

Solvation Structure of Calcium and Magnesium Ions in Water with the Presence of Hydroxide: a Study by Deep Potential Molecular Dynamics

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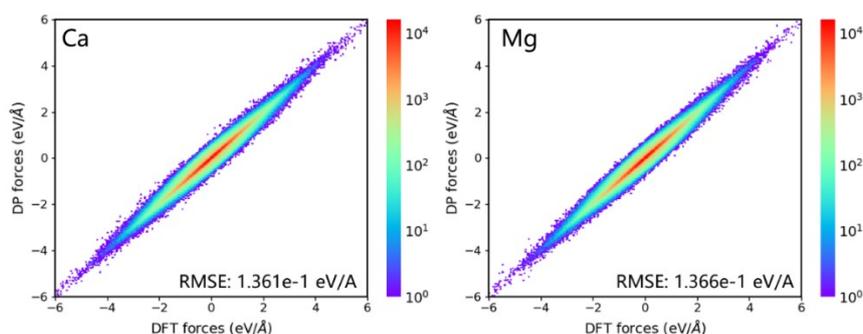


Figure S1. Correlation between atomic forces as predicted by the Deep Potential (DP) model and that calculated by Density Functional Theory (DFT) in the final training set. The color bar indicates the density of data.

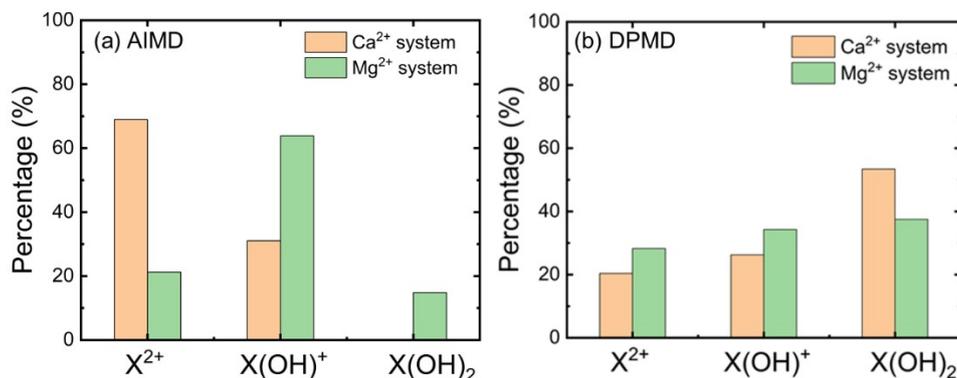


Figure S2. Relative concentrations of X²⁺, X(OH)⁺ and X(OH)₂ (X=Ca²⁺, Mg²⁺) from (a) *ab initio* molecular dynamics (AIMD) simulations and (b) DP molecular dynamics (DPMD) simulations. The different species have been defined by the number of OH⁻ ions in the first solvation shell of X²⁺.

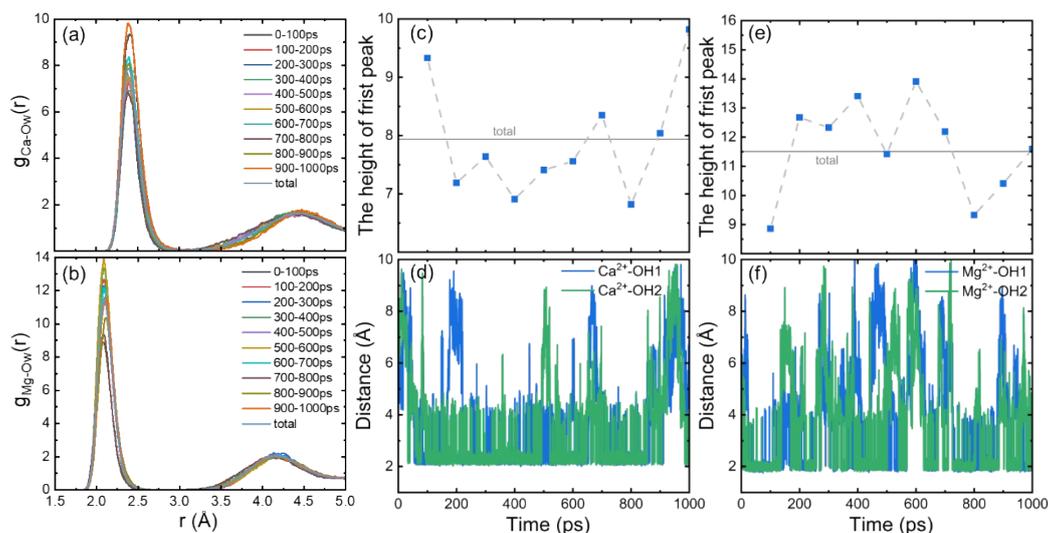


Figure S3. The 1-ns DPMD trajectories are equally divided into 10 slices. (a) and (b) show the radial distribution functions $g(r)$ of the slices of Ca^{2+} - O_w and Mg^{2+} - O_w (O_w represents the O atoms in a water molecule), respectively. We find that the height of the first peak changes with the simulation time, as shown in (c) and (e). However, the position of the RDF peak does not change over the simulation time. (d) and (f) show the distance between the $\text{Ca}^{2+}/\text{Mg}^{2+}$ cation and the two OH^- ions in the aqueous solution over the 1-ns simulation time of DPMD, where we find that the height of the first peak changes with the distance between the cation and OH^- , i.e., the number of water molecules around the cation decreases when OH^- is near the cation.

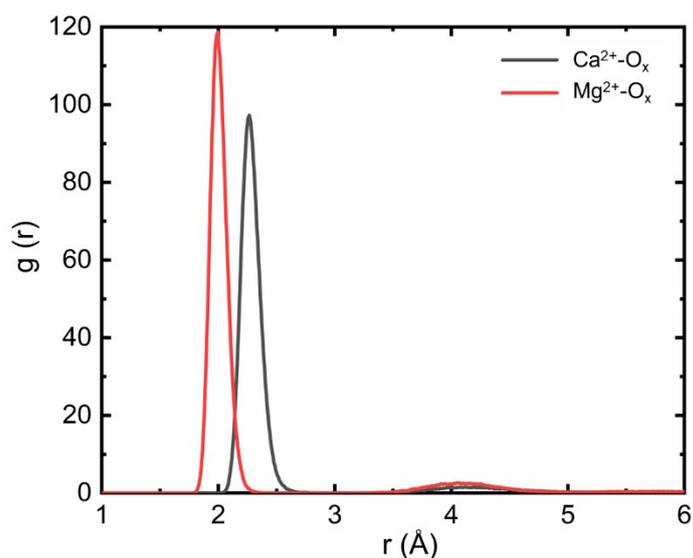


Figure S4. The radial distribution functions $g(r)$ of the Ca^{2+} - O_x and Mg^{2+} - O_x (O_x denote the oxygen atom of OH^-) as obtained from 1 ns DPMD simulations.

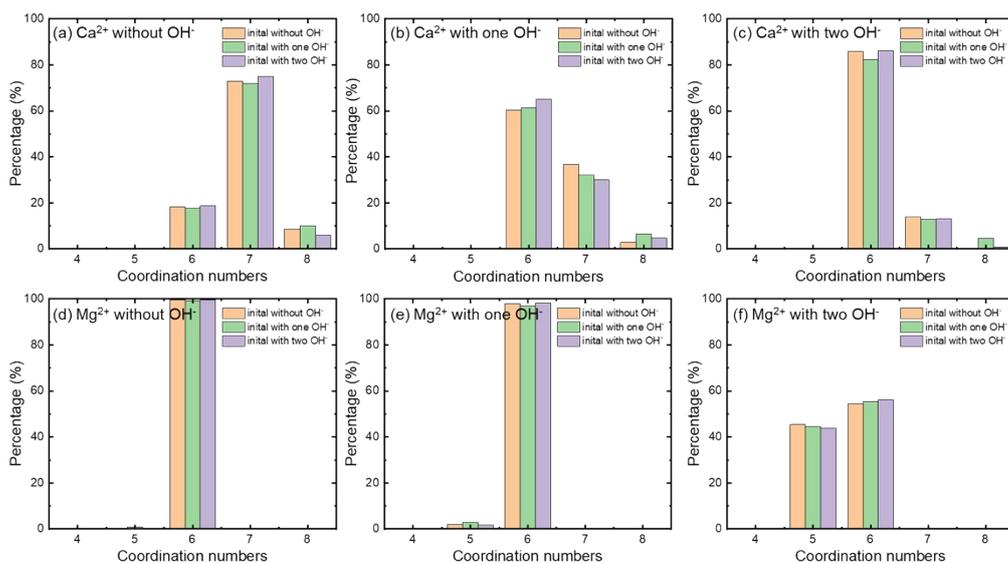


Figure S5. Probability distributions of the coordination numbers of the first coordination shells of (a)-(c) Ca^{2+} and (d)-(f) Mg^{2+} calculated from 1-ns DPMD trajectories. In detail, the distribution of coordination numbers for configurations of $\text{Ca}^{2+}/\text{Mg}^{2+}$ without OH^- in the first solvation shell, $\text{Ca}^{2+}/\text{Mg}^{2+}$ with one OH^- in the first solvation shell, and $\text{Ca}^{2+}/\text{Mg}^{2+}$ with two OH^- in the first solvation shell are illustrated in (a)/(d), (b)/(e), and (c)/(f), respectively. In each figure, we plot the distribution of coordination numbers with three different initial configurations in the DPMD trajectories, i.e., the cation ion without OH^- in the first solvation shell (orange), the cation ion with one OH^- in the first solvation shell (green), and the cation ion with two OH^- in the first solvation shell (purple).

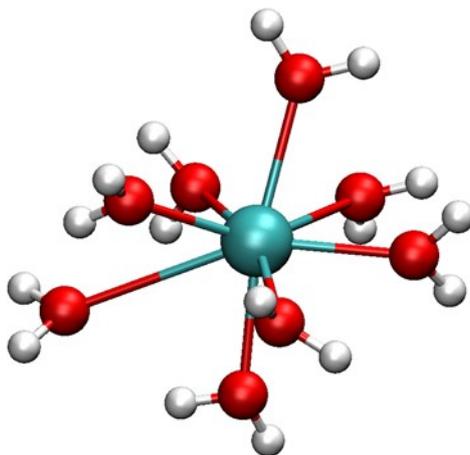


Figure S6. Representative solvation structure of Ca^{2+} with 8 water molecules. The solvation shell of Ca^{2+} tends to form a dodecahedron structure.

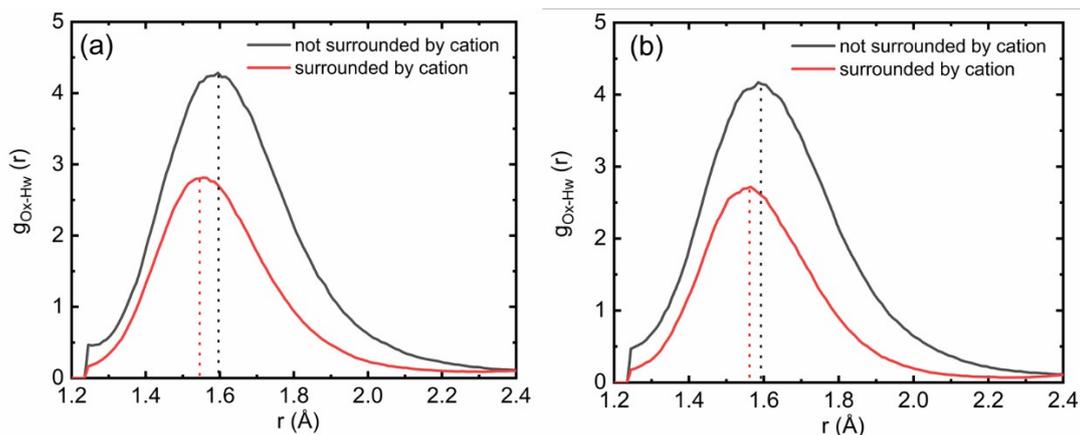


Figure S7. The radial distribution functions $g(r)$ of O_x-H_w of the OH^- ion in the (a) Ca^{2+} and (b) Mg^{2+} aqueous solutions from the 1-ns DPMD trajectories, where O_x and H_w denote the oxygen atom of OH^- and hydrogen atoms of water molecules, $g(r)$ for the two cases are considered: the OH^- ion is not surrounded by Ca^{2+} or Mg^{2+} , and the OH^- ion is surrounded by Ca^{2+} or Mg^{2+} . In general, we find the distance between O_x and H_w is shorter when OH^- is present in the first solvation shell of cations.

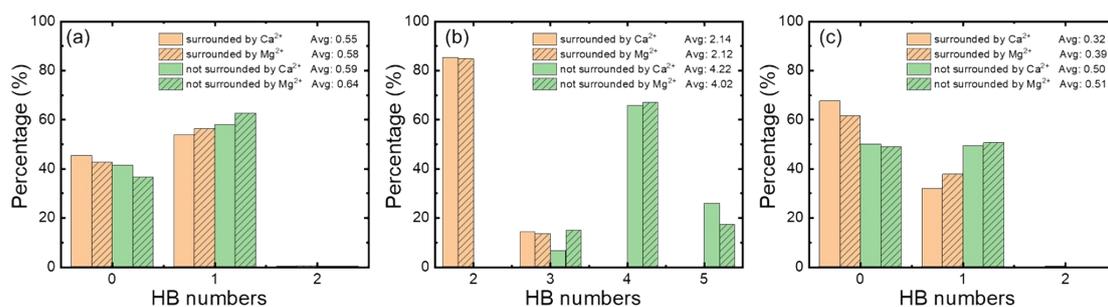


Figure S8. (a) Percentages of H-bonds (HBs) donated by OH^- from the 1-ns DPMD trajectories. (b) Percentages of HBs accepted by OH^- from the 100-ps AIMD trajectories, and (c) Percentages of HBs donated by OH^- from the 100-ps AIMD trajectories. The average (Avg) numbers of HBs are shown.