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

Encapsulation of charged halogens by the 5^{12} water cage

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Supplementary Information

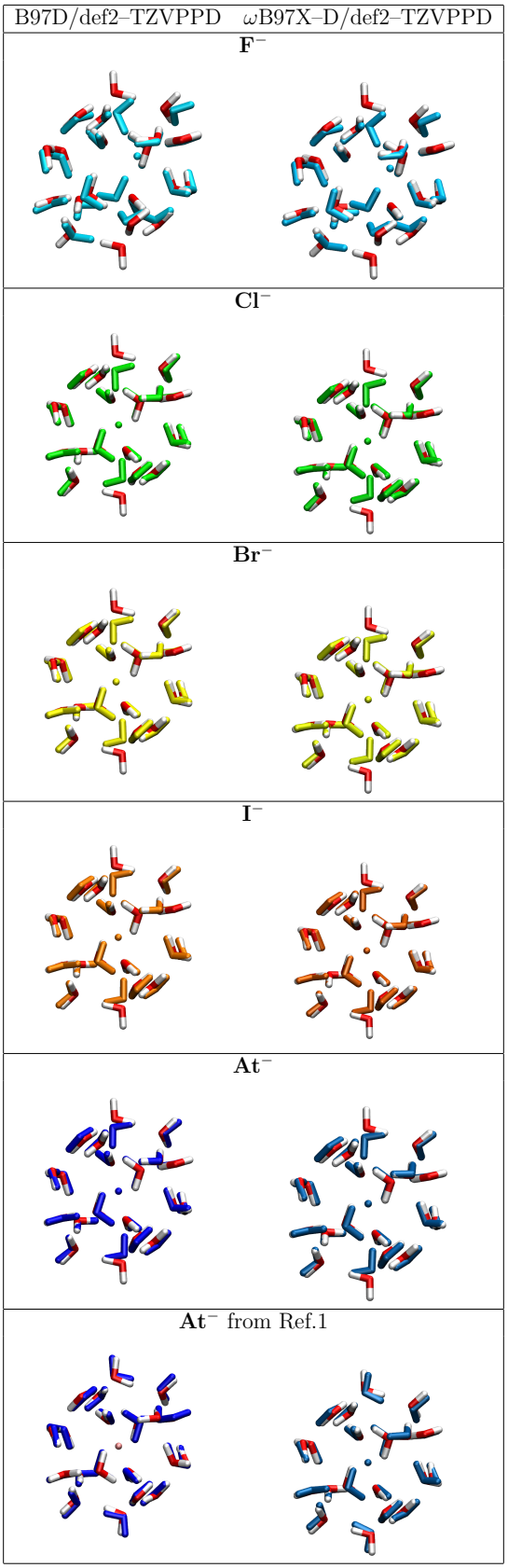

Figure S1: Superimposition of the structures of the $[X@(H_2O)_{20}]^-$ clusters (X = F, Cl, I, Br, At) and the 5^{12} bare cavity (red and white atoms). Geometries at the B97D/def2–TZVPPD (left) and ωB97X–D/def2–TZVPPD (right) levels of theory.

Table S1: Interaction and deformation energies in kcal/mol for the $[X@(H_2O)_{20}]^-$ clusters, X = F, Cl, Br, I, At. RMSD (in Å) with respect to the pristine cage and charge densities in C/mm^3 extracted from Refs. 2, 3 for the isolated anions are also listed. Level of theory: DLPNO-CCSD(T1)/def2-TZVPPD//ωB97X–D/def2-TZVPPD with TightPNO truncation setup. Extrapolated DLPNO-CCSD(T1) energies to CBS via TZ/QZ are also provided. Two $[At@(H_2O)_{20}]^-$ structures are included: one with no proton switch to the interior of the cage obtained here and in Ref. 1 and a hand constructed structure with two protons facing the interior of the cavity (see Figure 1)

Anion	E_{int}	$E_{int,\mathrm{CBS}}$	E_{def}	$E_{def,\mathrm{CBS}}$	E^*_{int}	$E^*_{int,\mathrm{CBS}}$	Charge density	RMSD
F^-	-69.7	-72.0	29.2	29.6	-98.8	-101.6	22.7	0.92
Cl^-	-42.7	-41.3	14.6	14.5	-57.3	-55.8	8.2	0.55
Br^-	-39.0	-37.5	14.6	14.6	-53.6	-52.2	6.3	0.51
I^-	-34.4	-30.6	15.0	15.1	-49.4	-45.7	4.4	0.47
At^-	-32.0	-27.5	15.4	15.5	-47.4	-43.0	3.2	0.46
At^- (Ref.1)	-22.3	-16.7	11.4	11.1	-33.7	-27.9	3.2	0.19

Table S2: Interaction and deformation energies in kcal/mol for the $[Ng@(H_2O)_{20}]$ clusters, X = Ne, Ar, Kr, Xe. RMSD (in Å) with respect to the pristine cage. Level of theory: B97D/def2-TZVPPD.

Noble gas	E_{int}	E_{def}	E^*_{int}	RMSD
Ne	-2.0	0.0	-2.0	0.01
Ar	-3.2	0.0	-3.2	0.01
Kr	-5.0	0.0	-5.0	0.01
Xe	-5.9	0.1	-5.8	0.01

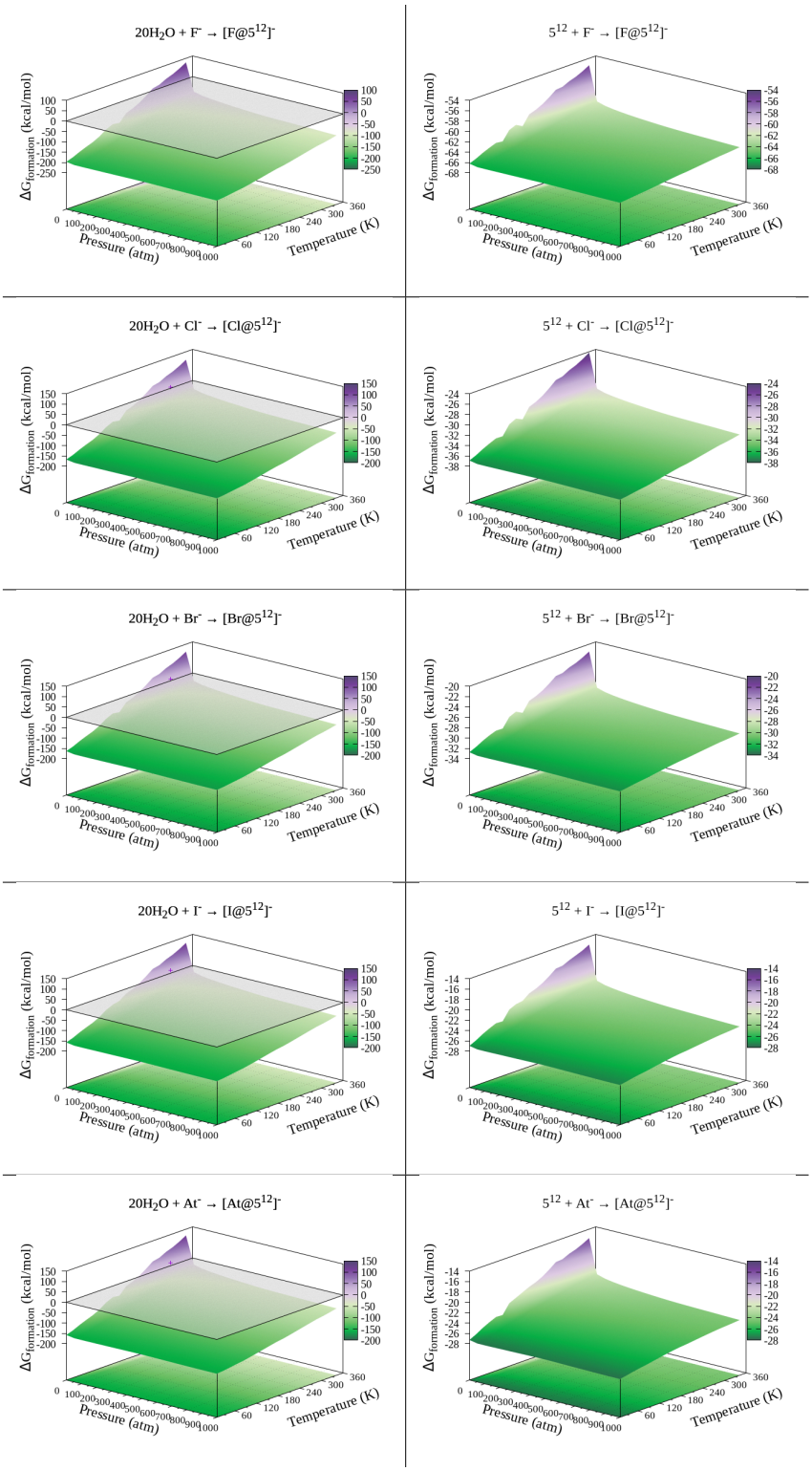

Figure S2: Thermal stability of the $[X@(H_2O)_{20}]^-$ cluster towards dissociation into $20H_2O$ + X^- (X = F, Cl, I, Br, At) on the left and towards the 5^{12} cavity + X^- on the right. All calculations are performed in the gas phase at the B97D/def2–TZVPPD level of theory. Points (+) mark the $\Delta G_{formation}$ values at T= 298 K and P = 1 atm.

References

[1] S. Gómez; E. Flórez; N. Acelas; C. Hadad; A. Restrepo, Encapsulation of Astatide by a water cage. *Phys. Chem. Chem. Phys.* **2023**, *25*, 12284–12289.

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