X-ray emission from pure and dilute H₂O and D₂O in a liquid microjet: Hydrogen bonds and nuclear dynamics

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Knowledge about the hydrogen bond network of water is essential for understanding its anomalies as well as its special role for biochemical systems. Different types of x-ray spectroscopy allow probing of the molecular orbitals of water, revealing the electronic structure which reflects the hydrogen bond conformations. In this work a recently developed high-resolution x-ray emission spectrometer was used in combination with the microjet technique for recording spectra of liquid H₂O and D₂O and their mixtures with acetonitrile. Variation of the nuclear dynamics via isotope substitution and variation of the hydrogen bond conformation via dissolution in acetonitrile was investigated. These two effects have two clearly distinguishable spectral fingerprints.

I. INTRODUCTION

The hydrogen bond (HB) network of water is the focus for a wide range of investigations.[1,2] X-ray absorption (XA) spectroscopy and x-ray emission (XE) spectroscopy belong to the methods which can provide essential information.[3] Whereas XA spectroscopy probes the unoccupied molecular orbitals, XE gives information about the occupied ones. While the orbitals are influenced by the chemical surroundings of the molecules, the spectra reflect the local HB conformation, from which conclusions can be drawn about the network. Since the electronic states are short-lived, x-ray spectra additionally hold information about the nuclear dynamics on the femtosecond timescale.

Due to the complexity of the interactions in the HB liquid the interpretation of the spectra cannot rely on rigorous theory, and there is a lively ongoing debate about the assignment of the spectral features, where notably various interpretations imply totally disparate HB conformations. Some years ago, an interpretation of the XA spectrum of liquid water based on comparison with the spectra of bulk and surface ice and density functional theory (DFT) calculations was presented that implied that the average HB coordination is much less than had earlier been assumed.[4] This interpretation has, however, been criticized in later experimental and theoretical works, which support the standard model of liquid water with approximately four hydrogen bonds.[5]

More recently XE spectra have been taken as the most important spectroscopic evidence for the existence of two different structural "motifs."[3,6,7] This interpretation has also been challenged.[8]

A crucial point of disagreement in the discussions concerns the role of nuclear dynamics and the role of static HB conformation for the spectrum formation. In attempts to settle this issue isotope and temperature effects have been thoroughly measured and discussed, without leading to a consensus regarding the assignment.[7,8] To isolate the HB conformation effects we recently compared the XE spectrum of neat H₂O with the spectrum of H₂O as a solute in acetonitrile.[9] In the latter case the number of HBs is significantly reduced, and we could thus isolate the corresponding spectral change. The question about the role of dynamics remained open because the dynamics is highly dependent on the HB coordination. In the present work we have varied the influence of dynamics by performing the corresponding study also for D₂O, where the nuclear dynamics is slower than in H₂O. The results demonstrate that the spectral response on increased HB coordination is significantly different from the response on increased nuclear rearrangement. The two effects can thus be separated experimentally, thereby establishing a firm ground for interpreting x-ray spectra of liquid water.

A further uncertainty in the current discussions stems from the fact that most experiments so far base the technique on ultrathin windows which potentially interact with the liquid. If the sample is only slowly replenished photolysis may also influence the structure and thus details in the spectra.[7,9–11] The present investigation uses a liquid microjet, by which such problems are avoided.

II. EXPERIMENTAL

The experiments were carried out at the U41 PGM undulator beamline of the BESSY II synchrotron facility using the LiXEdrom setup.[12] In this setup fresh sample is constantly introduced using a liquid microjet. The fluorescence yield XA spectra are recorded with a GaAsP diode. The XE spectrometer is based on Rowland geometry and is oriented perpendicular to the light path of the incident x-rays. For the oxygen *K*-edge emission lines a blazed grating of 7.5 m radius and a line density of 1200 lines per mm were used. The spectra are recorded with a MCP-CCD detection unit. The calibration of the spectra was done according to Tokushima *et al.*[6] The x-ray emission spectra in Fig. 2 were normalized on the 1*b*₂ intensity. The spectra in Fig. 3 were area normalized.

For the liquid microjet a nozzle of around 16 μm diameter was used. The samples were filtered and degassed before they were introduced with a flow rate of 0.4 ml/min to the
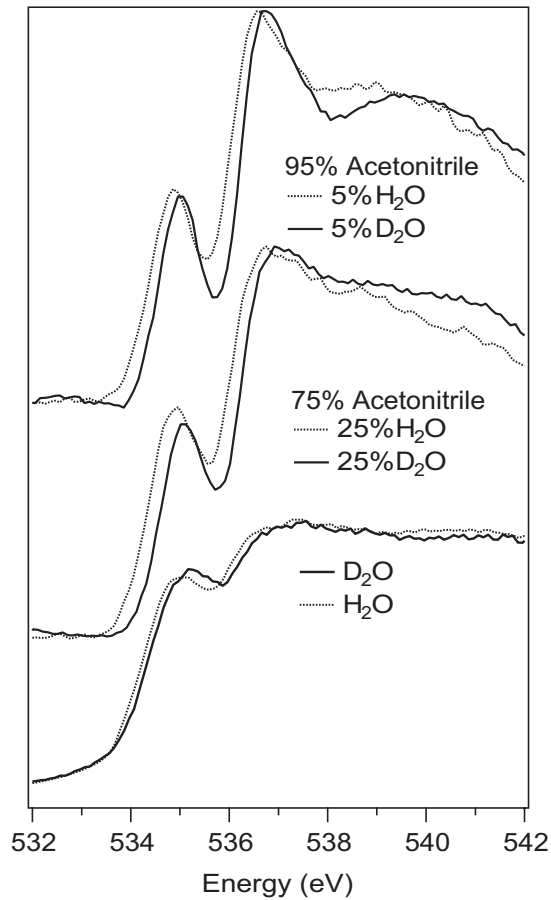
FIG. 1. K-edge x-ray absorption spectra of pure D_2O and D_2O-acetonitrile mixtures. For comparison the respective spectra of H_2O-acetonitrile mixtures are shown with dotted lines.

microjet. The spectra were recorded from the jet region of laminar flow with a distance of around 1 mm with respect to the nozzle opening. Evaporative cooling leads to a decrease of temperature along the jet axis. Based on the calculations

and the experimental data in Ref. 13 we estimated the temperature of the liquid in the probing zone to be around 15 °C.

III. RESULTS AND DISCUSSION

In agreement with earlier studies the fluorescence yield (FY) spectra of both H_2O and D_2O show three characteristic features (see Fig. 1): a pre-edge around 535 eV, a main edge around 537 eV, and a post-edge around 540 eV.[4] For the pure liquids the spectra are strongly saturated[14] which leads to an overemphasizing of the pre- and post-edge with respect to the main edge.[15] The saturation effects are reduced in the spectra of the 25 vol % solution, the post-edge intensity is relatively attenuated, and the pre-edge feature becomes a well separated peak. The changes can also partly be attributed to the reduced HB coordination,[11] which becomes even more accentuated in the 5 vol % solution.

The features of the D_2O spectra are very similar to the H_2O features at all measured concentrations. The principal differences comprise a general small (0.2 eV) high-energy shift of the entire spectrum, and an additional sharpening of the main features. This isotope effect has been discussed before for the pure liquids, and can be understood in terms of the slower dynamics and the shift of the ground-state zero-point energy,[16] due to the heavier nuclei. Thus, there is no need to refer to the small structural differences between the H_2O and D_2O liquids to describe the spectral differences.

Whereas the interaction between H_2O and acetonitrile has been well investigated over the whole concentration range, data sets for low D_2O concentrations in acetonitrile are rather scarce. The systematic changes in the XA spectra indicate that also for D_2O the number of intermolecular bonds is reduced upon dilution in acetonitrile, and the fact that the changes are similar in the two cases suggests that the reduction in HB coordination is similar for H_2O and D_2O.

In the following we turn our attention to the dramatic isotope and dynamic effects in the XE spectra (see Fig. 2). All spectra have a broad feature at 521 eV and a sharp peak
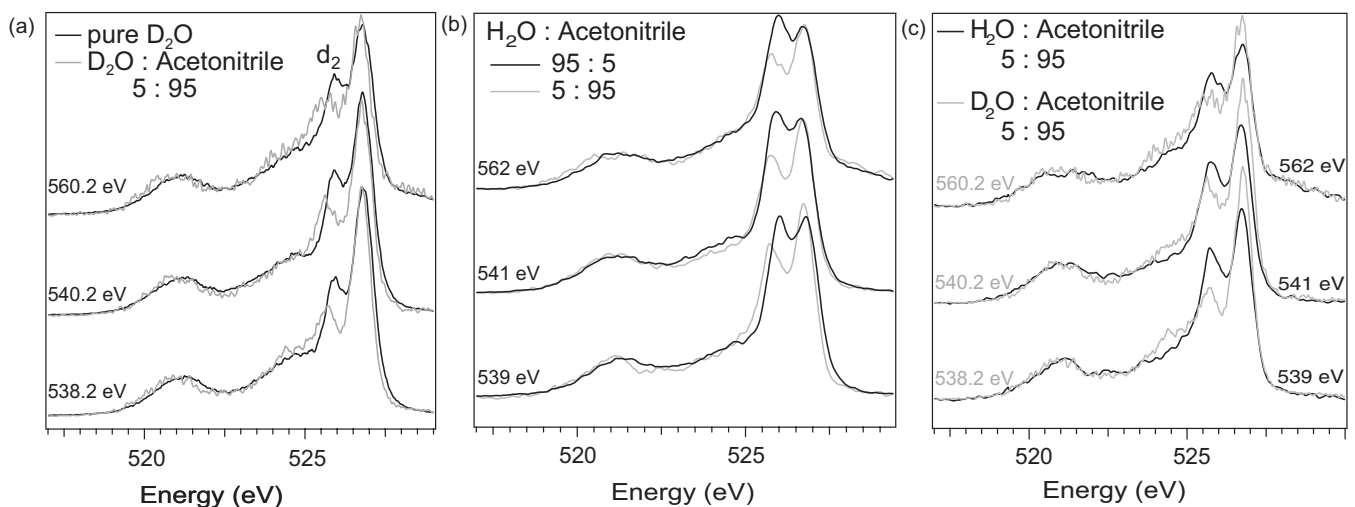

FIG. 2. X-ray emission spectra of (a) D_2O and of 5 vol % D_2O-acetonitrile mixtures, (b) H_2O and of 5 vol % H_2O-acetonitrile mixtures, and of (c) 5 vol % H_2O-acetonitrile mixtures and 5 vol % D_2O-acetonitrile mixtures for three different excitation energies.

at 526.7 eV in common. Led by the accepted interpretation of the gas-phase spectrum we associate these features with states derived from the bonding 1b_2 orbital and the "lone-pair" 1b_1 orbital, respectively. In the region between these two peaks we identify two features at around 524.4 eV and 525.6 eV,
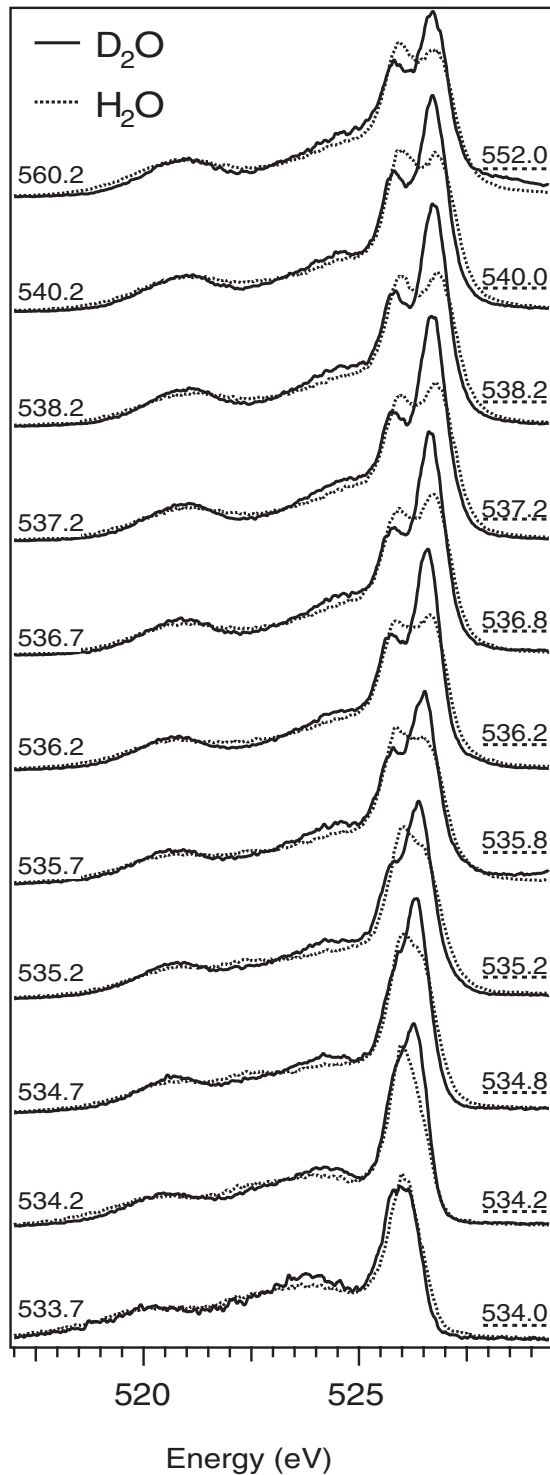

FIG. 3. Area normalized oxygen XE series of pure D$_2$O in comparison to pure H$_2$O obtained from a liquid microjet. The corresponding XA spectra are presented in Fig. 1. The excitation energies are indicated in eV on the left side for D$_2$O and on the right side for H$_2$O.

where especially the latter is very sensitive to changes in dynamics and coordination. Again led by the assignment in the XE spectra of the free molecule we associate the 524.4-eV feature with 3a_1-derived states, while we initially refrain from assigning an orbital symmetry to the 525.6-eV feature and label it d_2, in line with previous work.[8] We discuss the behavior in this energy range below.

The XE spectrum of the 5 vol % D$_2$O solution is shown in Fig. 2(a). We expect that this XE spectra of D$_2$O as a solute in acetonitrile should most closely mimic the spectra of a free molecule. Here the HB coordination as well as dynamics due to interaction with the surrounding is reduced. Indeed the spectra show similarities to the gas-phase XE spectrum of H$_2$O.[7,17] Whereas for XE spectra of free water molecules vibrational fine structure is expected if the experimental resolution allows,[18] in a HB liquid we expect that additional broadening due to the interaction with the environment will intrinsically smear out any vibrational fine structure.[19] Although our experimental resolution does not allow us to address this question here, the similarities to the gas-phase spectra suggest that internal vibrations are the main reason for the different widths of the 1b_1 and 1b_2 features also in the D$_2$O case.

The spectral change accompanying increased HB coordination [pure D$_2$O in Fig. 2(a)] is primarily an increase in intensity of the d_2 peak which simultaneously shifts towards higher energies. The enhancement is relative to all other features, and intensity is not redistributed from any specific part of the spectrum.

To address the role of dynamics we make the corresponding comparison of the spectra of 5 vol % H$_2$O in acetonitrile, with the spectra of the 95 vol % H$_2$O liquid [Fig. 2(b)]. Also in this case we observe an enhancement of the d_2 feature relative to all other features and a slight high-energy shift. The magnitude of this effect is similar for D$_2$O and H$_2$O, and we can therefore conclude that d_2 increases in intensity with increased HB coordination relative to all other features, almost independently of the nuclear dynamics.

We expect that the 5 vol % H$_2$O and 5 vol % D$_2$O solutions have rather similar and low HB coordination, and that the major difference is due to the faster nuclear dynamics as the deuterium atoms are replaced with hydrogen. Under this assumption we observe [Fig. 2(c)] that faster nuclear dynamics has a similar effect on the XE spectra as increased HB coordination: Intensity piles up in the d_2 region. However, a marked difference from the effect of increased HB coordination is that in this case the sharp 1b_1 peak significantly drops in relative intensity, as does, to some extent also, intensity in the 3a_1 region. The principal influence of the dynamics can accordingly be described as a redistribution of intensity from close-lying energy regions to d_2.

This intensity redistribution is very similar in the case when the spectra of neat H$_2$O and D$_2$O are compared (Fig. 3). We can therefore conclude that there is a redistribution of intensity primarily from the 1b_1 and 3a_1 regions to the d_2 feature due to nuclear dynamics, which is not much influenced by the HB coordination.

In the following we briefly speculate on the physical origin of the d_2 feature, considering experimental results based on other spectroscopic techniques. The XE transitions take place between states which are final states of the photoemission (PE)

process, and the interpretations of the results of the different methods must be consistent. In valence PE spectroscopy of H_2O as well as D_2O, emission from the $3a_1$ orbital is significantly broadened in the liquid, compared to the gas phase. The broadening is reminiscent of the Davydov splitting in ice, and has been fitted with two peaks 1.3–1.5 eV apart,[20,21] corresponding to bonding and antibonding interactions with the surrounding molecules. The PE spectra constitute clear evidence that the $3a_1$ orbital is mostly affected by condensation, and within state-of-the-art experimental accuracy the PE spectra of H_2O and D_2O are very similar.[20,22] It would be tempting to assign the XE structures in the d_2 energy region to changes in the $3a_1$ orbital under HB influence.

The phenomenology is, however, different in XE and PE. In PE the high-energy antibonding partner of the $3a_1$-derived double feature peak is situated 1.7 eV from the $1b_1$ peak, whereas the distance from the $1b_1$ peak to the d_2 feature here is only around 1.1 eV. Furthermore, this interpretation does not comply with the phenomenology when HB coordination increases. With increasing HB interaction we would expect a broadening/splitting of a $3a_1$ feature rather than a relative increase of the high-energy component.

The "two-motif interpretation"[6,7] assumes that intensity in the XE spectrum of liquid water in the region of the d_2 feature is due to emission from the $1b_1$ orbital of highly coordinated molecules, whereas the main part of the spectrum is due to less coordinated molecules. According to this interpretation, a large shift of the core level associated with HB formation gives rise to a correspondingly shifted XE spectrum. Thus, we would expect that not only d_2 but a full shifted XE spectrum grows as the HBs are switched on. When comparing spectra of 5 vol % D_2O and pure D_2O such a behavior is, however, not observed. The superposition of a low-energy shifted XE spectrum would imply, e.g., an enhancement of the low-energy flank of the $1b_2$ peak accompanying the growth of the 525.6-eV feature. In contrast a slight intensity increase on the high-energy flank is observed. Thus, the two-motif interpretation in this simple form is not supported by the present observations. It is consistent with the present data only if the XE spectrum of the coordinated molecules is very different from the spectrum of the less coordinated molecules.

In liquid water the PE peaks assigned to the $1a_1$ core level and the $1b_1$ lone-pair states are broad (FWHM $\approx$ 1.6 eV and $\approx$1.4 eV, respectively)[20,22] and rather structureless, whereas the XE transition between the two states shows a much sharper feature. Assuming that the core-level PE width originates in emission from a superposition of emission from various molecules shifted due to different HB conformations,[23] the narrowness in the XE spectrum could be understood if the shift of the $1b_1$ level due to interaction with the surrounding were similar to the core-level shift. Indeed, the binding energies of the two states both decrease upon condensation albeit with different magnitudes, 1.9 eV for the core level and 1.4 eV for the $1b_1$.[20,22] Therefore we assume that shifts due to increased coordination partially cancel, and that this is the principal reason for the observation of narrower $1b_1$ structures in XE than in PE spectra. Neglecting differences in excitation dynamics between PE and XE one would expect a low-energy shift of 0.5 eV in XE going from gas phase to liquid, which is not far from the observed 0.3 eV.[7] A low-energy feature

assigned to $1b_1$ states requires an additional XE shift of more than 0.7 eV. Such a shift, in principle, does not contradict the PE results because it can be accommodated in the broad PE peaks. A sharp $1b_1$ low-energy partner does require, however, that the shifts of the $1a_1$ and $1b_1$ levels are very different from the shifts leading to the main $1b_1$ peak associated with less coordinated molecules. In this case a low-energy shift of the core-level binding energy would *not* be accompanied by a corresponding $1b_1$ shift, but possibly the $1b_1$ binding energy may even shift in the opposite direction. For the "two-motif" interpretation this is still possible as the influence of the surrounding on $1b_1$ and $1a_1$ may have substantially different character.

As an alternative we note that the observed behavior may be explained beyond the one-center intensity model,[24,25] which is most often used in the interpretation of XE spectra of complex systems such as liquids. If "cross transitions" were prominent one would expect a low-energy shift for transitions from core hole states of molecules with high HB coordination or acceptor bonds broken (low BE) to $1b_1$ hole states on molecules with low coordination or donor bonds broken (high BE).[23] Such an interpretation would explain a $1b_1$ low-energy partner, and is in general consistent both with the observed XE and PE phenomenology. Since the first observation of cross transitions[26] their nature has been debated[27,28] and it has been argued that a degree of covalency is required to generate appreciable intensity. The intensity of cross transitions is difficult to assess beyond the one-center intensity approximation, especially in the case of a fluctuating HB liquid, and we hope that our suggestion will generate renewed theoretical interest.

The isotope effect consists primarily of a redistribution of intensity from the $1b_1$ and $3a_1$ peaks towards the d_2 region, and the present result shows that this redistribution occurs also when the HB influence is reduced in the acetonitrile solution. The major spectral differences induced by substitution are due to the difference in nuclear dynamics, and for the pure substances there have been major efforts to predict the spectra based on semiclassical models of the nuclear movement during the core hole lifetime.[7,29,30] One pertinent question in this context concerns how far the nuclei move before the decay, and it has been pointed out that intensity corresponding to d_2 almost coincides in energy with the expected intensity from dissociation fragments,[8] suggesting dissociation prior to emission. This interpretation is, however, not supported by simulations. Simulations differ in assigning $1b_1$ (Ref. [3]) or $3a_1$ (Ref. [29]) character to the d_2 feature. The present observation suggests that intensity is dynamically redistributed to this region from both $1b_1$ and $3a_1$ states.

This complex problem is notoriously difficult to treat using proper quantum mechanical theory. In time-independent Kramers-Heisenberg scattering formalism the nuclear wave-packet development is reflected in lifetime-vibrational interference, most readily demonstrated for diatomic molecules.[31,32] Recently, the dynamics of the HB proton in the water dimer has been treated in this way, demonstrating an isotope-dependent redistribution of intensity from the high-energy $1b_1$ feature towards lower energies,[30] a trend in line with observations. Although a quantum mechanical treatment is certainly called for, it remains to see to what extent the calculations of the

simple model system is relevant for the liquid phase. In a dipolar liquid, we expect that the interaction with the surrounding molecules intrinsically smears out any vibrational fine structure for electronically excited states.[19] In the condensed phase the spectral consequences of dissipation of vibrational energy have been discussed over the years,[10,33–35] and any counterpart to phonon damping[10] in the liquid will lead to an apparent loss of coherence and limit the applicability of a local Kramers-Heisenberg treatment.

IV. CONCLUSION

The use of a liquid microjet allows us to unambiguously measure XE spectra of dilute samples. In contrast to experiments based on ultrathin membranes the present spectra are free from distortions due to possible interactions with and contamination of the membranes. Due to the fast sample replenishment the influence of photolysis is minimized. A comparison of XE spectra of liquid H₂O and D₂O, in their pure form and as solutes in acetonitrile, allows us to identify and separate two distinctly different effects. First, one distinct spectral feature grows when HB coordination increases, rather independent of nuclear dynamics. Second, a redistribution of intensity from the peak associated with the $1b_1$ and $3a_1$ orbitals to the energy region of the HB feature is observed when nuclear dynamics becomes faster, rather independent of HB coordination. The consequences for current interpretations of the XE spectra of liquid water are briefly discussed, and we hope that the results will inspire theoretical developments.

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