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Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology

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F.K. Tittel, Yu. Bakhirkin, R.F. Curl, A.A. Kosterev, R. Lewicki, M. McCurdy, S.So and G. Wysocki

Rice Quantum Institute, Rice University, Houston, TX

http://ece.rice.edu/lasersci/

OUTLINE

IEEE LEOS
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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- Selected Applications of Trace Gas Detection
  - LAS with a Multipass Absorption Cell (NH_3, H_2CO)
  - Quartz Enhanced L-PAS (HCN, H_2CO)
  - OA-ICOS NO based Sensor Technology (NO, H_2CO)
- Future Directions and Conclusions

Work supported by NSF, NASA, DOE, DoD and Welch Foundation

Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, Aircraft and Marine Emissions
- **Rural Emission Measurements**
  - Agriculture & Forestry, Livestock
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Nuclear Safeguards, Pharmaceutical, Metals Processing & Food Industries
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Medicine and Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

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Trace Gas Monitoring in a Petrochemical Plant

University of Szeged, Hungary

Worldwide Megadirty Mega Cities

	Population, m 1990, ext.	2000, proj.	Sulphur dioxide	Particulate matter	Lead	Carbon monoxide	Nitrogen dioxide	Ozone
Bangkok	7.16	10.26	O	●	Ø	O	O	O
Beijing	9.74	11.47	●	●	O	-	O	Ø
Bombay	11.13	15.43	O	●	O	O	O	-
Buenos Aires	11.58	13.05	-	Ø	O	-	-	-
Cairo	9.08	11.77	-	●	●	Ø	-	-
Calcutta	11.83	15.94	O	●	O	-	O	-
Delhi	8.62	12.77	O	●	O	O	O	-
Jakarta	9.42	13.23	O	●	Ø	Ø	O	Ø
Karachi	7.67	11.57	O	●	●	-	-	-
London	10.57	10.79	O	O	O	Ø	O	O
Los Angeles	10.47	10.91	O	Ø	O	Ø	Ø	●
Manila	8.40	11.48	O	●	Ø	-	-	-
Mexico City	19.37	24.44	●	●	Ø	●	Ø	●
Moscow	9.39	10.11	-	Ø	O	Ø	Ø	-
New York	15.65	16.10	O	O	O	Ø	O	Ø
Rio de Janeiro	11.12	13.00	Ø	Ø	O	O	-	-
Sao Paolo	18.42	23.60	O	Ø	O	Ø	Ø	●
Seoul	11.33	12.97	●	●	O	O	O	O
Shanghai	13.30	14.69	Ø	●	-	-	-	-
Tokyo	20.52	21.32	O	O	-	O	O	●

Source: United Nations ● High pollution Ø Moderate to heavy pollution O Low pollution - No data available

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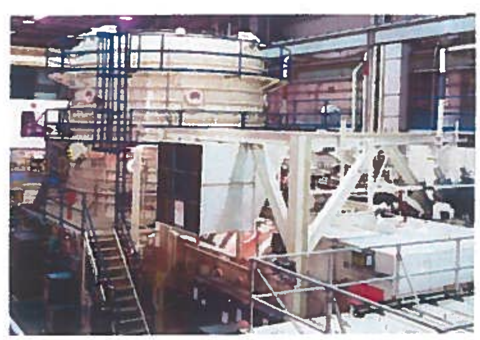
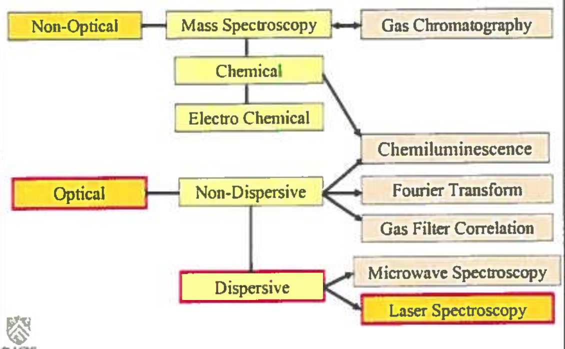
Megacity Air Pollution: Houston, TX

NASA–JSC Human-Rated Simulation Chamber



Existing Methods for Trace Gas Detection



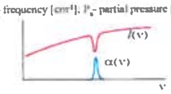
Fundamentals of Laser Absorption Spectroscopy

Beer-Lambert's Law of Linear Absorption

$$I(v) = I_0\, e^{-\alpha(v)\, P_a\, L}$$

$\alpha(v)$ - absorption coefficient [$cm^{-1} atm^{-1}$]; L - path length [cm]

v - frequency [cm^{-1}]; P_a - partial pressure [atm]



$$\alpha(v) = C\ S(T)\ g(v - v_0)$$

C - total number of molecules of absorbing gas/atm/cm³ [molecule cm⁻³ atm⁻¹]

S – molecular line intensity [cm/molecule⁻¹]

$g(v - v_0)$ – normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

Requirements: Sensitivity, specificity, Multi-gas Species, Rapid Data Acquisition, ...

Optimum Molecular Absorbing Transition

- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

Long Optical Pathlengths

- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Evanescent Field Monitoring (fibers & waveguides)

Spectroscopic Detection Schemes

- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy

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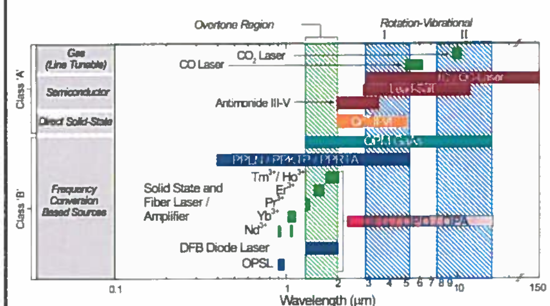
Mid-IR Source Requirements for Laser Spectroscopy

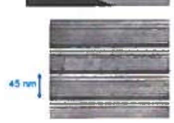
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Power
Selectivity	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelengths
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

IR Laser Sources and Wavelength Coverage

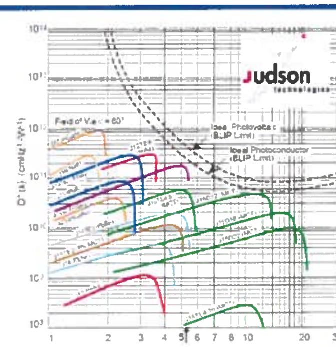


Quantum and Interband Cascade Laser: Basic Facts

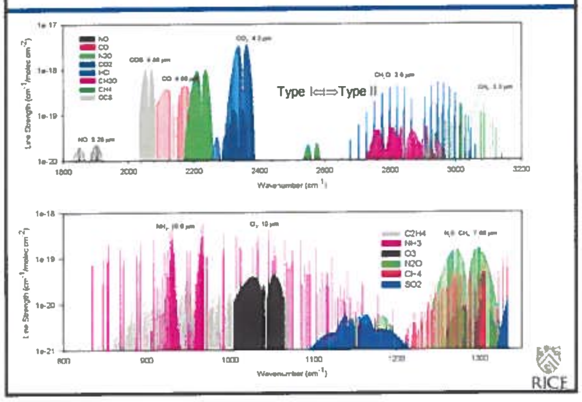
- Band – structure engineered devices (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 3.5 to 160 μm
  - Unipolar devices
  - Cascading (each electron creates N laser photons and the number of periods N determines laser power)
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- **Spectral tuning range in the mid-IR** (4-24 μm for QCLs and 3-5 μm for ICLs)
  - 1.5 cm^{-1} using current
  - 10-20 cm^{-1} using temperature
  - > 150 cm^{-1} using an external grating element
- **Narrow spectral linewidth** cw: 0.1 - 3 MHz & < 10Khz with frequency stabilization (0.0004 cm^{-1}); pulsed: ~ 300 MHz (chirp from heating)
- **High output powers at TEC/RT temperatures**
  - Pulsed peak powers of 1.6 W; high temperature operation ~ 425 K
  - Average power levels: 1-600 mW (wall plug η~4%)
  - ~ 50 mW, TEC CW DFB @ 5 and 10 μm (Alpes & Unine); Princeton, AdTech Optics, Maxion Technologies, Argos Tech. ~ 300 mW @ 8.3 μm (Agilent Technologies & Harvard)
  - >600 mW (CW FP) and >150 mW (CW DFB) at 298 K (Northwestern)



Wavelength Coverage of IR Detectors



HITRAN Simulation of Absorption Spectra (3.1-5.5 & 7.6-12.5 μm)



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Representative Trace Gas Detection Limits

Species	cm^{-1}	Precision 1 s RMS (ppt)	LOD 100 s (ppt)
NH_3	967	50	20
NO_2	1600	80	40
HONO	1700	200	80
CO	2190	120	50
N_2O	2240	100	50
HNO_3	1720	200	80
O_3	1050	500	200
NO	1905	200	100
CH_4	1270	400	200
SO_2	1370	310	120
C_2H_4	960	360	140
H_2CO	1765	350	100
H_2O_2	1267	1000	400

Limit of Detection (LOD) for S/N = 2

Pathlength: 210 m

Typical data acquisition times: 1-100 s

Mark S. Zahniser, SIRIS 2004, September 2004

Motivation for NH_3 Detection

- Monitoring of gas separation processes
- Spacecraft related gas monitoring
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver dysfunctions)

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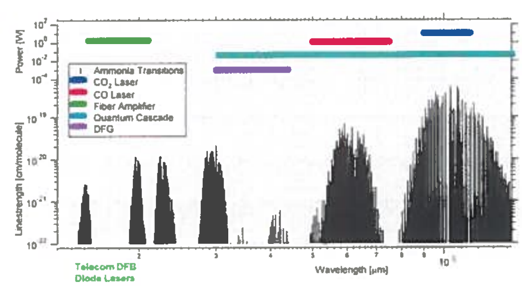
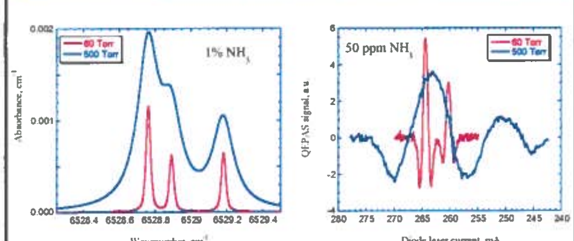
Simulated Infrared NH_3 Absorption Spectra



M. Webber et al. 2001, Pranalytica

Ammonia Detection using a 1.53 μm Telecom Diode Laser

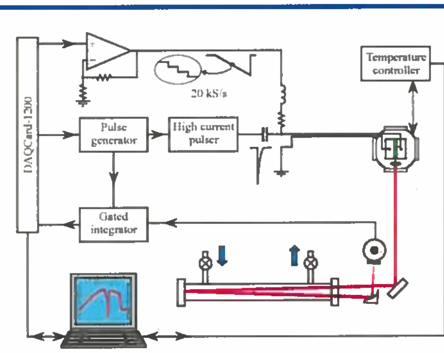


Spectral simulations based on data from Webber et al., APPLIED OPTICS 40, 2031-2042 (2001)]

QEPAS spectra at different pressures of NH_3:N_2 gas mixture; t=0.3s, 38 mW diode laser excitation power at 6529 cm^{-1}

Applied Optics 43, 6213-6217, 2004

Architecture of a Pulsed QC Laser Based Gas Sensor



A. Kosterev et al, Applied Optics 41, 573 2002

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Motivation for Monitoring of H_2CO

- Toxic pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products (eg. resins, foam)
- Atmospheric H_2CO is a key hydrocarbon oxidation product which leads to the photochemical generation of ozone and release of hydrogen radicals
- Medically important gas

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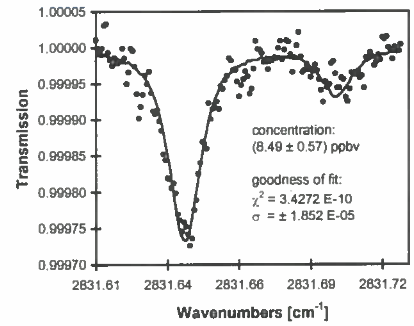
H_2CO Detection in Ambient Air at 3.53 μm



D. Rehle et al. Applied Physics B72, 947-952 (2001)

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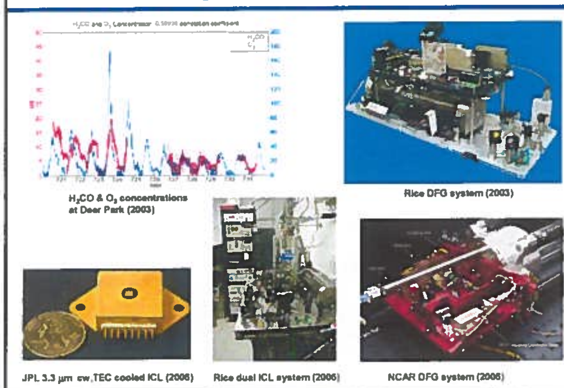
DFG and ICL based H_2CO Sensor for studying Urban Air Pollution



TexAQS II Field Campaign Summer 2006

- To study ozone formation and transport, a coordinated field study was conducted in August and September 2006 in Houston
- 5 aircraft, two ground chemistry sites, ~20 periphery and meteorological sites
- Participation by~300 scientists from academia, national laboratories, industry and government

Moody Tower, UH Campus

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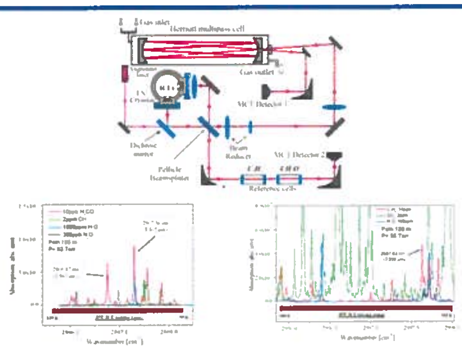
CW ICL Based H_2CO and C_2H_4 Sensor for TexAQS '06



HITRAN Based Simulation of a H_2CO H_2O-CH_4 Spectrum in Tuning Range of a 3.53μm IC Laser

HITRAN Based Simulation of C_2H_4-H_2O-CH_4 Spectrum in Tuning Range of a 3.33-3.35 μm IC Laser

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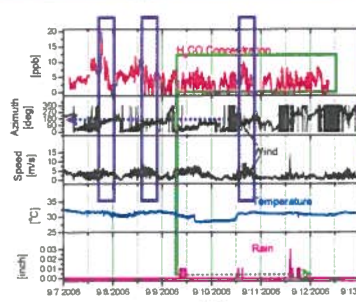
Comparison of LAS based H_2CO to Meteorological Data



- Peak concentration of H_2CO at winds blowing from E-SE-S (90-180deg)
- H_2CO concentration is usually lower after rainfalls

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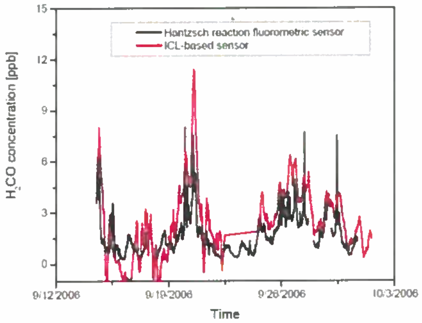
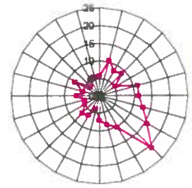
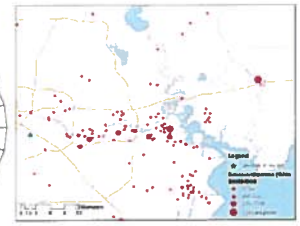
Comparison of H2CO measured by Rice ICL based sensor & UH commercial wet-chemical analyzer co-located at Moody Tower

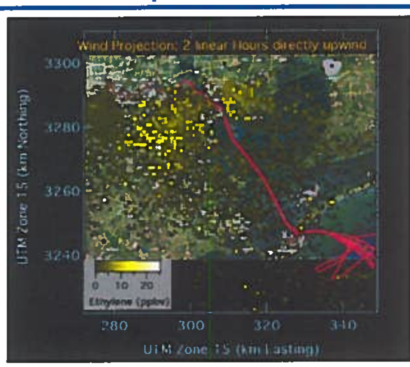


Maximum H_2CO (ppb) versus Wind Direction

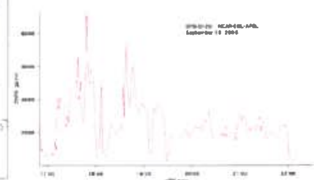




Ron Brown Ship Track in Houston Ship Channel, September 2006



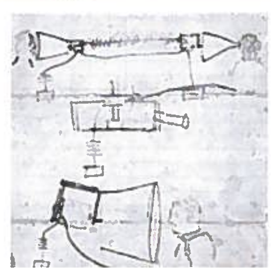
Airborne NASA P3 DFG based H_2CO Sensor



D. Richter, et al, NCAR EOL-APOL, Sept. 13 2006

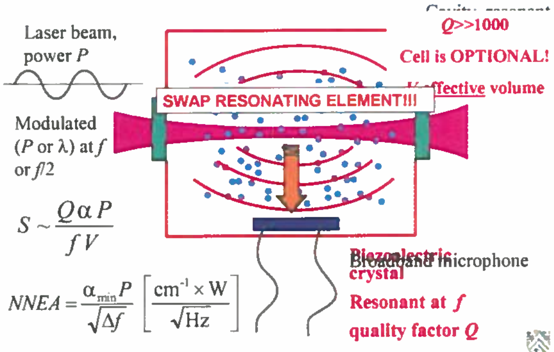
Photoacoustic Spectroscopy

First Report of PAS in 1880



Alexander Graham Bell's "photophone" used a voice coil to modulate a mirror which transmitted sunlight to a receiver containing a selenium resistor.
Nature, Sept. 23, 1880, pp. 500-503

From conventional PAS to QEPAS



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

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

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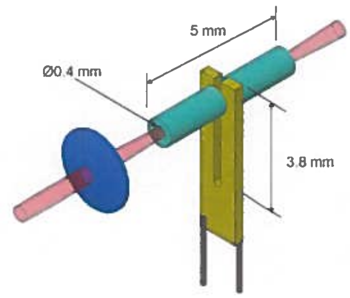
TF based spectrophone



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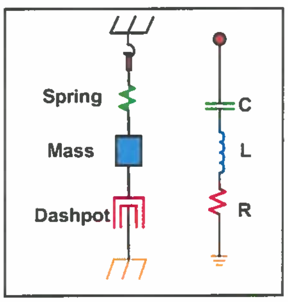
Equivalent Electrical Circuit of a Quartz TF



$$\omega_0 = \sqrt{\frac{1}{LC}}$$

$$Q = \frac{1}{R}\sqrt{\frac{L}{C}}$$

$$\sqrt{\langle I_N^2 \rangle} = \sqrt{\frac{4k_B T}{R}}$$

"QUARTZ CRYSTAL RESONATORS AND OSCILLATORS For Frequency Control and Timing Applications", tutorial by John R. Vig, U.S. Army Communications-Electronics Command (July 2001)

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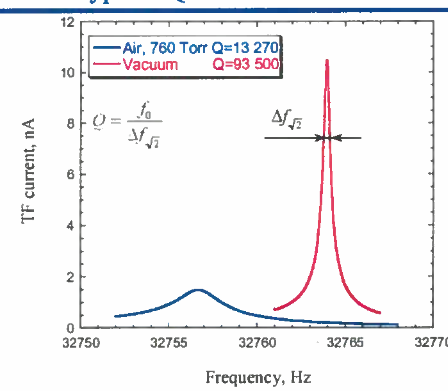
Typical QTF resonance curves



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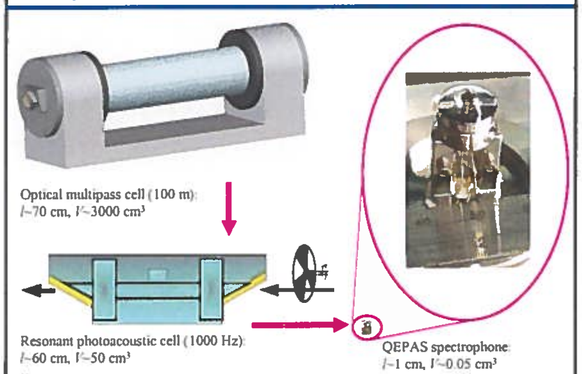
Comparative Size of Absorbance Detection Modules (ADM)



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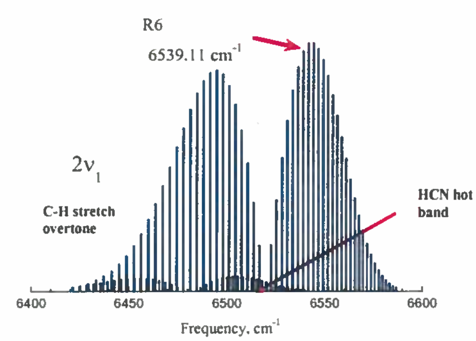
Simulated NIR absorption band of HCN centered at 1.53 μm



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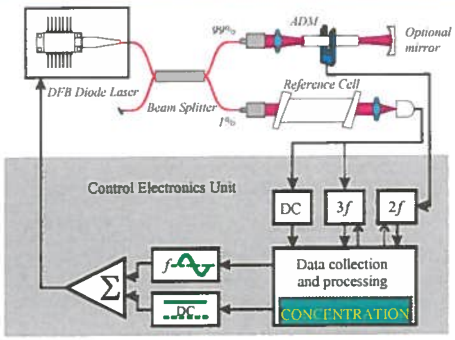
QEPAS based gas sensor architecture



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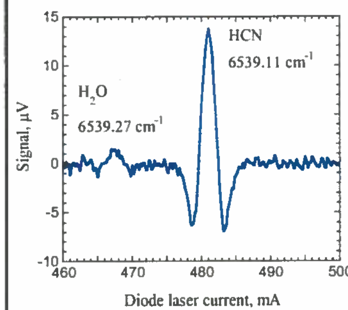
1.53 μm LPAS signal of a 6.25 ppmv HCN: air mixture



Estimated HCN toxicity concentration for 30 minutes exposure is 100 mg/m³ or ~85 ppmv

Laser power in the cell: 50 mW
Time constant: 1s, SNR=40

Room air, 50% RH (see plot):

Optimum pressure 60 Torr

NNEA=4.3×10^{-9} cm^{-1}W/(Hz)$^{1/2}$;
NEC=155 ppbv

Dry nitrogen or air:

Optimum pressure 300 Torr

NNEA=9.2×10^{-9} cm^{-1}W/(Hz)$^{1/2}$;
NEC=330 ppbv

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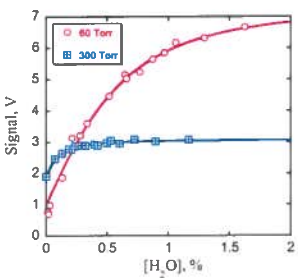
QEPAS HCN signal dependence on gas humidity



Addition of H_2O promotes V-T relaxation, resulting in a higher HCN detection sensitivity in humid air.

If the sensor is operated at 300 Torr, RH variations from 6% to 100% only change signal by 10%.

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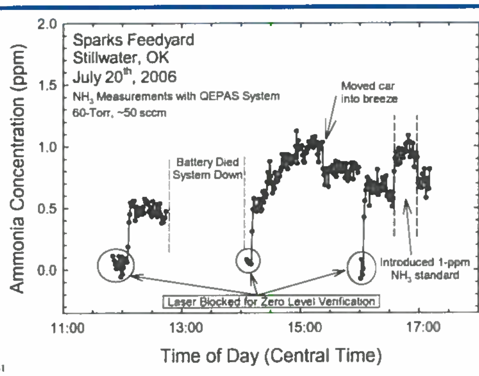
NH_3 Measurements at an Oklahoma State University Research Feedyard

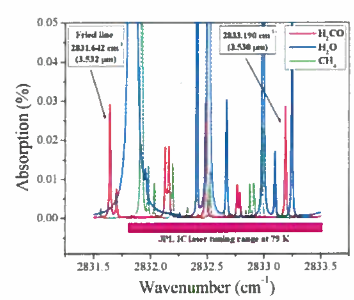
40 Ekips

Agricultural Ammonia Measurements



41 Ekips

HITRAN Based Simulation of a H_2CO-H_2O-CH_4 Spectrum in the Tuning Range of a 3.53μm IC Laser



- H_2CO: 10 ppb
- H_2O: 3%
- CH_4: 2 ppm
- Optical path: 100 m
- Total pressure: 30 Torr

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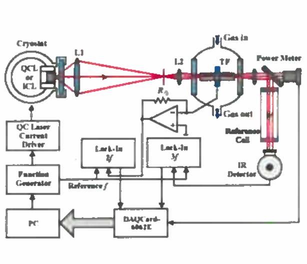
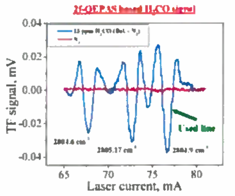
ICL based Quartz-Enhanced Photoacoustic Gas Sensor

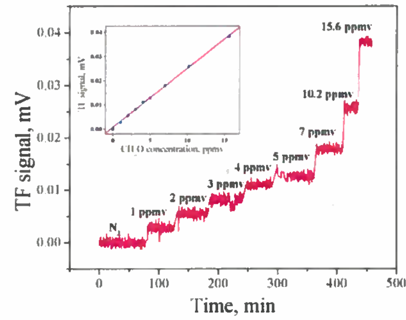




- $[H_2CO]$: 13 ppm (N_2 – balance gas)
- QEPAS NNEA Sensitivity (for 2804.9 cm^{-1}): 0.91×10^{-9}cm^{-1} W/√Hz;
- NEC (τ = 1s): 0.14 ppmv (~ 6.5 mW)

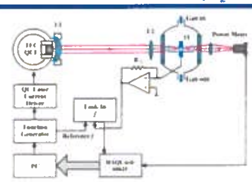
For comparison:
NIR QEPAS NNEA Sensitivity for NH_3 : 5.4×10^{-9}cm^{-1}W/ √ Hz
NEC (τ = 1s): 0.5 ppmv (38 mW)

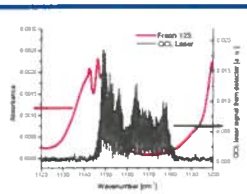
IC Laser based Formaldehyde Calibration Measurements with a Trace Gas Standard Generator



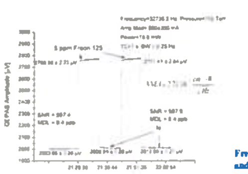
- H_2CO absorption frequency: 2804.9 cm^{-1}
- Lock-In time constant: 1 s
- QEPAS parameters
  - Resonance frequency: 32.760 KHz
  - Q-factor: ~ 8800
  - Pressure: 200 Torr
  - Gas Flow: ~50 sccm
  - IC laser power: ~ 6.8 mW

Amplitude Modulated 8.6 µm QCL based QEPAS Freon 125 (C_2HF_5) Sensor





Spectral comparison of Freon 125 with emission coverage from a 8.6 µm FP QCL based on the PNNL database



Freon 125 QEPAS signal and optical baseline noise

Merits of QEPAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to environmental noise- acoustic quadrupole
- Ultrasmall sample volume (< 1 mm³)
- Applicable over a wide range of temperatures and pressures, including atmospheric pressure
- Sensitivity is limited by the fundamental thermal TF noise: k_BT energy in the symmetric mode is directly observed
- Rugged and low cost compared to other spectroscopic techniques that require infrared detector(s)
- Sensitive to phase shift introduced by V-T relaxation processes – additional selectivity
- Potential for trace gas sensor networks

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QEPAS Performance for 10 Trace Gas Species (March 2007)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, cm^{-1}W/Hz^{½}	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10[illegible]	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	< 4.3×10[illegible]	50	0.16
C_2H_2 (N_2)**	6529.17	75	~2.5×10[illegible]	~40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10[illegible]	38	0.50
CH_4 (N_2)*	6057.09	700	5.2×10[illegible]	17.6	3.0
CO_2	6361.25	90	1.6×10[illegible]	26	410
CO_2 (N_2+1.5% H2O)*	4991.26	50	1.4×10[illegible]	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10[illegible]	7.2	0.12
CO (N_2)	2196.66	50	5.3×10[illegible]	13	0.5
CO (propylene)	2196.66	50	7.4×10[illegible]	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10[illegible]	19	0.007
C_2HF_5 (Freon 125)***	1208.62	770	2.6×10[illegible]	6.6	0.003

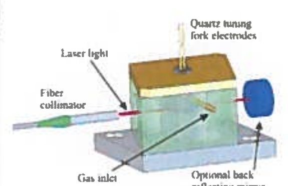
* - Improved microresonator
** - Improved microresonator and double optical pass through ADM
*** - With amplitude modulation and metal microresonator

NNEA – normalized noise equivalent absorption coefficient.
NEC – noise equivalent concentration for available laser power and τ=1s time constant.

For comparison: conventional PAS 2.2×10^{-9} cm^{-1}W/√Hz (1,800 Hz) for NH_3*

* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003)

Design of a 2nd Generation QTF based Absorption Detection Module



- **Compact & integrated design**
- **Laser-induced background reduction**
- **Machining precision of : +/- 10µm**
- **Two QTFs connected in parallel results in enhanced √2 SNR**
- **Minimum exposure of QTFs to QCL radiation**
- **Efficient for gas flow to microresonator**

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Cavity Enhanced Spectroscopy

ICOS vs. CRDS

ICOS

- High sensitivity
- High time resolution not required, slow detector is sufficient
- Multiple high-order transverse modes, off-axis propagation
- Relies on quasi-random mode structure, non-critical alignment
- Low throughput [(1-R)/2 max]
- No need for narrow line laser
- Sensitive to the source power fluctuations

CRDS

- Extremely high sensitivity possible – 10^{-11} cm^{-1} demonstrated in NIR
- Time resolved measurements, fast detector needed
- Single transverse mode, on-axis propagation – critical alignment
- Laser must be locked to the cavity mode
- High throughput in resonance for a narrow line (~kHz) laser
- Insensitive to the source power fluctuations

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Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_x monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1988 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection

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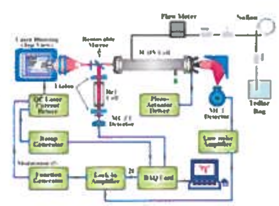
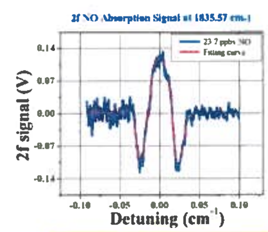
Laser-based ICOS Nitric Oxide Sensor





NO/N2 mixture @ 100 Torr; Effective L= 700 m

A 1σ deviation of the amplitude corresponds to a 700 ppt detection limit (1sec.)

Yu. A. Bakhirkin et al. "Sub-ppbv Nitric Oxide Concentration Measurements using CW Room-Temperature Quantum Cascade Laser based Integrated Cavity Spectroscopy", Applied Physics B 82,149-154 (2006)

Why is Breath so Useful ?

- Breath can be analyzed non-invasively from spontaneously breathing human subjects (neonate to the elderly), laboratory animals (from mice to horses), or from intubated patients (in ORs or ICUs).
- Breath can be sampled in the clinic, the home, the field, at the patient bedside, or in the physician's office by nurses, technicians, physicians and by the patient themselves.
- Breath analysis can be used for nutritional studies, exercise studies, to detect disease, stage disease, to monitor therapy or to monitor treatment

Terence Risby, Johns Hopkins University

Breath Biomarkers in Humans

As many as 400 different molecules in breath, many with well defined biochemical pathways

Compound	Concentration	Physiological basis/Pathology Indication
Acetaldehyde	ppb	Ethanol metabolism
Acetone	ppm	Decarboxylation of acetoacetate, diabetes
Ammonia	ppb	protein metabolism, liver and renal disease
Carbon dioxide	%	Product of respiration, Helicobacter pylori
Carbon disulfide	ppb	Gut bacteria, schizophrenia
Carbon monoxide	ppm	Production catalyzed by *heme oxygenase*
Carbonyl sulfide	ppb	Gut bacteria, liver disease
Ethane	ppb	Lipid peroxidation and oxidative stress
Ethanol	ppb	Gut bacteria
Ethylene	ppb	Lipid peroxidation, oxidative stress, cancer
Hydrocarbons	ppb	Lipid peroxidation/metabolism
Hydrogen	ppm	Gut bacteria
Isoprene	ppb	Cholesterol biosynthesis
Methane	ppm	Gut bacteria
Methanethiol	ppb	Methionine metabolism
Methanol	ppb	Metabolism of fruit
Methylamine	ppb	Protein metabolism
Nitric oxide	ppb	Production catalyzed by *nitric oxide synthase*
Oxygen	%	Required for normal respiration
Pentane	ppb	Lipid peroxidation, oxidative stress
Water	%	Product of respiration

Terence Risby, Johns Hopkins University

Dogs Can Smell Cancer

Integrative Cancer Therapies (March, 2006)

Diagnostic Accuracy of Canine Scent Detection in Early- and Late-Stage Lung and Breast Cancers

Michael McCulloch, Tadeusz Jezierski, Michael Broffman, Alan Hubbard, Kirk Turner, and Teresa Janecki

By smelling breath samples, dogs detected breast and lung cancer patients with accuracies of 88% and 97%, respectively.

The evidence is clear – gas phase molecules are uniquely associated with cancer

– We need sensors that can detect these biomarkers

The New York Times

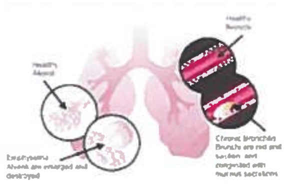
NO as a Biomarker

- NO is biochemically involved in most tissues and physiological processes in the human body
- NO excretion increases in exhaled breath in lung diseases such as :
  - ✓ Asthma[1]
  - ✓ Chronic Obstructive Pulmonary Disease[2]
  - ✓ Acute lung rejection[3]
  - ✓ Acute respiratory distress syndrome[4]
  - ✓ Pneumonia (useful for intubated patients)[5]

[1] Alving K, E Weitzberg, JM Lundberg. Increased amount of NO in exhaled air of asthmatics. Eur Respir J 1993, 6. 1368-1370.
[2] Wasem M, S Loukides, S Culpitt, P Sullivan, S Kharitonov, P Barnes. Exhaled NO in COPD. Am J Respir Crit Care Med 1998, 157. pp 998-1002.
[3] Silkoff PE et al. Exhaled NO in human lung transplantation. A noninvasive marker of acute rejection. Am J Respir Crit Care Med 1998, 157(6): 1822-1828
[4] Brett SJ, Evans TW. Measurement of endogenous NO in the lungs of patients with the ARDS. Am J Respir Crit Care Med 1998, 157 (3 Pt 1): 993-7
[5] Adrie C et al. Exhaled and nasal NO as a maker of pneumonia in ventilated patients. Am J Respir Crit Care Med 2001, 163(5):1143-9

Chronic Obstructive Pulmonary Disease

- **Chronic obstructive pulmonary disease (COPD)**
  - Accumulation of inflammatory products in the small airway lumen and wall
- **Alveolar NO**
  - Reflects peripheral lung inflammation and the response to anti-inflammatory treatment
  - Not affected by smoking or inhaled corticosteroids



Source: http://jama.ama-assn.org/cgi/content/full/290/17/2362

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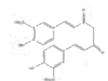
Curcumin Pilot Study

- Curcumin (Turmeric)
  - Polyphenol (diferuloylmethane)
  - Anti-inflammatory and anti-oxidant



- **Hypothesis:** Curcumin reduces indices of inflammation in individuals with severe COPD

BCM

Collaborator: Dr. Amir Sharafkhaneh

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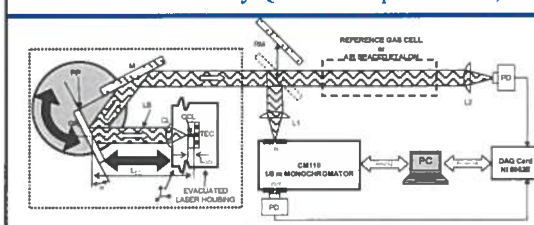
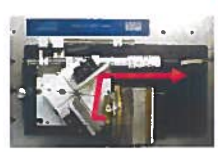
Widely Tunable, CW, TEC Quantum Cascade Lasers

Tunable external cavity QCL based spectrometer, 2006





- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + chilled water cooling)

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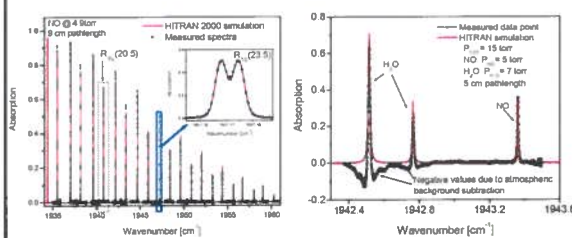
Mid-IR NO Absorption Spectra acquired with a Tunable TEC QCL



G. Wysocki et. al. Appl. Phys. B 81, 769-777 (2005)

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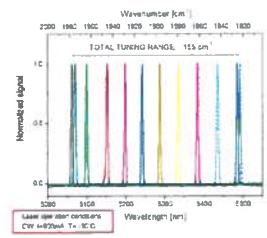
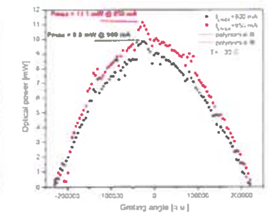
Performance of a 5.3 μm EC-QCL spectroscopic source



EC-QCL frequency tuning range



Output power vs. tuning range

Tunability **155 cm⁻¹** @5.3 μm

$P_{EC\text{-}opt}$ up to **11mW (cw)**

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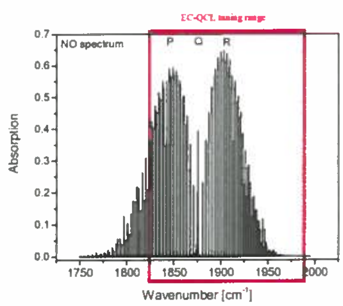
5.3 μm QCL spectral coverage superimposed on NO fundamental absorption band



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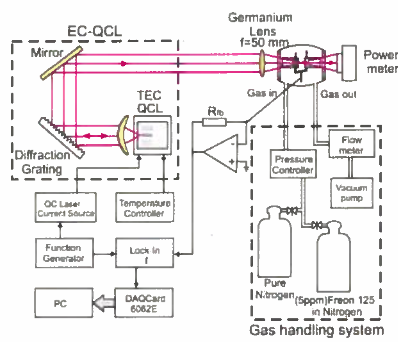
8.4 μm RT CW EC-QCL based QEPAS trace gas sensor



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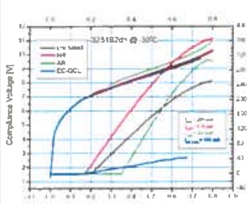
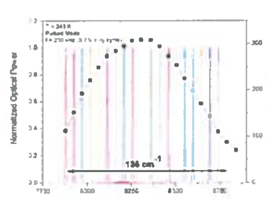
Performance of a 8.4 μm EC-QCL spectroscopic source



LIV curves for the MOCVD grown QCL gain medium operated at -30 oC. The curves were measured at different stages of the chip processing and after its incorporation into the EC-QCL configuration.



Laser frequency tuning range and corresponding optical power of the EC-QCL operating in the pulsed mode at 8.4 μm (the same tuning range was observed in cw operation).

Tunability is ~ **135 cm⁻¹**
@ 8.4 μm (7.8μm - 8.8μm)

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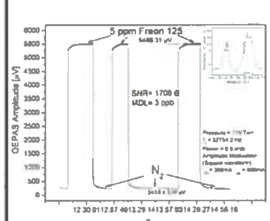
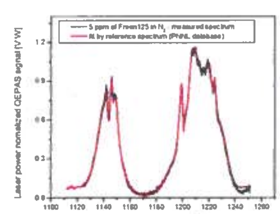
Freon 125 concentration measurements obtained with a tunable cw 8.4 μm EC-QCL based AM-QEPAS trace gas sensor



The inset depicts the spectral location of the laser frequency on the Freon 125 absorption spectrum.



QEPAS spectrum of Freon 125 measured between 1125 and 1250 cm-1 fitted to a reference spectrum from the PNNL spectral database.

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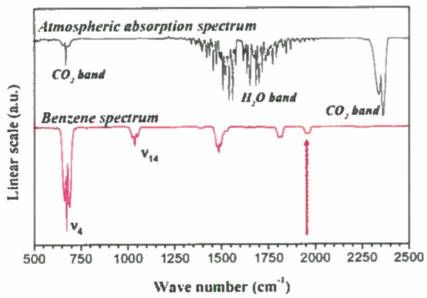
FT-IR survey absorption spectrum of benzene vapor (C_6H_6)



W. Chen, F. Cazier, F.K. Tittel and D. Boucher, Appl.Optics 39, 6238, 2000

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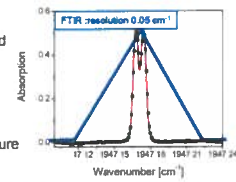
EC-QCL - Important Facts

- Laser spectroscopy provides superior resolution compared to other techniques e.g. FTIR
- Single mode operation of the laser is required for high resolution spectroscopy
- Wavelength tunability of single mode (DFB) mid-IR semiconductor lasers is ~$10 cm^{-1}$
- Gain chips, which can provide tunability of >200 ... ted in the literature
- Pote... EC... e.g. using tu... MS di... grat...



Commercial Tunable Mid-IR EC QCL

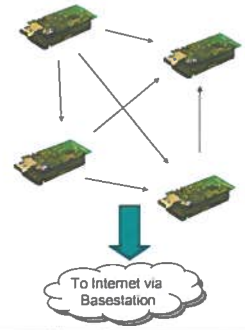
Introduced in 2006

Room Temperature—No Cryogenic Cooling

Center Wavelengths:	4.5 µm 5.5 µm 8.5 µm 9.5 µm 10.5 µm
Tuning Range:	>10%
Average Power (CW):	1 mW–10 mW

DAYLIGHT SOLUTIONS

Wireless Sensor Networks for Gas Sensing



- What is needed?
  - **Low cost**
  - **Small Size**
  - **Replicable**
  - **Autonomy**
  - **Low power**
  - **High sensitivity**

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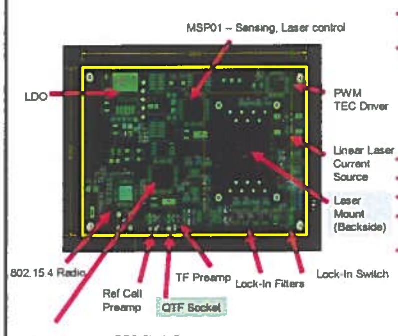
Future Work – Mini-QEPAS Sensor System



- **3.85 inch x 2.5 inch (9.8 cm x 6.4 cm)**
- Low power
  - 3W max for TEC
  - 3W max for Laser Bias
  - 0.5W max for electronics (µW sleep mode)
- Embedded Laser
- Embedded TF module
- Embedded Radio
- 2 cell Li-Pol Battery + Charging
- Low cost

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Summary & Future Directions of mid-IR Sensor Technology

- **Quantum and Interband Cascade Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity ($<10^{-4}$) and selectivity (3 to 500 MHz)
  - Fast data acquisition and analysis
  - Detected 12 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, SO_2, C_2H_5OH, C_2HF_5 and several isotopic species of C, O, N and H.
- **Applications in Trace Gas Detection**
  - Environmental monitoring (NH_3, CO, CH_4, C_2H_4, N_2O, CO_2 and H_2CO)
  - Industrial process control and chemical analysis (HCN, NO, NH_3, H_2O)
  - Medical & Biomedical Diagnostics (NO, CO, COS, CO_2, NH_3, C_2H_4)
  - Sensor Technologies for Law Enforcement and Homeland Security
- **Future Directions and Collaborations**
  - New applications using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR interband and intersubband quantum cascade lasers
  - Improvements of Cavity Enhanced and QEPAS based spectroscopic techniques using broadly wavelength tunable quantum cascade lasers
  - Development of optically multiplexed gas sensor networks based on QEPAS
  - Potential and limitations of amplitude modulated QEPAS for monitoring of broadband absorbers, in particular VOCs and HCs

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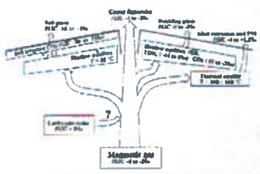
Volcanological Applications

- CO_2 the most abundant component of volcanic gases after H_2O
- $\delta^{13}C$ is a sensitive tracer of magmatic vs. hydrothermal or groundwater contributions to volcanic gases
- Monitoring $\delta^{13}C$ can be used in eruption forecasting and volcanic hazard assessment



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CO_2 Absorption Line Selection Criteria

- Three strategies:
  - Similar strong absorption of $^{12}CO_2$ and $^{13}CO_2$ lines
    - Very sensitive to temperature variations
  - Similar transition lower energies
    - Requires a dual path length approach to compensate for the large difference in concentration between major and minor isotopic species-or-
    - Can be realized if different vibrational transitions are selected for the two isotopes (4.35 μm for $^{13}CO_2$ and 2.76 μm for $^{12}CO_2$)*
- For the first 2 strategies both absorption lines must lie in a laser frequency scan window
- Avoid presence of other interfering atmospheric trace gas species

* Proposed scheme by Curl, Uehara, Kosterev and Tittel, Oct. 2002

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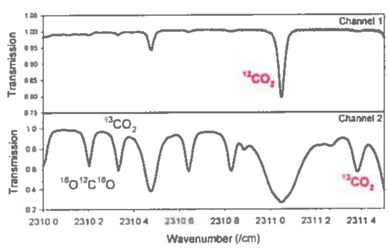
High resolution CO_2 absorption spectrum at 2311 cm^{-1}



OSAS Optics and Photonics News, May 2006

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