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Towards accurate first-principles computational protocols for light-element isotopic fractionation in the gas phases

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Computational quantum chemistry offers a unique ability to address equilibrium and kinetic isotopic effects by accounting for the mass dependence of electronic, translational, vibrational, and rotational states. However, the accuracy of the predictions depends on how well they describe the electronic correlations, with the most accurate methods suffering from the very high computational cost. For example, the “golden standard” of quantum chemistry, Coupled Cluster with singles, doubles, and perturbative triples excitations, shows canonical scaling of N^7 (where N is the number of electrons), which means that by doubling the size of the system, the computation time multiplies by a factor of 128. For decades, this prohibitive cost has prevented us from studying larger molecules; however, recent progress in the basis set extrapolation methods, explicitly correlated or local Coupled Cluster methods, allows routine computation of polyatomic molecules.

Here, we revisited the computational protocol proposed almost 50 years ago by Richet et al. Richet et al. [1] for diatomic and polyatomic molecules by using computationally determined spectroscopic constants. We accounted for anharmonicity, relativistic, and non-Born-Oppenheimer effects, showing that increasing the level of theory and accounting for these effects are necessary steps toward achieving experimental, spectroscopic accuracy. We compared three computational protocols built on the gold standard, considering 42 molecules composed of 11 elements from groups 13-17, periods 2-3, and hydrogen. In some cases, the calculated vibration frequencies are accurate to within 1 cm^{-1}; in other cases, especially for molecules exhibiting multireference character, the Coupled Cluster methods they deviate by several cm^{-1}. Nonetheless, we obtained accurate prediction of the temperature-dependent isotopic fractionation constants for a range of environmentally important isotope exchange reactions. We also illustrate site-specific and clumped isotopic fractionation in CO_2, CH_4, and CO_3^{2-} molecules, compared with the recent measurements carried out in our group.

[1] . Richet, Y. et al. A Review of Hydrogen, Carbon, Nitrogen, Oxygen, Sulphur, and Chlorine Stable Isotope Fractionation Among Gaseous Molecules, Annual Review of Earth and Planetary Sciences 567 (1977) 65–110.