Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Quantum molecular simulations of micro-hydrated halogen anions

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Supplementary material

Table S1 Energies (in kcal/mol) of low-lying structures of the indicated $X^-(H_2O)_{N=1-8}$ halide-water clusters, obtained from optimization of the i-TTM4 PESs.

X^-/N	1	2	3	4	5	6	7	8
F^-	-27.780	-49.556	-67.956 -67.073 -67.287 -66.505	-85.360 -84.621 -80.262 -80.851 -83.565 -82.875 -82.213	-101.786 -101.158 -98.314 -99.475 -99.755 -99.612 -100.096 -98.239 -97.734 -97.975	-115.668 -116.780 -115.864 -115.159 -113.976 -114.531 -114.389 -113.884 -113.576	-130.003 -128.907 -127.862 -129.832	-142.461 -141.082 -140.959 -139.635 -139.168 -138.940 -140.142
Cl^-	-14.974	-30.037	-46.230 -43.969 -44.235 -44.455	-60.385 -58.008 -55.544 -56.323 -57.967 -61.082 -58.235	-75.465 -74.999 -75.263 -73.562 -74.702 -73.759 -74.339 -72.523 -73.990 -73.067	-89.278 -88.244 -88.248 -88.454 -88.735 -87.310 -88.906 -86.725 -88.098 -87.034	-99.804 -102.741 -102.098 -100.190 -99.551, -97.659 -98.790 -101.633 -103.088	-115.358 -113.853 -111.882 -104.741 -111.744 -113.085 -111.734 -102.548
Br^-	-12.731	-26.639	-42.525 -39.861 -39.898	-56.268 -55.573 -53.740 -48.928 -51.714 -52.767 -56.071 -51.714 -51.891	-70.580 -70.007 -68.588 -69.584 -69.114 -68.691 -67.739 -69.127 -68.503	-83.645 -83.315 -83.998, -83.321 -82.427 -82.773 -83.261 -81.555 -82.772	-97.420 -94.089 -94.277 -91.675 -92.908 -96.210 -96.819 -97.330	-107.781 -106.130 -99.544 -105.811 -107.904 -107.032 -109.030 -105.748 -96.981
I^-	-10.662	-23.399	-38.958 -35.855 -35.230 -35.422 -34.162	-52.773 -50.778 -47.563 -49.505 -43.967 -47.321 -51.143 -50.677	-65.783 -65.148 -63.066 -63.648 -63.369 -63.868 -62.533	-79.142 -78.379 -78.544 -78.067 -78.866 -78.166 -77.581 -77.683 -76.381 -76.454	-90.985 -87.469 -86.985 -91.183 -87.835 -81.707 -86.994 -87.634 -88.557 -88.696 -91.493 -90.765	-103.38 -101.637 -99.673 -99.565 -103.410

Table S2 Minimun potential energy, and average kinetic, potential and total energies (in kcal/mol) computed from the classical MD and PIMD calculations at T=10 K for each $X^-(H_2O)_{N=1-8}$ cluster using the i-TTM4 potentials. The anharmonic ZPE (in kcal/mol) values from PIMC simulations, and harmonic $\mathcal{E}_{\mathrm{ZPE}^{(\mathrm{HA})}}$ estimates (in parenthesis) are also listed, in comparisom with those from DMC calculations, [a] from ref. 45.

N	$F^-(H_2O)_N$	MD			PIMD			
	E_{min}	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	ZPE
1	-27.780	-27.4605±0.0006	0.1556±0.0002	-27.6161±0.0003	-12.58±0.02	7.49±0.02	-20.073±0.007	15.20(15.58)/13.98[a]
2	-49.556	-49.0333±0.0009	0.2554±0.0004	-49.2887±0.0006	-19.00±0.02	14.98±0.01	-33.980±0.009	30.56(31.75)/29.45[a]
3	-67.956	-67.2531±0.0007	0.3429±0.0004	-67.5960±0.0005	-21.62±0.02	22.67±0.01	-44.29±0.01	46.33(48.46)/46.10[a]
4	-85.360	-84.4757±0.0009	0.4320±0.0004	-84.9077±0.0006	-22.17±0.03	30.89±0.02	-53.06±0.02	63.19(65.69)/62.21[a]
5	-101.786	-100.727±0.001	0.5176±0.0004	-101.2450±0.0006	-22.64±0.03	38.63±0.02	-61.27±0.02	79.15(82.66)/78.29[a]
6	-116.780	–115.539±0.001	0.6067±0.0004	-116.1457±0.0006	-21.69±0.04	46.42±0.02	-68.11±0.03	95.09(99.28)
7	-130.003	-128.572±0.001	0.6959±0.0005	-129.2680±0.0009	-18.79±0.05	54.34±0.02	-73.14±0.03	111.21(116.10)
8	-142.461	-140.860±0.001	0.7840±0.0004	-141.6443±0.0008	-16.12±0.05	61.81±0.03	-77.94±0.03	126.34(131.90)

N	$Cl^-(H_2O)_N$	MD			PIMD			
	E_{min}	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	ZPE
1	-14.974	-14.551±0.001	0.2054±0.0005	-14.7566±0.0006	-0.42±0.02	7.09±0.02	-7.514±0.008	14.55(15.03)/14.33[a]
2	-30.037	-29.4388±0.0009	0.2910±0.0004	-29.7298±0.0005	-0.24±0.02	14.53±0.01	-14.77±0.01	29.80(31.13)/29.78[a]
3	-46.230	-45.4739±0.0009	0.3693±0.0004	-45.8432±0.0005	-0.51±0.02	22.30±0.01	-22.81±0.01	45.72(47.85)/46.05[a]
4	-61.082	-60.1515±0.0009	0.4541±0.0004	-60.6056±0.0006	0.95±0.03	30.29±0.02	-29.34±0.02	62.03(64.56)/61.74[a]
5	-75.465	-74.3703±0.0009	0.5354±0.0004	-74.9057±0.0006	2.23±0.04	37.95±0.02	-35.72±0.02	77.70(81.26)/77.60[a]
6	-89.279	-88.0065±0.0009	0.6221±0.0004	-88.6287±0.0006	4.18±0.05	45.63±0.02	-41.44±0.03	93.46(97.68)
7	-103.088	-101.6405±0.001	0.7086±0.0005	-102.3492±0.0006	7.35±0.05	53.93±0.02	-46.58±0.03	110.44(115.27)
8	-115.358	-113.732±0.001	0.7953±0.0004	-114.5270±0.0008	9.78±0.04	61.13±0.02	-51.35±0.02	125.14(130.83)

N	$Br^-(H_2O)_N$	MD			PIMD			
	E_{min}	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	ZPE
1	-12.731	-12.030±0.002	0.3395±0.0008	-12.3699±0.0009	1.79±0.02	6.97±0.02	-5.17±0.01	14.52(14.87)/14.26[a]
2	-26.639	-25.843±0.001	0.3871±0.0005	-26.2298±0.0006	3.23±0.02	14.50±0.01	-11.27±0.01	29.87(31.01)/29.70[a]
3	-42.525	-41.620±0.001	0.4417±0.0005	-42.0614±0.0007	3.38±0.03	22.33±0.01	-18.96±0.02	45.91(47.91)/45.99[a]
4	-56.268	-55.219±0.001	0.5117±0.0005	-55.7311±0.0009	5.51±0.04	30.07±0.02	-24.56±0.02	61.78(64.26)/61.75[a]
5	-70.581	-69.385±0.001	0.5845±0.0005	-69.9699±0.0008	6.84±0.04	37.75±0.02	-30.91±0.02	77.42(80.95)/77.45[a]
6	-83.998	-82.642±0.001	0.6632±0.0005	-83.3055±0.0007	9.11±0.04	45.44±0.02	-36.33±0.03	93.11(97.40)
7	-97.420	-95.901±0.001	0.7440±0.0005	-96.6450±0.0008	11.32±0.05	53.19±0.02	-41.88±0.03	108.74(113.64)
8	-109.030	-107.339±0.001	0.8275±0.0005	-108.1664±0.0009	15.77±0.05	61.01±0.02	-45.24±0.04	124.80(130.25)

N	$I^-(H_2O)_N$	MD			PIMD			
	E_{min}	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	ZPE
1	-10.662	-9.632±0.002	0.496±0.001	-10.128±0.001	3.74±0.03	6.79±0.02	-3.05±0.02	14.40(14.70)/14.12[a]
2	-23.399	-22.388±0.002	0.4910±0.0008	-22.8792±0.0009	6.33±0.02	14.40±0.01	-8.07±0.02	29.72(30.87)/29.59[a]
3	-38.958	-37.895±0.001	0.5182±0.0006	-38.4133±0.0007	7.07±0.03	22.31±0.01	-15.23±0.02	46.03(47.94)/45.92[a]
4	-52.773	-51.600±0.001	0.5727±0.0006	-52.1725±0.0009	9.35±0.04	30.22±0.02	-20.87±0.02	62.12(64.42)/61.69[a]
5	-65.783	-64.485±0.001	0.6344±0.0005	-65.1199±0.0007	11.63±0.04	37.71±0.02	-26.08±0.03	77.41(80.76)/77.21[a]
6	-79.142	-77.696±0.001	0.7074±0.0006	-78.4029±0.0009	13.93±0.05	45.40±0.02	-31.47±0.03	93.07(97.20)
7	-91.494	-89.896±0.001	0.7811±0.0006	-90.6775±0.0008	18.12±0.05	53.48±0.02	-35.35±0.03	109.61(114.42)
8	-103.410	-101.649±0.001	0.8611±0.0005	-102.5101±0.0008	21.00±0.05	60.82±0.02	-39.82±0.03	124.41(129.96)

Table S3 Comparison of anharmonic ZPE values (in kcal/mol) obtained from the present PIMD simulations at T=10 K with those reported previously from DMC and variational quantum calculations. [a] ref. 55, [b] ref. 60, [c] ref. 44, [d] ref. 61, [e] ref. 45, [f] ref. 84, [g] ref. 85, [h] ref. 86.

PES/Method	$F^-(H_2O)$	$Cl^-(H_2O)$	$Br^-(H_2O)$	$I^-(H_2O)$
i-TTM4[a]/PIMD-This work	15.20	14.55	14.52	14.40
TTM-ngr[b]/RV4 code[c]	15.40	14.73	14.57	14.39
MB-ngr[d]/RV4 code[c]	14.80	14.48	14.36	14.20
MB-ngr [d]/DMC[e]	13.98	14.33	14.26	14.12
SLBCL/GENIUSH code[f]	13.81	–	–	–
RB[g]/QC[g,h]	–	14.36	–	–

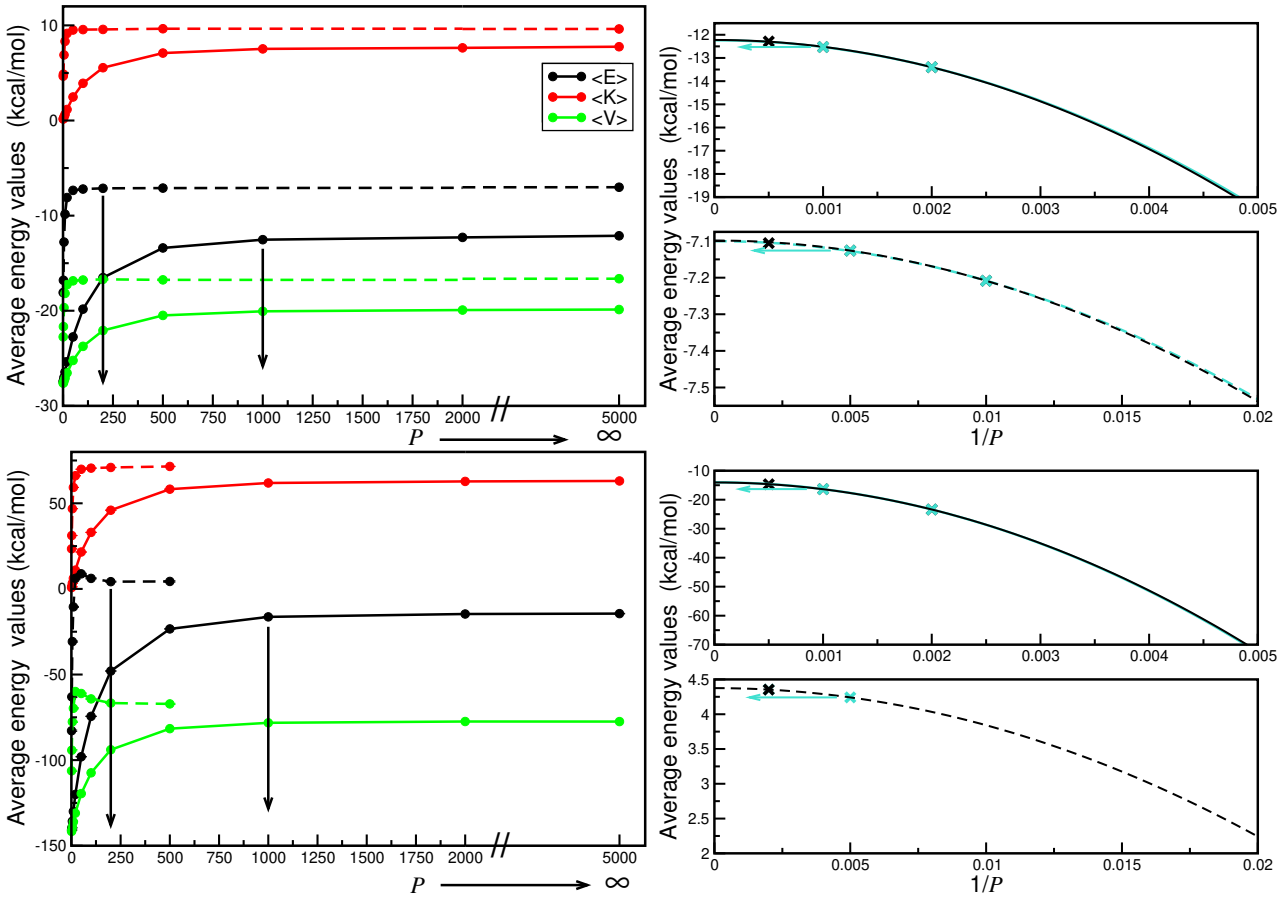

Fig. S1 Convergence of kinetic (<K>), potential (<V>), and total (<E>) energy as a function of the number of replicas ($\mathcal{P}$) (left panels), and extrapolation of the total energy in the $\mathcal{P} \rightarrow \infty$ limit (right panels), from the PIMD simulations for $F^-(H_2O)_N$ with N = 1 (upper panel) and 8 (lower panel at T = 10 and 300 K (see solid and dashed lines, respectively).

Table S4 Average kinetic, potential and total energies (in kcal/mol) computed from the classical MD and PIMD calculations at T=300 K for each $X^-(H_2O)_{N=1-8}$ cluster using the i-TTM4 potentials.

$F^-(H_2O)_N$	MD			PIMD		
	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$
1	-18.09±0.03	4.66±0.02	-22.75±0.02	-7.10±0.05	9.580±0.008	-16.74±0.05
2	-33.89±0.04	7.67±0.02	-41.56±0.03	-11.22±0.06	18.22±0.01	-29.52±0.06
3	-45.10±0.07	10.28±0.02	-55.38±0.06	-10.61±0.09	26.92±0.02	-37.6±0.1
4	-53.6±0.1	12.99±0.02	-66.6±0.1	-6.6±0.2	35.71±0.03	-42.9±0.2
5	-61.8±0.2	15.54±0.02	-77.34±0.2	-3.1±0.3	44.21±0.03	-47.5±0.3
6	-68.5±0.2	18.20±0.02	-86.7±0.2	0.2±0.3	53.14±0.03	-52.8±0.3
7	-75.8±0.3	20.86±0.02	-96.7±0.3	4.1±0.3	61.89±0.02	-58.00±0.2
8	-84.3±0.4	23.46±0.06	-107.7±0.4	9.1±0.3	70.90±0.06	-61.8±0.3

$Cl^-(H_2O)_N$	MD			PIMD		
	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$
1	-1.9±0.1	6.15±0.06	-8.05±0.09	7.3±0.2	9.34±0.03	-2.0±0.3
2	-10.8±0.1	8.80±0.06	-19.60±0.08	9.1±0.2	18.02±0.03	-8.9±0.2
3	-18.5±0.2	11.21±0.06	-29.7±0.1	12.3±0.2	26.68±0.04	-14.4±0.2
4	-25.8±0.2	13.74±0.06	-39.5±0.2	15.3±0.3	35.62±0.05	-20.4±0.3
5	-31.5±0.3	16.19±0.06	-47.7±0.2	22.9±0.4	43.89±0.05	-21.0±0.4
6	-38.1±0.3	18.72±0.07	-56.8±0.3	27.5±0.3	52.63±0.05	-25.1±0.3
7	-44.8±0.4	21.29±0.06	-66.1±0.4	28.7±0.3	61.54±0.06	-32.9±0.3
8	-51.8±0.5	23.96±0.06	-75.8±0.5	32.7±0.3	70.40±0.06	-37.7±0.3

$Br^-(H_2O)_N$	MD			PIMD		
	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$
1	11.5±0.4	10.01±0.09	1.4±0.4	13.3±0.3	9.19±0.03	4.2±0.3
2	2.3±0.4	11.87±0.07	-9.5±0.4	15.4±0.2	17.91±0.03	-2.5±0.2
3	-9.1±0.2	13.43±0.09	-22.6±0.2	18.5±0.2	26.56±0.04	-8.0±0.2
4	-16.0±0.2	15.65±0.07	-31.7±0.2	22.0±0.4	35.47±0.04	-13.5±0.4
5	-20.7±0.4	17.71±0.06	-38.5±0.4	29.5±0.4	43.78±0.05	-14.30±0.4
6	-30.3±0.3	19.91±0.07	-50.2±0.3	34.9±0.3	52.43±0.05	-17.5±0.3
7	-34.6±0.4	22.42±0.06	-57.0±0.4	38.1±0.3	61.29±0.06	-23.2±0.3
8	-40.6±0.5	24.95±0.07	-65.6±0.4	40.0±0.4	70.25±0.06	-30.3±0.4

$I^-(H_2O)_N$	MD			PIMD		
	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$
1	21.9±0.2	13.93±0.05	8.0±0.2	21.1±0.2	9.01±0.01	12.1±0.2
2	13.4±0.4	14.70±0.04	-1.3±0.4	23.0±0.2	17.62±0.01	5.4±0.2
3	2.3±0.3	15.88±0.03	-13.6±0.3	28.4±0.2	26.13±0.01	2.3±0.2
4	0.5±0.6	17.38±0.03	-16.9±0.6	33.2±0.3	34.97±0.02	-1.8±0.4
5	-13.0±0.2	19.18±0.03	-32.2±0.2	37.5±0.3	43.54±0.02	-6.0±0.3
6	-19.5±0.3	21.31±0.03	-40.8±0.3	43.2±0.4	52.15±0.03	-9.0±0.4
7	-25.2±0.3	23.58±0.02	-48.8±0.3	47.2±0.6	60.88±0.04	-13.7±0.6
8	-32.5±0.4	25.87±0.02	-58.3±0.4	52.8±0.3	69.57±0.03	-16.8±0.3

Table S5 Average total, kinetic and potential energies (in kcal/mol) computed from the classical MD and PIMD calculations at T=10 K for each $X^-\cdots(H_2O)_{N=1-8}$ system using the i-TTM4 potentials.

N	MD $(X^-\cdots(H_2O)_N)$			PIMD $(X^-\cdots(H_2O)_N)$		
	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$	$\langle E\rangle$	$\langle K\rangle$	$\langle V\rangle$
1	0.2540±0.0007	0.1559±0.0004	0.0981±0.0003	12.96±0.02	6.38±0.02	6.588±0.002
2	-4.4914±0.0008	0.2541±0.0004	-4.7455±0.0005	22.73±0.02	13.48±0.01	9.252±0.008
3	-14.2633±0.0008	0.3410±0.0004	-14.6043±0.0005	28.86±0.02	21.23±0.01	7.63±0.01
4	-26.3398±0.0008	0.4311±0.0004	-26.7709±0.0005	32.85±0.02	29.24±0.01	3.61±0.01
5	-34.810±0.001	0.5167±0.0004	-35.3263±0.0008	38.57±0.03	36.34±0.02	2.23±0.02
6	-44.929±0.001	0.6051±0.0005	-45.5345±0.0008	44.87±0.03	44.33±0.02	0.54±0.02
7	-56.987±0.001	0.6943±0.0005	-57.6814±0.0007	48.67±0.05	52.25±0.02	-3.58±0.04
8	-66.078±0.001	0.7830±0.0005	-66.8608±0.0009	54.53±0.04	59.67±0.02	-5.15±0.03

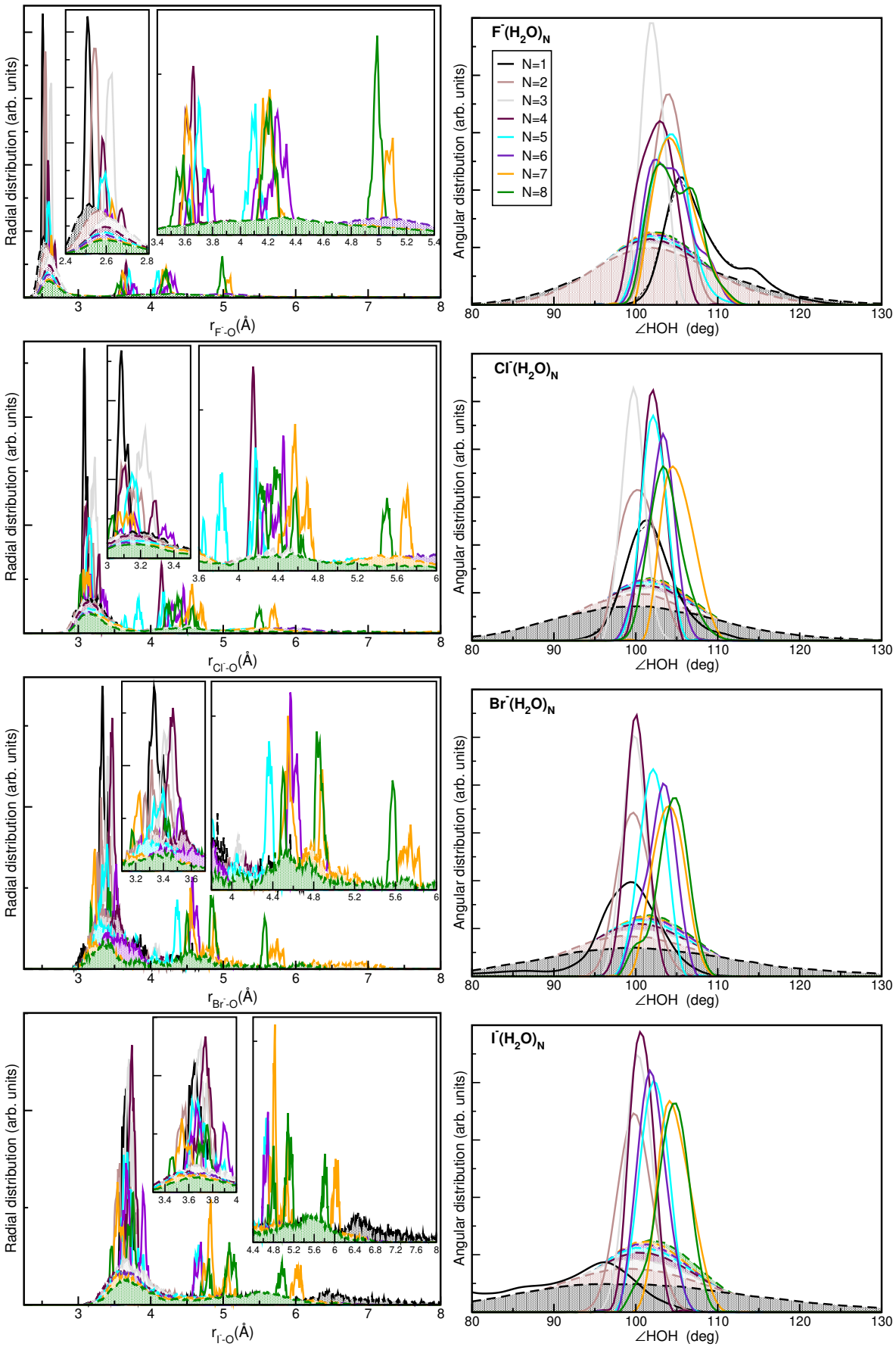

Fig. S2 Radial (left panel) and angular (right panel) distributions from the PIMD simulations for the indicated $X^-(H_2O)_n$ with n = 1 to 8 water molecules (X= F–I from upper to lower panels) at T = 10 (solid lines) and 300 K (dashed lines and shadow/pattern curves).

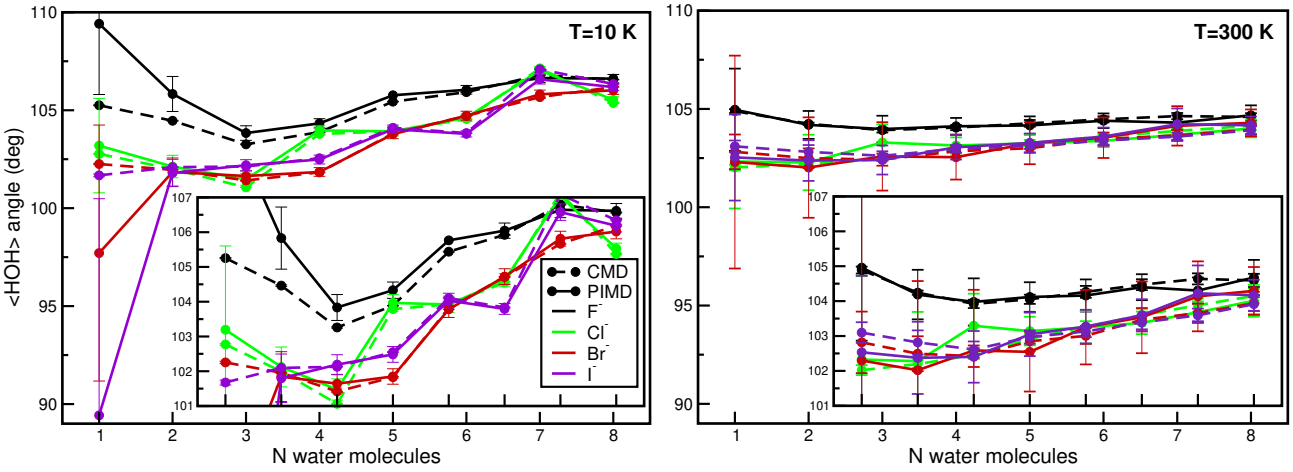

Fig. S3 Dependence of mean <HOH> angle values in the $X^-(H_2O)_N$ clusters, with X=F^-, Cl^-, Br^-, and I^-, from PIMD (solid lines) and classical MD (dashed lines) simulations at the indicated temperatures, as the number of the N water molecules increases.

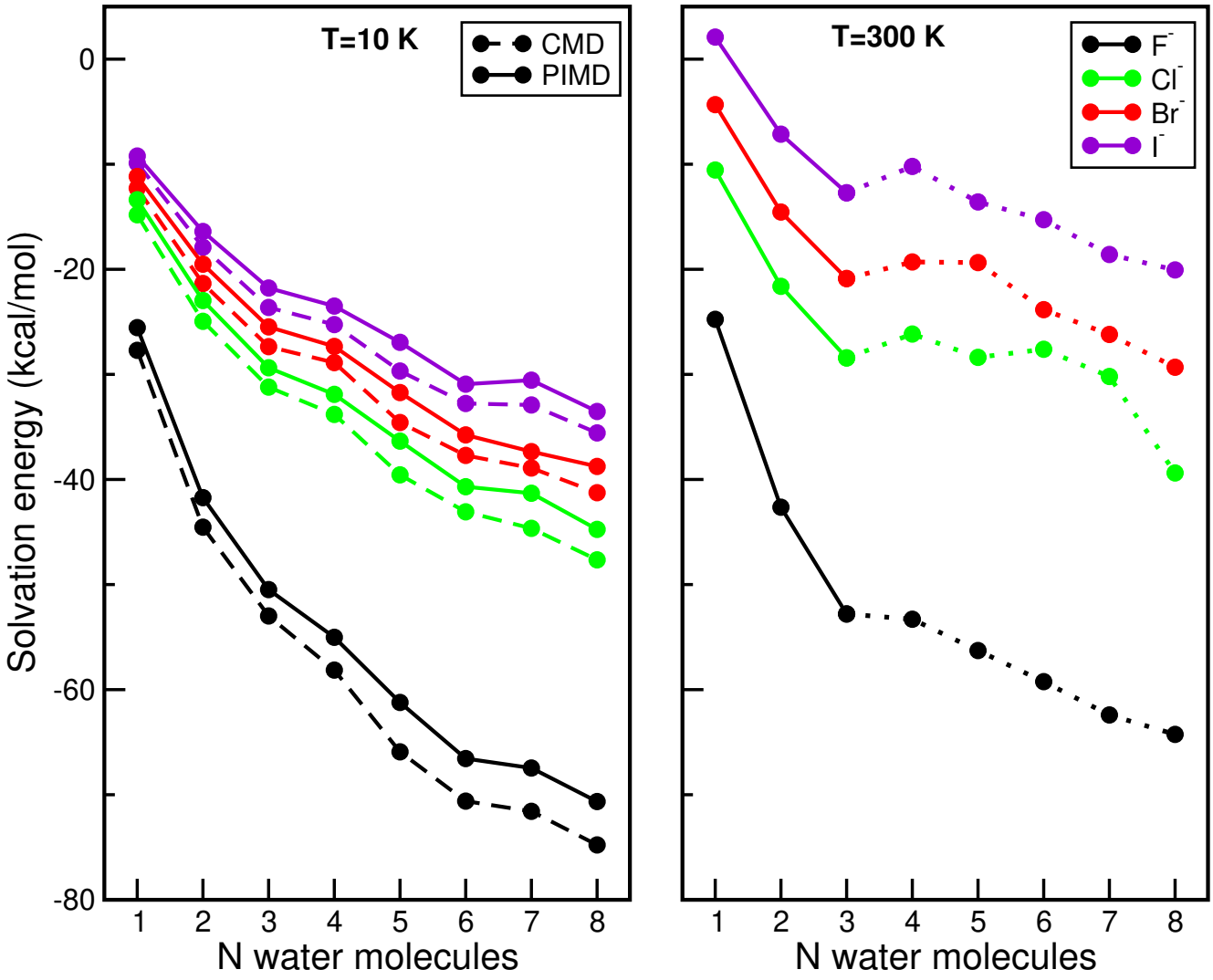

Fig. S4 Ion-cluster solvation energies as a function of the cluster size N from classical MD (dashed lines) and PIMD (solid lines) calculations at T=10 and 300 K for the indicated $X^-(H_2O)_N$ clusters.