Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology


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http://ece.rice.edu/lasersci/

• Motivation: Wide Range of Chemical Sensing
• Fundamentals of Laser Absorption Spectroscopy
• Selected Applications of Trace Gas Detection
  ▪ LAS with a widely tunable QCL sensor at 5.2 um (NO)
  ▪ Quartz Enhanced Laser-PAS (H$_2$CO, CO$_2$)
  ▪ QCL based CO2 isotopic ratio measurements

• Summary and Conclusions

Work supported by NASA, PNNL, NSF, NIH and Welch Foundation
Motivation: Wide Range of Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. early fire detection)
  - Automobile and Aircraft Emissions
- **Rural Emission Measurements**
  - Agriculture and Animal Facilities
- **Environmental Gas Monitoring**
  - Atmospheric Chemistry (e.g. ecosystems and airborne)
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Chemical, Pharmaceutical, Food & Semiconductor Industry
  - Toxic Industrial Chemical Detection
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Advanced Human Life Support Technology
- **Biomedical and Clinical Diagnostics** (e.g. breath analysis)
- **Forensic Science and 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, Cavity Ringdown & Intracavity 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

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

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

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

**Absorber**
Gas, Liquid or Solid

**Laser Source**

\( I_0 \)

**Detector**

\( I \)

\( L \)

\( C \) - total number of molecules of absorbing gas/atm/cm\(^3\)
\([\text{molecule} \cdot \text{cm}^{-3} \cdot \text{atm}^{-1}]\)

\( S \) – molecular line intensity \([\text{cm} \cdot \text{molecule}^{-1}]\)

\( g(\nu - \nu_0) \) – normalized spectral lineshape function \([\text{cm}]\),
(Gaussian, Lorentzian, Voigt)
<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (% to ppt)</td>
<td>Power</td>
</tr>
<tr>
<td>Selectivity</td>
<td>Single Mode Operation and Narrow Linewidth</td>
</tr>
<tr>
<td>Multi-gas Components, Multiple Absorption Lines</td>
<td>Tunable Wavelengths</td>
</tr>
<tr>
<td>and Broadband Absorbers</td>
<td></td>
</tr>
<tr>
<td>Directionality or Cavity Mode Matching</td>
<td>Beam Quality</td>
</tr>
<tr>
<td>Rapid Data Acquisition</td>
<td>Fast Time Response</td>
</tr>
<tr>
<td>Room Temperature Operation</td>
<td>No Consumables</td>
</tr>
<tr>
<td>Field deployable</td>
<td>Compact &amp; Robust</td>
</tr>
</tbody>
</table>
IR Laser Sources and Wavelength Coverage

Class 'A':
- Gas (Line Tunable)
- Semiconductor
- Direct Solid-State

Class 'B':
- Frequency Conversion
- Based Sources

- Solid State and Fiber Laser / Amplifier
  - Tm$^{3+}$/Ho$^{3+}$
  - Er$^{3+}$
  - Pr$^{3+}$
  - Yb$^{3+}$
  - Nd$^{3+}$
  - DFB Diode Laser
  - OPSL

- Rotation-Vibrational
  - I
    - CO Laser
    - CO$_2$ Laser
    - Lead-Salt
    - IC / QC-Laser
  - II
    - Antimonide III-V
    - Cr$^{3+}$ II-VI
    - QPM GaAs
    - PPLN / PPKTP / PPRTA
    - DFG / OPO / OPA

Wavelength (μm)
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 (limited by the CB offset on the short wavelength side)
  - Unipolar devices
  - Cascading (each electron creates N laser photons and the number of periods N determines laser power)

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

- Fabry-Perot (FP) or single mode (DFB)

- **Broad 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
  Linewidth is ~ 300 MHz of pulsed QCLs (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
  - ~ 50 mW, TEC CW DFB @ 5 and 10 µm (Alpes & Unine); Princeton
  - ~ 200 mW @8.3 µm (Agilent Technologies & Harvard)
  - >600 mW (CW FP) and >150 mW (CW DFB) at 298 K (Northwestern)
External Cavity QCL Based Spectrometer

- PZT controlled EC-length
- PZT controlled grating angle
- Optimization of cavity alignment performed by means of lens positioning using electrically controlled 3D translation stage
- 35 cm⁻¹ tunability with the present gain chip

Motivation for NO Detection

• Atmospheric Chemistry
• Environmental pollutant gas monitoring
  ▪ $\text{NO}_x$ monitoring from automobile exhaust and power plant emissions
  ▪ Photochemical smog
• Industrial process control
  ▪ Oswald process which converts $\text{NH}_3$ into $\text{HNO}_3$
• NO in medicine and biology
  ▪ Treatment of asthma
  ▪ Important signaling molecules in humans and mammals (1988 Nobel Prize in Physiology/Medicine)
Mid-IR NO Absorption Spectra Acquired with a Tunable TEC QCL

- **NO @ 4.9 torr**: 9 cm pathlength
  - $R_{3/2}(20.5)$
  - $R_{1/2}(23.5)$

- **HITRAN 2000 simulation**: Measured spectra

- **Absorption**: Wavenumber [cm$^{-1}$]

- **HITRAN simulation**:
  - $P_{\text{TOT}} = 15$ torr
  - $\text{NO}: P_{\text{NO}} = 5$ torr
  - $\text{H}_2\text{O}: P_{\text{H}_2\text{O}} = 7$ torr
  - 5 cm pathlength

- **Negative values due to atmospheric background subtraction**
Important facts of novel EC-QCL technology

- Laser spectroscopy provides superior resolution compared to other techniques e.g. FTIR
- Single mode operation of the laser is required
- Wavelength tunability of single mode (DFB) mid-IR semiconductor lasers is ~10cm⁻¹
- Demonstrated wavelength tunability of the Rice EC QCL is ~ 35 cm⁻¹ (limited by the gain chip properties and not by the designed EC configuration)
- Gain chips, which can provide tunability of >200 cm⁻¹ are already reported in the literature
QC lasers with inhomogeneously broadened gain

Alexander Graham Bell’s “photophone” used a voice coil to modulate a mirror which transmitted sunlight to a receiver containing a selenium resistor. 

*Nature*, Sept. 23, **1880**, pp. 500-503
From conventional PAS to QEPAS

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

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

Resonant at $f$

Quality factor $Q$

Piezoelectric crystal

SWAP RESONATING ELEMENT!!!
Motivation for Precision Monitoring of H$_2$CO

- Precursor to atmospheric O$_3$ production
- Potential trace contaminant in industrial manufactured products
- Pollutant due to incomplete fuel combustion processes
- Medically important gas
HITRAN Based Simulation of a H$_2$CO-H$_2$O-CH$_4$ Spectrum in Tuning Range of a 3.53µm IC Laser

- H$_2$CO: 10 ppb
- H$_2$O: 3%
- CH$_4$: 2 ppm
- Optical path: 100 m
- Total pressure: 30 Torr
QCL based Quartz-Enhanced Photoacoustic Sensor

2f-QEPAS based H₂CO signal at 3.53 µm (2832.48 cm⁻¹)

- [H₂CO]: 13.27 ppm
- QEPAS NNEA Sensitivity:
  1.1×10⁻⁸ cm⁻¹ W/√Hz;
  NEC (τ=1s): 0.28 ppmv (5 mW)

For comparison:
QEPAS Sensitivity for NH₃:
5.4×10⁻⁹ cm⁻¹ W/√Hz
NEC (τ=1s): 0.50 ppmv (38 mW)

M. Horstjann et. al., Applied Physics B 79, 799, 2004
CO$_2$ Detection at 2 $\mu$m

Line intensity [cm$^{-1}$/molecule cm$^{-2}$]

Wavenumber [cm$^{-1}$]

Telecom bands
Effect of H$_2$O on V-T relaxation

High concentration of H$_2$O in breath causes instantaneous thermalization of the absorbed laser power. In such a situation the optimal conditions depend mainly on the Q factor and absorption within the gas sample.
QEPAS signal for CO$_2$ in dry and humid air

- Significant difference in signal strength due to longer relaxation time for dry CO$_2$ mixture at lower pressures
- Further increase in signal phase difference between dry and moist gas mixture (60 deg. comparing 50 deg. at 300torr)
**CO₂ detection limit**

- SNR: ~ 91.4 (minimum detectable concentration ~110 ppm of CO₂)
- Laser power: ~ 4.6 mW
- Lock-in time constant: 1 s
- Peak absorption coefficient: ~ 1.4 × 10⁻³ cm⁻¹

**Normalized noise equivalent sensitivity for CO₂ in humid air:**

\[
\text{NES} = 1.25 \times 10^{-7} \text{cm}^{-1} W/\sqrt{\text{Hz}}
\]
### QEPAS Performance for 10 Trace Gas Species (Feb’05)

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm(^{-1})</th>
<th>Pressure, Torr</th>
<th>NNEA, cm(^{-1})W/Hz(^{1/2})</th>
<th>Power, mW</th>
<th>NEC (τ=1s), ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O (N(_2))(^{**})</td>
<td>7181.17</td>
<td>60</td>
<td>2.1×10(^{-9})</td>
<td>5.8</td>
<td>0.18</td>
</tr>
<tr>
<td>HCN (air: 50% hum) (^{**})</td>
<td>6539.11</td>
<td>60</td>
<td>&lt;2.6×10(^{-9})</td>
<td>50</td>
<td>0.1</td>
</tr>
<tr>
<td>C(_2)H(_2) ((N(_2))(^{**})</td>
<td>6529.17</td>
<td>75</td>
<td>~2.5×10(^{-9})</td>
<td>~40</td>
<td>0.06</td>
</tr>
<tr>
<td>NH(_3) (N(_2))(^{*})</td>
<td>6528.76</td>
<td>60</td>
<td>5.4×10(^{-9})</td>
<td>38</td>
<td>0.50</td>
</tr>
<tr>
<td>CO(_2) (exhaled air)</td>
<td>6514.25</td>
<td>90</td>
<td>1.0×10(^{-8})</td>
<td>5.2</td>
<td>890</td>
</tr>
<tr>
<td>CO(_2) (N(_2)) (^{***})</td>
<td>4990.00</td>
<td>300</td>
<td>1.25×10(^{-7})</td>
<td>4.6</td>
<td>110</td>
</tr>
<tr>
<td>CH(_2)O (N(_2)) (^{*})</td>
<td>2832.48</td>
<td>100</td>
<td>1.1×10(^{-8})</td>
<td>4.6</td>
<td>0.28</td>
</tr>
<tr>
<td>CO (N(_2))</td>
<td>2196.66</td>
<td>50</td>
<td>5.3×10(^{-7})</td>
<td>13</td>
<td>0.5</td>
</tr>
<tr>
<td>CO (propylene)</td>
<td>2196.66</td>
<td>50</td>
<td>7.4×10(^{-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>1.5×10(^{-8})</td>
<td>19</td>
<td>0.007</td>
</tr>
</tbody>
</table>

* - Improved microresonator  
** - Improved microresonator and double optical pass through QTF  
*** - Without microresonator

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

For comparison: conventional PAS 2.2×10\(^{-9}\) cm\(^{-1}\)W/√Hz (1,800 Hz) for NH\(_3\)*  

Volcanological applications

- CO₂ the most abundant component of volcanic gases after H₂O
- δ¹³C is a sensitive tracer of magmatic vs. hydrothermal or groundwater contributions to volcanic gases
- Monitoring δ¹³C can be used in eruption forecasting and volcanic hazard assessment
CO₂ Absorption Line Selection Criteria

• Three strategies:
  ➢ Similar strong absorption of ¹²CO₂ and ¹³CO₂ 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 ¹³CO₂ and 2.76 μm for ¹²CO₂)*

• 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
Dual path length gas cell design for infrared ratio spectrometry

To IR detector

2.4 cm

Short path cell

To IR detector

From QCL

Cell edge

Astigmatic Mirror

2.4 m Herriott multipass cell

Short cell

Herriott cell
High resolution CO$_2$ absorption spectrum at 2311 cm$^{-1}$

To appear in Optics and Photonics News, 2006
Summary 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 (~0.2 mm$^3$)
  - Detected 14 trace gases to date: 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
  - QE L-PAS based applications using novel thermoelectrically cooled cw and broadly wavelength tunable quantum and interband cascade lasers
  - Investigate QTFs with lower resonant frequencies
  - New target gases, in particular VOCs and HCs
  - Development of optically multiplexed gas sensor networks based on QE L-PAS
NASA Atmospheric & Mars Gas Sensor Platforms

Aircraft laser absorption spectrometers

Tunable laser planetary spectrometer

Tunable laser sensors for earth’s stratosphere
## Comparison of CO₂ line selection and strategy for different current US mid-IR laser-based isotopic ratiometers

<table>
<thead>
<tr>
<th>Group</th>
<th>Technology</th>
<th>Frequency 12/13 [cm⁻¹]</th>
<th>δT [K]</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCAR, UC and Rice U. A. Fried et al; Erdelyi</td>
<td>DFG with NIR TDLs and fiber amplifiers</td>
<td>2299.642 2299.795</td>
<td>0.005</td>
<td>0.8 ‰*</td>
</tr>
<tr>
<td>Aerodyne, Harvard U. M. Zahniser et al.</td>
<td>Direct Scan PbSalt TDL, QCL, DFG; Dual optical paths</td>
<td>2314.304 2314.408</td>
<td>0.213</td>
<td>0.2 ‰</td>
</tr>
<tr>
<td>Physical Sciences D. Sonnenfroh et al</td>
<td>QCL</td>
<td>2318.1</td>
<td></td>
<td>0.5 to 1‰</td>
</tr>
<tr>
<td>Rice University Tittel et al</td>
<td>QCL Dual optical paths</td>
<td>2311.105 2311.399</td>
<td>181</td>
<td>&lt;1 ‰</td>
</tr>
<tr>
<td>U. of Utah Bowling, Picarro</td>
<td>PbSalt TDLs Campbell Scientific Instrum.</td>
<td>2308.225 2308.171</td>
<td>0.006</td>
<td>0.2 ‰</td>
</tr>
<tr>
<td>JPL C. Webster</td>
<td>TDLs and QCL, LAS</td>
<td>2303.7 2303.5</td>
<td>0.007</td>
<td>TBD ‰</td>
</tr>
<tr>
<td>NASA-Ames Becker et al; Jost, LGR</td>
<td>Direct Scan PbSalt TDLs &amp; QCLs with ICOS</td>
<td>2291.542 2291.680</td>
<td>0.004</td>
<td>4 ‰</td>
</tr>
</tbody>
</table>
Motivation for Measuring $^{13}\text{CO}_2/^{12}\text{CO}_2$ Isotopic Ratios

- 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 isotopic ratios
    - Identification of carbon sources and sinks
  - Global carbon budget studies
- Study of planetary gases (e.g. for Mars: CO, CO$_2$, H$_2$O, CH$_4$, O$_3$, OCS)
- Volcano eruption forecasting and gas emission studies (CO$_2$, HCl, SO$_2$, HF, H$_2$S, CO, H$_2$O)
- Geochemistry
- Medical applications (non-invasive human health monitoring)