The state-of-the-art and grand Challenges of Mid-infrared Technology and Applications

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- New Laser Based Trace Gas Sensor Technology
  - Novel Multipass Absorption Cell & Electronics
  - Quartz Enhanced Photoacoustic Spectroscopy
- Seven Examples of Mid-Infrared Sensor Architectures
  - C₂H₆, NH₃, NO, CO, SO₂, CH₄ & N₂O
- Future Directions of Laser Based Gas Sensor Technology and Conclusions

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Mid-IR and THz Spectroscopic Phenomena

Size reference:
- Football field (10 m)
- Baseball (10 cm)
- Paperclip thickness (1 mm)
- Threat item, water molecule, virus, atom, subatomic particles

Wavelength (nm):
- 10^3 (10 m)
- 10^2 (1 cm)
- 10^1 (1 mm)
- 10^0 (1 mil)
- 10^{-1} (1 μm)
- 10^{-2} (1 nm)
- 10^{-3} (1 Å)
- 10^{-4} (1 pm)

Wavenumber (cm⁻¹):
- 10^{-5}
- 10^{-4}
- 10^{-3}
- 10^{-2}
- 10^{-1}
- 10^0
- 10^1
- 10^2
- 10^3
- 10^4
- 10^5
- 10^6
- 10^7
- 10^8
- 10^9
- 10^{10}

Electron volt (eV):
- 10^{-6}
- 10^{-5}
- 10^{-4}
- 10^{-3}
- 10^{-2}
- 10^{-1}
- 10^0
- 10^1
- 10^2
- 10^3
- 10^4
- 10^5
- 10^6

Frequency (Hz):
- 10^6
- 10^7
- 10^8
- 10^9
- 10^{10}
- 10^{11}
- 10^{12}
- 10^{13}
- 10^{14}
- 10^{15}
- 10^{16}
- 10^{17}
- 10^{18}
- 10^{19}
- 10^{20}
- 10^{21}

Radio Spectrum:
- Broadcast and Wireless
- Microwave

Terahertz:
- Far IR
- Mid IR
- Near IR

Infrared:
- Visible Light
- UV
- Soft X-ray

Ultraviolet:
- Hard X-ray

X-ray:
- Medical X-rays
- Cosmic ray observations

Gamma:
- PET imaging

Sources and Uses of Frequency Bands:
- AM radio
- FM radio
- Mobile Phones
- Radar
- Ultrasound
- TV Broadcast
- Wireless Data
- Microwave Oven
- "mm wave" sub-mm
- Night Vision
- Screening
- Remotes
- Baggage screen

Visible wavelength (nm):
- 700-600
- 600-570
- 570-540
- 540-470
- 470-440

Fiber telecom
- 0.7-1.4 μm
- Dental Curing
- 200-350nm

Biomedical imaging
- 850 nm
- 400-290 nm

Crystallography
- 0.1-0.01 Å

Visible Light
- 425-750 THz
- 700-400 nm

Mid-IR
- 18-100 cm⁻¹

RICE

Provided by: Prof. Daniel Mittleman, Rice University, Houston, TX
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, Isotopic Signatures
  - Volcanic Emissions

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

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

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

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

- **Fundamental Science and Photochemistry**
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 and Sentinel Photonics, Inc.)
  - 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
- 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>
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<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</td>
<td>Mode Hop-free Wavelength Tunability</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>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 – Feb 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 & <10 kHz 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;
Recent 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 ºC and < 30 ºC) 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 broad band 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…).
“Curiosity” landed on Mars on August 6, 2012
Motivation for Mid-infrared $C_2H_6$ 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 $C_2H_6$, $CH_4$, and $H_2O$
C$_2$H$_6$ Detection with a 3.36 µm 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)
NOAA Monitoring and Sampling Location: Alert (ALT), Nunavut, Canada

General view on Alert NOAA Facility

Ethane Concentration Measurements at ALT

CO$_2$ Concentration Measurements at ALT
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 Photoacoustic Spectroscopy (PAS)

Laser beam, power $P$

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

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

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

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

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.
NH₃ Detection due to a Fire resulting from a two 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.
Sporadic increased NH₃ Concentration Levels related to NOₓ Emission Reduction 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)
Atmospheric NH₃ measurements and implications for PM formation near Fort Worth

- Four specific aims are being pursued:
  - Investigation of the NH₃ dynamics (e.g., temporal variation);
  - Identification of NH₃ sources using auxiliary data for CO and NOₓ;
  - Performing NH₃ source apportionment using the EPA Positive Matrix Factorization 3.0 model including VOCs data;
  - Evaluation of NH₃ effects on local and regional air quality with respect to PM formation using aerosol/PM data collected by an Aerodyne High Resolution Time-of-Flight Mass Spectrometer, a Scanning Electrical Mobility Spectrometer, and a Mist Chamber-Ion Chromatography system.
NH₃ vs. Temperature data & Time series of NH₃, SO₂, CO

- 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 \( f/2 \)

\[ S \sim \frac{Q \alpha P}{f V} \]

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

Piezoelectric crystal

Resonant at \( f \)

quality factor \( Q \)

\( Q \gg 1000 \)
Cell is OPTIONAL!

\( V \)-effective volume
Quartz Tuning Fork as a Resonant Microphone for QEPAS

Unique properties

• Extremely low internal losses:
  ▪ Q~10,000 at 1 atm
  ▪ Q~100,000 in vacuum

• Acoustic quadrupole geometry
  ▪ Low sensitivity to external sound

• Large dynamic range (∼10^6) – linear from thermal noise to breakdown deformation
  ▪ 300 K noise: x~10^{-11} cm & breakdown: x~10^{-2} cm

• Wide temperature range: from 1.6K to ~700K

• Low cost (< $0.30)

• Resonant frequency;: ∼ 32.8 KHz

Acoustic Micro-resonator (mR) tubes

• Optimum inner diameter: 0.6 mm; mR-QTF gap is 25-50 µm

• Optimum mR tubes must be ∼ 4.4 mm long (∼λ/4<l<λ/2 for sound at 32.8 kHz)

• SNR of QTF with mR tubes: ×30 (depending on gas composition and pressure)
Simulated HITRAN high resolution spectra @ 130 Torr indicating two NH₃ absorption lines of interest

No overlap between NH₃ and CO₂ absorption lines was observed for the selected 967.35 cm⁻¹ NH₃ absorption line in the R branch of the ν₂ band.
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 40 sec.

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: 
$\sim 6$ ppbv at $967.35 \text{ cm}^{-1}$ ($1\sigma$; 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
CW TEC DFB QCL based QEPAS NO Gas Sensor

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

CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 630 mA and 20.5 deg C through tubes after ADM

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

2f QEPAS signal amplitude for 95 ppb NO when DFB-QCL was locked to the 1900.08 cm⁻¹ line.

Minimum detectable NO concentration is:
~ 3 ppbv (1σ; 1 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. CH$_4$).

• 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

CW DFB-QCL optical power and current tuning at a four different QCL temperatures.

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

Minimum detectable CO concentration is: ~ 2 ppbv (1σ; 1 s time resolution)

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.
**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 \( \rightarrow \) 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**

**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)
Motivation for CH₄ Detection
- Prominent greenhouse gas
- Leakage from Natural Gas Systems
- Animal Husbandry
- Fossil Fuel Production

Motivation for N₂O Detection
- Major greenhouse gas and air pollutant
- Agriculture
- Fossil Fuel Combustion
- Wastewater Management
- Industrial processes
- Medical Applications
QCL based QEPAS Performance for 10 Trace Gas Species (February 2013)

<table>
<thead>
<tr>
<th>Molecule (carrier gas)</th>
<th>Frequency cm(^{-1})</th>
<th>Pressure Torr</th>
<th>NNEA cm(^{-1})W/Hz(^{1/2})</th>
<th>QCL Power mW</th>
<th>NEC ((\tau=1)s) ppbV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)O (N(_2):75% RH)*</td>
<td>2804.90</td>
<td>75</td>
<td>8.7\times10^{-9}</td>
<td>7.2</td>
<td>120</td>
</tr>
<tr>
<td>CO (N(_2)+ 2.2% H(_2)O)*</td>
<td>2176.28</td>
<td>100</td>
<td>1.57\times10^{-8}</td>
<td>71</td>
<td>2</td>
</tr>
<tr>
<td>CO (propylene)</td>
<td>2196.66</td>
<td>50</td>
<td>7.4\times10^{-8}</td>
<td>6.5</td>
<td>140</td>
</tr>
<tr>
<td>N(_2)O (air+5%SF(_6))</td>
<td>2195.63</td>
<td>50</td>
<td>1.5\times10^{-8}</td>
<td>19</td>
<td>7</td>
</tr>
<tr>
<td>N(_2)O (N(_2)+2.37%H(_2)O)</td>
<td>2201.75</td>
<td>200</td>
<td>2.9\times10^{-8}</td>
<td>70</td>
<td>2.5</td>
</tr>
<tr>
<td>C(_2)H(_5)OH (N(_2))**</td>
<td>1934.2</td>
<td>770</td>
<td>2.2\times10^{-7}</td>
<td>10</td>
<td>9\times10^{4}</td>
</tr>
<tr>
<td>NO (N(_2)+H(_2)O)</td>
<td>1900.07</td>
<td>250</td>
<td>7.5\times10^{-9}</td>
<td>100</td>
<td>3.6</td>
</tr>
<tr>
<td>SO(_2) (N(_2)+2.4%H(_2)O)</td>
<td>1380.94</td>
<td>100</td>
<td>2.0\times10^{-8}</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>N(_2)O (air)</td>
<td>1275.49</td>
<td>230</td>
<td>5.3\times10^{-8}</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>CH(_4) (air)</td>
<td>1275.39</td>
<td>230</td>
<td>1.7\times10^{-7}</td>
<td>100</td>
<td>118</td>
</tr>
<tr>
<td>C(_2)HF(_5) (N(_2))***</td>
<td>1208.62</td>
<td>770</td>
<td>7.8\times10^{-9}</td>
<td>6.6</td>
<td>9</td>
</tr>
<tr>
<td>NH(_3) (N(_2))*</td>
<td>1046.39</td>
<td>110</td>
<td>1.6\times10^{-8}</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>SF(_6)**</td>
<td>943.73</td>
<td>75</td>
<td>2.7\times10^{-10}</td>
<td>40</td>
<td>5\times10^{-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 \(\tau=1\)s time constant, 18 dB/oct filter slope.

For comparison: conventional PAS 2.2 \((2.6)\times10^{-9}\) cm\(^{-1}\)W/\(\sqrt{\text{Hz}}\) (1,800; 10,300 Hz) for NH\(_3\)*. (**)  
Merits of QEPAS based Trace Gas Detection

• Very small sensing module and sample volume (a few mm\(^3\) to ~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 \(t\approx 3\) 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
Future Directions and Outlook

- New target analytes such as OCS, CH₂O, nitrous acid (HNO₂), H₂O₂, ethylene (C₂H₄), 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,…
- Low divergence surface emitting quantum cascade lasers
- Finite Element Modeling for on-axis and off-axis micro resonators for QEPAS
- Optical power build-up cavity designs
- Development of trace gas sensor networks
Potential Integration of a CW DFB-QCL and QEPAS Absorption Detection Module

A. Lyakh, et al. “1.6 W high wall plug efficiency, continuous-wave room temperature quantum cascade laser emitting at 4.6 \( \mu \text{m} \)”, Appl. Phys. Lett. 92, 111110 (2008)
Ring resonator-based surface emitting QCL

(a) Single-mode spectrum (b) Surface emission spectra recorded at different temperatures. (c) Linear tuning of the resonance. The inset illustrates the corresponding optical power curves.

Measured (left half) and simulated (right half) surface emission far-field pattern.
Hollow Core Waveguides

- Excellent Infrared transmission out to 20 µm
- Proven single mode delivery for bore size ~30λ
- No end reflections
- High damage threshold
- Very Robust
- Bending loss is a primary concern
Summary

- Laser spectroscopy with mid-infrared, TEC, CW, DFB laser diodes, high performance DFB QCLs and tunable EC-QCLs is a promising analytical approach for real time environmental, biomedical and industrial monitoring as well as technology for national security.

- Six mid-infrared from Nanoplus, Daylight Solutions, Maxion Technologies (Thor Labs), Hamamatsu, Northwestern University and Adtech Optics were used recently (2011-2013) in three sensor platforms: TDLAS, PAS and QEPAS.

- Seven target trace gas species were detected with a 1 sec sampling time:
  - $\text{C}_2\text{H}_6$ at $\sim 3.36 \mu\text{m}$ with a detection sensitivity of 130 pptv using TDLAS
  - $\text{NH}_3$ at $\sim 10.4 \mu\text{m}$ with a detection sensitivity of $\sim 1 \text{ ppbv}$ (200 sec averaging time);
  - NO at $\sim 5.26 \mu\text{m}$ with a detection limit of 3 ppbv
  - CO at $\sim 4.61 \mu\text{m}$ with minimum detection limit of 2 ppbv
  - $\text{SO}_2$ at $\sim 7.24 \mu\text{m}$ with a detection limit of 100 ppbv
  - $\text{CH}_4$ and $\text{N}_2\text{O}$ at $\sim 7.28 \mu\text{m}$ currently in progress with detection limits of 20 and 7 ppbv, respectively.