Advances in tunable infrared laser direct absorption spectroscopic measurements of clumped CH_4 isotopologues

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Measurements of methane isotopologues with two rare isotopes (e.g., $^{13}CH_3D$ and $^{12}CH_2D_2$) at natural abundances can provide new insights into the origin and evolution of methane[1]. Apparent equilibrium temperatures estimated from $\Delta^{13}CH_2D_2$ and $\Delta^{13}CH_3D$ can provide a novel geothermometer to constrain natural sources of methane gas production[1]. Whereas disequilibrium kinetic signals can provide information about the history and formation mechanism of the gas [2], as well as the presence or absence of multiple sources and sinks[3].

Here we present our progress on technological advancements using tuneable infrared laser direct absorption spectroscopy (TILDAS) for simultaneous measurements of two clumped methane isotopologues: $^{13}CH_3D$ and $^{12}CH_2D_2$. Using a 400 meter path length absorption cell and a new set of lasers, we are able to measure $\Delta^{13}CH_3D$ (deviation from stochastic abundance) with 0.02‰ precision (90-sec average). This is 10 times more precise than previously reported [4]. In addition, we are now capable of measuring $\Delta^{12}CH_2D_2$ with a precision of ~1‰ (90-sec average).

An automated inlet system allows the injection of reference and sample gases at a controlled pressure during a defined measurement cycle. We have run tests evaluating the repeatability of the measurements during 8 cycles (90-sec average) using the automatized inlet. These tests show 2 times better precision for $\Delta^{13}CH_3D$ than from the previous TILDAS instrument (0.08 vs. 0.15 ‰, respectively). The tests also showed 2 ‰ precision for $\Delta^{12}CH_2D_2$ for relatively large volume samples (about 40 mL STP).

[1] Stolper et al., *Geochim. Cosmochim. Acta*, 2015; [2] Young et al., *Geochim. Cosmochim. Acta*, 2017; [3] Haghnegahdar et al., *Global Biog. Cycles*, 2017; [4] Ono et al., *Anal. Chem.*, 2014.