P-05

Poster Session Day 1

Quantum chemical temperature dependent investigation of ^{13}C, D and clumped kinetic isotope effects in the reactions of methane with OH and Cl from 200 to 500 K

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Methane emissions source budgets based on $\delta^{13}C\text{-}CH_4$, $\delta D\text{-}CH_4$, $^{13}CH_3D$ and/or CH_2D_2 rely on a handful of measurements of the kinetic isotope effect (KIE) of the atmospheric methane oxidation reactions, results obtained at only a couple of temperatures. The goal of this study is to better characterize KIEs of the reactions and especially the temperature dependence of the KIEs. We have calculated the temperature dependent reaction rates using Eckart tunneling corrected Transition State Theory for temperatures ranging from 200 to 500 K. We examine the reaction of methane with chlorine and hydroxyl including all possible transition states with the isotopologues: CH_4, $^{13}CH_4$, $^{14}CH_4$, $^{13}CH_3D$, CH_3D, CH_2D_2, CHD_3, and CD_4. Transition State Theory has been used with M06-2X, ωB97X-D, and CAM-B3LYP level of theory, with the two basis sets 6-31++G(d,p) and 6-311++G(d,p). The KIE is calculated for all reactions and compared with literature. This study will increase our understanding of the oxidation of methane and compare the quantum chemical understanding of isotope budgeting to observations.