Isotopic Ratio Measurements of Atmospheric Carbon Dioxide Using a 4.3 μm Pulsed QC Laser

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HITRAN 2008 Conference – Cambridge, USA
June 23, 2008

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Outline

Importance of isotopic measurements of carbon dioxide and methane

Carbon Dioxide Isotopic Measurements

- Spectroscopic Approach - Real time, unattended, long term
- Optical design
- Achieving the necessary precision – Spectral Null Method
- Achieving the required accuracy – Dilution Calibration Method
- Comparison to standards – carbon dioxide
- Ambient CO_2 data acquired in Billerica, Massachusetts

Initial Methane Isotopic Measurements

Conclusions

Distribution of $\delta^{13}C$ in Ecosystems

Stable isotope ratios of CO_2 vary through ecosystem

Isotopic signature is an important tool for quantifying sources and sinks of CO_2 in the Earth's atmosphere

10 δ units = 1%

Well known example: C-3 and C-4 plants fractionate carbon differently

This effect can be used in forensics, medical testing, biology, etc…

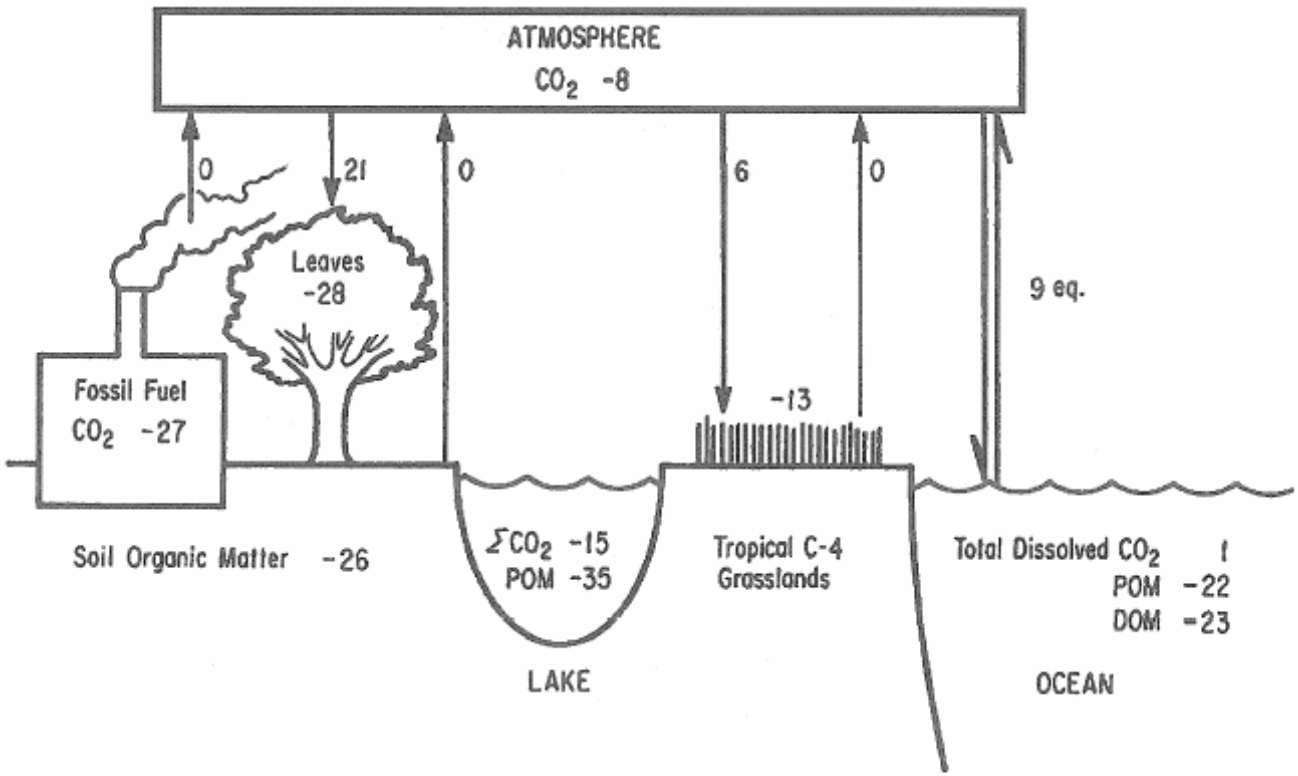
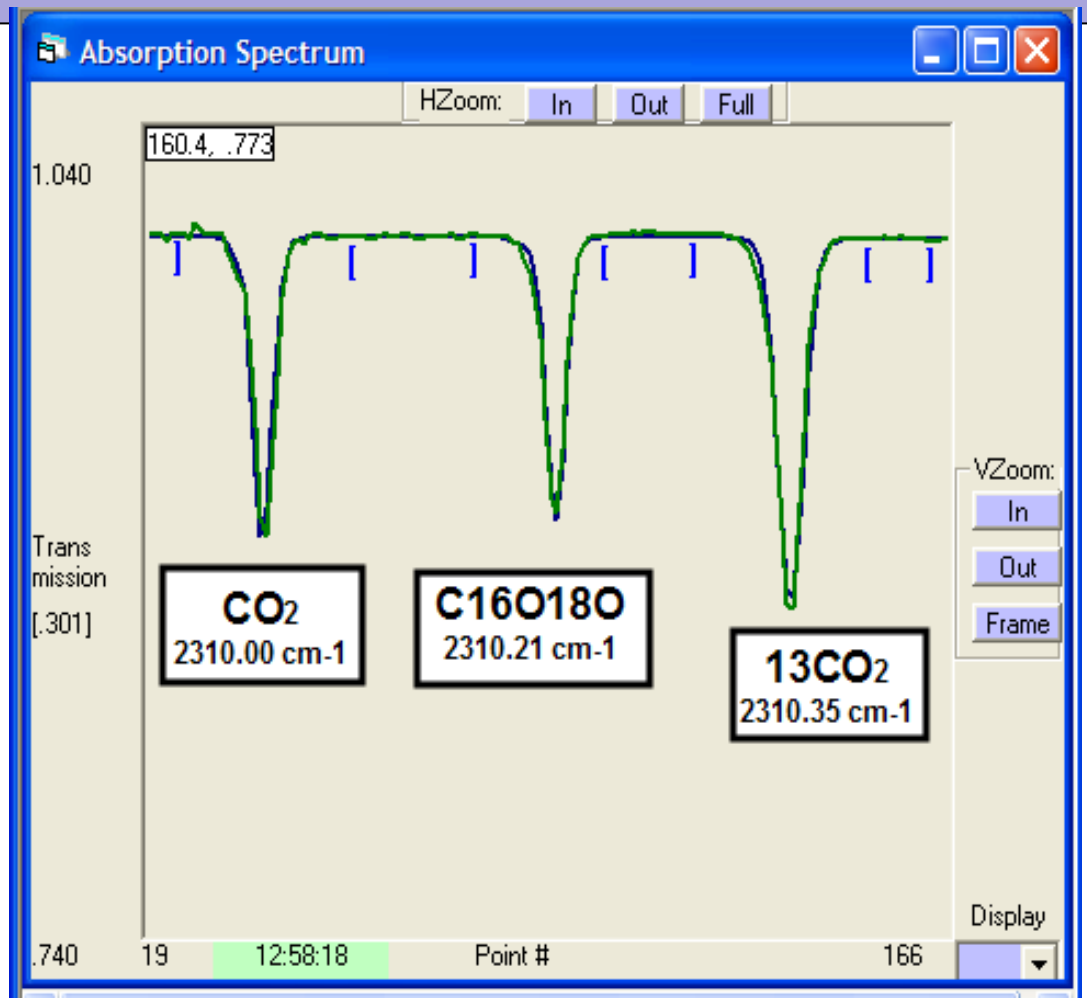


FIGURE 3.1. $\delta^{13}C$ distribution in ecosystems. Single arrows indicate CO_2 fluxes. The double arrow signifies an equilibrium isotope fractionation. Numbers for pools indicate $\delta^{13}C$ values (‰) and numbers of arrows indicate the fractionation (Δ, ‰) occurring during transfers. Negative $\delta^{13}C$ values indicate that less heavy isotope is present than in the standard (which has a 1.1% ^{13}C content; Table 1.2), not that isotope concentrations are less than zero. (From Peterson and Fry, 1987. Reprinted, with permission, from the *Annual Review of Ecology and Systematics*, Volume 18, copyright 1987 by Annual Reviews www.annualreviews.org.)

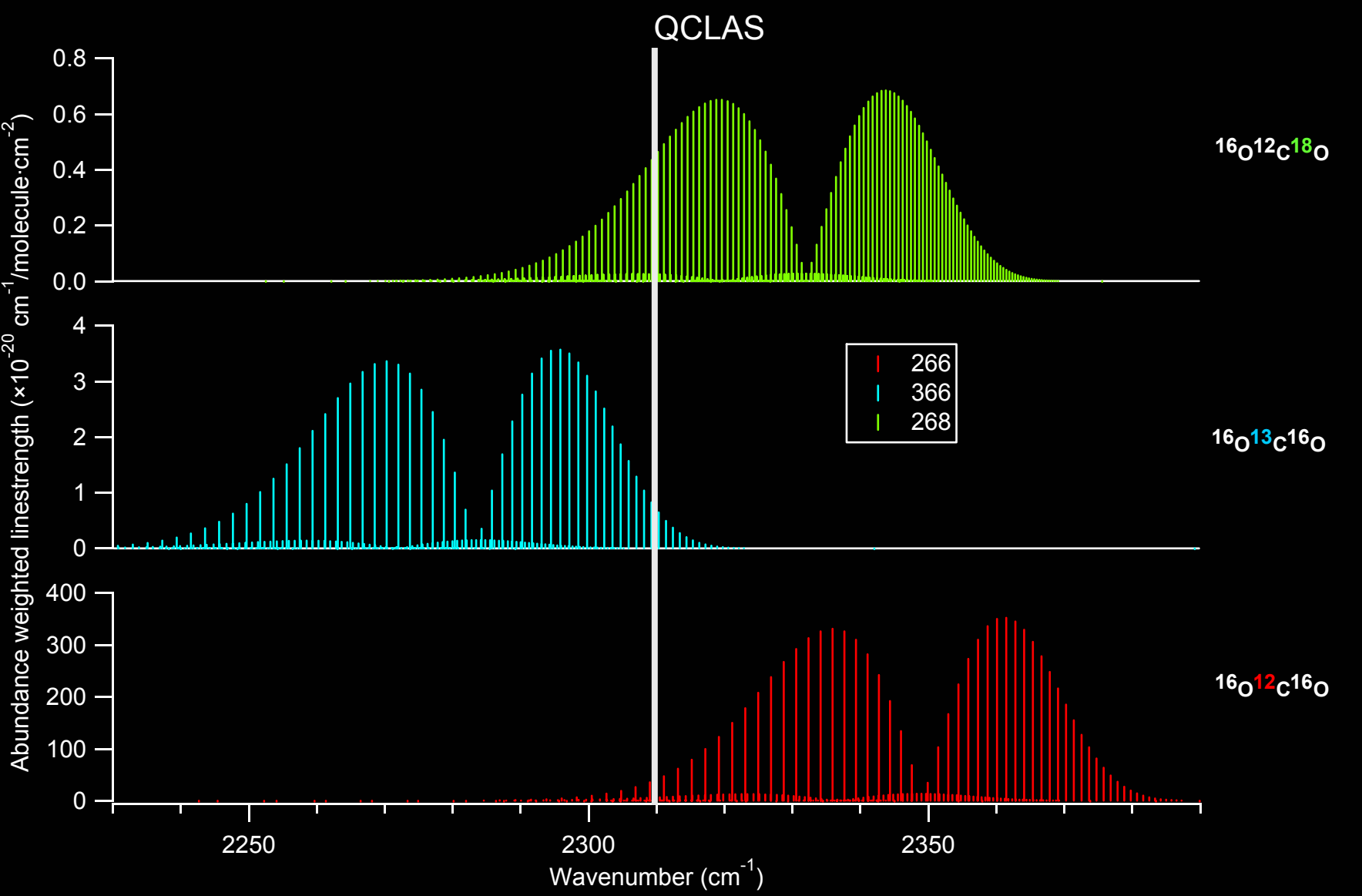
Spectroscopic Analysis

- Why use spectroscopy?
  - Fast.
  - Cheap – some day.
  - No sample prep.
  - Unattended operation!
- Originated by Bowling et al., 2001, using cryogenic TDL
- We focus on three spectral features near 2310 cm^{-1}
- Path length: 7 meters
- Optical depth: 10 – 15%, but concentrations are NOT similar
  - $[^{13}C] \sim [^{12}C]/90$
  - $[^{18}O] \sim [^{16}O]/500$
- Acquisition time: 1 sec
- Laser line width: 0.016 cm^{-1}
- Sample P: 70 Torr
- Data are plotted in green and the real time fit to the data is in blue.

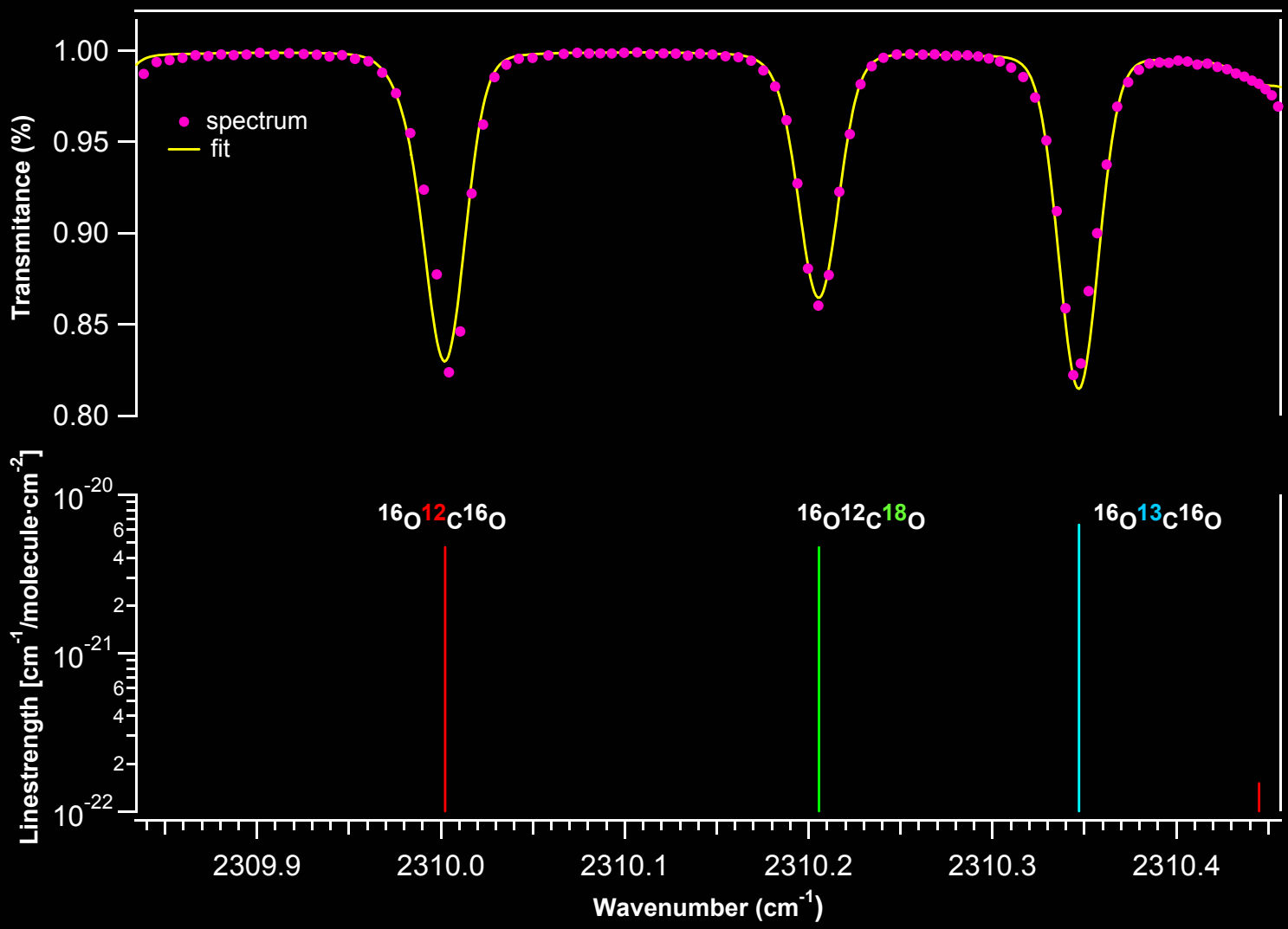


Looks easy, right?

Spectral Simulation of Isotope Specific CO_2 Bands



Measured vs. simulated spectra at 2311cm^{-1}



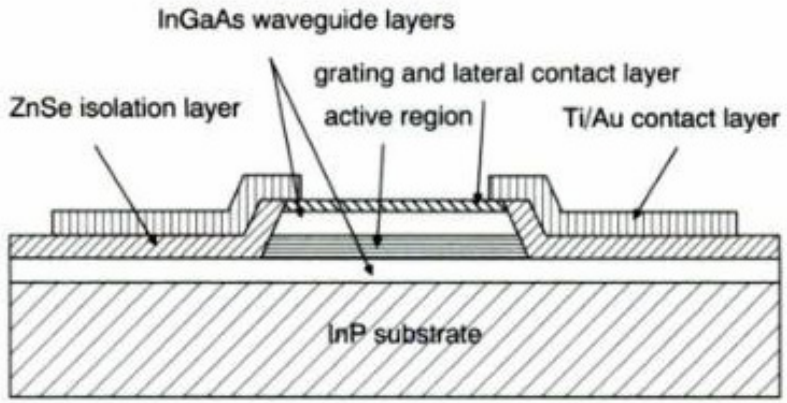
B. Tuzon et al., Infrared Physics & Technology (2007)

Quantum Cascade Lasers

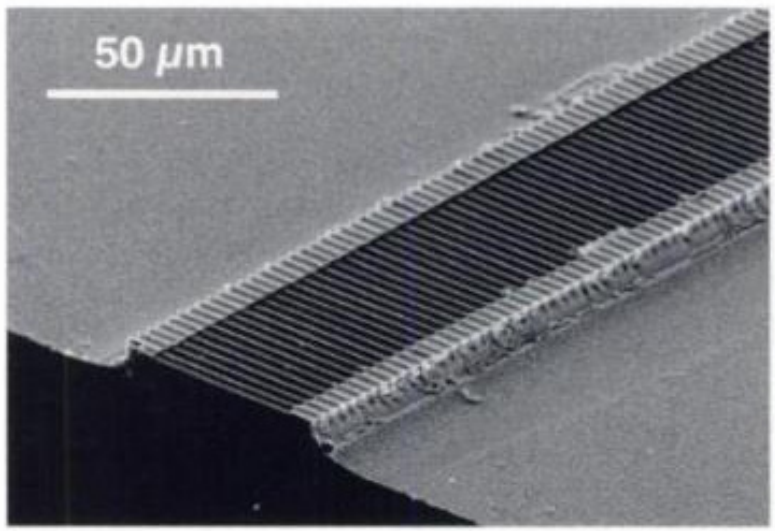
Alpes Lasers

MULITPLE LAYER STRUCTURE
eg InGaAs/AlInAs
DFB grating for single mode
Pulsed and/or CW operation
T_{max} ~300 K (TE-cooled)
P_{max} ~50 mW (CW – DFB)

Tuning Range (T) ~5 cm^{-1}
dF/dT -0.1 cm^{-1}/K
Tuning Range (I) ~ 1 cm^{-1}
dF/dI -0.002 cm^{-1}/mA
Linewidths <10^{-3} cm^{-1} CW
>5x10^{-3} Pulsed

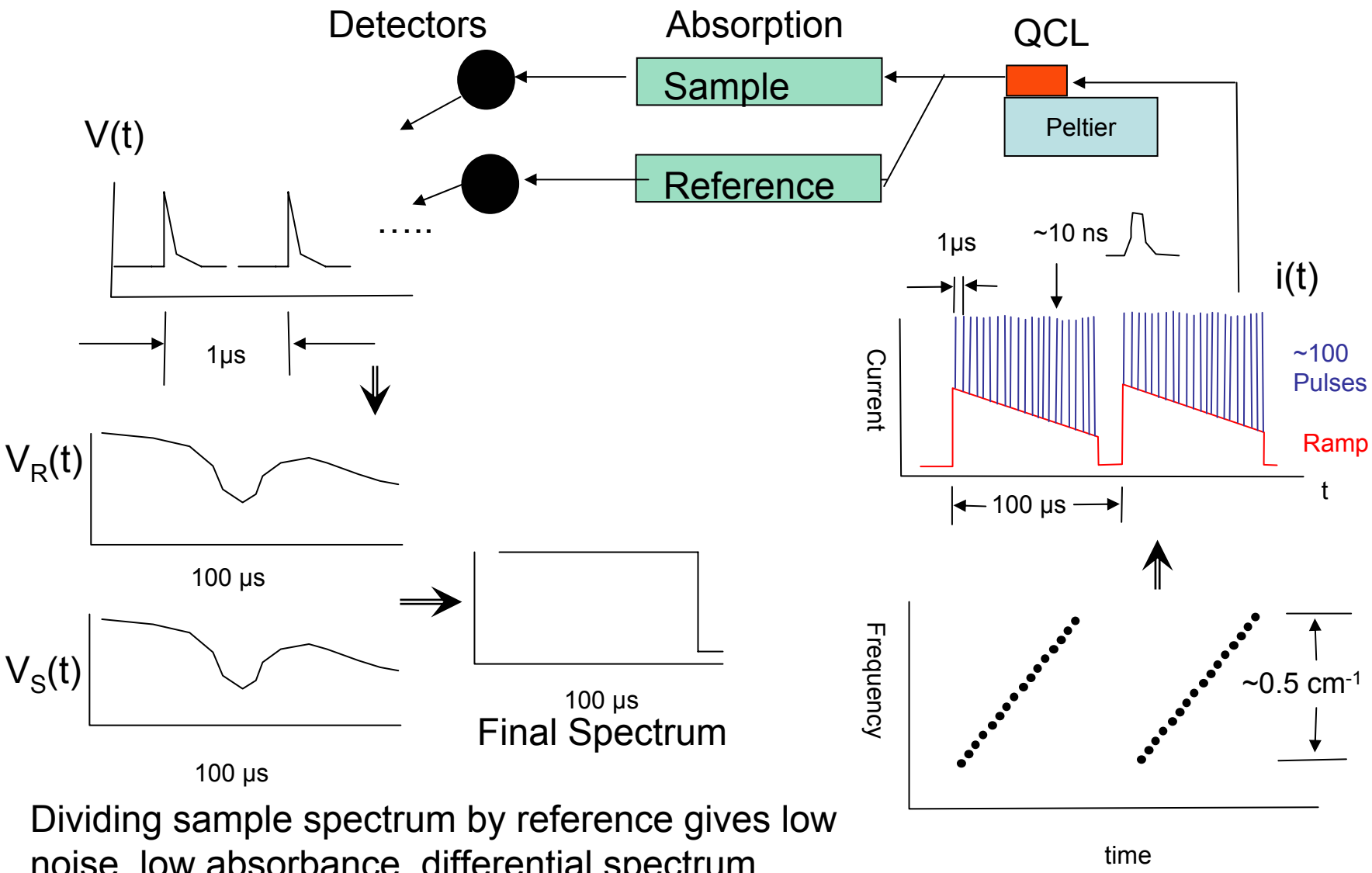


(a)



(b)

Laser Drive Cycle and Signal Processing



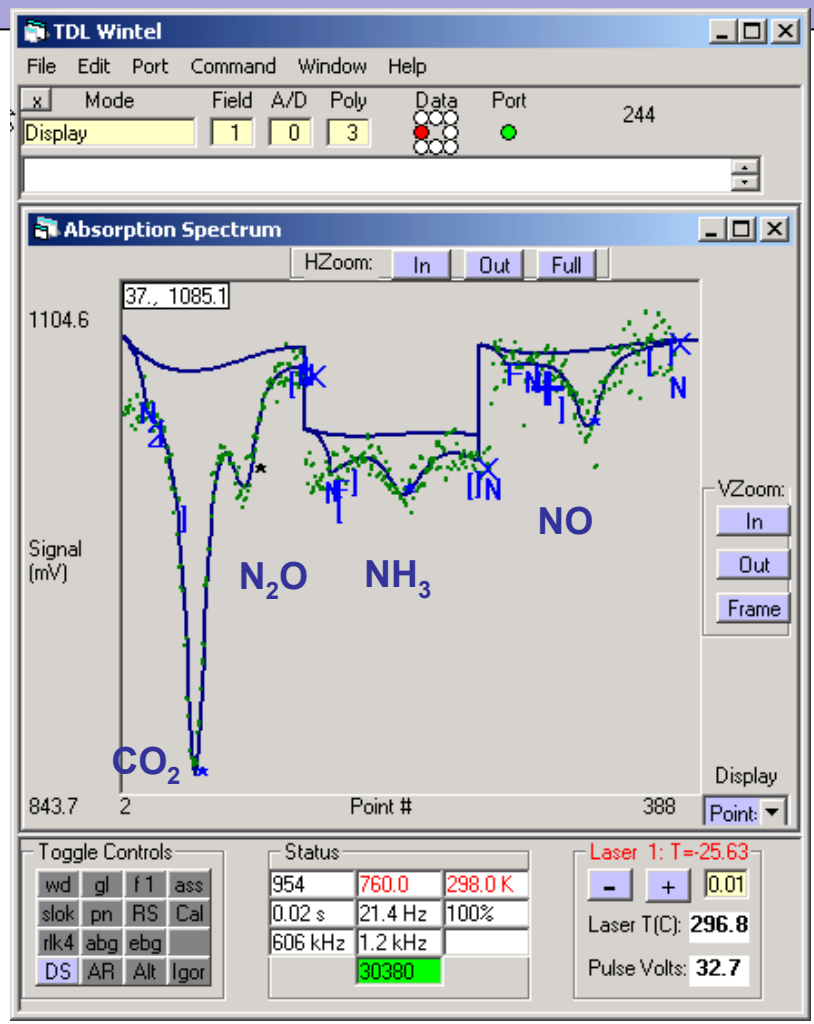
Dividing sample spectrum by reference gives low noise, low absorbance, differential spectrum.

“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
- Pulse normalization
- Rapid fitting [to 25 Hz]
- HITRAN based fit spectra
- Multi-gas concentrations
- Saved spectra
- Unattended operation
- External command language

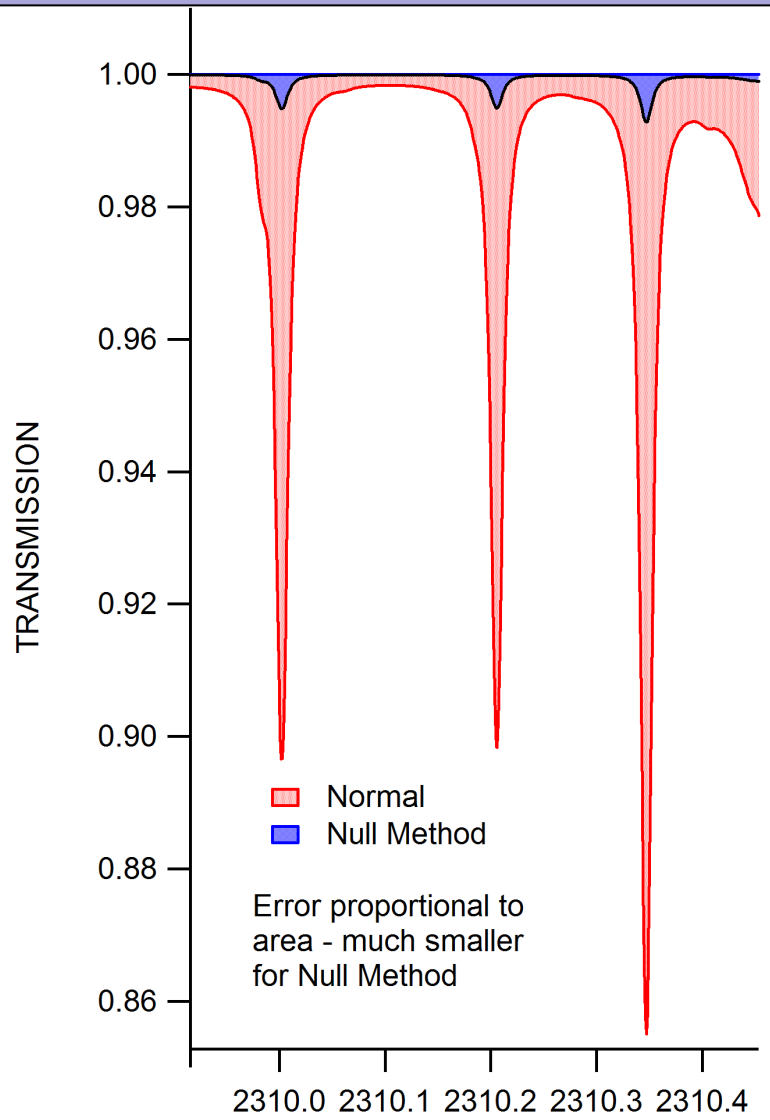


Absolute Concentrations Result

Data Sample: 3 lasers, 4 gases, 20 ms

Spectral Null Method

- Isotopic measurements require accuracy of ~ 0.1 δ or 1 in 10,000!
- Puts extreme demands on measurement of P, T, laser tuning rate, spectral fitting accuracy, etc..
- We relax these demands with spectral null method – process the ratio of the sample spectrum and a reference spectrum from a slow flow reference cell
- When sample and reference are identical, ratio shows no absorbance – it is nulled
- At this null point there is no sensitivity to tuning rate or fitting accuracy and greatly reduced sensitivity to errors in P and T



Optical Design of CO_2 Isotope Monitor

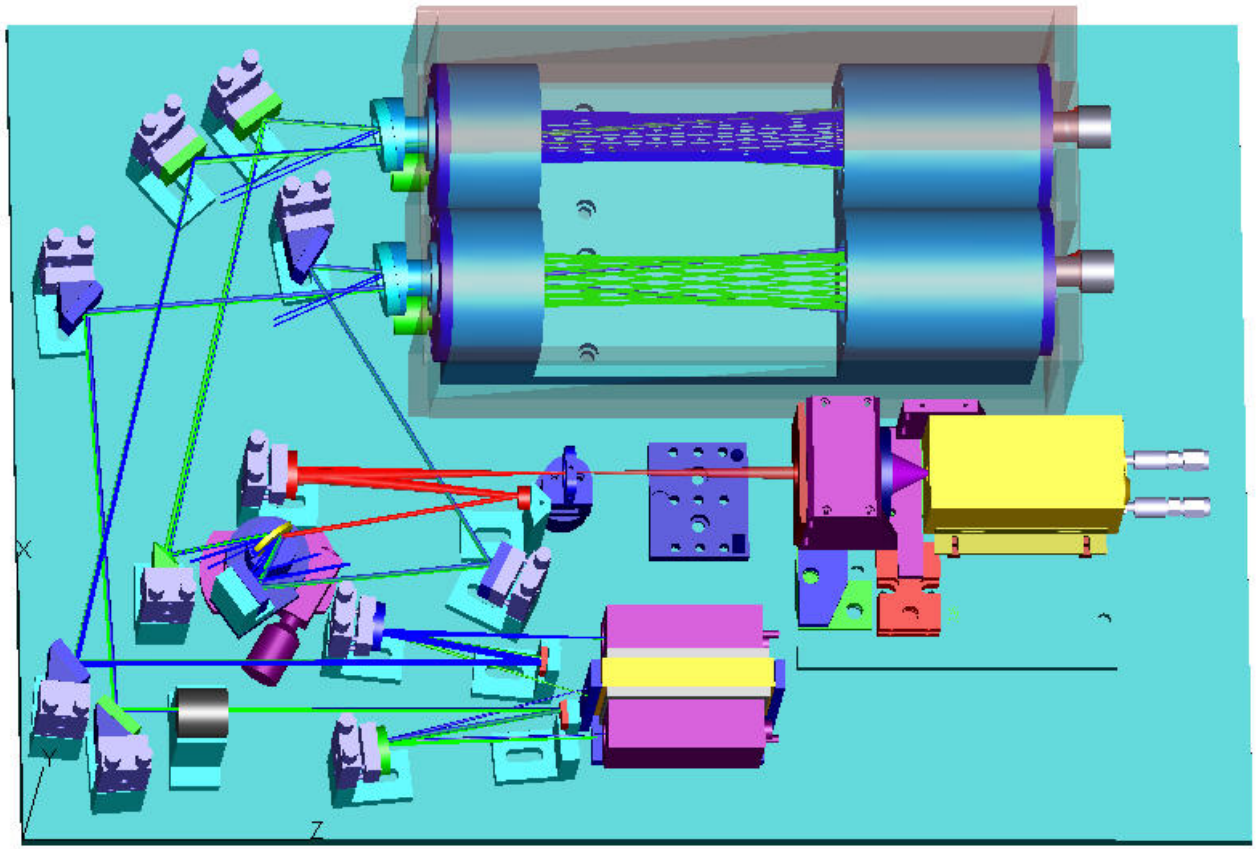
Pulsed QC laser output divided into 2 paths – reference cell and sample cell

Cells are matched in path length (7 m) and share a thermal zone

Laser beams exit cells and go to two IR detectors

Picture shows TEC detectors

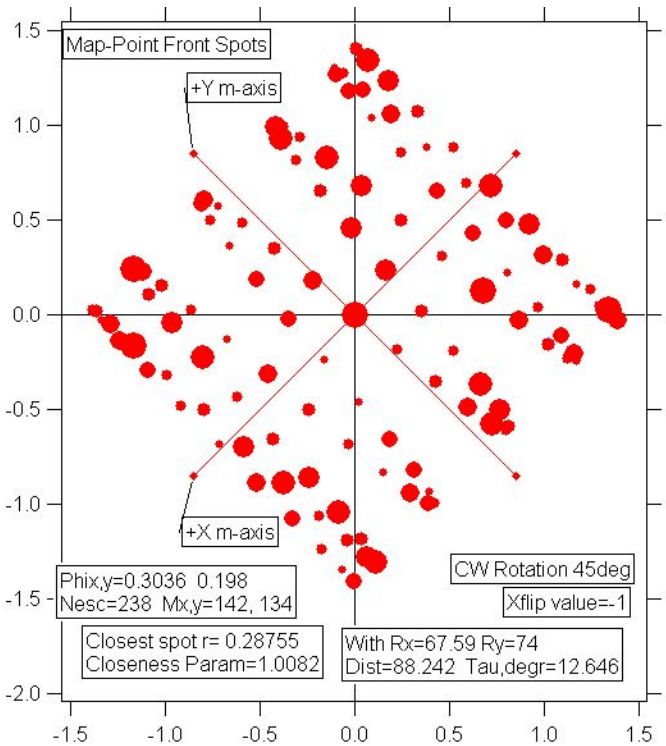
Liquid nitrogen cooled detectors are more sensitive but less convenient.

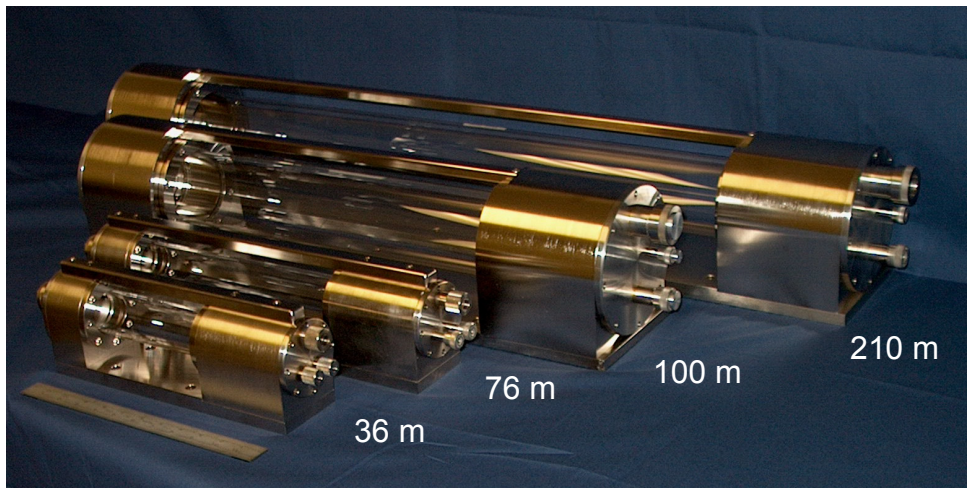


Astigmatic Multipass Cells

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





Instrument Package

Instrument package is relatively compact

Optics are on top in temperature controlled enclosure

Choice of cryogenic or thermo-electrically cooled infrared detectors

Electronics are on the bottom in rack mounted enclosure

Dimensions (cm): 53 W x 66 D x 71 H
Weight: 72 kg
Electrical Power 0.3 W, 120/240 V

New version has just been designed with a smaller footprint

Long Term Precision

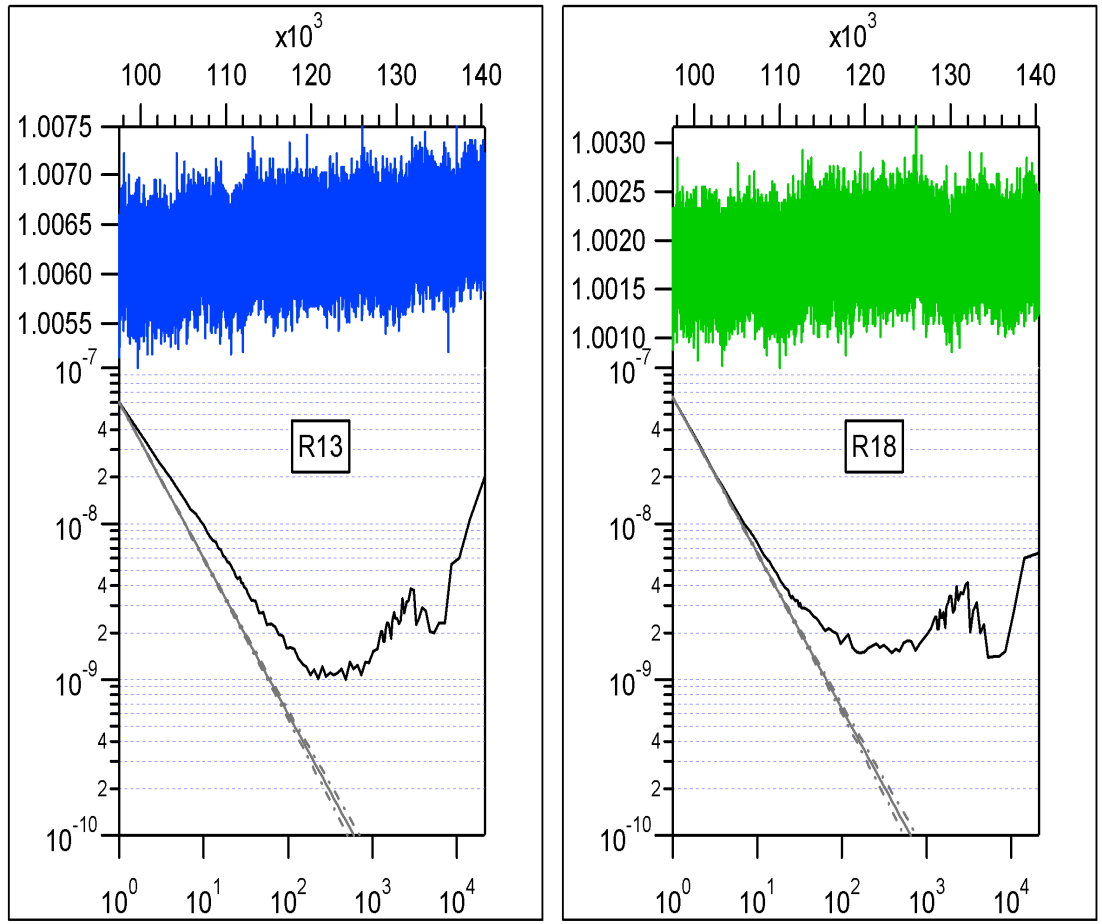
Allan variance plots of 1 sec data for R13 = $S(^{13}CO_2)/S(^{12}CO_2)$ and R18 over nearly 12 hours while monitoring room air wrt room air.

Upper traces are R vs. time with 1 s resolution.

Lower traces are the Allan variances vs. averaging time

The 1 sec rms noise for each plot is is 0.2 ‰.

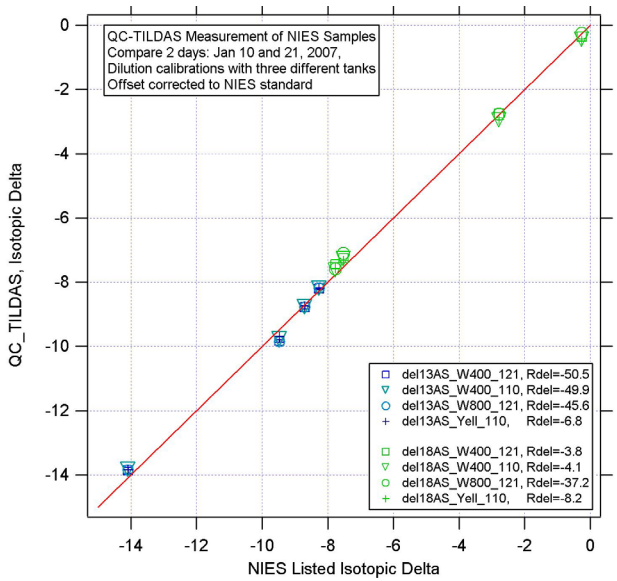
The minima in the plots correspond to σ_{Allan} = 0.03 ‰ after 300 s averaging time.

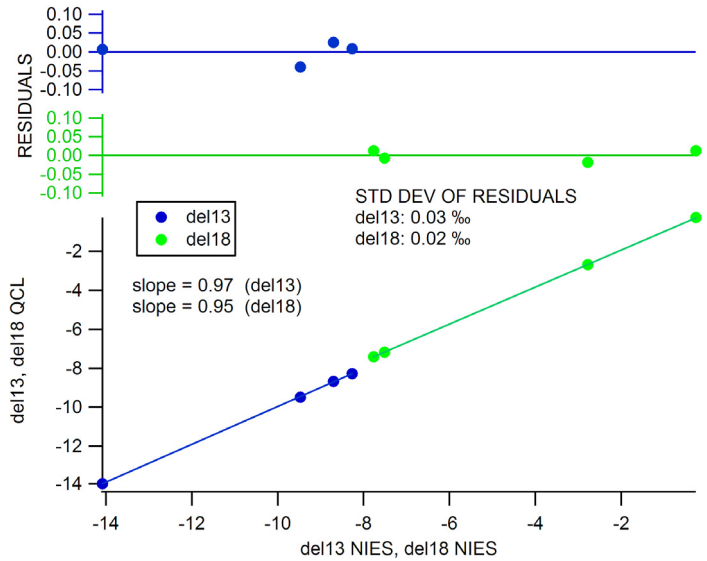


room air on room air
pn2; ref 375 ppm; poly3

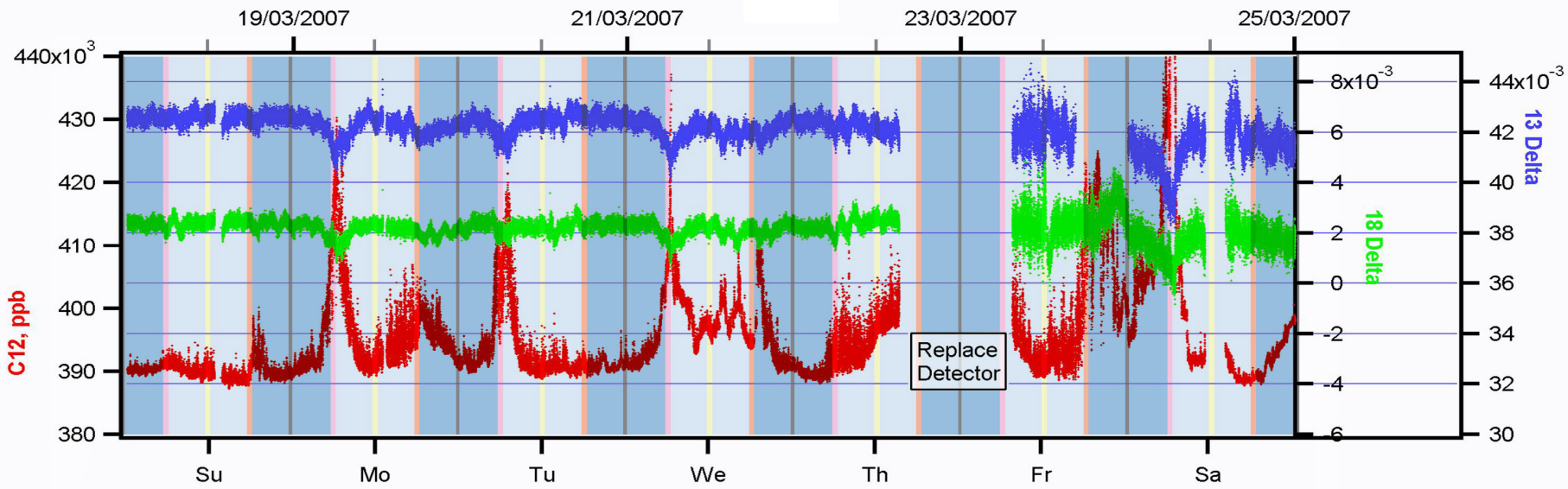
Measurement of NIES CO_2 Standards

- Challenged our instrument with isotopic standards provided by: Hiroshi Suto, National Institute for Environmental Studies, Tsukuba, Japan
- 4 carbon dioxide samples provided with known values of $\delta^{13}C$ (-14 to -8) and $\delta^{18}O$ (-8 to 0)
- Samples originally determined with Isotope Ratio Mass Spectroscopy (PDB,SMOW)
- Samples re-determined by us using IR laser spectroscopy – excellent precision
- Accuracy should approach precision with proper calibration





Week by Week



Continuous record of [CO_2], $\delta^{13}C$ and $\delta^{18}O$ for nearly one week. Time resolution is 4 seconds. More than 100,000 measurements plotted.

Traffic patterns are evident in the data.

Instrument has been running nearly continuously for nearly 6 months

No operator intervention – except for once daily liquid nitrogen addition to detector dewar.

Diurnal Variation

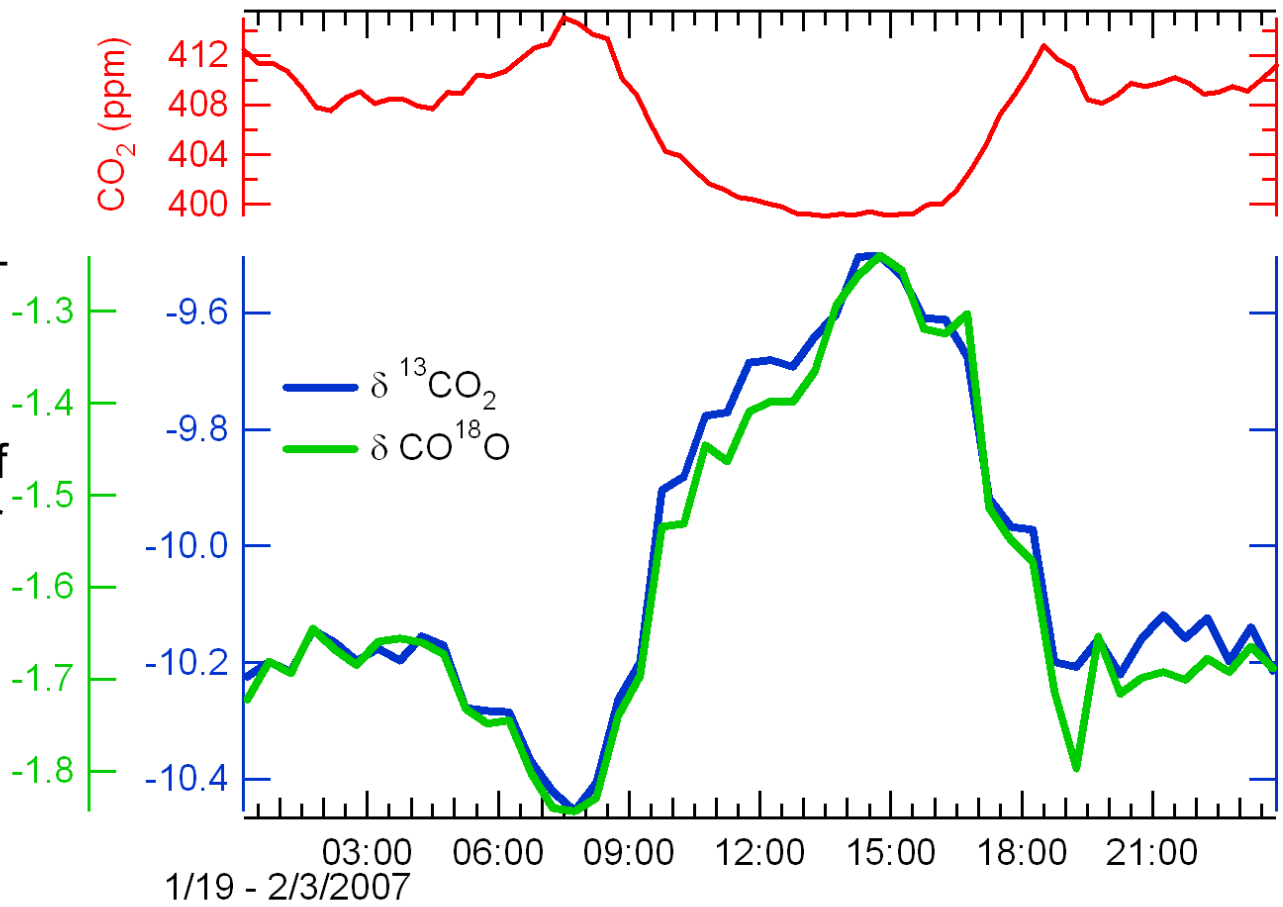
Diurnal average of two weeks of data acquired at Aerodyne Research, Billerica, MA

Aerodyne is 100 meters from interstate highway – strong CO_2 source

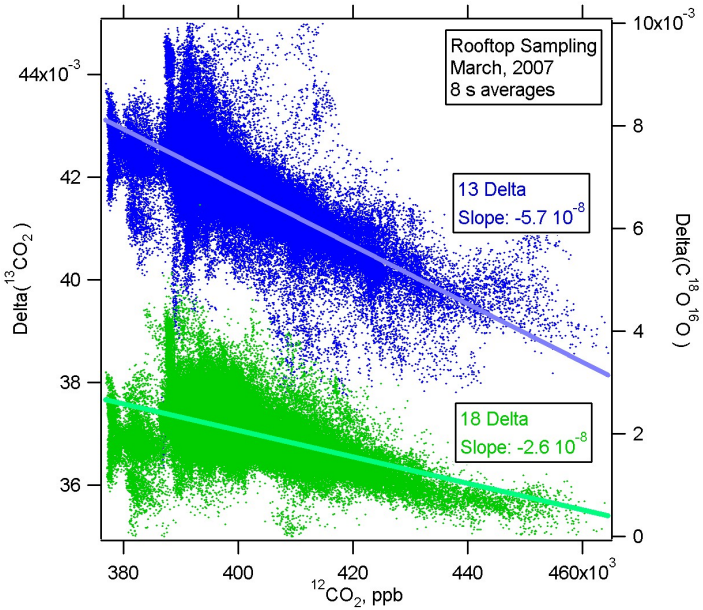
Early morning, late afternoon show effects of traffic emissions – higher CO_2 and lighter CO_2

Magnitude of $\delta^{13}C$ is reasonable for fossil fuel combustion

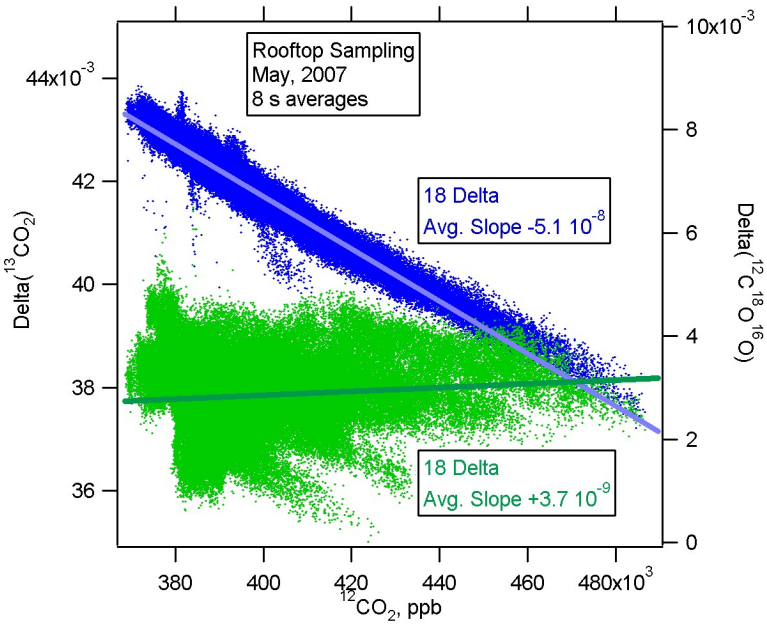
Overnight emissions probably integrate other sources besides highway



Rooftop Atmospheric Sampling Before and After Leaf Out: Correlations of Isotopic Deltas with $^{12}CO_2$



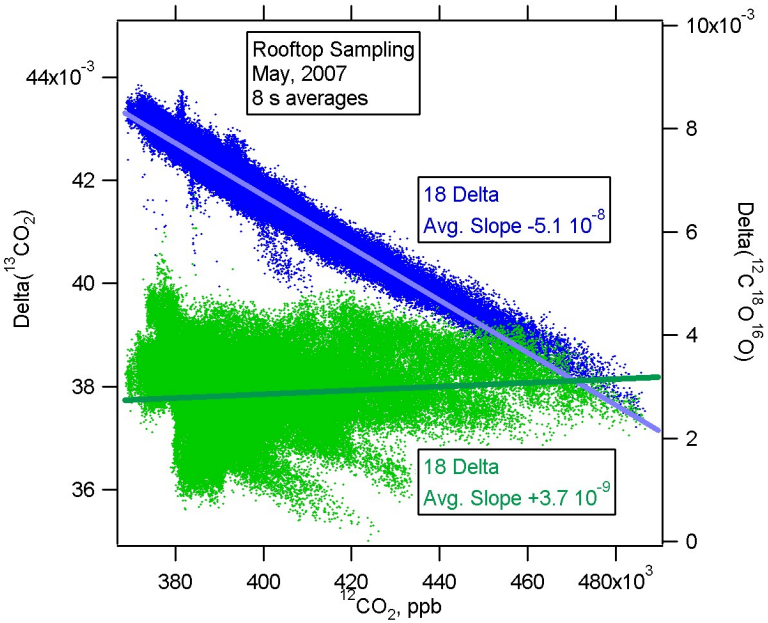
Global fits, deltas vs C12
March 2007



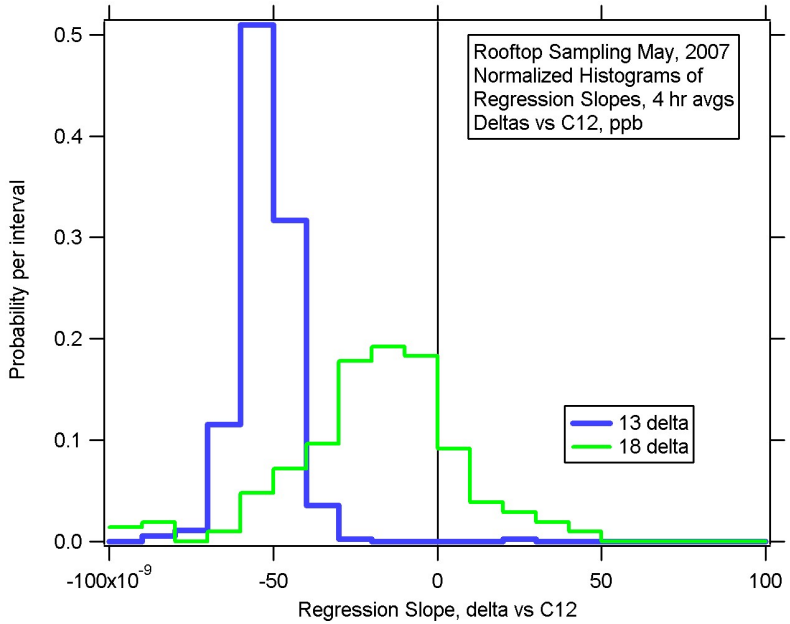
Global fits, deltas vs C12
May 2007

- Slopes for ^{13}C δ do not change much with the arrival of spring
- Slopes for ^{18}O δ increase and become far more variable. Leaf respiration?

Rooftop Atmospheric Sampling: May, 2007
Correlations of Isotopic Deltas with $^{12}CO_2$



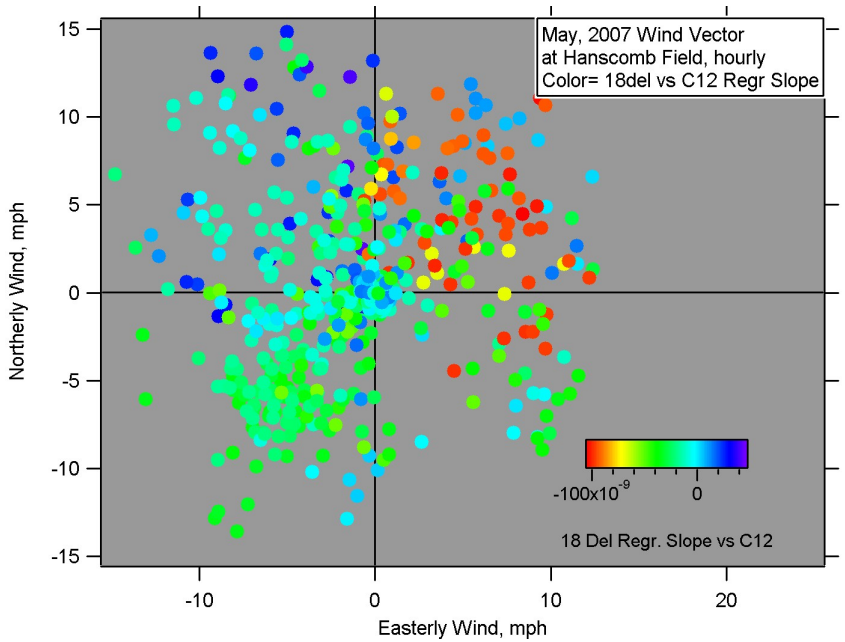
Global fits, deltas vs C12



Histogram of regression slopes,
deltas vs C12, 4 hr data windows

13 delta decreases with increasing $^{12}CO_2$, with a nearly constant slope.
18 delta has more variable regression slopes, showing a mix of sources.

Rooftop Atmospheric Sampling: May, 2007
Correlations of 18 Delta Slope vs $^{12}CO_2$ and Wind

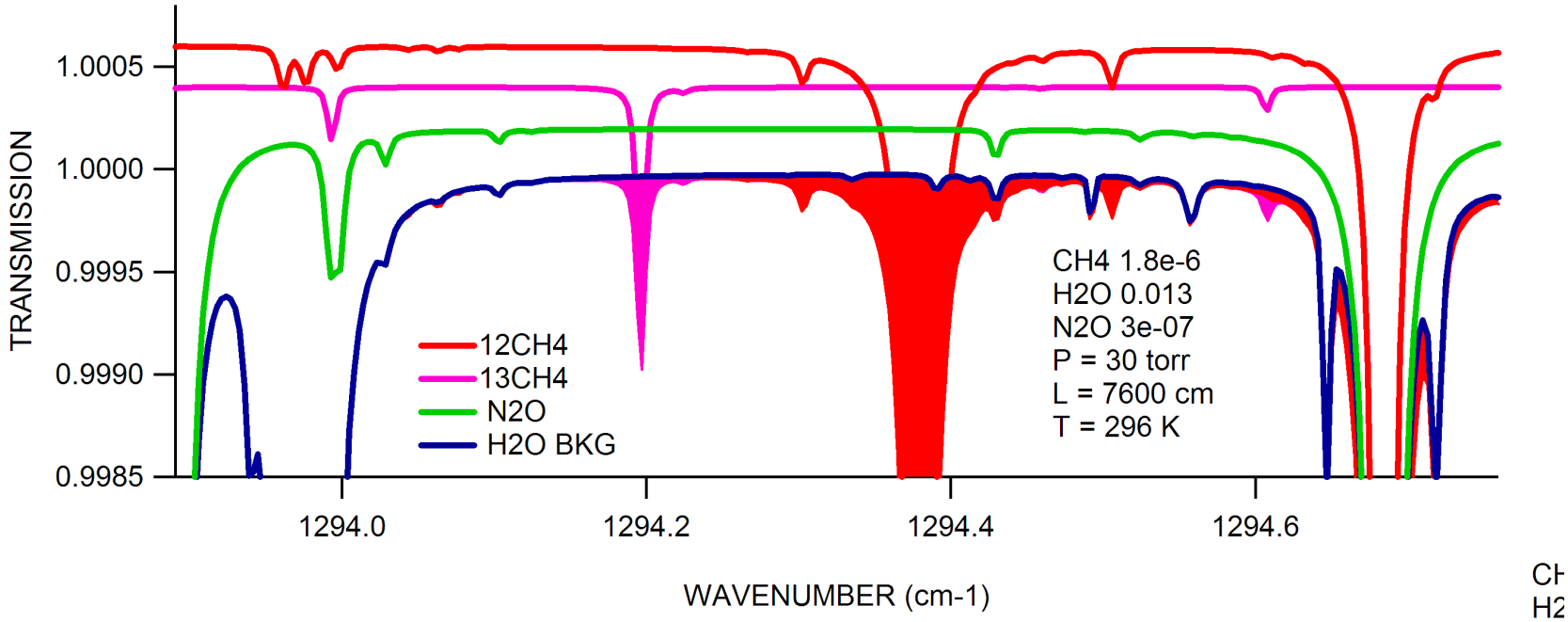


Regression slopes, 4 hr avgs.
18 delta vs C12, plotted vs
wind vector at Hanscom Field.

Area surrounding ARI from a Google map, ARI shown as red square.

Regression slope, 18 delta vs C12, shows a pattern when plotted against wind vector, suggesting directions of sources with different 18 deltas.

What about methane isotopes?



This is much harder because atmospheric abundance of methane is only 2 ppm compared to 380 ppm for carbon dioxide. Must have CW laser!

HITRAN becomes crucial – not to find lines – but to avoid lines!

Expected absorbance for $^{13}CH_4$ is only 0.1%. We want ratios that are good to 1 part in 10,000, so we must avoid spectral interference at the level of 1×10^{-7} absorbance.

Long Term Precision

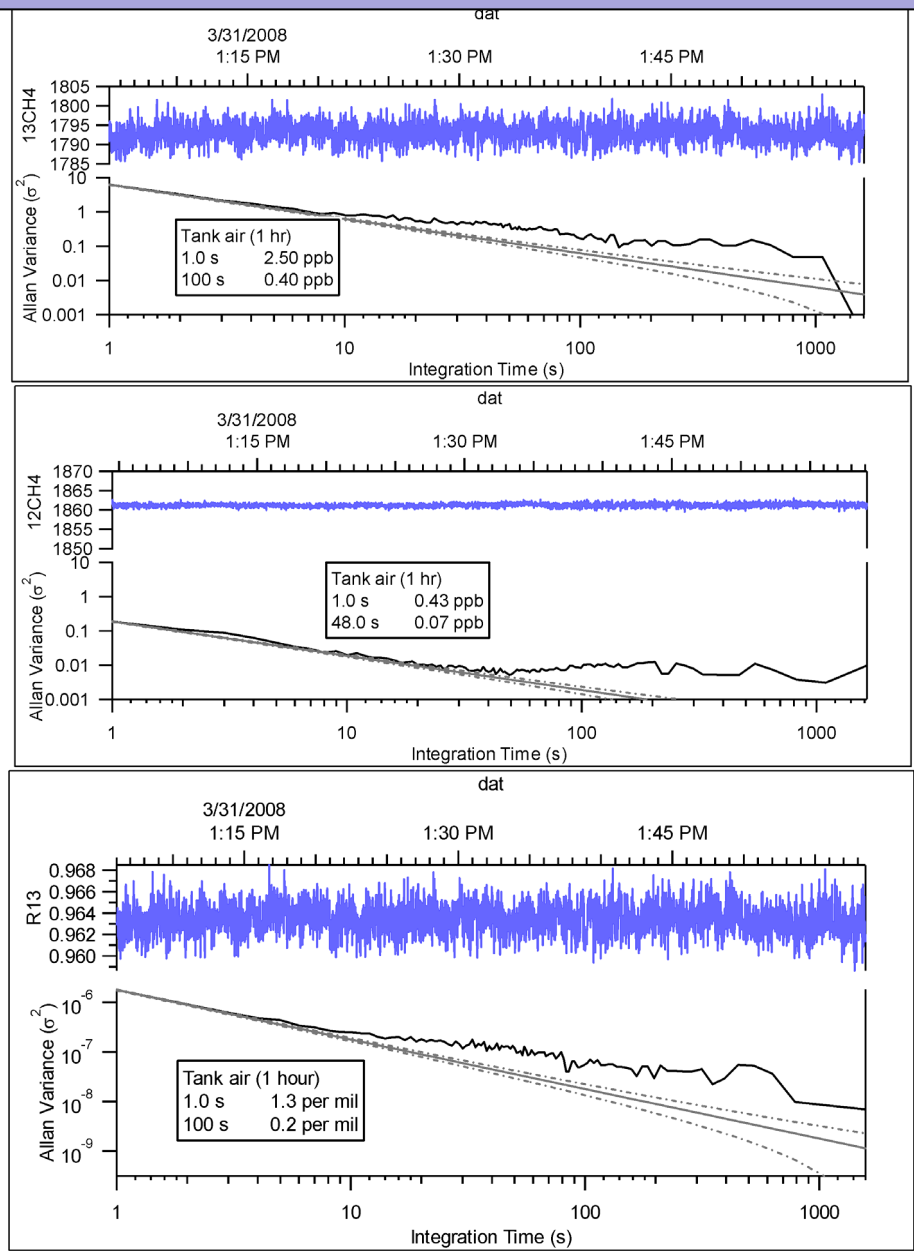
Allan variance plots of 1 sec data for 13C, 12C and R13 = $S(^{13}CH_4)/S(^{12}CH_4)$ over 1 hour while monitoring tank air.

Upper traces have time resolution of 1 s.

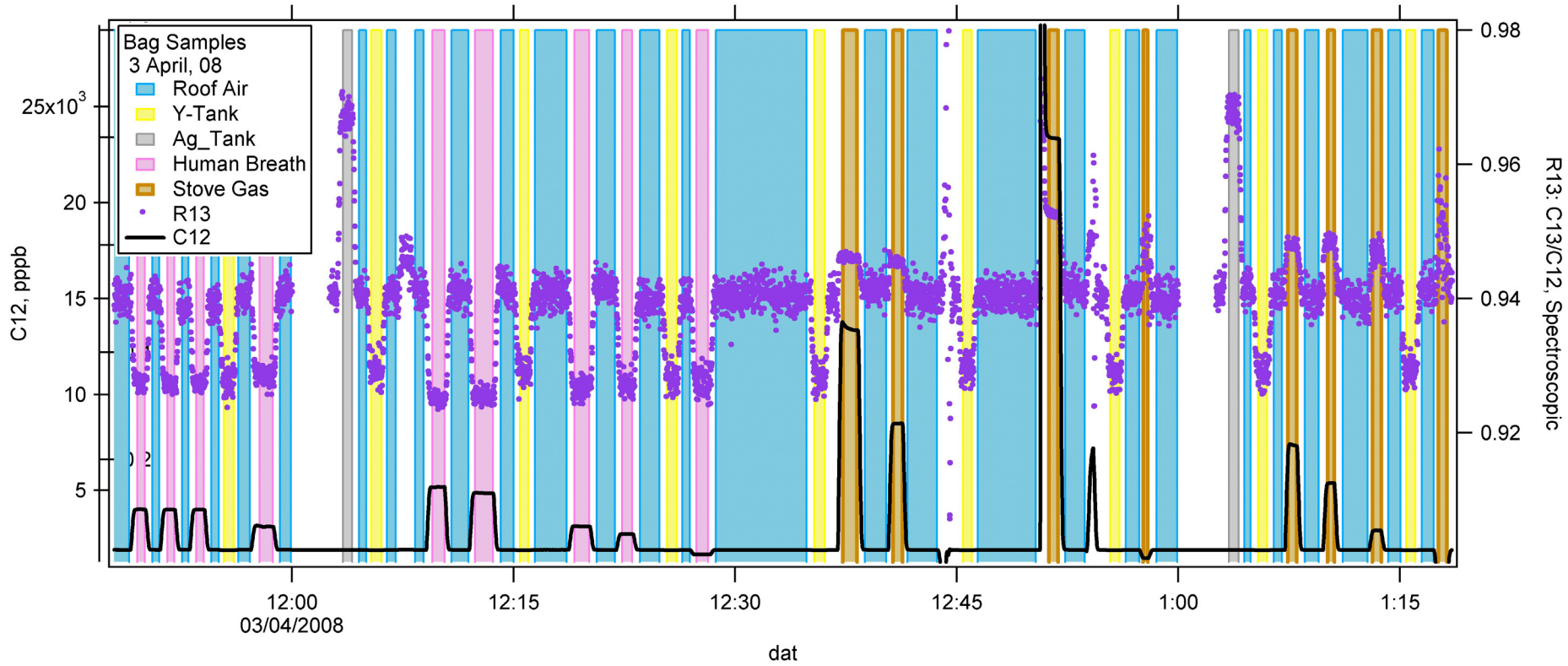
Lower traces are the Allan variances vs. averaging time

The 1 sec rms noise for the isotopic ratio is 1.3 ‰.

The minima in the ratio plot corresponds to σ_{Allan} = 0.2 ‰ after 100 s averaging time.



Comparing Methane Sources



Comparison of isotope ratios for various sources of methane: atmospheric, various tanks, human breath and stove gas.

Measured ratios are shown in purple and vary by about 40 δ.

Methane concentration is shown at bottom in black and varies from background (2 ppm) to more than 20 ppm.

Conclusions and Acknowledgements

Conclusions:

•We have demonstrated continuous, real time measurements of ambient carbon dioxide isotopic ratios

- •Both ^{13}C and ^{18}O are monitored
- •Time resolution is 1 second
- •No pre-concentration is required
- •Measurement precision of 0.2δ in one second, or 0.03δ in 300 sec.

•Initial results for $^{13}CH_4$ with CW QC laser are very promising: 1δ in one second

•Totally TE-cooled spectrometer will allow continuous, unattended, isotopic measurements – performance not yet fully evaluated

•Applications include:

- •Atmospheric monitoring of isotopic gradients from aircraft and other mobile platforms
- •Eddy covariance iso-flux measurements
- •Isotopic composition measurements

Acknowledgements:

Aerodyne acknowledges support from the DOE SBIR program

Null Method Details

Normal Method:

$M = A * T / \sigma(T) / P$

where M is mixing ratio and A is integrated absorbance or area.

Null Method:

$M = a * T / \sigma(T) / P + M_R * (P_R/P) * (T/T_R) * (\sigma(T_R)/\sigma(T))$

Where a is area in nulled spectrum. a << A.

- First term is accurate because a is small
- Second term is accurate because P and T enter as ratios

Correlations of Isotopic Deltas with $^{12}CO_2$, Source Deltas and Dillution

Measured concentrations, with D=dillution factor:

$$[^{12}CO_2]_{meas} = (1\text{-}D)\,[^{12}CO_2]_{bkgn} + D\,[^{12}CO_2]_{source}$$

$$[^{13}CO_2]_{meas} = (1\text{-}D)\,[^{13}CO_2]_{bkgn} + D\,[^{13}CO_2]_{source}$$

Measured delta, with 1-D ≈ 1,

$$^{13}\delta_{meas} \approx \{^{13}\delta_{bkgn}\,[^{12}CO_2]_{bkgn} + {}^{13}\delta_{source}\,D\,[^{12}CO_2]_{source}\} / \{[^{12}CO_2]_{bkgn} + D\,[^{12}CO_2]_{source}\}$$

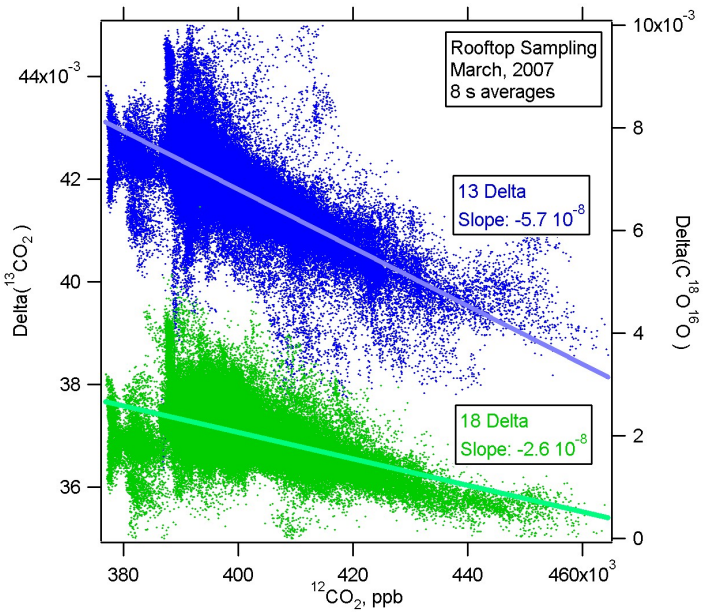
$$D \approx \{\,[^{12}CO_2]_{meas} - [^{12}CO_2]_{bkgn}\,\} / [^{12}CO_2]_{source}$$

$$^{13}\delta_{meas} \approx \{^{13}\delta_{bkgn}\,[^{12}CO_2]_{bkgn} + {}^{13}\delta_{source}(\,[^{12}CO_2]_{meas} - [^{12}CO_2]_{bkgn})\} / [^{12}CO_2]_{meas}$$

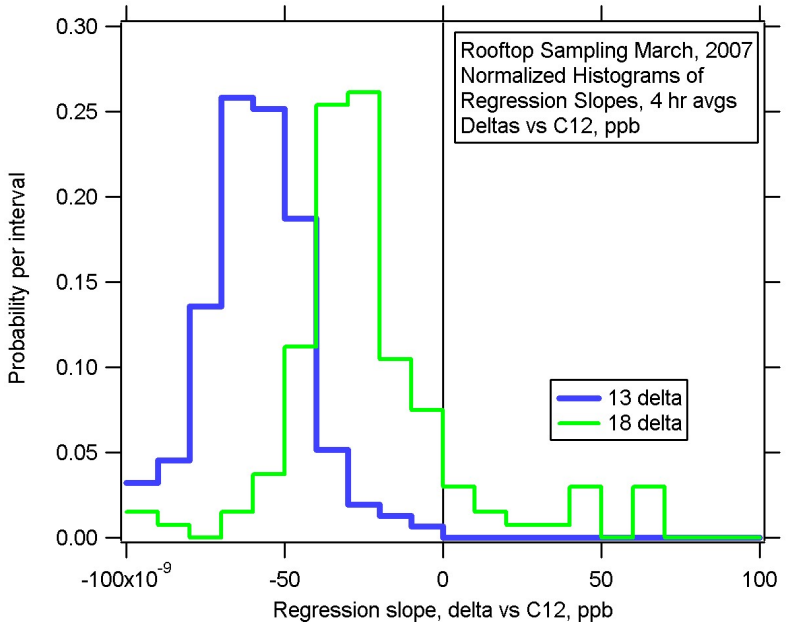
Regression slope, delta vs measured C12,

$$d(^{13}\delta_{meas}) / d([^{12}CO_2]_{meas}) \approx \{^{13}\delta_{source} - {}^{13}\delta_{bkgn}\}\,[^{12}CO_2]_{bkgn} / [^{12}CO_2]^2_{meas}$$

Rooftop Atmospheric Sampling: March, 2007
Correlations of Isotopic Deltas with $^{12}CO_2$



Global fits, deltas vs C12



Histogram of regression slopes, deltas vs C12, 4 hr data windows

Both 13 and 18 deltas decrease with increasing $^{12}CO_2$, with different regression slopes.

Our Standard Design Elements for High Sensitivity and Precision

Short Pulses: ~10 ns pulses for narrow linewidths, symmetrical lineshapes.
Balance effects of linewidth and light loss for best performance.

Pulse Normalization: Main and Pulse-Norm. on the same detector.
Matched path lengths, pulse-norm and main [external].

Background Subtraction: Periodically subtract saved spectrum with zero-gas.
Reduces effect of fluctuating baseline.

Reference Locking: Continuously lock laser center frequency,
Using either reference cell or main cell.

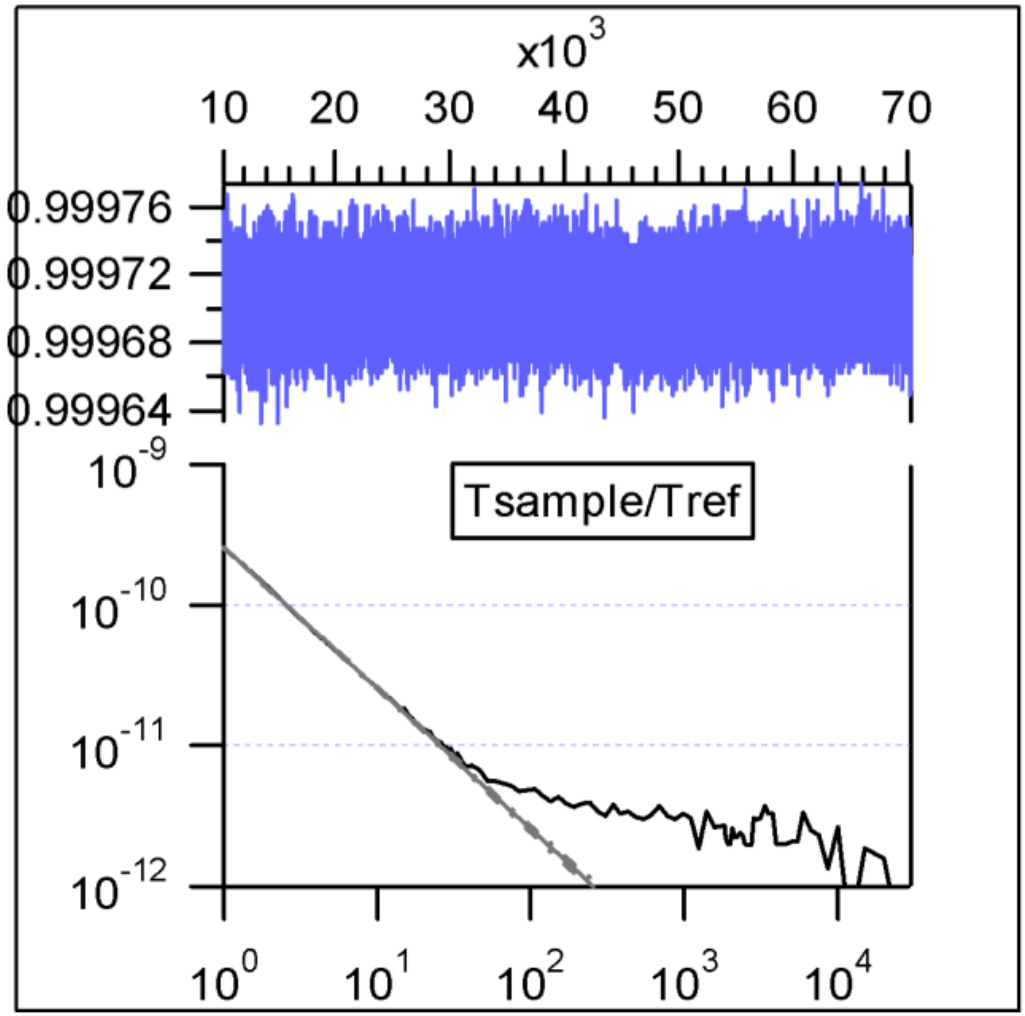
Efficient Optics: AMAC-76 cell for long path (76 m) in small volume (500 cc).
Field-sharing beam combination.

Temperature Stabilization: Temperature control of laser, electronics and optics.

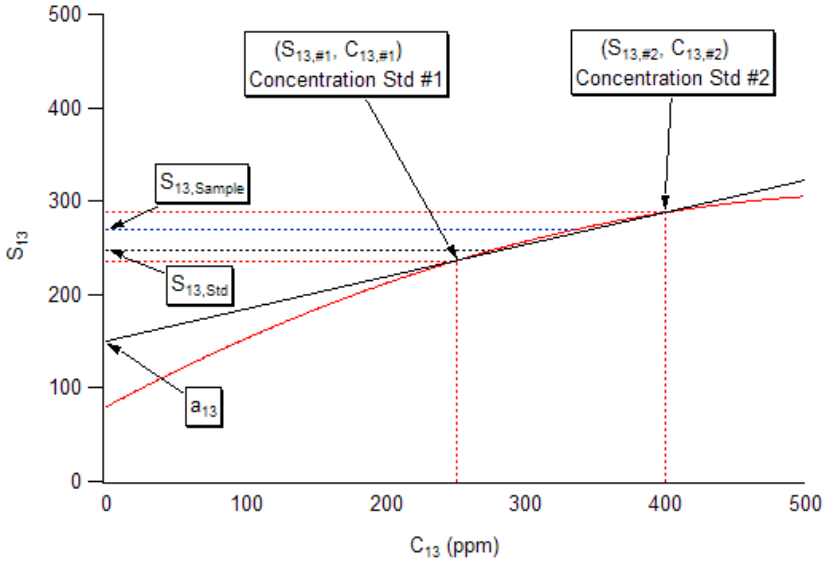
Great, but we want even more precision for isotopic measurements!

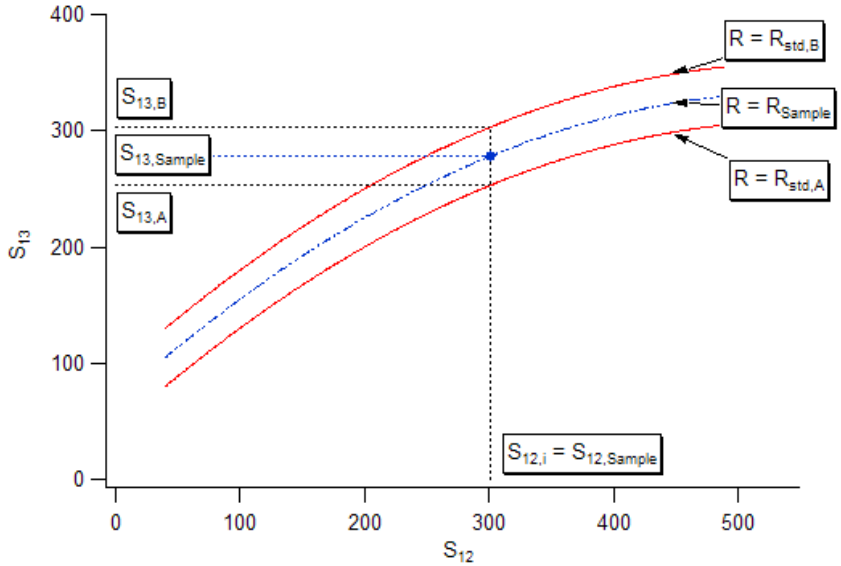
Precision Measurement of P and T

- Measurement of P and T to sufficient precision is hard
- Null method implies that we are sensitive to dP and dT.
- dP can be measured with differential pressure sensor
- dT can be measured to 1 mK in one minute – need 5 to 8 mK for 0.1 δ accuracy



Calibration via the Dilution Method





Concentration retrievals are not perfectly linear due to detector R's and finite laser line width

Hence, S vs. C must be addressed

Direct calibration is one approach but difficult to automate.

Need S vs. C for all three isotopes.

Alternative: Use dilution of secondary standards (S vs. S) to minimize or eliminate measurement of S vs. C

Dilution measurement is easily automated – we do hourly.

We use inexpensive concentrated CO_2 for dilution in nitrogen.

Implementation of Dilution Calibration

- Dilution calibrations are done hourly (350 to 500 ppm range)
- Extremely small flow of pure CO_2 is added to dry nitrogen flow
- Dilution factor is unknown and unneeded
- Also monitor zero gas and standard (500 ppm) hourly
- Detail of calibrations is shown in lower figure