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Session 5a) Novel Methodology 1: Application of Isotopologue Measurement

Rapid and high-sensitivity analysis of methane clumped isotopes ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$) using mid-infrared laser spectroscopy

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In the past decade, advancements in techniques for methane clumped isotope analysis ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$) have enabled a more detailed tracing of CH_4 pathways, especially in cases where multiple processes and sources are involved. These paired datasets can serve as proxy for investigating CH_4 formation temperatures or for studying the contributions of kinetically controlled processes [1]. To date, paired CH_4 clumped isotope ratios are mainly analyzed by HR-IRMS, achieving a precision of better than 0.3‰ for $\Delta^{13}CH_3D$ and 1.5‰ for $\Delta^{12}CH_2D_2$ with sample size of 3-5 mL [1,2]. Alternatively, mid-infrared laser absorption spectroscopy offers rapid, non-destructive analysis of CH_4 clumped isotopes. However, current method requires sample sizes of 20 mL, which significantly limits its applicability for natural samples [3].

To enhance the performance of spectroscopic measurement of CH_4 clumped isotopes, we established a laser spectroscopic platform with optimized spectral windows: 1076.97 cm^{-1} for CH_2D_2 and 1163.47 cm^{-1} for $^{13}CH_3D$, and a custom-built gas inlet system. This was achieved by conducting an extensive spectral survey on newly recorded HR-FTIR spectra across the wavelength range of 870 cm^{-1} to 3220 cm^{-1}, thereby addressing gaps in existing spectral databases for $^{12}CH_2D_2$. In addition, we implemented several key technological advances, which result in superior performance during sample injection and analysis.

We demonstrated the feasibility of reducing sample size down to 3–7 mL CH_4 gas, achieving precision levels comparable to that of HR-IRMS. Specifically, for sample sizes ranging from 3–10 mL, achieving a precision better than 1.5‰ in $\Delta^{12}CH_2D_2$ requires 4–6 repetitive measurements using a recycle-refilling system, while for sample volumes greater than 10 mL, measurements can be completed within 20 mins. These advancements in reducing sample size and shortening analysis time make the spectroscopic technique a more practical tool for analyzing the clumped isotope signatures of natural CH_4 samples, in particular for applications with low CH_4 concentrations or requiring consecutive analyses, potentially in conjunction with an automated pre-concentration system.

References

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