High resolution spectroscopy and trace-gas detection with thermoelectrically cooled cw quantum cascade lasers

F.K. Tittel, Y. Bakhirkin, R.F Curl, A.A Kosterev, R. Lewicki, M. McCurdy, S. So and G. Wysocki
Rice Quantum Institute, Rice University, Houston, TX , USA
http://ece.rice.edu/lasersci/

R. Maulini, J. Faist
Institute of Physics, University of Neuchatel, Switzerland.

L. Diehl, M. Troccoli, F. Capasso
Division of Engineering and Applied Science, Harvard University, Cambridge, MA, USA

D. Bour, S. Corzine, J. Zhu, G. Hoefler
Agilent Laboratories, Palo Alto, CA, USA

Work at Rice University supported by NASA, NSF, PNNL, DoE and Welch Foundation
Outline

• Motivation and Background Issues
• Mid-IR Quantum Cascade Laser based Gas Sensors
  ▪ CW, TEC cooled, high power DFB QCLs
  ▪ CW, TEC cooled, widely tunable QCLs
  ▪ CW, LN$_2$ & TEC cooled, DFB interband cascade lasers
• Selected Applications of Trace Gas Detection
  ▪ Off Axis-ICOS Detection of Nitric Oxide
  ▪ LAS based monitoring of formaldehyde and ethylene
  ▪ Quartz Enhanced PAS detection of HC$_2$O, CO, N$_2$O & broadband absorbers (C$_2$HF$_5$)
• Conclusions, Challenges and Future Directions
Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, Aircraft and Marine Emissions
- **Rural Emission Measurements**
  - Agriculture & Forestry, Livestock
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Nuclear Safeguards, Pharmaceutical, Metals Processing & Food Industries
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Medicine and Life Sciences**
- **Technologies for Law Enforcement and Homeland Security**
- **Fundamental Science and Photochemistry**
Fundamentals of Laser Absorption Spectroscopy

**Optimum Molecular Absorbing Transition**
- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

**Long Optical Pathlengths**
- Multipass Absorption Cell
- Cavity Enhanced and Cavity Ringdown Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Evanescent Field Monitoring (fibers & waveguides)

**Spectroscopic Detection Schemes**
- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy
- Remote Sensing

---

**Beer-Lambert’s Law of Linear Absorption**

\[ I(\nu) = I_0 e^{-\alpha(\nu) P_a L} \]

- \( \alpha(\nu) \) - absorption coefficient [cm\(^{-1}\) atm\(^{-1}\)]
- \( L \) - path length [cm]
- \( \nu \) - frequency [cm\(^{-1}\)]
- \( P_a \) - partial pressure [atm]

\[ \alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0) \]

- \( C \) - total number of molecules of absorbing gas/atm/cm\(^3\) [molecule·cm\(^{-3}\)·atm\(^{-1}\)]
- \( S \) – molecular line intensity [cm·molecule\(^{-1}\)]
- \( g(\nu - \nu_0) \) – normalized spectral lineshape function [cm],
  (Gaussian, Lorentzian, Voigt)
Tunable external cavity QCL based spectrometer

- PZT controlled EC-length
- PZT controlled grating angle
- QCL current control
- Optimization of cavity alignment performed by means of lens positioning using electrically controlled 3D translation stage
- 35 cm\(^{-1}\) wavelength tunability with present gain chip

Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - $\text{NO}_x$ monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1988 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection
Mid-IR NO Absorption Spectra Acquired with a Tunable EGC-QCL

Nitric oxide absorption spectra measured at different diffraction grating angles of the external cavity quantum cascade laser. The narrow EGC-QC laser linewidth allows resolution of two spectral peaks separated by ~ 0.006 cm⁻¹.

Single spectral scan of NO and strong neighboring H₂O lines. Background measurement was performed with the reference gas cell removed from the beam path.
Laser-based ICOS Nitric Oxide Sensor

A 1σ deviation of the amplitude corresponds to a 700 ppt detection limit (1 sec.)

Motivation for Monitoring of H$_2$CO

- Toxic pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products (e.g., resins, foam)
- Atmospheric H$_2$CO is a key hydrocarbon oxidation product which leads to the photochemical generation of ozone and release of hydrogen radicals
- Medically important gas
DFG and ICL based $\text{H}_2\text{CO}$ Sensor for studying Urban Air Pollution

$\text{H}_2\text{CO}$ and $\text{O}_3$ Concentration, 0.58938 correlation coefficient

$\text{H}_2\text{CO}$ & $\text{O}_3$ concentrations at Deer Park (2003)

Rice DFG system (2003)

JPL 3.3 $\mu$m cw, TEC cooled ICL (2006)

Rice dual ICL system (2006)

NCAR DFG system (2006)
CW ICL Based H₂CO and C₂H₄ Sensor for TexAQS ‘06

Moody Tower UH campus, earth Google satellite photo.

HITRAN Based Simulation of a H₁CO-H₂O-CH₄ Spectrum in Tuning Range of a 3.53μm IC Laser

HITRAN Based Simulation of C₂H₄-H₂O-CH₄ Spectrum in Tuning Range of a 3.33-3.35 μm IC Laser
From conventional PAS to QEPAS

Laser beam, power $P$

Modulated $(P$ or $\lambda$) at $f$ or $f/2$

$S_{PAS} \sim \frac{Q \alpha P}{fV}$

$Q \gg 1000$

Cell is OPTIONAL!

$V$-effective volume

Broadband microphone crystal

Resonant at $f$ quality factor $Q$

Cavity, resonant at $f$, volume $V$, quality factor $Q \sim 20-200$

SWAP RESONATING ELEMENT!!!
Quartz Tuning Fork as a Resonant Microphone for PAS

- Miniature size, 0.3 mm³ detection volume
- Dimensions in mm: length = 3.8, gap size = 0.3, thickness = 0.3, width = 0.58
- Piezo-active material
- Signal currents ≈ pA
- Intrinsically high $Q$ factor, $\sim$10,000 at ambient pressure; $Q_{\text{vacuum}} \sim$ 125,000
Design of a new QTF based Absorption Detection Module

• Compact & integrated design
• Laser-induced background reduction
• Machining precision of : +/- 10µm

• Two QTFs connected in parallel results in enhanced $\sqrt{2}$ SNR
• Minimum exposure of QTFs to QCL radiation
• Efficient for gas flow to micro-resonator
Merits of QE PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to ambient and flow acoustic noise, as well as laser noise and etalon effects
- Dramatic reduction of sample volume (< 1 mm$^3$)
- Applicable over a wide range of pressures, including atmospheric pressure
- Rugged and low cost compared to other spectroscopic techniques that require infrared detector(s)
- Sensitive to phase shift introduced by V-T relaxation processes – additional selectivity
- Potential for trace gas sensor networks
Motivation for H$_2$CO Monitoring

- Pollutant due to incomplete combustion processes
- Potential trace contaminant in industrial manufactured products
- Atmospheric H$_2$CO is a key hydrocarbon oxidation product which leads to the photochemical generation of ozone and release of hydrogen radicals
- Medically important gas
QCL or ICL based Quartz-Enhanced Photoacoustic Gas Sensor

- [H₂CO]: 13 ppm
- QEPAS NNEA Sensitivity (for 2804.9 cm⁻¹): 0.92×10⁻⁸ cm⁻¹ W/√Hz;
- NEC (τ=1s): 0.18 ppmv (~ 6.5 mW)

For comparison:
NIR QEPAS NNEA Sensitivity for NH₃: 5.4×10⁻⁹ cm⁻¹ W/√Hz
NEC (τ=1s): 0.5 ppmv (38 mW)
Calibration Measurements of a QEPAS based H$_2$CO Sensor with a Trace Gas Standard Generator

- H$_2$CO absorption frequency: 2804.9 cm$^{-1}$
- Lock-In time constant: 1 sec.
- QEPAS parameters
  - Resonance frequency: 32.760 KHz
  - Q-factor: ~ 8800
  - Pressure: 200 Torr
  - Gas Flow: ~50 sccm
  - IC laser power: ~ 6.5 mW
Amplitude Modulated 8.6 µm QCL based QEPAS Freon 125 Sensor

Spectral comparison of Freon 125 with emission coverage from a 8.6 µm FP QCL based on the PNNL database
# QEPAS Performance for 9 Trace Gas Species (Sept.’06)

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm(^{-1})</th>
<th>Pressure, Torr</th>
<th>NNEA, cm(^{-1})W/Hz(^{-1})</th>
<th>Power, mW</th>
<th>NEC ((\tau=1)s), ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O (N(_2))**</td>
<td>7306.75</td>
<td>60</td>
<td>1.9(\times)10(^{-3})</td>
<td>9.5</td>
<td>0.09</td>
</tr>
<tr>
<td>HCN (air: 50% RH )*</td>
<td>6539.11</td>
<td>60</td>
<td>&lt;4.3(\times)10(^{-3})</td>
<td>50</td>
<td>0.16</td>
</tr>
<tr>
<td>C(_2)H(_2) (N(_2))**</td>
<td>6529.17</td>
<td>75</td>
<td>(\sim)2.5(\times)10(^{-3})</td>
<td>(\sim)40</td>
<td>0.06</td>
</tr>
<tr>
<td>NH(_3) (N(_2))*</td>
<td>6528.76</td>
<td>60</td>
<td>5.4(\times)10(^{-3})</td>
<td>38</td>
<td>0.50</td>
</tr>
<tr>
<td>CO(_2) (exhaled air)</td>
<td>6514.25</td>
<td>90</td>
<td>1.0(\times)10(^{-8})</td>
<td>5.2</td>
<td>890</td>
</tr>
<tr>
<td>CO(_2) (N(_2)+1.5% H(_2)O )</td>
<td>4991.26</td>
<td>50</td>
<td>1.4(\times)10(^{-8})</td>
<td>4.4</td>
<td>18</td>
</tr>
<tr>
<td>CH(_2)O (N(_2):75% RH)*</td>
<td>2804.90</td>
<td>75</td>
<td>9.2(\times)10(^{-9})</td>
<td>6.5</td>
<td>0.18</td>
</tr>
<tr>
<td>CO (N(_2))</td>
<td>2196.66</td>
<td>50</td>
<td>5.3(\times)10(^{-7})</td>
<td>13</td>
<td>0.5</td>
</tr>
<tr>
<td>CO (propylene)</td>
<td>2196.66</td>
<td>50</td>
<td>7.4(\times)10(^{-8})</td>
<td>6.5</td>
<td>0.14</td>
</tr>
<tr>
<td>N(_2)O (air+5%SF(_6))</td>
<td>2195.63</td>
<td>50</td>
<td>1.5(\times)10(^{-8})</td>
<td>19</td>
<td>0.007</td>
</tr>
<tr>
<td>C(_2)HF(_5) (Freon 125)***</td>
<td>1162.79</td>
<td>700</td>
<td>1.9(\times)10(^{-8})</td>
<td>4.0</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* - Improved microresonator  
** - Improved microresonator and double optical pass through ADM  
*** - With amplitude modulation and microresonator

NNEA – normalized noise equivalent absorption coefficient.  
NEC – noise equivalent concentration for available laser power and \(\tau=1\)s time constant.

For comparison: conventional PAS 2.2\(\times\)10\(^{-9}\) cm\(^{-1}\)W/√Hz (1,800 Hz) for NH\(_3\)*  
Future Work – Mini-QEPAS Sensor System

- **3.85 inch x 2.5 inch (9.8 cm x 6.4 cm)**
- **Low power**
  - 3W max for TEC
  - 3W max for Laser
  - 0.5W max for electronics (μW sleep mode)
- **Embedded Laser**
- **Embedded TF module**
- **Embedded Radio**
- **2 cell Li-Pol Battery + Charging**
- **Low cost**
Summary, Technological Challenges and Future Directions of QCL based Applications

• **Quantum and Interband Cascade Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity (<10^-4) and selectivity (3 to 500 MHz)
  - Fast data acquisition and analysis
  - Detected 12 trace gases to date: NH₃, CH₄, N₂O, CO₂, CO, NO, H₂O, COS, C₂H₄, SO₂, C₂H₅OH, C₂HF₅ and several isotopic species of C, O, N and H.

• **Applications in Trace Gas Detection**
  - Environmental monitoring (NH₃, CO, CH₄, C₂H₄, N₂O, CO₂ and H₂CO)
  - Industrial process control and chemical analysis (HCN, NO, NH₃, H₂O)
  - Medical & Biomedical Diagnostics (NO, CO, COS, CO₂, NH₃, C₂H₄)
  - Sensor Technologies for Law Enforcement and Homeland Security

• **Future Directions and Collaborations**
  - New applications using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable near-IR interband and mid-IR intersubband quantum cascade lasers
  - Improvements of Cavity Enhanced and QEPAS based spectroscopic techniques using broadly wavelength tunable quantum cascade lasers
  - Development of optically multiplexed gas sensor networks based on QEPAS
  - Potential and limitations of amplitude modulated QEPAS for monitoring of broadband absorbers, in particular VOCs and HCs
Mt. Etna, Italy, Europe’s largest volcano

Photos provided by C. Oppenheimer, Cambridge University, UK
Volcanological Applications

• CO$_2$ the most abundant component of volcanic gases after H$_2$O
• δ$^{13}$C is a sensitive tracer of magmatic vs. hydrothermal or groundwater contributions to volcanic gases
• Monitoring δ$^{13}$C can be used in eruption forecasting and volcanic hazard assessment
CO₂ Absorption Line Selection Criteria

• Three strategies:
  
  ➢ Similar strong absorption of \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) lines
    ▪ Very sensitive to temperature variations
  
  ➢ Similar transition lower energies
    ▪ Requires a dual path length approach to compensate for the large difference in concentration between major and minor isotopic species—or—
    ▪ Can be realized if different vibrational transitions are selected for the two isotopes (4.35 μm for \(^{13}\text{CO}_2\) and 2.76 μm for \(^{12}\text{CO}_2\))

• For the first 2 strategies both absorption lines must lie in a laser frequency scan window

• Avoid presence of other interfering atmospheric trace gas species

* Proposed scheme by Curl, Uehara, Kosterev and Tittel, Oct. 2002
High resolution CO$_2$ absorption spectrum at 2311 cm$^{-1}$
Quantum and Interband Cascade Laser: Basic Facts

- Band – structure engineered devices (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 4 to 160 µm
  - Unipolar devices
  - Cascading (each electron creates N laser photons and the number of periods N determines laser power)

- Compact, reliable, stable, long lifetime, and commercial availability

- Fabry-Perot (FP), single mode (DFB) and multi-wavelength

- **Spectral tuning range in the mid-IR** (4-24 µm for QCLs and 3-5 µm for ICLs)
  - 1.5 cm⁻¹ using current
  - 10-20 cm⁻¹ using temperature
  - > 150 cm⁻¹ using an external grating element

- **Narrow spectral linewidth** cw: 0.1 - 3 MHz & <10KHz with frequency stabilization (0.0004 cm⁻¹); pulsed: ~ 300 MHz (chirp from heating)

- **High output powers at TEC/RT temperatures**
  - Pulsed peak powers of 1.6 W; high temperature operation ~ 425 K
  - Average power levels: 1-600 mW (wall plug η~4%)
  - ~ 50 mW, TEC CW DFB @ 5 and 10 µm (Alpes & Unine); Princeton, AdTech Optics, Maxion, Argos Technology.
  - ~ 300 mW @8.3 µm (Agilent Technologies & Harvard)
  - >600 mW (CW FP) and >150 mW (CW DFB) at 298 K (Northwestern)
Wavelength Coverage of IR Detectors
What are quantum cascade laser design requirements for improved trace gas sensor platform technology

- Availability of QCLs operating at key molecular target wavelengths
- Wavelength tunability and narrow spectral linewidth operation
- High power, cw operation at quasi room temperatures
- Packaging and reliability

Can we find both high value and high volume QCL based applications in Trace Gas Detection

- Environmental monitoring (HCHO, CO₂)
- Medical Diagnostics (NO, CO, COS, CO₂)
- Industrial process control and chemical analysis (eg. NO, CO, NH₃ and broad band absorbers)