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Analysis of methane clumped isotopologues with laser absorption spectroscopy

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Clumped isotope thermometry deals with the relative abundance of molecules that contain more than one of the rare isotopes. For methane, $^{13}CH_3D$ and $^{12}CH_2D_2$ isotopologues have been recently proposed as promising tracers in geological, biogeochemical, and atmospheric studies. Their relative abundance denoted as $\Delta^{13}CH_3D$ and $\Delta^{13}CH_3D$ is a direct temperature proxy which may, however, also be influenced by kinetic isotope effects. Therefore, thermometry using two independent clumped isotopologues increases the reliability of temperature reconstruction, since departures from thermodynamic equilibrium can be interpreted with respect to kinetic processes or mixing of methane from various methane formation pathways [1,2].

We present an analytical technique based on direct absorption laser spectroscopy for precise, direct, and simultaneous detection of all isotopologues involved in the isotope exchange reactions $^{12}CH_4 + {}^{13}CH_3D = {}^{13}CH_4 + {}^{12}CH_3D$ and $^{12}CH_4 + {}^{12}CH_2D_2 = 2\cdot{}^{12}CH_3D$. In contrast to HR-IRMS, which requires ultra-high mass-resolving power $M/\Delta M > 30000$ to achieve a reasonable selectivity for M/z = 18 isotopologues, optical detection is intrinsically free from isobaric interferences and is capable to analyze comparable amounts of sample within a measurement time of tens of minutes. We achieved a precision of 0.02‰ and 0.2‰ for $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, respectively, with an external reproducibility of better than 0.1‰ and 1‰ (1σ) for 10 reference-sample repetitions. The instrument employs two quantum cascade lasers (DFB QCL, Alpes Lasers) emitting around 8.6 µm and 9.3 µm spectral regions to simultaneously probe the transitions of all five above-mentioned isotopologues. An astygmatic Herriott-type optical multipass cell with 413 m optical path length (Aerodyne Research Inc.) allows for working with pure methane samples as little as 10 ml to enable the measurement of both $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$. Rare isotopologues line positions and intensities were surveyed using high-resolution FTIR spectroscopy and validated by laser spectroscopy. The instrument is coupled to a fully automated inlet system and a cryogen-free methane preconcentration unit [3]. Relevant aspects of instrument calibration using methane re-equilibrated in 50-300°C range over γ-Al_2O_3 catalyst and overview of future applications will also be discussed.

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