

Theoretical calculation of equilibrium clumped isotope signatures beyond the harmonic approximation

QI LIU AND YUN LIU*

Institute of Geochemistry, Chinese Academy of Sciences

(*correspondence: liuyun@vip.gyig.ac.cn)

Geological application of clumped isotope techniques has been broadened, but the studied objects mainly remain CO₂, or O₂. There is an urgent need to include other species into the inventory of clumped isotope geochemistry. In this study, we provide equilibrium Δ_i values of several common gaseous molecules which can be potential targets for the clumped isotope study in future. For improving the calculation accuracy, theoretical treatments beyond the harmonic level by including several higher-order corrections to the Bigeleisen-Mayer equation are used. We have evaluated contributions from many higher-order corrections (e.g., AnZPE, AnEXC, VrZPE, VrEXC, QmCorr and CenDist) to calculate the anharmonic effects of vibration, vibration-rotation coupling, quantum mechanics and centrifugal distortion for rotation, etc., which are ignored in the Bigeleisen-Mayer equation for the calculation of reduced partition function ratios. All calculations are performed at MP2/aug-cc-pVTZ level and no frequency scale factor has been used. The computational details of these higher-order corrections can be found in [1].

Our results provide detailed temperature dependencies of clumped isotope signatures of those molecules. We also find AnZPE is the most significant correction at room temperature. VrZPE plays second important role at room temperature, but may contribute equally important to AnZPE at higher temperature. Other corrections can contribute a little only if hydrogen atom is involved. With the increase of temperature, contributions of AnEXC, VrEXC and CenDist will become larger; contributions from AnZPE and QmCorr will become smaller. Our results suggest anharmonic corrections can significantly improve the estimation of clumped isotope signatures especially when hydrogen atom is in the clumps (e.g., H₂O, H₂S, NH₃ and CH₄). Higher-order anharmonic corrections are therefore recommended to the theoretical study of clumped isotope fractionations.

[1] Liu, Tossell and Liu (2010) *Geochim. Cosmochim. Acta* **74**, 6965-6983.