Hydrogen diffusion and lithium isotope fractionation: Cases of competing and (sometimes) surprising quantum effects

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The methodology of path integral molecular dynamics has advanced to a stage such that it is now possible to study condensed-phase quantum mechanical phenomena on a routine basis. In this talk, these important advances will be leveraged to investigate the temperature dependence of two particular interesting cases of quantum phenomena: Diffusion and isotope fractionation. For the former, I will consider the problem of hydrogen diffusion in structure-II clathrate at temperatures ranging from 8 K up to 200 K. Structure-II clathrate, which acts as a host for trapped gas molecules under high-pressure conditions, is an ice-like structure consisting of small water cages composed of 12 pentagonal faces and large cages composed of both pentagonal and hexagonal faces. Hydrogen molecules in structure-II clathrate are capable of diffusing from cage to cage mostly through the hexagonal faces, a process that exhibits strong quantum effects as a function of temperature. This effects are studied using path integral molecular dynamics (PIMD) and ring-polymer molecular dynamics (RPMD) to determine, respectively, equilibrium free energy profiles and approximate cage-to-cage transfer rates [1]. At the higher temperatures, quantum effects are found to slow the rate of diffusion while at low temperatures, when the deep tunneling regime is reached, they enhance the diffusion rate. For the problem of isotope fractionation, fractionation of lithium between aqueous solution and a phyllosilicate material, a phenomenon of geochemical interest, is investigated as a function of temperature. Isotope fractionation is a purely quantum mechanical process that is often estimated within the so-called harmonic approximation. In this study, it will be shown that the fractionation of lithium between the solution and solid phases is dominated by anharmonic effects that are most readily evaluated within the path-integral framework [2]. The severe breakdown of the harmonic approximation for this case and the prospect of similar breakdowns in other instances illustrates the impact that path integral methodology can have outside the traditional areas of physics and physical chemistry.

[1] J. R. Cendagorta, A. Powers, T. J. H. Hele, O. Marsalek, Z. Bacic, M. E. Tuckerman *Phys. Chem. Chem. Phys.* **18**, 32169 (2016).

[2] R. Dupuis, M. Benoit, M. E. Tuckerman, and M. Méheut *Acc. Chem. Res.* (in press)