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Recent progress of mid–infrared compact, field deployable sensors recent advances and their real world applications in industry, environment and defense

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OUTLINE

NEO Monitors
April 12, 2016
OSLO, Norway

- Novel Laser-Based Trace Gas Sensor Technology
  - Mid-IR TDLAS based on a Novel Multipass Gas Cell Design
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
- Examples of four Mid-infrared Trace Gas Species
  - CH_4, C_2H_6, H_2CO and H_2S
- Future Directions of QEPAS-Based Trace Gas Sensor Technologies and Conclusions
  - I (Intra-cavity) – QEPAS
  - New custom QTFs

Research support by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation as well as sub-awards ARPA-E from AERIS Technologies & Maxion-Thorlabs is acknowledged

Outline

- Novel Laser-Based Trace Gas Sensor Technology
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
  - Mid-infrared & THz spectral ranges
  - Recent near infrared QEPAS sensor technology
  - Sensor performance improvements resulting from custom QTFs
- **Applications of QEPAS based sensor systems**
- **Six mid-infrared Trace Gas Species**
- NO, NH_3, CO_2, CO, SF_6, H_2S
- **Two THz Trace Gas Species**
- H_2S and CH_3OH (Methanol)
- **Future Directions of QEPAS-Based Trace Gas Sensor Technologies and Conclusions**
  I (Intra-cavity) – QEPAS

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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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NASA's Horizons spacecraft flew past Pluto in July, 2015. Icy Heart of Pluto: Nitrogen snow and methane ice cover Tombaugh Region. Science March 14, 2016

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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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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

6

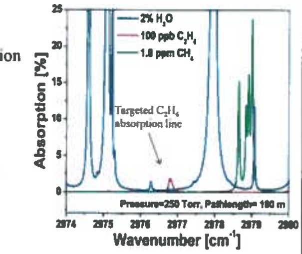
Key Characteristics of Mid-IR QCL & ICL Sources –April 2016

- **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 6 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 & ICLs at RT temperature**
  - TEC QCL pulsed peak power of ~203 W with 10% wall plug efficiency
  - CW QCL powers of ~ 5 W with 23% wall plug efficiency at 293 K
  - > 600 mW CW DFB at TEC/RT, wall plug efficiency 23% at 4.6 µm
  - > 5mW CW, DFB ICL at TEC/RT

4 mm

Motivation for Mid-infrared C_2H_6 Detection

- **Atmospheric chemistry and climate**
  - Fossil fuel and biofuel consumption
  - Biomass burning
  - Vegetation/soil
  - Natural gas loss
- **Application in medical breath analysis**
  - Asthma
  - Schizophrenia
  - Lung cancer
  - Vitamin E deficiency



HITRAN absorption spectra of C_2H_6, CH_4, and H_2O

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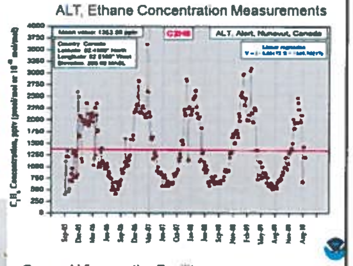
NOAA Monitoring & Sampling: Alert, Nunavut, Canada



General View on the Facility
Latitude: 82.4508° North
Longitude: 62.5056° West
Elevation: 200.00 m

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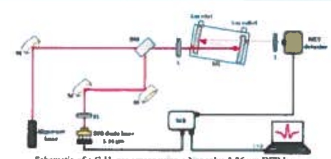
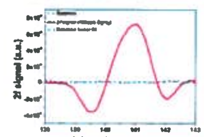
C_2H_6 Detection with a 3.36 µm CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics



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

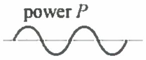
MGC dimensions: **17 x 6.5 x 5.5 (cm)**
Distance between the MGC mirrors: 12.5 cm

Minimum detectable C_2H_6 concentration:
~ 740 pptv (1σ; 1 s time resolution)

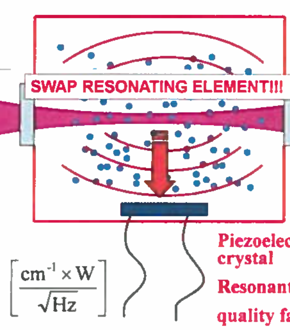
From Conventional PAS to Quartz Enhanced PAS (QEPAS)

Q>>1000
Cell is OPTIONAL!
V-effective volume

Laser beam, power *P*



Modulated (*P* or λ) at *f* or *f*/2



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

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

Piezoelectric crystal
Resonant at *f*
quality factor *Q*

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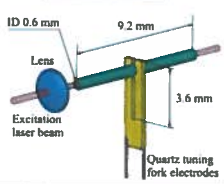
Quartz Tuning Fork as a Resonant Microphone for QEPAS



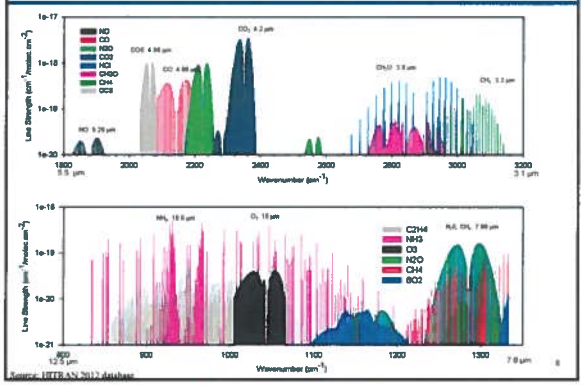
Unique Properties
- Extremely low internal losses:
  - Q ~ 10,000 at 1 atm
  - Q ~ 100,000 in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range (~10^6) – linear from thermal noise to breakdown deformation
  - 300K noise: $x \sim 10^{-11}$ cm
  - Breakdown: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

Acoustic Micro-resonator (µR) Tubes
- Optimum inner diameter: 0.6 mm; µR-QTF gap is 25-50 µm
- Optimum µR tubes must be ~ 4.4 mm long (~λ/4<l<λ/2 for sound at 32.8 kHz)
- SNR of QTF with µR tubes: × 30 (depending on gas composition and pressure)

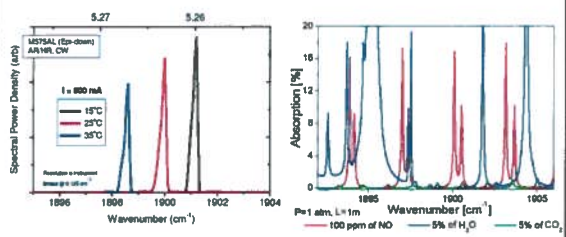
Motivation for Nitric Oxide Detection

- **NO in medicine and biology**
  - Important signaling molecule in physiological processes in humans and mammals (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, chronic obstructive pulmonary disease (COPD) & lung rejection
- **Environmental pollutant gas monitoring**
  - Ozone depletion
  - Precursor of smog and acid rain
  - NO_X monitoring from automobile exhaust and power plant emissions
- **Atmospheric Chemistry**

HITRAN Simulated Mid-Infrared Molecular Absorption Spectra

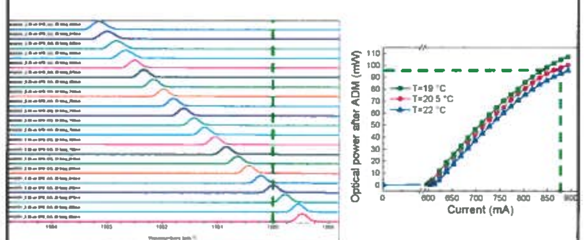


Emission spectra of a 1900 cm^{-1} TEC DFB QCL and HITRAN simulated spectra of NO, H_2O & CO_2



Output power: 117 mW @ 25 C
Thorlabs/Maxion

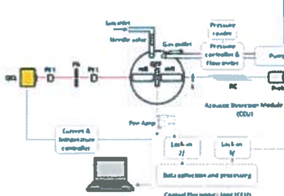
Performance of a 5.26 μm CW HHL TEC DFB-QCL



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

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

CW TEC DFB QCL based QEPAS NO Gas Sensor

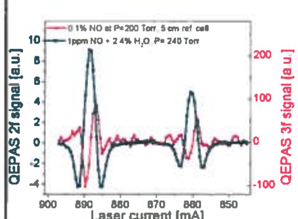


Schematic of a DFB-QCL based Gas Sensor.
PcL – plano-convex lens, Ph – pinhole,
QTF – quartz tuning fork, mR – microresonator,
RC- reference cell, P-elec D – pyro electric detector

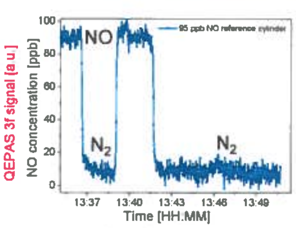
CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 630 mA and 20.5 deg C through tubes after ADM

Compact Prototype NO Sensor (September 2012)

Performance of CW DFB-QCL based WMS QEPAS NO Sensor Platform



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



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

Minimum detectable NO concentration is:
~3 ppbv (1σ; 1 s time resolution)

Motivation for NH_3 Detection

- **Medical diagnostics**
  - Kidney disease
  - Liver failure and Cirrhosis
  - Brain Cells dysfunction
  - Drowsiness and Coma
- **Atmospheric chemistry**
- **Pollutant gases monitoring**
- **Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques associated with electric power plants**
- **Spacecraft related trace gas monitoring**

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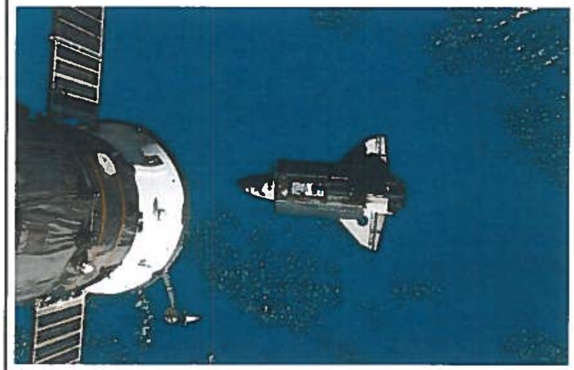
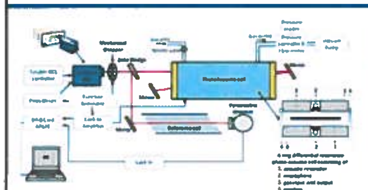
Ammonia Leaks from ISS May 2013

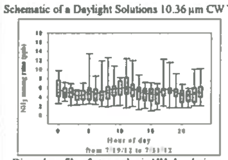


Atmospheric NH_3 Measurements using an EC-QCL PAS Sensor

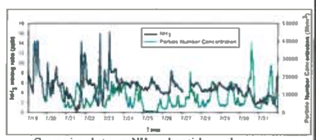


Schematic of a Daylight Solutions 10.36 µm CW TEC EC-QCL based PAS NH_3 Sensor.

NH_3 sensor deployed at the UH Moody Tower rooftop monitoring site.

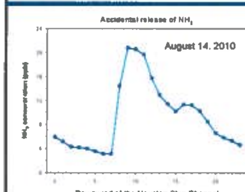


Diurnal profile of atmospheric NH_3 levels in Houston, TX.

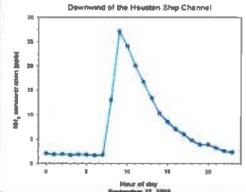


Comparison between NH_3 and particle number concentration time series from July 19 to July 31 2012

NH_3 Detection due to a Fire resulting from a Truck Collision



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



Estimated hourly NH_3 emission from the Houston Ship Channel area is about 0.25 ton. Mellqvist et al., (2007) Final Report, HARC Project H-53

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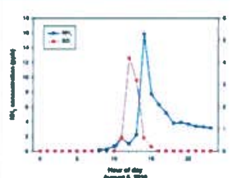
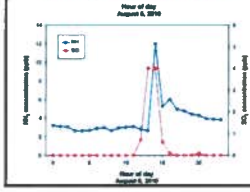
Sporadic increase in NH_3 concentration levels related to emissions by the Parish Electric Power Plant, TX





The Parish electric power plant is located near the Brazos River in Fort Bend County, Texas (~27 miles SW from downtown Houston)

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Fort-Worth, Dallas(TX) CAMS 75 & TCEQ monitoring site

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Instrumentation available at CAMS 75 & TCEQ monitoring site

Species/parameter	Measurement technique
NH_3	Daylight Solutions External Cavity Quantum Cascade Laser (Photo-acoustic Spectroscopy)
CO	Thermo Electron Corp. 48C Trace Level CO Analyzer (Gas Filter Correlation)
SO_2	Thermo Electron Corp. 43C Trace Level SO_2 Analyzer (Pulsed Fluorescence)
NO_x	Thermo Electron Corp. 42C Trace Level NO-NO_2-NO_x Analyzer (Chemiluminescence)
NO_y	Thermo Electron Corp. 42C-Y NO_y Analyzer (Molybdenum Converter)
HNO_3	Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)
HCl	Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)
VOC$_s$	IONICON Analytik Proton Transfer Reaction Mass Spectrometer and TCEQ Automated Gas Chromatograph
PBL height	Vaisala Ceilometer CL31 with updated firmware to work with Vaisala Boundary Layer View software
Temperature	Campbell Scientific 10MP45C Platinum Resistance Thermometer
Wind speed	Campbell Scientific 05103 R. M. Young Wind Monitor
Wind direction	Campbell Scientific 05103 R. M. Young Wind Monitor

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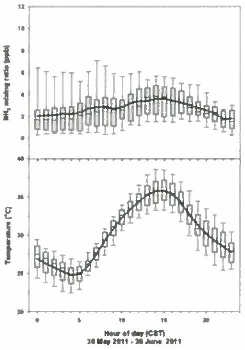
NH_3 Source Attribution & Temperature Variations

- Emission events from specified point sources (i.e., industrial facilities)
- Estimated NH_3 emissions from cows (1.3 tons/day)
- Estimated NH_3 emissions from soil and vegetation (0.15 tons/day)
- EPA PMF (biogenic:74.1%; light duty vehicles:12.1%; natural gas/industry: 9.4%; heavy duty vehicles:4.4%)
- Livestock might account for approximately 66.4% of total NH_3 emissions
- Increased contribution from industry (→18.9%)



Motivation for Carbon Monoxide Detection

- **CO in Medicine and Biology**
  - Hypertension and abnormality in heme metabolism
- **Public Health**
  - Extremely dangerous to human life even at a low concentrations. Therefore CO must be carefully monitored at low concentration levels (<35 ppm).
- **Atmospheric Chemistry**
  - Incomplete combustion of natural gas, fossil fuel and other carbon containing fuels.
  - Impact on atmospheric chemistry through its reaction with hydroxyl (OH) for troposphere ozone formation and changing the level of greenhouse gases (e.g. CH_4).

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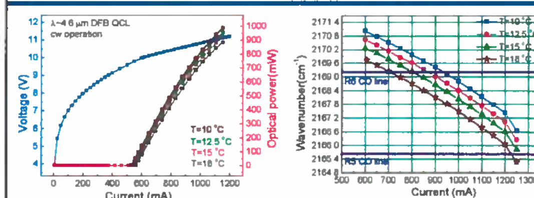
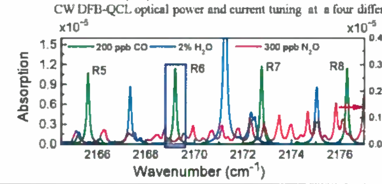
Performance of a 4.61µm high power CW TEC DFB QCL



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



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

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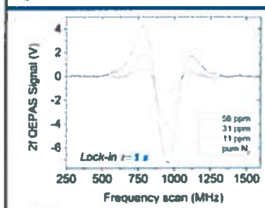
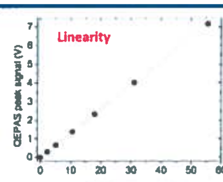
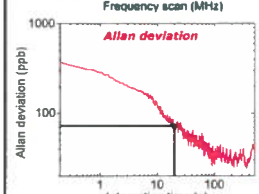
QEPAS Performance in locked mode and long term stability







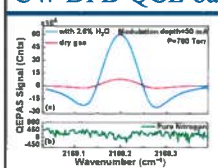
Noise Equivalent Concentration:

NEC = 72 ppb @ 20sec integration time

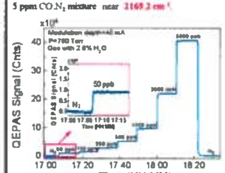
Normalized Noise Equivalent Absorption:

NNEA = 7.5×10^{-8} cm^{-1}W(Hz)$^{-1/2}$

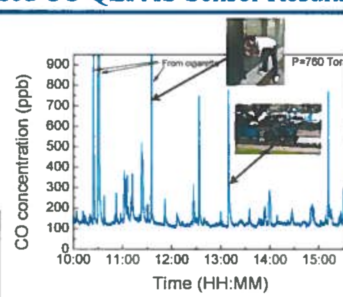
CW DFB-QCL based CO QEPAS Sensor Results



2f QEPAS signal for dry (red) and moisturized (blue) 5 ppm CO:N_2 mixture near 2169.2 cm^{-1}.



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



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

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

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Motivation for NH_3 Detection

- **Medical diagnostics**
  - Kidney disease
  - Liver failure and Cirrhosis
  - Brain Cells dysfunction
  - Drowsiness and Coma
- **Atmospheric chemistry**
- **Pollutant gases monitoring**
- **Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques associated with electric power plants**
- **Spacecraft related trace gas monitoring**

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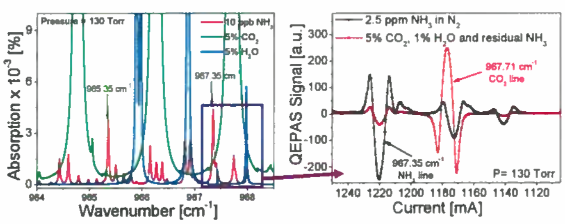
Important Breath Molecules

Molecule	Formula	Biological/Pathology Indication	Center wavelength [µm]
Pentane	C_5H_{12}	Inflammatory diseases, transplant rejection	6.8
Ethane	C_2H_6	Lipid peroxidation and oxidation stress, lung cancer (low ppbv range)	6.8
Carbon Dioxide isotope ratio	$^{13}CO_2/^{12}CO_2$	Helicobacter pylori infection (peptic ulcers, gastric cancer)	4.4
Carbonyl Sulfide	COS	Liver disease, acute rejection in lung transplant recipients (10-600 ppbv)	4.8
Carbon Disulfide	CS_2	Disulfiram treatment for alcoholism	6.6
Ammonia	NH_3	Liver and renal diseases, exercise physiology	10.3
Formaldehyde	CH_2O	Cancerous tumors (400-1500 ppbv)	5.7
Nitric Oxide	NO	Nitric oxide synthase activity, inflammatory and immune responses (e.g. asthma) and vascular smooth muscle response (6-100 ppb)	5.3
Hydrogen Peroxide	H_2O_2	Airway inflammation, oxidative stress (1-5 ppbv)	7.9
Carbon Monoxide	CO	Smoking response, lipid peroxidation, CO poisoning, vascular smooth muscle response	4.7
Ethylene	C_2H_4	Oxidative stress, cancer	10.5
Acetone	C_3H_6O	Ketosis, diabetes mellitus	7.3

Optimum NH_3 Line Selection for a 10.34 µm CW TEC DFB QCL



Simulated HITRAN high resolution spectra @ 130 Torr indicating two NH_3 absorption lines of interest

No overlap between NH_3 and CO_2 absorption lines was observed for the selected 967.35 cm^{-1} NH_3 absorption line in the v_2 R-band.

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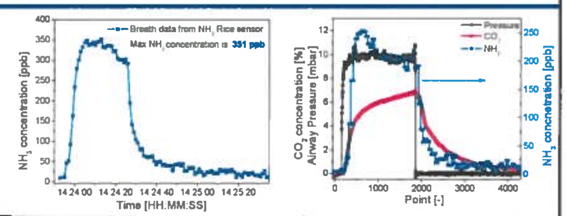
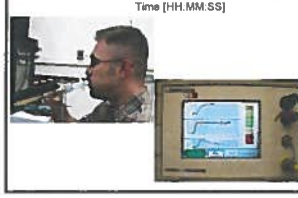
Real-time exhaled human NH_3 Breath Measurements



Airway pressure (black), CO_2 (red), and NH_3 (blue) profiles of a single breath exhalation lasting 40sec.



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

Minimum detectable concentration of NH_3 is:
~6 ppbv at 967.35 cm^{-1} (1σ; 1 s time resolution)

Motivation for  Detection

Industrial and semiconductor processes

- SF_6 is used in semiconductor manufacturing for plasma etching of metal silicides, nitrides and oxides
- SF_6 is an insulating material used as a dielectric in electrical transformers
- SF_6 is a tracer gas for leak detection

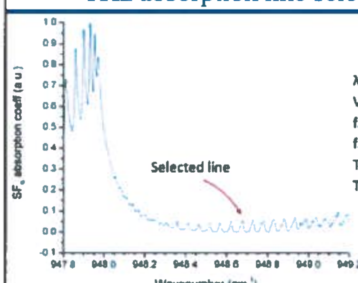
Line Selection Criteria for QEPAS:

1. High absorption strength
2. Well resolved spectral absorption features
3. Selected line far from interfering gases such as CO_2 and H_2O

} **Low gas Pressure**

Due to the fast vibrational-translation relaxation rate of SF_6, it is possible to work at low pressures (<100 Torr) and take advantage from the typically high quality factor Q of the QTF (>20,000) at these conditions

THz absorption line selection for SF_6

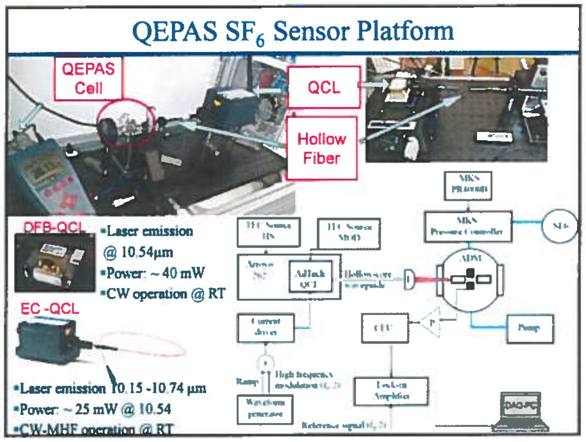


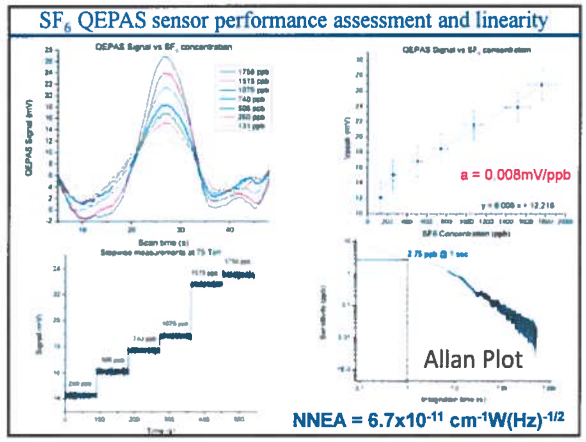
Working Conditions

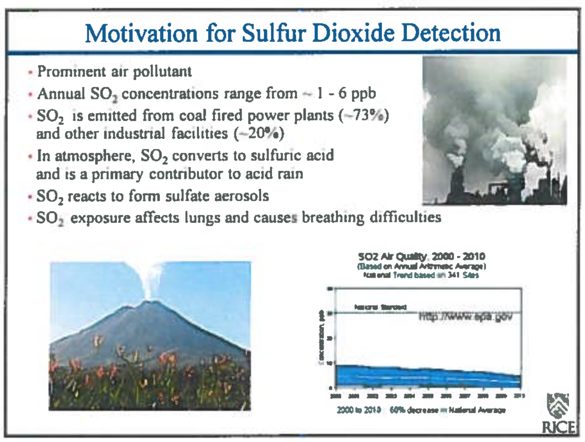
$λ_{QCL}$ = 948,68 cm^{-1}
V_{ramp} = 26 - 45 V
f_{ramp} = 5 mHz
$f_{modulation}$ = 16,37970 kHz
Tc (lock-in) = 100 ms
Tc (labview) = 300 ms

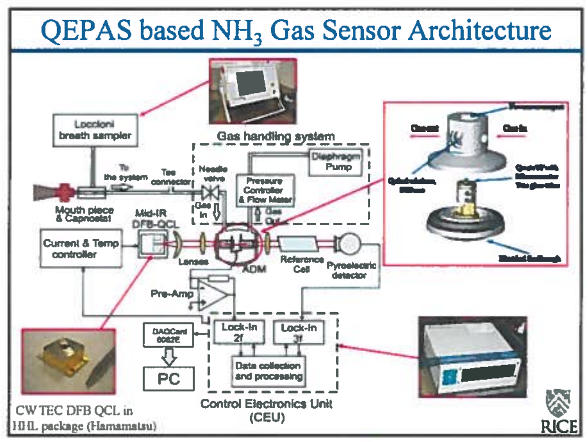
Selected Line	
Band	Wavenumber (cm^{-1})
v_3	948.68

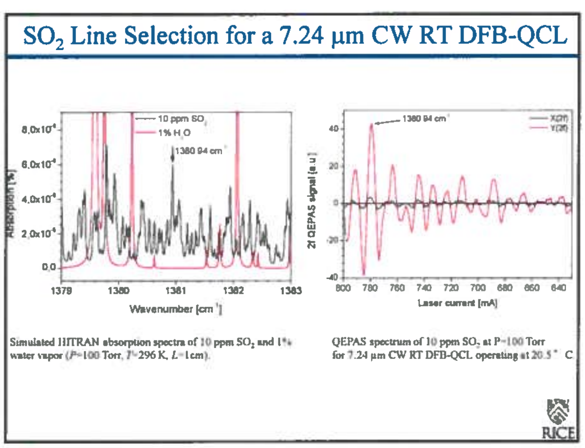
Main absorption lines for SF_6 in the range 947cm^{-1}-950cm^{-1} corresponding to the v_3 band (from the HITRAN database).

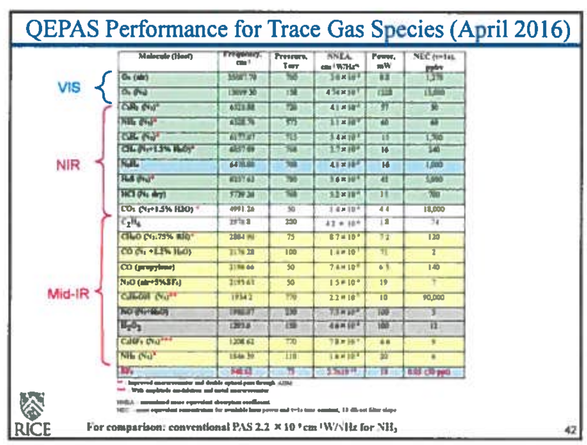

QEPAS SF6 Sensor Platform
QEPAS Cell
QCL
Hollow Fiber
DFB-QCL
•Laser emission @ 10.54µm
•Power: ~ 40 mW
•CW operation @ RT
EC -QCL
•Laser emission 10.15 -10.74 µm
•Power: ~ 25 mW @ 10.54
•CW-MHF operation @ RT
ADM
Pump
DAQ-PC


SF6 QEPAS sensor performance assessment and linearity
a = 0.008mV/ppb
Allan Plot
NNEA = 6.7x10-11 cm-1W(Hz)-1/2

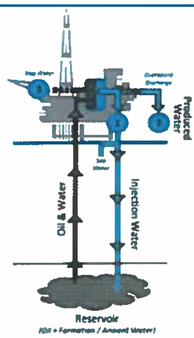

Motivation for Sulfur Dioxide Detection
• Prominent air pollutant
• Annual SO2 concentrations range from ~ 1 - 6 ppb
• SO2 is emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
• In atmosphere, SO2 converts to sulfuric acid and is a primary contributor to acid rain
• SO2 reacts to form sulfate aerosols
• SO2 exposure affects lungs and causes breathing difficulties
SO2 Air Quality, 2000 - 2010
http://www.epa.gov
RICE


QEPAS based NH3 Gas Sensor Architecture
Loccioni breath sampler
Gas handling system
Diaphragm Pump
Pressure Controller & Flow Meter
Needle valve
Tee connector
To the system
Mouth piece & Capnostat
Mid-IR DFB-QCL
Current & Temp controller
Lenses
ADM
Reference Cell
Pyroelectric detector
Pre-Amp
DAQCard 6062E
Lock-In 2f
Lock-In 3f
Data collection and processing
PC
Control Electronics Unit (CEU)
CW TEC DFB QCL in HHL package (Hamamatsu)
RICE


SO2 Line Selection for a 7.24 µm CW RT DFB-QCL
10 ppm SO2
1% H2O
1380.94 cm-1
Absorption [%]
Wavenumber [cm-1]
2f QEPAS signal [a.u.]
Laser current [mA]
X(2f)
Y(2f)
Simulated HITRAN absorption spectra of 10 ppm SO2 and 1% water vapor (P=100 Torr, T=296 K, L=1cm).
QEPAS spectrum of 10 ppm SO2 at P=100 Torr for 7.24 µm CW RT DFB-QCL operating at 20.5 °C
RICE


QEPAS Performance for Trace Gas Species (April 2016)
VIS
NIR
Mid-IR
For comparison: conventional PAS 2.2 × 10-9 cm-1W/√Hz for NH3
RICE
42

Oil in Water Detection



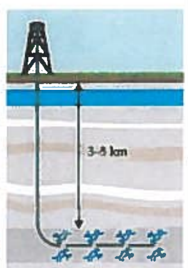
- Produced water
  - legislation: < 15 ppm
- Injection water
  - Economic reasons
    target value: < 5 ppm or lower

IQCLSW 2014, Policore, Italy: B. Lendl et al, Vienna University of Technology, Austria

A North Dakota Oil Facility in 2016.

RICE

Typical Oil & Gas Production Site near Houston, TX

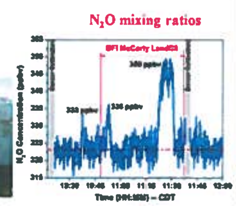


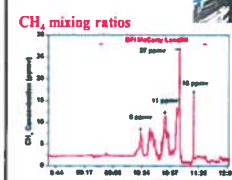
This figure depicts the result of a sequence of four fracking injections obtained by directional drilling which creates horizontal production in the target stratum.

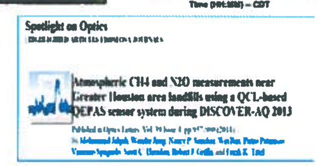
A proposed DOE-ARPA-E methane detection project at 3.327 µm will start in 2016 at various Texas located wellpad sites (typically,10 m x10 m with a 1 m spatial resolution.)

RICE

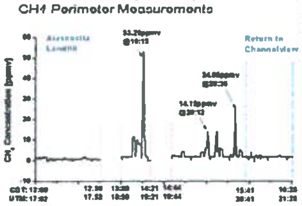
CH_4 and N_2O Measurements performed with a DFB-QCL based QEPAS Sensor installed in a mobile laboratory operated by Aerodyne, Inc. (Sept 7, 2013)







CH_4 Measurements performed with a DFB-QCL based QEPAS Sensor installed in the Aerodyne Mobile Laboratory (Sept 7, 2013)



A: 29.9599° North, 95.2334° West
B: 29.9364° North, 95.2508° West
C: 29.9547° North, 95.2462° West (Landfill)

M. Jahjah et. al., Opt. Letters., 39, 957-960, 2014

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

Size	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)

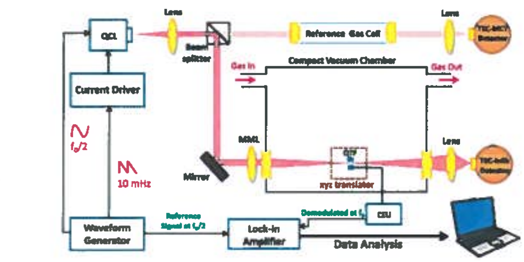
RICE

Motivation for Carbon Dioxide Detection

- **Atmospheric Chemistry**
  - Incomplete combustion of natural gas, fossil fuel and other carbon containing fuels.
  - Impact on atmospheric chemistry through its reaction with hydroxyl (OH) for troposphere ozone formation and changing the level of greenhouse gases (e.g. CH_4).
- **CO in Medicine and Biology**
- **Indoor Air Quality**
- **Beverage Carbonation**
- **Industrial process monitoring**
  - Hypertension and abnormality in heme metabolism
  - CO in Medicine and Biology
  - Hypertension and abnormality in heme metabolis

RICE

Schematic of single pass QEPAS CO_2 Detection

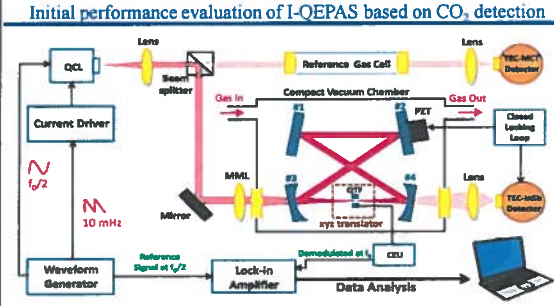


Optical power build up cavity can provide:

Standard single-pass QEPAS platform CO_2 Detection

- RT CW DFB QCL, λ=4.33 microns
- Low noise current driver → narrow QC laser linewidth ~1 MHz
- Optical Power of ~3 mW
- Gas pressure in the enclosure is 50 mbar
- Wavelength modulation approach and f_0 detection

Development of a novel I-QEPAS based sensor design: Initial performance evaluation of I-QEPAS based on CO_2 detection



At the same conditions of pressure and optical power,
Optical power build up cavity can provide:

- Bow-tie cavity → 4 high reflectivity mirrors, R=99.9%
- Electronic Control Loop + PZT driver lock of cavity resonant frequency to QCL frequency

P. Patimisco, G. Scamarcio, F.K. Tittel & V. Spagnolo, "Quartz-enhanced photoacoustic spectroscopy: a review", Sensors, 14, 6165-6206 (2014)

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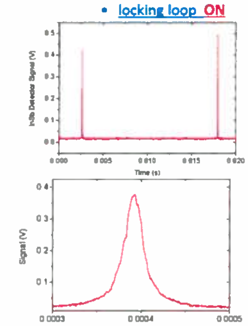
Optical properties of bow-tie cavity-I

Cavity response:
- Voltage ramp + modulation dither applied to QCL
- under vacuum
- locking loop ON



Cavity length L = 174mm

FSR = c/L = 1.725 GHz

Δν(FWHM) = 1.15 MHz

F = FSR/ Δν = 1505

G = F/π = 480

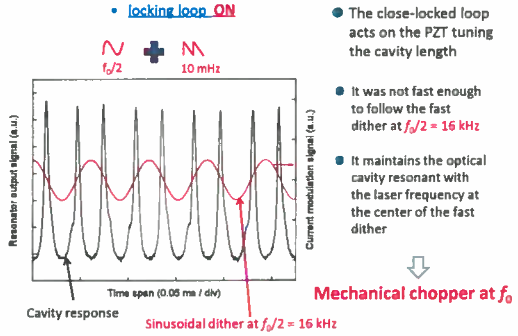
Mode matching 50%

Intracavity optical power enhancement factor = 240

Optical properties of bow-tie cavity-II

Cavity response:
- Voltage ramp + modulation dither applied to QCL
- under vacuum
- locking loop ON

$f_0/2$ + 10 mHz



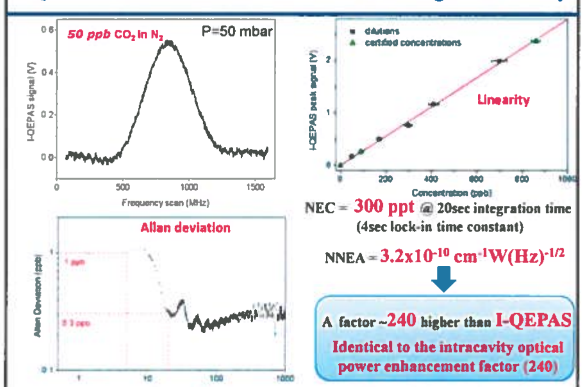
Cavity response

Sinusoidal dither at $f_0/2$ = 16 kHz

- The close-locked loop acts on the PZT tuning the cavity length
- It was not fast enough to follow the fast dither at $f_0/2$ = 16 kHz
- It maintains the optical cavity resonant with the laser frequency at the center of the fast dither

Mechanical chopper at f_0

I-QEPAS Performance in locked mode and long term stability



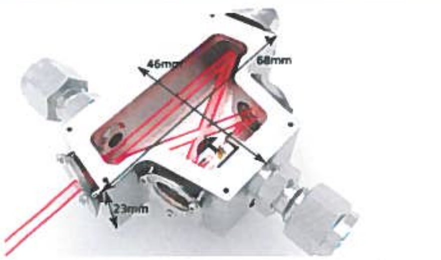
NEC = **300 ppt** @ 20sec integration time (4sec lock-in time constant)

NNEA = **3.2x10^-10^ cm^-1^W(Hz)^-1/2^**

A factor ~240 higher than I-QEPAS
Identical to the intracavity optical power enhancement factor (240)

S. Borri et al., Applied Physics Letters, 104, 091114 (2014)

Further Development of a novel I-QEPAS based Sensor Design

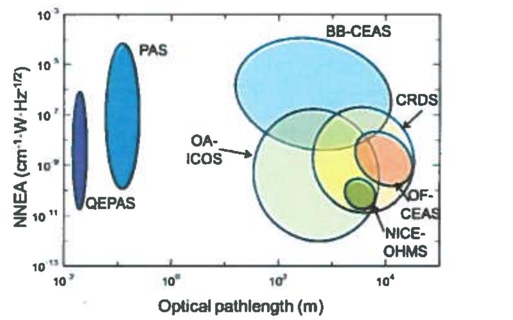


Computer Visualization of an Intra-Cavity Quartz Enhanced Photoacoustic Spectroscopy Optical Resonator

Bow-tie cavity resonator consists of 4 high reflectivity mirrors, R=99.9%

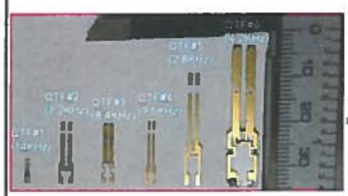
Electronic Control Loop + PZT driver for locking of the cavity resonant frequency to the frequency of the frequency Laser excitation source

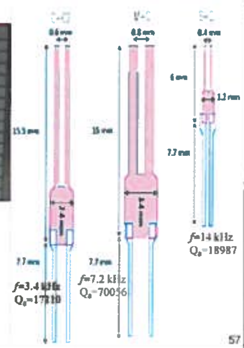
Comparison of I-QEPAS with Other Trace Gas Sensing Techniques



P. Patimisco, G. Scamarcio, F.K. Tittel & V. Spagnolo, "Quartz-enhanced photoacoustic spectroscopy: a review", Sensors, 14, 6165-6206 (2014)

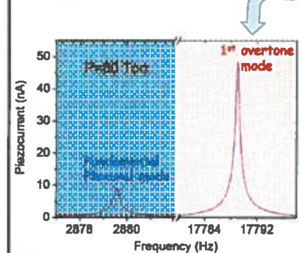
Custom fabricated QTFs with new Shapes and Dimensions optimized for mid-IR and THz QEPAS





- Standard photolithographic techniques were used to etch custom QTFs. Chromium/gold layer was deposited on both sides of the custom QTFs for electrical contacts.
- New generation of custom QTFs behave similar to "standard" QTFs in terms of their vibrational mode(s).

Comparison between fundamental and the first overtone QTF flexural modes for QTF#5 - Electrical Characterization



Comparison between the QTF fundamental and 1st overtone flexural modes

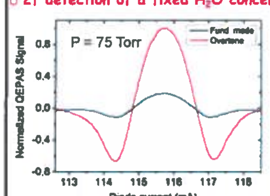
@ 760 torr	fundamental n = 0	1st overtone n = 1
Frequency (Hz)	2,879.5	17,788.9
Quality factor Q	12,099	31,374

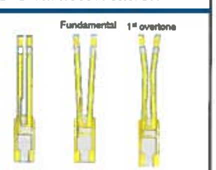
A ~ 5.3 higher piezocurrent is measured when operating with the first overtone flexural mode instead of the fundamental mode.

Gold coated electrode pattern was optimized for the fundamental vibrational mode, resulting in an enhanced piezo-charge collection for the 1st overtone flexural mode

Comparison between fundamental and first overtone QTF flexural modes for QTF#5 – QEPAS Characterization

○ 2f detection of a fixed H_2O concentration

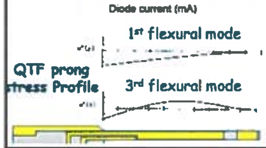




← Comparison between the 1st overtone (18KHz) and fundamental (3KHz) flexural modes of the B-C QTF @ P=75 torr.

The signal for the 3rd flexural mode is ~ 5 times higher.

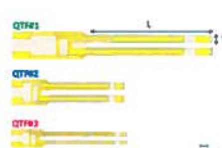
QTF prong stress Profile



The two vibrational modes differ in the stress profile.

A larger charge is generated for the high order modes

In-plane view of designs of three types of tuning forks realized in this work. The size scale is shown on the right bottom.

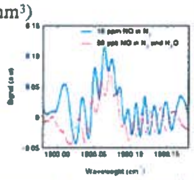


	QTF#1		QTF#2		QTF#3	
[illegible]	17		10		11	
[illegible]	1		0.9		0.5	
[illegible]	0.25		0.25		0.25	
[illegible]	n = 1	n = 2	n = 1	n = 2	n = 1	n = 2
[illegible]	2,813.42	16,245.48	7,577.81	47,466.54	3,479.25	21,780.04
[illegible]	17	3.7 17	10	2.2 10	11	2.4 11
[illegible]	0	0.8	0	0.53	0	0.58

F.K. Tittel, A. Sampaolo, P. Patimisco, L. Dong, A. Geras, T. Starecki, V. Spagnolo, Optics Express, 24, A683-A692, 2016

Why QEPAS sensors have not been developed in the THz range to-date?

Standard QTFs and are characterized by a very small sensitive volume (~0.3 × 0.3 × 3 mm^3)

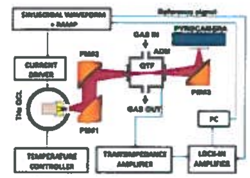


In QEPAS experiments, it is critical to avoid laser illumination of the QTF, since the radiation blocked by the QTF prongs results in an undesirable non-zero background which is associated with a shifting fringe- like interference pattern.

The narrow space (300 µm) between the QTF prongs is comparable with the wavelength of THz sources, which has so far represented the main limitation preventing the use of QEPAS system in THz range.

Hence, larger sized QTFs are required for operating in the THz regime.

Schematic of the QEPAS trace gas sensor using a THz Quantum Cascade Laser (THz QCL) as the excitation source



PM – Parabolic Mirror; ADM – Acoustic Detection Module; QTF – Quartz Tuning Fork; PC – Personal Computer.

Picture of the N-QTF including the size of the main geometrical parameters.

A. Sampaolo, P. Patimisco, M. Giglio, M. S. Vitiello, H. E. Beere, D. A. Ritchie, G. Scamarcio, F. K. Tittel, V. Spagnolo: "Improved tuning fork for terahertz quartz-enhanced photoacoustic spectroscopy", Sensors, 16, 439, 2016

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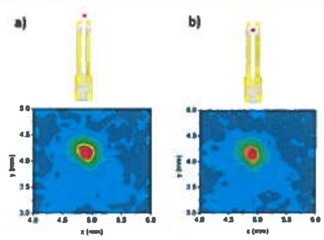
Two-dimensional beam profile of the THz-QCL acquired by means of an IR pyrocamera after mirror PM#3 (see Fig. 2) when the beam is focused out the N-QTF



(a) or between the two prongs (b). Both beam profiles are shown together with an illustration representing the position of the focused THz beam (red spot) with respect the N-QTF.

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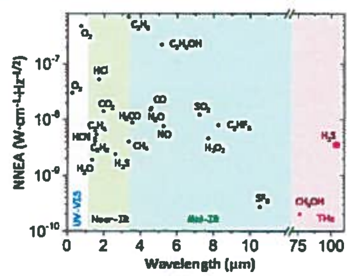
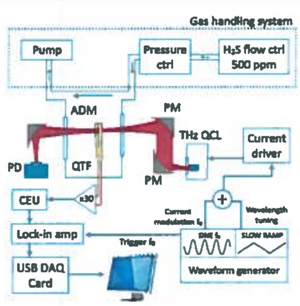
NNEA results obtained with QEPAS sensor for the gas species reported versus employed laser wavelength, in the UV-Vis, near-IR, mid-IR and THz spectral ranges

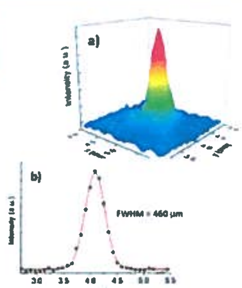


The red symbol (*) marks the result of present work.

Vincenzo Spagnolo, Pietro Patimisco, Riccardo Pennetta, Angelo Sampaolo, Gaetano Scamarcio, Miriam S. Vitiello, and Frank K. Tittel: "THz Quartz-enhanced photoacoustic sensor for H_2S trace gas detection", 23, 7574-7582, (2015)

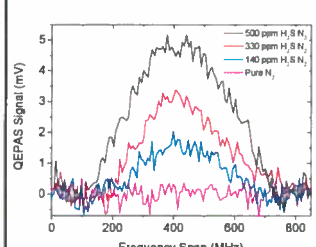
THz QEPAS H_2S Sensor employing QTF#5

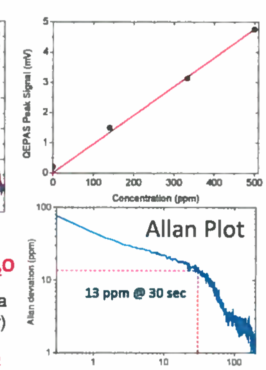




Selected Line			
Transition		[illegible]	[illegible]
(15 5 10-15 4 11)	rotational	97,114 (2.913	1.15x10^{-22} cm/mol

THz QEPAS H_2S Sensor Performance Assessment and Linearity



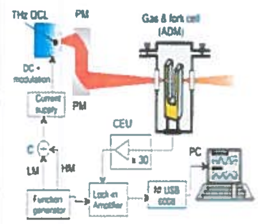


No signal changes with a few % of H_2O

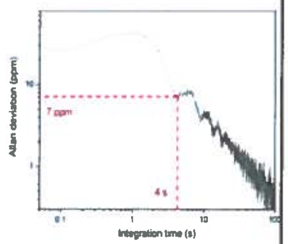
Absorption coefficient normalized to a detection bandwidth (*0.00556 Hz*) and an optical power (*240 µW*):

NNEA = 4.05x10^{-10} $cm^{-1}W(Hz)^{-1/2}$

THz QEPAS based Sensor for Methanol (CH_3OH) Detection



Schematic of THz QCL-based QEPAS sensor. PM – paraboloidal mirror; C – power combiner; LM, HM – low-frequency modulation (triangular ramp), high-frequency modulation; CEU – control electronics unit; PC – personal computer.



Allan deviation in ppm of the QEPAS signal as a function of the integration time. The initial growth from 0.1 to 1s reflects delays due to the signal sampling time (200 ms).

Spagnolo et. al. Appl. Phys. Lett. 103, 021105 (2013)

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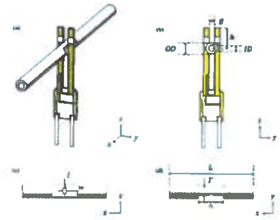
Schematic of the SO-QEPAS spectrophone



(b), (c), (d) symbols of the geometric parameters of the SO-QEPAS spectrophone where *g* is the QTF prong spacing, *l* is the slit length, *w* is the slit width, *L* is the acoustic resonator length, *ID* is the inner diameter, *OD* is the outer diameter, *T* is the waist thickness and *h* is the waist length.

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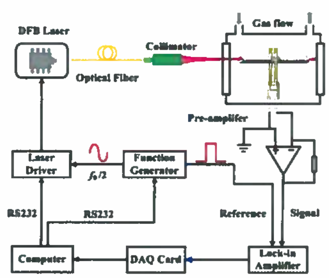
Schematic diagram of the experimental setup.



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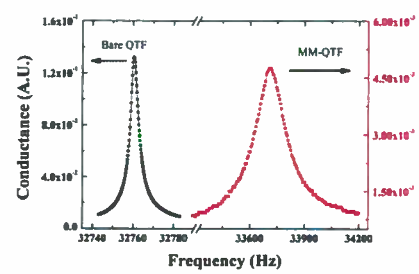
Conductance spectra of a QTF before (black) and after (red) modification by the PMMA microwire



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Summary, Conclusions and Future Work

- Development of robust, compact, sensitive, selective mid-IR trace gas sensor technology based on RT, CW high performance DFB ICLs & QCLs for environmental monitoring and medical diagnostics.
- ICLs and QCLs were used in TDLAS and PAS/QEPAS 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 resulted in a factor of 240 increase in detection sensitivity
  - CO_2 MDL of 300 pptv at 50mbar was achieved for a 20 sec integration time.
- THz-QEPAS H_2S sensing demonstration using a custom QTF resulted in a NNEA of 10^{-10} $cm^{-1}W(Hz)^{-1/2}$. The MDL was 13 ppmv for a 30 sec integration time.
- Novel implementation of QTF 1st overtone flexural l mode for QEPAS sensing
- Development of "active" I-QEPAS system for CO and NO detection in the ppt range
- Future development of trace gas sensors for monitoring of broadband absorbers: acetone(C_3H_6O), propane (C_3H_8), benzene (C_6H_6), acetone peroxide-TATP ($C_6H_{12}O_4$)
- Future development of mid-IR electrically pumped interband cascade optical frequency combs (OFCs) jointly with JPL, Pasadena, CA , NRL, Washington, DC and Bari (Italy)

Comparison of three QEPAS based sensors for H_2S detection operating in the near-IR, mid-IR and THz spectral ranges.

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	3788.56	1200.83	87.113
[illegible]	3	45	3.24
[illegible]	1.67·10 [illegible]	1.51·10 [illegible]	1.13·10 [illegible]
[illegible]	2.4·10 [illegible]	7.3·10 [illegible]	3.8·10 [illegible]
[illegible]	750 ppb	330 ppb	107 ppm

Companies Offering Infrared Laser Based Sensors

- ThorLabs, Newton, NJ
- Daylight Solutions Inc., San Diego, CA
- Neomonitors, Loerenskog, Norway
- Siemens, Goteborg, Sweden
- Focused Photonics, Hangzhou, China
- Yokogawa USA, Houston Texas
- Cascade Technologies, Sterling, UK
- Aerodyne Research Inc., Billerica, MA
- Physics Sciences Inc., Andover, MA
- California Analytical Instruments, Inc., Orange, CA
- Gasera Ltd., Turku, Finland
- Vista Photonics Inc., Santa Fe, NM
- Southwest Sciences Inc., Santa Fe, NM
- Spectra Sensors, Houston, TX
- Boreal Laser Inc., Spruce Grove, Alberta, Canada

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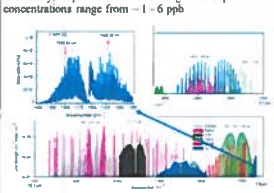
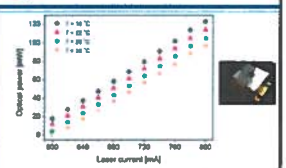
CW DFB-QCL based SO_2 QEPAS Results

Motivation for Sulfur Dioxide Detection

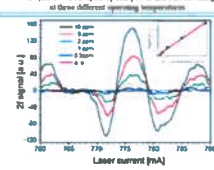
- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere SO_2 converts to sulfuric acid → primary contributors to acid rain
- SO_2 reacts to form sulfate aerosols
- Primary SO_2 exposure for 1 hour is 75 ppb
- SO_2 exposure affects lungs and causes breathing difficulties
- Currently, reported annual average atmospheric SO_2 concentrations range from ~1 - 6 ppb



Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



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



2f WMS QEPAS signals for different SO_2 concentrations when laser was tuned across 1380.9 cm^{-1} line

Minimum detectable SO_2 concentration is: ~100 ppbv (1σ; 1 s time resolution)