## Revising the <sup>13C</sup>KIE<sub>OH</sub> and <sup>D</sup>KIE<sub>OH</sub> values for the CH<sub>4</sub>-OH sink

## C.-C. Chen<sup>1\*</sup> & T. Röckmann<sup>1</sup>

<sup>1</sup> Institute for Marine and Atmospheric research Utrecht, Utrecht University, Utrecht, The Netherlands \*Presenting Author Email: c.c.chen@uu.nl

Methane (CH<sub>4</sub>) plays a critical role in the global carbon cycle and is the second most significant anthropogenic greenhouse gas after CO<sub>2</sub>. The current global CH<sub>4</sub> mole fraction is 2.5 times higher than preindustrial levels and its isotopic signatures,  $\delta^{13}$ C-CH<sub>4</sub> as well as  $\delta$ D-CH<sub>4</sub>, are essential tools for partitioning sources and tracing its atmospheric pathway. However, there is a discrepancy between the simulated and measured values of  $\delta^{13}$ C-CH<sub>4</sub>. A major uncertainty is the isotopic fractionation (kinetic isotope effect, KIE) for the CH<sub>4</sub>-OH reaction, which is the primary sink of CH<sub>4</sub> in troposphere. Previous literature reports various KIE values for this reaction, including <sup>13C</sup>KIE<sub>OH</sub> = 1.0054 and 1.0039 as well as <sup>D</sup>KIE<sub>OH</sub> = 1.294 and 1.25. These differences introduce significant uncertainty in the global CH<sub>4</sub> isotope budget. A better knowledge of KIE values could significantly improve estimates of CH<sub>4</sub> emission sources.

To address this, the aim of this study is to revise the KIE characterization by subjecting CH<sub>4</sub> in laboratory experiments to chemical reactions with hydroxyl radicals (OH·), generated through the photolysis of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) using a deep-UV light source (200-380 nm). The reactions take place in a triple-quartz-layered reactor maintained at stable pressure and temperature conditions. Secondary products are removed using a low-temperature trap. The reactor can be directly coupled to two Isotope Ratio Mass Spectrometers (IRMS), enabling continuous measurements of the  $\delta^{13}$ C,  $\delta$ D, and  $\delta^{18}$ O in remaining CH<sub>4</sub> and CO throughout the photochemical experiments.

References

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