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## High-precision determination of the temperature-dependent kinetic isotope effect for the CH<sub>4</sub> + OH reaction

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Methane (CH<sub>4</sub>) is a strong greenhouse gas, yet its global budget remains incompletely constrained. The uncertainties in its sources and sinks limit the implementation of successful mitigation. Stable isotope analysis ( $\delta^{13}\text{C-CH}_4$  and  $\delta^2\text{H-CH}_4$ ) offers powerful constraint for methane source attribution, but the accuracy of these constraints depends on accurate values of the kinetic isotope effects (KIEs) associated with its primary removal process, reaction with the OH radical.

Here, we present new laboratory measurements of both carbon and hydrogen isotope fractionation during the CH<sub>4</sub> + OH reaction. Our experimental design included extensive control runs to eliminate potential interferences from secondary radical species. In addition, we used kinetic chemical model and a reaction - transport model to verify that the observed fractionation results are exclusively driven by the OH oxidation.

We determined the fractionation across a wide temperature range to cover various atmospheric condition. Our data reveal a moderate but clear temperature dependence for both  $\delta^{13}\text{C-CH}_4$  and  $\delta^2\text{H-CH}_4$  fractionation, which is evaluated against theoretical estimates to assess its implications. These findings resolve previous literature discrepancies and provide a refined benchmark for inverse modeling applications.