P H Y S I C A L   R E V I E W   L E T T E R S

Isotope and Temperature Effects in Liquid Water Probed by X-Ray Absorption and Resonant X-Ray Emission Spectroscopy

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High-resolution x-ray absorption and emission spectra of liquid water exhibit a strong isotope effect. Further, the emission spectra show a splitting of the $1b_1$ emission line, a weak temperature effect, and a pronounced excitation-energy dependence. They can be described as a superposition of two independent contributions. By comparing with gas phase, ice, and NaOH/NaOD, we propose that the two components are governed by the initial state hydrogen bonding configuration and ultrafast dissociation on the time scale of the O $1s$ core hole decay.

The molecular structure of liquid water is very complex and remains a subject of ongoing vivid discussions [1–4]. A water molecule can have up to four hydrogen bonds (HBs) to neighboring molecules, preferably arranged in a tetrahedral configuration, as in ice Ih. Upon melting, the rigid HB network becomes dynamic, and some of the bonds break, but the exact nature of this process and the local structure of liquid water are still under discussion despite tremendous experimental and theoretical efforts [2–10].

Recently, well-established techniques for water studies such as neutron and x-ray scattering and infrared spectroscopy (see, e.g., [2,11]) were complemented by novel, synchrotron-based methods, viz., x-ray absorption (XAS) and resonant x-ray emission spectroscopy (XES) at the O K edge. These spectroscopies provide information on the unoccupied (XAS) and occupied (XES) electronic structure of liquid water. However, the interpretation of the spectra is quite difficult and relies mostly upon molecular dynamics simulations and first-principle calculations [2,3,5,7,9,10,12]. In XAS, absorption resonances related to the unoccupied $4a_1$ and $2b_2$ orbitals were observed, with the pre- and post-edge regions considered as signatures for distorted and fully coordinated HB configurations of water molecules, respectively [2,5,7,10]. In XES of liquid water, three emission peaks related to the occupied $1b_2$, $3a_1$, and $1b_1$ orbitals were recorded [13–15], as was the case for gas phase water [16] and ice [17]. As compared to gas phase, the emission peaks of liquid water and ice are significantly shifted and broadened due to the HB network [13,14]. Further, high-resolution XES (HRXES) spectra of ice show a clear splitting of the $1b_1$ orbital [17], while spectra of gas phase water [16] are dominated by a single $1b_1$ peak. As will be shown in this Letter, HRXES of liquid water clearly exhibits a splitting of the $1b_1$ peak similar to that in

ice. Furthermore, it is found to be sensitive to changes in a variety of physical parameters (discussed below).

Generally, thermodynamic and structural properties of normal (H_2O) and heavy (D_2O) water are slightly different [18]. In particular, it is believed that H_2O is slightly more disordered than D_2O at the same temperature [11,18,19]. This difference is claimed to be comparable to a $3.6\,°C$ temperature shift in pure H_2O at $45\,°C$, which increases to a $7.1\,°C$ temperature shift at $6\,°C$ [11]. For XAS, which is considered to be sensitive to the distribution of local HB configurations in liquid water [2,5,7,10], no isotope effect has been reported so far. For XES, noticeable isotope differences in form and spectral weight of individual emissions were observed and explained by different ultrafast core-excited-state dynamics of hydrogen and deuterium [15], similar to the case of ice, which shows ultrafast dissociation even for nonresonant excitation [20], while gas phase water only dissociates upon resonant excitation into the $4a_1$ orbital [21].

In this Letter, we report an isotope effect of liquid water in XAS and HRXES spectra and discuss the temperature and excitation-energy dependence in XES. The observed fine structure and dependencies can be interpreted as a combination of initial HB configurations and fast dissociation processes.

In addition to liquid H_2O and D_2O, we measured XAS and XES spectra of NaOH in H_2O and NaOD in D_2O solutions (both 25 wt%). Furthermore, we recorded XES spectra of amorphous H_2O and D_2O ice, grown on stainless steel below 200 K, which were used as reference to interpret the data for liquid water. All spectra were acquired at beam line 8.0.1 of the Advanced Light Source (ALS). XAS data were recorded in the total fluorescence yield (TFY) mode with a channeltron-based detector, while XES spectra were measured with the Rowland-circle spectrograph of

the SXF end station ($E/\Delta E > 1000$ in the present experiments). Note that this energy resolution is noticeably better than in previous liquid water XES studies [13–15]. We used a home-built Teflon flow cell (volume: 3 μl) [22] with a 100 nm thick Si$_3$N$_4$ membrane (Silson). To avoid local heating and x-ray damage effects, water was steadily pumped through the cell, with its content renewed 10–20 times per second. Further increase of the liquid flow rate or variation of the primary photon flux did not result in any spectral changes, ruling out contributions from long-living irradiation-induced species. The pressure in the cell was slightly lower than atmospheric, with a lower limit of 690 mbar. The water temperature was controlled by a thermostat and measured directly at the back side of the cell. Special care was taken to minimize contributions of the membrane to the XAS and XES spectra, including control measurements of oxygen-free liquids and with SiC membranes (NTT Advanced Technology Co.). In particular, a beam-induced oxidation of the inside surface of the Si$_3$N$_4$ membrane can lead to time-dependent and spuriously enhanced XES intensity at 526.7 eV (i.e., at the energy of the low-energy $1b_1$ component discussed below) [22]. In our case, spectral contributions related to the membrane are negligible.

In Fig. 1, we present O K-edge XAS spectra of liquid H$_2$O, D$_2$O, and NaOH/OD solutions ($T = 277$ K). The spectrum of H$_2$O shows typical pre-edge ($\sim$535 eV) and edge ($\sim$537 eV) features observed previously by other authors [2,3,5]. Because of self-absorption effects, the pre-edge feature is overemphasized as compared to electron yield spectra [8]. The spectrum of D$_2$O exhibits the same structure as that of H$_2$O but shows a significant
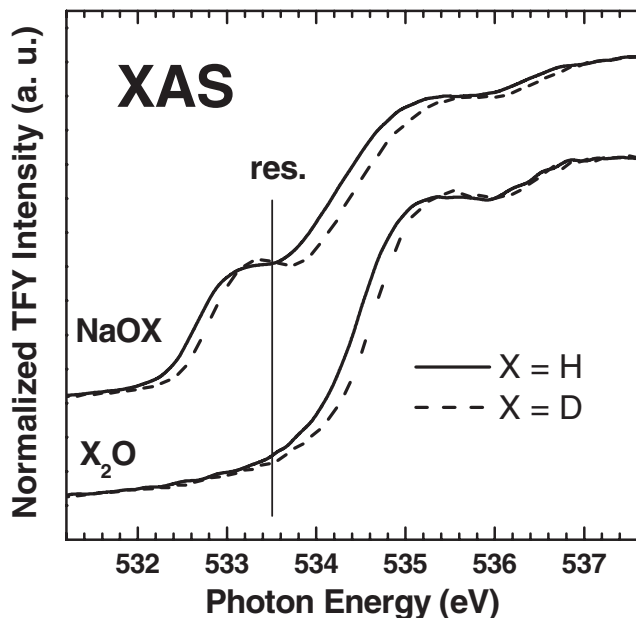
($\sim$160 meV) blue shift of the pre-edge peak and a smaller ($\sim$30–60 meV) shift of the absorption edge.

The NaOH/NaOD solutions exhibit pre-edge and edge features similar to H$_2$O and D$_2$O. In addition, both show a pre-pre-edge feature at $\sim$533 eV, stemming from the lowest unoccupied molecular orbital ($4\sigma^*$) of OH$^-$. Comparing the spectra of NaOH and NaOD, one finds a blue shift of $\sim$140, $\sim$200, and $\sim$175 meV for the pre-pre-edge, pre-edge, and edge features, similar to that of H$_2$O and D$_2$O. The observation of the isotope effect for both NaOH- and H$_2$O-related absorption resonances suggests its general character for water and water-based solutions. Note that such a shift is not present in gas phase XAS of H$_2$O and D$_2$O [23], which gives direct evidence that it is mainly correlated to differences in the local HB configuration of the liquid phase and not sufficiently explained by differences of zero-point energy. We speculate that this might be due to energetic differences in the initial state hydration shell between H$_2$O and D$_2$O.

In Fig. 2, we present resonant ($h\nu = 534.6$ and 536.3 eV) and nonresonant ($h\nu = 550.1$ eV) XES spectra of liquid H$_2$O and D$_2$O and resonant spectra of NaOH/NaOD solutions excited at the pre-pre-edge peak in the XAS spectrum (see Fig. 1). Since the latter excitation
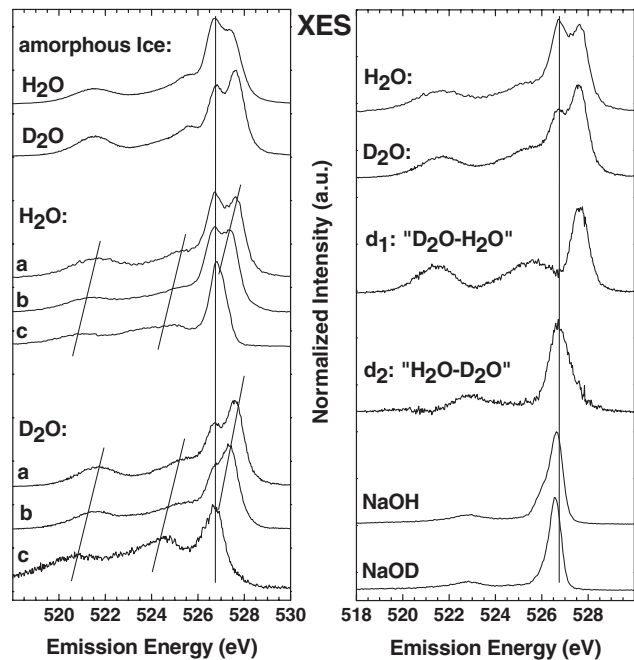

FIG. 1. O K-edge XAS spectra of liquid H$_2$O/D$_2$O and NaOH/OD solutions, acquired at $T = 277$ K.

FIG. 2. From top to bottom, left: nonresonant ($h\nu = 550.1$ eV) XES spectra of amorphous H$_2$O and D$_2$O ice, nonresonant ($h\nu = 550.1$ eV, labeled a), and resonant ($h\nu = 536.3$ and 534.6 eV, labeled b and c) XES spectra of liquid H$_2$O and D$_2$O; right: nonresonant spectra of H$_2$O and D$_2$O, differences between these spectra (d_1: D$_2$O-0.62 H$_2$O, d_2: H$_2$O-0.87 D$_2$O), and resonant spectra of NaOH/OD solutions ($h\nu = 533.5$ eV). The spectra of the liquids were acquired at $T = 277$ K, those of ice at $T \sim 100$ K.

occurred below the water absorption onset, the resonant
spectra of the NaOH/NaOD solutions do not contain no-
ticeable contributions from intact water molecules and can
be exclusively related to OH^- and OD^- ions. The XES
spectra of H_2O and D_2O exhibit characteristic emission
peaks, related to fluorescent decay from the three occupied
oxygen $2p$–derived molecular orbitals, $1b_2$, $3a_1$, and $1b_1$,
into the oxygen $1s$ core hole [16,17].

A novel feature of the HRXES spectra of liquid H_2O and
D_2O is the splitting of the $1b_1$ peak into two individual
components with similar full widths at half maximum, as
also observed in HRXES data of amorphous ice (see Figs. 2
here and in [17]). Comparing the XES spectra for excita-
tion energies between 534.6 and 550.1 eV (see Fig. 2), we
find that the low-energy (LE) component does not shift
with varying excitation energy, whereas the high-energy
component and the $1b_2$ and $3a_1$ emissions exhibit a notice-
able blue shift between 534.6 and 537.2 eV. At lower
energy resolution, such a behavior would result in one
broad $1b_1$ feature with different line shapes (widths) at
different excitation energies, as has been observed before
for liquid H_2O [13–15].

Comparing the XES spectra of liquid H_2O and D_2O in
Fig. 2, we find a pronounced isotope effect: the relative
intensity of the LE $1b_1$ component is significantly lower
for D_2O than for H_2O. Further, the intensity ratio between
both $1b_1$ components changes with temperature as shown
for H_2O in Fig. 3: the relative intensity of the LE peak
slightly decreases with increasing temperature.

The "splitting" of the $1b_1$ emission into two compo-
nents has not been predicted by any theoretical simulation
of XES spectra of liquid or solid H_2O/D_2O [13–15,24],
which means that one cannot use any of the available
theoretical models to account for this phenomenon.
Furthermore, the following experimental findings must
be explained. First, we observe a huge isotope effect with
a relative enhancement of the LE $1b_1$ peak for H_2O com-
pared to D_2O. Second, we find a relatively weak tempera-
ture effect for both D_2O and H_2O, with the LE $1b_1$ peak
decreasing with increasing temperature. Third, the LE $1b_1$
peak can be neither found for gas phase water [16] nor
observed in liquid water photoemission (PES) spectra [25].
Based on the temperature dependence of the LE $1b_1$ peak,
one would associate this feature with water molecules in a
highly coordinated HB environment. In this case, one
would expect the LE component of D_2O to be slightly
enhanced as compared to H_2O, since D_2O has a more
ordered structure. However, the observed LE $1b_1$ peak of
D_2O is substantially smaller than that of H_2O. Thus, both
magnitude and direction of the observed isotope effect
clearly show that an initial state description alone is not
sufficient to explain the results.

Therefore, we conclude that not initial but rather final
state effects have to be predominantly considered for a
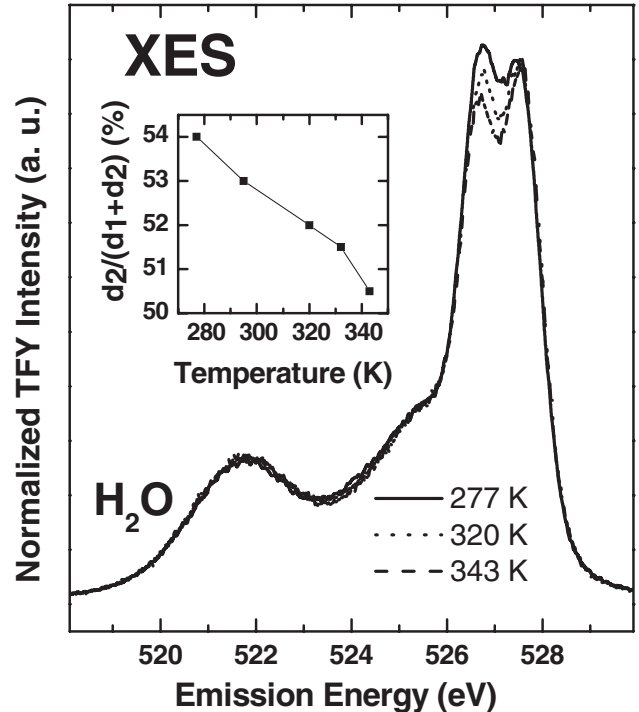description of our findings. Generally, XES spectra repre-

FIG. 3.   Nonresonant ($h\nu = 550.1$ eV) XES spectra of liquid
H_2O at different temperatures, normalized to the maximum of
the high-energy component of the $1b_1$ peak. Inset: relative
contribution of d_2 (see Fig. 2) as a function of temperature.

sent an average over different geometric configurations of
the excited molecule during the emission process [15,20].
The final state leading to the LE $1b_1$ peak obviously
requires proton dynamics during the core hole lifetime
(3.6 fs, [24]), since it is absent in PES [25] and significantly
reduced in the D_2O XES spectra. Furthermore, its absence
in gas phase XES [16] (and the observed decrease at higher
temperatures) suggests that the HB network plays an im-
portant role. Such influences of the initial state HB coor-
dination on the O-H bond dynamics have indeed been
predicted theoretically [15].

Since the bond dynamics show a strong isotope (H vs D)
dependence, we have analyzed the difference between the
XES spectra of D_2O and H_2O by subtracting one spectrum
from the other with a suitable weight factor. Optimized
values for the weight factors were determined by subtract-
ing a maximal amount of one spectrum from the other
while disallowing the residual to become negative at any
energy. The resulting difference spectra for the nonreso-
nant case, which we denote as d_1 ($D_2O - H_2O$) and d_2
($H_2O - D_2O$), are shown in Fig. 2 (right panel). Now, the
spectra of H_2O and D_2O can be described as a sum of d_1
and d_2, differing only by the weight ratio d_1/d_2, which is
1.08 for H_2O and 1.99 for D_2O at 277 K. When heating up
to 343 K (Fig. 3), this ratio increases to 1.28 for H_2O and
2.38 for D_2O. Most importantly, the above subtraction
procedure is applicable to all resonant HRXES spectra of

H_2O and D_2O with excitation energies between 534.6 and 550.1 eV, revealing a blue shift of the entire d_1 component of about 0.7 eV at excitation energies between 534.6 and 537.2 eV, while the d_2 component shows no shift at all. Except for this blue shift of d_1 in the resonant spectra, principal components very similar to those of the nonresonant case are obtained. d_1 exhibits three peaks, resembling the $1b_2$, $3a_1$, and $1b_1$ emissions in gas phase XES [16] and liquid water PES [25]. We thus interpret this component to be representative for intact water molecules. The d_2 component has no counterpart in liquid water PES and must therefore be specific for the dynamic processes inherent to the XES technique. d_2 exhibits only the LE $1b_1$ peak and a low-intensity component at ~523 eV. This spectrum is very similar to the spectra of NaOH/NaOD solutions in Fig. 2.

Based on the large isotope effect, the similarity of d_1 to the gas phase H_2O XES and liquid H_2O PES, and the resemblance of d_2 to the NaOH spectrum, we derive a phenomenological model which gives a physical meaning to d_1 and d_2 and is consistent with all experimental data. We propose that ultrafast dissociation occurs in liquid water, i.e., that a proton is removed during the core hole lifetime. Dissociation can lead to two predominant spectral components in XES [21,26], namely, a molecular and a dissociated fraction. Accordingly, d_1 is representative for the molecular species, while d_2 represents the dissociated species as derived from its similarity to OH^- XES. For NaOH/NaOD, nonresonant excitation of an OH^- ion yields a neutral OH species with a filled valence shell. Radiative decay transforms this species to a neutral OH radical. For nonresonantly excited water molecules which undergo ultrafast dissociation, the remaining OH is the same precursor of an OH radical as in the case of NaOH, again yielding a d_2 spectrum. Note that d_2 exhibits additional intensity at emission energies above 527.3 eV compared to NaOH/NaOD. This could be due to molecular species in intermediate states of the dissociation process.

We believe that our model is valid not only for liquid water but for ice as well, for which both a splitting of the $1b_1$ emission [17] and ultrafast dissociation [20] were observed. Considering that the splitting is not seen in the gas phase but in the condensed (ice or water) state only, and that the HRXES spectrum of crystalline ice is clearly dominated by the LE $1b_1$ peak [17] (i.e., by d_2), we deduce that the ultrafast dissociation is strongly facilitated by the presence of intact HBs, in agreement with theoretical results [15,20] and with the observed decrease of d_2 with increasing temperature.

In summary, we have observed significant isotope effects in both XAS and XES of liquid water. HRXES spectra of liquid H_2O and D_2O exhibit a pronounced splitting of the $1b_1$ emission and can be described as a superposition of two individual components. We ascribe one of these components to intact water molecules and relate the second to ultrafast molecular dissociation which is promoted by intact HBs of the probed water molecule. This tentative interpretation explains the observed splitting, the isotope, temperature, and excitation-energy effects, and XAS and XES spectra for NaOH/NaOD solutions.

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