

Simon Schreck,^{1,2,a)} Philippe Wernet^{1,b)}

¹ *Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str. 15, 12489 Berlin, Germany*

² *Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Strasse 24/25, 14476 Potsdam, Germany*

The effects of isotope substitution in liquid water are probed by x-ray absorption spectroscopy at the O K-edge as measured in transmission mode. Confirming earlier x-ray Raman scattering experiments, the D₂O spectrum is found to be blue shifted with respect to H₂O and the D₂O spectrum to be less broadened. Following the earlier interpretations of UV and x-ray Raman spectra, the shift is related to the difference in ground-state zero-point energies between D₂O and H₂O while the difference in broadening is related to the difference in ground-state vibrational zero-point distributions. We demonstrate that the transmission-mode measurements allow for determining the spectral shapes with unprecedented accuracy. Owing in addition to the increased spectral resolution and signal to noise ratio compared to the earlier measurements, the new data enable the stringent determination of blue shift and broadening in the O K-edge x-ray absorption spectrum of liquid water upon isotope substitution. The results are compared to UV absorption data and it is discussed to which extent they reflect the differences in zero-point energies and vibrational zero-point distributions in the ground-states of the liquids. The influence of the shape of the final-state potential, inclusion of the Franck-Condon structure and differences between liquid H₂O and D₂O resulting from different hydrogen-bond environments in the liquids are addressed. The differences between the O K-edge absorption spectra of water from our transmission-mode measurements and from the state-of-the-art x-ray Raman scattering experiments are discussed in addition. The experimentally extracted values of blue shift and broadening are proposed to serve as a test for calculations of ground-state zero-point energies and vibrational zero-point distributions in liquid H₂O and D₂O. This clearly motivates the need for new calculations of the O K-edge x-ray absorption spectrum of liquid water.

I. INTRODUCTION

The differences between light and heavy water H₂O and D₂O have ever since been addressed experimentally to study the effect of the quantum nature of hydrogen on various properties of water. In particular, the bulk structure of the liquid [1, 2], the structure of water at interfaces [3], the thermodynamical properties of water [4], the translational and rotational motions in liquid water [5] and the hydrogen-bond (H-bond) environment [6, 7] and its ultrafast dynamics [8] were investigated in light of these quantum effects.

^{a)} Current Address: Department of Physics, AlbaNova University Center, Stockholm University, SE-10691 Stockholm, Sweden.

^{b)} Author to whom correspondence should be addressed. Electronic mail: wernet@helmholtz-berlin.de.

Such experimental results can serve as benchmark tests for theoretical treatments of quantum effects in hydrogen bonding (H-bonding) in water [9, 10] and H-bonds in general [11]. Quantum effects are expressed in the electronic and geometric structure of the liquid and may be related to the structure and the properties of liquid water in general [12, 13].

One of the earliest experimental investigations addressing the manifestation of nuclear quantum effects in the electronic structure of water was performed by Franck and Wood where the ultraviolet (UV) absorption spectra of gaseous light and heavy water were measured [14]. This investigation also set the stage for the interpretation of the spectral differences: The blue shift of the UV absorption bands in heavy compared to light water were explained by the difference in the vibrational zero point energies which we refer to in here as the ground-state zero point energy (ZPE) difference (ΔZPE). The lower ZPE in D_2O compared to H_2O is expressed in a larger transition energy in D_2O and the measured shift [15, 16] can be directly related to the ΔZPE when assuming a transition from a bound to a dissociative state and a flat potential energy curve in the excited dissociative state [14]. Another representative manifestation of the isotope difference in the electronic structure of water was detected by Compton et al. in the energy-loss function or the electron-impact threshold excitation spectrum where the broader peaks in H_2O were related to the broader square of the vibrational ground-state wavefunction [17]. This broadening effect was verified later [18] and is referred to here as the difference in ground-state zero point spatial probability distribution (ΔZPD) where the ZPD is more confined in D_2O compared to H_2O and the line width is correspondingly smaller [17]. To date, the ΔZPE shift and the ΔZPD broadening in the UV absorption spectrum of liquid water are investigated experimentally [19] and theoretically [20]. This shows the importance to accurately quantify these effects to enable a correct interpretation of the fundamental processes upon photoionization of water and the related hydrated electron [21-24].

Over the last years, x-ray spectroscopy and x-ray scattering have been used increasingly to study liquid water [1, 6, 25-37]. The questions occur about how nuclear quantum effects are expressed in the x-ray spectroscopic observable and, in particular, how the effects of ΔZPE and ΔZPD can be transferred from the UV to the x-ray regime. This clearly motivates addressing isotope effects in liquid water with x-ray absorption spectroscopy (XAS) at the oxygen (O) K-edge. It was found indeed that the lowest-energy resonance in the O K-edge absorption spectrum (the so called pre-edge peak) at 535 eV shifts to higher absorption energies in D_2O and that this resonance is sharper in D_2O compared to H_2O [1, 6, 36]. Following the interpretation of the UV absorption spectra, these observations were readily attributed to the effects of ΔZPE and ΔZPD [1, 6]. In order to test the limits of this concept in the x-ray regime it is highly desirable to determine as accurately as possible shift and broadening of the pre-edge peak in the O K-edge absorption spectrum of liquid water. This could further help scrutinizing XAS as a method for probing H-bonded liquids, it could help validating theoretical approaches for calculating

the O K-edge absorption spectrum of liquid water [38-45] and it could allow for relating the x-ray spectroscopic observables to the properties of liquid H₂O and D₂O by, in particular, potentially enabling to correlate quantum effects, structure and density of states in the liquids.

The O K-edge absorption spectrum of liquid water was measured before by x-ray Raman scattering (XRS), fluorescence-yield XAS (FY-XAS) and by XAS in transmission mode. The so far most accurate determination of the shift and broadening of the pre-edge peak in the spectrum related to ΔZPE and ΔZPD were achieved with XRS [1, 6, 36]. FY-XAS of liquid H₂O and D₂O [26, 29, 37] was often analyzed alongside with investigating the x-ray emission spectrum at the O K-edge of light and heavy liquid water [1, 26, 27, 29, 34, 35, 37]. FY-XAS, however, suffers from well-known saturation effects which result in inaccurate determination of the spectral shape and, hence, the pre-edge peak shift and broadening cannot be accurately determined with FY-XAS. Transmission-mode XAS is the most direct way to determine the O K-edge absorption spectrum of water [46-53] but liquid H₂O and D₂O have not been addressed yet. Compared to FY-XAS we can expect the pre-edge peak shift and broadening to be determined more accurately with transmission-mode XAS as the spectral shape can be determined reliably. Compared to XRS we can expect better spectral resolution and, potentially, a better signal to noise ratio due to the higher cross section of XAS compared to XRS. In this work we show and discuss new transmission-mode XAS data for liquid H₂O and D₂O. The higher spectral resolution and the better signal to noise ratio compared to the state-of-the-art XRS spectra [1, 6, 36] enable a more accurate determination of the zero-point effects relating ΔZPE and ΔZPD and the pre-edge peak shift and broadening in the O K-edge x-ray absorption spectra. We furthermore compare in detail the respective XAS and XRS spectra and discuss possible reasons for their differences.

II. EXPERIMENTAL

We utilized a specialized sample holder to prepare ultra-thin liquid films of H₂O and D₂O of a few hundred nanometer thickness between two x-ray transparent silicon nitride membranes. To record the x-ray absorption spectra we measured the x-ray intensity transmitted through the liquid film and the silicon nitride membranes as a function of the incident photon energy. For a correct measure of the incident photon flux we measured the intensity transmitted through a pair of silicon nitride membranes with no liquid in between. The specialized sample holder, its performance as well as the data treatment are described and demonstrated in detail in Schreck *et. al.* [52].

The measurements were performed at the dipole beamline PM3 at the synchrotron radiation source BESSY II of the Helmholtz-Zentrum Berlin. Since we recorded spectra of H₂O and D₂O back to back at the same beamline using identical

monochromator settings, the relative energy scale of the H₂O and D₂O spectra is very accurate and the uncertainty can be regarded more than an order of magnitude smaller than the spectral shifts discussed in this work. The absolute energy scale was calibrated by setting the pre-edge peak in the H₂O spectrum to 535 eV [1, 54]. The bandwidth of the incident photon energy and thus the spectral resolution was about 250 meV at 535 eV.

We used D₂O purchased from Sigma Aldrich as received and deionized H₂O. Special care was taken to minimize the exposure to air and humidity for D₂O.

III. RESULTS AND DISCUSSION

The spectra of liquid H₂O and D₂O as measured in transmission mode are displayed in Figure 1. To the best of our knowledge this represents the first direct comparison of light and heavy liquid water spectra measured with XAS at the O K-edge. The spectra are shown on an extended incident photon energy range of up to 600 eV in Figure 1 (a) with their difference in Figure 1 (b). Because it is virtually impossible to prepare liquid water samples with the exact same thickness down to the nm range with our membrane-based sample holder, and because the measured transmission (not the absorption cross section) depends on the sample thickness, the absorption spectra need to be normalized in order to make them comparable. The normalized absorption that is calculated from the measured transmission is then plotted as relative intensities in arbitrary units. In principle, two ways of normalizing the spectra are viable: Normalized to the area of the near-edge region between 530 eV and 550 eV (area normalization) or normalization to the edge-jump at a photon energy far above the near edge, hence at 580-600 eV e.g. (edge-jump normalization, where the intensity oscillations due to the extended x-ray absorption fine structure, EXAFS, are small compared to our experimental accuracy) [48, 52]. We note that normalization is crucial to accurately determine small effects like those induced by isotope substitution in water. Determination of such small effects is facilitated here with the membrane-based sample holder that allows preparation of thin liquid water films with stable thickness over hours. We found that our spectra do not depend considerably on whether normalized at the edge jump or by area. Still, because a priori we could not exclude that the near-edge area is changed by isotope substitution we decided for edge-jump normalization.

With the difference spectrum (D₂O-H₂O) in Figure 1 (b) we show that isotope substitution effects are clearly concentrated to the near-edge region and, more specifically, to photon energies of 534-540 eV. Indeed, the near edge area in the spectrum is changed as evidenced by the exclusively negative difference. The zoom into the near-edge of the spectra in Figure 1 (c) and their difference in Figure 1 (d) now illustrates the high quality of our XAS data and motivates analyzing the effects of ΔZPE

and ΔZPD in more detail. For this we first concentrate on the ΔZPE shift of the pre-edge peak at 535 eV and analyze the ΔZPD broadening later. As expected from the simple consideration of the ΔZPE shift effect [14] in the UV absorption spectra and as measured before with XRS [1, 6] we observe the pre-edge peak to blue shift when going from liquid H_2O to D_2O . However, we also note that this is not simply a blue shift as in this case a difference spectrum with equally intense negative and positive intensities below and above 535 eV, respectively, was to be measured. The expected positive difference intensity at above 535 eV could be compensated for by the apparent blue shift of the main edge (main peak in the spectrum at around 537-538 eV) and the corresponding negative difference intensity at 536 eV. However, also at the main edge we do not observe the negative/positive differential spectrum as expected from a simple blue shift. This already points to limitations of the simple concept of relating ΔZPE to these blue shifts in the O K-edge x-ray absorption spectra. This is further illustrated by comparing the blue shift extracted from UV absorption to the shift in XAS. Before this we note that UV absorption experiments resulted in different values of 110 to 200 meV. Franck and Wood determined a shift of between 110 and 150 meV in gaseous water [14] while in the liquid at ambient conditions the early studies resulted in values of 120 meV [16], 160 meV [15], 140-160 meV [18] while a more recent study gave 200 meV [19]. Recent calculations of the joint density of states serving as an approximation to the UV absorption spectrum confirmed the 200 meV shift [20]. With the earlier XRS data an independent determination of the shift of the O K-edge XAS was not possible but the order of magnitude of the XAS pre-edge shift was found to agree with the UV absorption results. Here we aim at independently determine the shift in the O K-edge absorption spectrum and this is demonstrated with Figure 2. We plot in Figure 2 (a) the first derivatives of the liquid H_2O and D_2O spectra in the near edge region. As expected, they pass through zero at 535, 538 and 540 eV corresponding to the aforementioned pre-edge and main-edge peaks and the previously discussed post-edge peak at 540 eV [1, 54, 55]. The blue-shift of the liquid D_2O spectrum with respect to the liquid H_2O spectrum is clearly apparent and can be easily determined for the pre-edge by shifting the derivative of D_2O such that the root coincides with H_2O (Figure 2 (b)). We find for the so determined shift at the pre-edge peak a value of 117 meV and, taking into account uncertainties related to normalization of the spectra and to fitting the energy regions around the roots with linear functions, we arrive at a blue shift of 120 ± 20 meV for the pre-edge shift. This value is somewhat smaller than the 200 meV shift based on recent UV absorption spectra. Our data however also show that the shift determined with the main edge peak is not 120 meV: The root of the D_2O derivative shifted by 117 meV at the main edge does not coincide with the root of the H_2O derivative as illustrated in Figure 2 (c). Linear fits of the H_2O and D_2O derivatives in the energy region displayed in Figure 2 (c) result in a blue shift of the main edge in D_2O with respect to H_2O of 200 ± 20 meV now in perfect agreement with the UV absorption data. These results represent the first stringent determination of the ΔZPE related blue shift in the liquid water x-ray absorption spectrum at the

O K-edge upon isotope substitution. Within our experimental uncertainties we find no shift at the post edge at 540 eV. We also note that the ΔZPD related broadening effect for the pre-edge peak is already visible in Figure 2 (b): The derivative of the D_2O spectrum is steeper than that of the H_2O spectrum as a result of the narrower square of the vibrational ground-state wavefunction in D_2O or, correspondingly, the broadening of the H_2O pre-edge peak. This is analyzed in greater detail later and we stay for the moment with the ΔZPE related blue shift. The shift at the pre-edge peak apparently is considerably different from the shift at the main edge and the shift determined from UV absorption and we attempt to give a qualitative explanation with Figure 3 by considering the very basic approximations in relating ΔZPE and the spectral shift [14].

Following the graphical depiction for explaining the ΔZPE related blue shift in the O K-edge x-ray absorption spectrum of water by Nilsson *et al.* [1] we plot qualitative potential energy curves for the pre and main edges of liquid water in Figures 3 (a) and (b), respectively. XAS measures the energy difference (the vertical transition energy or the “Franck-Condon vertical transition”) between the electronic ground state (initial state) and the final (core-excited) state of the x-ray absorption process. Although the nature of the reaction coordinate in the core-excited XAS final states is not precisely known as exact potential energy curves are missing for liquid water, it can be concluded from previous discussions [1] and from a detailed study of the water dimer [44] that all core-excited XAS final states are dissociative or only weakly bound. Hence the reaction coordinate in Figure 3 for both the pre- and the main edge peak most likely is the intramolecular O-H/O-D distance. We concentrate our analysis here on this coordinate but note that a discussion of ground-state fluctuations of structures in liquid water would have to account for other distances and angles such as the H-O-H (D-O-D) angle in bending modes as well [9]. Following the reasoning in [1] we note that there is no ΔZPE in the core excited states because they are dissociative for both the pre and the main edge. A shift between the H_2O and D_2O spectra can thus be related to ground-state ΔZPE as illustrated in Figure 3. The fact that the final state potentials in UV absorption are dissociative as well makes the values from XAS and UV absorption comparable [1]. We believe, however, that the observed differences of the shifts at the pre and main edges points to the limitations of this concept. First, and as noted before [1, 14, 18], the exact shape of the final state (core-excited in our case) matters and, second, a more detailed description should take into account a calculation of the Franck-Condon factors of the transition. We start by elaborating the first aspect.

Depending on the shape of the core-excited state potential energy curve, we can qualitatively predict that the XAS transition energy can be smaller than the ground-state ΔZPE (for a particularly steep or steeply curved potential, Figure 3(a)) or larger (or, equally possible, identical for a less steep potential, Figure 3(b)). Note that for both scenarios the XAS transition energy in D_2O is still larger than in H_2O . What seems to matter for the line shift is the shape of the final state potential energy curve

while the slope (without changing the shape) leaves the shift largely unaffected on the 100-200 meV scale discussed here. This can be easily confirmed by evaluating the line shift with the potential from Figure 3 (b) and varying its slope. This qualitative depiction of the shapes of the core-excited state potentials could explain the different shifts at pre and main edges in the O K-edge x-ray absorption spectrum of water with a steeper (less steep) potential at the pre (main) edge. Indeed there is experimental and theoretical indication for this qualitative difference of the potential curves. O K-edge XAS of liquid water and ice measured by detecting the proton (H^+) yield indicates how efficiently the water molecules are de-protonated for the various photon energies in the spectrum. An increase of the proton-yield XAS intensity compared to the absorption cross section could thus be interpreted to be an indirect measure of the dissociative nature of the pre- and main-edge core excited states. In both liquid water and ice a much stronger pre-edge enhancement compared to the main-edge enhancement in proton-yield XAS was found with respect to the absorption cross section [56-59]. Irrespective of the concrete H-bond environment one could thus conclude that the core-excited states at the pre edge are more dissociative than at the main edge in line with the interpretation of our findings. This is also in agreement with the assignment of the transitions at the pre-edge peak to strongly antibonding molecular orbitals with $4a_1$ character [1, 54]. And it is in agreement with the theoretically derived notion that the core-excited states at the main edge have Rydberg-like character with, correspondingly, spatially more extended orbitals compared to the pre edge [43].

As noted before (second aspect to account for in a more detailed interpretation of the ΔZPE related blue shift), the vibrational structure in the core-excited states and in particular the Franck-Condon factors are not accounted for in the so far used simple conceptual depiction. Often, it already represents a challenge to theory to correctly describe the core-excited potentials. In addition, usually it is not necessary to accurately treat the Franck-Condon structure in XAS and hence this is often omitted for simplicity while first attempts have been realized for gaseous N_2 [60] and the water dimer [44, 61] e.g..

Given the agreement of our main-edge shift of 200 meV with the recently calculated shift based on the joint density of states of 200 meV the question occurs whether the agreement is coincidental or whether there may be a meaning to it. Concretely the question is whether there is any reason to believe that the main-edge shift corresponds to the ground-state ΔZPE while the pre-edge shift does not. Since the core-excited state potential at the pre edge is particularly dissociative and hence particularly steeply curved in contrast to the main edge this could explain why the pre-edge shift does not correspond to ΔZPE while the shift at the main edge does. This speculation could be further assessed by comparing the line shifts determined here with calculations of the ground-state ΔZPE . The necessary link between the two properties could be made by accurate calculations of the O K-edge x-ray absorption spectra of H_2O and D_2O with particular emphasize of accurately describing the core-excited

state potentials at the pre and main edges including the Franck-Condon structure in the core-excited states. Evaluating the at best quantitative agreement of state-of-the-art calculations of the O K-edge x-ray absorption spectrum of liquid water with experiment [38-45] shows that there is considerable improvement required in the theoretical descriptions to accurately reproduce and explain the small but significant differences between light and heavy liquid water x-ray absorption spectra.

We now proceed with analyzing the ΔZPD related broadening in the O K-edge absorption spectra of liquid H_2O and D_2O with Figures 4 and 5. In an attempt to analyze this effect separately from the ΔZPE related blue shift and following the analysis of the earlier XRS spectra in [1, 6] we first shifted the D_2O spectrum to lower energies to “correct” for the shift (Figure 4 (a)) and then evaluated the broadening quantitatively by comparing shifted and broadened D_2O spectra with the H_2O spectrum (Figure 4 (b)). The analysis aims at minimizing both the oscillation amplitudes and the integrated difference between the shifted D_2O and the H_2O spectra in order to determine the broadening of the H_2O spectrum with respect to D_2O . The first observation we make in the spectra shown in Figure 4 (b) is that the previously used broadening of the D_2O spectrum of 0.5 eV (throughout this paper Gaussian FWHM values are used) apparently is too large to explain the broadening of the H_2O spectrum compared to D_2O : The oscillation amplitudes in the resulting difference spectrum are clearly larger than for no broadening. A broadening of the D_2O spectrum by 0.23 eV instead results in the smallest number of oscillations and the smallest oscillation amplitudes hence a minimal integrated difference spectrum. The remaining spectral differences (lower pre and main edge in D_2O compared to H_2O) could now be interpreted as reflecting differences in the geometric and electronic structures between the two liquids due to isotope substitution. Indeed, they coincide with the generally accepted notion that the H-bond environment in D_2O is similar to H_2O but for a temperature that is lower by approximately 5 degrees [6]. This is evident when comparing the effects caused by isotope substitution (Figure 4 (a)) and caused by a change in temperature [1, 48, 54]. Further discussion of this comparison goes beyond the scope of this paper. We note that the main edge seems less affected by broadening than the pre edge while the post edge seems completely unaffected. This may be due to larger inhomogeneous broadening at these edges compared to the pre edge. Due to the larger spatial extent of the related orbitals structural fluctuations in the liquids could be picked up more effectively at the main and post edges compared to the pre edge.

As noted before, the detailed intensity differences throughout the spectra of liquid H_2O and D_2O on the level of accuracy discussed here may depend on how the spectra were normalized and we address this uncertainty with the data in Figure 5 with the aim to accurately determine the ΔZPD related broadening. The integrated D_2O - H_2O differences (difference spectra of shifted and broadened D_2O minus H_2O and integrated over the indicated photon energy range) are shown for four different

ways of area and intensity or edge-jump normalization and versus various broadenings of the D₂O spectrum between 0 and 0.5 eV. Apparently the integrated difference strongly depends on the normalization as is evident by the fact that four curves are strongly offset in the vertical. However, we also find that the dependence of the integrated difference with broadening of the D₂O spectrum follows the same trend irrespective of normalization with a minimal difference at broadening values of between 0.2 and 0.26 eV (legend in Figure 5) with a slow increase to lower values and a step increase for larger values. This makes us confident that the broadening resulting in a minimal integrated difference can be meaningfully extracted from this analysis. As a mean of the four values we find that the difference between the shifted and broadened D₂O spectrum and the H₂O spectrum is minimal for a broadening of the D₂O spectrum of 0.23 ± 0.05 eV where the uncertainty stems from the differences in minimal broadening for different ways of normalization. This represents the first stringent determination of the ΔZPD related broadening of the O K-edge x-ray absorption spectrum of water and could be used to test forthcoming calculations by relating the ground-state ΔZPD and the shape of the spectrum. The determination of this broadening value is more accurate than in the earlier investigations based on the XRS spectra, we believe, due to the higher resolution achieved here with transmission-mode XAS [1, 6]. Closer inspection of the transmission-mode XAS difference spectra in Figure 4 reveals that they are different from the XRS difference spectra. This motivates comparing in more detail the spectra of the different methods in order to also conclude on the generality of the extracted values for the ΔZPE related shift and the ΔZPD related broadening or whether they could depend on the experimental method used.

The O K-edge absorption spectra of light and heavy liquid water and their differences as measured here with transmission-mode XAS are compared to the earlier XRS spectra in Figure 6. In order to facilitate the analysis we compare in Figures 6 (a) and (b) the spectra of H₂O and D₂O for the same area normalization as in [1]. Deviations between the spectra from the different methods are apparent throughout the displayed photon energy range with higher pre and main edges and a somewhat reduced intensity at or above the post edge in the XRS spectra compared to the XAS spectra. In particular the differences at the pre and main edges could be explained by the lower spectral resolution in XRS compared to XAS. Furthermore, small remaining non-dipole contributions to the XRS spectrum could be the reason for the deviations although non-dipole effects were minimized as described in [1, 6]. Related, or more generally, to first approximation XRS and XAS coincide in what is probed and the deviations observed here may point to deviations from this approximation. Interestingly though, the D₂O-H₂O difference spectra from XAS and XRS almost perfectly coincide as evidenced with Figure 6 (c) for the raw D₂O minus H₂O difference and Figure 6 (d) for the difference of shifted and broadened D₂O minus H₂O. Note that the difference spectrum in Figure 6 (d) is different from the difference spectrum in Figure 4 (b, red line) due to the difference in normalization used. The ΔZPE related shift and the ΔZPD related broadening can be more reliably determined with

transmission-mode XAS but, once spectra have been corrected for them, we find that the remaining differences between liquid H₂O and D₂O O K-edge x-ray absorption spectra can be interpreted equally well with XRS or XAS in terms of remaining structural differences or differences in H-bond environment between light and heavy liquid water. This is the case in particular for the small intensity change upon isotope substitution in the post-edge region of the spectrum (Figure 6 (c) and (d)), which is essential in terms of structural interpretation [1]. Based on our analysis here we can claim that any difference of 0.5 % or larger between shift- and broadening corrected and normalized spectra can be reliably related to these structural differences. For that it will be interesting to test new calculations also in terms of these structural effects against the difference spectra shown in Figure 6 (d) (for area normalized calculated spectra) or in Figure 4 (b, red line) (for edge-jump normalized calculated spectra). We finally note in agreement with previous assessments from neutron scattering [2] and XAS [1] that we believe it is adequate for the interpretation of the observed isotope effects to stay within the Born-Oppenheimer approximation. In particular, the structural differences and the XAS differences between light and heavy liquid water can be explained by the differences arising from the ZPE differences in the electronic ground states in the anharmonic O-H/D potential (Figure 3) [9]. Still, it will be interesting in future calculations of XAS of light and heavy liquid water to quantify the effect of isotope substitution in the core-excited states in particular through vibronic coupling.

IV. SUMMARY AND CONCLUSIONS

We applied X-ray absorption spectroscopy at the O K-edge in transmission mode to light and heavy liquid water to address the spectral effects related to isotope substitution in the liquid. Confirming earlier results based on x-ray Raman scattering experiments we find the D₂O spectrum to be blue shifted with respect to H₂O and the D₂O spectrum to be less broadened than the H₂O spectrum. Following the conceptual explanation of the related shift and broadening effects in UV absorption spectra the shift is related to the difference in ground-state zero-point energies between D₂O and H₂O while the difference in broadening is related to the difference in ground-state vibrational zero-point distributions. The shift in the O K-edge absorption spectrum is accurately determined separately for two absorption edges in the spectrum (the pre and the main edge) and a significant difference is observed. This is discussed and qualitatively explained by addressing the limitations of the conceptual explanation by, in particular, evoking the influence of the shape of the final-state potential. A more strongly curved potential for the final states at the pre edge is thought to cause a shift smaller than the ground-state zero-point energy difference while a less strongly curved potential for the main edge could result in a shift equal to or even larger than the ground-state zero-point energy difference. We also accurately determine the broadening effect related to the difference in ground-state vibrational zero-point distributions between liquid H₂O and D₂O. Both extracted values of the blue shift and the

broadening could be used in the future to stringently test new calculations of ground-state zero-point energies and vibrational zero-point distributions in H₂O and D₂O. As a link between the experimental observables of shift and broadening and the ground-state properties, new calculations of the O K-edge x-ray absorption spectra of liquid H₂O and D₂O are deemed necessary. Proper description of the final core-excited state potentials and inclusion of the Franck-Condon structure seems necessary to reproduce the small spectral differences determined experimentally. In addition, we correct the O K-edge absorption spectra for the shift and broadening effects. These benchmark spectra reflect the remaining structural differences between liquid H₂O and D₂O resulting from different environments due to the different hydrogen-bond fluctuations in the liquids and could serve to quantify the possible influence of nuclear quantum effects on the structures of light and heavy liquid water.

ACCEPTED MANUSCRIPT

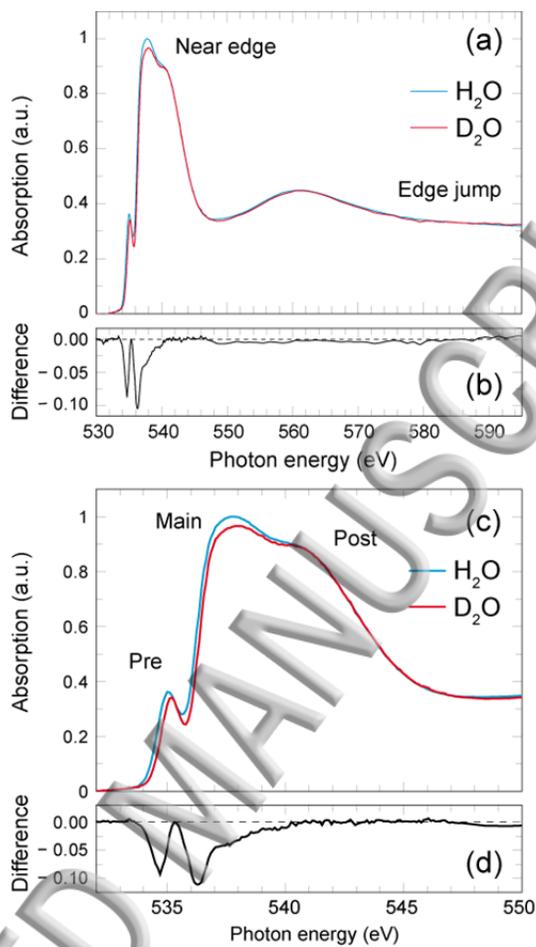


FIG. 1. (a) O K-edge x-ray absorption spectra of liquid H₂O and D₂O measured in transmission mode at room temperature. The spectra are normalized to the same intensity at 580-600 eV. (b) D₂O-H₂O difference of the spectra in (a). (c) and (d) Zooms into the near-edge regions of the spectra in (a) and (b).

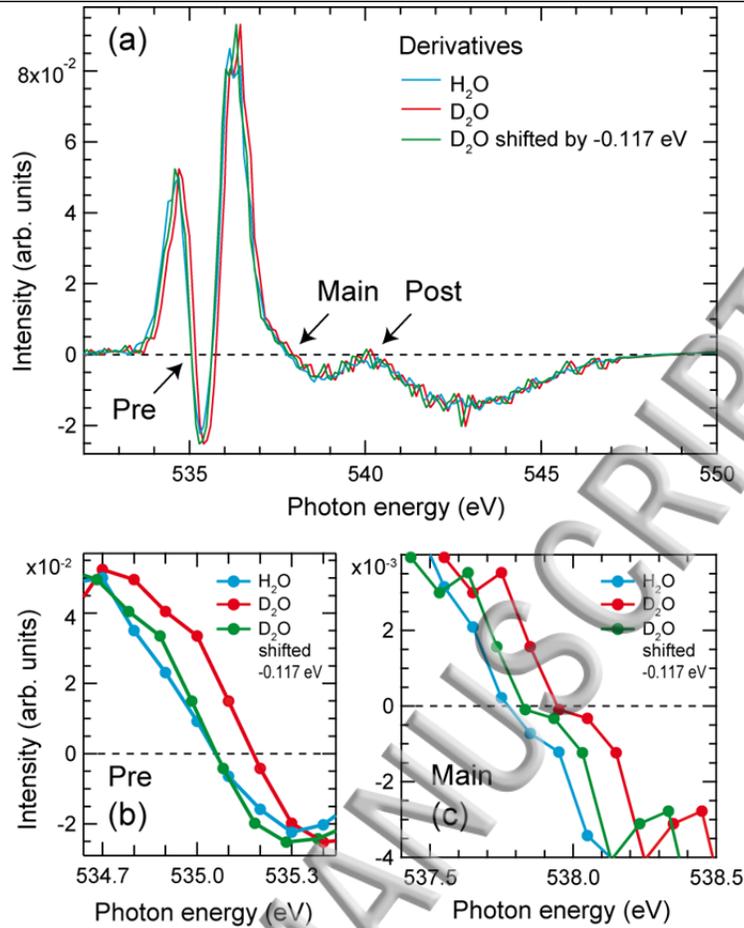


FIG. 2. (a) Derivatives of the liquid H₂O (blue) and D₂O (red) O K-edge x-ray absorption spectra from Figure 1. For comparison the derivative of the D₂O spectrum shifted by -117 meV (green) is displayed. (b) Zoom into the pre-edge region around 535 eV. (c) Zoom into the main-edge region around 538 eV.

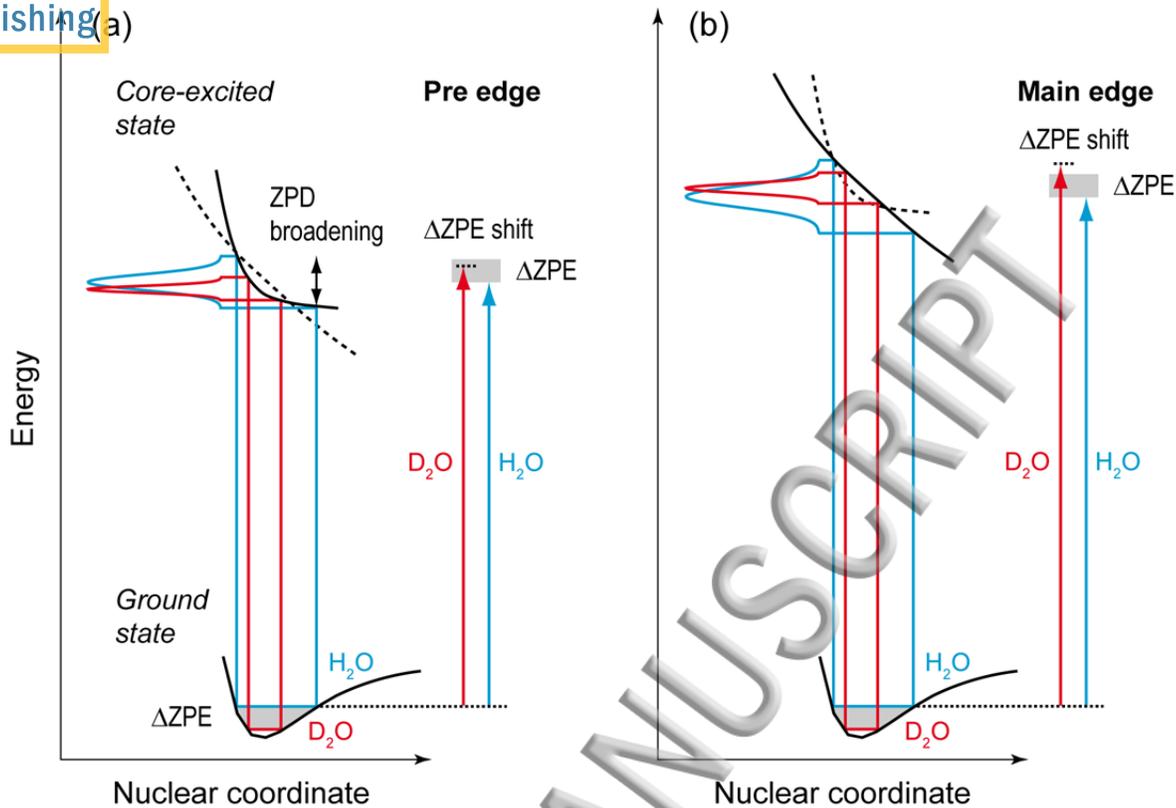


FIG. 3. Schematic illustration of the isotope effect on the x-ray absorption spectrum of water. The zero-point energy difference in the ground state (ΔZPE) causes the ΔZPE shift of the absorption or vertical transition energies between H₂O and D₂O. The different zero-point spatial probability distributions in the ground states (ZPD) are projected on the same core-excited state potential energy surface causing the ZPD broadening of x-ray absorption spectral features to be different in H₂O compared to D₂O (smaller in D₂O). The shape of the core-excited state energy potential surface affects both the ZPD broadening and the vertical transition energy. The latter can be (a) smaller or (b) larger than the ground state ΔZPE as in the measured pre and main edges, respectively, of the water O K-edge absorption spectra.

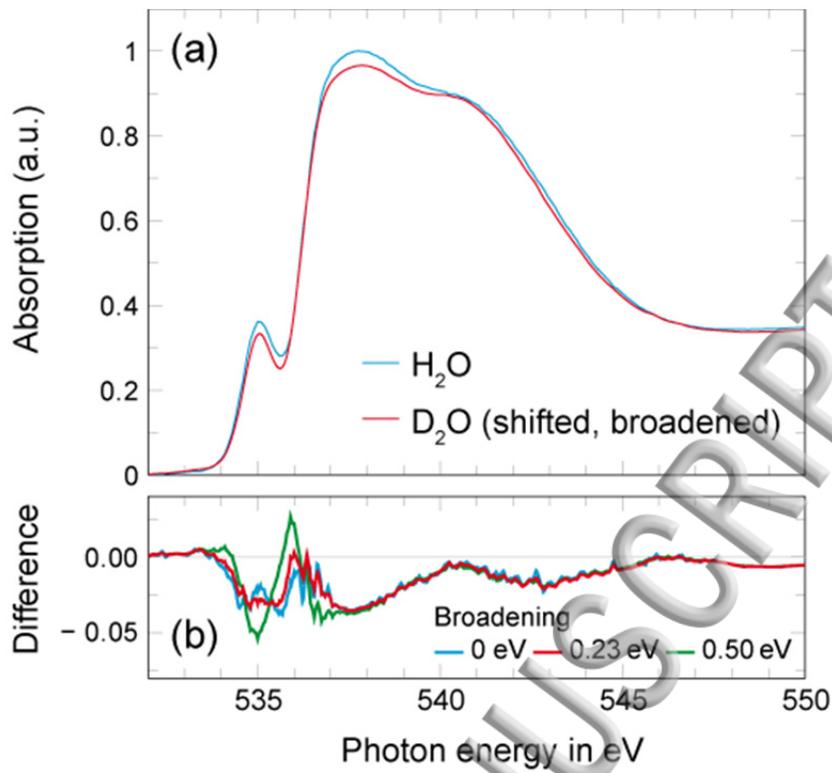


FIG. 4. (a) O K-edge x-ray absorption spectra of liquid H_2O and D_2O where the D_2O spectrum was shifted by -120 meV and broadened with a Gaussian of 0.23 eV FWHM compared to the spectrum in Figure 1. The spectra are normalized to the same intensity at 580 - 600 eV (see Figure 1). (b) D_2O - H_2O differences of the spectra in (a) for different broadenings of the D_2O spectrum prior to performing the difference: FWHM of 0.23 eV (red), 0 eV (blue, unbroadened case) and 0.50 eV (green). In all cases the D_2O spectrum was shifted by -120 meV prior to performing the difference.

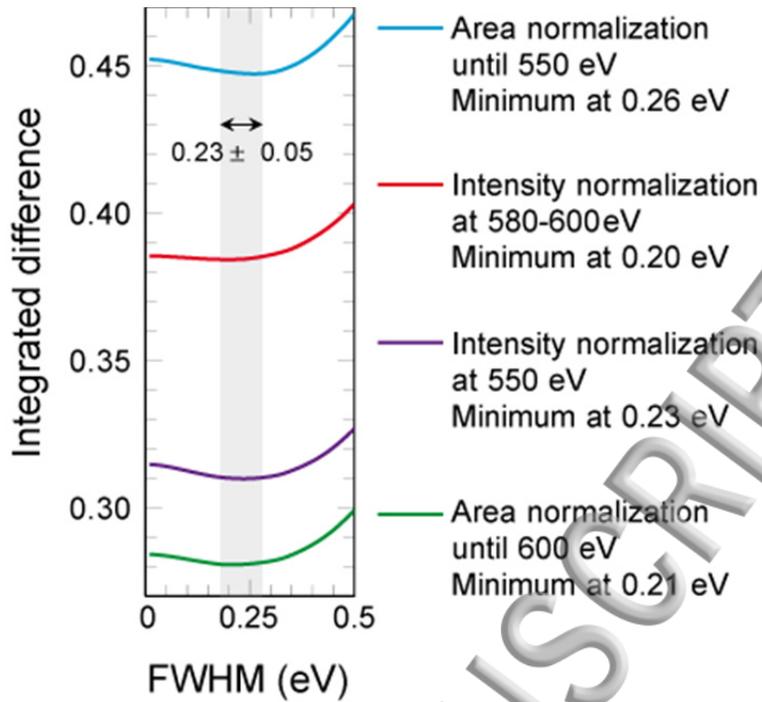


FIG. 5. Integrated D₂O-H₂O differences (absolute value) with integration over the photon energy range from 530 – 550 eV versus the Gaussian FWHM in eV used to broaden the D₂O spectrum prior to performing the difference and integrating it. The four curves reflect four different normalization procedures for normalizing the H₂O and D₂O spectra prior to performing the difference and integrating it [the differences for 0, 0.23 and 0.5 eV broadening are shown for intensity normalization at 580-600 eV in Figure 4 (b)]. The minimum of each curve (broadening where the integrated difference is smallest) is given in the legend. The gray region marks the mean value of broadening at minimum integrated difference (0.23 eV) including uncertainties introduced by the different ways of normalizing the spectra (± 0.05). The D₂O spectrum was shifted by -120 meV in all cases prior to performing the differences and integrating them.

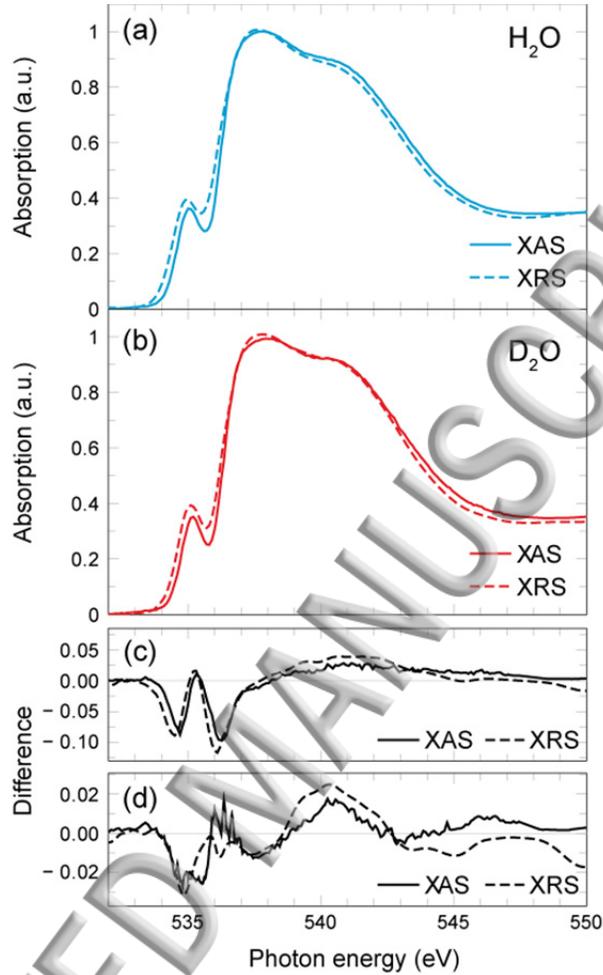


FIG. 6. (a) Liquid H_2O and (b) liquid D_2O O K-edge x-ray absorption spectra measured with transmission-mode x-ray absorption spectroscopy (XAS, solid line, this work) and with x-ray Raman scattering (XRS, dashed line, ref. [1]). The spectra are normalized to the same area in the region from 530 eV to 550 eV as it was done in ref. [1]. (c) D_2O - H_2O difference of the spectra in (a) and (b) for XAS (solid line, this work) and with XRS (dashed line, ref. [1]). (d) D_2O - H_2O difference minimized by shifting and broadening the D_2O spectrum prior to performing the difference for XAS (solid line, this work, -120 meV shift, 0.23 eV broadening) and with XRS (dashed line, ref. [1], 160 meV shift and 0.5 eV broadening). The XAS difference in (c) and the minimized XAS difference in (d) are different from the respective differences in Figure 1 (d) and Figure 4 (b) due to the different normalizations of the spectra prior to performing the differences.

ACKNOWLEDGMENTS

We gratefully acknowledge the continuous support by the BESSY II staff and we thank HZB for the allocation of synchrotron radiation beamtime. We are grateful in particular to Christian Weniger for providing the silicon nitride membranes. We thank L. G. M. Pettersson and A. Nilsson for fruitful discussions.

REFERENCES

1. Nilsson, A., et al., *X-ray absorption spectroscopy and X-ray Raman scattering of water and ice; an experimental view*. Journal of Electron Spectroscopy and Related Phenomena, 2010. **177**(2-3): p. 99-129.
2. Soper, A.K. and C.J. Benmore, *Quantum Differences between Heavy and Light Water*. Phys Rev Lett, 2008. **101**(6): p. 065502.
3. Nagata, Y., et al., *Nuclear quantum effects affect bond orientation of water at the water-vapor interface*. Phys Rev Lett, 2012. **109**(22): p. 226101.
4. Gainaru, C., et al., *Anomalously large isotope effect in the glass transition of water*. Proceedings of the National Academy of Sciences, 2014. **111**(49): p. 17402-17407.
5. Hardy, E.H., et al., *Isotope effect on the translational and rotational motion in liquid water and ammonia*. The Journal of Chemical Physics, 2001. **114**(7): p. 3174.
6. Bergmann, U., et al., *Isotope effects in liquid water probed by x-ray Raman spectroscopy*. Physical Review B, 2007. **76**(2).
7. Giuliani, A., et al., *Quantum effects and the local environment of water hydrogen: Deep inelastic neutron scattering study*. Physical Review B, 2012. **86**(10).
8. Nibbering, E.T.J. and T. Elsaesser, *Ultrafast Vibrational Dynamics of Hydrogen Bonds in the Condensed Phase*. Chem Rev, 2004. **104**: p. 1887-1914.
9. Ceriotti, M., et al., *Nuclear Quantum Effects in Water and Aqueous Systems: Experiment, Theory, and Current Challenges*. Chem Rev, 2016.

10. Giberti, F., et al., *The role of quantum effects on structural and electronic fluctuations in neat and charged water*. J Phys Chem B, 2014. **118**(46): p. 13226-35.

11. Li, X.Z., B. Walker, and A. Michaelides, *Quantum nature of the hydrogen bond*. Proceedings of the National Academy of Sciences, 2011. **108**(16): p. 6369-6373.

12. Nilsson, A. and L.G.M. Pettersson, *The structural origin of anomalous properties of liquid water*. Nat Commun, 2015. **6**: p. 8998.

13. Nilsson, A. and L.G.M. Pettersson, *Perspective on the structure of liquid water*. Chemical Physics, 2011. **389**(1-3): p. 1-34.

14. Franck, J. and R.W. Wood, *Ultraviolet Absorption of Heavy Water Vapor*. Physical Review, 1934. **45**(10): p. 667-668.

15. Fox, M.F. and E. Hayon, *Far-Ultraviolet Solvent Spectroscopy*. J Phys Chem, 1972. **76**(19): p. 2703-2750.

16. Verrall, R.E., *Vacuum-Ultraviolet Study of Liquid H₂O and D₂O*. The Journal of Chemical Physics, 1969. **50**(6): p. 2746.

17. Compton, R.N., et al., *Threshold Electron Impact Excitation of Atoms and Molecules: Detection of Triplet and Temporary Negative Ion States*. The Journal of Chemical Physics, 1968. **48**(2): p. 901-909.

18. Heller, J.M., R.D. Birkhoff, and L.R. Painter, *Isotopic effects on the electronic properties of H₂O and D₂O in the vacuum uv*. The Journal of Chemical Physics, 1977. **67**(5): p. 1858.

19. Marin, T.W., K. Takahashi, and D.M. Bartels, *Temperature and density dependence of the light and heavy water ultraviolet absorption edge*. J Chem Phys, 2006. **125**(10): p. 104314.

20. Del Ben, M., J. Hutter, and J. VandeVondele, *Probing the structural and dynamical properties of liquid water with models including non-local electron correlation*. J Chem Phys, 2015. **143**: p. 054506.

21. Bartels, D.M. and R.A. Crowell, *Photoionization Yield vs Energy in H₂O and D₂O*. J Phys Chem A, 2000. **104**: p. 3349-3355.

22. Elles, C.G., et al., *Excitation-energy dependence of the mechanism for two-photon ionization of liquid H(2)O and D(2)O from 8.3 to 12.4 eV*. J Chem Phys, 2006. **125**(4): p. 44515.
23. Lian, R., R.A. Crowell, and I.A. Shkrob, *Solvation and Thermalization of Electrons Generated by above-the-Gap (12.4 eV) Two-Photon Ionization of Liquid H2O and D2O*. J Phys Chem A, 2005. **109**: p. 1510-1520.
24. Sander, M.U., et al., *Liquid water ionization: mechanistic implications of the H/D isotope effect in the geminate recombination of hydrated*. Chemical Physics, 2000. **258**: p. 257-265.
25. Fransson, T., et al., *X-ray and Electron Spectroscopy of Water*. Chem Rev, 2016.
26. Fuchs, O., et al., *Isotope and temperature effects in liquid water probed by x-ray absorption and resonant x-ray emission spectroscopy*. Phys Rev Lett, 2008. **100**(2): p. 027801.
27. Harada, Y., et al., *Selective probing of the OH or OD stretch vibration in liquid water using resonant inelastic soft-x-ray scattering*. Phys Rev Lett, 2013. **111**(19): p. 193001.
28. Huang, C., et al., *Increasing correlation length in bulk supercooled H2O, D2O, and NaCl solution determined from small angle x-ray scattering*. J Chem Phys, 2010. **133**(13): p. 134504.
29. Lange, K.M., et al., *X-ray emission from pure and dilute H2O and D2O in a liquid microjet: Hydrogen bonds and nuclear dynamics*. Physical Review B, 2012. **85**(15).
30. Nilsson, A., et al., *Resonant inelastic X-ray scattering of liquid water*. Journal of Electron Spectroscopy and Related Phenomena, 2013. **188**: p. 84-100.
31. Nishizawa, K., et al., *High-resolution soft X-ray photoelectron spectroscopy of liquid water*. Phys Chem Chem Phys, 2011. **13**(2): p. 413-7.
32. Nygard, K., et al., *Isotope quantum effects in the electron momentum density of water*. J Chem Phys, 2007. **126**(15): p. 154508.
33. Thurmer, S., et al., *On the nature and origin of dicationic, charge-separated species formed in liquid water on X-ray irradiation*. Nat Chem, 2013. **5**(7): p. 590-6.

34. Tokushima, T., et al., *High resolution X-ray emission spectroscopy of liquid water: The observation of two structural motifs*. Chemical Physics Letters, 2008. **460**(4-6): p. 387-400.
35. Tokushima, T., et al., *Polarization dependent resonant x-ray emission spectroscopy of D₂O and H₂O water: assignment of the local molecular orbital symmetry*. J Chem Phys, 2012. **136**(4): p. 044517.
36. Tse, J.S., et al., *X-ray Raman spectroscopic study of water in the condensed phases*. Phys Rev Lett, 2008. **100**(9): p. 095502.
37. Weinhardt, L., et al., *Nuclear dynamics and spectator effects in resonant inelastic soft x-ray scattering of gas-phase water molecules*. J Chem Phys, 2012. **136**(14): p. 144311.
38. Fransson, T., et al., *Requirements of first-principles calculations of X-ray absorption spectra of liquid water*. Phys Chem Chem Phys, 2016. **18**(1): p. 566-83.
39. Hetenyi, B., et al., *Calculation of near-edge x-ray-absorption fine structure at finite temperatures: spectral signatures of hydrogen bond breaking in liquid water*. J Chem Phys, 2004. **120**(18): p. 8632-7.
40. Iannuzzi, M., *X-ray absorption spectra of hexagonal ice and liquid water by all-electron Gaussian and augmented plane wave calculations*. J Chem Phys, 2008. **128**(20): p. 204506.
41. Kong, L., X. Wu, and R. Car, *Roles of quantum nuclei and inhomogeneous screening in the x-ray absorption spectra of water and ice*. Physical Review B, 2012. **86**(13).
42. Kuhne, T.D. and R.Z. Khaliullin, *Electronic signature of the instantaneous asymmetry in the first coordination shell of liquid water*. Nat Commun, 2013. **4**: p. 1450.
43. Leetmaa, M., et al., *Theoretical approximations to X-ray absorption spectroscopy of liquid water and ice*. Journal of Electron Spectroscopy and Related Phenomena, 2010. **177**(2-3): p. 135-157.
44. Ljungberg, M.P., L.G.M. Pettersson, and A. Nilsson, *Vibrational interference effects in x-ray emission of a model water dimer: implications for the interpretation of the liquid spectrum*. J Chem Phys, 2011. **134**(4): p. 044513.

45. Prendergast, D. and G. Galli, *X-ray absorption spectra of water from first principles calculations*. Phys Rev Lett, 2006. **96**(21): p. 215502.
46. Gavrilu, G., et al., *Time-resolved X-ray absorption spectroscopy of infrared-laser-induced temperature jumps in liquid water*. Applied Physics A, 2009. **96**(1): p. 11-18.
47. Huse, N., et al., *Probing the hydrogen-bond network of water via time-resolved soft X-ray spectroscopy*. Phys Chem Chem Phys, 2009. **11**(20): p. 3951-7.
48. Meibohm, J., S. Schreck, and P. Wernet, *Temperature dependent soft x-ray absorption spectroscopy of liquids*. Rev Sci Instrum, 2014. **85**(10): p. 103102.
49. Nagasaka, M., et al., *Development of a liquid flow cell to measure soft X-ray absorption in transmission mode: A test for liquid water*. Journal of Electron Spectroscopy and Related Phenomena, 2010. **177**(2-3): p. 130-134.
50. Nagasaka, M., H. Yuzawa, and N. Kosugi, *Development and application of in situ/operando soft X-ray transmission cells to aqueous solutions and catalytic and electrochemical reactions*. Journal of Electron Spectroscopy and Related Phenomena, 2015. **200**: p. 293-310.
51. Näslund, L.Å., et al., *X-ray Absorption Spectroscopy Measurements of Liquid Water*. J Phys Chem B, 2005. **109**: p. 13835-13839.
52. Schreck, S., et al., *A sample holder for soft x-ray absorption spectroscopy of liquids in transmission mode*. Rev Sci Instrum, 2011. **82**(10): p. 103101.
53. Wernet, P., et al., *Ultrafast temperature jump in liquid water studied by a novel infrared pump-x-ray probe technique*. Applied Physics A, 2008. **92**(3): p. 511-516.
54. Wernet, P., et al., *The structure of the First Coordination Shell in Liquid Water*. Science, 2004. **304**: p. 995-999.
55. Myneni, S., et al., *Spectroscopic probing of local hydrogen-bonding structures in liquid water*. J Phys Condens Matter, 2002. **14**: p. L213-L219.

56. Coulman, D., et al., *Excitation, deexcitation, and fragmentation in the core region of condensed and adsorbed water*. The Journal of Chemical Physics, 1990. **93**(1): p. 58.

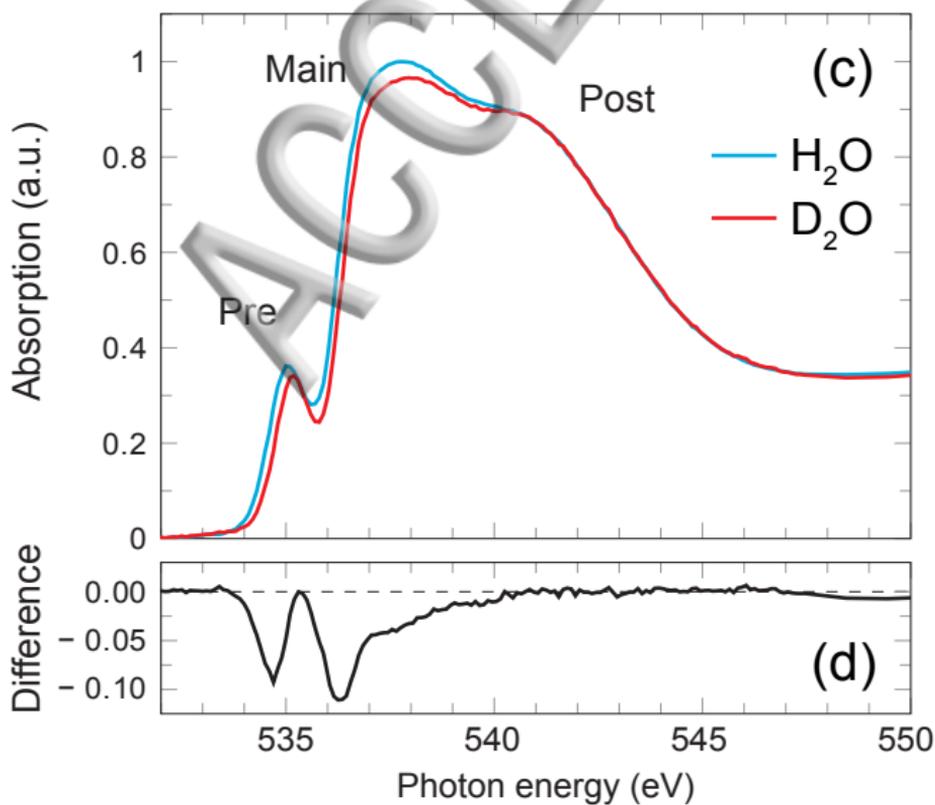
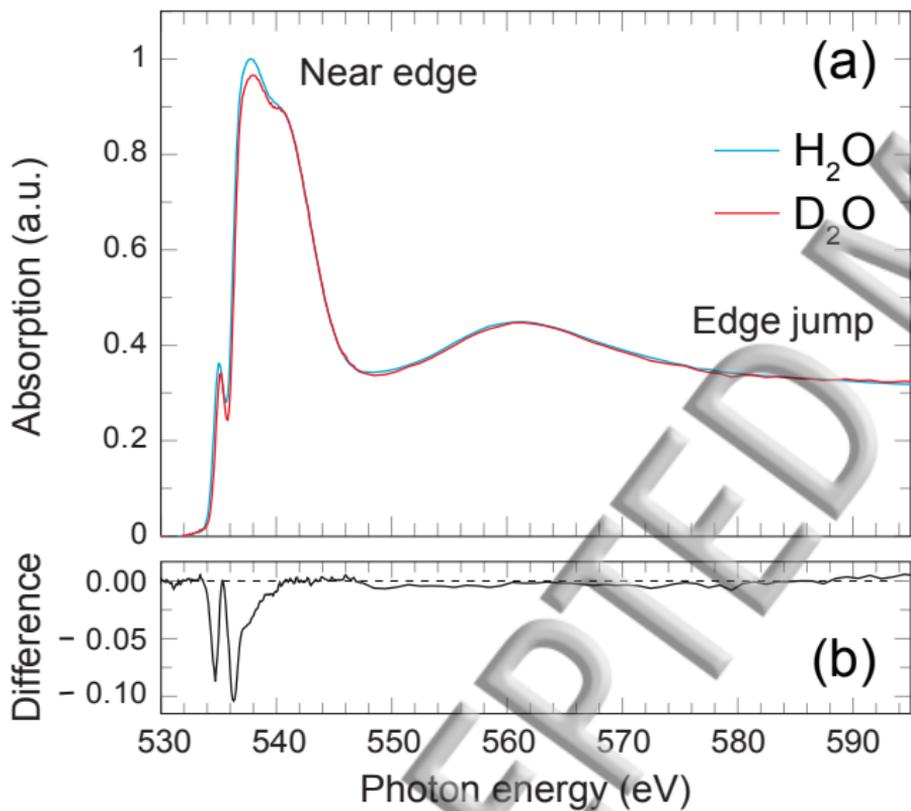
57. Parent, P., et al., *Structure of the water ice surface studied by x-ray absorption spectroscopy at the O K-edge*. The Journal of Chemical Physics, 2002. **117**(23): p. 10842.

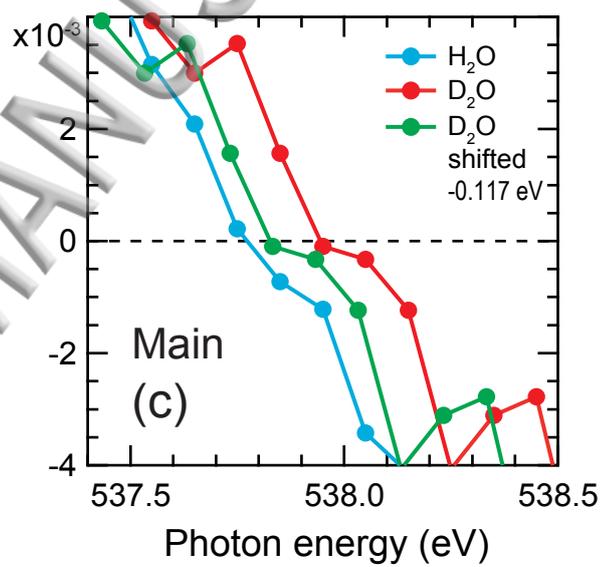
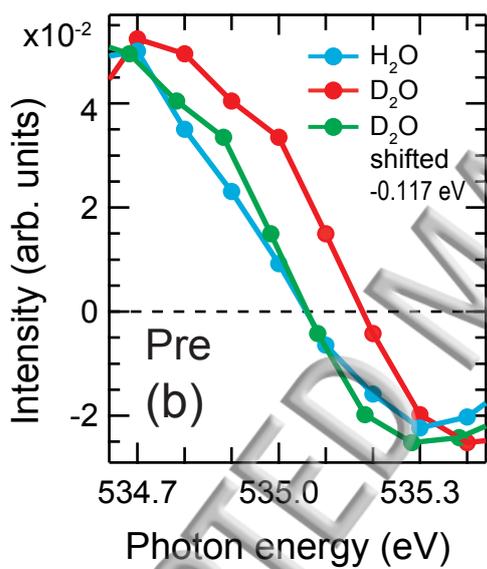
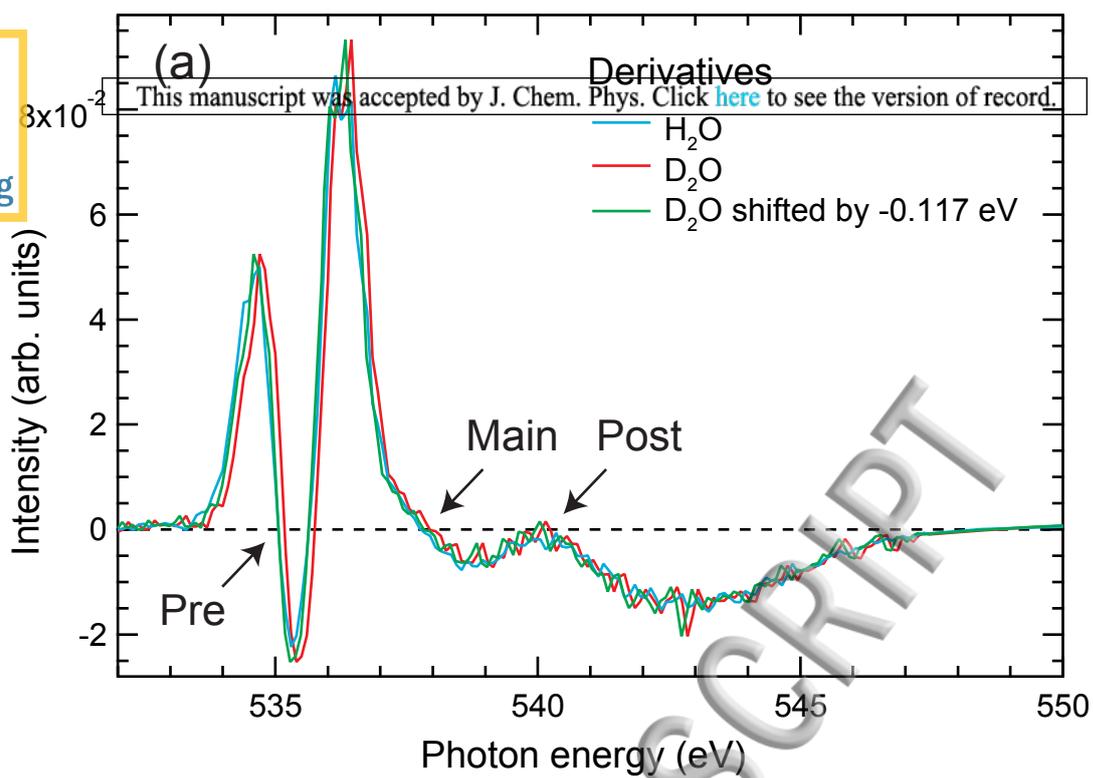
58. Romberg, R., et al., *Photon stimulated desorption of neutral hydrogen atoms from condensed water and ammonia by resonant O1s and N1s excitation: search for the signature of ultrafast bond breaking*. Surface Science, 2000. **451**: p. 116-123.

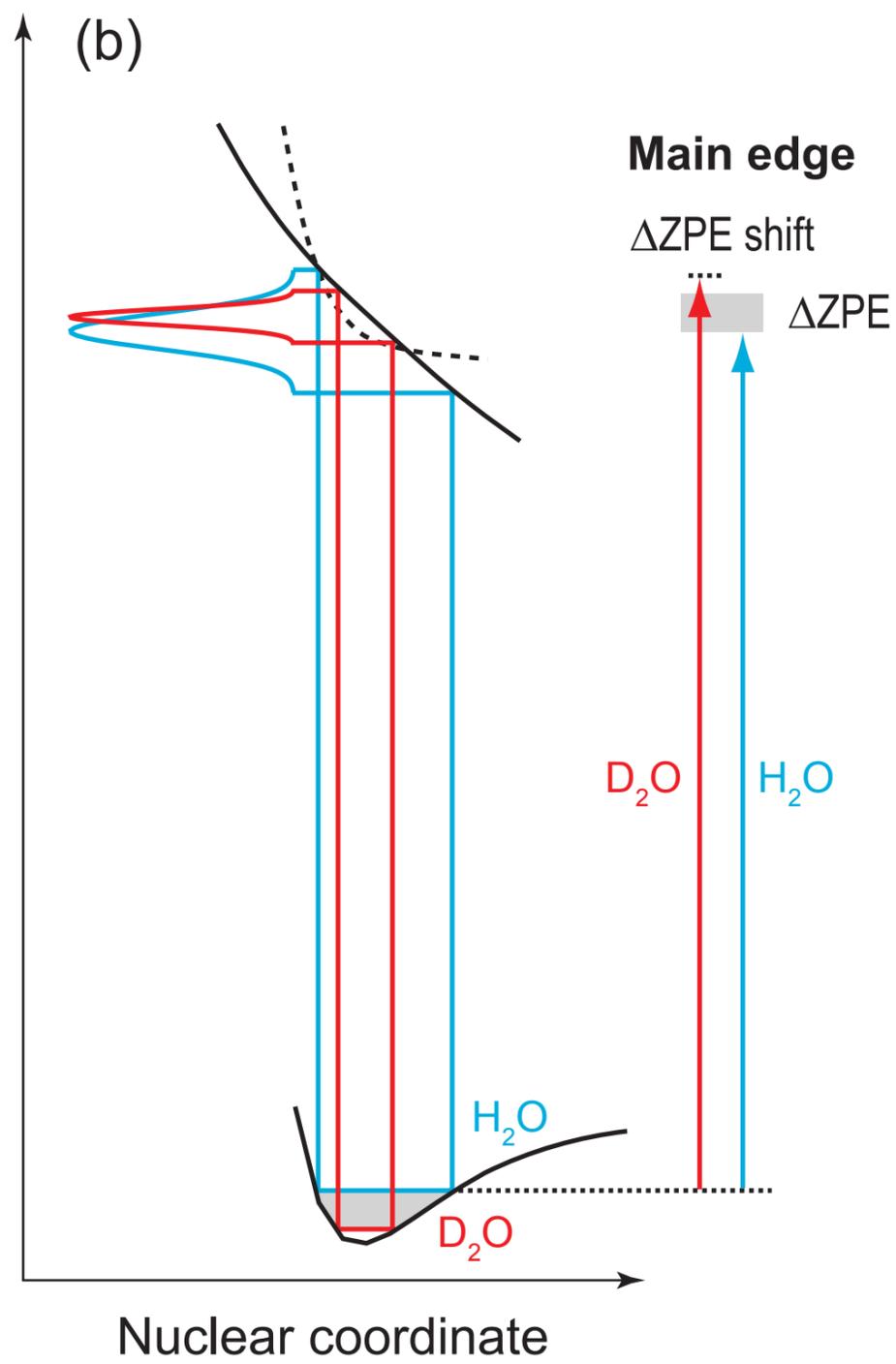
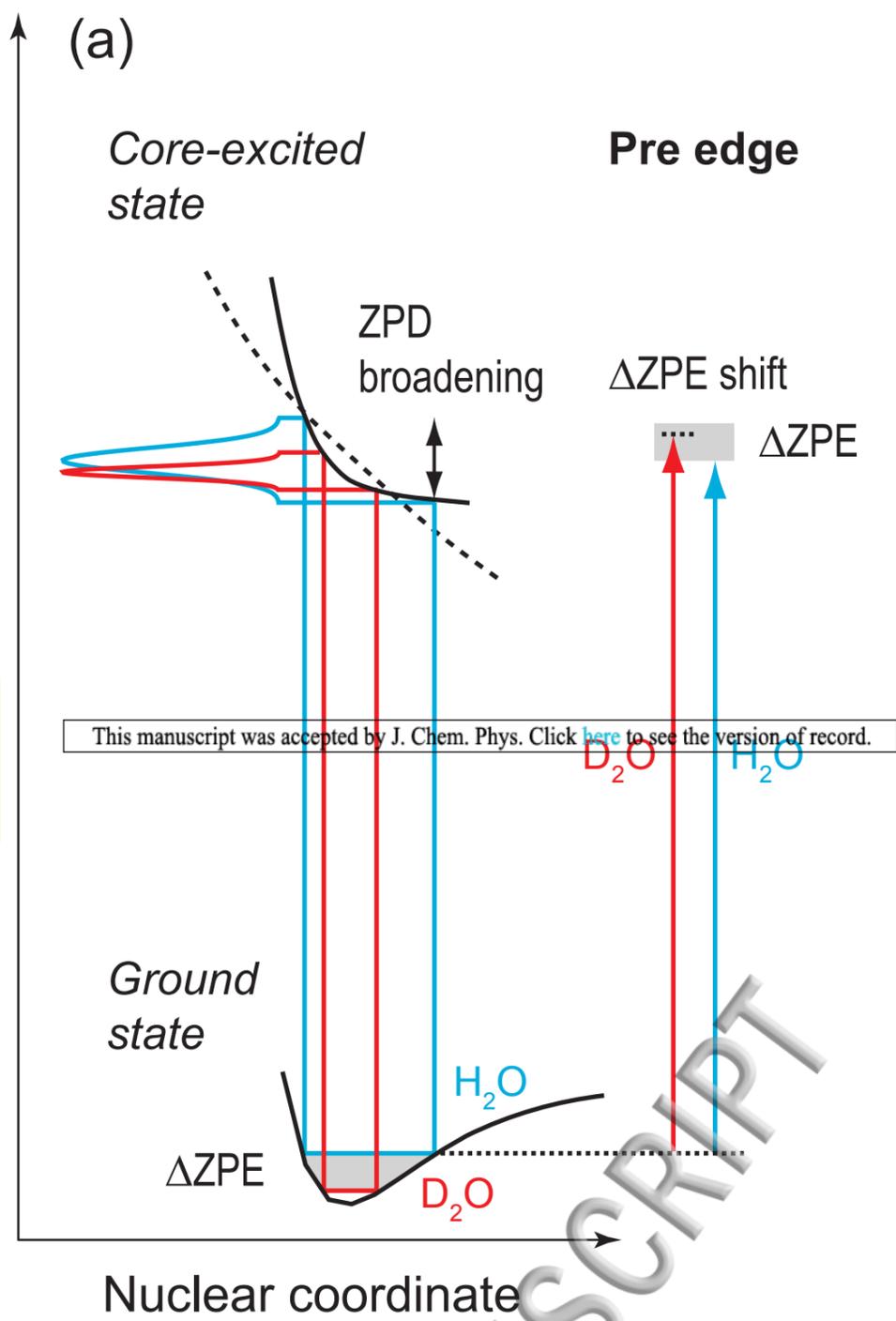
59. Wilson, K.R., et al., *X-ray Spectroscopy of Liquid Water Microjets*. J phys Chem B, 2001. **105**: p. 3346-3349.

60. Fatehi, S., et al., *Nuclear quantum effects in the structure and lineshapes of the N2 near-edge x-ray absorption fine structure spectrum*. J Chem Phys, 2010. **132**(9): p. 094302.

61. Felicissimo, V.C., et al., *A theoretical study of the role of the hydrogen bond on core ionization of the water dimer*. Chemical Physics, 2005. **312**(1-3): p. 311-318.

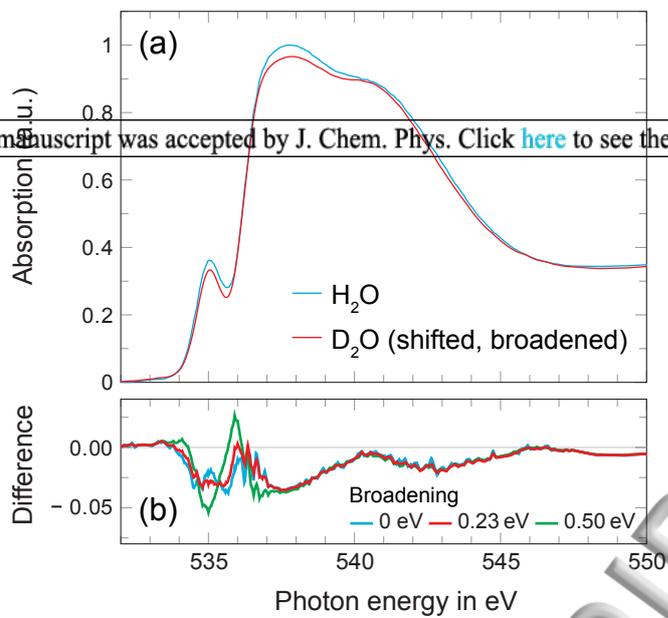




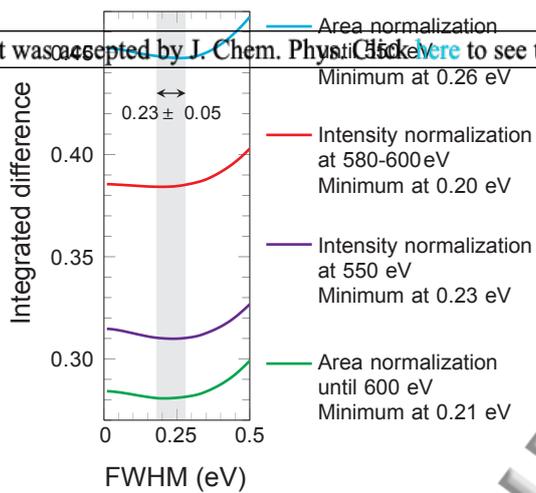


ACCEPTED MANUSCRIPT

This manuscript was accepted by J. Chem. Phys. Click [here](#) to see the version of record.



ACCEPTED MANUSCRIPT



ACCEPTED MANUSCRIPT

