Mid-infrared semiconductor laser based trace gas technologies: recent advances and applications

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- New Laser Based Trace Gas Sensor Technology
  - Novel Multipass Absorption Cell & Electronics
  - Quartz Enhanced Photoacoustic Spectroscopy
- Examples of Mid-Infrared Sensor Architectures
  - C₂H₆, NH₃, NO, CO, and SO₂
- Future Directions of Laser Based Gas Sensor Technology and Conclusions

Research support by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation, Scinovation, Inc., Testo AG and Sentinel Photonics Inc. via an EPA Phase 1 SBIR sub-award is acknowledged.
Mid-IR and THz Spectroscopic Phenomena

Provider: Prof. Daniel Mittleman, Rice University
Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, Truck, Aircraft and Marine Emissions

- **Rural Emission Measurements**
  - Agriculture & Forestry, Livestock

- **Environmental Monitoring**
  - Atmospheric Chemistry (e.g. isotopologues, climate modeling,...)
  - Volcanic Emissions

- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Pharmaceutical, Metals Processing, Food & Beverage Industries; Nuclear Technology & Safeguards

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

- **Applications in Medical Diagnostics and the Life Sciences**

- **Technologies for Law Enforcement, Defense and Security**

- **Fundamental Science and Photochemistry**
“Curiosity” landed on Mars on August 6, 2012.
Laser based Trace Gas Sensing Techniques

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (Mid-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot, Chernin, Sentinel Photonics)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector): Standoff and Remote Detection
  - Fiberoptic Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic & Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
Other spectroscopic methods

- Faraday Rotation Spectroscopy (limited to paramagnetic chemical species)
- Differential Optical Dispersion Spectroscopy (DODiS)
- Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)
- Frequency Comb Spectroscopy
- Laser Induced Breakdown Spectroscopy (LIBS)
HITRAN Simulated Mid-Infrared Molecular Absorption Spectra

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>Optimum Wavelength, Power</td>
</tr>
<tr>
<td>Selectivity (Spectral Resolution)</td>
<td>Stable Single Mode Operation and Narrow Linewidth</td>
</tr>
<tr>
<td>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</td>
<td>Mode Hop-free Wavelength Tunability</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>High wall plug efficiency, no cryogenics or cooling water</td>
</tr>
<tr>
<td>Field deployable in harsh environments</td>
<td>Compact &amp; Robust</td>
</tr>
</tbody>
</table>
Key Characteristics of Mid-IR QCL & ICL Sources – May 2013

• **Band – structure engineered devices**
  Emission wavelength is determined by layer thickness – MBE or MOCVD; Type I QCLs operate in the 3 to 24 µm spectral region; Type II and GaSb based ICLs can cover the 3 to 6 µm spectral range.
  - Compact, reliable, stable, long lifetime, and commercial availability
  - Fabry-Perot (FP), single mode (DFB) and multi-wavelength devices

• **Wide spectral tuning ranges in the mid-IR**
  - 1.5 cm\(^{-1}\) using injection current control for DFB devices
  - 10-20 cm\(^{-1}\) using temperature control for DFB devices
  - ~100 cm\(^{-1}\) using current and temperature control for QCL DFB Array
  - ~525 cm\(^{-1}\) (22% of c.w.) using an external grating element and FP chips with heterogeneous cascade active region design; also QCL DFB Array

• **Narrow spectral linewidths**
  - CW: 0.1 - 3 MHz & <10kHz with frequency stabilization (0.0004 cm\(^{-1}\))
  - Pulsed: ~300 MHz

• **High pulsed and CW powers of QCLs at TEC/RT temperatures**
  - Room temperature pulsed power of >30 W with 27% wall plug efficiency and CW powers of ~5 W with 21% wall plug efficiency
  - >1W, TEC CW DFB @ 4.6 µm
  - >600 mW (CW FP) @ RT; wall plug efficiency of ~17% at 4.6 µm;
Improvements and New Capabilities of QCLs and ICLs

- Optimum wavelength ( > 3 to < 20 µm) and power ( >10 mw to < 1 W) at room temperature (> 15 °C and < 30 °C) with state-of-the-art fabrication/processing methods based on MBE and MOCVD, good wall plug efficiency and lifetime (> 20,000 hours) for detection sensitivities from % to pptv with low electrical power budget
- Stable single TEM$_{00}$ transverse and axial mode, CW and pulsed operation of mid-infrared laser sources (narrow linewidth of ~ 300 MHz to < 10kHz)
- Mode hop-free ultra-broad wavelength tunability for detection of broadband absorbers and multiple absorption lines based on external cavity or mid-infrared semiconductor arrays
- Good beam quality for directionality and/or cavity mode matching. Implementation of innovative collimation concepts.
- Rapid data acquisition based on fast time response
- Compact, robust, readily commercially available and affordable in order to be field deployable in harsh operating environments (temperature, pressure, etc…)
Motivation for Mid-infrared C$_2$H$_6$ Detection

- Atmospheric chemistry and climate
  - Fossil fuel and biofuel consumption,
  - biomass burning,
  - vegetation/soil,
  - natural gas loss
- Oil and gas prospecting
- Application in medical breath analysis
  (a non-invasive method to identify and monitor different diseases):
  - asthma,
  - schizophrenia,
  - Lung cancer,
  - lung cancer,
  - vitamin E deficiency.

HITRAN absorption spectra of C$_2$H$_6$, CH$_4$, and H$_2$O
**C$_2$H$_6$ Detection with a 3.36 µm CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics**


- Innovative long path, small volume multipass gas cell: 57.6 m with 459 passes

- 2f WMS signal for a C$_2$H$_6$ line at 2976.8 cm$^{-1}$ at a pressure of 200 Torr

**Minimum detectable C$_2$H$_6$ concentration is:**

~ 130 pptv (1σ; 1 s time resolution)

**MC dimensions:** 17 x 6.5 x 5.5 (cm)

Distance between the MGC mirrors: 13 cm
NOAA Monitoring & Sampling Location: Alert, Nunavut, Canada

General View on the Facility
Latitude: 82.4508° North
Longitude: 62.5056° West
Elevation: 200.00 m
Motivation for NH$_3$ Detection

- Atmospheric chemistry
- Pollution gas monitoring
- Monitoring NH$_3$ concentrations in the exhaust stream of NO$_x$ removal systems based on selective catalytic reduction (SCR) techniques
- Spacecraft related trace gas monitoring
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Monitoring of gas separation processes
- Medical diagnostics (kidney & liver diseases)
- Detection of ammonium-nitrate explosives
Conventional PAS

Laser beam, power $P$

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

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

$NNEA = \frac{\alpha_{\text{min}} P}{\sqrt{\Delta f}} \left[ \frac{\text{cm}^{-1} \times W}{\sqrt{\text{Hz}}} \right]$
Atmospheric NH₃ Measurements using an EC-QCL PAS Sensor

Schematic of a Daylight Solutions 10.36 µm CW TEC EC-QCL based PAS NH₃ Sensor.

NH₃ sensor deployed at the UH Moody Tower rooftop monitoring site.

Diurnal profile of atmospheric NH₃ levels in Houston, TX.

Comparison between NH₃ and particle number concentration time series from July 19 to July 31 2012.
NH$_3$ Detection due to a Fire resulting from a Truck Collision

A chemical incident occurred at ~ 6 a.m. after two trucks collided on I-59. Both trucks caught fire. [www.chron.com]

Estimated hourly NH$_3$ emission from the Houston Ship Channel area is about 0.25 ton. Mellqvist et al., (2007) Final Report, HARC Project H-53.
Sporadic increased NH$_3$ Concentration Levels related to Emissions by the Parish Electric Power Plant, TX

The Parish electric power plant is located near the Brazos River in Fort Bend County, Texas (~27 miles SW from downtown Houston)
NH₃ Detection due to a Fire resulting from a Truck Collision

A chemical incident occurred at ~ 6 a.m. after two trucks collided on I-59. Both trucks caught fire. [www.chron.com]

Estimated hourly NH₃ emission from the Houston Ship Channel area is about 0.25 ton. Mellqvist et al., (2007) Final Report, HARC Project H-53.
Fort-Worth, Dallas (TX) CAMS 75 & TCEQ monitoring site

- Laboratory trailer in this study
- Eagle Mountain Lake continuous ambient monitoring station (CAMS 75) operated by Texas Commission on Environmental Quality (TCEQ)
<table>
<thead>
<tr>
<th>Species/parameter</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>Daylight Solutions External Cavity Quantum Cascade Laser (Photo-acoustic Spectroscopy)</td>
</tr>
<tr>
<td>CO</td>
<td>Thermo Electron Corp. 48C Trace Level CO Analyzer (Gas Filter Correlation)</td>
</tr>
<tr>
<td>SO₂</td>
<td>Thermo Electron Corp. 43C Trace Level SO₂ Analyzer (Pulsed Fluorescence)</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Thermo Electron Corp. 42C Trace Level NO-NO₂-NOₓ Analyzer (Chemiluminescence)</td>
</tr>
<tr>
<td>NOᵧ</td>
<td>Thermo Electron Corp. 42C-Y NOᵧ Analyzer (Molybdenum Converter)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)</td>
</tr>
<tr>
<td>HCl</td>
<td>Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)</td>
</tr>
<tr>
<td>VOCₙ</td>
<td>IONICON Analytik Proton Transfer Reaction Mass Spectrometer and TCEQ Automated Gas Chromatograph</td>
</tr>
<tr>
<td>PBL height</td>
<td>Vaisala Ceilometer CL31 with updated firmware to work with Vaisala Boundary Layer View software</td>
</tr>
<tr>
<td>Temperature</td>
<td>Campbell Scientific HMP45C Platinum Resistance Thermometer</td>
</tr>
<tr>
<td>Wind speed</td>
<td>Campbell Scientific 05103 R. M. Young Wind Monitor</td>
</tr>
<tr>
<td>Wind direction</td>
<td>Campbell Scientific 05103 R. M. Young Wind Monitor</td>
</tr>
</tbody>
</table>
NH₃ source attribution & temperature variations

- Emission events from specified point sources (i.e., industrial facilities)
- Estimated NH₃ emissions from cows (1.3 tons/day)
- Estimated NH₃ emissions from soil and vegetation (0.15 tons/day)
- EPA PMF (biogenic: 74.1%; light duty vehicles: 12.1%; natural gas/industry: 9.4%; and heavy duty vehicles: 4.4%)
- Livestock might account for approximately 66.4% of total NH₃ emissions
- Increased contribution from industry (→ 18.9%)
From Conventional PAS to QEPAS

Laser beam, power $P$

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

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

$$NNEA = \frac{\alpha_{\min} P}{\sqrt{\Delta f}} \left[ \frac{\text{cm}^{-1} \times W}{\sqrt{\text{Hz}}} \right]$$

$Q >> 1000$

Cell is OPTIONAL!

$V$-effective volume

Piezoelectric crystal

Resonant at $f$

quality factor $Q$
Quartz Tuning Fork as a Resonant Microphone for QEPAS

**Unique properties**
- Extremely low internal losses:
  - $Q \approx 10\,000$ at 1 atm
  - $Q \approx 100\,000$ in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range ($\sim 10^6$) – linear from thermal noise to breakdown deformation
  - 300K noise: $x \approx 10^{-11}$ cm
  - Breakdown: $x \approx 10^{-2}$ cm
- Wide temperature range: from 1.6K to $\sim 700$K

**Acoustic Micro-resonator (mR) tubes**
- Optimum inner diameter: 0.6 mm; mR-QTF gap is 25-50 $\mu$m
- Optimum mR tubes must be $\sim 4.4$ mm long ($\sim \lambda/4 < l < \lambda/2$ for sound at 32.8 kHz)
- SNR of QTF with mR tubes: $\times 30$ (depending on gas composition and pressure)
Simulated HITRAN high resolution spectra @ 130 Torr indicating two NH$_3$ absorption lines of interest.

No overlap between NH$_3$ and CO$_2$ absorption lines was observed for the selected 967.35 cm$^{-1}$ NH$_3$ absorption line in the $\nu_2$ R band.
QEPAS based NH$_3$ Gas Sensor Architecture

CW TEC DFB QCL in HHL package (Hamamatsu)
Real-time exhaled human NH$_3$ Breath Measurements

Airway pressure (black), CO$_2$ (red), and NH$_3$ (blue) profiles of a single breath exhalation lasting 40sec.

Successful testing of a 2nd generation breath ammonia monitor installed in a clinical environment. (Johns Hopkins, Baltimore, MD and St. Luke’s Hospital, Bethlehem, PA)

Minimum detectable concentration of NH$_3$ is: ~ 6 ppbv at 967.35 cm$^{-1}$ (1σ; 1 s time resolution)
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
- Photofragmentation of nitro-based explosives
Molecular Absorption Spectra within two Mid-IR Atmospheric Windows and NO absorption @ 5.26µm

Source: HITRAN 2000 database
Performance of a 5.26 μm CW HHL TEC DFB-QCL

Single frequency QCL radiation recorded with FTIR for different laser current values at a QCL temperature of 20.5°C.

CW DFB-QCL optical power and current tuning at three different temperatures.
Emission spectra of a 1900cm$^{-1}$ TEC CW DFB QCL and HITRAN Simulated spectra

Output power: 117 mW @ 25 C
Schematic of a DFB-QCL based Gas Sensor.
PcL – plano-convex lens, Ph – pinhole,
QTF – quartz tuning fork, mR – microresonator,
RC - reference cell, P-elec D – pyro electric detector

Compact Prototype NO Sensor
(September 2012)
Performance of CW DFB-QCL based WMS QEPAS NO Sensor Platform

2f QEPAS signal (navy) and reference 3f signal (red) when DFB-QCL was tuned across $1900.08 \text{ cm}^{-1}$ NO line.

Minimum detectable NO concentration is:

$\sim 3 \text{ ppbv} \ (1\sigma; \ 1 \text{ s time resolution})$
Motivation for Carbon Monoxide Detection

- Atmospheric Chemistry
  - Incomplete combustion of natural gas, fossil fuel and other carbon containing fuels.
  - Impact on atmospheric chemistry through its reaction with hydroxyl (OH) for troposphere ozone formation and changing the level of greenhouse gases (e.g. CH₄).

- Public Health
  - Extremely dangerous to human life even at a low concentrations. Therefore CO must be carefully monitored at low concentration levels.

- CO in medicine and biology
  - Hypertension, neurodegenerations, heart failure and inflammation have been linked to abnormality in CO metabolism and function.
Performance of a NWU 4.61 μm high power CW TEC DFB QCL

\[ \lambda \approx 4.6 \mu m \text{ DFB QCL} \]
\[ \text{cw operation} \]

Voltage (V) vs. Current (mA)

- T=10 °C
- T=12.5 °C
- T=15 °C
- T=18 °C

Optical power (mW) vs. Wavenumber (cm\(^{-1}\))

Current (mA)

- R5 CO line
- R6 CO line

Estimated max wall-plug efficiency (WPE) is \(\approx 7\%\) at 1.25A QCL drive-current.

Absorption vs. Wavenumber (cm\(^{-1}\))

- 200 ppb CO
- 2% H\(_2\)O
- 300 ppb N\(_2\)O
CW DFB-QCL based CO QEPAS Sensor Results

2f QEPAS signal for dry (red) and moisturized (blue) 5 ppm CO:N₂ mixture near 2169.2 cm⁻¹.

Dilution of a 5 ppm CO reference gas mixture when the CW DFB-QCL is locked to the 2169.2 cm⁻¹ R6 CO line.

Atmospheric CO concentration levels on Rice University campus, Houston, TX

Minimum detectable CO concentration is: ~ 2 ppbv (1σ; 1 s time resolution)
Motivation for Sulfur Dioxide Detection

- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere SO₂ converts to sulfuric acid (primary contributors to acid rain)
- SO₂ reacts to form sulfate aerosols
- Primary SO₂ exposure for 1 hour is 75 ppb
- SO₂ exposure affects lungs and causes breathing difficulties
- Currently, reported annual average atmospheric SO₂ concentrations range from ~ 1 - 6 ppb

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

7.24 µm CW DFB-QCL optical power and current tuning at three different operating temperatures.

2f WMS QEPAS signals for different SO₂ concentrations when laser was tuned across 1380.9 cm⁻¹ line.

Minimum detectable SO₂ concentration is:

~ 100 ppbv (1σ; 1 s time resolution)
# QCL based QEPAS Performance for 10 Trace Gas Species (May 2013)

<table>
<thead>
<tr>
<th>Molecule (carrier gas)</th>
<th>Frequency cm⁻¹</th>
<th>Pressure Torr</th>
<th>NNEA cm⁻¹W/Hz⁰.⁵</th>
<th>QCL Power mW</th>
<th>NEC (τ=1s) ppbV</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>120</td>
</tr>
<tr>
<td>CO (N₂+ 2.2% H₂O)*</td>
<td>2176.28</td>
<td>100</td>
<td>1.57×10⁻⁸</td>
<td>71</td>
<td>2</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>140</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>7</td>
</tr>
<tr>
<td>N₂O (N₂+2.37%H₂O)</td>
<td>2201.75</td>
<td>200</td>
<td>2.9×10⁻⁸</td>
<td>70</td>
<td>2.5</td>
</tr>
<tr>
<td>C₂H₅OH (N₂)**</td>
<td>1934.2</td>
<td>770</td>
<td>2.2×10⁻⁷</td>
<td>10</td>
<td>9×10⁻¹</td>
</tr>
<tr>
<td>NO (N₂+H₂O)</td>
<td>1900.07</td>
<td>250</td>
<td>7.5×10⁻⁹</td>
<td>100</td>
<td>3.6</td>
</tr>
<tr>
<td>SO₂ (N₂+2.4%H₂O)</td>
<td>1380.94</td>
<td>100</td>
<td>2.0×10⁻⁸</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>N₂O (air)</td>
<td>1275.49</td>
<td>230</td>
<td>5.3×10⁻⁸</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>CH₄ (air)</td>
<td>1275.39</td>
<td>230</td>
<td>1.7×10⁻⁷</td>
<td>100</td>
<td>118</td>
</tr>
<tr>
<td>C₂HF₅ (N₂)***</td>
<td>1208.62</td>
<td>770</td>
<td>7.8×10⁻⁹</td>
<td>6.6</td>
<td>9</td>
</tr>
<tr>
<td>NH₃ (N₂)*</td>
<td>1046.39</td>
<td>110</td>
<td>1.6×10⁻⁸</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>SF₆***</td>
<td>943.73</td>
<td>75</td>
<td>2.7×10⁻¹⁰</td>
<td>40</td>
<td>5×10⁻²</td>
</tr>
</tbody>
</table>

* - Improved microresonator
** - Improved microresonator and double optical pass through ADM
*** - 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, 18 dB/oct filter slope.

For comparison: conventional PAS 2.2 (2.6)×10⁻⁹ cm⁻¹W/√Hz (1,800; 10,300 Hz) for NH₃*. (**)

Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm$^3$ to $\sim$2cm$^2$)
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range
- Frequency and spatial selectivity of acoustic signals
- Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
- Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise: $k_B T$ energy in the TF symmetric mode
- Absence of low-frequency noise: SNR scales as $\sqrt{t}$, up to $t=3$ hours as experimentally verified

QEPAS: some challenges

- Cost of Spectrophone assembly
- Sensitivity scales with laser power
- Effect of H$_2$O
- Responsivity depends on the speed of sound and molecular energy transfer processes
- Cross sensitivity issues
Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module

Hollow core waveguide

Hollow Core Glass Waveguides:

- Excellent Infrared transmission out to 20 µm
- Proven single mode delivery for bore size ~ 30λ
- No end reflections
- High damage threshold
- Very Robust
- 20+ years of experience at Rutgers

Bending loss is the primary concern
HWG Fiber with 300 µm bore size allows single mode beam delivery @ 10,5 µm

<table>
<thead>
<tr>
<th>Bore Size</th>
<th>300 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight Losses</td>
<td>1 dB/m</td>
</tr>
<tr>
<td>Bending Losses</td>
<td>0,1 dB/m</td>
</tr>
</tbody>
</table>

Beam Profiling measurement setup and sample beam profiles
Future Directions and Outlook

- New target analytes such as carbonyl sulfide (OCS), formaldehyde (CH₂O), nitrous acid (HNO₂), hydrogen peroxide (H₂O₂), ethylene (C₂H₄), ozone (O₃), nitrate (NO₃), propane (C₃H₈), and benzene (C₆H₆)
- Ultra-compact, low cost, robust sensors (e.g. C₂H₆, NO, CO……)
- Monitoring of broadband absorbers: acetone (C₃H₆O), acetone peroxide (TATP), UF₆……
- Optical power build-up cavity designs
- Development of trace gas sensor networks
Mid-IR and THz Ring Cavity Surface Emitting QCLs

(a) Two-dimensional far-field plot emanating from a MIR RCSE-QCL and recorded with a micro-bolometer camera in a distance of 40 mm. (b) Polarization dependent intensity measurement.

(a) Three-dimensional illustration of a ring cavity surface emitting laser. (b) Scanning electron microscopy image of a processed MIR device. Close-up of a (c) MIR and (d) a THz waveguide section holding second order gratings.
Summary

- Laser spectroscopy with a mid-infrared, room temperature, continuous wave, DFB laser diodes and high performance DFB QCL is a promising analytical approach for real time atmospheric measurements and breath analysis.

- Six infrared semiconductor lasers from Nanoplus, Daylight Solutions, Maxion Technologies (PSI), Hamamatsu, Northwestern University and AdtechOptics were used recently (2011-2012) by means of TDLAS, PAS and QEPAS.

- Seven target trace gas species were detected with a 1 sec sampling time:
  - C₂H₆ at ~ 3.36 µm with a detection sensitivity of 130 pptv using TDLAS
  - NH₃ at ~ 10.4 µm with a detection sensitivity of ~1 ppbv (200 sec averaging time);
  - NO at ~5.26µm with a detection limit of 3 ppbv
  - CO at ~ 4.61µm with minimum detection limit of 2 ppbv
  - SO₂ at ~7.24µm with a detection limit of 100 ppbv
  - CH₄ and N₂O at ~7.28 µm currently in progress with detection limits of 20 and 7 ppbv, respectively.

- New target analytes such as OCS, CH₂O, HONO, H₂O₂, C₂H₄,

- Monitoring of broadband absorbers such as acetone, C₃H₈, C₆H₆ and UF₆

- Compact, robust sensitive and selective single frequency, mid-infrared sensor technology that is capable of performing precise, accurate and autonomous concentration measurements of trace gases relevant in environmental, biomedical, industrial monitoring and national security.