

## SINGLE SUBSTITUTION KINETIC ISOTOPE EFFECT MEASUREMENTS FOR CH<sub>4</sub> + O(<sup>1</sup>D) USING CAVITY RING-DOWN SPECTROSCOPY

DOUGLAS OBER, TZULING CHEN, MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA.*

As the most abundant atmospheric hydrocarbon and potent greenhouse gas, methane plays a major role in the chemistry of Earth's atmosphere. The study of kinetic isotope effects (KIEs) for H–D and <sup>12</sup>C–<sup>13</sup>C substitutions on the reaction rates for methane is of importance for modelers, but is challenging because the effects are small, and producing methane oxidants results in a variety of secondary chemistry.

In this work, the single-substitution methane KIEs were produced using the flash photolysis of different O(<sup>1</sup>D) precursors: N<sub>2</sub>O and O<sub>3</sub>, and the methane isotopic compositions were determined via frequency-stabilized cavity ring-down spectroscopy using a dual wavelength near-IR DBF laser system. Despite the different chemistry of the oxidative samples, the KIEs for both methods were found to be consistent with the literature values at room temperature of 1.060 for H–D and 1.013 for <sup>12</sup>C–<sup>13</sup>C substitutions. Further, the expected lack of a temperature-dependence of the KIE over the range 170 – 300 K was seen regardless of O(<sup>1</sup>D) precursor.