Importance of a fully anharmonic treatment of equilibrium isotope fractionation properties

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Natural isotopic signatures give essential insights on the geological processes that happened on Earth. The dearth of reliable estimates of equilibrium fractionation factors creates a need for accurate computational approaches. Since many years, the harmonic approximation is often considered[1]. A priori, this method might be too crude for dissolved species.

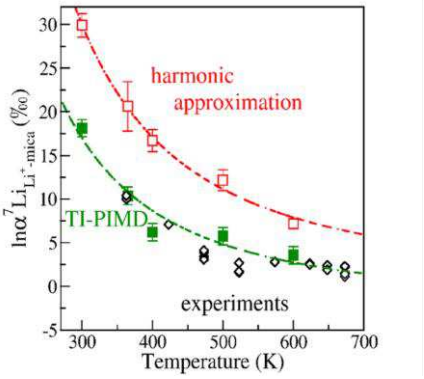

Figure 1. Isotopic fractionation properties of Li

We developed an efficient path integral approach that goes beyond the harmonic approximation, using the Feynman path integral. We estimated isotopic fractionation properties of Li in minerals and dissolved in water[2]. We find that the harmonic approximation overestimates isotope fractionation factor between minerals and liquids by 30% at room temperature. This new approach yields to results that are in agreement with experimental data and relevant natural data.

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[2]R. Dupuis, M. Benoît, M. Tuckerman and M. Méheut, Acc. of Chem. Res. (2017), DOI: 10.1021/acs.accounts.6b00607