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Calculating Singly and Doubly-Substituted Methane KIE Values in Atmospheric Sink Reactions Using CCSD and CCSD(T)

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Methane (CH_4) is the second most important long-lived atmospheric greenhouse gas with the global average increase of ~6 ppb/year. With an atmospheric lifetime of ~10 years, the primary sink of atmospheric methane is •OH (~90%); reactions with Cl• in the stratosphere and the marine boundary are responsible for an additional ~6%. The remaining sinks include soil reactions as well as a small loss due to reaction with O(1D), mostly occurring in the stratosphere. However, there is still a lack of information on the precise methane lifetime, the processes that govern atmospheric methane removal, and the concentrations of sink radicals in the atmosphere.

Due to the Kinetic Isotope Effect (KIE), atmospheric sink reactions are slower for heavier methane molecules with rare heavy isotopes especially in the D-substituted methane isotopologues. Therefore, KIE generates a distinct signature of higher D/H in air relative to the total source composition. Methane KIEs provide crucial insights into methane transformation processes in atmospheric chemistry, biogeochemical cycles, as well as constraining more precise atmospheric models. Atmospheric methane sinks and the KIEs and their temperature dependency have been the subject of experimental and theoretical studies. Recent developments in analytical techniques have offered the opportunity of measuring doubly- substituted isotopologues of methane along with the singly-substituted ones and applying them as a tool for tracking atmospheric methane sinks. *Ab initio* calculations which provide information about all isotopologues have not yet converged on same KIE as measured in experiments. Here we use first-principles electronic structure calculations using CCSD and CCSD(T)/aug-cc-pVTZ level of theory to recalculate KIE for $^{12}CH_4$, $^{13}CH_4$, $^{13}CH_3D$, and $^{12}CH_2D_2$ using transition state theory (TST) framework. All electronic structure calculations are made with the Gaussian 16 software package. These model chemistries do well at reproducing previous measurements and providing a higher precision theoretical calculations of structural and vibrational properties of methane in sink reactions.