

Strengthening of the Coordination Shell by Counter Ions in Aqueous Th^{4+} Solutions

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Supporting Information

1. COMPUTATIONAL METHODOLOGY

1.1 Metadynamics

Metadynamics (MTD) is a powerful, non-equilibrium molecular dynamics method which accelerates the sampling of the multidimensional free energy surfaces of chemical reactions on a simulation time scale that is easily accessible on modern computers.¹⁻³ This is achieved by adding an *external time-dependent bias potential* which is a function of the *collective variables*, $\mathbf{S}$, to the Hamiltonian of the system. The bias potential discourages the system from sampling previously visited values of $\mathbf{S}$ (i.e., encourages the system to explore new values of $\mathbf{S}$), and its accumulation in low energy wells allows the system to cross energy barriers much more quickly than would occur in standard molecular dynamics. The collective variable $\mathbf{S}$ is defined as a generic function of the system coordinates, $\mathbf{R}^N$ (e.g. bond distance, bond angle, etc.) that is capable of describing the chemical reaction of interest. $\mathbf{S}(\mathbf{R}^N)$ can be regarded as a *reaction coordinate* if it can distinguish between the reactant, transition, and products states, and also capture the kinetics of the reaction. The biasing is achieved by “flooding” the energy landscape with *repulsive* Gaussian “hills” centered on the current location of $\mathbf{S}(\mathbf{R}^N)$ at a constant time interval τ . In between the addition of Gaussians, the system is propagated by normal (but out of equilibrium) dynamics. Suppose that prior to any time t during an MTD simulation, $N+1$ Gaussians centered on $\mathbf{S}_{ig}$ are deposited along the trajectory of $\mathbf{S}(\mathbf{R}^N)$ at times $t_g = 0, \tau, 2\tau, \dots, N\tau$. Then, the value of the bias potential, V , at an arbitrary point, $\mathbf{s}$, along the trajectory of $\mathbf{S}(\mathbf{R}^N)$ at time t is given by

$$V(\mathbf{s}, t) = \sum_{\substack{t_g=0, \tau, 2\tau, \dots, N\tau \\ t_g < t}} H \exp\left(-\frac{(\mathbf{s} - \mathbf{S}_{t_g})^2}{2\omega^2}\right) \quad (\text{S1})$$

where H and ω are respectively the height and width of the Gaussian, T is the simulation temperature, k_B is Boltzmann's constant, and $V(\mathbf{S}_{t_g})$ is the bias potential at the center position $\mathbf{S}_{t_g}$. For a sufficiently large t , $V(\mathbf{s}, t)$ will nearly flatten the free energy surface, $F(\mathbf{s})$, along $\mathbf{S}$, and an unbiased estimator of $F(\mathbf{s})$ is given by

$$F(\mathbf{s}) \approx -\lim_{t \rightarrow \infty} V(\mathbf{s}, t) + \text{constant} \quad (\text{S2})$$

In this work, the collective variable is the primary hydration number of Th^{4+} , i.e., the coordination number of Th^{4+} with respect to all O atoms present⁴:

$$\xi_c(R_{\text{Th-O}}) = \frac{1}{1 + \exp[\kappa(R_{\text{Th-O}} - R_{\text{cut}})]} \quad (\text{S3})$$

where $R_{\text{Th-O}}$ is the Th-O distance, R_{cut} is the cut-off radius (determined from the Th-O RDF), and $\kappa > 0$ is the smearing parameter. In this work, $R_{\text{cut}} = 3.4 \text{ \AA}$ and $\kappa = 20/3 \text{ \AA}^{-1}$ were found to be the optimal choice.

1.2 Set-up of the ab initio dynamics and metadynamics simulations

The ab initio dynamics were carried out using Car-Parrinello molecular dynamics (CPMD)⁵ simulation in the canonical ensemble at 300 K. Pseudopotential plane-wave DFT⁶ as implemented in the NWChem code⁷ was employed for the electronic structure computations. Each system comprised a Th^{4+} and in a periodic cubic cell of length 12.4172 $\text{\AA}$ containing 64 water molecules (the density of water is 1 g/cm^3). In the case where no counter ions were employed, the charge on the metal center was compensated with uniform a background charges of opposite sign and equal magnitude. In the cases where counter ions were employed, the charge was neutralized by Cl^- , Br^- , or ClO_4^- ions. The Perdew-Burke-Ernzerhof (PBE) generalized-corrected exchange-correlation functional⁸ and norm-conserving pseudopotentials modified into a separable form due to Kleinman and Bylander⁹ were employed. The plane wave kinetic energy cut-off was 100 Ry. The simulation time step was $\Delta t = 5 \text{ a.u.}$ (0.121 fs). Nose-Hoover thermostats were used to control the temperature.¹⁰⁻¹¹ Starting with a well-equilibrated cell the metadynamics simulation was carried out using the following parameters: $H = 0.06 \text{ kcal/mol}$, $\omega = 0.1$, $\tau = 100\Delta t$ (12.1 fs). As mentioned earlier, we employed $R_{\text{cut}} = 3.4 \text{ \AA}$ and $1/\kappa = 0.15 \text{ \AA}$ for the coordination number collective variable in the metadynamics simulations.

1.3 Analysis Hydration Shell Properties

The hydration shell properties were analyzed using the partial pair radial distribution functions (RDF), the average first and second shell coordination numbers, the average interatomic distances within the first and second shell, the first shell water tilt angle, and configuration averaged EXAFS.

The radial distribution function provides an average static picture of the structure of water molecules around Th^{4+} as well as the size of the hydration shell. The partial pair radial distribution function (partial RDF) of atoms of type j around atoms of type i , $g_{i-j}(r)$ is defined as

$$g_{i-j}(r) = \frac{1}{N_{total} N_i} \sum_{k=1}^{N_i} \sum_{t=1}^{N_{total}} n_{kj}(r, r + \delta r; t) \quad (S4)$$

where N_{total} is the total number of production time steps, t denotes the time step, N_i is the total number of particles of type i , $n_{ij}(r, r + \delta r; t)$ is the total number of particles of type j in the region between concentric spheres of radii r and $r + \delta r$ centered on a particle of type i at time t , $V(r, r + \delta r) = \frac{4}{3} \pi [(r + \delta r)^3 - r^3]$ is the volume of the region between the concentric spheres, and $\rho_j = \frac{N_j}{V_{tot}}$ is the ideal density of particles of type j , with V_{tot} being the total volume of the system.

The numerator of Eq. S4 is the simply the average number of number atoms of type j located at a distance r from atoms of type i , while the denominator is the *ideal* number atoms of type j at a distance r from atoms of type i assuming the system is homogeneous. The hydration number in the interval was measured using the running coordination up a distance r :

$$n_{i-j}(r) = 4\pi\rho_j \int_{r_{min}}^r r'^2 g(r') dr' \quad (S5)$$

The first minima of the partial RDFs were used as the cut-off values for the computation of the average bond distances and bond angles.

The tilt angle θ_{tilt} of the water with respect to the Th^{4+} -O bond can be used to gauge the flexibility of the water molecules around the metal ion in the first solvation shell, and often used in neutron diffraction studies. Using the first shell parameters in Table 4 of the manuscript, ψ_{tilt} was computed as:

$$\theta_{\text{tilt}} = \arccos \left[\frac{r_{\text{Th-HI}}^2 - r_{\text{Th-OI}}^2 - r_{\text{OI-HI}}^2}{2r_{\text{Th-OI}}r_{\text{OI-HI}} \cos\left(\frac{\theta_{\text{HI-OI-HI}}}{2}\right)} \right] \quad (S6)$$

where $r_{\text{Th-HI}}$, $r_{\text{Th-OI}}$, and $r_{\text{OI-HI}}$ are respectively the average first shell Th-H, Th-O, and O-H bond distances. $\theta_{\text{HI-OI-HI}}$ is the average first H-O-H bond angle.

The ended X-ray absorption fine spectra (EXAFS) of the $\text{Th}(\text{ClO}_4)_4$ system was computed using the MD-EXAFS method.¹² In the MD-EXAFS method is quite straightforward: (i) the atomic coordinates the absorber (Th), and scatterers (O, H, and Cl) of each snapshot are

collected over the production times; (ii) A cluster of radius 6 Å centered on Th is carved out snapshot and used as input to calculate the EXAFS spectrum using the FEFF8 *ab initio* scattering code.¹³; (iii) Finally, the spectra from the individual snapshots are combined to create the ensemble-averaged spectrum.

2. HYDROGEN BOND DYNAMICS

2.1 Geometric criteria for the existence of a hydrogen bond

A hydrogen bond (HB) exists between a pair of molecules (or an ion-molecule pair) if the following three geometric conditions are simultaneously satisfied:

- (i) The $X\cdots O$ distance should be less than some cutoff $R_{X\cdots O}^{cut}$
- (ii) The $X\cdots H$ distance should be less than some cutoff $R_{X\cdots H}^{cut}$
- (iii) The angle between $X\cdots O$ and $O-H$ should be less than some cutoff $\theta_{X\cdots O-H}^{cut}$.

Here $X=O$, Cl or Br . It must be noted that in literature conditions (i) and (iii) are often used to define the existence of an HB. However including condition (ii) makes the existence of a hydrogen bond more stringent. In this work all three conditions were used in the HB dynamical analysis. The cutoff distances $R_{X\cdots O}^{cut}$ and $R_{X\cdots H}^{cut}$ are chosen as first minimum of the partial pair radial distribution function (RDF)¹⁴ of the equilibrated systems shown on the left of Fig. S3. $\theta_{X\cdots O-H}^{cut}$ is the first minimum of the $X\cdots O-H$ angular distribution for all molecular pairs subject to condition (i) above (see Fig. S2 and S3). The cutoff parameters are summarized in Table S1.

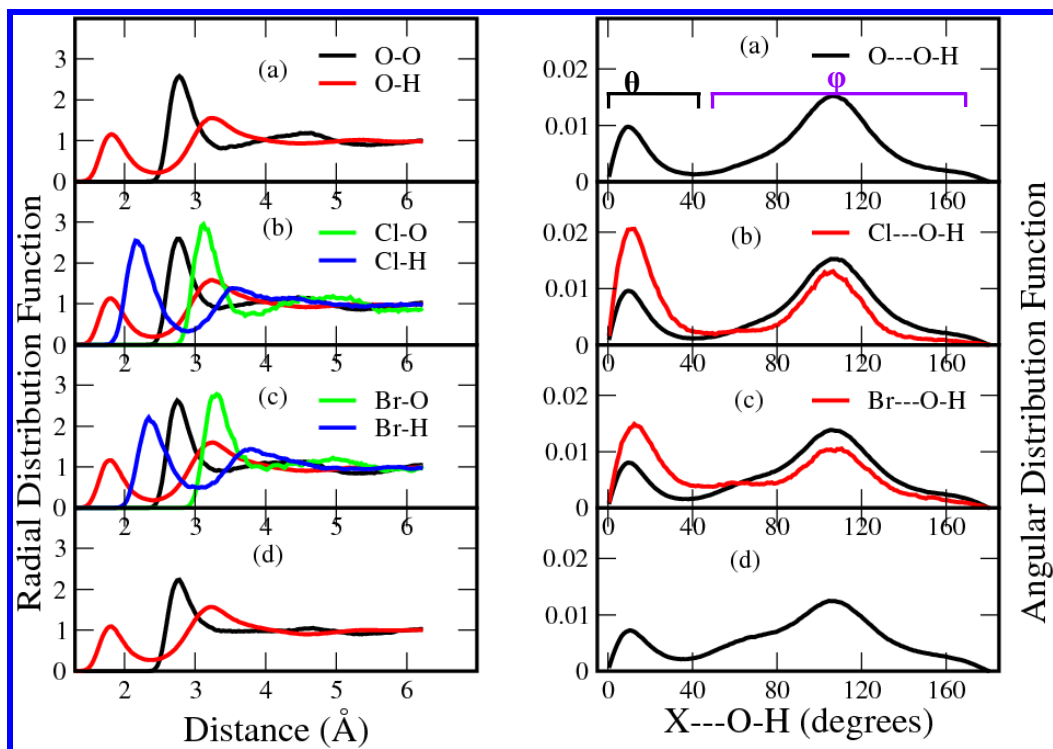


Figure S1: Left figure: Partial RDFs for : (a) dilute solution (b) ThCl₄ (c) ThBr₄ (d) Th(ClO₄)₄. Right figure: HB angle distribution subject to condition (i) above for (a) dilute solution (b) ThCl₄ (c) ThBr₄ (d) Th(ClO₄)₄. The range spanned by angles θ and ϕ are also shown (see Fig. S3 for the definitions of θ and ϕ).

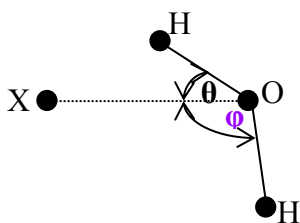


Figure S2: Cartoon depiction of the two characteristic HB angles θ and ϕ , where X=O, O_p, Cl, or Br.

Table S1: Hydrogen bond cut-off parameters for each system.

System	$R_{X\cdots O}^{cut}$ (Å)				$R_{X\cdots H}^{cut}$ (Å)				$\theta_{X\cdots O-H}^{cut}$ (degrees)			
	X				X				X			
	O	O _p	Cl	Br	O	O _p	Cl	Br	O	O _p	Cl	Br
Th ⁴⁺	3.4		–	–	2.45		–	–	40		–	–
Th ⁴⁺ + 4ClO ₄ [–]	3.4	4.0	–	–	2.35	2.30	–	–	40	25	–	–
Th ⁴⁺ + 4Cl [–]	3.4		3.8	–	2.35		2.9	–	40		40	–
Th ⁴⁺ + 4Br [–]	3.4		–	4.0	2.35		–	3.0	40		–	40

2.2 Hydrogen bond lifetimes

In the dynamical equilibrium of aqueous solutions, the hydrogen bonds break and reform due to librational and translational motion of water molecules.¹⁵ We commence the analysis of the HB dynamics by defining two HB population variables $h_{ij}(t)$ and $H_{ij}(t)$ for a pair of molecules i and j at time t ¹⁶⁻¹⁷:

$$h_{ij}(t) = \begin{cases} 1 & \text{if } i \text{ and } j \text{ are hydrogen bonded at time } t \\ 0 & \text{otherwise} \end{cases} \quad (S7)$$

$$H_{ij}(t) = \begin{cases} 1 & \text{if } i \text{ and } j \text{ are continuous ly hydrogen bonded from time 0 to time } t \\ 0 & \text{otherwise} \end{cases}$$

The HB lifetime is estimated by computing the time correlation function^{15, 17-21}

$$S(t) = \frac{\langle \delta h_{ij}(t_0) \delta H_{ij}(t+t_0) \rangle_{\{i,j\},t_0}}{\langle \delta h_{ij}(t_0) \delta h_{ij}(t_0) \rangle_{\{i,j\},t_0}} \quad (S8)$$

where $\delta h_{ij}(t) = h_{ij}(t) - \bar{h}_{ij}$, $\bar{h}_{ij}$ is the time average of $h_{ij}(t)$ over the entire trajectory, and $\langle \cdots \rangle_{\{i,j\},t_0}$ denotes average over all possible molecular pairs $\{i, j\}$ and time origins t_0 . We point out that in literature, $\bar{h}_{ij}$ is usually assumed to zero, that is, the correlation function is computed as $S(t) = \frac{\langle h_{ij}(t_0) H_{ij}(t+t_0) \rangle_{\{i,j\},t_0}}{\langle h_{ij}(t_0)^2 \rangle_{\{i,j\},t_0}}$. However, this assumption is true if the system size is very large. To eliminate finite size effects, the correlation function must be computed per Eq. S8. Since our system sizes are not very large, we have used Eq. S8. In computing $S(t)$, the atomic positions were saved every 12.1 fs over a total simulation time of 18-22 ps.

$S(t)$ is interpreted as the probability that an initially hydrogen bonded pair *remains continuously bonded* up to time t . The characteristic decay time-constant, τ_{LT} , of $S(t)$, given by

$$\tau_{LT} = \int_0^{\infty} S(t) dt \quad (\text{S9})$$

measures the average hydrogen bond “lifetime.” τ_{LT} is obtained by fitting $S(t)$ to $\exp(-t/\tau_{LT})$. In some systems (for example, ThBr_4) the decay of $S(t)$ and cannot be described by a single time-constant (that is, it each cannot be accurately fitted to $\exp(-t/\tau)$). In such cases, $S(t)$ is well-described by the sum of exponential functions: $S(t) = \sum_{i=1}^n a_i \exp(-t/\tau_i)$, where τ_i and a_i are

the decays time-constants and corresponding amplitudes respectively, and a_i satisfies $\sum_{i=1}^n a_i = 1$.

The average decay time-constant, τ , is the sum of the decays constants τ_i weighted by their corresponding amplitudes a_i : $\tau = \sum_{i=1}^n a_i \tau_i$. Typically, $n = 2$ or 3 .

3. RESULTS

3.1 Th-O radial distribution functions

Figure S3 the partial Th—O radial distribution function (upper panel) and running coordination number. The first shell peak height of $\text{Th}(\text{ClO}_4)_4$ is slightly less than that of the remaining plots, implying that the solvent coordination around the ion is slightly less structured in the former. The running coordination number indicates that the second shell ($3.5 < r < 5.2 \text{ \AA}$) of $\text{Th}(\text{ClO}_4)_4$ is slightly more than the other solutions because the ClO_4^- oxygen were included in the count.

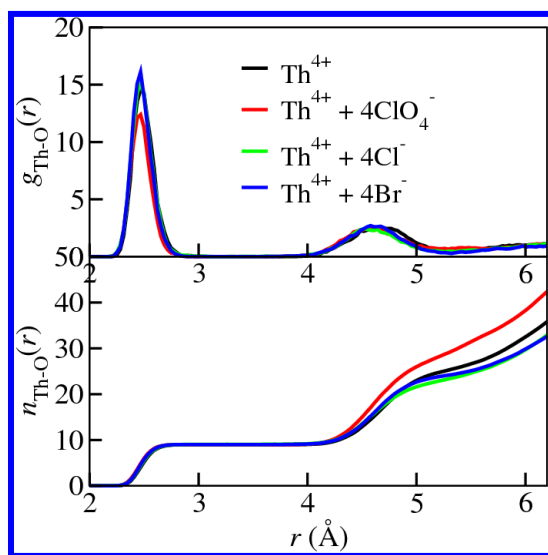


Figure S3: Partial Th—O RDF (top) and running coordination number (bottom).

3.2 Geometry of the first shell solvents around Th^{4+}

Figure S4 show the distribution of the first shell O—Th—O angles from the equilibrium run. When the distribution was compared to several ideal (crystalline) Th^{4+} hydrates, the tricapped trigonal prismatic (TTP) geometry yielded the best match. Obviously, the delta functions in the crystal (vertical blue lines) are difficult to reproduce in the molecular dynamics structures due to severe thermal distortion—particularly the peaks located at 92° and 120° .

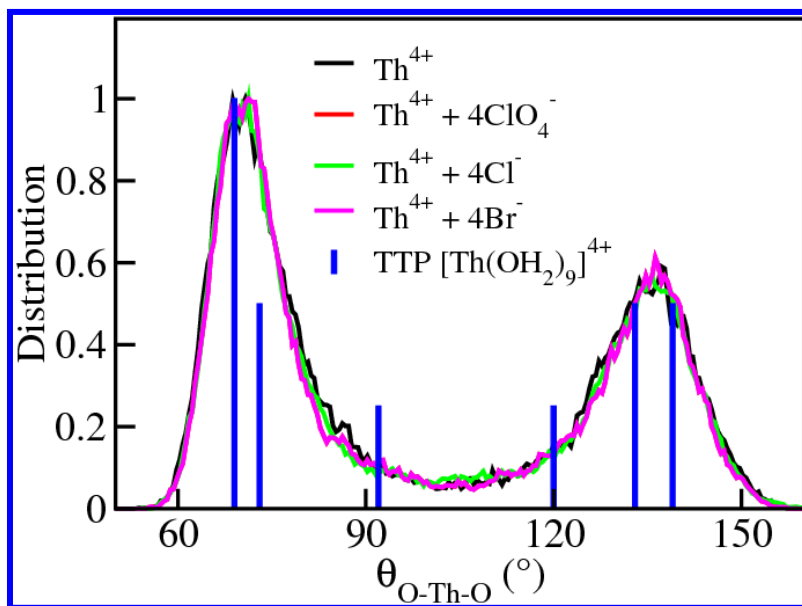


Figure S4: Comparison of the first shell O-Th-O angular distribution to the ideal tricapped trigonal prismatic (TTP) geometry.

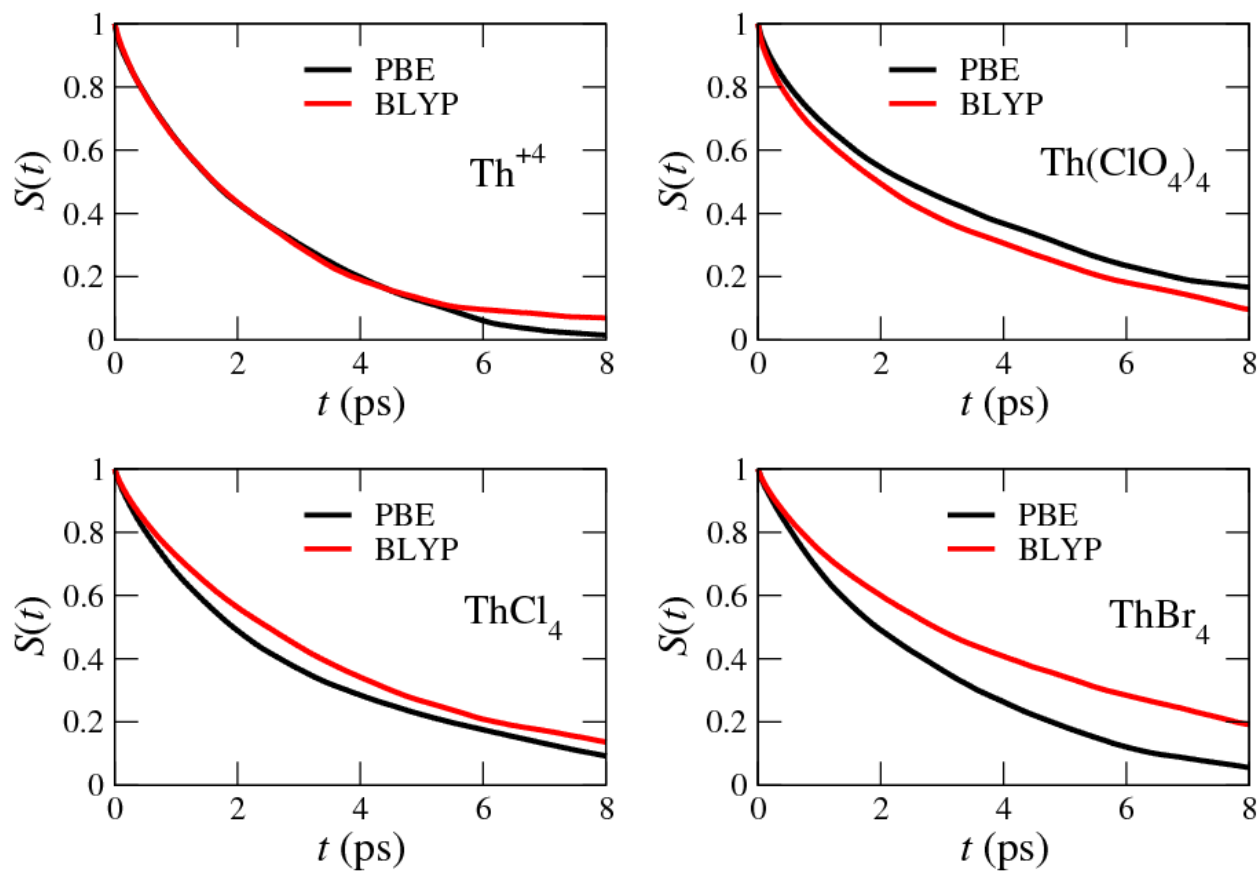


Figure S5: Comparison of the PBE and BLYP hydrogen bond (HB) lifetimes distribution. HB is between first shell water ligands and bulk water-and-anions.

3.3 Metadynamics convergence

In standard metadynamics, convergence is achieved if it can be demonstrated that the free energy surface (the negative of the accumulated bias potential) at some later time, is a constant shift from the free energy surface at some initial time—this, in essence, is equation S1. Convergence is generally difficult to reach, particularly in ab initio molecular dynamics where the sampling time is limited. There is no hard-and-fast rule for determining the initial and final times, and subsequently the shift in the free energy curves. The easiest way to is to systematically track the free energy profiles as a function of time and look for similar trends in pairs of energy profiles. From the 0.1 nanoseconds metadynamics trajectory for Th^{4+} , ThCl_4 , $\text{Th}(\text{ClO}_4)_4$ and a 0.15 ns trajectory for ThBr_4 , we identified the free energy curves that shift by a near constant amount; this is depicted by the black and red curves in Fig. S6. The representative free energy of each system, which is reported in the manuscript, is then the arithmetic average of the two curves (blue curve in the figure).

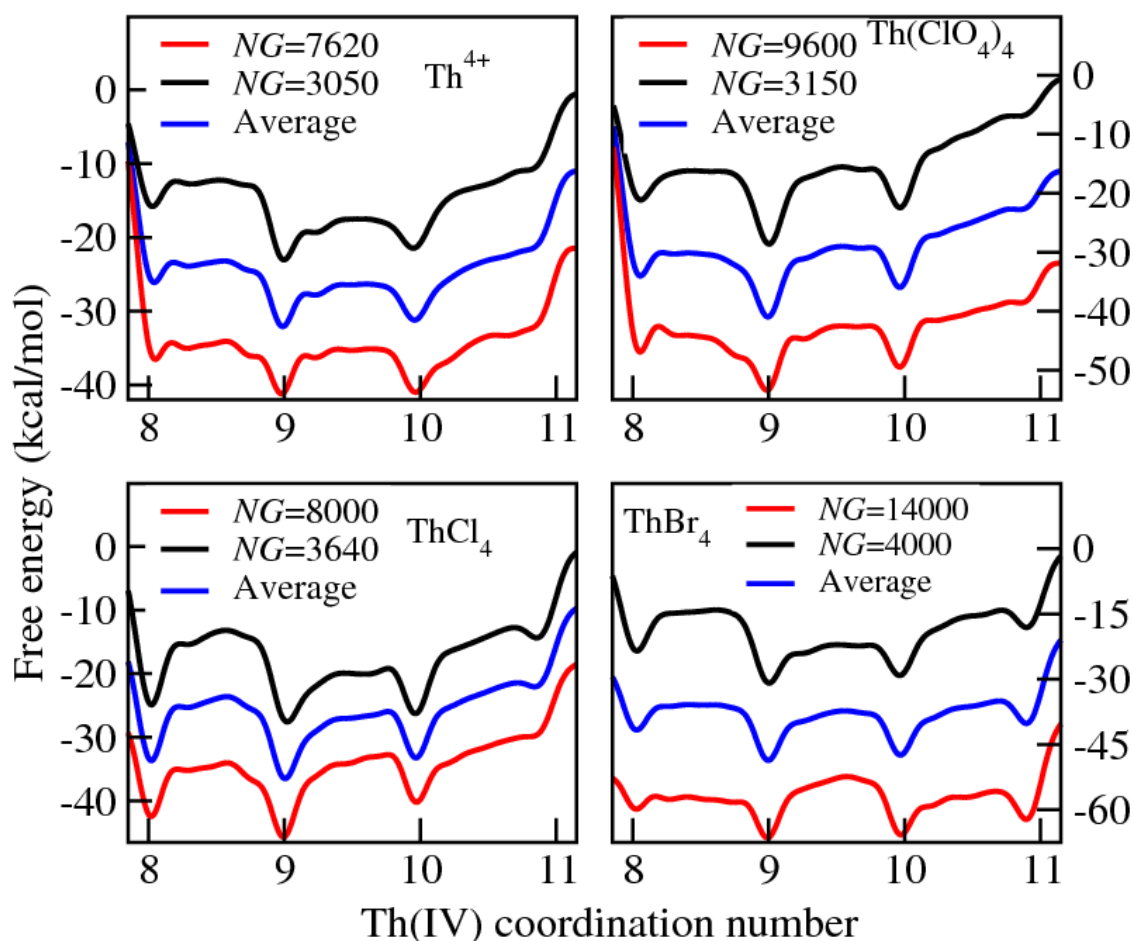
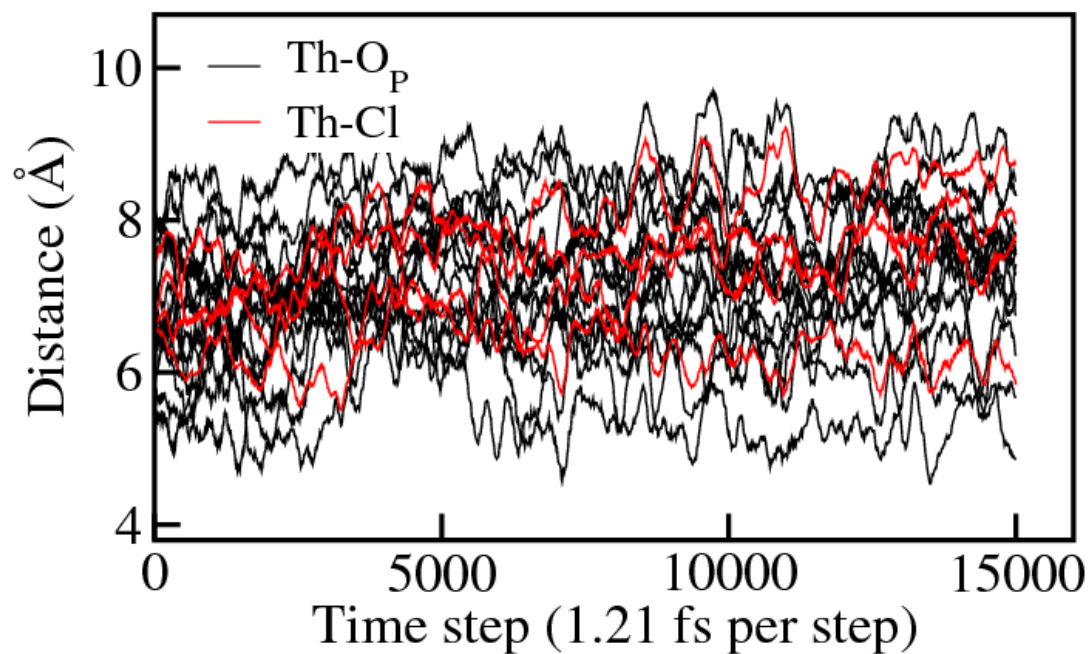


Figure S6: Depiction of the convergence of the metadynamics potential for each system. NG is the total number Gaussians hills used to construct the free energy surface. The black and red in energy curves differ by nearly a constant. The blue curve is the average of the blue and red curves.

(a) Counterions initially placed in the bulk region



(b) Counterions initially placed near the second shell

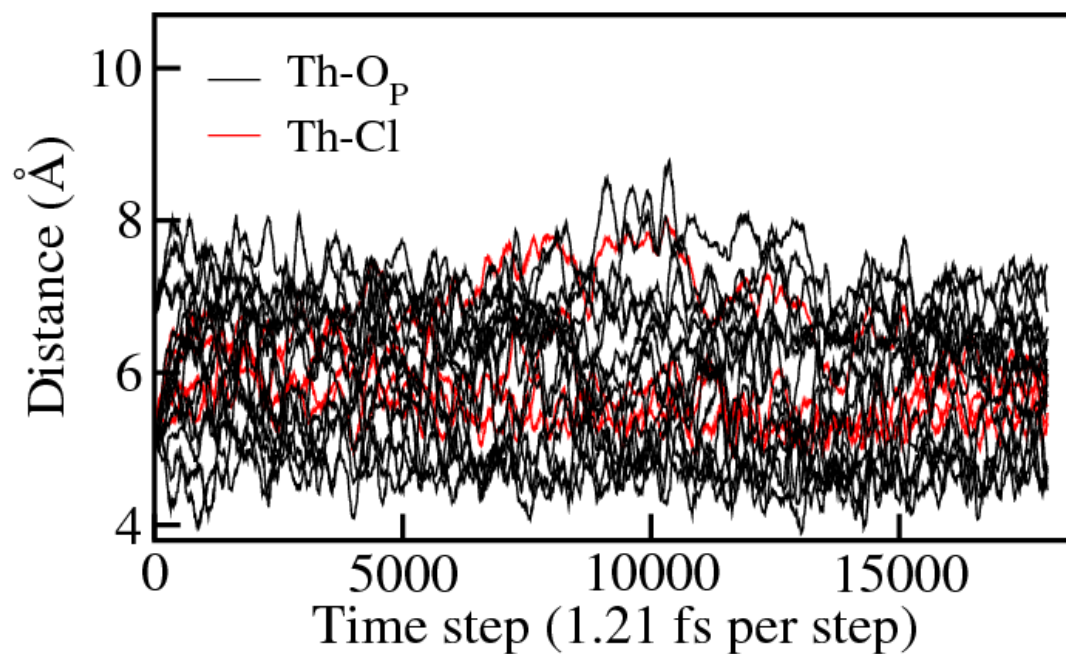


Figure S7: Depiction of the time evolution of the distance between Th and the counterions (O_P denotes the oxygen atom in the counterion) for the case where (a) the counterions were initially placed in the bulk and (b) the counterions were initially placed in the second shell.

References

1. Laio, A.; Parrinello, M., Escaping Free-Energy Minima. *Proceedings of the National Academy of Sciences* **2002**, *99*, 12562.
2. Laio, A.; Gervasio, F. L., Metadynamics: A Method to Simulate Rare Events and Reconstruct the Free Energy in Biophysics, Chemistry and Material Science. *Reports on Progress in Physics* **2008**, *71*, 126601.
3. Barducci, A.; Bussi, G.; Parrinello, M., *Phys. Rev. Lett.* **2008**, *100*, 020603.
4. Sprik, M., Coordination Numbers as Reaction Coordinates in Constrained Molecular Dynamics. *Faraday Discussions* **1998**, *110*, 437.
5. Car, R.; Parrinello, M., Unified Approach for Molecular Dynamics and Density-Functional Theory. *Phys. Rev. Lett.* **1985**, *55*, 2471.
6. Kohn, W.; Sham, L. J., Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133.
7. Valiev, M., et al., Nwchem: A Comprehensive and Scalable Open-Source Solution for Large Scale Molecular Simulations. *Comput. Phys. Commun.* **2010**, *181*, 1477.
8. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
9. Kleinman, L.; Bylander, D. M., Efficacious Form for Model Pseudopotentials. *Physical Review Letters* **1982**, *48*, 1425-1428.
10. Nose, S., A Molecular Dynamics Method for Simulations in the Canonical Ensemble. *Mol. Phys.* **1984**, *52*, 255.
11. Hoover, W. G., Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31*, 1695.
12. Dang, L. X.; Schenter, G. K.; Glezakou, V. A.; Fulton, J. L., Molecular Simulation Analysis and X-Ray Absorption Measurement of Ca^{2+} , K^{+} and Cl^{-} Ions in Solution. *J. Phys. Chem. B* **2006**, *110*, 23644.
13. Rehr, J. J.; Kas, J. J.; Vila, F. D.; Prange, M. P.; Jorissen, K., Parameter-Free Calculations of X-Ray Spectra with Feff9. *Physical Chemistry Chemical Physics* **2010**, *12*, 5503-5513.
14. The partial RDF is computed using the intermolecular distances. For example: the intramolecular O-H distances in water and the intramolecular Cl-O distances in the perchlorate anion were not included.
15. Chowdhuri, S.; Chandra, A., Hydrogen Bonds in Aqueous Electrolyte Solutions: Statistics and Dynamics Based on Both Geometric and Energetic Criteria. *Physical Review E* **2002**, *66*, 041203.
16. Stillinger, F. H., Theory and Molecular Models for Water. *Adv. Chem. Phys.* **1975**, *31*, 1.
17. Rapaport, D. C., Hydrogen Bonds in Water. *Mol. Phys.* **1983**, *50*, 1151.
18. Luzar, A.; Chandler, D., Effect of Environment on Hydrogen Bond Dynamics in Liquid Water. *Phys. Rev. Lett.* **1996**, *76*, 928.
19. Luzar, A.; Chandler, D., Structure and Hydrogen Bond Dynamics of Water-Dimethyl Sulfoxide Mixtures by Computer Simulations. *J. Chem. Phys.* **1993**, *98*, 8160.
20. Luzar, A., Resolving the Hydrogen Bond Dynamics Conundrum. *J. Chem. Phys.* **2000**, *113*, 10663.
21. Chandra, A., Effects of Ion Atmosphere on Hydrogen-Bond Dynamics in Aqueous Electrolyte Solutions. *Phys. Rev. Lett.* **2000**, *85*, 768.

