Recent Advances and Applications of Mid-infrared Semiconductor Laser based Trace Gas Sensor Technologies

RICE

F.K.Tittel[1], Q. He[1], W. Ye[1], H. Zheng[1], M. Giglio[1,2], P. Patimisco[2], A. Sampaolo[2], J.M. Kriesel[3], V. Spagnolo[2]
[1]Departments of Electrical & Computer Engineering and Bioengineering, Rice University, Houston, TX 77005
[2]Dipartimento Interateneo di Fisica, University and Politecnico of Bari,
[3]Opto-Knowledge Systems, Inc. (OKSI).
http://www.ece.rice.edu/~lasersci/

OUTLINE

- Novel Laser-Based Trace Gas Sensor Technologies
  - Mid-IR Laser Absorption Spectroscopy (LAS) based on novel Multipass Gas Cell Designs
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
- Examples of Mid-infrared & THz Trace Gas Sensor Systems
- Future Directions of QEPAS-Based Trace Gas Sensor Technologies
  - I (Intra-cavity) – QEPAS
  - New custom QTFs

4th Intl WORKshop on Infrared Technologies

Nov. 8-9, 2017

Tempe, AZ

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

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)

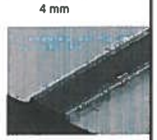
RICE

2

Key Characteristics of Mid-IR QCL & ICL Sources – Nov 2017

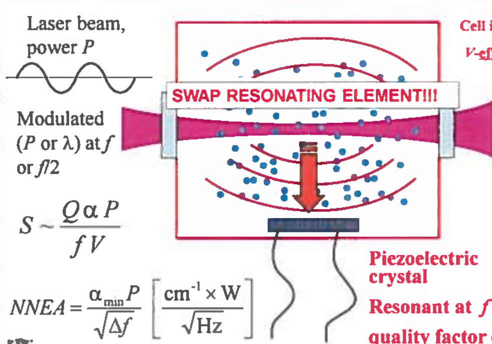
- **Band – structure engineered devices**
  Emission wavelength is determined by layer thickness – MBE or MOCVD; QCLs operate in the 3 to 24 μm spectral region and ICLs can cover the 3 to 6 μm spectral range.
  - Compact, reliable, stable, long lived, and commercially available
  - Fabry-Perot (FP), 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

4 mm



3

From Conventional PAS to Quartz Enhanced PAS (QEPAS)



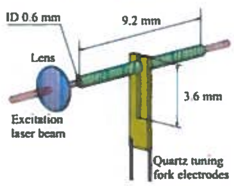
$$S \sim \frac{Q \alpha P}{f V}$$

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

RICE

4

Quartz Tuning Fork as a Resonant Microphone for QEPAS



Unique Properties

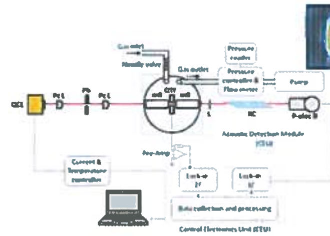
- Extremely low internal losses:
  - Q ~ 10,000 at 1 atm
  - Q ~ 100,000 in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range (~10^6) – linear from thermal noise to breakdown deformation
  - 300K noise: x~10^{-11} cm
  - Breakdown: x~10^{-2} cm
- Wide temperature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

5

CW TEC DFB QCL based QEPAS NO Gas Sensor



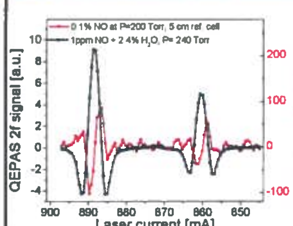
CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 430 mA and 20.5 deg C through tubes after ADM

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

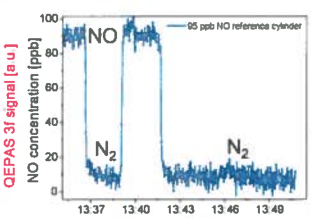
Compact Prototype NO Sensor
(September 2012)

RICE

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.



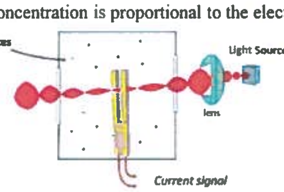
2f QEPAS signal amplitude for 95 ppb NO when DFB-QCL was locked to the **1900.08 cm⁻¹** line.

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

RICE

Quartz-Enhanced Photoacoustic Spectroscopy Introduction and Basic Operation

- Optical radiation is focused between the prongs of a quartz tuning fork
- Trace gases absorb optical energy at characteristic frequencies
- A pressure wave (sound) is generated by modulating the laser power
- Resonant mechanical vibrations are excited by the sound waves
- The mechanical vibration is converted to an electrical signal via the piezoelectric effect
- The trace gas concentration is proportional to the electrical signal



P. Patimisco et al., "Quartz-enhanced photoacoustic spectrophones exploiting custom tuning forks: a review", Advances in Physics X 2, 169-187, 2016

RICE

Quartz-Enhanced Photoacoustic Spectroscopy: Merits and main characteristics

- Very small sensing module and sample volume (a few cm^3)
- Extremely low dissipative losses
- **Optical detector is not required**
- Wide dynamic range (from % down to ppt)
- Immune to environmental acoustic noise
- Acoustic micro-resonators to enhance the QEPAS signal

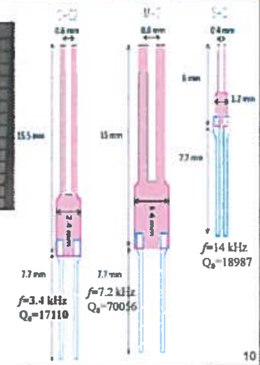
- Sensitivity scales with laser power
- Cross sensitivity issues
- Alignment requirement is that no incident radiation will hit the QTF or micro-resonators)
- Responsivity depends on the molecular energy transfer processes

Record sensitivity: 50 part-per-trillion
$\lambda = 10.54\ \mu m$ (mid – IR), SF_6

V. Spagnolo et al., Optics Letters, 37, 4461-4463, 2012.
P. Patimisco et al., "Quartz-Enhanced Photoacoustic Spectroscopy: a Review", Sensors 14, 6165, 2014

RICE

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).

QEPAS Performance for Trace Gas Species (Sept. 2017)

	Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppbv
VIS	O_2 (air)	13087.70	760	3.0×10[illegible]	0.8	1,270
VIS	O_2 (N_2)	13099.30	158	4.74×10[illegible]	1228	13,000
NIR	C_2H_2 (N_2)*	6523.88	720	4.1×10[illegible]	57	30
NIR	NH_3 (N_2)*	6528.76	575	3.1×10[illegible]	60	60
NIR	C_2H_4 (N_2)*	6177.07	715	5.4×10[illegible]	15	1,700
NIR	CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10[illegible]	16	240
NIR	N_2H_4	6470.00	700	4.1×10[illegible]	16	1,000
NIR	H_2S (N_2)*	6357.63	780	5.6×10[illegible]	45	5,000
NIR	HCl (N_2 dry)	5739.26	760	5.2×10[illegible]	15	700
NIR	CO_2 (N_2+1.5% H_2O)*	4991.26	50	1.4×10[illegible]	4.4	18,000
Mid-IR	C_2H_6	2976.8	200	4.2×10[illegible]	1.8	74
Mid-IR	CH_2O (N_2:75% RH)*	2804.90	75	8.7×10[illegible]	7.2	120
Mid-IR	CO (N_2 +2.2% H_2O)	2176.28	100	1.4×10[illegible]	71	2
Mid-IR	CO (propylene)	2196.66	50	7.4×10[illegible]	6.5	140
Mid-IR	N_2O (air+5%SF_6)	2195.63	50	1.5×10[illegible]	19	7
Mid-IR	C_2H_5OH (N_2)**	1934.2	770	2.2×10[illegible]	10	90,000
Mid-IR	NO (N_2+H_2O)	1900.07	250	7.5×10[illegible]	100	3
Mid-IR	H_2O_2	1295.6	150	4.6×10[illegible]	100	12
Mid-IR	C_2HF_5 (N_2)***	1208.62	770	7.8×10[illegible]	6.6	9
Mid-IR	NH_3 (N_2)*	1046.39	110	1.6×10[illegible]	20	6
Mid-IR	SF_6	948.62	75	2.7×10[illegible]	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=1 s time constant, 18 dB/oct filter slope

RICE

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

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 four 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 mode for QEPAS sensing
- Development of an "active" I-QEPAS system for CO and NO detection in the ppt range
- Future development of a pulsed QEPAS sensor system
- 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)