Using Tunable Infrared Laser Direct Absorption Spectroscopy technique for precise $^{12}CH_2D_2$ measurements.

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Measurements of clumped methane isotopologue, $^{13}CH_3D$, can provide a temperature at which methane is generated or last equilibrated, a critically important constraint on natural gas generation[1]. It has also been shown, however, that active microbial methanogenesis can produce kinetic signals that yield methane with high apparent clumped temperatures[2].

Recently, we have used Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS) for $^{13}CH_3D$ measurements with 0.2‰ precision[3]. We will present our progress on a further technological advancement measuring $^{12}CH_2D_2$ using TILDAS. Measurements of $^{12}CH_2D_2$ (with fractional abundance 144 ppb) is challenging but is worthwhile since it can be used to distinguish equilibrium vs non-equilibrium methane[2].

We simulated and measured line positions and strengths of $^{12}CH_2D_2$ in the spectral region corresponding to C-H and C-D bending vibrational bands $\nu_4(A_1)$, $\nu_7(B_1)$, $\nu_9(B_2)$, $\nu_5(A_2)$ and $\nu_3(A_1)$ at 900 to 1500 cm^{-1} regions. We identified a $^{12}CH_2D_2$ line at ~ 1090 cm^{-1} that is free of spectral interference from absorption by other methane isotopologues. Using a newly developed 400 meter absorption cell and probing two spectral regions, we are able to simultaneously measure the five major methane isotopologues. The precision of the instrument approaches to ~ 1 ‰ for $^{12}CH_2D_2$ abundance. Since $^{12}CH_2D_2$ presents aproximately five times larger clumped isotope effect compared to $^{13}CH_3D$, we expect to have similar precision on the temperature estimation from our previous $^{13}CH_3D$ TILDAS instrument[2]. In equilibrium, consistent temperatures estimated from $\Delta^{12}CH_2D_2$ and $\Delta^{13}CH_3D$ will provide reliable thermometry.

[1]Wang et al., *Science*, 2015; [2]Young et al., *Geochim. Cosmochim. Acta*, 2017; [3] Ono, S., et al., *Anal. Chem.*, 2014.