Development of QCL Based Sensor Technology for Trace Gas Monitoring Applications

Rice Quantum Institute, Rice University, Houston, TX
http://ece.rice.edu/lasersci/

- Motivation and Technology Issues
- Fundamentals of Laser Absorption Spectroscopy
- Selected Applications of Trace Gas Detection
  - Off Axis-ICOS based detection of NO
  - Direct Absorption Spectroscopy of OCS
  - Quartz Enhanced Laser-PAS of \( \text{N}_2\text{O} \) and \( \text{H}_2\text{CO} \)
  - \( \text{CO}_2 \) Flux and Isotopic Ratio Measurements
- Conclusions and Outlook
Motivation: Wide Range of Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (eg. early fire sensing)
  - Automobile and Aircraft Emissions

- **Rural Emission Measurements**
  - Agriculture and Animal Facilities

- **Environmental Monitoring**
  - Atmospheric Chemistry (eg ecosystems and airborne)
  - Volcanic Emissions

- **Chemical Analysis and Industrial Process Control**
  - Chemical, Pharmaceutical, Food & Semiconductor Industry

- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Human Life Support Program

- **Medical Diagnostics** (eg. breath analysis)

- **Biohazard and Toxic Chemical Detection**

- **Fundamental Science and Photochemistry**
**Fundamentals of Laser Absorption Spectroscopy**

**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 \cdot cm\(^{-3}\) \cdot atm\(^{-1}\)]
- \( S \) - molecular line intensity [cm \cdot molecule\(^{-1}\)]
- \( g(\nu - \nu_0) \) - normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

**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)

**Spectroscopic Detection Schemes**
- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy
HITRAN Simulation of Absorption Spectra (3.1-5.5 & 7.6-12.5 μm)
## CW IR Source Requirements for Laser Spectroscopy

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR SOURCE</th>
</tr>
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<tbody>
<tr>
<td>Sensitivity (% to ppt)</td>
<td>Power</td>
</tr>
<tr>
<td>Selectivity</td>
<td>Narrow Linewidth</td>
</tr>
<tr>
<td>Multi-gas Components</td>
<td>Tunable Wavelength</td>
</tr>
<tr>
<td>Directionality</td>
<td>Beam Quality</td>
</tr>
<tr>
<td>Rapid Data Acquisition</td>
<td>Fast Response</td>
</tr>
<tr>
<td>Room Temperature</td>
<td>No Consumables</td>
</tr>
</tbody>
</table>
Key Characteristics of Mid-IR Quantum Cascade Lasers for Spectroscopy

QC laser wavelengths cover entire mid-IR range from 3.3 to 24 μm determined by thickness of the quantum well and barrier layers of the active region

Intrinsically high power lasers (determined by number of stages of injector-active quantum well gain regions)

- CW: ~100 mW @ 80°C and 1-640 mWes @ 295 °K
- Pulsed: >1 W peak at room temperature, ~50 mW avg. @ 0 °C (up to 80% duty cycle) to 100 mWes (56% d.c)

High spectral purity (single frequency:<kHz - 330MHz)

Wavelength tunable by current (~1cm⁻¹) or temperature scanning (~10 cm⁻¹); ~150 cm⁻¹ with external cavity grating

High reliability: long lifetime, robust operation and reproducible emission wavelengths
# Important Biomedical Target Gases

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Biological/Pathology Indication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>( \text{CH}_3(\text{CH}_2)_3\text{CH}_3 )</td>
<td>Lipid peroxidation, oxidative stress associated with inflammatory diseases, transplant rejection, breast and lung cancer</td>
</tr>
<tr>
<td>Ethane</td>
<td>( \text{C}_2\text{H}_6 )</td>
<td>Lipid peroxidation and oxidative stress</td>
</tr>
<tr>
<td>( \text{CO}_2 ) isotope ratio</td>
<td>( ^{13}\text{CO}_2 / ^{12}\text{CO}_2 )</td>
<td>Marker for Heliobacter pylori infection, Gastrointestinal and hepatic function</td>
</tr>
<tr>
<td>Carbonyl Sulfide</td>
<td>( \text{COS} )</td>
<td>Liver disease and acute rejection in lung transplant recipients (10-500 ppb?)</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>( \text{CS}_2 )</td>
<td>Schizophrenia</td>
</tr>
<tr>
<td>Ammonia</td>
<td>( \text{NH}_3 )</td>
<td>Hepatic encephalopathy, liver and renal diseases, fasting response</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>( \text{HCHO} )</td>
<td>Cancerous tumors, breast cancer (400-1500 ppb)</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>( \text{NO} )</td>
<td>Inflammatory and immune responses (e.g., asthma) and vascular smooth muscle response (6-100 ppb)</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>( \text{H}_2\text{O}_2 )</td>
<td>Airway Inflammation, Oxidative stress (1-5 ppb)</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>( \text{CO} )</td>
<td>Smoking response, CO poisoning, vascular smooth muscle response, platelet aggregation (400-3000 ppb)</td>
</tr>
<tr>
<td>Ethylene</td>
<td>( \text{H}_2\text{C} = \text{CH}_2 )</td>
<td>Oxidative stress, cancer</td>
</tr>
</tbody>
</table>
- Novel compact gas cell design of length: 3.8 - 5.3 cm and cell volumes < 80 cm³;
- Low loss mirrors (ROC 1m): ~60-250 ppm, R~99.975, L_eff = 170-800 m
- Rapid eNO concentration measurements during a single breath cycle feasible
Off-axis ICOS Detection of NO

- 95 and 490 ppb NO/N₂ calibration mixture at 100 Torr total pressure
- Effective optical path ~ 70 m (1,350 passes)

Voigt fit of measured NO absorption line at 1920.7 cm⁻¹ for a concentration of 95 ppb

Noise-equivalent sensitivity is 10 ppb for 1σ deviation of the best fit coefficient.
Detection sensitivity: $1.0 \times 10^{-7}$ cm⁻¹ Hz⁻¹/²
OCS Sensor Architecture

QCL – quantum cascade laser chip
LH - laser housing
CL – collimating lens
SB – sample beam
RB – reference beam
M – mirror
BS – beam splitter
PM – off-axis parabolic mirror

DAQ CARD NI 6062E

FUNCTION GENERATOR

PULSED QCL DRIVER

GATE GENERATOR

PULSE AMPLITUDE CONTROL

TRACK & HOLD's

REFERENCE SAMPLE

TRIGGER PULSE GENERATOR

PC

PCMCIA
OCS ro-vibrational Spectrum

- Line intensity: $7.49 \times 10^{-19} \text{ cm}^{-1}/\text{molecule-cm}$
- Minimal spectral interference by nearby CO$_2$ and H$_2$O absorption lines
- Availability of a CO$_2$ line with the fast tuning range of the QCL for ventilation monitoring simultaneously with an OCS measurement
OCS Concentration Calibration of QCL Sensor

Calibration curve

Theoretical sensitivity:

\[ 0.27 \text{ ppb} \cdot \sqrt{1000/100} = 0.85 \text{ ppb} \]

Scattering of the concentration measurement: \( \sigma = 1.2 \text{ ppb} \)

Reference concentration [ppb]

1000 spectra averaged acquired within \( t = 4 \text{ s} \)
and fitted to 300 ppb OCS reference spectrum

Measurement No.

100 spectra averaged acquired within \( t = 0.4 \text{ s} \)
and fitted to 300 ppb OCS reference spectrum
OCS and CO\textsubscript{2} Concentration Measurements in Exhaled Breath

- Sample was taken from lung transplant patient with suspected bronchiolitis*
- Sampling was performed using chemically inert 1 liter Tedlar sampling bags and analyzed within 2 hours after collection
- Spectrum was measured at a total pressure of 60 torr

*The authors wish to thank Dr. Remzi Bag and Carolyn M. Paraguaya from Baylor College of Medicine, Houston, TX for supplying breath samples
QC laser based measurements of CO trace gas above cell cultures

- Measured CO production rates of viable cultures of vascular smooth muscle cells
- Achieved a detection limit of for CO of ∼20 ppb

Towards CW Mode Operation of DFB QCLs

- Main drawbacks of QCL pulsed operation
  - Pulse to pulse intensity variation
  - Linewidth broadening by thermal chirp
  - Requirement of nanosecond electronics

- Efforts towards achieving quasi-RT CW DFB QCLs
Direct Absorption Based Gas Sensor Architecture

Temperature control

Current source

QCL

Aspheric lens

Flow output

Flow input

21" absorption cell (53.34 cm)

MCT Detector + preamplifier

Acquisition
Wavelength Modulation Spectroscopy

- QCL Drive Current: Quasi CW + Wavelength modulation

- Calibration with a 1038 ppm NH$_3$ : N$_2$ mixture

  $1\sigma$ extrapolated sensitivity 82 ppb.m/$\sqrt{\text{Hz}}$

$\Rightarrow$ Improvement by a factor of 3 compared to direct absorption spectroscopy
Resonant photoacoustic spectroscopy

Laser beam, power $P$

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

Absorption: $\alpha(\lambda)$

Cavity, resonant at $f$, volume $V$, quality factor $Q$

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

Sensitivity $[k] = \frac{\text{cm}^{-1} \times \text{W}}{\sqrt{\text{Hz}}}$

RICE
Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)

Laser beam, power $P$

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

Absorption: $\alpha(\lambda)$

$S_{QEPAS} \sim \frac{Q\alpha P}{f}$

Sensitivity $[k] = \frac{\text{cm}^{-1} \times W}{\sqrt{\text{Hz}}}$

Piezoelectric quartz crystal (instead of microphone)

Resonant at $f$, quality factor $Q$ is $>10,000$ instead of 20-200 for PAS.

*Resonant Cavity in L-PAS
*Cell is OPTIONAL in QEPAS.
Comparative Size of Absorbance Detection Modules (ADM)

Optical multipass cell (100 m):
l~70 cm, V~3000 cm³

Resonant photoacoustic cell (1000 Hz):
l~60 cm, V~50 cm³

QEPAS ADM:
l~0.5 cm, V~0.05 cm³
QCL based Quartz-Enhanced Photoacoustic Spectromete

Noise-equivalent sensitivity ($\alpha_{\text{min}}$): $8.1 \times 10^{-9} \text{ cm}^{-1} \text{W}/\sqrt{\text{Hz}}$ (Rice Dec. 2003)

f. traditional PAS $1.1 \times 10^{-8} \text{ cm}^{-1} \text{W}/\sqrt{\text{Hz}}$ (Webber et al. Appl. Phys. B 77, 381, 2003)
$\text{N}_2\text{O}$ Detection in Ambient Air at 4.6 $\mu$m (2195.6 cm$^{-1}$)

**Graph 1:**
- ICL power in TF cell: 11 mW
- Gas pressure: 50 Torr
- Ambient air + 5% SF$_6$

**Graph 2:**
- SNR = 48
- $[\text{N}_2\text{O}] = 315$ ppb
- Total gas pressure: 50 Torr
- ICL power in TF cell: 9 mW
- $\sigma(\tau=1\text{s}) = 0.7$ $\mu$V

[Graph showing signal vs. detuning with relevant parameters]
Merits of QE Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to ambient and flow acoustic noise, laser noise and etalon effects
- Significant reduction of sample volume (< 1 mm³)
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive
- Rugged and low cost compared to LAS that requires a multipass absorption cell and infrared detector(s)
- Potential for optically multiplexed concentration measurements
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Traditional PAS</th>
<th>QEPAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$, Hz</td>
<td>100 to 4000</td>
<td>Presently $\sim$32 760</td>
</tr>
<tr>
<td>$Q$</td>
<td>20 to 200</td>
<td>10 000 to 30 000</td>
</tr>
<tr>
<td>$Q$ vs. pressure</td>
<td>INCREASES (high spectral resolution is problematic)</td>
<td>DECREASES (high spectral resolution is achievable)</td>
</tr>
<tr>
<td>Sample volume</td>
<td>$&gt;10$ cm$^3$</td>
<td>$&lt;1$ mm$^3$</td>
</tr>
<tr>
<td>Sensitivity to ambient acoustic and flow noise</td>
<td>Usually high</td>
<td>None observed</td>
</tr>
<tr>
<td>Pathlength involved</td>
<td>$\sim$10 cm</td>
<td>(a) 0.3mm, (b) 5mm</td>
</tr>
</tbody>
</table>
HITRAN Based Simulation of a $\text{H}_2\text{CO}-\text{H}_2\text{O}-\text{CH}_4$ Spectrum in Tuning Range of a 3.53$\mu$m IC Laser

- $\text{H}_2\text{CO}$: 10 ppb
- $\text{H}_2\text{O}$: 3%
- $\text{CH}_4$: 2 ppm
- Optical path: 100 m
- Total pressure: 30 Torr
2f QEPAS based H₂CO signal at 3.53 μm (2832.48 cm⁻¹)

- [H₂CO]: 13.27 ppm
- Sensitivity: 7.10⁻⁸ cm⁻¹ W/√Hz
- QEPAS NE sensitivity for NIF: 8.10⁻⁹ cm⁻¹ W/√Hz
  (For comparison)
C laser based formaldehyde calibration measurement with a gas standard generator

- $\text{H}_2\text{CO}$ absorption frequency: 2832.5 cm$^{-1}$
- Lock-In time constant: 10 s
- Photoacoustic cell:
  - Resonance frequency: 32.760 KHz
  - Q-factor: 17336
  - Pressure: 200 Torr
  - Gas Flow: 75 sccm
  - IC laser power: 6 mW
Each Point
Replicate Precision
Over 1 min, $N = 60$
And
Avg. Channel Std. Dev

$$1_{\text{min}} = \frac{\sigma_{1\text{sec}}}{\sqrt{n}} \approx \frac{200 \text{ ppt}}{\sqrt{60}} \approx 26 \text{ ppt}$$

Each Point
1-second data points

Concentration determined by least squares fit of Calibration spectrum to Sample spectra

Data provided by Alan Fried et. al., NCAR Boulder, CO
Motivation for Measuring $^{13}\text{CO}_2/^{12}\text{CO}_2$ Isotopic Ratios

- Volcano eruption forecasting and gas emission studies ($\text{CO}_2$, $\text{HCl}$, $\text{SO}_2$, $\text{HF}$, $\text{H}_2\text{S}$, $\text{CO}$, $\text{H}_2\text{O}$)
- Atmospheric Chemistry: Environmental monitoring of $C_y$ gases ($\text{CO}_2, \text{H}_2\text{O}, \text{CO}, \text{N}_2\text{O}, \text{CH}_4$)
  - Global warming studies
  - Temporal and spatial variations of the isotopic ratios
  - Identification of carbon sources and sinks
  - Global carbon budget studies
- Study of planetary gases (e.g. for Mars: $\text{CO}$, $\text{CO}_2$, $\text{H}_2\text{O}$, $\text{CH}_4$, $\text{O}_3$, $\text{OCS}$)
- Medical applications (non-invasive human health monitoring)
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 \(\mu\text{m}\) for \(^{13}\text{CO}_2\) and 2.76 \(\mu\text{m}\) 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

Ro-vibrational bands suitable for $^{12}\text{CO}_2/^{13}\text{CO}_2$ ratio measurements

[Graph showing line strength vs. wavenumber for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$.]

Strongest band in the overlapping region:

- $^{12}\text{CO}_2$ transition 00$^0_1$-00$^0_0$
- $^{13}\text{CO}_2$ transition 00$^0_1$-00$^0_0$
- $^{12}\text{CO}_2$ transition 01$^1_1$-01$^1_0$
- $^{13}\text{CO}_2$ transition 01$^1_1$-01$^1_0$
Dual path length gas cell design

To IR detector

2.4 cm Short path cell

From QCL

2.4 m Herriott multipass cell

Cell edge

Astigmatic Mirror

Short cell

Herriott cell
QC laser based Isotopic Ratio Sensor Layout

Bread board: 12x18” (30x45 cm)
The sensor must be operated in a dry nitrogen atmosphere to eliminate atmospheric CO₂ background
$^{16}\text{O}^{12}\text{C}^{18}\text{O}$ Spectra at 2320.2 cm$^{-1}$

a) Channel 1

b) Channel 2

Wavenumber (cm$^{-1}$)
Conclusions and Future Directions

- **Quantum Cascade Laser based Trace Gas Sensors**
  - Compact and robust sensors based on QC-LAS and QE L-PAS
  - High sensitivity ($10^{-4}$-$10^{-5}$) and selectivity (3 to 500 MHz)
  - Dramatic reduction of sample volume ($\sim$0.2 mm$^3$)
  - Detected trace gases: NH$_3$, CH$_4$, N$_2$O, CO$_2$, CO, NO, H$_2$O, COS, C$_2$H$_4$, C$_2$H$_5$OH, SO$_2$, H$_2$CO and several isotopic species of C, O, N and H.

- **Applications in Trace Gas Detection**
  - Environmental monitoring (NH$_3$, CO, CH$_4$, C$_2$H$_4$, N$_2$O, CO$_2$)
  - Industrial process control and chemical analysis (NO, NH$_3$)
  - Medical Diagnostics (NO, CO, COS, CO$_2$, C$_2$H$_4$)

- **Future Directions and Collaborations**
  - Cavity enhanced (ICOS) and QE L-PAS spectroscopy based applications using novel thermoelectrically cooled cw and broadly wavelength tunable quantum cascade lasers
  - Applications using new near IR interband and far-IR intersubband quantum cascade lasers
NASA Atmospheric & Mars Gas Sensor Platforms

Aircraft based laser absorption spectrometer

Tunable laser planetary spectrometer

Tunable laser based sensor for stratospheric measurements