

Electronic Supplementary Information for

Evidence of asymmetric cation solvation from the instability of $[\text{Pb}(\text{H}_2\text{O})_n]^{2+}$ complexes.

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Experimental and computational details

ESI-MS. All experiments were run on an unmodified Micromass Q-ToF microTM mass spectrometer at a capillary voltage of 2900 V and an ion energy of 1.0 V. $[\text{Pb}(\text{H}_2\text{O})]^{2+}$ clusters were generated by injecting 5 mmol $\text{Pb}(\text{NO}_3)_2$ into the mass spectrometer at a rate of 50 $\mu\text{L min}^{-1}$. The cone voltage was maximized to 200 V and the source and desolvation temperatures were set to 60 °C and 20 °C, respectively. The cone gas was turned off and the desolvation gas flow rate was 100 L h^{-1} . The formation of water clusters was little affected by other parameters in the normal working range.

EDESI-MS/MS. EDESI-MS/MS experiments were carried out by performing MS/MS on a selected peak at slightly higher than unit mass resolution and increasing the collision voltage in one volt increments from 2 to 85 V for Sr^{2+} and from 2 to 43 V for Pb^{2+} (ion current dropped to near-zero above this value). Individual MS/MS spectra were collected for 30 s and 120 s, respectively. Automation of MassLynx® to carry out the EDESI experiments was achieved using AutoHotkey (freely available from www.autohotkey.com).

DFT calculations. Density functional B3LYP 6-31G* equilibrium geometry calculations were carried out in Spartan using the lanl2DZ pseudopotential. The convergence criteria were lowered to 10⁻⁵ to ensure convergence of all structures. The lowest energy geometries were identified by manual searching of a limited number of possible starting geometries. Note that Wander and Clark (M. C. F. Wander and A. E. Clark, *Inorg. Chem.*, 2008, **47**, 8233.) have criticized the use of the lanl2DZ basis set in describing $[\text{Pb}(\text{H}_2\text{O})_n]^{2+}$ structures, preferring instead the aug-cc-pvdz-PP basis set. Their method predicts that ions with all values of n , including 1, should be stable, and that the lowest energy structures are all holodirected.

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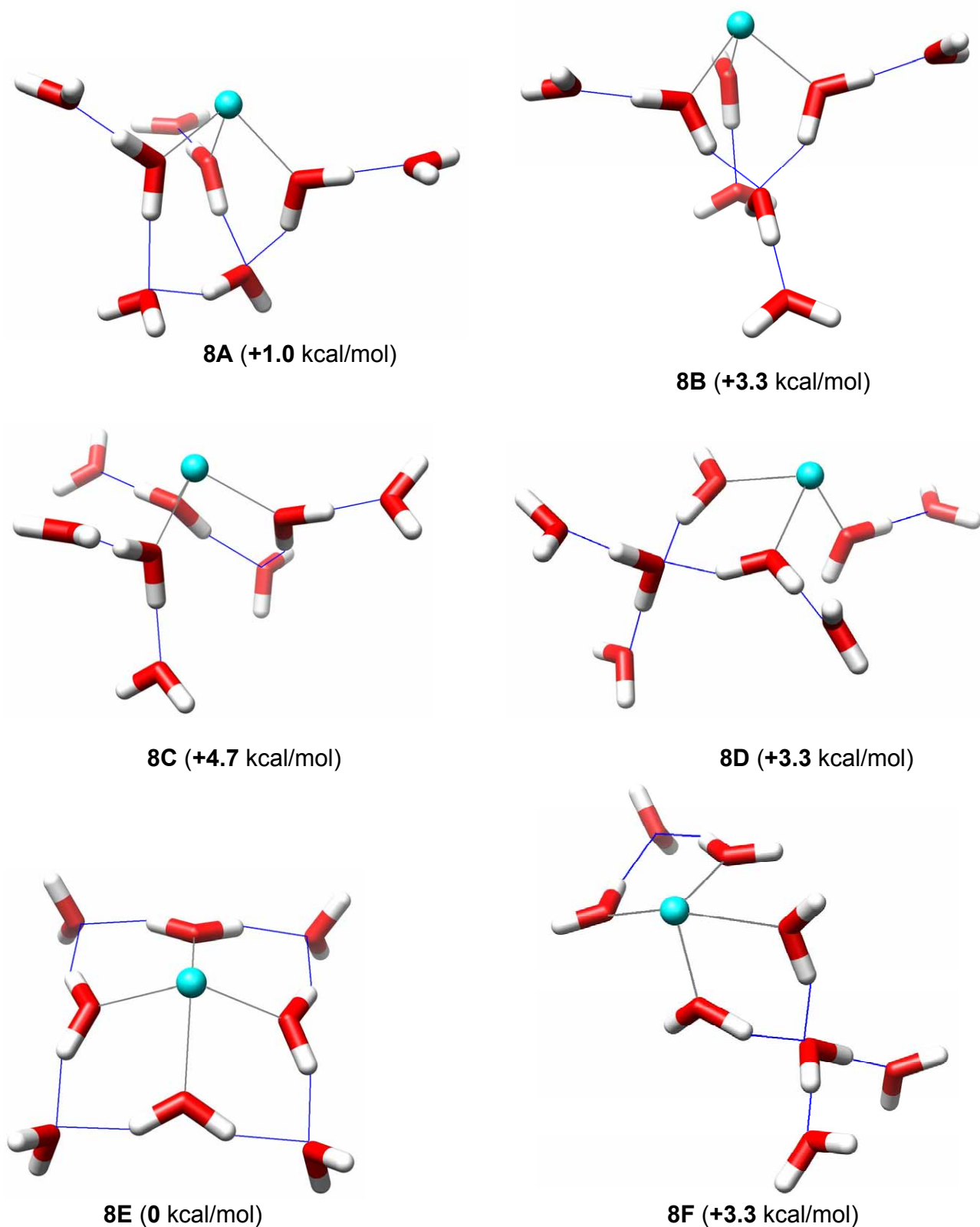


Figure S1. Geometry optimized structures of $[\text{Pb}(\text{H}_2\text{O})_8]^{2+}$ using DFT B3LYP/LANL2DZ 6-31G*. Grey lines represent ion-molecule bonds while blue lines represent hydrogen bonds. The energy of each structure can be seen in Table S1.

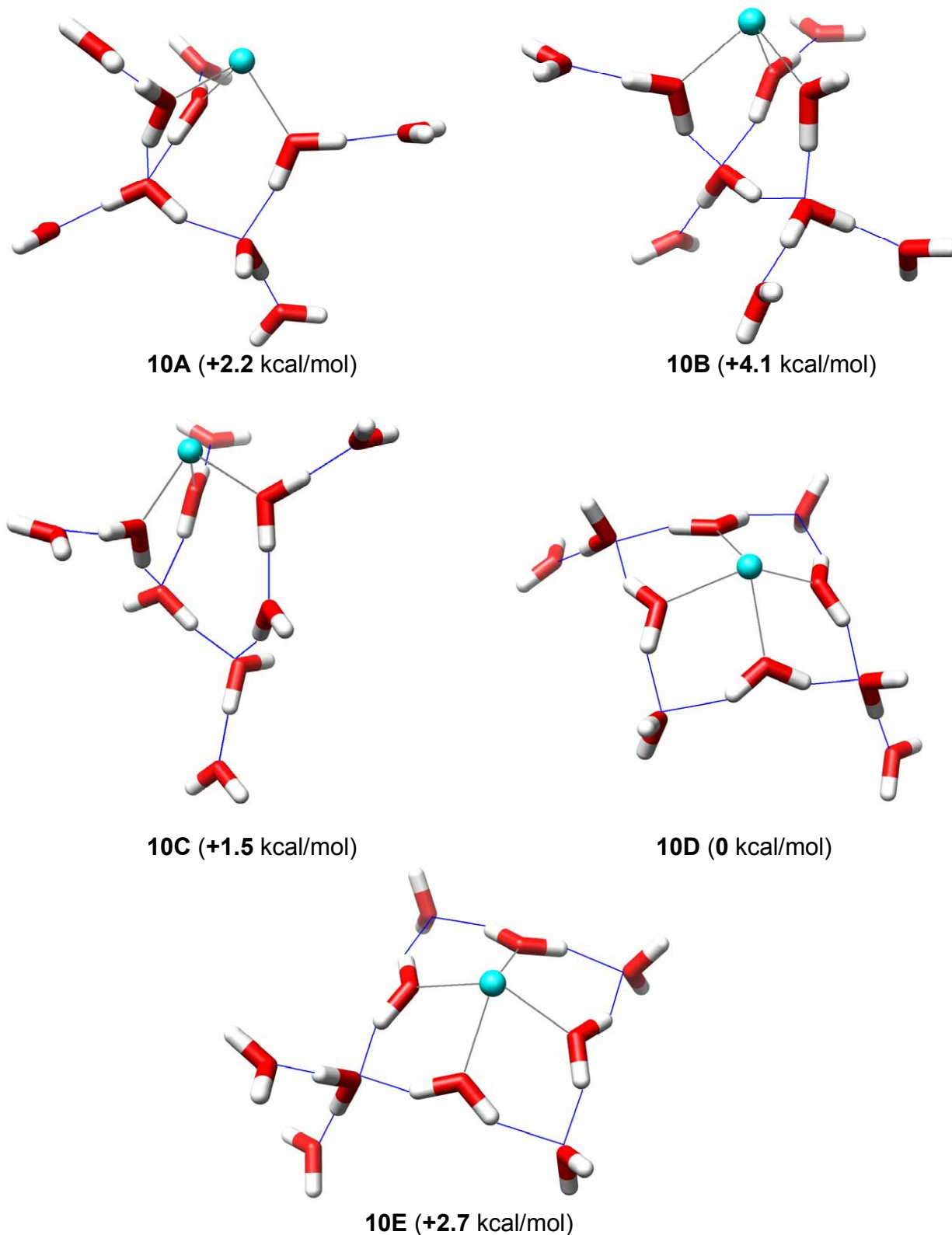


Figure S2. Geometry optimized structures of $[\text{Pb}(\text{H}_2\text{O})_{10}]^{2+}$ using DFT B3LYP/LANL2DZ 6-31G*. Grey lines represent ion-molecule bonds while blue lines represent hydrogen bonds. The energy of each structure can be seen in Table S1.

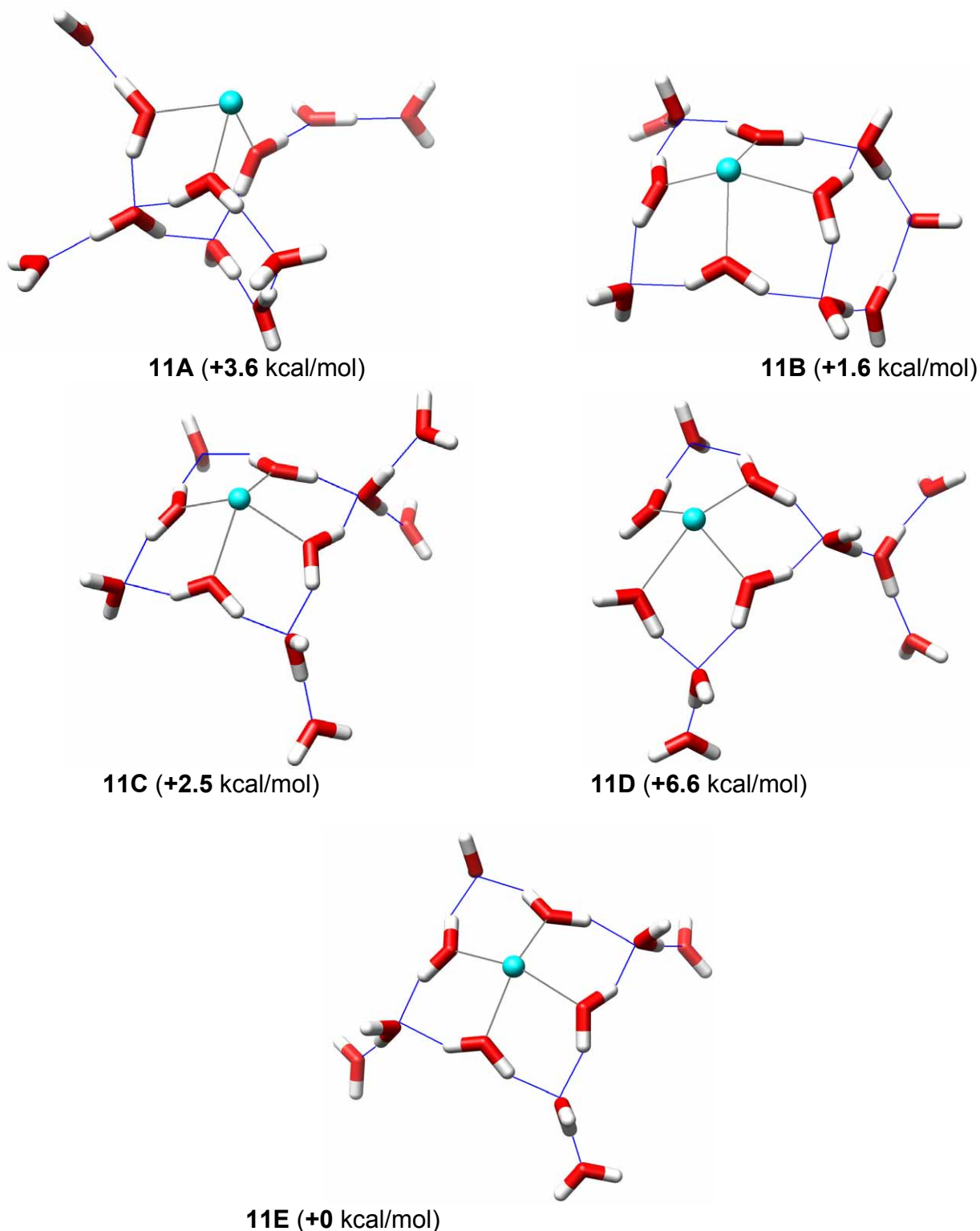


Figure S3. Geometry optimized structures of $[\text{Pb}(\text{H}_2\text{O})_{11}]^{2+}$ using DFT B3LYP/LANL2DZ 6-31G*. Grey lines represent ion-molecule bonds while blue lines represent hydrogen bonds. The energy of each structure can be seen in Table S1.

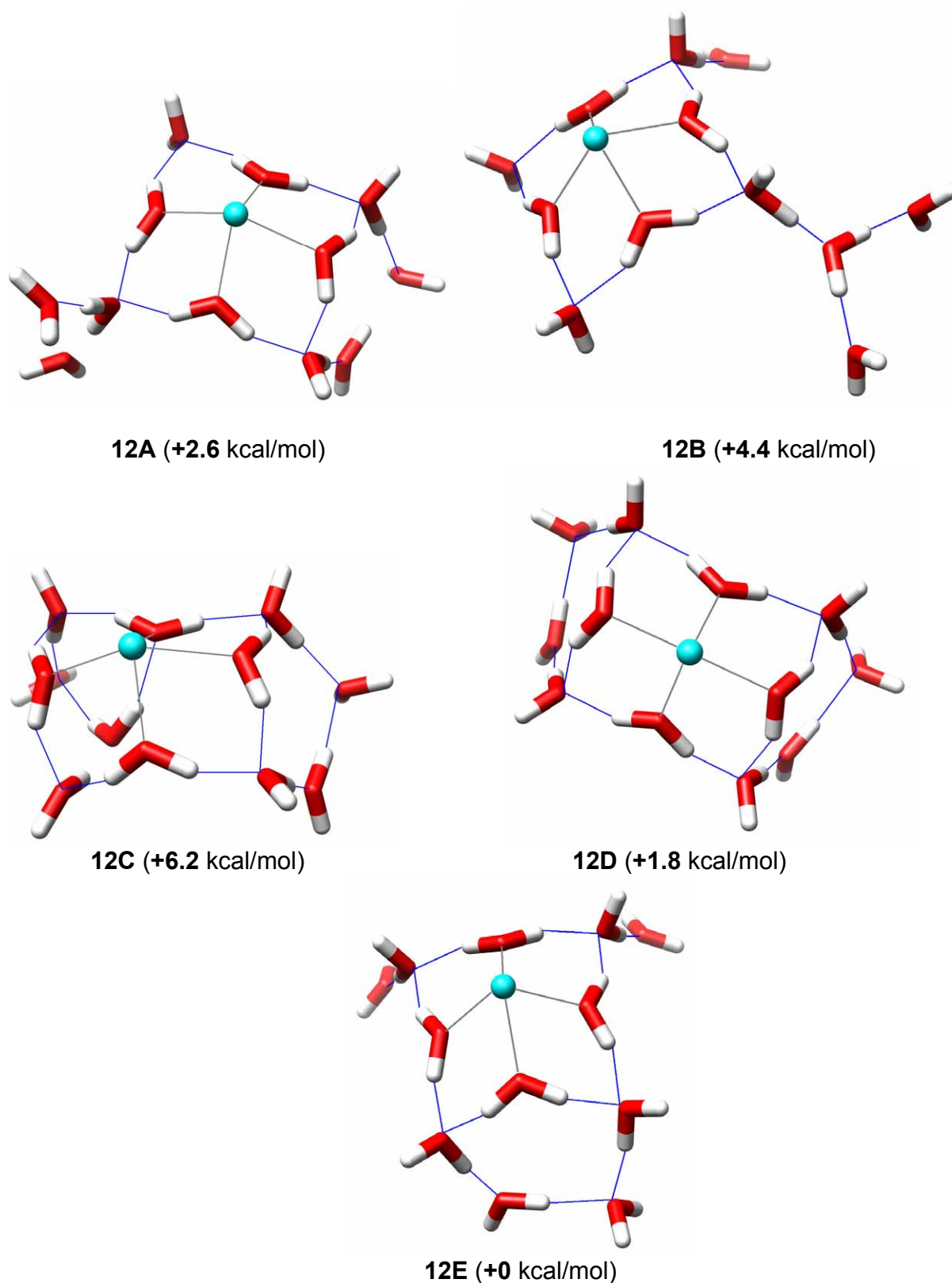


Figure S4. Geometry optimized structures of $[\text{Pb}(\text{H}_2\text{O})_{12}]^{2+}$ using DFT B3LYP/LANL2DZ 6-31G*. Grey lines represent ion-molecule bonds while blue lines represent hydrogen bonds. The energy of each structure can be seen in Table S1.

Table S1. Zero point energy-corrected absolute and relative energies of geometry-optimized Pb^{2+} structures (DFT B3LYP/LANL2DZ 6-31G*^a).

Cluster size	Structure	Energy (kcal/mol)	Relative energy (kcal/mol)
$[\text{Pb}(\text{H}_2\text{O})_8]^{2+}$	8A	-385377.2	1.0
	8B	-385374.9	3.3
	8C	-385373.5	4.7
	8D	-385374.9	3.3
	8E	-385378.2	0.0
	8F	-385375.0	3.2
$[\text{Pb}(\text{H}_2\text{O})_{10}]^{2+}$	10A	-481263.4	2.2
	10B	-481261.6	4.1
	10C	-481264.2	1.5
	10D	-481265.7	0.0
	10E	-481263.0	2.7
$[\text{Pb}(\text{H}_2\text{O})_{11}]^{2+}$	11A	-529203.9	3.6
	11B	-529206.0	1.6
	11C	-529205.0	2.5
	11D	-529200.9	6.6
	11E	-529207.6	0.0
$[\text{Pb}(\text{H}_2\text{O})_{12}]^{2+}$	12A	-577144.7	2.6
	12B	-577142.9	4.4
	12C	-577141.1	6.2
	12D	-577145.6	1.8
	12E	-577147.4	0.0

^a Calculations at this level of theory are not meant to provide quantitative energy values, but the small differences in energy between closely related ion structures do suggest that the hemi-directed hydration spheres have a great deal of structural flexibility.

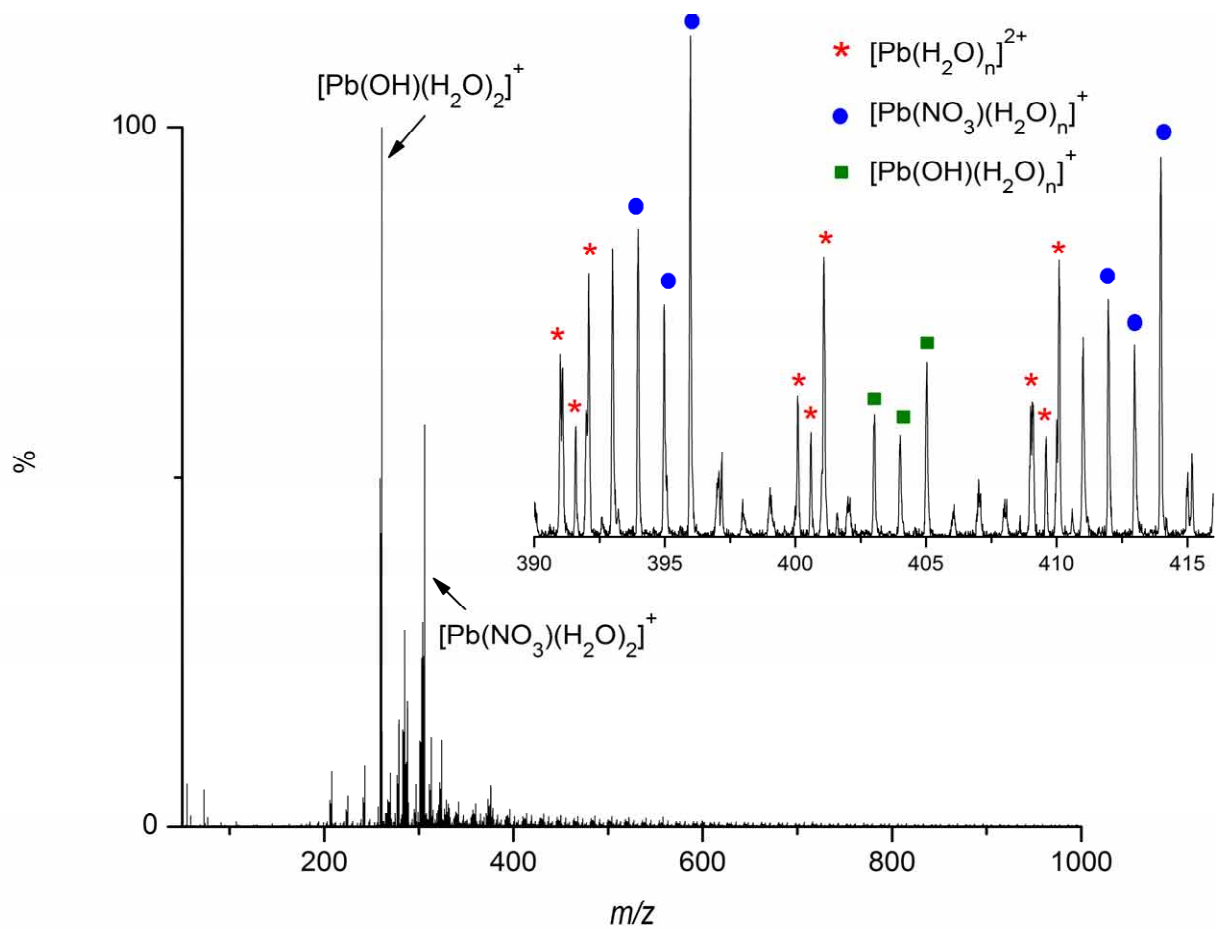


Figure S5. ESI-MS of $\text{Pb}(\text{NO}_3)_2$ solution in water. Three discrete series of ions are observed (see inset).

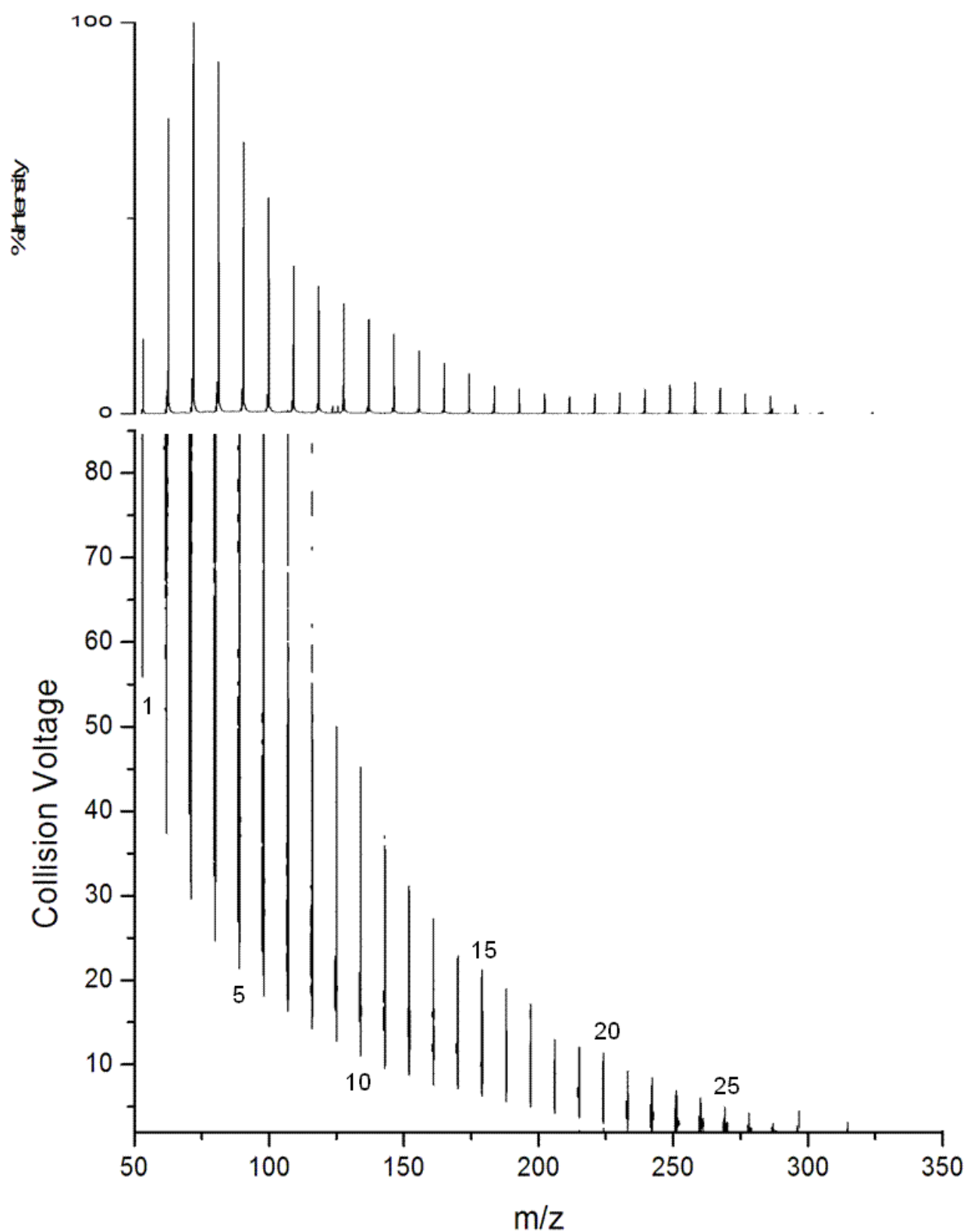


Figure S6. Positive ion EDESI-MS/MS of $[\text{Sr}(\text{H}_2\text{O})_{30}]^{2+}$. Water molecules are sequentially removed through multiple collisions, producing $[\text{Sr}(\text{H}_2\text{O})_N]^{2+}$ ($N = 1-29$). No charge separation occurs. Sr^{2+} is not observable as it is below the minimum m/z value for the instrument (50).