



## Advanced Measurement Concepts for Mid-infrared Semiconductor Laser based Trace Gas Sensor Technologies: Opportunities & Challenges

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### OUTLINE

MIOMD 2014  
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France.

Oct. 5-9, 2014

- New Laser Based Trace Gas Sensor Technology
  - Novel Multipass Gas Absorption Cells & Electronics
  - Quartz Enhanced Photoacoustic Spectroscopy
- Examples of seven Mid-infrared Trace Gas Species
  - NO, CO, SO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> & C<sub>3</sub>H<sub>6</sub>O
- Future Directions of 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 I SBIR sub-award is acknowledged

## 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**

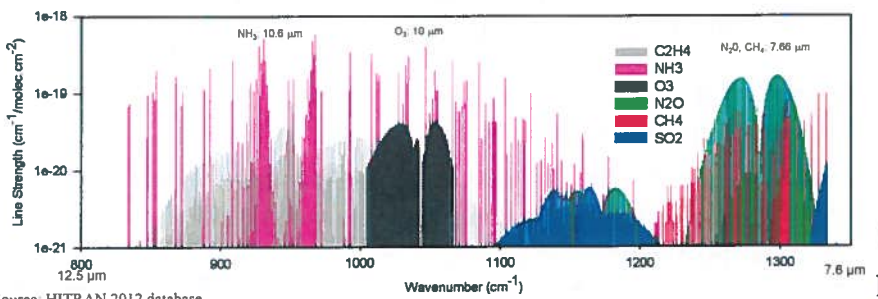
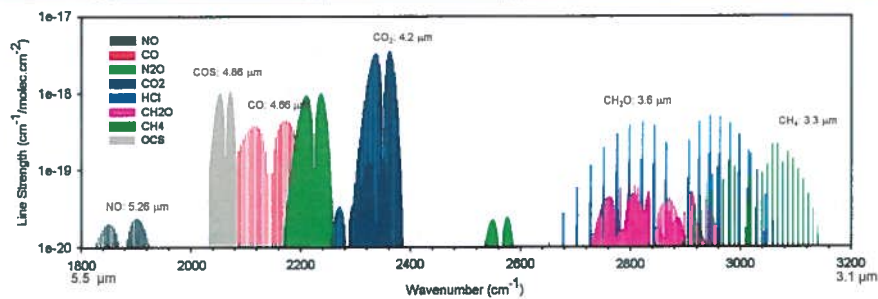


## Laser based Trace Gas Sensing Techniques

- **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; Circular Cylindrical: Empa & Loncar)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector): 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)**



## HITRAN Simulated Mid-Infrared Molecular Absorption Spectra



Source: HITRAN 2012 database

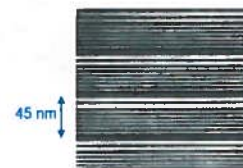


## Mid-IR Source Requirements for Laser Spectroscopy

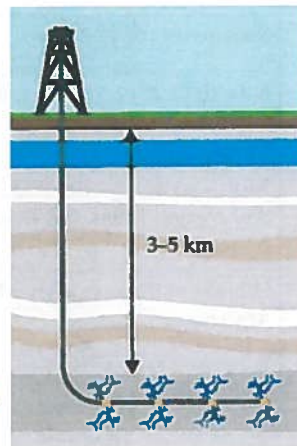
<u>REQUIREMENTS</u>	<u>IR LASER SOURCE</u>
Sensitivity (% to pptv)	Optimum Wavelength, Power
Selectivity (Spectral Resolution)	Stable Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Mode Hop-free Wavelength Tunability
Directionality or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

## Key Characteristics of Mid-IR QCL & ICL Sources – Oct. 2014

- Band – structure engineered devices**  
 Emission wavelength is determined by layer thickness – MBE or MOCVD; Type I QCLs operate in the 3 to 24  $\mu\text{m}$  spectral region; Type II and GaSb based ICLs can cover the 3 to 6  $\mu\text{m}$  spectral range.
  - 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**
  - 1.5  $\text{cm}^{-1}$  using injection current control for DFB devices
  - 10-20  $\text{cm}^{-1}$  using temperature control for DFB devices
  - ~100  $\text{cm}^{-1}$  using current and temperature control for QCL DFB Array
  - ~ 525  $\text{cm}^{-1}$  (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 (0.0004  $\text{cm}^{-1}$ )
  - Pulsed: ~ 300 MHz
- High pulsed and CW powers of QCLs at TEC/RT temperatures**
  - Room temperature pulsed 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  $\mu\text{m}$



## Typical Oil & Gas Production Site near Houston, TX

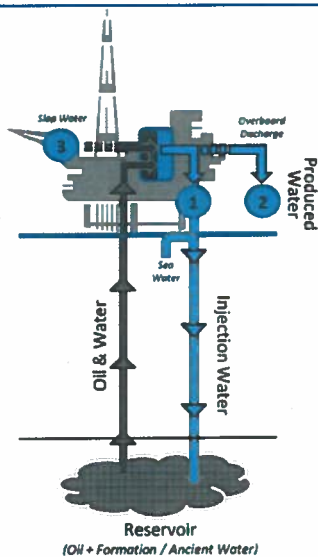


This figure shows the result of a sequence of four fracking injections obtained by directional drilling which creates horizontal production in target stratum.

A proposed DOE-ARPA-E CH<sub>4</sub> detection project at 3.327  $\mu\text{m}$  will start in 2015 at a wellpad of 10 m x 10 m with a 1 m spatial resolution.



## 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

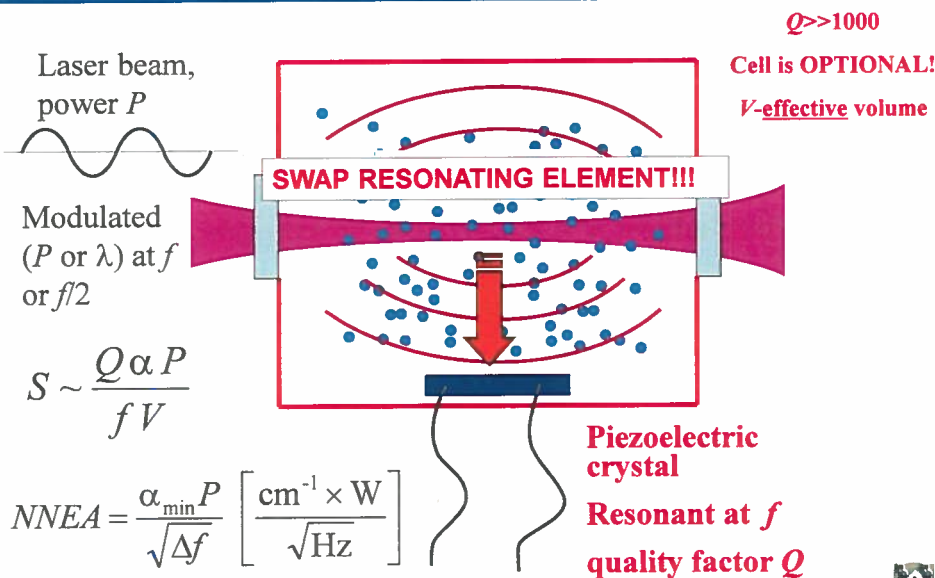
## Comparison of proposed Rice CH<sub>4</sub> Sensor System and current commercially available CH<sub>4</sub> Platforms

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)

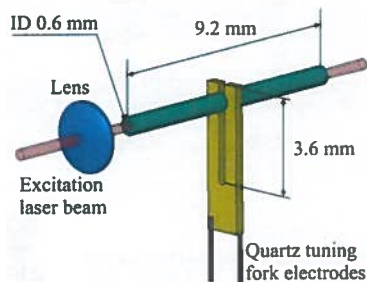


## From Conventional PAS to Quartz Enhanced PAS (QEPAS)





## Quartz Tuning Fork as a Resonant Microphone for QEPAS



### Unique Properties

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

### Acoustic Micro-resonator ( $\mu$ R) Tubes

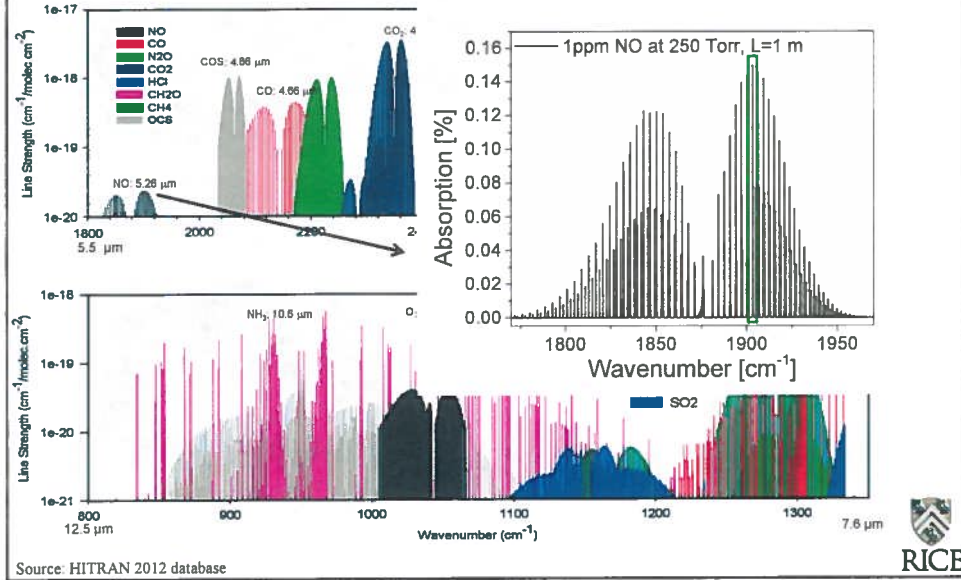
- Optimum inner diameter: 0.6 mm;  $\mu$ R-QTF gap is  $25\text{--}50\ \mu\text{m}$
- Optimum  $\mu$ R tubes must be  $\sim 4.4\ \text{mm}$  long ( $\sim \lambda/4 < l < \lambda/2$  for sound at 32.8 kHz)
- SNR of QTF with  $\mu$ R tubes:  $\times 30$  (depending on gas composition and pressure)

## Motivation for Nitric Oxide Detection

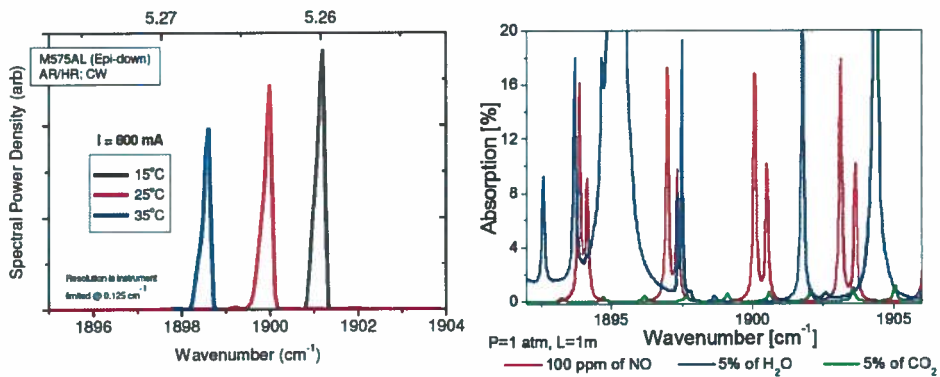
- **NO in medicine and biology**
  - Important signaling molecule in physiological processes in humans and mammals (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, chronic obstructive pulmonary disease (COPD) & lung rejection
- **Environmental pollutant gas monitoring**
  - Ozone depletion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



## Molecular Absorption Spectra within two Mid-IR Atmospheric Windows and NO absorption @ 5.26 $\mu\text{m}$



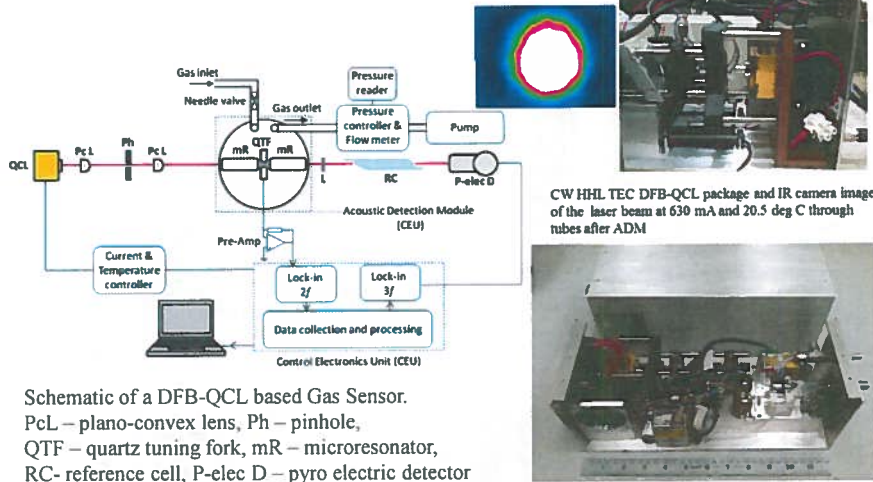
## Emission Spectra of a 1900 $\text{cm}^{-1}$ TEC DFB QCL and HITRAN simulated spectra of NO, H<sub>2</sub>O & CO<sub>2</sub>



Output power: 117 mW @ 25 C  
Thorlabs/Maxion



## 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

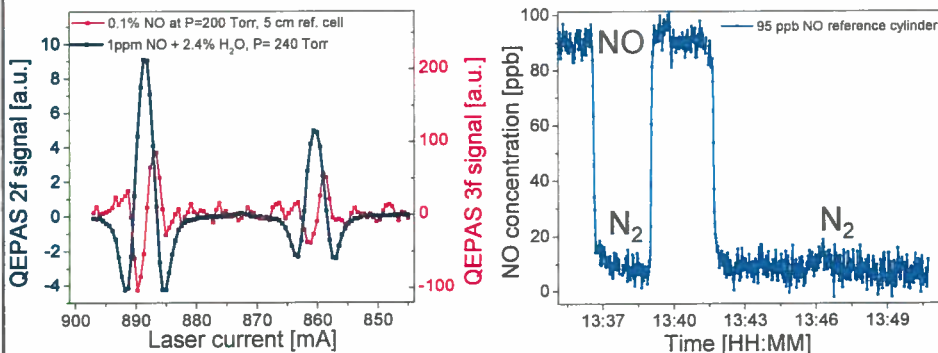
CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 630 mA and 20.5 deg C through tubes after ADM



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  $1900.08 \text{ cm}^{-1}$  NO line.

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

Minimum detectable NO concentration is:  
 **$\sim 3 \text{ ppbv}$  ( $1\sigma$ ; 1 s time resolution)**



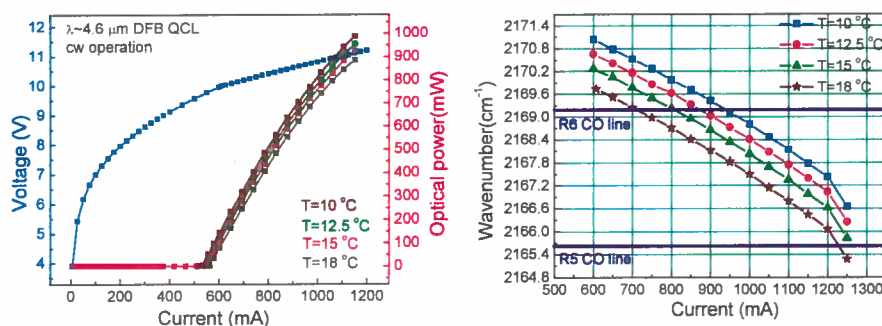


## Motivation for Carbon Monoxide Detection

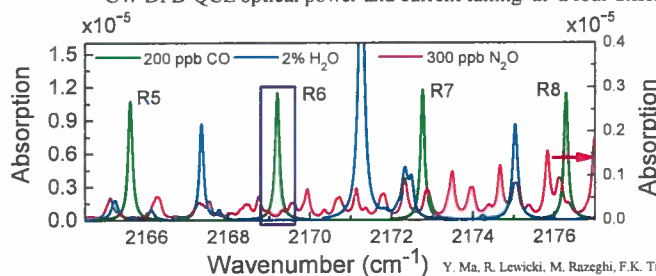
- **CO in Medical Diagnostics**
  - Hypertension and abnormality in heme metabolism
- **Public Health**
  - Extremely dangerous to human life even at a low concentrations. CO must be monitored at low concentration levels (<35 ppm).
- **Atmospheric Chemistry**
  - Incomplete combustion of natural gas, fossil fuel and other carbon containing fuels.
  - Impact on atmospheric chemistry through its reaction with hydroxyl (OH) for troposphere ozone formation and changing the concentration levels of greenhouse gases (e.g. CH<sub>4</sub>).



## Performance of a 4.61 $\mu$ m high power CW TEC DFB QCL



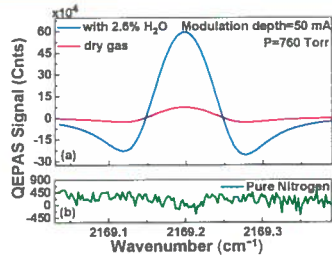
CW DFB-QCL optical power and current tuning at a four different QCL temperatures.



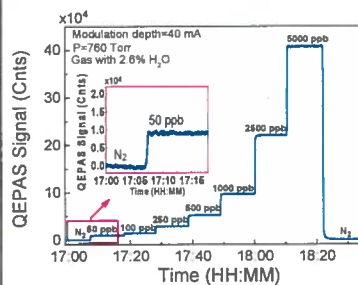
Estimated max wall-plug efficiency (WPE) is  $\sim 7\%$  at 1.25A QCL drive-current.



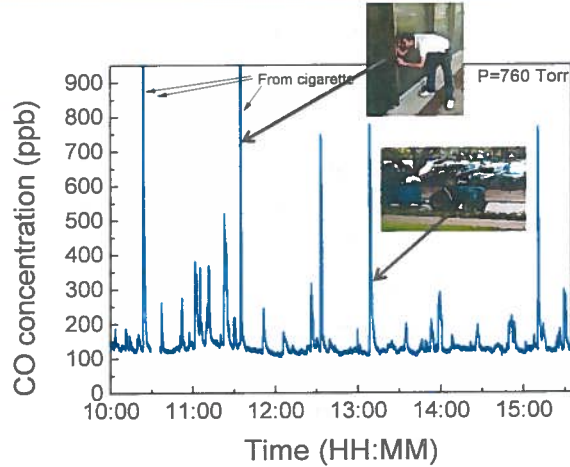
## CW DFB-QCL based CO QEPAS Sensor Results



2f QEPAS signal for dry (red) and moistured (blue) 5 ppm CO N<sub>2</sub> mixture near 2169.2 cm<sup>-1</sup>.



Dilution of a 5 ppm CO reference gas mixture when the CW DFB-QCL is locked to the 2169.2 cm<sup>-1</sup> 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)

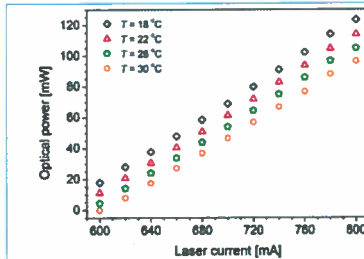
P. Stefanski et al., Appl. Phys. B, online June 3 2014



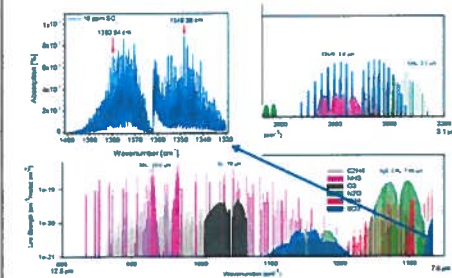
## CW DFB-QCL based SO<sub>2</sub> QEPAS Results

### Motivation for Sulfur Dioxide Detection

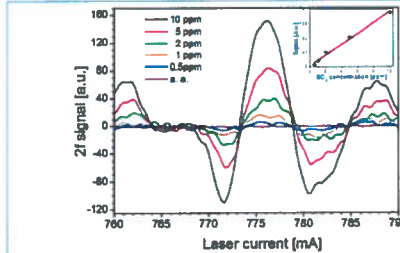
- SO<sub>2</sub> exposure affects lungs and causes breathing difficulties, bronchitis, cardiovascular disease
- Currently, reported annual average atmospheric SO<sub>2</sub> concentrations range from ~ 1 - 6 ppb
- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In the atmosphere SO<sub>2</sub> converts to sulfuric acid → primary contributors to acid rain
- SO<sub>2</sub> reacts to form sulfate aerosols
- Primary SO<sub>2</sub> exposure for 1 hour is 75 ppb



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



Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



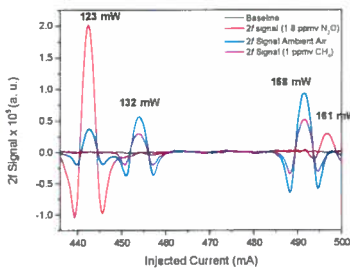
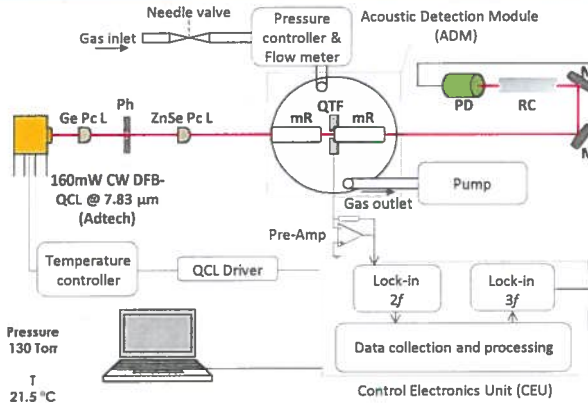
2f WMS QEPAS signals for different SO<sub>2</sub> concentrations when laser was tuned across 1380.9 cm<sup>-1</sup> line.

Minimum detectable SO<sub>2</sub> concentration is:  
~ 100 ppbv (1σ; 1 s time resolution)

# QEPAS based CH<sub>4</sub> and N<sub>2</sub>O Gas Sensor

## Motivation for CH<sub>4</sub> and N<sub>2</sub>O Detection

- **Medical Diagnostics**
  - Nausea, blurred vision, vomiting
- **Prominent greenhouse gases**
- **Sources: wetlands, leakage from natural gas systems, fossil fuel production and agriculture**



Pressure  
130 Torr  
T  
21.5 °C  
AM  
4 mA  
f  
32760 Hz  
f<sub>mod</sub>  
16380 Hz

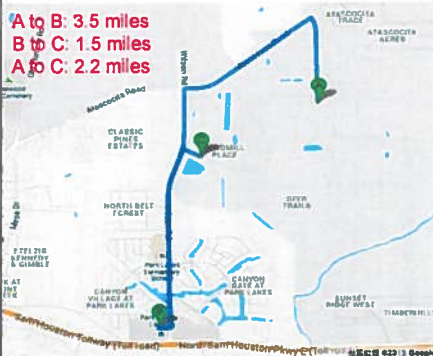
**Detection Limit (1σ) with a 1-sec averaging time**  
Methane (CH<sub>4</sub>) (1275.04 cm<sup>-1</sup>) **13 ppbv**  
Nitrous Oxide (N<sub>2</sub>O) (1275.5 cm<sup>-1</sup>) **6 ppbv**

Deduced N<sub>2</sub>O concentration in the ambient laboratory air: **331 ppbv**

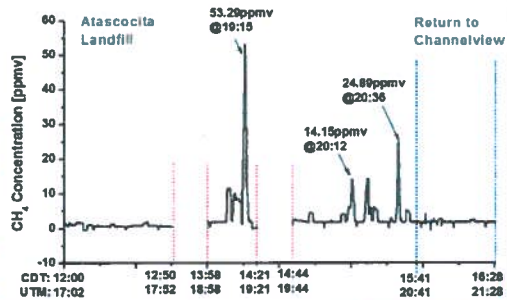
M. Jahjah et al., Analyst, 139, 2063-2069, 2014 & Appl. Lett., 39, 957-960, 2014



## CH<sub>4</sub> Measurements performed with a DFB-QCL based QEPAS Sensor installed in the Aerodyne Mobile Laboratory (Sept 7, 2013)



### Atascocita Landfill, Humble, TX 77396 CH<sub>4</sub> Perimeter Measurements



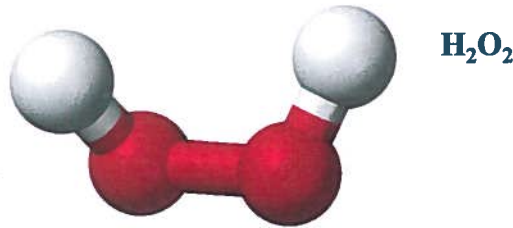
- A: 29.9599° North, 95.2334° West
- B: 29.9364° North, 95.2508° West
- C: 29.9547° North, 95.2462° West (Landfill)



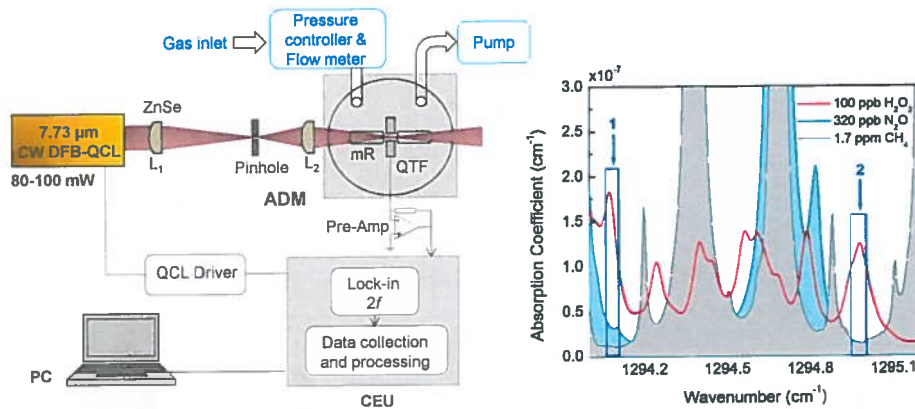
M. Jahjah et al., Opt. Letters, 39, 957-960, 2014

## Motivation of H<sub>2</sub>O<sub>2</sub> Detection

- Oxidative capacity of atmosphere and balance of HO<sub>x</sub>;
- Acid rain formation & In-cloud oxidation of S(IV) to S(VI);
- Active agent in decontamination and sterilization systems;
- H<sub>2</sub>O<sub>2</sub> in breath is a biomarker of oxidative stress;
- H<sub>2</sub>O<sub>2</sub> concentration levels in Houston have not been reported despite of atmospheric conditions, such as high humidity, high solar radiation levels, and the presence of the petrochemical industry.



## QEPAS based Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) Sensor System



Schematic of QCL based QEPAS sensor:  
ADM – acoustic detection module; CEU – control electronics unit; PC – personal computer.

Simulated spectra (HITRAN) of H<sub>2</sub>O<sub>2</sub> at 296 K and 130 Torr, along with atmospheric interfering molecules of CH<sub>4</sub> and N<sub>2</sub>O; two target wavelengths at 1294.1 and 1294.9 cm<sup>-1</sup> are shown.



H<sub>2</sub>O<sub>2</sub> Exposure limit is set at 1 ppmv by OSHA

W Ren et al., Appl. Phys. Lett., 114, 041117, 2014




## QEPAS Performance for Trace Gas Species (October 2014)

	Molecule (Host)	Frequency, cm <sup>-1</sup>	Pressure, Torr	NNEA, cm <sup>2</sup> W/Hz <sup>2</sup>	Power, mW	NEC (τ=1s), ppmv
VIS	O <sub>2</sub> (air)	15087.70	700	3.0×10 <sup>-2</sup>	0.8	1.27
	O <sub>2</sub> (N <sub>2</sub> )	13099.30	158	4.74×10 <sup>-2</sup>	1228	13
	C <sub>2</sub> H <sub>2</sub> (N <sub>2</sub> )*	6523.88	720	4.1×10 <sup>-9</sup>	57	0.03
NIR	NH <sub>3</sub> (N <sub>2</sub> )*	6528.76	575	3.1×10 <sup>-9</sup>	60	0.06
	C <sub>2</sub> H <sub>2</sub> (N <sub>2</sub> )*	6177.07	715	5.4×10 <sup>-9</sup>	15	1.7
	CH <sub>4</sub> (N <sub>2</sub> +1.2% H <sub>2</sub> O)*	6057.09	760	3.7×10 <sup>-9</sup>	16	0.24
	N <sub>2</sub> H <sub>4</sub>	6470.00	700	4.1×10 <sup>-9</sup>	16	1
	H <sub>2</sub> S (N <sub>2</sub> )*	6357.63	780	5.6×10 <sup>-9</sup>	45	5
	HCl (N <sub>2</sub> dry)	5739.26	760	5.2×10 <sup>-9</sup>	15	0.7
	CO <sub>2</sub> (N <sub>2</sub> +1.5% H <sub>2</sub> O)*	4991.26	50	1.4×10 <sup>-8</sup>	4.4	18
	CH <sub>2</sub> O (N <sub>2</sub> :75% RH)*	2804.90	75	8.7×10 <sup>-9</sup>	7.2	0.12
	CO (N <sub>2</sub> +2.2% H <sub>2</sub> O)	2176.28	100	1.4×10 <sup>-7</sup>	71	0.002
	CO (propylene)	2196.66	50	7.4×10 <sup>-8</sup>	6.5	0.14
Mid-IR	N <sub>2</sub> O (air+5%SF <sub>6</sub> )	2195.63	50	1.5×10 <sup>-8</sup>	19	0.007
	C <sub>2</sub> H <sub>5</sub> OH (N <sub>2</sub> )**	1934.2	770	2.2×10 <sup>-7</sup>	10	90
	NO (N <sub>2</sub> +H <sub>2</sub> O)	1900.07	250	7.5×10 <sup>-8</sup>	100	0.003
	H <sub>2</sub> O <sub>2</sub>	1295.6	150	4.6×10 <sup>-8</sup>	100	12
	C <sub>2</sub> HF <sub>5</sub> (N <sub>2</sub> )***	1208.62	770	7.8×10 <sup>-9</sup>	6.6	0.009
	NH <sub>3</sub> (N <sub>2</sub> )*	1046.39	110	1.6×10 <sup>-8</sup>	20	0.006
	SF <sub>6</sub>	948.62	75	2.7×10 <sup>-10</sup>	18	5×10 <sup>-3</sup> (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.

For comparison: conventional PAS 2.2 ×10<sup>-9</sup> cm<sup>2</sup>W/√Hz for NH<sub>3</sub>

## Use of Canines in Non-invasive & Sensitive Cancer Detection



**Bladder Cancer**  
 Urine  
 Sensitivity 73%  
 Specificity 56-92%

**Ovarian cancer**  
 Carcinoma Tissue  
 Sensitivity 100%, Specificity 98%  
 Blood  
 Specificity 100%, Sensitivity 95%

**Lung Cancer**  
 Breath  
 Sensitivity 99%  
 Specificity 99%

**Breast Cancer**  
 Breath  
 Sensitivity 88%  
 Specificity 98%

**Prostate Cancer**  
 urine  
 Sensitivity 99%

**Melanoma**  
 Skin VOCs  
 Potential!

**Colorectal cancer**  
 Sensitivity Specificity  
 Breath 91% 99%  
 Stool 97% 99%

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





## Advantages & Disadvantages of Canines in Cancer 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
- Potential of VOCs are 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

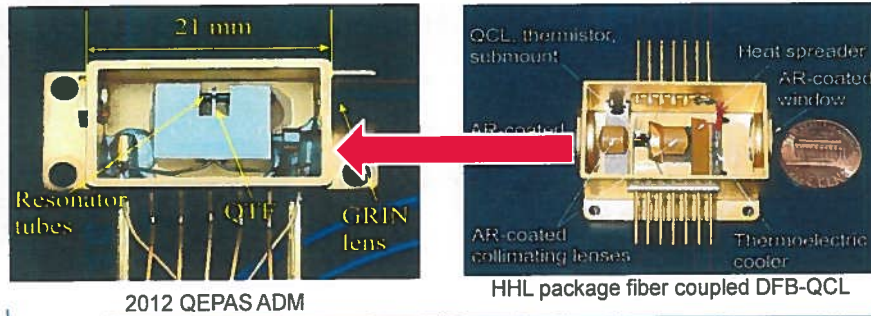


## Future Directions and Outlook

- New target analytes: formaldehyde ( $\text{CH}_2\text{O}$ ), ethylene ( $\text{C}_2\text{H}_4$ ), ozone ( $\text{O}_3$ ) and nitrate ( $\text{NO}_3$ )
- Ultra-compact, low cost, robust sensors (e.g.  $\text{CH}_4$ ,  $\text{NO}$ ,  $\text{CO}$ ...)
- QCL based ultra-portable atmospheric carbon isotope monitor for  $^{12}\text{CH}_4$  &  $^{13}\text{CH}_4$
- Monitoring of broadband absorbers: acetone ( $\text{C}_3\text{H}_6\text{O}$ ): MDL of 1.5 ppm with a 7mW ICL & AM, or 20ppb with a 100mW QCL @ 8.23 $\mu\text{m}$ ; benzene ( $\text{C}_6\text{H}_6$ )...
- Optical power build-up cavity designs (I-QEPAS)
- THz QEPAS based sensors
- Development of trace gas sensor networks

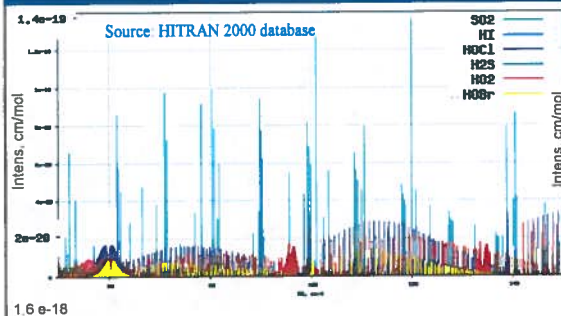


## Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module



A. Lyakh, et al "1.6 W high wall plug efficiency, continuous-wave room temperature quantum cascade laser emitting at 4.6  $\mu\text{m}$ ", Appl. Phys. Lett. 92, 111110 (2008)

## Why is THz based Trace Gas Sensing useful ?



Several gas species such as HF, OH, HCN, HCl, HBr, NH<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>O & 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

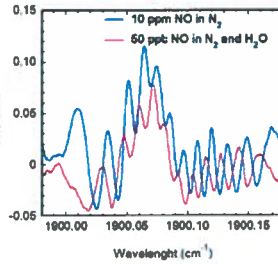


**QEPAS signal strongly depends on the energy relaxation rates due to the possibility to operate at low pressure, & thereby taking advantages of the typically very high QTF Q-factors.**

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

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

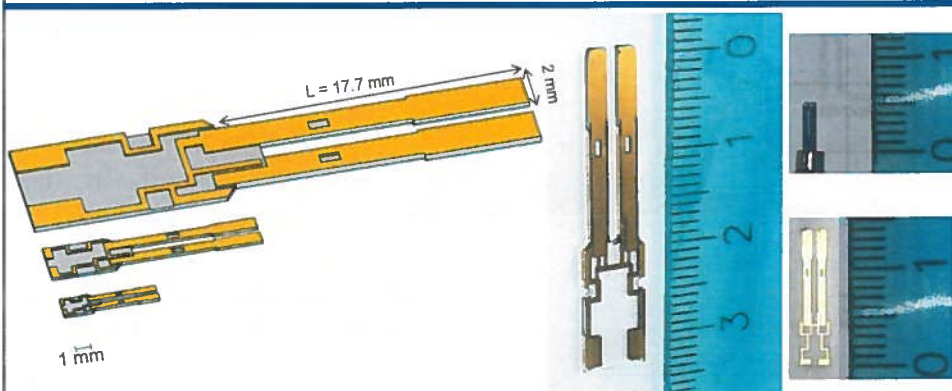
In QEPAS sensor systems, it is critical to avoid laser illumination of the QTF, since the radiation blocked by the QTF prongs results in an undesirable non-zero background as well as a shifting fringe-like interference pattern.



Standard QTF

The standard QTF prong separation of  $330 \mu\text{m}$  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 scaled in Dimensions that are $\sim 7$ & $3$ times larger than standard QTFs



Standard photolithographic techniques were used to etch the custom QTF, starting from a z-cut quartz wafer. Chromium/gold contacts were deposited on both sides of the custom QTF.

Currently verification that the larger QTFs behave similar to a “standard” QTF in terms of vibrational modes and Q factor is in progress

## THz QCL Sources via Nonlinear Optics

Use intra-cavity DFG in mid-IR QCLs



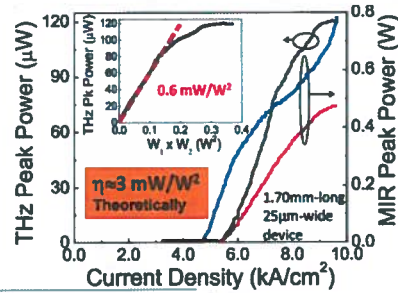
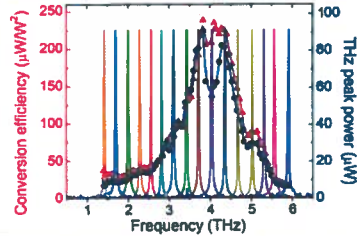
$$W(\omega_{THz}) \propto |\chi^{(2)}|^2 W(\omega_1) W(\omega_2) \times I_{eff}^2$$

THz QCL source based on intra-cavity DFG

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



2.3-mm-long, 22-μm-wide device @ room temperature

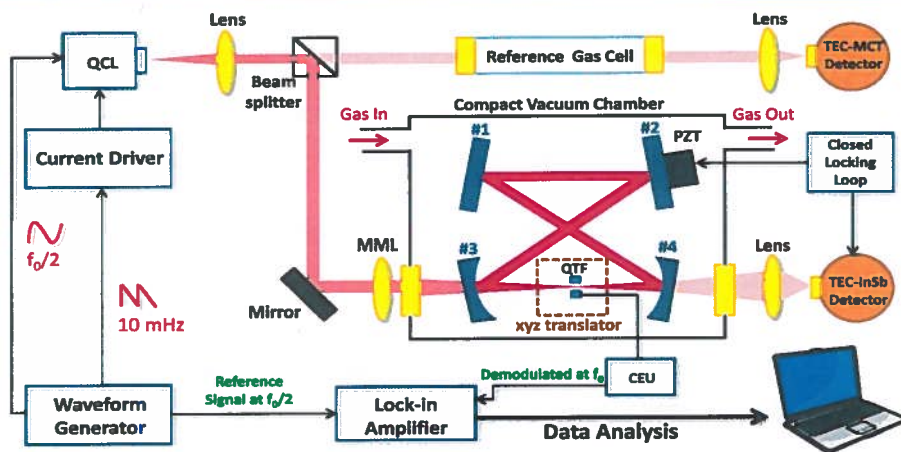


Vijayraghavan et al., Nature Comm. 4, 2021 (2013)

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

Vijayraghavan et al., Nature Comm. 4, 2021 (2013); Jiang et al., J. Opt. 18, 094002 (2014)  
Monolithic tuners: 0.58 THz of tuning - Jung et al., Nature Comm. 5, 4267 (2014)

## Proposed Intracavity-QEPAS (I-QEPAS) Sensor System

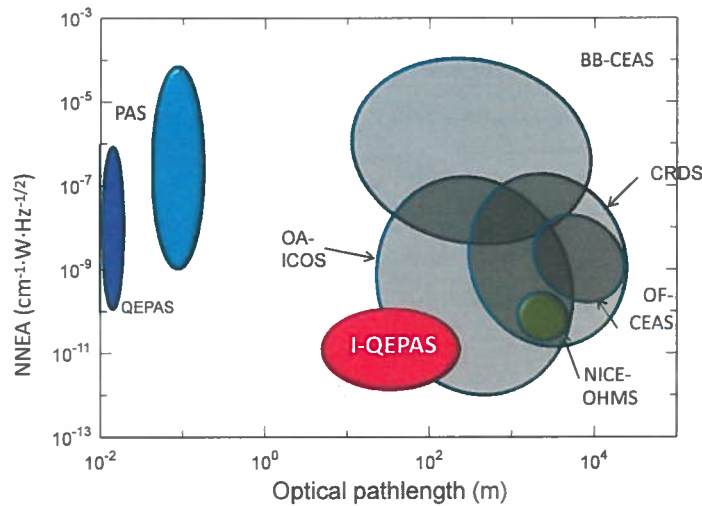


Optical power build up cavity can provide:

- RT CW DFB QCL,  $\lambda=4.33$  microns
- Low noise current driver  $\rightarrow$  narrow QC laser linewidth  $\sim 1$  MHz
- Bow-tie cavity  $\rightarrow$  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 DFB laser diodes and high performance QCLs for **environmental monitoring and medical diagnostics**.
- Interband cascade and quantum cascade lasers were used in QEPAS and TDLAS based sensor platforms
- Six target trace gas species were detected with a 1 sec sampling time:
  - NO:  $\sim 5.26 \mu\text{m}$ , detection limit of 3 ppbv
  - CO:  $\sim 4.61 \mu\text{m}$ , minimum detection limit of 2 ppbv
  - SO<sub>2</sub>:  $\sim 7.24 \mu\text{m}$ , detection limit of 100 ppbv
  - CH<sub>4</sub> and N<sub>2</sub>O:  $\sim 7.28 \mu\text{m}$ , detection limits of 13 and 6 ppbv, respectively
  - H<sub>2</sub>O<sub>2</sub>:  $\sim 7.73 \mu\text{m}$ , detection limit of 75 ppb
  -
- New target analytes: CH<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub>O

