Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology

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

OUTLINE

- 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
- Future Directions and Conclusions

Radboud University Nijmegen

Nov 27, 2006

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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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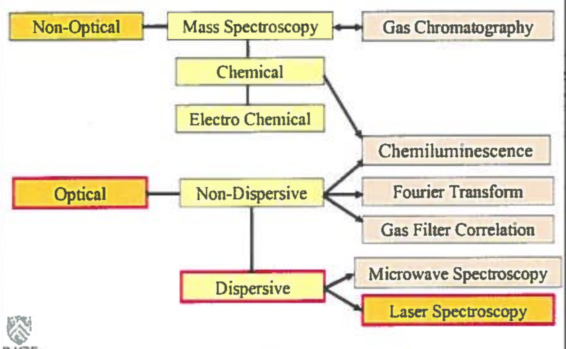
Megacity Air Pollution: Houston, TX

NASA–JSC Human-Rated Simulation Chamber

Existing Methods for Trace Gas Detection



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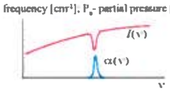
Fundamentals of Laser Absorption Spectroscopy

Beer-Lambert's Law of Linear Absorption

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

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

ν - frequency [cm^{-1}], P_a - partial pressure [atm]



$$\alpha(\nu) = C \; S(T) \; g(\nu - \nu_0)$$

C - total number of molecules of absorbing gas/atm/cm^3 [molecule cm^{-3} atm^{-1}]

S - molecular line intensity [cm/molecule]

$g(\nu - \nu_0)$ - 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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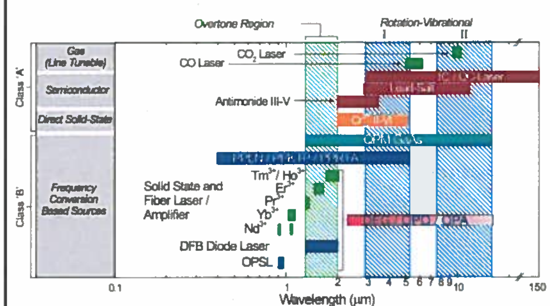
Mid-IR Source Requirements for Laser Spectroscopy

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



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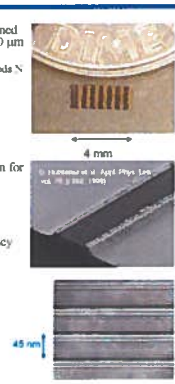
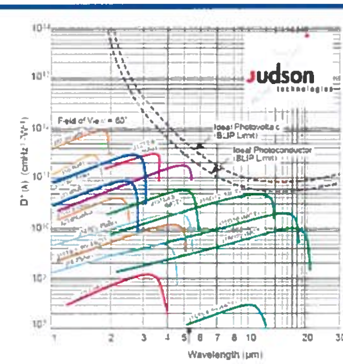
Quantum and Interband Cascade Laser: Basic Facts

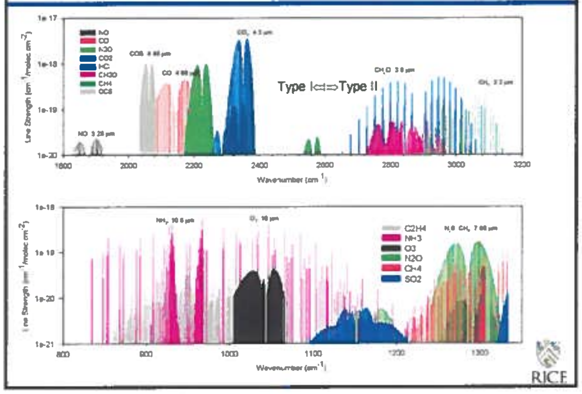
- Band – structure engineered devices (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 3.5 to 160 µm
  - Unipolar devices
  - Cascading (each electron creates N laser photons and the number of periods N determines laser power)
- Compact, reliable, stable, long lifetime, 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 Technology
    ~ 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)



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
HCHO	1765	350	100
H_2O_2	1267	1000	400

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

Pathlength: 210 m

Typical data acquisition time: 1-100 s

Mark S. Zahniser, SIRIS 2004, September 2004

NASA Target Gas Opportunity Matrix

Molecule	Detection Limit (ppb)	QEPAS detectable? 1.3-1.7 μm	QEPAS detectable? 2-5 μm
Formaldehyde	10	No	X
Acetaldehyde	20	Experiments required	
Ammonia	100	X	X
Carbon monoxide	1000	Probably not	X
Hydrogen cyanide	100	X	X
Carbon dioxide	<2%	X	X
Nitrogen dioxide	100	Probably not	X
HF	100	Experiments required	
Acrolein (2-Propenal)	5	Unlikely	
Water vapor	10-90%	X	X

X – Demonstrated

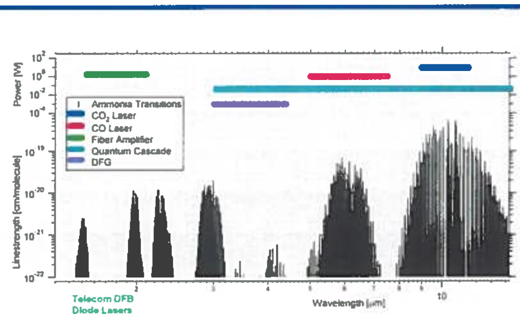
X – Highly expected based on the existing technology level

X – Expected with the technology advance

Motivation for NH_3 Detection

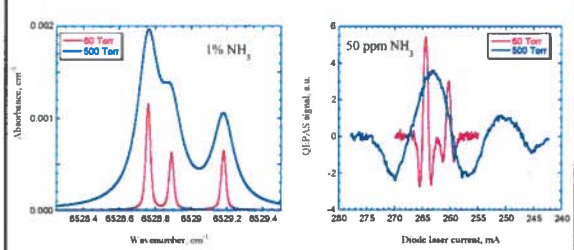
- Monitoring of gas separation processes
- Spacecraft related gas monitoring
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities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

Simulated Infrared NH_3 Absorption Spectra



M. Webber et al. 2003, Pranalytica

Ammonia Detection using a 1.53 μm Telecom Diode Laser

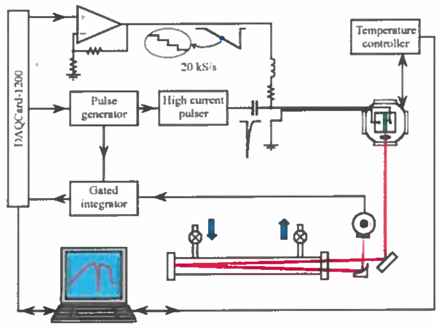


Spectral simulations based on data from Webber et al., APPLIED OPTICS 40, 2031-2042 (2001)

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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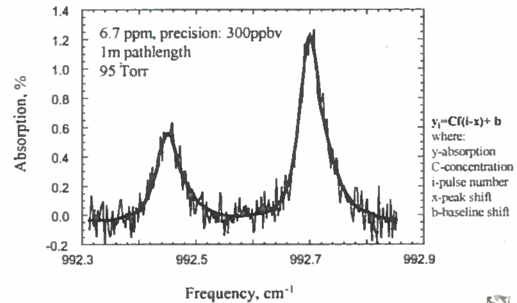
Ammonia Absorption Spectrum @ 993 cm^{-1}



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

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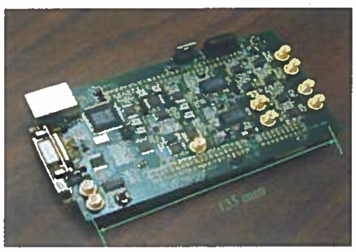
Dedicated DSP-based electronics for trace gas sensing using a pulsed QC laser



A pulsed quantum cascade laser requires a high speed pulsed processing system for a minimum detection limit

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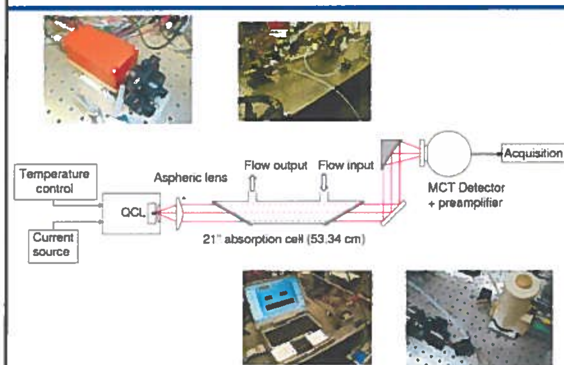
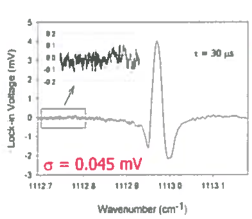
CW RT DFB QC laser based NH_3 Sensor @ 9 µm (1113 cm^{-1})



Wavelength Modulation Spectroscopy of NH_3

- QCL Drive Current : Quasi CW + Wavelength modulation



- Calibration with a 1038 ppm $NH_3:N_2$ mixture

1σ extrapolated sensitivity 82 ppb.m/√Hz

⇒ Improvement by a factor of 3 compared to direct absorption spectroscopy

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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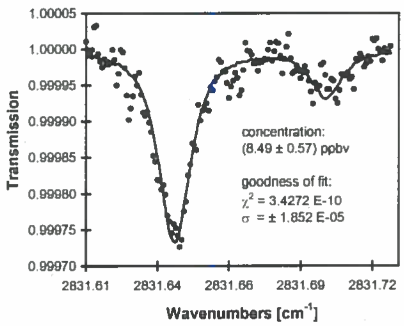
H_2CO Detection in Ambient Air at 3.53 μm



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

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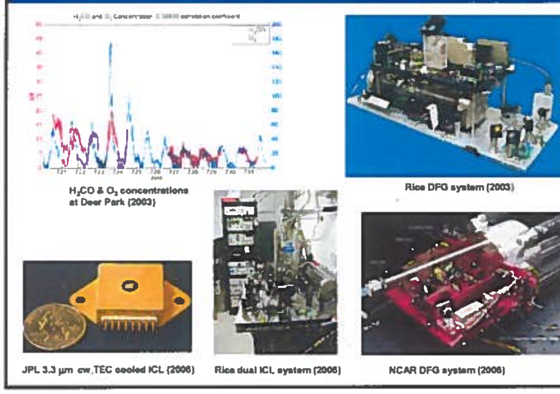
DFG and ICL based H_2CO Sensor for studying Urban Air Pollution



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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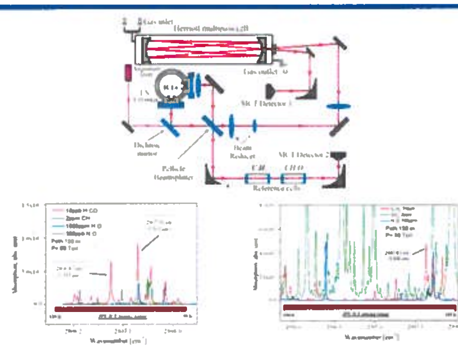
CW ICL Based H_2CO and C_2H_4 Sensor for TexAQS '06



HITRAN Based Simulation of a H_2CO-H_2O-CH_4 Spectrum in Tuning Range of a 3.5μm 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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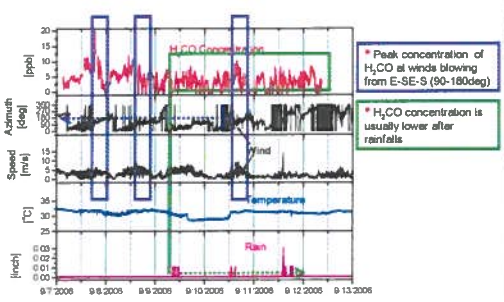
Comparison to Meteorological Data



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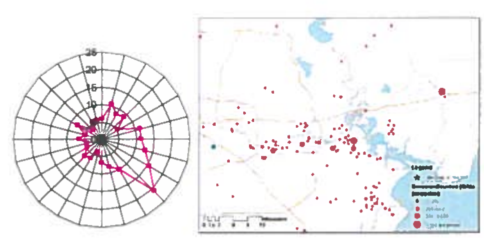
Maximum HCHO (ppb) versus Wind Direction



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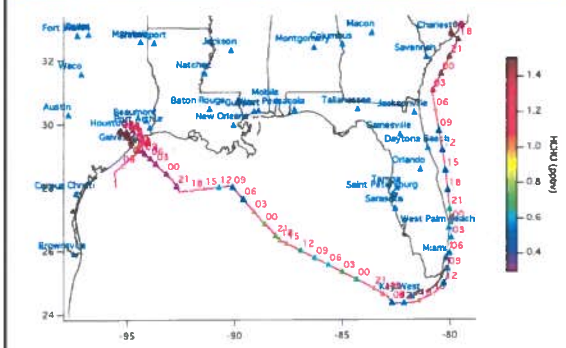
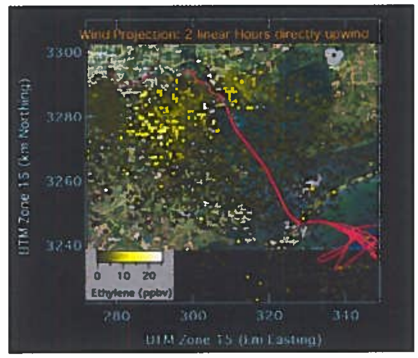
Ron Brown Ship Track, August 2006

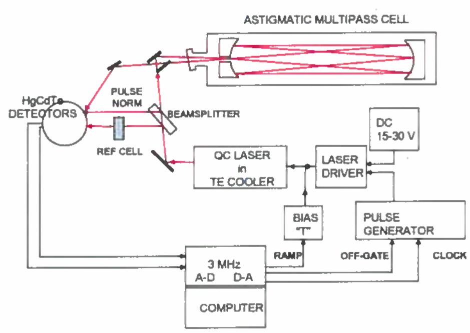


Aerodyne Inc., Billerica, MA

Ron Brown Ship Track in Houston Ship Channel, September 2006

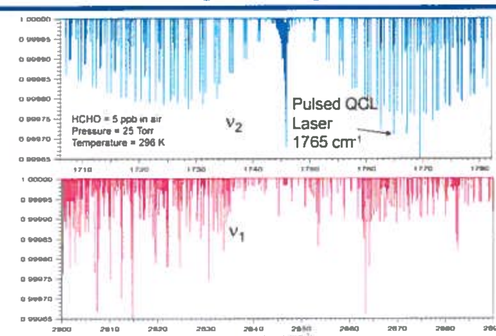


Pulsed QC-TILDAS Sensor Platform



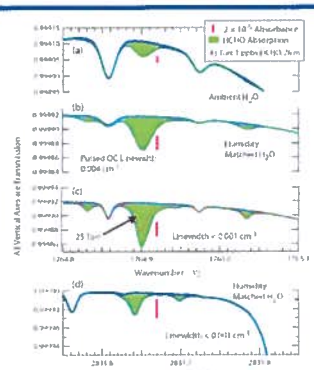
Aerodyne Inc., Billerica, MA

Infrared Spectroscopic Bands



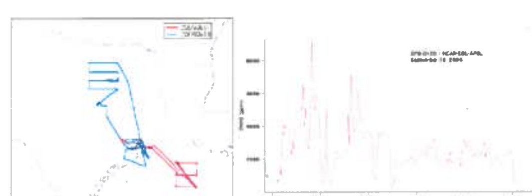
Aerodyne Inc., Billerica, MA

Formaldehyde Absorption Data



Aerodyne Inc., Billerica, MA

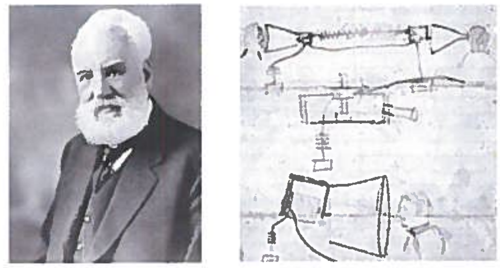
Airborne (NASA P3) DFG based CH_2O Sensor



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

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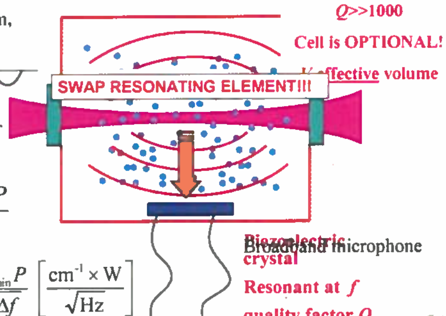
From conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$



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

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

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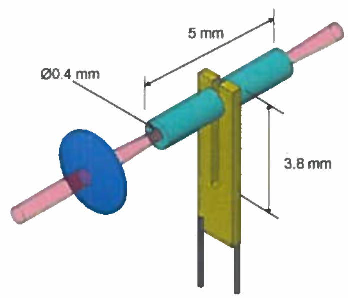
TF based spectrophone



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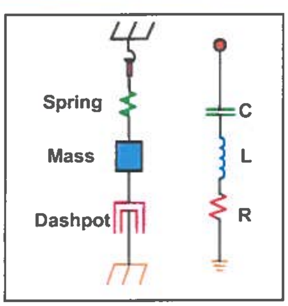
Equivalent Electrical Circuit of a Quartz TF



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

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

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

41 "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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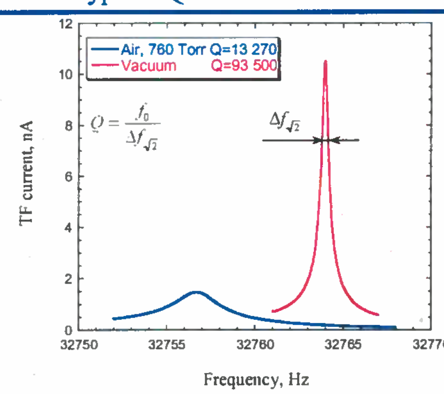
Typical QTF resonance curves



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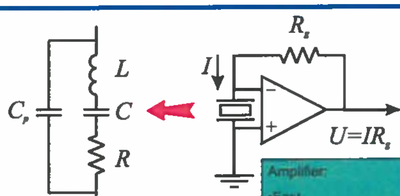
Noise analysis



Amplifier:
- Fast
- Low noise
- High impedance
- Low 1/f noise

$S_1 = \sqrt{4k_B T R_g}$; $R_g = 10\,\mathrm{M\Omega} \Rightarrow S_1 = 4.1\cdot$ [illegible]

$S_2 = \sqrt{\frac{4k_B T}{R}} R_g$; $R = 100\mathrm{k\Omega} \Rightarrow S_2 = 4.1\cdot10$ [illegible] $\frac{}{\sqrt{\mathrm{Hz}}}$ (at 760 Torr)

$S = \sqrt{S_1^2 + S_2^2} \approx S_2$ (at resonance)   Noise goes up as $\sqrt{Q}$.

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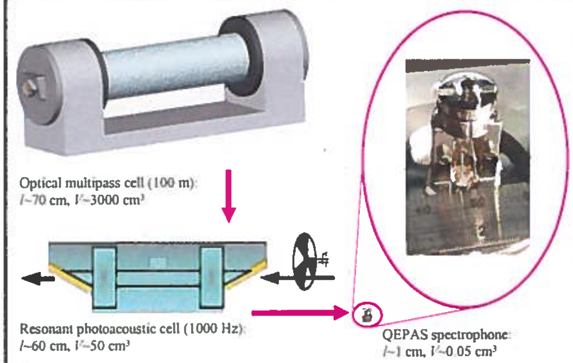
Comparative Size of Absorbance Detection Modules (ADM)



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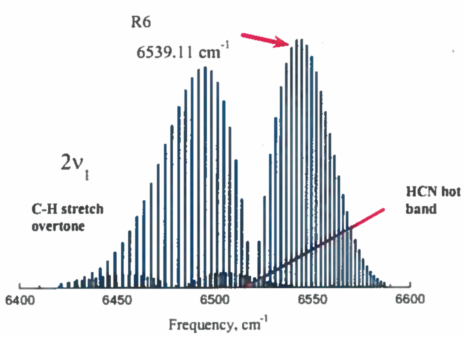
Simulated NIR absorption band of HCN centered at 1.53 μm



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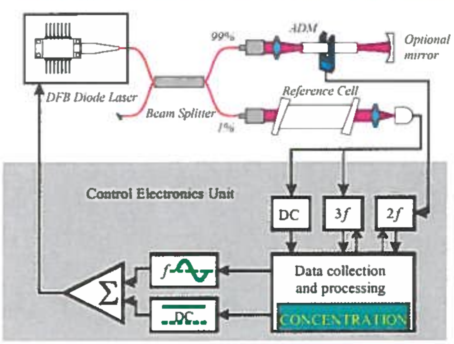
QEPAS based gas sensor architecture



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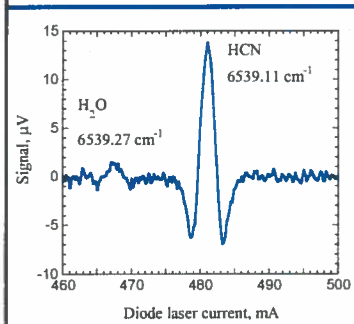
1.53 μm LPAS signal of a 6.25 ppmv HCN: air mixture



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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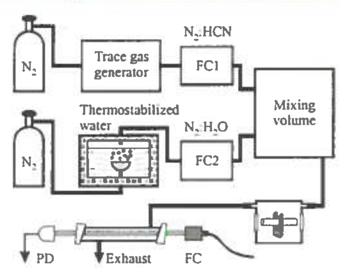
Generation of controlled H_2O concentrations in HCN gas flow



Humidifier was developed for HCN sensor characterization in Phase I and will be used in current Phase II project to study water interference and relaxation effects when targeting broadband absorbers, such as Freon 125.

FC1,2 – mass flow controllers, FC – fiber collimator to couple the diode laser radiation at 1.37 mm into the optical gas cell, PD – photodiode

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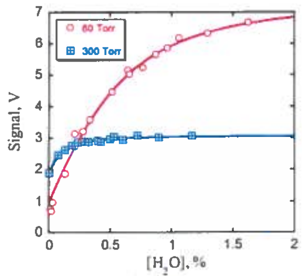
QEPAS HCN signal dependence on gas humidity



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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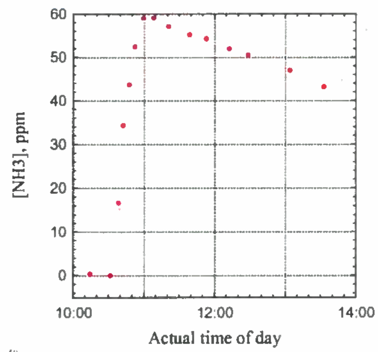
NH_3 in H_2: SRNL, reaction bed products



The spectrophone was not optimized for H_2 (different speed of sound), therefore the response was ~7 times weaker compared to N_2 as a carrier.

However, the sensitivity was still sufficient to monitor the NH_3 content in the post-reaction bed H_2 flow.

SRNL

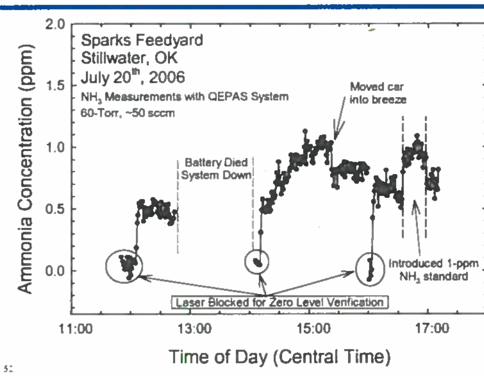
50

Oklahoma State University research feedyard

51

Ekips

Agricultural Ammonia Measurements



52

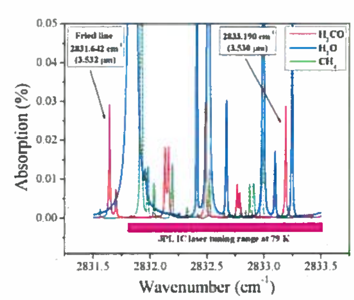
Ekips

Motivation for Precision Monitoring of H_2CO

- Pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products
- Precursor to atmospheric O_3 production
- Medically important gas

RICE

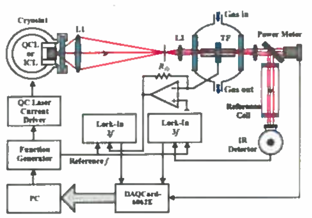
HITRAN Based Simulation of a H_2CO-H_2O-CH_4 Spectrum in the Tuning Range of a 3.53μm IC Laser

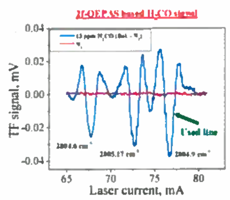


- H_2CO : 10 ppb
- H_2O : 3%
- CH_4 : 2 ppm
- Optical path: 100 m
- Total pressure: 30 Torr

NASA JPL RICE

ICL based Quartz-Enhanced Photoacoustic Gas Sensor



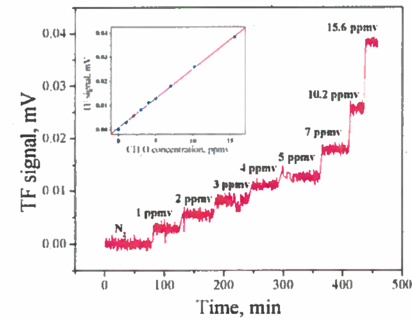


- $[H_2CO]$: 13 ppm (N_2 - balance gas)
- QEPAS NNEA Sensitivity (for 2804.9 cm^{-1}): $0.91\times10^{-8} cm^{-1} W/\sqrt{Hz}$;
- NEC (τ = 1s): 0.14 ppmv (~ 6.5 mW)

For comparison:
NIR QEPAS NNEA Sensitivity for NH_3 :
$5.4\times10^{-9} cm^{-1}W/\sqrt{Hz}$
NEC (τ = 1s): 0.5 ppmv (38 mW)

JPL RICE

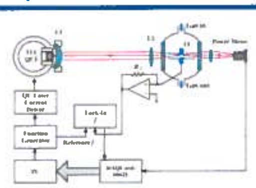
IC Laser based Formaldehyde Calibration Measurements with a Trace Gas Standard Generator

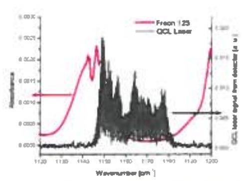


- H_2CO absorption frequency: 2804.9 cm^{-1}
- Lock-In time constant: 1 s
- QEPAS parameters
  - Resonance frequency: 32.760 KHz
  - Q-factor: ~ 8800
  - Pressure: 200 Torr
  - Gas Flow: ~50 sccm
  - IC laser power: ~ 6.8 mW

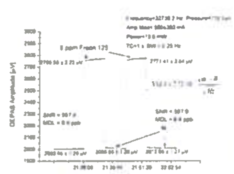
JPL RICE

Amplitude Modulated 8.6 µm QCL based QEPAS 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

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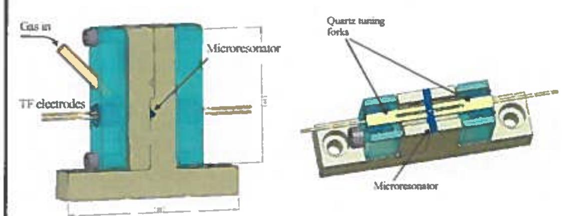
Design of a new QTF based Absorption Detection Module



- **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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Merits of QE PAS 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 mm^3)
- 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 9 Trace Gas Species (Nov.'06)

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
CO_2 (exhaled air)	6514.25	90	1.0×10[illegible]	5.2	890
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	9.1×10[illegible]	6.5	0.14
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)***	1162.79	700	2.7×10[illegible]	18.60	0.008

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

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

For comparison: conventional PAS $2.2\times10^{-9} cm^{-1}W/\sqrt{Hz}$ (1,800 Hz) for NH_3*
* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003)

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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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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, Heliobacter 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

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

The New York Times

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

- We need sensors that can detect these biomarkers.

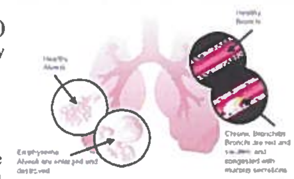
NO as a Biomarker

- 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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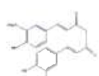
Curcumin Pilot Study

- 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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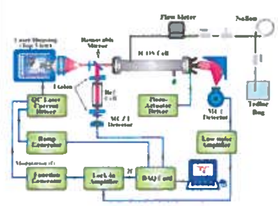
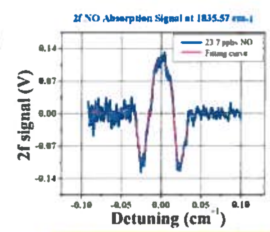
Laser-based ICOS Nitric Oxide Sensor





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

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

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)

Target: Kidney and Liver Disease

- Top-10 causes of death
  - result in morbidity for millions
- Prevalence markedly increasing
- Kidney Failure: Dialysis
- Liver Failure: Hepatic encephalopathy
- Management "imprecise": hindered by the lack of a reliable, rapid, and inexpensive monitoring
- Treatments "suboptimal": unpleasant→ serious side effects, unpredictable dose-response profiles

T. Risby, Johns Hopkins University, Baltimore, MD

Applications of Oxidative Stress and Antioxidant Defenses in Medicine

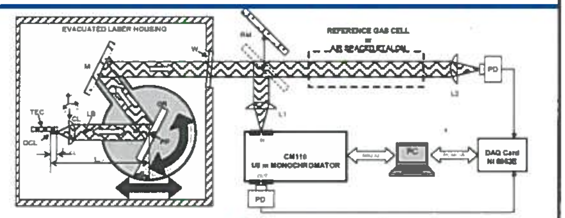
Reactive oxygen species (ROS) are involved in:

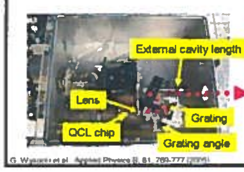
- Diseases of prematurity
- Cardiovascular disease
- Airway reactivity and pulmonary diseases
- Diabetes
- Liver disease
- Cancer
- Alzheimers, and Parkinson diseases
- Amyotrophic lateral sclerosis
- Scleroderma
- Infections
- Ischemia/reperfusion injuries
- Radiation damage

T. Risby, Johns Hopkins University, Baltimore, MD

Widely Tunable, CW, TEC Quantum Cascade Lasers

Tunable external cavity QCL based spectrometer, 2005





- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Electrically controlled 3D lens positioning for cavity alignment optimization

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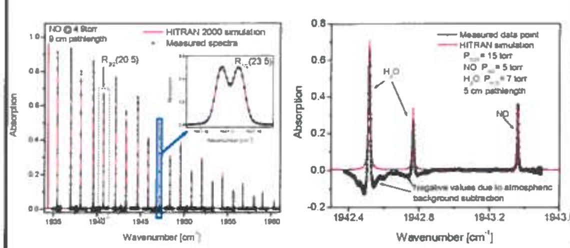
Mid-IR NO Absorption Spectra acquired with a Tunable TEC QCL



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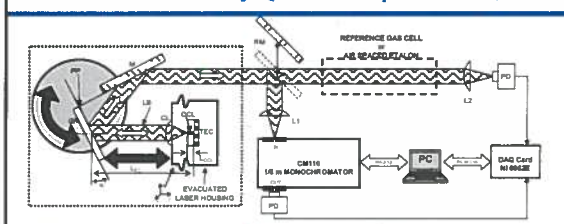
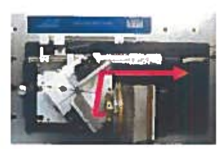
Tunable external cavity QCL based spectrometer, 2006





- 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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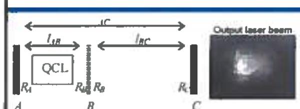
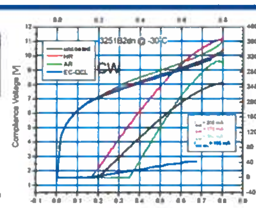
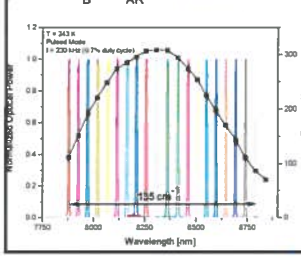
Preliminary results with a RT CW EC-QCL emitting at $\lambda = 8.4\ \mu m$





$R_B = R_{AR} \approx 2 \times 10^{-4}$



$P_{EC\text{-}opt}$ up to 50mW (cw)

Tunability 135 cm^{-1} @8.4 μm (7.8μm - 8.8μm)

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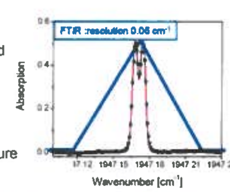
EC-QCL - Important Facts

- 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 ~10cm^{-1}
- Gain chips, which can provide tunability of >200 [illegible] ted in the literature
- Potential for [illegible] EC-QCL systems [illegible] using [illegible] MS different gratings



EC QCL in 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 Wavelength
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

Trace Gas Sensor Control and Data Processing

- Computer control of a laser-based spectroscopic sensor using PC (Windows, LabView) is convenient but does not always achieve optimum sensor performance
- Reliable systems such as NI Real-Time devices are costly, in part because of their multifunction abilities
- Dedicated electronic modules for autonomous sensor control and data processing are reliable, compact, and utilize inexpensive components
- Today's technology such as DSP and FPGA offers convenience and flexibility of design

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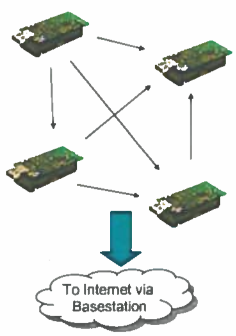
Wireless Sensor Networks for Gas Sensing



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

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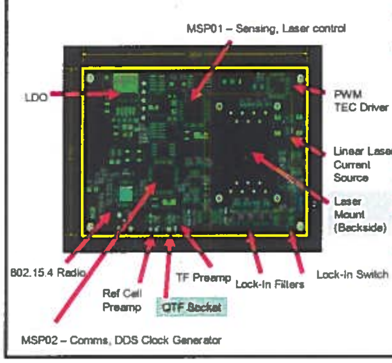
Future Work – Mini-QEPAS Sensor System



- **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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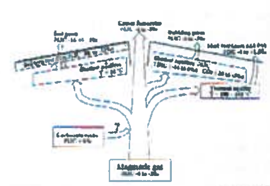
Volcanological Applications

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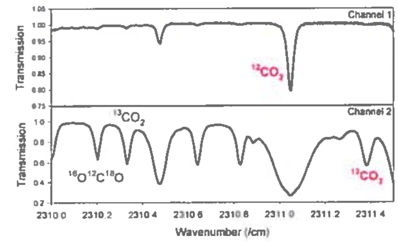
High resolution CO_2 absorption spectrum at 2311 cm^{-1}



OSAS Optics and Photonics News, May 2006

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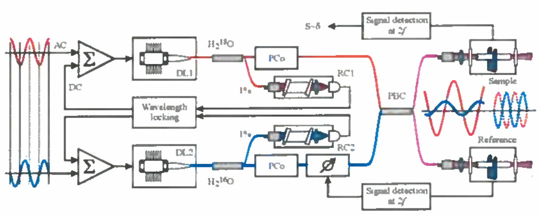
Proposed $H_2{}^{18}O$/ $H_2{}^{16}O$ Isotopic Ratiometer Scheme



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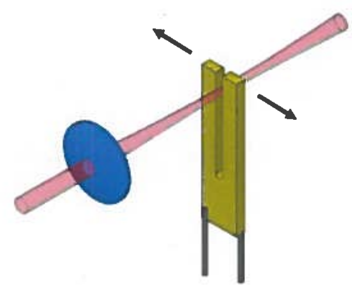
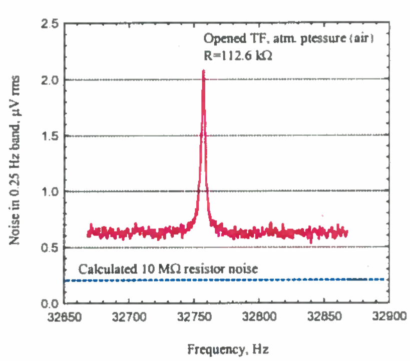
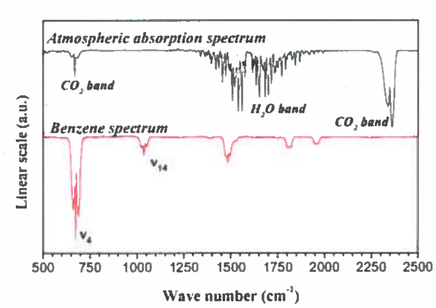
TF based spectrophone



Measured noise spectrum



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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