



Semiconductor Laser based Trace Gas Sensor Technology: Advances and Opportunities

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OUTLINE

Oklahoma University
Norman, OK
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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
 - Quartz Enhanced Laser-PAS
 - 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** (Explosive, CW, etc.)
- **Fundamental Science and Photochemistry**



Trace Gas Monitoring in a Petrochemical Plant



University of Szeged, Hungary

Worldwide Megadirty Mega Cities

	Population, m	Sulphur dioxide	Particulate matter	Lead	Carbon monoxide	Nitrogen dioxide	Ozone
	1990, est.	2000, proj.					
Bangkok	7.16	10.26	0	0	0	0	0
Beijing	9.74	11.47	0	0	0	0	0
Bombay	11.13	15.43	0	0	0	0	0
Buenos Aires	11.58	13.05	-	0	-	-	-
Cairo	9.08	11.77	-	0	-	-	-
Calcutta	11.83	15.94	0	0	0	0	0
Delhi	8.62	12.77	0	0	0	0	0
Jakarta	9.42	13.23	0	0	0	0	0
Karachi	7.67	11.57	0	0	0	0	0
London	10.57	10.79	0	0	0	0	0
Los Angeles	10.47	10.91	0	0	0	0	0
Maria	8.40	11.48	0	0	-	-	-
Mexico City	19.37	24.44	0	0	0	0	0
Moscow	9.39	10.11	-	0	0	0	0
New York	15.65	16.10	0	0	0	0	0
Rio de Janeiro	11.12	13.00	0	0	0	0	0
Sao Paulo	18.42	23.60	0	0	0	0	0
Saudi	11.33	12.97	0	0	0	0	0
Shanghai	13.30	14.69	0	0	-	-	-
Tokyo	20.52	21.32	0	0	0	0	0

Source: United Nations. 0 High pollution, 1 Moderate to heavy pollution, 2 Low pollution, - No data available

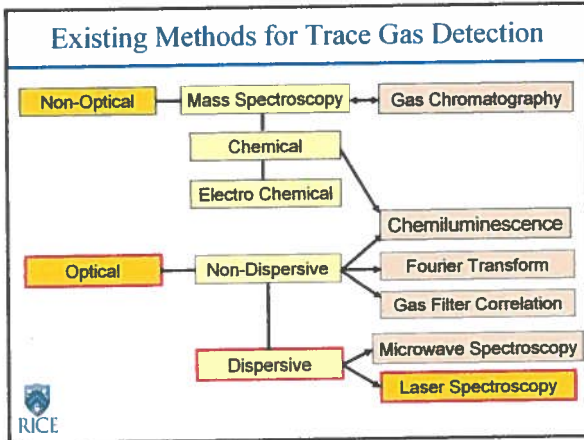


Megacity Air Pollution: Houston, TX



NASA-JSC Human-Rated Simulation Chamber





Fundamentals of Laser Absorption Spectroscopy

Beer-Lambert's Law of Linear Absorption

$$I(\nu) = I_0 e^{-n(\nu) P \cdot L}$$

$\alpha(\nu)$ - absorption coefficient [$\text{cm}^{-1} \text{atm}^{-1}$], L - path length [cm]
 ν - frequency [cm^{-1}], P - partial pressure [atm]

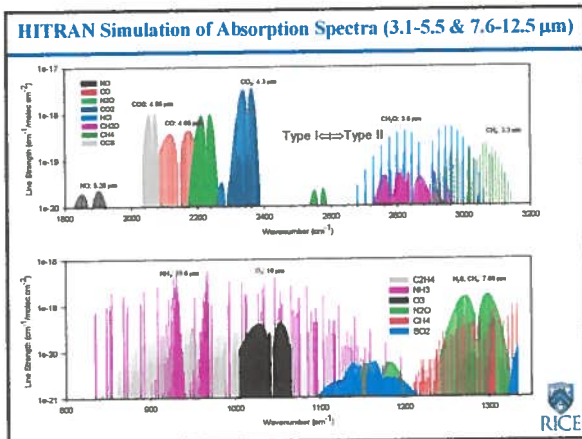
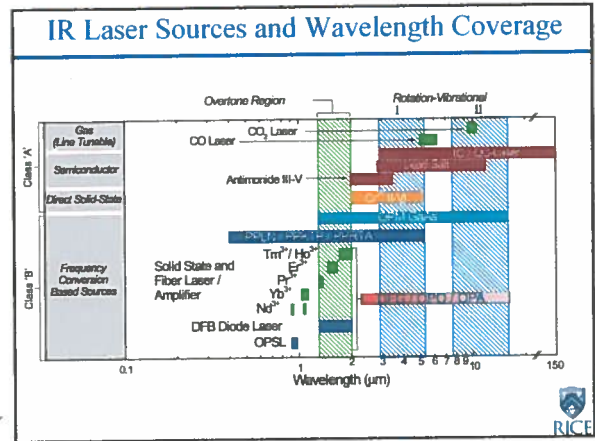
$$\alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0)$$

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

Mid-IR Source Requirements for Laser Spectroscopy

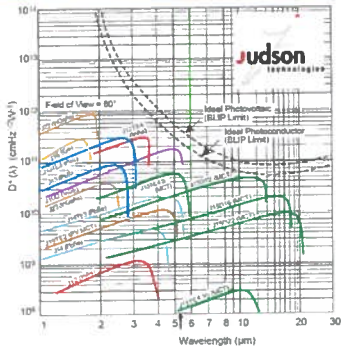
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt) ✓	Power
Selectivity	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelengths
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response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



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
 - Linewidth is ~ 300 MHz of pulsed QCLs (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 microns (Alpes & Unime)
 - > 600 mW (CW FP) and > 150 mW (CW DFB) at 298 K (Northwestern)

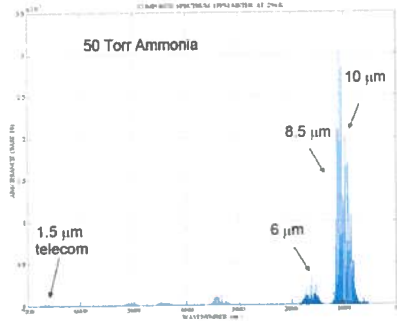
Wavelength Coverage of IR Detectors



Motivation for NH₃ Detection

- Monitoring of gas separation processes
- Spacecraft related gas monitoring
- Monitoring NH₃ 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 NH₃ Absorption Spectrum (Near-IR to Mid-IR)



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$I(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0)$
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 S - molecular line intensity [$\text{cm} \cdot \text{mole}^{-1}$]
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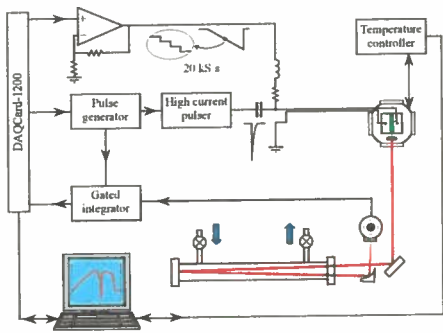
Long Optical Pathlengths

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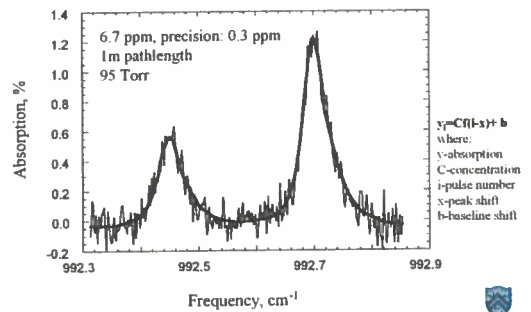
Spectroscopic Detection Schemes

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

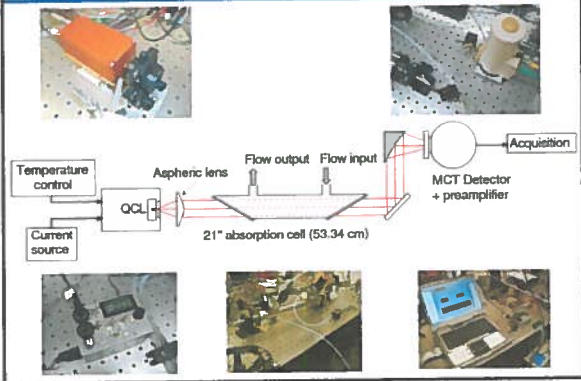
Pulsed QC Laser Based Gas Sensor



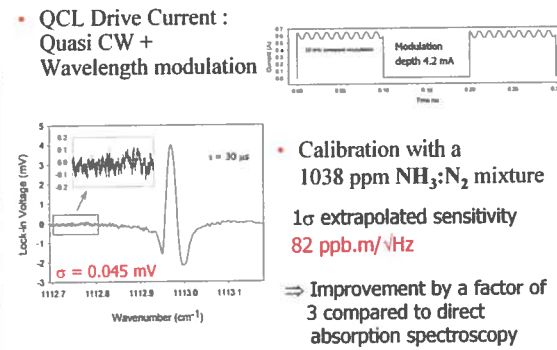
Ammonia Absorption Spectrum @ 993 cm⁻¹



CW RT DFB QC laser based NH₃ Sensor @ 9 μm (1113 cm⁻¹)



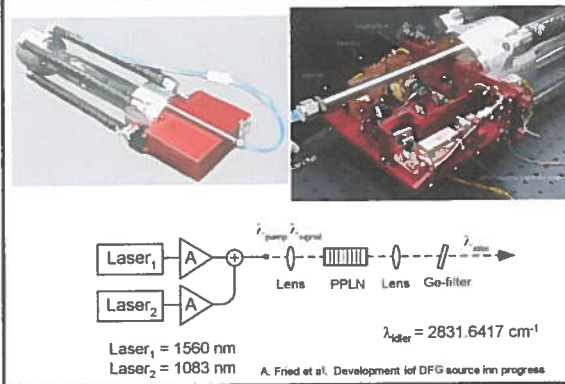
Wavelength Modulation Spectroscopy of NH₃



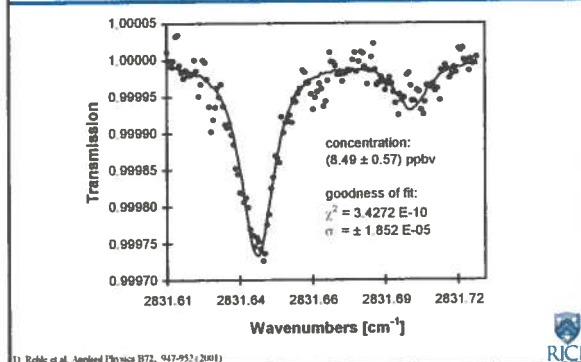
Motivation for Precision Monitoring of H₂CO

- Pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products
- Precursor to atmospheric O₃ production
- Medically important gas

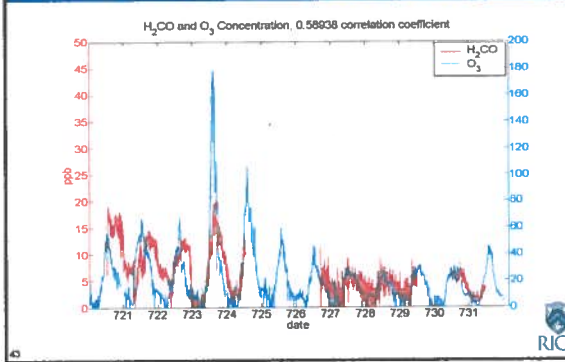
Advanced DFG System for H₂CO Detection




H₂CO Detection in Ambient Air at 3.53 μm



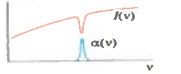
H₂CO and O₃ Concentrations at Deer Park, TX for July 20-31, 2003



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 ν - frequency [cm^{-1}]; P_0 - partial pressure [atm]



$\alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0)$
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 $g(\nu - \nu_0)$ - normalized spectral lineshape function [cm]
 (Gaussian, Lorentzian, Voigt)

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- Fundamental Absorption Bands (MID-IR)

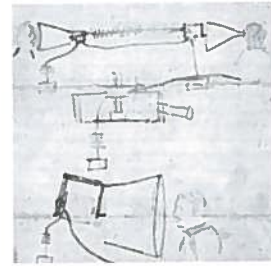
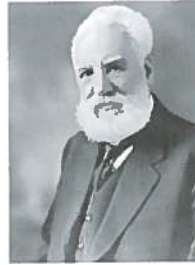
Long Optical Pathlengths

- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector)
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Spectroscopic Detection Schemes

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

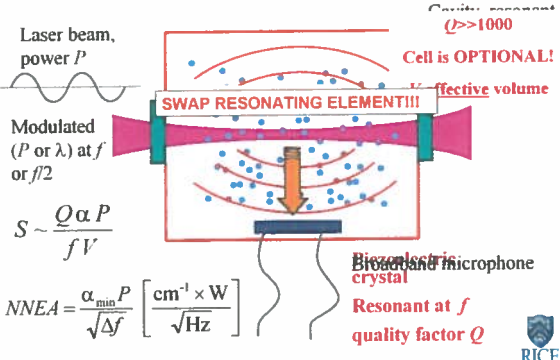
Motivation: Wide Range of Gas Sensing Applications



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



Laser beam, power P

Modulated (P or λ) at f or $f/2$

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

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

Cell is **OPTIONAL!**

SWAP RESONATING ELEMENT!!!

Biacoustic crystal

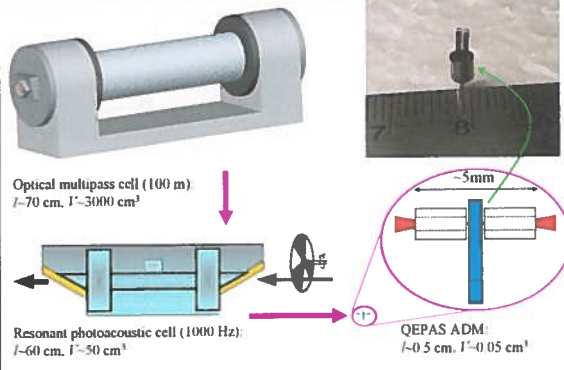
Resonant at f quality factor Q

$Q \gg 1000$

Effective volume

RICE

Comparative Size of Absorbance Detection Modules (ADM)



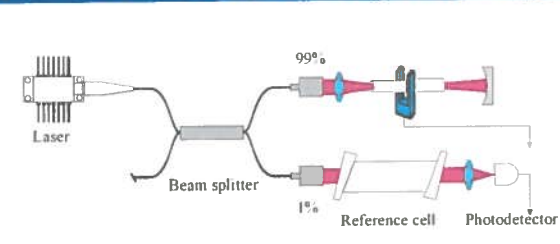
Optical multipass cell (100 m)
 $l \sim 70 \text{ cm}$, $V \sim 3000 \text{ cm}^3$

Resonant photoacoustic cell (1000 Hz)
 $l \sim 60 \text{ cm}$, $V \sim 50 \text{ cm}^3$

QEPAS ADM:
 $l \sim 0.5 \text{ cm}$, $V \sim 0.05 \text{ cm}^3$

RICE

QEPAS based gas sensor architecture



Laser

Beam splitter

99%

1%

Reference cell

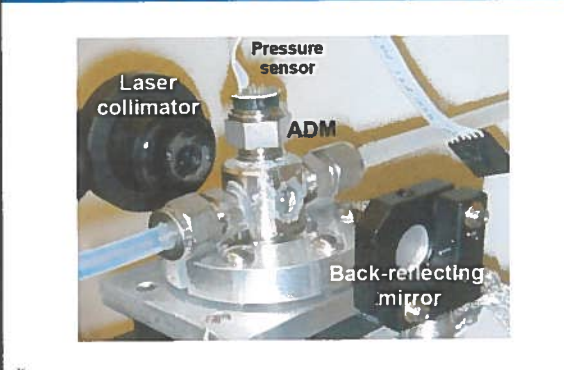
Photodetector

ADM

The laser is wavelength modulated at half the resonant frequency of the TF, signal is detected at the TF resonant frequency - 2f/modulation spectroscopy

RICE

QEPAS Trace Gas Sensing Module



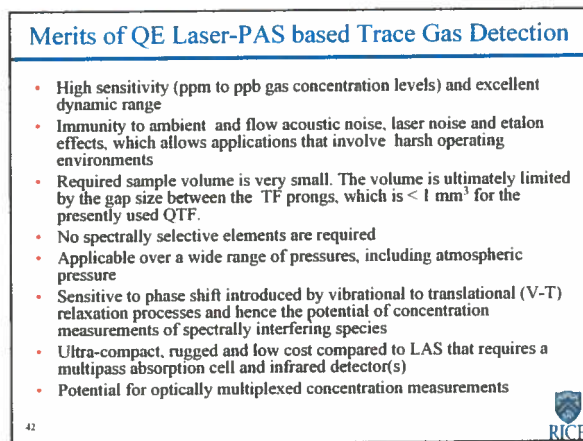
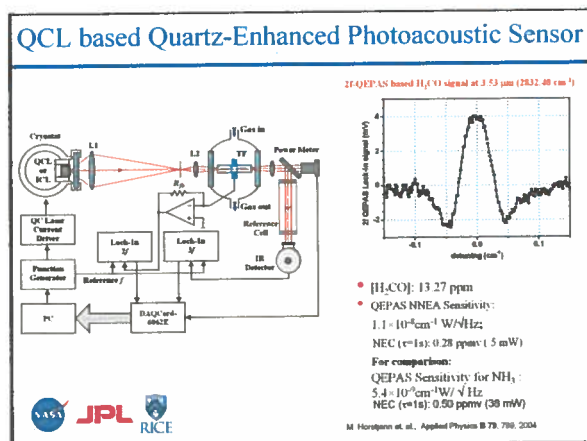
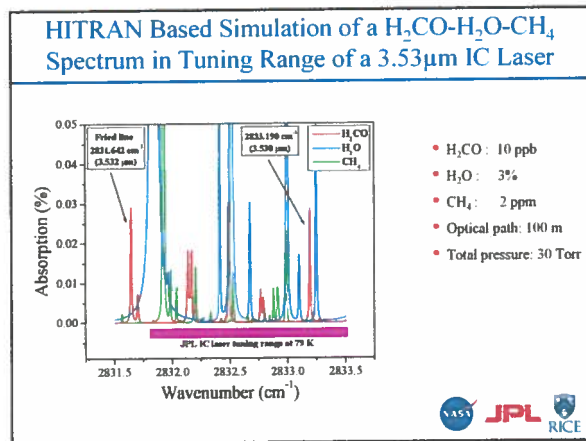
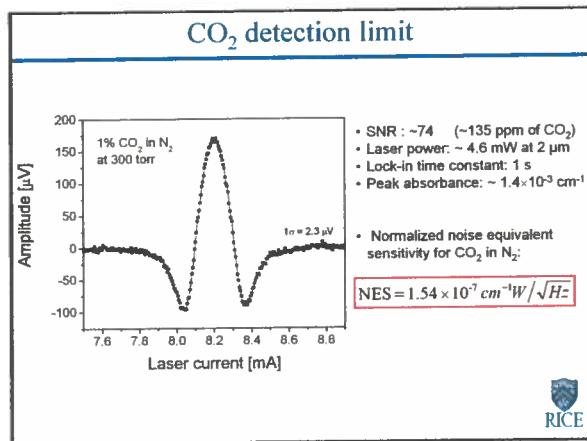
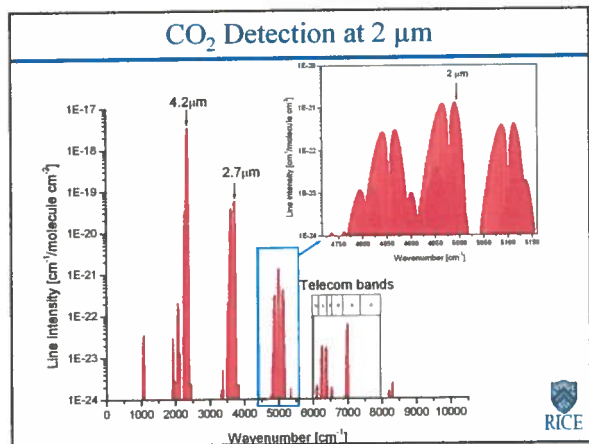
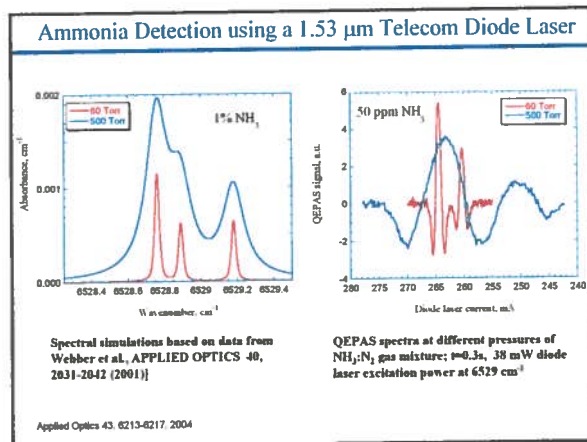
Laser collimator

Pressure sensor

ADM

Back-reflecting mirror

RICE



QEPAS Performance for 10 Trace Gas Species (Jan'06)

Molecule (Host)	Frequency, cm ⁻¹	Pressure, Torr	NNEA, cm ² W/Hz ²	Power, mW	NEC (τ=1s), ppbav
H ₂ O (N ₂)**	7181.17	60	2.1 · 10 ⁻⁹	5.8	0.18
HCN (air: 50% humid)**	6539.11	60	-2.6 · 10 ⁻⁹	50	0.1
C ₂ H ₂ (N ₂)**	6529.17	75	-2.5 · 10 ⁻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 ₄ O (N ₂)*	2832.48	100	1.1 · 10 ⁻⁸	4.6	0.28
CO (N ₂)	2196.66	50	5.3 · 10 ⁻⁹	13	0.5
CO (propylene)	2196.66	50	7.4 · 10 ⁻⁹	6.5	0.14
N ₂ O (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

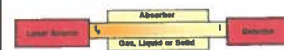
NNEA - normalized noise equivalent absorption coefficient.
 NEC - noise equivalent concentration for available laser power and τ=1s time constant.

For comparison: conventional PAS 2.2 × 10⁻⁸ cm²W/Hz (1,800 Hz) for NH₃*

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



Fundamentals of Laser Absorption Spectroscopy

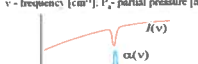


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(Gaussian, Lorentzian, Voigt)

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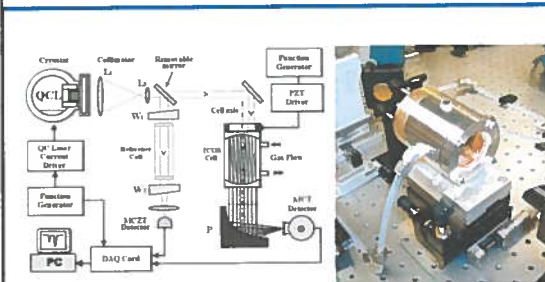
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Important Biomedical Target Gases

Molecule	Formula	Biological/Pathology Indication
Pentane	CH ₃ (CH ₂) ₃ CH ₃	Lipid peroxidation, oxidative stress associated with inflammatory diseases, transplant rejection, breast and lung cancer
Ethane	C ₂ H ₆	Lipid peroxidation and oxidative stress
CO ₂ isotope ratio	¹³ CO ₂ / ¹² CO ₂	Marker for Helicobacter pylori infection, Gastrointestinal and hepatic function
Carbonyl Sulfide	COS	Liver disease and acute rejection in lung transplant recipients (10-500 ppb?)
Carbon disulfide	CS ₂	Schizophrenia
Ammonia	NH ₃	Hepatic encephalopathy, liver and renal diseases, fasting response
Formaldehyde	HCHO	Carcinogenic tumors, breast cancer (400-1500 ppb)
Nitric Oxide	NO	Inflammatory and immune responses (e.g., asthma) and vascular smooth muscle response (6-100 ppb)
Hydrogen Peroxide	H ₂ O ₂	Airway Inflammation, Oxidative stress (1-5 ppb)
Carbon Monoxide	CO	Smoking response, CO poisoning, vascular smooth muscle response, platelet aggregation (400-3000 ppb)
Ethylene	H ₂ C=CH ₂	Oxidative stress, cancer
Acetone	CH ₃ COCH ₃	Fasting response, diabetes mellitus response, ketosis

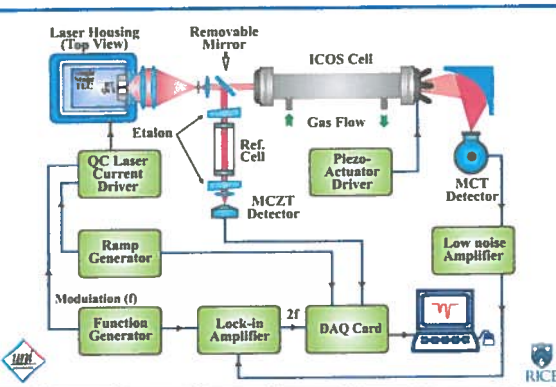
Off-Axis Integrated Cavity Output Spectroscopy (ICOS) Based Gas Sensor



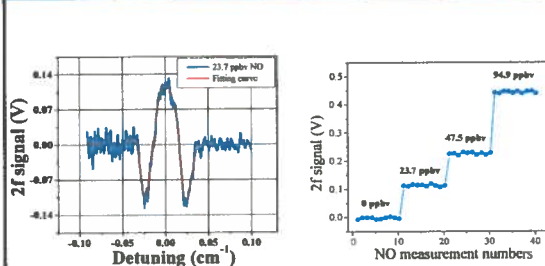
• Novel compact gas cell design of length 3.8 - 5.3 cm and cell volumes 80 cm³
 • Low loss mirrors (ROC 1m) - 60-250 ppm, R - 99.97%, L_{eff} = 170-800 m
 • Rapid eNO concentration measurements during a single breath cycle are feasible



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



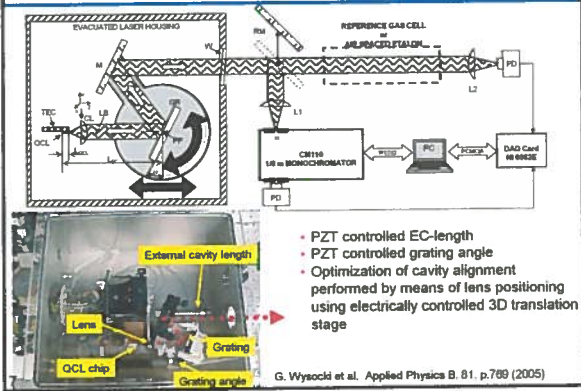
2f NO Absorption Signal at 1835.57 cm⁻¹



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

Noise equivalent sensitivity:
 0.7 ppbv (1σ)

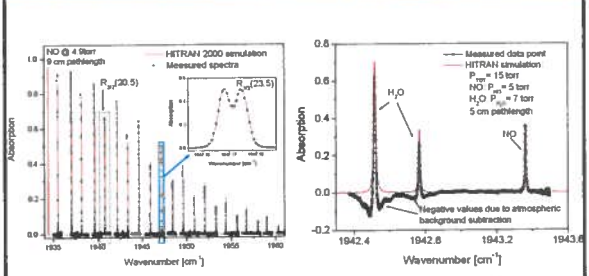
External Cavity QCL Based Spectrometer



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

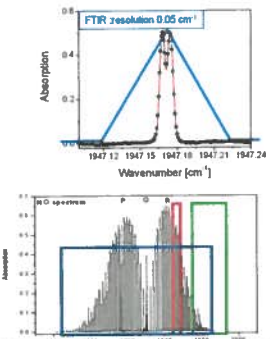
G. Wysocki et al. Applied Physics B. 81, p.789 (2005)

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

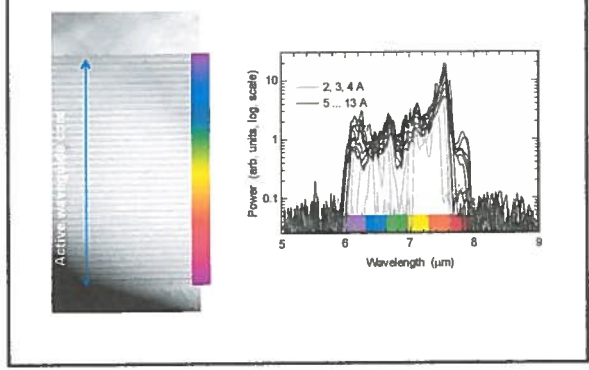


Important facts of novel EC-QCL Technology

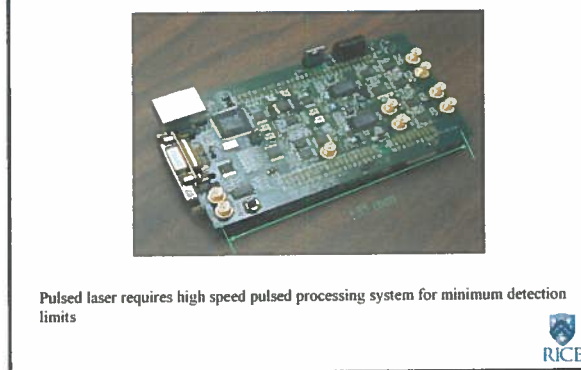
- Laser spectroscopy provides superior resolution compared to other techniques e.g. FTIR
- Single mode operation of the laser is required
- Wavelength tunability of single mode (DFB) mid-IR semiconductor lasers is ~10cm-1
- Demonstrated wavelength tunability of the Rice EC QCL is ~35 cm-1 (limited by 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



QC lasers with inhomogeneously broadened gain



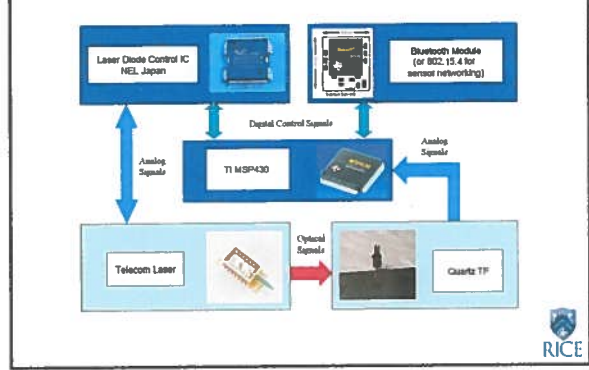
Dedicated DSP-based electronics for trace gas sensing using a pulsed QC laser



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



Concept of a ultra-miniature QEPAS gas sensor



Conclusions and Future Directions

- **Laser based Trace Gas Sensors**
 - Ultra compact (~ 0.2 mm³), 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⁻¹W^{1/2}/Hz for H₂O/N₂
 - QEPAS exhibits a low 1/f noise level, allowing data averaging for more than 3 hours
 - Detected 14 trace gases to date: NH₃, CH₄, N₂O, CO₂, CO, NO, H₂O, COS, HCN, C₂H₂, C₂H₄, C₂H₅OH, SO₂, H₂CO and several isotopic species of C, O, N & H
- **Applications in Trace Gas Detection**
 - Environmental & Spacecraft Monitoring (NH₃, CO, CH₄, C₂H₂, N₂O, CO₂, and H₂CO)
 - Medical Diagnostics (NO, CO, COS, CO₂, NH₃, C₂H₄)
 - Industrial process control and chemical analysis (NO, NH₃, H₂O)
- **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

NASA Atmospheric & Mars Gas Sensor Platforms



Tunable laser sensors for earth's stratosphere

Aircraft laser absorption spectrometers



Tunable laser planetary spectrometer

