## Exploring isotopic clumping in organic molecules using DFT calculations

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Recent technological advances paved the way to applications of multiply-substituted ('clumped') isotope analysis of simple organic molecules such as methane [1] or ethane [2,3]. The deviation of the abundance of clumped isotopologues from a stochastic distribution, named  $\Delta$  values, provides invaluable information on the origin and history of these molecules. In particular, when a system is at equilibrium, they reflect temperature and can thus be used as geothermometers.

In this context, theoretical calculations provide powerful methods to determine  $\Delta$  values at equilibrium. Yet, theoretical calculations have been limited so far to simple molecules and to C and H isotopes, leading to a gap in our understanding of what controls equilibrium clumped isotope fractionation factors in organic molecules.

Here, we calculate 143 equilibrium  $\Delta$  values corresponding to DD, <sup>13</sup>CD, <sup>13</sup>C<sup>13</sup>C, <sup>13</sup>C<sup>15</sup>N and <sup>13</sup>C<sup>18</sup>O clumping for a total of 29 organic molecules. The calculations are made using the harmonic oscillator approach with B3LYP/6-311++G(d,p) method. At first-order approximation, and expectedly, the  $\Delta$  values are governed by the mass of both isotopes as well as the bond order. On a refined scale, variations within a single clumped isotope system (same isotopes and same bond order) can be explained by neighboring atoms and bonds associated. Similar to the "isotopic bond number" approach taken by Galimov [4] for <sup>13</sup>C equilbrium position-specific fractionation factors, we provide coefficients that allow equilibrium isotope fractionation factor determination for a given clumping system without the need for time-consuming DFT calculations. These data can prove useful for future studies aiming at developing measurement methods as well as interpreting natural data.

References

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