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, Semiconductors, 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

**CO$_2$ absorption spectrum**

HITRAN Simulation of Absorption Spectra

**Spectroscopic techniques for trace-gas detection**

Mid-IR Source Requirements for Laser Spectroscopy

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (% in ppt)</td>
<td>Wavelength, Power</td>
</tr>
<tr>
<td>Selectivity (Spectral Resolution)</td>
<td>Single Mode Operation and Narrow Lineswidth</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>
**Quantum Cascade Laser: Basic Facts**

- Semiconductor lasers (IR-V materials)
- Multiple-quantum-well heterostructure
- Intersubband transitions (emission wavelength defined by bandstructure engineering and independent of material energy bandgap)
- Laser wavelengths cover the mid-IR range (3-24 μm)
- High quantum efficiency (Cascading: 1 electron + N photons)
- High laser power (≥500 mW cw, ≥1W peak for pulsed)
- High spectral purity - single frequency with DBR structure (≥10 cm⁻¹ tunability) or external cavity (≥200 cm⁻¹ tunability - 18 mW peak for pulsed)
- High reliability, long lifetime
- Capable of room temperature operation (Pulsed: up to +150°C CW: up to RT)
- Compact

**Tunable external cavity QCL based spectrometer, 2006**

- Wide wavelength tuning
  - PZT controlled cavity length
  - PZT controlled grating angle
  - QCL current control
  - Motorized coarse grating angle tuning
  - Vacuum tight QCL enclosure with built-in 3D lens positioner (TEC laser cooling + chilled water cooling)

**High resolution spectroscopy with a 5.3μm EC-QCL**

- Mode hop free scan of up to 3 cm⁻¹ with a resolution <0.001 cm⁻¹ (30 MHz) can be performed anywhere within the tuning range

**Wide Wavelength Tuning of a 5.3μm EC-QCL**

- Coarse wavelength tuning of 155 cm⁻¹ is performed by varying diffraction grating angle
- Max. CW power ~11 mW
- Access to QCL transition of NO at 1075.6 cm⁻¹ for LMR spectroscopy

**Breath Biomarkers in Humans**

As many as 400 different molecules in breath, many with well defined biochemical pathways.
QCLs for Absorption Spectroscopy

QCLs, ICLs:
- Pulsed (DPP - RT)
  - Easily achievable RT operation
  - High peak power
  - Little quantum confinement effects
  - Limited availability due to pulsed operation
- CW (DPP - LN and RT)
  - Spectral line smoothness
  - Low noise
  - Limited availability for RT operation
- QCLs (CW - LN and RT)
  - Wide frequency tuning range
  - Still under development
  - Limited availability

EC-QCL emitting at $\lambda = 8.5$ $\mu$m

$P_{\text{EC-QCL}}$ up to 50 mW (cw)

AR coating: $R_{\text{AR}}^2 = 2 \times 10^{-4}$

Tunability 182 cm$^{-1}$

@6.4 $\mu$m (7.77$\mu$m - 9.05$\mu$m)

15.3% of the center wavelength

QCL based Quartz-Enhanced Photoacoustic Gas Sensor

QEPAS characteristics:
- High sensitivity (ppb to ppt)
- Excellent dynamic range
- Insensitive to environmental noise
- Ultra-small sample volume (< 1 mm$^3$)
- Sensitivity is limited by the fundamental thermal IR noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

Motivation for Monitoring of Freon 125 and acetone

- Freon 125 (C$_2$H$_2$F$_5$)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals e.g. chemical warfare agents
- Acetone (CH$_3$COCH$_3$)
  - Recognized biomarker for diabetes

Spectroscopy of Broadband Absorbers with Widely Tunable EC-QCL at $\lambda = 8.5$ $\mu$m

EC-QCL in Laser Spectroscopy

<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 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>
Summary & Future Directions

- Widely tunable, continuous wave and thermoelectrically cooled EC-QCLs operating at 5.3μm and 6.5μm were demonstrated.
- Mode-hop free wavelength tuning enables high resolution (<0.001cm⁻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 18% 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.