

A Mid-IR, Wavelength-Scanned, Cavity Ring-Down Spectrometer for Continuous Trace N₂O and Nitrogen Isotope Measurements

PICARRO

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Abstract

We report the design and performance of a first-generation, wavelength-scanned, cavity ring-down spectroscopy (WS-CRDS)-based analyzer utilizing a QCL with a center wavelength near 4.55 μm. Its design is based on Picarro's commercial WS-CRDS. These portable gas and isotope analyzers currently utilize one or more tunable, narrowband, near-infrared lasers to provide ppbv-level detection of several gases including CO₂, CH₄, H₂O and various isotopes. However, detection of N₂O at the ppbv level requires the use of longer, mid-infrared wavelengths. The advent of compact, tunable, quantum cascade lasers (QCLs) operating at room temperature in the mid-IR has recently enabled practical instrumentation at this wavelength range. Moreover, the long effective optical path length—over 15 km—of WS-CRDS and corresponding high signal-to-noise ratio inherent in this time-based measurement means that high precision can be achieved with simple thermoelectric cooling of the laser and detector.

Based on the field performance of existing WS-CRDS-based greenhouse gas analyzers and the known extinction coefficients for the target mid-IR N₂O spectral lines, the targeted precision is <0.1 ppbv in only seconds of data acquisition time. Nitrogen isotopes in N₂O can also be analyzed at the sub-permil level with this instrument. We are designing a turnkey solution with the same ease of use and reliability as Picarro's existing near-IR instrumentation.

Need for high-precision analyzers

Nitrous oxide (N₂O) is an important trace atmospheric gas with both a greenhouse effect and a role in ozone depletion. The globally averaged surface abundance of N₂O was 314 ppb in 1998, corresponding to a global burden of 1510 TgN. The atmospheric burden of nitrous oxide continues to increase by about 0.25%/yr. The detailed impact of N₂O cannot, however, be accurately assessed or mitigated as there is currently no quantitative analysis tool for N₂O (and isotopes of nitrogen) that combines the requisite precision (sub-ppbv) with the rugged simplicity, low-drift and hands-free operation necessary for real-time field studies at unattended monitoring stations. In fact, the only laboratory tool capable of delivering this sensitivity—gas chromatography—is slow, relatively complex and labor intensive. Further, the utility of in-situ atmospheric nitrogen isotope analysis is practically nonexistent due to the impracticality of using isotope ratio mass spectrometry equipment in the field.

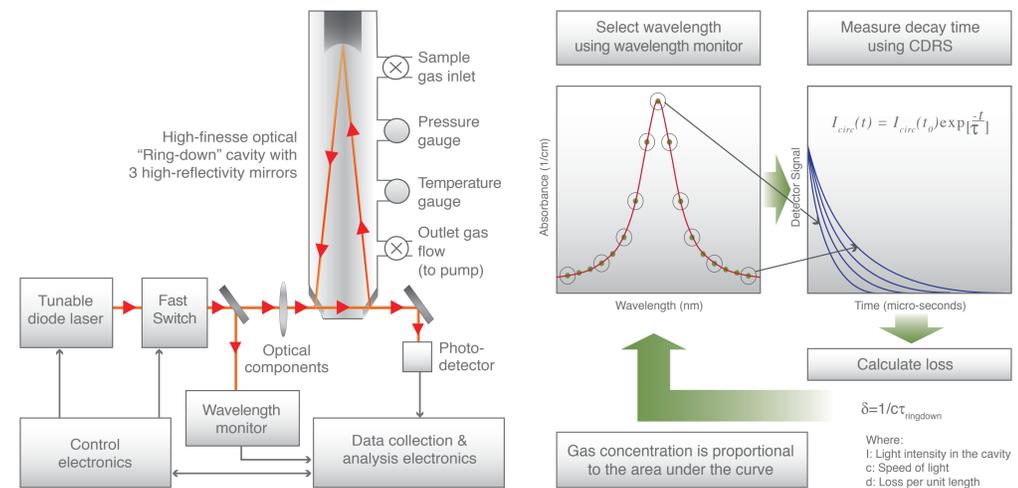
Why work in the mid-IR? Pluses and Minuses

- + The absorption signals correspond to fundamental rotational and vibrational modes of gaseous molecules; hence the lines are much stronger
- + Many molecules have weak or no absorption in the near-IR and visible ranges. Spectroscopy of these compounds is accessible only in the mid-IR
- Optical technology is not very mature at wavelengths beyond the telecommunication band (1.6 μm) making instrument design challenging (e.g. commonly available components like optical isolators are not commercially available)
- The energy of mid-IR photons is significantly closer to the thermal energy (proportional to kT). This leads to detection systems that have lower signal to noise ratios or require cooling to below room temperature and are ultimately limited by background black-body radiation

Performance Goals

N₂O Concentration < 0.2 ppbv in 30s
 <0.2 ppbv drift in 24 hours
 < 0.5 ppbv drift in 1 month
 $\delta^{15/14}\text{N} < 1\text{‰}$ in 5 minutes
 $\delta^{18/16}\text{O} < 1\text{‰}$ in 5 minutes

How can a measurement of time be used to quantify concentrations or isotope ratios?



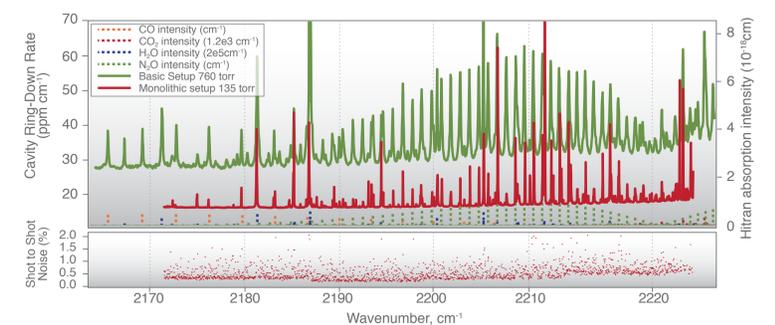
Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) – How it Works

- Light from a tunable semiconductor diode laser is directed into an optical resonator cavity containing the continuously-flowing analyte gas.
- When the optical frequency matches the resonance frequency of the cavity, energy builds up in the cavity.
- When the build-up is complete, the laser is shut off.
- Light circulates in the cavity ~100,000 times, traveling many km. The high precision of WS-CRDS comes from this long interaction pathlength providing parts-per-trillion detection levels for some gases.
- The energy decays from the cavity (through a partially-reflective mirror) exponentially in time, or "rings down," with a characteristic decay time. This energy decay is measured, as a function of time, on a photodiode.
- The ring down time measurement is continuously repeated (~100 times per second) at several different well-controlled points in wavelength as the laser is tuned across the molecular signature of the analyte gas.
- WS-CRDS is a measurement of time not of absorbance. When the laser is at a wavelength where the gas in the cavity is strongly absorbing, the ring down time is short; when the wavelength is such that the gas does not absorb, the ring down time is long. WS-CRDS has complete immunity to laser noise since the laser is actually off during the measurement.
- The gas concentration or isotope ratio is determined by a multi-parameter fit to this lineshape (red curve) and is proportional to the area under the curve. The vertical axis is loss (or absorption, measured with cavity ring down); the horizontal axis is wavelength (measured with Picarro Wavelength meter).

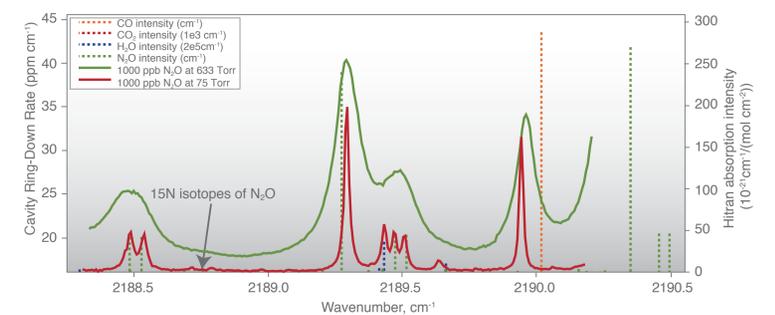
Instrument design

- Utilize newly available room-temperature (TE cooled) mid-IR sources and detectors
- Single-frequency, CW, continuously tuned QC laser
- Photovoltaic MCT detector
- Utilize Picarro's proven wavelength monitor and ringdown cavity designs
- Mid-IR optical materials are required
- Integrate onto a common rugged baseplate

Results

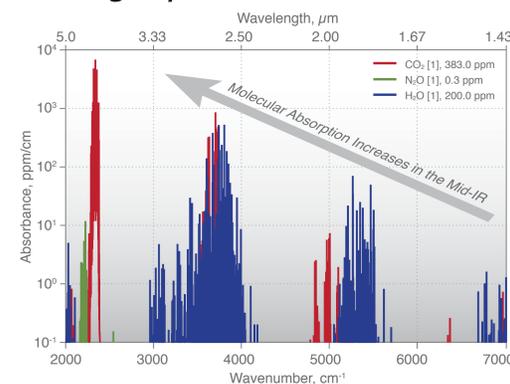


Wide scan showing the cavity ringdown rate as a function of laser wavenumber. The laser setpoint resolution is not fine enough to accurately sample the absorption lines at lower pressures. The inset shows the variation in the measured ringdown time (Shot to Shot Noise) an important measure of instrument performance as it ultimately limits the sensitivity of the concentration measurement.

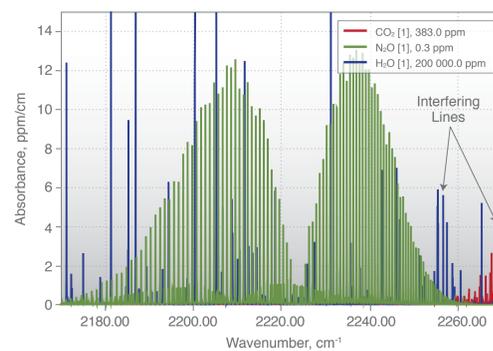


High resolution scan showing interfering and Nitrogen isotope lines.

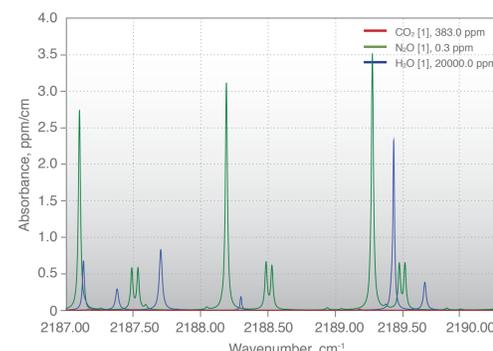
Choosing a spectral line



Hundreds of lines for any given species are available for analysis (only need one line per species to measure its concentration). We must choose which line to use.



Molecular absorption (i.e. signal) is stronger in the mid-IR.



Zooming in: choose the strongest possible molecular feature that is as free from interference as possible (example of N₂O in ambient air).

Maximizing the Advantage of CRDS

- Compact, high-finesse, ring cavity provides high sensitivity with high stability
- The 35 ml cavity volume is small enough for very rapid sample exchange with moderate flow while giving a pathlength >15 km
- High precision inline wavelength monitor with femtometer resolution maximizes selectivity resulting in spectral resolution orders of magnitude higher than FT-IR
- Accurate spectral location isolates individual spectral features and yields a measurement with high linearity
- Sub-ambient pressure operation enhances selectivity through line narrowing
- Precise temperature and sub-torr pressure stability enhances accuracy and minimizes drift
- Temperature controlled to 1 part in 3000, pressure to 1 part in 500

Summary

The analyzer is designed for continuous use both in the field and in the laboratory. Because this small-footprint instrument will not require frequent calibration and will maintain high linearity, precision, and accuracy over changing environmental conditions, the analyzer will offer low operating costs and thereby enable high-density field deployment. The ability to measure N₂O and nitrogen isotopes with both high accuracy and high precision will reduce the uncertainty in determination of terrestrial sources and sinks of this important greenhouse gas. Such knowledge is needed to improve predictive models that lead to a better understanding of the human contribution to global warming.



Planned Field Testing
 1-2 months at agricultural test site in Jylland, DK