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Mid–infrared interband and quantum cascade laser based trace gas sensor technologies: recent advances and applications

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http://www.ece.rice.edu/~lasersci/

OUTLINE

OASIS V 2015
TEL AVIV,
ISRAEL

March 3-4, 2015

- Novel Laser-Based Trace Gas Sensor Technologies
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
  - Mid-IR TDLAS based on a Novel Multipass Gas Cell Design
- Motivation for CH_4 and C_2H_6 Detection
- HITRAN Simulation for CH_4 and C_2H_6
- Performance Evaluation of CH_4 & C_2H_6 Sensor Platform
- Future Directions of Mid-IR Laser based Trace Gas Sensor Technologies and Conclusions

Research support by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation, and Sentinel Photonics Inc. via an EPA Phase 1 SBIR sub-award is acknowledged

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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 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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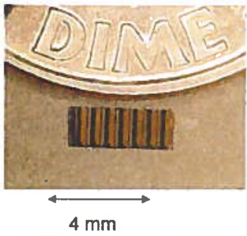
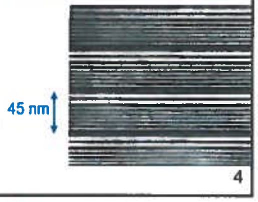
Mid-IR Source Requirements for Laser Spectroscopy

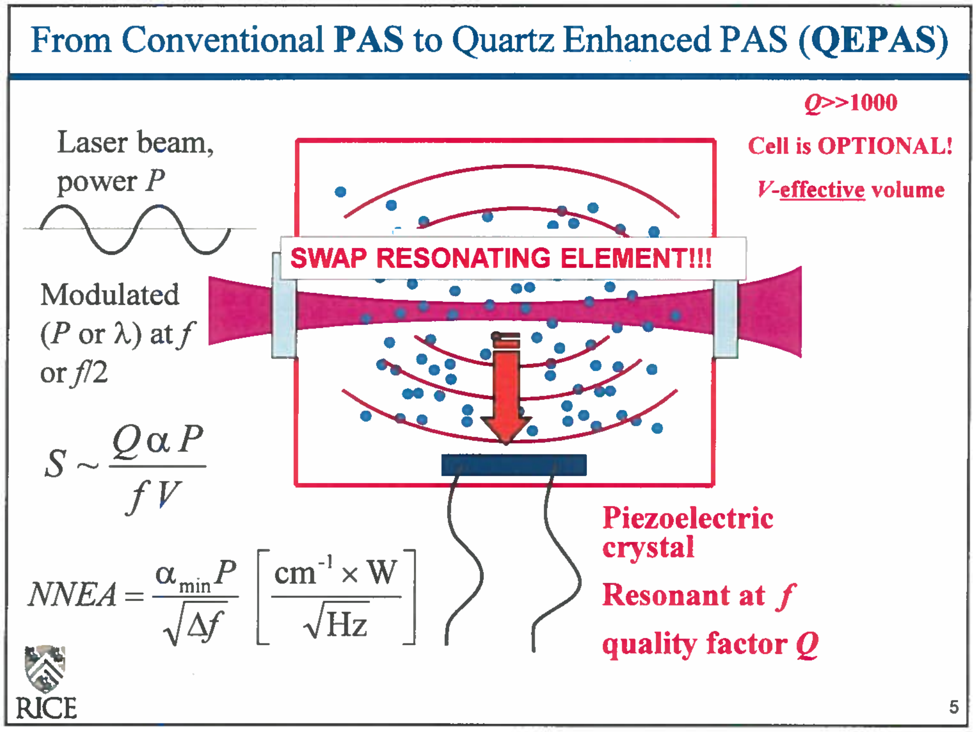
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to pptv)	**Optimum Wavelength, Power**
Selectivity (Spectral Resolution)	**Stable Single Mode Operation and Narrow Linewidth**
Multi-gas Components, Multiple Absorption Lines, and Broadband Absorbers	**Mode Hop-Free Wavelength Tunability**
Directionality or 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 and Robust**

Key Characteristics of Mid-IR QCL & ICL Sources – March 2015

- **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 QCL DFB Array
  - ~ 525 cm^{-1} (22% of c.w.) using an external grating element and FP chips with heterogeneous cascade active region design; also QCL DFB Array
- **Narrow spectral linewidths**
  - CW: 0.1 - 3 MHz & <10kHz with frequency stabilization
  - Pulsed: ~ 300 MHz
- **High pulsed and CW powers of QCLs at TEC/RT temperatures**
  - Room temperature pulsed peak power of > 30 W with 44% wall plug efficiency
  - CW powers of ~ 5 W with 23% wall plug efficiency at 293 K
  - > 600 mW CW DFB @ 285 K; wall plug efficiency 23% at 4.6 µm







From Conventional **PAS** to Quartz Enhanced PAS (**QEPAS**)

Laser beam,
power *P*

Modulated
(*P* or λ) at *f*
or *f*/2

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

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

SWAP RESONATING ELEMENT!!!

***Q*>>1000**

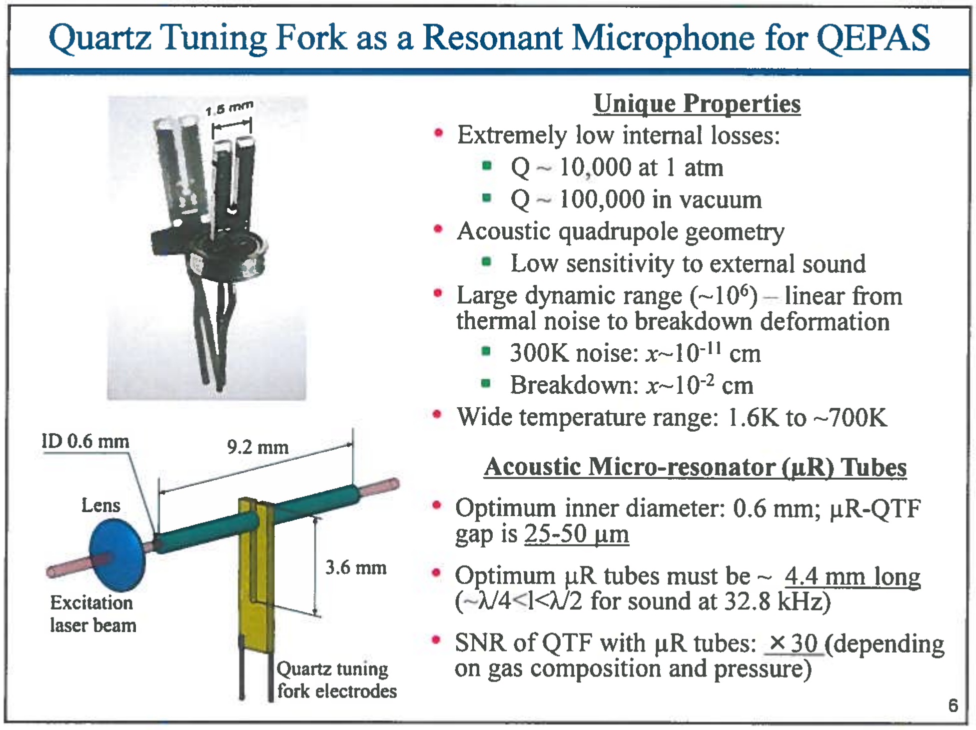
Cell is OPTIONAL!

***V*-effective volume**

Piezoelectric crystal

Resonant at *f*

quality factor *Q*



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

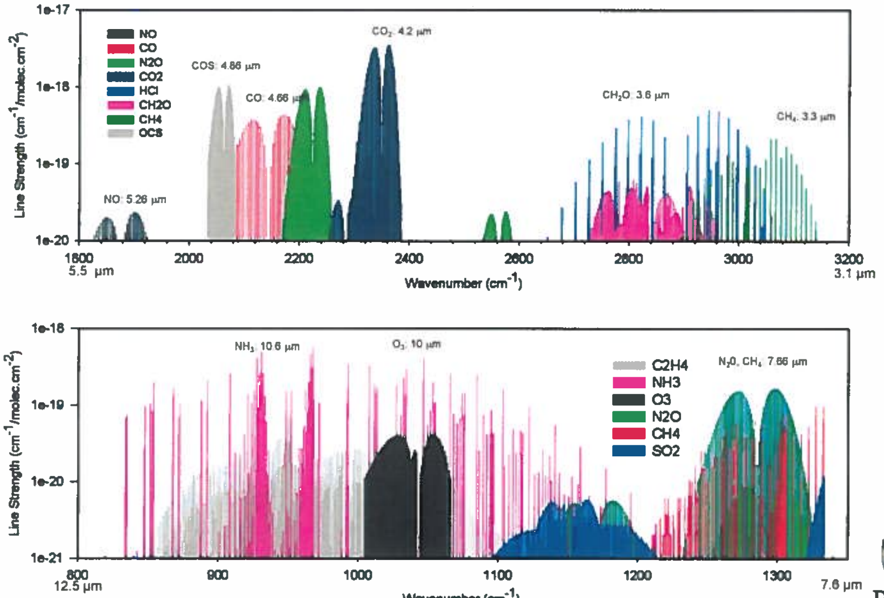
Acoustic Micro-resonator (μR) Tubes

- 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)

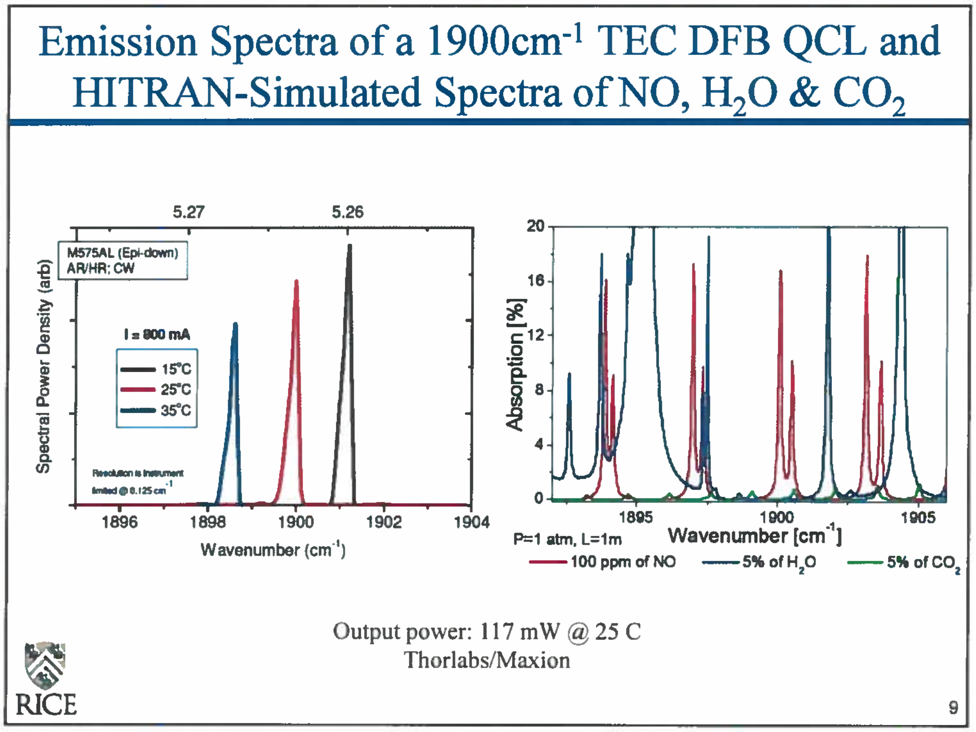
Chemicals of interest in defense & security applications

- **Chemical warfare agents**
  - Nerve agents
  - Blister agents
  - Pulmonary agents
  - Blood agents
- **Explosives**
- TNT, RDX, PETN, RTN
- **High Threat Toxic Industrial Chemicals (TICs)**
  - Ammonia, Arsine, Boron trichloride, Carbon disulphide, Chlorine, Ethylene oxide, Fluorine, Formaldehyde, Hydrogen bromide, Hydrogen chloride, Hydrogen cyanide, Hydrogen fluoride, Hydrogen sulphide, Nitric acid, Phosgene, Sulphur dioxide, Sulphuric acid, Tungsten hexafluoride
- **Environmental pollutant gas monitoring**
  - Naval vessels in particular Submarines
  - Aircraft and drones
  - Exposure to combat personnel in battle field.

HITRAN Simulated Mid-Infrared Molecular Absorption Spectra



Source: HITRAN 2012 database



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

Output power: 117 mW @ 25 C
Thorlabs/Maxion

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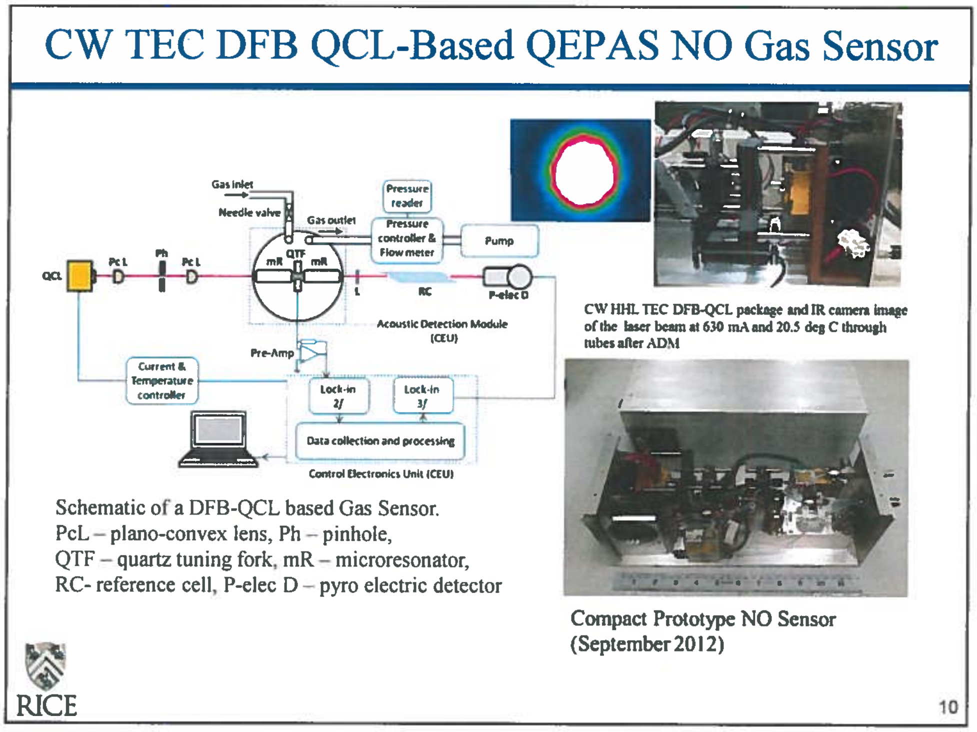

CW TEC DFB QCL-Based QEPAS NO Gas Sensor

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

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

Compact Prototype NO Sensor
(September 2012)

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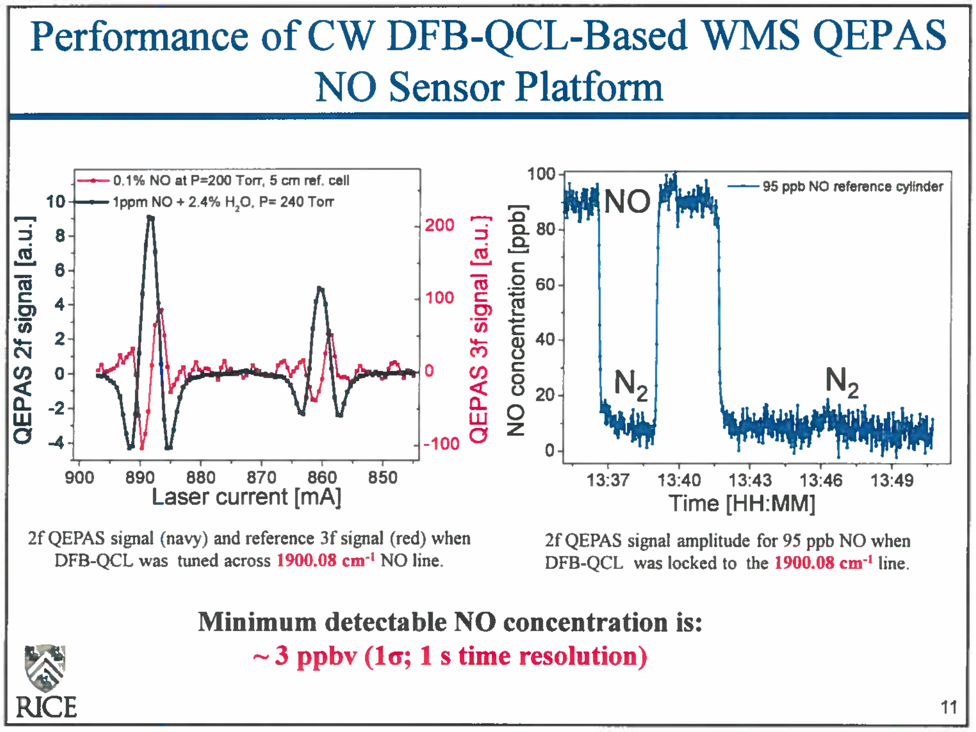

Performance of CW DFB-QCL-Based WMS QEPAS NO Sensor Platform

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)

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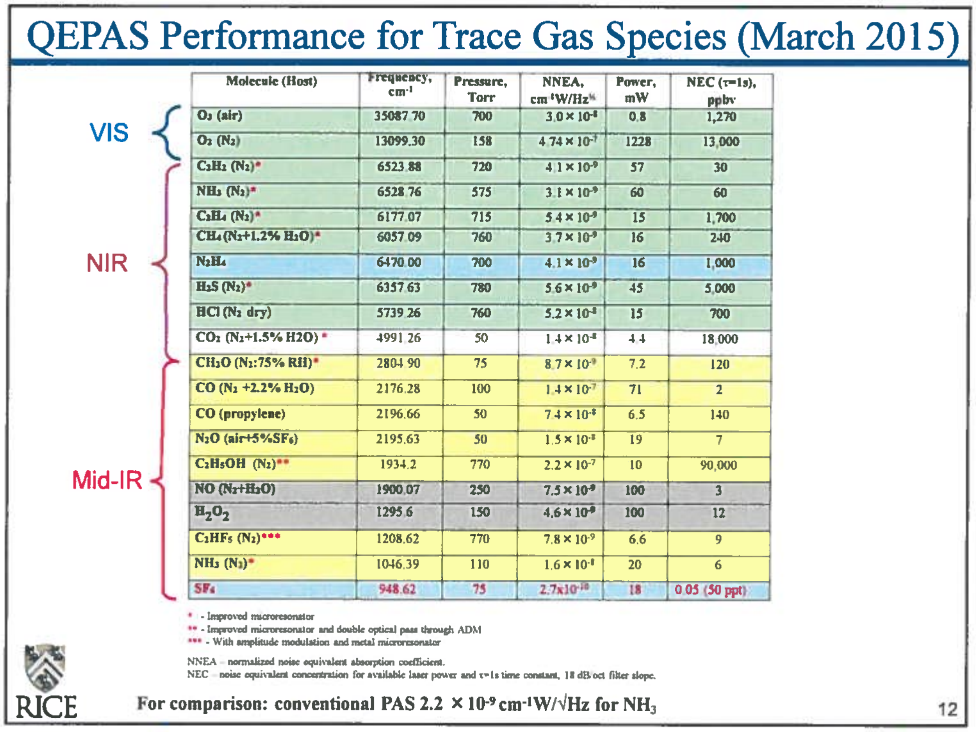

QEPAS Performance for Trace Gas Species (March 2015)

	Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, cm^{-1}W/Hz^{½}	Power, mW	NEC (τ=1s), ppbv
VIS	O_3 (air)	35087.70	700	3.0×10^{-8}	0.8	1,270
	O_2 (N_2)	13099.30	158	4.74×10^{-7}	1228	13,000
NIR	C_2H_2 (N_2)*	6523.88	720	4.1×10^{-9}	57	30
	NH_3 (N_2)*	6528.76	575	3.1×10^{-9}	60	60
	C_2H_4 (N_2)*	6177.07	715	5.4×10^{-9}	15	1,700
	CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10^{-9}	16	240
	N_2H_4	6470.00	700	4.1×10^{-9}	16	1,000
	H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	5,000
	HCl (N_2 dry)	5739.26	760	5.2×10^{-8}	15	700
	CO_2 (N_2+1.5% H2O) *	4991.26	50	1.4×10^{-8}	4.4	18,000
Mid-IR	CH_2O (N_2:75% RH)*	2804.90	75	8.7×10^{-9}	7.2	120
	CO (N_2 +2.2% H_2O)	2176.28	100	1.4×10^{-7}	71	2
	CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	140
	N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	7
	C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	90,000
	NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	3
	H_2O_2	1295.6	150	4.6×10^{-9}	100	12
	C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	9
	NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	6
	SF_6	948.62	75	2.7×10^{-10}	18	0.05 (50 ppt)

* - 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.

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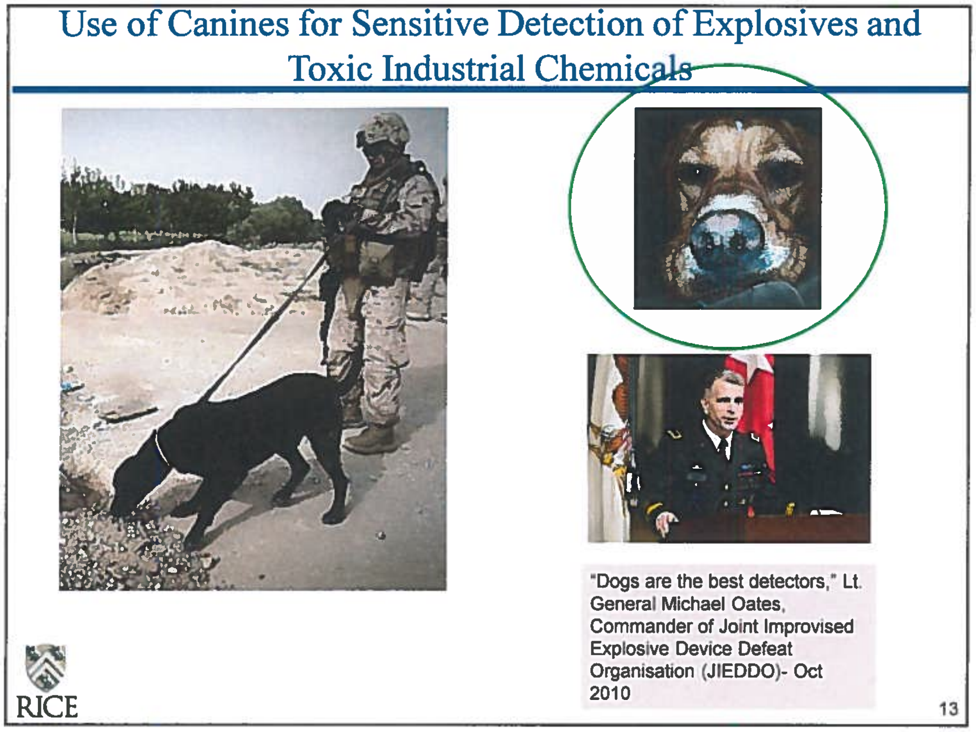
For comparison: conventional PAS 2.2 × 10^{-9} cm^{-1}W/√Hz for NH_3



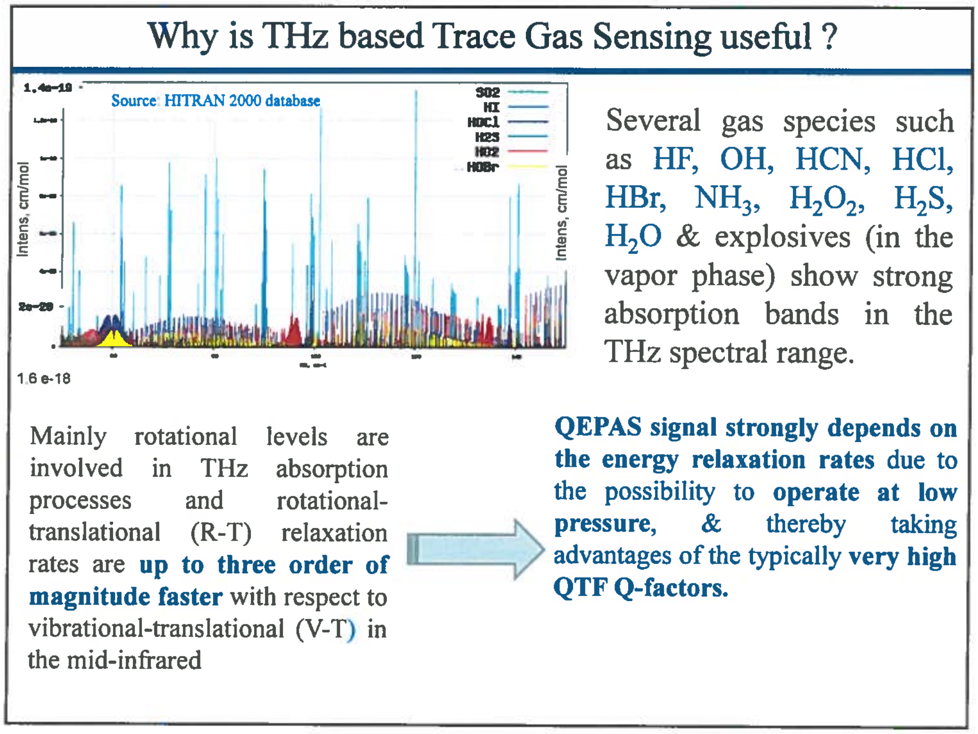
Use of Canines for Sensitive Detection of Explosives and Toxic Industrial Chemicals

"Dogs are the best detectors," Lt. General Michael Oates, Commander of Joint Improvised Explosive Device Defeat Organisation (JIEDDO)- Oct 2010

Advantages & Disadvantages of Canines in Explosive and TICs Detection

- **Advantages**
  - Non-invasive, safe and easy sample collecting
  - Relatively easy training and interpretation of dogs' indications
  - Odor samples can be tested several times
  - Extremely high detection sensitivity and specificity
  - Potentially useful in search, rescue and emergency applications
- **Disadvantages**
  - To-date a "black-box technology"
  - It is a method based on earning a reward, which becomes unreliable after ~ 4 years
  - Variation of sensitivity and specificity
  - Re-training of dogs is not effective

Breath 2014, Torun, Prof. T. Jezierski et al.,
Institute of Genetics and Animal Breeding, PAS, Poland

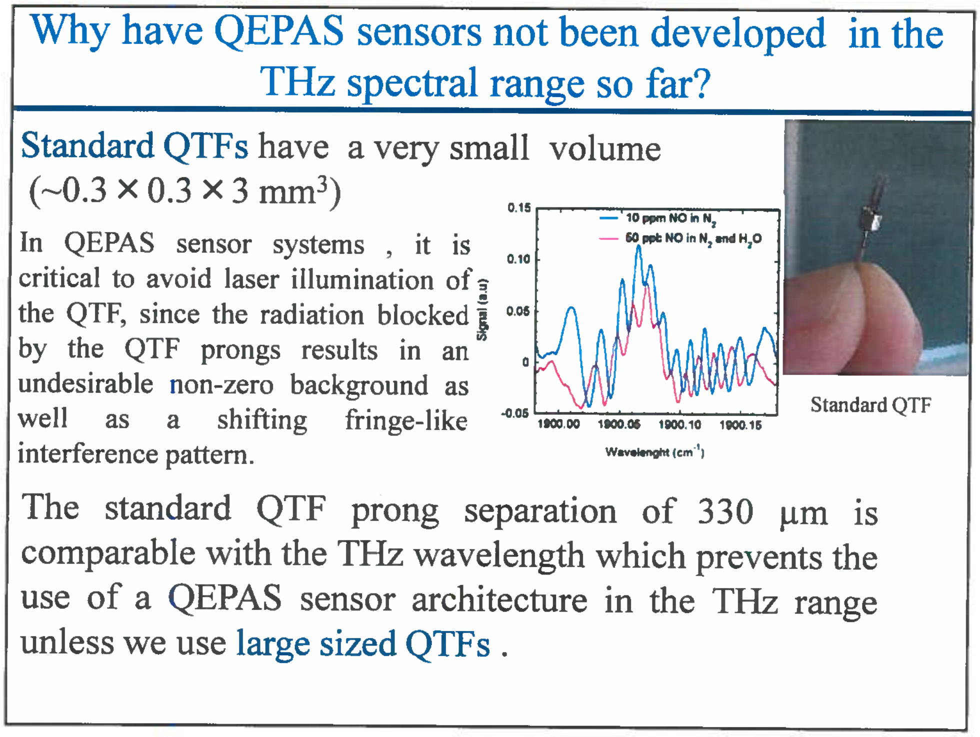


Why is THz based Trace Gas Sensing useful ?

Several gas species such as HF, OH, HCN, HCl, HBr, NH_3, H_2O_2, H_2S, H_2O & explosives (in the vapor phase) show strong absorption bands in the THz spectral range.

Mainly rotational levels are involved in THz absorption processes and rotational-translational (R-T) relaxation rates are **up to three order of magnitude faster** with respect to vibrational-translational (V-T) in the mid-infrared

QEPAS signal strongly depends on the energy relaxation rates due to the possibility to **operate at low pressure,** & thereby taking advantages of the typically **very high QTF Q-factors.**



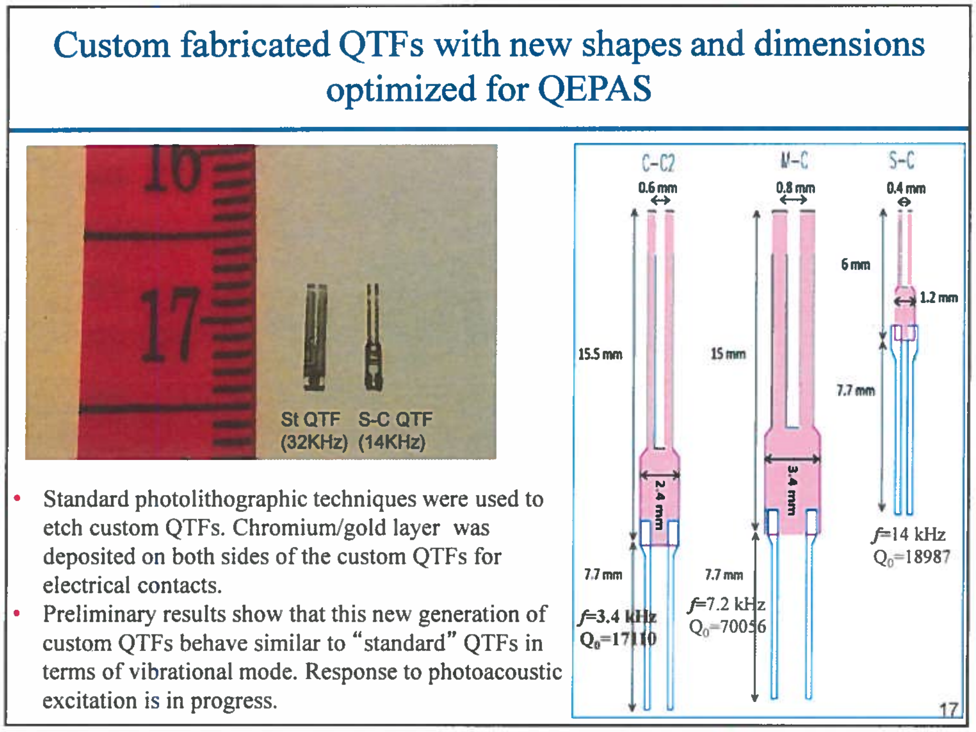
Why have QEPAS sensors not been developed in the THz spectral range so far?

Standard QTFs have a very small volume ($\sim 0.3 \times 0.3 \times 3\ mm^3$)

In QEPAS sensor systems , 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 as well as a shifting fringe-like interference pattern.

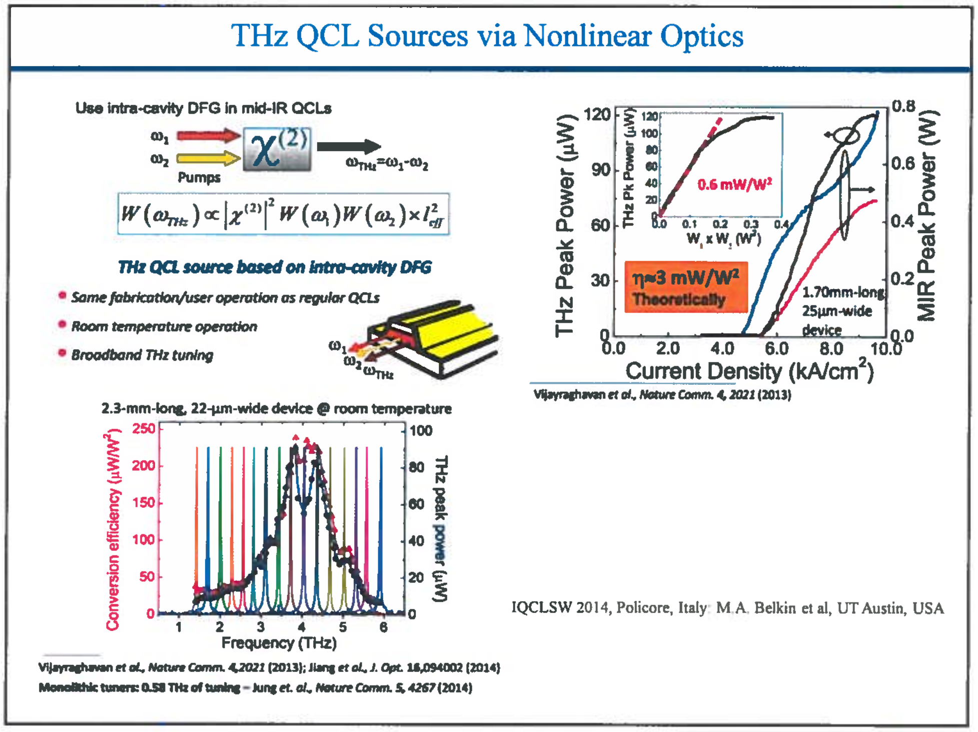
Standard QTF

The standard QTF prong separation of 330 μm is comparable with the THz wavelength which prevents the use of a QEPAS sensor architecture in the THz range unless we use large sized QTFs .



Custom fabricated QTFs with new shapes and dimensions optimized for 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.
- Preliminary results show that this new generation of custom QTFs behave similar to "standard" QTFs in terms of vibrational mode. Response to photoacoustic excitation is in progress.



THz QCL Sources via Nonlinear Optics

Use intra-cavity DFG in mid-IR QCLs

$$W(\omega_{THz}) \propto |\chi^{(2)}|^2 W(\omega_1) W(\omega_2) \times l_{eff}^2$$

THz QCL source based on intra-cavity DFG

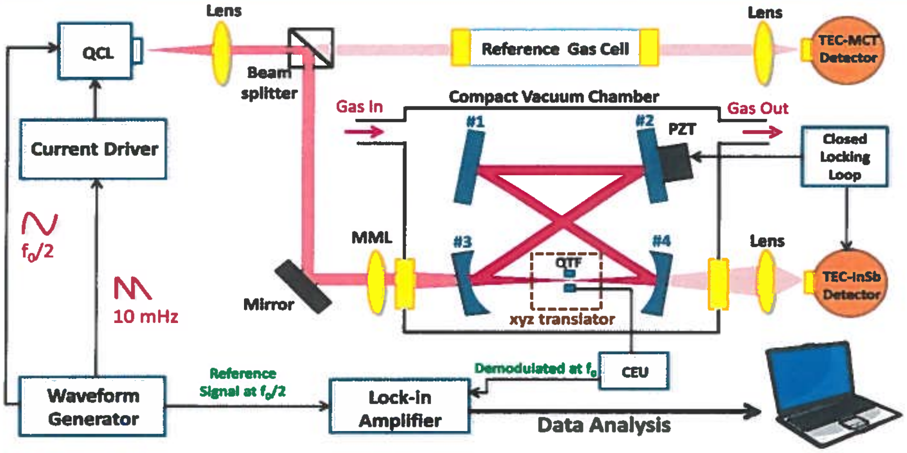
- *Same fabrication/user operation as regular QCLs*
- *Room temperature operation*
- *Broadband THz tuning*

Vijayraghavan *et al., Nature Comm. 4,2021* (2013); Jiang *et al., J. Opt. 16*,094002 (2014)
Monolithic tuners: 0.58 THz of tuning – Jung *et. al., Nature Comm. 5, 4267* (2014)

Vijayraghavan *et al., Nature Comm. 4, 2021* (2013)

IQCLSW 2014, Policore, Italy: M.A. Belkin et al, UT Austin, USA

Proposed Intracavity-QEPAS (I-QEPAS) Sensor System

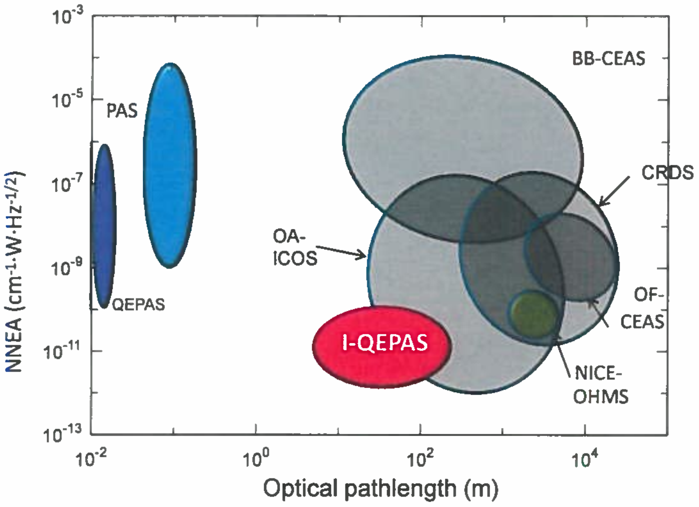


Optical power build up cavity can provide:

- RT CW DFB QCL, λ=4.33 microns
- Low noise current driver → narrow QC laser linewidth ~1 MHz
- 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)

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)

Summary and Conclusions

- Development of robust, compact, sensitive, selective mid-infrared trace gas sensor technology based on room temperature, continuous wave 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
- To date six target trace gas species were detected with a 1 sec sampling time:
    - NO: ~5.26 µm, detection limit of 3 ppbv
    - CO: ~4.61 µm, minimum detection limit of 2 ppbv
    - SO_2: ~7.24 µm, detection limit of 100 ppbv
    - CH_4 and N_2O: ~7.28 µm, detection limits of 13 and 6 ppbv, respectively
    - H_2O_2: ~7.73 µm, detection limit of 75 ppb

    :
- New target analytes: CH_2O and C_3H_6O
- Mid-Infrared Optical Frequency Comb

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