Measuring the Drivers of Global Climate Change: Using Quantum Cascade Lasers to Quantify Atmospheric Greenhouse Gases

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OUTLINE

- Motivation: Greenhouse Gases
- Measurement Principles
  - Mid IR Laser Absorption
  - CW vs Pulsed-QCLs
  - Longer optical paths, lower volumes
- Aerodyne Instruments
- Isotopes of CO_2
- Isotopes of CH_4
- N_2O and Its Isotopes
- Other Applications

Global Warming is Driven by Greenhouse Gases

- Primary Cause of Global Warming over last 100 years is the accumulation of "Greenhouse Gases" in Earth's atmosphere
  - CO_2 is the most important
  - But CH_4 and N_2O are also quite significant

- What is the cause of the rise in Greenhouse Gases?
  - In each case there are natural and anthropogenic sources.
  - In each case there is large uncertainty about the sources and sinks.
  - This makes it difficult to predict future and to plan political response

- So there is a need to measure Greenhouse Gases
  - Need high sensitivity – especially for N_2O and CH_4
  - Need fast time response – eddy covariance
  - Need isotopic resolution – for source determination

Measurement Principle - Absorption Spectroscopy

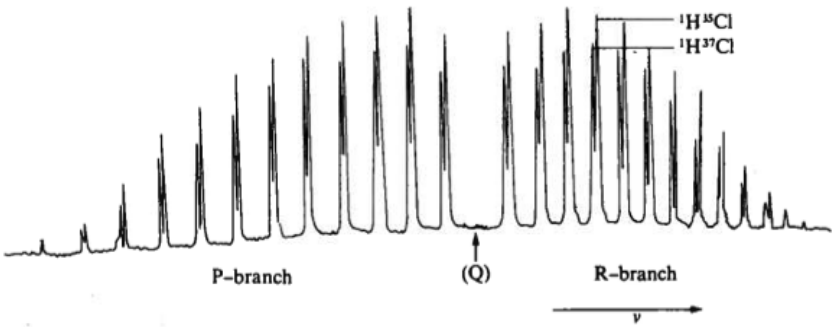


Fig. 17.14. A high-resolution vibration–rotation spectrum of HCl.

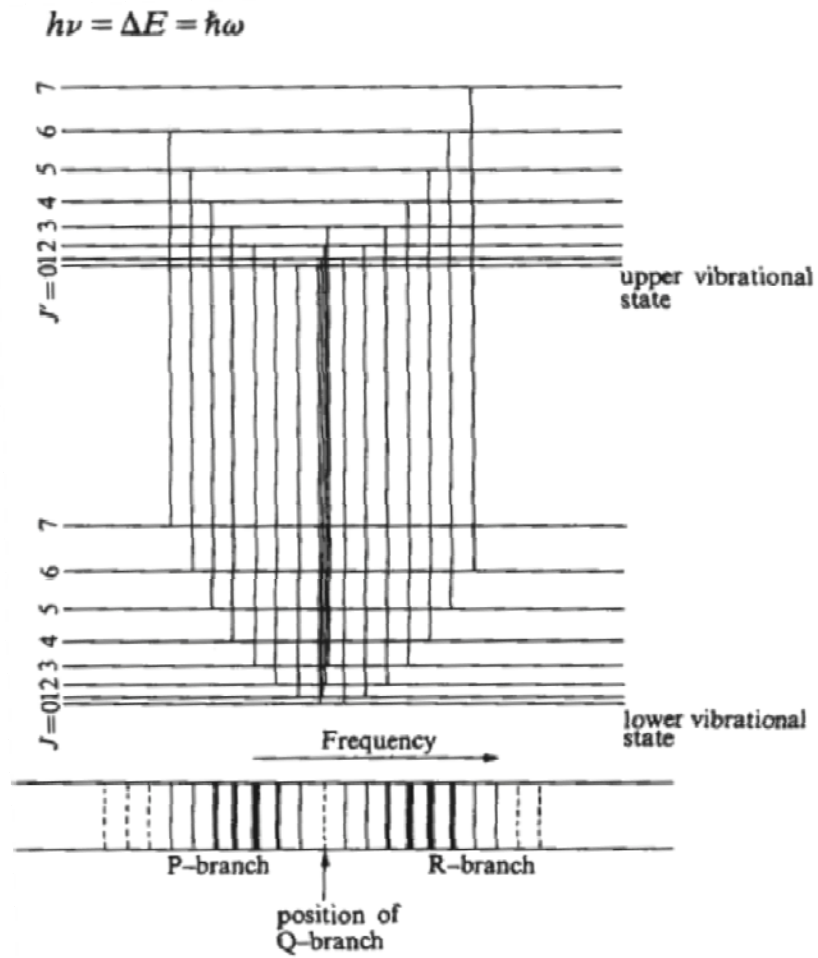


Fig. 17.15. The formation of P, Q, and R branches.

Why do we observe a spectrum?

Quantum mechanics explains:

- Each molecule absorbs light at specific frequencies
- Absorption adds energy to vibration and rotation levels
- Additional energy must be specific quantity
- Every molecule has unique spectrum

J is rotational quantum number.

Measurement Principle – Beer's Law

How much light is absorbed by the sample?

$$A = N \times \sigma \times L$$

A is fractional absorption – we measure this

N is number density – we want to know this

σ is the absorption cross section – property of molecule – we want it big

L is the optical path length – we want it big

$$N = A / (\sigma \times L)$$

Measurement of N is absolute – no need for calibration!

Trace Gas Measurements with Mid-Infrared Quantum Cascade Lasers

Why Laser Spectroscopic Instrumentation?

- Specific and verifiable detection.
- High sensitivity.
- Fast time response.
- Rugged instruments – field ready.

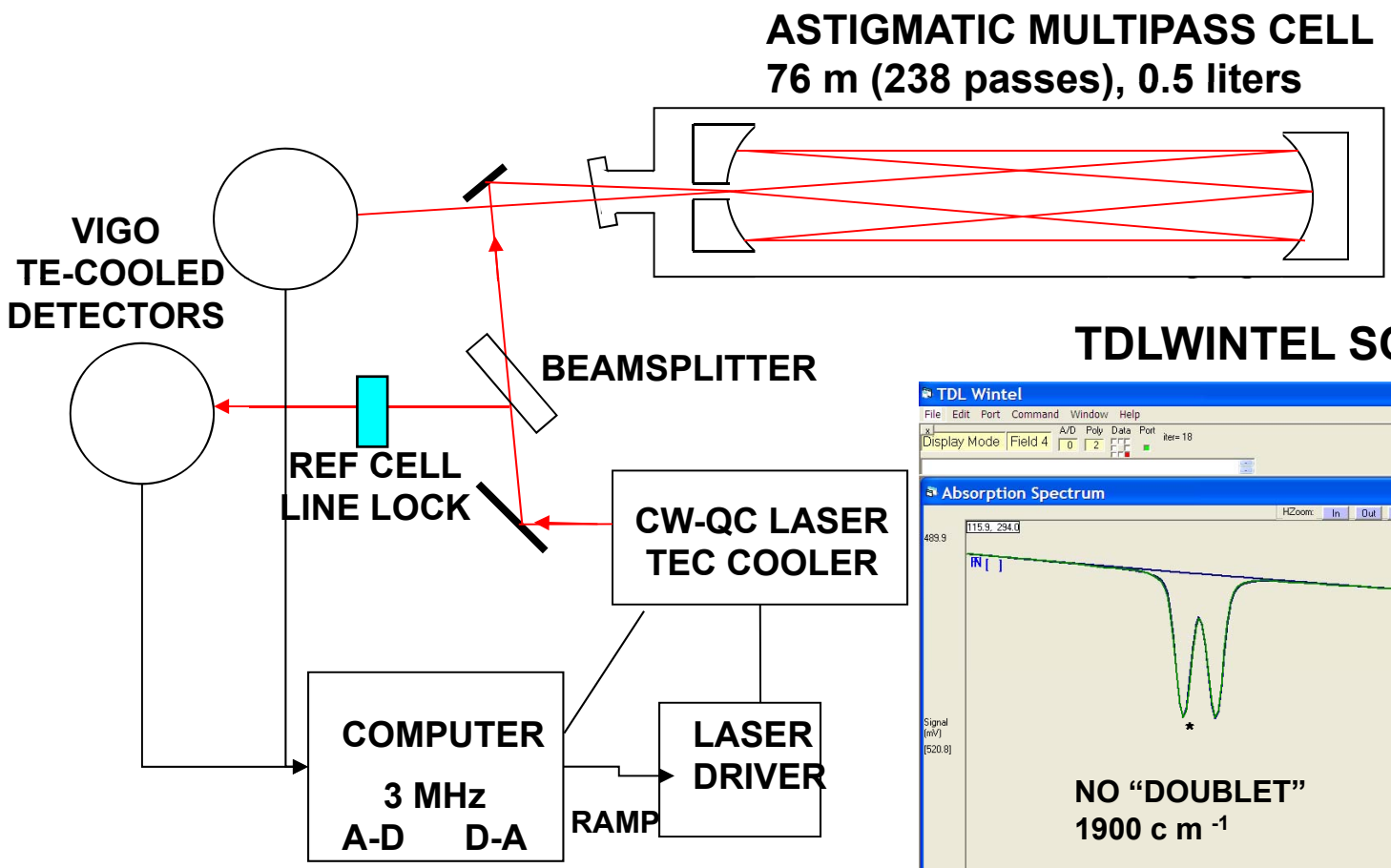
Why Mid-IR?

- Fingerprint spectra for many molecules.
- Strongest absorption, Highest sensitivity.

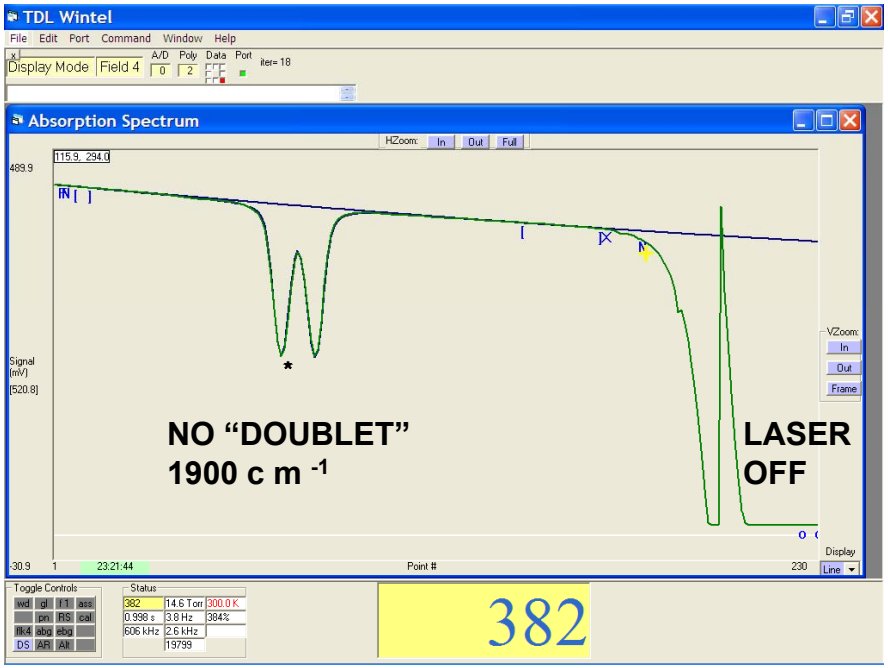
Why Quantum Cascade Lasers?

- Spectroscopic quality IR lasers at near room temperature.
- High power, continuous operation for high sensitivity.

DIRECT ABSORPTION - CW-QCLs

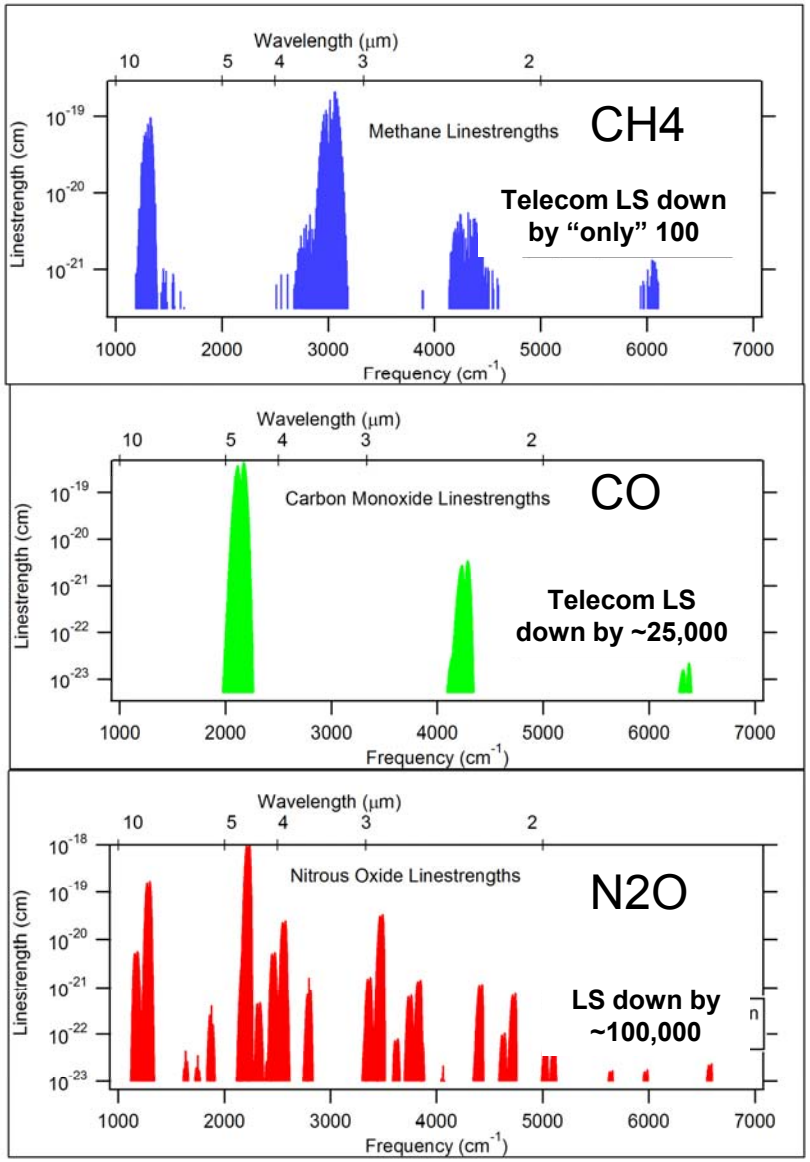


TDLWINTEL SOFTWARE



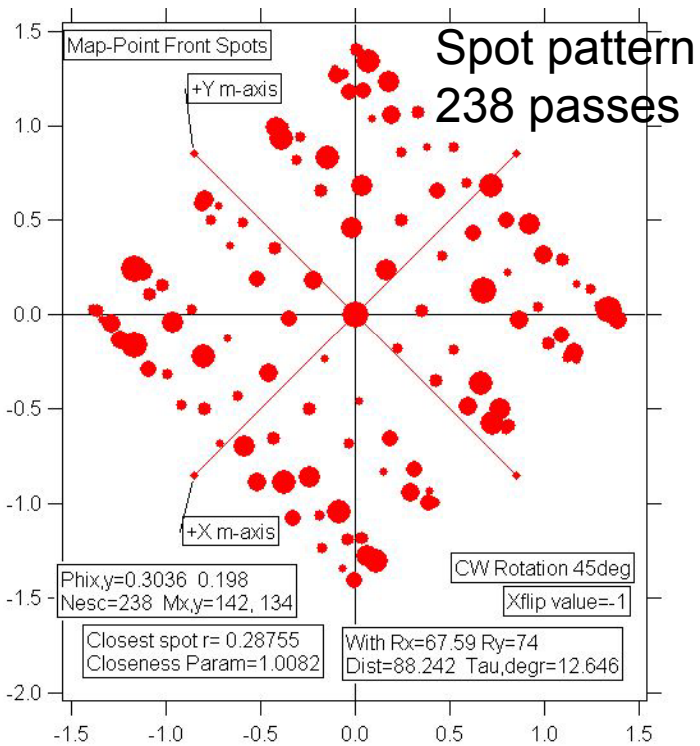
Advantages of Mid-IR Detection

- Linestrengths in mid-IR are **much** stronger than near-IR
- 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

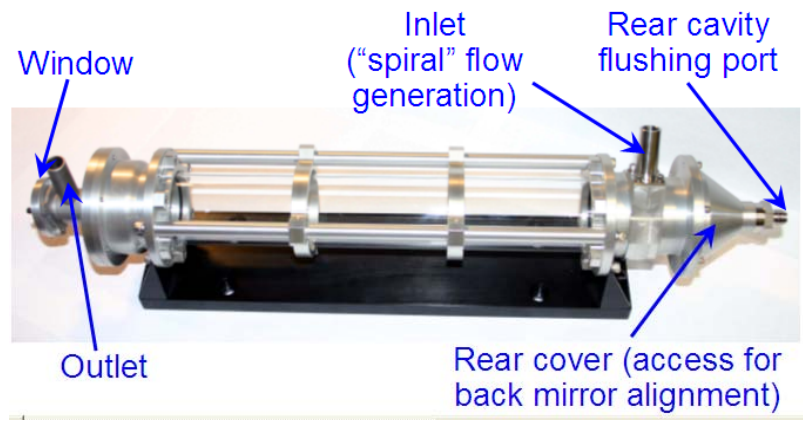


Astigmatic Multipass Cells

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.



AMAC-76-Lightweight (Daube Cell)



Aerodyne Research
QCL Instrument Models

Mini QCL instrument:
single laser, 76 meter path

Dual QCL instrument:
one or two lasers,
up to 260 meter path

Why Measure Isotopes? 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…

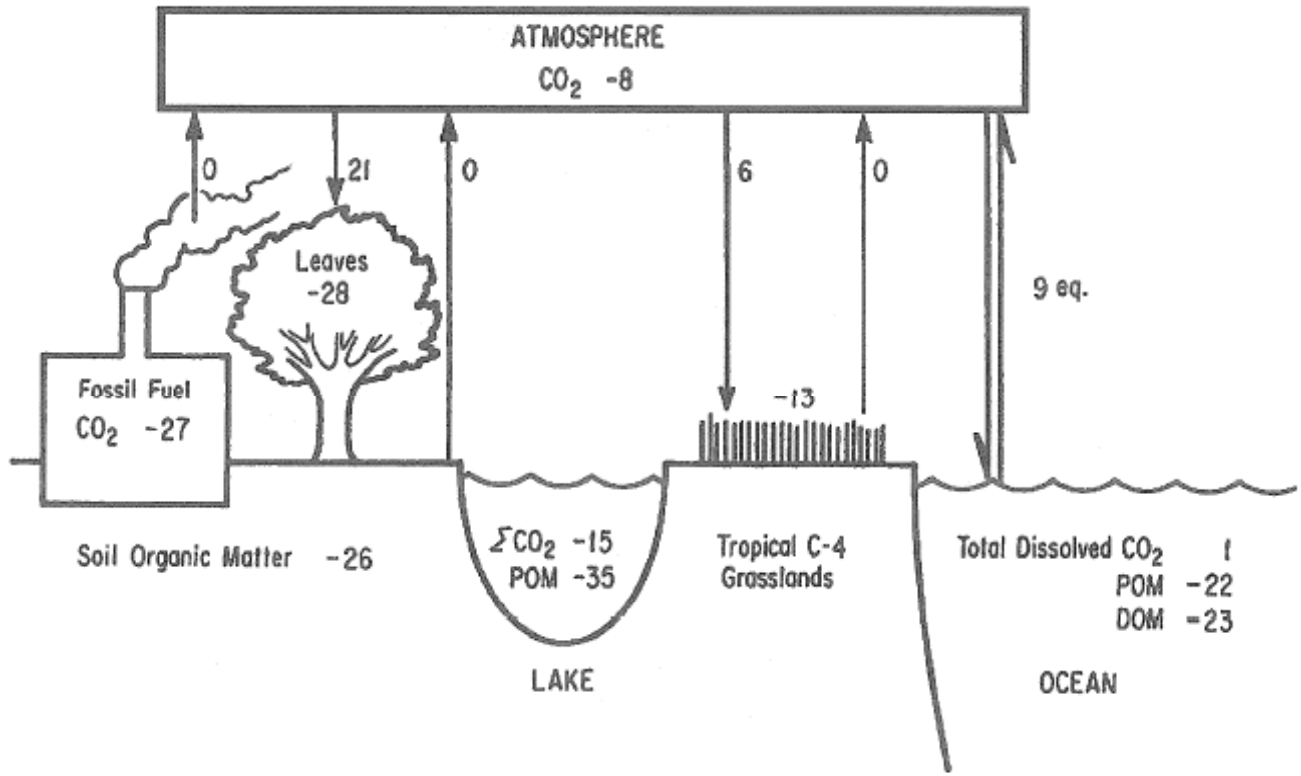
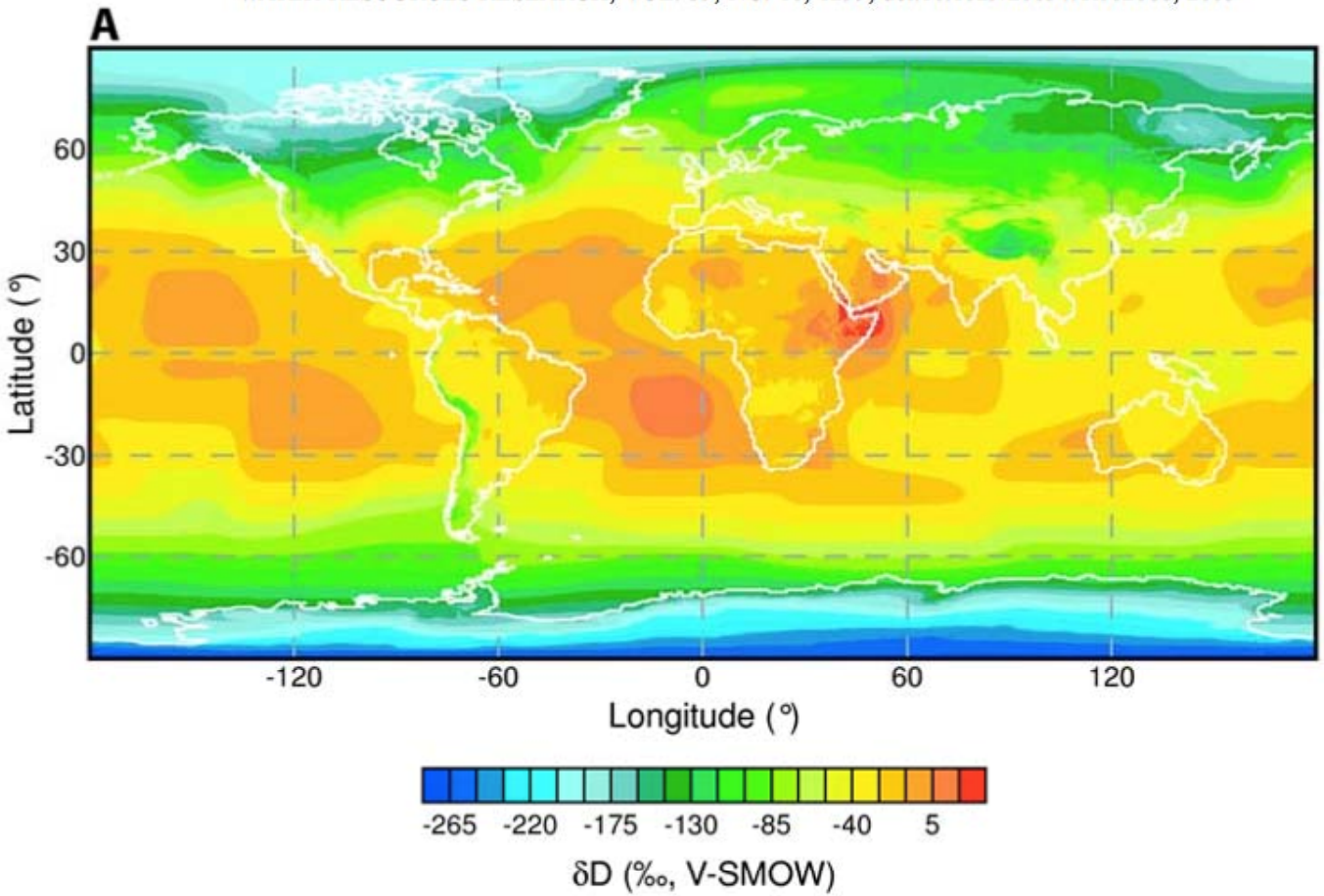


FIGURE 3.1. $\delta^{13}C$ distribution in ecosystems. Single arrows indicate CO_2 fluxes. The double arrow signifies an equilibrium isotope fractionation. Numbers for pools indicate $\delta^{13}C$ values (‰) and numbers of arrows indicate the fractionation (Δ, ‰) occurring during transfers. Negative $\delta^{13}C$ 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.)

Why Measure Isotopes?
Distribution of δD in Rain Water

BOWEN AND REVENAUGH: ISOTOPIC COMPOSITION OF MODERN PRECIPITATION SWC

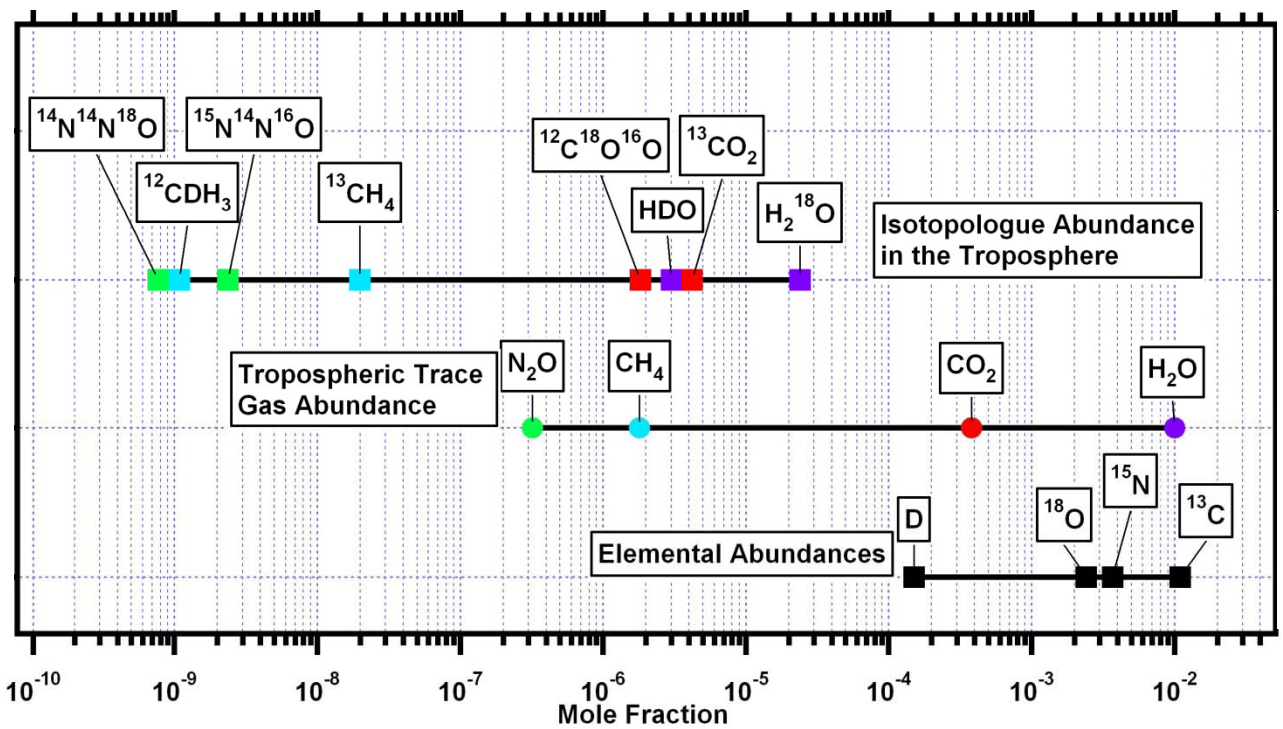
WATER RESOURCES RESEARCH, VOL. 39, NO. 10, 1299, doi:10.1029/2003WR002086, 2003



- Water is fractionated both during evaporation and condensation
- Used in many applications including bird migration studies

Measuring Isotopologues of Atmospheric Trace Gases at Ambient Concentrations is Very Challenging

Trace gas isotopologues are present at very low concentrations:

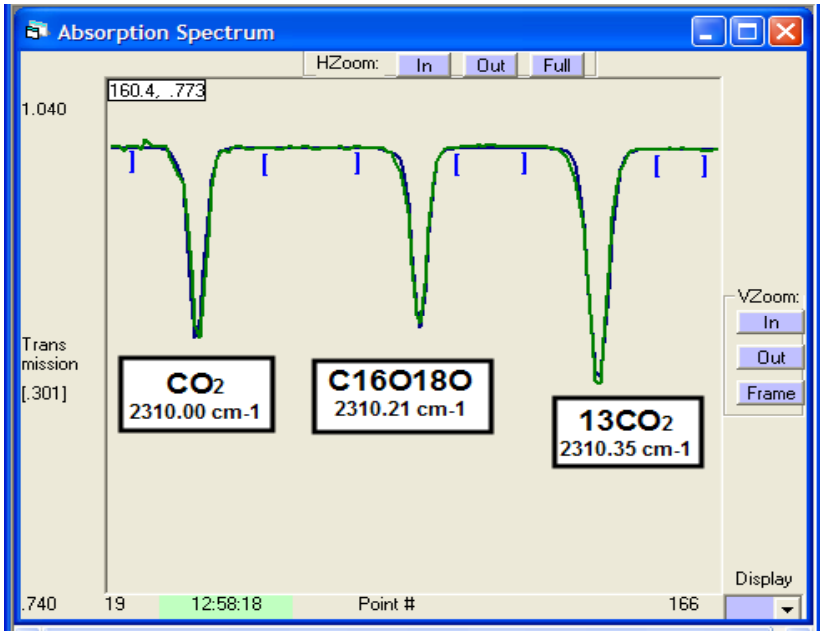


Measurement challenge:
High precision measurements are needed on the minor and major isotopologues, 10^{-3} to 10^{-4} !

CO_2 Isotope Instrument

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

- Both ^{13}C and ^{18}O are monitored
- Time resolution is 0.1 seconds
- Measurement precision of 0.1‰ in one second, or 0.03 ‰ in 300 sec.
- Atmospheric monitoring of isotopic gradients
- Eddy covariance iso-flux measurements
- Determination of Net Ecosystem Exchange of CO_2

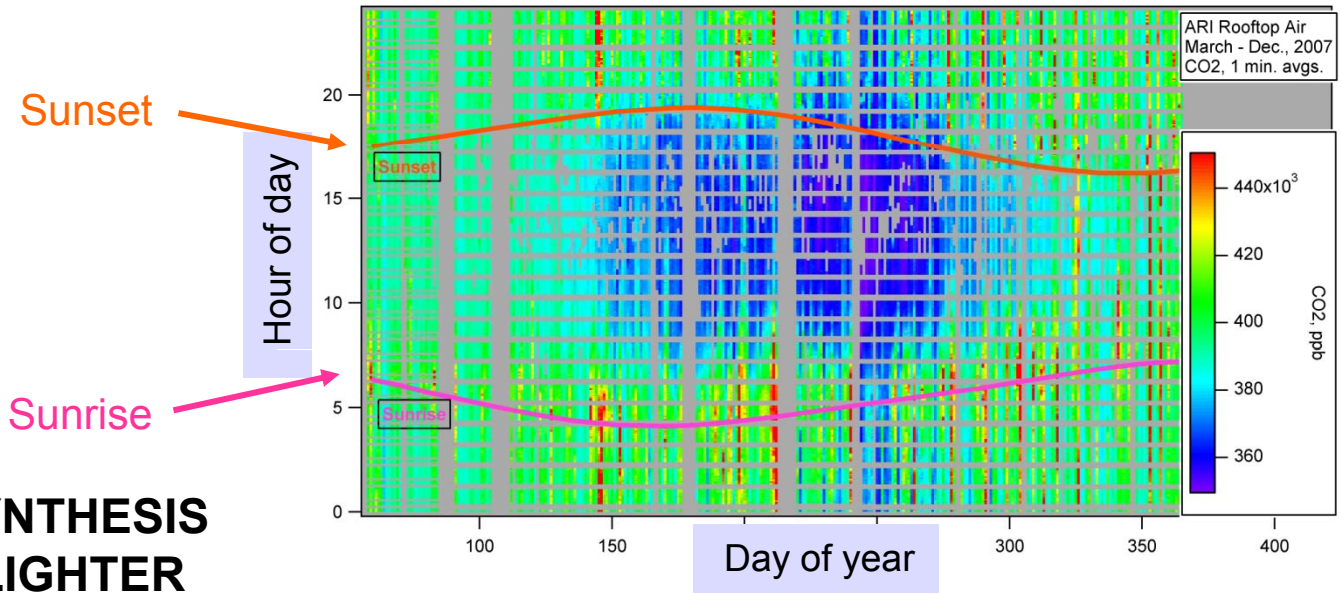


D. D. Nelson et al., Appl. Phys. B90, 310-309 (2008), "New method for isotopic ratio measurements of atmospheric carbon dioxide using a 4.3 μm pulsed quantum cascade laser".

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"

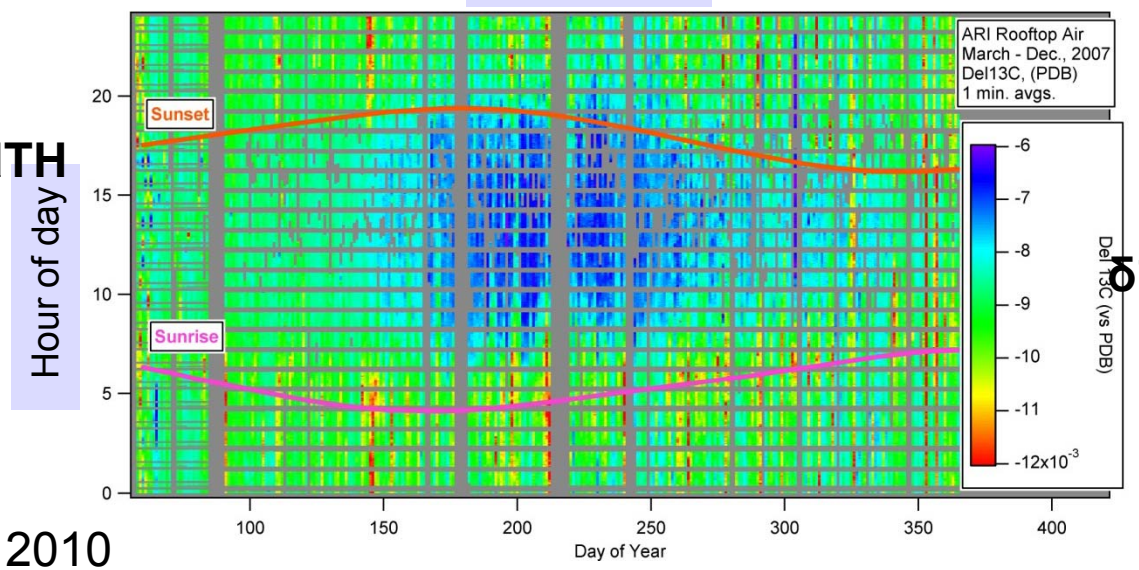
10 Months of ambient air data at Aerodyne

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



PHOTOSYNTHESIS FAVORS LIGHTER ISOTOPE

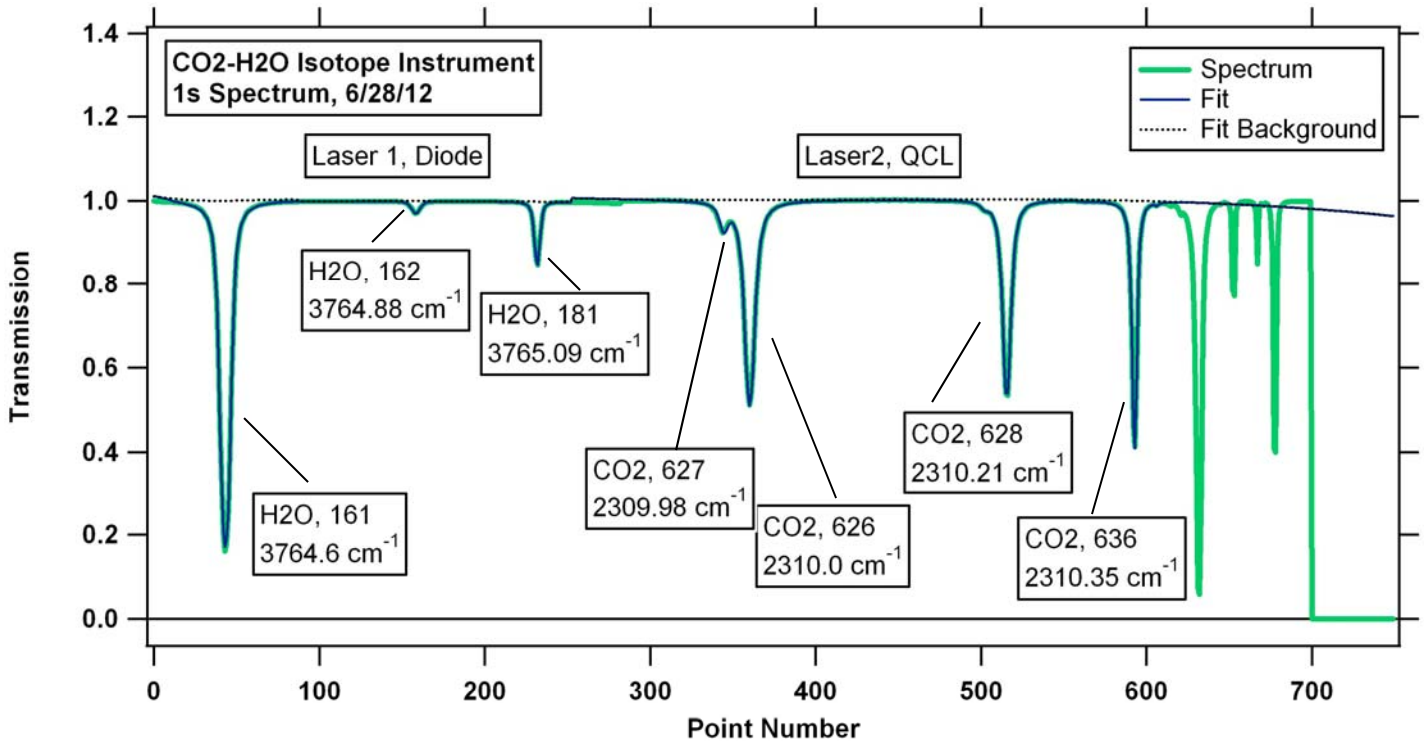
DIURNAL CYCLE WITH RESPIRATION AT NIGHT



McManus et al., IEHS 2010

CO_2 H_2O Dual Isotope Instrument

Sample spectrum with fit: 1s average of spectra
2 multiplexed lasers sweeping at 2 kHz



CO_2 H_2O Dual Isotope Instrument

Typical ratio noise performance at ambient levels,
1 s average (as of June, 2012):

H_2O:	R 162/161	0.3 ‰	(D/H)
	R 181/161	0.1 ‰	($^{18}O/^{16}O$)
CO_2:	R 628/626	0.08 ‰	($^{18}O/^{16}O$)
	R 636/626	0.13 ‰	($^{13}C/^{12}C$)

This is excellent measurement precision!

Application #1:
Carbon Dioxide Iso-Flux at Harvard Forest

Link to application 1

$^{13}CH_4$ 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

CURRENT INSTRUMENT PERFORMANCE:

$\delta\ ^{13}C$ 0.2 ‰ in 60 s WITHOUT PRE-CONCENTRATION

CRYOGEN FREE OPERATION

FIELD PORTABLE

IMPROVEMENTS COMING

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, RELAXED EDDY ACCUMULATION AND FOR LARGE FLUX EDDY COVARIANCE

Application #2:
Isotopic Methane Flux at Sallie's Fen, New Hampshire

Link to application

Typical N_2O Measurement Precision with CW QCL

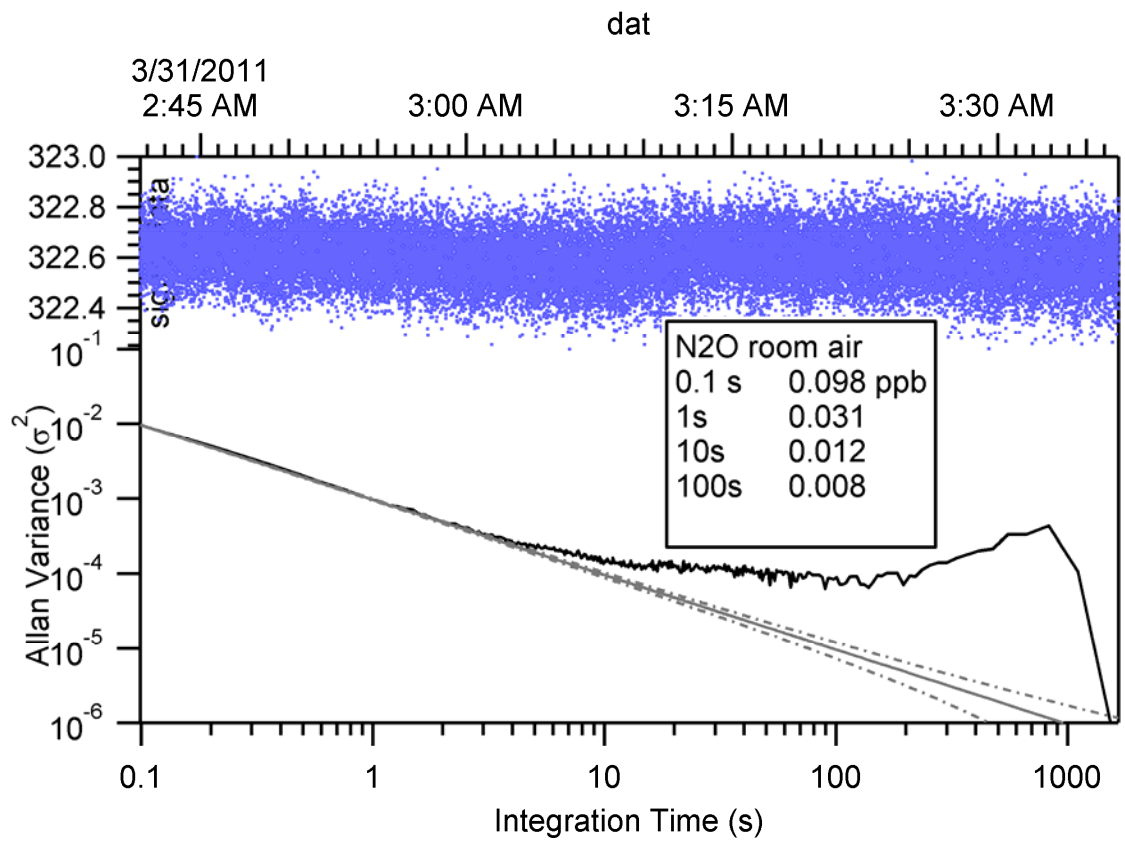
76 meter pathlength

Single laser system

Excellent laser frequency stability of 600 kHz in one ms

Perfectly suited for nitrous oxide eddy covariance measurements

Also, measures water vapor and either CO, CO_2 or CH_4 simultaneously.



Measurement precision for nitrous oxide expressed as an Allan plot. The noise with 1 second of signal averaging is 31 ppt or just 0.1 per mil!

Application #3:
Nitrous Oxide Flux from Corn Field in Tennessee

Link to application

N_2O Isotope Monitor

- N_2O isotope monitor is part of general development of dual CW QCL instruments with >200 meter path length
- Aerodyne is funded by NSF to further develop this instrument for AGAGE network (see below)
- Detects three most significant isotopologues: $^{15}N^{14}NO$, $^{14}N^{15}NO$ and $N_2{}^{18}O$ with precision approaching 1‰ for ambient N_2O concentrations
- Instrument is flexible – could be reconfigured with additional lasers to monitor other trace gases like: NO, NO_2, HONO, many others.
- Mechanical specs:
  - Dimensions: 530 mm x 660 mm x 710 mm
  - Weight: 72 kg
  - Electrical Power: 500 W, 120/240 V, 50/60 Hz (with Varian IDP-3 vacuum pump)

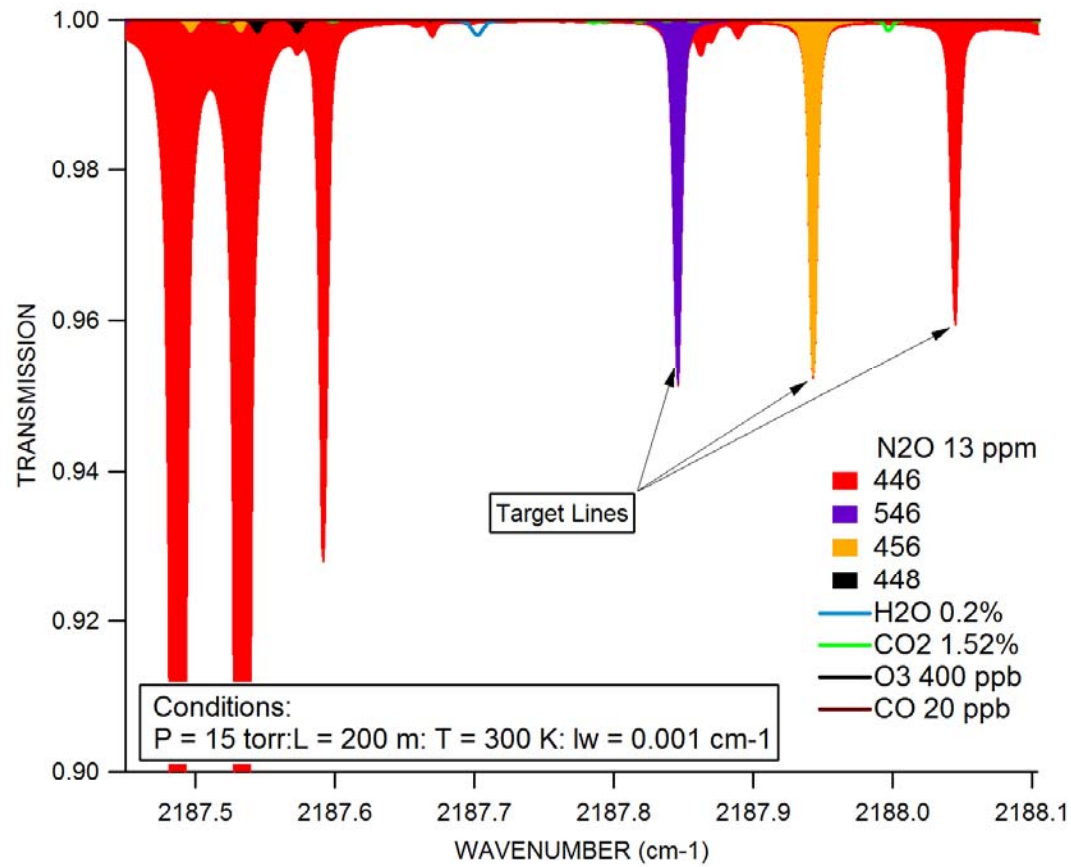
Spectral Simulation for Detection of ^{15}N Isotopomers

Spectral region near 2188 cm^{-1} is ideal for detecting $^{15}N^{14}NO$ and $^{14}N^{15}NO$

Simulation assumes 200 meter pathlength and 40X pre-concentration of ambient N_2O concentration

Projected sensitivity for each isotopic ratio is 0.025‰ with 100 seconds of averaging

Without pre-concentration, the projected sensitivity is 1‰ with 100 seconds of averaging for ambient N_2O concentrations



This spectral region has been demonstrated for detecting $^{15}N^{14}NO$ and $^{14}N^{15}NO$ by our colleagues at ETH and EMPA using an Aerodyne instrument:

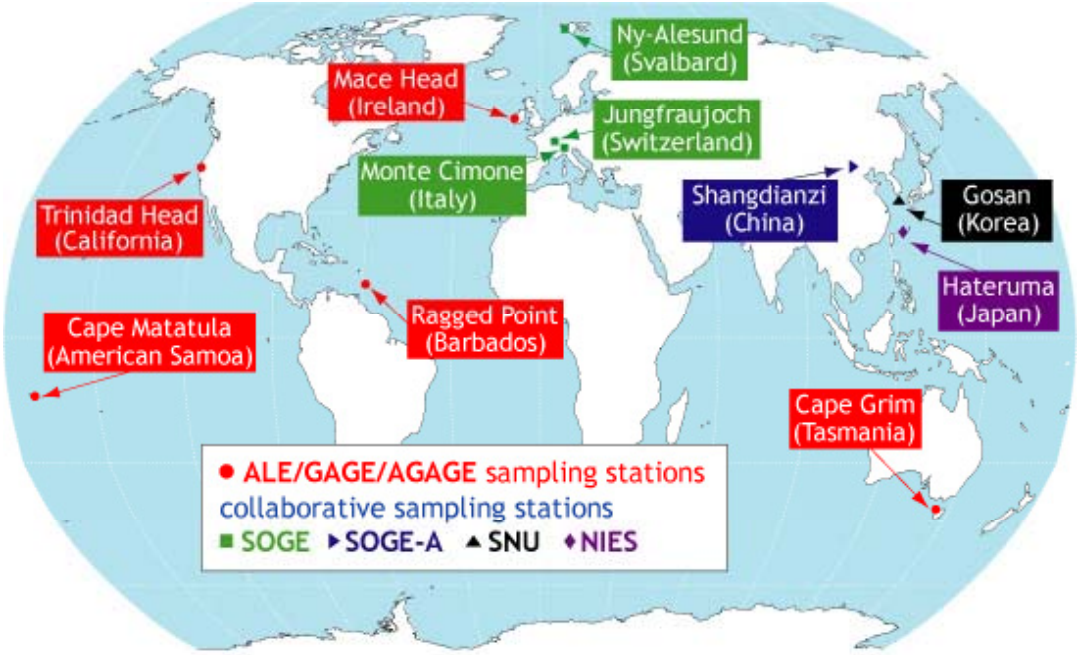
Waechter, H., J. Mohn, B. Tuzson, L. Emmenegger and M. Sigrist (2007). "Determination of N 2 O isotopomers with quantum cascade laser based absorption spectroscopy." Soil Sci. Soc. Am. J **71**: 1-7.

N2O Isotope Monitors at AGAGE Network

NSF MRI project to design, construct and deploy a dual QCL N2O isotope monitor as part of the AGAGE monitoring network

This project is a collaboration with Shuhei Ono and Ron Prinn of MIT. Prinn is the PI and founder of the AGAGE network.

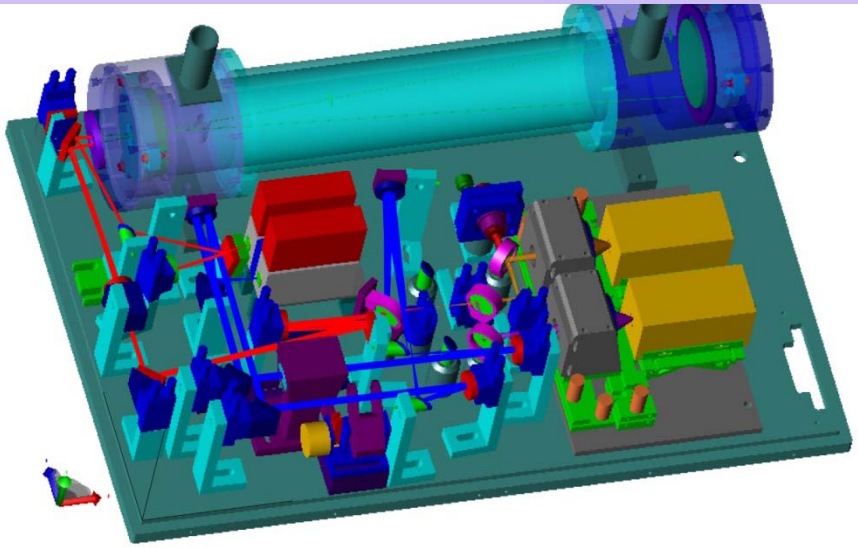
AGAGE (Advanced Global Atmospheric Gases Experiment) network has monitored the trace gas composition of the global atmosphere since 1978



Our long term goal is to deploy nitrous oxide, carbon dioxide and methane isotope monitors at multiple AGAGE sites.

New Dual CW QCL Spectrometer

200 m sample cell
Volume 1.8 liters
Mirror reflectivity >0.999
Two CW QC lasers
TE cooled detectors



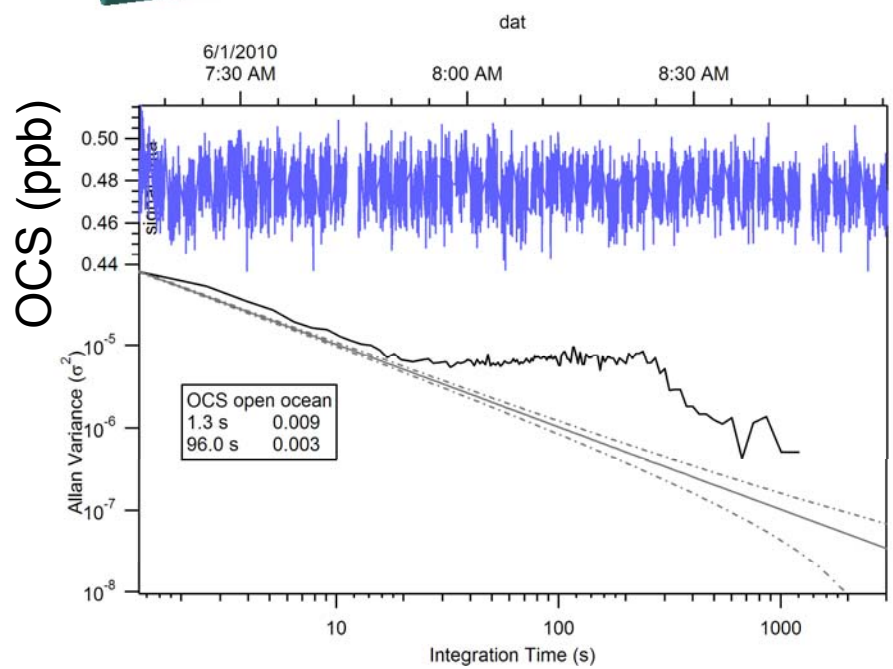
Recent results with CW-QCLs

NO_2	7 ppt $Hz^{-1/2}$
HCHO	40 ppt $Hz^{-1/2}$
HCOOH	50 ppt $Hz^{-1/2}$
OCS	10 ppt $Hz^{-1/2}$

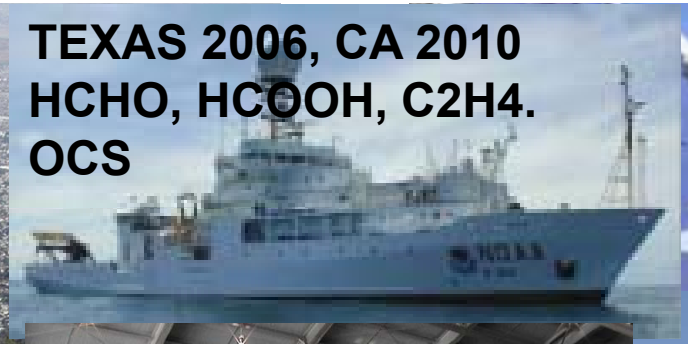
Next applications

$^{13}CH_4$ - CH_3D

^{15}NNO – $N_2{}^{18}O$



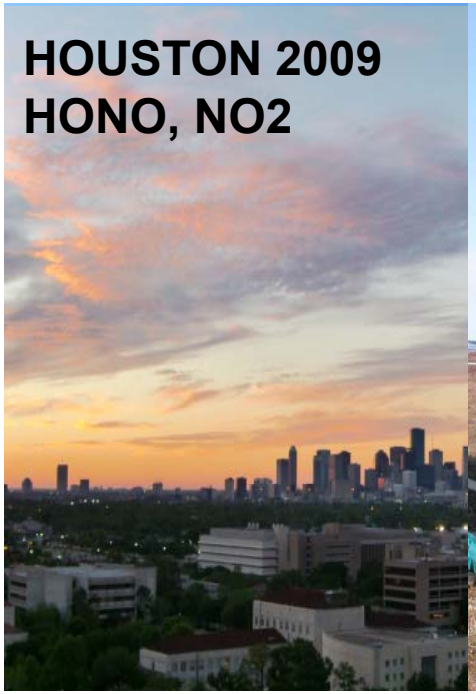

Mexico City 2003, 2006
NH3,NO2, CO, HCHO, C2H4
AERODYNE MOBILE LABORATORY


TEXAS 2006, CA 2010
HCHO, HCOOH, C2H4.
OCS


Jungfraujoch
(EMPA) 2008-2010
CO2 isotopes


NEW ENGLAND 2004
HCHO, HCOOH


COLORADO 2008-2010
CH4, N2O, CO, CO2


HOUSTON 2009
HONO, NO2


RUSSIAN
TUNDRA 2008
(U. Copenhagn)
CH4


SALLIE's FEN, NH 2009
13CH4 – 12CH4 ISOTOPES

SUMMARY

- Advances in CW-QCL technology are revolutionizing isotopic trace gas measurements by infrared absorption
- Single laser QCL instruments for $^{13}CO_2$ and $^{13}CH_4$ now approach IRMS precision and these instruments are field deployable
- Dual-QCL instruments now available for
  - CO_2 and H_2O isotopes
  - $^{13}CH_4$ and CH_3D
  - ^{15}NNO, $N^{15}NO$, and $N_2{}^{18}O$
- Dual QCL instruments are highly flexible – easily reconfigured for other molecular species

Acknowledgments

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  - Mark Zahniser
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