Equilibrium clumped-isotope effects in doubly substituted isotopologues of ethane

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Abstract

We combine path-integral Monte Carlo methods with a new intramolecular potential energy surface to quantify the equilibrium enrichment of doubly substituted ethane isotopologues due to clumped-isotope effects. Ethane represents the simplest molecule to simultaneously exhibit ^{13}C–^{13}C, ^{13}C–D, and D–D clumped-isotope effects, and the analysis of corresponding signatures may provide useful geochemical and biogeochemical proxies of formation temperatures or reaction pathways. Utilizing path-integral statistical mechanics, we predict equilibrium fractionation factors that fully incorporate nuclear quantum effects, such as anharmonicity and rotational-vibrational coupling which are typically neglected by the widely used Urey model. The magnitude of the calculated fractionation factors for the doubly substituted ethane isotopologues indicates that isotopic clumping can be observed if rare-isotope substitutions are separated by up to three chemical bonds, but the diminishing strength of these effects suggests that enrichment at further separations will be negligible. The Urey model systematically underestimates enrichment due to ^{13}C–D and D–D clumped-isotope effects in ethane, leading to small relative errors in the apparent equilibrium temperature, ranging from 5 K at 273.15 K to 30 K at 873.15 K. We additionally note that the rotameric dependence of isotopologue enrichment must be carefully considered when using the Urey model, whereas the path-integral calculations automatically account for such effects due to configurational sampling. These findings are of direct relevance to future clumped-isotope studies of ethane, as well as studies of ^{13}C–^{13}C, ^{13}C–D, and D–D clumped-isotope effects in other hydrocarbons.
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1. INTRODUCTION

The isotopic composition of a material embeds a wealth of information regarding its origin and history (Schoell, 1984; Whiticar, 1990; Sturup et al., 2008; Wolfsberg et al., 2009; Eiler, 2013). Although stable isotope analysis typically focuses on the bulk isotopic composition of materials, which is often dominated by the concentration of molecules containing only one rare isotope, recent advancements in analytical methods enable the explicit and precise measurement of multiply substituted isotopologues (isotopologues

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with two or more rare-isotope substitutions) at natural abundances (Eiler and Schauble, 2004; Affek and Eiler, 2006; Eiler, 2007; Yeung et al., 2012; Eiler et al., 2013; Stolper et al., 2014; Ono et al., 2014; Wang et al., 2015; Magyar et al., 2016; Young et al., 2016). The rich diversity of both equilibrium and non-equilibrium fractionation behavior of multiply substituted isotopologues could help to identify or place additional constraints on formation temperatures, sources, or reaction pathways in a variety of molecular systems and organic compounds (see Eiler, 2013; Eiler et al., 2014, and references therein).

Recent innovations in isotope-ratio mass spectrometry, infrared absorption spectroscopy, nuclear magnetic resonance techniques, and other instrumentation that can preserve the original bonding connectivity of the analyte enable measurements of isotopically 'clumped' species, in which rare isotopes are spatially co-localized in a molecule (Eiler, 2007; Eiler et al., 2014). At equilibrium, this co-localization of rare isotopes leads to relative enrichment of clumped isotopologues compared to what would be expected from the random distribution of the composite isotopes at natural abundance (Wang et al., 2004). Importantly, this relative enrichment at equilibrium is a function of temperature that depends only on the energetics of homogeneous isotope exchange among isotopologues and not on the absolute abundances of the isotopes themselves, which can vary based on sample origin. Therefore, a useful application of clumped-isotope measurements is to provide a paleothermometer based on the extent of ^{13}C–^{18}O ordering in carbonate ions (Ghosh et al., 2006; Eiler, 2011), which has been employed to reconstruct ancient marine ocean environments (Finnegan et al., 2011; Grauel et al., 2013), estimate mountain uplift rate (Ghosh et al., 2006), characterize diagenesis (Huntington et al., 2011), and understand the thermal physiology of extinct vertebrates (Eagle et al., 2010, 2011). More applications of clumped-isotope measurements are emerging, as recent studies have demonstrated capabilities to source methane (Eiler, 2007; Stolper et al., 2014; Stolper et al., 2014; Stolper et al., 2015; Wang et al., 2015; Douglas et al., 2016; Young et al., 2016; Wang et al., 2016) and to identify biological signatures in molecular oxygen (Yeung et al., 2015 and nitrous oxide Magyar et al., 2016).

A natural extension of existing clumped-isotope applications would be to utilize clumped-isotope signatures in hydrocarbon exploration or in stable isotope studies of other organic matter. Carbon and hydrogen isotope ratios have long been used to unravel the complex origins or source processes of samples in geochemistry and biogeochemistry (Craig, 1953; Schoell, 1984; Freeman et al., 1990; Hayes et al., 1990; Clayton, 1991; Sessions et al., 1999), and clumped-isotope measurements would add additional constraints and dimensions to this analysis (Ma et al., 2008; Stolper et al., 2014; Eiler, 2013; Wang et al., 2015; Young et al., 2016). Ethane is the simplest molecule that feasibly exhibits ^{13}C–^{13}C, ^{13}C–D, and D–^{12}C–D (henceforth referred to as D–D) clumping effects that could be used to probe fractionation history. Clumping effects in ethane would indicate the balance of thermodynamic and kinetic factors affecting the distribution of isotopes in kero-

gen, coal, petroleum, and natural gases (Clog et al., 2012; Clog and Eiler, 2014; Clog et al., 2014) and may additionally provide insights into the chemistry of more complex organic molecules. Many factors–including gas wetness, diffusion, maturation, and degradation–are likely to affect observed experimental signatures in ethane and other hydrocarbons. However, measurements of clumping in some methane isotopologues have either indicated isotopic equilibrium or partial equilibrium conditions, and deviations can otherwise characterize kinetically controlled formation pathways (Stolper et al., 2014,, 2015; Ono et al., 2014; Wang et al., 2015; Douglas et al., 2016; Young et al., 2016; Wang et al., 2016). Therefore, a natural starting point for ethane is quantify the enrichment of isotopologues due to isotopic clumping at equilibrium conditions.

In previous work, we used path-integral methods to compute equilibrium clumped-isotope effects in carbon dioxide and methane (Webb and Miller, 2014), finding that results obtained within the harmonic approximation via the widely used Urey model (Urey, 1947; Bigeleisen and Mayer, 1947) benefited from a large cancellation of errors. However, clumped-isotope effects were not examined in any molecules that exhibit torsional motions. Here, we rigorously and accurately compute equilibrium clumped-isotope effects for the flexible ethane molecule using path-integral Monte Carlo methods and a new full-dimensional, isotopically independent intramolecular potential energy surface that is parameterized from more than 900 energies and gradients at the B3LYP/aug-cc-pVTZ level of theory. We compute fractionation factors for five double-isotope exchange reactions of ethane as functions of temperature. The path-integral calculations are converged to within anticipated experimental precisions of high-resolution mass spectrometry, and comparison among the various equilibrium constants reveals the effect of isotopic clumping on the enrichment of doubly substituted ethane isotopologues. The results of the path-integral calculations are further compared to those obtained via the Urey model, elucidating the errors in this widely used model.

2. METHODOLOGY

2.1. Enrichment of doubly substituted isotopologues

The relative equilibrium enrichment of an isotopologue is quantified as

$$\Delta_i = 1000 \left[\frac{(x_i/x_0)_{eq}}{(x_i/x_0)_r} - 1 \right], \tag{1}$$

where x_i/x_0 is the abundance of an isotopologue, i, relative to that with no rare-isotope substitutions. The notation $(\cdots)_{eq}$ indicates an observed quantity at equilibrium conditions, while $(\cdots)_r$ indicates a quantity obtained from the stochastic distribution, in which the composite isotopes are distributed randomly among all isotopologues subject to their absolute abundance (Wang et al., 2004; Affek and Eiler, 2006; Eiler, 2007). While x_i in Eq. (1) depends on the absolute abundances of its composite isotopes, Δ_i does not, instead indicating the propensity for rare isotopes to