

Electronic Supplementary Information (ESI) for

The hydration of the heavy-alkalines Rb^+ and Cs^+ through Molecular Dynamics and EXAFS Spectroscopy: surface clusters and eccentricity

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Intermolecular ion-water potential and MCDHO2 water potential

The monoatomic cation, M(I), (M being Rb or Cs) is described by a positive charge, $Z_M = 3$, and a mobile negative charge density, ρ_M with a total charge, $q_M = -2$, joined to the nucleus by a spring of force constant, k_M (see Figure S1). The intra-atomic energy is defined by:

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

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 $U_{intra} = 0$.

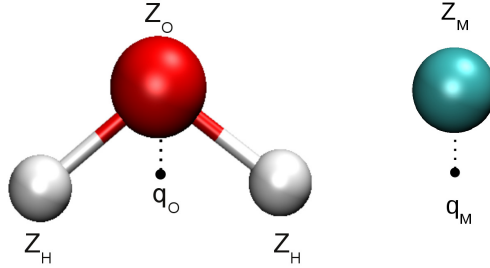


Figure S1: Schematic representation of MCDHO model for the water molecule and the metal cation.

The incorporation of the MCDHO2 model to the new potential needs the consideration of the following intermolecular terms for the M(I)-H₂O interaction:

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

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

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 ($i \equiv O, H$), is given by a two-exponential function as well:

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

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 :

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

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 MCDHO2 paper (Villa, A.; Hess, B.; Saint-Martin, H. J. Phys. Chem. B **2009**, *113*, 7270-7281).

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

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

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:

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

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

The MCDHO2 water molecules are described by a positive charge in the hydrogens $Z_H = 0.62$ and in the oxygen $Z_O = 2.00$ and with a negative charge in the mobile charge density $q_M = -3.92$ joined to the oxygen by a spring of force constant, k (see Figure S1):

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

The charge density is modelled by λ :

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

being the charge:

$$q = 4\pi \int_0^\infty \rho(r) r^2 dr \quad (9)$$

The interatomic distance is modelled by a Morse potential:

$$U_{d_{\text{OH}}} = D_{\text{OH}} \left(e^{-2\gamma(R_{\beta}-r_e)} - 2e^{-\gamma(R_{\beta}-r_e)} \right) \quad (10)$$

The internal angle is defined by a quartic potential:

$$U_{\Theta_{\text{HOH}}} = a_1(\Theta - \Theta_e) + a_2(\Theta - \Theta_e)^2 + a_3(\Theta - \Theta_e)^3 + a_4(\Theta - \Theta_e)^4 \quad (11)$$

Being the internal energy of a water molecule:

$$U_{\text{internal}} = \frac{1}{2}kr_{\text{O}}^2 + \frac{Z_{\text{H}}^2}{R_{1,2}} + \frac{qZ_{\text{H}}}{r_{\beta}} \left[1 - \left(\frac{r_{\beta}}{\lambda} + 1 \right) e^{-2r_{\beta}/\lambda} \right] + U_k + U_{d_{\text{OH}}} + U_{\Theta_{\text{HOH}}} \quad (12)$$

The energy of a cluster of N water molecules is defined by a Lennard-Jones potential for the interactions between oxygens, between hydrogens and between oxygen and hydrogen.

$$U_{\text{total}} = \sum_{n=1}^N \sum_{m=1}^{n-1} \left(\frac{A}{r_{nm}} \right)^{12} - \left(\frac{B}{r_{nm}} \right)^6 + \frac{q^2}{r_{nm}} + \frac{qZ_{\beta}}{r_{n\beta}} \left[1 - \left(\frac{r_{n\beta}}{\lambda} + 1 \right) e^{-2r_{n\beta}/\lambda} \right] \\ + \sum_{\beta \in m}^q \left(\frac{A_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left(\frac{B_{\alpha\beta}}{r_{\beta\alpha}} \right)^6 + \frac{Z_{\alpha\beta}}{r_{\alpha\beta}} \quad (13)$$

Table S1: Fitted parameters of the $\text{M}^+\text{-H}_2\text{O}$ potentials (in a.u.).

	Rb	Cs
k_{M}	0.217025	0.364708
λ'_{M}	0.621742	0.995166
A_{MO}	539.102465	449.494649
α_{MO}	1.357374	1.413723
B_{MO}	-383.448443	-362.094604
β_{MO}	1.293485	1.371814
C_{MH}	1857.808870	1776.523448
γ_{MH}	0.857618	0.834310
D_{MH}	-1859.064561	-1776.616635
δ_{MH}	0.857790	0.834339

Table S2: Parameters of the MCDHO2 water potential (in a.u)

Z_H	0.62
Z_O	2.0
q	-3.24
k	1.00
λ	1.90
D_{OH}	0.42954902
r_e	1.3440633
γ	1.1131102
θ_e	1.927
a_1	0.031621
a_2	0.043914
a_3	-0.012721
a_4	-0.00866
A_{OM}	3.228656
B_{OM}	1.962046
A_{OH}	2.037891
A_{HH}	0

Details of MD simulations

- 1 cation + 1000 water molecules.
- Cubic 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 (P.J.Mitchell and D. Fincham, *J. Phys. Condens. Matter* **1993**, 5, 1031-1038) to account for the polarizable MCDHO2 model.
- A modified version of the DL-POLY Classic code (W. Smith, T.R. Forester and I.T. Todorov, DL-POLY v. 2.19; STFC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, Cheshire, UK 2012).
- 1ns production time.

Quantum Mechanical Potential Energy Surface

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

Octahydrates



Nonahydrates

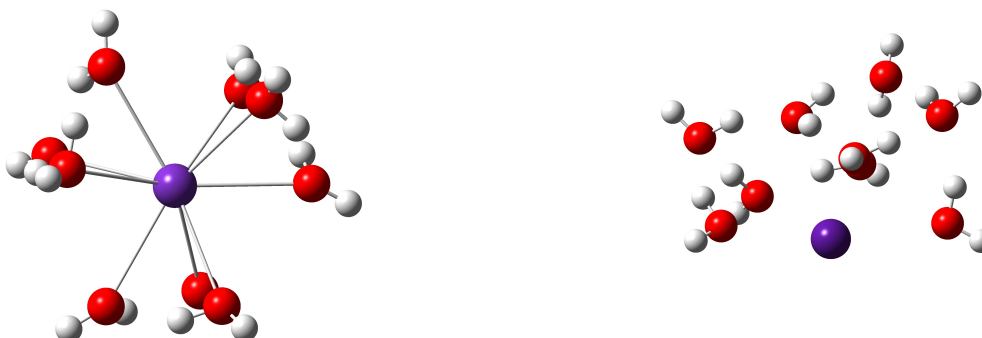


Figure S2: Quantum-mechanical optimized structures for $[\text{Rb}(\text{H}_2\text{O})_n]^+$

Table S3: Quantum mechanical methods^a

M(I)	DFT	Pseudopotential ^b
Rb	M062x	ECP28MBW
Cs	M062x	ECP46MBW

^(a) Basis sets from:

M. Dolg et al. *Theor.Chem.Acc.* **1989**, *75*, 173-194; **1993**, *85*, 441-450

J. Yang et al. *Theor.Chem.Acc.* **2005**, *113*, 212-224.

^(b) Pseudopotentials taken from <http://www.theochem.uni-stuttgart.de>

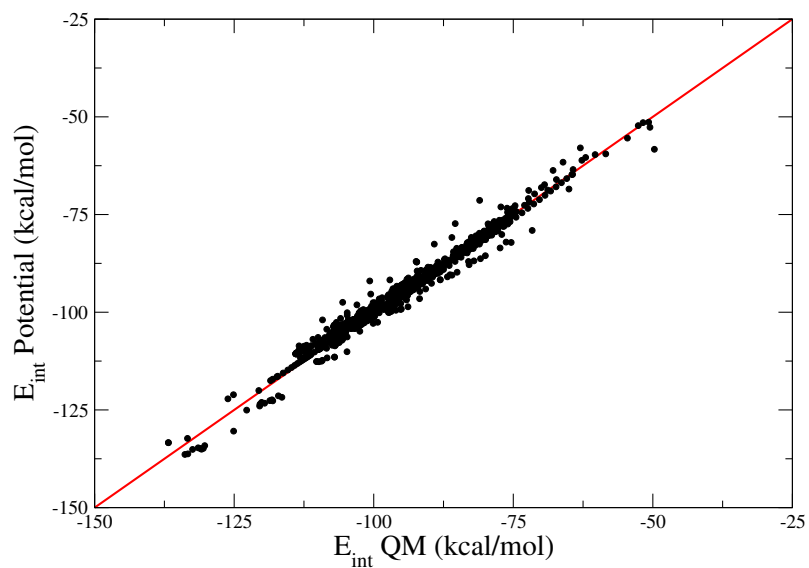


Figure S3: Fitting of the exchangeable HI Rb⁺-H₂O interaction potential to the set of QM structures.

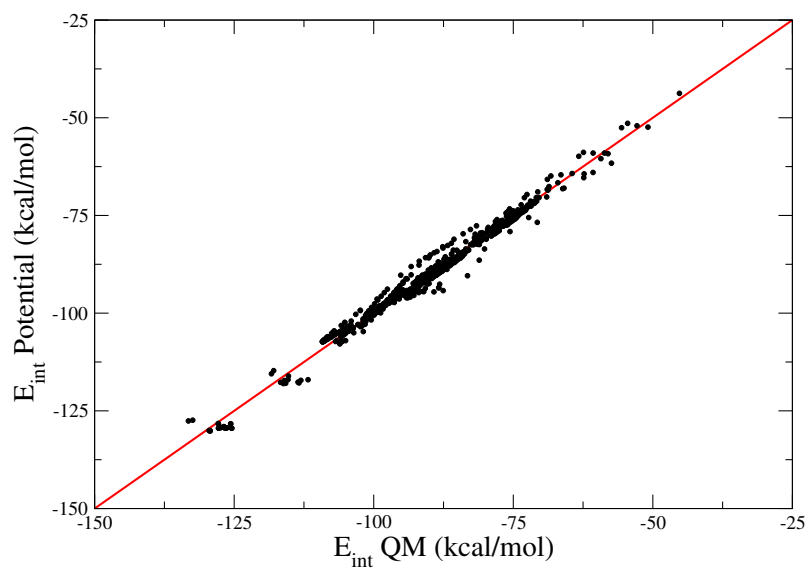


Figure S4: Fitting of the exchangeable HI Cs⁺-H₂O interaction potential to the set of QM structures.

Example of EXAFS inputs used in the FEFF simulation

```
TITLE_Rb_structure_snapshot_NVT

EDGE K
S02 1.0

CONTROL 1 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

RPATH 6.0
TDLDA 1
SCF 6.0
EXCHANGE 0 -5.0 0.
POTENTIALS
  0 37 Rb 3 3
  1 8 0 3 3
  2 1 H 2 2

ATOMS
  0.0000000 0.0000000 0.0000000 0 Rb 0.0000000
  2.5040010 -1.0831000 -0.4564000 1 O 2.7661214
  2.6410000 -1.8961000 -0.9654000 2 H 3.3914707
  3.2770000 -1.2231000 0.1245000 2 H 3.5000290
 -1.4640000 -0.1747000 -2.4274000 1 O 2.8400857
  .
  .
END
```

Figure S5: Part I of the input used on the EXAFS simulation

```
TITLE_Rb_structure_snapshot_NVT

EDGE K
S02 1.0

CONTROL 0 1 1 1 1 1
PRINT 0 0 0 3 0 0

COREHOLE RPA
EXAFS 16.0
CRITERIA 4.0 2.5
RPATH 6.0
NLEG 4

RPATH 6.0
TDLDA 1
SCF 6.0
EXCHANGE 0 -5.0 0.
POTENTIALS
  0 37 Rb 3 3
  1 8 0 3 3

ATOMS
  0.0000000 0.0000000 0.0000000 0 Rb 0.0000000
  2.5040010 -1.0831000 -0.4564000 1 O 2.7661214
 -1.4640000 -0.1747000 -2.4274000 1 O 2.8400857
  .
  .
END
```

Figure S6: Part II of the input used on the EXAFS simulation

For the EXAFS simulation of the K-edge of Rubidium $\Delta E_0 = -5.0$ eV whereas for the L3-edge of Cesium $\Delta E_0 = -2.0$ eV.

Example of XANES inputs used in the FEFF simulation

```
TITLE_Rb_structure_snapshot_NVT
EDGE K
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 -2.0 2
POTENTIAL
  0 37 Rb 3 3
  1 8 0 3 3
  2 1 H 2 2

ATOMS
0.0000000 0.0000000 0.0000000 0 Rb 0.0000000
2.5040010 -1.0831000 -0.4564000 1 O 2.7661214
2.6410000 -1.8961000 -0.9654000 2 H 3.3914707
3.2770000 -1.2231000 0.1245000 2 H 3.5000290
-1.4640000 -0.1747000 -2.4274000 1 O 2.8400857
.
.
END
```

Figure S7: Part I of the input used on the XANES simulation

```
TITLE_Rb_structure_snapshot_NVT
EDGE K
CONTROL 0 1 1 1 1 1
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 -2.0 2

POTENTIALS
  0 37 Rb 3 3
  1 8 0 3 3

ATOMS
0.0000000 0.0000000 0.0000000 0 Rb 0.0000000
2.5040010 -1.0831000 -0.4564000 1 O 2.7661214
-1.4640000 -0.1747000 -2.4274000 1 O 2.8400857
.
.
END
```

Figure S8: Part II of the input used on the XANES simulation

The XANES simulation of the K-edge of Rubidium uses a broadening of -2.0 eV whereas the simulation of the L3-edge of Cesium uses a broadening of 0.9 eV.

Equation and parameters of Ohta's equation for multi-electron excitation removing from EXAFS spectrum.

The damped sine equation of Ohta et. al :

$$f_{\chi}(k) = (Ak^2 + B)\exp(-Ck^2)\sin(Dk^2 + Ek + F) + G + Hk \quad (14)$$

Table S4: Damped sine coefficients

Coefficient	Rb ⁺	Cs ⁺
A	0.194812	0.202138
B	0.281428	0.103479
C	0.0661385	0.0804508
D	0.100565	-0.00237742
E	3.4741	4.82325
F	2.24634	-3.3454
G	0.05852	-0.000956909
H	-0.0243885	0.000416375

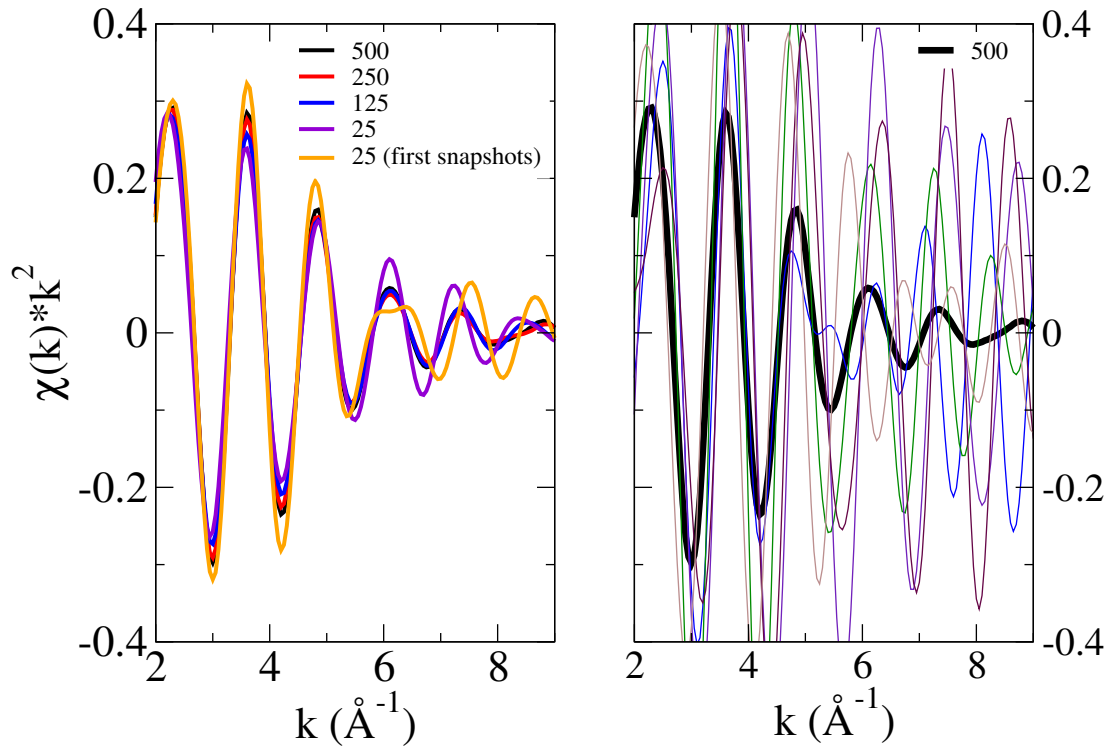


Figure S9: Left: Simulated EXAFS spectrum of Cs⁺ obtained with a different number of snapshots evenly taken from trajectory, (500, 250, 125 and 25), and spectrum derived from the average of the first 25 snapshots of the trajectory. Right: Comparison of the average EXAFS spectrum with five different spectra derived from different snapshots.

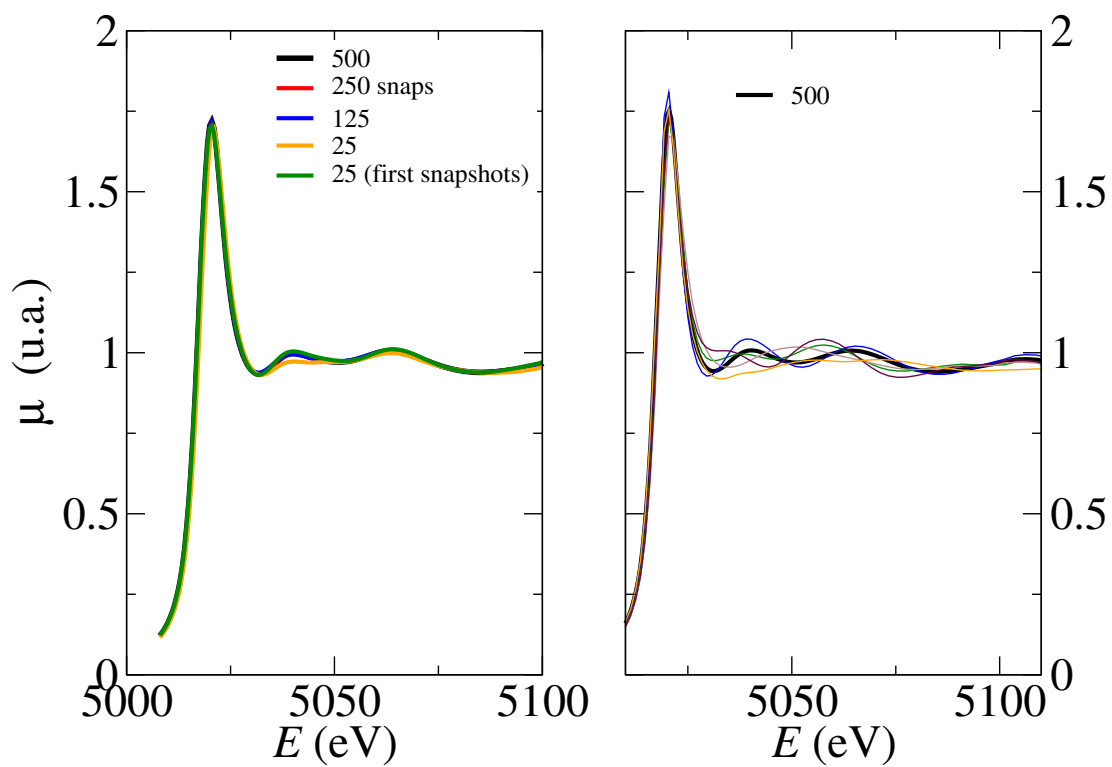


Figure S10: Left: Simulated XANES spectrum of Cs^+ obtained with a different number of snapshots evenly taken from trajectory, (500, 250, 125 and 25), and spectrum derived from the average of the first 25 snapshots of the trajectory. Right: Comparison of the average XANES spectrum with five different spectra derived from different snapshots.