Quantum Cascade Laser Applications to Chemical and Environmental Analysis

RICE

F.K. Tittel, A.A. Kosterev, Y. Bakhirkin, C. Roller, D.Weidmann and R.F.Curl

Rice Quantum Institute, Rice University, Houston, TX
http://www.ece.rice.edu/lasersci

C.Gmachl and D.L Sivco
Lucent Technologies, Murray Hill, N.J.

NEST-INFM & SNS
Pisa, Italy
May 7, 2003

- Motivation and Technology Issues
- Mid-IR QC Laser based Gas Sensors
  - Pulsed quasi-room temperature sensors
  - CW cryogenically cooled sensors
- Selected Applications of Trace Gas Detection
  - NH_3, CO, C_2H_4, COS and NO
- Outlook and Summary

Rice University, Houston TX

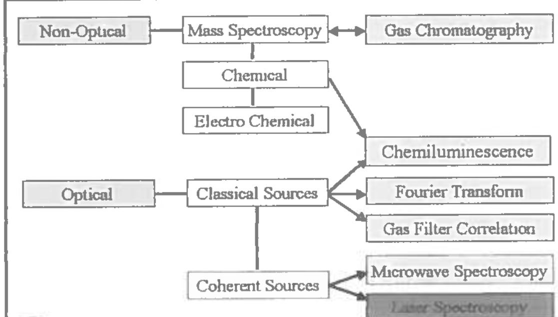
RICE

Wide Range of Gas Sensor Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes
  - Automobile
- **Rural Emission Measurements**
  - Agriculture
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Chemical, Pharmaceutical & Semiconductor Industry
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Medical Applications**
- **Fundamental Science and Photochemistry**

RICE

Existing Methods for Trace Gas Detection



RICE

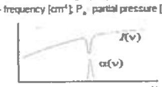
Laser Absorption Spectroscopy

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 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 (White, Herriot)
- Cavity Enhanced and Cavity Ringdown Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Fiberoptic Evanescent Wave Spectroscopy

Spectroscopic Detection Schemes
- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy
- Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)

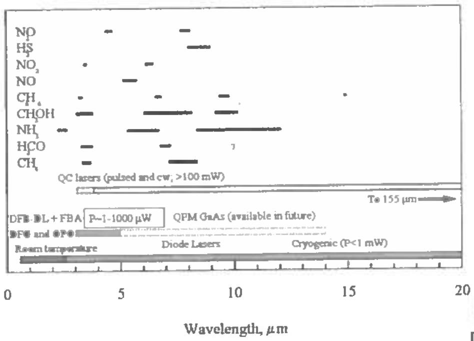
CW IR Source Requirements for Spectroscopy

REQUIREMENTS	**IR SOURCE**
• **Sensitivity**	• **Power**
• **Selectivity**	• **Line Width**
• **Multi-gas Components**	• **Tunable λ**
• **Directionality**	• **Beam Quality**
• **Rapid Data Acquisition**	• **Fast Response**
• **Room Temperature**	• **No Consumables**

RICE

6

Near & Mid-Infrared CW Spectroscopic Sources



RICE

Key Characteristics of Mid-IR Quantum Cascade Lasers

- QC laser wavelengths cover entire mid-IR range from 3.5 to 24 μm determined by thickness of the quantum well and barrier layers of the active region
- Intrinsically high power lasers (determined by number of stages of injector-active quantum well gain regions)
  - CW: ~100 mW @ 80°K and mWs @ 300 °K
  - Pulsed: 1 W peak at room temperature, ~50 mW avg. @ 0 °C (up to 80 % duty cycle)
- High spectral purity (single frequency: <kHz - 330MHz)
- Wavelength tunable by current (~1cm^{-1}) or temperature scanning (~10cm^{-1}); ~150cm^{-1} with external cavity grating
- High reliability: long lifetime, robust operation and reproducible emission wavelengths

RICE

QC-DFB Lasers: Pulsed vs. CW operation

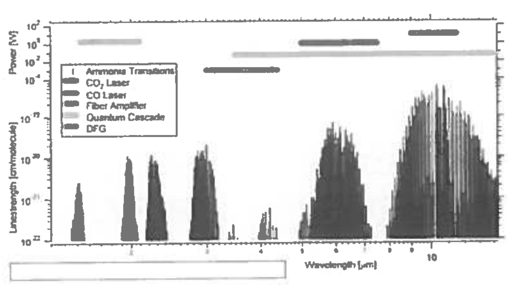
ADVANTAGES	SPECIFIC DEVICE ISSUES
• Laser can be operated at near-room temperature (TE cooling) • Facilitates temperature control • No consumables (liquid N_2) • Unattended remote monitoring • Decreased instrument size & weight	• Broad asymmetric linewidth (>170 MHz FWHM) related to heating during excitation pulse • Reduced average power • Optimum frequency tuning • More sophisticated electronics for driving QC laser and data acquisition system are required

RICE

Motivation for NH_3 Detection

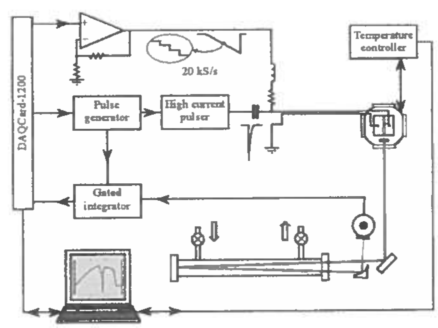
- Monitoring & control of NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Spacecraft related gas monitoring
- Pollutant gas monitoring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

Infrared NH_3 Absorption Spectra



M. Webber et al 2003, Pranalytica

Pulsed QC Laser Based Gas Sensor

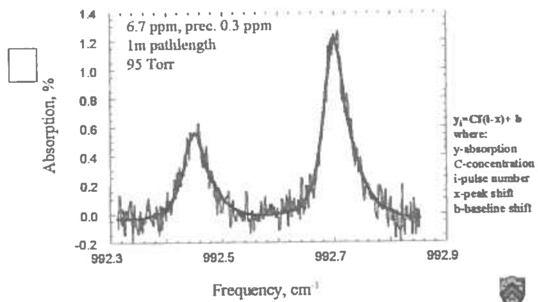


A. Kosterev et al, Applied Optics 41, 573 2002

RICE

12

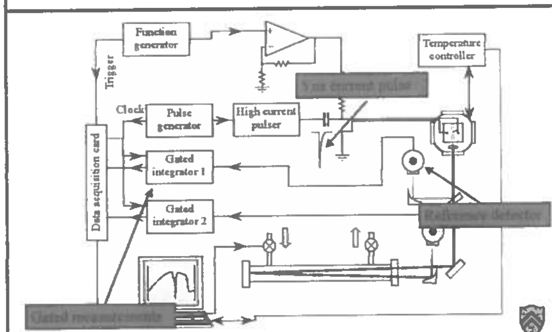
Ammonia Absorption Spectrum @ 993 cm-1



RICE

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

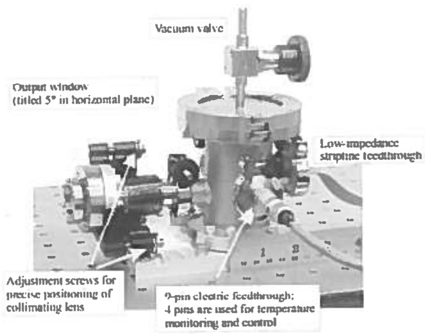
Pulsed QC Laser Based CO Gas Sensor



RICE

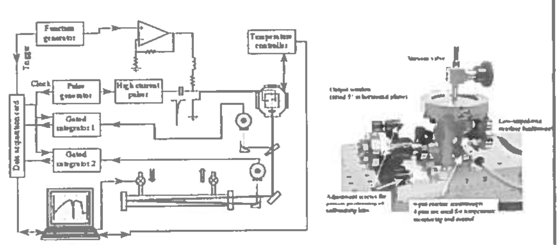
A. Kosterev et al, Applied Optics 41, 1170 2002

TEC cooled QC Laser Housing



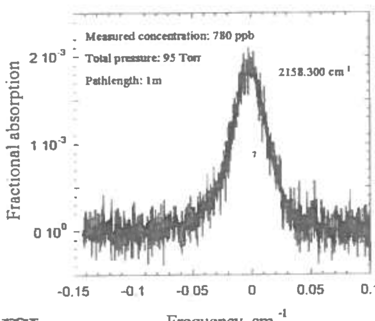
RICE

Pulsed QC Laser Based CO Gas Sensor



A. Kosterev et al, Applied Optics 41, 1170 2002

CO absorption in ambient air @ 2158 cm-1



Two IR detectors

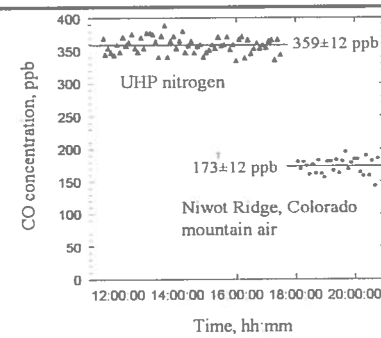
Sensitivity ~7 ppb

ISI

RICE

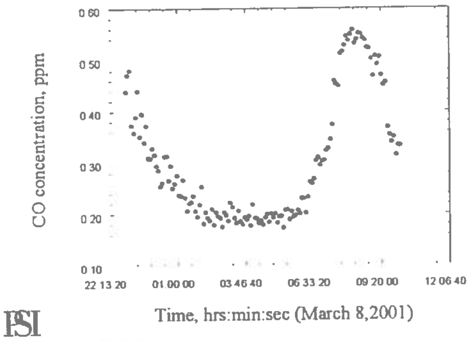
A. A. Kosterev et al, Applied Optics 41, 1169, 2002

CO concentration in two gas cylinders



ISI RICE

CO Concentration Measurements in Houston



FSI RICE

A. A. Kosterev et al. Applied Optics 41, 1169, 2002

Important Biomedical Target Gases

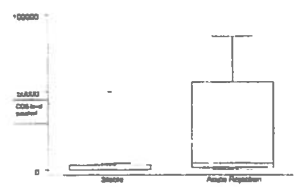
Molecule	Formula	Trace Concentration in Breath (ppb)	Biological/Pathology Indication
Nitric Oxide	NO	6 - 100	Inflammatory and immune responses (e.g., asthma) and vascular smooth muscle response
Carbon Monoxide	CO	400 - 3000	Smoking response, CO poisoning, vascular smooth muscle response, platelet aggregation
Hydrogen Peroxide	H_2O_2	1 - 5	Airway inflammation, Oxidative stress
Carbonyl Sulfide	COS	100 – 1000	Liver disease & acute rejection in lung transplant recipients
Formaldehyde	HCHO	400 - 1500	Cancerous tumors, breast cancer

FSI RICE

Exhaled Carbonyl Sulfide

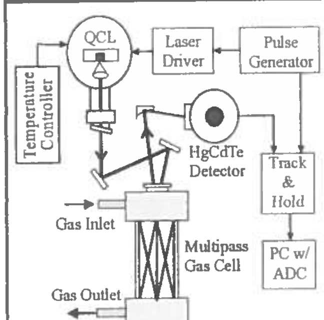
- A 2001 study by the T. H. Risby group at John Hopkins University demonstrated that elevated levels of COS could have a diagnostic role in the detection of acute allograft rejection in lung transplant recipients
  - S. M. Studer, et. al., J. of Heart and Lung Transplantation, 20(11), 1158-66 (2001).

Measured with gas chromatography and flame ionization detection



15

QC-LAS Gas Sensor Architecture

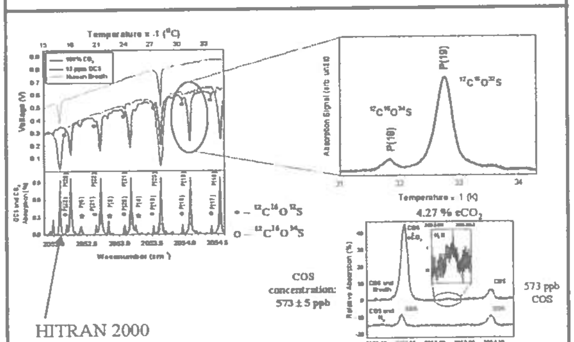


- Effective Pathlength of Gas Cell: 36 m
- Cell Pressure: 40 Torr
- QC Laser Pulse Duration: ~14 ns
- Laser linewidth: ~500 MHz
- Pulse Repetition Rate: 500 kHz

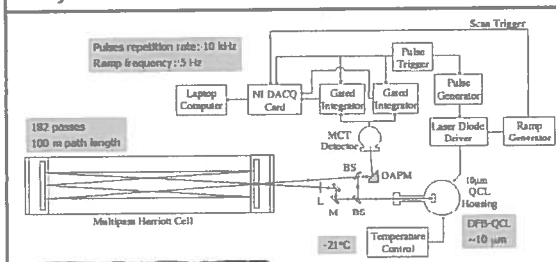
RICE

16

Measured & Simulated Absorption Spectra of COS @ 2053.5 cm⁻¹



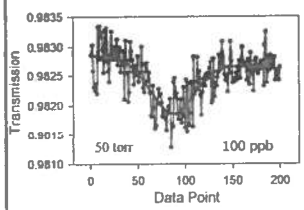
Ethylene QC laser based Sensor Architecture



Motivation for Ethylene Monitoring
- Atmospheric Monitoring
  - Main Source: Vehicle Exhaust
  - Precursor of tropospheric Ozone
- Medical Applications
  - Cell membrane breakdown produces Ethylene
- Agronomy and Plant Biology
  - Ethylene is a plant hormone

24 (1/2)

ν_7 Ethylene Spectrum at 993.45 cm^{-1}

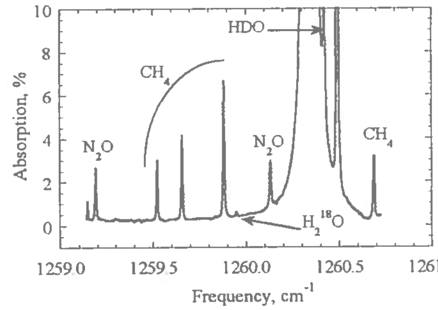


- Noise equivalent sensitivity (to-date): 30 ppb
- By using the strongest ro-vibrational C_2H_4 line: 6 ppb
- By using optimum detection system: 2 ppb

Real World Applications

- Automotive exhaust monitoring
  - 6 cylinder 1998 SUV with engine idling
  - 1 foot behind the exhaust pipe: 670 ppb
- Washburn Tunnel (Houston) monitoring
  - Two tests were made in tunnel
    - 1) Ethylene concentration too low to be detected
    - 2) We detected 51 ± 17 ppb of ethylene
- Application to medical diagnostics
  - Detection of ethylene produced by skin after sun exposure

Absorption Spectrum of Room Air @ 1260 cm^{-1}

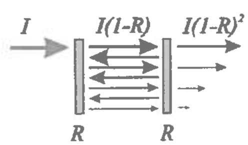


RICE

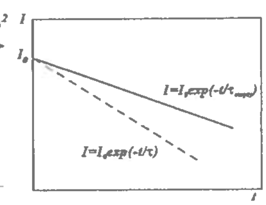
NO in the human body

- NO is biochemically involved in most tissues in the body
- In many lung diseases, NO excretion increases in breath
  - Asthma[1]
    - ➢ Chronic bronchial hyper-responsiveness, variable airway obstruction & airway inflammation
    - ➢ Prevalence: affects 17 million Americans[1]
    - ➢ Typical Asthmatic Range of eNO Levels: **20 to 80 ppb**
  - Chronic Obstructive Pulmonary Disease
  - Acute lung rejection[3]
  - Acute respiratory distress syndrome
  - Pneumonia (esp. useful for intubated patients)

Cavity Ring-down Spectroscopy



$R>0.999...$

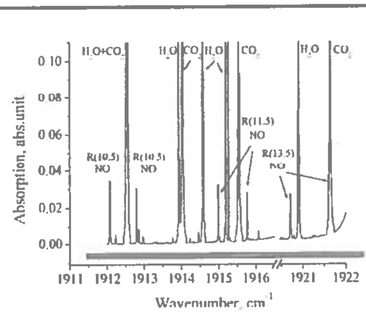


$$I = I_0 \exp\left(-\frac{t}{\tau}\right)$$

$$\tau = \frac{l}{c} \cdot \frac{1}{\alpha l - \ln\sqrt{R_1 R_2}}$$

$$\alpha = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_{empty}}\right)$$

HITRAN Based Simulation of NO-H_2O-CO_2 Mixture Spectrum in Mid-IR Region



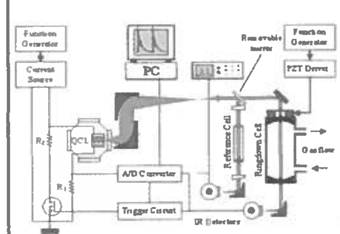
Optical path – 100 m;
Total pressure – 50 Torr
NO – 0.5 ppm;
H_2O – 2.5 %;
CO_2 – 4.0 %

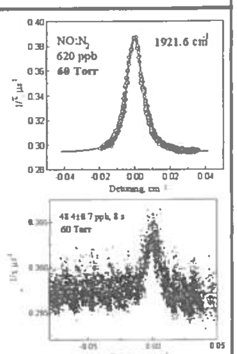
R(10.5) line intensity is $5.17 \cdot 10^{-20}$ cm^{-1}/mol•cm^{-2}

QC lasers tuning range

RICE

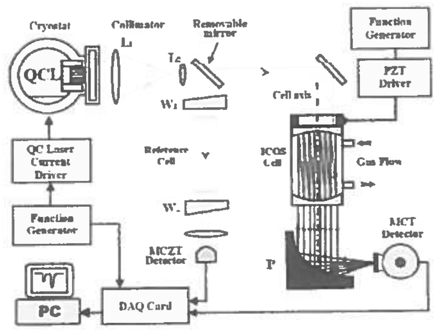
CRDS based NO Sensor @ 1922 cm^{-1}





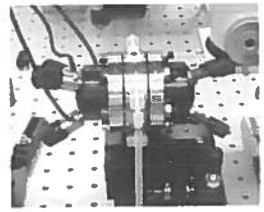
30

Off-Axis Integrated Cavity Output Spectroscopy Based Gas Sensor System



RICE

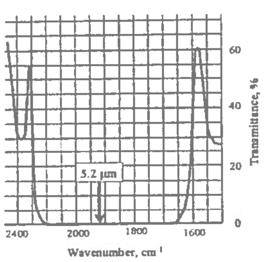
Novel compact gas cell designs for Off-Axis ICOS

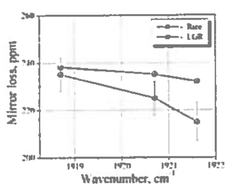


- Cell length 3.8 – 5.3 cm ;
- Cell volumes < 100 cm^3;
- Enables rapid on-line and off-line measurements of eNO in gas flow during a single breath cycle.

PSI LGR RICE

Ultra low-loss MIR mirror reflectivity characteristics centered at 5.2 microns





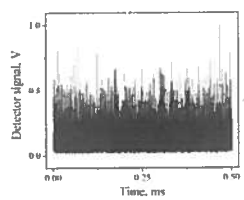
Losses of the mirrors are defined by measuring ringdown time of a cavity TEM_{00} mode

- 2.0" ZnSe, 1m ROC
- Losses ~ 240 – 250 ppm (R>0.9997)

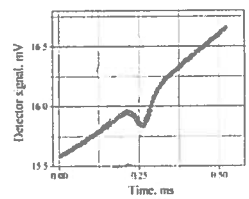
RICE LGR

Off-axis ICOS Cavity Throughput

- NO : N_2 Calibration mixture: 100 Torr
- NO concentration: 490 ppb
- R(13.5) NO line at 1920.7 cm^{-1}



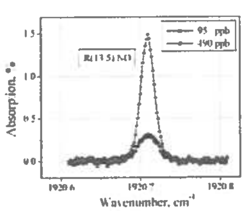
Typical transmitted intensity through the OA-ICOS cavity for a single laser current scan.



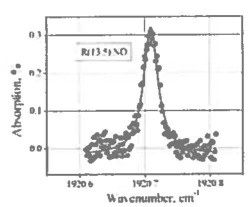
Averaged OA-ICOS cavity throughput

RICE

Off-axis ICOS Detection of NO



- 95 and 490 ppb NO/N_2 calibration mixture at 100 Torr total pressure;
- effective optical path ~ 70 m (1,350 passes)



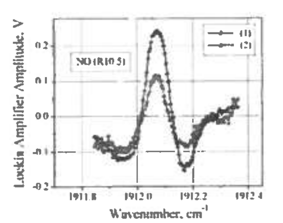
Voigt fit of the measured NO absorption line for a concentration of 95 ppb

Noise equivalent sensitivity is 10 ppb for 1σ deviation of the best fit coefficient (Detection sensitivity: $1.0*10^{-7}$ cm^{-1} Hz$^{-1/2}$

RICE

NO from Nasal Exhaled Air
(OA-ICOS and wavelength modulation spectroscopy)

"Quintron" breath sample bag and mouth piece



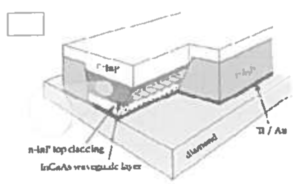
Averaged 2f signal of the OA-ICOS cavity output

(1) Nasal NO concentration: 53 ppb
(2) 95 ppb NO/N_2 calibration mixture

RICE

36

CW DFB QC Laser on a Peltier Cooler



- Operating wavelength – 1115 cm^{-1}
- Tuning range ~5cm^{-1} (200-245 K)
- Output Power 18mW (180 K) & 1mW (250 K)

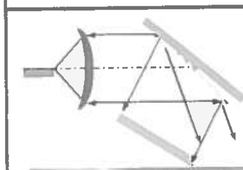
APL

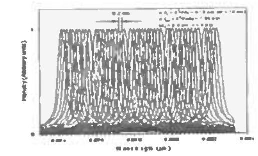
RICE

T Aellen, et al. Applied Physics Letters Sept 8, 2003

NH_3, SO_2, formic acid

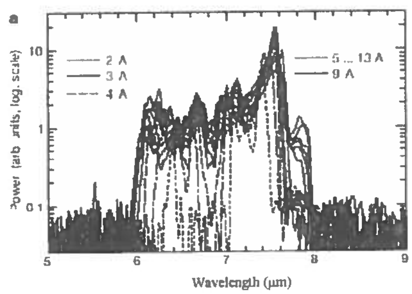
Broadly Wavelength-Tunable External-Cavity Quantum Cascade Lasers





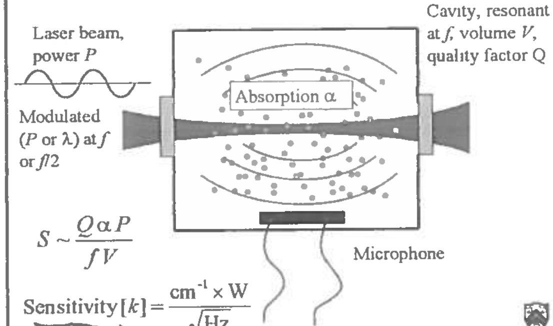
- Littmann-Metcalf configuration
- Single-mode pulse operation, 7-12-dB side mode suppression ratio
- Wavelength bands: 4.6, 5.2, 7.1, 9 μm
- Tuning range – 2-2.5% of center wavelength, limited by the gain band
- Power ~1 - 40 mW peak (up to 5% d.c.)

Laser Spectrum of Ultra-Broadband QC Laser



C Gmachl et al Nature, 145, 883 (2002)

Resonant photoacoustic spectroscopy



$$S \sim \frac{Q\alpha P}{fV}$$

$$\text{Sensitivity}\,[k] = \frac{cm^{-1} \times W}{\sqrt{Hz}}$$

40

RICE

Merits of PAS based Trace Gas Detection

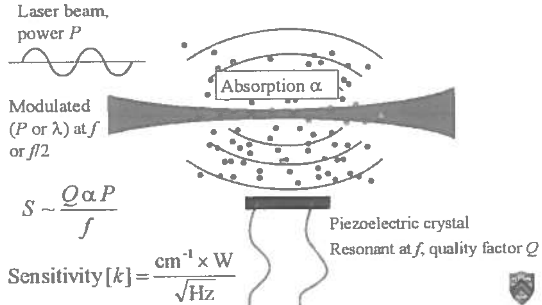
- High sensitivity
- Zero background
- Low cost (compared to multipass cell + IR detector)
- (*) Linear response to gas concentration
- Small volume cells
- Immune to laser noise
- Immune to etalon effects

(*) microphone (insensitive ~~to wavelength~~

41

RICE

Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)



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

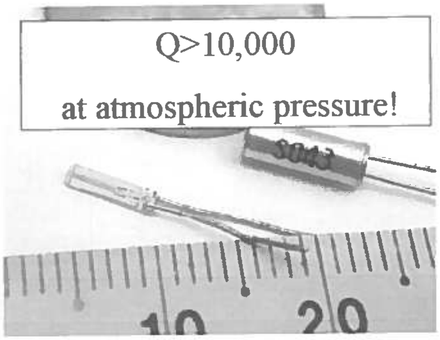
$$\text{Sensitivity}\,[k] = \frac{cm^{-1} \times W}{\sqrt{Hz}}$$

42

RICE

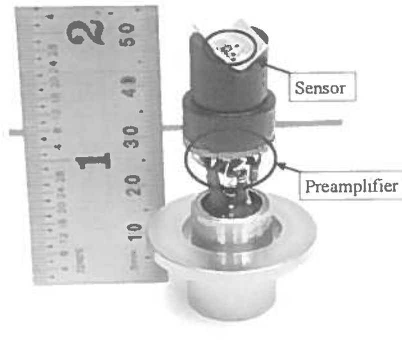
42

Watch tuning fork



43

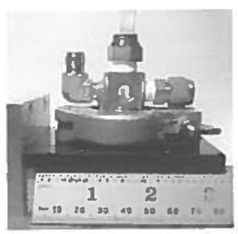
QEPAS based Gas Sensor Assembly



44

QEPAS based Gas Sensor Module

Bottom part with a mounted TF

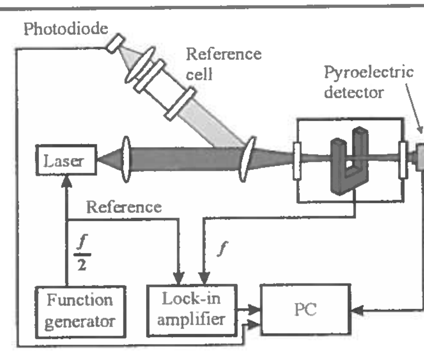


Assembled cell with a pressure sensor on top

RICE

45

Laboratory setup for QEPAS based gas sensor evaluation

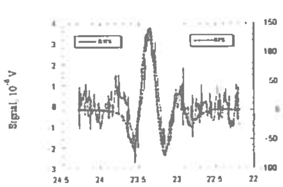


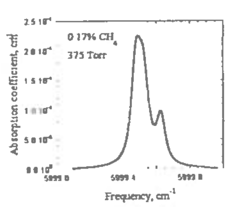
RICE

46

reject (?)

Measured and Simulated CH_4 Spectrum



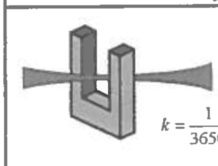


- QEPAS is immune to random noise
- Best sensivity to date is 1 2 x10⁻⁷cm⁻¹WHz⁻¹ᐟ²

RICE

A. A. Kosterev et al, Optics Letters 27, 1902 (2002)

Sensitivity Estimate of QEPAS



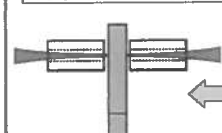
At 265 Torr:

SNR=(2.7V/200)/3 7μV=3650

Assuming SNR=1,

$$k = \frac{1}{3650} \times \frac{0\,023\ \text{cm}^{-1} \times 0.027\ \text{W}}{\sqrt{0.53\text{Hz}}} = 2.3\times10^{-7}\ \frac{\text{cm}^{-1}\text{W}}{\sqrt{\text{Hz}}}$$

Previously reported (Opt.Lett. 2002) $k=8.8\times10^{-7}$ a 3.8 times improvement!
Most probably due to the RIGHT OA in transimpedance preamplifier



Was reported to be 7 times more sensitive ($1\,2\times10^{-7}$ $cm^{-1}WHz^{-1/2}$) There is hope!

RICE

48

48

prior art

Webber, Miklos

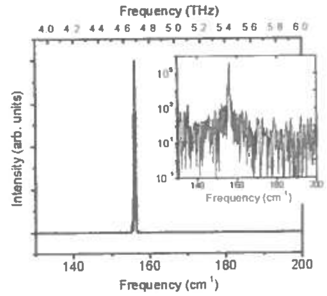
AK

What does such a sensitivity mean ?

- Acetylene P(11), $\nu 1+\nu 3$, SNR=1, k=1.2×10^{-7} cm^{-1}WHz$^{-1/2}$, 40 mW, ~1min data acquisition time (Δf=0.01 Hz) ⇒ 180 ppb
- Ammonia in near-IR (6528.76 cm^{-1}) - 7 times weaker line ⇒ ~1.25 ppm
- Mid IR - ~100 times stronger absorption ⇒ ~10 ppb range for reliable (3×SNR level) detection with ~1min data acquisition time
- Sensitivity is directly proportional to the laser power
- We expect to reach k<2×10^{-7} cm^{-1}WHz$^{-1/2}$ due to better selection of TF geometry and acoustic microcavity optimization

49 RICE

Terahertz quantum cascade laser

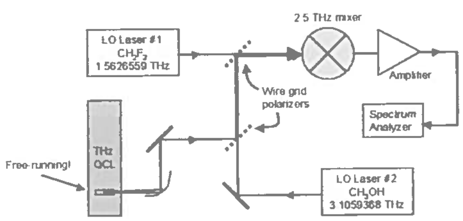


Operating temperature: cryo

Frequency range: 2.4 - 5 THz
Power: up to 50 mW (multi-mode)
Linewidth: ?
Tunability: ?

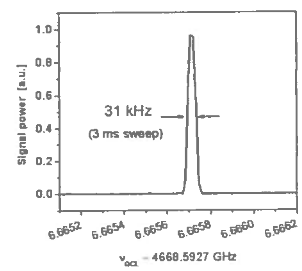
Laser courtesy of: Giacomo Scalari, Lassaad Ajili, and Jérôme Faist, University of Neuchâtel; Harvey Beere and Edmund Linfield, University of Cambridge

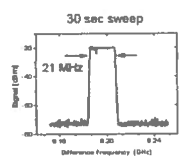
Linewidth measurements



A collaboration with: Robert Dengler and Peter Siegel, Jet Propulsion Laboratory

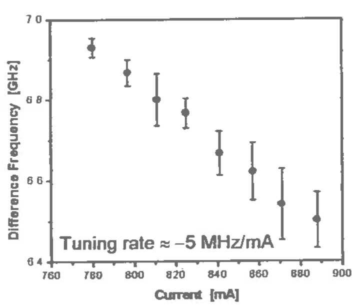
Instrumentation-limited line



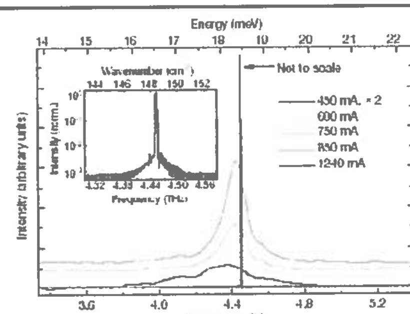


Schawlow-Townes limit: a few 10's of kHz!

Current tuning



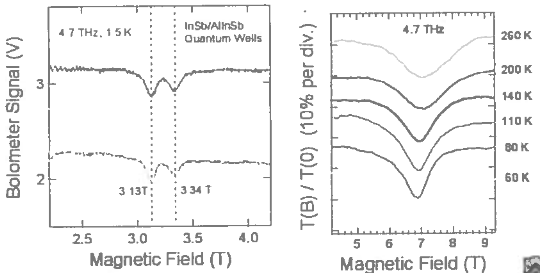
Emission Spectra from a 4.4 THz QC Laser



A. Tredicucci et al., Nature 147, 156-159, May 2002, also B4 ... J Faist et al Appl. Phys Letters 81, 1381-1383 Aug 2002

54

Cyclotron Resonance in Semiconductor Quantum Wells



InSb/InAlSb quantum wells
M. B. Santos (U. of Oklahoma)

InAs/AlSb quantum wells
S. Sasa & M. Inoue (OIT)

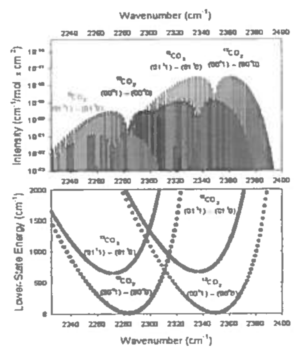
RICE

Motivation for Isotopic Ratio Measurements

- **Atmospheric chemistry** [Environmental monitoring C_y gases: $\mathbf{CO_2}$, CO, CH_4..]
- **Volcanic gas emission studies. ($\mathbf{CO_2}$** H_2O, HCl, SO_2 ,HF, H_2S, CO), eg Colli Albani ; Solfatara; Mammoth Mt., Long Valley Caldera, CA (north of L.A.)
- Combustion diagnostics
- Non-invasive medical diagnostics (NO, CO, $\mathbf{CO_2}$, NH_3)
- Biology (Photosynthesis)

Solfatara Crater near Pozzuoli (Naples)

CO_2 Spectra & Lower State Energies @ 2300 cm^{-1}



Strong bands of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ around 2300 cm^{-1}. Shown are

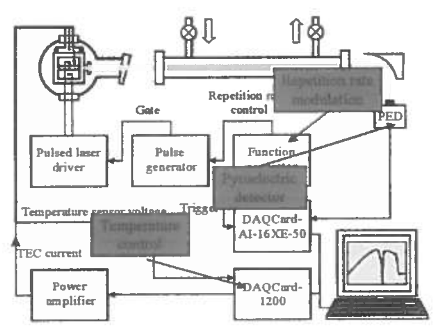
- Line Intensities
- Lower-state energy of each line.

Summary and Future Directions

- **Quantum Cascade Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity ($<10^{-4}$) and selectivity (3 to 300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, C_2H_5OH, SO_2 and isotopic species
- **Applications in Trace Gas Detection**
  - Environmental monitoring (HCHO, CO_2)
  - Medical Diagnostics (NO, CO, COS, CO_2)
  - Industrial process control and chemical analysis (NO)
- **Future Directions**
  - Cavity ring down and QE-PAS spectroscopy based applications
  - Applications using novel thermoelectrically cooled cw and broadly wavelength tunable quantum cascade lasers
  - Applications using new near IR interband and far-IR intersub-band quantum cascade lasers

RICE

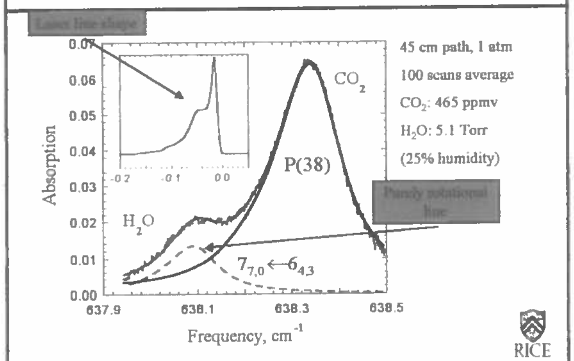
16 µm QC laser based gas sensor



RICE

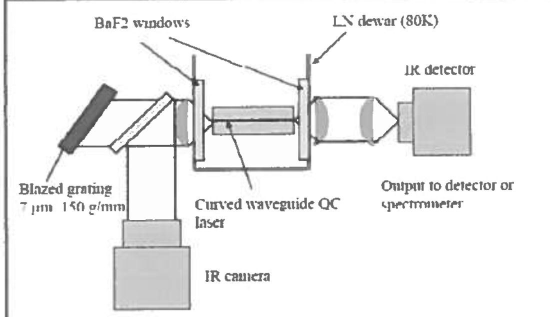
60

Absorption Spectrum of Ambient Air

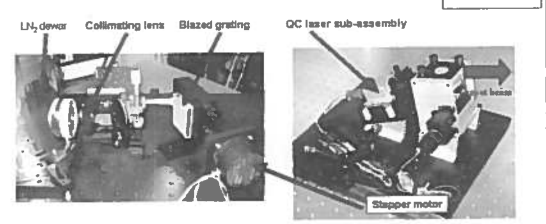


RICE

External Cavity Configuration for a Cryogenic Cooled QC Laser



UH Wavelength Tunable QC Laser Sources



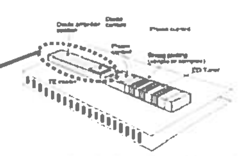
Grating first-order direct feedback

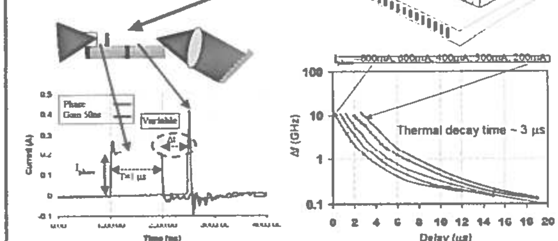
Littman-Metcalf feedback (TE-cooled package)

Tunable MRIR EC Two-Segment QC Laser

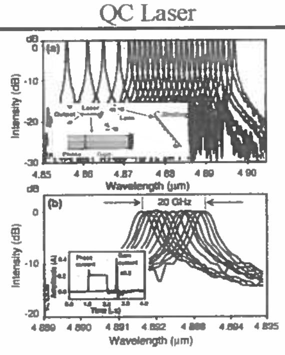
2-segment laser phase tuning

- Use thermo-optic effect
- Separate wavelength and power control
- A key test of miniature module design

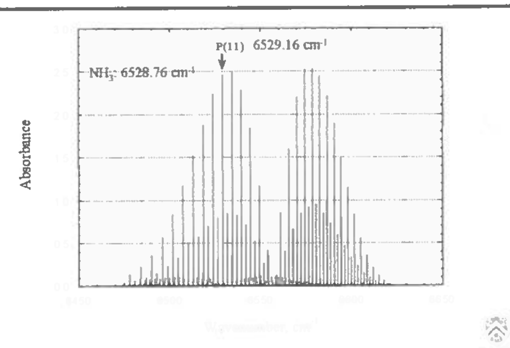


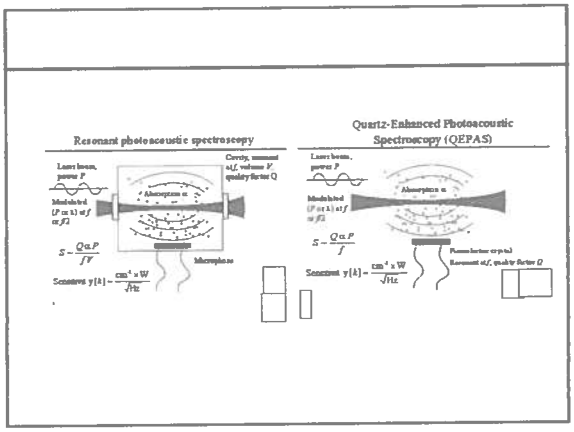


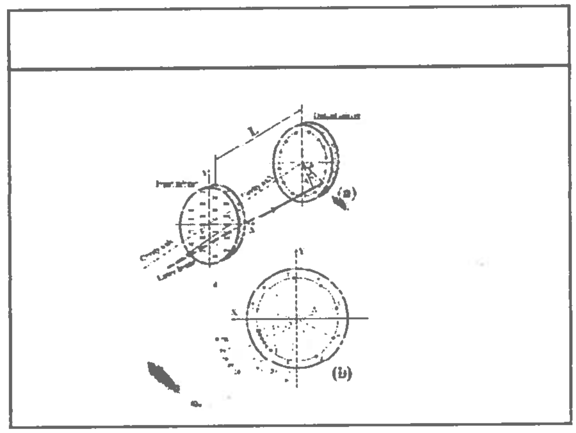
Normalized Coarse & Fine Tuning Spectra of 4.9 µm QC Laser



Absorption of C_2H_2 in the $\nu_1+\nu_3$ band region




Resonant photoacoustic spectroscopy
Laser beam, power P
Cavity, resonant at f, volume V, quality factor Q
Absorption α
Modulated (P or λ) at f or f/2
$S \sim \frac{Q \alpha P}{f V}$
Microphone
Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)
Laser beam, power P
Absorption α
$S \sim \frac{Q \alpha P}{f}$
Resonant at f, quality factor Q


L
(a)
(b)

Import