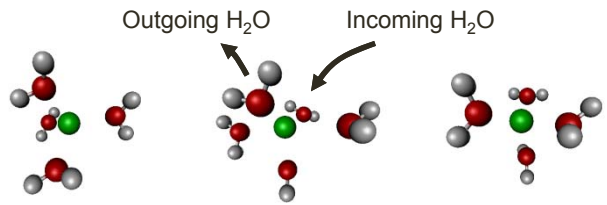
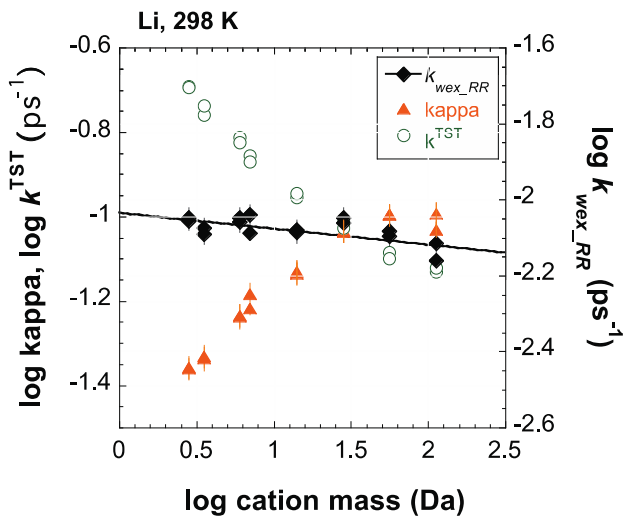
METAL LIGAND-EXCHANGE REACTIONS: A NEW MECHANISM OF KINETIC ISOTOPE FRACTIONATION



Snapshots (taken at ~100 ps intervals) of $^7Li^+$ and the water molecules in its first solvation shell during a water-exchange event. The central image shows a short-lived 5-fold coordination that occurs during the event.



Reaction rate theory predictions of log k_{wex} vs. log m for Li^+ isotopes. According to the theory, $k_{wex} = \kappa\, k_{TST}$, where the transition-state theory constant k_{TST} has an inverse square root dependence on metal-ion reduced mass (green circles) and κ is a transmission coefficient with a poorly characterized mass dependence (orange triangles). Our reaction rate theory calculations show that the mass-dependence of κ almost cancels that of k_{TST}, such that $k_{wex} \propto m^{-0.05}$, in agreement with our MD simulation results.

Scientific Achievement

The water-exchange rate k_{wex} of aquated metals decreases with increasing isotopic mass. This type of kinetic isotope effect had never been previously shown.

Significance and Impact

Any reaction that involves a rate-limiting metal desolvation step (or more broadly, a ligand exchange step) may cause significant kinetic isotope fractionation. This includes carbonate precipitation and several other types of reactions (metal adsorption, binding to organic ligands, interfacial redox reactions).

Research Details

- Molecular dynamics simulations of a single metal ion (Li, K, Rb, Ca, Sr, Ba) in liquid water at 5, 25, and 50°C.
- For all solutes studied, $k_{wex} \propto m^{-0.05\pm0.01}$.
- MD simulation results are consistent with reaction rate theory calculations.
- Results are consistent existing measurements of kinetic isotope fractionation during metal binding to mineral surfaces and organic ligands.

Hofmann A.E., Bourg I.C., DePaolo D.J. Ion desolvation as a mechanism for kinetic isotope fractionation in aqueous systems. *Proceedings of the National Academy of Sciences of the U.S.A.* 109, 18689-18694 (2012).