# Theoretical calculation of $^{13}$C-D clumped isotope effects in methyl of several organic compounds

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Recent developments in mass spectrometry [1] and tunable infrared laser direct absorption spectroscopy [2] make it possible to measure $^{13}$C-D clumped isotope effects of methane. These techniques can be further applied to determine $^{13}$C-D clumped isotope effects of methyl fragments, therefore need accurate equilirbium $\Delta_i$ values to calibrate experimental measurements. In this study, we calculate temperature depandences of $^{13}$C-D clumped isotope signatures in methyl of several organic compounds including ethane, propane, acetic acid, etc. Our calculation are performed at CCSD/6-311+G(3df,3pd) by using Gaussian 03 program with no scale treament.

Our results show that the $\Delta_i$ values of $^{13}$C-D clumping in methyl fragments of different organic compounds yield similar signals (~5.5‰ at 25˚C, slightly lower than $\Delta_i$ value of $^{13}$C-D clumping in methane). For testing the calculated accuracy, theoretical treaments beyond the harmonic level by including 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 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. The results show that the higher-order corrections contribute ~0.05‰ at 25˚C, which is similar to the contribution for calculating $^{13}$C-D clumped isotope signature of methane. By comparing our calculated frequencies to the measured ones, the uncertainty of our calculation of $\Delta_i$ values $^{13}$C-D clumping in methyl fragments is considered to be within ~0.05‰ at room temperature.

[1] Stolper et al. (2014) *Geochim. Cosmochim. Acta* **126**: 169-191. [2] Ono et al. (2014) *Anal. Chem.* **86**:6487-6494.