Cations Strongly Reduce Electron Hopping Rates in Aqueous Solutions

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Abstract

We study how the ultrafast inter-molecular hopping of electrons excited from the water O1s core level into unoccupied orbitals depends on the local molecular environment in liquid water. Our probe is the resonant Auger-decay of the water O1s core-hole (lifetime \(\sim 3.6\) fs), by which we show that the electron hopping rate can be significantly reduced when a first-shell water molecule is replaced by an atomic ion. Decays resulting from excitations at the O1s post-edge feature (\(\sim 540\) eV) of 6m LiBr and 3m MgBr\textsubscript{2} aqueous solutions reveal electron hopping-times of approximately 1.5 and 1.9 fs, respectively – the latter represents a four-fold increase compared to the corresponding value in neat water. The slower electron hopping in electrolytes, which shows a strong dependence on the charge of the cations, can be explained by ion-induced reduction of water-water orbital mixing. Density functional theory (DFT) electronic structure calculations of solvation geometries obtained from molecular dynamics simulations reveal that this phenomenon largely arises from electrostatic perturbations of the solvating water molecules by the solvated ions. Our results demonstrate that it is possible to deliberately manipulate the rate of charge-transfer via electron hopping in aqueous media.
1. Introduction

Charge-transfer phenomena in aqueous environments are essential for numerous chemical, biochemical as well as technological processes and applications.\(^1\) While charge-transfer rates in the electronic ground state of most redox-systems are relatively well described by standard Marcus theory,\(^2\) there lies great interest in improving models for charge-transfer between neighboring sites initiated by photo-induced electronic transitions in solution. For example, such processes play a key role in the function of electrolyte-based dye-sensitized solar-cells.\(^3\) In most cases, the solvent is considered to only passively assist such processes, e.g. by enabling the redox-couple to interact in favorable geometries, and is therefore not really involved in the charge-transfer \textit{per se}. Nevertheless, there exists several charge-transfer phenomena where the solvent molecules play a much more active role, such as charge-transfer-to-solvent (CTTS) absorption processes\(^4\) and solvent-mediated proton transfer reactions, which are ubiquitous in aqueous environments.\(^5\)

One important mechanism for charge transfer is electron hopping, which for liquid water has recently been reported to extend down to attosecond time-scales upon resonant excitation of a core electron into unoccupied orbitals.\(^6\) The ultrafast time scale makes these processes extremely challenging to study directly in the time domain, and an attractive alternative is to use the short lifetime associated with the decay of the O 1s core-hole (~3.6 fs) itself to indirectly probe the concurrent ultrafast electron hopping. The dynamical information can be accessed by analysis of the different channels in the associated Auger electron spectra, which reflect whether the excited electron has left the initial excitation site during the core-hole lifetime.\(^7\) The principle is schematically illustrated in figure 1, showing the relevant electronic decay processes of core-ionized/core-excited molecules (see figure captions for details). On a microscopic scale the rate of electron hopping depends on the both spatial and energetic overlap between the orbital the electron has been excited into and the empty orbitals of the neighboring molecules. Due to the locally disordered nature of liquids, this is not as easily defined as in crystalline systems, for which hopping rates can be connected to bandwidth. Locally, however, the hopping rates in liquid water are determined by the same basic mechanisms.\(^8\)

In this work we demonstrate that the addition of simple inorganic salts strongly slows down the ultrafast electron delocalization from a resonantly core-excited water
molecule into the H-bonding network. Even though we experimentally cannot fully disentangle the effects of anions and cations, the comparison between solutions of different salts reveals that the magnitude of the effect strongly depends on the cationic charge. Further insight into the microscopic mechanism is given by molecular dynamics (MD) simulations and electronic structure calculations using density functional theory (DFT). Based on our findings, we propose a qualitative model in which the resonantly excited electron is “back-polarized” toward the parental core-excited water molecule when engaged in cation solvation. This reduces the electronic overlap with other neighboring molecules in the excited state, slowing down the ultra-fast delocalization dynamics observed in pure water.

2. Methods

2a. Experimental

O1s resonant Auger spectra of liquid water as well as of 6m LiBr and 3m MgBr2 aqueous solutions were recorded at the U-41 PGM micro-focus undulator beamline at the BESSY synchrotron facility, Berlin, Germany, which delivers soft X-ray photons in the 180-1500 eV range. The experimental setup has previously been described in detail.9,10 Briefly, the liquid samples are injected into the evacuated experimental chamber as a 15 µm jet, traveling at a velocity of approximately 100 m/s. The liquid jet propagates in the plane of the linearly polarized synchrotron radiation and is perpendicular to the detection axis of the hemispherical electron analyzer. The expelled electron enters the analyzer through a circular opening with a diameter of 0.2 mm, situated 0.5 mm from the liquid surface. Such an arrangement allows for good differential pumping of the spectrometer (at approx. 10⁻⁸ mbar) while a sufficiently small fraction of the photoelectrons are lost in the short passage through the vapor. Further, the favorable overlap between the synchrotron focal spot at the U-41 PGM beamline (23x12 µm²) and the liquid micro-jet results in negligible gas-phase contributions to the spectra.

All samples were prepared from highly de-mineralized water. Salts were purchased from Sigma-Aldrich and were used without further purification (LiBr > 99.9% and MgBr2 > 99.8%).

2b. Molecular Dynamics simulations
Classical MD simulations were performed for LiBr(aq) and MgBr$_2$(aq), as well as for pure water. For the salt solutions, systems of two different sizes were used. For LiBr(aq), the large system contained 1512 water molecules, 162 Li$^+$, and 162 Br$^-$ ions. The small system contained 76 water molecules, 8 Li$^+$ and 8 Br$^-$ ions. For MgBr$_2$(aq), the large system contained 1512 water molecules, 81 Mg$^{2+}$, and 162 Br$^-$ ions, while the small system contained 76 water molecules, 4 Mg$^{2+}$, and 8 Br$^-$ ions. The pure water simulation contained 1024 water molecules. The SPC/E water model was used in all cases. The Li$^+$ and Br$^-$ ions were described by the ion-water Lennard-Jones parameters of Horinek et al. Lorenz-Berthelot combination rules were used to derive the Li$^+$-Li$^+$, Br$^-$-Br$^-$, and Li$^+$-Br$^-$ Lennard-Jones interactions. The Mg$^{2+}$-water potentials used were the three-body potentials of Spångberg and Hermansson, while the Mg$^{2+}$-Mg$^{2+}$ and Mg$^{2+}$-Br$^-$ interactions were derived using Lorenz-Berthelot combination rules from the Mg$^{2+}$-water Lennard-Jones parameters of Åqvist. Standard cubic periodic boundary conditions were used, with short range interactions truncated using a spherical cutoff distance of 13 Å for the pair interactions and an ion-oxygen distance of 6 Å for the three body interactions in the Mg$^{2+}$-water potential. Ewald lattice sums were used for the Coulomb interactions. The temperature was set to 300K and the pressure to 0 Pa using Nosé-Hoover extended system dynamics to obtain the NPT ensemble. The water molecules were kept rigid using the RATTLE algorithm with successive over-relaxation (SOR) to increase the speed of convergence. The equations of motion were integrated with the velocity Verlet integrator employing a timestep of 1.5 fs.

The starting positions and angles for the species in the LiBr(aq) simulations were selected randomly on a primitive cubic lattice, while for the MgBr$_2$(aq) simulations, it was ensured that each Mg$^{2+}$ ion was surrounded by six water molecules initially, since the mean residence time of water molecules in the first solvation shell of Mg$^{2+}$ is about 1 ms, substantially longer than the possible timescale for the simulations. Thus, should the initial configuration of the simulation contain bromide ions in the first solvation sphere of magnesium ions, a long time might be required to displace the bromide ions by water molecules. The simulations were equilibrated for 300 ps, followed by 1.2 ns of production. The obtained average volume for the small and large LiBr(aq) simulations, were 2776 Å$^3$ and 55315 Å$^3$, respectively, while for the small and large MgBr$_2$(aq) simulations the volumes were 2576 Å$^3$ and 47500 Å$^3$, respectively. The concentrations of
the salt solutions are thus 4.8M and 4.9M for the small and large LiBr(aq) simulations, respectively. The corresponding values for the small and large MgBr$_2$(aq) simulations are 2.6M and 2.8M.

2c. Electronic structure calculations

We have investigated the electronic structure in single snapshots from the small classical MD simulations with 76 water molecules in concentrated LiBr(aq) and MgBr$_2$(aq) solutions to guide the interpretation of the experimental spectra. The partial density of states in the ground state is derived to resolve the chemical bonding and mixing of the states in electrolyte solution.

Electronic structure calculations performed in a density functional framework of the CPMD code$^{22}$ were used to derive partial density of states and X-ray absorption spectra as previously implemented.$^{23-25}$ The gradient-corrected density functional, BLYP,$^{26,27}$ was used. The calculations in CPMD employed pseudo-potentials in combination with a 85 Ry kinetic energy plane-wave cut-off in the expansion of the Kohn-Sham wave-functions. To cover the spectral region of interest a large number of unoccupied orbitals were required, and 800 Kohn-Sham states was calculated in each system. A Troullier–Martins type pseudo-potential$^{28}$ expressed in the Kleinman-Bylander form$^{29}$ was used for bromine. The cations were described by Goedecker pseudo-potentials.$^{30,31}$

We calculate averages for different classes of environment to investigate how the electronic structure varies locally in the electrolyte. By transformation of the intensities into the molecular frame$^{32}$ before averaging, we obtain a comprehensive picture of the chemical bonding in terms of the symmetry classes of the isolated water molecule. The $b_1$ component is perpendicular to the molecular plane, the $a_1$ component is along the molecular axis and the $b_2$ component is their cross-product, approximately along the intramolecular H-H direction.

3. Results and Discussion

Figure 1 shows a series of Auger spectra in the 488-523 eV kinetic energy (KE) range, obtained from pure liquid water, 6m LiBr and 3m MgBr$_2$ (i.e. with equal Br$^-$ concentrations) at varying excitation energies. The top-left inset shows a X-ray absorption (XA) spectrum of liquid water with labeled arrows (a-d) that indicate the choice of photon
energies used to obtain the associated Auger spectra. The three lowest energies correspond to excitations into the three main features of the water XA spectra; in the following we will adopt the terminology of Wernet et al. and refer to these as the pre- (a), main- (b) and post-edge (c), respectively. Most important for the present study is that excitations into successively higher core-excited states lead to distinguishable spectator shifts in resonant absorption spectroscopy (RAS) as function of photon energy throughout the near-edge absorption fine-structure. This behavior implies a persistent excitonic particle-hole interaction in the core-excited states, which induces a localization of the excited electron at the core-excited molecule during the core-hole lifetime.

As we are interested in ion-induced effects, each trace in figure 1 shows difference spectra formed from the respective solution spectra minus that of water at the same photon energy (magnified by a factor 3 for better visibility). In the following we go though the electronic decay spectra associated with each of the excitations. We first consider the simpler cases of the lowest and highest photon energies, i.e. (a) and (e), before we proceed with the more complex and intriguing intermediate cases (b)-(d).

At the pre-edge resonance (a) we observe a pronounced spectator shift of ~5 eV to higher KE relative to off-resonance excitations. This has previously been interpreted as a fingerprint of a high degree of localization of the excited electron. We here make the observation that the spectra of electrolyte solutions look nearly identical to that of the pure water reference. This is a strong indication that the localization in the corresponding core-excitations is not substantially affected by solvated ions. Even though the molecular environment is typically quite different in the two cases, the core-hole of an excited water molecule is similarly screened and the resulting spectator spectra are therefore very similar.

Trace e) is taken at 650 eV photon energy and is therefore clearly off-resonant – the O1s BE of liquid water is 538.1 eV. We again note that the solution spectra and the water reference look nearly identical. Even though ab initio electronic structure calculations have shown that water molecules residing in the first solvation shell of solvated ions display significant polarization (gradually increasing with charge from monovalent, to trivalent species), we have recently demonstrated that the only clear effect of ions on the off-resonance O1s Auger spectrum of liquid water is limited to the high-energy region (507-515 eV KE), pertaining to various delocalized two-hole final states. Briefly, the
positive features around 514 eV KE in the difference spectra of trace e) originates from bromide-water double hole final-states. In a similar fashion, the decrease centered around 510 eV originates from a reduced number of water-water delocalized final states due to hydrogen bonding interactions, a relaxation channel that has been discussed in great detail elsewhere. While this striking overall insensitivity in the off-resonance Auger spectra to ion-induced electronic structure modification may at first sight seem disappointing, this actually simplifies the interpretation of the resonant Auger spectra (a-c) considerably.

Turning to the decay spectra associated with resonant excitation in the main-edge region (b) we start to observe pronounced differences between the solution spectra and the water reference. These differences become even more pronounced at the post-edge (c), and gradually diminish at higher excitation energies – grey boxes in figure 1 highlight the important regions. In all cases we see intensity redistribution (indicated by the arrow) from a region centered around 500 eV for all cases to a band at higher KEs, which moves to lower energies upon going from main- to post-edge excitations.

As indicated by the vertical lines in figure 1, the high KE region is associated with spectator Auger decays, where a neutral core-excited water molecule (H$_2$O$^*$) is transformed to an excited, singly valence-ionized H$_2$O$^+$. As previously mentioned, these Auger transitions lie at high KEs due to the screening of the core-hole by the resonantly excited electron, and signify that it has remained localized on its parental molecule until the decay occurred. We note that the difference with respect to pure water is strongest for post-edge core-excitations but it is also present at higher energies indicating an influence from resonances even at 550 eV.

The X-ray absorption spectrum in liquid water is strongly influenced by hydrogen-bonding, and the main- and post-edge features are due to resonances from valence-excitations in the conduction band. The presence of resonances in the continuum will induce a localization of the core-excited electron, and as a result the resonant Auger spectra deviate from the normal Auger spectrum. As expected, the spectator features decrease in KE with increasing excitation energy, as the screening efficiency of the excited electron decreases for higher, and spatially more extended, intermediate states. In contrast, the low KE region originates from normal Auger decays, i.e. a transition from the singly core-ionized H$_2$O$^+$ to the double valence-ionized H$_2$O$^{2+}$, meaning that the electron has delocalized prior to the core-hole decay. This means that the intermediate state has lost its
“memory” of the initial excitation and the final state KE is independent of excitation energy.

The differences in localization of the excited electron between pure water and the ionic solutions revealed by the features in the difference spectra unambiguously show that the introduction of ions into the H-bonding network of liquid water changes the electron delocalization times in the excited states. Since the fraction of Auger decays where the excited electron remains localized is larger with ions than without, we conclude that the ions slow down the electron delocalization dynamics. Figure 2 illustrates this picture in some further detail: Core-ionization (left branch) produces a H$_2$O$^+$ state where the electron has instantaneously been delocalized, due to the sudden nature of the photo-ionization process. There is then no other electronic decay path available except for normal Auger decay, leading to a variety of H$_2$O$^{2+}$ two-hole final states. The possibilities become more diverse upon resonant core-excitation (right branch in figure 2), producing neutral H$_2$O$^-$ intermediate states. For completeness, we have included the participator Auger channel to the far right in figure 2, in which the excited electron has participated in the decay. However, these states overlap with the direct valence photoemission features and lie outside the KE window here considered. Furthermore, these features are very weak compared to the spectator contributions. For the present discussion we are therefore concerned with the branching ratio between the spectator channel producing H$_2$O$^-$ (two hole-one electron) final states, and the doubly ionized states reached via the intermediate core-ionized state through ultra-fast delocalization of the excited electron into the H-bonded surroundings. The latter closely resembles the mechanism of “internal ionization” observed for similar excitations in other non-metallic systems. The channels of main interest are marked with a grey triangle in figure 2.

O1s X-ray absorption spectroscopy has been applied to aqueous electrolyte solutions in several studies. The ion-induced variations in the XA spectra have been analyzed primarily either in terms of changes in local electronic structure on the solvating water molecules or in terms of hydrogen bonding effects. The present study of the resonant Auger decay of the core-excited states is naturally linked to the XA data and can contribute to our understanding of the XA spectral features and the electronic structure of electrolyte solution. Cappa et al. have reported XA spectra from aqueous solutions of divalent cations (including Mg$^{2+}$), showing considerably more structure in the main and post-edge
regions compared to that of pure water. This was interpreted to arise due to the strong electrostatic perturbation of the cations on the solvating water molecules. This fits well with the picture emerging from the current experiments, as 3m MgBr₂ leads to stronger RAS difference features at these resonances than 6M LiBr, suggesting that the electron delocalization rates are highly dependent on the nature of the solvated cation. The higher degree of structure in the solution XA spectra also signifies the presence of resonances further up in the continuum which could explain why we see a weak effect of ion-induced electron localization as far up as at 550 eV excitation energy whereas the normal Auger contribution totally dominates for pure water at this energy.

If a reliable de-composition of the resonant spectra in figure 1 could be made we could apply the “core hole-clock” method to obtain a value of $\tau_{\text{deloc.}}$ for the respective excitations of each solution. In practice this is challenging given that we do not have access to the isolated spectator spectrum at higher excitation energies. If we knew the respective spectator and normal Auger fractions in the corresponding pure water spectra we could however estimate the changes in delocalization time based on the respective difference spectra in figure 1 – the details on how to estimate this are given in the supplementary information (SI). Assuming $\tau_{\text{deloc.}} = 0.5$ fs for post-edge excitation in pure water as reported in ref. we can in this way determine the corresponding values in 6m LiBr and 3m MgBr₂ to approximately 1.5 and 1.9 fs, respectively, meaning that the ions slows down the hopping rate up to almost 400% in the latter case. Note that this value is an ensemble average and that molecules in different binding environment may well contribute to very different extents. Since the value of $\tau_{\text{deloc.}}$ for main-edge excitation of pure water has not been reported (and cannot be accurately determined in the present study), it is not possible to make the corresponding estimation for the ion-induced reduction of the electron hopping rate at this resonance. The reason why the large ion-induced variations in electron hopping times upon post-edge excitation lead to rather small spectral changes (figure 1c) is due to the non-linear relation between lifetime variations and corresponding changes in spectral intensity – an inherent property of the core-hole clock method.

In order to rationalize the experimental findings in terms of molecular and electronic structure and to separate various contributions to the ion-induced changes in electron delocalization times we have calculated occupied and un-occupied electronic density
of states of p-character (PDOS) from the MD simulations as described in sections 2b and c. The difference in structure obtained from the large and small size classical MD simulations are small, validating the use of the small simulations in the electronic structure calculations, see the SI for details. We limit the analysis to the oxygen p-character, which can be related to the transition probabilities for core-excitations. We are especially interested in identifying what inter-molecular configurations that are primarily contributing to the spectral redistribution observed upon main- and post-edge excitations in figure 1. Therefore, the water molecules from each MD snapshot have been divided into discrete classes of environments based on their ion coordination and hydrogen (H) bonding configuration – details on the criteria and the resulting H-bonding statistics are given in the SI. While as many as 187 discrete classes can be identified they fall into four natural main categories, namely those which

1) are “water-like”, i.e. only coordinate to other water molecules
2) coordinate to at least one Mg$^{2+}$ cation
3) coordinate to at least one Br$^{-}$ anion
4) coordinate to both Mg$^{2+}$ and Br$^{-}$

Figure 3 shows the calculated PDOS for these four categories (b–e) together with the H$_2$O monomer in the gas-phase (a). The black lines show the total PDOS while the red, green and blue components reveal the respective contributions of $a_1$, $b_2$ and $b_1$ symmetry, respectively. Local p-character in each orbital is projected onto the axes in the molecular frame which allows for a symmetry decomposition of the PDOS. This analysis is motivated by the clear symmetry separation of the features in the occupied PDOS. Relative to the occupied orbitals, the larger spatial extension of the unoccupied orbitals makes them more sensitive to a mixing of states due to symmetry-breaking intermolecular interactions, in particular hydrogen bonding, and the analysis has to be performed with caution. However, when applied, we observe systematic trends in the symmetry decomposed unoccupied PDOS which are naturally correlated with the changes in the occupied orbitals. Hence, we conclude that the symmetry analysis is a valuable tool to resolve changes in the electronic structure, which is contained in the total PDOS.

By comparing traces (a) and (b) we see that the H-bonding in the condensed phase causes a significant broadening of all electronic states. Importantly, the $3a_1$ orbital in the occupied DOS, which is engaged in forming the intramolecular O-H bond, is known to
mix with neighboring water molecules upon H-bonding due to the spatial and energetic overlap of the 3a$_1$ orbitals.\textsuperscript{24} This causes the characteristic splitting into a bonding and anti-bonding component, seen around -5 to -1 eV in trace (b) of figure 3. Note that this phenomenon has no counterpart in the gas-phase as the orbital remains fully localized. When engaged in ion solvation the 3a$_1$ orbital is pulled down in energy compared to that of the “water-like” molecules, and the splitting is also reduced (see traces c-e), revealing that the occupied electronic structure is more localized on these water molecules. This effect is more pronounced for the Mg$^{2+}$-coordinated molecules than for Br$^-$-coordination. Similarly, the unoccupied electronic structure is strongly influenced by the presence of ions. The orbitals originating from 4a$_1$ give a PDOS which is smooth and broad for “water-like” molecules with a maximum around 12.5 eV. Upon ion solvation this state starts to show more structure (compare with the PDOS of the “water-like” molecule) and almost breaks up into two discrete bands. Once again, this effect is the most pronounced for Mg$^{2+}$-coordinated molecules. This resembles the ion-induced effects seen in the XA spectrum of MgCl$_2$ solutions.\textsuperscript{44} In order to better understand the connection between XAS and RAS of the current systems we have calculated X-ray absorption spectra from our MD snapshots; the computational methods and detailed results are given in SI. Briefly, the analysis shows that it is indeed the cationic charge that, to a large extent, causes the increased structuring in the XA spectrum of cation-coordinated water, which here has been shown to result in a reduced electron delocalization dynamics into the H-bonded surrounding.

The reduced electronic mixing with the environment, as observed in both the occupied and unoccupied orbitals for ion-coordinated water molecules, can thus be seen as having two different (but closely related) causes: First, the water-ion bonds perturb the H$_2$O electronic states and shift them down in energy. This leads to an energetic mismatch with the “water-like” neighbors, which decreases the mixing in the H-bonding between the different class of molecules. Secondly, the electrostatic interaction between a water molecule and the solvated ions will influence the spatial extension of the orbitals, both in the ground and excited states. A core-excited electron of a water molecule (which has high density along the H-donor bond) located in the first solvation shell of a cation will hence be “back-polarized” toward the parental molecule. This effect limits the spatial overlap with the acceptor site (thereby reducing the delocalization rate) and should scale
with the charge of the cation, in agreement with the experimental observations in fig. 1. The mechanism is schematically illustrated in figure 4, where a core-excited water molecule is either binding with its oxygen side to a) another water molecule, b) Li⁺, or c) Mg²⁺ - resulting in gradually weaker electronic overlap with the right-hand molecule to which it donates a H-bond. Note that the presence of the cationic core-hole, which was not taken into account in the PDOS calculations shown in figure 4 (but in the XA spectra discussed in the SI), will further increase this effect. Interaction with anions also results in changes in the PDOS of coordinating water molecules, but the effect is less pronounced than for cation coordination, especially in the unoccupied orbitals.

4. Conclusions

By a combination of O1s resonant Auger spectroscopy and electronic structure calculations of geometries obtained from MD simulations we have studied the effects of ion solvation on the electron-dynamics upon core-excitation of water molecules in LiBr and MgBr₂ aqueous solutions. The solute-induced changes in the resonant Auger spectra at the main- and post-edge excitations reveal an increased localization of the excited electron in the final states. At the pre-edge, however, the excited electron remains localized in both pure water and in the electrolytes – as a consequence the Auger spectra are very similar. Using the core-hole clock method we have determined the electron delocalization times to approximately 1.5 and 1.9 fs upon post-edge excitation in aqueous 6m LiBr and 3m MgBr₂, respectively, i.e. up to a four-fold increase compared to the corresponding value for pure water. Electronic structure calculations have revealed that water-molecules engaged in ion solvation show a reduced orbital mixing with the H-bonded surroundings. This effect, which provides a rationalization for the experimental results, has been found to be most pronounced for cation-coordinated molecules and increases with the cationic charge. Based on our findings we have proposed a molecular mechanism in which the excited electron of a core-excited cation-coordinated water is “back-polarized” towards its parental molecules, reducing its propensity to jump through one of its donor H-bond during the core-hole lifetime.

The present work identifies a sign- and charge-dependence for the efficiency of electron-transfer in aqueous solutions on the direct local environment of the electron-donating water molecules. Such effects may need to be considered in accurate models of
charge-transfer in strongly perturbed aqueous media, such as intra-cellular water.

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**Supporting Information Available:** Description of model for calculation of changes in electron delocalization times from resonant Auger spectra, details on analysis of MD simulations, description of X-ray absorption spectra calculations and complete reference 39. This material is available free of charge via the Internet http://pubs.acs.org
Figure and table captions

Figure 1) Schematic electronic level diagram illustrating how different auto-ionization pathways of a core-ionized/core-excited molecule in solution can be used to identify ultrafast charge-transfer mechanisms. a) shows the normal Auger process; the core-hole of a core-ionized molecule is re-filled by a valence electron, causing the ejection of another valence electron and leaving the system in a doubly ionized state. b) shows the most probable decay channel from a molecule where the initial excitation does not lead to ionization, but rather promotes a core electron to an initially unoccupied energy level (dashed line). The Auger decay now occurs in the presence of the excited electron, and hence the final state will be different from that shown in a), due to the screening of the excited electron – this process is referred to as spectator Auger decay. c) illustrates the situation where a resonantly excited molecule (to the right) quickly donates the excited electron to neighboring molecule through charge transfer (labeled 1), prior to the decay of the core-hole. The subsequent auto-ionization process will thus locally look like a normal Auger decay (labeled 2). If the delocalization and core-hole decay rates are comparable, the Auger spectra upon resonant excitation will contain both spectator and “normal-like” contributions. From their relative intensities together with the core-hole lifetime, the delocalization time-scale and rate can be deduced.

Figure 2) O1s resonant/off-resonant Auger spectra of liquid water and 6m LiBr / 3m MgBr₂ aqueous solutions. The inset (top left) shows the excitation energies, projected onto the water X-ray absorption spectrum. The dotted lines under each trace are the difference spectra of the respective solution minus water at the given photon energy. The grey boxes in the difference spectra of traces (b) and (c) highlight a characteristic spectral redistribution at the main and post edges discussed in the main text.

Figure 3) Top figure A shows a schematic flow diagram of how different final states can be reached through Auger decay after O1s core-ionization/resonant absorption of a water molecule in the aqueous phase. The core-ionized H₂O⁺ state can solely decay through normal Auger decay (left branch). Resonant absorption (right branch) however produces a wide range of intermediated states, whose nature depends on the excitation energy.
Depending on the efficiency for delocalization of the electron in the excited state (characterized by the lifetime $\tau_{\text{deloc}}$), either a doubly charged [2h] cationic state or a singly charged valence-excited [2h1e] state is reached, each with a distinct signature in the resulting Auger spectrum. Since the core-hole lifetime (here denoted $\tau_{\text{de-exc.}}$) is known (3.6 fs), the delocalization time $\tau_{\text{deloc}}$ can be derived by analysis of the spectral branching ratio. Bottom figure B conceptually illustrates how ion coordination of a resonantly excited molecule reduces the delocalization rate during the core-hole lifetime, and how this is reflected in the final Auger spectrum.

**Figure 4** Calculated occupied and unoccupied density of states of p-character (PDOS) for a) the water molecule in the gas-phase and b-e) different classes of water molecules from MD simulations of $\sim 3$ m MgBr$_2$: b) “water-like” water, i.e. those which only coordinate to other water molecules, c) those which coordinate to at least one Mg$^{2+}$, d) those which coordinate to at least one Br$^-$, and e) those which coordinate to both Mg$^{2+}$ and Br$^-$. 

**Figure 5** Principle sketch of how we schematically can understand why ions have an effect on the electron hopping-rate in the resonantly excited states of water molecules in aqueous solutions. a) shows the situation where a water-coordinated molecule is resonantly excited on the main/post edge. The electron in the excited orbital, which is extended toward the accepting H$_2$O to the right, can jump to this molecule through its H-donor bond on the timescale of the core-hole decay. In b) the excited molecule is sitting in the first solvation shell of a lithium cation. The excited orbital will then be “back-polarized” toward the parental molecule and the overlap with the neighboring water molecule on the donor side will be reduced. When going from lithium to Mg$^{2+}$ (c) this effect is increased, which is consistent with the experimental observations in figure 1. Note that the cationic core-hole on the central O1s atom (denoted by *) also will limit the spatial extension of the excited electron.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
References


