Understanding Reversible Mg Deposition and Stripping in Non-Aqueous Electrolytes —Supplementary Information—

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S1 Adsorption energies of THF with respect to its thermodynamic gas reference

Figure S1 shows the adsorption energies of THF molecules on the Mg (0001) surface when the gas THF reference is used.

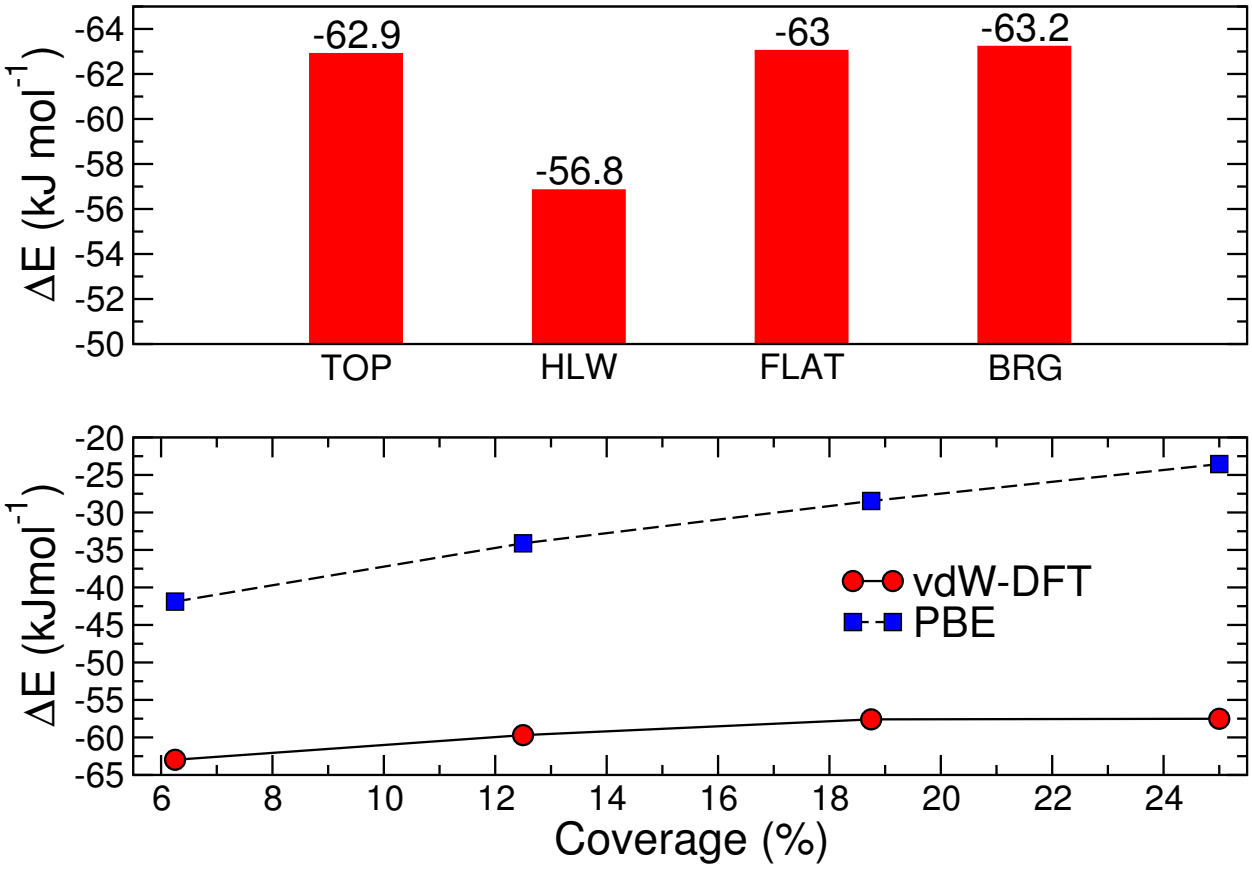

Figure S1: (Color online) top panel ΔE (in kJ mol^{-1}) of THF molecules at the Mg (0001) surface and bottom panel adsorption energies versus coverage. Gas reference for THF is used.

S2 Adsorption energies of $(MgCl)^+$ with respect to its liquid and gas thermodynamic references

Figure S2 shows all the adsorption energies computed in this work for $(MgCl)^+$ (coordinated by THF) at the Mg (0001) surface when a liquid reference for $(MgCl)^+$ is used.

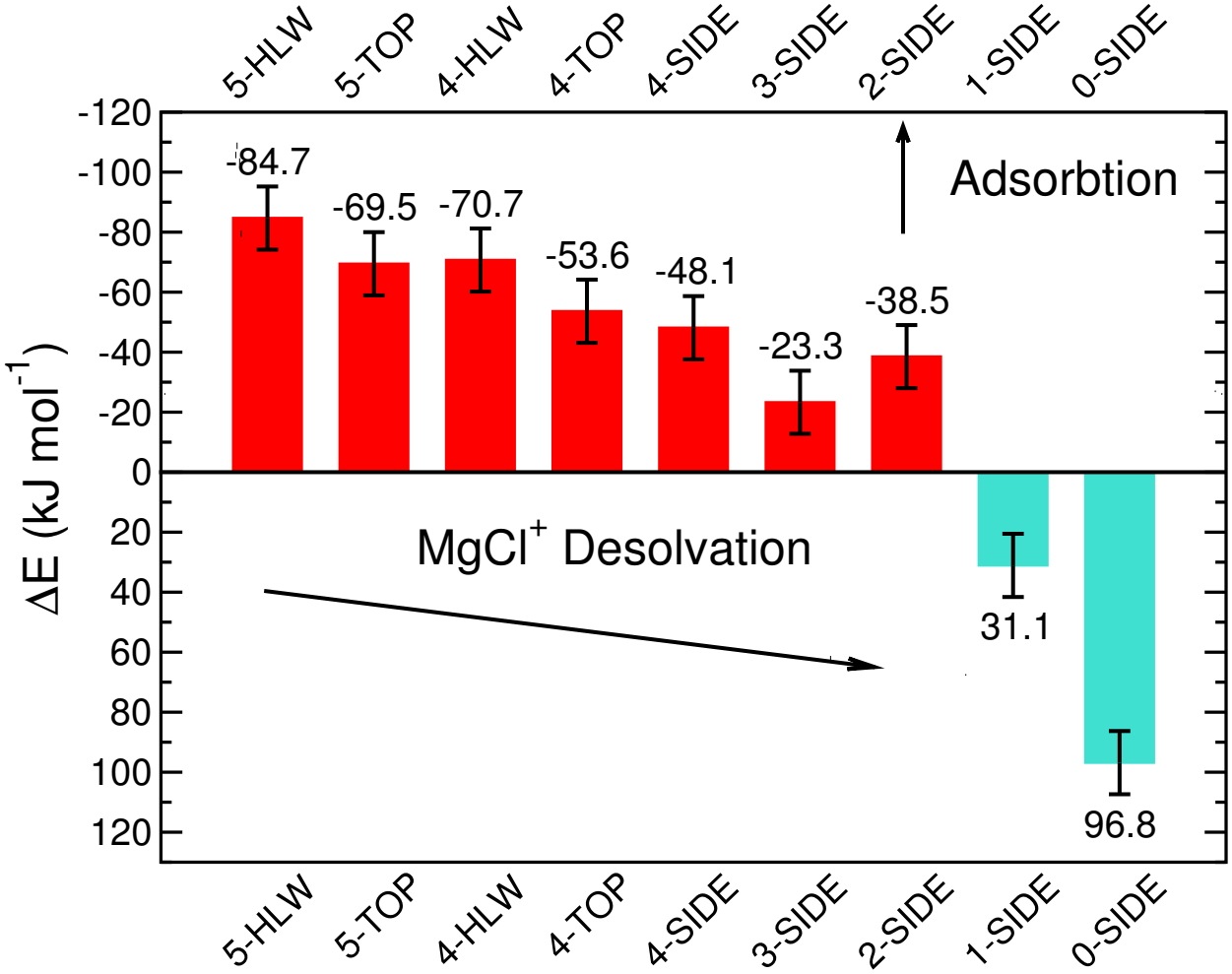

Figure S2: (Color online) adsorption energies ΔE (in kJ mol^{-1}) for $(MgCl)^+$ as function of number coordinating THF molecules at the Mg (0001) surface with reference to the liquid state. Labels HLW, TOP, SIDE mark the type of adsorption site and orientation (see Fig. 3 in the manuscript for details). Upper and lower bounds indicated by the bars on ΔEs are from using 3-THF (as determined by Wan et al.[1]) and 5-THF bulk liquid reference states, respectively

Figure S3 shows the adsorption energies of THF coordinated $(MgCl)^+$ at the Mg (0001) surface when a gas reference for $(MgCl)^+$ is used.

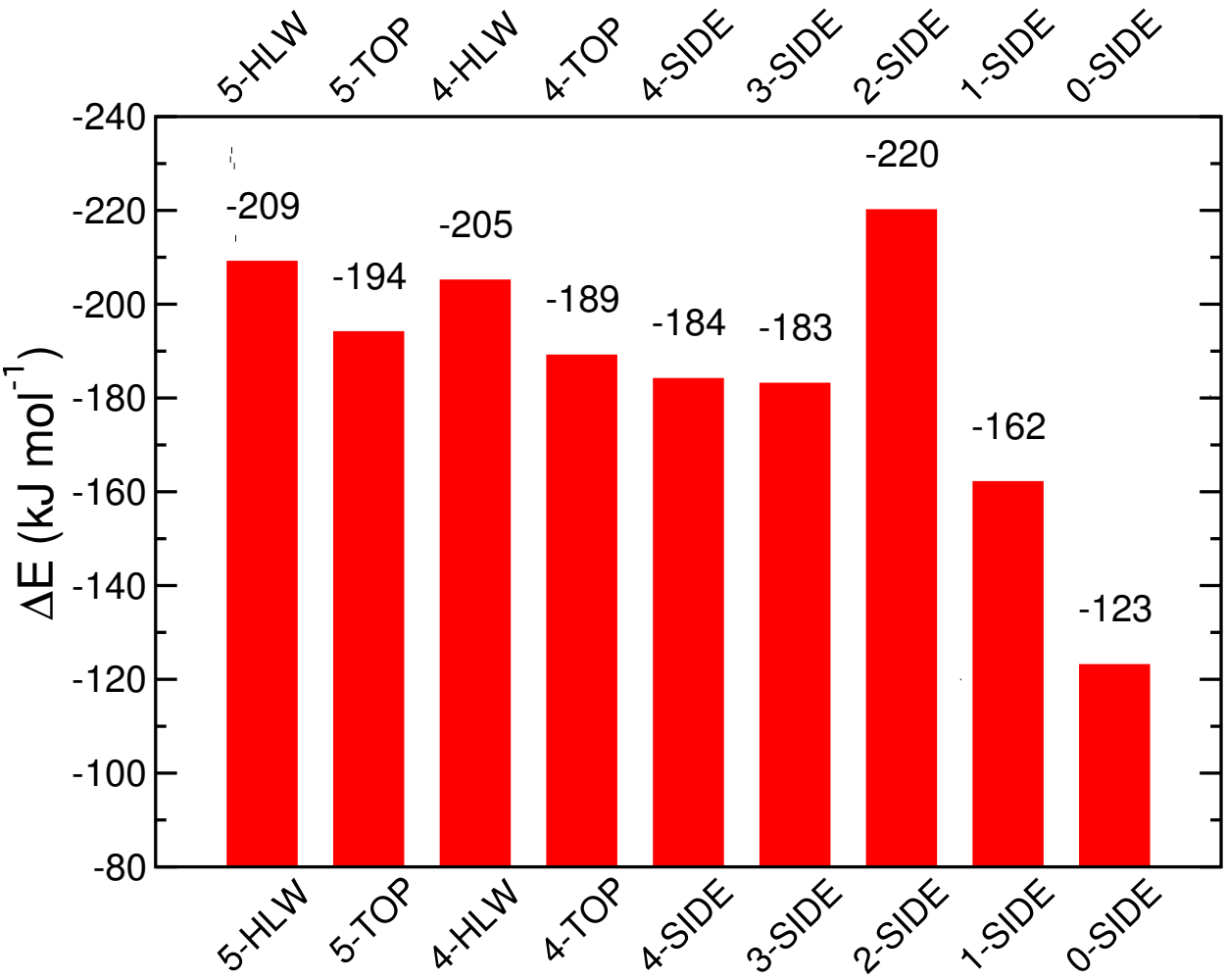

Figure S3: (Color online) adsorption energies ΔE (in kJ mol^{-1}) for $(MgCl)^+$ as function of number coordinating THF molecules at the Mg (0001) surface and with reference to the gas-phase. Labels HLW, TOP, SIDE mark the type of adsorption site and orientation (see Fig. 3 in the manuscript for details).

S3 Mg-Cl pair distribution functions for $(MgCl)^+$ salt cases

Figure S4 shows the Mg_{Salt}-Cl pair distribution functions for three important $(MgCl)^+$ salt configurations, and confirm that Cl is always bound to Mg.

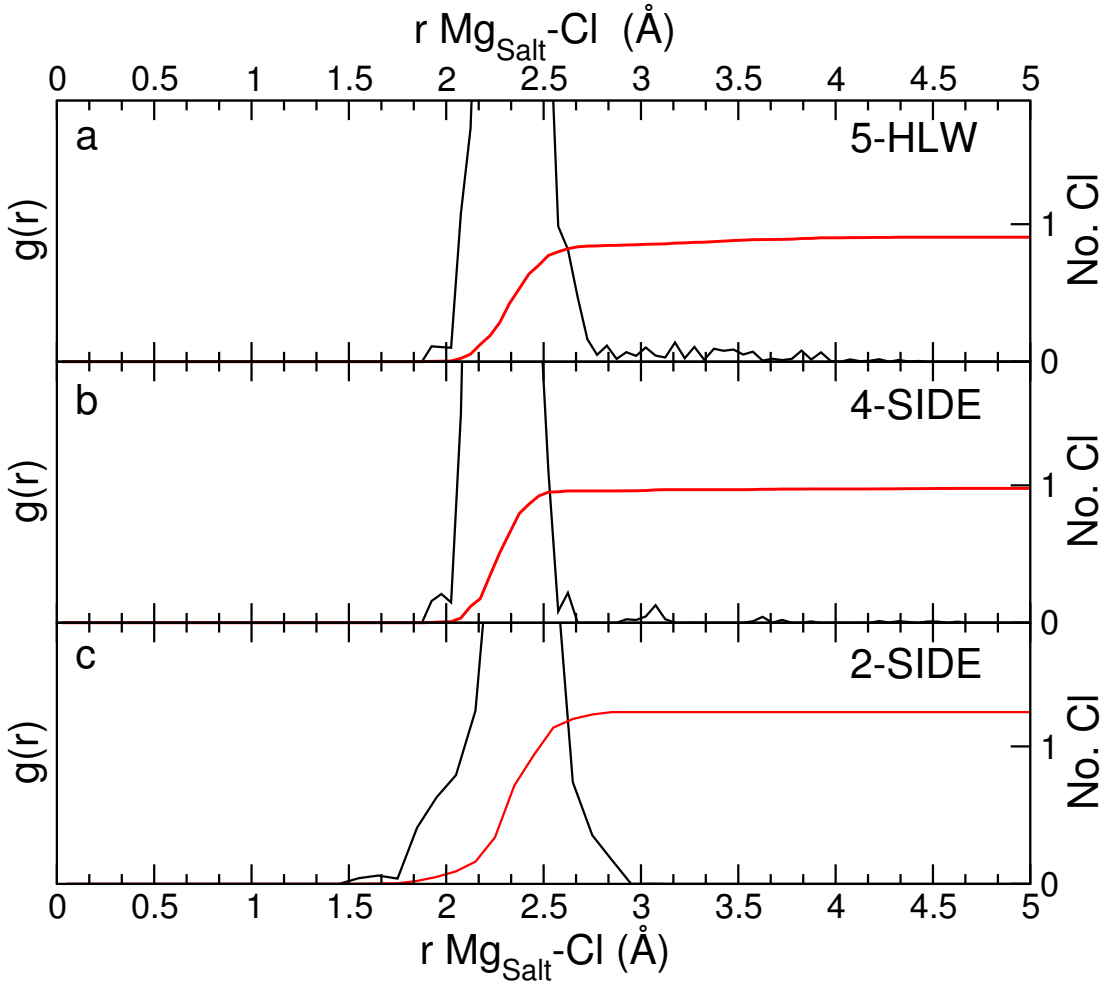

Figure S4: (Color online) PDFs g(r), and coordination number of Mg atoms by Cl atoms of models 5-HLW, 4-SIDE and 2-SIDE $(MgCl)^+$, respectively (see Fig. 3 in the manuscript). Insets show the structural evolution of the salts at the surface.

S4 $MgCl_2$ adsorption models

Figure S5 depicts three models for $MgCl_2$ adsorbed at the Mg (0001) surface.

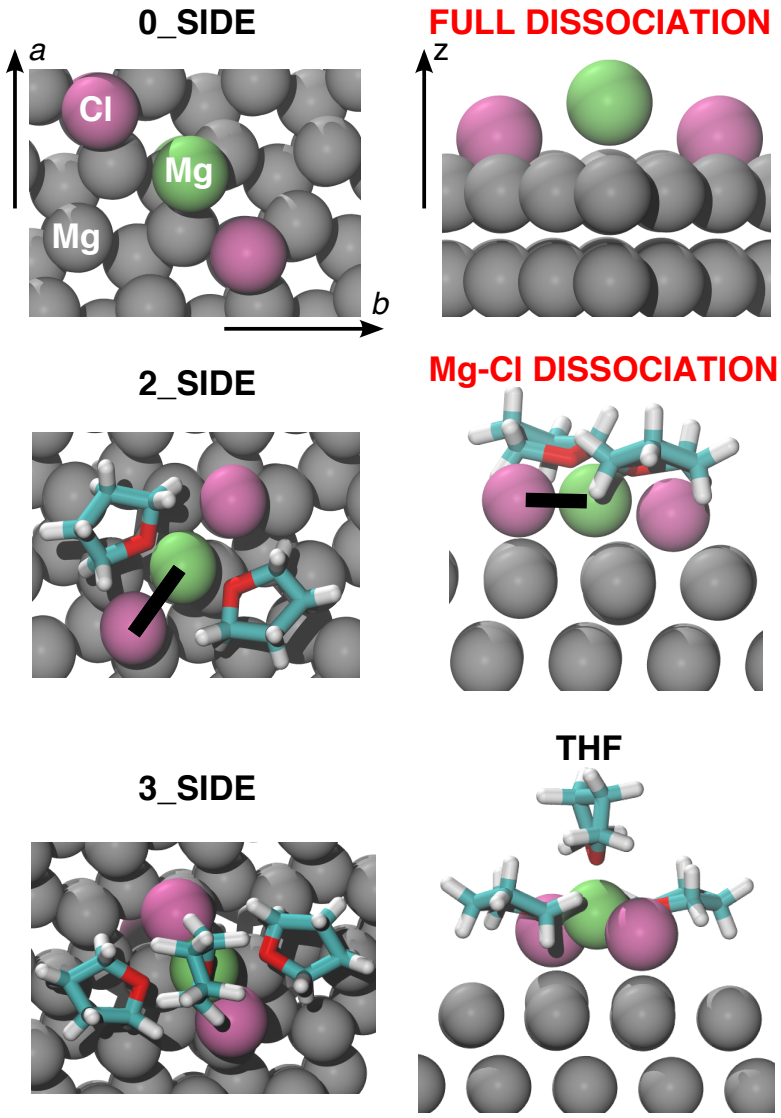

Figure S5: (Color online) top and side view of relevant adsorption models for $MgCl_2$ at the Mg (0001) surface.

S5 Adsorption energies of $MgCl_2$ with respect to its liquid and gas thermodynamic references

Figure S6 shows the adsorption energies of THF coordinated $MgCl_2$ at the Mg (0001) surface.

Note model 1-SIDE was not computed.

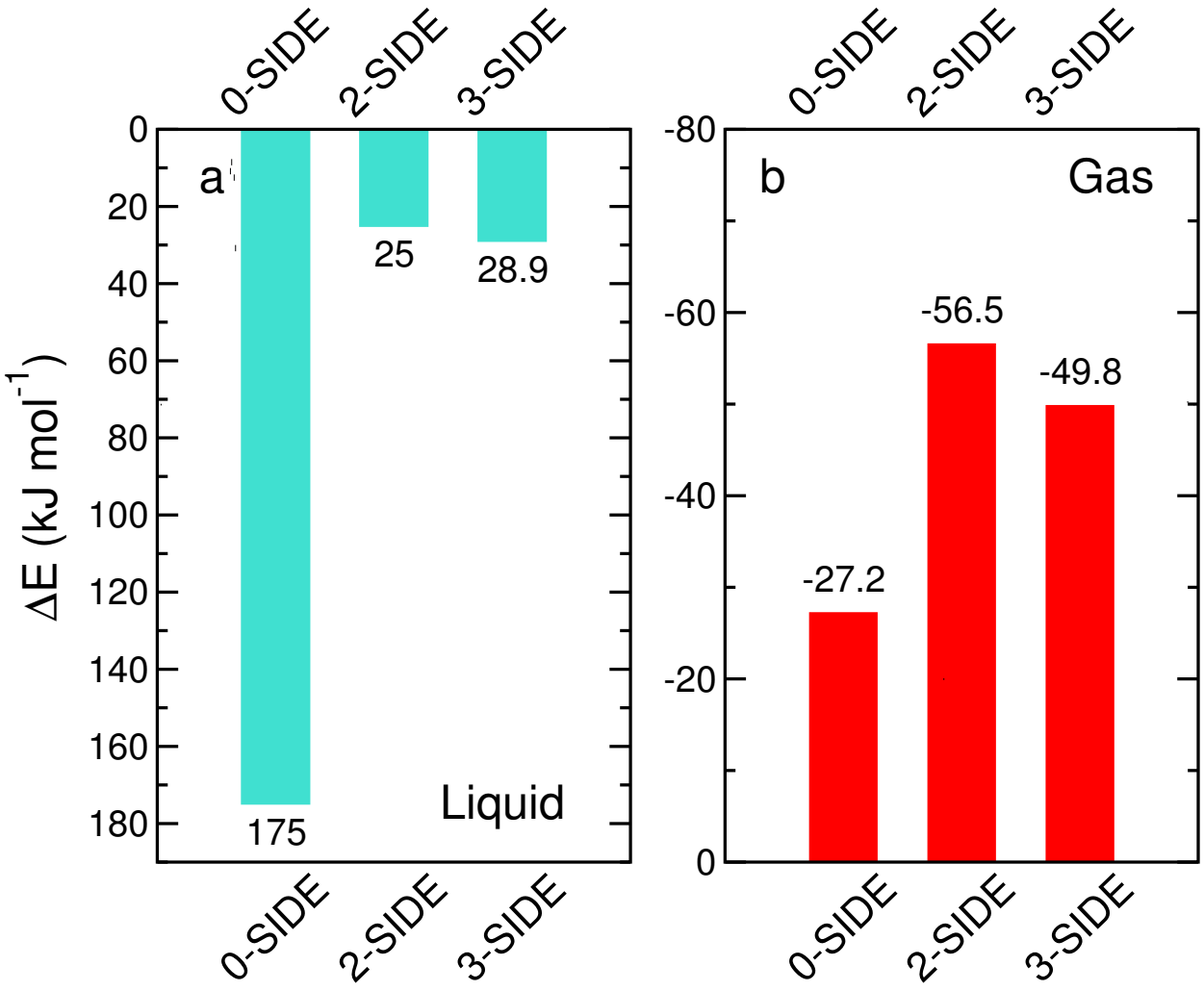

Figure S6: (Color online) adsorption energies ΔE (in kJ mol^{-1}) for $MgCl_2$ as function of coordinating THF molecules at the Mg (0001) surface with reference to (a) liquid, and (b) gas. Label SIDE marks the type of adsorption site and orientations see Fig. S5

References

(1) Wan, L. F.; Prendergast, D. The Solvation Structure of Mg Ions in Dichloro Complex Solutions from First-Principles Molecular Dynamics and Simulated X-ray Absorption Spectra. *J. Am. Chem. Soc.* **2014**, *136*, 14456–14464.