

Supporting Information for “ $1b_1$ splitting in the X-ray emission spectrum of liquid water is dominated by ultrafast dissociation”

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Table of Contents

1. Liquid-phase simulations of pure H ₂ O and D ₂ O.....	2
2. Distribution of hydrogen-bonding in the initial structures used in the core-ionized and core-excited simulations.....	2
3. O-H dissociation in core-ionized and core-excited simulations	3
4. Protocol to identify orbital symmetry.....	6
5. Core-hole dynamical effects in the X-ray emission spectrum with emphasis on orbital symmetry.....	7
6. Time-averaged X-ray emission spectrum with emphasis on orbital symmetry.....	10
7. Core-hole dynamical effects in the X-ray emission spectrum with emphasis on hydrogen-bonding environment.....	11
8. X-ray emission spectrum predictions with EOM-IP-CCSD	14
9. Non-resonant $1b_1'$ peak gains intensity as proton is transferred from core-ionized water to the first solvation shell	16
10. X-ray emission spectrum with different core-hole lifetimes.....	17
11. Computational estimates for core-hole lifetimes from Auger decay rates in the gas-phase.....	17
12. Generation of core-ionized and core-excited states	18
REFERENCES	18

1. Liquid-phase simulations of pure H₂O and D₂O

In **Figure S1**, we present the radial distribution functions obtained from the MB-pol molecular dynamics simulations for H₂O and D₂O. **Figure S1** suggests that the equilibrium structures of H₂O and D₂O are almost indistinguishable.

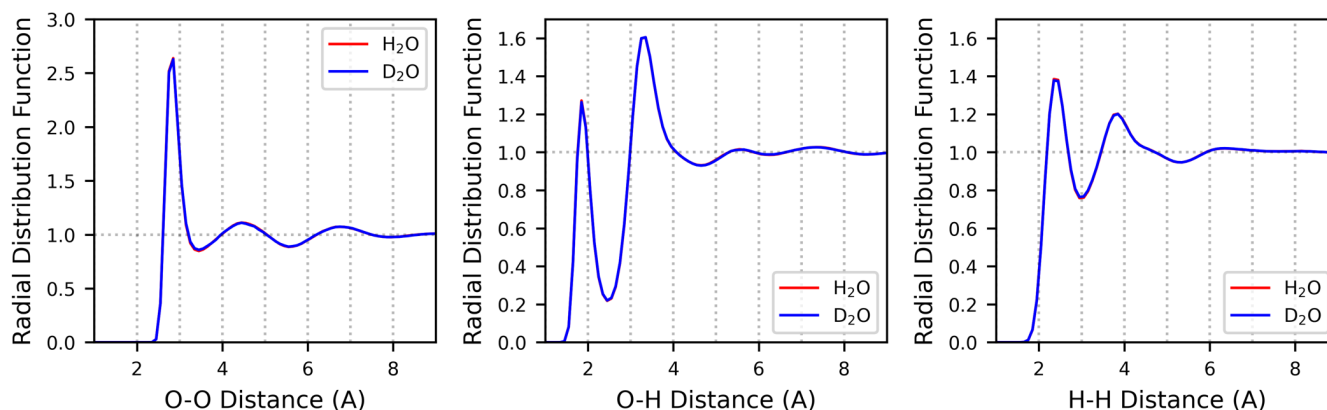


Figure S1: Oxygen-oxygen (left), oxygen-hydrogen (middle), and hydrogen-hydrogen (right) radial distribution functions in pure H₂O (red) and pure D₂O (blue) MB-pol simulations.

2. Distribution of hydrogen-bonding in the initial structures used in the core-ionized and core-excited simulations

Table S1 shows the populations of various hydrogen-bonding topologies computed for the central water molecule at $t = 0$ fs in the core-ionized and core-excited simulations described in the main text; therefore, 1000 structures were considered for liquid H₂O and 1000 for D₂O.

Table S1: Distribution of hydrogen-bonding topologies for the core-ionized and core-excited water molecules upon excitation (at the initial timestep of the simulations). D denotes a donor hydrogen-bond, A represents an acceptor hydrogen-bond, and F indicates a free molecule without any hydrogen bonds.

Hydrogen-bonding topology	Liquid H ₂ O 1 atm, 298 K	Liquid D ₂ O 1 atm, 298 K
DDAA	39.7%	39.4%
DDA	19.9%	19.5%
DA	15.1%	13.5%
DAA	15.2%	17.3%
A	3.2%	2.6%
D	1.0%	1.1%
DDAAA	2.0%	2.2%
AA	1.8%	1.3%
DD	1.5%	1.6%
F	0.4%	0.7%
DAAA	0.2%	0.8%

3. O-H dissociation in core-ionized and core-excited simulations

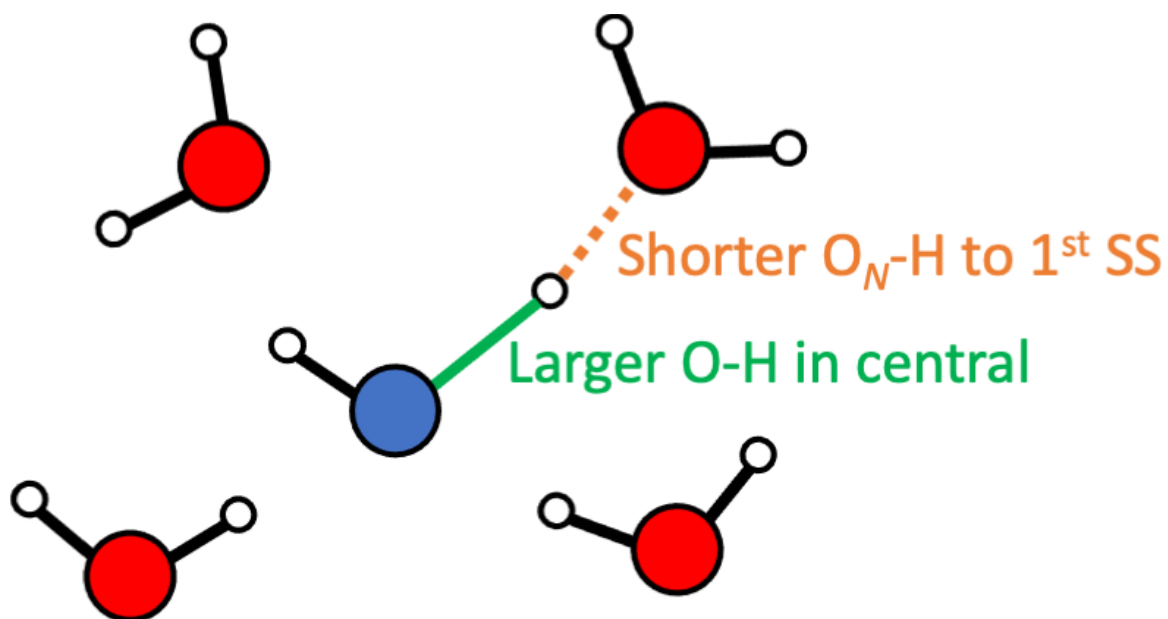


Figure S2: Illustration of the x and y axes in Figures S3 and S4, which depict the central water molecule (blue) that has been core-ionized or core-excited, surrounded by molecules in the first solvation shell (SS). The illustration highlights two O-H distances: the larger within the central water molecule and the shorter between a hydrogen atom in the central molecule and an oxygen atom in the first solvation shell (denoted as O_N).

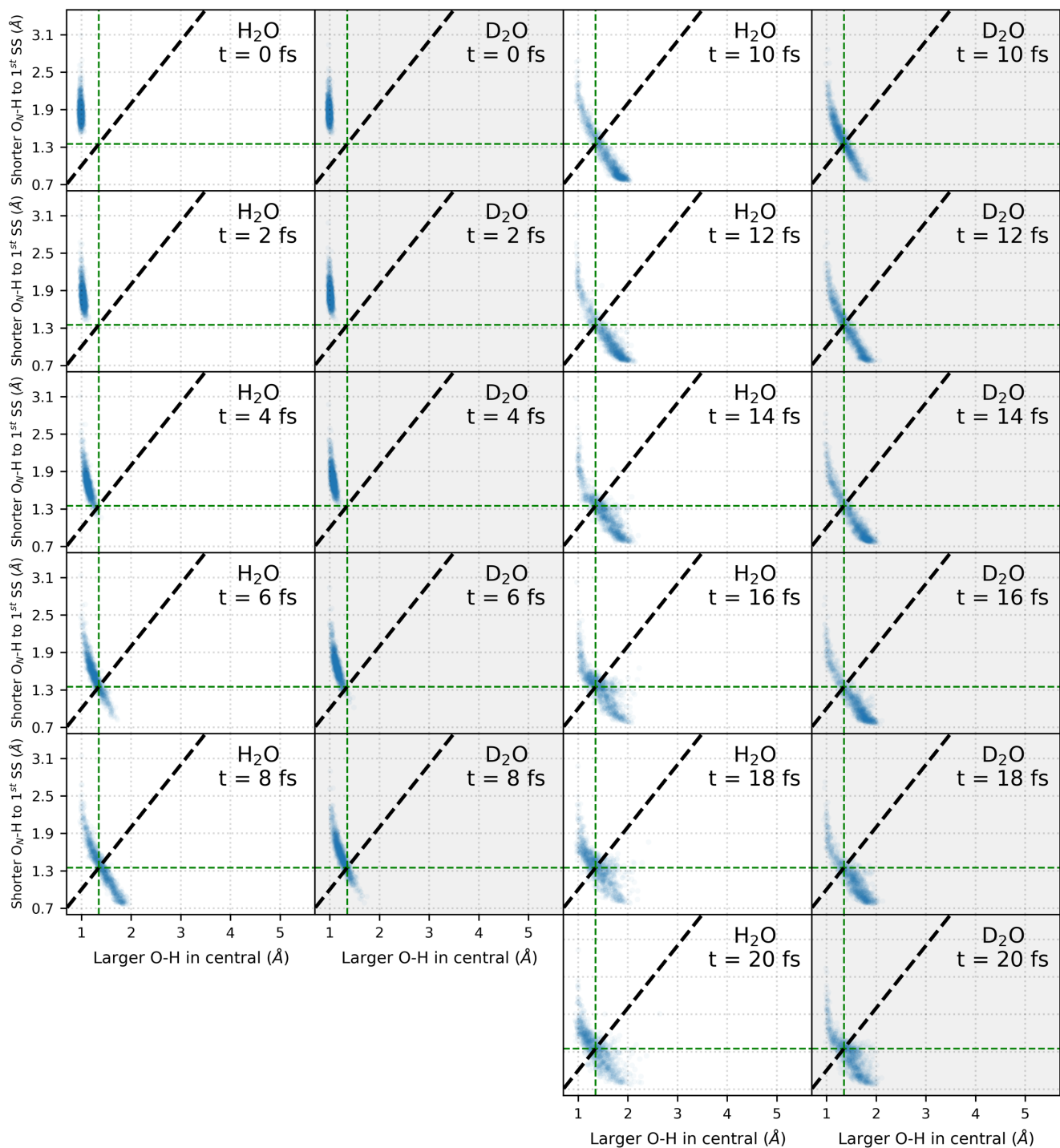


Figure S3: Distribution of two O-H distances for different simulation times in the simulations with core-ionized water molecules. The distances, illustrated in Figure S2, are the larger distance within the central water molecule (x-axis) and the shorter distance between a hydrogen atom in the central molecule and an oxygen atom (denoted as O_N) in the first solvation shell (y-axis). The dashed black line indicates where the two O-H distances are equal, while the dashed green lines represent the cutoff used to evaluate whether the hydrogen is bound to the central water molecule or the first solvation shell (SS).

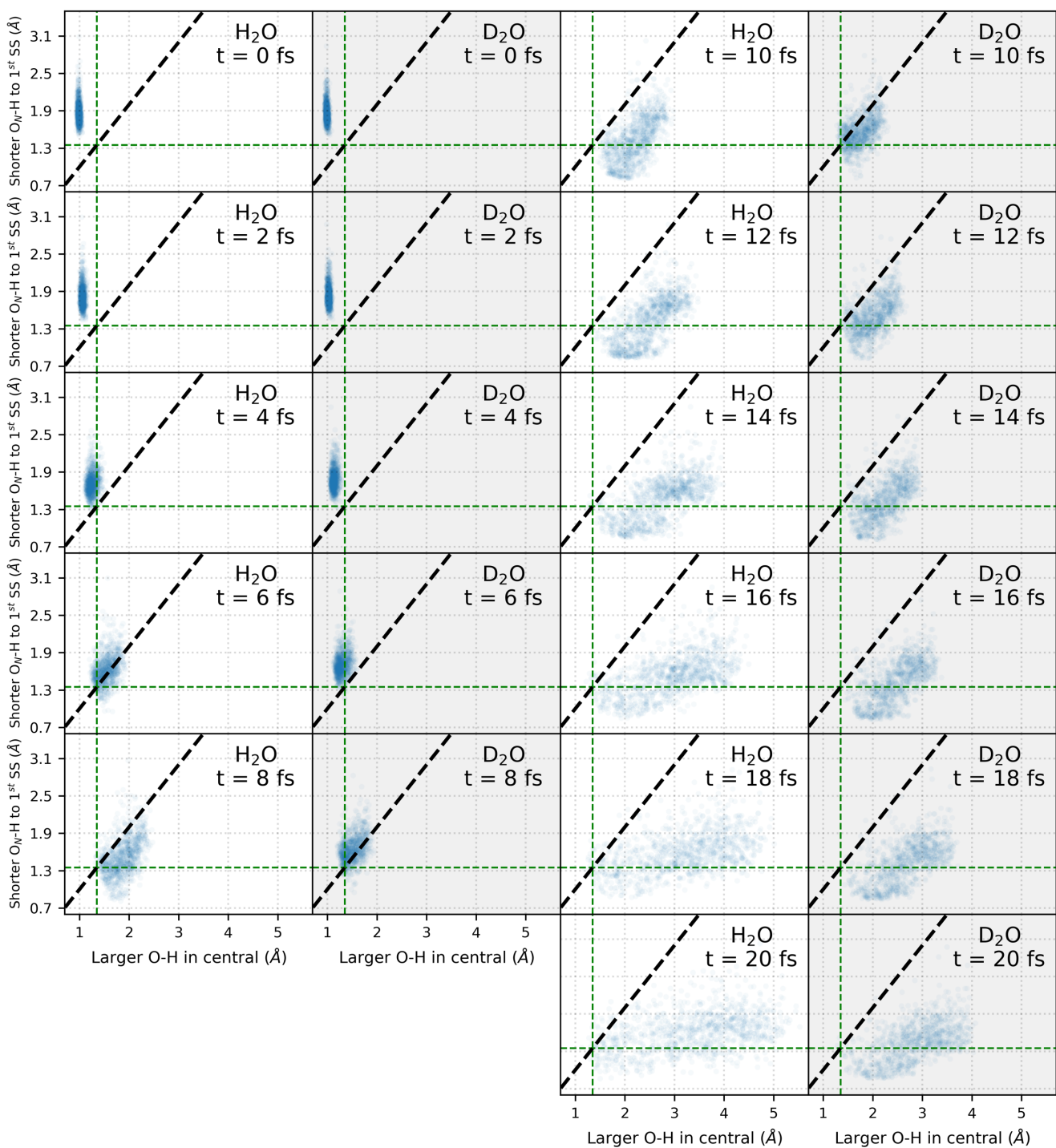


Figure S4: Distribution of two O-H distances for different simulation times in the simulations with core-excited water molecules. The distances, illustrated in Figure S2, are the larger distance within the central water molecule (x-axis) and the shorter distance between a hydrogen atom in the central molecule and an oxygen atom (denoted as O_N) in the first solvation shell (y-axis). The dashed black line indicates where the two O-H distances are equal, while the dashed green lines represent the cutoff used to evaluate whether the hydrogen is bound to the central water molecule or the first solvation shell (SS).

4. Protocol to identify orbital symmetry

The X-ray emission spectrum of liquid water involves electronic transitions between valence orbitals with localization in the core-ionized or core-excited molecule and the core-hole orbital localized at the oxygen atom of the same molecule. Since the O 1s core-hole orbital exhibits spherical symmetry, the transition dipole moment of an excited state will reflect the characteristics of the wavefunction distribution of the corresponding valence orbital. As depicted in **Figure S5**, in an optimized water molecule with C_{2v} symmetry, the $1b_1$ orbital will be aligned out of the molecular plane, the $3a_1$ orbital will be aligned along the bisector between the two O-H bonds, and the $1b_2$ orbital will be aligned along the H-H direction.

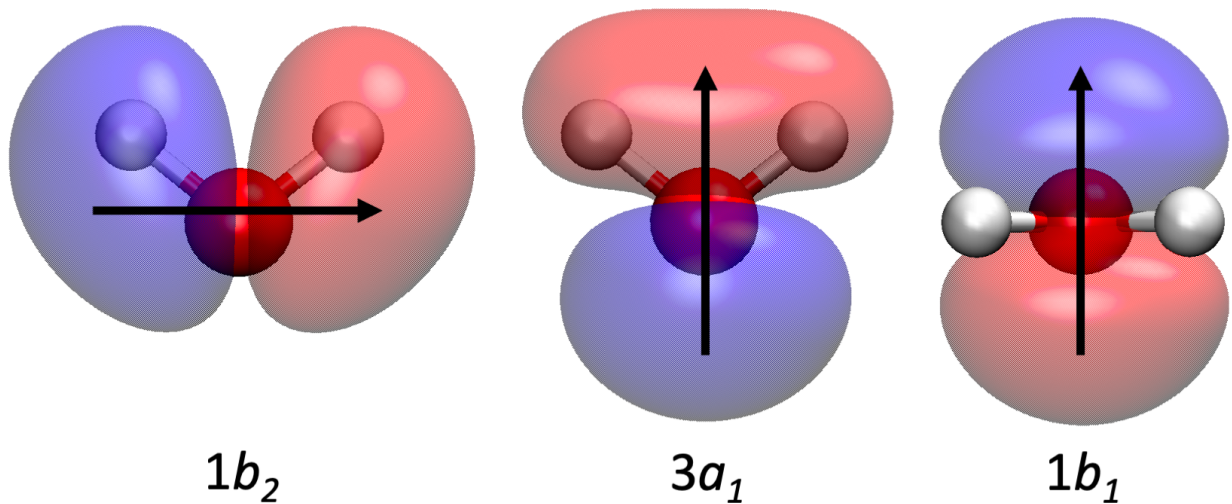


Figure S5: $1b_2$, $3a_1$ and $1b_1$ molecular orbitals of a water molecule in its optimized geometry. The arrows illustrate to the axes along which each orbital is oriented.

To compute the contributions of different orbital symmetries, we start from the coordinates of the central water molecule ($\vec{r}_O$, $\vec{r}_{H1}$, and $\vec{r}_{H2}$), define $\vec{r}_{O-H1} = \vec{r}_{H1} - \vec{r}_O$ and $\vec{r}_{O-H2} = \vec{r}_{H2} - \vec{r}_O$, and define unit vectors along the $1b_1$, $3a_1$, and $1b_2$ directions around the central water molecule:

$$\begin{aligned}\widehat{1b_1} &= \frac{\vec{r}_{O-H1} \times \vec{r}_{O-H2}}{|\vec{r}_{O-H1} \times \vec{r}_{O-H2}|} \\ \widehat{3a_1} &= \left(\frac{\vec{r}_{O-H1}}{|\vec{r}_{O-H1}|} + \frac{\vec{r}_{O-H2}}{|\vec{r}_{O-H2}|} \right) / \left| \frac{\vec{r}_{O-H1}}{|\vec{r}_{O-H1}|} + \frac{\vec{r}_{O-H2}}{|\vec{r}_{O-H2}|} \right| \\ \widehat{1b_2} &= \widehat{3a_1} \times \widehat{1b_1}\end{aligned}$$

Based on these unit vectors, a given excited state can be decomposed into contributions from the $1b_1$, $3a_1$, and $1b_2$ symmetries, computed as $|\hat{T}_i \cdot \widehat{1b_1}|^2$, $|\hat{T}_i \cdot \widehat{3a_1}|^2$, and $|\hat{T}_i \cdot \widehat{1b_2}|^2$, respectively, where $\hat{T}_i$ is the unit vector along the transition dipole moment of excited state i . These factors are used as weights when making the orbital symmetry decompositions. This means that if all the factors for a given excited state are non-zero, the contribution of this state will appear in the decomposition of different orbital symmetries. Notably, since $\widehat{1b_1}$, $\widehat{3a_1}$, and $\widehat{1b_2}$ are orthonormal, we have that $|\hat{T}_i \cdot \widehat{1b_1}|^2 + |\hat{T}_i \cdot \widehat{3a_1}|^2 + |\hat{T}_i \cdot \widehat{1b_2}|^2 = 1.0$.

5. Core-hole dynamical effects in the X-ray emission spectrum with emphasis on orbital symmetry

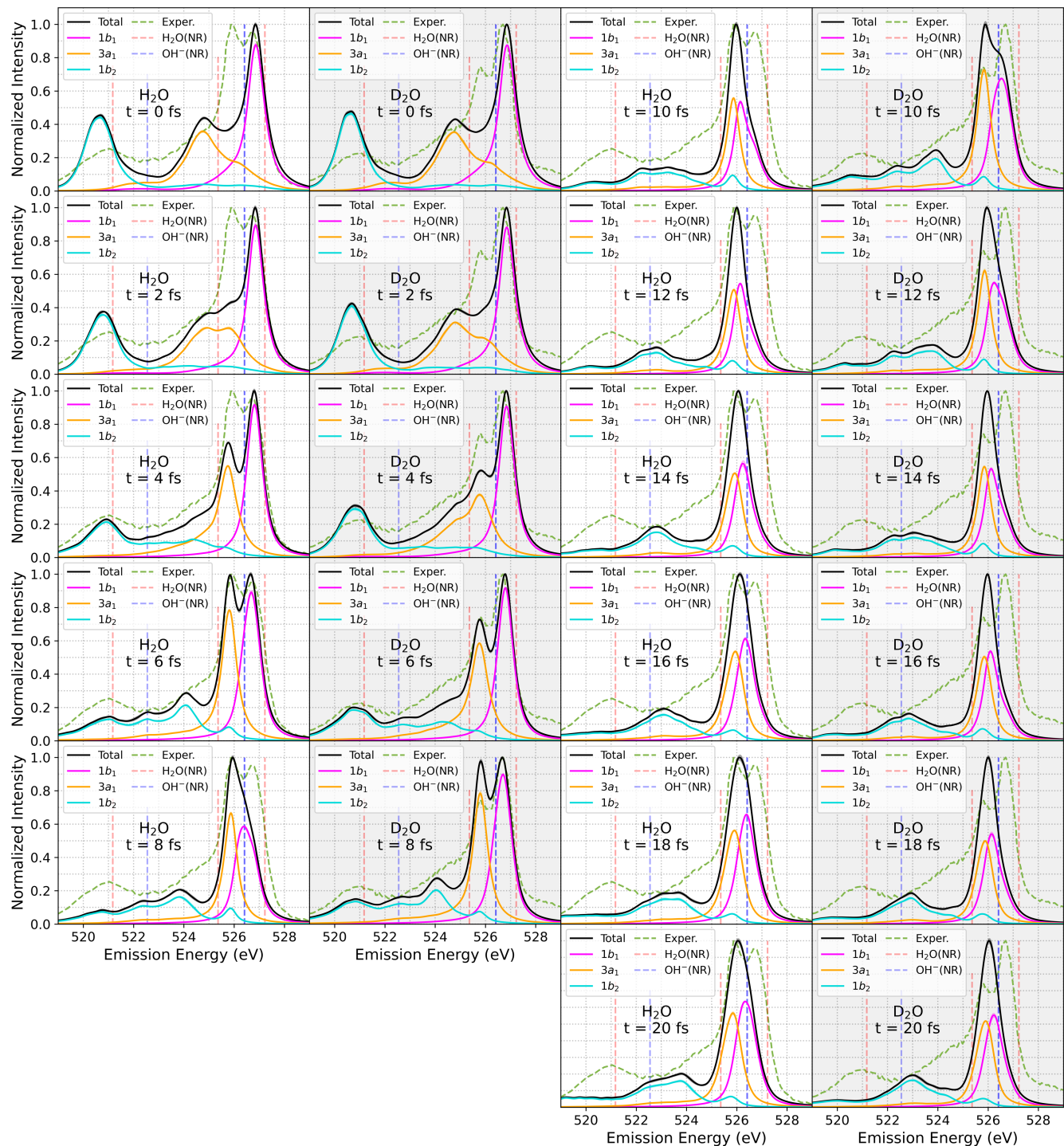


Figure S6: Non-resonant X-ray emission spectrum for liquid H₂O (white background) and D₂O (light grey background) at various core-hole simulation times. The figure also displays the contributions from different orbital symmetries and, for comparison, the experimental spectra¹ and the gas-phase emissions of the optimized H₂O and OH⁻ molecules. NR corresponds to non-resonant.

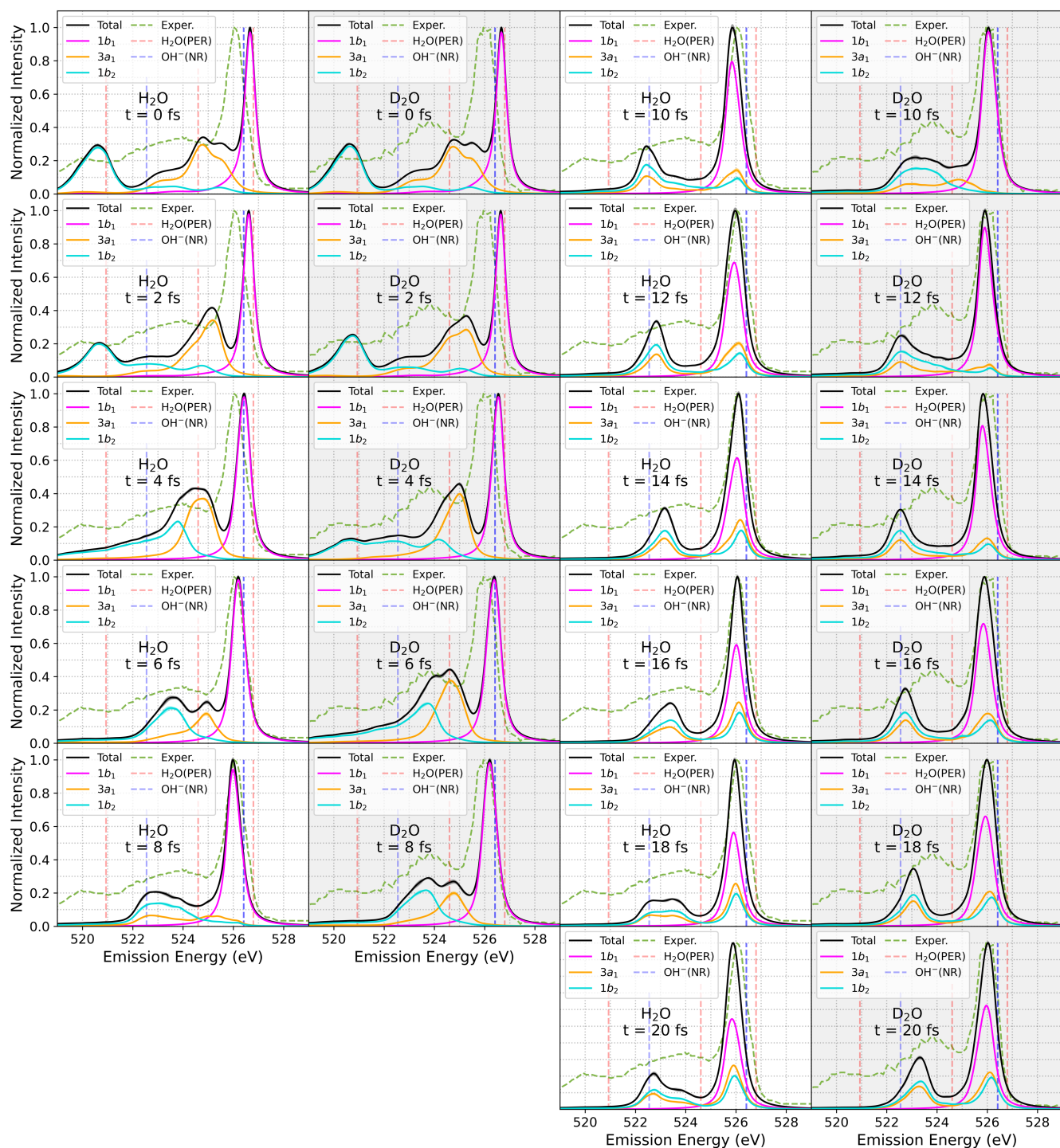


Figure S7: Pre-edge resonant X-ray emission spectrum for liquid H₂O (white background) and D₂O (light grey background) at various core-hole simulation times. The figure also displays the contributions from different orbital symmetries and, for comparison, the experimental spectra¹ and the gas-phase emissions of the optimized H₂O and OH⁻ molecules. NR and PER correspond, respectively, to non-resonant and pre-edge resonant, and OH-(NR) is shown in all panels because the product of dissociation.

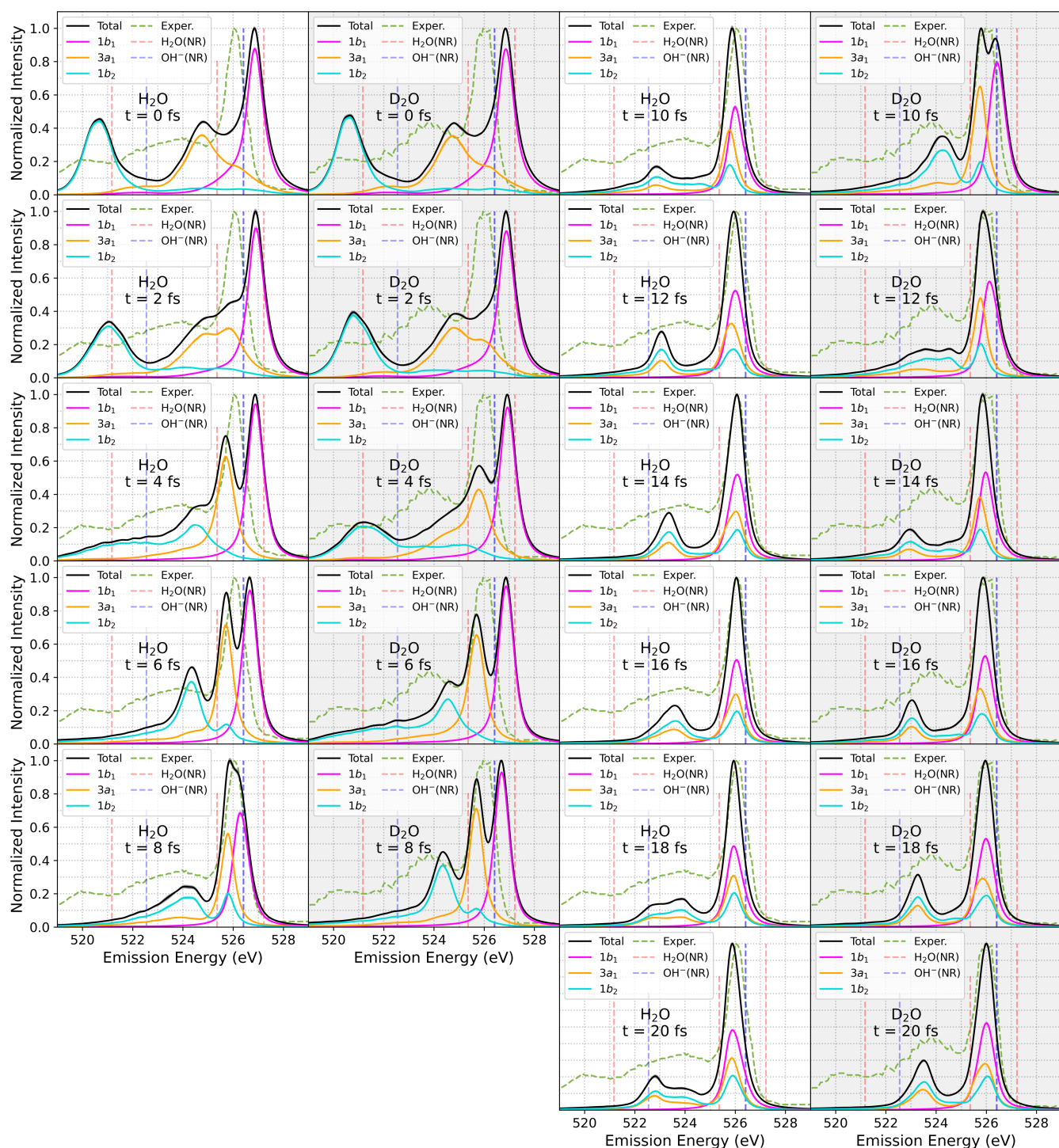


Figure S8: X-ray emission spectrum using core-excited dynamics and core-ionized electronic structure. Figure shows liquid H₂O (white background) and D₂O (light grey background) at various core-hole simulation times. The figure also displays the contributions from different orbital symmetries and, for comparison, the experimental spectra¹ and the gas-phase emissions of the optimized H₂O and OH⁻ molecules. NR corresponds to non-resonant.

6. Time-averaged X-ray emission spectrum with emphasis on orbital symmetry

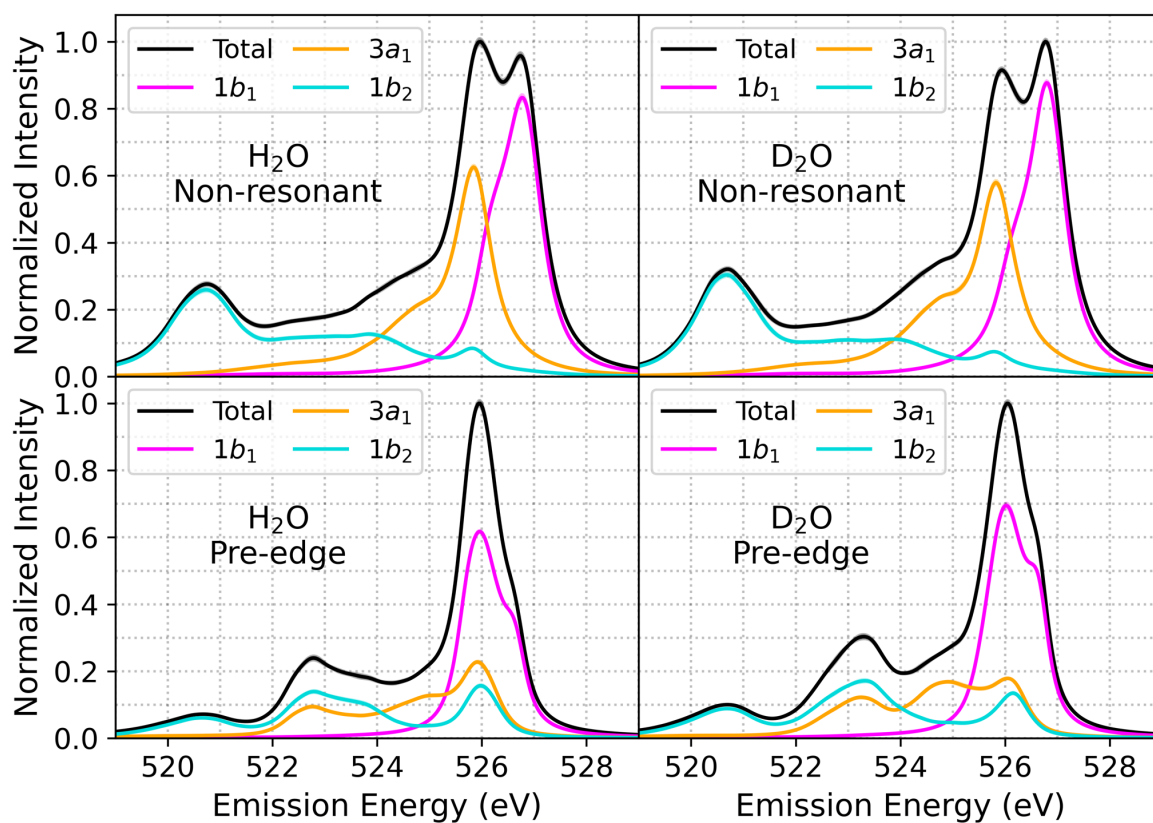


Figure S9: Time-averaged non-resonant (top panels) and pre-edge resonant (bottom panels) X-ray emission spectrum for liquid H₂O (left panels) and D₂O (right panels), using a core-hole lifetime of 4.0 fs for non-resonant and 10.0 fs for pre-edge resonant. The figure displays the contributions from different orbital symmetries to the overall spectrum (Total).

7. Core-hole dynamical effects in the X-ray emission spectrum with emphasis on hydrogen-bonding environment

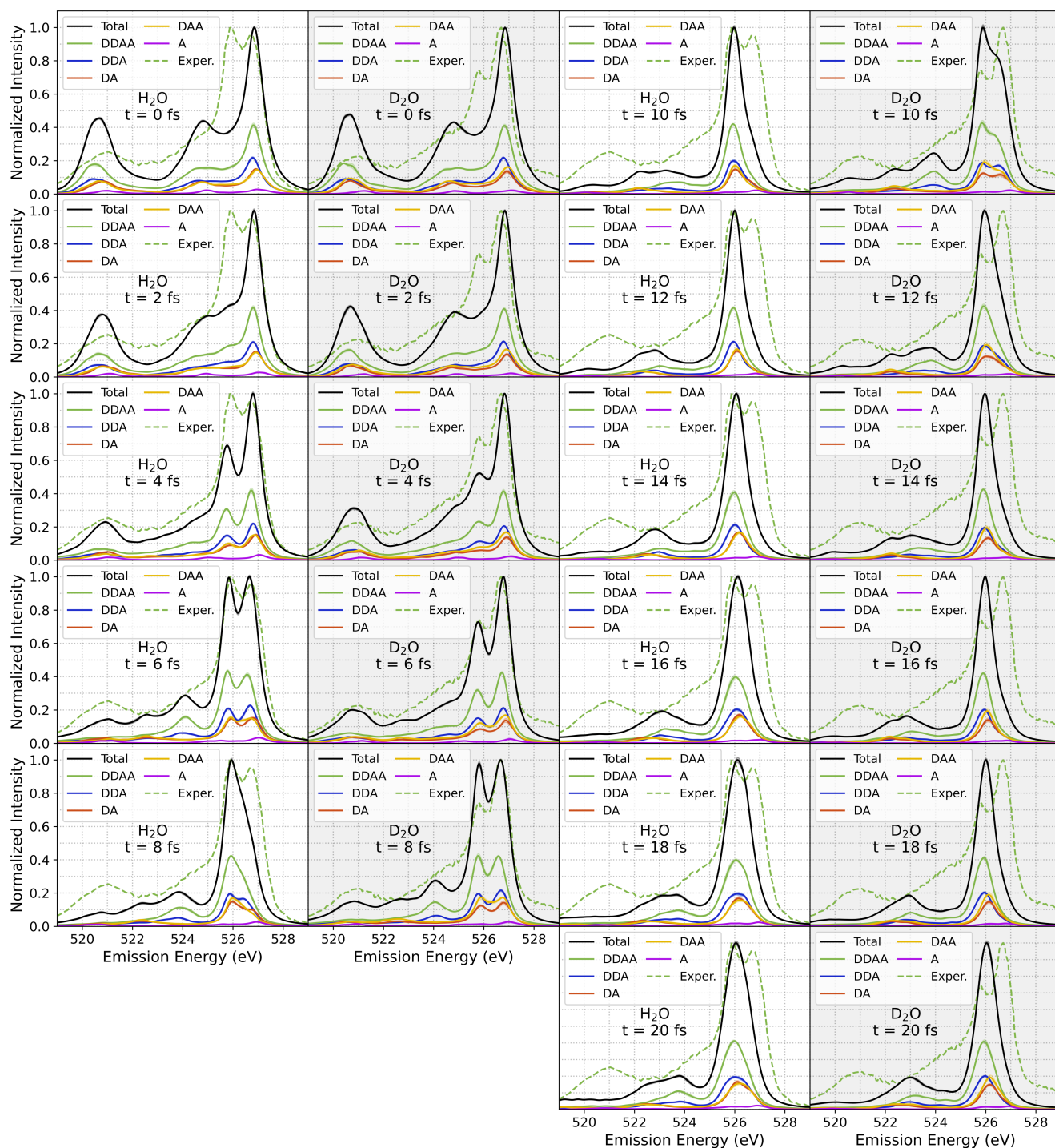


Figure S10: Non-resonant X-ray emission spectrum for liquid H₂O (white background) and D₂O (light grey background) at various core-hole simulation times. The figure also displays the contributions from distinct hydrogen-bonding environments, computed at $t = 0$ fs, where D denotes donor and A indicates acceptor. For comparison, the experimental spectra¹ is also shown.

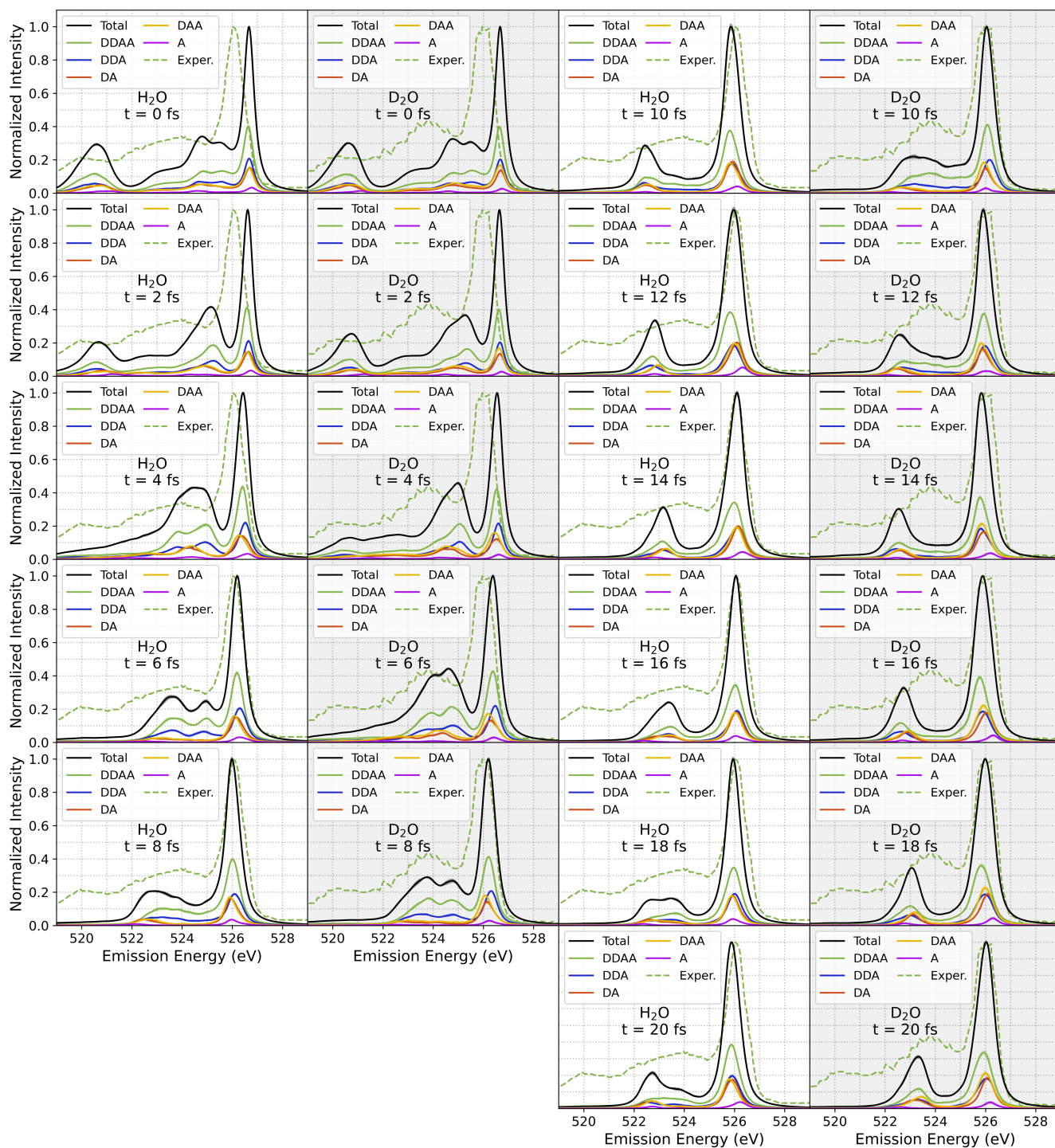


Figure S11: Pre-edge resonant X-ray emission spectrum for liquid H₂O (white background) and D₂O (light grey background) at various core-hole simulation times. The figure also displays the contributions from distinct hydrogen-bonding environments, computed at $t = 0$ fs, where D denotes donor and A indicates acceptor. For comparison, the experimental spectra¹ is also shown.

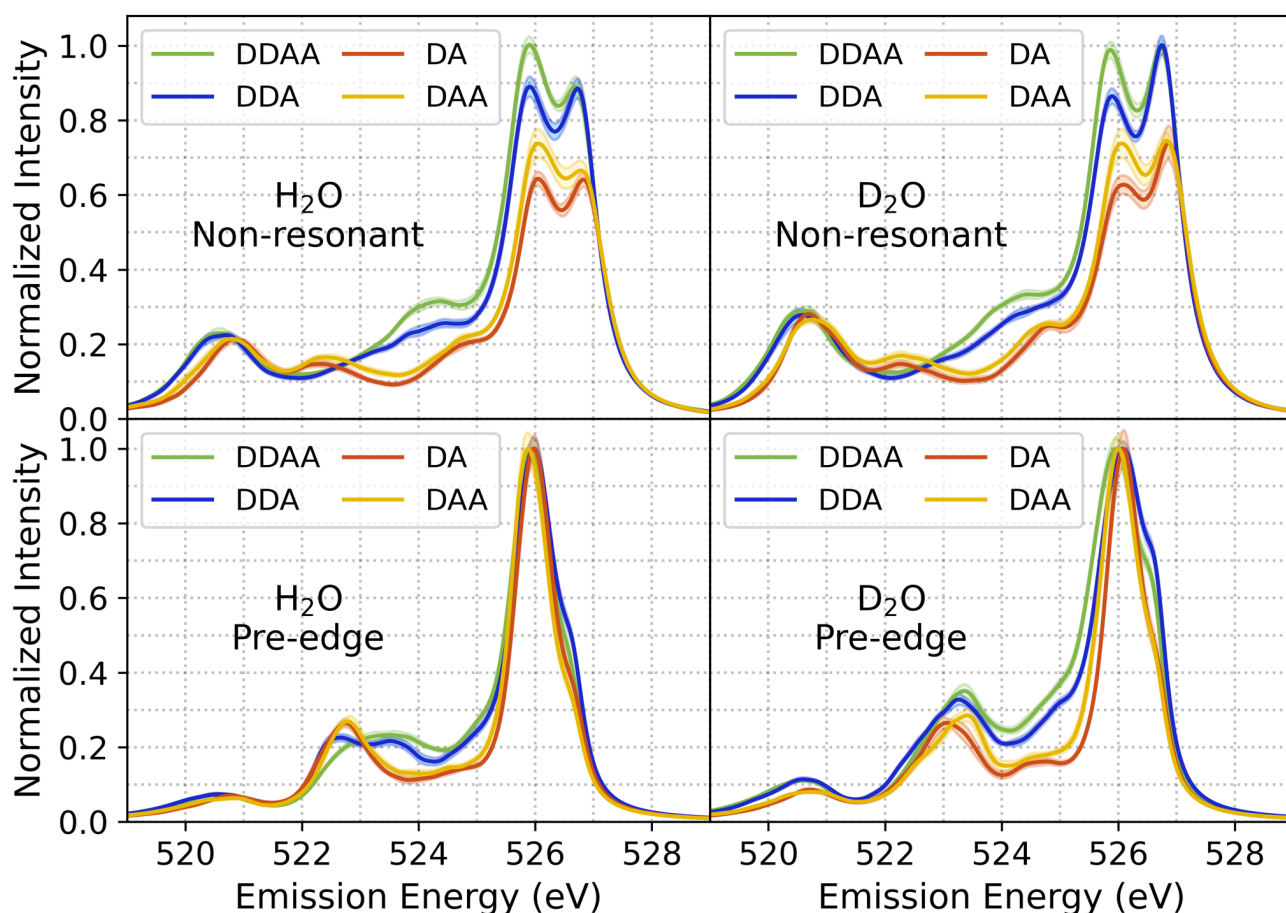


Figure S12: Time-averaged non-resonant X-ray emission spectrum of different hydrogen-bonding topologies for liquid H₂O (left) and D₂O (right), using a core-hole lifetime of 4.0 fs for non-resonant and 10.0 fs for pre-edge resonant. For comparison, the spectra have been aligned at the $1b_2$ band. Hydrogen-bonding topologies were computed at $t = 0$ fs, where D denotes a donor hydrogen-bond and A represents an acceptor.

Table S2: Fraction of core-ionized water molecules that remain intact after 20 fs of core-hole simulation time for each hydrogen-bonding topology. The table shows the percentage of core-ionized molecules that maintain both O-H distances below 1.35 Å throughout the entire simulation. D denotes a donor hydrogen-bond, A represents an acceptor hydrogen-bond, and F indicates a free molecule without any hydrogen bonds.

Hydrogen-bonding topology	Intact core-ionized, Liquid H ₂ O	Intact core-ionized, Liquid D ₂ O
DDAA	2.8%	6.6%
DDA	7.5%	13.8%
DA	11.3%	21.5%
DAA	8.6%	11.0%
A	84.4%	84.6%
D	20.0%	45.5%
DDAAA	0.0%	9.1%
AA	55.6%	76.9%
DD	20.0%	18.8%
F	100%	85.7%
DAAA	0.0%	0.0%

8. X-ray emission spectrum predictions with EOM-IP-CCSD

Theoretical spectra were computed using the equation-of-motion ionization potential coupled-cluster with singles and doubles (EOM-IP-CCSD) method. To facilitate comparison with the TD-B3LYP predictions from the main text and experimental spectrum, the computed spectra were convoluted using the same procedure as described in the main text, but with a 3.9 eV redshift. Due to expensive computational cost, EOM-IP-CCSD calculations were performed only for liquid H₂O, considering 5% of the structures used in the TD-DFT calculations discussed in the main text. **Figure S13** presents the non-resonant X-ray emission spectra at various core-hole simulation times in comparison to the TD-B3LYP predictions and the experimental spectrum. **Figure S14** shows the decomposition of the spectrum from different orbital symmetries.

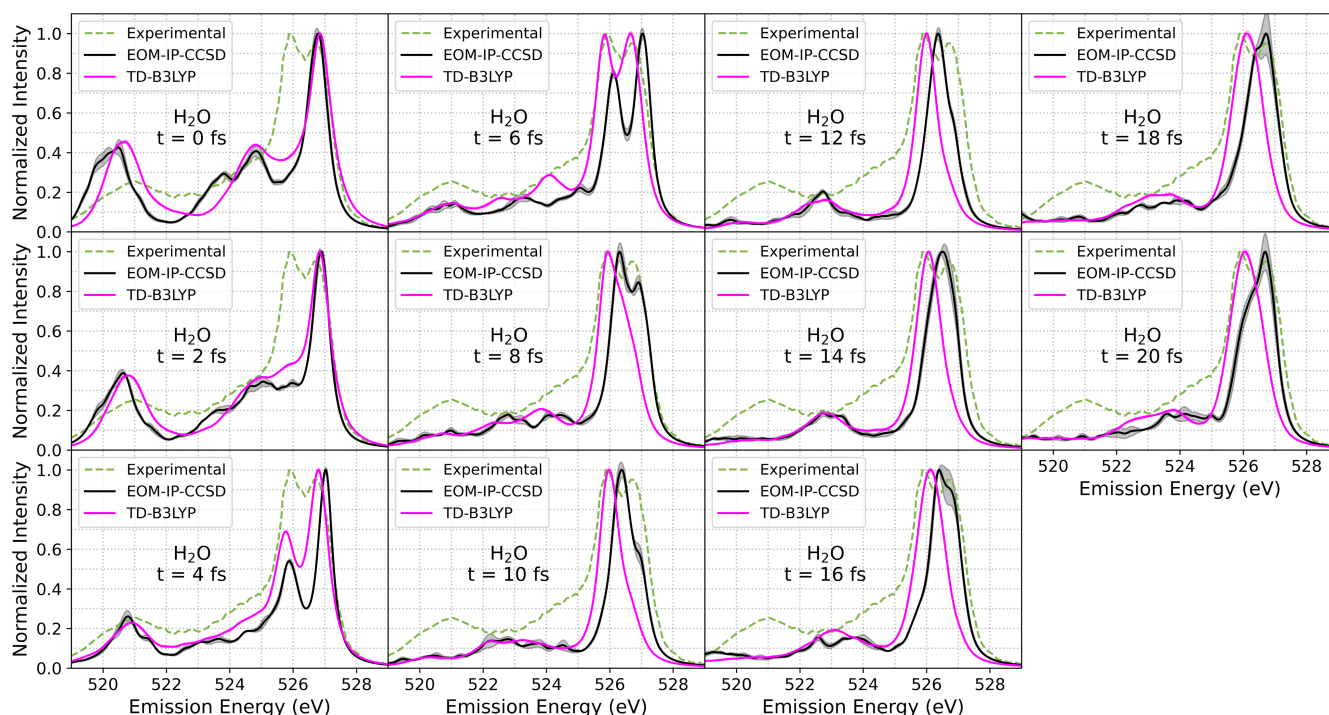


Figure S13: Non-resonant X-ray emission spectrum for liquid H₂O at various core-hole simulation times comparing electronic excitations computed with EOM-IP-CCSD and TD-B3LYP. The figure also displays, for comparison, the experimental spectra.¹

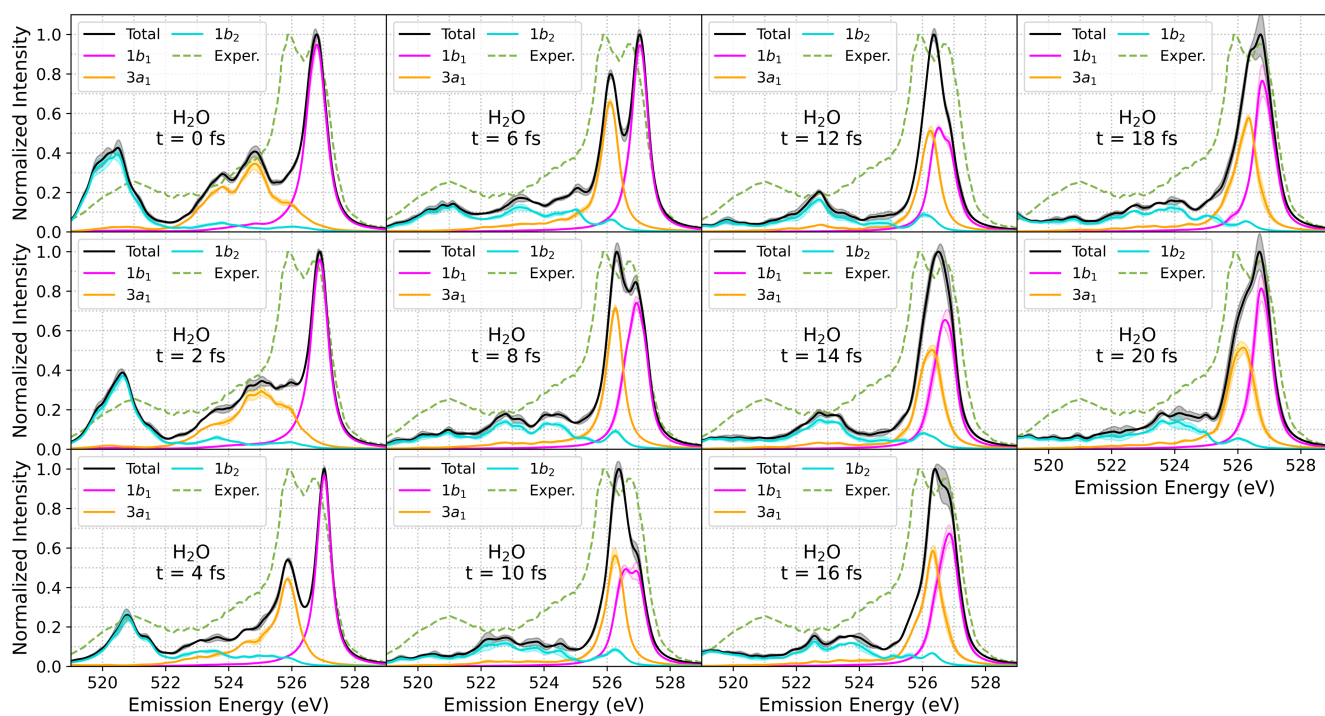


Figure S14: Non-resonant X-ray emission spectrum for liquid H₂O at various core-hole simulation times with electronic excitations computed with EOM-IP-CCSD. The figure also displays the contributions from different orbital symmetries and, for comparison, the experimental spectra.¹

9. Non-resonant $1b_1'$ peak gains intensity as proton is transferred from core-ionized water to the first solvation shell

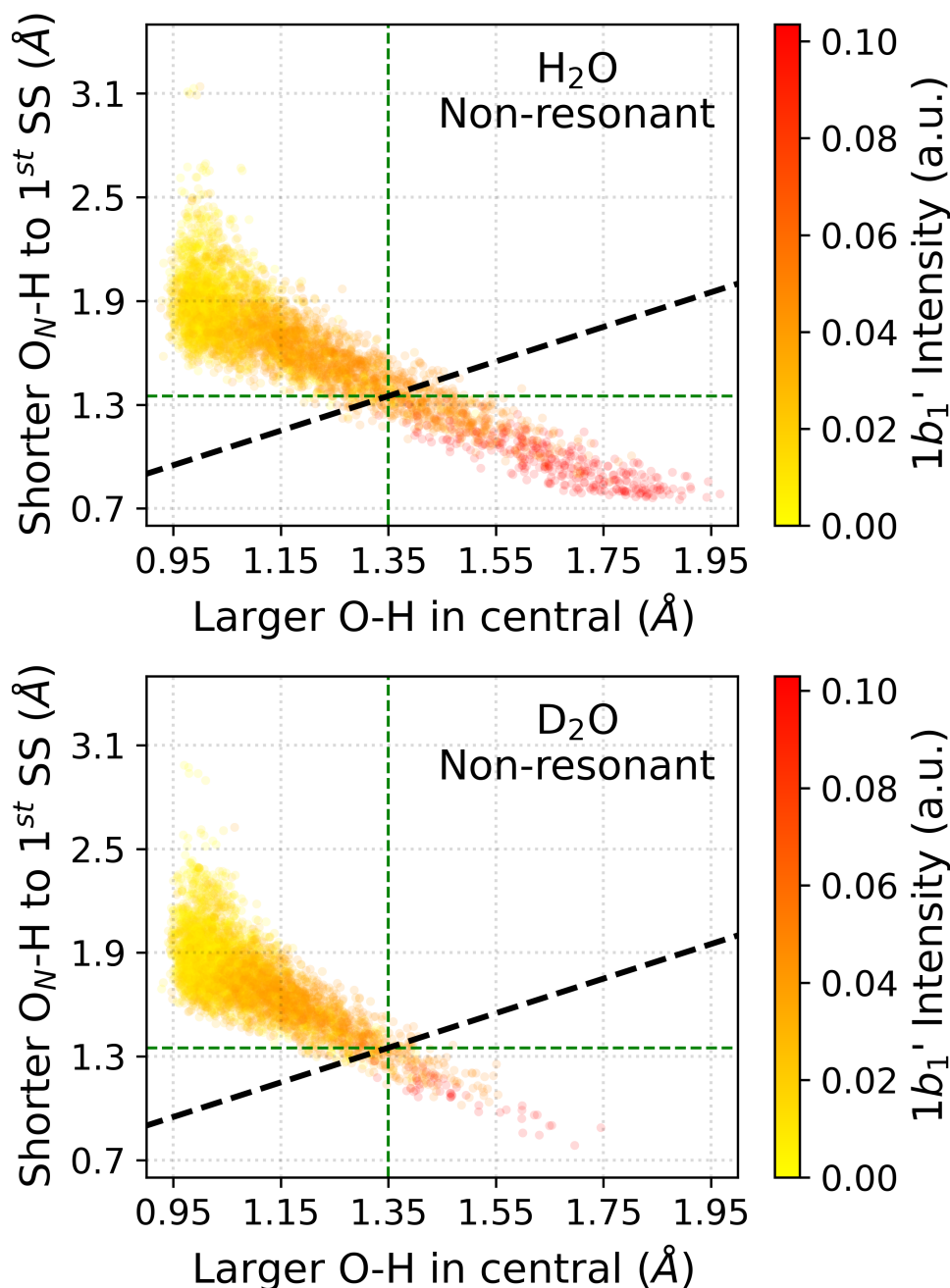


Figure S15: Distribution of two O-H distances for during the first 8 fs in the simulations with core-ionized water molecules for liquid H_2O (top) and D_2O (bottom). The colors represent the intensity of the $1b_1'$ peak at the non-resonant X-ray emission spectrum (sum of contributions between 525.6 eV and 526.3 eV). The distances, illustrated in Figure S2, are the larger distance within the central water molecule (x-axis) and the shorter distance between a hydrogen atom in the central molecule and an oxygen atom (denoted as O_N) in the first solvation shell (y-axis). The dashed black line indicates where the two O-H distances are equal, while the dashed green lines represent the cutoff used to evaluate whether the hydrogen is bound to the central water molecule or the first solvation shell (SS).

10. X-ray emission spectrum with different core-hole lifetimes

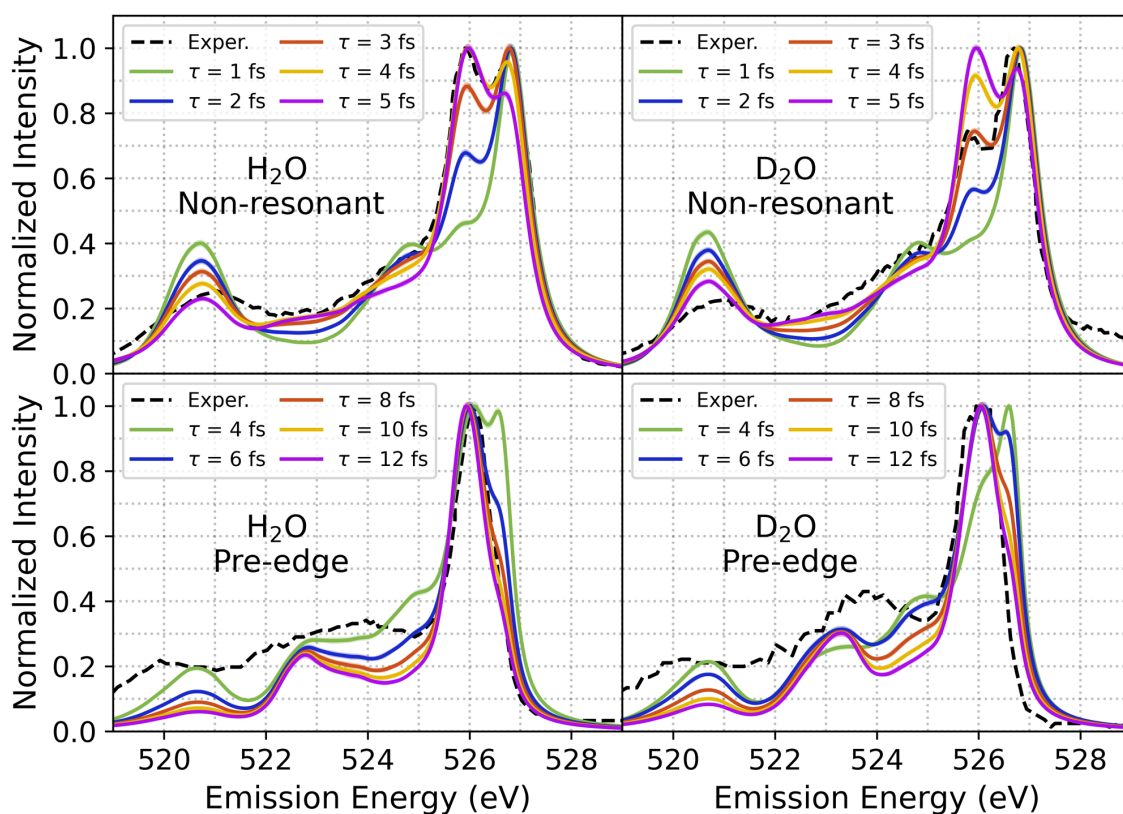


Figure S16: Time-averaged non-resonant (top panels) and pre-edge resonant (bottom panels) X-ray emission spectra for liquid H₂O (left panels) and D₂O (right panels) for different core-hole lifetimes. For comparison, the experimental spectra¹ are shown.

11. Computational estimates for core-hole lifetimes from Auger decay rates in the gas-phase

We observed a striking difference in the core-hole lifetimes of liquid water between the non-resonant (4.0 fs) and pre-edge (10.0 fs) states, based on our simulations. This prompted us to explore whether a similar contrast exists for isolated water molecules in the gas-phase. Using a Feshbach-Fano formalism² implemented in Q-Chem,³ we estimated the Auger decay rates of a single water molecule in the core-ionized state (analogous to the non-resonant state in liquid water) and the first core-level excited state ($1a_1 \rightarrow 4a_1$ excitation, analogous to the pre-edge state in liquid water) with EOM-CCSD calculations. We included the 100 lowest energy states that could result from the Auger process and modeled the ejected electron as a plane wave. The Auger widths were 176 meV for the core-ionized state and 103 meV for the lowest core-excited state, corresponding to Auger decay lifetimes of 3.74 fs and 6.39 fs, respectively. These gas phase calculations are not directly comparable to the liquid-phase, but they suggest that the core-ionized state has a much shorter Auger decay lifetime than the core-excited state, in agreement with our findings at the liquid-phase. One possible factor that could enhance the difference in lifetime between the pre-edge resonant and non-resonant cases is the suppression of partial Rydberg character in the pre-edge excitation of the condensed phase, compared to the gas-phase. We used the experimental equilibrium structure⁴ of the water molecule (0.958 Å bond length, 104.48° bond angle) and the aug-cc-pCVTZ basis in Auger decay rate calculations.

12. Generation of core-ionized and core-excited states

We use the following procedure to generate the initial states for the core-hole QM/MM simulations and in the TD-DFT calculations. First, we select the QM and MM regions for each structure and perform a ground state calculation with total charge 0 and spin multiplicity 1. The wavefunction of the calculation is the initial guess for the following calculation. Next, we swap the beta 1s orbital of the oxygen atom in the central water molecule of the cluster (the target of core-ionization or core-excitation) with the beta valence orbital. We then perform a single point calculation with total charge 1 and spin multiplicity 2, which creates a core-hole in the beta 1s orbital of the central water molecule. This is the core-ionized state. We use the maximum overlap method (MOM) to prevent the core-hole from moving to another molecule during the SCF procedure. To construct the core-excited state, we perform another single point calculation, where we swap the beta 1s orbital of the oxygen atom with the beta orbital of the lowest unoccupied molecular orbital (LUMO). The LUMO has $4a_1$ symmetry in the gas-phase optimized molecule and is localized on the central water molecule as a consequence of the previous calculation for the core-ionized state. The total charge is 0 and the spin multiplicity is 1. The core-hole and the core-excited electron are both located on the central water molecule. We again use MOM to keep them fixed during the SCF procedure.

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