

Theoretical calculation of position-specific carbon and hydrogen 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 and hydrogen isotope fractionation at equilibrium of several organic compounds obtained by using quantum chemistry methods (e.g., butane, acetic acid, etc.). Our calculation are performed by using Gaussian 09 program without scaling frequencies.

For testing the calculated accuracy, theoretical treatments beyond the harmonic level by considering several higher-order corrections to the Bigeleisen-Mayer equation are used. Contributions from higher-order corrections (e.g., AnZPE, AnEXC, VrZPE, VrEXC, QmCorr and CenDist) are estimated to repair the ignoring 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. The results show that the higher-order corrections contribute less than 0.9 at room temperature, which can be considered as negligible effects for this calculation comparing to the current experimental precisions.

The results show that position-specific isotope effects of similar fragments present similar behaviors at equilibriums. There are significant differences in thermodynamics between different functional groups. 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.