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Laser Spectroscopic Monitoring and Calibration of 13C18O16O and 12C17O16O in Atmospheric Carbon Dioxide

David Nelson (1), Joanne Shorter (1), Shuhei Ono (2), Barry McManus (1), and Mark Zahniser (1)

(1) Aerodyne Research, Inc., Billerica, United States (ddn@aerodyne.com), (2) MIT, Earth, Atmospheric, and Planetary Sciences, Cambridge, United States

One of the main challenges to making accurate predictions of future changes in CO_2 concentration is the capability to determine what fraction of human produced CO_2 remains in the atmosphere. We present our progress in the application of Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS) to the measurement of the primary clumped (13C18O16O) as well as 17O (12C17O16O) isotopologues of atmospheric CO_2. We expect unique isotopologue signals in CO_2 from high-temperature combustion sources, plants, soils, and air-sea exchange processes. High sampling frequency (a few minutes for each sample) can be achieved and is expected to reveal local heterogeneous sources and temporal variations.

The TILDAS is equipped with a 400-meter optical absorption cell which provides sufficient sensitivity for direct measurements of the rare clumped isotopologue. We designed a dual pressure measurement technique in which the clumped isotopologue, 13C18O16O, and 13C16O16O are first measured at $\sim$ 30 torr cell pressure. This is followed by measurement of the more abundant isotopologues, 12C17O16O, 12C18O16O and 12C16O16O, at much lower ($\sim$5 torr) cell pressure. Isotopologue ratios are compared between reference and sample gases. Preliminary tests demonstrated a precision approaching 0.03 ‰ for the ratio 13C18O16O/13C16O16O and 0.08‰ for Δ13C18O16O value (1σ repeatability for 4 min sample vs. reference cycle). Sample size for a single analysis is approximately 100 mL of air (1.6μmol of CO_2). Given the previously observed range of variations for Δ13C18O16O and Δ17O in atmospheric samples (as large as 0.6 and 0.3 ‰ respectively), TILDAS offers the possibility of real time, nearly continuous monitoring of these signals.

Achieving better than 0.1‰ precision requires careful matching of CO_2 mixing ratios between reference and sample air. A primary cause of pressure and mixing ratio dependence is inaccurate baseline fitting (analogous to abundance sensitivity or pressure baseline for IRMS). Given that mixing ratios of atmospheric CO_2 can vary as much as 50% or more, a dynamic dilution scheme, where sample air is diluted by CO_2 free air to match the reference mixing ratio, is being developed. An in-line calibration source that equilibrates the clumped isotope of CO_2 over a heated catalyst is also being tested and shows promise. We will discuss the current instrument performance, areas for improvement, and future applications.