A New Quantum-Cascade Laser Based Spectrometer for High-Precision Airborne CO_2 Measurements

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Abstract

We present a new, compact, fast response mid-IR laser spectrometer for high-precision airborne measurements of CO_2. The instrument is based on a thermoelectric-cooled, pulsed-operated DFB quantum-cascade (QC) laser. Unlike conventional cryogenically-cooled Pb-salt diode lasers, QC lasers display high mode purity and wavelength stability, and can be operated at near room temperature. This last attribute allows for a compact design and simplified operation.

The CO_2 concentration is derived from direct absorption dual-cell spectra obtained by electrical modulation at ~5-10 kHz of the laser wavelength across a selected ν_3-band transition at around 4.3 μm (typically 2311 or 2314 cm^{-1}). The measurements are thus fully specific of the CO_2 molecule and free from interference of H_2O or other mid-IR light absorbers. Sample gas humidity is nevertheless reduced to less than ~100 ppmv in order to restrain density variation effects.

Absorption spectra of the sample and a flowing standard (reference) along a 10-cm (or 5-cm) path are simultaneously detected by LN_2-cooled InSb detectors. The CO_2 concentration difference is retrieved from the differential spectrum (sample/reference). The advantages of this "null" mode operation are discussed in detail.

The spectrometer includes a mechanism that allows directing the sample beam either to the cell or to a 25-mm Ge etalon for accurate wavelength tuning rate determination. Additional technical details are discussed, including the impact of laser linewidth on the linearity of the measurements.

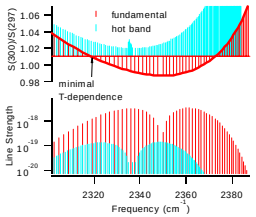
The spectrometer is enclosed in a temperature controlled, hermetically sealed vessel. The enclosure is flushed with CO_2-free dry air previous operation in order to avoid light absorption in the external path. Details on the gas temperature, pressure, and flow rate controls are also presented.

The demonstrated short-term precision of the instrument is better than ~75 ppbv $Hz^{-1/2}$ (1-sigma in 1-s integration time) for CO_2 concentrations within ±100 ppmv of the reference concentration. An accuracy of ±0.2 ppmv or better is insured through periodic calibration with high, low and "archival" standards traceable to NOAA CMDL.

Motivation

- Two NDIR CO_2 instruments developed at Harvard University have demonstrated long-term precisions better than ±0.1 ppmv during more than 300 flights [Daube, 2002]
- This stability has been achieved through tight control of temperatures and pressures and careful calibration. This is necessary because of the strong, non-linear temperature and pressure dependences inherent to the NDIR technique
- First demonstrated in 1994 [Faist, 1994], and rapidly progressing thereafter [Gmachl, 2001], the quantum-cascade laser (QCL) is today a practical laser alternative to thermal (broadband) light sources for spectroscopic detection in the mid-IR
- Unlike conventional cryogenically-cooled Pb-salt diode lasers, QC lasers display high mode purity and wavelength stability, and can be operated at near room temperature (in pulsed mode). This last attribute allows for a compact design and simplified operation

Optimal transition



- Selection criterion: Minimum temperature dependence of the linestrength (rather than maximum absorption)
- Optimum = 2319.18 cm^{-1} (P(34)) → Relative temperature dependence ~10^{-6} K^{-1} (see figure above)
- Laser not yet found at this wavelength
- Measurements have been performed at 2311.10 cm^{-1} and 2313.16 cm^{-1}. T-dependence ~ 0.3% per K
- Design insures T-stability (including of any thermal gradients) better than ±0.1 K → Allows meeting relative precision requirement of ~3×10^{-4} or better

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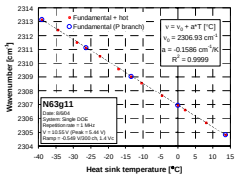
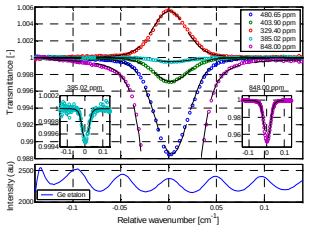
Conceptual design

- ✓Direct absorption spectroscopy
- ✓Dual beam absorption: simultaneous detection of sample and reference (~370 ppmv) spectra of absorption through optical paths of identical length (5 or 10 cm). Benefits:
  - ✓Covariant noise removal (pulse-to-pulse and scan-to scan)
  - ✓Accuracy increases as $\Delta[CO_2] \rightarrow 0$
  - ✓Cancellation to a large extent of externally-produced interference fringes and external path CO_2 absorption. This last one produces baseline distortion mainly due to detector non-linearity (saturation). In order to reduce this effect, the external paths are matched to better than ~2%, and the enclosure is flushed with CO_2-free air.
  - ✓Systematic retrieval errors are dramatically reduced. These include errors due to linewidth variation and wavelength drift
  - ✓Differential spectrum is optically thinner
- ✓Relative CO_2 concentrations (sample – reference) are derived on first principles from differential spectra (sample/reference) of fully-resolved rovibrational transitions around 2320 cm^{-1} (non-calibrated mixing ratios are accurate within better than ±5%). Periodic calibration insures an accuracy of ±0.2 ppmv or better. Real-time concentration retrieval using non-linear least squares fitting. Target precision ~ 100 ppb $Hz^{-1/2}$ or better
- ✓Measurements are fully specific of CO_2 (free from spectral interferences). Sample gas humidity is reduced to less than ~100 ppmv → Restrain density variation effects.
- ✓InSb photovoltaic detectors engineered for improved linearity (relatively high bias voltage applied)

Driving a QCL

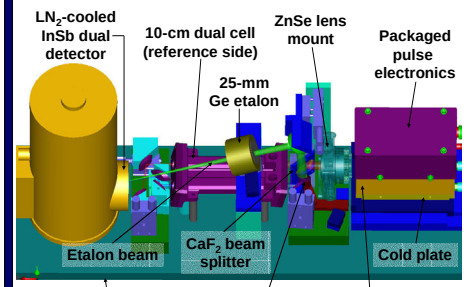


- Lasers are operated just above threshold with the shortest possible electrical pulses (12 ns) repeated at 1 MHz (~1.2% duty cycle)
- Wavelength modulation (5-10 kHz) is achieved by applying a sub-threshold current ramp, which raises the laser temperature
- Laser temperature (T_L) stability is a critical parameter. We achieve ±1 mK stability with compact commercial T-controllers
- N63g11:
  - Tuning rate ~ 0.01 cm^{-1}/mA (~50 mA → $\Delta T_L \approx$ 3 K)
  - Linewidth @ optimum ~ 0.011 cm^{-1} HWHM
- Unipolar semiconductor. Pulsed operation → Thermoelectric cooling (–40 °C to + 40 °C)
- Distributed feedback (DFB) →
  - Single mode (most cases)
  - Wavenumber is a linear function of temperature ($-\nu_0 \cdot d\nu/dT = n_{0,B} \cdot dn_B/dT \approx 7\times10^{-5}$, where n_B is the refractive index of the Bragg waveguide (figure above)
  - Linewidth is proportional to electrical pulse length (≥ 12 ns) and voltage above threshold



1-Hz differential P(40) line (2313.16 cm^{-1}) spectra relative to a 378.30 ppmv reference. Ge etalon (lower panel). Residuals ~2×10^{-4} (peak-to-peak). 3rd Degree polynomial baseline.

Airborne spectrometer



Mechanics:

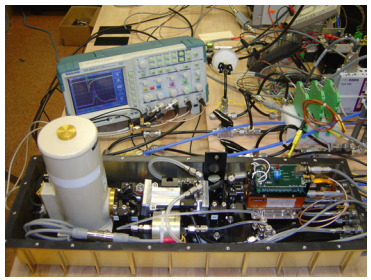
- ✓Spectrometer mounted on a vibrationally isolated optical table housed in a hermetically sealed, temperature-controlled pressure vessel (61 cm (L) × 20 cm (W) × 18 cm (H) + 10 cm dewar hat)
- ✓Components are stabilized along the detection axis

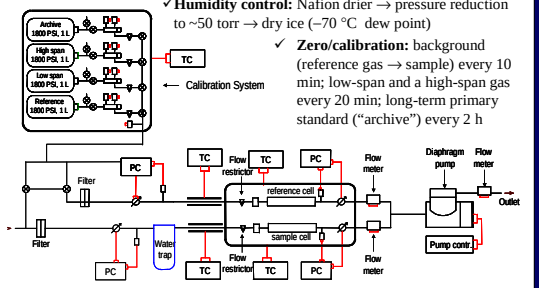
Thermal management:

- ✓Thermoelectric cooler (Peltier) heat is dumped into a small, close-circuit chiller (coolant temperature control better than ±0.2 K)
- ✓Boiled LN_2 vented outside the enclosure → 2 control valves in series
- ✓Heat generation by other components in the enclosure is negligible
- ✓Thermal control of enclosure and flowing gases will be better than ±0.1 K

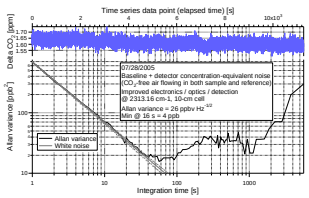
Electronics:

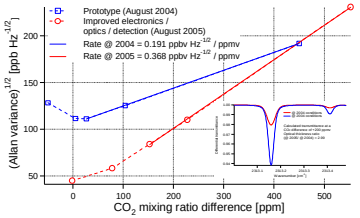
- ✓Signal generation / acquisition with 5-MHz NI cards on a PXI computer
- ✓Computer and other components are shared with a dual QCL system (CO, CH_4, N_2O – [Jiménez, 2005])
- ✓Initialization / control / housekeeping data with a CR-10 datalogger
- ✓Cell response time ~ 1 s @ ~100 sccm
- ✓Pressure, temperature and flow rates controlled similar to the NDIR CO_2 Harvard instruments
- ✓**Humidity control:** Nafion drier → pressure reduction to ~50 torr → dry ice (–70 °C dew point)
- ✓ **Zero/calibration:** background (reference gas → sample) every 10 min; low-span and a high-span gas every 20 min; long-term primary standard ("archive") every 2 h



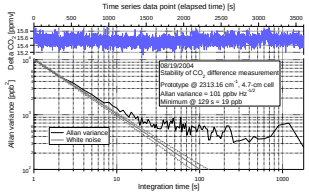


What controls the precision?





- Ratio of proportional noise slopes ~ ratio of apparent optical thicknesses (different cell length: 4.7 cm in 2004 compared to 10 cm currently) →
- Penalty on proportional noise for higher optical thickness
- Zeroing → Low-order degree polynomial → Less uncertainty in fitting (lower proportional noise)



Current concentration-equivalent noise share:

- Detector (dark) noise ~ 20 ppbv $Hz^{-1/2}$
- Baseline noise (no absorption) ~ 20 ppbv $Hz^{-1/2}$
- Dark + baseline ~ 30 ppbv $Hz^{-1/2}$ (top, left figure)
- Proportional noise ≈ fitting + shot noise (see figure above)
  - Dominates from |Δ[CO2]| ≥ 75 ppmv on
  - Rate ~ 40 ppbv $Hz^{-1/2}$ per 100 ppmv
- The overall precision is ~50 ppbv $Hz^{-1/2}$ or better for CO_2 concentration differences within ±50 ppmv. Concentrations differences above this range are only rarely encountered in the free troposphere / stratosphere (provided the reference concentration is close to the tropospheric background, ~370 ppmv)

Conclusions and perspectives

- ✓Improved linearity compared to NDIR instruments
- ✓Significant improvement in precision has been already achieved. Precision is currently better than ~50 ppbv $Hz^{-1/2}$ for small concentration differences (± 50 ppmv)
- ✓Further improvement of the short-term precision is expected. Major improvement in mid- and long-term precision is expected upon the application of rigorous control of temperatures, pressures, flow rates and water content as previously achieved with the Harvard NDIR instruments
- ✓Spectrometer is suitable for eddy covariance measurements
- ✓QCL measurements of the CO_2 isotopic composition have been also demonstrated with the same or similar lasers [McManus, 2005; Saleska, 2005; Weidmann, 2005]

Acknowledgements

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