Quantum Cascade Laser based Trace Gas Technology: Recent Advances and Applications

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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New laser sources and sensing technologies
- Selected Applications of Trace Gas Detection
  - Detection of nitric oxide and ethanol
  - Quartz Enhanced L-PAS (Freon 125, acetone)
- Future Directions and Conclusions

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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 National Security
- Fundamental Science and Photochemistry
Fundamentals of Laser Absorption Spectroscopy

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

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

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

\[ \alpha(v) = C \cdot S(T) \cdot g(v - v_0) \]

- \( C \) - total number of molecules of absorbing gas/atm/cm\(^3\) [molecule\cdot cm\(^{-3}\) \cdot atm\(^{-1}\)]
- \( S \) - molecular line intensity [cm \cdot molecule\(^{-1}\)]
- \( g(v - v_0) \) - normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

**Requirements:** Sensitivity, specificity, multi-gas species, rapid data Acquisition, ….

**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
Key Characteristics of mid-IR QCLs and ICL Sources

- **Band** – *structure engineered devices* (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 3 to 160 μm

- 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
  - > 200 cm\(^{-1}\) using an external grating element

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

- **High pulsed and cw powers at TEC/RT temperatures**
  - Pulsed peak powers of 1.6 W; high temperature operation ~ 425 K
  - Average power levels: 1-600 mW (current wall plug η~4%)  
    - ~ 50 mW, TEC CW DFB @ 5 and 10 μm Alpes; Princeton,  
    - Adtech Optics, Maxion Technologies, Argos Tech.  
    - ~ 300 mW @8.3 μm (Agilent Technologies & Harvard)  
    - >600 mW (CW FP) and >150 mW (CW DFB) at 298 K (Northwestern)
Example Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

Source: HITRAN 2000 database
### Mid-IR Source Requirements for Laser Spectroscopy

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (% to ppt)</td>
<td>Wavelength, Power</td>
</tr>
<tr>
<td>Selectivity (Spectral Resolution)</td>
<td>Single Mode Operation and Narrow Linewidth</td>
</tr>
<tr>
<td>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</td>
<td>Tunable Wavelength</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>
Widely Tunable, CW, TEC Quantum Cascade Lasers
Tunable external cavity QCL based spectrometer

- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + chilled water cooling)
Mid-IR NO Absorption Spectra acquired with a Tunable TEC QCL

Wide Wavelength Tuning of a 5.3μm EC-QCL

- Coarse wavelength tuning of 155 cm⁻¹ is performed by varying diffraction grating angle
- Power output is ~ 11mW
- Access to Q(3/2) transition of NO at 1875.8 cm⁻¹ for LMR spectroscopy

Performance of 8.4 μm EC-QCL Spectroscopic Source

Tunability $180 \text{ cm}^{-1}$ @8.4 μm (1100 to 1280 cm$^{-1}$)

AR coating: $R_{AR} \approx 2 \times 10^{-4}$  
$P_{EC-opt}$ up to 50 mW (cw)  
($I_{QCL} = 680 \text{ mA} \rightarrow P = 44 \text{ mW}$)

Quartz Enhanced
Photoacoustic Spectroscopy
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

Laser beam, power $P$

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

or $f/2$

$$S \sim \frac{Q \alpha P}{f V}$$

$NNEA = \frac{\alpha_{\min} P}{\sqrt{\Delta f}} \left[ \frac{\text{cm}^{-1} \times W}{\sqrt{\text{Hz}}} \right]$
TF based spectrophone
TF based spectrophone
Comparative Size of Absorbance Detection Modules (ADM)

Optical multipass cell (100 m):
$L \sim 70$ cm, $V \sim 3000$ cm$^3$

Resonant photoacoustic cell (1000 Hz):
$L \sim 60$ cm, $V \sim 50$ cm$^3$

QEPAS spectrophone:
$L \sim 1$ cm, $V \sim 0.05$ cm$^3$
Trace Gas Sensing Examples
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 (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection
Biomarkers Present in Exhaled Human Breath

As many as 400 different molecules in breath; many with well defined biochemical pathways

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
<th>Physiological basis/Pathology Indication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>ppb</td>
<td>Ethanol metabolism</td>
</tr>
<tr>
<td>Acetone</td>
<td>ppm</td>
<td>Decarboxylation of acetoacetate, diabetes</td>
</tr>
<tr>
<td>Ammonia</td>
<td>ppb</td>
<td>Protein metabolism, liver and renal disease</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>%</td>
<td>Product of respiration, Heliobacter pylori</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>ppb</td>
<td>Gut bacteria, schizophrenia</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>ppm</td>
<td>Production catalyzed by <em>heme oxygenase</em></td>
</tr>
<tr>
<td>Carbonyl sulfide</td>
<td>ppb</td>
<td>Gut bacteria, liver disease</td>
</tr>
<tr>
<td>Ethane</td>
<td>ppb</td>
<td>Lipid peroxidation and oxidative stress</td>
</tr>
<tr>
<td>Ethanol</td>
<td>ppb</td>
<td>Gut bacteria</td>
</tr>
<tr>
<td>Ethylene</td>
<td>ppb</td>
<td>Lipid peroxidation, oxidative stress, cancer</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>ppb</td>
<td>Lipid peroxidation/metabolism</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>ppm</td>
<td>Gut bacteria</td>
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<tr>
<td>Isoprene</td>
<td>ppb</td>
<td>Cholesterol biosynthesis</td>
</tr>
<tr>
<td>Methane</td>
<td>ppm</td>
<td>Gut bacteria</td>
</tr>
<tr>
<td>Methanethiol</td>
<td>ppb</td>
<td>Methionine metabolism</td>
</tr>
<tr>
<td>Methanol</td>
<td>ppb</td>
<td>Metabolism of fruit</td>
</tr>
<tr>
<td>Methylamine</td>
<td>ppb</td>
<td>Protein metabolism</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>ppb</td>
<td>Production catalyzed by <em>nitric oxide synthase</em></td>
</tr>
<tr>
<td>Oxygen</td>
<td>%</td>
<td>Required for normal respiration</td>
</tr>
<tr>
<td>Pentane</td>
<td>ppb</td>
<td>Lipid peroxidation, oxidative stress</td>
</tr>
<tr>
<td>Water</td>
<td>%</td>
<td>Product of respiration</td>
</tr>
</tbody>
</table>

Terence Risby, Johns Hopkins University
High resolution spectroscopy with a 5.3μm EC-QCL

- Mode hop free scan of up to ~2cm⁻¹ with a resolution <0.001cm⁻¹ (30MHz) can be performed anywhere within the tuning range.

Optimum NO absorption line for atmospheric measurements

FTIR resolution ~0.1cm⁻¹


High resolution EC-QCL based QEPAS

External Amplitude Modulation:

- QTF is used as a mechanical chopper at $f \approx 32\text{kHz}$
- No chirp associated with the laser current modulation
- High resolution mode-hop-free tuning is possible
Monitoring of broadband absorbers

- **Freon 125** ($\text{C}_2\text{HF}_5$)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals e.g. chemical warfare agents
- **Acetone** ($\text{CH}_3\text{COCH}_3$)
  - Recognized biomarker for diabetes
QCL based Quartz-Enhanced Photoacoustic Gas Sensor

QEPAS characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume (< 1 mm³)
- Sensitivity is limited by the fundamental thermal TF noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks
Spectroscopy of Freon 125 and Acetone with a Widely Tunable 8.4 $\mu$m CW EC-QCL

QEPAS concentration measurement of Freon 125 (5ppm mixture in N$_2$)

- Minimum detection limit (1$\sigma$) of $\sim$4.5 ppb was obtained for Freon 125 with an average laser power of 6.6 mW

QEPAS concentration measurement of a Freon 125 and acetone mixture

- Wide tunability enables excellent molecular selectivity for broad band absorbers

R. Lewicki et al Optics Express 15, 7357, 2007
Reference spectrum from the PNNL spectral database (red line). Sharp features on the ethanol spectrum correspond to the atmospheric water absorption lines (blue line depicts water absorption spectrum simulated using HITRAN database).
Future of Chemical Trace Gas Sensing
Future development of EC-QCL technology

- Complete mid infrared wavelength coverage
- Faster tuning speed
- Solid state designs
  - MEMS

- Electrical tuning (in collaboration with QCL-research groups)
  - Tunable Distributed Bragg Reflectors (DBR) (carrier-induced refractive index tuning)
  - Electronically tunable extraordinary transmission gratings (tunable mirrors and filters) (work presently carried out at Princeton)
New designs of fast broadly tunable EC-QCLs (2007)

- Optical configuration based on the previous EC-QCLs
- Fast tuning capabilities:
  - Broadband tuning up to 1KHz
  - High resolution mode-hop free tuning up to 400Hz

- New optical configuration
- Fast tuning capabilities:
  - Broadband tuning up to 6 KHz
  - High resolution mode-hop free tuning up to 6 KHz
Commercial Tunable Mid-IR EC QCL

Introduced in 2006

Room Temperature—No Cryogenic Cooling
Center Wavelengths:
- 4.5 μm
- 5.5 μm
- 8.5 μm
- 9.5 μm
- 10.5 μm

Tuning Range: >10%
Average Power (CW): 1 mW–10 mW
Summary & Future Directions of mid-IR Sensor Technology

- **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: NH$_3$, CH$_4$, N$_2$O, CO$_2$, CO, NO, H$_2$O, COS, C$_2$H$_4$, SO$_2$, C$_2$H$_5$OH, C$_2$HF$_5$ and several isotopic species of C, O, N and H.

- **New Applications of Trace Gas Detection are the main driving force to the field**
  - Distributed sensor networks for Environmental monitoring (NH$_3$, CO, CH$_4$, C$_2$H$_4$, N$_2$O, CO$_2$ and H$_2$CO)
  - Inexpensive and sensitive sensors for Industrial process control and chemical analysis (HCN, NO, NH$_3$, H$_2$O)
  - Wearable sensors for Medical & Biomedical Diagnostics (NO, CO, COS, CO$_2$, NH$_3$, C$_2$H$_4$)
  - Hand-held sensors and sensor network technologies for Law Enforcement and Homeland Security

- **Future Directions and Collaborations**
  - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR interband and intersubband quantum cascade lasers
  - New applications enabled by novel broadly wavelength tunable quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs)
  - Development of optically multiplexed gas sensor networks based on QEPAS
Summary & Future Directions

- Widely tunable, continuous wave and thermoelectrically cooled EC-QCLs operating at 5.3\( \mu \)m and 8.5\( \mu \)m were demonstrated.
- **Mode-hop free wavelength tuning** enables high resolution (<0.001\( \text{cm}^{-1} \)) spectroscopic applications.
- **PZT actuated mode tracking system** allows employing gain chips operating at both shorter and longer wavelengths without modification of its mechanical construction (chips with lower efficiency AR coatings can be used).
- Wavelength tunability up to 15\% of the center wavelength was demonstrated.
- Output optical power up to 50 mW.
- The main limitations in the scanning speed (limited by the mechanical resonances of the EC-QCL construction), which will be addressed in future EC-QCL designs.
- The novel broadly wavelength tunable quantum cascade lasers enable **new applications in laser based trace gas sensing**
  - Sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs
  - Multi-species detection
FT-IR survey absorption spectrum of benzene vapor ($\text{C}_6\text{H}_6$)

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 other optical sensor architectures)
QCL based Quartz-Enhanced Photoacoustic Gas Sensor

QEPAS characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume (< 1 mm³)
- Sensitivity is limited by the fundamental thermal quartz tuning fork (QTF) noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

R. Lewicki, G. Wysocki, A.A. Kosterev, F. K. Tittel “QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.5 µm”, submitted to Optics Express, April 2007
Miniature QEPAS CO$_2$ sensor ($\lambda=2\mu$m) v2.0 boards

- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0.2W control system power consumption
- Projected sensitivity* to CO$_2$ 110 ppm with 1sec. lock-in TC
- Over $10^3$ improvement in sensitivity @4.2$\mu$m

Wireless Sensor Networks for Gas Sensing

- Each point called "mote"
- Advantages?
  - Spatial resolution
  - Measure fluxes
- What is needed?
  - Low power
  - Low cost
  - Ultra miniature
  - Replicable
  - Autonomy

To Internet via Base-station
# QCL based QEPAS Performance for 5 Trace Gas Species

(May 2007)

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm⁻¹</th>
<th>Pressure, Torr</th>
<th>NNEA, cm⁻¹W/Hz¹/₂</th>
<th>Power, mW</th>
<th>NEC (τ=1s), ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂O (N₂:75% RH)*</td>
<td>2804.90</td>
<td>75</td>
<td>8.7×10⁻⁹</td>
<td>7.2</td>
<td>0.12</td>
</tr>
<tr>
<td>CO (N₂)</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>N₂O (air+5%SF₆)</td>
<td>2195.63</td>
<td>50</td>
<td>1.5×10⁻⁸</td>
<td>19</td>
<td>0.007</td>
</tr>
<tr>
<td>C₂H₅OH **</td>
<td>1934.2</td>
<td>770</td>
<td>2.2×10⁻⁷</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>C₂HF₅ (Freon 125)***</td>
<td>1208.62</td>
<td>770</td>
<td>2.6×10⁻⁹</td>
<td>6.6</td>
<td>0.003</td>
</tr>
</tbody>
</table>

* - Improved microresonator
** - Preliminary (estimated) with amplitude modulation and metal microresonator
*** - With amplitude modulation and metal microresonator

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

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For comparison: conventional L-PAS 2.2×10⁻⁹ cm⁻¹W/√Hz (1,800 Hz) for NH₃*