Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology

RICE

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

Universität Düsseldorf

July 4, 2006

- 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 Laser-PAS (H_2CO)
  - OA-ICOS NO based Sensor Technology
- Outlook and Conclusions

Work supported by NASA, PNNL, NSF, NIH and Welch Foundation

Motivation: Wide Range of Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (eg. early fire detection)
  - Automobile and Aircraft Emissions
- **Rural Emission Measurements**
  - Agriculture and Animal Facilities
- **Environmental Gas Monitoring**
  - Atmospheric Chemistry (eg ecosystems and airborne)
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Chemical, Pharmaceutical, Food & Semiconductor Industry
  - Toxic Industrial Chemical Detection
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Advanced Human Life Support Technology
- **Biomedical and Clinical Diagnostics** (eg. breath analysis)
- **Forensic Science and 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, est.	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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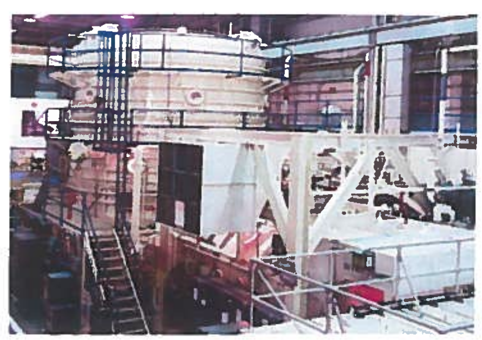
Megacity Air Pollution: Houston, TX

NASA–JSC Human-Rated Simulation Chamber



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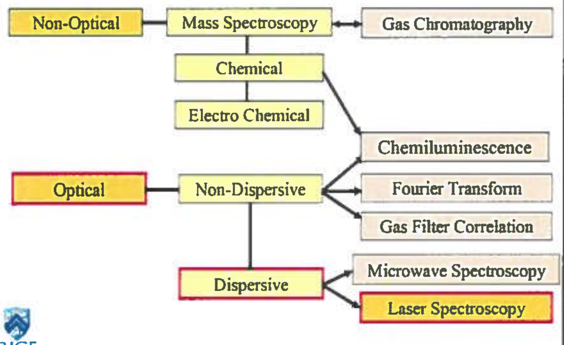
Existing Methods for Trace Gas Detection



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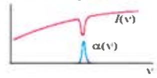
Fundamentals of Laser Absorption Spectroscopy

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]



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

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

S – molecular line intensity [cm·molecule^{-1}]

$g(\nu - \nu_0)$ – normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

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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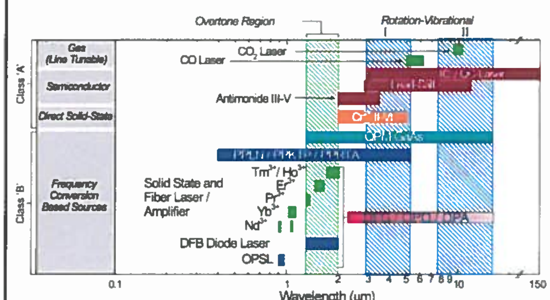
Mid-IR Source Requirements for Laser Spectroscopy

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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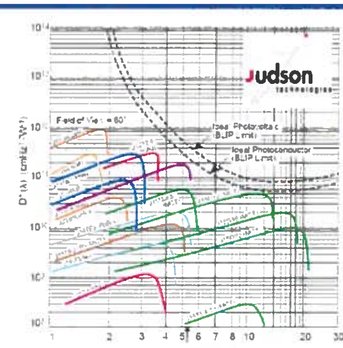
Quantum and Interband Cascade Laser: Basic Facts

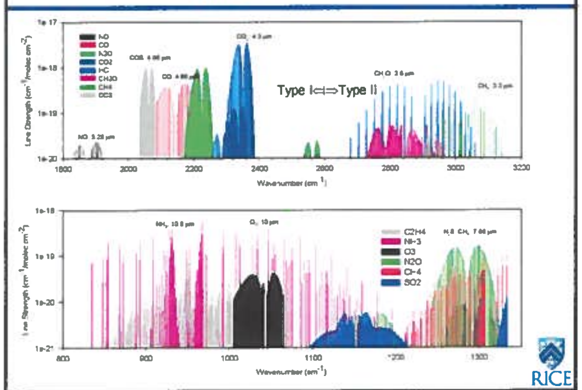
- Band – structure engineered devices (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 4 to 160 μm (limited by the CB offset on the short wavelength side)
  - Unipolar devices
  - Cascading (each electron creates N laser photons and the number of periods N determines laser power)
- Compact, reliable, stable, long lifetime, commercial availability
- Fabry-Perot (FP) or single mode (DFB)
- Broad 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; 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
  - ~ 50 mW, TEC CW DFB @ 5 and 10 μm (Alpes & Cnrne); Princeton, AdTech Optics, Maxion, Argos Tech.
    ~ 300 mW @8.3 μm (Agilent Technologies & Harvard)
  - >600 mW (CW FP) and >150 mW (CW DFB) at 298 K (Northwestern)

4 mm

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
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

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NASA Target Gas Opportunity Matrix

Molecule	Detection Limit (ppb)	QEPAS detectable?	
		1.3-1.7 μm	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

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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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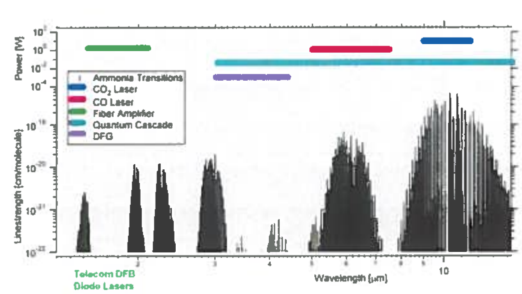
Infrared NH_3 Absorption Spectra



M. Webber et al. 2003, Praxis...

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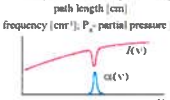
ν - frequency [cm^{-1}]; P_a - partial pressure [atm]



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

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

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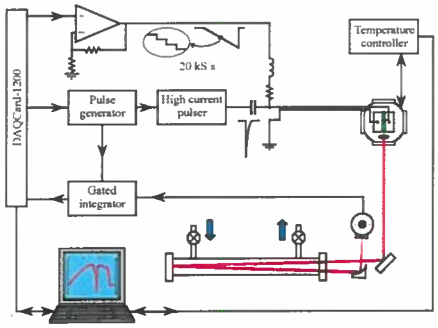
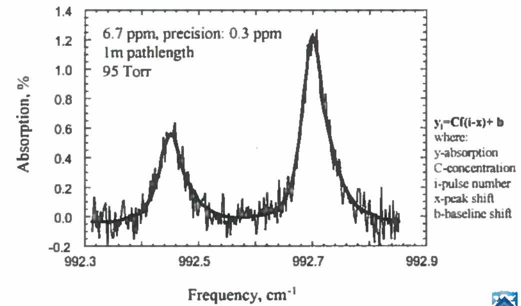
Pulsed QC Laser Based Gas Sensor



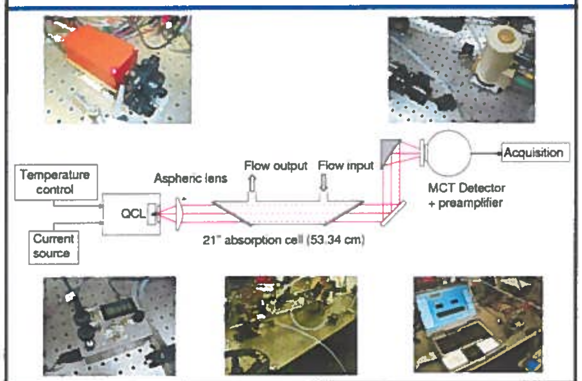
A. Kosterev et al, Applied Optics 41, 573 2002

Ammonia Absorption Spectrum @ 993 cm-1



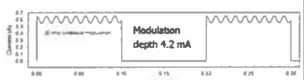
A. Kosterev et al, Applied Optics 41, 573 2002

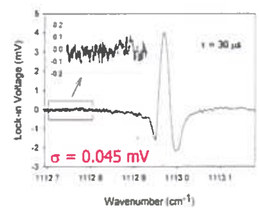
CW RT DFB QC laser based NH_3 Sensor @ 9 μm (1113 cm^{-1})



Wavelength Modulation Spectroscopy of NH_3

- QCL Drive Current : Quasi CW + Wavelength modulation



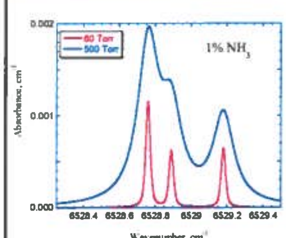


- Calibration with a 1038 ppm NH_3:N_2 mixture

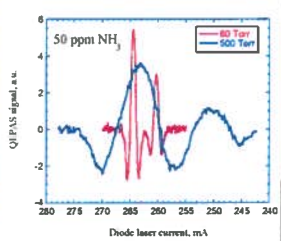
1σ extrapolated sensitivity
82 ppb.m/√Hz

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

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)]

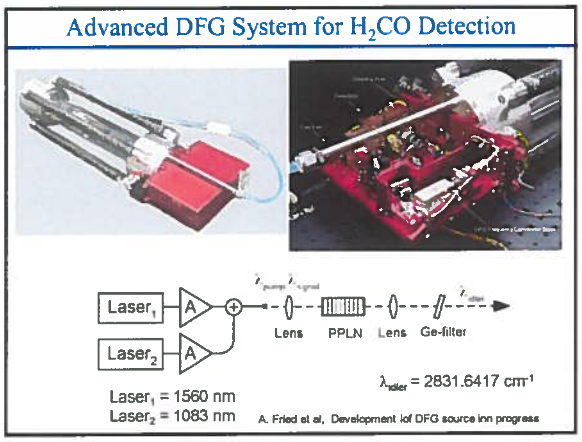


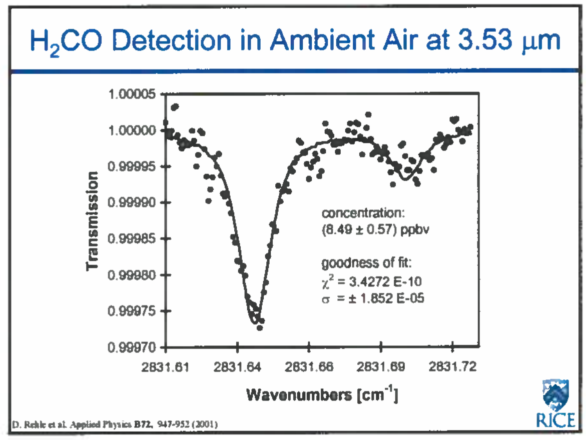
QEPAS spectra at different pressures of NH_3:N_2 gas mixture; t=0.3s, 38 mW diode laser excitation power at 6529 cm^{-1}

Applied Optics 43, 6213-6217, 2004

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


Advanced DFG System for H_2CO Detection
Laser$_1$
Laser$_2$
A
A
Lens
PPLN
Lens
Ge-filter
λ_{idler} = 2831.6417 cm^{-1}
Laser$_1$ = 1560 nm
Laser$_2$ = 1083 nm
A. Fried et al, Development lof DFG source inn progress


H_2CO Detection in Ambient Air at 3.53 μm
Transmission
1.00005
1.00000
0.99995
0.99990
0.99985
0.99980
0.99975
0.99970
concentration:
(8.49 ± 0.57) ppbv
goodness of fit:
χ^2 = 3.4272 E-10
σ = ± 1.852 E-05
2831.61
2831.64
2831.66
2831.69
2831.72
Wavenumbers [cm^{-1}]
D. Rehle et al. Applied Physics B72, 947-952 (2001)
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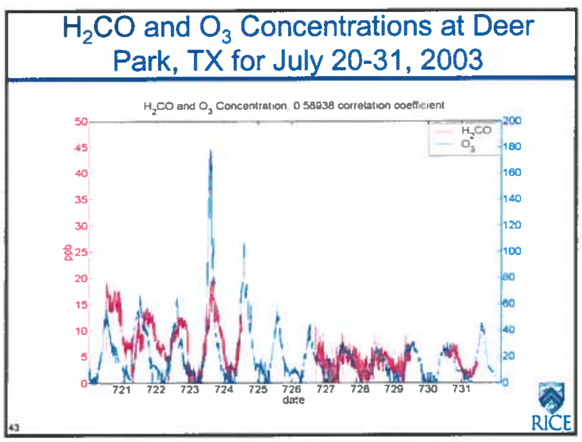
H_2CO and O_3 Concentrations at Deer Park, TX for July 20-31, 2003
H_2CO and O_3 Concentration, 0.58938 correlation coefficient
ppb
date
721
722
723
724
725
726
727
728
729
730
731
H_2CO
O_3
43
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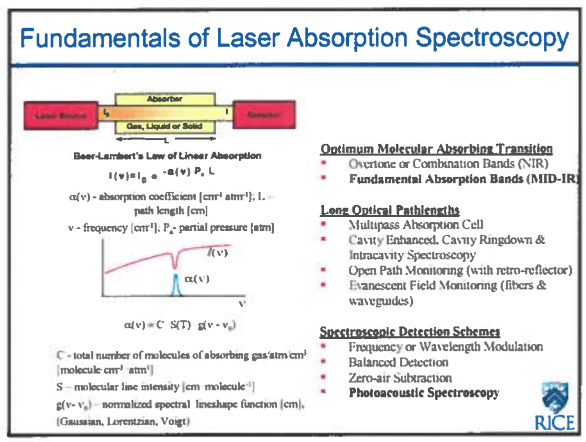
Fundamentals of Laser Absorption Spectroscopy
Absorber
Gas, Liquid or Solid
Beer-Lambert's Law of Linear Absorption
$I(\nu) = I_0 e^{-\alpha(\nu) P_a L}$
α(ν) - absorption coefficient [cm^{-1} atm^{-1}]; L - path length [cm]
ν - frequency [cm^{-1}]; P_a - partial pressure [atm]
I(ν)
α(ν)
$\alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0)$
C - total number of molecules of absorbing gas/atm/cm^3 [molecule cm^{-3} atm^{-1}]
S – molecular line intensity [cm molecule^{-1}]
$g(\nu-\nu_0)$ – normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)
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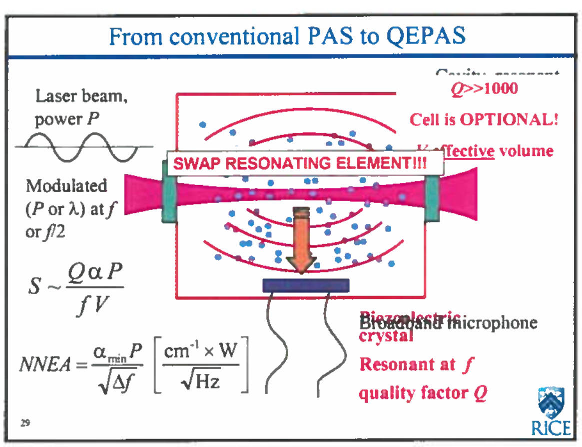
From conventional PAS to QEPAS
Laser beam, power P
Modulated (P or λ) at f or f/2
$S \sim \frac{Q \alpha P}{f V}$
$NNEA = \frac{\alpha_{min} P}{\sqrt{\Delta f}} \left[\frac{cm^{-1} \times W}{\sqrt{Hz}}\right]$
Q>>1000
Cell is OPTIONAL!
effective volume
SWAP RESONATING ELEMENT!!!
Broadband microphone
Piezoelectric crystal
Resonant at f
quality factor Q
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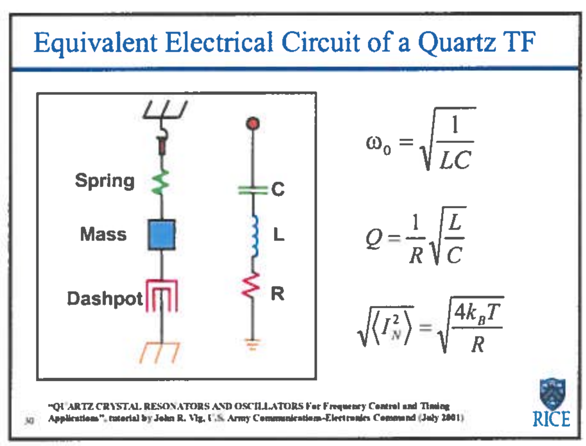
Equivalent Electrical Circuit of a Quartz TF
Spring
Mass
Dashpot
C
L
R
$\omega_0 = \sqrt{\frac{1}{LC}}$
$Q = \frac{1}{R}\sqrt{\frac{L}{C}}$
$\sqrt{\langle I_N^2 \rangle} = \sqrt{\frac{4k_B T}{R}}$
"QUARTZ CRYSTAL RESONATORS AND OSCILLATORS For Frequency Control and Timing Applications", tutorial by John R. Vig, U.S. Army Communications-Electronics Command (July 2001)
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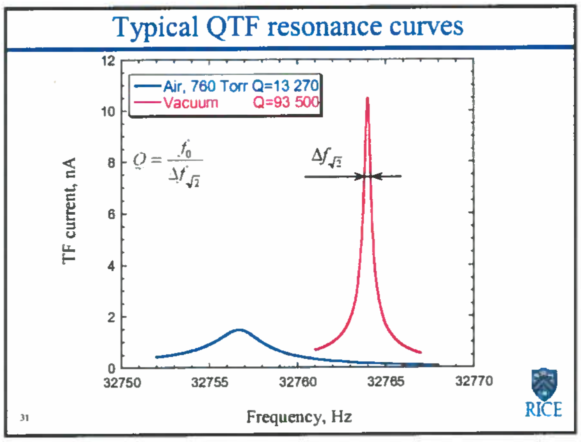
Typical QTF resonance curves
Air, 760 Torr Q=13 270
Vacuum Q=93 500
$Q = \frac{f_0}{\Delta f_{\sqrt{2}}}$
$\Delta f_{\sqrt{2}}$
TF current, nA
Frequency, Hz
32750
32755
32760
32765
32770
31
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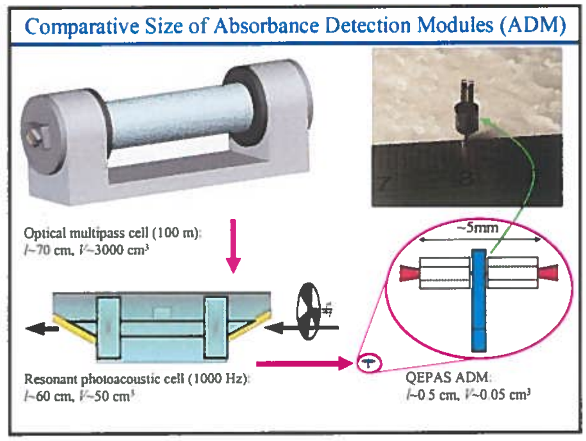
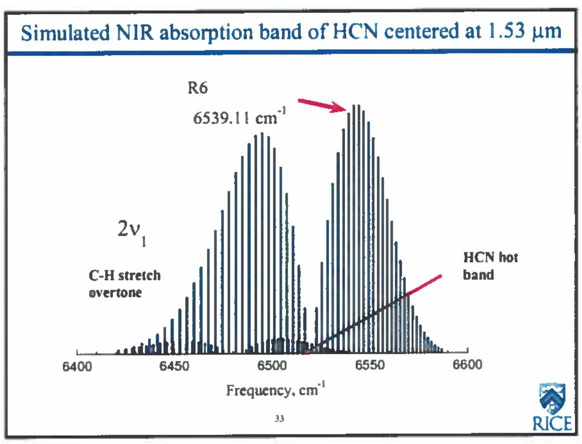

Comparative Size of Absorbance Detection Modules (ADM)
Optical multipass cell (100 m):
l~70 cm, V~3000 cm³
~5mm
Resonant photoacoustic cell (1000 Hz):
l~60 cm, V~50 cm³
QEPAS ADM:
l~0.5 cm, V~0.05 cm³


Simulated NIR absorption band of HCN centered at 1.53 μm
R6
6539.11 cm-1
2ν1
C-H stretch
overtone
HCN hot
band
6400
6450
6500
6550
6600
Frequency, cm-1
33
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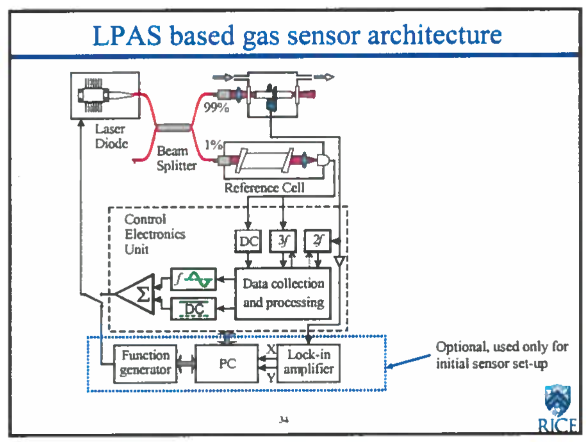
LPAS based gas sensor architecture
Laser
Diode
99%
1%
Beam
Splitter
Reference Cell
Control
Electronics
Unit
DC
3f
2f
Data collection
and processing
Function
generator
PC
Lock-in
amplifier
Optional, used only for
initial sensor set-up
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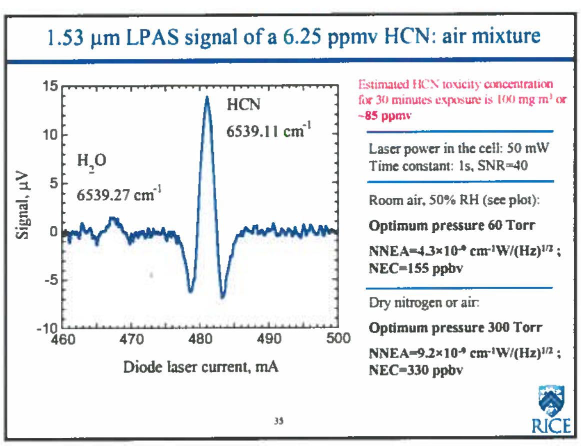
1.53 μm LPAS signal of a 6.25 ppmv HCN: air mixture
HCN
6539.11 cm-1
H2O
6539.27 cm-1
Signal, μV
Diode laser current, mA
Estimated HCN toxicity concentration
for 30 minutes exposure is 100 mg/m³ or
~85 ppmv
Laser power in the cell: 50 mW
Time constant: 1s, SNR=40
Room air, 50% RH (see plot):
Optimum pressure 60 Torr
NNEA=4.3×10-9 cm-1W/(Hz)1/2 ;
NEC=155 ppbv
Dry nitrogen or air:
Optimum pressure 300 Torr
NNEA=9.2×10-9 cm-1W/(Hz)1/2 ;
NEC=330 ppbv
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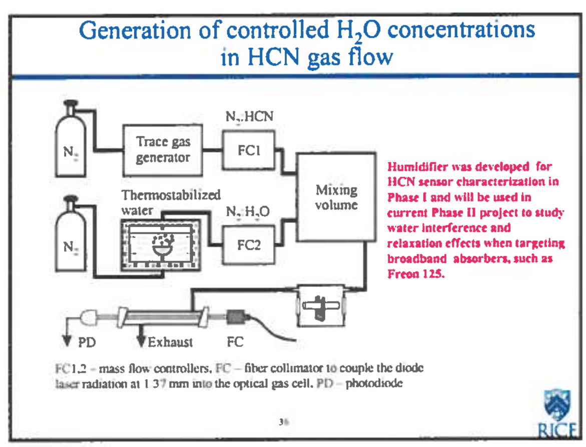
Generation of controlled H2O concentrations
in HCN gas flow
N2
Trace gas
generator
N2:HCN
FC1
Mixing
volume
Thermostabilized
water
N2:H2O
FC2
PD
Exhaust
FC
Humidifier was developed for
HCN sensor characterization in
Phase I and will be used in
current Phase II project to study
water interference and
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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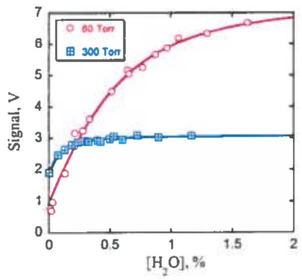
LPAS HCN signal dependence on gas humidity



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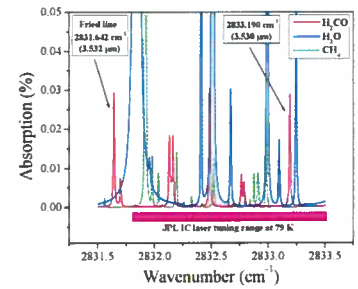
HITRAN Based Simulation of a H_2CO-H_2O-CH_4 Spectrum in Tuning Range of a 3.53μm IC Laser



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

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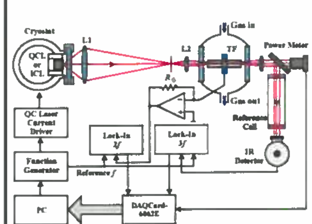
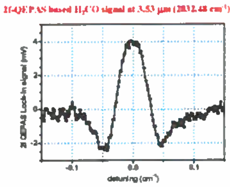
QCL based Quartz-Enhanced Photoacoustic Sensor





- $[H_2CO]$: 13.27 ppm
- QEPAS NNEA Sensitivity: $1.1\times10^{-9} cm^{-1} W/\sqrt{Hz}$; NEC (τ=1s): 0.28 ppmv (5 mW)

For comparison:
QEPAS Sensitivity for NH_3 : $5.4\times10^{-9} cm^{-1} W/\sqrt{Hz}$
NEC (τ=1s): 0.50 ppmv (38 mW)

M. Horstjann et al., Applied Physics B 79, 799, 2004

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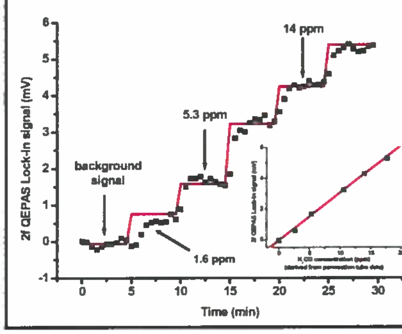
IC Laser based Formaldehyde Calibration Measurements with a Gas Standard Generator



- H_2CO absorption frequency: 2832.5 cm^{-1}
- Lock-In time constant: 10 s
- QEPAS parameters
  - Resonance frequency: 32.760 KHz
  - Q-factor: 17336
  - Pressure: 200 Torr
  - Gas Flow: 75 sccm
  - IC laser power: 6 mW

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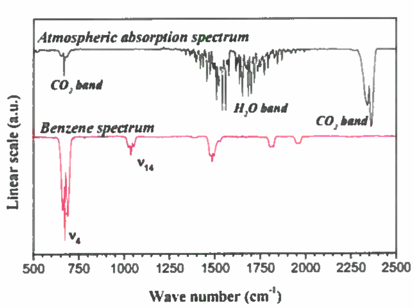
FT-IR survey absorption spectrum of benzene vapor (C_6H_6)



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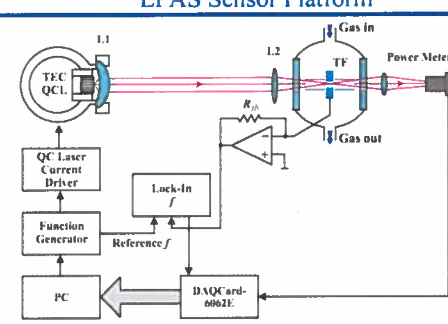
W Chen, F Cazier, F K Tittel and D Boucher, Appl.Optics 39, 6238, 2000

Amplitude Modulated 8.6 μm QCL based LPAS Sensor Platform



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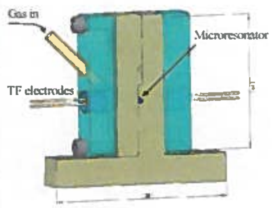
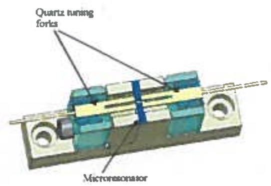
Design of a new QTF based absorption detection module





- 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 Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immunity to ambient and flow acoustic noise, laser noise and etalon effects, which allows applications that involve harsh operating environments
- Required sample volume is very small. The volume is ultimately limited by the gap size between the TF prongs, which is < 1 mm^3 for the presently used QTF.
- No spectrally selective elements are required
- Applicable over a wide range of pressures, including atmospheric pressure
- Sensitive to phase shift introduced by vibrational to translational (V-T) relaxation processes and hence the potential of concentration measurements of spectrally interfering species
- Ultra-compact, rugged and low cost compared to LAS that requires a multipass absorption cell and infrared detector(s)
- Potential for optically multiplexed concentration measurements

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QEPAS Performance for 8 Trace Gas Species (June'06)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{1/2}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10^{-9}	9.5	0.09
HCN (air: 50% hum) *	6539.11	60	$< 4.3\times10^{-9}$	50	0.16
C_2H_2 (N_2)**	6529.17	75	$\sim2.5\times10^{-9}$	~40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	0.50
CO_2 (exhaled air)	6514.25	90	1.0×10^{-8}	5.2	890
CO_2 (N_2) ***	4990.00	300	1.5×10^{-7}	4.6	130
CH_2O (N_2) * , H_2O	2832.48	100	1.1×10^{-8}	4.6	0.28
CO (N_2)	2196.66	50	5.3×10^{-7}	13	0.5
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007

* - Improved microresonator
** - Improved microresonator and double optical pass through QTF
*** - Without 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} $cm^{-1}W/\sqrt{Hz}$ (1,800 Hz) for NH_3*

* M. E. Webber, M. Pushkarsky and C. K. N Patel, Appl. Opt. 42, 2119-2126 (2003)

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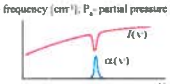
Fundamentals of Laser Absorption Spectroscopy

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]



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

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

S – molecular line intensity [cm molecule^{-1}]

$g(\nu - \nu_0)$ – normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

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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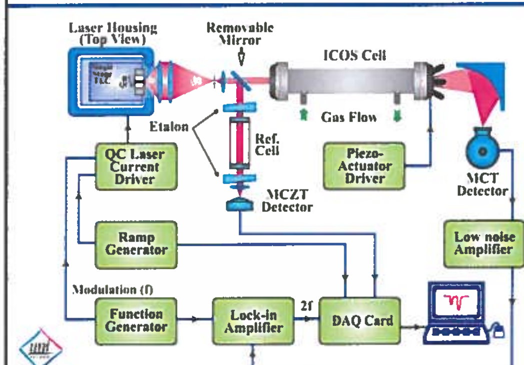
NO as a Biomarker

- 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 marker of pneumonia in ventilated patients. Am J Respir Crit Care Med 2001, 163(5): 1143-9

TEC – CW-DFB QCL based Nitric Oxide OA-ICOS Sensor



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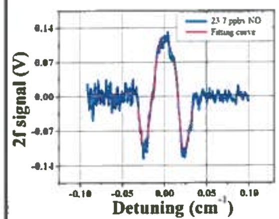
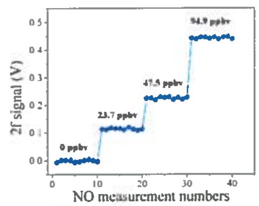
2f NO Absorption Signal at 1835.57 cm^{-1}





$NO:N_2$ mixture @ 100 Torr
Effective L= 700 m

Noise equivalent sensitivity:
0.7 ppbv (1σ)

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Chronic Obstructive Pulmonary Disease

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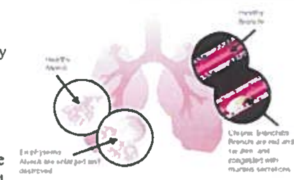
- Chronic obstructive pulmonary disease (COPD)
  - Accumulation of inflammatory products in the small airway lumen and wall
- Alveolar NO
  - Reflects peripheral lung inflammation and the response to anti-inflammatory treatment
  - Not affected by smoking or inhaled corticosteroids



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

Curcumin Pilot Study

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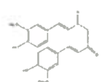
- Curcumin (Turmeric)
  - Polyphenol (diferuloylmethane)
  - Anti-inflammatory and anti-oxidant



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

Collaborator: Amir Sharafkhaneh, MD

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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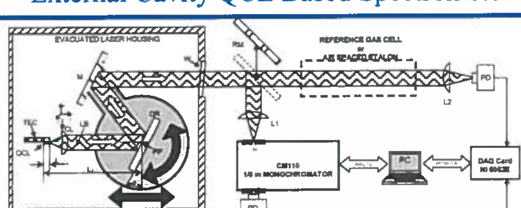
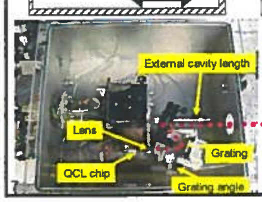
External Cavity QCL Based Spectrometer

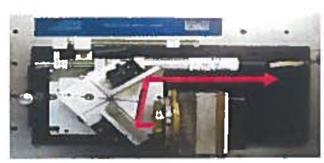




- PZT controlled EC-length
- PZT controlled grating angle
- Optimization of cavity alignment performed by means of lens positioning using electrically controlled 3D translation stage

G. Wysocki et al. Applied Physics B, 81, p 769 (2005)

Tunable external grating cavity QCL based spectrometer II



Compact ECG QCL design, June 2006

Housing for high power cw QCL and lens positioning assembly

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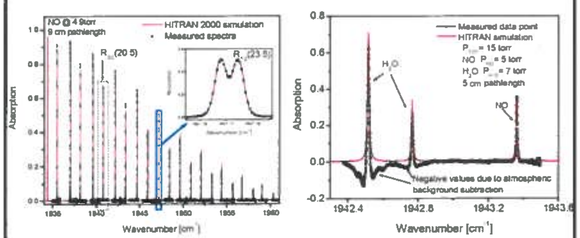
Mid-IR NO Absorption Spectra Acquired with a Tunable TEC QCL



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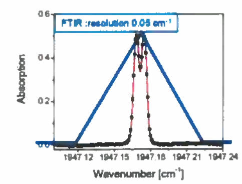
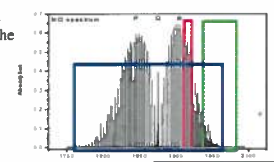
Important facts of novel EC-QCL Technology

- Laser spectroscopy provides superior resolution compared to other techniques e.g. FTIR
- Single mode operation of the laser is required
- Wavelength tunability of single mode (DFB) mid-IR semiconductor lasers is ~10cm-1
- Demonstrated wavelength tunability of the Rice EC QCL is ~ 35 cm-1 (limited by the gain chip properties and not by the designed EC configuration)
- Gain chips, which can provide tunability of >200 cm^{-1} are already reported in the literature





Sensor control and data processing

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

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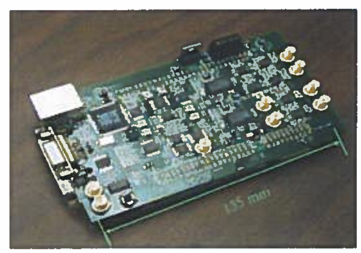
Dedicated DSP-based electronics for trace gas sensing using a pulsed QC laser



Pulsed laser requires high speed pulsed processing system for minimum detection limits

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Conclusions and Future Directions

- **Laser based Trace Gas Sensors**
  - Ultra compact (~ 0.2 mm^3), robust & low cost sensors based on QE L-PAS
  - QEL-PAS is immune to ambient noise. The measured noise level coincides with the thermal noise of the QTF
  - Best to date demonstrated QEPAS sensitivity is 2.1×10^{-9} $cm^{-1}W/\sqrt{Hz}$ for H_2O:N_2
  - QEPAS exhibits a low 1/*f* noise level, allowing data averaging for more than 3 hours
  - Detected 14 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, HCN, C_2H_4, C_2H_2, C_2H_5OH, SO_2, H_2CO and several isotopic species of C, O, N & H
- **Applications in Trace Gas Detection**
  - Environmental & Spacecraft Monitoring (NH_3, CO, CH_4, C_2H_4, N_2O, CO_2 and H_2CO)
  - Medical Diagnostics (NO, CO, COS, CO_2, NH_3, C_2H_4)
  - Industrial process control and chemical analysis (NO, NH_3, H_2O)
- **Future Directions and Collaborations**
  - QE L-PAS based applications using novel thermoelectrically cooled cw and broadly wavelength tunable quantum and interband cascade lasers
  - Investigate QTFs with lower resonant frequencies
  - Investigate amplitude modulation QEPAS potential and limitations
  - New target gases, in particular VOCs and HCs
  - Development of optically multiplexed gas sensor networks based on QE L-PAS

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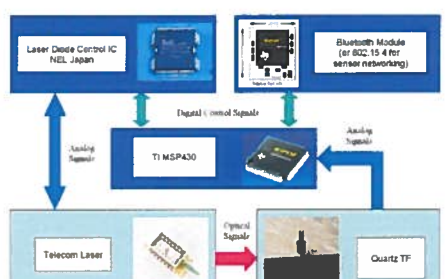
Concept of a ultra-miniature QEPAS gas sensor



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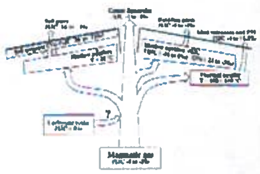
Volcanological applications

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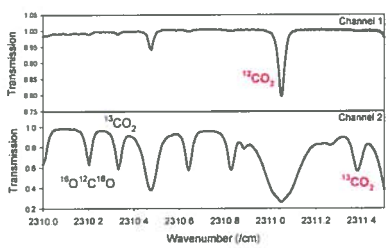
High resolution CO_2 absorption spectrum at 2311 cm^{-1}



To appear in Optics and Photonics News 2006

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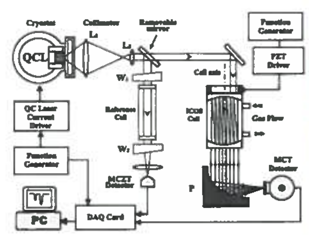
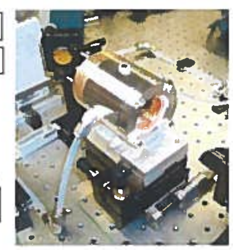
Off-Axis Integrated Cavity Output Spectroscopy (ICOS) Based Gas Sensor





- Novel compact gas cell design of length: 3.8 – 5.3 cm and cell volumes < 80 cm³.
- Low loss mirrors (ROC 1m) ~60-250 ppm, R~99.975, L_{eff} ~170-800 m
- Rapid eNO concentration measurements during a single breath cycle are feasible

ISI LGR RICE

Weladee pg 44 CLEO 2006 (May 22 2006)