

Supplementary Material: Structure of Liquid and Aqueous Water Isotopologues at Ambient Temperature from *ab initio* Path Integral Simulations

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We herein assess the bead convergence of the results presented in the main text, and provide a fair comparison to previous *ab initio* PIMD studies with $P = 16$ beads.^{1,2} All the results presented in this Supplementary Material are from the *ab initio* PIMD simulation with the same setup as in the main article using the RPBE-D3 functional. Figure S1 shows a zoom in of the region around the first peak of the OO RDFs of H₂O(l), D₂O(l), and T₂O(l) and the first peak of the O*O RDFs of HDO(aq) and HTO(aq). Figure S2 and Table SI compares the RDF peak heights and positions between the simulations using $P = 1, 16$ and 32 beads. Table SII compares the average bond lengths and angles of water molecules of the simulations using $P = 1, 16$ and 32 beads. Table SIII compares the mean proton kinetic energies of the simulations using $P = 16$ and 32 beads. Figure S3 shows the $g(\text{O}^*\text{H}^*)$ and $g(\text{O}^*\text{H}^*)$ of the HDO(aq) and HTO(aq) simulations. Figure S4 shows the proton/deuteron/tritium sharing coordinates of the liquid phase simulations. Figure S5 shows the distribution of the tetrahedral order parameter in the liquid phase simulations. Figure S6 show a decomposition of the OO and O*O RDFs into contributions from the first and second hydration shell and from oxygen atoms not participating in the hydrogen bond network. Figure S7 shows the distribution of the bond angles and bond lengths in the liquid and gas phase simulations of the water isotopologues.

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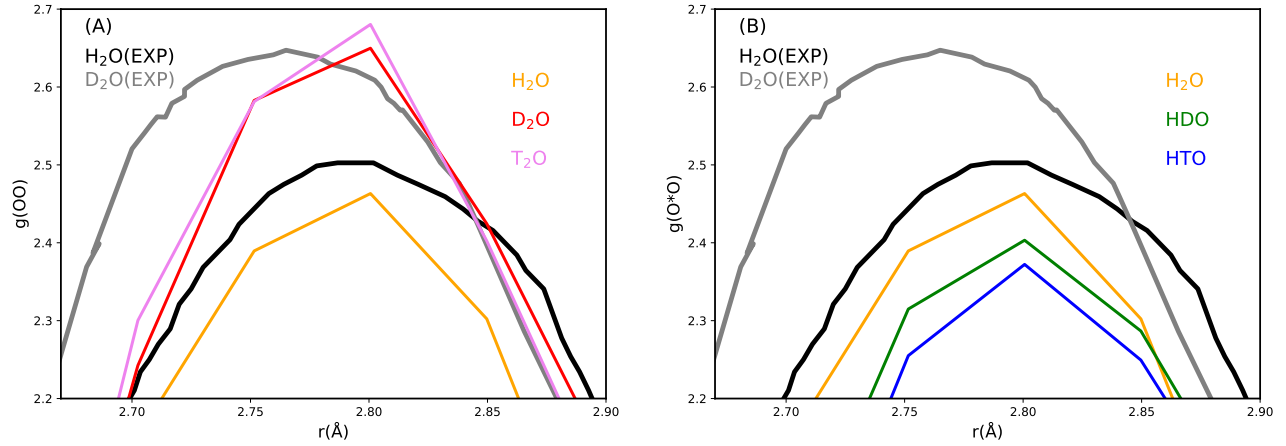


FIG. S1. (A) Zoom in of first peak the The OO RDFs of $\text{H}_2\text{O}(l)$ (orange), $\text{D}_2\text{O}(l)$ (red) and $\text{T}_2\text{O}(l)$ (violet). (B) Zoom in of the first peak of the O^*O RDFs of $\text{HDO}(aq)$ (green) and $\text{HTO}(aq)$ (blue), the OO RDFs of $\text{H}_2\text{O}(l)$ (orange) is also included here for reference. The black trace are the experimental RDFs of water and the grey trace shows the experimental RDFs of heavy water from Refs. 3, 4 and 5, for both figure (A) and (B). The peak heights and positions are given in Table 1.

Table SI. The peaks in the radial distributions of liquid water in the ambient condition.^a

Pair ^c	Peak Number	Peak Value	Expt. ^b		Quantum - 16 Beads		Quantum - 32 Beads	
			H ₂ O	D ₂ O	H ₂ O	D ₂ O	H ₂ O	D ₂ O
OO	1	<i>r</i>	2.80	2.76	2.78±0.01	2.81±0.01	2.78±0.02	2.79±0.02
	1	<i>h</i>	2.50	2.62	2.58±0.02	2.56±0.02	2.48±0.02	2.65±0.02
	2	<i>r</i>	4.40	4.49	4.24±0.10	4.15±0.20	4.39±0.20	4.27±0.20
	2	<i>h</i>	1.13	1.15	1.28±0.08	1.23±0.07	1.23±0.04	1.33±0.05
OH	1	<i>r</i>	0.975	...	0.985±0.01	0.985±0.01	0.985±0.01	0.985±0.01
	1	<i>h</i>	11.2	...	13.8±0.1	15.9±0.1	13.2±0.1	15.4±0.1
	2	<i>r</i>	1.85	1.77	1.81±0.02	1.83±0.02	1.80±0.02	1.79±0.02
	2	<i>h</i>	1.09	1.10	1.16±0.02	1.19±0.02	1.14±0.02	1.27±0.02
	3	<i>r</i>	3.27	3.20	3.30±0.03	3.31±0.02	3.31±0.03	3.30±0.01
	3	<i>h</i>	1.53	1.48	1.56±0.01	1.61±0.01	1.60±0.02	1.61±0.01
HH	1	<i>r</i>	1.62	...	1.58±0.01	1.57±0.01	1.57±0.02	1.57±0.00
	1	<i>h</i>	1.54	...	1.63±0.01	1.89±0.01	1.57±0.01	1.87±0.01
	2	<i>r</i>	2.34	2.33	2.35±0.04	2.35±0.03	2.37±0.02	2.35±0.03
	2	<i>h</i>	1.35	1.41	1.25±0.03	1.28±0.04	1.28±0.01	1.37±0.02
	3	<i>r</i>	3.81	3.84	3.80±0.05	3.79±0.05	3.83±0.02	3.82±0.02
	3	<i>h</i>	1.15	1.21	1.19±0.02	1.22±0.01	1.21±0.00	1.24±0.02

^aIf the error is represented as all digits being filled with zero, e.g., 0.00, it means that the error is less than the reported precision.

^b *r* refers to the position of the peak, while *h* refers to the peak height.

^cData interpolated from Refs. 3, 4 and 5

^dPrevious study at 300 K and 1.00 g/mL.²

^eThis study at 298 K and 1.00 g/mL.

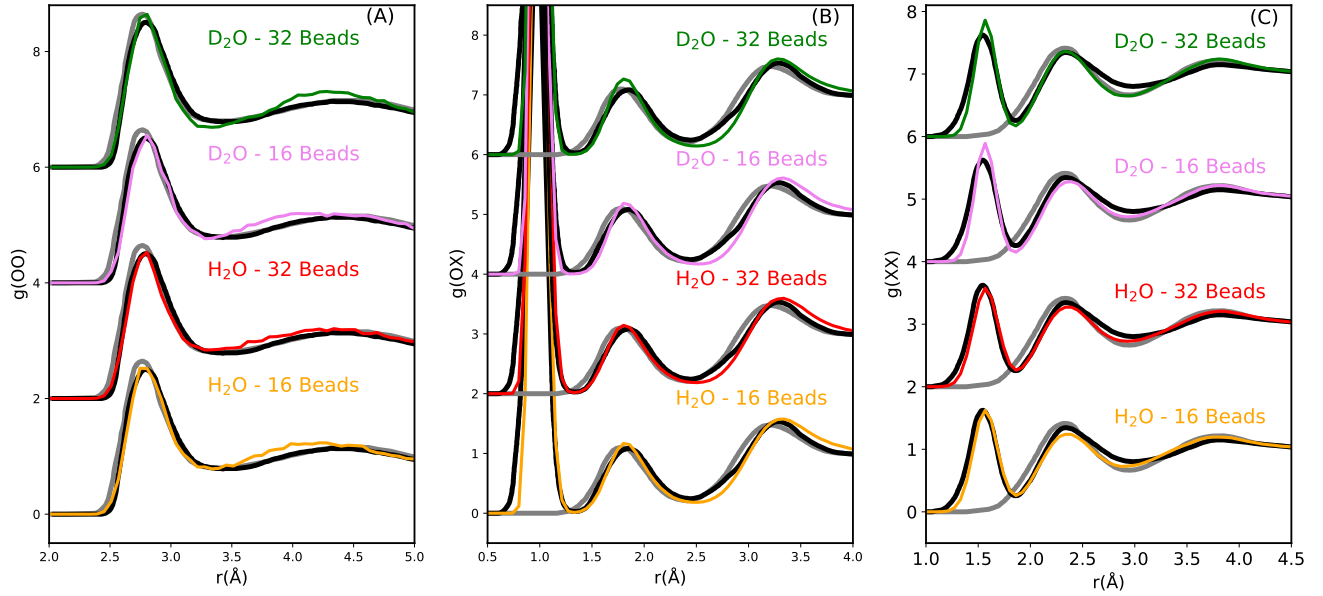


FIG. S2. The RDFs calculated by *ab initio* PIMD for water using 16 beads (orange), using 32 beads (red), heavy water using 16 beads (violet), and using 32 beads (green). The black trace are the experimental RDFs of water and the grey trace shows the experimental RDFs of heavy water from Refs. 3, 4 and 5. α refer to H and D for $\text{H}_2\text{O}(l)$ and $\text{D}_2\text{O}(l)$ respectively. The peak heights and positions are given in Table S1.

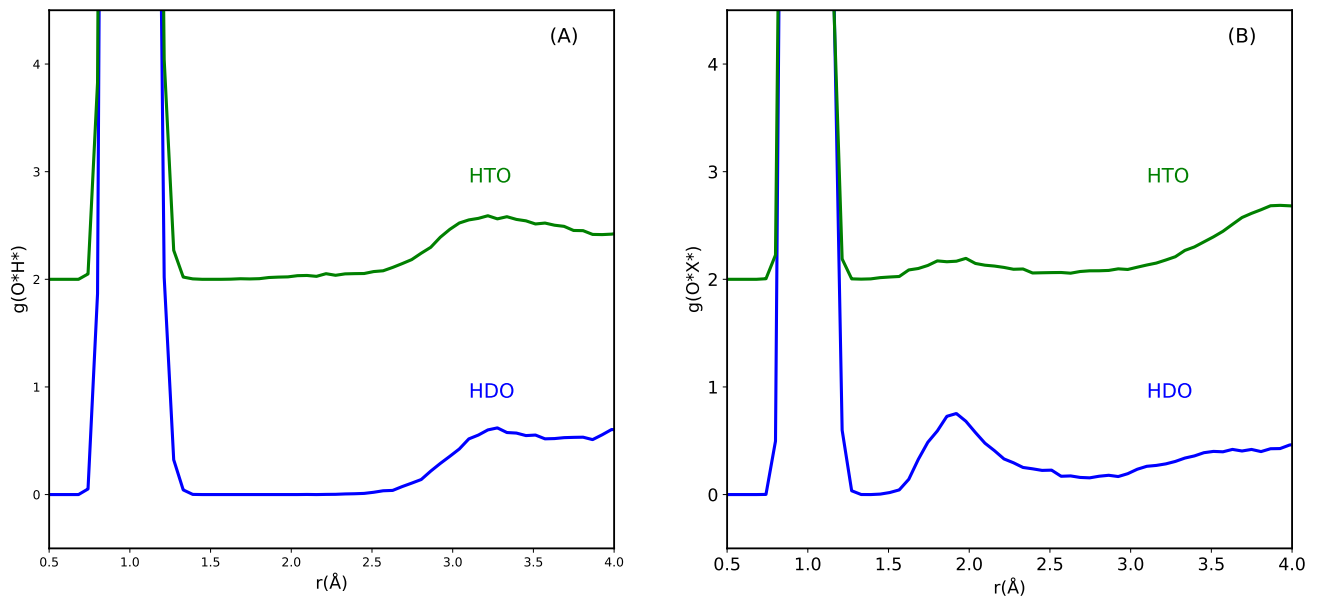


FIG. S3. The O^*H^* and O^*X^* RDFs for $\text{HDO}(\text{aq})$ and $\text{HTO}(\text{aq})$, the star labels are explained in the main text.

Table SII. Temperature dependence of bond lengths and angles of water molecules.

Method	Temperature (K)	Density (g/mL)	State	$\langle r_{OH} \rangle (\text{\AA})$	$\langle \theta_{HOH} \rangle (\text{deg})$
MD	298	1.00	Liquid	0.987 ± 0.000	105.31 ± 0.02
	298	-	Gas	0.972 ± 0.000	103.94 ± 0.02
PIMD (16 Beads)	298	1.00	Liquid	1.003 ± 0.000	105.12 ± 0.01
	298	-	Gas	0.985 ± 0.000	103.78 ± 0.01
PIMD (32 Beads)	298	1.00	Liquid	1.004 ± 0.000	105.23 ± 0.01
	298	-	Gas	0.987 ± 0.000	103.67 ± 0.01
Expt. ^a	-	-	Gas	0.9743	104.52

^aReference 6 and references within.

Table SIII. Mean proton kinetic energy estimated from ab initio PIMD simulations compared with the results from deep inelastic neutron scattering.

Temperature (K)	Density (g/mL)	State	Beads	PIMD (mEv)	Experiment ^a (mEv)
298	1.00	Liquid	16	140.4 ± 0.0	143 ± 3^b
298	-	Gas	16	134.2 ± 0.4	-
298	1.00	Liquid	32	148.2 ± 0.0	143 ± 3^b
298	-	Gas	32	142.3 ± 0.6	-

^aReference 7.

^bThe experimental result is reported at 300 K.

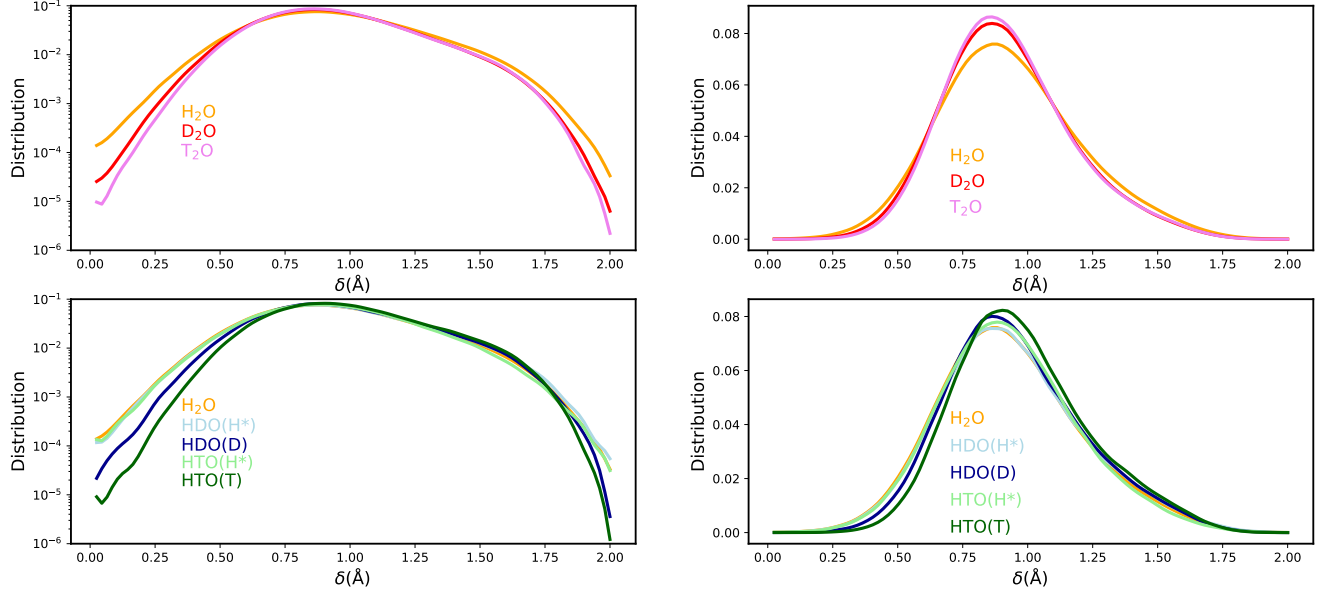


FIG. S4. The proton/deuteron/tritium sharing coordinate of the particles participating in hydrogen bonds as defined in the main text.

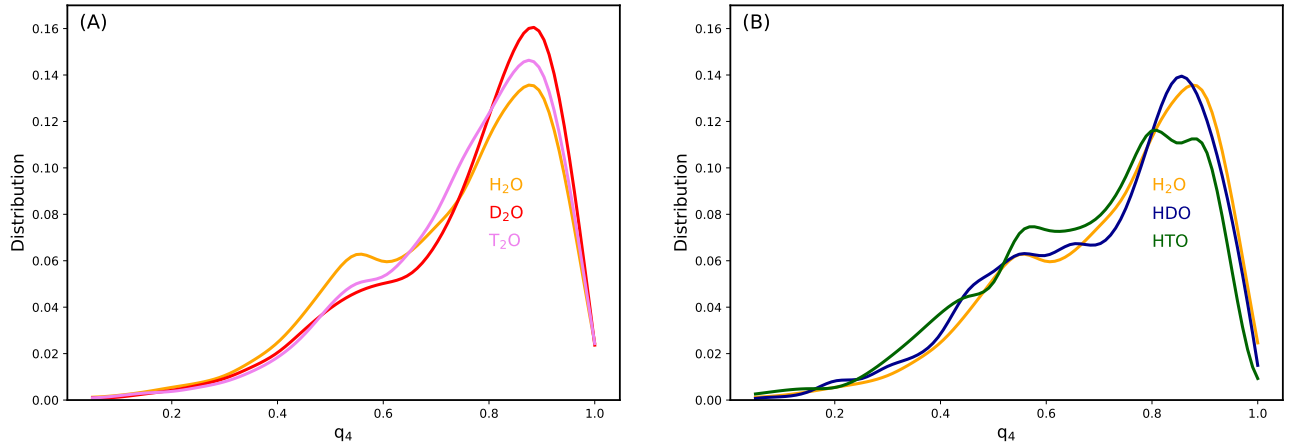


FIG. S5. The distribution of the tetrahedral order parameter $q_4 = 1 - \langle \frac{3}{8} \sum_j^3 \sum_{k=j+1}^4 (\cos(\theta_{jik}) - \frac{1}{3})^2 \rangle$, where θ_{jik} is the angle between the central oxygen i and two of its four closest neighbours j, k .

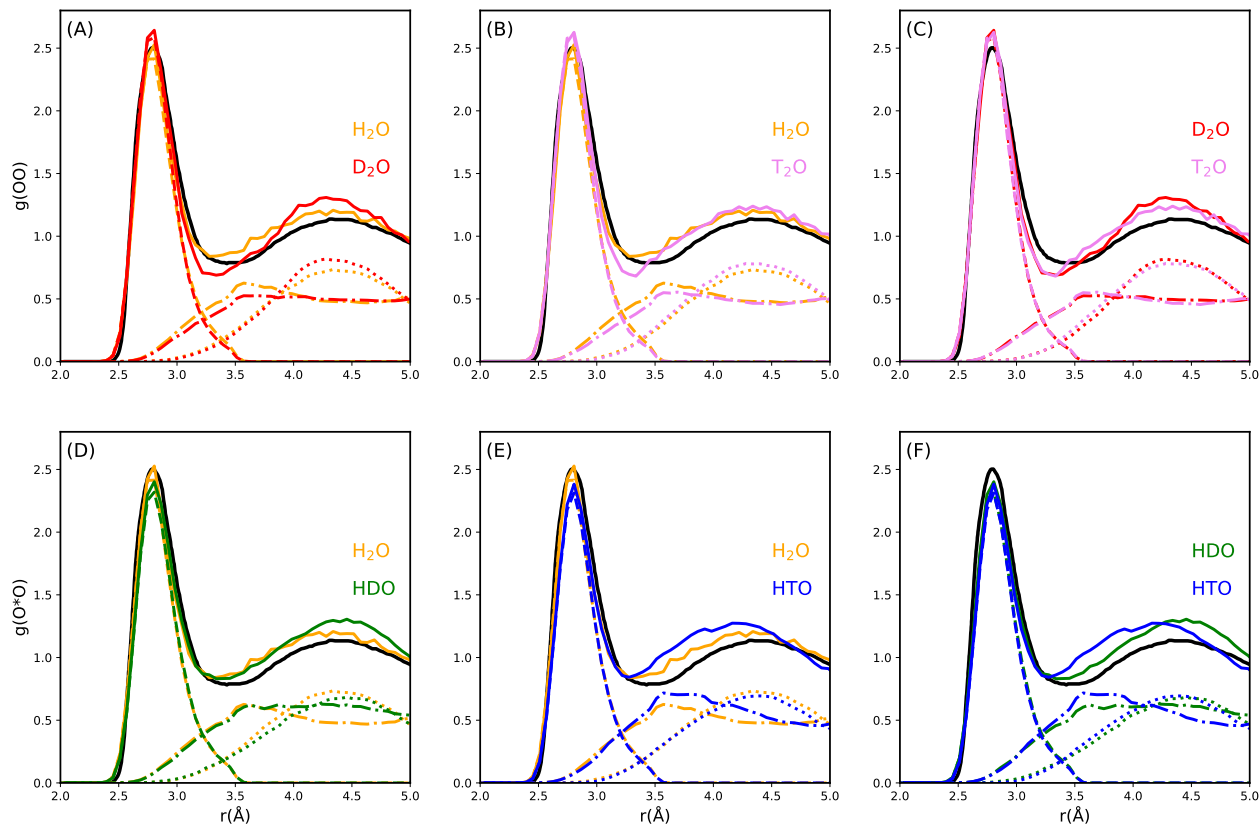


FIG. S6. Comparison of the OO and O*O RDFs of (A) $\text{H}_2\text{O}(\text{l})$ and $\text{D}_2\text{O}(\text{l})$, (B) $\text{H}_2\text{O}(\text{l})$ and $\text{T}_2\text{O}(\text{l})$, (C) $\text{D}_2\text{O}(\text{l})$ and $\text{T}_2\text{O}(\text{l})$, (D) $\text{H}_2\text{O}(\text{l})$ and $\text{HDO}(\text{aq})$, (E) $\text{H}_2\text{O}(\text{l})$ and $\text{HTO}(\text{aq})$, and (F) $\text{HDO}(\text{aq})$ and $\text{HTO}(\text{aq})$. The solid lines does in all cases indicate the full OO or O*O RDFs of each system. The dashed lines indicate the contribution to the OO RDFs from the first hydration shell. The dotted lines indicate the contribution to the OO RDFs from the second hydration shell. The dash-dotted lines indicate the contribution to the OO RDFs from the oxygens which are not hydrogen bonded to either the first or second hydration shell.

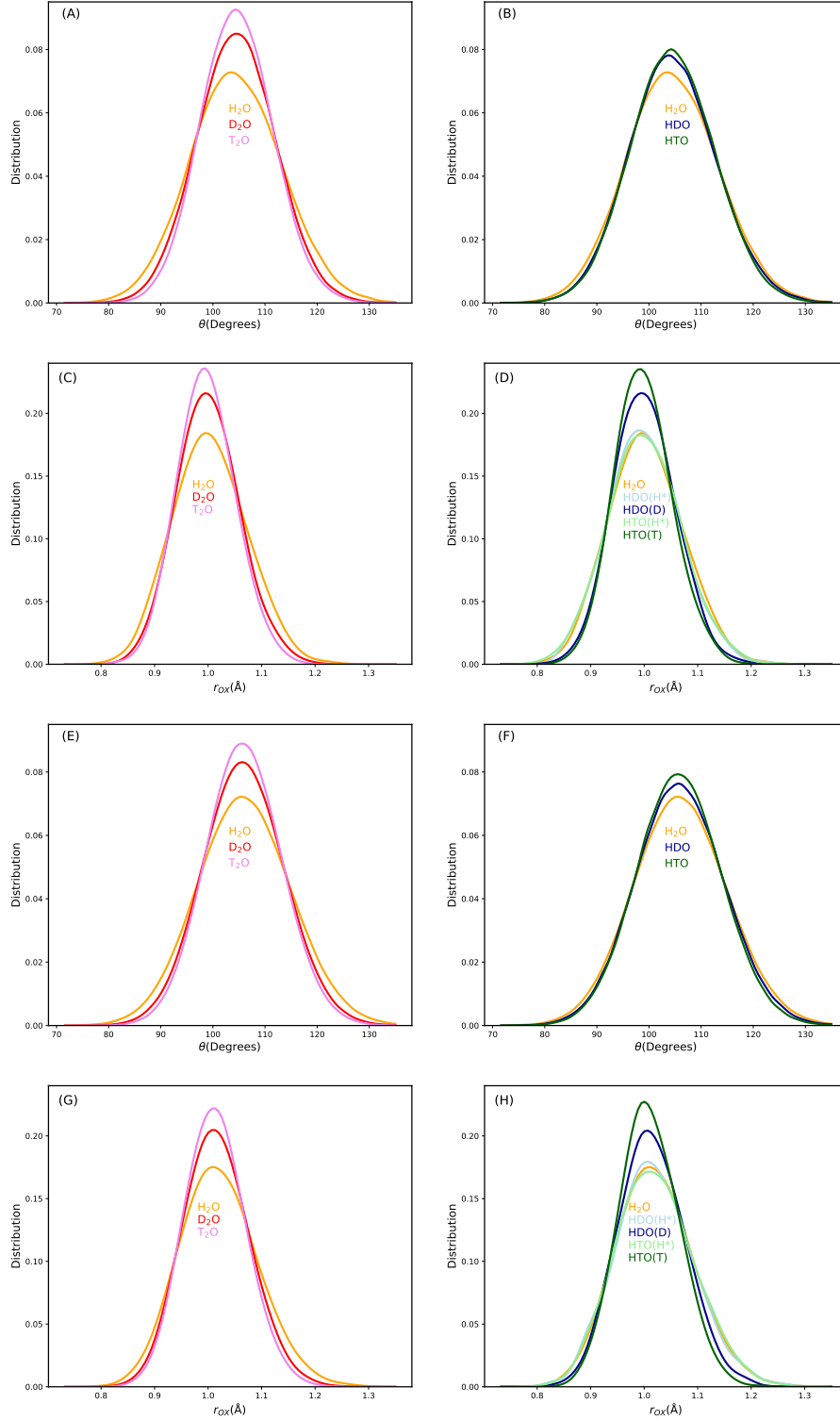


FIG. S7. The distributions of bond angles and distances in the gas (A) - (D) and liquid (E) - (H) phase simulations of water isotopologues.

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