Mid-Infrared Quantum Cascade Laser based Trace Gas Sensor Technologies: Recent Advances and Applications

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OUTLINE

IAEA Visit

Rice University

- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New Mid-IR Sensing Technologies
- Laser Absorption Spectroscopy of UF_6 at 7.8, 12.2 and 16µm
- NH_3 Sensor Technology for Urban Environmental Monitoring at 10.3µm
- Future Directions and Conclusions

Work supported by NSF-ERC, NASA, DOE and The Robert Welch Foundation

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
  - 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 Biomedical and the Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

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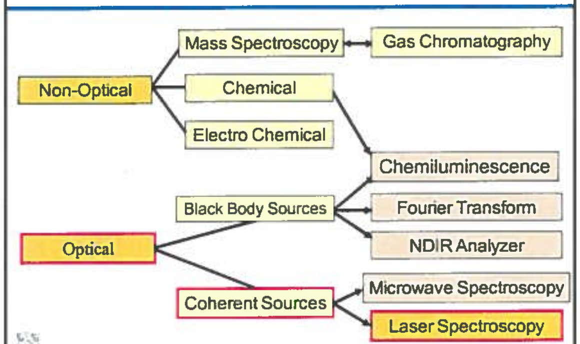
Methods for Trace Gas Detection



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Sensitivity Enhancement Techniques for Laser Spectroscopy

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot, Chernin)
  - Cavity Ringdown and Cavity Enhanced Spectroscopy
  - Open Path Monitoring (with & without retro-reflector): Standoff and Remote Detection
  - Fiberoptic Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy (PAS and QEPAS)
  - Laser Induced Breakdown Spectroscopy (LIBS)

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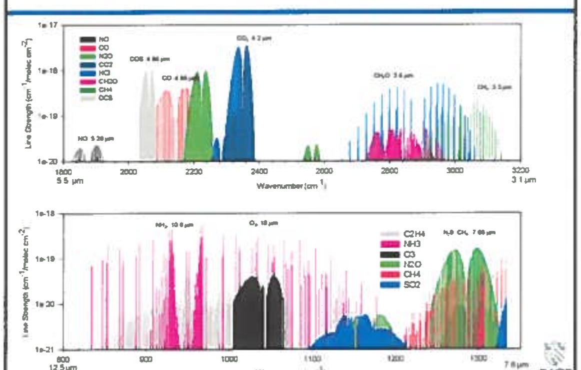
Simulated Mid-Infrared Molecular Absorption Spectra



Source: HITRAN 2000 database

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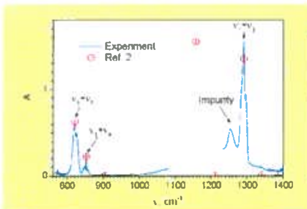
CW IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Optimum Wavelength, Power
Selectivity (Spectral Resolution)	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
Room Temperature Operation	High wall plug efficiency, no cryogenics or cooling water
Field deployable in harsh environments	Compact & Robust

UF_6 mid-infrared absorption bands

Absorption spectrum of UF_6 is broadband with unresolved rotational-vibrational spectral covering several tens of wavenumbers (cm^{-1}).



Assignment	ν, cm^{-1}	σ, cm^{-1}/atm
$2\nu_3+\nu_6$	1386±2	0.0018
$\nu_1+\nu_2+\nu_6$	1341	0.0088
$\nu_1+\nu_3$	1290.9±0.5	0.72
$2\nu_2+\nu_6$	1211±2	0.0007
$\nu_2+\nu_3$	1156.9±0.5	0.82
$\nu_3+2\nu_6$	905±2	0.0035
$\nu_1+\nu_4$	852.8±0.5	0.12
$\nu_3+\nu_5$	821	0.33
ν_3	625	350

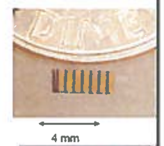
Absorption spectrum of gas mixture under investigation and observed spectral features identification.

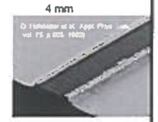
R.S. McDowell, L.B. Asprey, R.T. Paine, Vibrational spectrum and force field of uranium hexafluoride. -J. of Chemical Physics, Vol. 61, No. 9, 1974.

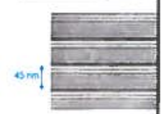
A. Nadezhdinskii et al., "Tunable Diode Laser Spectroscopy Application for Detection and Isotopes Ratio Measurements of UF6 Molecules."GPI, Moscow, March 2008

Key Characteristics of mid-IR QCL and ICL Sources – Jan '11

- **Band – structure engineered devices**
  (Emission wavelength is determined by layer thickness – MBE or MOCVD); mid-infrared QCLs operate from 3 to 24 μm (AlInAs/GaInAs)
  - 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**
  (4-24 μm for QCLs Type I) and 3-5 μm for ICLs (Type II) and GaSb based ICLs
  - 1.5 cm^{-1} using injection current control for DFB devices
  - 10-20 cm^{-1} using temperature control for DFB devices
  - > 430 cm^{-1} 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 and CW powers of > 30 W and 3 W respectively
  - >280 mW, TEC CW DFB @ 5 μm
  - > 600 mW (CW FP) @ RT, wall plug efficiency of ~17 % at 4.6 μm;







Motivation for High Wall Plug Efficiency

$$\eta_{wp} = \frac{P_{optical}}{P_{electrical}}$$

- High WPE essential for applications limited by:
  - Electrical power (Battery Capacity)
  - Thermal Control
  - Size
  - Weight

Optimization by Design, Processing & Packaging →

- CW, RT QC laser state of the art:
  - 2006: ~1%
  - 2008: ~12%
  - 2010: ~17%

Strategies for Improving WPE

Voltage Efficiency:
- Lower voltage defect
- Reduce contact resistance

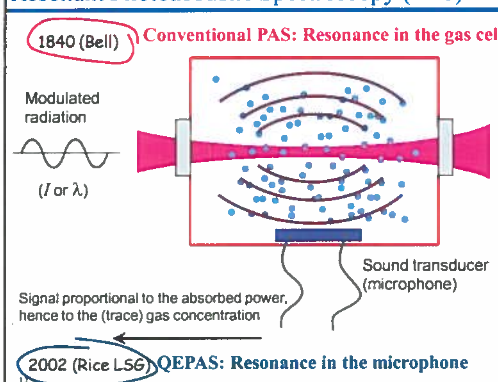
Extraction Efficiency:
- Implement high reflection (HR) and anti-reflection (AR) coatings
- Employ low loss waveguides
- Optimize cavity length

Internal Efficiency:
- Reduce thermionic emission
- Improve heat removal from active core
- Optimize injector barriers

Current Efficiency:
- Design high gain, low loss structures
- Lower threshold currents

Traditional and Quartz Enhanced Photoacoustic Spectroscopy

Resonant Photoacoustic Spectroscopy (PAS)



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Quartz Tuning Fork as a Resonant Microphone

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
  - 300K noise: x~10^{-11} cm
  - Breakdown: x~10^{-2} cm
- Wide temperature range: from 1.56K (superfluid helium) to ~700K
- Low cost (<$1)

Other parameters

- Resonant frequency ~32.8 kHz
- Force constant ~26800 N/m
- Electromechanical coefficient ~7□10⁻⁶ C/m

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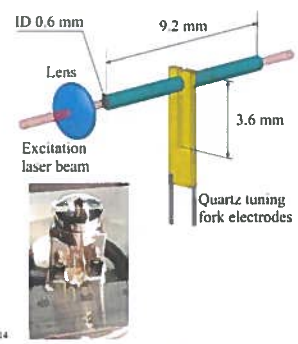
QEPAS spectrophone (QTF & Micro-resonator)



Micro-resonator (mR) tubes

- Must be close to QTF but not touch QTF (25-50 μm gaps).
- Optimum inner diameter: 0.6 mm
- Optimum micro-resonator tubes are 4.4 mm long (~□/4<l<□/2 for sound at 32.8 kHz)
- **Maximum SNR of QTF with mR tubes: ×30** (depending on gas composition and pressure)

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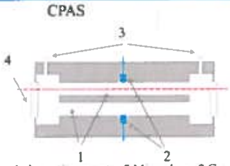
Comparison of State-of-the-Art CPAS & QEPAS Detection Modules

CPAS

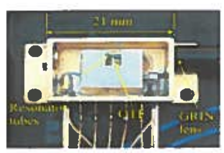


1. Acoustic resonator;2 Microphone;3 Gas inlet-outlet; 4. Windows

l=136 mm, Ø56.5 mm
Resonator: 4500 mm³
Optical pathlength: 90 mm
f_0=1790 Hz in N_2
Q=49 in N_2

C.-M. Lee, K. V. Bychkov, V. A. Kapitanov, A. I. Karapuzikov, Y. N. Ponomarev, I. V. Sherstov, V. A. Vasiliev, High-sensitivity laser photoacoustic leak detector, Opt. Eng. 46, 064302(2007)

QEPAS



21×12.7×8.5 mm
Resonator: 2 mm³
Optical pathlength: 9 mm
f_0=32735 Hz in N_2
Q=3630 in N_2

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CPAS vs. QEPAS: C_2H_2 and CO_2 Sensitivity Comparison

C_2H_2 : absorption line at 6529.17cm⁻¹, 10 ppmv

CO_2: 6361.25 cm⁻¹ , 100%

	10 ppm C_2H_2 in N_2		Pure CO_2	
	QEPAS	CPAS	QEPAS	CPAS
Signal, µV	6280	46	13880	413
Noise, µV	53	0.49	74	0.91
SNR	119	94	188	455
Laser Power, mW	37.2	39.0	21.1	24.3
NNEA, cm⁻¹W/√Hz	4.1×10^{-9}	5.4×10^{-9}	16.0×10^{-9}	7.6×10^{-9}

NNEA: normalized noise-equivalent absorption coefficient
(lower NNEA means better sensitivity)
Equivalent noise detection bandwidth is 0.833 Hz

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Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm³)
- 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_BT energy in the TF symmetric mode
- Absence of low-frequency noise: SNR scales as □t, up to t=3 hours as experimentally verified

QEPAS: some technical challenges

- Responsivity depends on the speed of sound and molecular energy transfer processes
- Sensitivity scales with laser power
- Effect of H_2O
- Cross sensitivity issues
- **Alignment cost**

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QEPAS Performance for 15 Trace Gas Species (Jan. '11)

Molecule (Host)	Frequency, cm⁻¹	Pressure, Torr	NNEA, cm⁻¹W/Hz^½	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10[illegible]	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	4.6×10[illegible]	50	0.16
C_2H_2 (N_2)*	6523.88	720	4.1×10[illegible]	57	0.03
NH_3 (N_2)*	6528.76	575	3.1×10[illegible]	60	0.06
C_2H_4 (N_2)*	6177.07	715	5.4×10[illegible]	15	1.7
CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10[illegible]	16	0.24
CO_2 (breath ~50% RH)	6361.25	150	8.2×10[illegible]	45	40
H_2S (N_2)*	6357.63	780	5.6×10[illegible]	45	5
HCl (N_2 dry)	5739.26	760	5.2×10[illegible]	15	0.7
CO_2 (N_2+1.5% H_2O)*	4991.26	50	1.4×10[illegible]	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10[illegible]	7.2	0.12
CO (N_2)	2196.66	50	5.3×10[illegible]	13	0.5
CO (propylene)	2196.66	50	7.4×10[illegible]	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10[illegible]	19	0.007
NO (N_2+H_2O)	1900.07	250	7.5×10[illegible]	100	0.003
C_2H_5OH (N_2)**	1934.2	770	2.2×10[illegible]	10	90
C_2HF_5 (N_2)***	1208.62	770	7.8×10[illegible]	6.6	0.009
NH_3 (N_2)*	1046.39	110	1.6×10[illegible]	20	0.006

* - 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 NH_3*,**

* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003); ** J. S. Pilgrim et al, SAE Intl. ICES 2007-01-3152

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Groups working on Quartz Enhanced Photoacoustic Spectroscopy

- Rice University
- UMBC, Baltimore, MD
- Savannah River National Laboratory, Aikin, SC
- Pacific Northwest National Laboratory, Richland, WA
- NASA- JSC, Houston, TX
- JPL, Pasadena, CA
- Woods Hole Oceanographic Institution, MA
- United States Naval Academy, Annapolis, MD
- Daylight Solutions Inc., San Diego, CA
- NKT Flexibles, Copenhagen, Denmark
- University of Bari, Italy
- TU Clausthal, Germany
- TU Vienna, Austria
- University of Montpellier, France
- Institute of Spectroscopy, Troitsk, Russia
- University of Littoral, Dunkerque, France
- Anhui Institute of Optics and Fine Mechanics, Heifei, China
- Zhejiang University, Hangzhou, China

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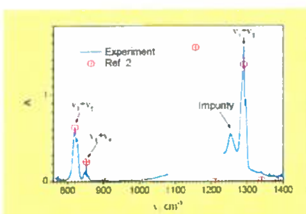
Recent Applications of Mid-Infrared Laser based Trace Gas Sensors

UF_6 mid-infrared Absorption Bands

Absorption spectrum of UF_6 is broadband with unresolved rotational-vibrational spectral covering several tens of wavenumbers (cm^{-1}).



Absorption spectrum of gas mixture under investigation and observed spectral features identification.

Assignment	ν, cm^{-1}	σ, cm^{-1}/atm
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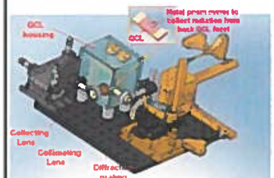
A. Nadezhdinskii et al. "Tunable Diode Laser Spectroscopy Application for Detection and Isotopes Ratio Measurements of UF6 Molecules "GPI, Moscow, March 2008

Opto-mechanical Platform for Evaluation of CW TEC FP QCL Gain Chips



Design schematic of FP-QCL optical mechanical evaluation platform

FP-QCL in quasi-Littrow configuration:
- feedback to the front facet (diffraction grating)
- back facet radiation analyzed by FTIR

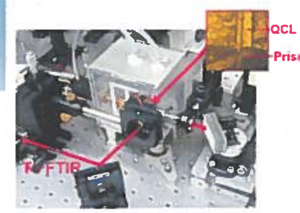


Photo of FP-QCL evaluation platform

Laser parameters that are investigated:
- Wavelength tunability
- Optical power
- Threshold value

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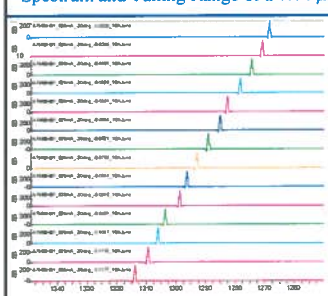
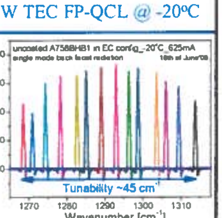
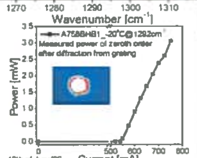
Spectrum and Tuning Range of a 7.74 μm CW TEC FP-QCL @ -20°C



FTIR spectra for 3mm cavity length 7.74 μm FP-QCL (A758BHB1) in external cavity





Resistance @ RT is R= 540Ω

Threshold with grating I_{th}= 543mA

Threshold without grating I_{th}= 568mA

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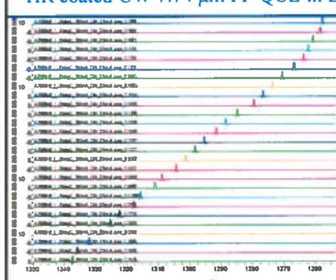
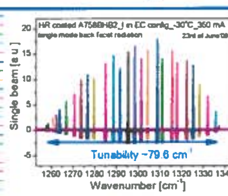
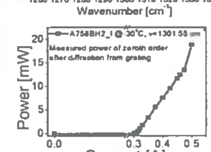
HR coated CW 7.74 μm FP-QCL in EC-configuration @ -30°C



FTIR spectra for 2mm cavity length 7.74 μm FP-QCL (A758BHB2.1) in external cavity





Resistance @ RT is R= 650Ω

Threshold with grating I_{th}= 301.5mA

Threshold without grating I_{th}= 350mA

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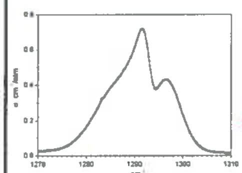
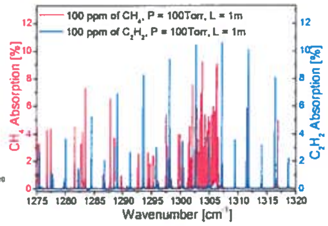
Simulant molecules for UF_6

Single mode spectral frequency tuning range of the tested FP-QCLs cover the $v_1 + v_3$ UF_6 combination band centered at ~1291cm^{-1} (7.745 μm) and several methane (CH_4) and acetylene (C_2H_2) absorption lines.



Experimental spectrum of absorption cross-section σ of the analyzed uranium hexafluoride sample (circles) as well as the obtained model spectra of $^{238}UF_6$ (solid line) and 235UF6 (dotted line) [1].



HITRAN simulation for 100 ppm of CH_4 and C_2H_2 concentrations. Spectra were simulated at a 100 Torr pressure and 1 meter pathlength.

Ref 1: A. G. Berezin,et al, Spectrochimica Acta Part A 66, 796-802 (2007).

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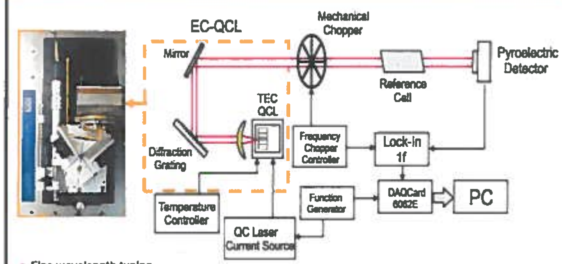
EC-QCL based LAS system for CH_4 measurements



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

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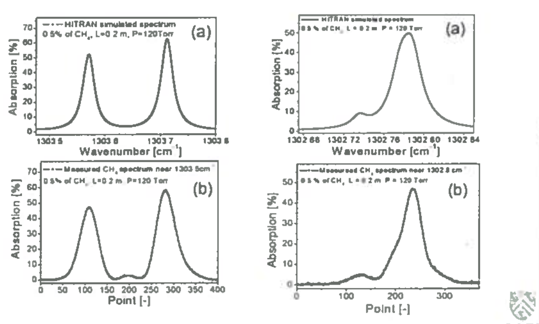
Preliminary Results of LAS for CH_4 detection



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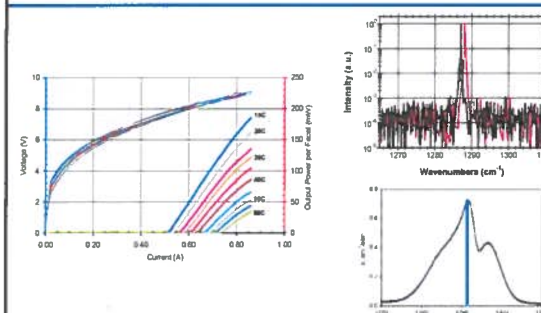
A 7.74μm DFB-QCL for AM-QEPAS detection technique



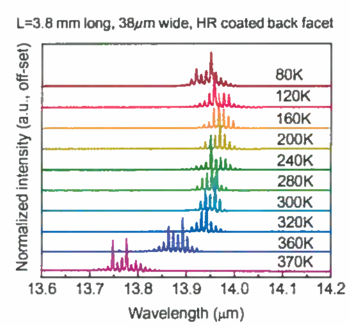
High power DFB-QCL and a sufficiently high UF_6 absorption value permit using a compact QEPAS sensor for laboratory measurements.

AdTech optics

Long-wavelength Quantum Cascade lasers

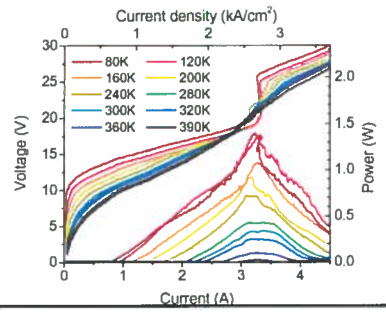
Laser Spectra of a pulsed 14 μm QCL

L=3.8 mm long, 38μm wide, HR coated back facet



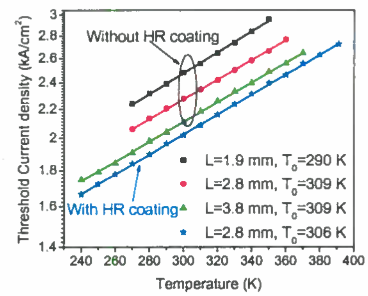
Pulsed Light-Current-Voltage (LIV) Characteristics

L=2.8 mm long, 38μm wide, 100 ns pulsewidth,~ 335 mW avg. power



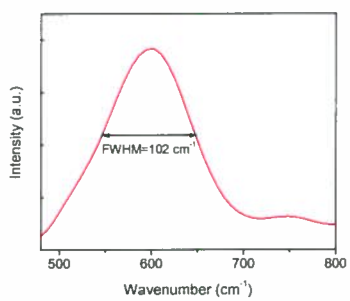
Threshold Current Density of a 14 μm QCL

38μm wide, 2.8 mm long laser with HR coated back facet



Electroluminescence Spectrum of a 16 μm QC Laser Structure

Preliminary results: Wavelength shifted to 16 μm (625 cm^{-1})



Motivation for NH_3 Detection

- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- Spacecraft related gas monitoring
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver diseases)

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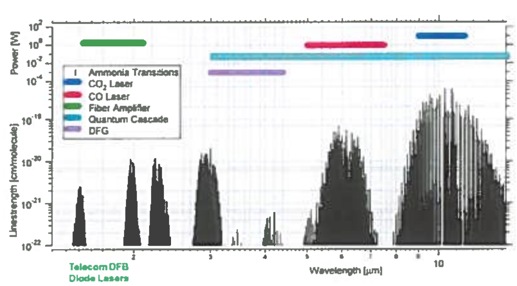
Infrared NH_3 Absorption Spectra



M. Webber et al. 2003, Pranalytica

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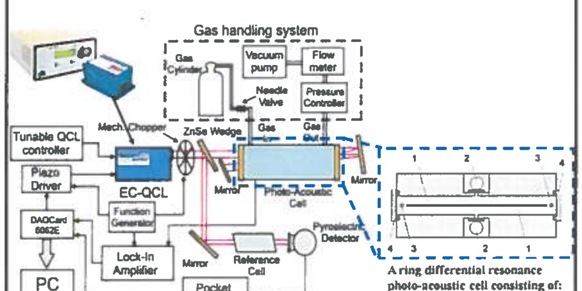
Mid-IR EC-QCL based AM-PAS Sensor Architecture for Atmospheric NH_3 Detection



A ring differential resonance photo-acoustic cell consisting of:
1. acoustic resonator,
2. microphone,
3. gas input and output,
4. window

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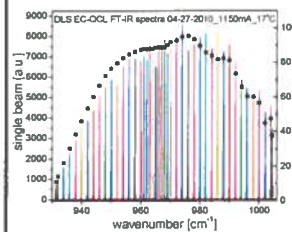
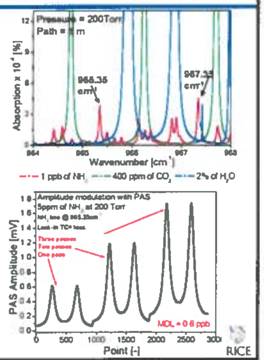
PAS based NH_3 Measurements with a 10.34μm DLS EC-QCL Spectroscopic Source





- Tuning range and optical power profile for the DLS Mid-IR CW EC-QC laser
- Tunability 73 cm⁻¹ (931 cm⁻¹ – 1004 cm⁻¹)
- P_{EC}-opt up to 95 mW (CW)
- Optimum wavelength 965.35 cm⁻¹

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NH_3 Sensor Deployment at the 60 m high Moody Tower Rooftop Site (U of H campus)

Moody Tower at the U of H campus, Houston

Monitoring of atmospheric NH_3 in the Greater Houston Area

View on Houston downtown from roof of the Moody Tower

Location of Moody Tower, University of Houston campus

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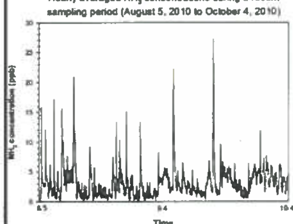
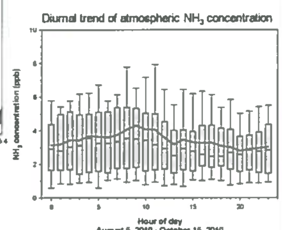
Data of Atmospheric NH_3 Concentration Levels for Houston

Hourly averaged NH_3 concentrations during a recent sampling period (August 5, 2010 to October 4, 2010)



- Range: 0.16 - 27.1 ppb.
- Mean: 3.2 ppb.

Diurnal trend of atmospheric NH_3 concentration



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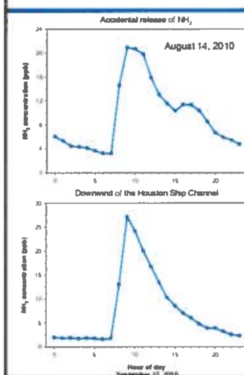
NH_3 detection due to fire resulting from truck collision



Aug 14 2010
The chemical incident happened at ~ 6 a.m. after two 18-wheelers headed southbound side-by-side collided. 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) HARC Project H-53.

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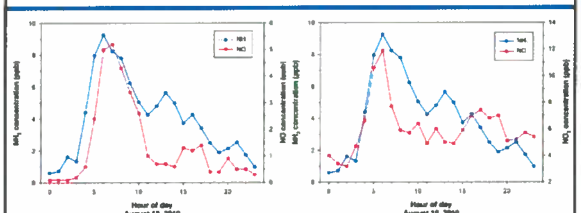
Increased NH_3 Concentrations related to Traffic Emissions during Houston, TX Rush Hour



NH_3 concentrations significantly increased on Aug 18, 2010 during rush hour and the wind direction was from the northwest to the Moody tower. During the same time period TCEQ Site No.408 located in northwest Houston measured NO and NO_2 enhancements at Site No.408, coincident with the increased NH_3 concentrations measured at the Moody Tower test site.

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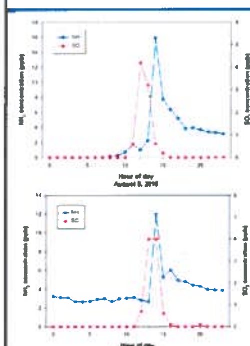
Sporadic increased NH_3 Concentration Levels related to Emissions by Parish Electric Power Plant, TX



The Parish power plant

Outlook of future optical Chemical Sensor Technology

- Improvements of mid-infrared QCL. and ICLs in areas such as wall plug efficiency, temperature performance, beam shape, packaging and price reduction
- Improvements of the existing sensing technologies (LAS, CES, QEPAS, EWS) using novel, thermoelectrically cooled, cw, distributed feedback (DFB), high power and broadly wavelength tunable mid-IR QCLs and ICLs.
- New applications enabled by novel broadly wavelength tunable and ultra-compact single frequency quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular , UF_6, VOCs and HCs)

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Performance evaluation of UF_6 Detection with a 16 μm LIDAR using Reflection from a topographic Target

Ideal conditions:

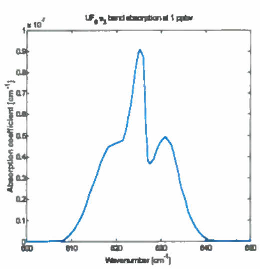
- Light source: 100 mW CW RT DFB QCL at 16 μm (625 cm-1)
- Collection mirror :~10" in diameter
- Photodetector:
  Hamamatsu MCT photoconductive LN-cooled detector, tuned to the peak sensitivity at 16 μm. Detector area 1 × 1 mm², $D^* = 10^{10}$ cm·Hz$^{1/2}$/W, NEP = 10^{-11} W/Hz$^{1/2}$.
- Distance between source/receiver to target: 200 m
- Diffuse reflectivity from target: ~50%
- Neglecting scattering and background absorption
- Neglecting turbulence

Potential problems:

- Background absorption of water, CO_2 and O_3
- Concentration of UF_6 in air is unknown. It can be low due to the reaction of UF_6 with water. This will require a special investigation.
- Differential reflectivity of natural targets at 16 μm is unknown. May impact detectivity. Investigation is required.

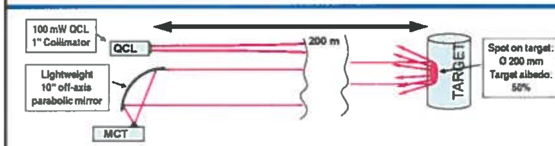
Properties of UF_6 ν_3 absorption band at 16 μm

- Very large absorption coefficient, peak fractional absorption $k{\cdot}L$ for a roundtrip path L = 400 m and a 1 ppbv concentration is 3.5×10^{-3}
- Absorption feature is too broad for wavelength modulation spectroscopy. An External Cavity QCL with a tuning range of ~30 cm^{-1} will be needed.
- High value of absorption permits using a compact QEPAS sensor



G. Baldaccini, et. al., "Diode Laser Absorption of UF_6 at Room Temperature around 16 μm.", Nuovo Cimento, **8**, No 2, pp. 203 – 210 (1986)

Potential LIDAR System Layout and Performance



The power P_r received by a topographic target DIAL (LIDAR Equation)[1]

$$P_r = \frac{P_t \rho A \eta \cos(\theta)}{\pi R^2} \exp[-2(\alpha C + \beta) R]$$

Parameters:

Transmitter laser power	P_t = 100 mW
Target albedo	ρ = 0.5
Detector area (10")	A = 0.051 m²
System optical efficiency	η = 1
Attenuation due to scatter and absorption	β = 0 cm-1
Distance to target	R = 200 m

α and C are the analyte absorption coefficient and concentration

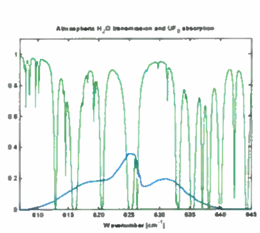
Results:

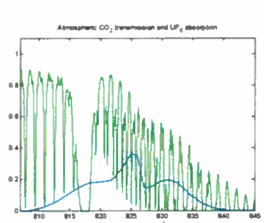
Received power T_r:	20 nW
With detector NEP of 10 pW/√Hz the S/N ratio is	2000/√Hz
Noise equivalent UF_6 concentration	140 pptv/√Hz

[1] W Grant, Applied Optics, 21, pp 2390 – 2394 (1982)

Challenge: Atmospheric Water and CO_2

Transmission spectra for 200 m roundtrip of atmospheric water (50% relative humidity @ 25°C) and carbon dioxide with the overlap of the 16 μm ν_3 absorption band of 100 ppb UF_6 (blue spectrum)



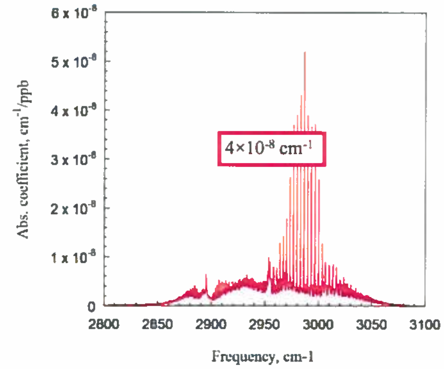


16 μm (625 cm^{-1}) UF_6 LIDAR Summary

- LIDAR performance assuming ideal conditions and a QCL power of 100 mW allows a detection of 140 pptv of UF_6 at a distance of 200m from the target
- Absorption bands of atmospheric water and carbon dioxide overlap strongly with the ν_3 absorption band of UF_6 at 16 μm
- With a broadly and rapidly tunable (>30 cm^{-1} and >1000 Hz) 100mW EC-QCL it may be possible to detect UF_6 concentrations in air of ~ 1 ppbv
- Strong UF_6 absorption may permit a design of an ultra-compact, portable QEPAS detector with a detection sensitivity of ~1 ppbv using the effect of the QEPAS signal phase shift difference of UF_6 and interfering gases (see A. Kosterev et al. "Photoacoustic phase shift as a chemically selective spectroscopic parameter" *Applied Physics B* **78**, 673-676, 2004)

Future Directions and Outlook of Chemical Trace Gas Sensing Technology

Ethane Absorption Spectrum



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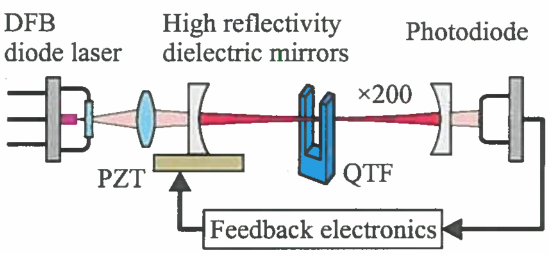
Proposed QEPAS-OPBC Sensor Configuration



Circulating power = Source power / (1-*R*)

Very conservatively, ×100

Alex Kachanov Skymoon Research R & D

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QEPAS MDAL Comparison with CRDS, ICOS & TDLAS

Minimum Detectable Absorption Loss (MDAL) [cm^{-1}/□Hz] can be used for comparison of different techniques:

- Cavity Ring Down Spectroscopy (CRDS) : ~ 3×10^{-11}
- Integrated Output Spectroscopy (ICOS): ~ 3×10^{-11}
- Multipass Gas Cell based TDLAS: ~ 2×10^{-11}

- QEPAS (Sept 2009) MDAL (DFB 100mW): 1.9×10^{-8}
- QEPAS-OPBC MDAL (DFB 20 mW): 3.2×10^{-10}
- QEPAS-OPBC + micro-resonator (estimated): ~ 7×10^{-12}

QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS and retain most of the performance merits of QEPAS

52 Alex Kachanov, Skymoon Research R & D

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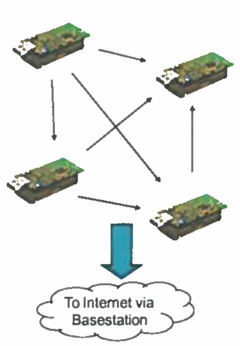
Wireless Sensor Networks for Trace Gas Sensing



- Advantages?
  - Spatial resolution
  - Measure fluxes
  - Detect spike before diffusion
- What is needed?
  - Ultra low power
  - Fast duty cycling capability
  - Low cost, Replicable
  - Ultra miniature
  - Autonomy (no consumables; auto-processing; auto start)

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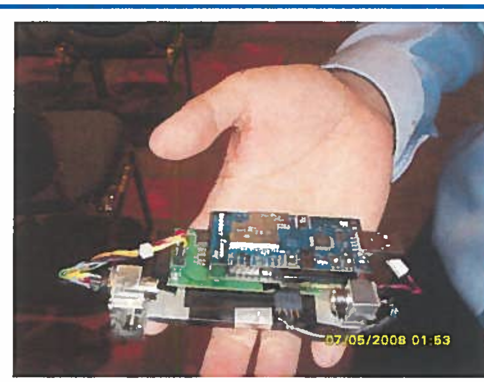
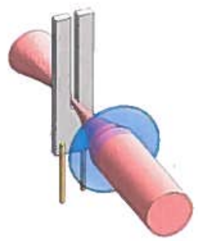
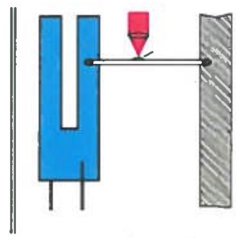
Ultra-compact Diode Laser based Trace Gas Sensor



Resonant Optothermoacoustic Detection (ROTADE)



Rotade sensor for measuring weak optical absorption in gases



Rotade sensor for detecting optical absorption by micro-objects via linked thermal effects

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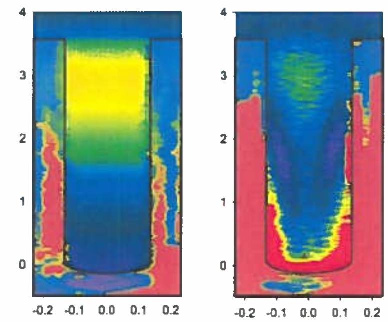
Near infrared QTF and ROTADE Images



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