Mid-infrared Semiconductor laser based Trace Gas Sensor Technologies: Recent Advances and Applications

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OUTLINE

- 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 Mid-infrared & THz Trace Gas Species
- Future Directions of QEPAS-Based Trace Gas Sensor Technologies
  - I (Intra-cavity) – QEPAS
  - New custom QTFs

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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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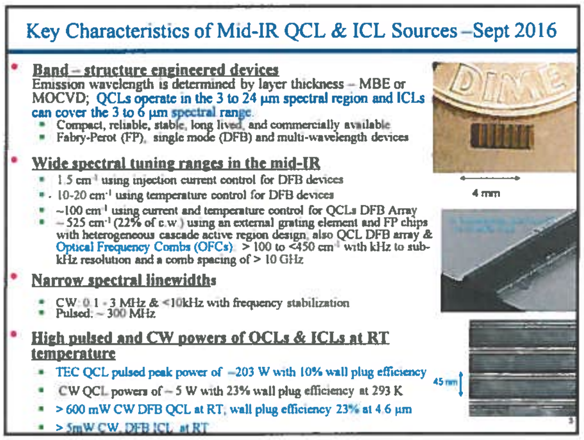
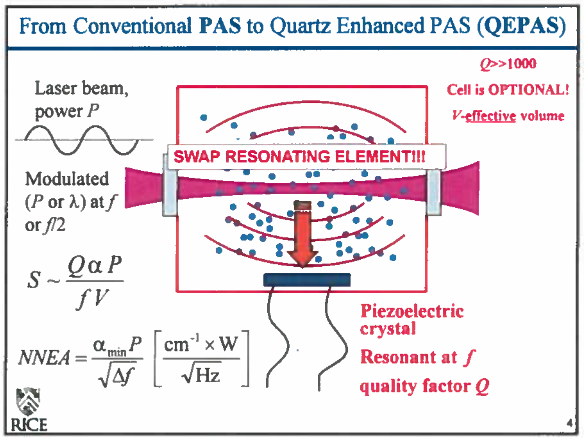


Key Characteristics of Mid-IR QCL & ICL Sources –Sept 2016

- **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 QCL at RT, wall plug efficiency 23% at 4.6 µm
  - > 5mW CW DFB ICL at RT



From Conventional PAS to Quartz Enhanced PAS (QEPAS)

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

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

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

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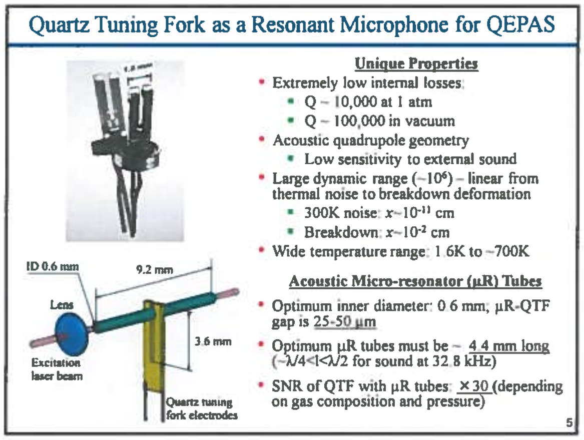


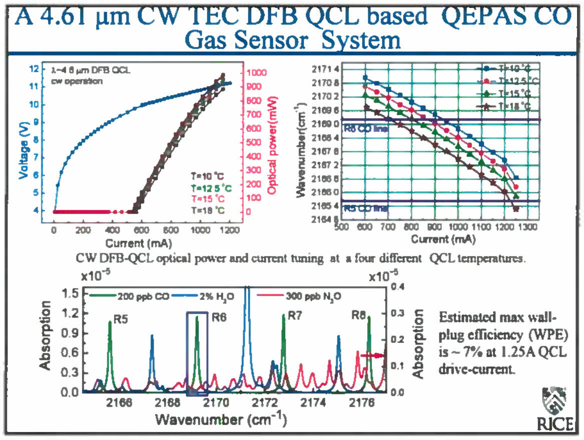
Quartz Tuning Fork as a Resonant Microphone for QEPAS

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)



A 4.61 µm CW TEC DFB QCL based QEPAS CO Gas Sensor System

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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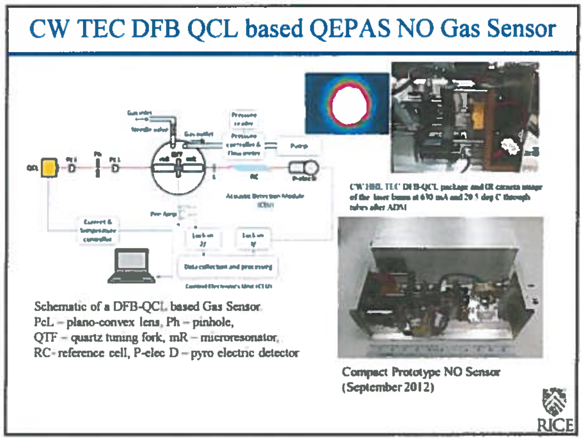
CW TEC DFB QCL based QEPAS NO Gas Sensor

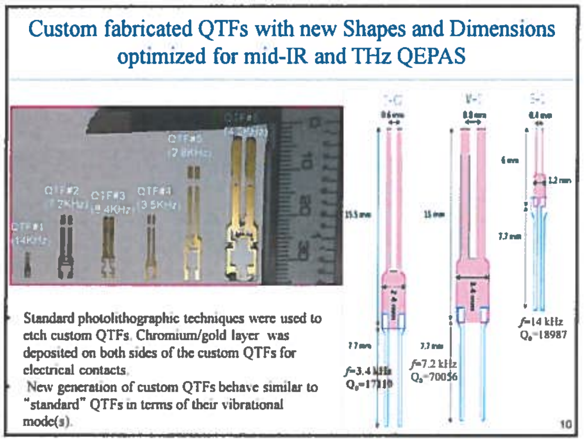


Schematic of a DFB-QCL based Gas Sensor
PcL – plano-convex lens, Ph – pinhole,
QTF – quartz tuning fork, mR – microresonator,
RC- reference cell, P-elec D – pyro electric detector

CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 610 mA and 20.5 deg C through tubes after ADM

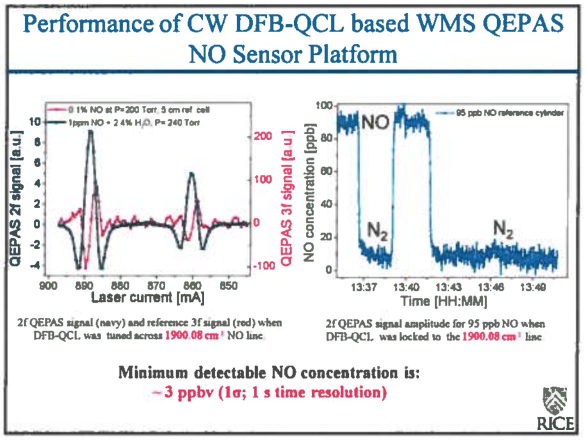
Compact Prototype NO Sensor
(September 2012)

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).

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

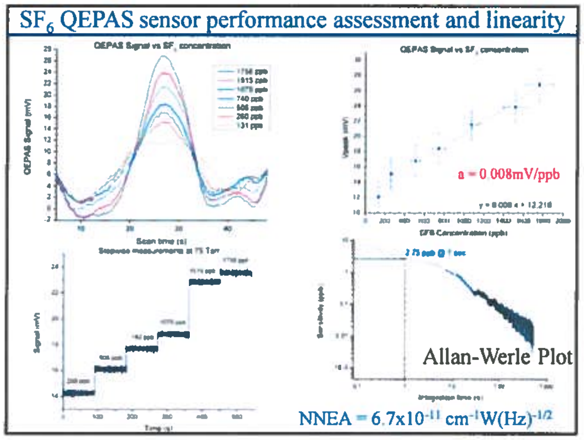


2f QEPAS signal (navy) and reference 3f signal (red) when DFB-QCL was tuned across 1900.08 cm-1 NO line.

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

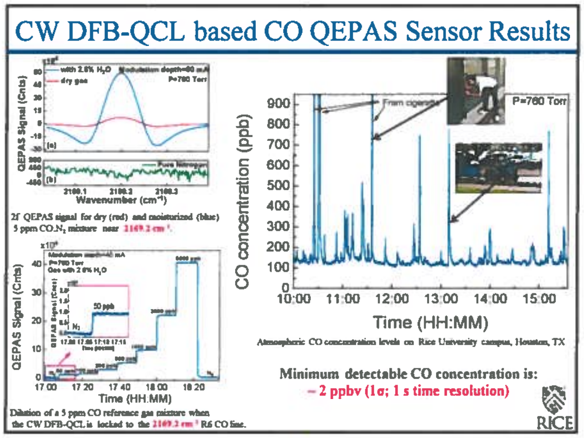
Minimum detectable NO concentration is:
~3 ppbv (1σ; 1 s time resolution)

SF_6 QEPAS sensor performance assessment and linearity



NNEA = 6.7×10^{-11} cm^{-1}W(Hz)$^{-1/2}$

CW DFB-QCL based CO QEPAS Sensor Results



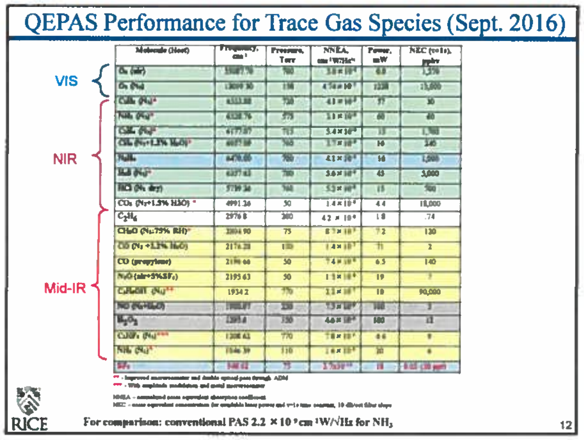
2f QEPAS signal for dry (red) and moisturized (blue) 5 ppm CO:N2 mixture near 2169.2 cm-1.

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)

QEPAS Performance for Trace Gas Species (Sept. 2016)

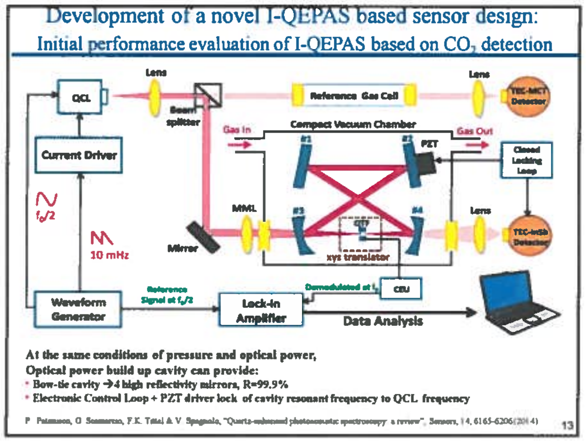


	Molecule (Host)	Frequency, cm-1	Pressure, Torr	NNEA, cm-1W/Hz½	Power, mW	NEC (τ=1s), ppbv
VIS	O_2 (air)	13087.70	760	3.8×10^{-9}	6.0	1,370
	O_2 (N_2)	13099.30	150	4.74×10^{-7}	1228	13,000
NIR	C_2H_2 (N_2)*	6523.88	720	4.1×10^{-9}	57	30
	NH_3 (N_2)*	6528.76	575	3.1×10^{-9}	60	60
	C_2H_4 (N_2)*	6177.07	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% H_2O)*	4991.26	50	1.4×10^{-8}	4.4	18,000
Mid-IR	C_2H_6	2976.8	200	4.2×10^{-9}	1.8	.74
	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 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 × 10^{-9} cm^{-1}W/√Hz for NH_3

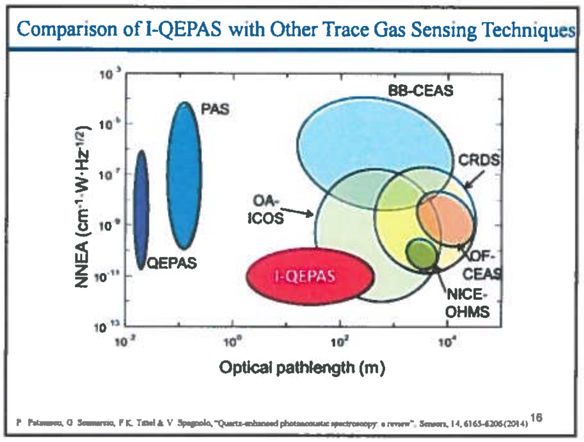


Development of a novel I-QEPAS based sensor design:
Initial performance evaluation of I-QEPAS based on CO_2 detection

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

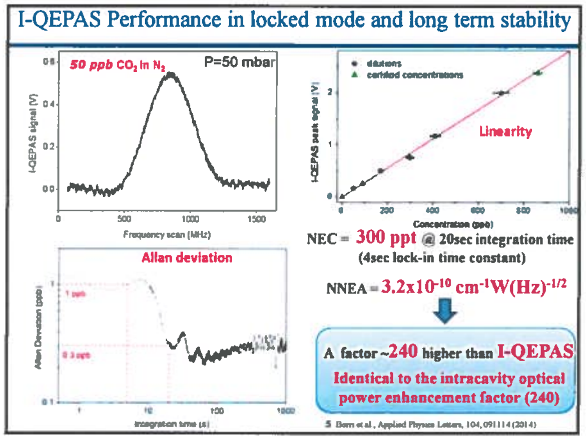
- **Bow-tie cavity →4 high reflectivity mirrors, R=99.9%**
- **Electronic Control Loop + PZT driver lock of cavity resonant frequency to QCL frequency**

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



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)



I-QEPAS Performance in locked mode and long term stability

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

NNEA = 3.2×10^{-10} $cm^{-1}W(Hz)^{-1/2}$

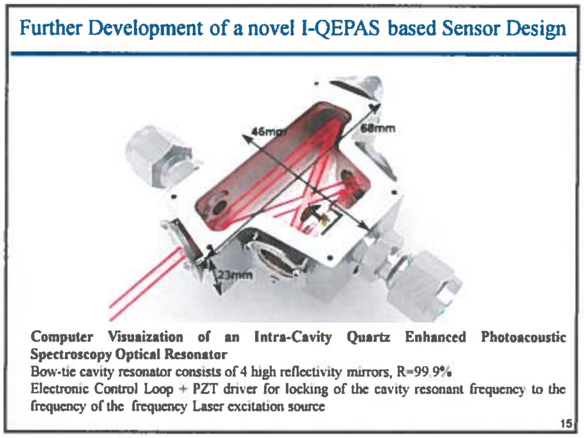
A factor ~240 higher than I-QEPAS

Identical to the intracavity optical power enhancement factor (240)

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

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.
- 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} $cm^{-1}W(Hz)^{-1/2}$. 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 pulsed QEPAS sensor systems
- 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)



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