Hydrogen Bonds

On the Origin of the Hydrogen-Bond-Network Nature of Water: X-Ray Absorption and Emission Spectra of Water–Acetonitrile Mixtures**

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Liquid water plays a significant role, especially as a solvent in the fields of biology and biochemistry. Its strong impact on protein function and activity in the direct surrounding of proteins led to the coining of the term biological water.[1] Investigations of the hydration of polar and nonpolar protein sites, or of systems which can mimic this interaction, such as mixtures of water with solvents of different polarity, are of great interest. However, even for pure liquid water the complex nature of the hydrogen-bond (HB) network is still in the course of clarification. One open question in this context is whether in the dynamic bond-building and -breaking equilibrium of liquid water a continuum of almost tetrahedral bond configurations[2] or rather a number of distinct preferential species of broken and unbroken HB configurations exists.[3] X-ray absorption (XA) and X-ray emission (XE) spectroscopy, which reveal information about the local electronic structure, have been used to pursue this question.[3b,4] In XA spectroscopy a core electron is excited to the unoccupied states of a molecule, and thus probes the corresponding local electronic structure. The oxygen K-edge XA spectrum of liquid water shows three main features: a pre-edge at 535 eV, a main edge around 537 eV and a post-edge around 540 eV. Isotope-, temperature-, and phase-dependent measurements on water in combination with

theoretical simulations led to the proposal that these features are correlated to distinct HB conformations: the post-edge to tetrahedrally bonded water molecules and the pre- and main edges to conformations with broken HBs.[3,5] This interpretation indicated that a significant number of water molecules with only one strong donating and one strong accepting HB is present in the liquid phase, challenging the traditional tetrahedral model. This new interpretation has been questioned, and based on theoretical modeling it has been argued that XA spectra are rather insensitive to the HB network.[6]

X-ray emission spectroscopy probes the occupied electronic states on detecting the energy distribution of the radiative decay of the core-hole state. The recent development of high-resolution XE spectrometers for liquid samples drew particular attention to the observation of the splitting of the sharpest peak in the spectrum associated with the lone-pair orbital of the free water molecule.[4a,f,g] Tokushima et al. interpreted the double feature as further proof for the existence of two different structures, the tetrahedral and strongly distorted H-bonded species.[4g] Fuchs et al. assign the two distinct peaks to emission from species before and after core-hole-induced ultrafast dissociation.[4a] Experimental approaches to clarify the origin of the peak splitting included temperature-, isotope-, and state-of-aggregation-dependent measurements, as well as the study of the proposed dissociated species.

To shed further light on this issue we present XA and XE spectra of the water molecule in a chemical environment in which the HB configuration is radically different from that of liquid water. To mimic polar surroundings, acetonitrile was chosen as solvent.

Figure 1 shows the fluorescence yield spectra at the O K-edge of water–acetonitrile mixtures of 95, 25, 5, and 1 vol% water content. At 95 vol% the spectrum is very similar to that of neat liquid water, and shows the three principal pre- (535 eV), main (537 eV) and post- (540 eV) edge features. However, its strong saturation[7] leads to overemphasis of pre- and post-edge with respect to the main-edge intensity.[8] With decreasing water concentration saturation is significantly reduced and, compared to the spectrum of pure liquid water, enhancement of the main edge is observed. In addition, the shape of the spectrum changes character, so that at 1 vol% the pre-edge structure becomes clearly resolved, the main edge appears as a sharp feature, and the relative intensity of the post-edge is attenuated. Thus, the XA spectrum of the 1 vol% water–acetonitrile mixture now deviates considerably from the spectrum of neat water, and

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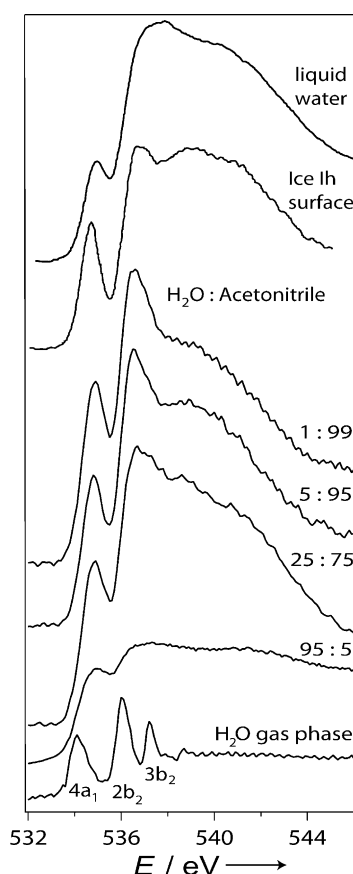© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 1. Oxygen K-edge X-ray absorption spectra of water–acetonitrile mixtures of four different concentrations. The spectra of an Ih ice surface[3b] and liquid-[3b] and gas-phase H_2O are shown for comparison

instead it increasingly resembles the spectrum of gas-phase water (Figure 1), with the pre- and the main-edge correlating with the $4a_1$ and the $2b_2$ resonances of the free molecule. We note that the XA spectra shown here differ significantly from previous XA measurements in a membrane cell.[4c] The present data are free from any artifacts which may be introduced by structuring due to interaction with a membrane. As the sample is rapidly renewed in the microjet setup we can also rule out any photoinduced restructuring. Previously published spectra may be influenced by such effects (for further details see Supporting Information).

Before we discuss our experimental results further we consider the molecular arrangement of water and acetonitrile in the mixture. The number of HBs per water molecule is considerably reduced compared to water molecules in pure water. At 1 vol %, there are around 34 acetonitrile molecules per water molecule and the water molecules are mostly surrounded by the acetonitrile molecules.[9] Acetonitrile is usually considered to be a pure HB acceptor, although it has been proposed that interactions of the methyl protons of acetonitrile with the oxygen atom of water are also possible.[10] Using molecular dynamics (MD) simulations in combination with infrared and far-infrared measurements, Venables et al.[11] concluded that the number of HBs accepted by a water molecule significantly drops from 1.75 for neat

water to 0.5 for a 7 vol % mixture, whereas the number of donated HBs decreases only slightly from 1.75 to 1.65. At lower concentrations, any water clustering is absent, and based on calibrated multiple attenuated total reflection spectroscopy Bertie and Lan conclude that the fraction of bonded OH groups decreases from about 0.865 in neat water to 0.45 in the limit of low water concentration,[12] in which the remaining O−H⋯N donor bonds are weaker than the O−H⋯O bonds in liquid water.[4c] Compared to the free molecule we note that condensation effects are present even without hydrogen bonds, and we expect that features corresponding to resonances in the free molecule will be broadened and shifted due to dipole–dipole interaction and different relaxation in gas and condensed phases. Even in the absence of HBs, Rydberg resonances will be smeared out in the liquid due to the large extension of the orbitals.

Thus, hydrogen bonds break with decreasing water concentration, and in the 1 % solution we may expect only some remaining donor bonds to acetonitrile. In general, this explains why the 1 % spectrum shows similarities with the gas-phase spectrum. The character of the first two unoccupied orbitals is retained to the extent that they give rise to two distinct peaks, and the third gas-phase resonance is smeared out due to its Rydberg character. The relative attenuation of post-edge intensity is in line with its interpretation as due to highly coordinated water molecules and with the absence of a corresponding resonance in the gas phase. Similar trends are observed in the XA spectrum of an surface layer of ice Ih (Ref. [3b], shown in Figure 1 for comparison), in which asymmetric H-bonding prevails. The surface molecules were estimated to have 1.2 donor HBs on average. Note that our XA spectra are very similar to recently measured hard X-ray Raman spectra of acetonitrile–water solutions.[13]

For each water–acetonitrile mixture a series of XE spectra was recorded (Figure 2). For high water concentrations the spectra are in agreement with previously published XE spectra of liquid water,[4a,d,f,g] showing a sharp $1b_1$ lone-pair-derived peak around 527 eV, followed by broader $3a_1$- (≈ 525 eV) and (≈ 521 eV) $1b_2$-derived features. With increasing excitation energy the $1b_1$ feature splits into two distinct features, denoted in the following d_1 (high-energy) and d_2 (low-energy) after Fuchs et al.[4a] The relative intensity of the d_2 feature is dramatically attenuated when the water concentration is reduced. Following the discussion above this behavior can be unambiguously attributed to the breaking of hydrogen bonds. Conversely, this directly demonstrates that a substantial part of the d_2 intensity indeed is due to the formation of HBs, in line with earlier interpretations.[4f,g] In addition we note that, apart from this striking influence of HB formation, the spectra (Figure 2) seem rather little influenced by the chemical environment. The nonresonantly excited spectrum approaches with decreasing water concentration to gas-phase spectra, which show only one $1b_1$-related feature.[4g, 14] Note, however, that even for the 1 vol % solution the additional d_2 feature is still present. Although published gas-phase spectra differ from each other considerably in intensity ratios and peak broadening,[4g, 14] the further major difference compared to the low-concentration spectra appears to be a uniform energy shift.
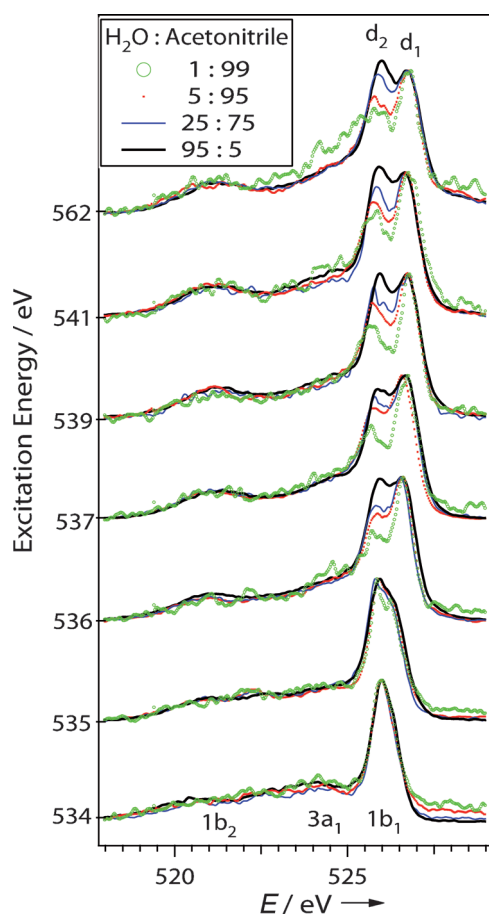
Figure 2. Series of X-ray emission spectra of water–acetonitrile mixtures of four different concentration ratios obtained from a microjet. The spectra are normalized to d_1 intensity.

The expected XE shift on going from gas-phase to liquid water can be estimated by comparing the shift of the binding energies of the core and valence holes states. According to reference [15] the core-level binding energy decreases by 1.91 eV, while the $1b_1$ shift is 1.39 eV. Neglecting differences in excitation dynamics between direct photoemission and XE, we would thus expect a low-energy shift of the $1b_1$-derived feature of 0.52 eV, whereas a direct measurement[4g] gives a low-energy shift of around 0.3 eV if the d_1 feature is identified with the $1b_1$ hole state. For weakly interacting molecules it is known that the major effect of condensation is a uniform shift of all spectral features, while the overall spectral shape is preserved.[16] The observations are fully consistent with the notion that the water molecules in the low-concentration solution interact only weakly with the surroundings. At increasing water concentration the interaction increases, and the changes in the spectra can be unambiguously assigned to this interaction. Obviously the spectrum is largely independent of the stronger HB interaction, while the most striking change is the increasing relative intensity of the d_2 feature.

The association of the d_1 feature to less coordinated species and a major part of the d_2 intensity to highly coordinated species can thus be done on firm experimental grounds. This conclusion is reached without any advanced theoretical considerations, which in complex situations like

this necessarily invoke approximations which can be questioned. In the following we will briefly discuss some details in the light of the current debate on the origin of the splitting of the lone-pair-derived feature.[4a,17]

To emphasize the spectral changes induced by HB formation we subtract the spectra of solutions with low water content from the 95 vol% spectrum (Figure 3). The result of the subtraction is critically dependent on the relative normalization of the spectra, and we chose to subtract the
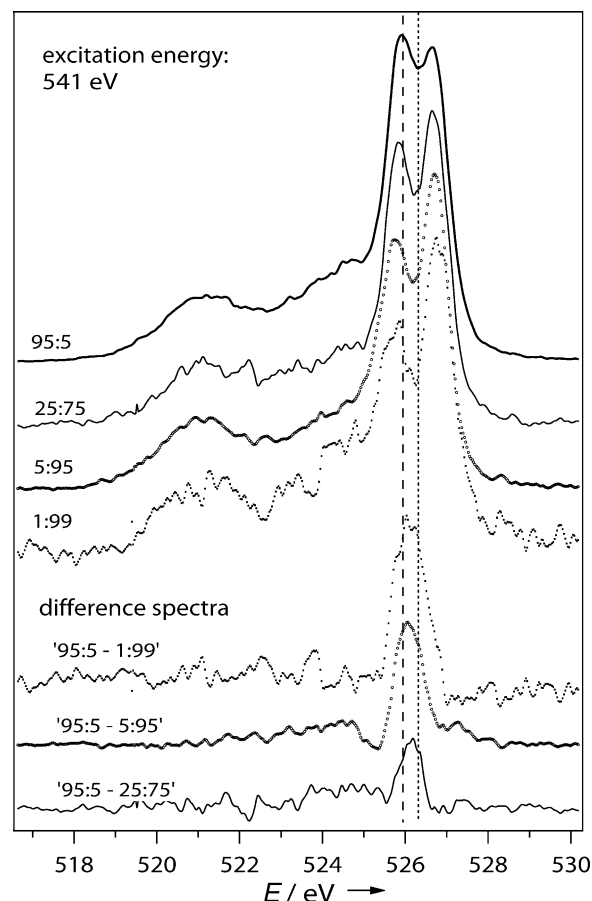

Figure 3. Spectra of water–acetonitrile mixtures excited at 541 eV and difference spectra. To avoid negative residuals, weight factors were used for the subtraction.

maximum intensity which does not lead to negative residual intensity. The difference spectra for further excitation energies can be found in the Supporting Information (Figures S3, S4).

The difference spectra are completely dominated by a feature at an emission energy of about 526.0 eV, and this energy position is independent of concentration. Furthermore it has internal structure, showing intensity not only at the d_2 peak but also a high-energy shoulder extending under the d_1 peak (see dashed and dotted lines in Figure 3). In the case of ultrafast dissociation we would expect the residual to resemble the XE spectrum of the dissociation product OH$^-$, which, upon resonant excitation, is dominated by a peak very close in energy to the d_2 peak. Although this is in line with the

present observations, the internal structure observed in the residuals shows the limitation of any attempt to describe the water XE spectra as a simple superposition of emission from intact and dissociated species.

If the d_2 emission were due to intact molecules,[4f] one would expect that the residuals resemble a shifted spectrum of water molecules. Recently, it was predicted that HBs cause an asymmetry in the d_1 peak towards lower energies, and that the variation in relative intensity of this low-energy flank significantly contributes to the apparent variation of the d_2 intensity.[18] The fact that much intensity in the difference spectra is found between the d_1 and d_2 peaks speaks is in line with this prediction. If the residual has contributions both from d_2 and changes in the asymmetry of the d_1 peak, $1b_2$ and $3a_1$ intensity of the shifted spectrum may be below the detection limit.

Finally, we note that the spectra resonantly excited at the XA pre-peak are virtually independent of the water concentration. This is in line with the notion that the pre-peak largely is due to species in which HBs are already broken in liquid water and that the excitation in this case is local at a specific molecular site.

In conclusion, we have studied the impact on XA and XE spectra of water as the number of HBs is reduced with decreasing water concentration in a mixture with acetonitrile. Our results confirm that both techniques are very sensitive to the HB environment. The XA intensity at the pre- and main edges is enhanced relative to the post-edge intensity upon HB breaking, and we find that condensation effects are important for the XA spectrum even without HBs. In the XE spectra the low-energy component of the sharp double feature is relatively reduced upon HB breaking, and its relative intensity can thus be used as a probe for H-bonding. This can be concluded without theoretical modeling. To understand the detailed mechanisms behind the variations, however, further investigations are needed, and we hope that our results will inspire new theoretical and experimental developments.

Experimental Section

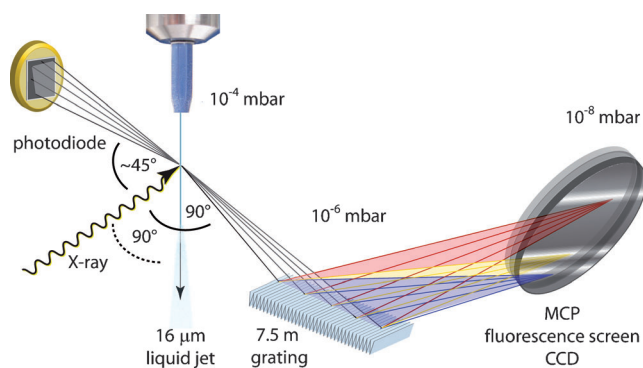The measurements were carried out at the U41 PGM undulator beamline of the BESSY II third-generation synchrotron facility of the HZB using the LiXEdrom setup. Figure 4 shows a schematic of the experimental setup, and detailed information about the setup can be found in the literature.[4d] Briefly, the samples were introduced through a 16 μm microjet directly into the vacuum. The XA spectra were recorded with a GaAsP photodiode. For the XE measurements a Rowland spectrometer with a grating of 7.5 m radius and a line density of 1200 lines per millimeter was used. The oxygen emission lines were recorded in second order. The energy of the XES series was calibrated according to the water spectra of Tokushima et al.[4f]

Figure 4. Schematic of the LiXEdrom setup for XA and high-resolution XE measurements.

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