A pulsed QC-laser based dual-spectrometer instrument for airborne measurements of CO_2, CO, CH_4 and N_2O

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Outline

- Rationale
- Spectroscopic considerations
- QCL operation
- Spectrometers and spectra (2-QCL and CO_2)
- Control systems
- Calibration
- Integration
- Conclusions and perspectives

Rationale: significance / requirements

- CO_2, CH_4 , N_2O: most important long-lived GHG
- CO → OH scavenging → oxidative capacity reduction → indirect effect on radiative balance

	Long term accuracy		(1-s) Precision [ppbv Hz$^{-1/2}$]		Atmospheric range [ppbv]		Figure of merit (FOM)	
Tracer	**ppbv**	**%**	**Target**	**Lab**	**BL-FT**	**TTL-LS**	**BL-FT**	**TTL-LS**
CO_2	200	0.05%	100	20	50,000	10,000	250	50
CO	1	1%	0.5	0.3	1,000	100	1000	100
CH_4	2	0.1%	1	0.6	500	40	250	20
N_2O	0.2	0.06%	0.1	0.06	5	20	25	100

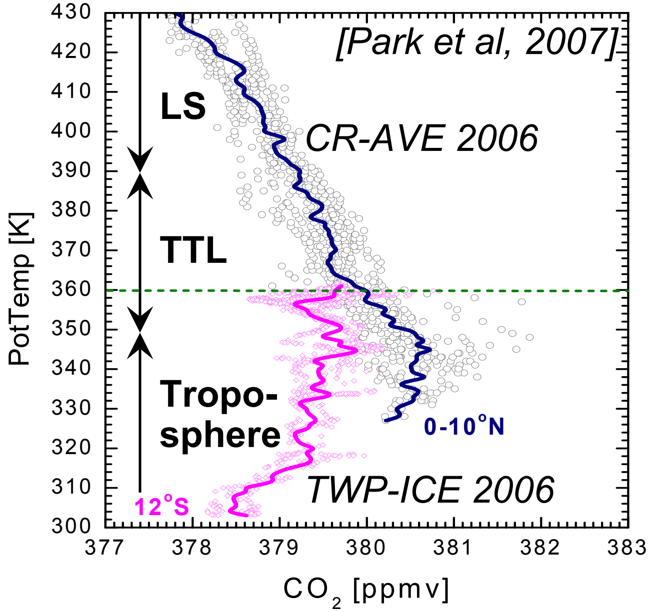
FOM = range / accuracy

Calibrations traceable to world standards;
BL: boundary layer; FT: free troposphere; TTL: tropical tropopause layer; LS: lower stratosphere

- Long-lived species (CO moderately long lived) → small atmospheric concentration range → **high fractional precision/accuracy required (≤ 0.1%)**
- Ability to resolve variation (FOM) → TTL-LS very demanding!
- Airborne → **fast response required (~1 Hz)**

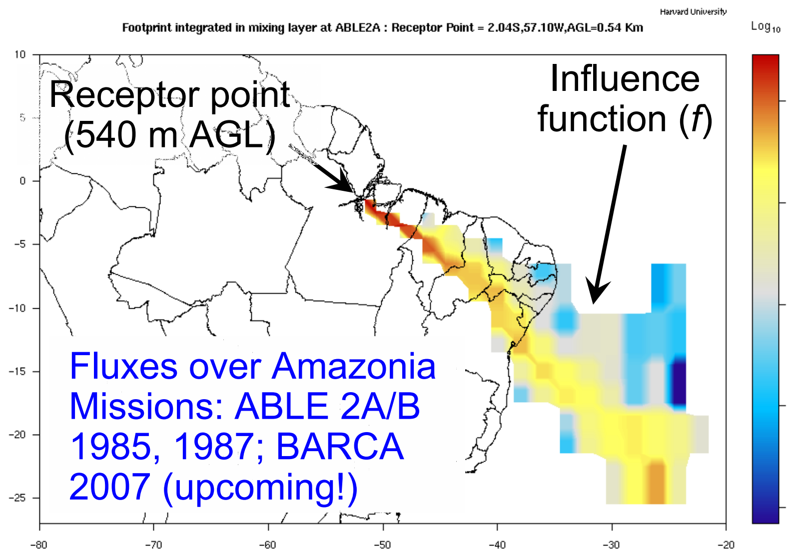
Rationale: atmospheric science goals

UT→LS transport



- TTL: stratosphere source (H_2O, GHG, SLS) region
- CO_2 clock → mean age (±100 ppbv → ±3 day precision)
- CH_4 (inter-hemispheric mix), CO, N_2O (tropo-, stratospheric influence) → constraints

GHG flux estimation



- Lagrangian approach:

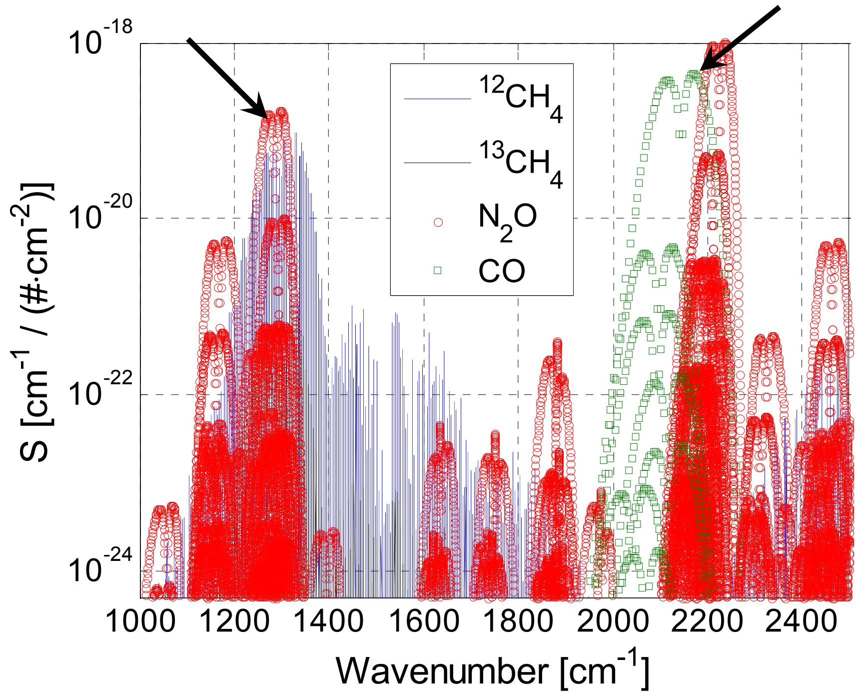
$$c = c_{BG} + \Delta c$$

$$\Delta c = \int dt \cdot \int_A E'' \cdot f \, d^2x$$

- STILT → back trajectories → (BL) influence (*f*)
- *A priori* fluxes (E") → Bayesian *a posteriori* E"

Spectroscopic considerations: DUAL

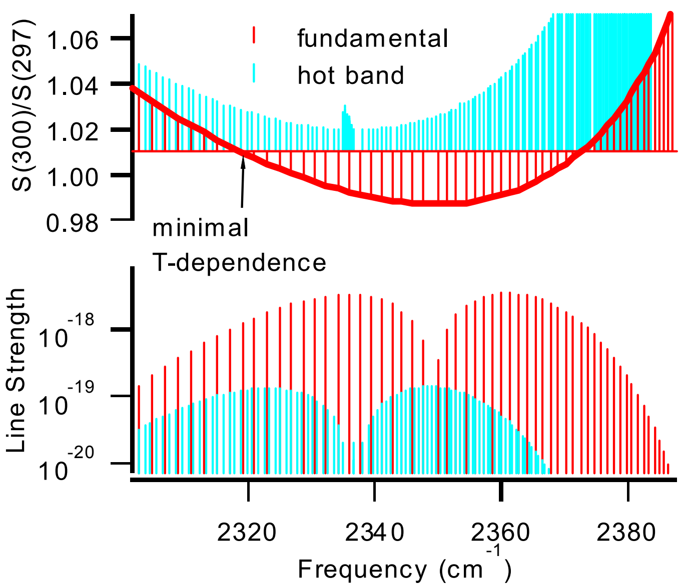
- Fundamental rovibrational transitions
- QCLs available at $\lambda > 4$ μm
- **4 species → 3 DFB QCL required** (CO_2, CO and CH_4)
- [CO_2] >> [other species] → **2 spectrometers:**
  - ***CO_2***
  - ***2-QCL* (CO, CH_4, N_2O)**
- QCLs at 7.8 μm perform better than at 4.6 μm → **N_2O measured along with CH_4**



- CH_4: υ_4, P-branch
- N_2O: υ_1, P(11) or P(16)
- CO measured at (or near) highest S (R(7), 2172.76 cm^{-1})

Spectroscopic considerations: CO_2

- CO_2 → most demanding fractional precision requirement (~0.01%)
- High stability → minimum $\partial S/\partial T$ rather than S_{max}
- Optimum at 2319.18 cm^{-1} (υ_3, P(34)) → $1/S \cdot \partial S/\partial T \approx 10^{-6}\ K^{-1}$

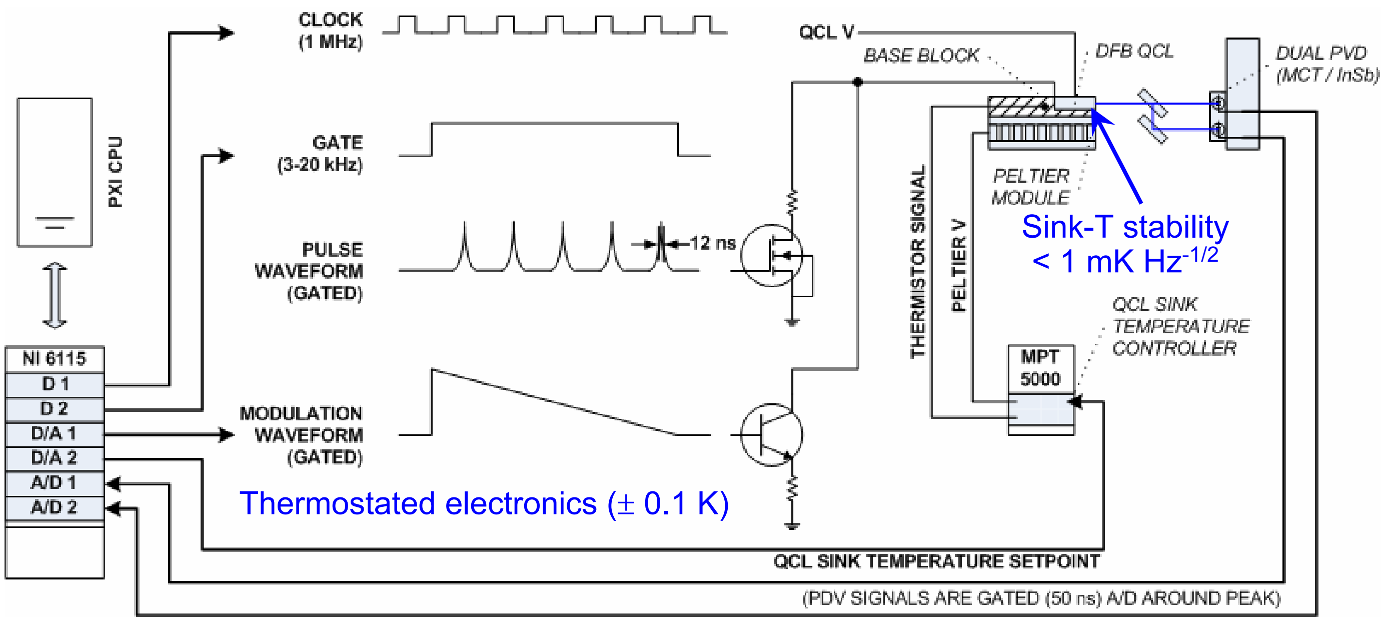


Conceptual design

- **Null method:** dual beam, differential absorption (sample / reference)
- **External paths matched**
- Balanced detection → covariance removal (e.g. due to pulse-to-pulse and linewidth variations, and wavelength drift)
- Accuracy increases as $\Delta[CO_2] \rightarrow 0$
- Differential spectrum is optically thinner
- Cancellation of external interference fringes

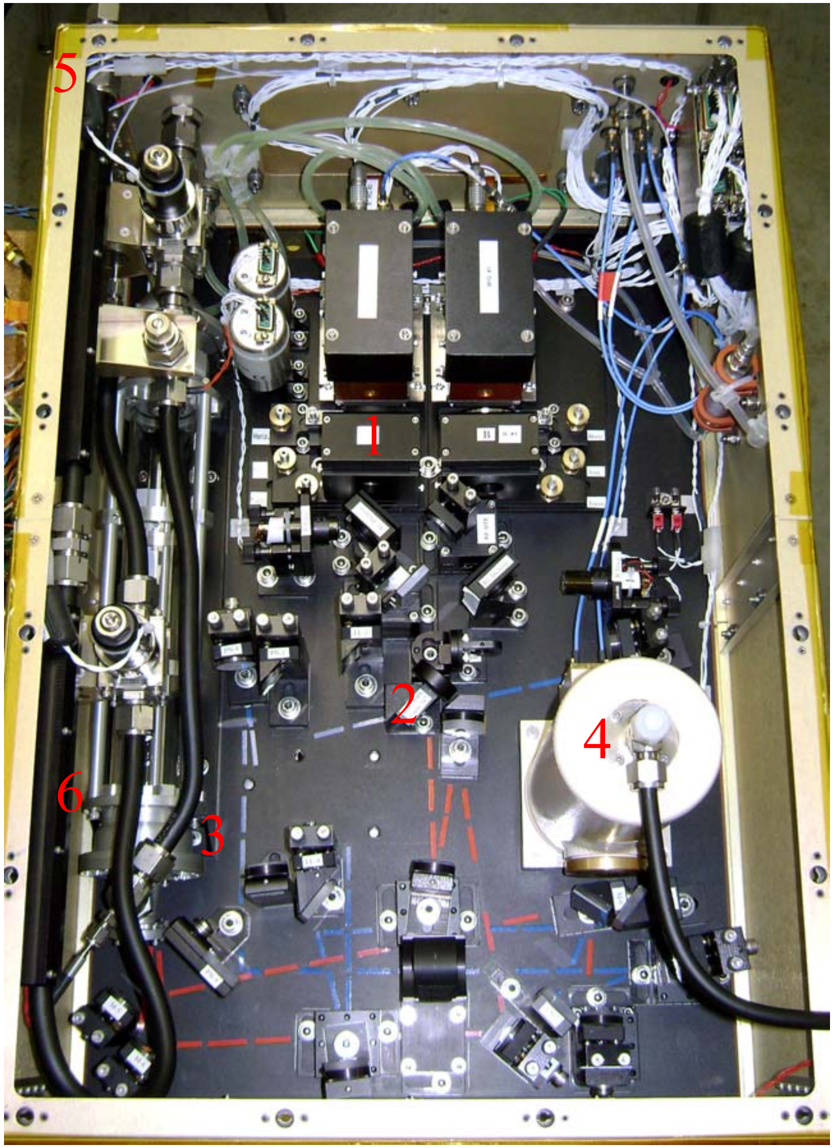
QCL operation

TDL Wintel
- QCL control (FG)
- Data acquisition
- Real-time retrieval

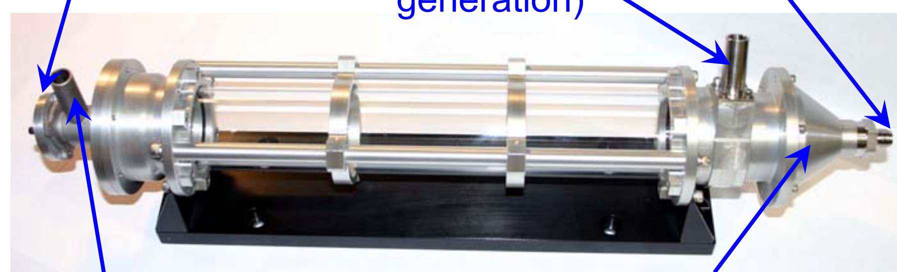


- Pulsed (TEC) mode → short coherence length → **weak (or non observable) fringes!**
- **Excitation with shortest possible pulses** → max power and min chirping (pulses → $\Delta T \approx 0.2$ K → $\Delta\nu \approx 0.02$ cm^{-1})
- **"Smallest" sub-threshold ramp** (quadratic modulation)
- **Direct absorption** (harmonic detection not suitable)
- **Balanced detection** → covariance removal

2-QCL spectrometer

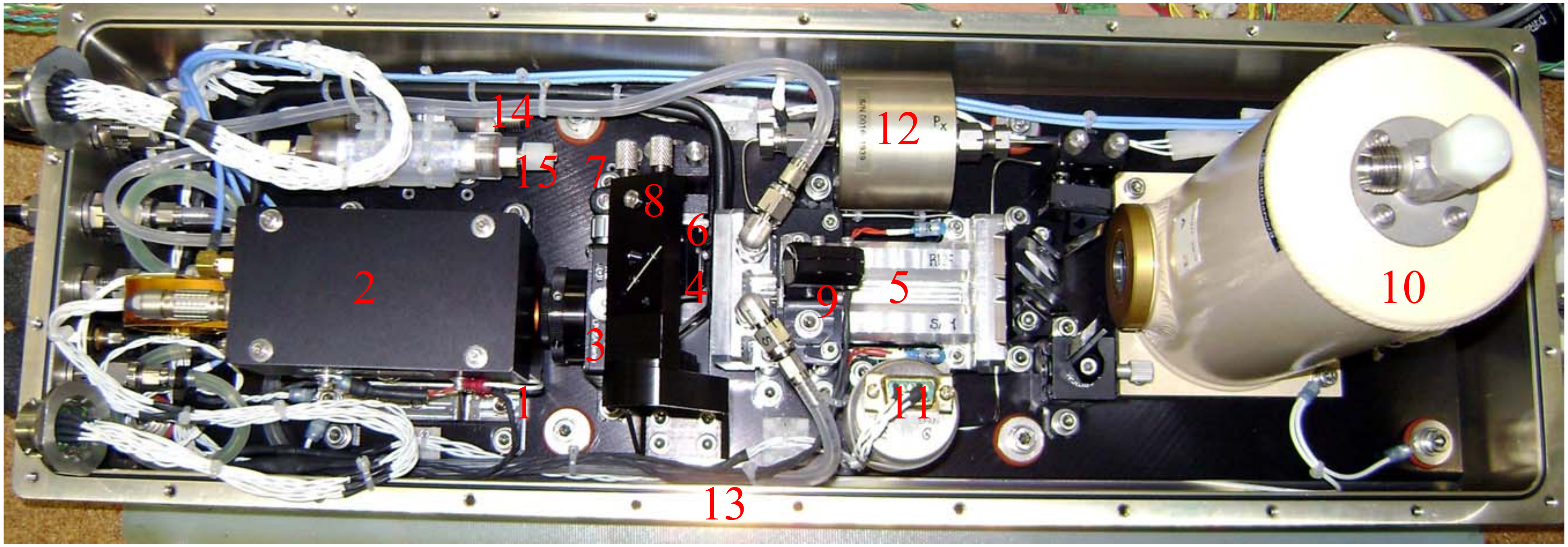


1. Alignment mount for Schwarzschild objective (15X, 0.4 NA)
2. Wedged BaF_2 beam splitter
3. Light (Al), fast response ($\tau \approx 1$ s), astigmatic-mirror multipass cell (238 passes, 76 m pathlength)



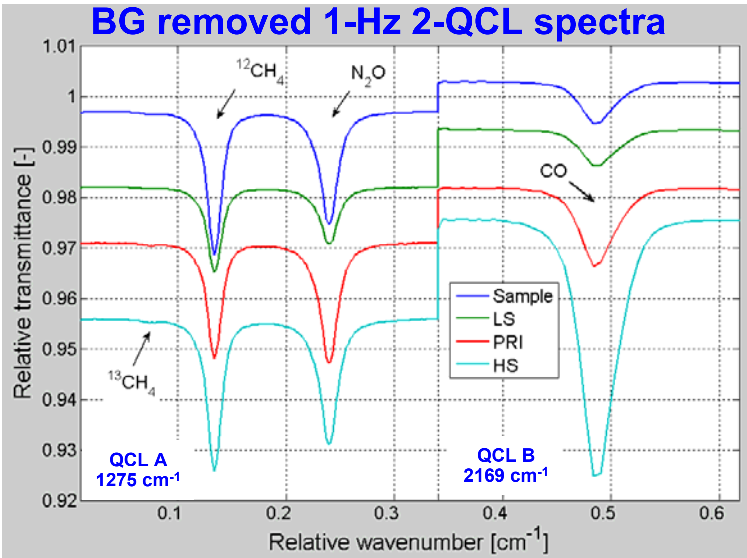
4. LN_2–cooled dual MCT detector (D* $\approx 6 \cdot 10^{10}$ cm $Hz^{1/2}$ W^{-1}, NEP $\approx$ 3 nW)
5. T-controlled enclosure ($\pm$0.1 K)
6. Gas-T conditioner (heat exchanger)

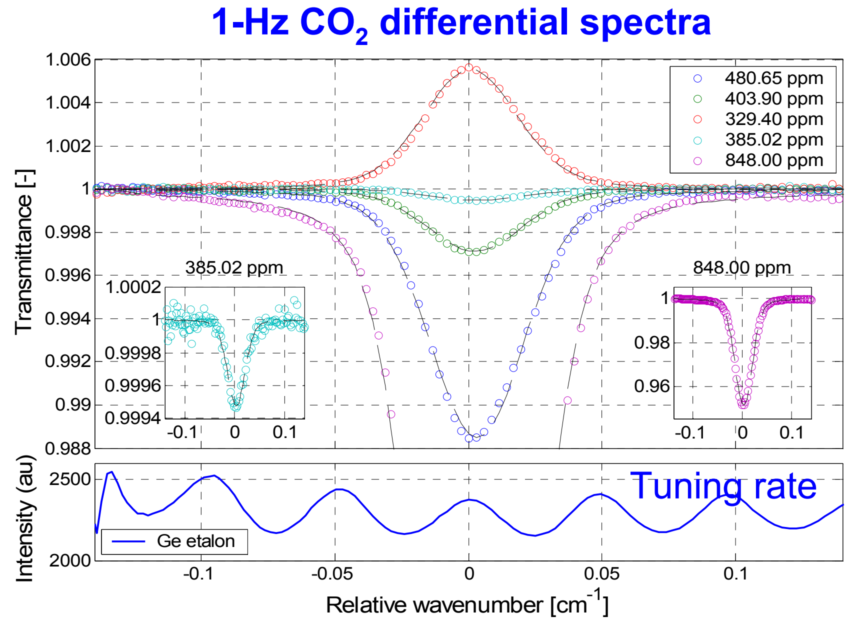
CO_2 QCL spectrometer



1. QCL house
2. Electronics (pulse generator / bias-T)
3. **Aspheric AR ZnSe lens** (15.5 mm ϕ, 13 mm f) in mount
4. CaF_2 beam splitter
5. **10-cm dual absorption cells** ($\tau \approx 1$ s; wedged/tilted windows)
6. Diverting mirror
7. Actuator for diverting mirror
8. Etalon aiming flat mirror
9. 25-mm Ge etalon
10. **LN_2–cooled dual InSb detector** ($D^* \approx 9 \cdot 10^{10}$ cm $Hz^{1/2}$ W^{-1}, NEP $\approx$ 2 nW)
11. Sample absolute P-transducer
12. Differential P-transducer
13. **Thermostated ($\pm$0.1 K) pressure vessel**
14. Pressure vessel P-transducer
15. QCL house desiccant

Spectra



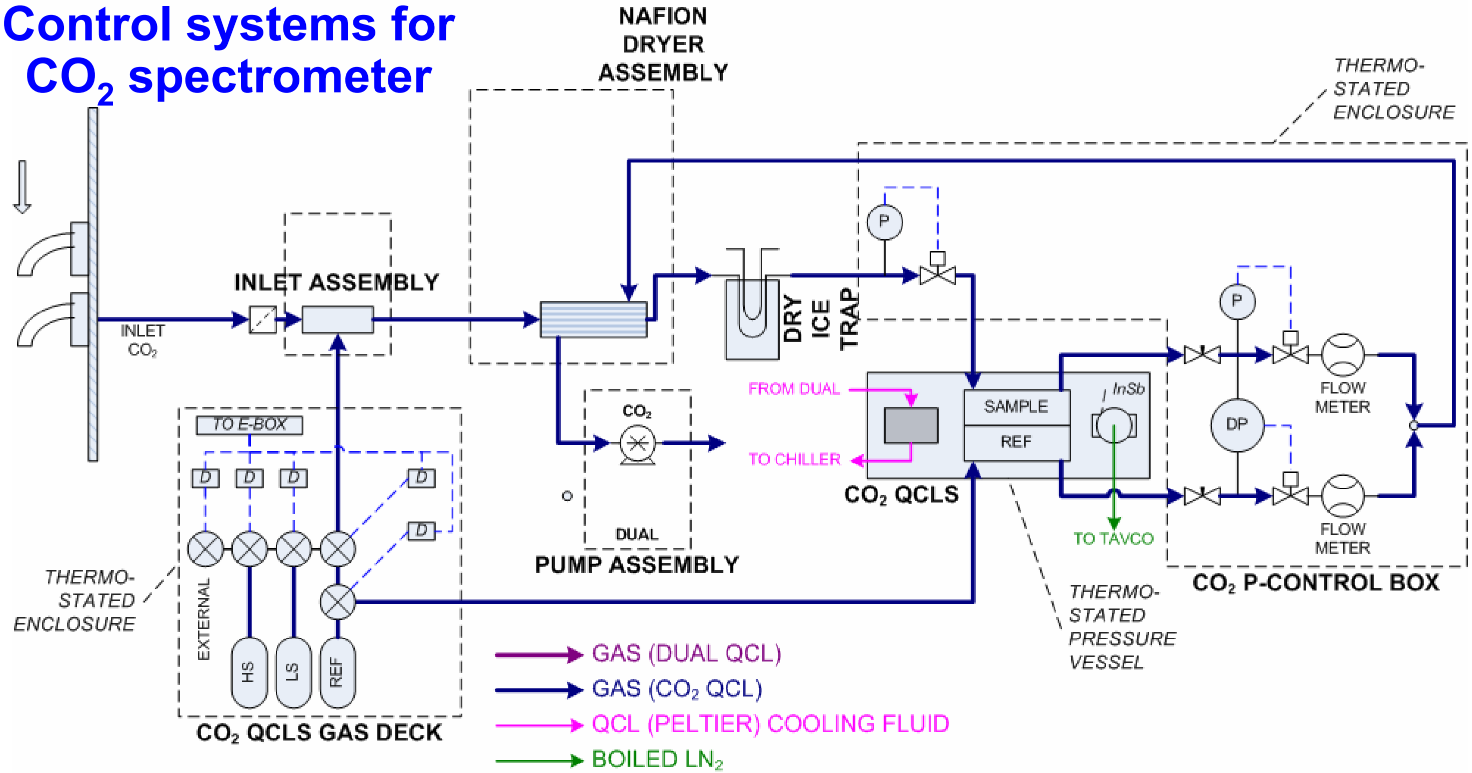


- **Cell pressure ≈ 60 torr → Voigt linewidth ≈ QCL Δν** ((5-17)·10^{-3} cm^{-1} HWHM)
- Broad QCL LW → linear response requires small OT
- **Best performance → linewidth-power tradeoff**
- Chirping noticeable on CO

- CO_2 differential spectra at 2313.16 cm^{-1} (reference = 378.30 ppmv CO_2)
- Residuals ≈ 2·10^{-4} peak-to-peak
- Absolute spectra absorptance ≈ 20%

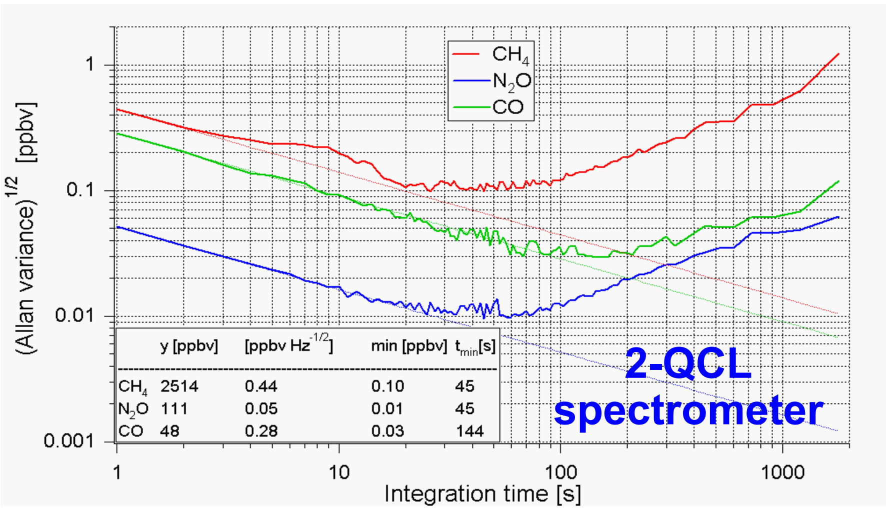
Control systems

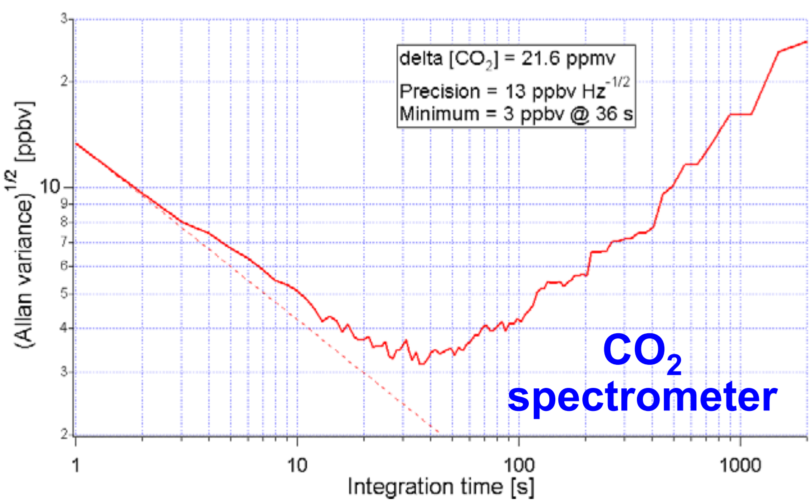
Control systems for CO_2 spectrometer



- **Water removal prior detection** (Nafion→trap) → $\delta\rho<0.01\%$
- Pressure controlled IN and OUT of absorption cells → **Absolute-P stability better than ±0.1 hPa**
- **Gas / spectrometers thermostated to ±0.1 K**
- Boiled LN_2 → 2 TAVCO valves (±2 hPa) → DC level stability

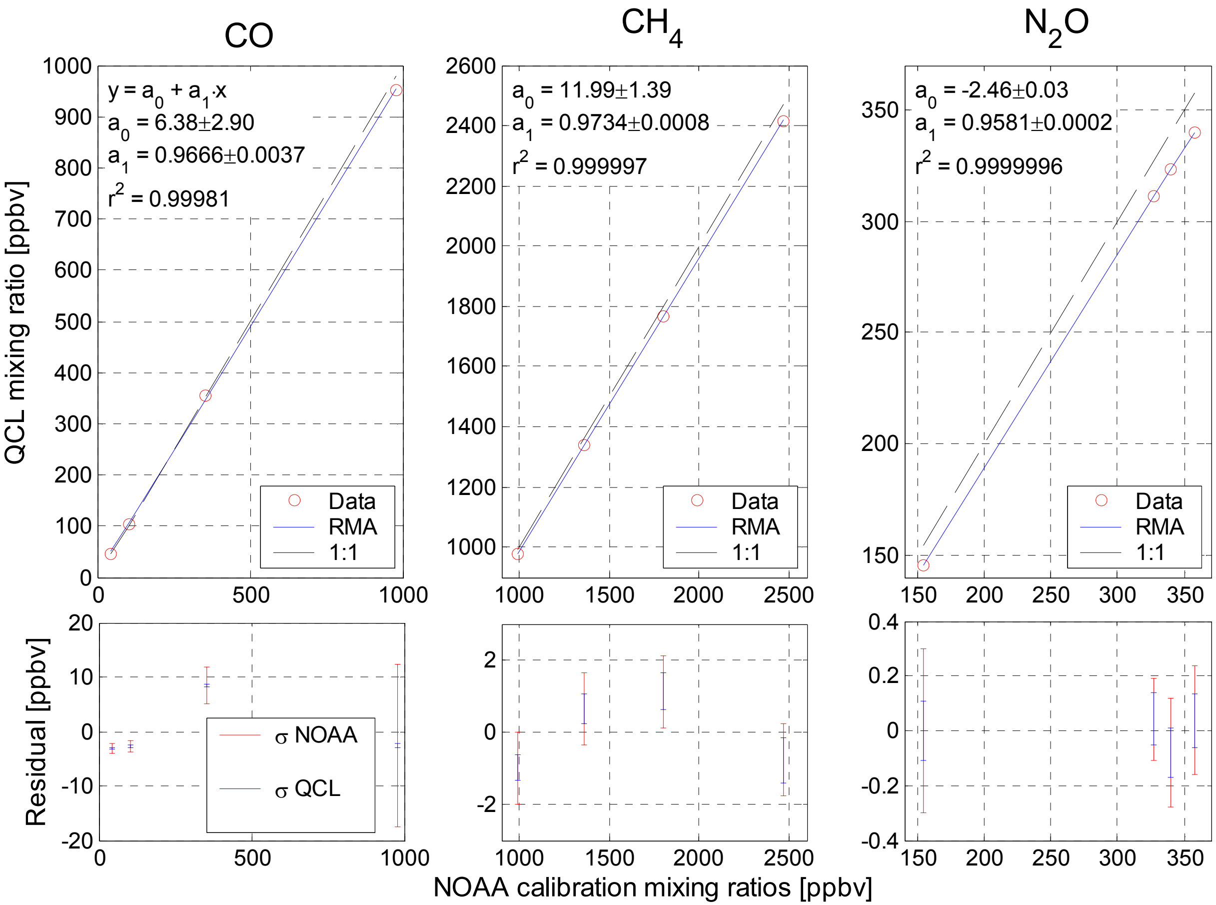
Stability





- Fractional precision → absorbance RMS < $3 \cdot 10^{-5}$
- **Short-term precision determined by QCL power (SNR) and linewidth**
- **Undetectable mode competition!**
- Middle-term precision seems to be controlled by alignment drift (PVD non-linearity artifact)
- **Negligible proportional noise at atmospheric concentrations**
- CO_2 precision and accuracy increases as $\Delta[CO_2] \rightarrow 0$

Calibration



FLT calibration

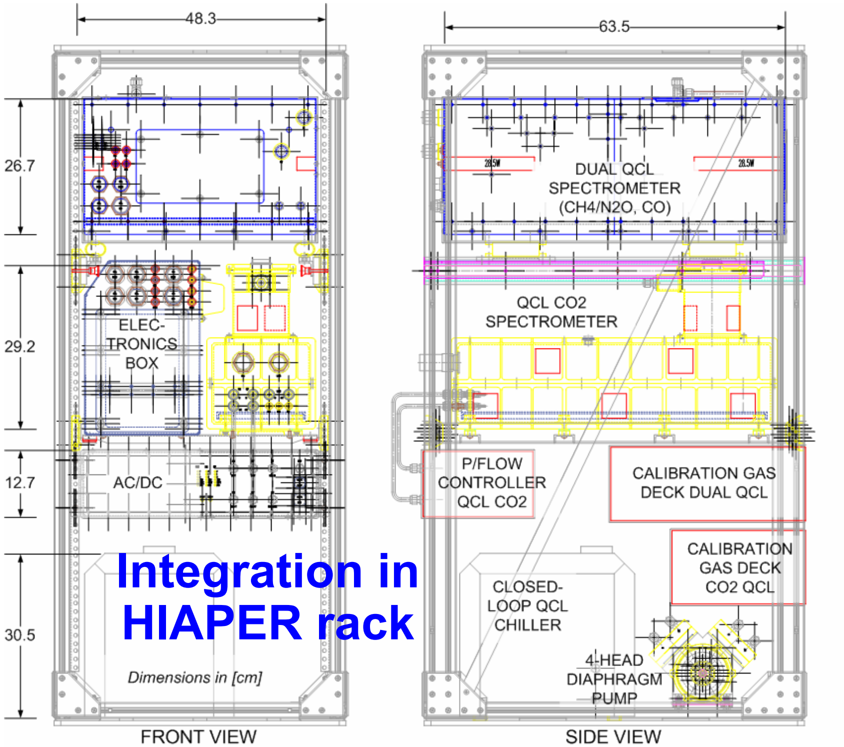
- BG (4-6 h^{-1})
- LS/HS (2 h^{-1})
- PRI (0.5-1 h^{-1})

PRI: mission-long "archive" gas

Source / gas deck tanks calibrated in the laboratory before / after mission

- Excellent linearity and precision over atmospheric range
- NOAA CO accuracy dominate residuals and obscure apparent non-linearity; CH4 non-linearity < 2·sigma

At a glance



- Ready for integration in NASA's WB-57 and Lear35a (BARCA 2007)
- Integration for HIAPER in preparation

- Precision:
  - CO_2 < 100 ppb $Hz^{-1/2}$
  - CO < 0.5 ppb $Hz^{-1/2}$
  - CH_4 < 1 ppb $Hz^{-1/2}$
  - N2O < 0.1 ppb $Hz^{-1/2}$
- Calibrated with low span, high span and "archive" gases traceable to world standards
- Total weight < 150 kg (platform dependent)
- Power: 28 VCD or 3-phase 115 VAC / 400Hz
- Power consumption: steady state = 700 W; peak = 1.8 kW

Conclusions and perspectives

- We have developed a dual-spectrometer instrument that **fulfill the requirements for airborne measurements** from the ground to the stratosphere
- **Stability, precision and accuracy maximized through:**
  - Operation wavelength selection
  - Optimized pulsed QCL operation
  - Balanced detection (null mode operation for CO_2)
  - Short coherence length minimizes interference fringes
  - Tight controls on temperature, pressure, flow and density
  - Frequent calibration with gases traceable to world standards
- Instrument provides **excellent precision and linearity** over the atmospheric concentration range
- **Data processing algorithms** will account for background (BG) discontinuity and PVD non-linearity
- Ready for **integration** on NASA's WB-57 and Lear35a (BARCA 2007); Integration in HIAPER in preparation (START 2008)

HU QCLS team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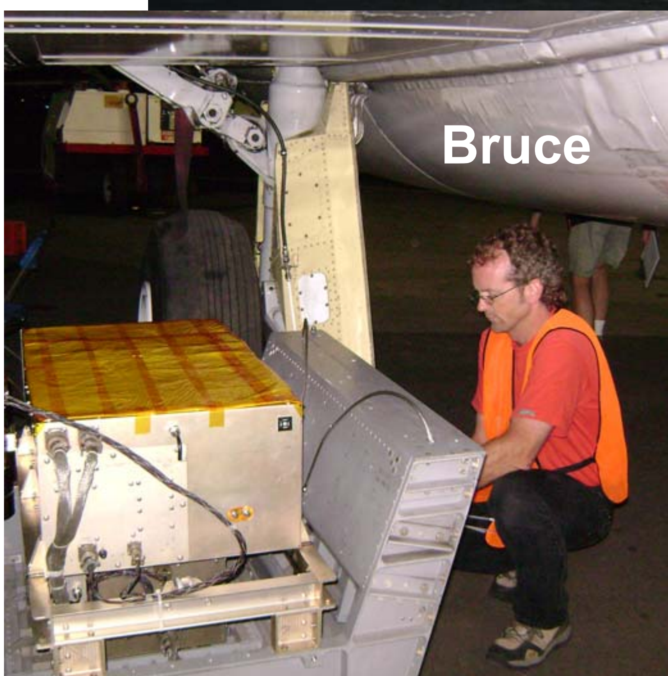
Bruce


Rodrigo

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