

Probing the Electron Delocalization in Liquid Water and Ice at Attosecond Time Scales

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We determine electron delocalization rates in liquid water and ice using core-hole decay spectroscopy. The hydrogen-bonded network delocalizes the electrons in less than 500 as. Broken or weak hydrogen bonds—in the liquid or at the surface of ice—provide states where the electron remains localized longer than 20 fs. These asymmetrically bonded water species provide electron traps, acting as a strong precursor channel to the hydrated electron.

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The dynamics of excess electrons in water leading to the hydrated electron, discovered more than 40 years ago [1], has received intense theoretical and experimental interest [2–10]. Although final structures of the hydrated electron have been proposed [11], there is still debate over both the structure of the solvation shell [2–5] and the ultrafast solvation dynamics [6–10]. The quantum states of the hydrated electron consist of a localized s ground state, a triply degenerate localized p state, and a delocalized conduction band. The generation of the s state involves rich dynamics over a large temporal range: ultrafast librational dynamics (tens of femtoseconds, fs) [8,9], localization of the electron in preexisting traps (~ 100 fs) [3,12], and solvation dynamics involving translational motion of surrounding molecules (< 300 fs) [9]. There have been numerous studies of the excitation process and on the ultrafast decay (100–400 fs) between the s and p states [1,10], but dynamics of the conduction band and the nature of potential trapping states for the hydrated electron are still relatively unexplored. In order to investigate electron transport in the conduction band for differently hydrogen-bonded (H-bonded) molecules it is essential to use techniques that allow electron dynamics to be probed in an atom-specific way on a time scale below 1 fs for different excitation energies.

Ultrafast processes on a subfemtosecond time scale can be accessed using core excitations to generate an electronic state which subsequently decays in an Auger process on a time-scale related to the lifetime of the core hole [13]. Here we use the O $1s$ x-ray absorption (XA) process to pump electrons in a near-instantaneous process (≥ 8 as) [14] into specific unoccupied states in liquid water and ice. The O $1s$ core-level decay, with a lifetime of ~ 3.6 fs, is used to probe electron dynamics down to a few hundred attosecond time resolution by analyzing the ejected Auger electrons. We observe (Fig. 1) whether the excited electron is still

present or already delocalized when the core-hole decays. If the excited electron delocalizes faster than the core-hole decay process, the Auger decay reaches the same two-valence-hole final state as in nonresonant Auger decay (denoted *normal* Auger decay). An excited electron that remains localized during the core-hole decay process results in a screened Auger final state (denoted *spectator* Auger decay).

In this work we consider the O KLL Auger-electron decay, where L corresponds to molecular orbitals with $O2p$ character ($1b_2$, $3a_1$, and $1b_1$ in the water molecule). The spectra in Fig. 1 show the simulated kinetic energy of the outgoing electron for the two different O KLL Auger decay channels, modeled by a water tetramer with a double hole in the L shell with the excited electron completely removed (normal Auger decay spectrum) or localized in the LUMO orbital (spectator Auger decay spectrum). The *spectator* Auger spectrum is shifted approximately 5 eV towards higher kinetic energy relative to the *normal* Auger spectrum, reflecting a general spectral trend of spectator decay to higher kinetic energy due to the screening of the final state by the localized (spectator) electron. If separable, the intensity ratio of the two final states and the core-hole lifetime will experimentally determine the electron hopping rate [13].

The liquid water experiments were performed using the ambient pressure photoemission end station at beam line 11.0.2 at the Advanced Light Source in Berkeley, CA. The end station is equipped with a differentially pumped electrostatic lens system [15] that transfers the electrons from the sample surface (background pressures < 7 torr) to the entrance slit of a Specs Phoibos 150 hemispherical electron spectrometer kept in high vacuum. A liquid droplet (volume ~ 5 mm³) was condensed onto a thin Au film on a Cu substrate. The droplet was kept in thermodynamical equilibrium with its vapor at a background pressure of about

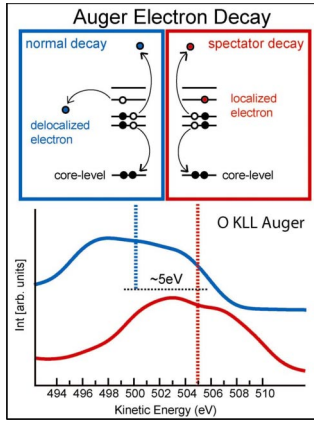


FIG. 1 (color online). Auger-electron decay processes used to derive site-specific time scales in this work. (Top) *Normal* Auger decay (left), where the excited electron is delocalized from the decaying atom and *spectator* Auger decay (right), where the excited electron remains localized during the decay. (Bottom) Simulated spectra of a cluster model (see text) indicate a shift of ~ 5 eV between the two decay channels due to screening by the spectator electron.

4 torr, with the temperature of the sample substrate held at $\sim 1^\circ\text{C}$ (controlled by a Peltier element). By using a positive bias (150 V) on the sample, the gas-phase signal was experimentally shifted to lower kinetic energies and smeared out. This low kinetic energy background, along with the inelastically scattered liquid water signal, was removed by subtracting a Shirley-type background prior to the area normalization. The $2a_1$ direct photoemission channel, modeled by a Gaussian function fitted to the $2a_1$ peak in the nonresonant (550 eV) O $1s$ decay spectra, was subtracted from all spectra shown in Fig. 2. Variations in incoming photon flux were taken into account and the direct photoemission cross section assumed constant in the range 535–548 eV.

The ice experiments were performed at the surface end station on the undulator beam line I511 at MAX-lab (Sweden) [16], equipped with a Scienta SES 200 hemispherical electron spectrometer. The crystalline ice film was epitaxially grown by slow deposition on Pt (111) at 130 ± 5 K using a thickness of 10 bilayers (like in Ref. [17]), but a certain degree of amorphous ice cannot be excluded). D_2O was used to increase the beam-damage threshold and the thin layer to allow detecting the Fermi level and avoid charging. The photon source had a bandwidth of 0.14 eV, and the electron spectrometer was operated at 0.2 eV resolution. A gold mesh mounted in front of the sample measured the incoming photon flux. By detecting the O $1s$ decay perpendicular to the incoming E -vector axis, the $2a_1$ direct photoemission channel was suppressed. As for the liquid water spectra, a Shirley-type background was removed prior to the area normalization.

The O $1s$ XA spectra of liquid water and ice are shown in the insets of Fig. 2 [17,18]. There are three main regions of

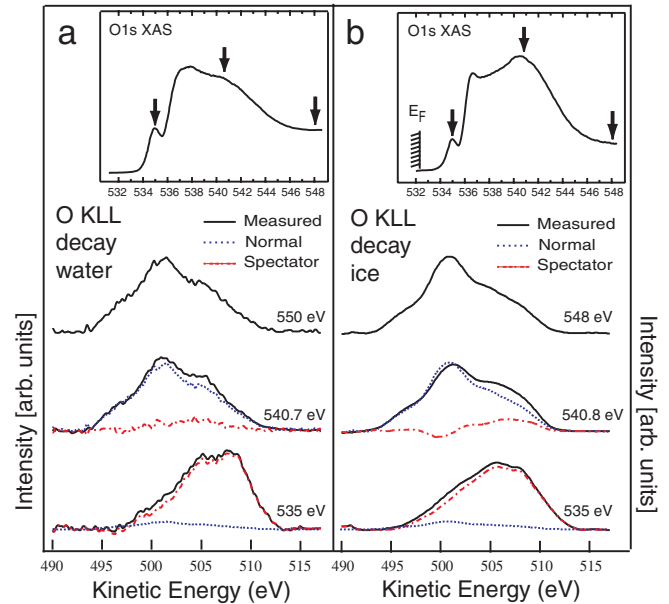


FIG. 2 (color online). O $1s$ x-ray absorption spectra (insets) of liquid water (A) and ice (B) with corresponding O KLL Auger decay spectra for selective excitations. Using the decay from nonresonant excitation at 550(548) eV as model spectra for normal Auger decay, the normal Auger fraction (f_{Aug}) is quantified for the excitation at the postedge (~ 541 eV) and at the preedge (~ 535 eV). The difference between the measured spectra (line) and the normal Auger fraction (dotted) is associated with the spectator decay spectra (dashed), shifted to ~ 5 eV higher kinetic energy in agreement with theory (see Fig. 1). All spectra were area normalized in the region 495–510 eV prior to the quantification.

interest: a preedge around 535 eV, a main-edge at 537–538 eV and a postedge centered at 541 eV. Antibonding states localized along the H-bond have been assigned to the postedge intensity [19,20]; in ice this forms the conduction band due to the well-ordered H-bond network [18,21] with large intensity since both OH groups are involved in donor hydrogen bonds. In the liquid, the preedge intensity is associated with states localized along the weakly H-bonded OH group in single donor (SD) water species with strongly asymmetrical H-bonding on the donor side [18]. In ice, the preedge is due to similar non-H-bonded species at the ice surface (ammonia termination ascertains that the preedge states we excite into almost exclusively reside at the ice surface [18]). The relative fraction of broken or weak hydrogen bonds in the liquid phase is debated [18,19,22,23], whereas the assignment of the preedge to SD species seems well established, in particular, supported by ion-yield experimental data [24].

In Fig. 2, the O KLL Auger decay spectra for selected excitation energies in liquid water and ice are shown. The insets show the corresponding XA spectra and arrows indicating excitation energies. We observe marked excitation energy dependence for both liquid water and ice. Upon excitation at the preedge (535 eV), the *spectator* Auger

intensity (center around 506 eV) is pronounced, whereas the *normal* Auger intensity (centered around 501 eV) is very small. Upon excitation to the postedge, it is the other way around, with *normal* Auger intensity dominating the spectra. Thus, for core excitations into the preedge state, associated with the weakly H-bonded OH groups in SD species in the liquid or free OH groups at the ice surface, the electron remains localized far longer than the core-hole lifetime. For excitations into the postedge state, associated with OH groups involved in strong hydrogen bonds, the delocalization rate is instead much faster than the core-hole lifetime. To quantify the delocalization rate τ_{CT} experimentally, we determine by scaled subtraction the relative intensity of the normal Auger electron (f_{Aug}) using the measured nonresonant Auger spectrum at 550 (548) eV to describe the normal Auger spectral shape (dotted in Fig. 2). Applying the relation $\tau_{CT} = \tau_c(f_{Aug}^{-1} - 1)$ [13], where τ_c is the O 1s core-hole lifetime, τ_{CT} is determined to be faster than 500 as for postedge excitation (*normal* Auger fraction $f_{Aug} > 0.88$), and slower than 20 fs for preedge excitation ($f_{Aug} < 0.15$).

In Fig. 3, we show representative orbital plots for typical preedge and postedge excited state wave functions, simulated using cluster-based DFT [25] of an MD snap shot. The postedge [Fig. 3(a)] is dominated by states delocalized along the H bonds over many atomic centers. This is consistent with the large fraction of normal Auger decay at this excitation energy [Figs. 2(a) and 2(b)], showing that the excited electron is propagated into the H-bonded network at the time of the core-hole decay. In contrast to this, the orbital corresponding to the preedge excitation for a typical single-donor configuration [Fig. 3(b)] is localized along the internal non-hydrogen-bonded O-H bond [18]. The confinement of the wave function causes a large difference in localization character of the preedge excited state in the liquid and at the ice surface compared to the conduction band in both water and ice.

It is interesting to put the present results into the context of electron transport in the liquid phase. Electrons immersed in liquid water are known as hydrated electrons and are thought to be trapped in an electrophilic cavity

consisting of approximately six water molecules with broken donating hydrogen bonds pointing towards and creating the electrophilic cavity [4,11]. The preedge state associated with weak hydrogen bonds in the liquid phase [18] is electrophilic and resides in the band gap. Comparison of the orbital plot of the preedge state [Fig. 3(b)] with a plot of the ground state orbital for a solvated electron in a model cavity using six molecules [Fig. 3(c)] shows certain similarities. The preedge orbital in Fig. 3(b) extends out from the hydrogen atom with strong O-H antibonding character and we can generate a wave function similar to the hydrated electron if the water molecules orient their OH groups towards the center cavity. Whereas the exact geometry of the hydrated structure is debated, the connection to uncoordinated OH groups is suggested both by theory and experiments (see, e.g., Ref. [2] and references therein).

The experiments (Fig. 2) show that broken H bonds at the ice surface and weak or broken H bonds in liquid water have unique electronic states that trap the excited electron for longer than 20 fs, suggestive of such states acting as precursors to form hydrated electrons in the liquid. In the present study the trapping states are populated with electrons through a core excitation process; the fast decay of the core-hole effectively excludes actual solvation effects from the probe which greatly simplifies the interpretation. Note that the core excitation process used here is not a common path for creating solvated electrons (typically produced by radiolysis, photoionization, or chemical reactions), but is merely a tool to obtain site-specific electronic structure information in terms of delocalization rates. The presence of the core-hole at the trapping site could affect the electronic structure, but comparison with time-resolved two-photon photoemission (2PPE) measurements of thin ice films [26] indicate that the electronic states we observe are similar to states populated through electron scattering. Our measured preedge peak energy position is 2.8 eV above the Fermi level similar to the value (2.9 eV) from the 2PPE study, which furthermore indicated rapid electron transfer in the bulk while at the interface traps with bound electronic states below the vacuum level were found. By Xe titration of D₂O clusters on a Cu(111) surface, solvated electrons were shown to preferentially bind on the cluster surface [27], in agreement with the results presented here.

As depicted in Fig. 4, electron transfer rates on attosecond timescales are found in liquid water in electronic states extending over the H-bond network, similar to that in bulk ice (steps 1 and 2). The electron hopping rate (<500 as) is then extremely fast compared to the molecular motion in the liquid [28] and the structural rearrangement of water to form an electron-stabilizing cavity would not be favored. However, the trapping of the electron at the broken H-bond (step 3) provides a time scale long enough for librational response of the water molecules [7,8,10], and early-time dynamics can then lead to the hydrated electron (steps 4 and 5). Single-donor species in liquid water are

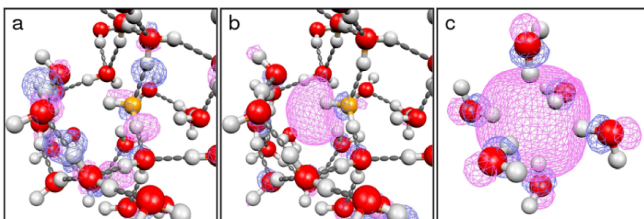


FIG. 3 (color online). Orbital plots of core-excited states in (a) the postedge region and (b) the preedge region compared to (c) the solvated electron, represented by the relaxed HOMO orbital of a $-1e$ charged cluster of six water molecules oriented around a central cavity.

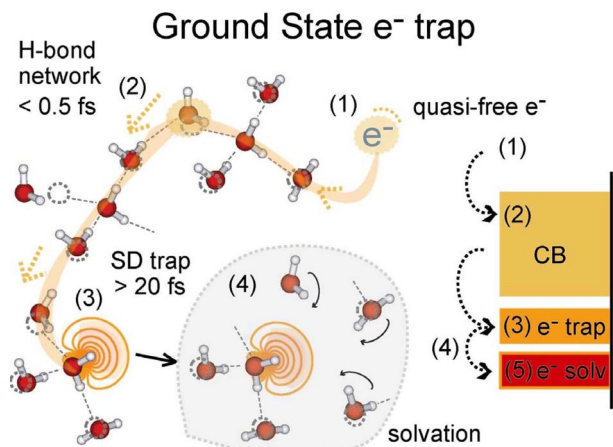


FIG. 4 (color online). Schematic diagram of electron trapping in liquid water: (1 & 2) an excess electron propagating along the H-bond network, (3) trapping at a weakly H-bonded OH group of a single-donor site followed by (4) electron solvation dynamics to reach the solvated electron (5).

thus suggested as strong preexisting traps for the hydrated electron, localizing the electrons long enough for initial electron solvation to occur. This experiment adds to previous studies with a probe of early-time dynamics of electron trapping and localization that has not yet been achieved by traditional optical pump-probe measurements.

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Note added in proof.—Recently, another resonant Auger study of liquid water was submitted [29].

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