Strange isotopic fractionation of noble gases diffusing through water

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(Atmospheric) noble gases are routinely used as natural physical tracers to reconstruct past climate conditions as well as to analyse water transport and (aquatic) phase partitioning (e.g. mixing in lakes, air-water exchange). Molecular diffusion often contributes to such exchange. Most authors axiomatically assume molecular diffusion to force mass ($m_{i,j}$) dependent fractionation of (noble) gases and their isotopes scaling with $(m_i/m_j)^{1/2}$ [1]. Thus, isotopic fractionation could allow pinning down noble gas transport by diffusion. However, classical molecular dynamics simulations (MD) reported only negligible isotopic fraction within a noble gas element and challenged the common assumption [2]. In contrast experiments showed Ne, Kr and Xe not to be isotopically fractionated upon molecular diffusion in water, although He and Ar isotopes were fractionated similar to the assumed root square relation [3].

By applying ab initio MD accounting explicitly for the quantum-mechanical behavior of electrons we assessed the conflict between computational and experimental results by elucidating the molecular-resolved mechanisms ruling noble gases diffusing through bulk water. Our excercice shows the particle size and polarizability of a hydrophobic (noble gas) atom mechanstically control its molecular motion through dense and polar liquids like water. Such small-scale transport is subject to different 'diffusive regimes' forcing He and Ar to isotopically fractionate, but much less so for Ne, Kr and Xe [4]

[1] Richter et al. (2006) GCA, 70, 277-289. [2] Bourg and Sposito (2008) GCA, 72, 2237-2247. [3] Tyroller et al. (2014) GCA, 136, 60-66. [4] de Magalhães et al. (2017) Env. Sci. Process, DOI: 10.1039/c6em00614k.