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Recent progress in development of infrared laser based instruments for real-time ambient measurements of isotopologues of carbon dioxide, water, methane, nitrous oxide and carbon monoxide

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The capacity for real time precise in situ measurements of isotopic ratios of a variety of trace gases at ambient concentrations continues to create new opportunities for the study of the exchanges and fluxes of gases in the environment. Aerodyne Research has made rapid progress in laser based instruments since our introduction in 2007 of the first truly field worthy instrument for real time measurements of isotopologues of carbon dioxide. We have focused on two instrument design platforms, with either one or two lasers. Absorption cells with more than 200 meters path length allow precise measurements of trace gases with low ambient concentrations. Most of our systems employ mid infrared quantum cascade lasers. However, recently available 3 micron antimonide based diode lasers are also proving useful for isotopic measurements. By substituting different lasers and detectors, we can simultaneously measure the isotopic composition of a variety of gases, including: H_2O, CO_2, CH4, N2O and CO.

Our newest instrument for true simultaneous measurement of isotopologues of CO_2 ($12CO_2$, $13CO_2$, 12C18O16O) has (1 s) precision better than 0.1 per mil for both ratios. The availability of 10 Hz measurements allows measurement of isotopic fluxes via eddy correlation. The single laser instrument fits in a 19 inch rack and is only 25 cm tall. A two laser instrument is larger, but with that instrument we can also measure clumped isotopes of CO_2, with 1 second precisions of: 2.3 per mil for 13C18O16O, and 6.7 per mil for 13C17O16O. The sample size for such a measurement corresponds to 0.2 micromole of pure CO_2. Another variation on the two laser instrument simultaneously measures isotopologues of CO_2 ($12CO_2$, $13CO_2$, 12C18O16O) and H_2O (H216O, H218O, HD16O). Preliminary results for water ratio precisions (in 1s) are 0.1 per mil for H218O and 0.3 per mil for HD16O, simultaneous (1 s) precisions for isotopologues of CO_2 of $\sim$0.1 per mil.

Methane, nitrous oxide and carbon monoxide have such low ambient concentrations that real-time isotopologue measurements are a serious challenge. For these gases, we typically use our 200 m absorption cell. Several of these instruments have already been used for long term field measurements of isotopologues of methane, (12CH4, 13CH4), with a demonstrated (1 s) precision of 1.5 per mil. A new version of this instrument operating near 3.3 microns has recently been developed to quantify 13CH4 and CH3D simultaneously. In separate experiments at MIT, using trapped concentrated samples, we have made highly precise measurements of the abundance of the clumped isotope of methane: 13CH3D.

We are also developing methods to monitor the isotopic abundance of the isotopes of CO and N2O. We have achieved a measurement precision for ambient 13CO (1 s) of 1.9 per mil. For the isotopologues of N2O (14N216O, 14N15N 16O, 15N14N 16O, 14N218O), we have demonstrated (1 s) precision at ambient levels (320 ppb) of $\sim$3 per mil. For N2O, a quasi continuous preconcentrator has been used to give even better precisions (<0.1 per mil) and one is being developed for CO.