

Theoretical calculation of position-specific carbon isotope fractionation of several organic compounds

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High precision position-specific (sometimes called site-specific) isotope fractionation signatures at equilibrium determined by theoretical methods are imperatively needed as references for the application of the intramolecular isotope effects. This study provides the position-specific carbon isotope fractionation at equilibrium of several organic compounds obtained by using quantum chemistry methods (e.g., propane, acetic acid, etc.). Our calculation are performed at CCSD/6-311+G(3df,3pd) by using Gaussian 09 program without scaling frequencies.

For testing the calculated accuracy, theoretical treatments beyond the harmonic approximation by including several higher-order corrections to the Bigeleisen-Mayer equation are used [1]. Contributions from higher-order corrections (e.g., AnZPE, AnEXC, VrZPE, VrEXC, QmCorr and CenDist) are estimated to repire the ignorings of the Bigeleisen-Mayer equation (the anharmonic effects of vibration, vibration-rotation coupling, quantum mechanics and centrifugal distortion for rotation, etc.) for the calculation of partition function ratios [2].

Our prediction of position-specific carbon isotope fractionation offers a theoretical framework to study the thermodynamics of the intramolecular isotope exchange reactions, or track kinetic processes such as biogenic effects during the formation of the organic compounds.

[1] Liu and Liu. (2016) *Geochim. Cosmochim. Acta* **175**: 252-270. [2] Liu et al. (2010) *Geochim. Cosmochim. Acta* **74**: 6965-6983.