Measurement of Nighttime Nitrogen Oxides and Ozone by Cavity Ring Down Spectroscopy during SENEX 2013

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Figure 1. Nitrogen oxide CRDS instrument during CalNex 2010

Nitrogen oxides play important roles in numerous atmospheric chemical cycles. Daytime chemical cycling of NO and NO_2 is the mechanism for tropospheric ozone production, while nighttime chemistry of NO_3 and N_2O_5 is important to nitrogen oxide and ozone budgets, biogenic VOC oxidation, aerosol formation, and halogen activation. Cavity ring-down spectroscopy (CRDS) is a high sensitivity optical technique for the measurement of trace gas concentration applicable to the measurement of nitrogen oxides. The NOAA CRDS instrument for nitrogen oxides and ozone is based on two visible diode lasers at 662 nm (for detection of NO_3) and 405 nm (for detection of NO_2) [*Wagner et al.*, 2011]. Inlet conversions allow the measurement of additional species. Figure 2 shows a schematic of the instrument.

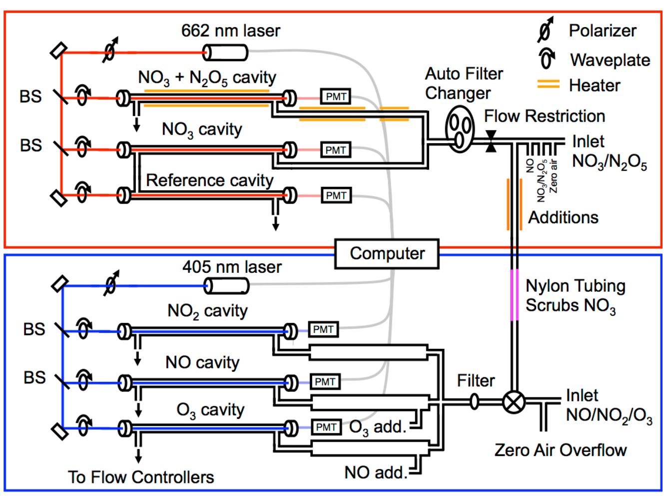

Figure 2. Schematic of the nitrogen oxide CRDS instrument

One 662 nm channel provides a direct measurement of NO_3, while a second 662 nm channel with a heated inlet provides a measurement of the sum of NO_3 and N_2O_5 via thermal dissociation of N_2O_5 to NO_3. Both channels are zeroed by addition of NO to the inlet, which reacts rapidly with NO_3, but not with other species that absorb 662 nm light, such as ambient NO_2, O_3 or water vapor.[*Dubé et al.*, 2006]

$$NO_3 + NO \rightarrow 2NO_2 \qquad (1)$$

The NO_2 produced in this reaction has an absorption cross section nearly 10^4 times smaller than NO_3 and does not interfere with the NO_3 measurement.

There are three channels at 405 nm. The first detects NO_2 directly by total optical extinction at this wavelength, which is specific to NO_2. The second channel has an addition of excess O_3 to convert NO to NO_2 to measure total NO_x (=NO + NO_2) via reaction (2) [*Fuchs et al.*, 2009].

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2)$$

A third 405 nm channel has an addition of excess NO to quantitatively convert O_3 to NO_2 to measure total O_x (=O_3 + NO_2), also via reaction (2) [*Washenfelder et al.*, 2011]. Differencing between the NO_x, O_x channels and the NO_2 channel provides measurement of NO and O_3, respectively. The zero for the 405 nm channel consists of addition of scrubbed air to the inlet. All channels operate at a repetition rate of 4 Hz, with 1 Hz measurement precision (2σ) of < 3 pptv for NO_3 and N_2O_5, < 100 pptv for NO_2 and < 150 pptv for NO and O_3.

The CRDS operation during SENEX will be similar to that of the CalNex 2010 campaign, although with several design improvements for ease of calibration and instrument automation.

References

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