Calculating Isotopic Equilibria: Clumped Isotopes in H_2O and CH_4

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Recent advances in mass spectrometry have allowed for precise (±0.2‰) measurements of clumped isotopologues of methane at natural abundances, giving rise to its use as a geothermometer in equilibrated systems [1]. For this technique to be used, accurate models need to be developed that quantify equilibrium shifts of all isotopologues away from stochastic distributions. These shifts can be calculated using modern quantum chemical methods and programs with results that vary in accuracy depending on the particular methods chosen. Our objective here is to explore methods and pitfalls when using these calculations at the harmonic and anharmonic levels and to determine the magnitude of the anharmonic shifts for various isotopologues of methane.

H/D exchange in water ($H_2O + D_2O = 2HDO$) is one of the most widely studied systems and should be useful as a benchmark, but the results for $K(T)$ are still somewhat controversial. We review historical results as determined by the three principal methods: statistical mechanics and vibrational spectroscopy, direct measurement of compositions, and statistical mechanics and quantum chemistry. We show that there is consensus among at least some studies for all three methods for $K(298K) \sim 3.85$ as opposed to the widely quoted values $K(298K) \sim 3.80$. We then show that anharmonic effects for water are small and that MP2 and B3LYP calculations with triple-zeta basis sets can produce values close to those from the best experiments or high-level calculations.

For methane, we show that anharmonic effects are not large for doubly-substituted $^{13}CH_3D$, but that they are increasingly significant for CH_2D_2 and other species with higher levels of deuterium substitution. Since the different isotopologues of methane suffer from various levels of "resonance", it is critical to generate anharmonic corrections using a suitably "deperturbed" method. We show that the hybrid degeneracy-corrected perturbation model of Bloino, Miczysko, and Barone gives reasonable and consistent corrections which vary little between B3LYP and MP2.

[1] D.A. Stolper *et al* (2014), *Geoch. et Cosmo. Acta* **126**.