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

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July 2012
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$_2$O 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
  • $\text{CO}_2$ is the most important
  • But $\text{CH}_4$ and $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ and $\text{CH}_4$
  • Need fast time response – eddy covariance
  • Need isotopic resolution – for source determination
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

\[ h\nu = \Delta E = h\omega \]

\[ J \] 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

\( \sigma \) is the absorption cross section – property of molecule – we want it big

L is the optical path length – we want it big

\[ N = \frac{A}{(\sigma \times L)} \]

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

ASTIGMATIC MULTIPASS CELL
76 m (238 passes), 0.5 liters

VIGO TE-COOLED DETECTORS

BEAMSPLITTER

CW-QC LASER

TEC COOLER

COMPUTER

3 MHz
A-D  D-A

LASER DRIVER

RAMP

NO "DOUBLET"
1900 cm⁻¹

LASER OFF

TDLWINTEL SOFTWARE

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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 N₂O, telecom detection will be very hard due to lower atmospheric abundance and extremely small linestrengths.
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.
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 $\delta$ 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 ($\Delta$, ‰) 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 $\delta^D$ in Rain Water

- 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 $\mu$m

- 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$_2$


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$_2$O Dual Isotope Instrument

Sample spectrum with fit: 1s average of spectra
2 multiplexed lasers sweeping at 2 kHz
Typical ratio noise performance at ambient levels, 1 s average (as of June, 2012):

\[
\begin{align*}
\text{H}_2\text{O:} & \quad R \frac{162}{161} \quad 0.3 \, \% \quad (\text{D}/\text{H}) \\
& \quad R \frac{181}{161} \quad 0.1 \, \% \quad (^{18}\text{O}/^{16}\text{O}) \\
\text{CO}_2: & \quad R \frac{628}{626} \quad 0.08 \, \% \quad (^{18}\text{O}/^{16}\text{O}) \\
& \quad R \frac{636}{626} \quad 0.13 \, \% \quad (^{13}\text{C}/^{12}\text{C})
\end{align*}
\]

This is excellent measurement precision!
Application #1: Carbon Dioxide Iso-Flux at Harvard Forest

Link to application 1
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.

<table>
<thead>
<tr>
<th>CURRENT INSTRUMENT PERFORMANCE:</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ 13C 0.2 ‰ in 60 s</td>
</tr>
<tr>
<td>WITHOUT PRE-CONCENTRATION</td>
</tr>
<tr>
<td>CRYOGEN FREE OPERATION</td>
</tr>
<tr>
<td>FIELD PORTABLE</td>
</tr>
<tr>
<td>IMPROVEMENTS COMING</td>
</tr>
</tbody>
</table>

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
N₂O Isotope Monitor

- N₂O 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: ¹⁵N¹⁴NO, ¹⁴N¹⁵NO and N₂¹⁸O with precision approaching 1‰ for ambient N₂O concentrations
- Instrument is flexible – could be reconfigured with additional lasers to monitor other trace gases like: NO, NO₂, 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$_2$O 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$_2$O 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:

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
- NO₂ 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
- $^{13}$CH₄ - CH₃D
- $^{15}$NNO – N₂₁⁸O
Mexico City 2003, 2006
NH3, NO2, CO, HCHO, C2H4

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

Jungfraujoch (EMPA) 2008-2010
CO2 isotopes

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

New England 2004
HCHO, HCOOH

COLORADO 2008-2010
CH4, N2O, CO, CO2

Jungfraujoch (EMPA) 2008-2010
CO2 isotopes

COLORADO 2008-2010
CH4, N2O, CO, CO2

Sallie’s FEN, NH 2009
13CH4 – 12CH4 isotopes

Sallie’s FEN, NH 2009
13CH4 – 12CH4 isotopes

HOUSTON 2009
HONO, NO2

Russian Tundra 2008 (U. Copenhagen)
CH4

HOUSTON 2009
HONO, NO2

Russian Tundra 2008 (U. Copenhagen)
CH4
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$_2$O isotopes
- $^{13}$CH$_4$ and CH$_3$D
- $^{15}$NNO, N$^{15}$NO, and N$_2$$^{18}$O

Dual QCL instruments are highly flexible – easily reconfigured for other molecular species.
Acknowledgments

- Aerodyne Colleagues
  - Mark Zahnisser
  - Barry McManus
  - Joanne Shorter
  - Scott Herndon
  - Dan Glenn
  - Ryan McGovern
  - Stanley Huang
  - Ezra Wood

- Harvard University
  - Greg Santoni
  - Ben Lee
  - Roisin Commane
  - Bruce Daube
  - William Munger
  - Steve Wofsy

- Alpes Lasers
  - Antoine Müller
  - Stephan Blaser

- Collaborators
  - Rick Wehr
  - Scott Saleska U. Arizona
  - Bela Tuzson
  - Lukas Emmenegger EMPA

FUNDING

- US DOE, NSF, NASA, EPA, NIST, NIH
  Small Business Innovation Research Programs

- NOAA Global Change, NSF Atmospheric Chemistry Programs