Mid-Infrared Laser based Trace Gas Sensor Technologies: Recent Advances and Applications

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OUTLINE

Rice University ECE Affiliates Day

Mar. 23, 2018

Houston, TX

- 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
- Field Deployment of Trace Gas Sensors

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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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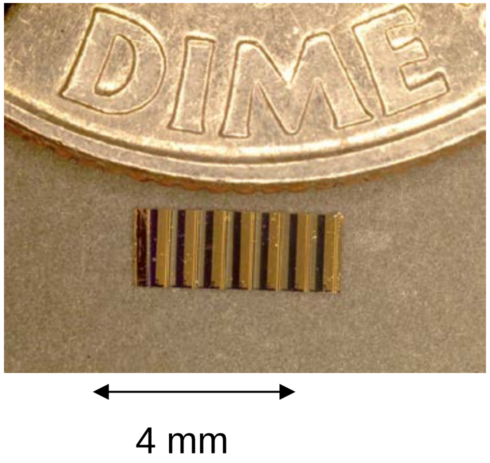
Key Characteristics of Mid-IR QCL & ICL Sources – March 2018

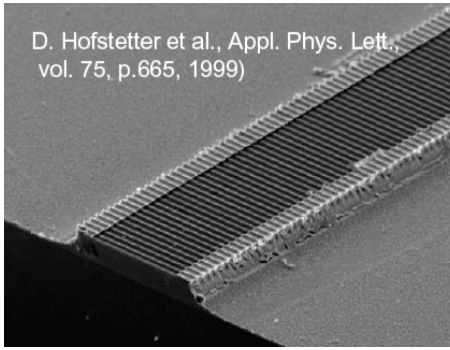
- **Band – structure engineered devices**
  Emission wavelength is determined by layer thickness – MBE or MOCVD; QCLs operate in the 3 to 24 µm spectral region and ICLs can cover the 3 to 6 µm spectral range.
  - Compact, reliable, stable, long lived, and commercially available
  - Fabry-Perot (FP),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

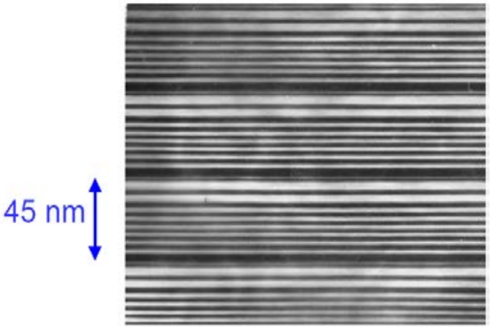
- **Wide spectral tuning ranges in the mid-IR**
  - 1.5 cm^{-1} using injection current control for DFB devices
  - 10-20 cm^{-1} using temperature control for DFB devices
  - ~100 cm^{-1} using current and temperature control for QCLs DFB Array
  - ~ 525 cm^{-1} (22% of c.w.) using an external grating 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

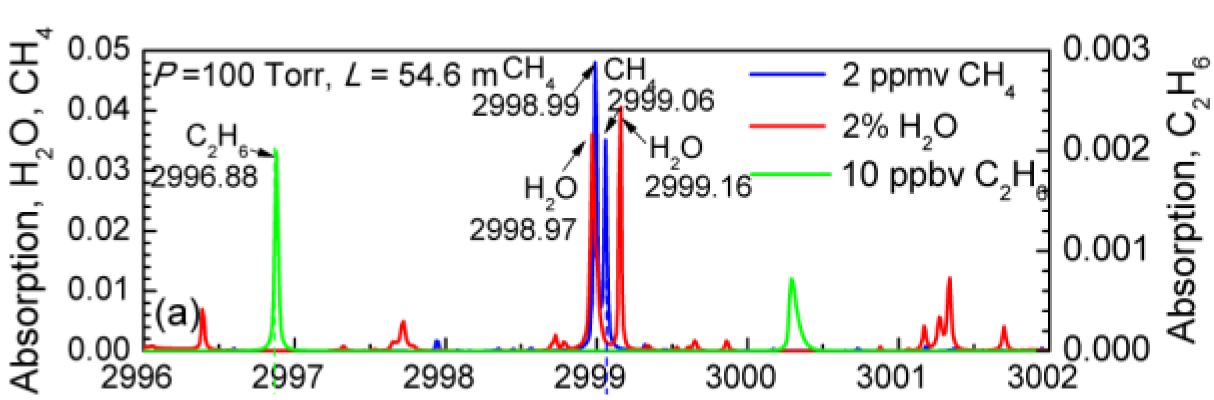
- **High pulsed and CW powers of QCLs & ICLs at RT temperature**
  - TEC QCL pulsed peak power of ~203 W with 10% wall plug efficiency
  - CW QCL powers of ~ 5 W with 23% wall plug efficiency at 293 K
  - > 600 mW CW DFB QCL at RT; wall plug efficiency 23% at 4.6 µm
  - > 5mW CW, DFB ICL at RT



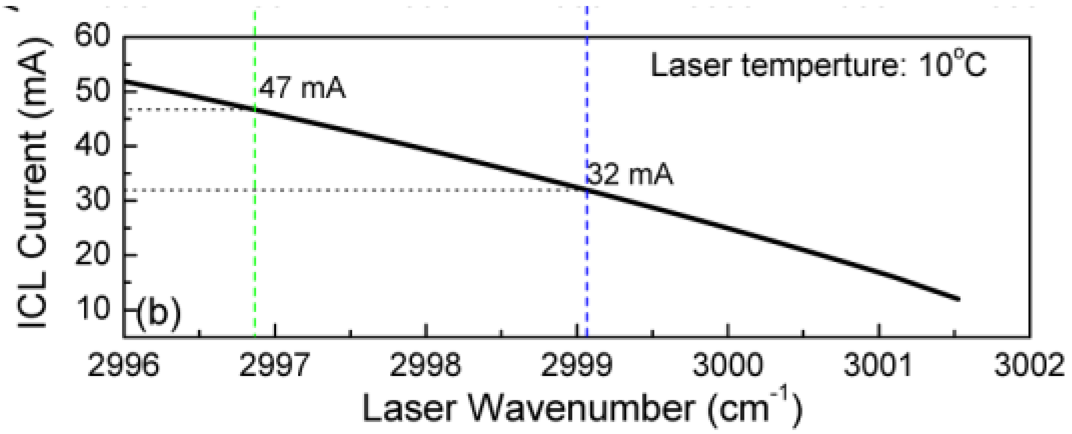




HITRAN Line Selection for a CH_4 & C_2H_6 Sensor



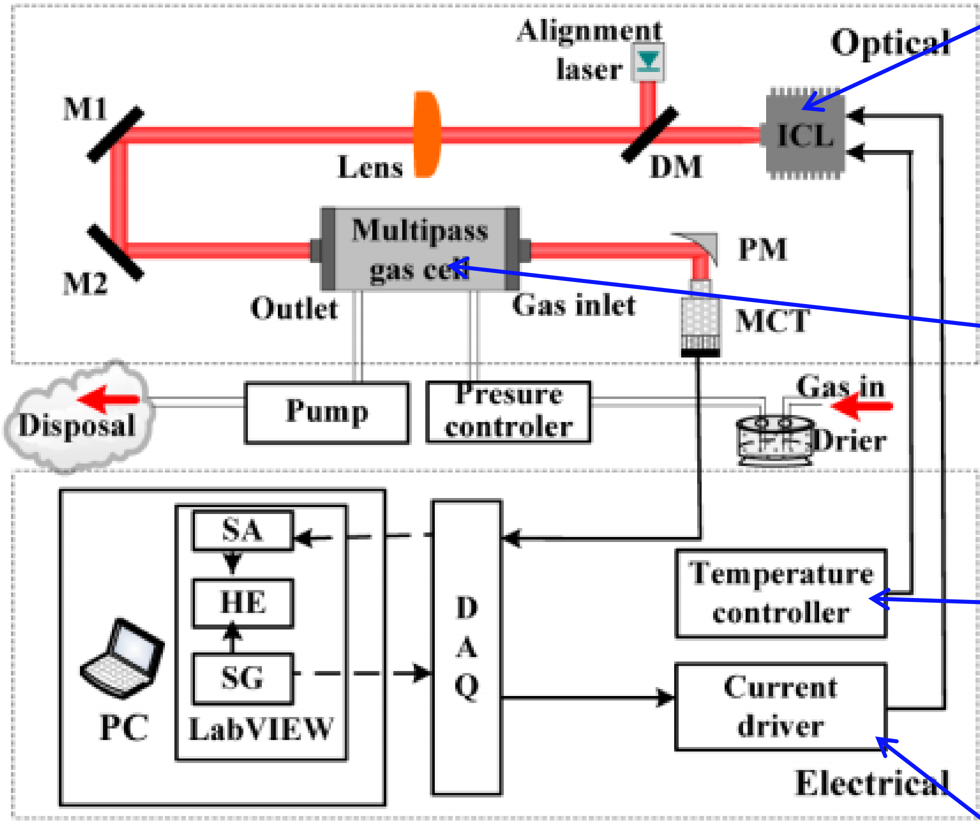
(a) HITRAN based absorption spectra of C_2H_6 (10 ppbv), CH_4 (2 ppmv), and H_2O(2%) in a narrow spectral range from 2996 cm^{-1} to 3002 cm^{-1} at a pressure of 100 Torr and an absorption length of 54.6 m. C_2H_6, CH_4, and H_2O lines are shown in green, blue and red, respectively.



(b) Plot of the ICL emission wavenumber as a function of the ICL drive current at 10 ° C.

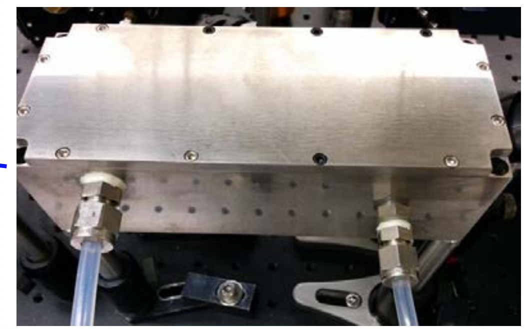
Laser Absorption Spectroscopy based CH_4 & C_2H_6 Dual-gas Sensor

Sensor structure

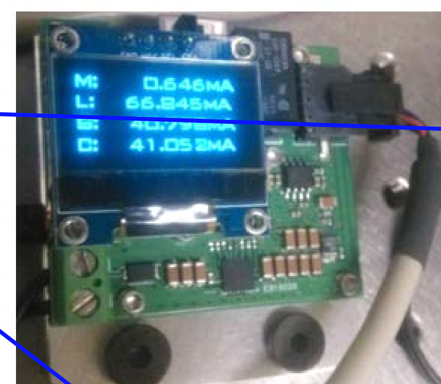


Schematic of a mid-infrared dual-gas sensor for simultaneous detection of methane and ethane using a single continuous-wave ICL

3.327μm CW ICL



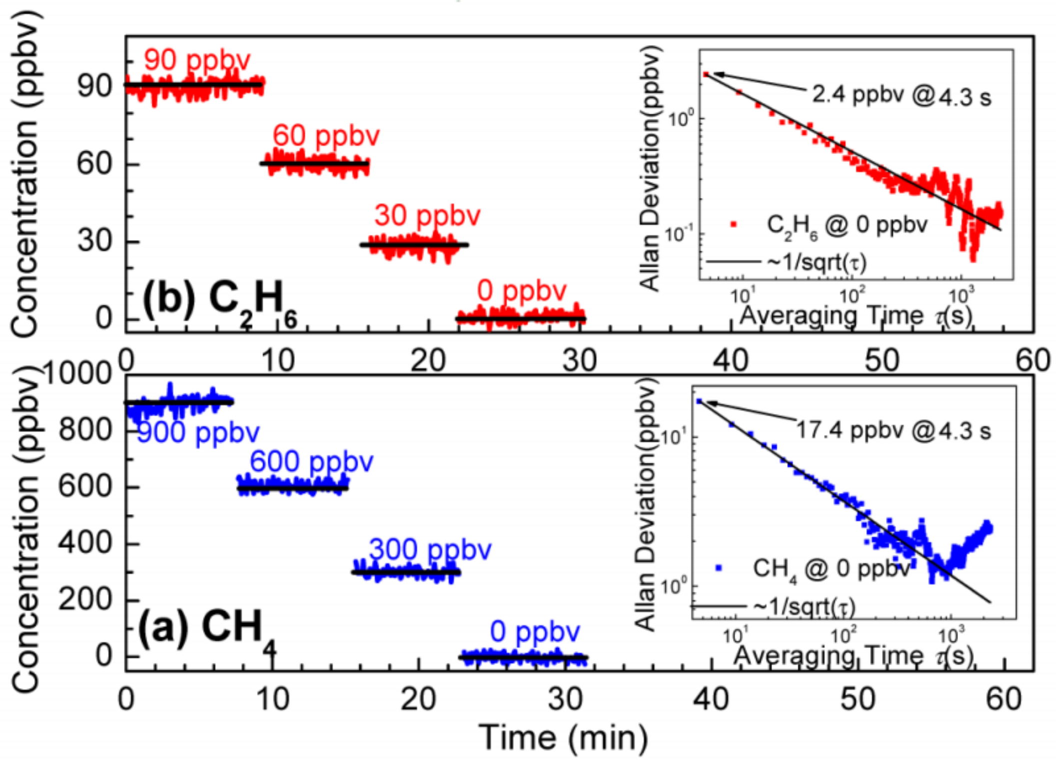
54.6 m MPC with dimensions of $17 \times 6.5 \times 5.5$ cm^3



Laser current driver with dimensions of $4.2 \times 4.8 \times 2.0$ cm^3

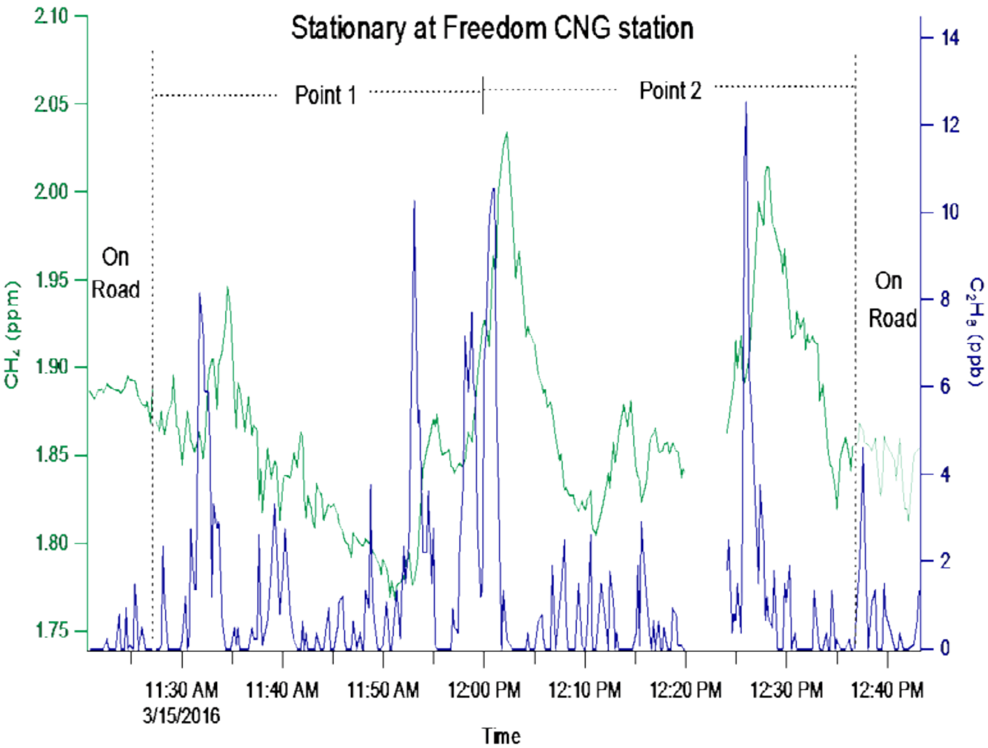
Temperature controller with dimensions of $4.5 \times 3.6 \times 2.0$ cm^3

Chemical Sensing Performance of CH_4 & C_2H_6



Measurement results of concentration levels of (a) four CH_4 samples (0, 300, 600, 900 ppbv) and (b) four C_2H_6 samples (0, 30, 60, 90 ppbv). The insets in (a) and (b) exhibit the Allan deviation plots obtained from long-term measurements on 0 ppmv CH_4 and 0 ppbv C_2H_6 samples for ~40 min, respectively, using the calibrated dual-gas sensor system.

Optical CH_4 Sensor: Gas Leakage Monitoring



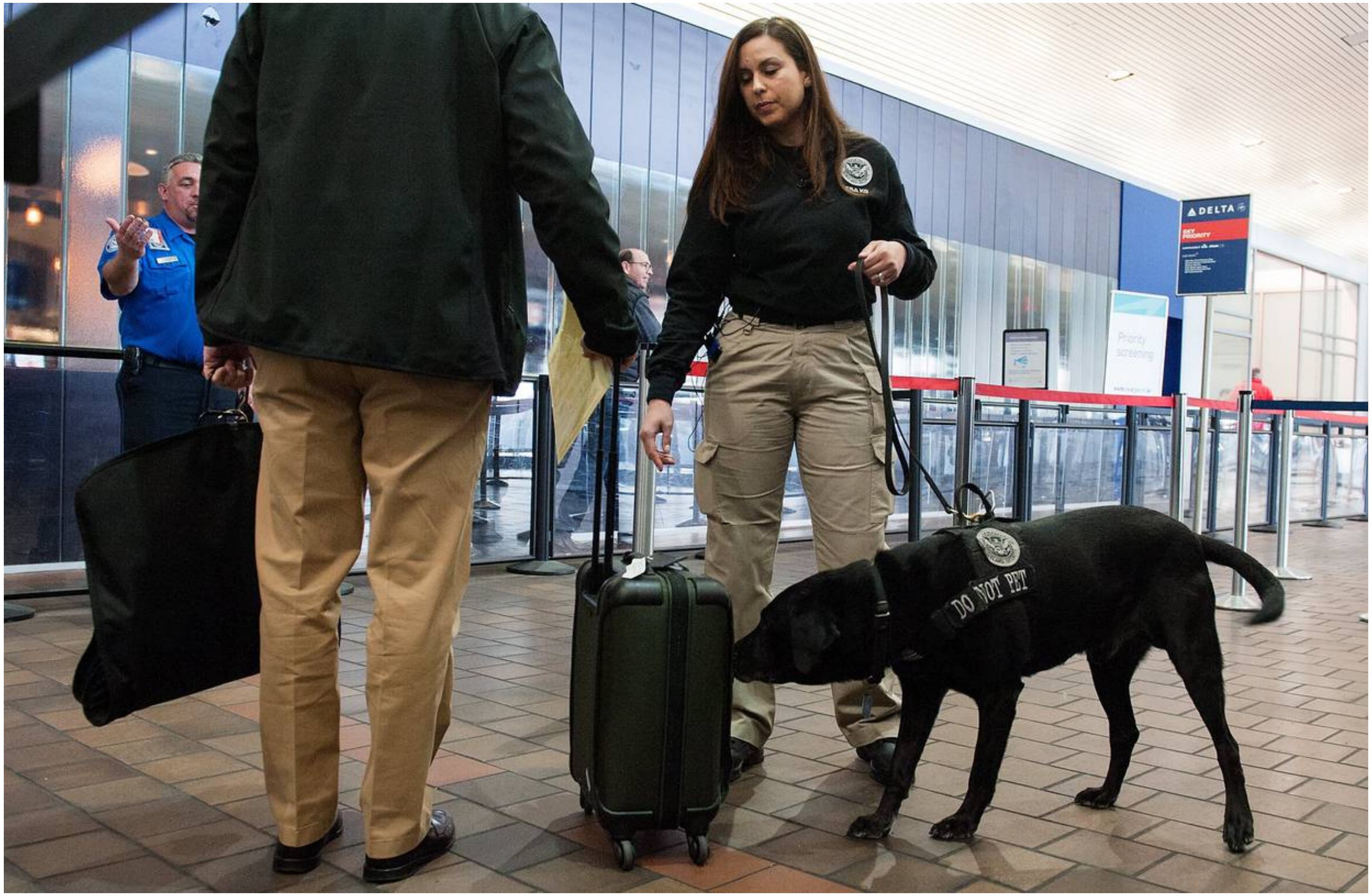
CH_4 Field Test at the Freedom Energy CNG Station, Pasadena, TX. An C_2H_6 sensor was also included in the field test for dual-gas monitoring

Both CH_4 and C_2H_6 were measured at two points at the Freedom Energy CNG station in March 2016. Points 1 & 2 correspond to two different locations at the CNG station where the vehicle was stationary (in the proximity of two different gas dispensing units). Each point was tested for ~ 0.5 hour.

Comparison of Rice CH_4 Sensor System and current commercially available CH_4 Platforms

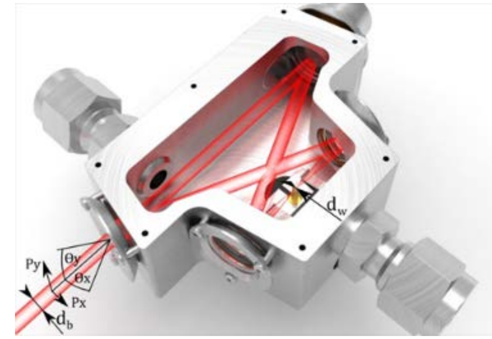
Size	Rice	Picarro	ABB-LGR I	ABB-LGR II	Aerodyne
Opt. Path length and method	MIR TDLAS: ~ 9 m	NIR CRDS: >2000m	NIR OA-ICOS: > 1000m	NIR OA-ICOS: > 2000m	MIR TDLAS: 70-100 m
Sensitivity/sec	< 5-10 ppb	1-2 ppb	5 ppb	2 ppb	<1 ppb
Accuracy (drift)	2 ppb stabilized	2 ppb	20 ppb, temp. stabilized	2 ppb	2 ppb
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

Dogs in smell test still beat trace gas technologies in 2017

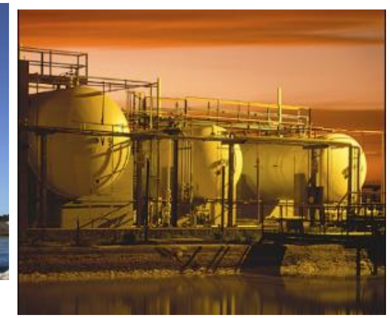


Rice Laser Science - Research Activities

- **Novel gas sensing techniques development and implementation**
- **Highly sensitive trace gas sensors portable for in-situ & real time detection**



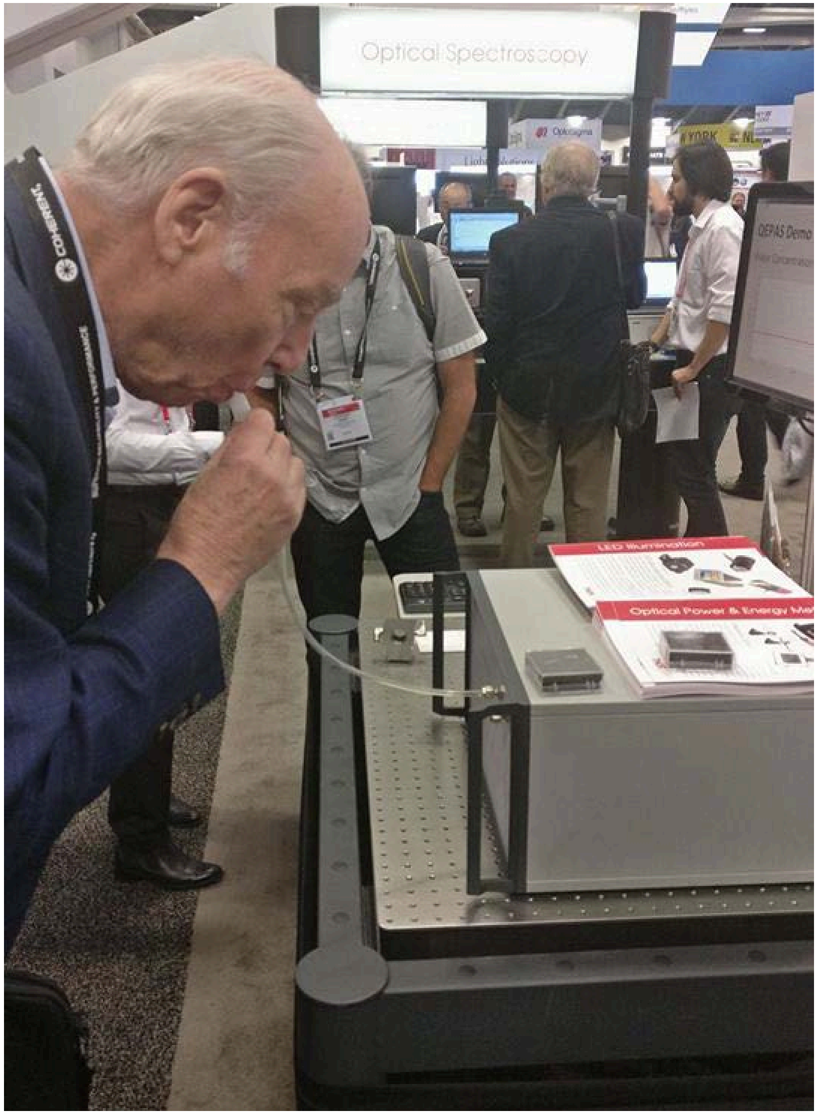
- **Potential applications:**
  - Breath analysis
  - Hydrocarbon gas monitoring
  - Environmental monitoring
  - Leak detection
  - Monitoring of hotspot areas (toxic gases,explosive precursors)

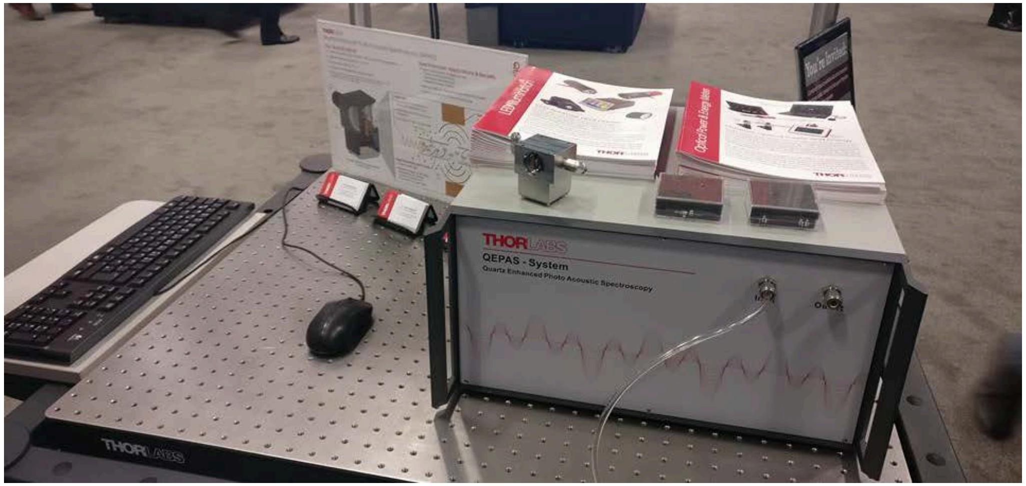




- **On-demand chemical sensing**
- **Third party consulting**



Visit by Frank Tittel to Photonics West 2018 ThorLabs Booth





First commercial QEPAS prototype

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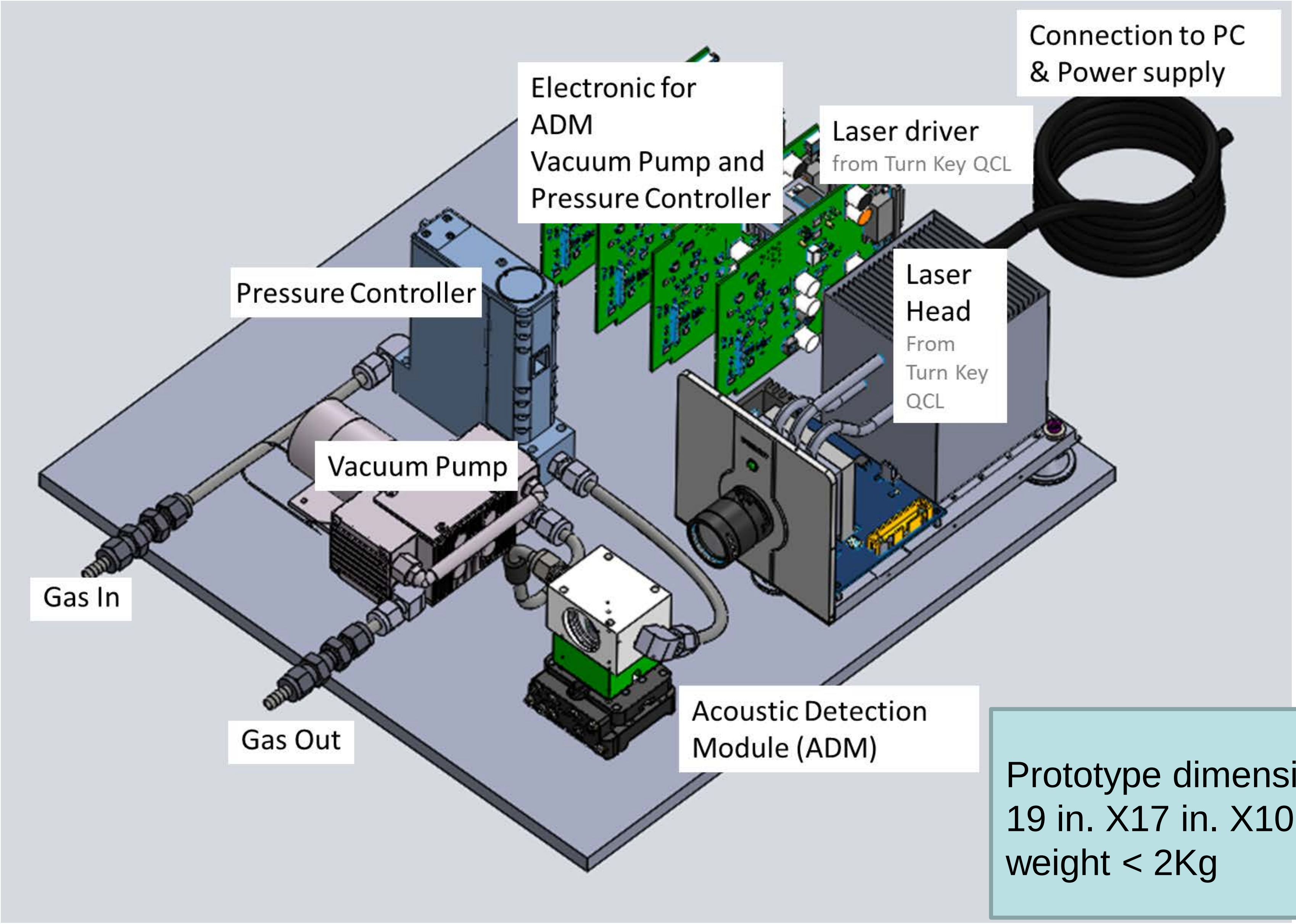
First commercial QEPAS prototype in collaboration with THORLABS



Prototype dimensions
19 in. X17 in. X10 in.
weight < 2Kg

Future development

Deployment of QEPAS prototype on drone system
In collaboration with Prof. E. Knightly and Dr. R. Petroli

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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, atmospheric chemistry, industrial process control and medical diagnostics.
- ICLs and QCLs were used in both TDLAS and QEPAS based sensor platforms
- Performance evaluation of four target trace gas species (xyzz) were reported
- I-QEPAS demonstration resulted in a factor of 240 increase in the 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.
- Development of mid-IR electrically pumped interband cascade optical frequency combs (OFCs) was performed jointly with NASA- JPL, Pasadena, CA , NRL, Washington, DC and Polysense, University of Bari (Italy)
- Development of an "active" I-QEPAS system for CO and NO detection in the ppt range
- 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 ($C_6H_{12}O_4$)
- Development of QEPAS sensor on drone System in collaboration with the Knightly Research tteam

A North Dakota Oil Facility in 2016.

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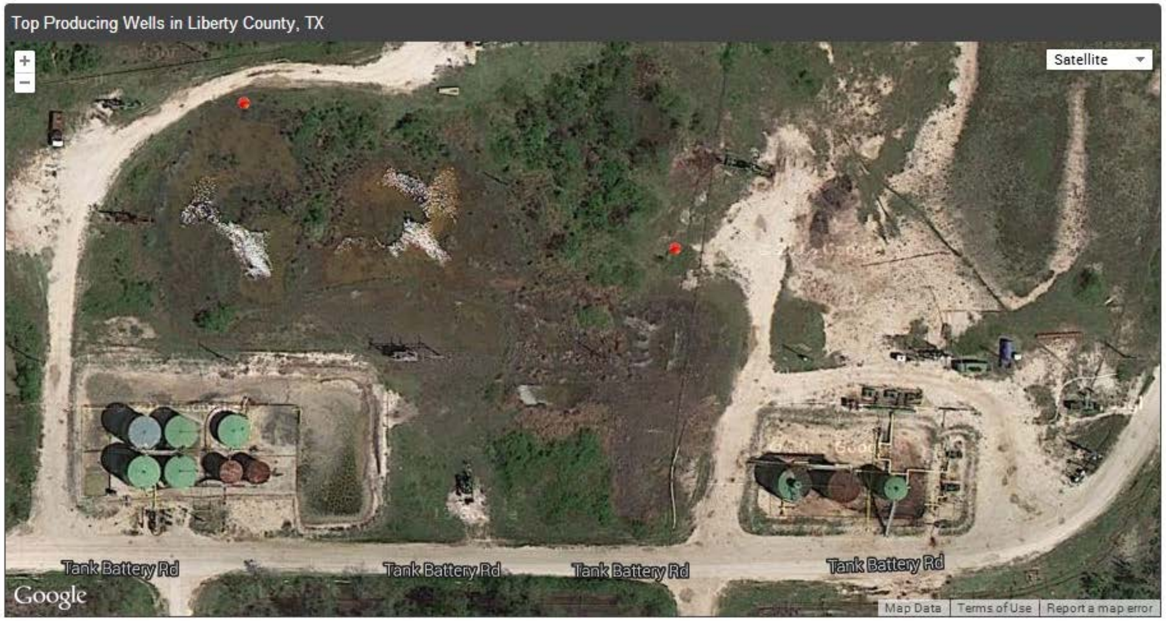
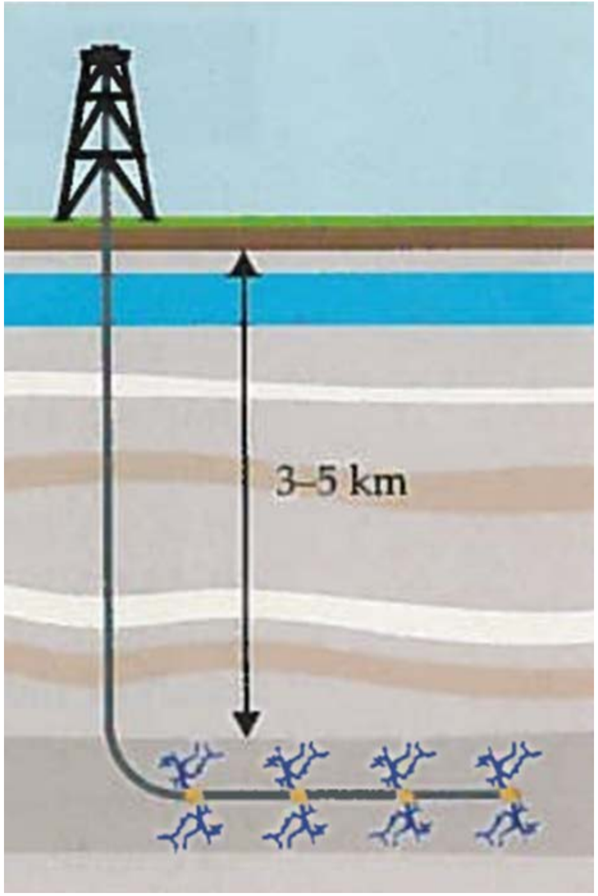
Typical Oil & Gas Production Site near Houston, TX





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

A DOE-ARPA-E methane detection project at 3.327 µm started at an ARPA-E CSU site in 2017

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