Supporting Information

Probing calcium solvation by XAS, MD and DFT calculations

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MD simulation details:

The simulations were initially equilibrated using LAMMPS[1] under isothermal-isobaric (NPT) ensemble at a temperature of 300 K and a pressure of 1 atmosphere, followed by the canonical ensemble (NVT). A cut-off distance of 13 Å and 14 Å were used for nonbonded interactions in aqueous and methanol solution, respectively. For all electrostatic interactions, the mesh Ewald method was used[2]. Each of the simulations was run for at least 20 ns with a time step of 1fs and the last 1 ns data were used for analysis.

References:

1) S. Plimpton, *J. Comput. Phys.*, 1995, **117**, 1-19.
2) U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee and L. G. Pedersen, *J. Chem. Phys.*, 1995, **103**, 8577–8593.

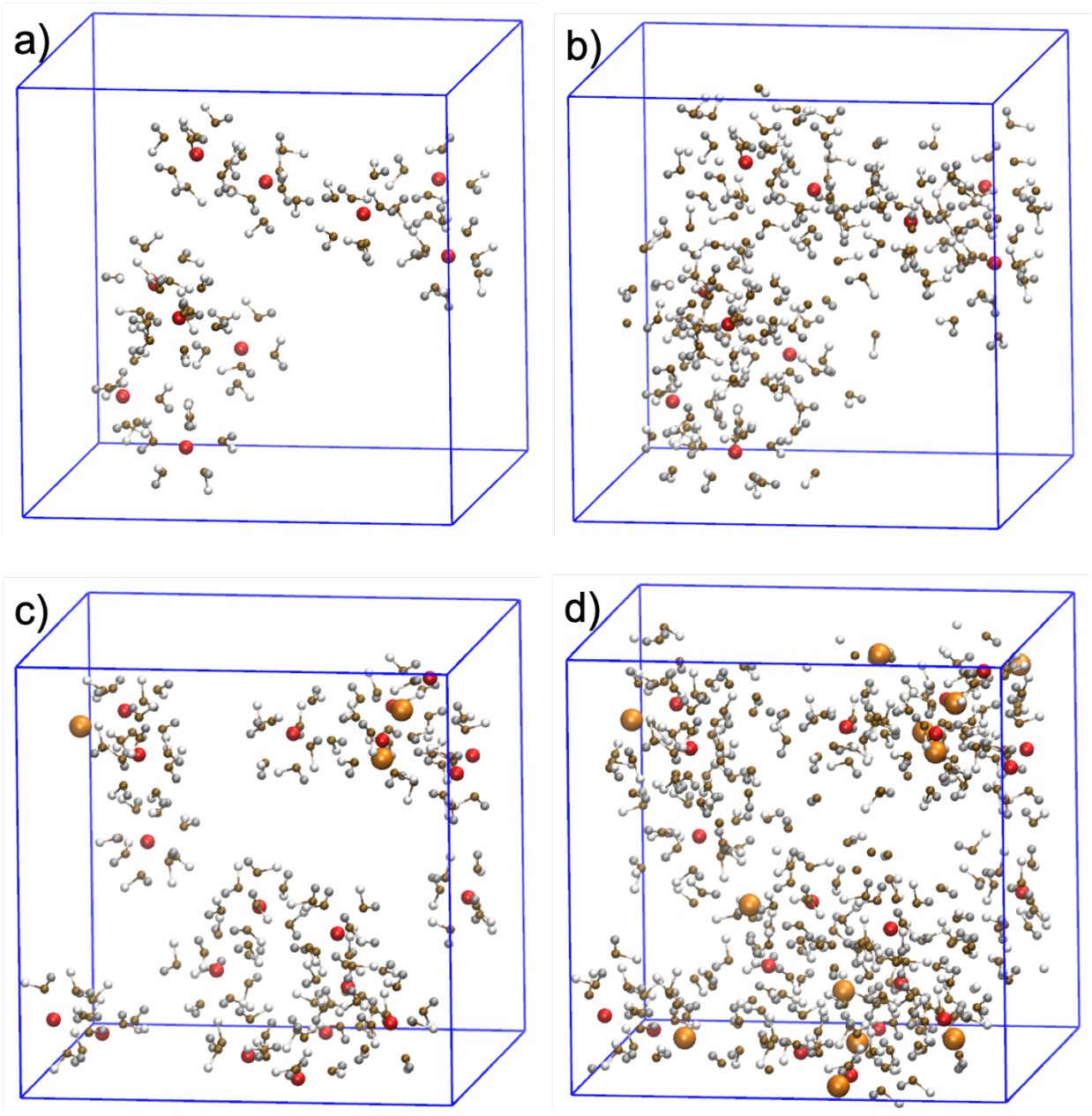

Figure S1 Molecular dynamics (MD) simualtion for (a) the first solvation shell around Ca^{2+} in 0.5 M $CaCl_2 \cdot 2H_2O$ methanol solution; (b) the first and second solvation shells around Ca^{2+} in 0.5 M $CaCl_2 \cdot 2H_2O$ methanol solution; (c) the first solvation shell around Ca^{2+} in 1.0 M $CaCl_2 \cdot 2H_2O$ methanol solution; (d) the first and second solvation shells around Ca^{2+} in 1.0 M $CaCl_2 \cdot 2H_2O$ methanol solution. (Red: Ca^{2+}, Orange: Cl^-)

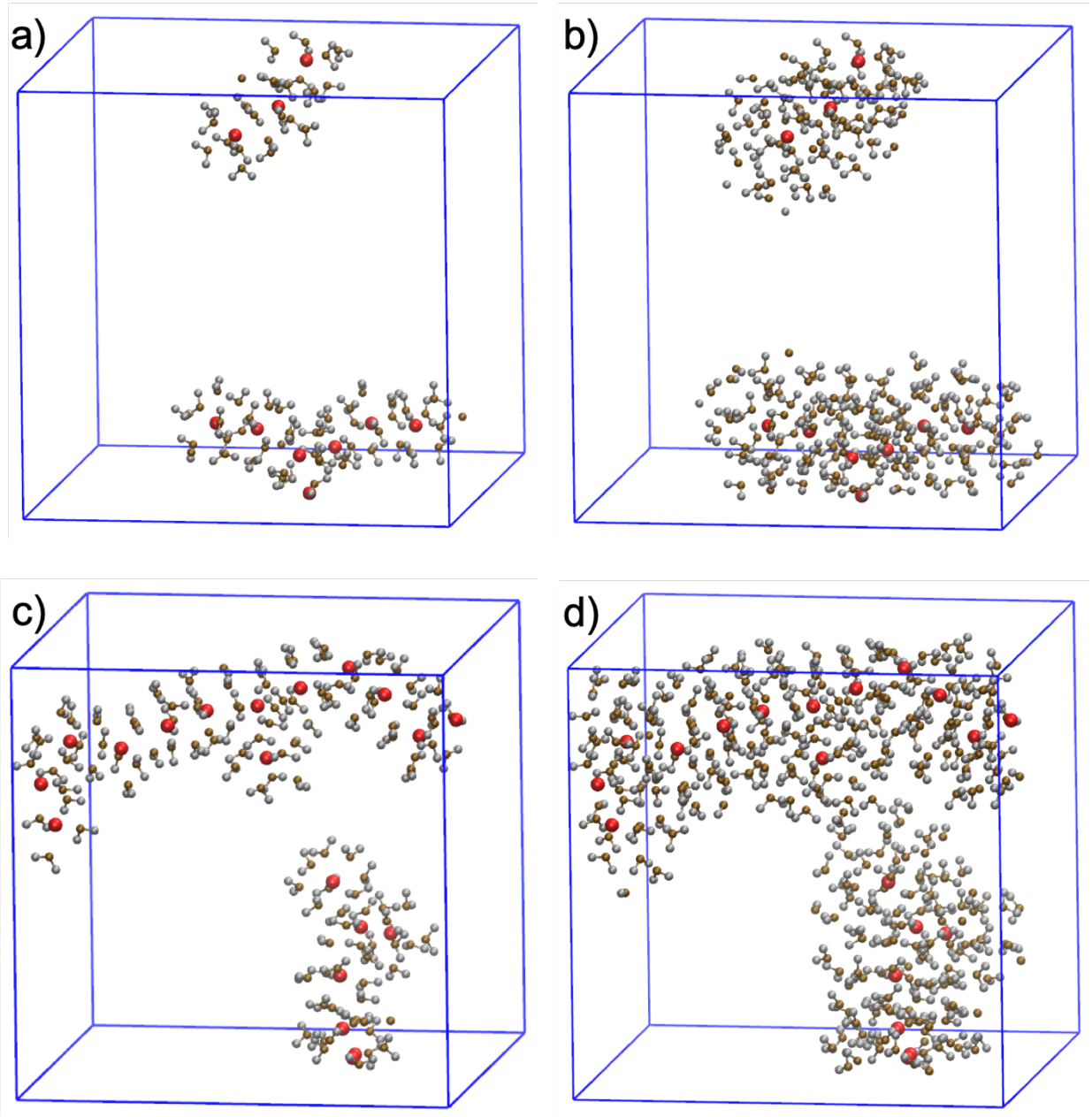

Figure S2 Molecular dynamics (MD) simualtion for (a) the first solvation shell around Ca^{2+} in 0.5 M $CaCl_2 \cdot 2H_2O$ aqueous solution; (b) the first and second solvation shells around Ca^{2+} in 0.5 M $CaCl_2 \cdot 2H_2O$ aqueous solution; (c) the first solvation shell around Ca^{2+} in 1.0 M $CaCl_2 \cdot 2H_2O$ aqueous solution; (d) the first and second solvation shells around Ca^{2+} in 1.0 M $CaCl_2 \cdot 2H_2O$ aqueous solution.

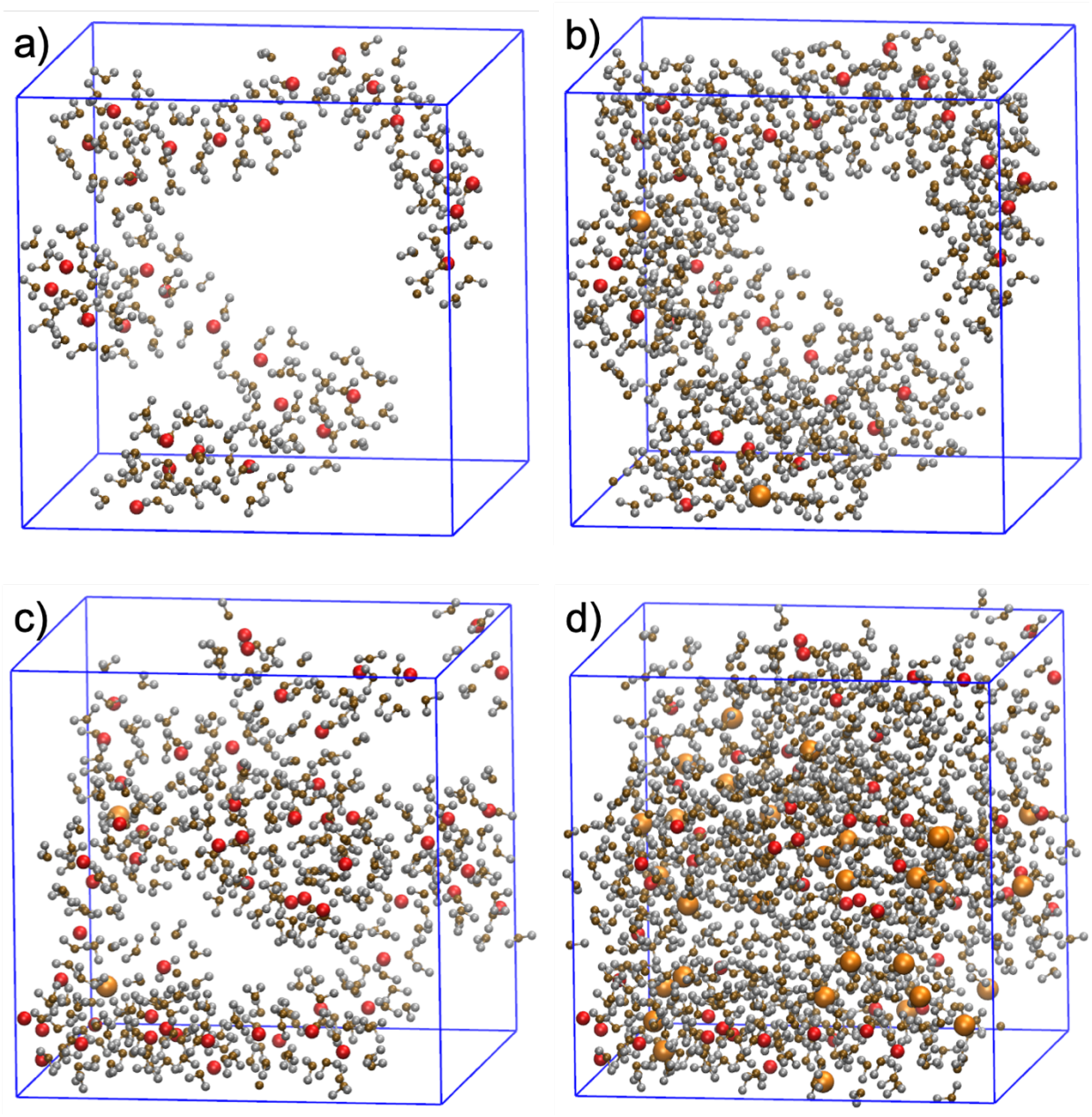

Figure S3 Molecular dynamics (MD) simualtion for (a) the first solvation shell around Ca^{2+} in 1.5 M $CaCl_2 \cdot 2H_2O$ aqueous solution; (b) the first and second solvation shells around Ca^{2+} in 1.5 M $CaCl_2 \cdot 2H_2O$ aqueous solution; (c) the first solvation shell around Ca^{2+} in 3.0 M $CaCl_2 \cdot 2H_2O$ aqueous solution; (d) the first and second solvation shells around Ca^{2+} in 3.0 M $CaCl_2 \cdot 2H_2O$ aqueous solution.