

Core-Ionization Spectrum of Liquid Water: Supplemental Information

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1. DATA DEPOSITION

The equilibrium dynamics trajectory files for the MD and AIMD simulations as well as raw data for the $1s_O$ IE spectrum from the AIMD/400, 1w/20QM simulations were deposited in *Zenodo* archive¹.

2. EQUILIBRIUM SAMPLING: MOLECULAR DYNAMICS VERSUS AB INITIO MOLECULAR DYNAMICS

Fig. S1 and Table S1 compare the structural properties of water computed from the MD (TIP3P) and AIMD trajectories. For adequate comparison, in both simulations we computed $g_{OO}(r)$ (O-O radial distribution function, RDF) between the selected central water molecule and the rest of the waters, so that in AIMD simulations the short-range structure of $g_{OO}(r)$ comes from the QM part. We note that water molecules within 6.5 Å radius of the central water were included in the QM region in the AIMD simulation. It covers part of the third shell and has more structure than TIP3P and experiment. Below we compare the RDF from our simulations with that generated from the neutron diffraction data refined with X-ray data (experimental)².

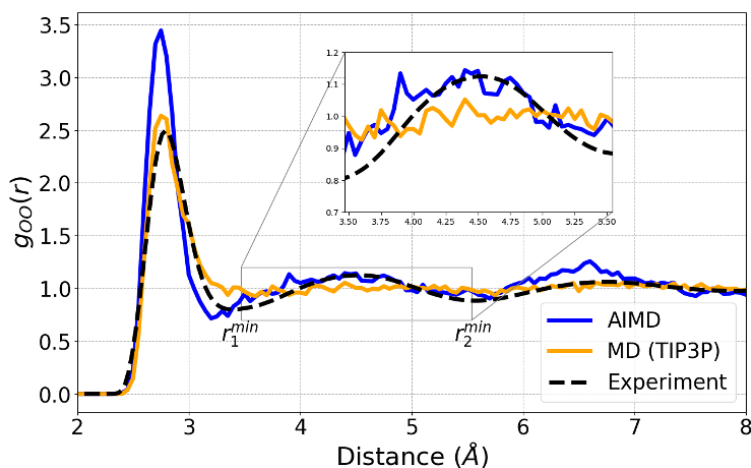


FIG. S1: The O-O radial distribution function computed from the AIMD and MD trajectories compared with the experimental $g_{OO}(r)$ ²

The first peak of the radial distribution function for TIP3P water is closer to the experimental one than that generated from the AIMD simulation. However, the average coordination number generated from the two calculation and from the experiment are not very different and lie between 4.5 and 4.9. These results indicate that the first shell is just more structured in case of water described by ω B97X-D/6-31G* than TIP3P water and experiment. As discussed in the main manuscript, an important aspect which determines the XPS spectra of water is its hydrogen bonding environment. It is only indirectly captured by the radially averaged structure of $g_{OO}(r)$. Therefore, we calculated the average number of

TABLE S1: Structural properties of liquid water from the O–O radial distribution function, $g_{OO}(r)$, obtained from the AIMD and MD simulations around the central water molecule of their respective simulation boxes and experimental data.^a

$g_{OO}(r)$	$r_1^{min}, \text{Å}$	$r_2^{min}, \text{Å}$	n_1	n_2
MD	3.54	5.76	4.91	23.41
AIMD	3.28	5.51	4.53	23.46
Expt ²	3.39	5.58	4.73	23.31

r_1^{min} and r_2^{min} are the first and the second minima of $g_{OO}(r)$, which define the first and second coordination shells; n_1 and n_2 are the number of water molecules inside the first and the second coordination shells.

hydrogen bonds around the central water molecule and compared it to the experiment which uses a three dimensional distribution of water molecules³. The later uses the same definition of hydrogen bonding as used to construct Fig. 13 of the main draft. The experiments show that the total number of hydrogen bonds formed by a water molecule is 3.58, which is same as that obtained from the AIMD trajectory while we get an average of 3.28 hydrogen bonds from the MD trajectory.

The $g_{OO}(r)$ calculated from the three methods have first peak at the same radial distance. While both the first minima and second minima (r_1^{min} and r_2^{min}) is systematically shifted to larger r values for the MD (TIP3P) simulation, MD yields much flatter 2nd peak. The ω B97X-D functional⁴ reproduces the second shell accurately, but produces over-structured 1st solvation shell. Table S2 shows the breakdown of different hydrogen-bonding motifs in our simulations and in previous studies.

TABLE S2: The fraction of water molecules with double-donor (DD), single-donor (SD), and non-donor (ND) configurations from different computational methods.

Method	DD	SD	ND
AIMD/ ω B97X-D ^a	81	16	3
TIP3P	65	27	8
AIMD/MP2 ^{b,c}	53	40	7
PIMD/MBPOL ^d	58	36	6
CPMD ^c	79	20	1
TIP3PF ^c	75	22	3
Exp ^c	15±25	80±20	5±5

^a This work.

^b Fragment-based method parameterized by MP2.

^c Quoted from Ref. 5.

^d From Ref. 6.

3. CONVERGENCE WITH RESPECT TO THE QM SIZE AND NUMBER OF SNAPSHOTS: ADDITIONAL RESULTS

Including 5 or 6 water molecules in the QM region produces similar spectra because an water molecule can have 4-5 molecules in its first solvation shell. The energy peaks are similar when taking just the central water to construct the spectra but the shape may differ. However, it is nearly the same when including all waters from the first solvation shell in the QM region. The snapshots are from the AIMD trajectory.

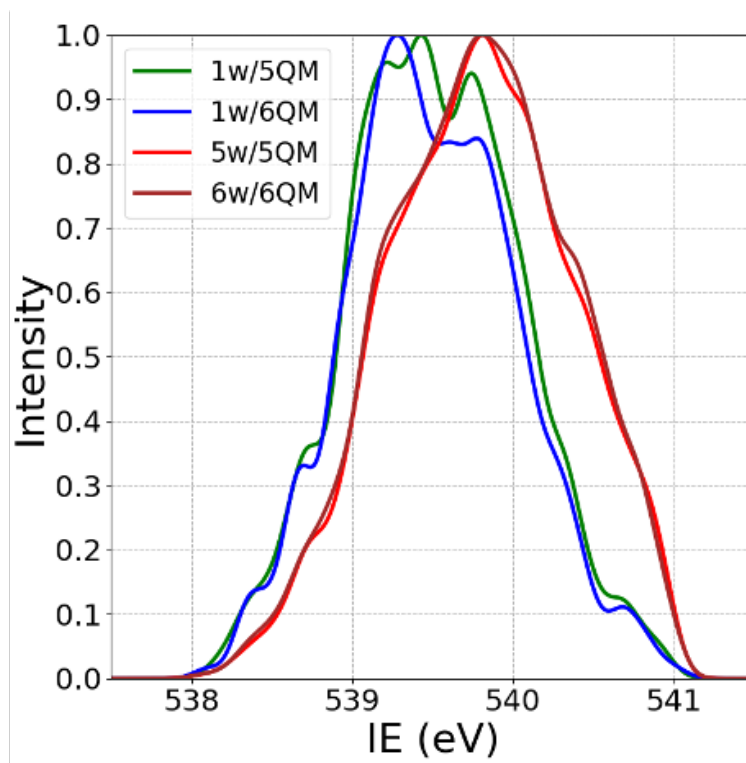


FIG. S2: The O edge ionization spectra computed 5 and 6 water QM systems.

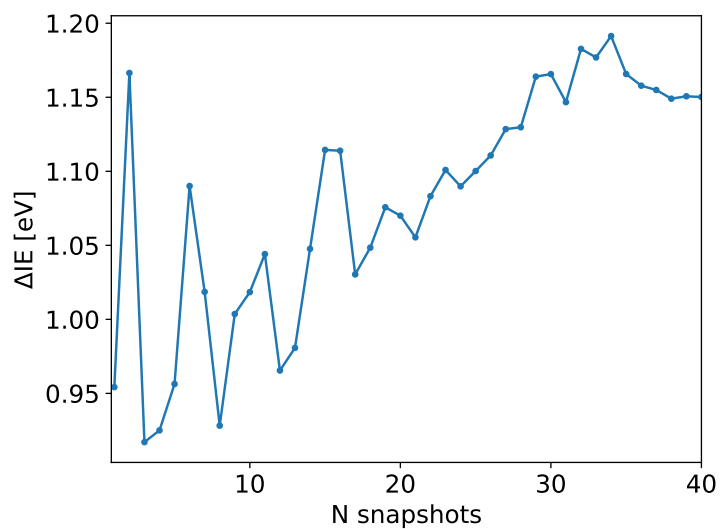


FIG. S3: Convergence of CVS-EOM-IP-CCSD shift (from eT calculations) with respect to the number of snapshots. $\Delta IE=1.15$ eV, with standard deviation of 0.55 eV.

4. ANALYSIS OF THE COMPUTED SPECTRA

Table IV in the main paper gives the peak position and width of the $1s_O$ spectra of water calculated using different setups. The peak and the FWHM of the spectra were calculated by convoluting the core IEs with gaussians of FWHM=0.5 eV. Figure S4 shows the $1s_O$ spectra of AIMD/400, 5w/20QM system convoluted with gaussians with FWHM equals 0.5, 0.2, and 0.3 eV, respectively. The peak for FWHM = 0.5 eV is 538.996 eV and the peak for FWHM = 0.2 eV is 538.929 eV, whereas the spectrum with FWHM = 0.05 eV is noisy and its peak maximum is difficult to determine. The width of the spectra for FWHM = 0.5, 0.2 and 0.05 eV is 1.44, 1.345, and 1.331 eV, respectively.

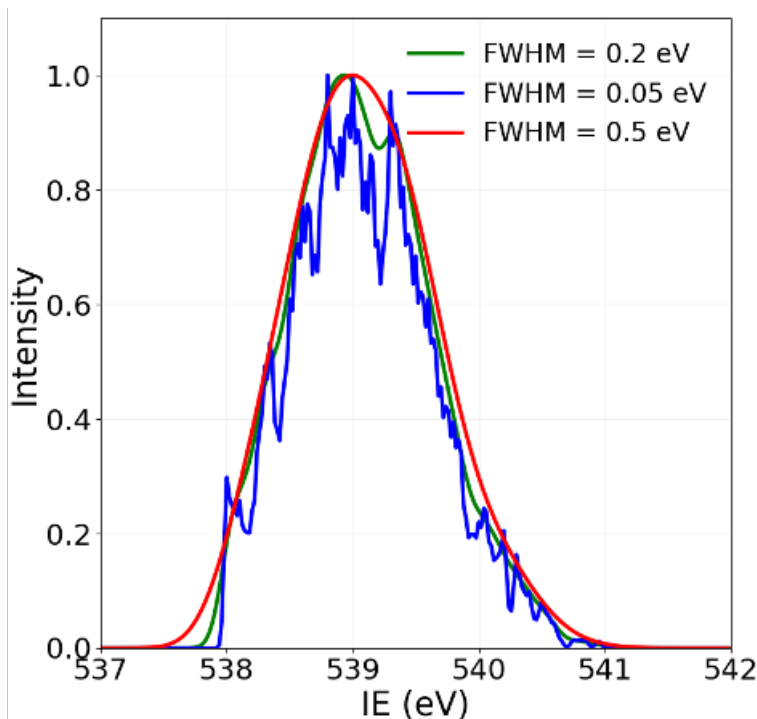


FIG. S4: The O edge ionization spectra of the AIMD/400, 5w/20QM system convoluted with gaussians of width (FWHM) 0.5, 0.2 and 0.05 eV respectively.

5. RECALCULATING THE SPECTRA USING DIFFERENT HYDROGEN-BOND DISTRIBUTIONS

Figure S5 shows the $1s_O$ spectra MD/400, 1w/5QM system and the AIMD/400, 1w/5QM spectra constructed by re-weighting with the dominant hydrogen-bond distributions from

the trajectory of TIP3P water.

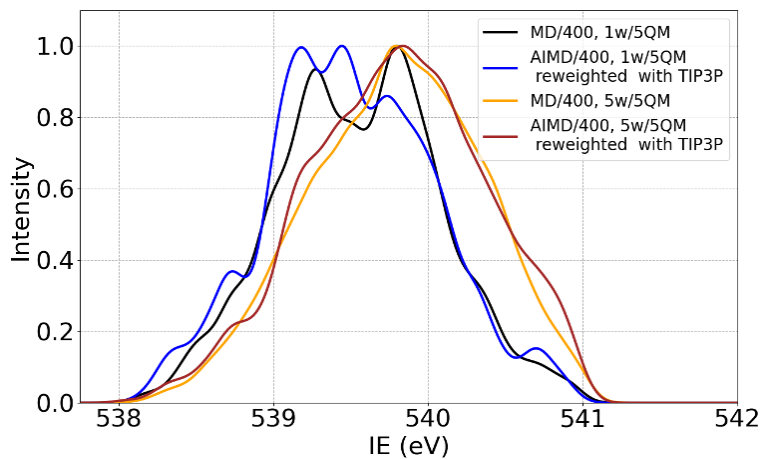


FIG. S5: The $1s_O$ spectra of liquid water constructed from the MD trajectory and re-weighting the contributions from the dominant hydrogen-bonding patterns to match the distributions from the MD trajectory.

**6. Q-CHEM INPUT FOR CVS-EOM-CCSD CALCULATIONS FOR 20 QM
WATERS**

```
$REM
BASIS = MIXED
SCF_GUESS = CORE
SCF_CONVERGENCE = 8
MAX_SCF_CYCLES = 200
THRESH = 14
METHOD = EOM-CCSD
CVS_IP_STATES = [20]
MEM_TOTAL = 230000
N_FROZEN_CORE = 20
SYM_IGNORE = TRUE
NO_REORIENT = TRUE
CC_TRANS_PROP = 1
STATE_ANALYSIS = TRUE
MOLDEN_FORMAT = TRUE
CC_BACKEND = VM
$END
```


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- ¹ S. Dey, S. D. Folkestad, A. Paul, H. Koch, and A. I. Krylov, Core-ionization spectrum of liquid water, <https://doi.org/10.5281/zenodo.7978306>, 2023.
- ² A. K. Soper, The radial distribution functions of water as derived from radiation total scattering experiments: Is there anything we can say for sure?, *ISRN Phys. Chem.* 2013 **7**, 074506 (2013).
- ³ A. K. Soper, F. Bruni, and M. A. Ricci, Site-site pair correlation functions of water from 25 to 400°—the methanol hydration case, *J. Mol. Liq.* **300**, 112258 (2020).
- ⁴ J.-D. Chai and M. Head-Gordon, Systematic optimization of long-range corrected hybrid density functionals, *J. Chem. Phys.* **128**, 084106 (2008).
- ⁵ J. Liu, X. He, and J. Z. H. Zhang, Structure of liquid water—a dynamical mixture of tetrahedral and ‘ring-and-chain’ like structures, *Phys. Chem. Chem. Phys.* **19**, 11931 (2017).
- ⁶ V. W. D. Cruzeiro, A. Wildman, X. Li, and F. Paesani, Relationship between hydrogen-bonding motifs and the $1b_1$ splitting in the x-ray emission spectrum of liquid water, *J. Phys. Chem. Lett.* **12**, 3996 (2021).