Importance of a fully anharmonic treatment of equilibrium isotope fractionation properties of dissolved species as evidenced by Li+(aq)

Romain Dupuis¹, Magali Benoît², Mark Tuckerman³ and Merlin Méheut⁴

¹DIPC, San Sebastian, Spain. rdupuisbelin@gmail.com ²CEMES CNRS, Toulouse, France. Magali.benoit@cemes.fr ³NYU, New York, United States. mark.tuckerman@nyu.edu ⁴GET, OMP, Toulouse, France. Merlin.meheut@get.omp.eu

Isotopic signatures recorded in geological objects constitute a primary source of information on the processes that shaped our planet. The dearth of reliable estimates of equilibrium fractionation factors, from experiment or natural observations, creates a need for accurate computational approaches. In these calculations, a severe approximation is often made, in which it is assumed that the system can be decomposed into a set of independent harmonic oscillators. In particular, one might expect the harmonic approximation (HA) to perform poorly for the isotopic fractionation between solid and solution phases. In this work, we have considered the fractionation of Li isotopes between solution and phyllosilicate minerals, where we find that the HA overestimates isotope fractionation factors by 30% at 25°C.

Moving beyond the harmonic approximation requires tackling the problem of performing exact quantum calculations, which can be performed using the Feynman path integral (PI) formulation of quantum statistical mechanics. Recent developments of efficient PI approaches now allow the case of the aforementioned dissolved Li fractionation properties to be studied in detail. We find that the calculations yield results that are in good agreement with both experimental and natural data. Importantly, PI methods, being fully atomistic, allow us to identify the origins of anharmonic effects and to make reliable predictions at temperatures that are experimentally inaccessible yet are, nevertheless, relevant for natural phenomena.