Supporting Information

Ion-Solvation-Induced Molecular Reorganization in Liquid Water Probed by Resonant Inelastic Soft X-ray Scattering

Yekkoní L. Jeyachandran,1,§ Frank Meyer,2 Sankaranarayanan Nagarajan,1,# Andreas Benkert,2,3 Marcus Bär,4,5,6 Monika Blum,6 Wanli Yang,7 Friedrich Reinert,2 Clemens Heske,3,6,8 Lothar Weinhardt,3,6,8,9 and Michael Zharnikov1*

1 Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany
2 Experimentelle Physik VII, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
3 Institute for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology (KIT), Hermann-v.-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
4 Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
5 Institut für Physik und Chemie, Brandenburgische Technische Universität Cottbus-Senftenberg, Platz der Deutschen Einheit 1, 03046 Cottbus, Germany
6 Department of Chemistry, University of Nevada, Las Vegas (UNLV), 4505 Maryland Pkwy., Las Vegas, Nevada 89154-4003, USA
7 Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA
8 ANKA Synchrotron Radiation Facility, Karlsruhe Institute of Technology (KIT), Hermann-v.-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
9 Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstrasse 18/20, 76128 Karlsruhe, Germany
§ Currently at Department of Physics, Bharathiar University, Coimbatore 641046, India
# Currently at Department of Chemistry, National Institute of Technology, Tiruchirappalli – 620015, India
Qualitative analysis of the RIXS data and XE spectra

**Figure S1.** Representative O K-edge XA spectra extracted from the RIXS maps presented in Fig. 1 (left panel) and selected O K-edge XE spectra of pure liquid water and the KCl solutions of different concentrations (right panel). The absorption resonances (XAS) and emission lines (XES) are labeled. The XA spectra represent the integrated intensity over an emission energy range of 519 - 529 eV. The XE spectra are area-normalized; the main-edge and non-resonant (550 eV) spectra are additionally normalized to the maximum of the respective HE intensity. The label D corresponds to the same feature as in the RIXS maps of Fig. 1.

To qualitatively analyze the changes upon admixture of KCl into water in the spectator emission region (i.e., below an emission energy of 529 eV), O K-edge partial fluorescence yield (PFY) XA spectra were generated by integrating over the emission energy range between 519 and 529 eV. They are shown in Fig. S1 (left), together with representative XE spectra for several selected excitation energies (right). Note that, to enhance the signal-to-noise ratio, these XE spectra were recorded separately from the RIXS map series; nevertheless, they are identical to the analogous spectra that can be extracted from the maps. As expected,\(^1\)^\(^-\)^\(^4\) the XA spectra show the characteristic pre- (534.3 eV), main- (~536 eV), and post-edge (~540 eV) absorption features. All these spectra exhibit the saturation effects typical of the PFY acquisition mode,\(^5\)^\(^-\)^\(^7\) overemphasizing the signal in the pre- and post-edge ranges with respect to the main-edge. Whereas the saturation effects are quite strong for pure
water, they are progressively reduced for the KCl solutions, increasingly resembling electron yield XA spectra, as in a similar study based on water-acetonitrile solutions. This creates a challenge to correctly interpret the target effects in PFY XA spectra: speculating that the decrease of the saturation effects in the KCl solutions could be due to the presence of additional absorption edges associated with the K$^+$ and Cl$^-$ ions (and associated modifications of the attenuation coefficients), it is difficult to isolate the “true” ion-related changes. For example, the intensity of the pre-edge feature does not increase but decrease as a function of salt concentration, in contrast to literature data taken with a liquid jet (see, e.g., refs 9 and 10). For this reason, we will in the given case primarily rely on the XE spectra for an unimpeded view of the solvation-induced effects.

The O K XE spectra shown in Fig. S1 (right) exhibit the characteristic spectator emission lines of water molecules, related to fluorescent decay from three occupied, O2p-derived molecular orbitals, 1$b_2$, 3$a_1$, and 1$b_1$, into the O 1$s$ core hole. For excitation energies corresponding to the main edge resonance and above, the spectra show the previously observed splitting of the 1$b_1$ line into the LE and HE components, which, as discussed earlier, are assigned to dissociated and intact water molecules, respectively. For excitation into the pre-edge resonance, the LE and HE lines shift and merge into a single asymmetric 1$b_1$ emission feature (labeled D in Figs. 1 and S1), an effect that can be attributed to spectator shifts. Moreover, the pre-edge resonant XE spectra exhibit an additional weak emission line around 522.7 eV that is highlighted by the arrow in Fig. S1. Note that this feature is also present at higher excitation energies, but is less visible due to a partial overlap with the dominant 1$b_2$ emission line. It can, however, be clearly identified by the difference of the spectra of H$_2$O and D$_2$O (see refs 3 and 11). Furthermore, for pre-edge excitation, it can be observed that the spectral center-of-gravity of the 1$b_1$ emission feature is at LE, shifting to HE at the main-edge, and back to LE for the higher excitation energies, in agreement with previous reports.

In the pre-edge excited XE spectra of the KCl solutions, the intensities of the 1$b_1$ emission and the emission at 522.7 eV decrease with increasing salt concentration. At the higher excitation energies (main edge and above), the relative intensity of the LE component decreases and that of the 1$b_2$ and 3$a_1$ emissions increases with increasing salt concentration. Note that a similar decrease in the intensity of the LE component, reported recently for a variety of aqueous chloride solutions, was attributed to ion-induced disruption of the HB network of water.
Additional experimental data

**Figure S2.** Left panels: pre- (534.2 eV, top) and main-edge (536 eV, bottom) resonant O K-edge XE spectra of pure liquid water and the KCl solutions. The spectra are normalized to the maximum of the $1b_1$ emission and HE component, respectively, and fitted with three principal components (shown in the right panels) with varying weights. The components are color-coded according to the right panel. The sum of all the residuals is plotted at the bottom of the left panels.
Figure S3. Comparison of the 'residual' spectra ($d_R$; black curves), obtained by the principal component decomposition of the XE spectra, with the difference spectra ($d_S$; red curves), obtained by subtraction of the weighted XE spectra of pure water from the spectra of the salt solutions (apart from the spectral weight, $d_R$ is independent of the KCl concentration). The $d_R$ and $d_S$ component spectra are similar for the pre- (534.2 eV; left panel) and main-edge (536 eV; middle panel) excitation, but are substantially different for the non-resonant (550 eV; right panel) case. We assume that the calculated $d_R$ component represents the salt-induced changes better than the $d_S$ spectrum calculated by the simple subtraction step.
Figure S4. Ion/water molecule composition ratio (red line and circles) and the weight of the d_R component in the non-resonant and resonant XE spectra (black lines and symbols) as functions of the KCl concentration. The K^+ and Cl^- ions are counted together, independent of the charge. As can be expected, the gain of the d_R component with increasing KCl concentration correlates well with the change in the ion/water ratio.
Figure S5. Participant decay spectra of pure liquid water and the aqueous KCl solutions obtained for pre-edge (left panel) and main-edge (right panel) excitations. The spectra are normalized to the primary x-ray flux and the acquisition time to monitor changes in the low-energy tail represented by the dotted box. This tail, extending down to the spectator $1b_1$ emission (Figs. 1 and 2), is a characteristic of the ultrafast dissociation process of the water molecules. The observed decrease in the intensity of this tail with increasing KCl concentration can be associated with the decrease in the dissociation probability of water molecules in the KCl solutions, as established by the spectator emission analysis (Fig. 2).
Experimental details and monitoring of the membrane

A high-transmission soft x-ray spectrometer at the SALSA endstation has a slitless design, a spherical collecting mirror, a variable line spacing grating, and a soft x-ray CCD detector. The spectrometer allows the collection of an entire RIXS map on the time scale of a few tens of minutes. For our experiments, the resolving power $E/\Delta E$ was set to be better than 1000 for both x-ray spectrometer and beamline. The optical axis of the spectrometer was oriented at ~45° relative to that of the beamline in the polarization plane of the undulator. The excitation and emission energy scales were calibrated using the XA spectrum of TiO$_2$ (anatase) and elastically scattered (Rayleigh) lines, respectively.

Special care was taken to monitor and minimize spectral contributions due to a possible oxidation of the membrane, especially for the prolonged (~30 min) exposure to x-rays during the acquisition of RIXS maps. This was achieved by timely exchange of the membrane, control measurements of oxygen-free liquids (acetonitrile), and frequent recording of reference water spectra. Some of the respective data are presented in Figs. S6 and S7.

Figure S6. Non-resonant O $K$-edge XE spectra of pure liquid water measured at regular intervals during the acquisition of the RIXS maps (Fig. 1). These measurements were used to monitor a possible oxidation or contamination of the window membrane (Si$_3$N$_4$ in the present case; only one membrane was used for the entire measurement series). The reproduction of the same XE spectrum each time showed that any potential changes in the composition of the membrane had negligible effect on the measurements.
Figure S7. O K-edge XE spectrum measured under acetonitrile flow (red curves) against a reference spectrum of pure liquid water (blue curve). This measurement was used, in addition to the acquisition of the pure water spectra (Fig. S6), to monitor a possible oxidation-related contamination of the Si₃N₄ window membrane. As acetonitrile is nominally oxygen-free, the resulting spectrum is a conservative estimate of the extent of oxidation of the membrane (including a potential oxygen-contamination of the acetonitrile itself). The presented acetonitrile spectrum was collected after the measurement of all RIXS maps and XE spectra of Figs. 1, 2, and S2, and thus represents the cumulative oxidation of the membrane. The observed low intensity of the acetonitrile spectrum compared to that of the reference water spectrum (bottom curves) suggests a very low level of membrane oxidation during the entire set of the experiments, which is therefore considered to have a negligible effect on the experimental spectra. Significantly, the enlarged (multiplied by a factor of 45) acetonitrile spectrum (top curve) showed a strong peak at the position of the LE emission line of the water spectrum. Thus, an increase in the intensity of the LE component with time (corresponding to increase in the salt concentration in our experiments) would be expected in the case of a membrane oxidation. In contrast, a decrease of the LE intensity was observed (Figs. 1, 2, and S3).
References


