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

OUTLINE

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GE Global Research

Houston, TX

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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, 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**

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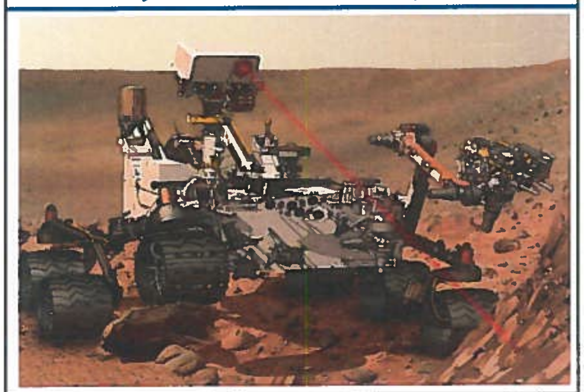
"Curiosity" Landed on Mars on August 6, 2012



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)

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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)

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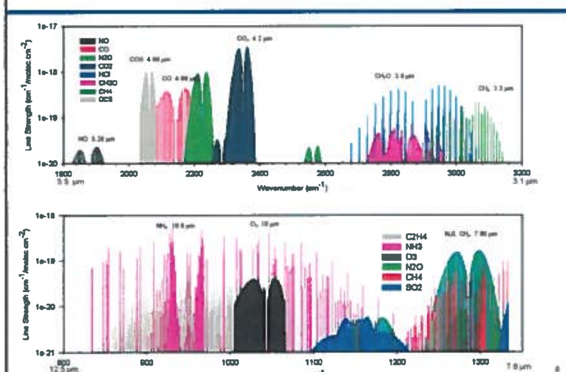
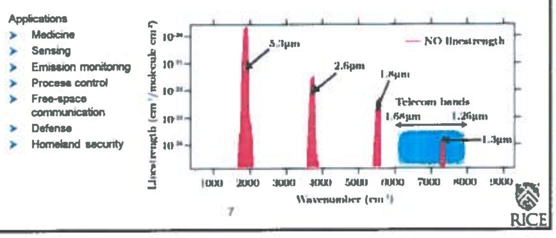
HITRAN Simulated Mid-Infrared Molecular Absorption Spectra



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)



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Mid-IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to pptv)	Optimum Wavelength and Power
Selectivity (Spectral Resolution) or Specificity	Stable Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines, and Broadband Absorbers	Mode Hop-Free Wavelength Tunability
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response Time
Room Temperature Operation	High Wall Plug Efficiency, No Cryogenics or Cooling Water
Field Deployable in Harsh Environments	Compact and Robust

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Key Characteristics of Mid-IR QCL & ICL Sources – March 2016

- **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

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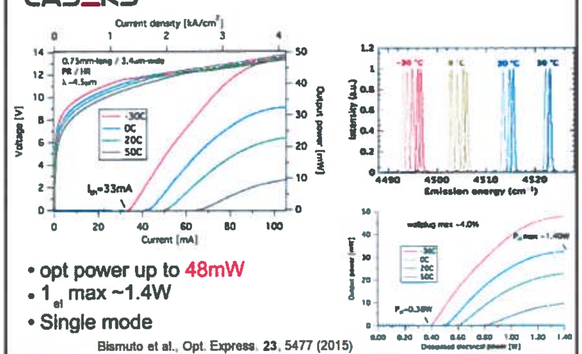
ALPES LASERS Low-dissipation DFB devices at 4.5 μm

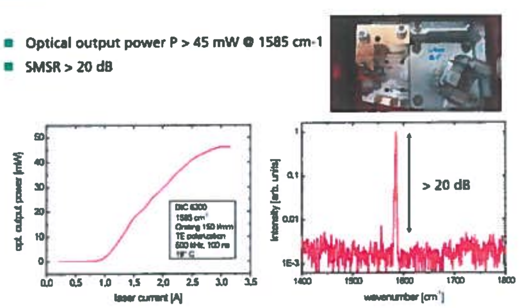


- opt power up to 48mW
- I_{el} max ~1.4W
- Single mode

Bismuto et al., Opt. Express. 23, 5477 (2015)

A miniaturized External Cavity QCL with MEMS Technology

- Optical output power P > 45 mW @ 1585 cm-1
- SMSR > 20 dB



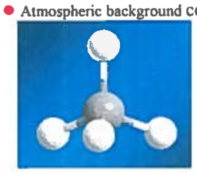
11 Fraunhofer

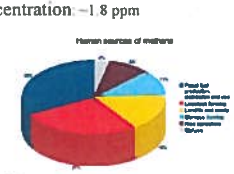
Methane Detection

Methane is one of the major atmospheric greenhouse gases contributing to global warming and climate change.

ARPA-E Monitor: Aeris Technologies, Inc and Thorlabs, Inc

- 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_2O
- Atmospheric background concentration: ~1.8 ppm





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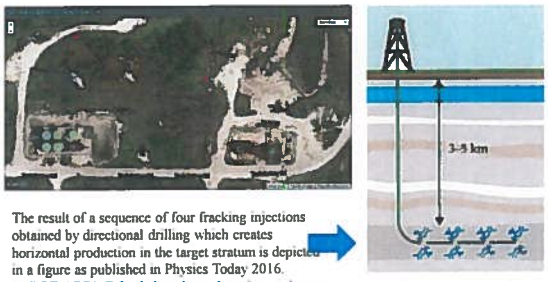
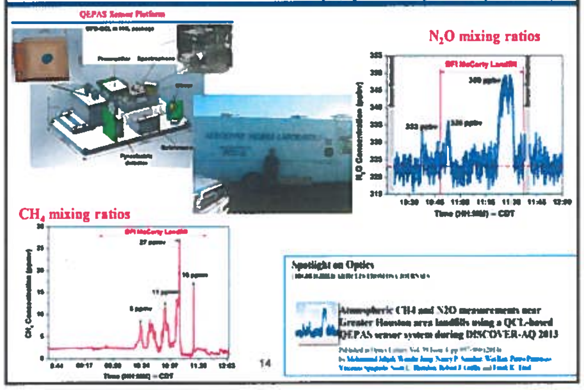
Typical Texas Oil & Gas Production Site near Houston



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_2O Measurements performed with a DFB-QCL based QEPAS Sensor installed in a Mobile Laboratory (operated by Aerodyne, Inc.)



Comparison of proposed Rice CH_4 Sensor System and current commercially available CH_4 Sensor Platforms

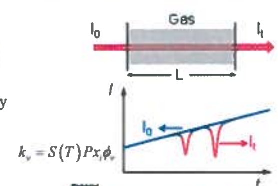
	Rice	Picarro	ABB-LGR I	ABB-LGR II	Aerodyne
Opt. Path length and method	MIR TDLAS: ~9 m	NIR CRDS: >2000m	NIR OA-ICOS: > 1000m	NIR OA-ICOS: > 2000m	MIR TDLAS: 70-100 m
Sensitivity/sec	< 5-10 ppb	1-2 ppb	5 ppb	2 ppb	<1 ppb
Accuracy (drift)	2 ppb stabilized	2 ppb	20 ppb, temp. stabilized	2 ppb	2 ppb
Cell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

US Department of Energy Advanced Research Project Agency - Energy (ARPA-E), Methane Observation Networks with Innovative Technology to obtain Reductions (MONITOR)

Spectroscopy Fundamentals

Beer's Law: $\frac{I_t}{I_o} = \exp(-k_v L)$

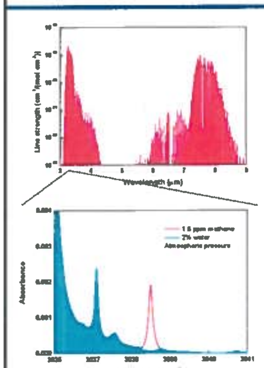
where: I_t is transmitted light intensity
I_0 is incident light intensity
k_v is absorption coefficient
L is optical path



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)

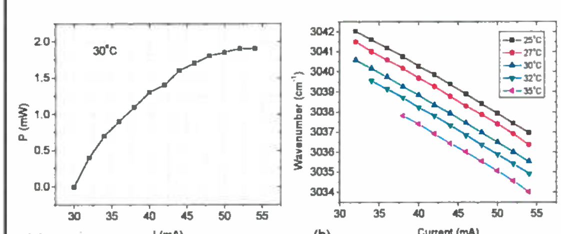
CH_4 Absorption Line Selection



- The fundamental ν_1 and ν_3 CH_4 bands are located at ~7.7 µm and ~3.3 µm, respectively
- A high detection sensitivity for methane measurements using quantum cascade lasers (QCLs) at 7.7 µm was previously reported
- Compact, TEC, CW, DFB ICLs emitting at 3-4 µm 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 3.3µm CH_4 absorption line can be used at atmospheric pressure

ICL Characterization & Performance Evaluation

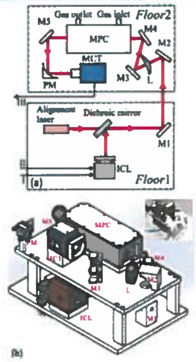
Nanoplus ICL, 3.291 µm center-wavelength



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

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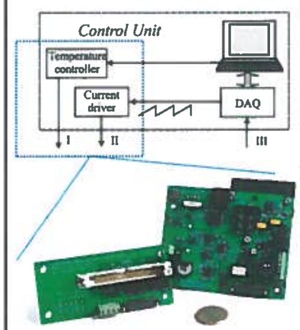
Current Electronics Controller for CH_4 Sensor System



- 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^2
  - Low noise characteristic: ≤1 nA/√Hz
  - On-board TEC driver: ±3 A, 15 V
  - Single voltage power supply 12-24V

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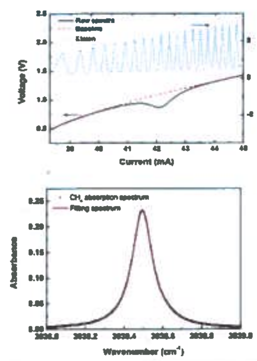
Data Processing for CH_4 Detection



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.

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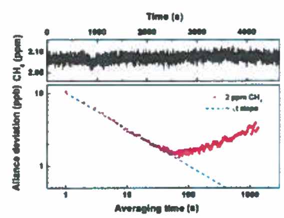
Allan-Werle Deviation Analysis



An Allan-Werle deviation plot was acquired in a time period of ~ 1.5 hours using a certified 2 ppm CH_4 cylinder with a 1 Hz sampling rate

1-s measurement precision is σ=10.53 ppb
60-s measurement precision is σ=1.43 ppb

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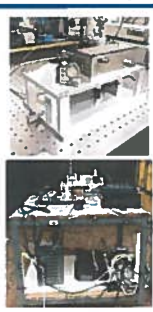
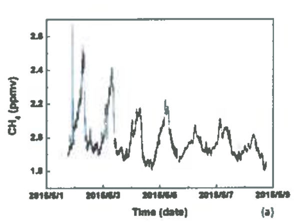
Stationary Laboratory Measurements





CH_4 concentrations measured over a 7-day period in ambient air on the Rice University campus during May 2015.

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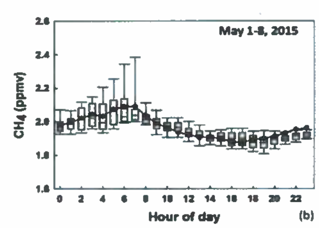
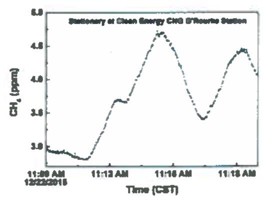
Laboratory Stationary Measurements



Diurnal variations of CH_4 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.

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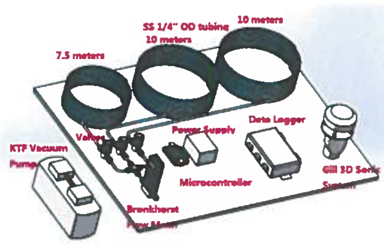
CH_4 Sensor System Summary (2015-2016)

- A 3.291 µm 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



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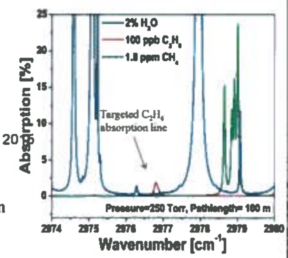
Motivation for mid-infrared Ethane (C_2H_6) Detection

- **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 C_2H_6, CH_4, and H_2O

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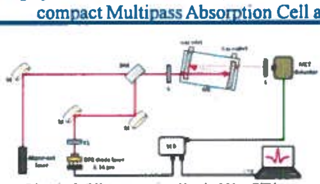
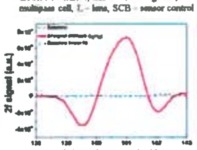
C_2H_6 Detection with a 3.36 µm CW DFB Diode Laser using a novel compact Multipass Absorption Cell and Control Electronics

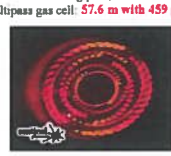


Schematic of a C_2H_6 gas sensor using a Nanoplus 3.36 µm DFB laser diode. M – mirror, CL – collimating lens, DM – dichroic mirror, MC – multipass cell, L – lens, SCB – sensor control board.

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



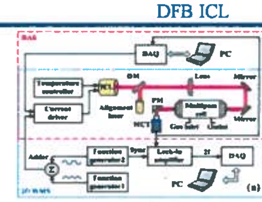
2f WMS signal for a C_2H_6 line at 2976.8 cm^{-1} at 200 Torr



Minimum detectable C_2H_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

Improved C_2H_6 sensor system using novel MPGC and a 3.337µm CW, DFB ICL



The upper part surrounded by red dash line is the detection scheme using direct absorption spectroscopy (DAS) technique, and the lower part surrounded by blue dot line is the detection scheme using second harmonic wavelength modulated spectroscopy (2f-WMS) technique. ICL: interband cascade laser; DM: dichroic mirror; M: plane mirror; PM: parabolic mirror; MCT: mercury-cadmium-telluride detector.

Minimum detectable C_2H_6 concentration:
7.92 ppbv @ 1s for DAS and ~1.19 ppbv @ 4s for WMS were obtained, which are limited by interference fringes due to unwanted etalons. A detection limit of 299 pptv for a data acquisition time of 108s with the use of WMS compared with 777 pptv @166s with DAS can be realized.

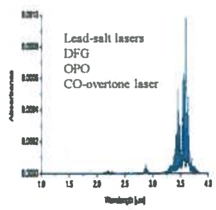
Innovative long path, small volume multipass gas cell: **57.6 m with 459 passes**

2f WMS signal for a C_2H_6 line at 2976.8 cm^{-1} and 200 Torr

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 H_2CO sources are vehicle exhaust and fugitive industrial emissions
  - Secondary H_2CO sources orginate 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 H_2CO

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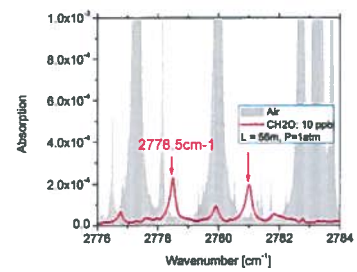
Formaldehyde Line Selection in the 3-4 μm Spectral Region



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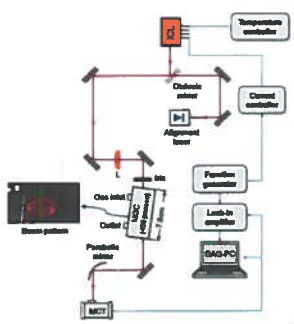
H_2CO Sensor Configuration

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

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

λ-modulation scheme



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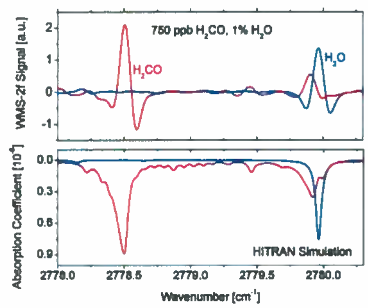
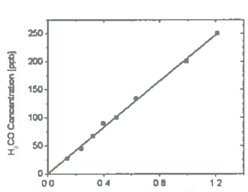
Representative H_2CO Sensor Calibration Results

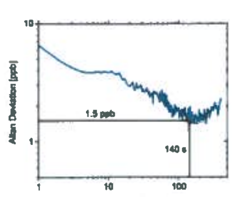
- H_2CO gas standard: Kin-Tek gas standard generator



H_2CO Detection Sensitivity

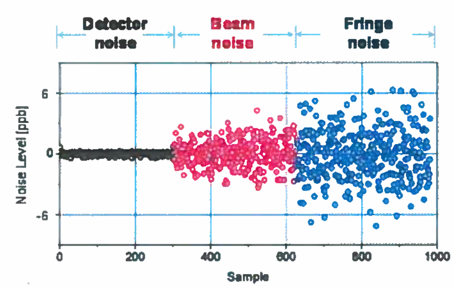
- Minimum detection concentration: 1.5 ppb with a 140 sec averaging time





Noise Limitations

- Zero air measurements: 1s sampling rate



Summary and Future Work (2014-15)

- Development of laser-based absorption sensors for H_2CO 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.

Summary, 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.

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- 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_2O_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)

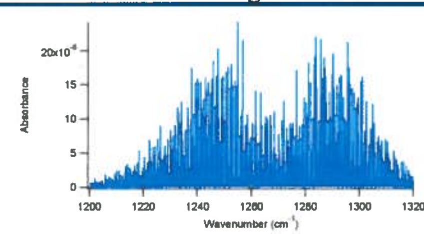
- VPHP is used for:
  - Decontamination of health-care and pharmaceutical facilities
  - Sterilization of medical equipment and packing materials in the food industry
- VPHP units: gas-phase H_2O_2 generated from concentrated liquid H_2O_2 solutions
- H_2O_2 concentrations between 200-1200 ppm are produced in the gas-phase and maintained for ~10 min
- After decontamination procedures, ambient H_2O_2 concentrations need to be monitored

Source: Bioquell UK Ltd

Techniques for H_2O_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

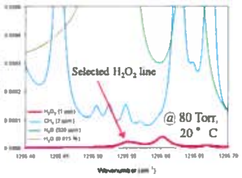
H_2O_2 Absorption in the mid-infrared spectral Region



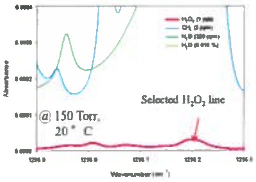
Fundamental ν_6 H_2O_2 band located at ~7.5-8.3 µm

Previous Employed Absorption Lines

Previous mid-IR sensor systems developed for H_2O_2 detection suffer from significant interferences from other gas species, particularly N_2O and H_2O vapor



1295.55 cm^{-1}
QEPAS-based sensor system *(Rei, et al., APL, 2014)*



1296.2 cm^{-1}
Multipass absorption-based sensor system *(Cao, et al., Adv. Opt. Tech 2014)*

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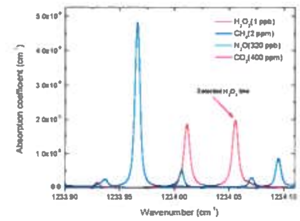
Selection of optimum Absorption Line

- A comprehensive spectral study was conducted
- Potential interferences from H_2O vapor, N_2O, CH_4 and CO_2 were considered
- An interference-free absorption line at 1234.05 cm^{-1} was selected for H_2O_2 detection



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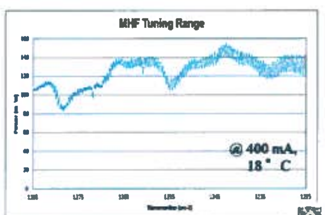
EC-QCL Operating Characteristics

- 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



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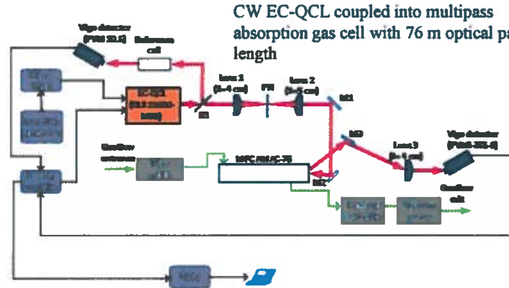
Sensor Architecture

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

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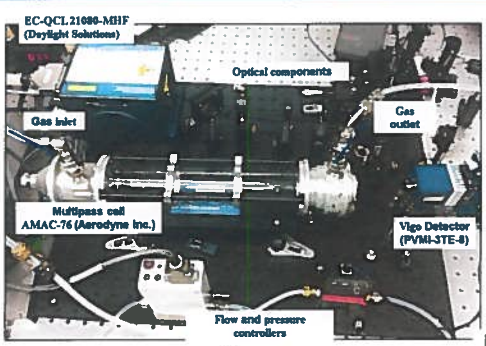
Photo of H_2O_2 Sensor Configuration



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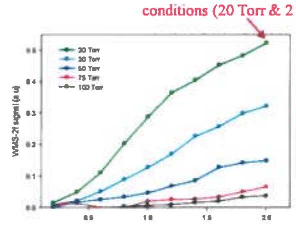
Parameter Optimization

- 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

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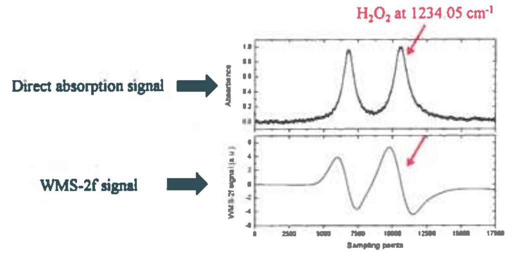
Sensor System Response



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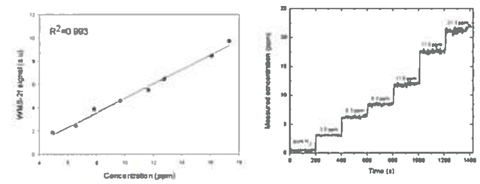
Calibration Results

- Different gas-phase H_2O_2 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 H_2O_2 concentrations between 3 and 21 ppm

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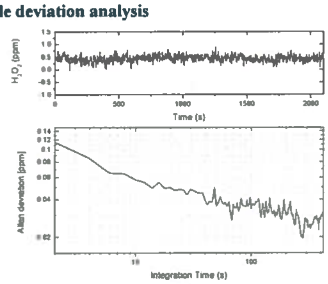
Sensor System Sensitivity

Allan-Werle deviation analysis



Minimum detection limit (MDL): 25 ppb @ 280-sec integration time

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H_2O_2 Sensor System Summary

- Selected absorption line at 1234. 05 cm^{-1} effectively alleviates interference issues identified previously for H_2O_2 detection
- MDL and ability to operate with no interference from water make our sensor system suitable for the monitoring of H_2O_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

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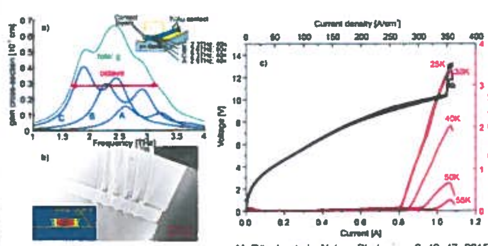
Broadband THz QCLs

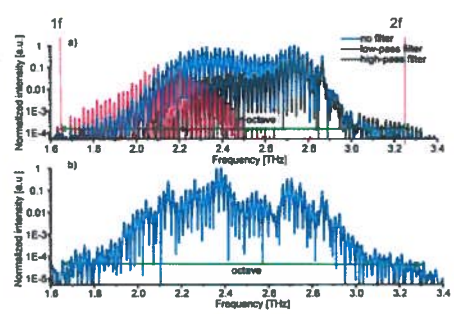
- Multistack QC laser with four quantum well active regions



M. Rösch, et al., *Nature Photonics*, 9, 42–47, 2015

RICE

Broadband Spectrum



M. Rösch, et al., *Nature Photonics*, 9, 42–47, 2015

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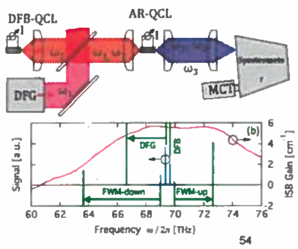
Experimental setup

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



P. Friedli, et al., Appl Phys Lett. 102, 222104, 2013.

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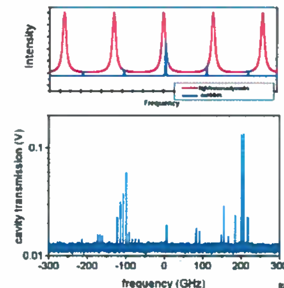
Use a Fabry-Perot as a spectroscopy tool

- Can be used to measure the spectrum
- S/N limited by stability



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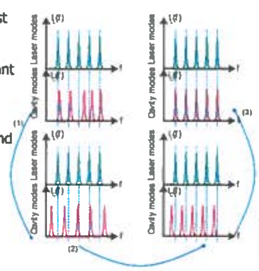
Cavity enhanced optical frequency comb spectroscopy

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.
   Intracavity dispersion compensation
1) Separation of the cavity eigenmodes and the separation of the frequency comb modes must be equal.
   Matching both cavity length
1) ntire comb must be shifted to overlap with the cavity eigenfrequencies.
   Alignment of the eigenfrequencies



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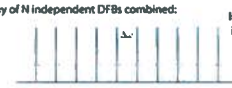
What is an optical frequency comb?

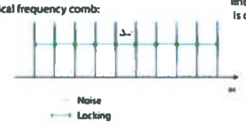
Array of N independent DFBs combined:



line-to-line frequency noise is uncorrelated

$\delta(\omega_i - \omega_j) \approx \sqrt{2}\delta(\omega_i)$

Optical frequency comb:



line-to-line frequency noise is correlated

$\delta(\omega_i - \omega_j) << \delta(\omega_i)$

The beat tone has a very narrow linewidth in a comb

Still, the array source may still be very interesting for some applications!!

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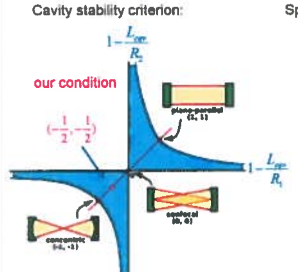
Cavity design for ICL-comb source

HR mirrors radius of curvature calculation

Cavity stability criterion:



R_1 : radius of curvature of mirror #1
R_2 : radius of curvature of mirror #2

Specs for cavity mirrors design:

For L_{cav} = 30 mm

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

$R_1 = R_2$ = 20 mm

- ✓ Plano-concave
- ✓ Diameter: ½"
- ✓ Radius of curvature: 20mm

H. Kogelnik, Proc. IEEE 54,1312-1329, 1966
N. Hodgson & H. Weber, "Laser Resonators & Beam Propagation" Chapter 1, Springer 2005

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Cavity design for ICL-comb source

Optical Cavity Performances:

- ✓ For effective length:

  Number of half round-trip:

  $$N = \frac{L_{eff}}{L_{cav}} = 6667$$

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

  $$R_{mirror}^{N} = 26\%$$

- ✓ Finesse $\Im$:

  $$\zeta = \frac{\pi}{1-R_{mirror}} \approx 15700$$

- ✓ Width of the cavity mode:

  $$\Delta\nu = \frac{FSR}{\zeta} = 637KHz$$

- ✓ Intra-cavity power enhancement factor:

  $$G = \frac{\zeta}{\pi} = 5000$$

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Cavity design for an ICL-comb source

Cavity length calculation

Frequency comb spacing: $\Delta f = \frac{c}{2nL}$

For ICL cavity length: $L = 2 \sim 4$ mm

L	ν
2mm	20GHz
3mm	15GHz
4mm	10GHz

Cavity mode spacing: $FSR = \frac{c}{2L_{cav}}$

Mode matching between comb and cavity modes: $\Delta f = n \cdot FSR$

For n=2

ν	L_{cav}
20GHz	15 mm
15GHz	20 mm
10GHz	30 mm

The possibility to tune the comb modes spacing allows us to choose a cavity length of 30mm, maximizing the effective absorption length.

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Sensing cavity design for ICL-comb 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)

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]

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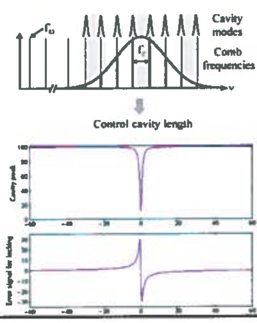
Proposed Sensing Cavity Locking to JPL-NRL ICL

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.

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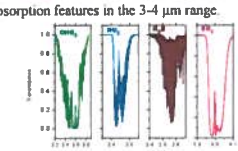
Schematic of CE-OFC sensor system

CE-OFC-SENSOR

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:

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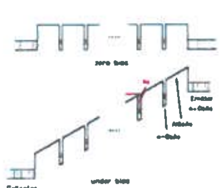
Fast detector

- Use an intersubband Quantum Well Infrared Photoconductor (QWIP) detector



Detector: H.C. Liu
Ref: H. Schneider and H.C. Liu, Springer book

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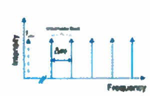
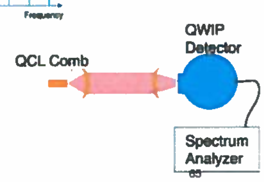
Is it a comb?

- Beat note measurement of the photocurrent (at 7.5GHz)
  - For modes of amplitude E_k, the photocurrent at $\Delta\omega$



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



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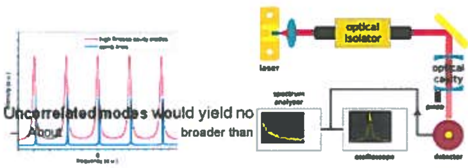
Frequency noise of a comb

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



- Uncorrelated modes would yield no
  - About broader than

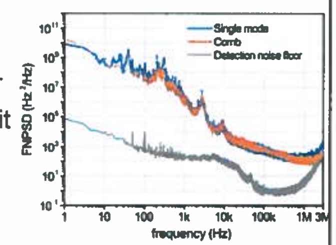
$N\sqrt{N} \approx 300\times$

$\sqrt{N}\delta\omega_i$

F. Cappelli, G. Villares et al, ArXiv

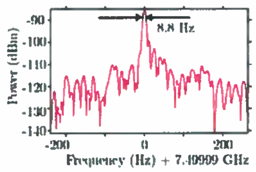
Frequency noise power spectral density

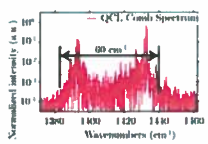
- Single mode versus comb
- Above noise floor
- No significant limit



Beatnote spectrum

- 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





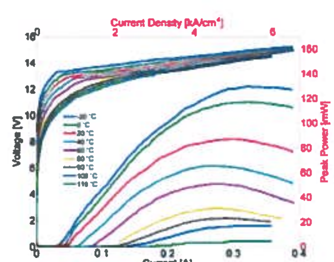
Summary, Conclusions and Future Developments

- 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.
- I-QEPAS demonstration with a power enhancement factor of 240 providing a corresponding increase in detection sensitivity
  - CO_2: for the P(42) absorption line located at ~ 4.33 µm (2311.105 cm⁻¹), a MDL of 300 pptv at 50mbar was achieved for a 20 sec integration time.
- Development of "active" I-QEPAS system for CO and NO detection in the few ppt range
- Development of Trace Gas Sensors for the monitoring of broadband absorbers: acetone(C_3H_6O), propane (C_3H_8), benzene (C_6H_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 & Maxion Technologies; DE-XXX
- National Science Foundation (NSF) ERC MIRTHE award
- NSF-ANR (France) award for international collaboration in chemistry
- Robert Welch Foundation grant C-0586

New QCL data at l ~ 3.3µm



I_{th} ~ 30mA
Pulsed operation

Johanna Wolf et al, unpublished, Feb 15, 2016