FIELD MEASUREMENTS OF ATMOSPHERIC TRACE GASES USING QUANTUM CASCADE LASERS

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Billerica Massachusetts USA

IQCLWS 2008

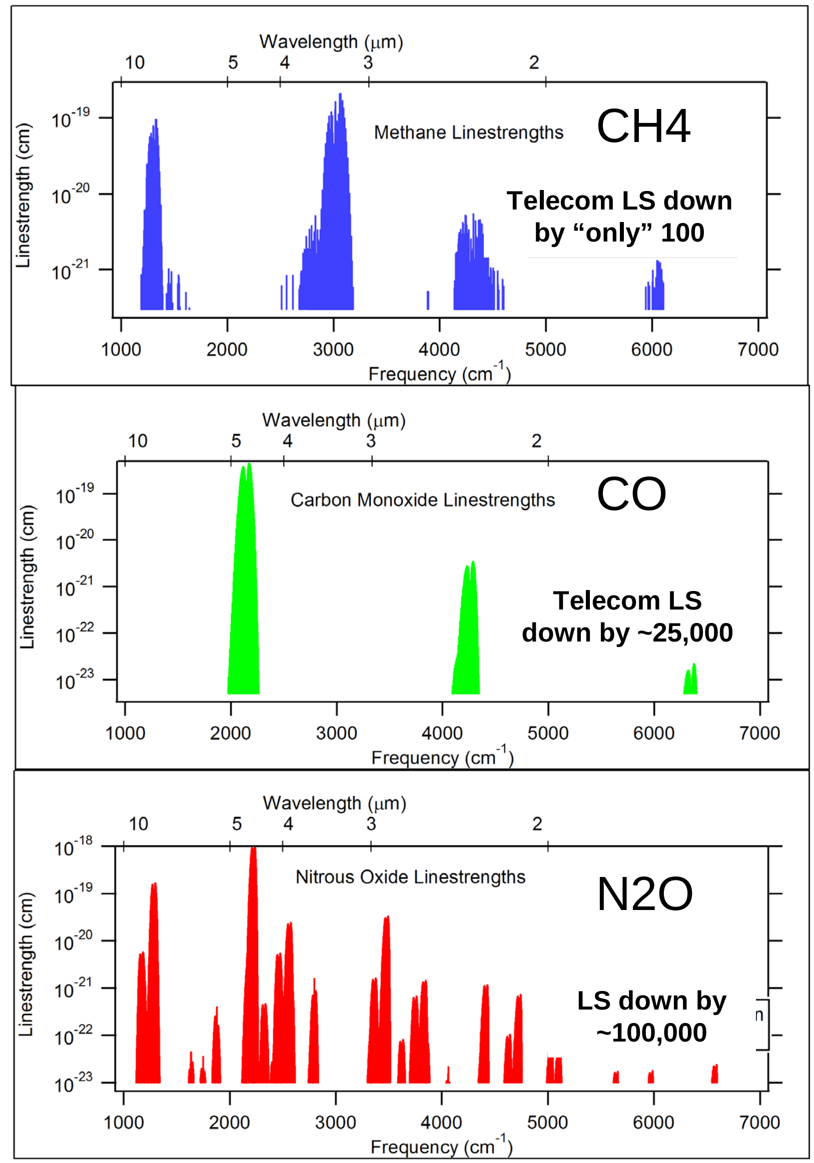

Mexico City 2003, 2006
NH3,NO2, CO, HCHO, C2H4
AERODYNE MOBILE LABORATORY
HOUSTON 2006
HCHO, HCOOH, C2H4
NOAA
Jungfrau
(EMPA) 2008
CO2 isotopes
COLORADO 2008
CH4, N2O, CO, CO2
NEW ENGLAND 2004
HCHO, HCOOH
UNITED STATES
Netherlands
(ECN) 2006-2008
N2O, CH4
RUSSIAN
TUNDRA 2008
(U. Copenhagn)
CH4
SCOTLAND 2005. 2008
(U. MANCHESTER, UK)
NH3, HNO3

OUTLINE

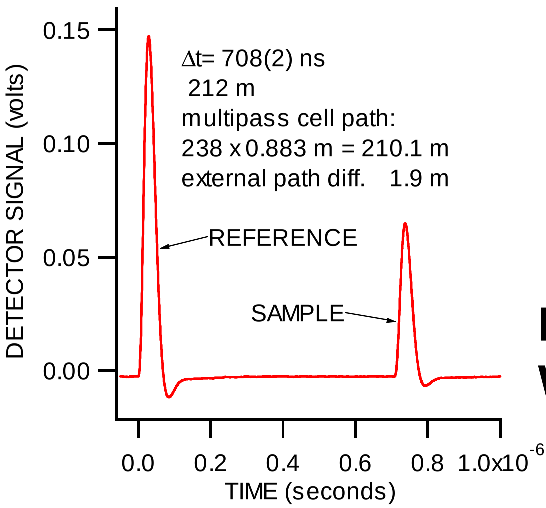
- Instrumentation Requirements
  - Robust Optical Systems
  - Easy Turn-on
  - Continuous, Unattended, Operation
  - Long Component Lifetime
- Application Examples
  - Airborne CH_4, N_2O, CO, CO_2
  - Carbonyl Sufide (COS)
  - Methane Isotopologues
- CW vs Pulsed QCLs
- Wish List

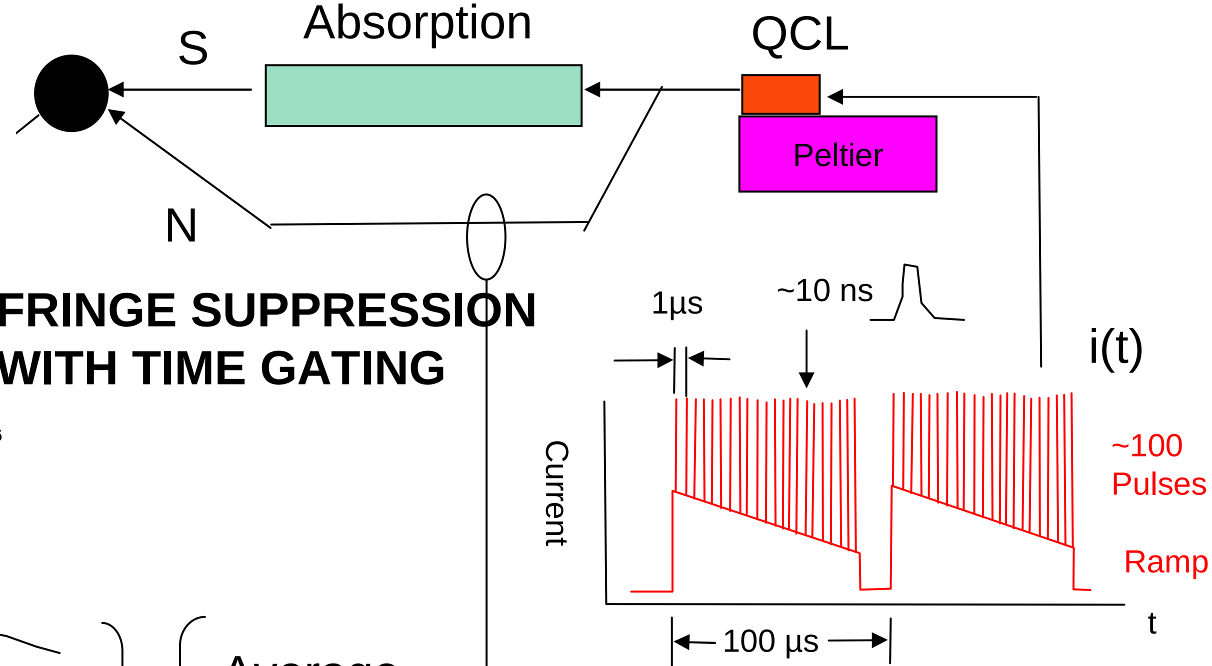
Advantages of Mid-IR Detection

- Linestrengths in mid-IR are **much** stronger
- For methane, the loss of 100x in LS is mitigated by superior lasers, optics, detectors and methane's large ambient concentration (2 ppm)
- For CO and N_2O, telecom detection will be very hard due to lower atmospheric abundance and extremely small linestrengths

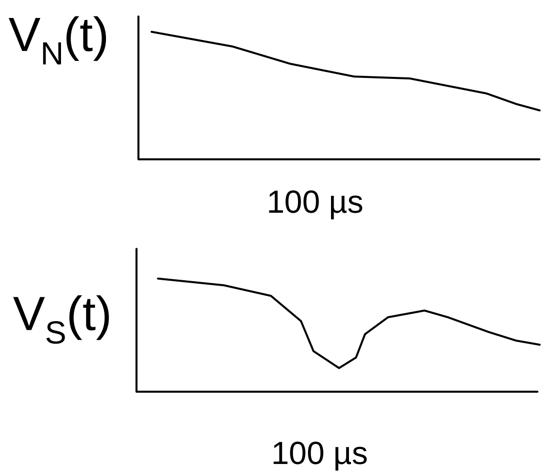


DIRECT ABSORPTION WITH PULSED-QCLs

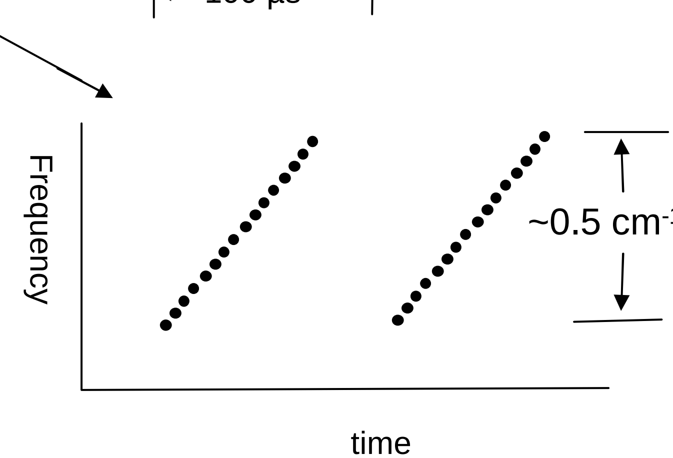




FRINGE SUPPRESSION WITH TIME GATING



Average
Divide
Fit spectra
Calc. Conc.
Adj. Peltier



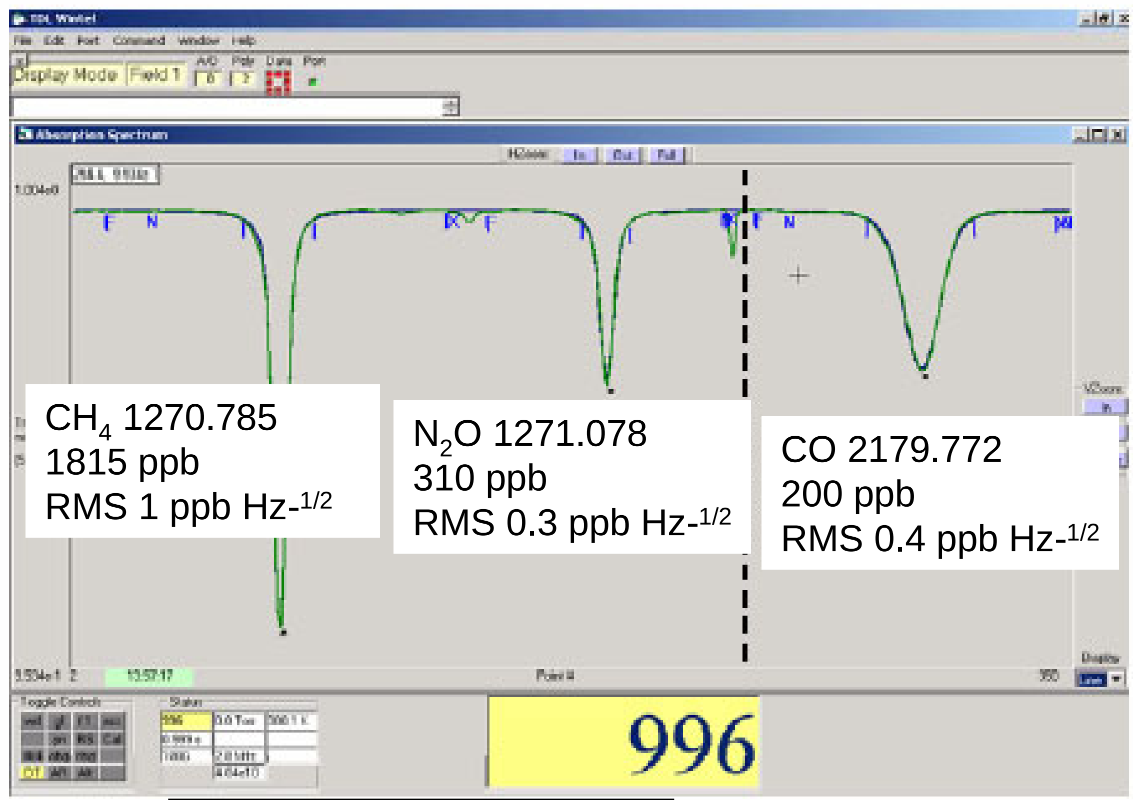
"TDLWINTEL"
Laser Control and Signal Processing Software

Laser Drive Control:
- Pulsed or CW lasers
- Tuning ramp & gate
- Multiplex up to 4 lasers
- Lock to reference lines

Event Control:
- Reference gas valves
- Background subtraction

Signal Processing:
- Direct absorption
- Sweep Integration
- Pulse normalization
- Rapid scan [5-10 kHz]
- Rapid fitting [to 25 Hz]
- HITRAN based fit spectra
- Multi-gas concentrations
- Saved spectra
- Unattended operation

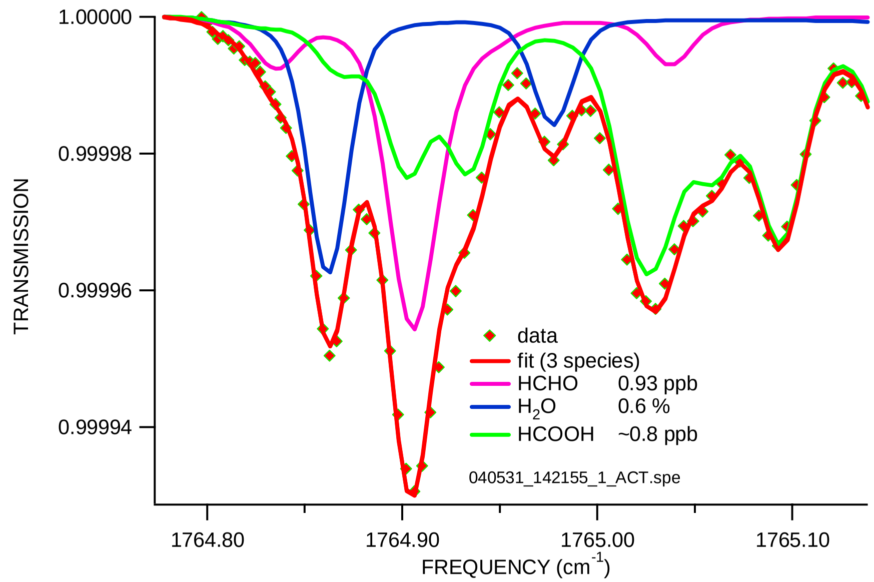
Absolute Concentrations Result



LASER 1
Line width 0.003 cm^{-1} hwhm
76 m; 54 Torr

LASER 2
Line width 0.01 cm^{-1}

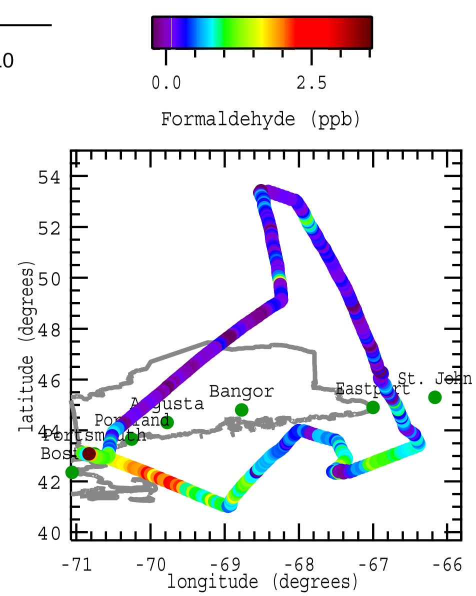
FORMALDEHYDE and FORMIC ACID - NEAQS-2004

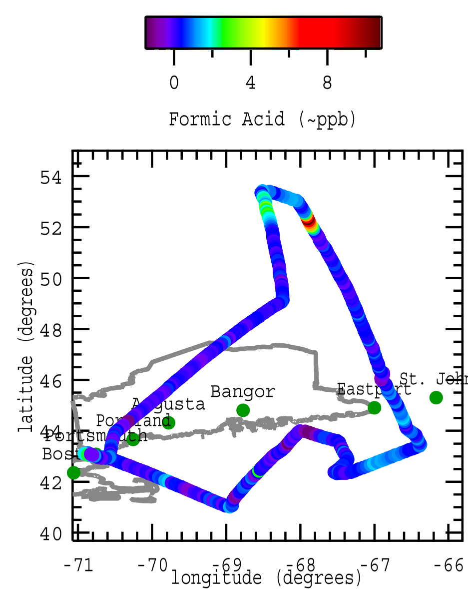


Formic Acid Linestrength Data
Agnes Perrin, U. Paris Sud &
Jean Vander Auwera, Free U. Brussels

MULTIPLE SPECIES FITTING:
HCHO, HCOOH, H_2O
RESIDUALS ~2×10^{-6} ABSORBANCE
(15 min SPECTRAL AVERAGE)

HCHO DETECTION LIMIT ~0.1 ppb





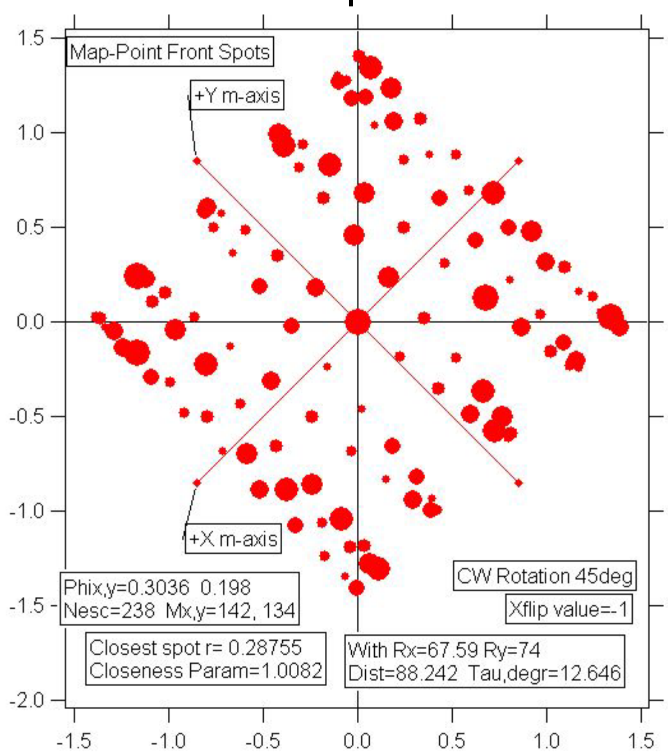
FLIGHT TRACK 09 JULY 2004
HCOOH > 10 ppb IN
FOREST FIRE PLUME FROM
ALASKA

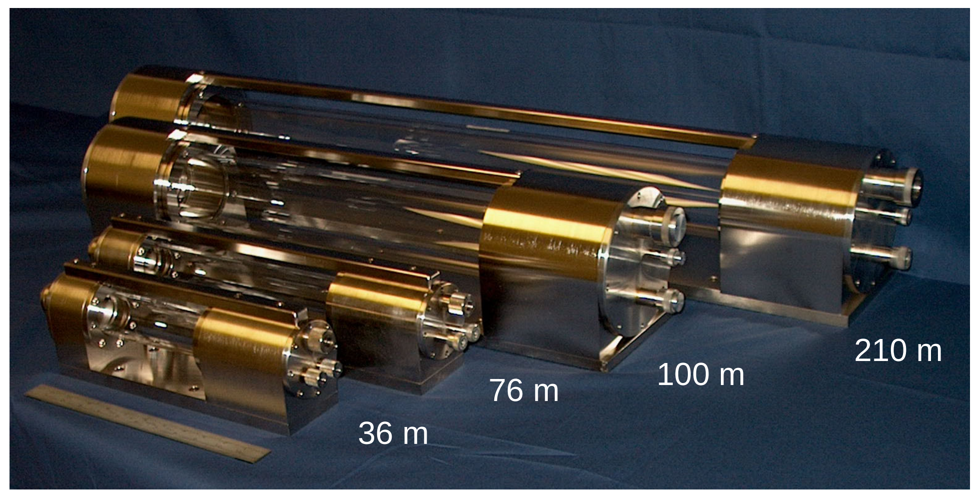
HERNDON et al., JGR 2007

Astigmatic Multipass Cells

Astigmatic mirrors in an off-axis resonator produce mirror filling recirculation patterns with high pass number (>200), in low volumes (e.g. 76 m in 0.5 Liter), with controllable pass number.

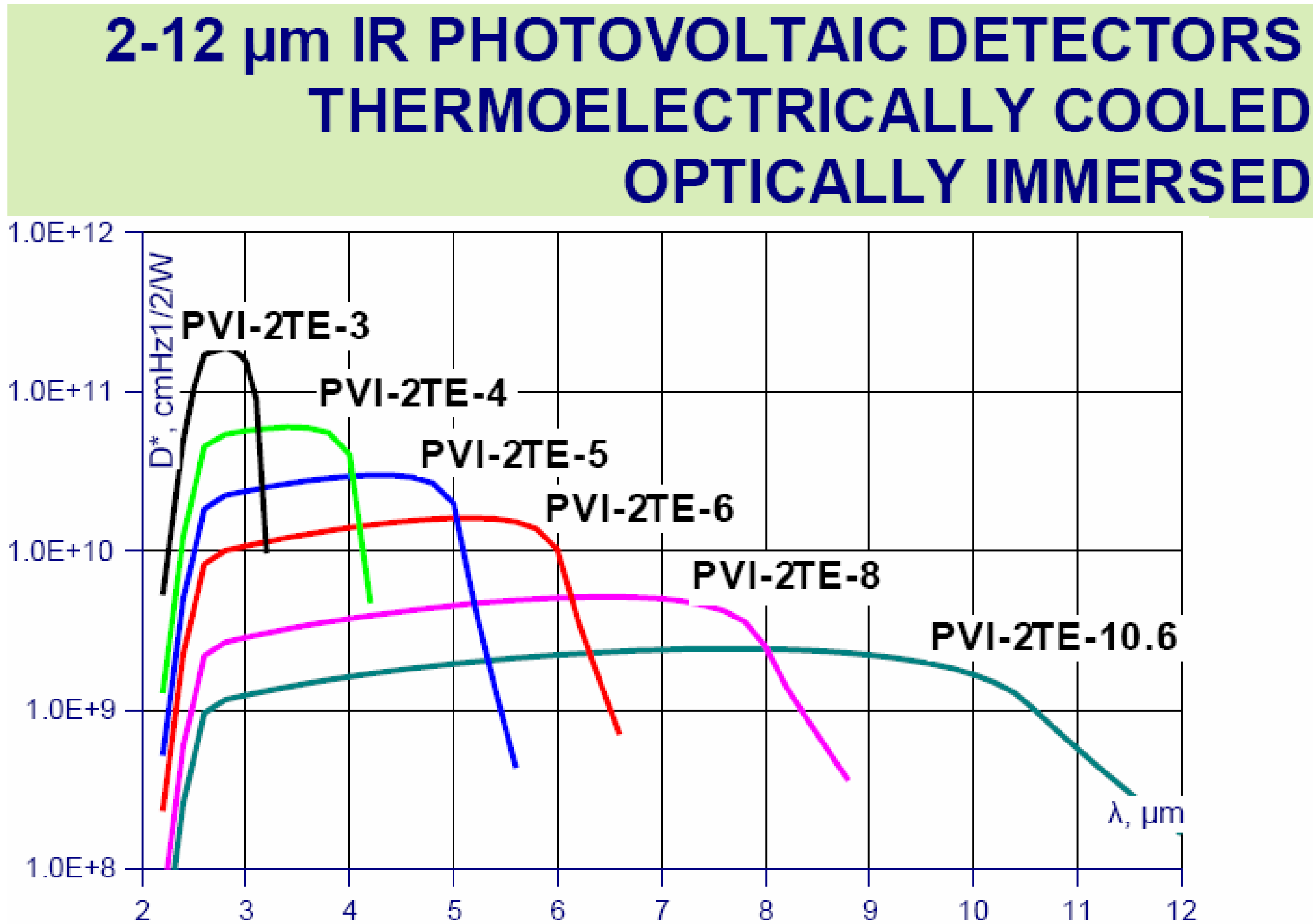
Beam pattern





D* for Optically Immersed, TE-Cooled PV Detectors

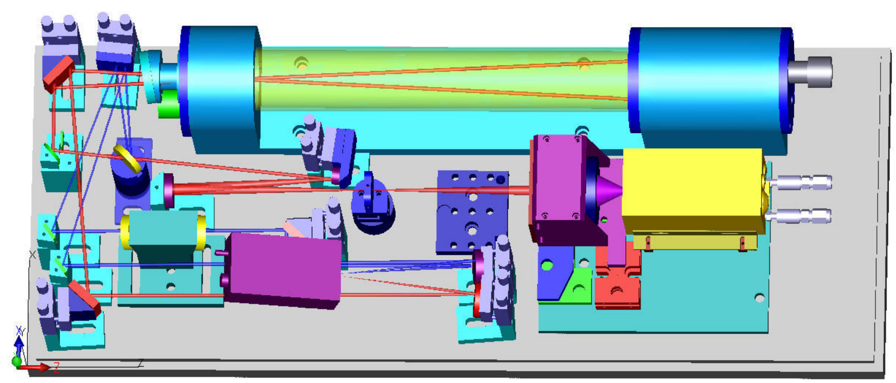
- Detector performance versus wavelength for TE cooled PV detectors made by Vigo Systems, S.A. in Poland
- Note the sharp decrease in D* with increasing wavelength caused by thermal noise
- Detector performance at 5 microns approaches that of an LN2 cooled InSb
- Performance at 10 microns is much worse than a cryogenic detector



SYSTEM S.A.

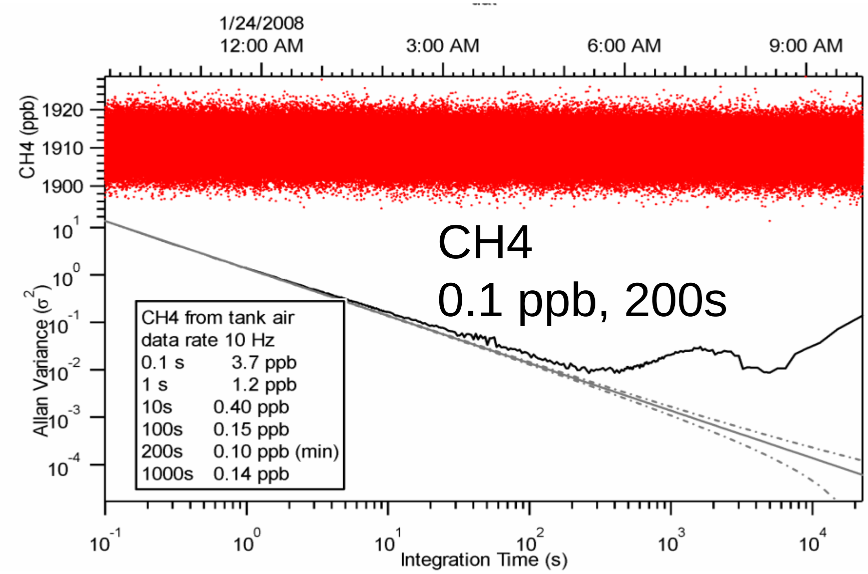
COMPACT SINGLE QCL

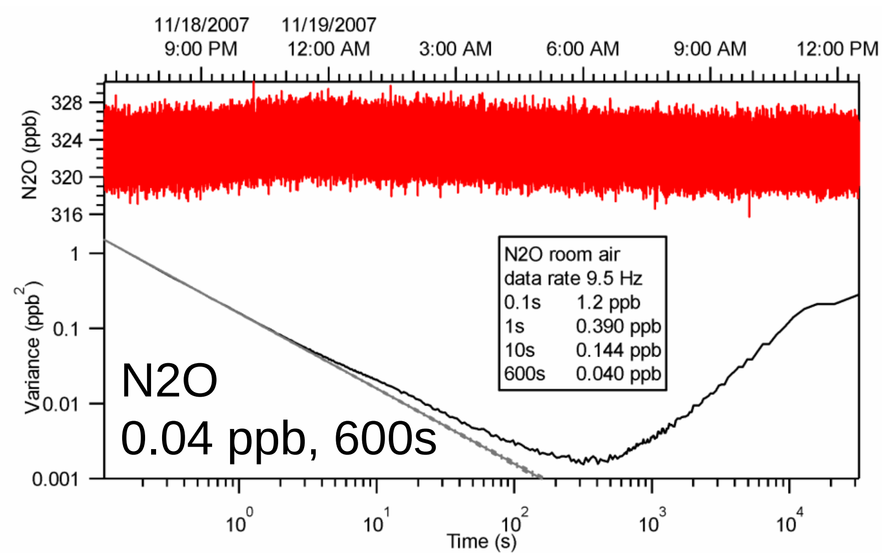
- TE-COOLED LASER and DETECTOR
- COMBINED OPTICS & ELECTRONICS
- STANDARD 19” RACK MOUNT
- WEIGHT 25 kg
- 76 m ASTIGMATIC MULTIPASS CELL



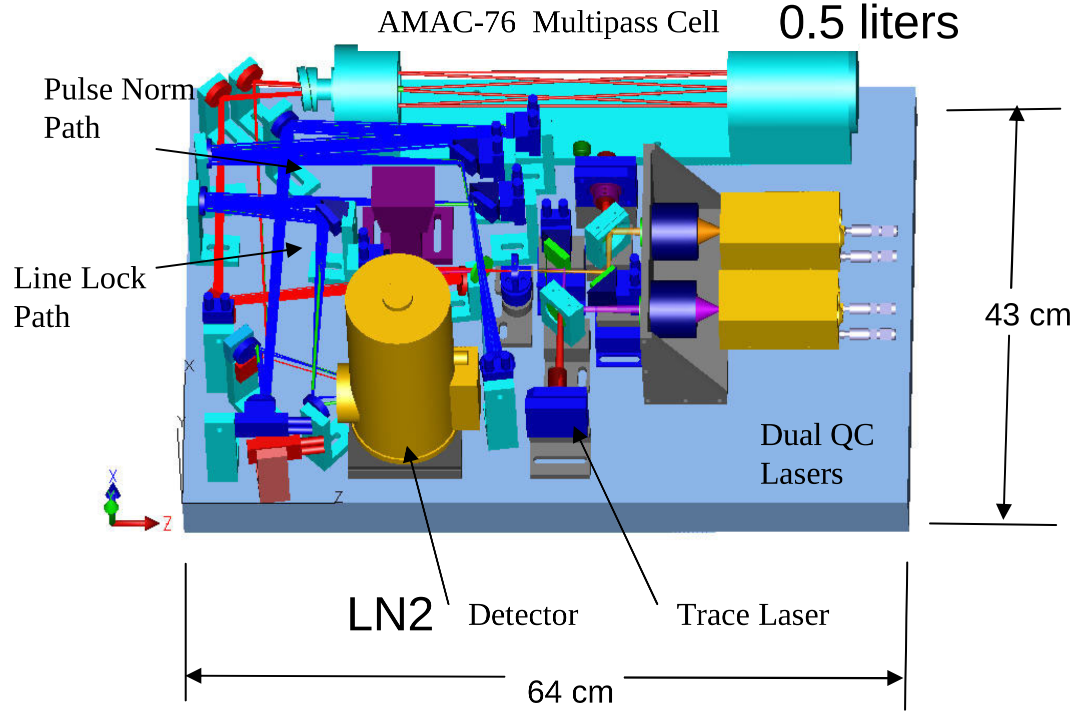
CH_4 and N_2O MEASUREMENT PRECISION

- ALLAN VARIANCE
  - SHORT TERM PRECISION
  - LONG TERM DRIFT
- PULSED-QCL (1271 cm^{-1})
- TE-COOLED LASER AND DETECTOR
- SHOWN FOR SINGLE SPECIES DETECTION at 10Hz DATA RATE
- SIMULTANEOUS DETECTION FEASIBLE AT 8 μm BUT REDUCES PRECISON BY ~2 x





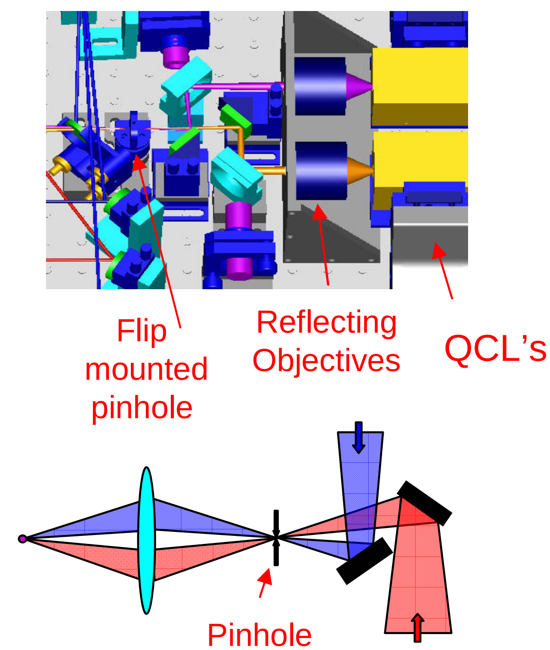
Compact Dual QCL Instrument Optical Layout



Beam combining by sharing angular field:

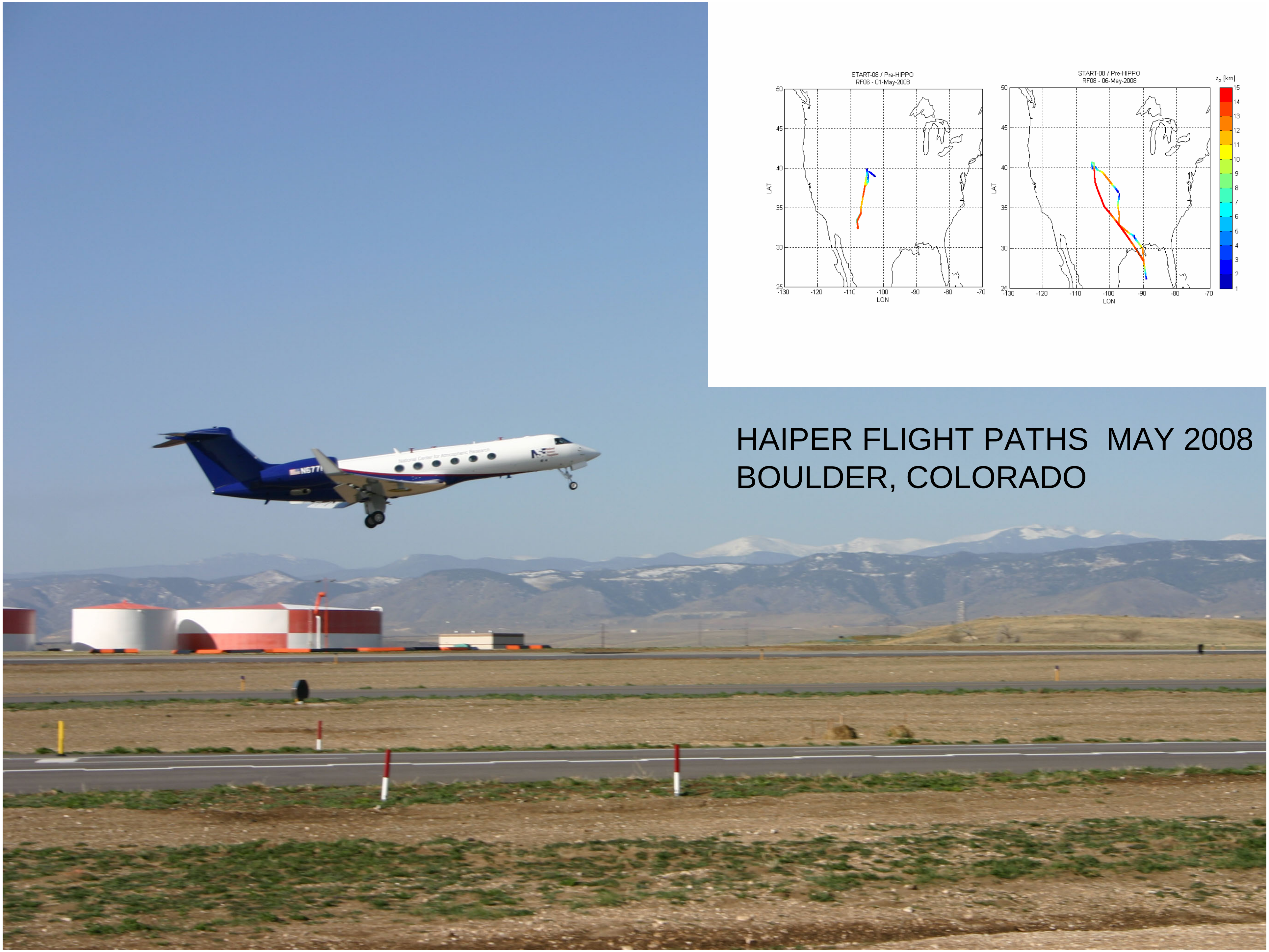
Both beams are focused through a common pinhole. Beams overlap again when re-imaged.

Power efficient and wavelength independent.



Reduced sensitivity to ambient fluctuations with path matching:

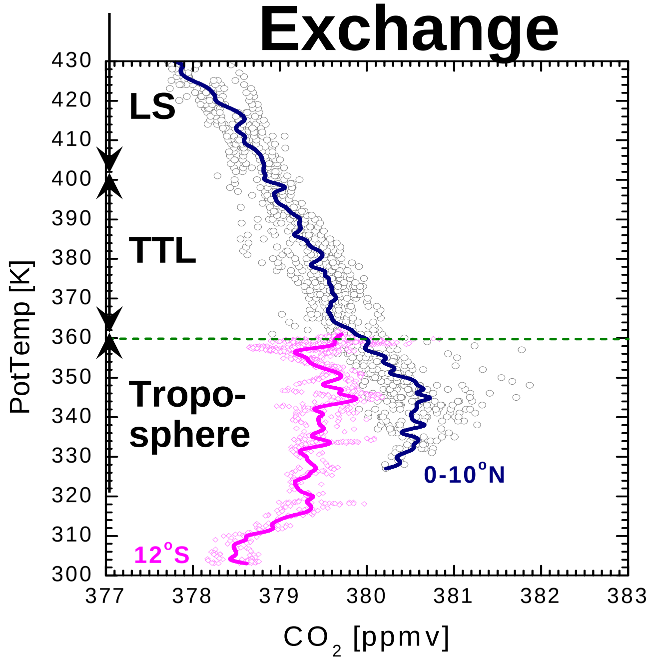
Pulse normalization path length equals main path length, outside multipass cell.


START-08 / Pre-HIPPO
RF06 - 01-May-2008
START-08 / Pre-HIPPO
RF08 - 06-May-2008
LAT
LON
z_p [km]
HAIPER FLIGHT PATHS MAY 2008
BOULDER, COLORADO

Airborne measurements of CO_2, CO, CH_4 and N_2O

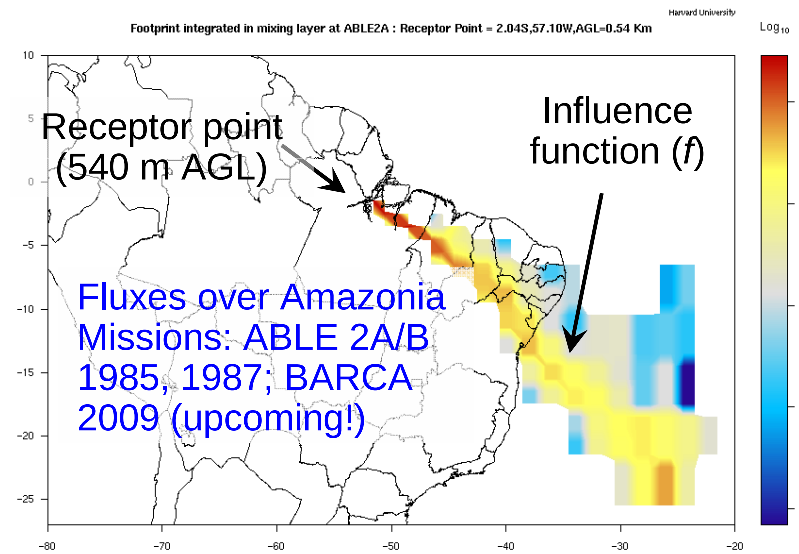
Rodrigo Jiménez, B.C. Daube, S. Park, E.A. Kort, E. Gottlieb, S.C. Wofsy
HARVARD UNIVERSITY

Troposphere →Stratosphere Exchange



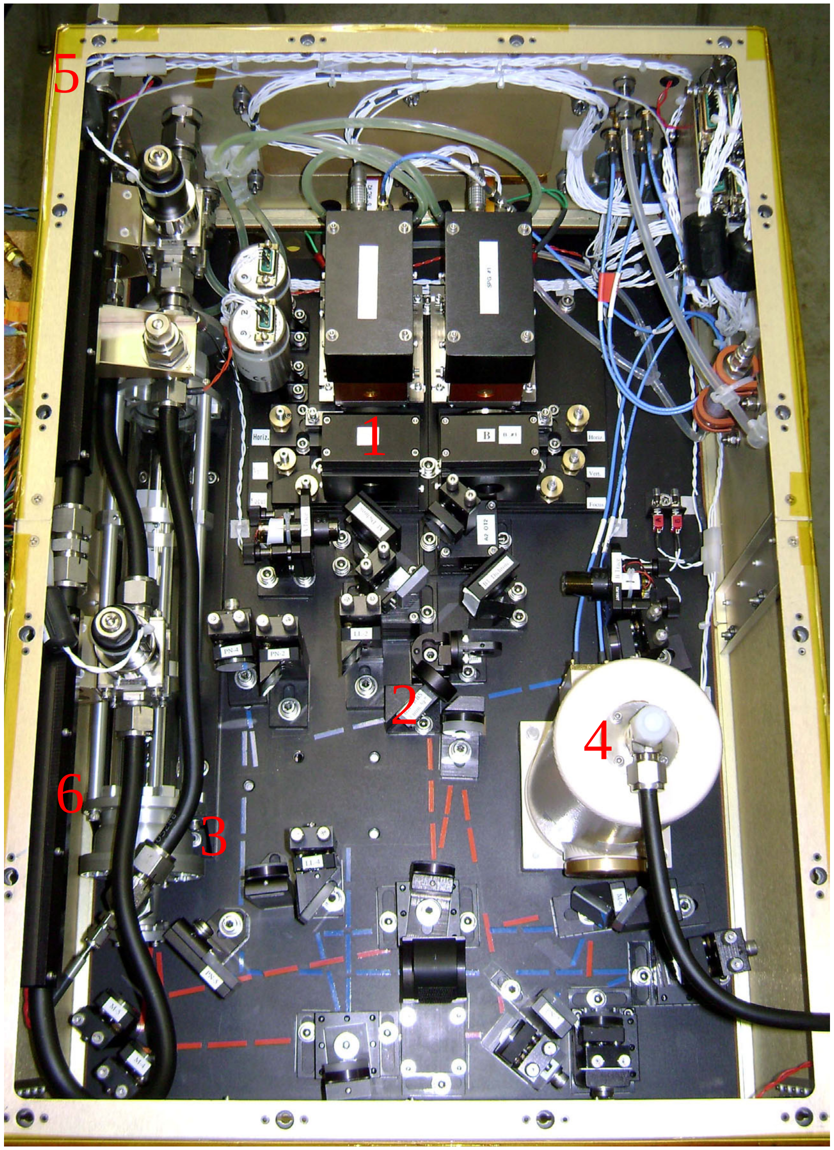
- TTL: stratosphere source of H_2O, GHG, Sulfur Gases
- CH_4 inter-hemispheric mixing, CO, N_2O tropo-stratosphere mixing

Green House Gas Flux Estimation

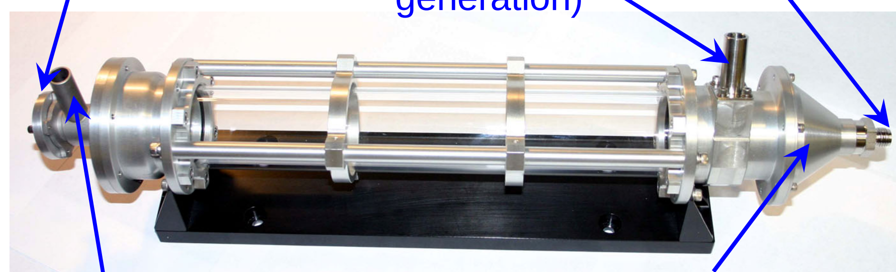


- Lagrangian models
- Back trajectories
- High precision requirements

2-QCL spectrometer

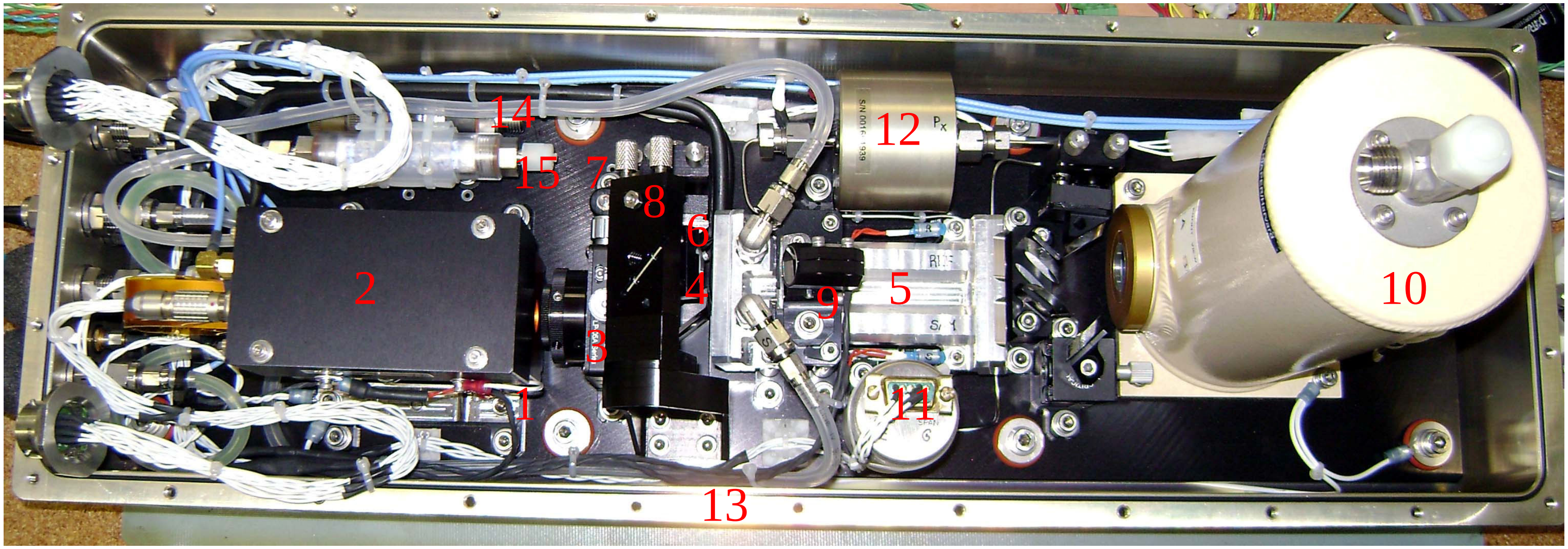


1. Alignment mount for Schwarzschild objective (15X, 0.4 NA)
2. Wedged BaF_2 beam splitter
3. Light (Al), fast response ($\tau \approx 1$ s), astigmatic-mirror multipass cell (238 passes, 76 m pathlength)



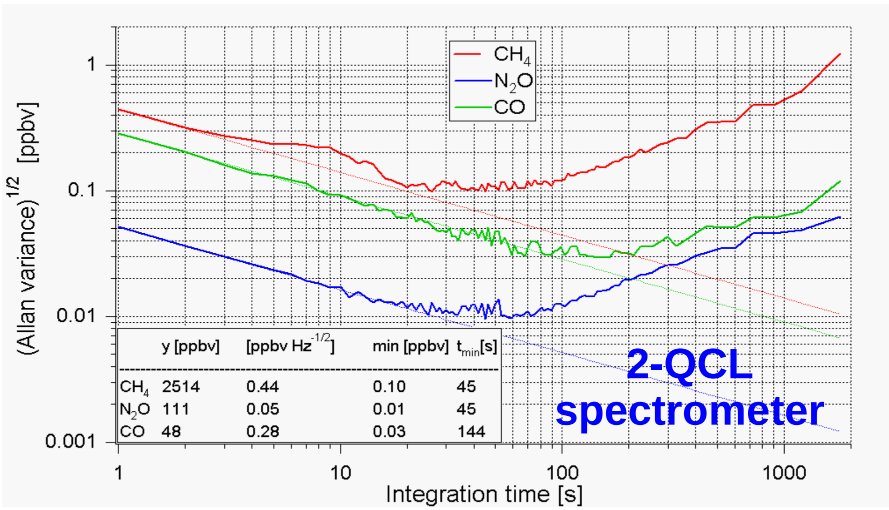
4. LN_2–cooled dual MCT detector ($D^* \approx 6{\cdot}10^{10}$ cm $Hz^{1/2}$ W^{-1}, NEP $\approx$ 3 nW)
5. T-controlled enclosure ($\pm$0.1 K)
6. Gas-T conditioner (heat exchanger)

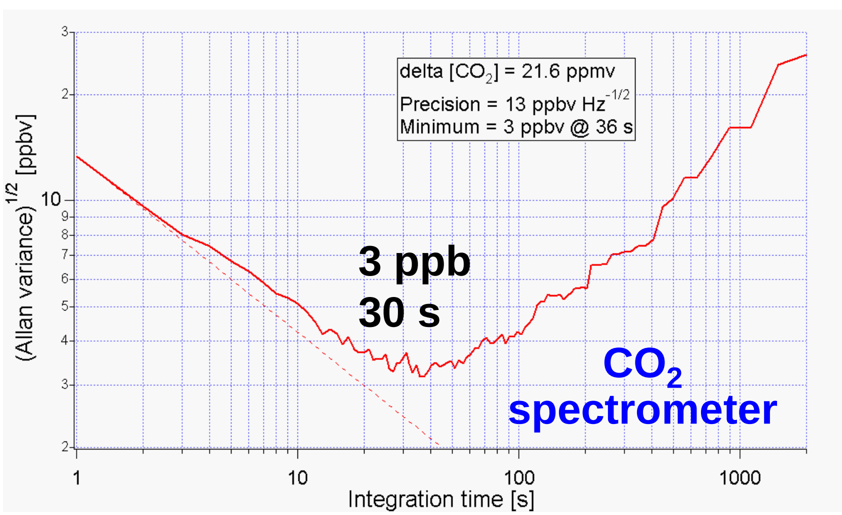
CO_2 QCL spectrometer



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 ≈ 2 nW)
11. Sample absolute P-transducer
12. Differential P-transducer
13. **Thermostated (±0.1 K) pressure vessel**
14. Pressure vessel P-transducer
15. QCL house desiccant

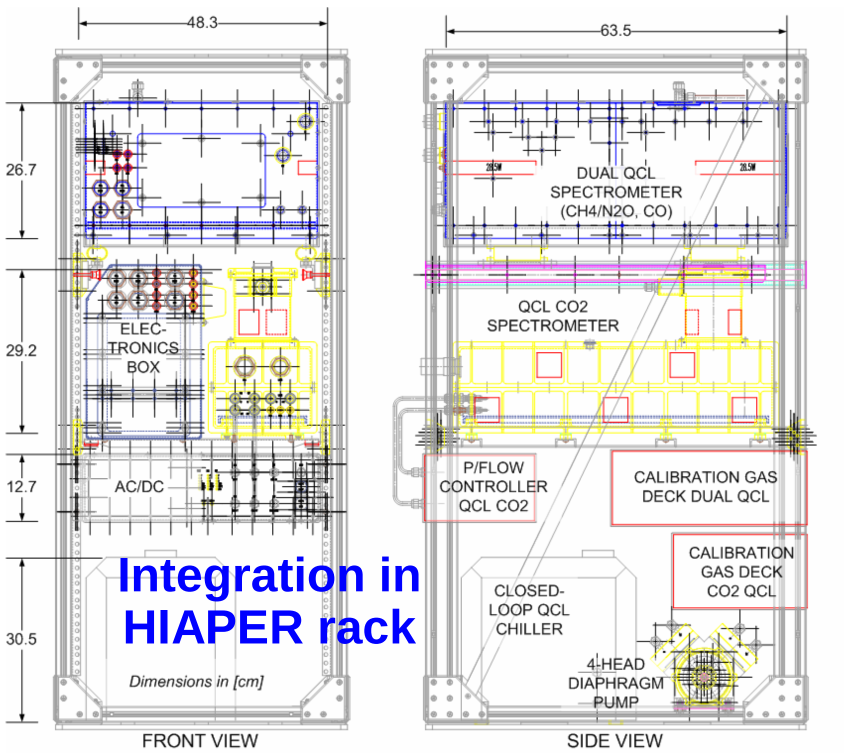
Stability





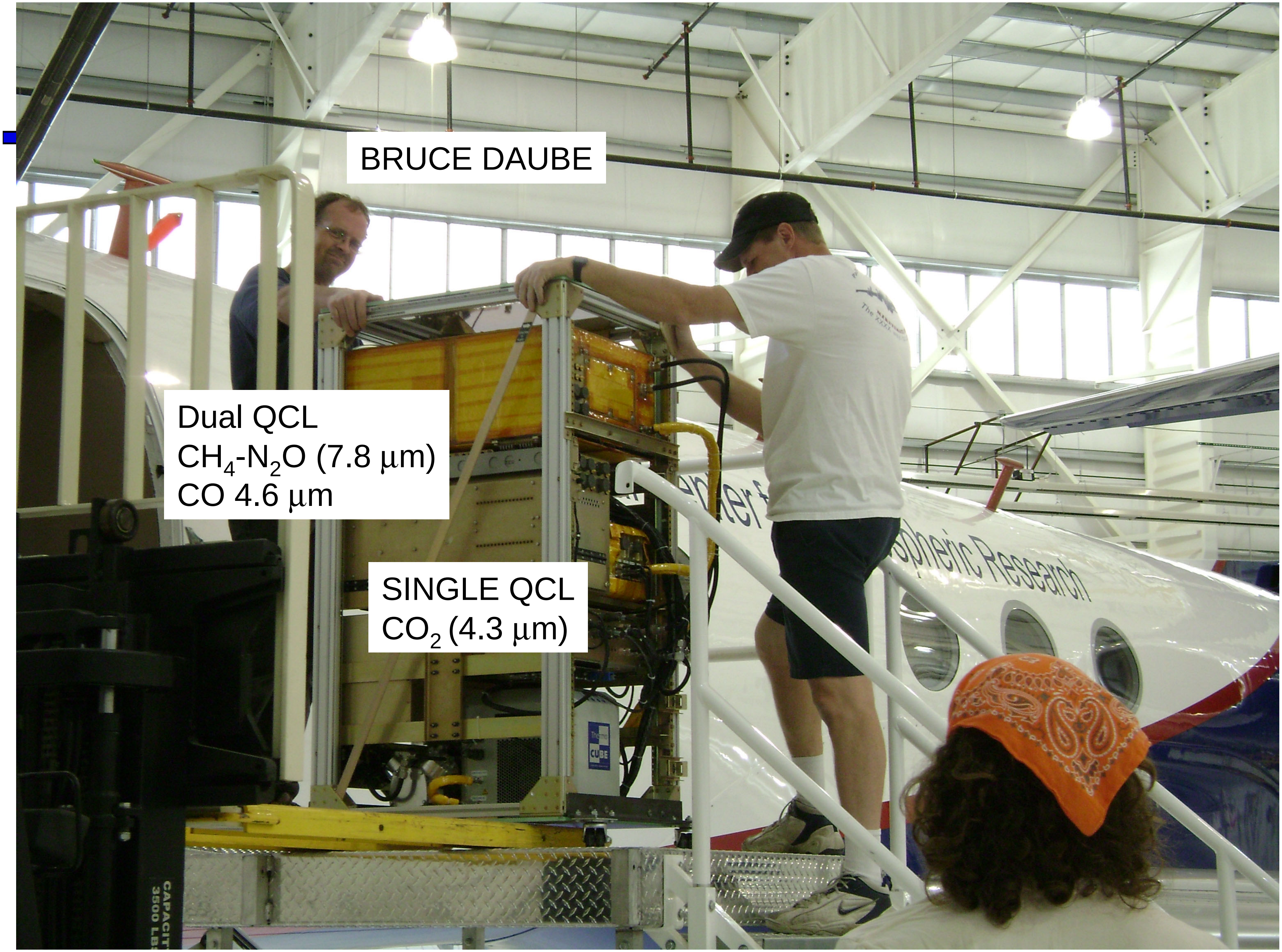
- Fractional precision → absorbance RMS ~ $1 \cdot 10^{-5}$
- **Short-term precision determined by QCL power (SNR) and linewidth**
- **Undetectable mode competition!**
- Middle-term precision seems to be controlled by alignment drift
- **Negligible proportional noise at atmospheric concentrations**
- CO_2 precision and accuracy increases as $\Delta[CO_2] \rightarrow 0$

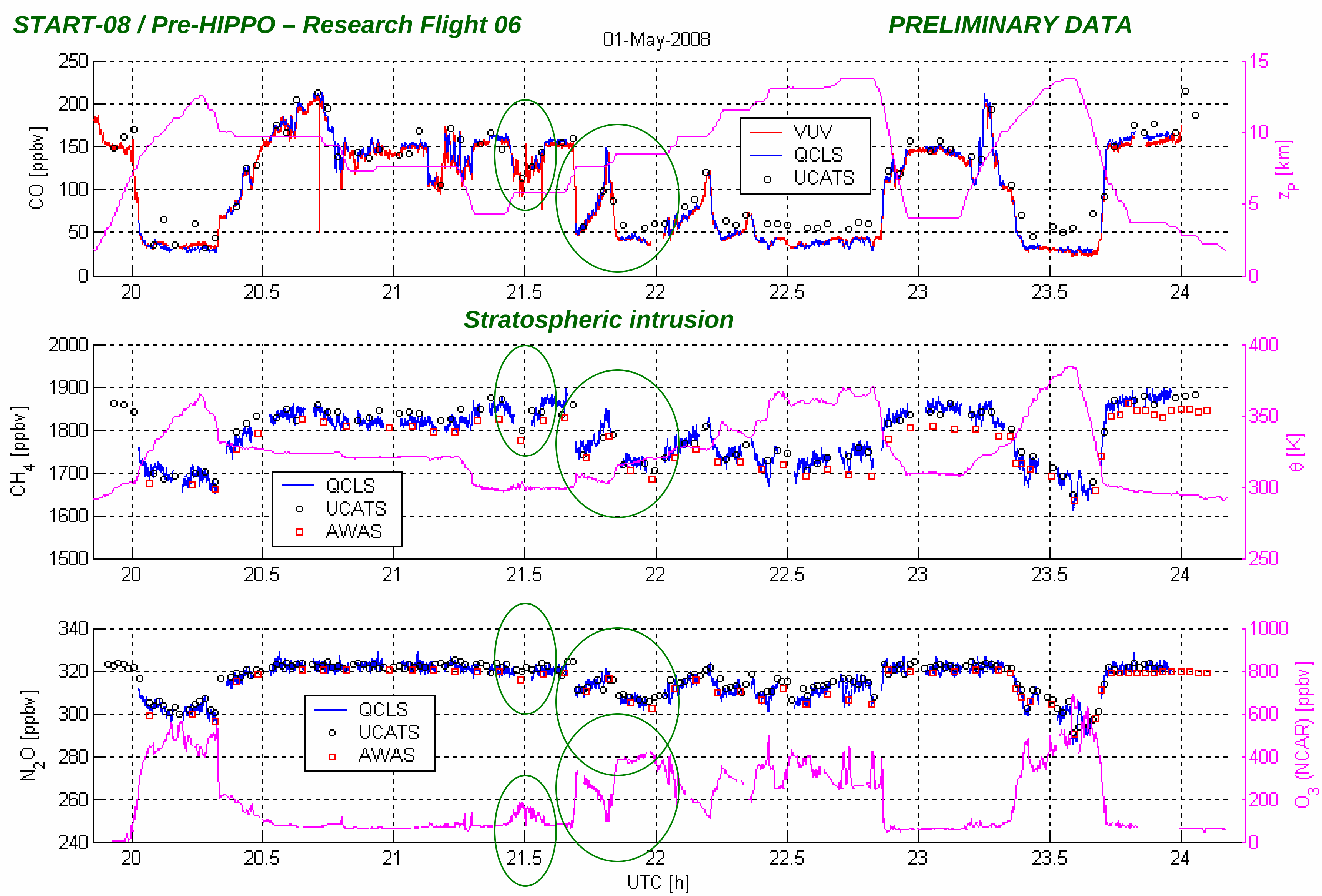
At a glance



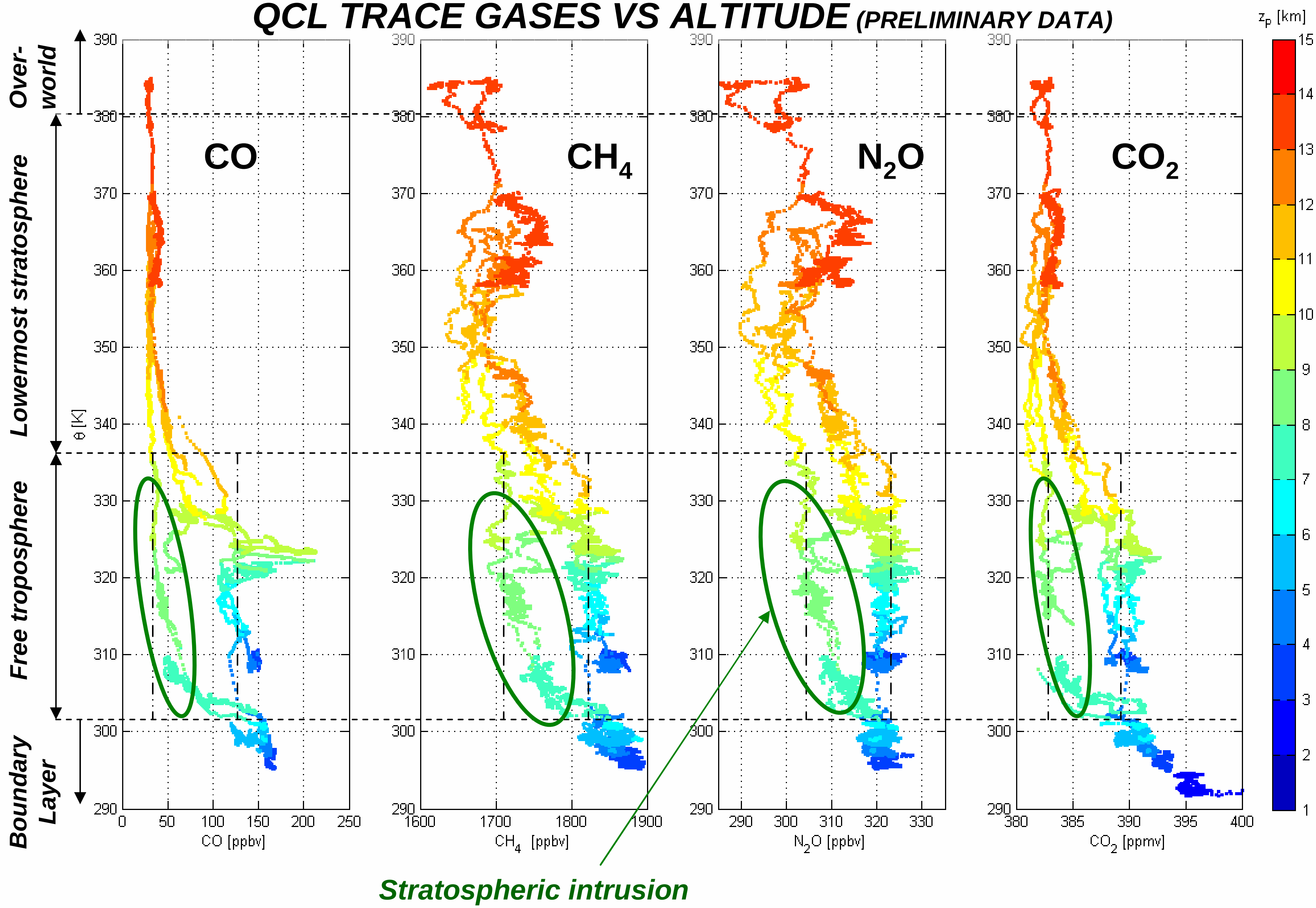
- Integration for HIAPER completed May 2008
- Ready for integration in NASA's WB-57 and Lear35a (BARCA 2009)

- 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


BRUCE DAUBE
Dual QCL
CH4-N2O (7.8 µm)
CO 4.6 µm
SINGLE QCL
CO2 (4.3 µm)
CAPACITY
3500 LBS


START-08 / Pre-HIPPO – Research Flight 06
PRELIMINARY DATA
01-May-2008
CO [ppbv]
z_p [km]
VUV
QCLS
UCATS
Stratospheric intrusion
CH_4 [ppbv]
θ [K]
QCLS
UCATS
AWAS
N_2O [ppbv]
O_3 (NCAR) [ppbv]
QCLS
UCATS
AWAS
UTC [h]

QCL TRACE GASES VS ALTITUDE (PRELIMINARY DATA)



CARBON DIOXIDE STUDIES

We have demonstrated continuous, real time measurements of ambient carbon dioxide isotopic ratios using pulsed-QCLs at 4.3 μm

- Both ^{13}C and ^{18}O are monitored
- Time resolution is 1 second
- Measurement precision of 0.2δ in one second, or 0.03δ in 300 sec.
- Atmospheric monitoring of isotopic gradients
- Eddy covariance iso-flux measurements
- Determination of Net Ecosystem Exchange of CO_2

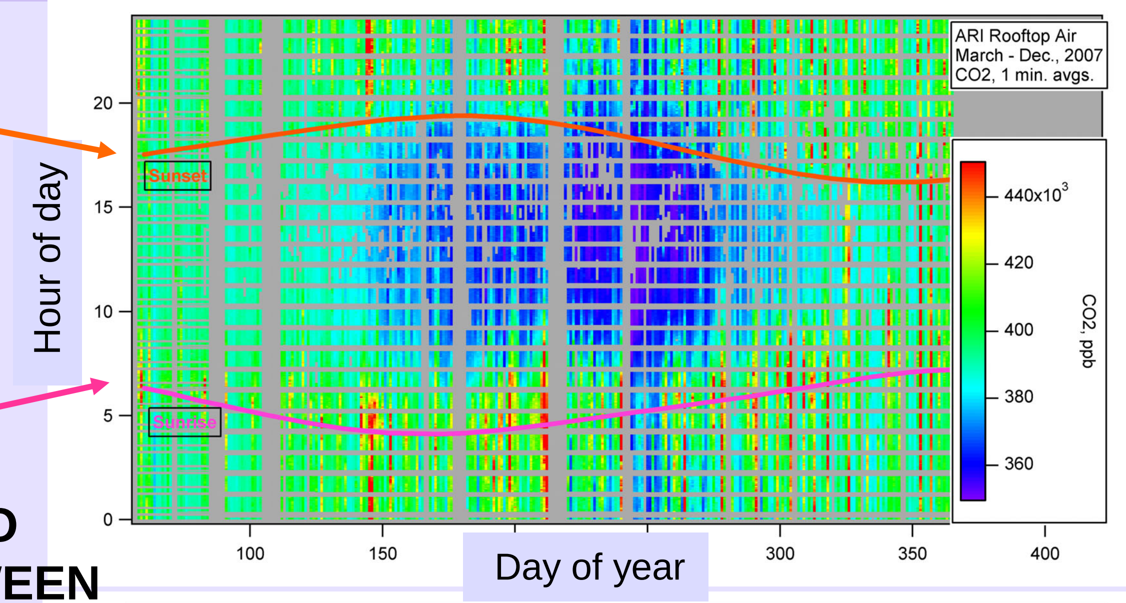
Collaborators: **Bela Tuzson and Lukas Emmenegger**
EMPA, Air Pollution/Environmental Technology Lab, Uberlandstr. 129, CH-8600 Duebendorf, Switzerland

D. D. Nelson et al., Appl. Phys. B90, 310-309 (2008),
“New method for isotopic ratio measurements of atmospheric carbon dioxide using a 4.3 μm pulsed quantum cascade laser”.

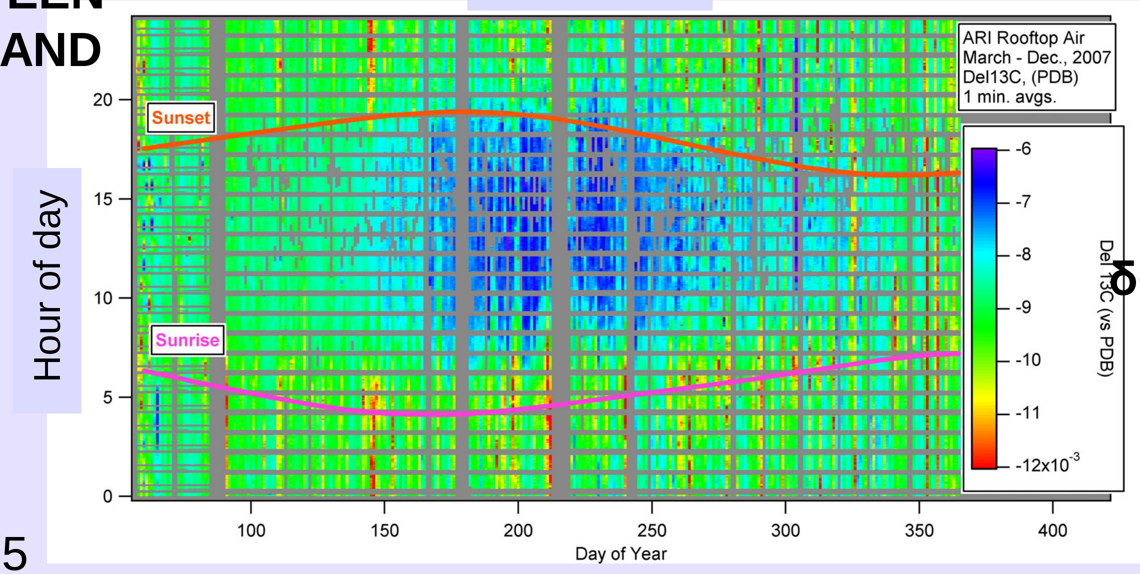
B. Tuzson et al., Appl. Phys. B90, DOI: 10.1007/ s00340-008-3085-4 (2008),
“High precision and continuous field measurements of $\delta^{13}C$ and $\delta^{18}O$ in carbon dioxide with a cryogen-free QCLAS”

10 Months of ambient air data at Aerodyne

Rooftop Sampling $^{12}CO_2$ & $\delta^{13}C$, 1 min Avg's, February 26 – December 31, 2007



$[^{12}CO_2]$



$\delta^{13}C$ (vs PDB)

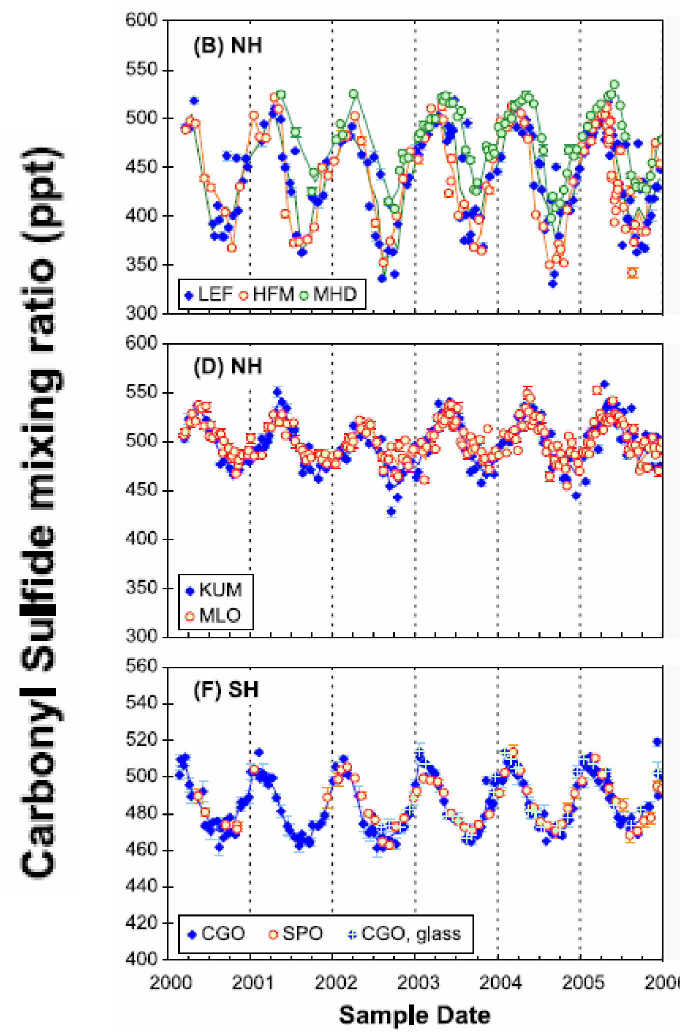
PROBLEM: HOW TO DISTINGUISH BETWEEN PHOTOSYNTHESIS AND RESPIRATION?

ALPESLASERS
QCL N63g11
In operation since 2005

ATMOSPHERIC CARBONYL SULFIDE (COS)

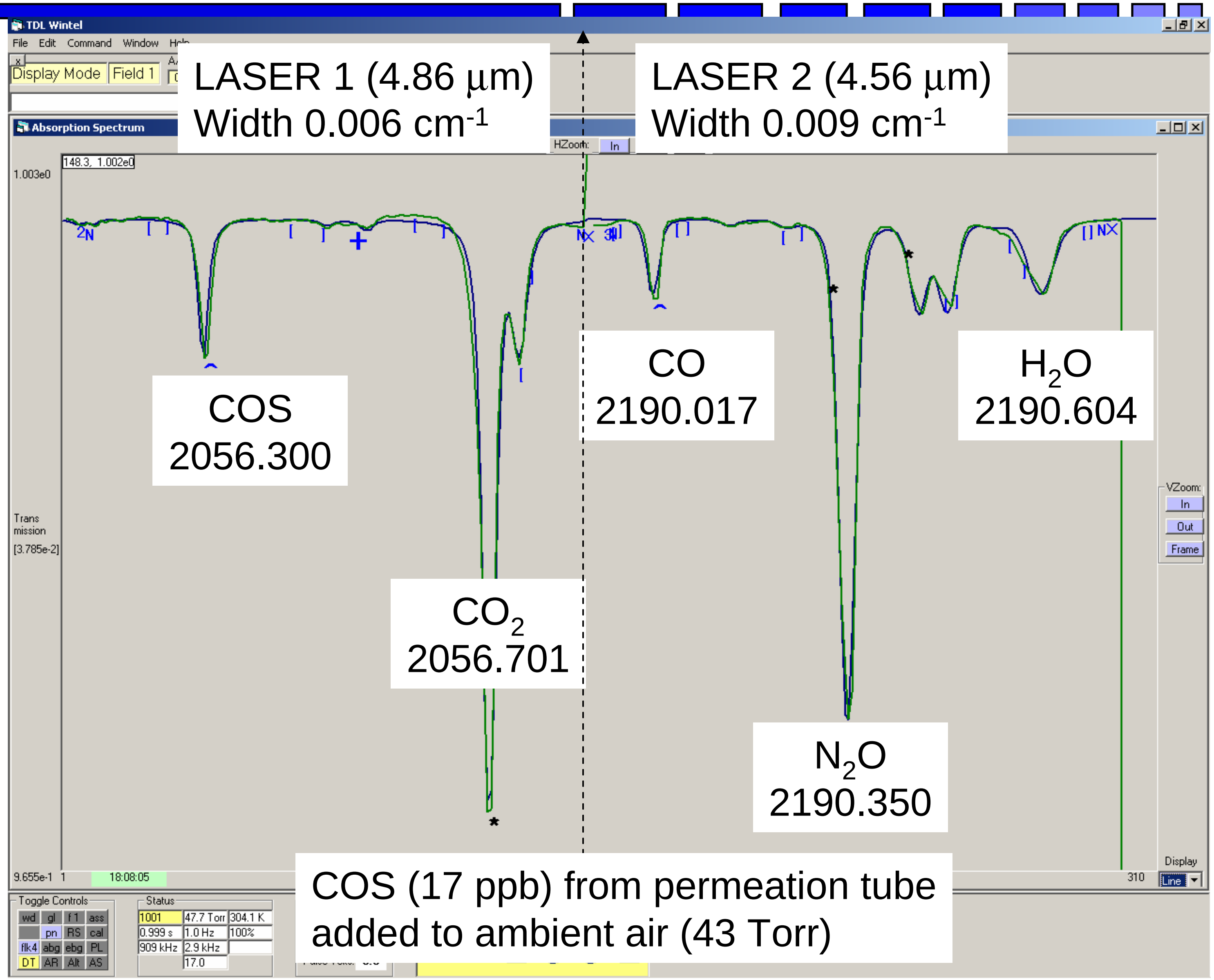
- Source: oceans
- Sink: vegetation
- Mixing ratio ~400 ppt (10^{-12})
- Seasonal Variability 30% (NH), 10% (SH)
- **Uptake by vegetation mimics CO_2 but without respiration component**
- On-line continuous COS measurements can be used for determining Net Ecosystem Exchange of CO_2

Collaborators: Keren Stimler, Dan Jakir
Weizmann Institute



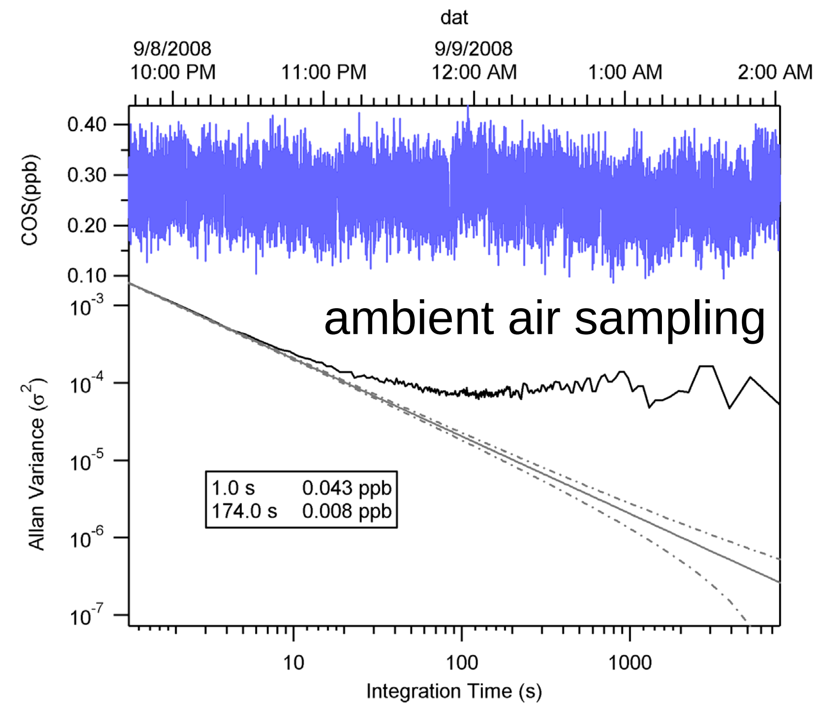
Montzka et al.,
JGR 112 D09302 (2007)

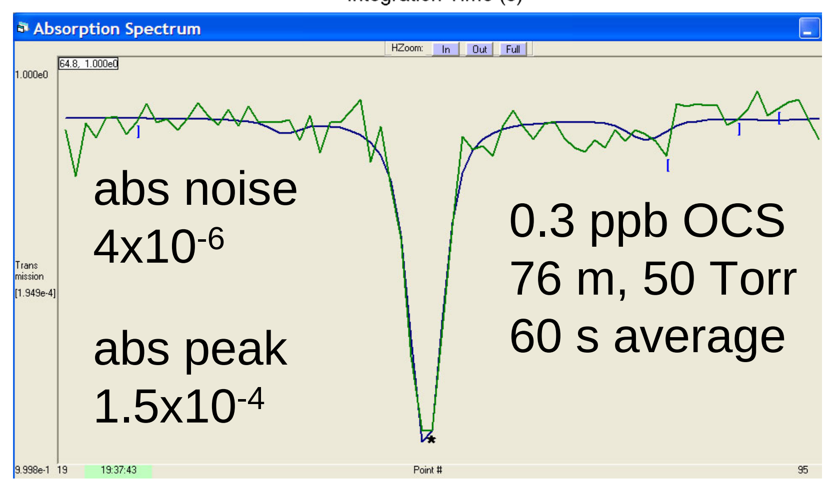
Dual pulsed-QCL system for COS ecology studies



COS Detection with pulsed-QCLs

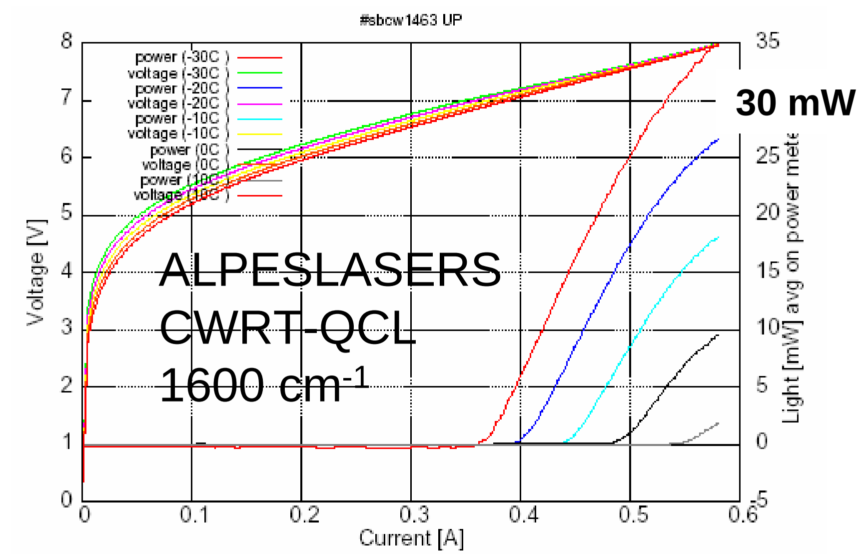
- Strong IR absorber
  ($S=2e^{-18}\,cm^3\,molec^{-1}\,cm^{-1}$)
- Allan variance plot
  short term noise and
  long term stability
- 43 ppt $Hz^{-1/2}$ ($ppt=10^{-12}$)
- Minimum 8 ppt, 100s
- Spectral averaging
  agrees with Allan
  plot residual rms

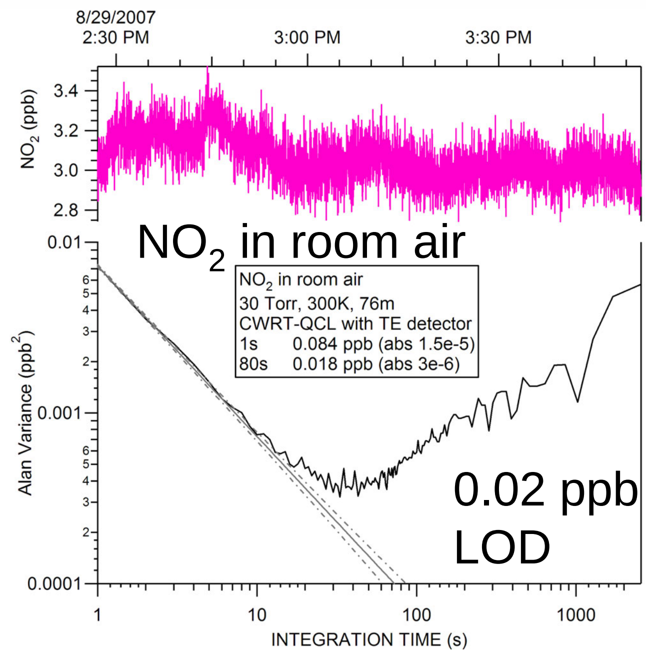




CRYOGEN-FREE CW QCLs

- Narrow Linewidth
  - Improved specificity
  - Greater absorption
- Higher Power
  - **TE-cooled detectors**
  - Longer path lengths
- **But, can be more susceptible to optical fringes**



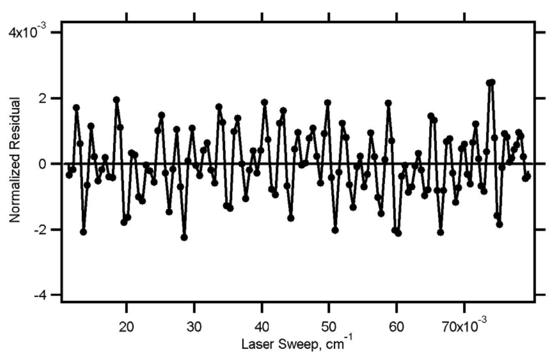


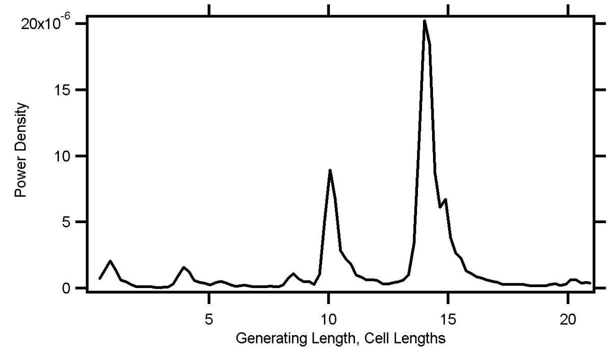
Interference Fringes with QCL SYSTEMS

Pulsed: Fringes not observed. 10 ns electrical pulse, ~5 ns optical pulse

CW: Cell fringes observed, and can limit stability

Amplitude 10^{-4} to 10^{-3}, FSR: Even multiples of base length, Pattern dependent.

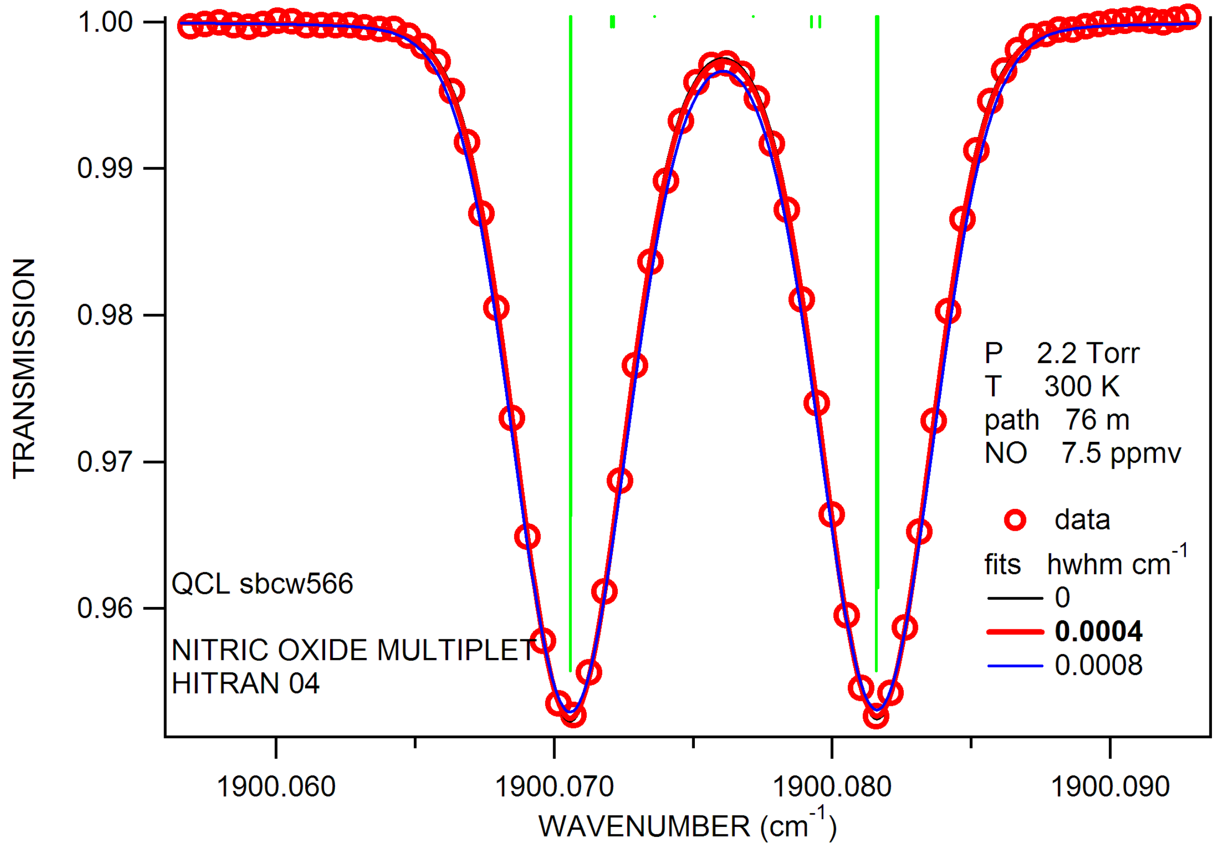




Reduction: Cell- Mirror dither

Cell pattern selection for long generating lengths

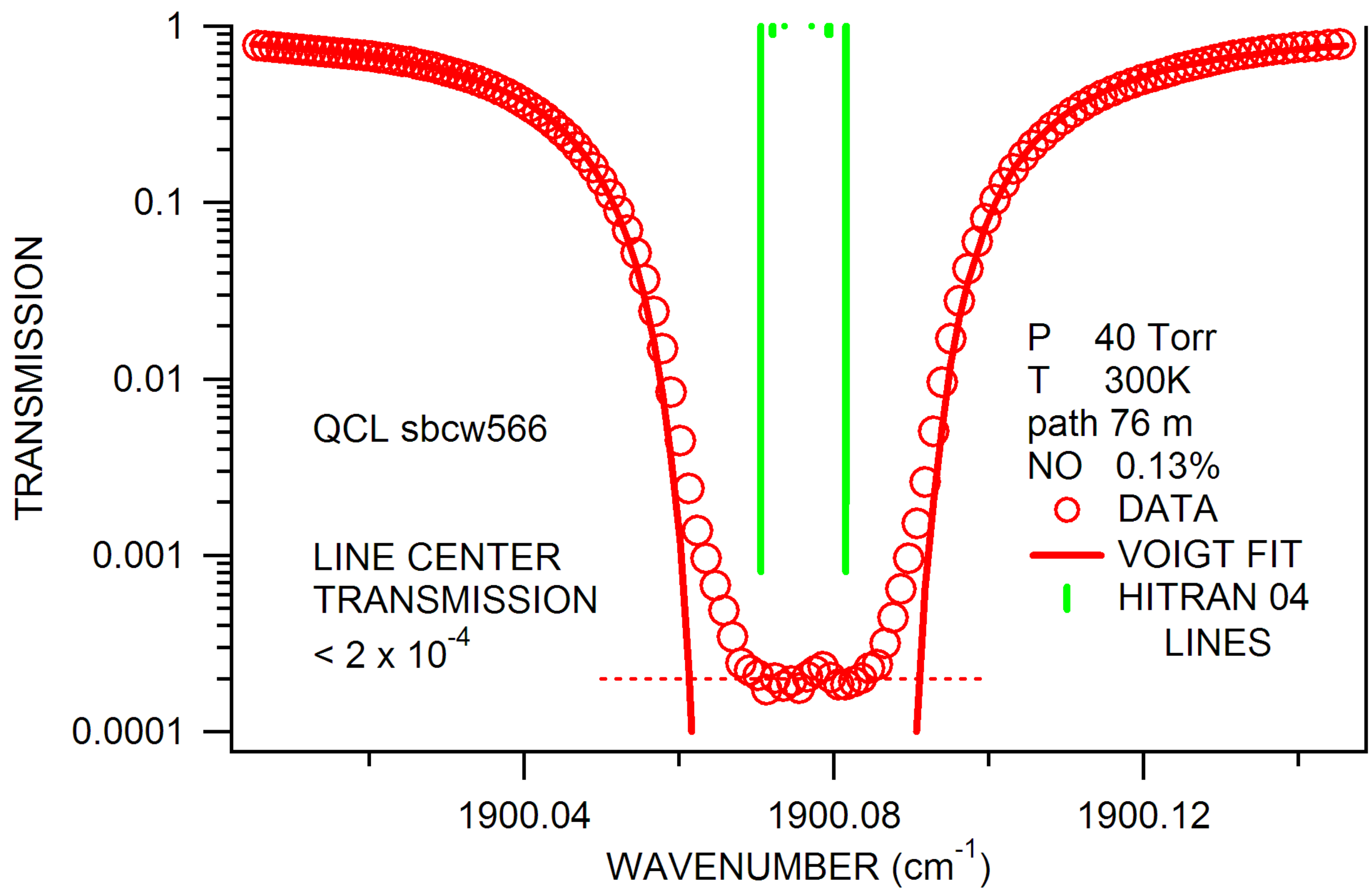
CONTINUOUS WAVE TE-COOLED QCLs



Reference: Nelson et al.,
Opt. Lett. **31**, 2012-2014 (2006)

Doppler broadened NO spectrum
Laser Line width < 0.0004 cm^{-1}

CW-RT QCL MODE PURITY



Reference: Nelson et al.,
Opt. Lett. **31**, 2012-2014 (2006)

"BLACK" NITRIC OXIDE SPECTRUM
Laser Single Mode Purity > 99.98%

Pulsed vs CW QCL Detectivity

Laser chirp during the pulse leads to the appearance of wider absorption lines.

The effective laser line width under the best-compromise pulsed operating conditions was 0.006 cm^{-1} hwhm.

Nitric Oxide Detection
with TE-cooled Laser
and TE-cooled Detector

1 s average

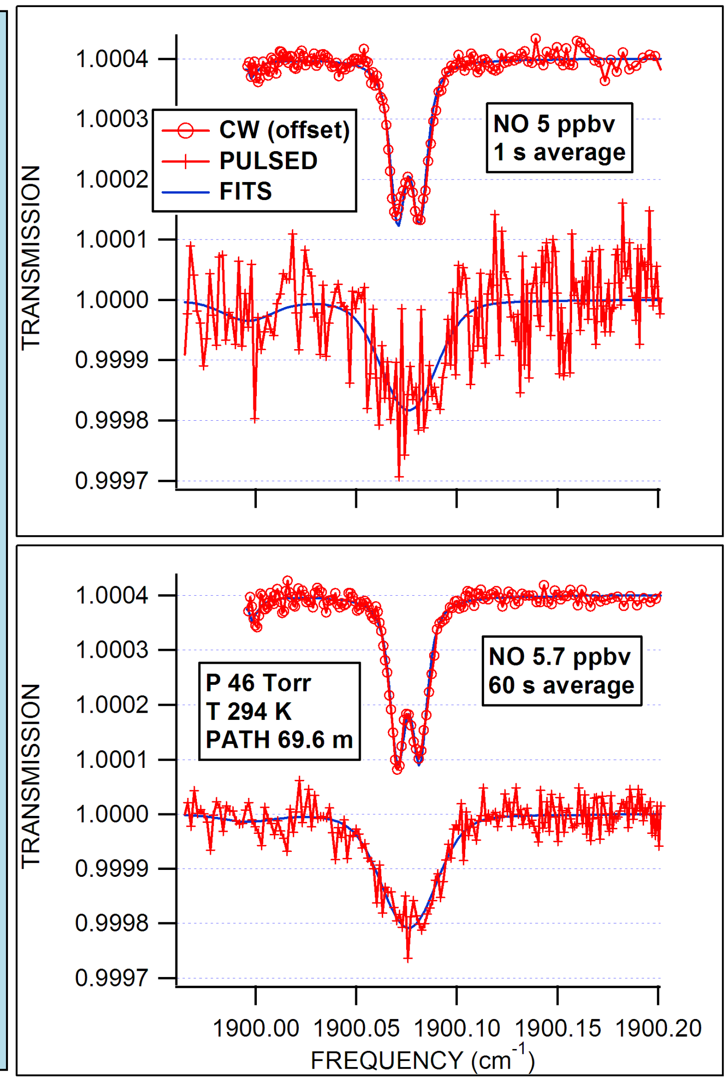
CW

Pulsed

60 s average

CW

Pulsed



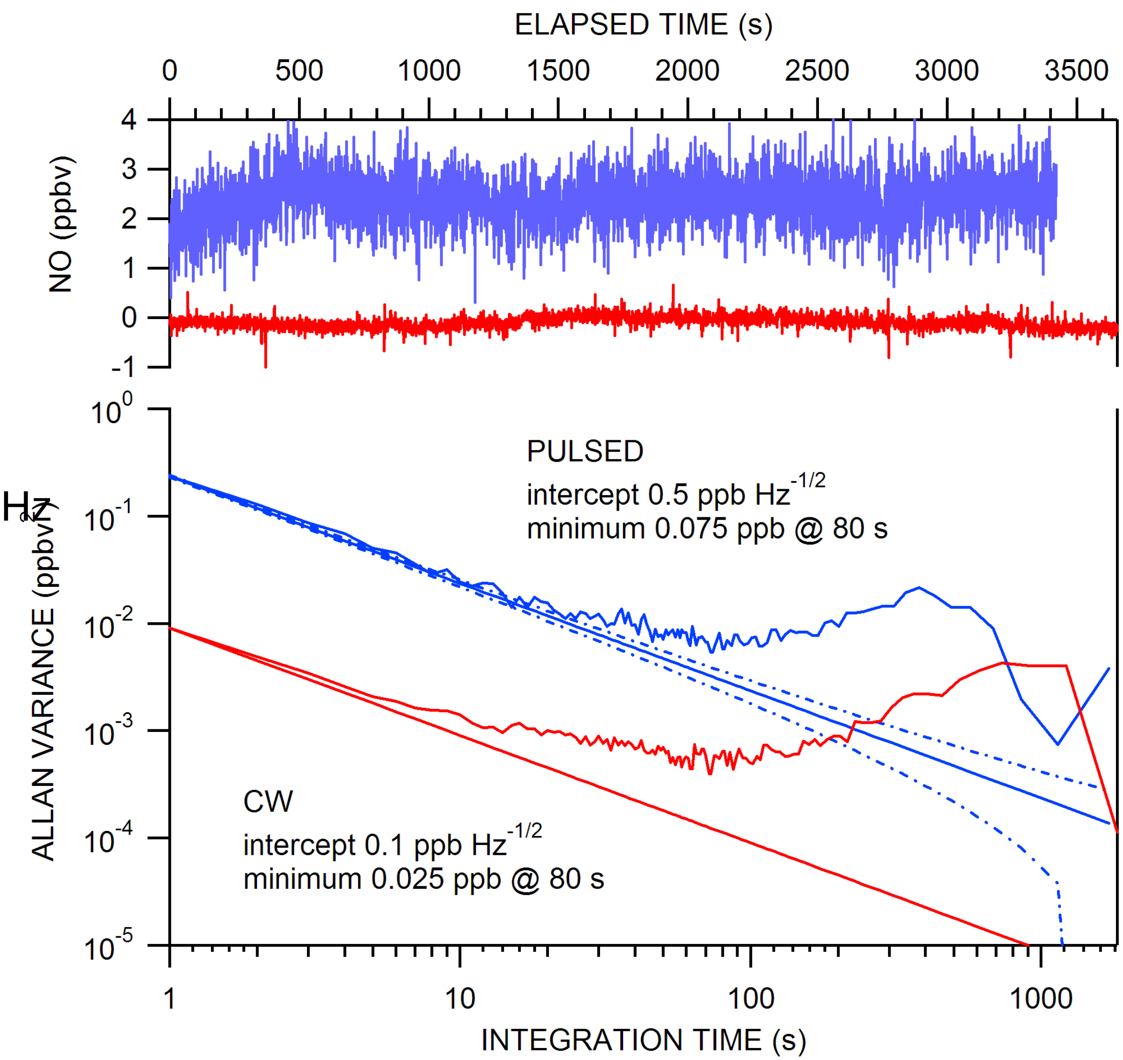
CW vs Pulsed: Allan Variance for Measured NO

TE-Cooled Detector (VIGO)

Variance vs integration time shows the limits of averaging.

NO line at 1900 cm^{-1} measured CW and pulsed, same laser.

Concentration noise, sdev @ 1 Hz
CW: 0.1 ppb
Pulsed: 0.5 ppb



$^{13}CH_4$ ISOTOPOLOGUE STUDIES

High precision measurements of ecosystem CH4 isotopic composition (13C/12C) can be used to determine specific production processes
e.g. plant emissions vs. microbial oxidation in soils;
anaerobic microbial production in wetlands vs. CO2 reduction pathways

INSTRUMENT DESIGN GOALS:

$\delta^{13}C$ 0.5 ‰ in 30 s WITHOUT CONCENTRATION

CRYOGEN FREE OPERATION

FIELD PORTABLE

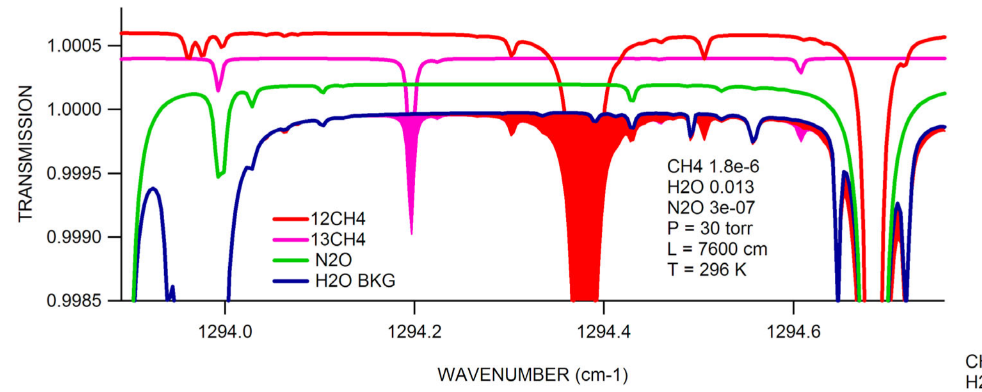
METHANE SOURCE SIGNATURES:

RICE PADDIES	-63 ±5 ‰
PEATLANDS	-60 ±5 ‰
TROPICAL FORESTS	-62 ±5 ‰
ATMOSPHERE CH4	-47 ‰
FUEL COMBUSTION	-35 ±5 ‰
BIOMASS BURNING	-25 ±5 ‰

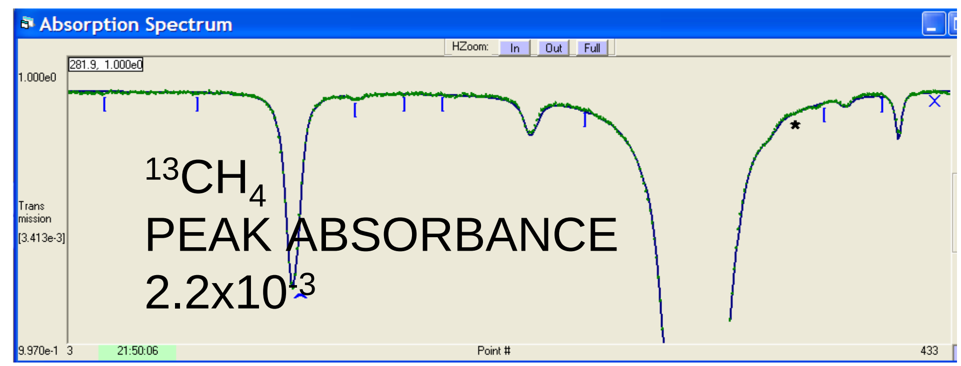
PRECISION OF 0.5 ‰ SUFFICIENT
FOR CHAMBER STUDIES AND RELAXED EDDY ACCUMULATION METHODS
BUT NOT (YET) FOR EDDY COVARIANCE

$^{13}CH_4$ SPECTRUM

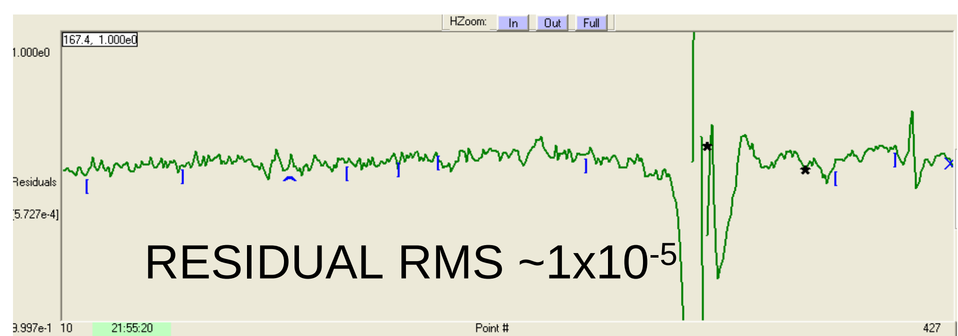
HITRAN SIMULATION
CH4 1800 ppb
Path 76m, 30 Torr



EXPERIMENTAL SPECTRUM
CW QCL LASER (1294 cm^{-1})
Path 210m, 30 Torr
Laser line width 0.0012 cm-1
30s sample, 30s background



RMS NOISE in fitted 1s data
3 ppb (1.5 per mil of ambient)



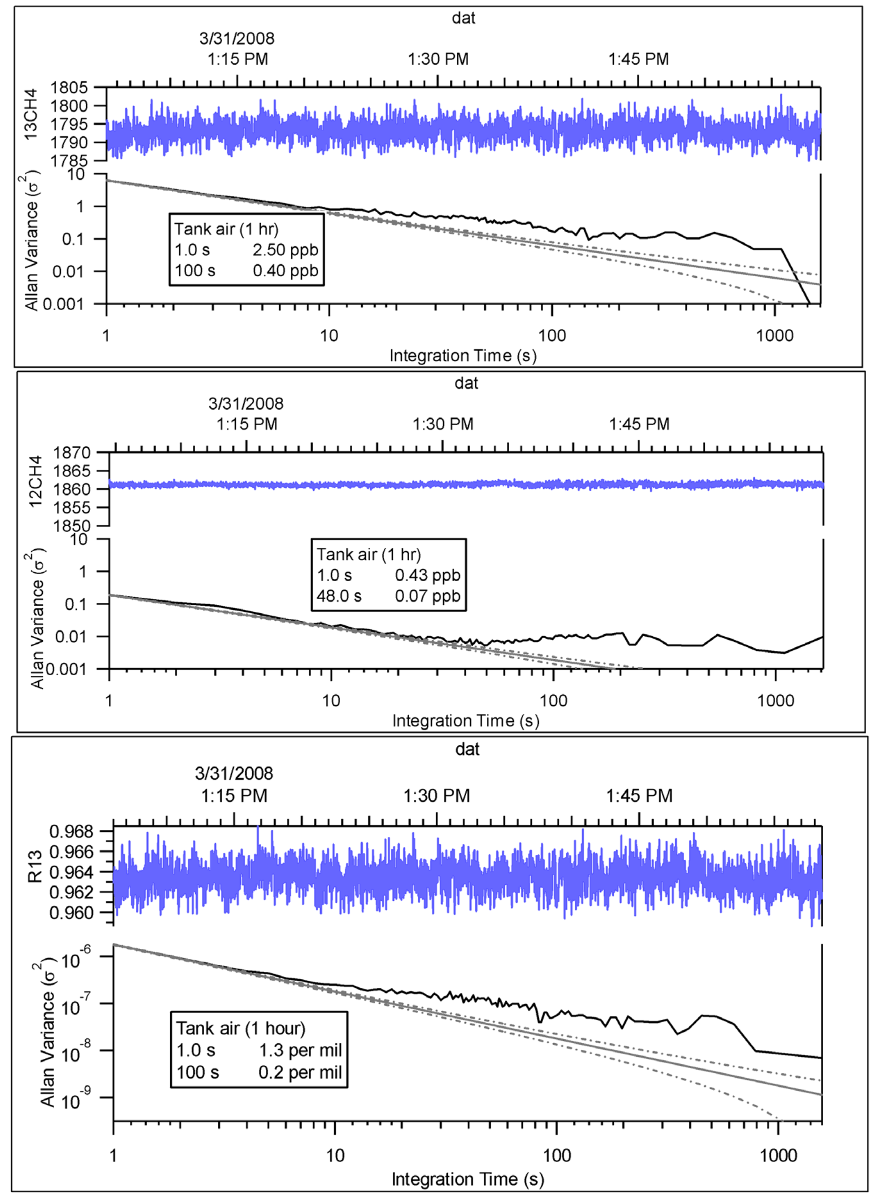
$^{13}CH_4/^{12}CH_4$ PRECISION

TANK AIR
1 s data stream for 1 hour

PRECISION LIMITED BY BASELINE VARIATIONS IN $^{13}CH_4$ SPECTRUM

$^{13}CH_4$	2.5 ppb $Hz^{-1/2}$
$^{12}CH_4$	0.4 ppb $Hz^{-1/2}$
R13	1.3 per mil $Hz^{-1/2}$
	0.2 per mil 100 s

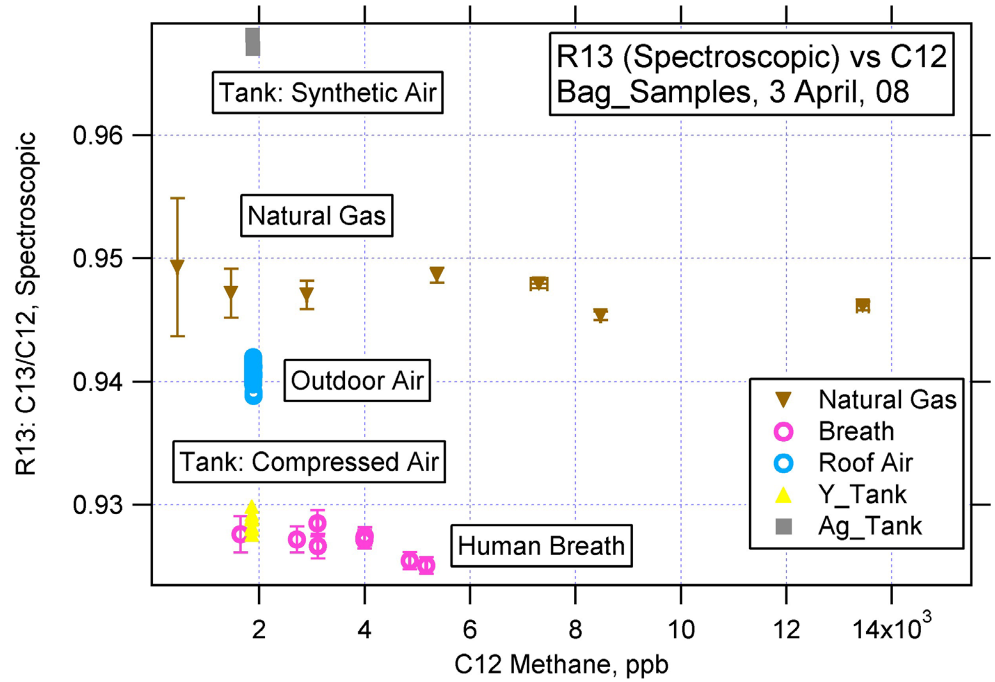
SPECTROSCOPIC ACCURACY
± 1% of TANK VALUE FOR CH_4



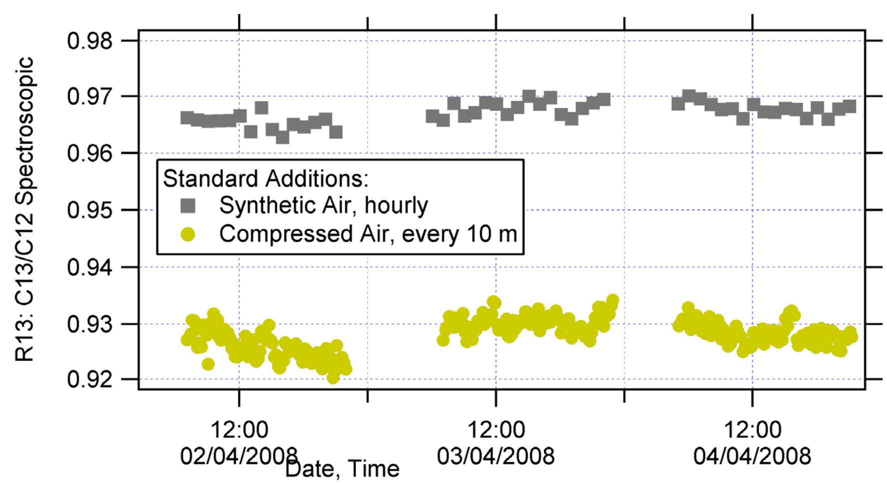
$R13 = {}^{13}CH_4/{}^{12}CH_4$ SAMPLE MEASUREMENTS

LARGE VARIATION OBSERVED IN R13 AMONG SAMPLES

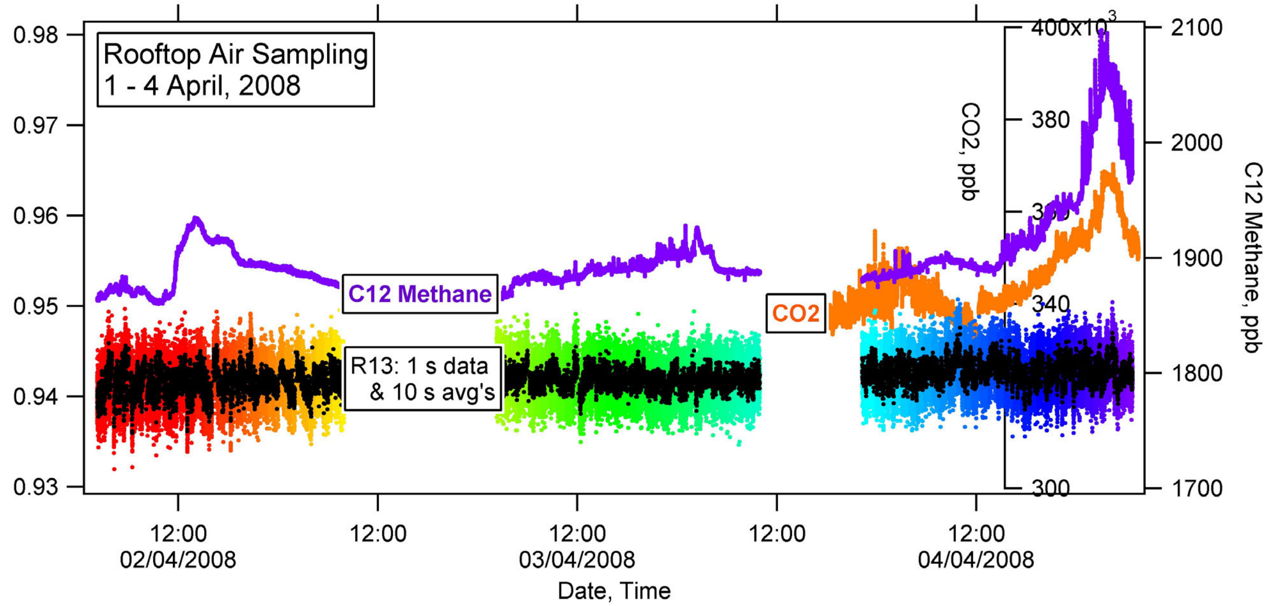
- SYNTHETIC AIR TANK
- NATURAL GAS (DILUTED)
- OUTDOOR AIR
- COMPRESSED AIR TANK
- HUMAN BREATH (McMANUS)



INSTRUMENT DRIFT CORRECTED BY PERIODIC ADDITIONS OF TANK AIR

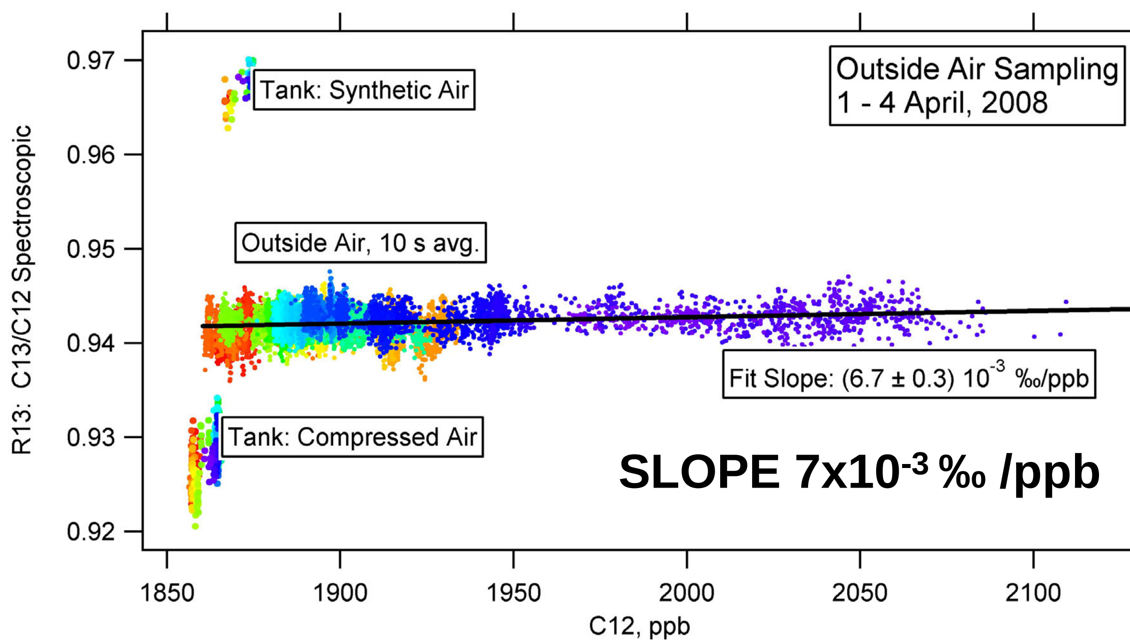


MONITORING $^{13}CH_4/^{12}CH_4$ IN AMBIENT AIR



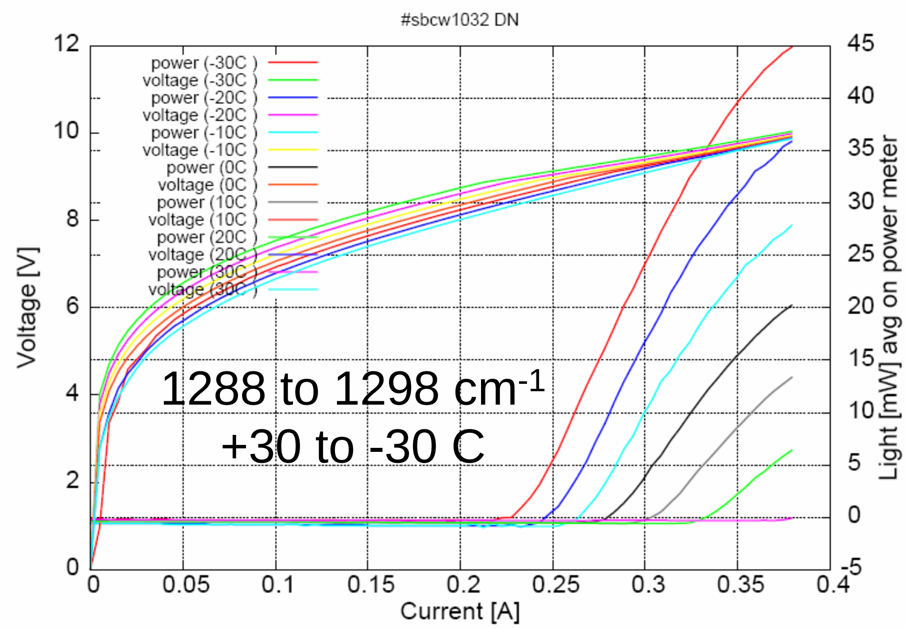
POSITIVE SLOPE
OF R13 vs $^{12}CH_4$
SOURCE SIGNATURE
-35 ‰ (14 ‰ > ATM)

FOSSIL FUEL
COMBUSTION,
NOT WETLAND,
IS DOMINANT
LOCAL METHANE
SOURCE (APRIL 2008)



CH_4 ISOTOPOLOGUE MEASUREMENTS

- EXTREME STABILITY REQUIRED FOR ALL INSTRUMENTAL PARAMETERS
  - Pressure 0.01 Torr
  - Cell T 2 mK
  - Laser T 1 mK
  - Laser amplitude stability <0.01%
- LASER POWER >30 mW
- GOOD DETECTOR LINEARITY (LN2-cooled HgCdTe)
- CELL MIRROR REFLECTIVITY >99.3%
- LONG PATH LENGTHS >200m



ALPESLASERS CWRT QCL 7.8 μm

CONCLUSION:

CONTINOUS MEASUREMENTS OF $^{13}CH_4/^{12}CH_4$ WITH PRECISION <1 ‰ ARE NOW POSSIBLE WITHOUT PRECONCENTRATION USING MID-IR CW-RT QC LASERS

SUMMARY

- **PULSED QC LASERS PROVIDE CRYOGEN-FREE ATMOSPHERIC TRACE GAS DETECTION**
- **DETECTION SENSITIVITY AND PRECISION WITH PULSED-QC LASERS IS SUFFICIENT FOR MANY ATMOSPHERIC MONITORING APPLICATIONS**
- **IMPROVEMENTS OBTAINED WITH CONTINUOUS-WAVE, ROOM TEMPERATURE QCLs**

SPECIES DETECTED AT ARI USING ALPESLASERS QCLs

TRACE GAS	*cm^{-1}*	*1 s RMS ppb 76 m path*	*LoD ppb 100 s*
NH_3	967	0.2	0.06
C_2H_4	960	1	0.5
O_3	1050	1.5	0.6
CH_4	1270	1	0.4
N_2O	1270	0.4	0.2
H_2O_2	1267	3	1
SO_2	1370	1	0.5
NO_2	1600	0.2	0.1
HONO	1700	0.6	0.3
HNO_3	1723	0.6	0.3
HCHO	1765	0.3	0.15
HCOOH	1765	0.3	0.15
NO	1900	0.6	0.3
OCS	2071	0.06	0.03
CO	2190	0.4	0.2
N_2O	2240	0.2	0.1
$^{13}CO_2/^{12}CO_2$	2311	0.5 ‰	0.1 ‰

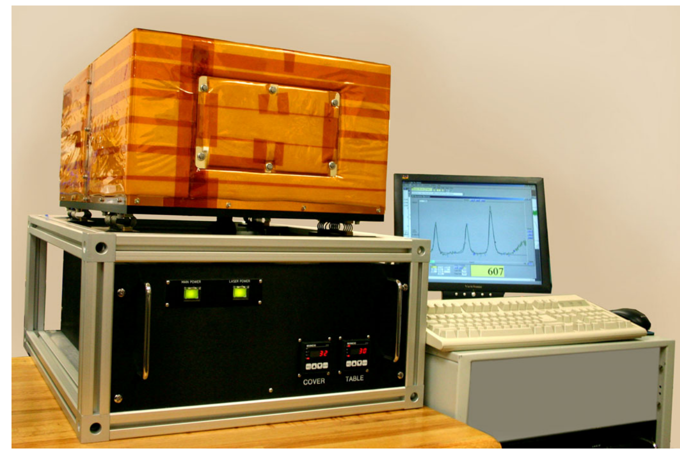
RED: OBSERVED
BLACK: ANTICIPATED

“COMMERCIALIZATION” SUMMARY

- Aerodyne Research QCL INSTRUMENTS FOR TRACE GAS DETECTION 2004-2008
  - SINGLE LASER SYSTEMS 12
  - ISOTOPE SYSTEMS (CO_2) 6
  - DUAL LASER SYSTEMS 15
  - QUAD LASER SYSTEMS 6

  ~40 UNITS OVER 4 YEARS

- CURRENT PRICE OF INSTRUMENT: 100K to 200K (USD)
- PRESENT MARKET MAINLY RESEARCH INSTITUTIONS
- FUTURE MARKET FOR MONITORING NETWORKS AS COST DECREASES, SIMPLICITY INCREASES
- LARGER INDUSTIAL MONITORING MARKET AFTER PROVEN RELIABILITY OF DEVICES AND COMPONENTS



“WISH LIST” for mid-IR QCLs

- Extend CWRT QCLs to 11 μm
  - Compensate for weaker TE-detectors with stronger laser power
- Extend pulsed-QCLs to 3.3 μm ➔ C-H stretch
- Lower heat dissipation ➔ smaller packaging
- Manufacturing efficiency ➔ lower cost
- Improve integration laser and pulse electronics
- Better TE-cooled mid-IR detectors
  - Improved linearity, longer wavelength performance

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