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

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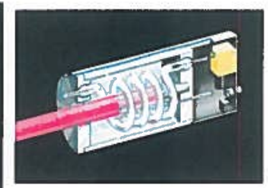
- Development of robust, compact, highly sensitive & selective mid-IR trace gas sensor technology based on high performance interband cascade lasers (ICLs) & quantum cascade lasers (QCLs) for medical diagnostics, environmental monitoring, atmospheric chemistry and industrial process control
- Development of Laser Absorption Spectroscopy (LAS)
- Photoacoustic Spectroscopy (PAS) , Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) and I-QEPAS based trace gas sensor systems
- Future development of trace gas sensors for monitoring broadband absorbers, such as acetone (C_3H_6O), propane (C_3H_8), benzene (C_6H_6) & acetone peroxide-TATP ($C_6H_{12}O_4$)
- Drone based sensor systems

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 and DOD-SCOUT from JPL is acknowledged

LASER is an acronym for: Light Amplification by Stimulated Emission of Radiation



Charles H. Townes (Columbia University) and Arthur L. Schawlow (Stanford University) conceived the laser in 1960. Theodore Maiman (Hughes Aircraft Company) demonstrated the first laser: a flash-pumped ruby laser in the same year. Gordon Gould was a graduate student of Prof. Townes, and first used the acronym "LASER."

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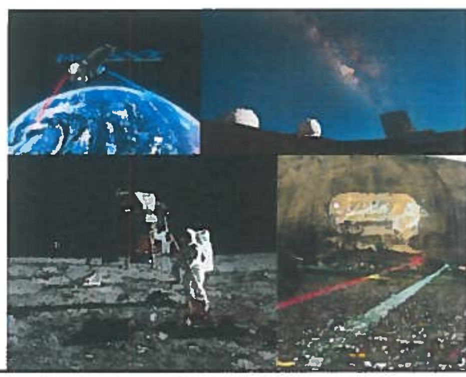
High-Power Lasers in Space



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A North Dakota Oil Facility in 2016.

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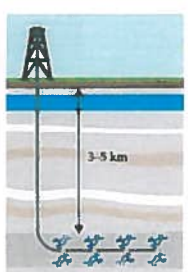
Typical Oil & Gas Production Site near Houston, TX



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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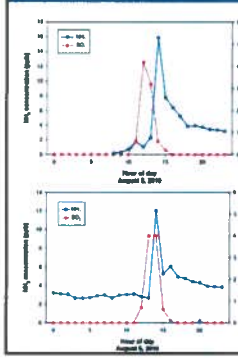
Sporadic increased NH_3 Concentration Levels related to Emissions by the Parish Electric Power Plant, TX



The Parish electric power plant is located near the Brazos River in Fort Bend County, Texas (~27 miles SW from downtown Houston)

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Laser-Based Absorption Spectroscpy

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (Mid-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Gas Cell (e.g Astigmatic Herriot - Aerodyne, Aeris DoE Monitor Bow-Tie)
  - 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
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

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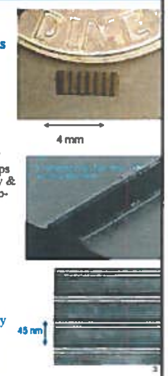
Key Characteristics of Mid-IR QCL & ICL Sources – July 2018

- **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



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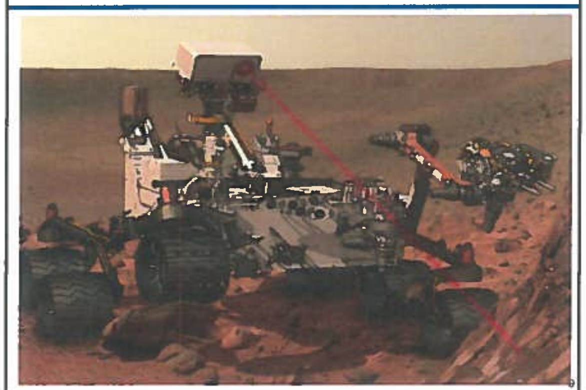
"Curiosity" landed on Mars on August 6, 2012



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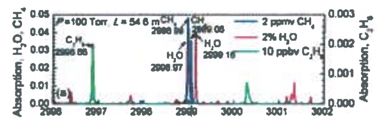
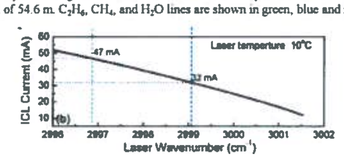
HITRAN Line Selection for a CH_4 & C_2H_6 Sensor



(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

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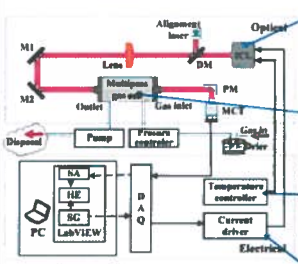
Laser Absorption Spectroscopy based CH_4 & C_2H_6 Dual-gas Sensor

Sensor structure



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

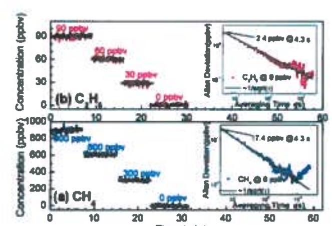
3.327μm CW ICL

54.6 m MPC with dimensions of 17 × 6.5 × 5.5 cm^3

Laser current driver with dimensions of 4.2 × 4.8 × 2.0 cm^3

Temperature controller with dimensions of 4.5 × 3.6 × 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.

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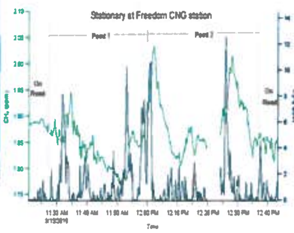
Optical CH_4 & CH_6 Sensor: Gas Leakage Monitoring



CH_4 & CH_6 field test at the Freedom Energy CNG Station, Pasadena, TX, for dual-gas monitoring

Both CH_4 and C_2H_6 were measured at two locations 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 location was tested for ~0.5 hour.

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

Site	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)

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Dogs in smell test still beat trace gas technologies in 2018

https://k2canine.com/2017/07/wsj-making-sense-of-a-dogs-olfactory-powers/

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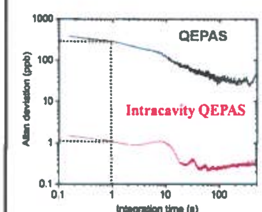
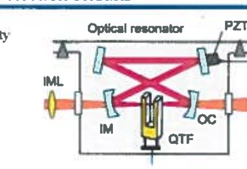
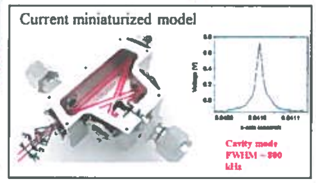
Intracavity Quartz Enhanced Photoacoustic Spectroscopy (I-QEPAS) and Nitric Oxide Detection Results

- Tuning fork placed inside an high finesse cavity for optical power enhancement

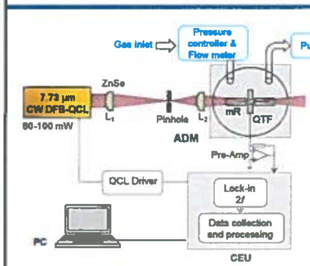


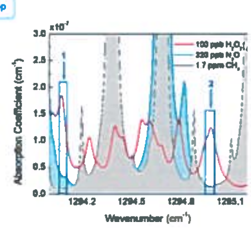




P. Patimisco, et al., Sens. Actuators A 267, 70-75, 2017

QCL based QEPAS Sensor for Hydrogen Peroxide (H_2O_2)





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

Simulated spectra (HITRAN) of H_2O_2 at 296 K and 130 Torr, along with atmospheric interfering molecules of CH_4 and N_2O; two target wavelengths at 1294.1 and 1294.9 cm^{-1} are shown.

H_2O_2 Exposure limit is set at 1 ppmv by OSHA

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QEPAS Performance for Trace Gas Species (August 2018)

	Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{1/2}$	Power, mW	NEC (τ=1s), ppmv
VIS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
VIS	O_2 (N_2)	13099.30	150	4.74×10^{-7}	1228	13
NIR	C_2H_2 (N_2)*	6523.88	720	4.1×10^{-9}	57	0.03
NIR	NH_3 (N_2)*	6528.76	575	3.1×10^{-9}	60	0.06
NIR	C_2H_4 (N_2)*	6177.07	715	5.4×10^{-9}	15	1.7
NIR	CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10^{-9}	16	0.24
NIR	N_2H_4	6470.00	700	4.1×10^{-9}	16	1
NIR	H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	5
NIR	HCl (N_2 dry)	5739.26	760	5.2×10^{-8}	15	0.7
NIR	CO_2 (N_2+1.5% H_2O)*	4991.26	50	1.4×10^{-8}	4.4	18
Mid-IR	CH_2O (N_2, 75% RH)*	2804.90	75	8.7×10^{-9}	7.2	0.12
Mid-IR	CO (N_2+2.2% H_2O)	2176.28	100	1.4×10^{-7}	71	0.002
Mid-IR	CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	0.14
Mid-IR	N_2O (air+5% SF_6)	2195.63	50	1.5×10^{-8}	19	0.007
Mid-IR	C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	90
Mid-IR	NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	0.003
Mid-IR	C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	0.009
Mid-IR	NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	0.006
Mid-IR	SF_6	948.62	75	2.7×10^{-10}	18	5×10^{-5} (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^{-9} $cm^{-1}W/\sqrt{Hz}$ for NH_3

Visit by Frank Tittel to ThorLabs Booth at Photonics West Feb. 2018

First commercial QEPAS prototype

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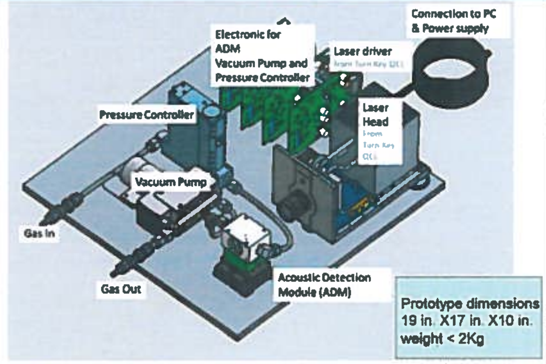
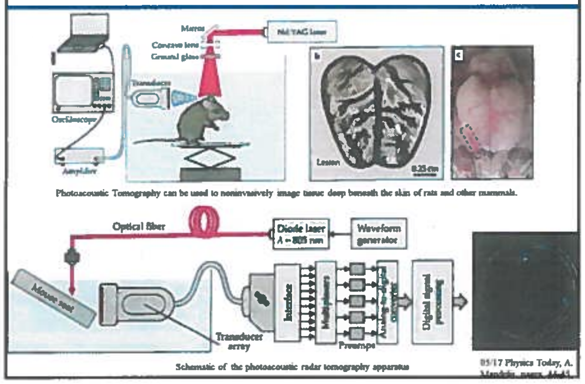
First commercial QEPAS prototype in collaboration with ThorLabs-USA/Germany



Imaging cancer with Photoacoustic Radar



Future development of a Drone mounted I-QEPAS Chemical Sensor System

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Volcanic gas & thermal emission measurements in collaboration with by Prof. C. Oppenheimer, Cambridge University, Cambridge, UK

Summary, Conclusions and Future Developments

- 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
- Development and demonstration of I-QEPAS resulted in a factor of 240 increase in the detection sensitivity
- Demonstration of THz-QEPAS H_2S sensing using a custom QTF resulted in a Minimum Detection Limit of 13 ppmv for a 30 sec integration time.
- 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 a Drone mounted QEPAS sensor in collaboration with Shell and Adamco, Houston, TX