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

ab initio molecular dynamics studies of hydroxide coordination of alkaline earth metals and uranyl

Olivia Lynes[1], Jonathan Austin[2] and Andy Kerridge[1]*

[1] Department of Chemistry, Faraday Building, Lancaster University, Lancaster, LA1 4YB, UK

[2] National Nuclear Laboratory Limited, 5th Floor, Chadwick House, Birchwood Park, Warrington, WA3 6AE, UK

Electronic Supplementary Information

Determining simulation conditions

Simulation Temperature of 400 K

Initial simulations were carried out on a simulation cell containing 64 water molecules. Firstly, the simulation temperature was considered, with the motivation lying in the well-established fact that pure GGA functionals have a tendency to overbind in water simulations[141–143]. This overbinding manifests itself in an elevated melting temperature in AIMD simulations[144,145], leading to previous studies[41,143,146,147] selecting a simulation temperature of 400 K in order to ensure a liquid phase. Figure S1 presents O—H, O—O and H—H RDFs obtained from 300 and 400 K simulations and compares to experimental data. For each RDF clearly improved agreement with experimental data can be seen for the higher temperature simulations, particularly when considering the second and third peaks in the O-H and O-O RDFs. There is still significant deviation from the experimental data which might perhaps be improved with further optimisation of the simulation temperature but a value of 400 K is retained throughout the remainder of this contribution in order to ease comparison with literature data. It should be noted the data presented in Figure S1 incorporates Grimme's D2 dispersion correction.[130] This was included to better represent bonding interactions and again leads to improved agreement with experimental data at 400K, as shown in Figure S2, at extremely modest computational cost.

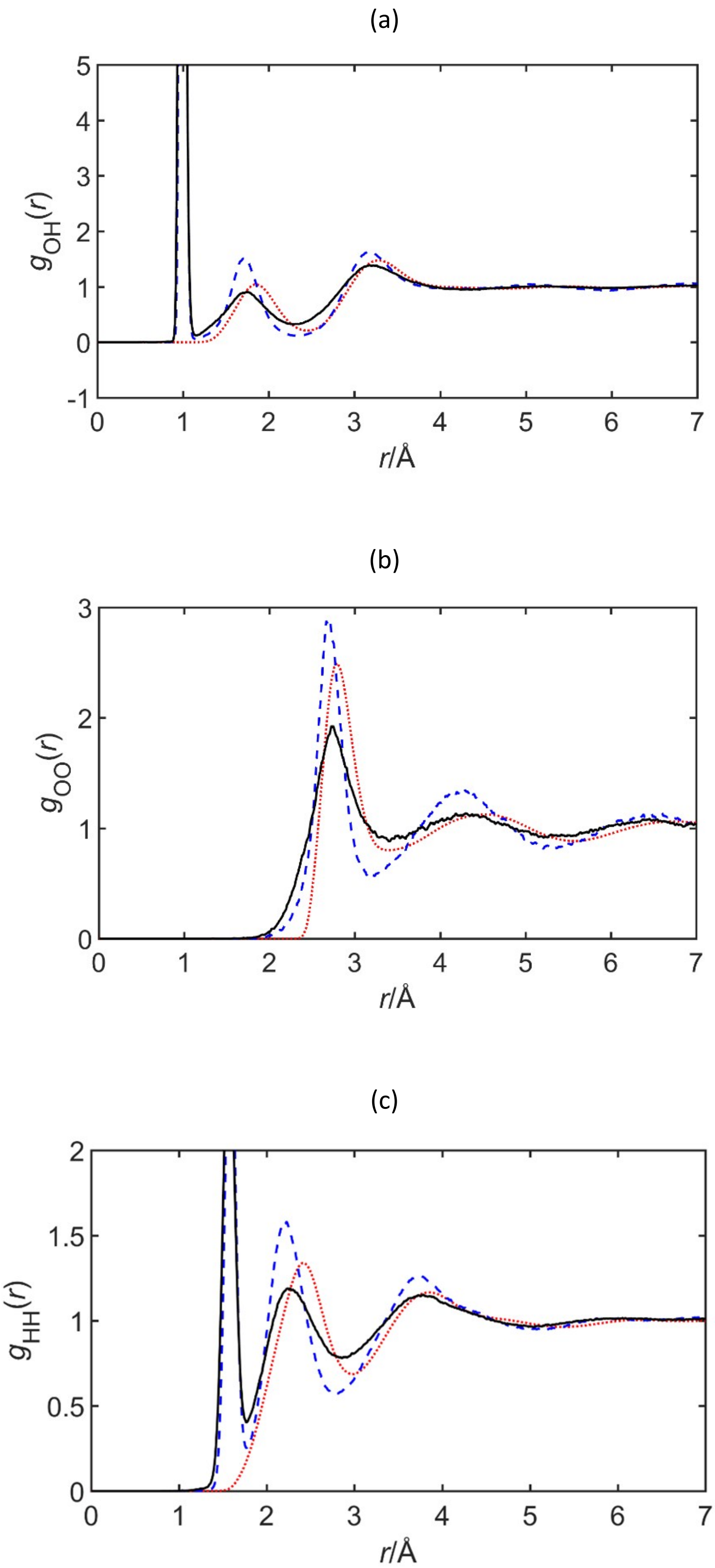


Figure S1. (a) O—H, (b) O—O and (c) H—H radial distribution functions, *g*(*r*), generated using simulation temperatures of 300 K (dashed blue) and 400 K (solid black), compared to experimental data from reference [148] (dotted red)

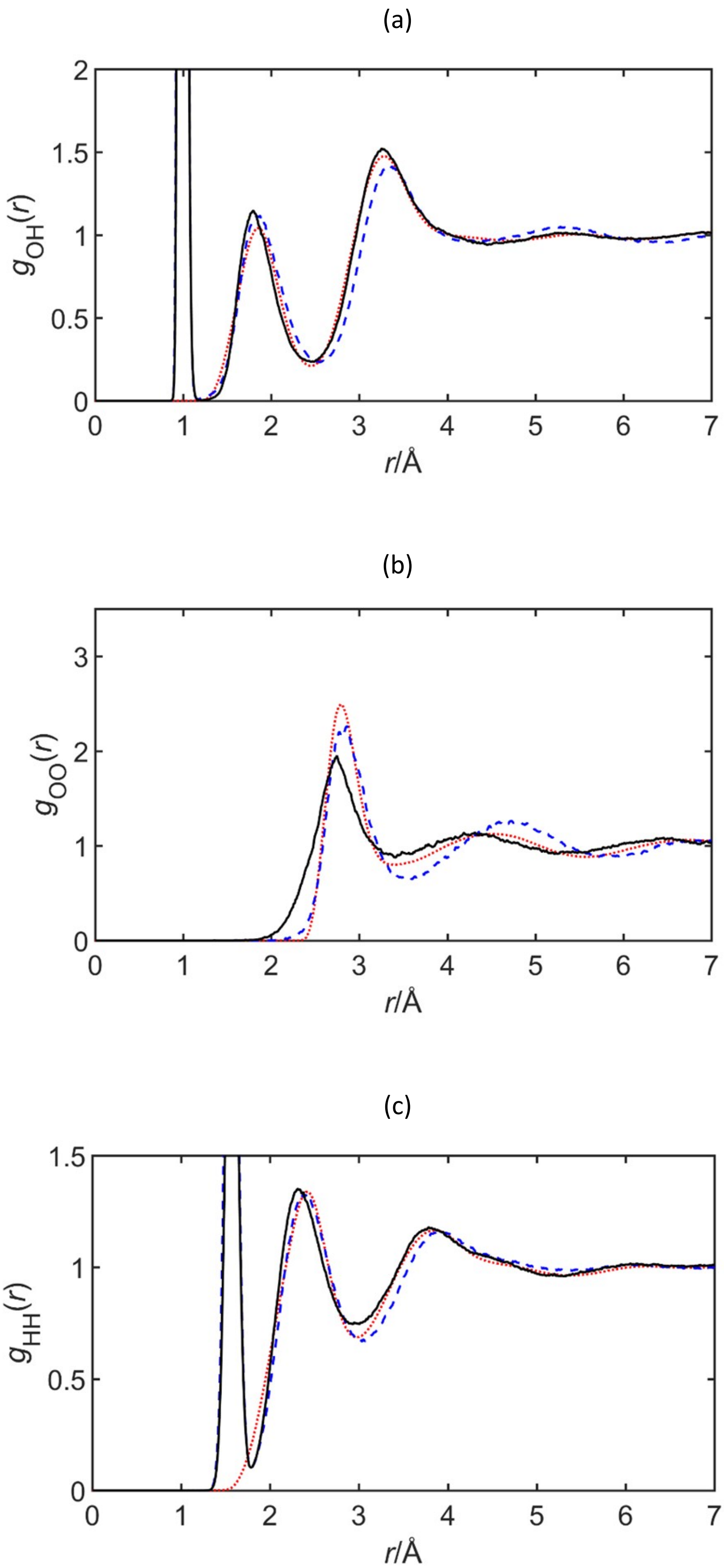


Figure S2. (a) O—H, (b) O—O and (c) H—H radial distribution functions, calculated at 400 K with (solid black) and without (dashed blue) Grimme's D2 dispersion correction, and compared to experimental data from reference [148] (dotted red).

Choice of Ensemble

Our attention then turned to simulation of the Sr^{2+} ion solvated by 64 molecules and the effect of allowing the volume of the simulation box to be varied was considered. Figure S3 compares a trajectory generated using the NVT ensemble and a fixed simulation cell to one generated using the NPT_I ensemble and a flexible simulation cell. The first peak of the Sr—O RDF occurs at 2.60 Å and 2.63 Å, for the NVT and NPT_I simulations, respectively. Literature values for this peak range between 2.52 and 2.67 Å (see Table 1). While the differences were small, the improved agreement with literature values obtained from the NPT_I simulations led us to adopt this approach for the remainder of the study.

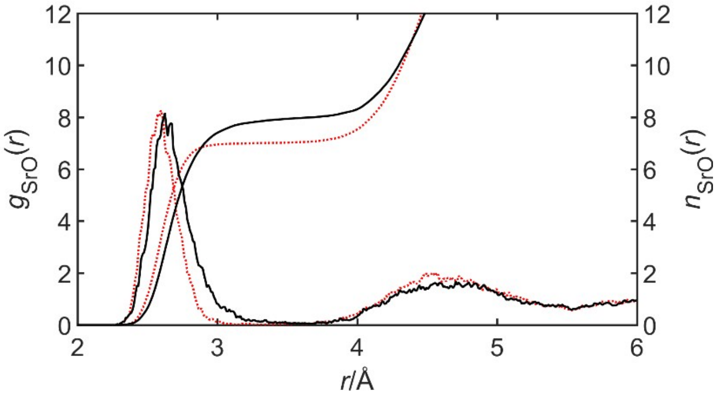


Figure S3. Sr—O radial distribution functions, $g(r)$, generated from trajectories in which the volume of the simulation cell was held fixed (NVT, dotted red) or allowed to vary (NPT_I, solid black).

Impact of 400 K on First Shell Bonding

To investigate the impact of a 400 K simulation temperature on calculated M—O bonds lengths, we considered the effect of temperature in our simulations of the Sr aquo complex, performing simulations at temperatures of 300 and 400 K. Analysing a single 15 ps trajectory at each temperature revealed RDF peaks at 2.65 and 2.62 Å at 300 and 400 K, respectively (see Figure S4), indicating that the elevated temperature had only a small effect on the calculated structural properties. The increase in Sr—O separation at 300K is presumably a reflection of the stronger H-bonding.

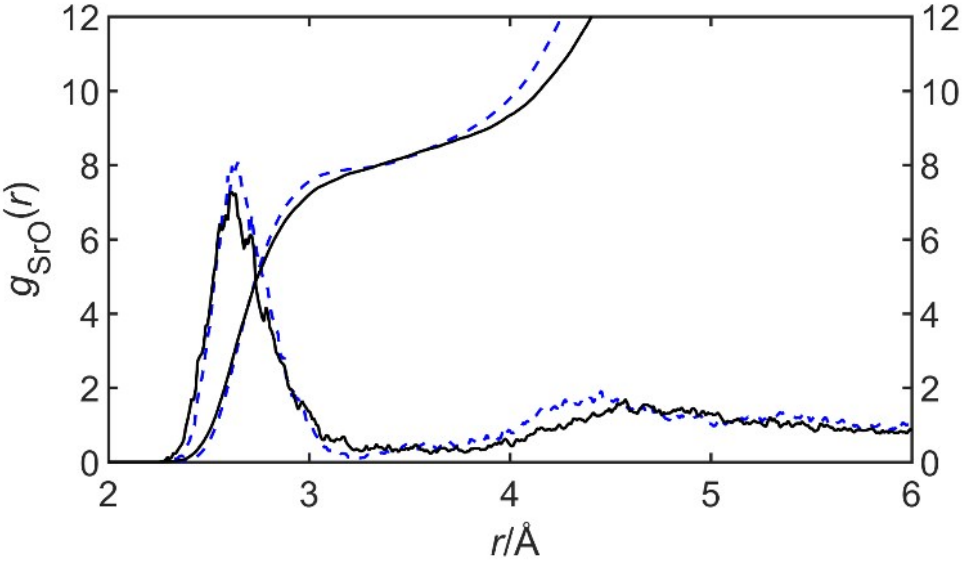


Figure S4. Sr—O RDFs for Sr^{2+} in a pure aqueous environment, calculated from 15ps simulations at 300K (dashed blue) and 400k (solid black).

RDFs for Aquo Alkaline Earth Metals.

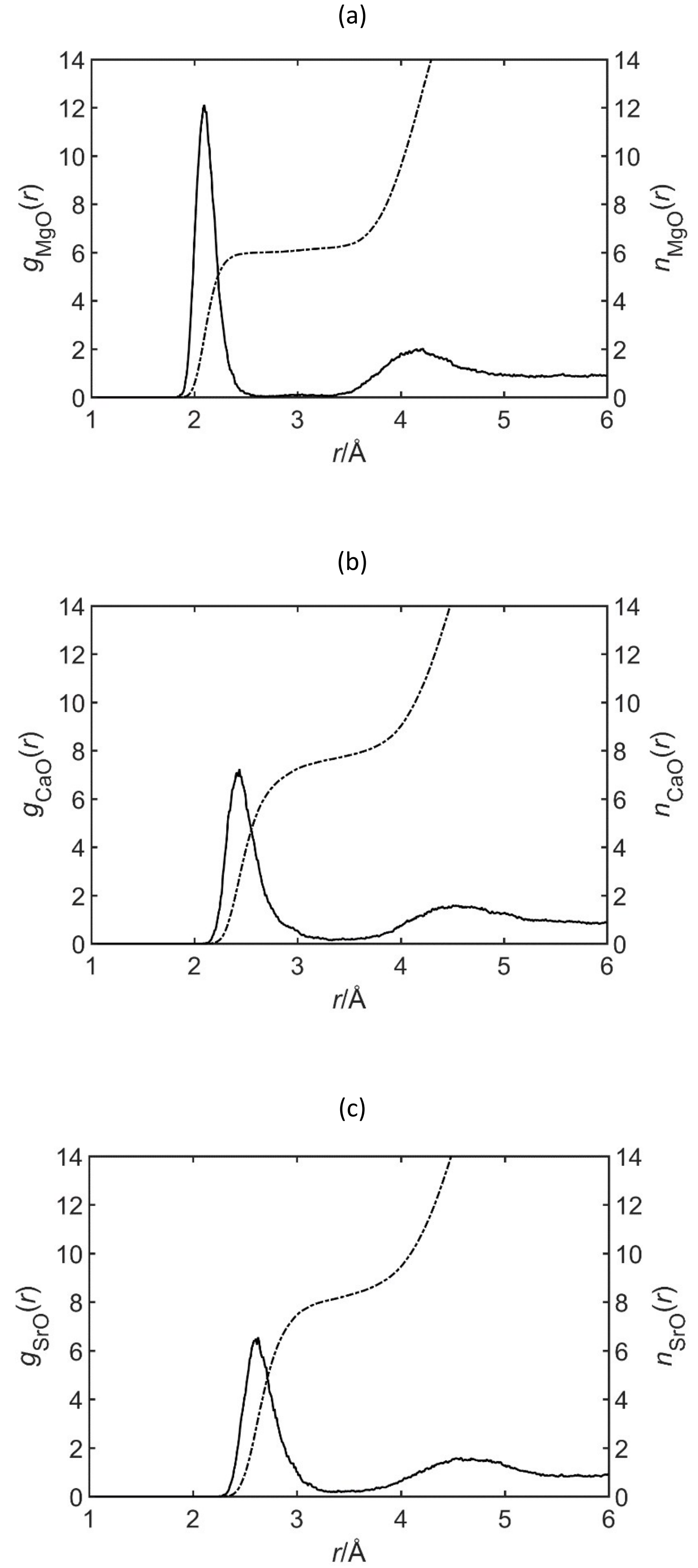
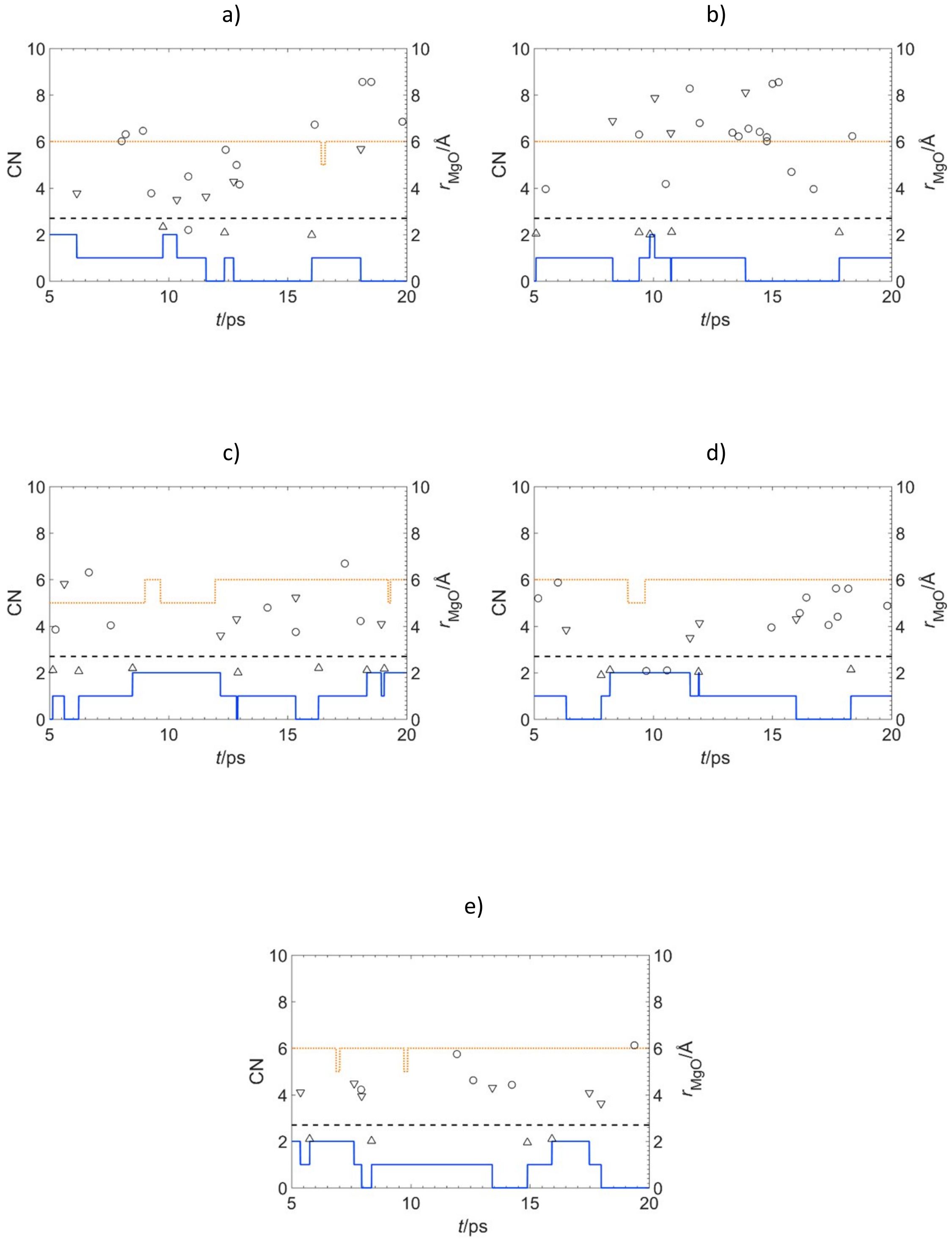


Figure S5: Calculated M—O RDFs for each alkaline earth ion in a pure aqueous environment, generated using a total of 75 ps of simulation time.



1. Magnesium dihydroxide trajectory analysis

Figure S6. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each magnesium dihydroxide

AIMD trajectory in which both hydroxides were initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 2.7 Å.

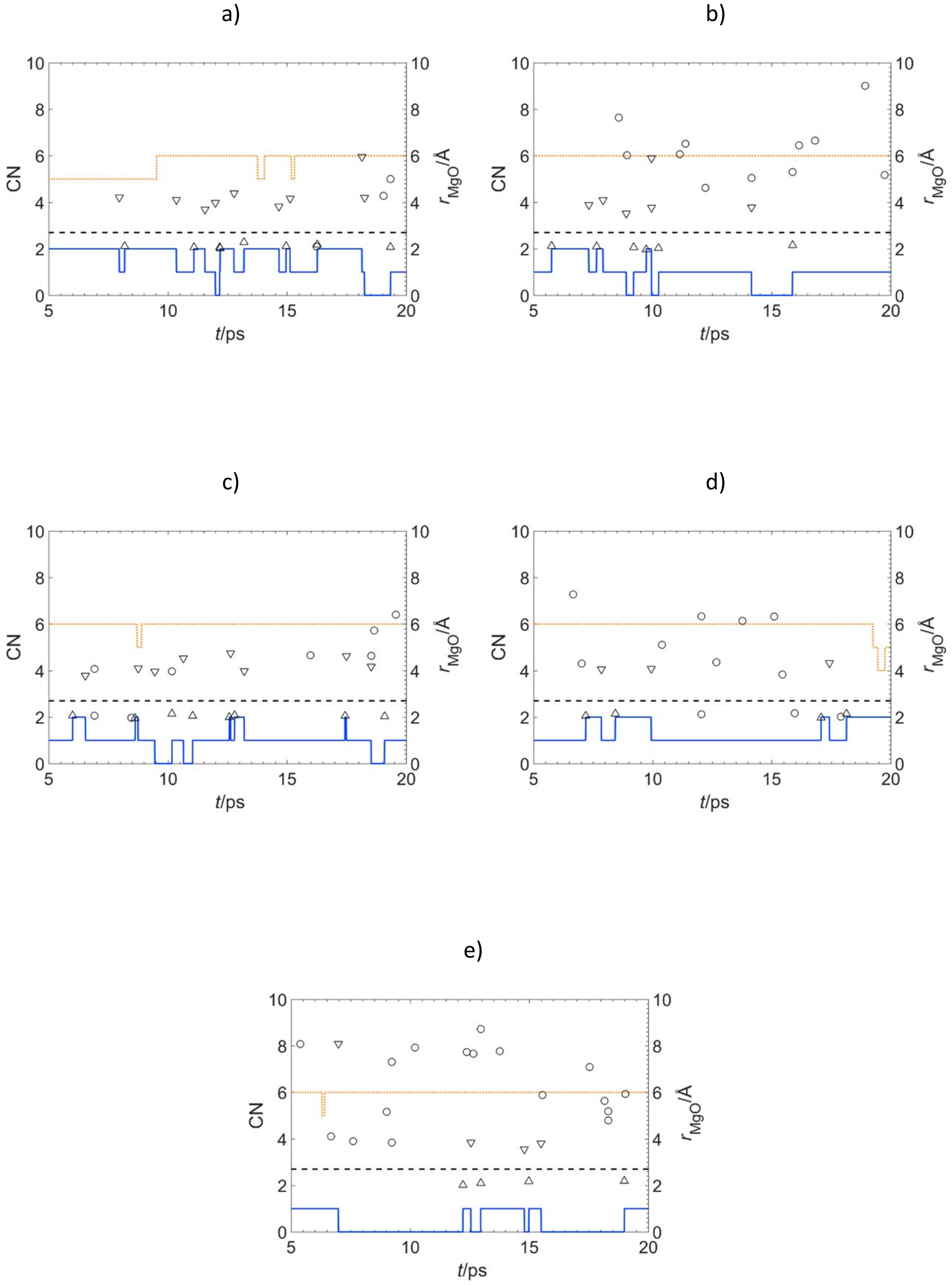


Figure S7. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each magnesium dihydroxide

AIMD trajectory in which neither hydroxide was initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 2.7 Å.

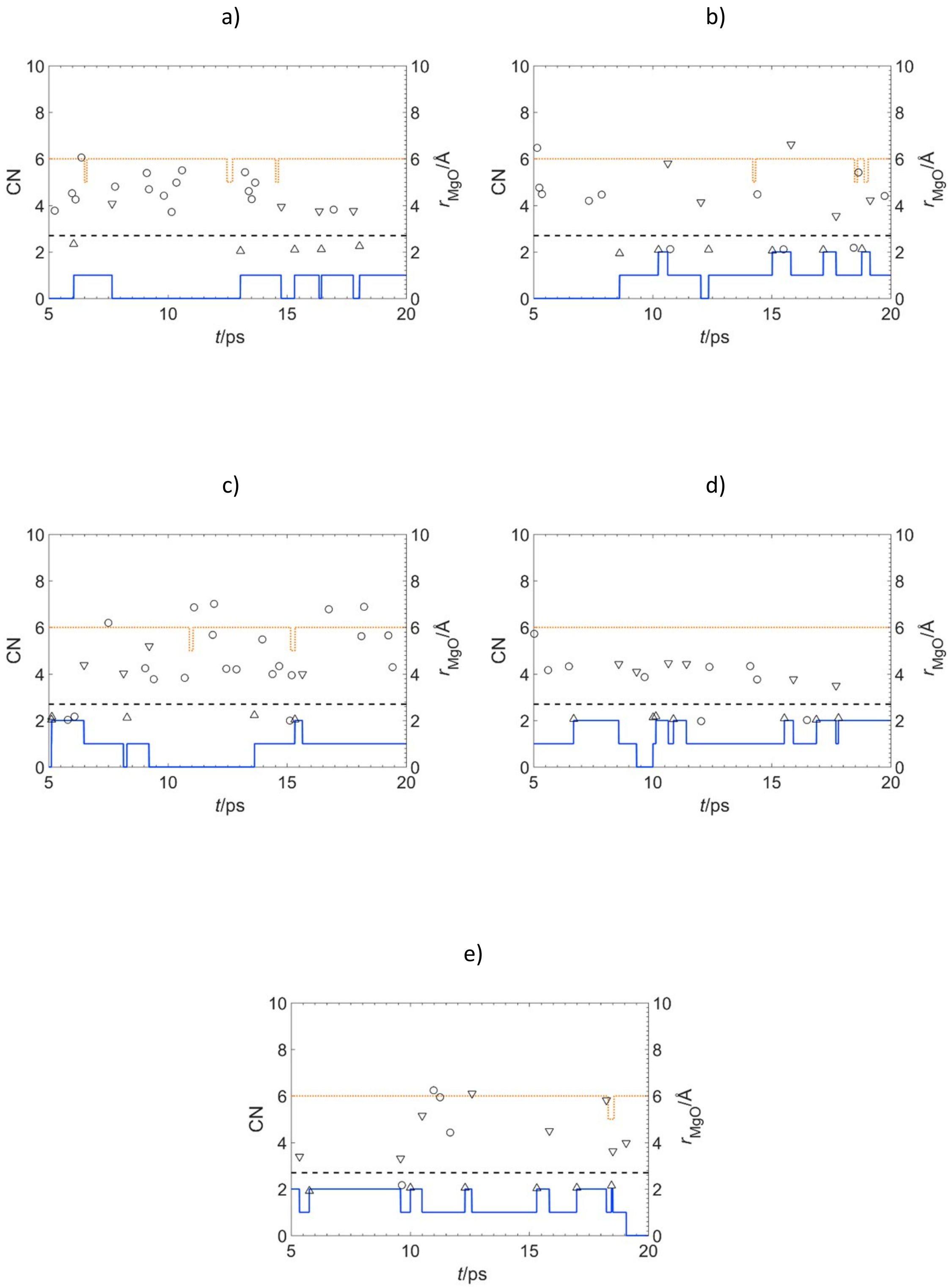
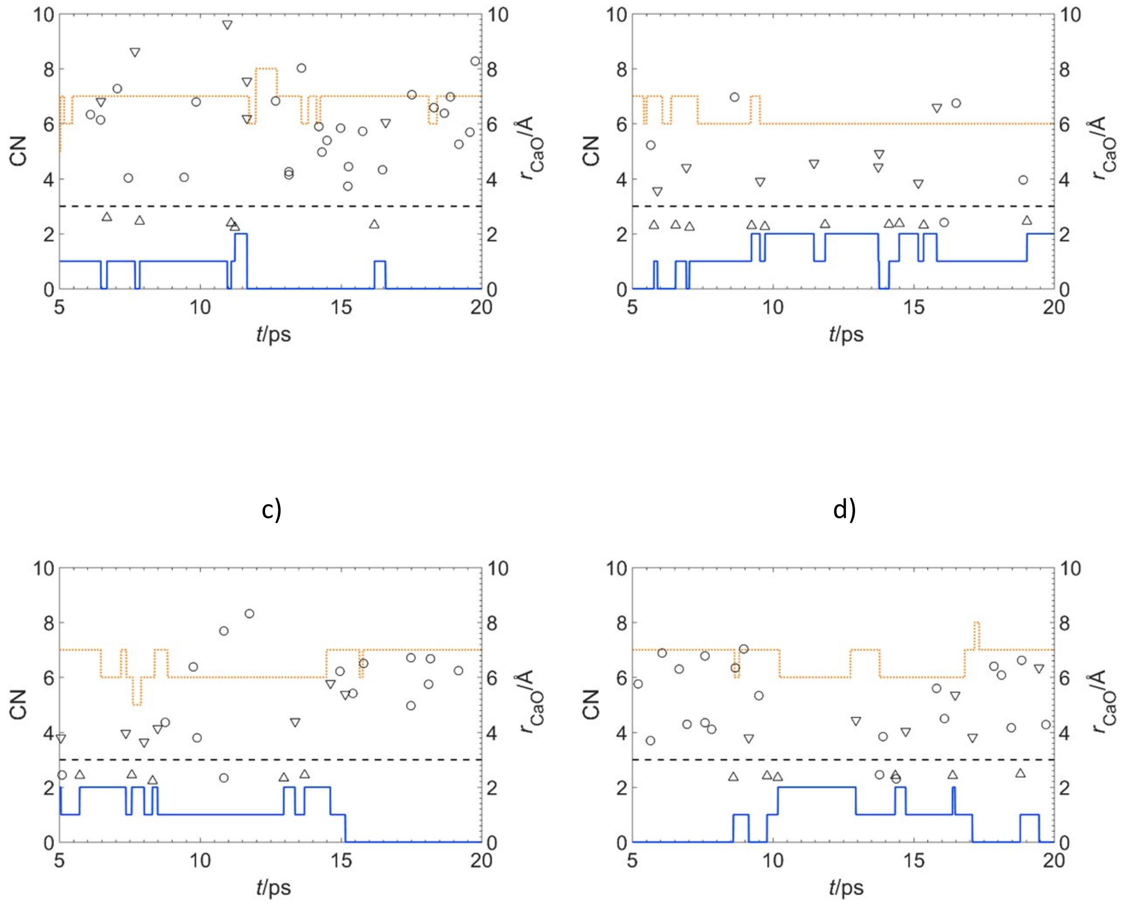

a)
b)
c)
d)
e)

Figure S8. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each magnesium dihydroxide AIMD trajectory in which one hydroxide was initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 2.7 Å.

2. Calcium dihydroxide trajectory analysis



a)

b)

c)

d)

e)

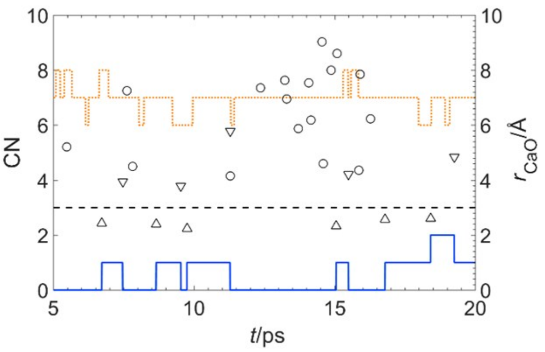
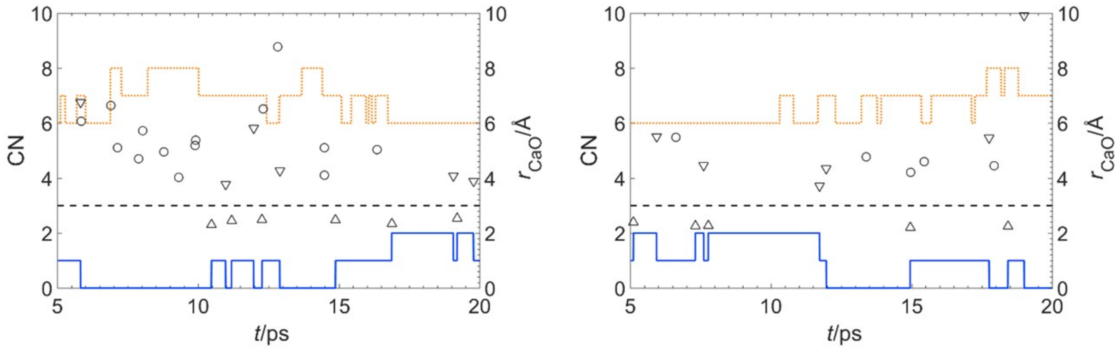
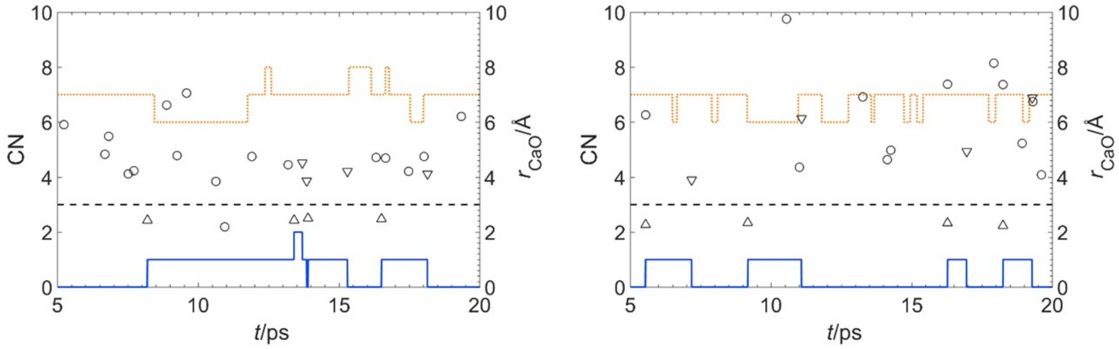


Figure S9. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each calcium dihydroxide AIMD trajectory in which both hydroxides were initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 3.0 Å.

a) b)



c) d)



e)

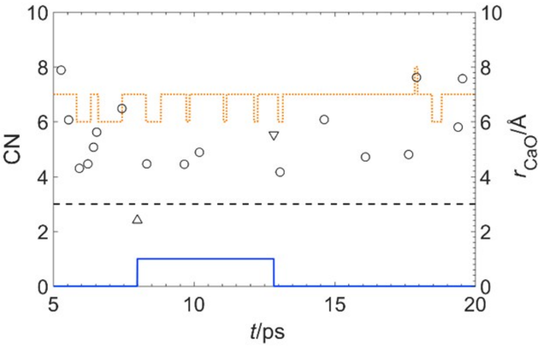
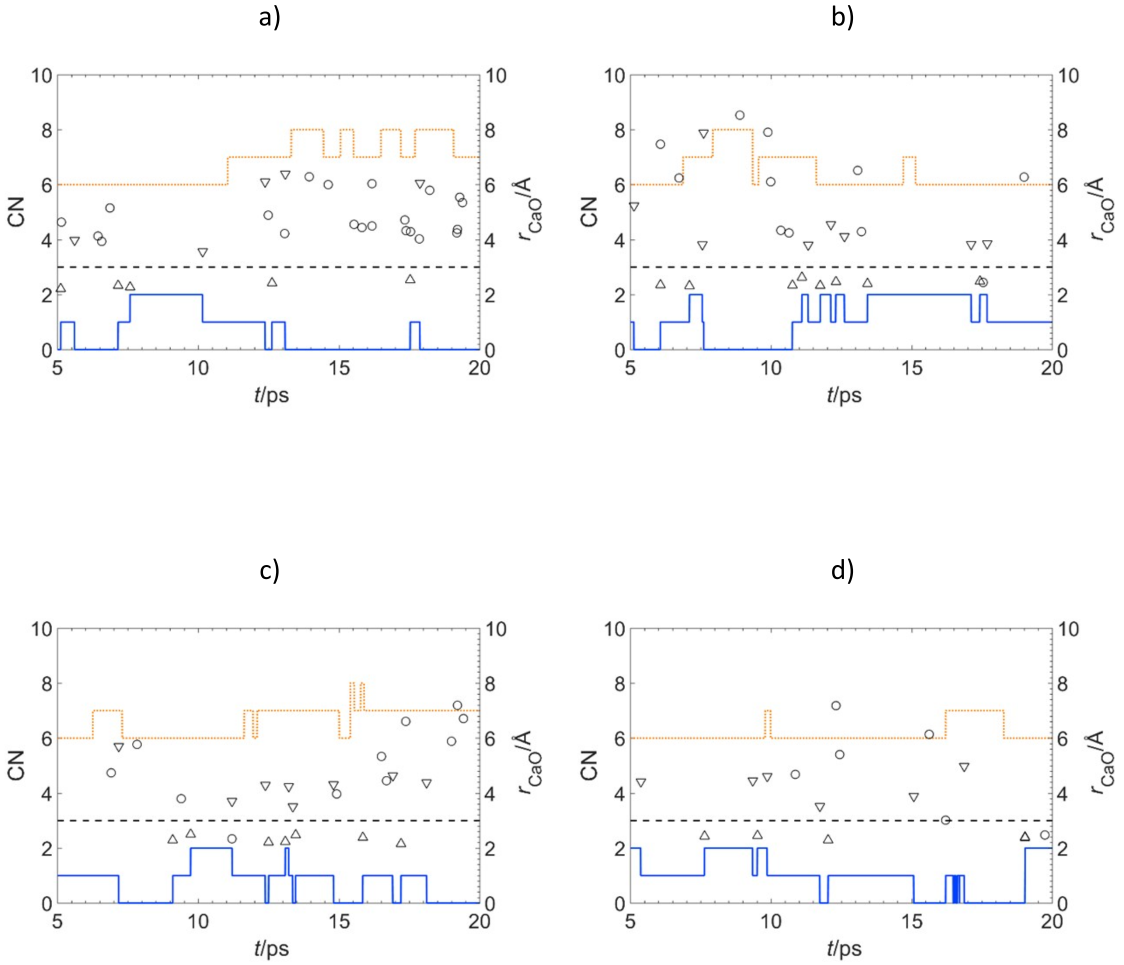


Figure S10. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each calcium dihydroxide AIMD trajectory in which neither hydroxide was initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 3.0 Å.



e)

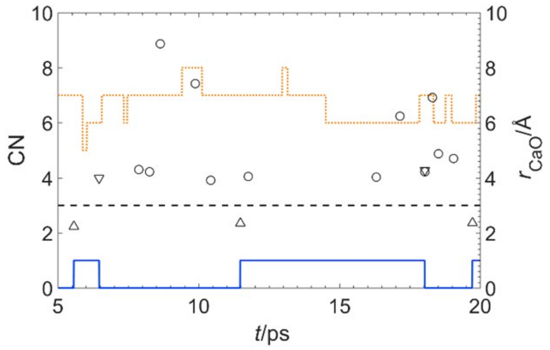
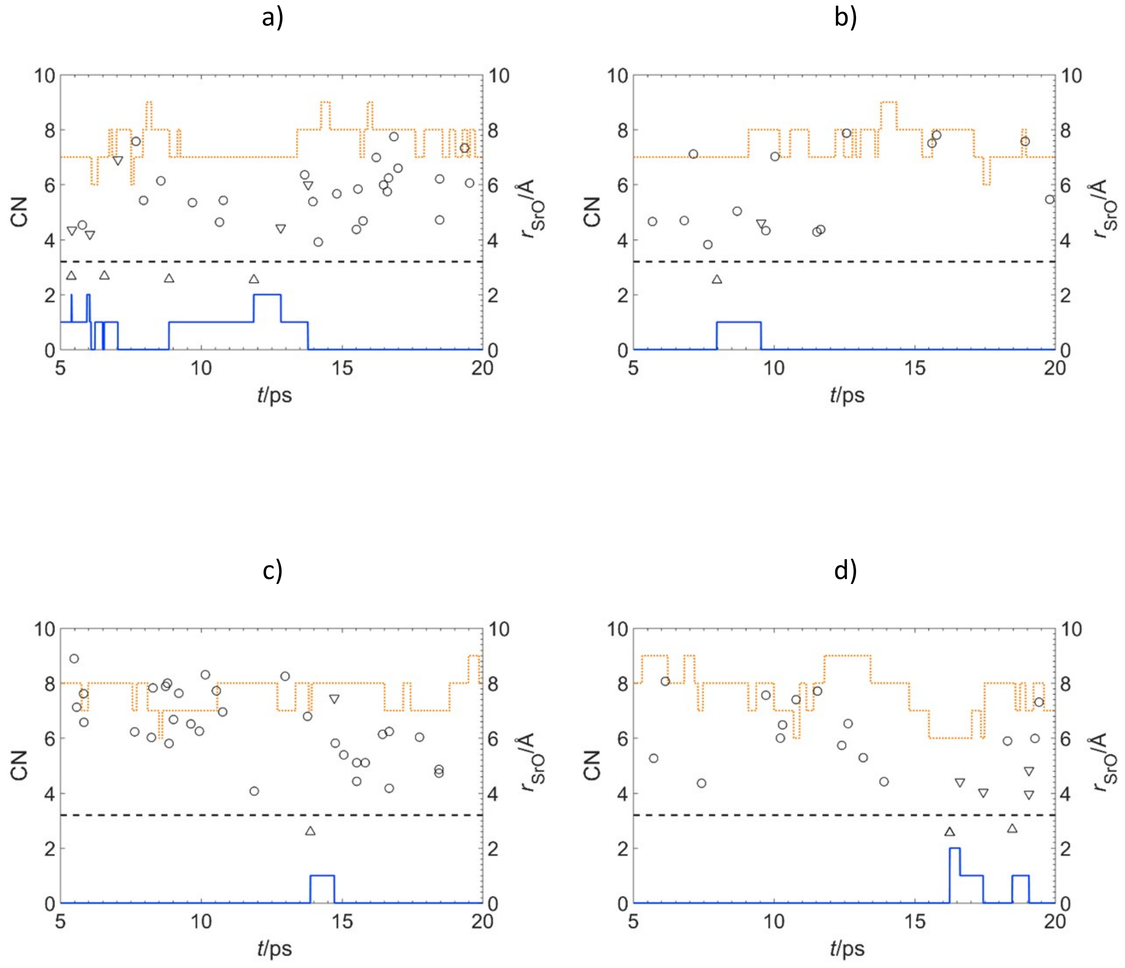


Figure S11. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each calcium dihydroxide AIMD trajectory in which one hydroxide was initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 3.0 Å.

3. Strontium dihydroxide trajectory analysis



e)

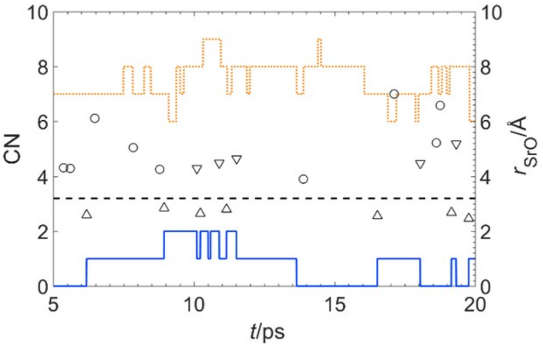
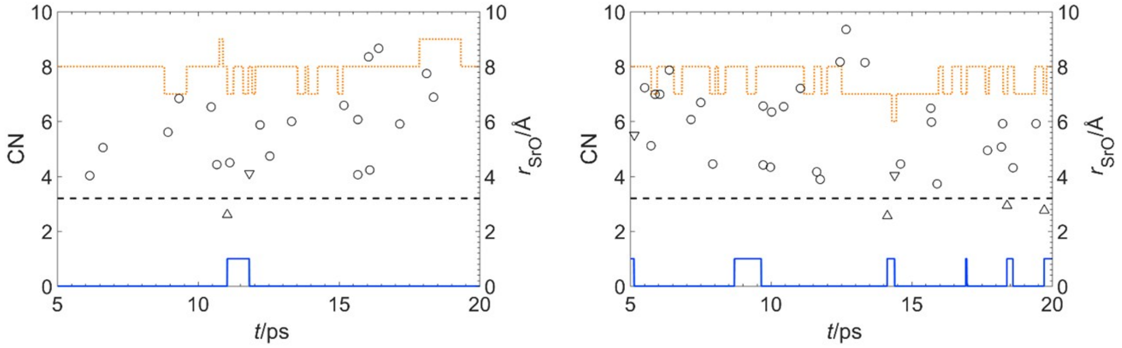
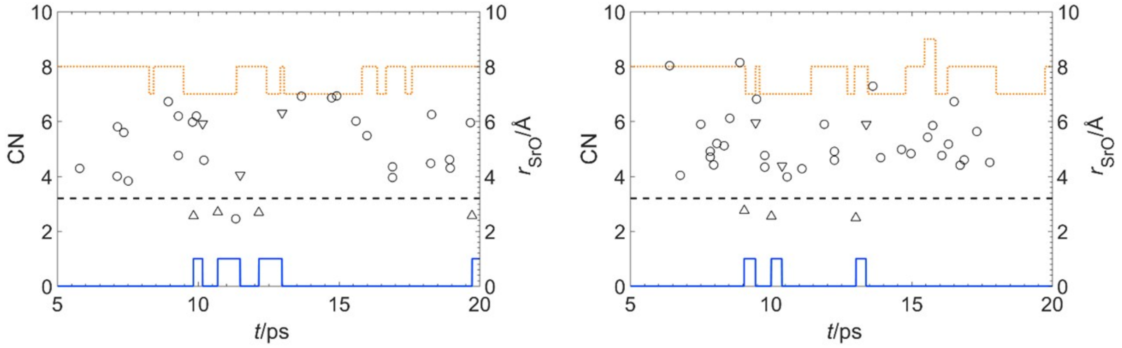


Figure S12. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each strontium dihydroxide AIMD trajectory in which both hydroxides were initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 3.2 Å.



a) b)



c) d)

e)

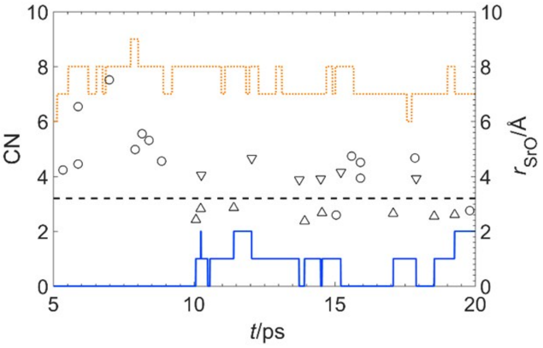
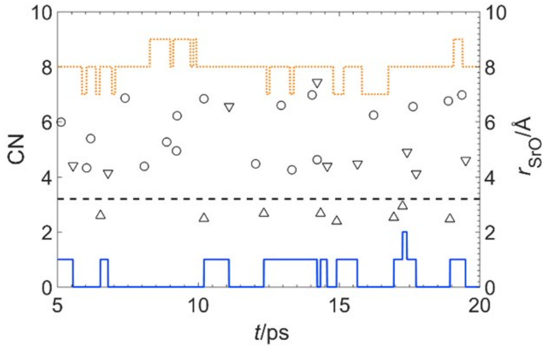
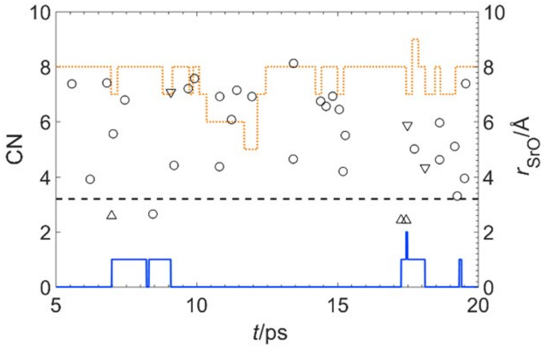


Figure S13. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each strontium dihydroxide AIMD trajectory in which neither hydroxide was initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 3.2 Å.

a)

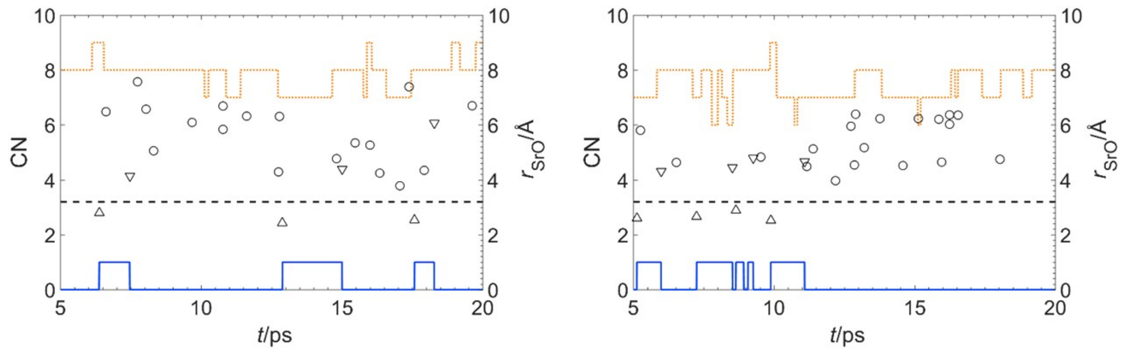


b)



c)

d)



e)

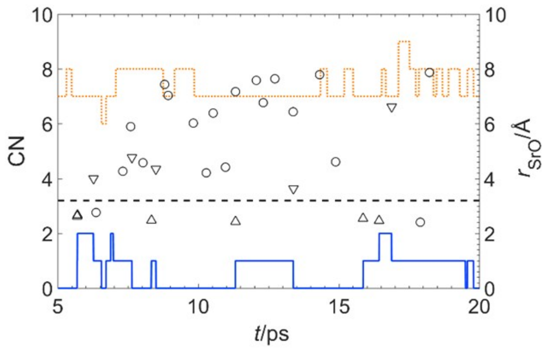
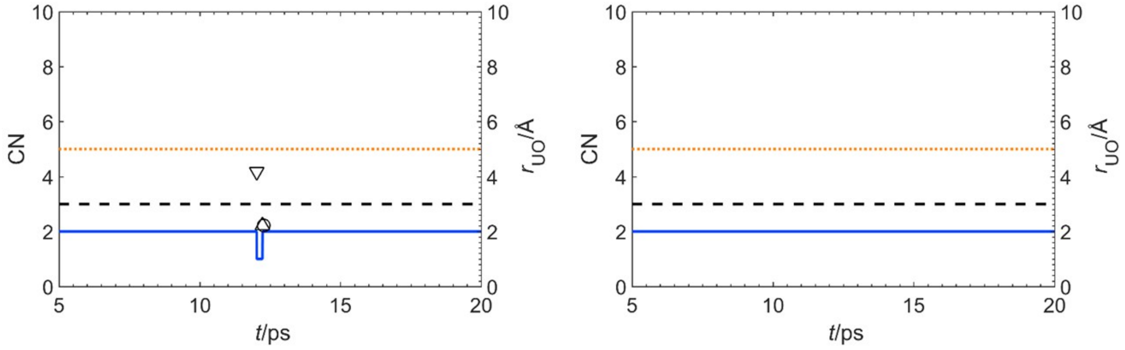
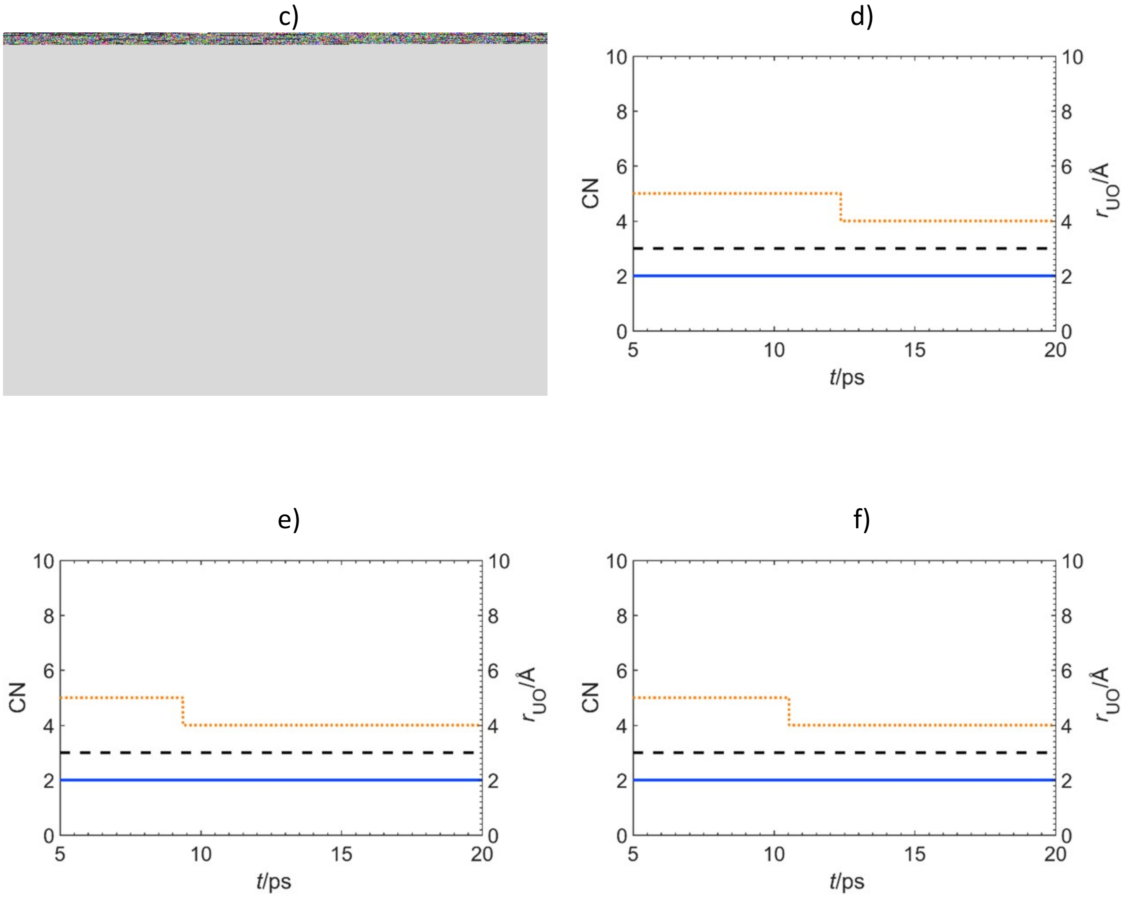


Figure S14. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each strontium dihydroxide AIMD trajectory in which one hydroxide was initially in the first solvation shell. The dashed black line indicates the first shell cutoff distance of 3.2 Å.

4. Uranyl dihydroxide trajectory analysis


a)

b)


c)

d)

e)

f)

Figure 15. Total (dotted orange) and hydroxide (solid blue) coordination number and proton transfer events (Δ: 1st shell → 2nd shell, ∇: 2nd shell → 1st shell, ○: intrashell) for each uranyl dihydroxide AIMD trajectory. The dashed black line indicates the first shell cutoff distance of 3.0 Å.