Measurements of Clumped Methane Isotopologue ($^{13}CH_3D$) by Tunable Mid-Infrared Laser Spectroscopy

SHUHEI ONO[1], DAVID WANG[1], DANIELLE GRUEN[1], BARBARA SHERWOOD LOLLAR[2], BARRY MCMANUS[3], MARK ZAHNISER[3] AND DAVID NELSON[3]

[1]Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA. sono@mit.edu

[2]Department of Geology, University of Toronto, Toronto ON Canada

[3]Center for Atmospheric and Environmental Chemistry, Aerodyne Research, Inc., Billerica, Massachusetts, USA

We report the application of a tunable infrared laser direct absorption spectroscopy (TILDAS) instrument for precise measurement of doubly-isotope substituted methane, $^{13}CH_3D$. The relative abundance of $^{13}CH_3D$ may indicate the temperature at which methane is formed or thermally-equilibrated, and thus provide a new dimension of constraints on the origin of methane in various geologic settings.

The TILDAS instrument simultaneously measures absorption line strengths of four methane isotopologues ($^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$, and $^{13}CH_3D$) using two quantum cascade lasers. The narrow line width (<10 MHz) of the laser enables high spectral resolution and measurement of $^{13}CH_3D$ line strength virtually free from interference.

A dual-inlet sample introduction manifold with two adjustable bellow volumes was constructed and interfaced with the TILDAS instrument. Long term (>2 months) precisions (2σ) are ±0.1‰ for the ratio $^{13}CH_4/^{12}CH_4$ and $^{12}CH_3D/^{12}CH_4$, and ±0.2‰ for the ratio $^{13}CH_3D/^{12}CH_4$, evaluated by repeated measurements of a pair of methane samples. Our isotopologue thermometry scale is calibrated by thermally-equilibrating methane between 200 and 400°C, and is consistent with theoretical prediction within this temperature range. Calibration for lower temperatures using methanogen cultures is currently in progress [1].

The accuracy of our technique is ±0.5‰, evaluated by thermally-equilibrating methane with a range of δD-SMOW values (from -380 to +180‰). An accuracy of ±0.5‰ allows estimation of the apparent isotopologue temperature to within ±30 °C for methane scrambled at 100 °C. Our technique has been applied for measurement of $^{13}CH_3D$ in methane from natural gas [2] and other geologic sources.

[1] Gruen *et al* Goldschmidt 2014; [2] Wang *et al* Goldschmidt 2014.