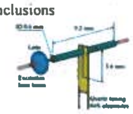
Current Status of Mid-Infrared Quantum and Interband Cascade Lasers Based Trace Gas Detection in Exhaled Breath

F.K.Tittel, W. Ren, W. Jiang, Y. Cao, J.J. Allred, L. Luo, D. Jiang & L. Dong

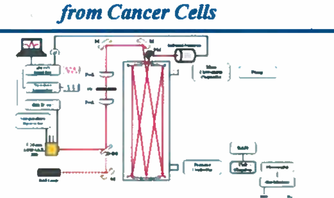
Department of Electrical and Computer Engineering,
Rice University, Houston, TX 77005
website: http://www.ece.rice.edu/lasersci

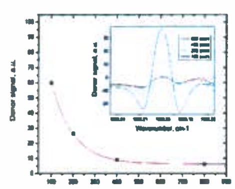
Outline

- New Laser Based Trace Gas Sensor Technology
  - Novel Multipass Absorption Cell (MGC) & Electronics
  - Quartz Enhanced Photoacoustic Spectroscopy
    - Unique Properties of Quartz Tuning Fork
    - Acoustic Micro-resonator Tubes
- Examples of five Mid-Infrared Sensor Architectures
  - NH_3, NO, CO, CH_4, N_2O and H_2O_2
  - Future Directions of Laser based Gas Sensor Technologies and Conclusions



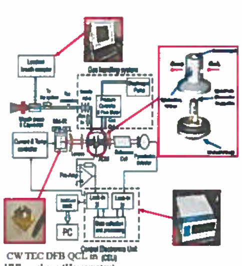
TDLAS Sensor for Detecting NO Emission from Cancer Cells



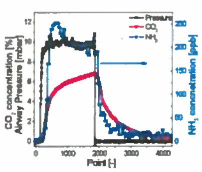


Dependence of the sensor signal from biological samples on the overall gas flow of the sensor system (black squares). The inset shows spectra corresponding to the data points.

QEPAS based NH_3 Gas Sensor and Real-time Measurements

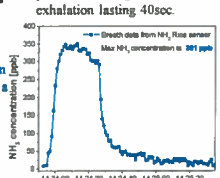


CW TEC DFB QCL in CS1 HHL package (Hamamatsu)



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)



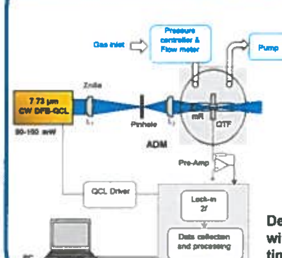
Minimum detectable concentration of NH_3 is:
~ 6 ppbv at 967.35 cm^{-1} (1σ; 1 s time resolution)

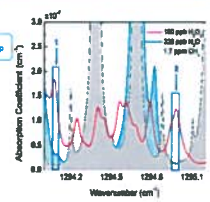
CW TEC DFB QCL based QEPAS NO Gas Sensor

Schematic of a QCL QEPAS based Gas Sensor. M – mirror, PcL – plano-convex lens, Ph – pinhole, QTF – quartz tuning fork, mR – acoustic micro-resonator, RC – reference cell

Compact Prototype NO Sensor (September 2012)

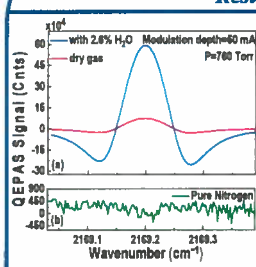
CW TEC DFB QCL based QEPAS H_2O_2 Gas Sensor



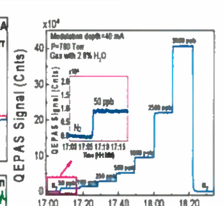


Detection limit of 75 ppbv with 1 sec data acquisition time, and 12 ppbv with 100 sec averaging time

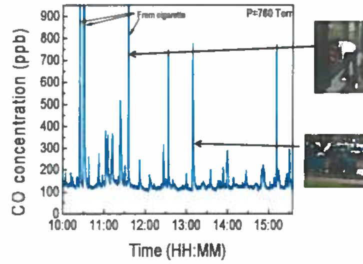
CW DFB-QCL based CO QEPAS Sensor Results



2f QEPAS signal for dry (red) and moisturized (blue) 5 ppm CO:N_2 mixture near **2169.2 cm^{-1}** (R6 CO line).



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.

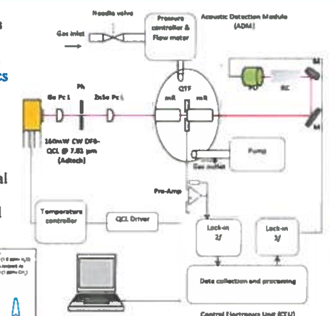


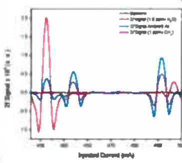
Minimum detectable CO concentration is:
~ 2 ppbv (1σ; 1 s time resolution)

QEPAS based CH_4 and N_2O Gas Sensor

Motivation for CH_4 and N_2O Detection

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





The Analyst Aug 2013

Detection Limit (1σ) with a **1-sec** averaging time
Methane (CH_4) (1275.04 cm^{-1}) **13 ppbv**
Nitrous Oxide (N_2O) (1275.5 cm^{-1}) **6 ppbv**

Deduced N_2O concentration in the ambient laboratory air: **331 ppbv**

QEPAS Performance for Trace Gas Species (July 2014)

	Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppmv
VIS	O_3 (air)	35087.70	700	3.0×10[illegible]	0.8	1.27
VIS	O_2 (N_2)	13099.30	158	4.74×10[illegible]	1228	13
VIS	C_2H_2 (N_2)*	6523.88	720	4.1×10[illegible]	57	0.03
NIR	NH_3 (N_2)*	6528.76	575	3.1×10[illegible]	60	0.06
NIR	C_2H_4 (N_2)*	6177.07	715	5.4×10[illegible]	15	1.7
NIR	CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10[illegible]	16	0.24
NIR	N_2H_4	6470.00	700	4.1×10[illegible]	16	1
NIR	H_2S (N_2)*	6357.63	780	5.6×10[illegible]	45	5
NIR	HCl (N_2 dry)	5739.26	760	5.2×10[illegible]	15	0.7
NIR	CO_2 (N_2+1.5% H_2O)*	4991.26	50	1.4×10[illegible]	4.4	18
Mid-IR	CH_2O (N_2:75% RH)*	2804.90	75	8.7×10[illegible]	7.2	0.12
Mid-IR	CO (N_2 +2.2% H_2O)	2176.28	100	1.4×10[illegible]	71	0.002
Mid-IR	CO (propylene)	2196.66	50	7.4×10[illegible]	6.5	0.14
Mid-IR	N_2O (air+5%SF_6)	2195.63	50	1.5×10[illegible]	19	0.007
Mid-IR	C_2H_5OH (N_2)**	1934.2	770	2.2×10[illegible]	10	90
Mid-IR	NO (N_2+H_2O)	1900.07	250	7.5×10[illegible]	100	0.003
Mid-IR	C_2HF_5 (N_2)***	1208.62	770	7.8×10[illegible]	6.6	0.009
Mid-IR	NH_3 (N_2)*	1046.39	110	1.6×10[illegible]	20	0.006
Mid-IR	SF_6	948.62	75	2.7×10[illegible]	18	5×10[illegible] (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.

Future Directions and Outlook

- New target analytes: formaldehyde (CH_2O), ethylene (C_2H_4), ozone (O_3), nitrate (NO_3),
- Ultra-compact, low cost, robust sensors (e.g. C_2H_6, NO, CO) capable of high precision and accuracy
- QCL based ultra-portable atmospheric carbon isotope monitor for $^{12}CH_4$ and $^{13}CH_4$
- Monitoring of broadband absorbers: acetone (C_3H_6O), propane (C_3H_8), benzene (C_6H_6)
- Optical power build-up cavity designs (I-QEPAS)
- THz QEPAS based sensors: H_2S,
- Development of trace gas sensor networks