

Supporting Information

Hydration Structure of the Elusive Ac(III) Aqua Ion: Interpretation of X-ray Absorption Spectroscopy (XAS) Spectra on the Basis of Molecular Dynamics (MD) Simulations

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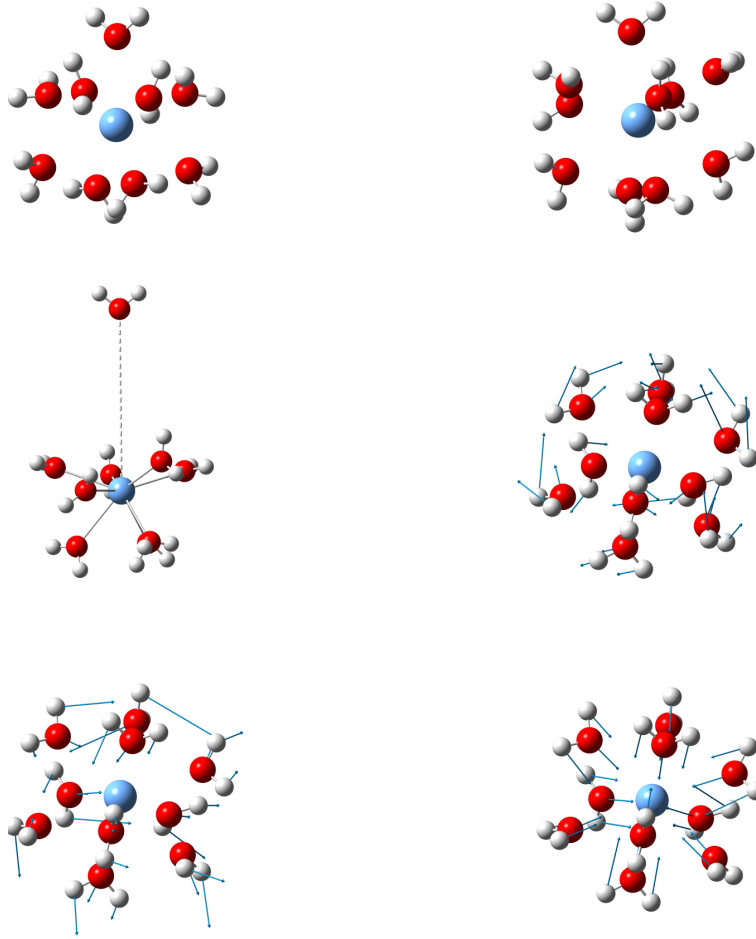


Figure S1: Representative structures of Ac^{3+} hydrates employed in the development of the Ac^{3+} - H_2O interaction potential: (top) optimized structures of $[\text{Ac}(\text{H}_2\text{O})_m]^{+3}$ for $m=9,10$; (medium) left, scan of a water molecule from the hydrate, right, structures derived from a bending vibrational mode; (bottom) structures derived from stretching vibrational modes.

Intermolecular ion-water potential

The monoatomic cation, $\text{Ac}(\text{III})$, is described by a positive charge, $Z_M = 4$, and a mobile negative charge density, ρ_O with a total charge, $q_M = -1$, joined to the nucleus by a spring of force constant, k_M (see Figure S2).

The intra-atomic energy is defined by:

$$U_{\text{intra}} = \frac{1}{2} k_M \cdot r^2 \quad (1)$$

where r is the distance between the nucleus and its associated mobile charge density. In the absence of an external field, the equilibrium position of the oscillator is located on the nucleus and $U_{\text{intra}} = 0$.

The incorporation of the MCDHO2 model to the new potential needs the consideration of the following intermolecular terms for the $\text{Ac}(\text{III})$ - H_2O interaction:

- Classical interaction between the mobile charge densities, q_O and q_M , given by a two-exponential function:

$$U_{\text{inter}}(q_O, q_M) = A_{\text{MO}} \cdot e^{-\alpha_{\text{MO}} \cdot R_{\text{MO}}} + B_{\text{MO}} \cdot e^{-\beta_{\text{MO}} \cdot R_{\text{MO}}} \quad (2)$$

where R_{MO} is the distance between the mobile charge densities. A_{MO} , α_{MO} , B_{MO} and β_{MO} are fitting parameters.

- Classical interaction between the M nucleus, Z_M , and those of the water molecule, Z_i ($i \equiv \text{O}, \text{H}$), is given by a two-exponential function as well:

$$U_{\text{inter}}(Z_i, Z_M) = C_{\text{Mi}} \cdot e^{-\gamma_{\text{Mi}} \cdot R_{\text{Mi}}} + D_{\text{Mi}} \cdot e^{-\delta_{\text{Mi}} \cdot R_{\text{Mi}}} \quad (3)$$

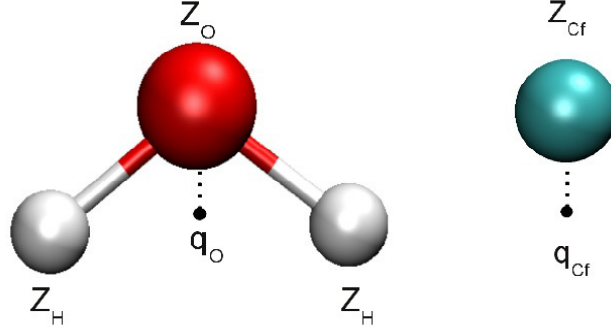


Figure S2: Schematic representation of MCDHO2 model for the water molecule and the metal cation.

where R_i is the distance between the M nucleus and each i -th nucleus of the water molecule, and C_{Mi} , γ_{Mi} , D_{Mi} and δ_{Mi} are fitting parameters.

- Electrostatic interaction between the water mobile charge density, q_O and the M nucleus, Z_M :

$$U_{inter}(q_O, Z_M) = \frac{q_O Z_M}{r'_{OM}} \left[1 - \left(\frac{R'_{MO}}{\lambda'} + 1 \right) e^{-2R'_{MO}/\lambda'} \right] \quad (4)$$

where R' is the distance between the center of ρ_O and the M nucleus and λ' is the intermolecular screening described in the original MCDHO model[1].

- Electrostatic interaction between the M mobile charge density, q_M , and each of the charges on the water molecule nuclei, $Z_i (i \equiv O, H)$:

$$U_{inter}(Z_i, q_M) = \frac{Z_i q_M}{R_{iM}} \left[1 - \left(\frac{R_{iM}}{\lambda'_M} + 1 \right) e^{-2R_{iM}/\lambda'_M} \right] \quad (5)$$

where R_i is the distance from the ρ_M center to Z_i and λ'_M is the corresponding intermolecular screening.

Thus, the interaction energy for a cluster with N water molecules is computed by the expression:

$$U = \sum_{S=1}^N \left(\sum_{i \in S} \sum_{j \in T} [U_{inter}(Z_i, Z_j) + U_{inter}(q_i, q_j)] + U_{inter}(q_i, Z_j) + U_{inter}(q_j, Z_i) \right) + \sum_{i \in S} \frac{1}{2} k_i \cdot r_{ii}^2 + \frac{1}{2} k_M \cdot r^2 \quad (6)$$

where S runs over the water molecules and T over the M.

Harmonic constant, k_M , is in E_h/a_0^2 , ion electrostatic decaiment, λ'_M , is in a_0 , pre-exponential terms are in E_h and exponential terms are in a_0^{-1} .

Table S1: Fitted parameters of the Ac-H₂O interaction potential (in a.u.)

Parameters	values
k_{Ac}	1.01107
λ'_M	0.613765
A_{AcO}	295.115153
α_{AcO}	1.56067
B_{AcO}	-146.907148
β_{AcO}	1.455453
C_{AcH}	49.771715
γ_{AcH}	11.235805
D_{AcH}	0.00227
δ_{AcH}	4.635531

The MCDHO2 water molecule is described by a positive charge in the oxygen atom, $Z_O = 2$, and the hydrogen atoms, $Z_H = 0.62$, and a mobile charge density linked at the oxygen atom with charge, $q_O = -3.24$.

The polarizability of the water molecule is modeled by a harmonic function connecting the mobile charge density and the oxygen nucleus:

$$U_k = \frac{1}{2}k \cdot r^2 \quad (7)$$

The mobile charge is defined as a Gaussian charge distribution having a decaying constant λ :

$$\rho(r) = \frac{q}{\pi\lambda^3} e^{-2\frac{r}{\lambda}} \quad (8)$$

The oxygen-hydrogen bond flexibility is defined by a Morse potential:

$$U_{d_{OH}} = D_{OH} \left(e^{-2\gamma(R_\beta - r_e)} - 2e^{-\gamma(R_\beta - r_e)} \right) \quad (9)$$

The water internal angle is defined by a quartic function:

$$U_{\Theta_{HOH}} = a_1(\Theta - \Theta_e) + a_2(\Theta - \Theta_e)^2 + a_3(\Theta - \Theta_e)^3 + a_4(\Theta - \Theta_e)^4 \quad (10)$$

The internal energy of a water molecule is then given by the addition of all the previous contributions:

$$U_{\text{internal}} = \frac{1}{2}kr_O^2 + \frac{Z_H^2}{R_{1,2}} + \frac{qZ_H}{r_\beta} \left[1 - \left(\frac{r_\beta}{\lambda} + 1 \right) e^{-2r_\beta/\lambda} \right] + U_k + U_{d_{OH_1}} + U_{d_{OH_2}} + U_{\Theta_{HOH}} \quad (11)$$

The intermolecular energy of a cluster of N water molecules is defined by the electrostatics and a Lennard-Jones potential for the interactions among oxygen and hydrogen atoms and mobile charges of the different solvent molecules.

$$U_{\text{total}} = \sum_{n=1}^N \sum_{m=1}^{n-1} \left(\frac{A}{r_{nm}} \right)^{12} - \left(\frac{B}{r_{nm}} \right)^6 + \frac{q^2}{r_{nm}} + \frac{qZ_\beta}{r_{n\beta}} \left[1 - \left(\frac{r_{n\beta}}{\lambda} + 1 \right) e^{-2r_{n\beta}/\lambda} \right] + \sum_{\beta \in m}^q \left(\frac{A_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left(\frac{B_{\alpha\beta}}{r_{\alpha\beta}} \right)^6 + \frac{Z_\alpha\beta}{r_{\alpha\beta}} \quad (12)$$

Harmonic constant, k_M , is in E_h/a_0^2 , electrostatic decaiment, λ_O , is in a_0 , distances are in a_0 and angles are in radians.

Table S2: MCDHO2 parameters (in a.u.)

Parameters	values
Z_H	0.62
Z_O	2.00
q_O	-3.24
k_O	1.00
λ_O	1.90
D_{OH}	0.42954802
r_{OH}	1.3440633
α_{OH}	1.1131102
θ_{HOH}	1.927
a_{HOH}	0.031621
b_{HOH}	0.043914
c_{HOH}	-0.012721
d_{HOH}	-0.00866

Details of MD simulations

- 1 cation + 1000 water molecules.
- Cubix box with length chosen to get experimental water density= 0.997 g/cm⁻³ at simulation conditions.
- NVT ensemble with T=300K.
- PBC and Ewald sum.
- MD simulations have been carried out using the Dynamical shell model [3].
- A modified version of the DL-POLY Classic code [4].
- 1 ns production time.

Potential Energy Surface Building

The interaction energies to be fitted are obtained from ab initio calculations obtained at the level indicated in the following table.

Table S3: Quantum mechanical methods

M(III)	DFT	Pseudopotential
Ac	TPSSH	ECP78MBW

It is worth pointing out that the quasi-relativistic effective core potential (RECP) were specifically developed by Dolg and col.[5] for the lanthanides and actinides trivalent cations. Their recommended basis sets for the valence orbitals were used and aug-cc-pvdz basis sets for the O and H atoms.

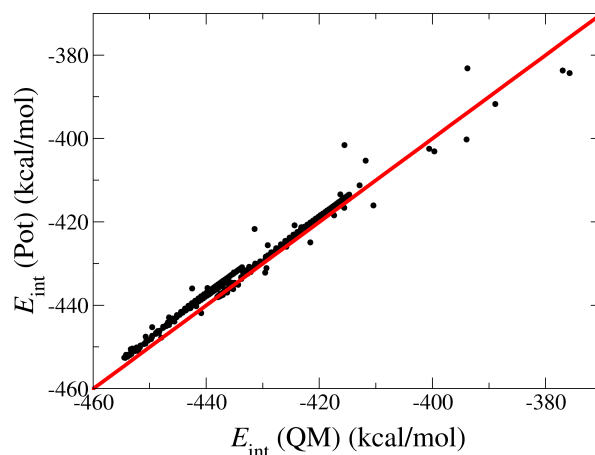


Figure S3: Ac³⁺-H₂O fitting: Comparison of interaction energy derived from the potential with that derived from the quantum-mechanical computations for all structures employed in the potential fit.

Table S4: Ac-O distances of several Ac^{3+} hydrates obtained from QM and potential optimized geometries.

Structure	$R_{\text{M-O}} \text{ (\AA)}$	
	R^{QM}	R^{Pot}
$\text{Ac}(\text{H}_2\text{O})_8^{3+}$	2.68	2.67
$\text{Ac}(\text{H}_2\text{O})_8^{3+}(\text{H}_2\text{O})_1$	8x2.66, 1x4.79	8x2.65, 1x4.76
$\text{Ac}(\text{H}_2\text{O})_8^{3+}(\text{H}_2\text{O})_2$	8x2.66, 2x4.79	8x2.65, 2x4.76
$\text{Ac}(\text{H}_2\text{O})_8^{3+}(\text{H}_2\text{O})_{16}$	8x2.66, 16x4.79	8x2.65, 16x4.77
$\text{Ac}(\text{H}_2\text{O})_9^{3+}$	2.71	2.71
$\text{Ac}(\text{H}_2\text{O})_9^{3+}(\text{H}_2\text{O})_1$	9x2.69, 1x4.86	9x2.68, 1x4.82
$\text{Ac}(\text{H}_2\text{O})_9^{3+}(\text{H}_2\text{O})_{18}$	9x2.69, 18x4.93	9x2.68, 18x4.87
$\text{Ac}(\text{H}_2\text{O})_{10}^{3+}$	4x2.72, 4x2.76, 2x2.80	

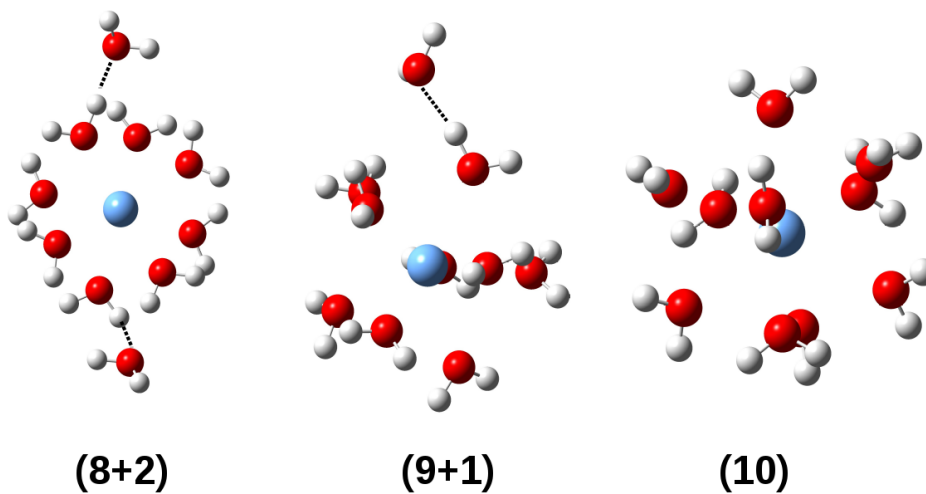


Figure S4: $[\text{Ac}(\text{H}_2\text{O})_m]^{3+}(\text{H}_2\text{O})_n$ clusters structures for a total coordination number of 10

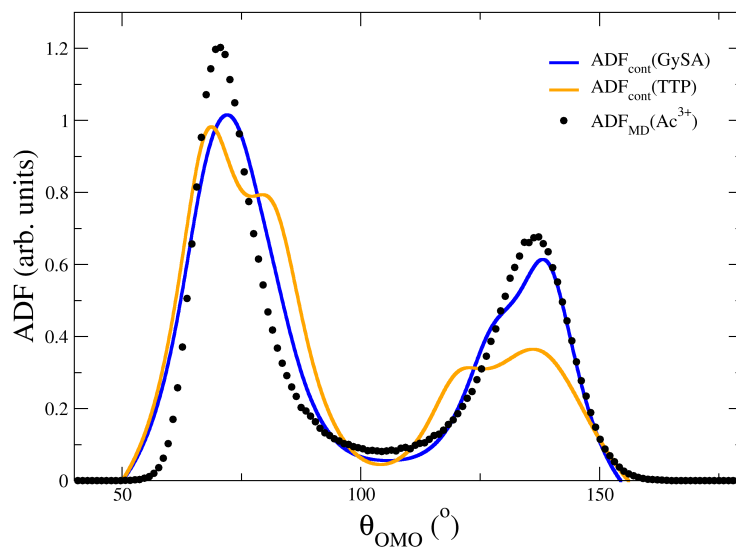


Figure S5: Comparison of the Angular Distribution Function (ADF) of OAcO angles in the first hydration shell from the Ac^{3+} simulation (black dots) and the continuous ADF for the gyro-elongated square antiprism (blue line) and trigonal tricapped prism (orange line) 9-coordination polyhedra [6].

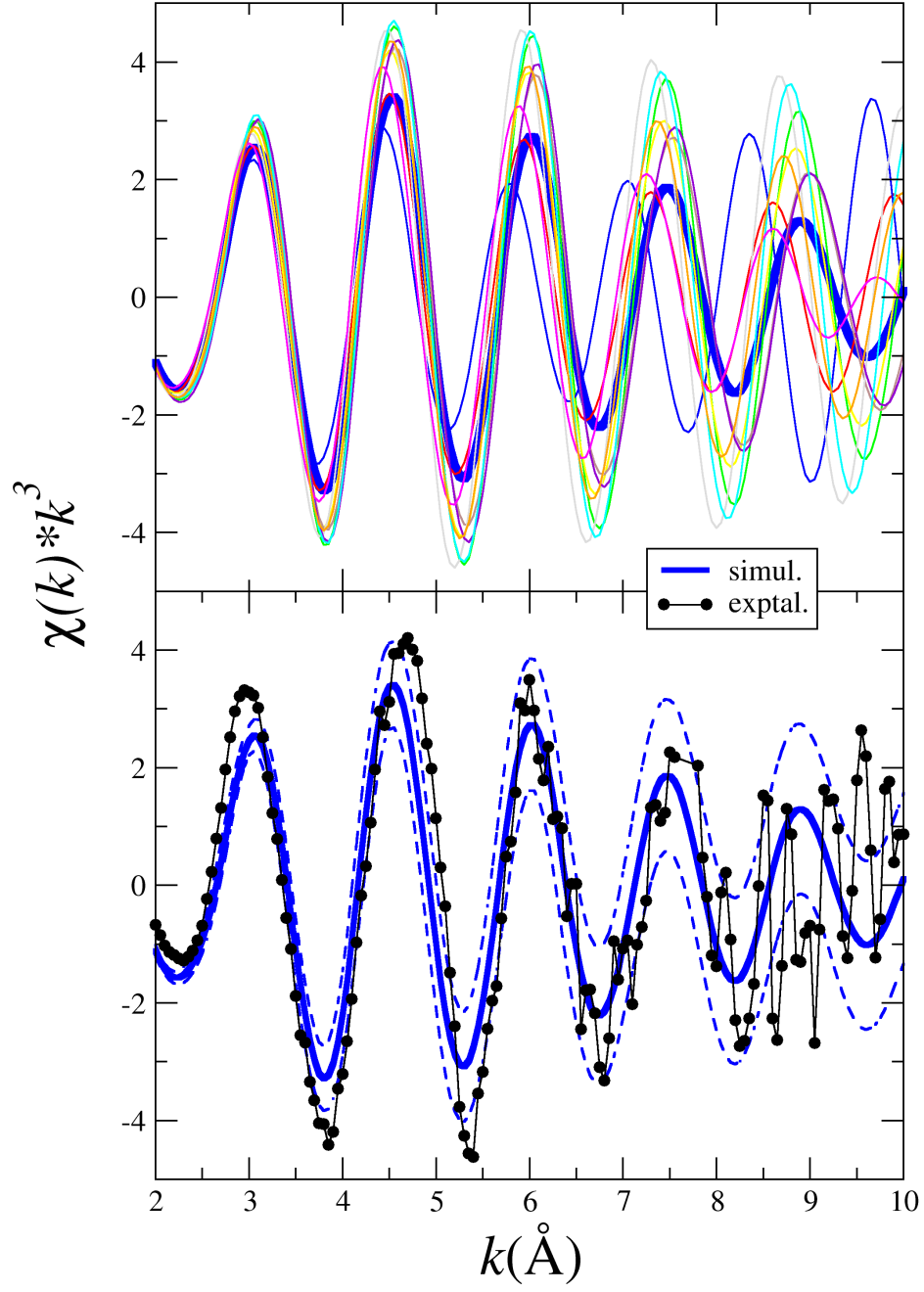


Figure S6: Ac L_3 -edge k^3 -weighed EXAFS spectrum of the Ac^{3+} aqueous solution: (top) 10 individual simulated spectra from snapshots of the MD trajectory and the simulated spectrum averaged from 500 snapshots. (bottom) Simulated spectrum (blue line) with its statistical uncertainty of the 500-snapshots average (blue dashed lines) and experimental spectrum (black dotted line).

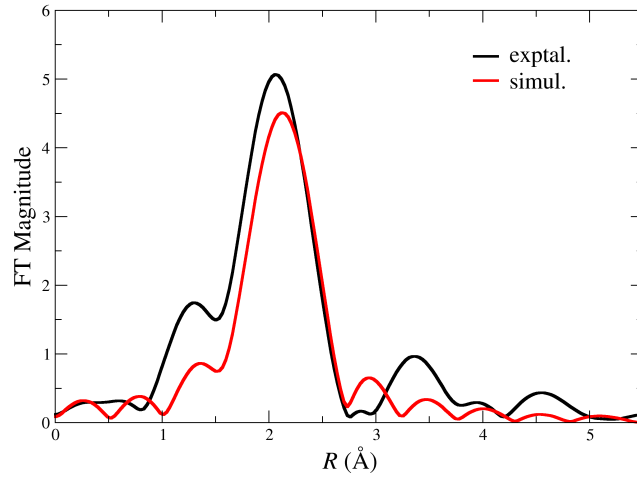


Figure S7: Comparison of the experimental Fourier Transform k^3 -EXAFS spectrum (black line) of the Ac^{3+} aqueous solution obtained by Ferrier et al. [7] with the simulated spectrum obtained from a set of 500 snapshots taken from the MD simulation.

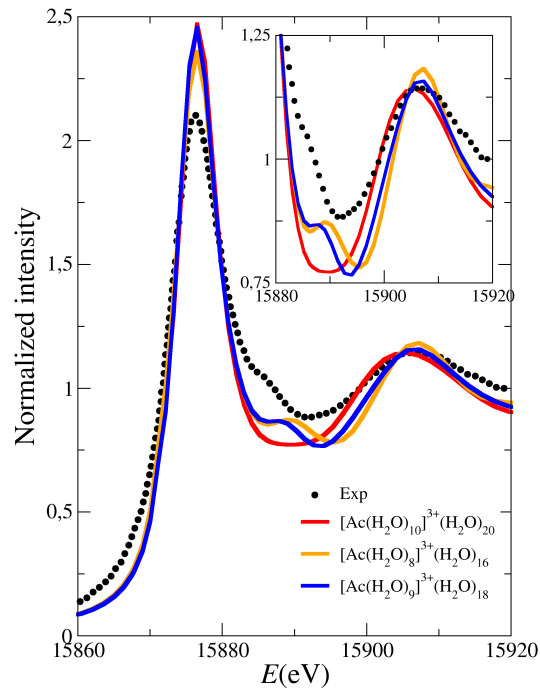


Figure S8: Comparison of the experimental XANES spectra of the Ac^{3+} aqueous solution obtained by Ferrier et al. [7] with the computed spectra obtained from three Ac^{3+} hydrates including two hydration shells.

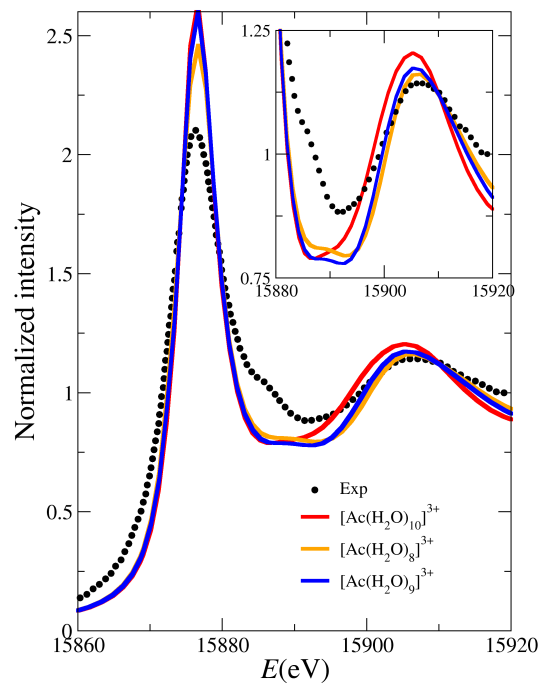


Figure S9: Comparison of the experimental XANES spectra of the Ac^{3+} aqueous solution obtained by Ferrier et al. [7] with the computed spectra obtained from three Ac^{3+} hydrates including one hydration shell.

```
EDGE L3
S02 1.0
CONTROL 1 0 0 0 0 0
PRINT 0 0 0 3 0 0
COREHOLE RPA
EXAFS 16.0
CRITERIA 4.0 2.5
RPATH 6.0
NLEG 4
TDLDA 1
SCP 6.0
EXCHANGE 0 1.5 0.
POTENTIALS
0 89 Ac 3 3
1 8 O 3 3
2 1 H 2 2
ATOMS
```

Figure S10: FEFF input files for computation of simulated EXAFS spectrum

```

CONTROL 1 0 0 0 0 0
PRINT 2 2 0 0 0 0

XANES
FMS 6.0 1
AFOLP
OPCONS
MPSE 2

COREHOLE RPA

TDLDA 1
SCF 6.0 0

EXCHANGE 0 0.0 -1.5 2
POTENTIAL
      0      89   Ac    3    3
      1       8    O    3    3
      2       1    H    2    2

ATOMS

```

Figure S11: FEFF input files for computation of simulated XANES spectrum

References

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