

Supplementary material for “Requirements on first-principles calculations of X-ray absorption spectra of liquid water”

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Geometries of the water complexes were optimized using deMon2k.¹

TABLE I. Gas phase geometry, as obtained using the PBE² exchange-correlation functional and the TZVP basis set for oxygen³ and IGLO-II for both hydrogen atoms.⁴ All distances expressed in Ångström.

Atom	X	Y	Z
O	0.000000	0.000000	0.000000
H	0.771185	0.596798	0.000000
H	-0.771185	0.596798	0.000000

TABLE II. Dimer geometry, as obtained using the PBE² exchange-correlation functional and the aug-cc-pVTZ^{5,6} basis set, and the optimization was performed under the constraint that the distance between the oxygens was equal to 2.8 Å. All distances expressed in Ångström.

Atom	X	Y	Z
O (acceptor)	0.000000	0.000000	0.000000
H	0.772161	0.366173	-0.463961
H	-0.772161	0.366173	-0.463961
O (donor)	0.000000	-2.800000	0.000000
H	0.000000	-1.817880	0.000000
H	0.000000	-3.049212	0.938813

TABLE III. Trimer geometries, as obtained using the PBE exchange-correlation functional and the TZVP basis set for oxygen and IGLO-II for both hydrogen atoms. The geometries were partially optimized with constraints used in order to get the desired H-bonding structure. First, the O–O distances to the solute waters were set at 2.8 Å, as for the dimer. Secondly, the angle to the two solute oxygens was fixed close to the tetrahedral angle or to 180°, and the position of the two hydrogens involved in H-bonding were fixed. All distances expressed in Ångström.

Atom	X	Y	Z
<u>acceptor-acceptor</u>			
O (solute)	0.000000	0.000000	0.000000
H	-0.539331	0.758557	-0.294135
H	-0.513460	-0.793847	-0.243252
O	2.701875	-0.002673	-0.734753
H	1.758737	0.000000	-0.555635
H	2.785041	-0.035542	-1.705095
O	-0.035019	-0.043860	2.799438
H	0.898025	-0.036204	3.083162
H	0.000000	0.000000	1.841080
<u>donor-acceptor</u>			
O (solute)	0.000000	0.000000	0.000000
H	-0.076942	0.060653	-0.983252
H	0.944576	0.158791	0.187749
O	0.000000	0.000000	2.799997
H	-0.348082	0.054196	1.881485
H	-0.059525	-0.948690	3.018355
O	0.000000	0.000306	-2.800000
H	-0.327748	-0.855552	-3.136021
H	-0.528984	0.675829	-3.265261

TABLE IV. Trimer geometries, *cont.*

Atom	X	Y	Z
donor-donor			
O (solute)	0.000000	0.124013	2.797253
H	0.868791	-0.085670	3.147731
H	0.000000	0.000000	1.845297
O	0.000000	0.000000	0.000000
H	-0.414969	-0.807689	-0.357915
H	-0.607295	0.723455	-0.246664
O	2.667979	-0.206625	3.579921
H	2.924313	0.714221	3.380799
H	2.864939	-0.321393	4.529015

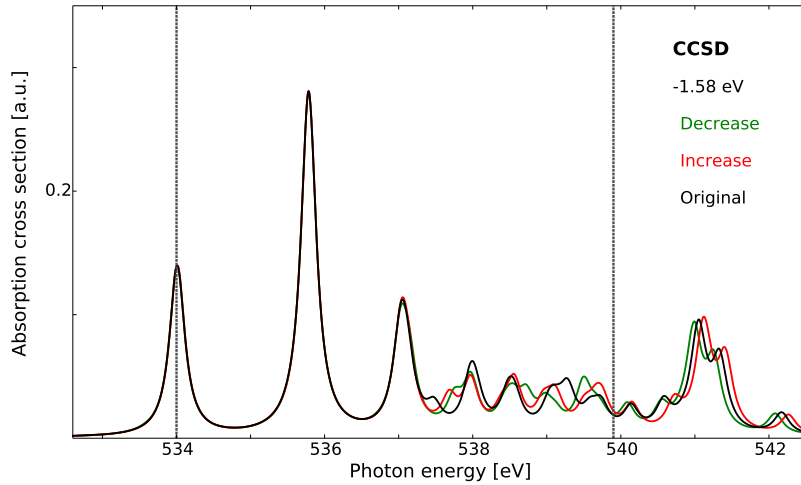


FIG. 1. X-ray absorption spectra of gas-phase water as obtained using damped CCSD response theory with a Lanczos chain length of 8000. Basis set exponents changed by factors of 1.0, 0.98, and 0.98^{-1} . For additional information, see main article.

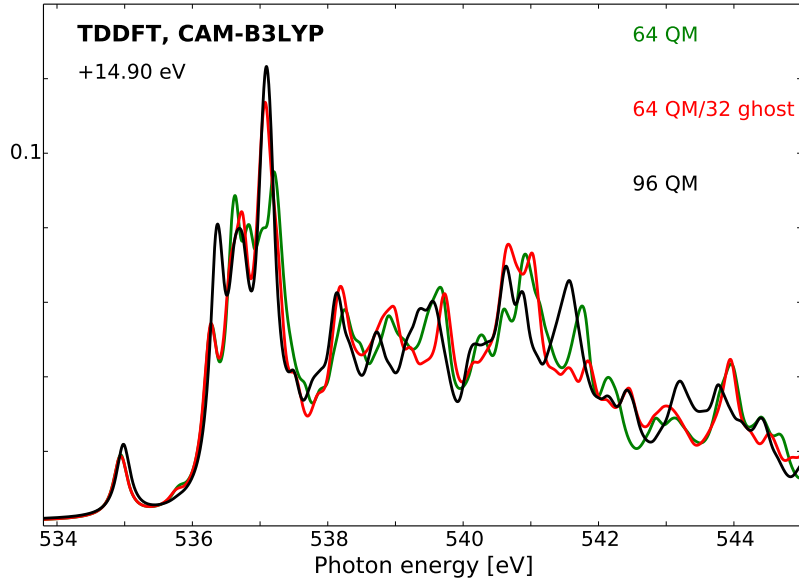


FIG. 2. X-ray absorption spectra of a single water cluster, comparing 64 QM and 96 QM calculations with 64 QM using the basis set of 96 QM. For additional information, see main article.

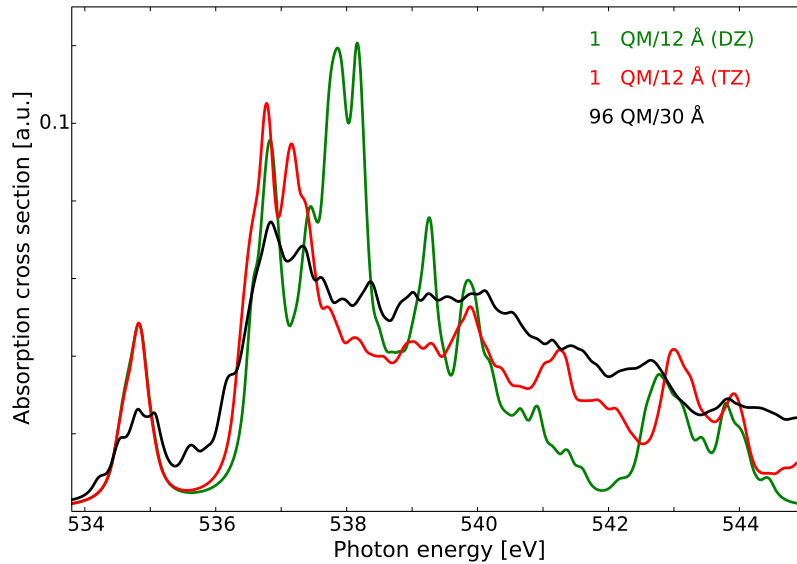


FIG. 3. Summed up X-ray absorption spectra of a 10 MD structures, as obtained using time-dependent DFT with a polarizable embedding. Comparing 1 QM/12 Å calculations using the basis set employed in this study to that used in Ref. [7]. Spectra shifted by 14.9 eV, as well as an additional 0.5 eV for the 1 QM/12 Å (TZ) results. For additional information, see main article.

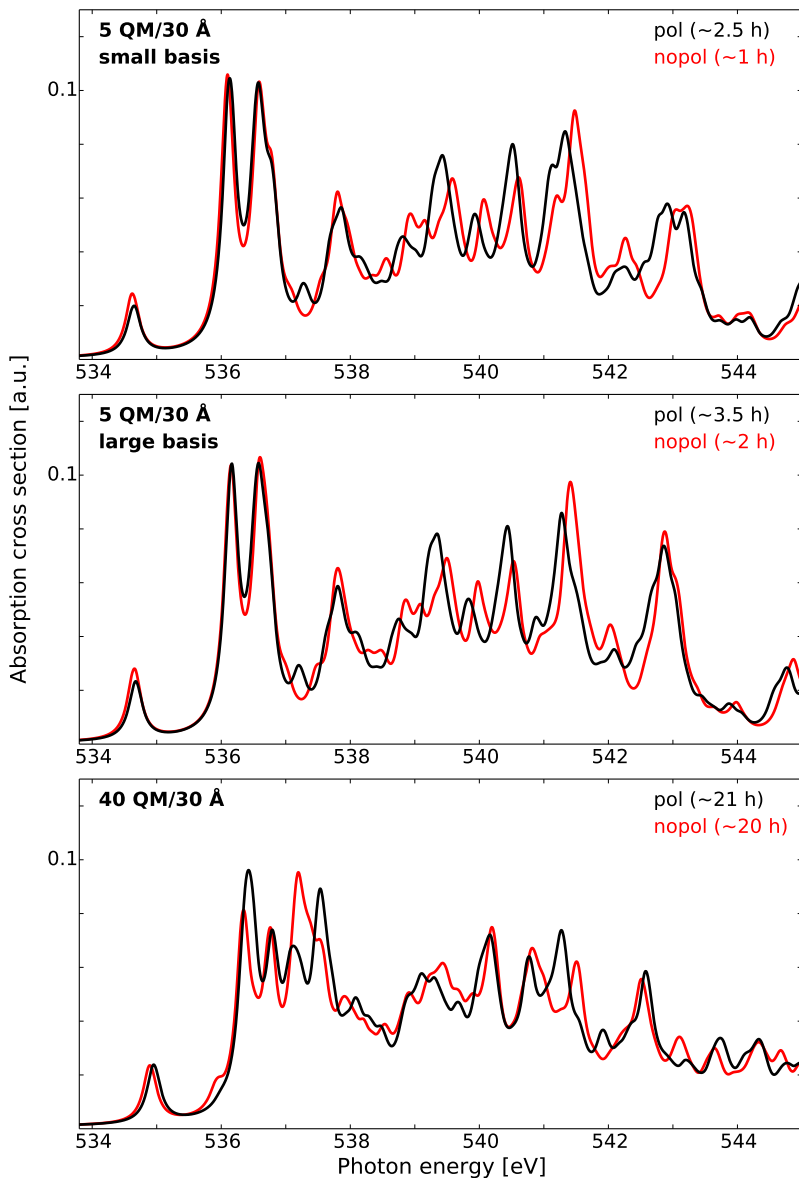


FIG. 4. X-ray absorption spectra of a single water cluster, including and excluding polarizabilities in the MM-region. Small and large basis sets are designations for the four QM solvent molecules, given a DZ or TZ basis set. Also included are the time differences for the calculations (only to be compared within the same panel). Spectra shifted by 14.9 eV. For additional information, see main article.

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