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Unraveling the Mass-dependent Mystery of Kinetic Isotope Fractionation in Aqueous Environments

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Dynamic processes in liquid systems - for example, molecular diffusion, ligand exchange, mineral growth, and liquid evaporation - are classic, well-studied problems in physical chemistry that are highly relevant to aqueous geochemistry and many other fields of chemistry, biology, and materials sciences. An important question in the fundamental studies of these processes is their sensitivity to collective solvation dynamics. Collective solvation dynamics play an important role in geochemistry since they underlie much of our current fundamental understanding of geochemical kinetics in areas such as cloud formation, metal biogeochemical cycling, noble gas geochemistry, water evaporation to the atmosphere, and the thermal history of rocks and, also, because they determine the kinetic isotope effects (KIEs) associated with elementary geochemical processes. These KIEs are powerful investigative tools in the geosciences, but their utility could be significantly enhanced by additional understanding of their molecular basis and magnitude.

In the present study we use classical molecular dynamics to examine the mass-dependency of kinetic isotope fractionation. In particular, we show that a mass-dependent diffusion coefficient (conflicting with Einstein's model of Brownian motion) can be described due to the collective couplings of the isotopic ion with the surrounding solvents collective modes of motion.