charge delocalization dynamics of ammonia in different hydrogen bonding environments: free clusters and in liquid water solution. *Phys. Chem. Chem. Phys.* **11**, 1758-1764, (2009).

21 Stoychev, S. D., Kuleff, A. I. & Cederbaum, L. S. Intermolecular Coulombic Decay in Small Biochemically Relevant Hydrogen-Bonded Systems. *J. Am. Chem. Soc.* **133**, 6817-6824, (2011).

22   Aziz, E. F., Ottosson, N., Faubel, M., Hertel, I. V. & Winter, B. Interaction between liquid water and hydroxide revealed by core-hole de-excitation. *Nature* **455**, 89-91, (2008).

23   Pokapanich, W. *et al.* Auger Electron Spectroscopy as a Probe of the Solution of Aqueous Ions. *J. Am. Chem. Soc.* **131**, 7264-7271, (2009).

24   Pokapanich, W. *et al.* Ionic-Charge Dependence of tie Intermolecular Coulombic Decay Time Scale for Aqueous Ions Probed by the Core-Hole Clock. *J. Am. Chem. Soc.* **133**, 13430-13436, (2011).

25   Pokapanich, W. *et al.* Bond Breaking, Electron Pushing, and Proton Pulling: Active and Passive Roles in the Interaction between Aqueous Ions and Water as Manifested in the O 1s Auger Decay. *J. Phys. Chem. B* **116**, 3-8, (2012).

26   Ottosson, N., Öhrwall, G. & Björneholm, O. Ultrafast charge delocalization dynamics in aqueous electrolytes: New insights from Auger electron spectroscopy. *Chem. Phys. Lett.* **543**, 1-11, (2012).

27   Öhrwall, G. *et al.* The electronic structure of free water clusters probed by Auger electron spectroscopy. *J. Chem. Phys.* **123**, 054310, (2005).

28   Stoychev, S. D., Kuleff, A. I. & Cederbaum, L. S. On the intermolecular Coulombic decay of singly and doubly ionized states of water dimer. *J. Chem. Phys.* **133**, (2010).

29   Kryzhevoi, N. V. & Cederbaum, L. S. Non local Effects in the Core Ionization and Auger Spectra of Small Ammonia Clusters. *J. Phys. Chem. B* **115**, 5441-5447, (2011).

30   Hjelte, I. *et al.* Evidence for ultra-fast dissociation of molecular water from resonant Auger spectroscopy. *Chem. Phys. Lett.* **334**, 151-158, (2001).

31   Björneholm, O., Nilsson, A., Sandell, A., Hernnas, B. & Martensson, N. Determination of Time Scales for Charge-Transfer Screening in Physisorbed Molecules. *Phys. Rev. Lett.* **68**, 1892-1895, (1992).

32   Schnadt, J. *et al.* Experimental evidence for sub-3-fs charge transfer from an aromatic adsorbate to a semiconductor. *Nature* **418**, 620-623, (2002).

33   Föhlisch, A. *et al.* Direct observation of electron dynamics in the attosecond domain. *Nature* **436**, 373-376, (2005).

34   Odelius, M. *et al.* Ultrafast Core-Hole-Induced Dynamics in Water Probed by X-Ray Emission Spectroscopy. *Phys. Rev. Lett.* **94**, 227401, (2005).

35   Fuchs, O. *et al.* Isotope and temperature effects in liquid water probed by x-ray absorption and resonant x-ray emission spectroscopy. *Phys. Rev. Lett.* **100**, 027801, (2008).

36   Tokushima, T. *et al.* High resolution X-ray emission spectroscopy of liquid water: The observation of two structural motifs. *Chem. Phys. Lett.* **460**, 387-400, (2008).

37   Odelius, M. Molecular dynamics simulations of fine structure in oxygen K-edge x-ray emission spectra of liquid water and ice. *Phys. Rev. B* **79**, 144204, (2009).

38   Ljungberg, M. P., Nilsson, A. & Pettersson, L. G. M. Semiclassical description of nuclear dynamics in x-ray emission of water. *Phys. Rev. B* **82**, 245115, (2010).

39   Ljungberg, M. P., Pettersson, L. G. M. & Nilsson, A. Vibrational interference effects in x-ray emission of a model water dimer: Implications for the interpretation of the liquid spectrum. *J. Chem. Phys.* **134**, 044513, (2011).

40   Winter, B., Aziz, E. F., Hergenhahn, U., Faubel, M. & Hertel, I. V. Hydrogen bonds in liquid water studied by photoelectron spectroscopy. *J. Chem. Phys.* **126**, 124504, (2007).

41   Winter, B., Hergenhahn, U., Faubel, M., Björneholm, O. & Hertel, I. V. Hydrogen bonding in liquid water probed by resonant Auger-electron spectroscopy. *J. Chem. Phys.* **127**, 094501, (2007).

42   Nordlund, D. *et al.* Probing the electron delocalization in liquid water and ice at attosecond time scales. *Phys. Rev. Lett.* **99**, 217406, (2007).

43   Soper, A. K. & Benmore, C. J. Quantum differences between heavy and light water. *Phys. Rev. Lett.* **101**, 065502 (2008).

44   Winter, B. *et al.* Full valence band photoemission from liquid water using EUV synchrotron radiation. *J. Phys. Chem. A* **108**, 2625-2632, (2004).

45   Nishizawa, K. *et al.* High-resolution soft X-ray photoelectron spectroscopy of liquid water. *Phys. Chem. Chem. Phys.* **13**, 413-417, (2011).

46   Barth, S. *et al.* Valence Ionization of Water Clusters: From Isolated Molecules to Bulk. *J. Phys. Chem. A* **113**, 13519-13527, (2009).

47   Takahashi, O. *et al.* Auger decay calculations with core-hole excited-state molecular-dynamics simulations of water. *J. Chem. Phys.* **124**, 064307, (2006).

48   Felicissimo, V. C., Guimaraes, F. F., Gel'mukhanov, F., Cesar, A. & Agren, H. The principles of infrared-x-ray pump-probe spectroscopy. Applications on proton transfer in core-ionized water dimers. *J. Chem. Phys.* **122**, 094319, (2005).

49   Felicissimo, V. C. *et al.* A theoretical study of the role of the hydrogen bond on core ionization of the water dimer. *Chem. Phys.* **312**, 311-318, (2005).

50   Stia, C. R. *et al.* Theoretical investigation of the ultrafast dissociation of core-ionized water and uracil molecules immersed in liquid water. *Eur. Phys. J. D* **60**, 77-83, (2010).

51   Vendrell, O., Stoychev, S. D. & Cederbaum, L. S. Generation of Highly Damaging H_2O^+ Radicals by Inner Valence Shell Ionization of Water. *Chem. Phys. Chem.* **11**, 1006-1009, (2010).

52   Marsalek, O. *et al.* Chasing charge localization and chemical reactivity following photoionization in liquid water. *J. Chem. Phys.* **135**, 224510, (2011).

53   Anicich, V. G. Evaluated biomolecular ion-molecule gas-phase kinetics of positive ion for use in modeling planetary atmosphere, cometary comae, and interstellar clouds. *J. Phys. Chem. Ref. Data* **22**, 1469-1569, (1993).

54   Pimblott, S. M. & LaVerne, J. A. Stochastic simulation of the electron radiolysis of water and aqueous solutions. *J. Phys. Chem. A* **101**, 5828-5838, (1997).

55   Garrett, B. C. Ions at the air/water interface. *Science* **303**, 1146-1147, (2004).

56   Jahnke, T. *et al.* Ultrafast energy transfer between water molecules. *Nat. Phys.* **6**, 139-142, (2010).

57 Winter, B. & Faubel, M. Photoemission from liquid aqueous solutions. *Chem. Rev.* **106**, 1176-1211, (2006).

58 Winter, B. Liquid microjet for photoelectron spectroscopy. *Nucl. Intrum. Meth. A* **601**, 139-150, (2009).

59 Seidel, R., Thürmer, S. & Winter, B. Photoelectron spectroscopy meets aqueous solution: Studies from a vacuum liquid microjet. *Phys. Chem. Lett.* **2**, 633-641, (2011).

60 MOLPRO, version 2010.1, a package of ab initio programs (Cardiff, UK, 2010).

(a) Energy, valence, core — e_{photo}

$[HO^* - H^+ \cdots H_2O]_{(aq)}$

Auger decay

(b) $2h_v$ — e_{Auger}, $2+$

$[H_2O^{2+} \cdots H_2O]_{(aq)}$

ICD

(c) $1h_v \cdot 1h_v$

ET — e_{ICD}

$[H_2O^+ \cdots H_2O^+]_{(aq)}$

(d) Proton transfer mediated charge separation (PTM-CS)

$[HO^* \cdots H^+ \cdots H_2O]_{(aq)}$ ① * + — 2' — $[HO^+ \cdots H^+ \cdots H_2O]_{(aq)}$ e_{Auger} + +

3'

e_{ICD}

Internal Conversion

ET

$[HO \cdots H^+ \cdots H_2O^+]_{(aq)}$

2'' proton hop

$[OH^+ \cdots H_3O^+]_{(aq)}$

3''

$[H_2O^+ \cdots H_2O^+]_{(aq)}$

a Core ionization: 1h

b Doubly ionized final state

e_{Auger}

e_{photo}

X-ray

$[OH^+ \cdot H_3O^+]_{(aq)}$