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

Frank K. Tittel

Dept. of Electrical & Computer Engineering, Rice University, Houston, TX 77005

http://www.ece.rice.edu/~lasersci/
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 Gas Cell** (e.g., White, Herriot, Chernin, Aeris Technologies, and Circular Cylindrical Multipass Cell)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector or back scattering from topographic target): Standoff and Remote Detection
  - Fiberoptic & Wave-guide 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 2012 database
Selection of Absorption lines in the mid-IR Spectral Range (3 – 5 µm)

- 2.5 µm < l < 5 µm (4000 cm\(^{-1}\) – 1900 cm\(^{-1}\))
- Access to molecular fundamental rotational-vibrational states
- Atmospheric window (3.5-4.8 µm)

Applications
- Medicine
- Sensing
- Emission monitoring
- Process control
- Free-space communication
- Defense
- Homeland security
## 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 pptv)</td>
<td>Optimum Wavelength and Power</td>
</tr>
<tr>
<td>Selectivity (Spectral Resolution) or Specificity</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 Time</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 and Robust</td>
</tr>
</tbody>
</table>
• **Band – structure engineered devices**
  Emission wavelength is determined by layer thickness – MBE or MOCVD; QCLs operate in the 3 to 24 µm spectral region and ICLs can cover the 3 to 5 µm spectral range.
  - Compact, reliable, stable, long lived, and commercially available
  - 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 QCLs 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 & Optical Frequency Combs (OFCs) > 100 to <450 cm⁻¹ with kHz to sub-kHz resolution and a comb spacing of > 10 GHz

• **Narrow spectral linewidths**
  - CW: 0.1 - 3 MHz & <10kHz with frequency stabilization
  - Pulsed: ~ 300 MHz

• **High pulsed and CW powers of QCLs and ICLs at TEC/RT temperatures**
  - Room temperature pulsed peak power of ~203 W with 10% wall plug efficiency for QCLs
  - ~1 W CW DFB TEC/RT QCL; wall plug efficiency 23% at 4.6 µm
  - ~ 5-10mW CW DFB ICLs at TEC/RT in the 3 to 4 µm spectral range
Low-dissipation DFB devices at 4.5 $\mu$m

- **opt power up to 48mW**
- $P_{\text{max}} \approx 1.4$W
- Single mode

A miniaturized External Cavity QCL with MEMS Technology

\[ \text{wavenumber [cm}^{-1}\text{]} \]

\[ > 20 \text{ dB} \]
Methane is one of the major atmospheric greenhouse gases contributing to global warming and climate change.

- Global warming potential (GWP) of 25 compared to GWP of 1 for CO$_2$ for a 100-year period)
- Short lifetime in the atmosphere (~12 yrs) compared to CO$_2$ and N$_2$O
- Atmospheric background concentration: ~1.8 ppm
The result of a sequence of four fracking injections obtained by directional drilling which creates horizontal production in the target stratum is depicted in a figure as published in Physics Today 2016. A DOE-ARPA-E funded methane detection project at 3.33 µm was started in 2015. Texas located wellpad sites (Texas located well pad sites typically measure 10-30 m with a 1 m spatial resolution)
CH$_4$ and N$_2$O Measurements performed with a DFB-QCL based QEPAS Sensor installed in a Mobile Laboratory (operated by Aerodyne, Inc.)

CH$_4$ mixing ratios

N$_2$O mixing ratios

Spotlight on Optics

Atmospheric CH$_4$ and N$_2$O measurements near Greater Houston area landfills using a QCL-based QEPAS sensor system during DISCOVER-AQ 2013
# Comparison of proposed Rice CH$_4$ Sensor System and current commercially available CH$_4$ Sensor Platforms

<table>
<thead>
<tr>
<th></th>
<th>Rice</th>
<th>Picarro</th>
<th>ABB-LGR I</th>
<th>ABB-LGR II</th>
<th>Aerodyne</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Opt. Path length and method</strong></td>
<td>MIR TDLAS: ~ 9 m</td>
<td>NIR CRDS: &gt;2000m</td>
<td>NIR OA-ICOS: &gt; 1000m</td>
<td>NIR OA-ICOS: &gt; 2000m</td>
<td>MIR TDLAS: 70-100 m</td>
</tr>
<tr>
<td><strong>Sensitivity/sec</strong></td>
<td>&lt; 5-10 ppb</td>
<td>1-2 ppb</td>
<td>5 ppb</td>
<td>2 ppb</td>
<td>&lt;1 ppb</td>
</tr>
<tr>
<td><strong>Accuracy (drift)</strong></td>
<td>2 ppb stabilized</td>
<td>2 ppb</td>
<td>20 ppb, temp. stabilized</td>
<td>2 ppb</td>
<td>2 ppb</td>
</tr>
<tr>
<td><strong>Cell Volume, cc</strong></td>
<td>60</td>
<td>30</td>
<td>500</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td><strong>Pump Size (10 sec flush time)</strong></td>
<td>~ 1 lpm</td>
<td>~ 0.5 lpm</td>
<td>~ 11 lpm</td>
<td>~ 45 lpm</td>
<td>~ 45 lpm</td>
</tr>
<tr>
<td><strong>Cavity Mirror Reflectance</strong></td>
<td>98.5%-99%</td>
<td>&gt;99.99%</td>
<td>&gt;99.99%</td>
<td>&gt;99.99%</td>
<td>&gt;99.99%</td>
</tr>
<tr>
<td><strong>Power Consumption</strong></td>
<td>2-20 W</td>
<td>200 W</td>
<td>70 W</td>
<td>200 W</td>
<td>400 W</td>
</tr>
<tr>
<td><strong>Weight</strong></td>
<td>~ 2-4 kg</td>
<td>~ 20 kg</td>
<td>~ 15 kg</td>
<td>~ 40 kg</td>
<td>~ 40 kg</td>
</tr>
<tr>
<td><strong>Cost</strong></td>
<td>~ 20-25K USD</td>
<td>~ 40-50K USD</td>
<td>~ 25K USD</td>
<td>~ 40K USD</td>
<td>~ 100K USD</td>
</tr>
</tbody>
</table>

US Department of Energy Advanced Research Project Agency – Energy (ARPA-E), Methane Observation Networks with Innovative Technology to obtain Reductions (MONITOR)
Beer’s Law: \[ \frac{I_t}{I_0} = \exp(-k_v L) \]

where: 
- \( I_t \) is transmitted light intensity
- \( I_0 \) is incident light intensity
- \( k_v \) is absorption coefficient
- \( L \) is optical path

**Multipass Gas Cell (MPGC):**
The minimum detection limit can be improved by increasing the effective optical path without increasing the physical length.

3D Rice LSG simulation of a multipass cell
Based on RLSG custom software
(L=100mm R=100mm D=15mm)
The fundamental $v_1$ and $v_3$ CH$_4$ bands are located at $\sim7.7$ $\mu$m and $\sim3.3$ $\mu$m, respectively.

A high detection sensitivity for methane measurements using quantum cascade lasers (QCLs) at $7.7$ $\mu$m was previously reported.

Compact, TEC, CW, DFB ICLs emitting at 3-4 $\mu$m wavelengths became recently commercially available.

An interference-free CH$_4$ absorption line located at 3038.5 cm$^{-1}$ was selected as the optimum target absorption line.

The 3.3$\mu$m CH$_4$ absorption line can be used at atmospheric pressure.
Performance evaluation for a 3.291-µm CW RT ICL at different operating temperatures and injection currents. (a) ICL output power response curves; (b) Emission wavenumber curves.

Current turning rate: -0.232308 cm\(^{-1}\)/mA; Temperature turning rate: -0.23994 cm\(^{-1}\)/°C
Schematic of current CH$_4$ Gas Sensor System

- **ICL source (Nanoplus)**
  - Current: 42 mA
  - Temperature: 30 °C
  - Power: 1.5 mW

- **Multipass gas cell (Sentinel Photonics/Aeris Technologies, Inc)**
  - 54.6 meter, 435-passes, sealed
  - Sampling volume: 220 mL
  - Dimensions: 16.9 x 6.6 x 5.3 cm$^3$

- **Sensor system platform**
  - Two-floor design with folded optical path
  - Low power consumption: 6 W
  - Dimensions: 32 x 20 x 17 cm$^3$
Current Electronics Controller for CH\textsubscript{4} Sensor System

- **Control unit**
  - Laptop+NI DAQ+OEM laser driver
  - Direct absorption spectroscopy
  - DAQ: acquiring data & scanning the ICL wavelength

- **OEM laser driver for ICL**
  - Neo Monitors, Oslo, Norway
  - Size: 10 x 8 cm\textsuperscript{2}
  - Low noise characteristic: $\leq 1$ nA$/\sqrt{\text{Hz}}$
  - On-board TEC driver: $\pm 3$ A, 15 V
  - Single voltage power supply 12-24V
A 4-step algorithm for CH$_4$ detection

- 150 spectra were averaged
- Baseline of the spectral scan was fitted and eliminated
- Linearized spectrum using fringe spacing of a germanium etalon
- Lorentzian line shape fitting to retrieve concentration information

Interference-free absorption line of CH$_4$ at 3038.5 cm$^{-1}$ obtained from laboratory air at atmospheric pressure together with a fitted baseline and a transmission signal from a germanium etalon.
An Allan-Werle deviation plot was acquired in a time period of \( \sim 1.5 \) hours using a certified 2 ppm CH\(_4\) cylinder with a 1 Hz sampling rate.

1-s measurement precision is \( \sigma=10.53 \) ppb
60-s measurement precision is \( \sigma=1.43 \) ppb
CH$_4$ concentrations measured over a 7-day period in ambient air on the Rice University campus during May 2015.
Diurnal variations of CH₄ mixing ratio. Bottom whisker, bottom box line, top box line and top whisker indicate the 5th, 25th, 75th and 95th percentile, respectively. Line inside the boxes and continuous solid line represent the hourly median and mean of the data respectively.

The diurnal profile of the methane concentration shows an increase in concentration during the early morning with a subsequent gradual decrease after ~8:00 am CDT to its typical background level of ~1.87 ppm in the Greater Houston area in May 2015.
Recent mobile Field Tests: December 2015

CH$_4$ concentrations measured for a sampling period of ~ 10 minutes at a Clean Energy CNG O’Rourke Natural Gas Station in Houston, TX.
CH$_4$ Sensor System Summary (2015-2016)

- A 3.291 $\mu$m CW room-temperature ICL based absorption sensor was developed for methane detection using a 54.6 m optical path length multipass gas cell.

- A two-floor mechanical design with a folded optical path resulted in a sensor system dimension of 32 x 20 x 17 cm$^3$.

- Good electrical power management resulted in a low power consumption of the CH$_4$ sensor system: 6 W.

- A minimum detectable Limit (MDL) of 10.5 ppb for CH$_4$ with a 1 sec integration time was achieved.

- Laboratory measurements and mobile-mode field tests were conducted and results demonstrate the suitability of the sensor system to generate CH$_4$ spatial distributions in a typical U.S. urban area and at an oil and gas storage facility in Houston, TX.
Portable three Line Methane Sampling System for Laboratory and Field Deployment
Motivation for mid-infrared Ethane ($\text{C}_2\text{H}_6$) Detection

- **Application in medical breath analysis**
  - Asthma
  - Schizophrenia
  - Lung cancer
  - Vitamin E deficiency

- **Atmospheric chemistry and climate**
  - Fossil fuel and biofuel consumption
  - Biomass burning
  - Vegetation/soil
  - Natural gas loss

HITRAN absorption spectra of $\text{C}_2\text{H}_6$, $\text{CH}_4$, and $\text{H}_2\text{O}$

Targeted $\text{C}_2\text{H}_6$ absorption line
C$_2$H$_6$ Detection with a 3.36 µm CW DFB Diode Laser 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 200 Torr

Minimum detectable C$_2$H$_6$ concentration: ~ 740 pptv (1σ; 1 s time resolution)

MGC dimensions: 17 x 6.5 x 5.5 (cm)
Distance between the MGC mirrors: 12.5 cm
Motivation for mid-infrared Formaldehyde Detection

- **Atmospheric chemistry and climate**
  - Important volatile organic compound (VOC) present in all regions of the atmosphere which reacts in the presence of sunlight to yield ozone.
  - Primary $\text{H}_2\text{CO}$ sources are vehicle exhaust and fugitive industrial emissions
  - Secondary $\text{H}_2\text{CO}$ sources originate from the breakdown of primary VOCs via photochemical oxidation
- **Industrial Applications**
  - Textile industry
  - Automobile industry
  - Adhesive resins for use in carpeting & plywood

![HITRAN absorption spectra of $\text{H}_2\text{CO}$](image)

- Lead-salt lasers
- DFG
- OPO
- CO-overtone laser
Formaldehyde Line Selection in the 3-4 µm Spectral Region

Absorption

1.0x10^{-3}
8.0x10^{-4}
6.0x10^{-4}
4.0x10^{-4}
2.0x10^{-4}
0.0

Wavenumber [cm^{-1}]

2776 2778 2780 2782 2784

2778.5 cm^{-1}

Air
CH2O: 10 ppb
L = 56 m, P = 1 atm
Sensor Configuration

Laser source
- Nanoplus ICL, 3.6 μm
- Injection current: 50 mA
- Output power: 3mW

Compact multipass cell
- Sentinel Inc.
- 7.6 cm multipass cell length
- 32 ml sampling volume
- 3.7 m effective optical length

$\lambda$-modulation scheme
Representative $\text{H}_2\text{CO}$ Sensor Calibration Results

- $\text{H}_2\text{CO}$ gas standard: Kin-Tek gas standard generator
H$_2$CO Detection Sensitivity

- Minimum detection concentration: 1.5 ppb with a 140 sec averaging time
Noise Limitations

- Zero air measurements: 1s sampling rate
- Development of laser-based absorption sensors for H$_2$CO detection using an interband cascade laser & a compact xx m multipass absorption cell.
- A minimum detection concentration of 1.5 ppb with 140 sec averaging time was achieved.
- Future work is planned to further improve the sensor detectivity to sub-ppb concentration level by using a multipass cell with an increased effective optical path length. Preliminary results show that a minimum detection concentration of 1 ppb with 10 sec averaging time can be achieved.
Conclusions and Future Developments

• Development of robust, compact, sensitive, selective mid-IR trace gas sensor technology based on RT, CW high performance DFB ICLs & QCLs for detection of explosives and TICs as well as environmental monitoring and medical diagnostics.

• Interband cascade and quantum cascade lasers were used in QEPAS and TDLAS based sensor platforms

• Performance evaluation of seven target trace gas species were reported. The minimum detection limit (MDL) with a 1 sec sampling time were:
  - C_2H_6: MDL of .24 ppbv at ~3.36 µm; CH_4: MDL of 13 ppbv at ~7.28 µm; N_2O: MDL of 6 ppbv at ~7.28 µm.

• Development of Trace Gas Sensors for the monitoring of broadband absorbers: acetone(C_3H_6O), propane (C_3H_8), benzene (C_6H_6)
Hydrogen Peroxide (H$_2$O$_2$)

- Strong oxidant species in the atmosphere
- Associated with the formation of acid rain and atmospheric aerosols
- Employed in the synthesis of multiple chemical products & as bleaching agent in the pulp and paper industry
- Used for decontamination and sterilization of medical and pharmaceutical facilities
- Biomarker of lung and respiratory system diseases in exhaled breath
Vapor-Phase Hydrogen Peroxide (VPHP)

- VPHP units: gas-phase \( \text{H}_2\text{O}_2 \) generated from concentrated liquid \( \text{H}_2\text{O}_2 \) solutions
- \( \text{H}_2\text{O}_2 \) concentrations between 200-1200 ppm are produced in the gas-phase and maintained for \(~10\) min
- After decontamination procedures, ambient \( \text{H}_2\text{O}_2 \) concentrations need to be monitored

VPHP is used for:
- Decontamination of health-care and pharmaceutical facilities
- Sterilization of medical equipment and packing materials in the food industry

Source: Bioquell UK Ltd
Techniques for $\text{H}_2\text{O}_2$ Detection

• Wet-chemistry methods based on fluorescence spectroscopy, colorimetric analysis and chemiluminescence
  - Transfer from gas to liquid phase required for subsequent analysis
  - Interference from other species and formation of sampling artifacts

• Mid-infrared laser based spectroscopy
  - Direct detection in the gas-phase
  - Real-time detection
  - High sensitivity and specificity
H$_2$O$_2$ Absorption in the mid-infrared spectral Region

Fundamental $\nu_6$ H$_2$O$_2$ band located at $\sim$7.5-8.3 $\mu$m
Previous mid-IR sensor systems developed for \( \text{H}_2\text{O}_2 \) detection suffer from significant interferences from other gas species, particularly \( \text{N}_2\text{O} \) and \( \text{H}_2\text{O} \) vapor.

**Previous Employed Absorption Lines**

@ 80 Torr, 20 ° C

**Selected \( \text{H}_2\text{O}_2 \) line**

1295.55 cm\(^{-1}\)

QEPAS-based sensor system *(Rei, et al., APL, 2014)*

@ 150 Torr, 20 ° C

**Selected \( \text{H}_2\text{O}_2 \) line**

1296.2 cm\(^{-1}\)

Selection of optimum Absorption Line

- A comprehensive spectral study was conducted
- Potential interferences from H$_2$O vapor, N$_2$O, CH$_4$ and CO$_2$ were considered
- An interference-free absorption line at 1234.05 cm$^{-1}$ was selected for H$_2$O$_2$ detection
EC-QCL Operating Characteristics

- CW EC-QCL (Model 21080-MHF, Daylight Solutions)
- Tuning range: 1175-1300 cm\(^{-1}\)
- Mode-hop-free range: 1225-1285 cm\(^{-1}\)
- Power output: < 200 mW
Sensor Architecture

CW EC-QCL coupled into multipass absorption gas cell with 76 m optical path length

Wavelength modulation spectroscopy (WMS) with 2f detection implemented for data processing
Photo of H₂O₂ Sensor Configuration

EC-QCL 21080-MHF (Daylight Solutions)

Multipass cell
AMAC-76 (Aerodyne Inc.)

Optical components

Gas inlet

Gas outlet

Vigo Detector
(PVMI-3TE-8)

Flow and pressure controllers
Parameter Optimization

- Pressure and modulation amplitude levels were optimized for improved SNR

Selected operation conditions (20 Torr & 2 V)

- EC-QCL current & relative temperature: 300 mA & 0 °C
- Laser power output: ~ 66 mW
Sensor System Response

Direct absorption signal → WMS-2f signal

H₂O₂ at 1234.05 cm⁻¹
Calibration Results

- Different gas-phase H₂O₂ concentrations were generated by flowing air over aqueous solutions of different strengths.
- Gas-phase concentrations were determined by fitting the direct absorption signals using the HITRAN database.

Calibration curve and sensor response at H₂O₂ concentrations between 3 and 21 ppm.
Sensor System Sensitivity

Allan-Werle deviation analysis

Minimum detection limit (MDL): 25 ppb @ 280-sec integration time
H$_2$O$_2$ Sensor System Summary

- Selected absorption line at 1234.05 cm$^{-1}$ effectively alleviates interference issues identified previously for H$_2$O$_2$ detection

- MDL and ability to operate with no interference from water make our sensor system suitable for the monitoring of H$_2$O$_2$ in:
  - Industrial sites to establish possible exceedances of OSHA permissible exposure levels (PELs)
  - Decontamination/sterilization locations using VPHP
  - Exhaled breath as biomarker of lung-related diseases

- Further improvement of the MDL is necessary for application in other fields such as atmospheric monitoring
**Broadband THz QCLs**

- Multistack QC laser with four quantum well active regions

Broadband Spectrum

Mix a DFB QCL with a source operating by DFG (widely tunable)

Use a Fabry-Perot as a spectroscopy tool

- Can be used to measure the spectrum
- S/N limited by stability
Cavity enhanced optical frequency comb spectroscopy

For an optimum build-up of pulses inside a sensing cavity resonator, three conditions must be met:

1) Sensing cavity has to support equidistant frequency eigenmodes.
   \textit{Intracavity dispersion compensation}

1) Separation of the cavity eigenmodes and the separation of the frequency comb modes must be equal.
   \textit{Matching both cavity length}

1) Entire comb must be shifted to overlap with the cavity eigenfrequencies.
   \textit{Alignment of the eigenfrequencies}
Cavity design for ICL-comb source

HR mirrors radius of curvature calculation

Cavity stability criterion:

\[ 1 - \frac{L_{cav}}{R_2} = 1 - \frac{L_{cav}}{R_1} = -\frac{1}{2} \]

Specs for cavity mirrors design:

For \( L_{cav} = 30 \text{ mm} \)

\[ R_1 = R_2 = 20 \text{ mm} \]

✓ Plano-concave
✓ Diameter: 1/2”
✓ Radius of curvature: 20mm

\( R_1 \) : radius of curvature of mirror #1
\( R_2 \) : radius of curvature of mirror #2

Cavity design for ICL-comb source

Optical Cavity Performances:

✓ For effective length:

\[ L_{\text{eff}} = 200 \text{m} \]

Number of half round-trip:

\[ N = \frac{L_{\text{eff}}}{L_{\text{cav}}} = 6667 \]

Fraction of residual optical intra-cavity power after N half round-trips

\[ R_{\text{mirror}}^N \approx 26\% \]

✓ Finesse \( \mathcal{F} \):

\[ \zeta \approx \frac{\pi}{1 - R_{\text{mirror}}} \approx 15700 \]

✓ Width of the cavity mode:

\[ \Delta \nu = \frac{\text{FSR}}{\zeta} = 637 \text{KHz} \]

✓ Intra-cavity power enhancement factor:

\[ G = \frac{\zeta}{\pi} = 5000 \]
Cavity design for an ICL-comb source

Cavity length calculation

Frequency comb spacing:

\[ \Delta f = \frac{c}{2nL} \]

For ICL cavity length:

\[ L = 2 \sim 4 \text{ mm} \]

<table>
<thead>
<tr>
<th>( L )</th>
<th>( \Delta f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mm</td>
<td>20 GHz</td>
</tr>
<tr>
<td>3 mm</td>
<td>15 GHz</td>
</tr>
<tr>
<td>4 mm</td>
<td>10 GHz</td>
</tr>
</tbody>
</table>

Cavity mode spacing:

\[ FSR = \frac{c}{2L_{cav}} \]

Mode matching between comb and cavity modes:

\[ \Delta f = n \cdot FSR \]

For \( n=2 \)

<table>
<thead>
<tr>
<th>( \Delta f )</th>
<th>( L_{cav} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 GHz</td>
<td>15 mm</td>
</tr>
<tr>
<td>15 GHz</td>
<td>20 mm</td>
</tr>
<tr>
<td>10 GHz</td>
<td>30 mm</td>
</tr>
</tbody>
</table>

The possibility to tune the comb modes spacing allows us to choose a cavity length of 30 mm, maximizing the effective absorption length.
Sensing cavity design for ICL- OFC source

Specifications for cavity mirror material

- Transmittance within the 3-4 μm spectral range
- Transparent in the visible (red diode laser for pump beam alignment)
- High surface quality (for HR and AR coatings to be applied)

AR coatings:

@ 3590 nm
plano substrate surface

HR coatings:

✓ @ λ = 3590 nm
✓ plano concave surface
✓ $R_{\text{mirror}} \geq 99.98\%$

LohnStar Optics was contacted on Jan.14, 2016 for a quotation of AR & HR coatings on sapphire optics from Mellor Optics. Inc [http://www.lohnstaroptics.com; www.melleroptics.com]
Proposed Sensing Cavity Locking to JPL-NRL ICL

Cavity locking system

Critical requirement: resonances of the optical cavity must coincide with the comb teeth of the optical source

Cavity length must be adjusted

Locking of feedback loop will be realized by means of a piezo-actuator

Rice team will design a quasi Pound-Drever-Hall circuit to lock the output of the optical comb to the external cavity.
TARGET: detection and identification of toxic industrial chemicals with strong absorption features in the 3-4 µm range.

Sensor system will offer:
- High detection sensitivity
- High spectral stability and purity
- High selectivity
- Possibility of multi-gas detection

Two Sensor Configurations:

Comb laser is locked to a high finesse cavity

Cavity is locked to comb laser
Fast Mid-infrared detector

- Use of an intersubband Quantum Well Infrared Photoconductor (QWIP) detector
• Beat note measurement of the photocurrent (at 7.5GHz)
  – For modes of amplitude $E_k$, the photocurrent at $\Delta \omega$

$$I^{\Delta \omega} = \sum_k E_k E_{k+1} \cos(\phi_{k+1} - \phi_k)$$
Frequency noise of a comb

- Use a (matched) optical cavity as an optical discriminator
- Measures all the modes at once

Uncorrelated modes would yield noise broader than

\[ N \sqrt{N} \approx 300 \times \sqrt{N} \delta \omega_i \]

F. Cappelli, G. Villares et al, ArXiv
Frequency noise power spectral density

- Single mode versus comb
- Above noise floor
- No significant limit

![Graph showing frequency noise power spectral density (FNPSD) for single mode, comb, and detection noise floor over various frequency ranges.](image)
The very narrow width confirms the correlations between modes

- Uncorrelated lines could not be narrower than Schawlow-Townes (100’s Hz)
- However the signal is only about 2% of the c.w. photocurrent
Development of robust, compact, sensitive, selective mid-IR trace gas sensor technology based on RT, CW high performance DFB ICLs & QCLs for detection of explosives and TICs as well as environmental monitoring and medical diagnostics.

Interband cascade and quantum cascade lasers were used in QEPAS and TDLAS based sensor platforms.

Performance evaluation of seven target trace gas species were reported. The minimum detection limit (MDL) with a 1 sec sampling time were:
- $\text{C}_2\text{H}_6$: MDL of 0.24 ppbv at ~3.36 $\mu$m; $\text{CH}_4$: MDL of 13 ppbv at ~7.28 $\mu$m; $\text{N}_2\text{O}$: MDL of 6 ppbv at ~7.28 $\mu$m.

Development of Trace Gas Sensors for the monitoring of broadband absorbers: acetone($\text{C}_3\text{H}_6\text{O}$), propane ($\text{C}_3\text{H}_8$), benzene ($\text{C}_6\text{H}_6$).

Development of Mid-IR Electrically pumped Interband Cascade Optical Frequency Combs (OFCs) with JPL, Pasadena, CA, NRL, Washington, and the U. of Bari (Italy).
Acknowledgements

- DoE ARPA-E MONITOR Program: Aeries Technologies & ThorLabs
- DOD SCOUT Program: NRL and NASA-JPL
- National Science Foundation (NSF) ERC MIRTHE award
- NSF-ANR (France) award for international collaboration in chemistry
- Robert Welch Foundation grant C-0586