Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology

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OUTLINE

SRNL

Aiken,SC
Dec 5, 2005

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

Source: United Nations ● High pollution ◐ Moderate to heavy pollution ○ Low pollution - No data available

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Megacity Air Pollution: Houston, TX

NASA–JSC Human-Rated Simulation Chamber

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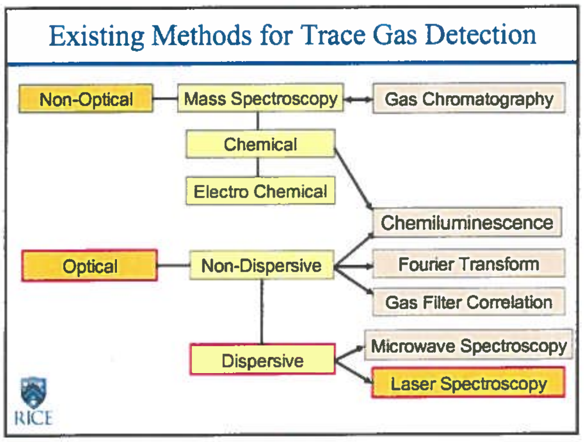
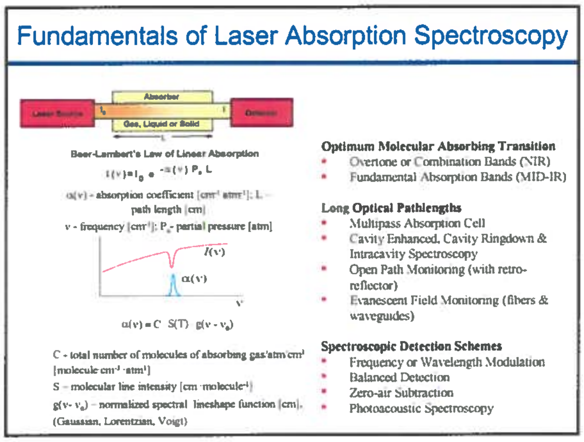


Existing Methods for Trace Gas Detection



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/cm³ [$molecule\cdot cm^{-3}\cdot atm^{-1}$]

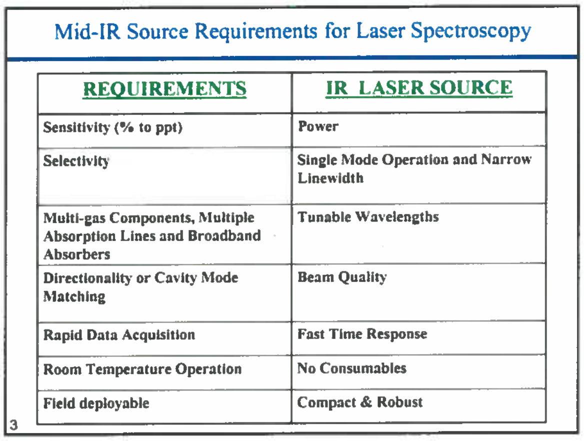
S – molecular line intensity [$cm \cdot molecule^{-1}$]

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

Optimum Molecular Absorbing Transition
- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

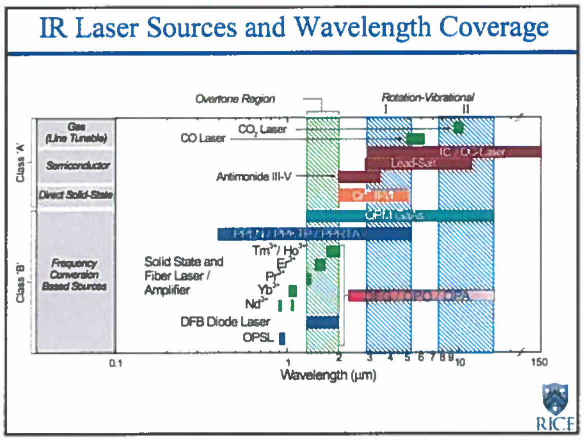
Long Optical Pathlengths
- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Evanescent Field Monitoring (fibers & waveguides)

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

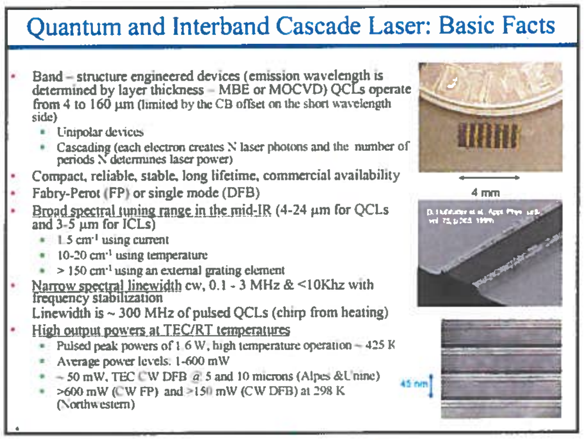


Mid-IR Source Requirements for Laser Spectroscopy

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
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

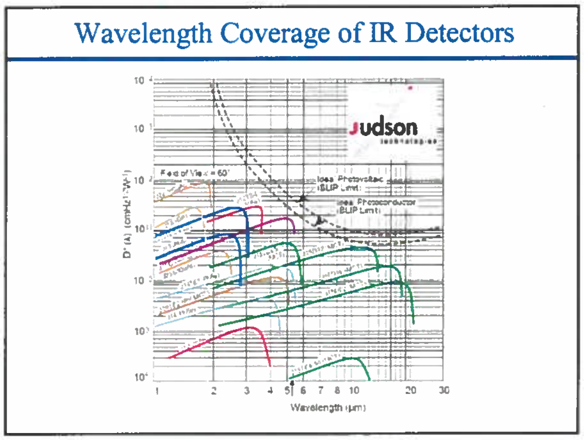


IR Laser Sources and Wavelength Coverage

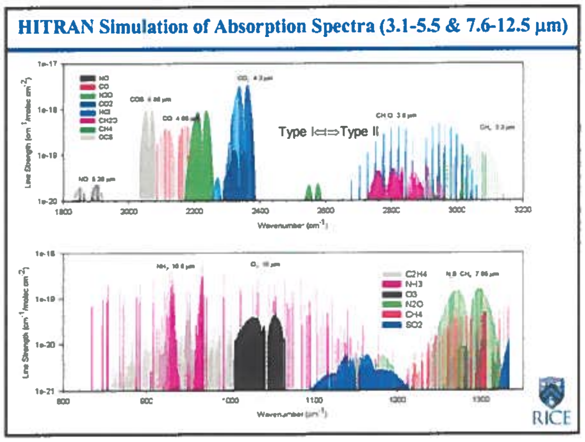


Quantum and Interband Cascade Laser: Basic Facts

- Band – structure engineered devices (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 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
  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 &Unine)
  - >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

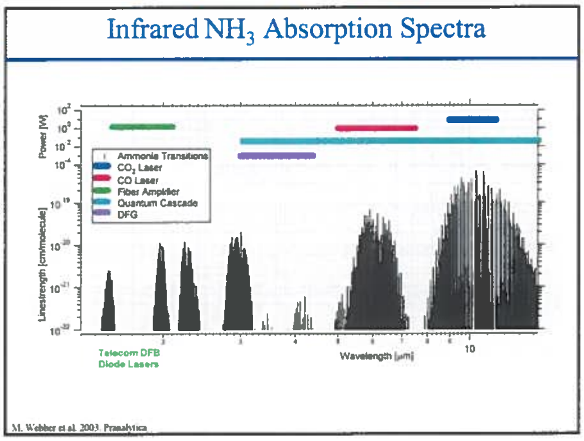
Pathlength: 210 m

Typical data acquisition time: 1-100 s

Mark S. Zahniser, SIRIS 2004, September 2004

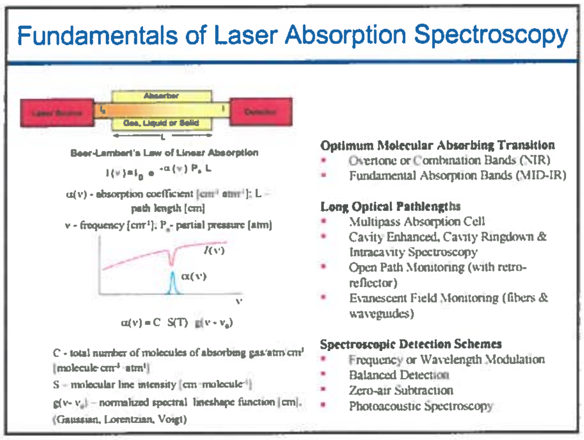
Motivation for NH_3 Detection

- 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)



Infrared NH_3 Absorption Spectra

M. Webber et al. 2003, Pranalytica



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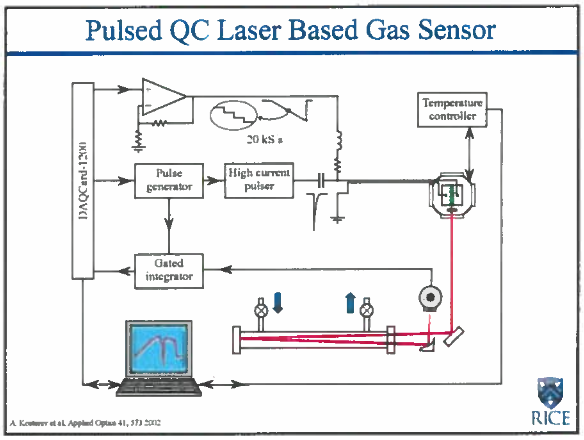
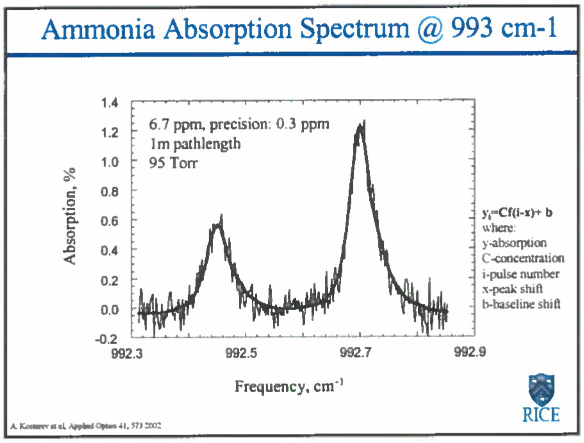
Spectroscopic Detection Schemes

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



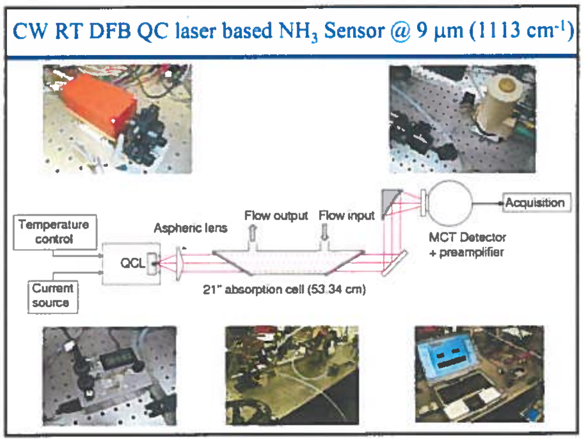
Pulsed QC Laser Based Gas Sensor

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

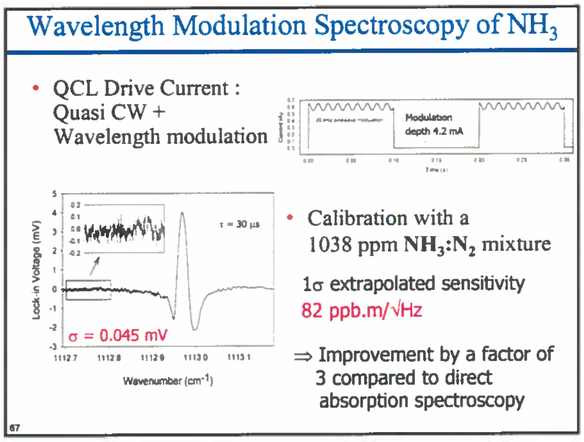


Ammonia Absorption Spectrum @ 993 cm-1

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

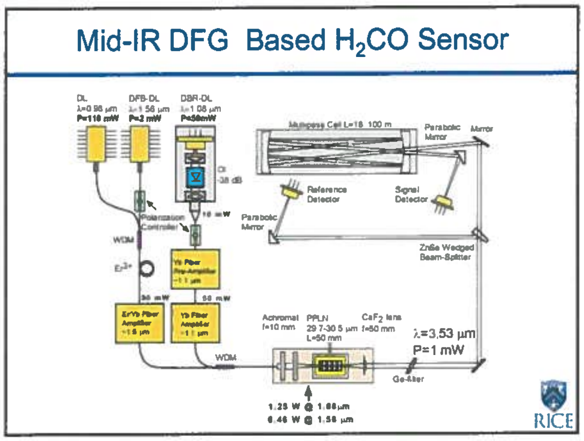
- Calibration with a 1038 ppm **NH_3:N_2** mixture

1σ extrapolated sensitivity
82 ppb.m/√Hz

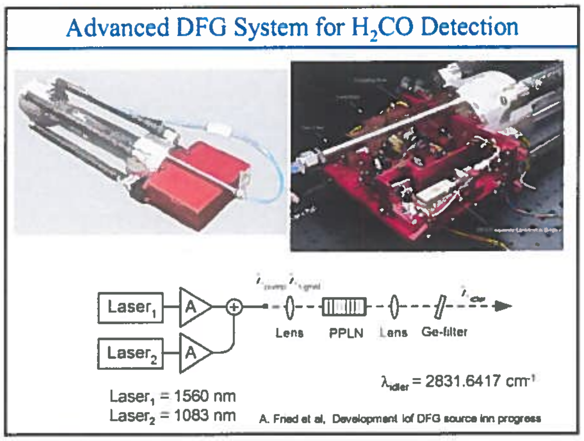
⇒ Improvement by a factor of 3 compared to direct absorption spectroscopy

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



Mid-IR DFG Based H_2CO Sensor

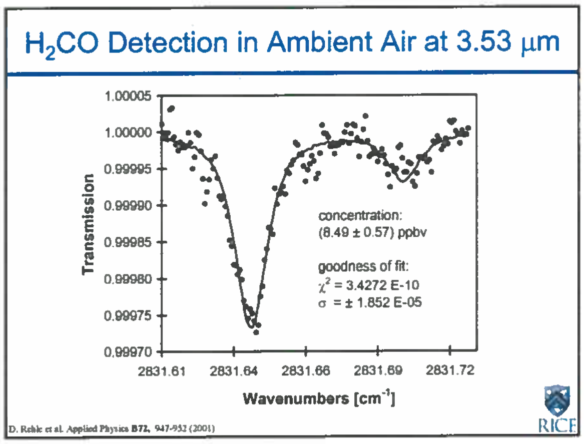


Advanced DFG System for H_2CO Detection

λ_{idler} = 2831.6417 cm^{-1}

$Laser_1$ = 1560 nm
$Laser_2$ = 1083 nm

A. Fried et al, Development of DFG source in progress



H_2CO Detection in Ambient Air at 3.53 µm

concentration: (8.49 ± 0.57) ppbv

goodness of fit:
χ^2 = 3.4272 E-10
σ = ± 1.852 E-05

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

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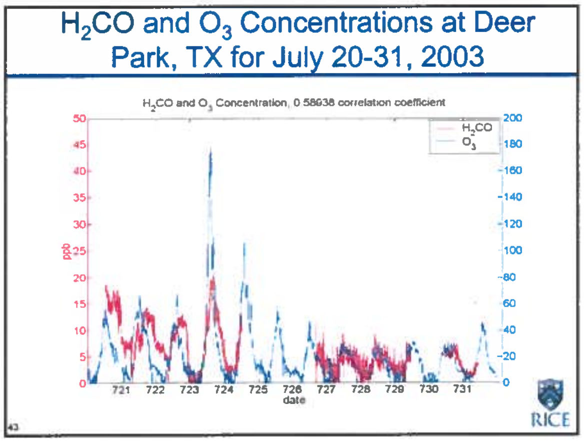

H_2CO and O_3 Concentrations at Deer Park, TX for July 20-31, 2003

H_2CO and O_3 Concentration, 0.58938 correlation coefficient

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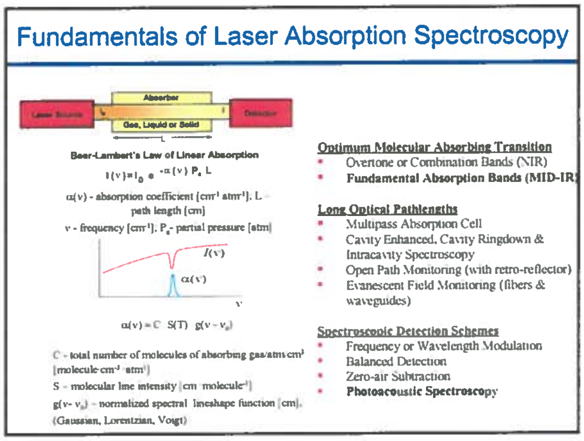

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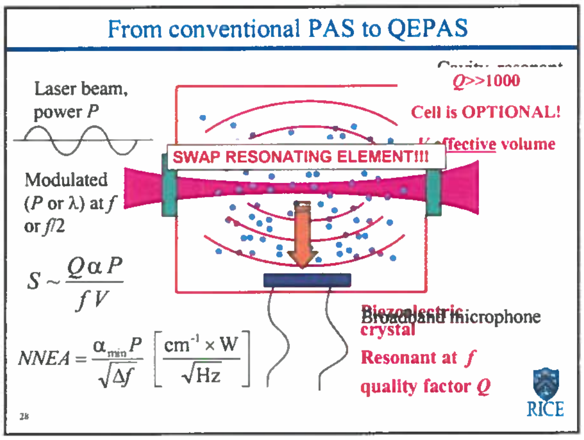
- **Photoacoustic Spectroscopy**



From conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$

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

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

Q>>1000

Cell is OPTIONAL!

V effective volume

SWAP RESONATING ELEMENT!!!

Broadband microphone

Piezoelectric crystal

Resonant at f

quality factor Q

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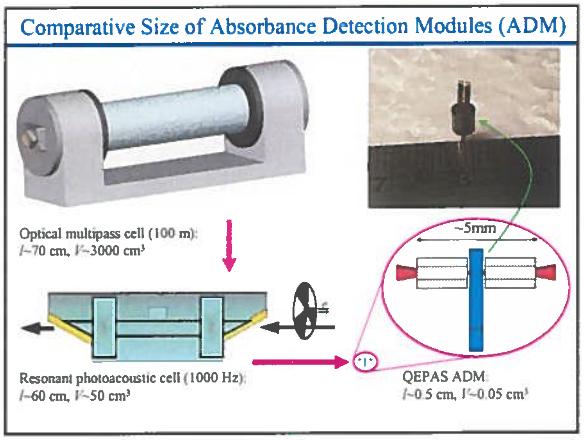
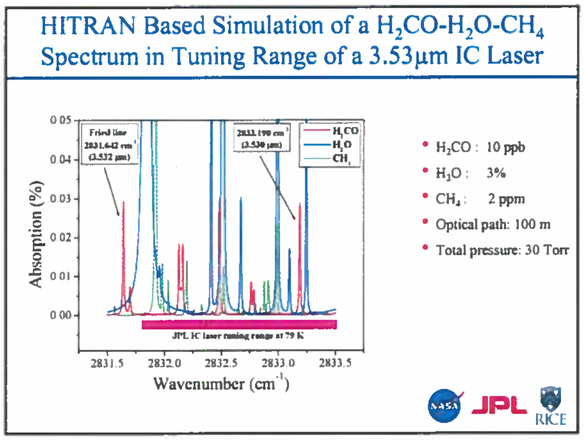


Comparative Size of Absorbance Detection Modules (ADM)

Optical multipass cell (100 m): l~70 cm, V~3000 cm³

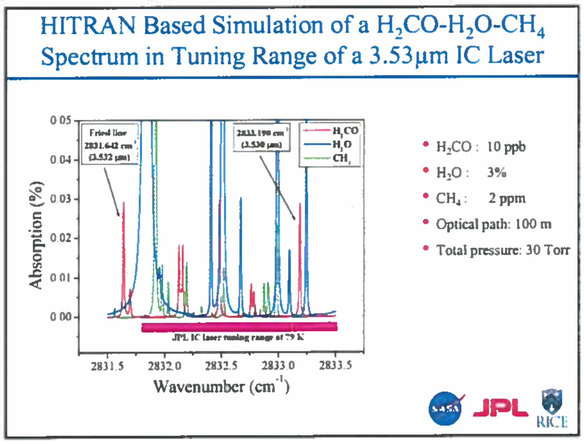
Resonant photoacoustic cell (1000 Hz): l~60 cm, V~50 cm³

QEPAS ADM: l~0.5 cm, V~0.05 cm³



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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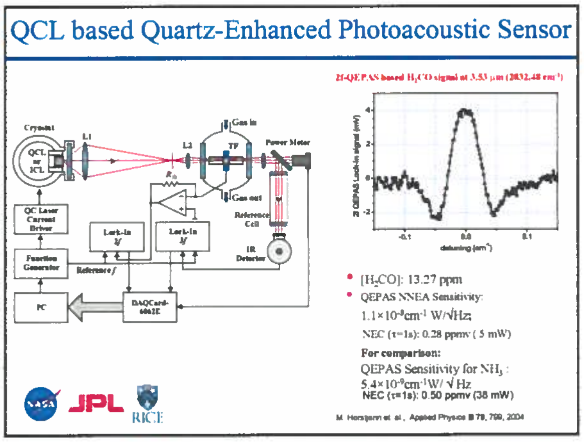


QCL based Quartz-Enhanced Photoacoustic Sensor

- $[H_2CO]$: 13.27 ppm
- QEPAS NNEA Sensitivity:

  1.1×10^{-8}cm^{-1} W/√Hz;

  NEC (τ=1s): 0.28 ppmv (5 mW)

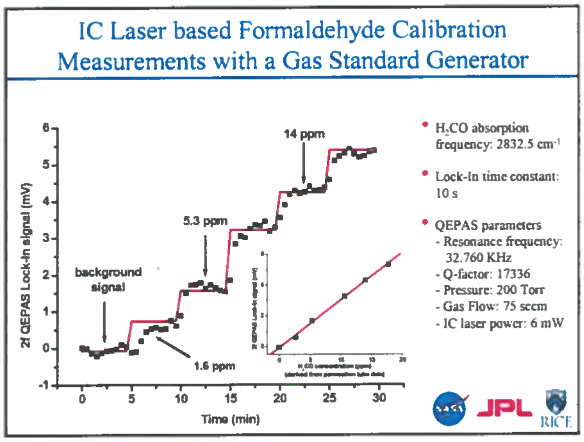
  For comparison:

  QEPAS Sensitivity for NH_3 :

  5.4×10^{-9}cm^{-1}W/ √ Hz

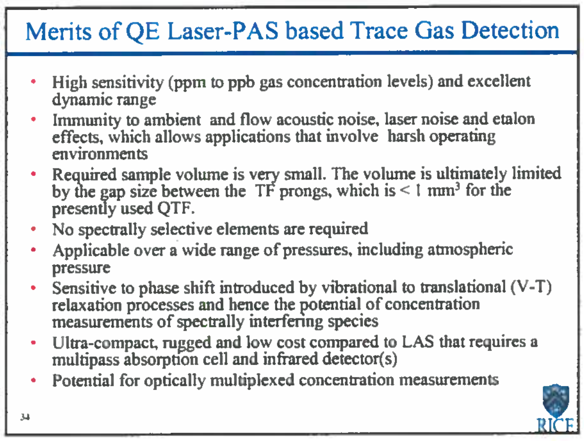
  NEC (τ=1s): 0.50 ppmv (38 mW)

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



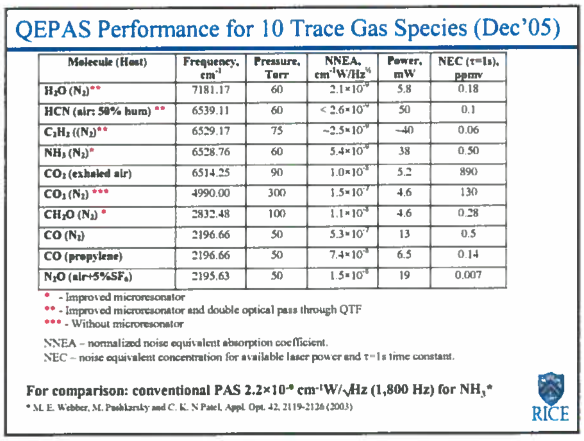
IC Laser based Formaldehyde Calibration Measurements with a Gas Standard Generator

- 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



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 mm³ 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



QEPAS Performance for 10 Trace Gas Species (Dec'05)

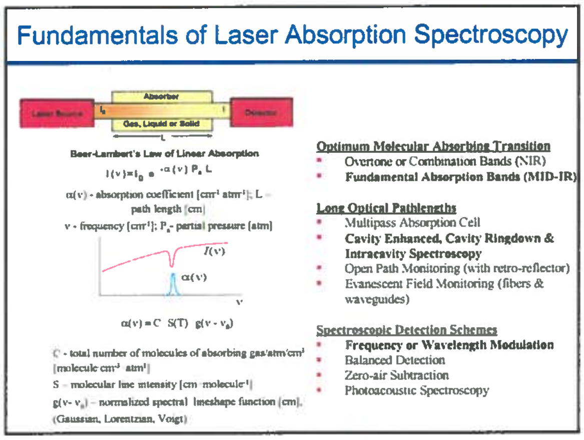
Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, cm^{-1}W/Hz^{½}	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7181.17	60	2.1×10^{-9}	5.8	0.18
HCN (air: 50% hum) **	6539.11	60	$< 2.6\times10^{-9}$	50	0.1
C_2H_2 ((N_2)**	6529.17	75	$\sim2.5\times10^{-9}$	~40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	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) *	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/√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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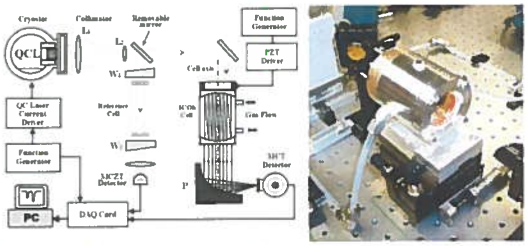
- Photoacoustic Spectroscopy

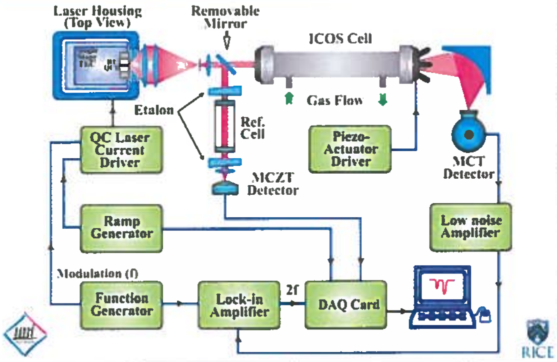
Off-Axis Integrated Cavity Output Spectroscopy (ICOS) Based Gas Sensor



- 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

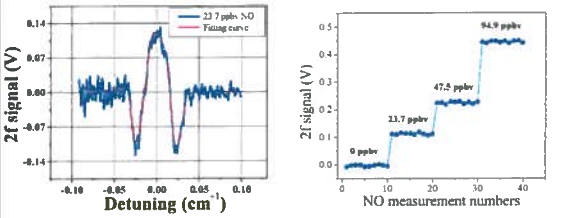
TEC – CW-DFB QCL based Nitric Oxide OA-ICOS Sensor



Laser Housing (Top View)
Removable Mirror
ICOS Cell
Gas Flow
Etalon
Ref. Cell
QC Laser Current Driver
Piezo-Actuator Driver
MCT Detector
MCZT Detector
Ramp Generator
Low noise Amplifier
Modulation (f)
Function Generator
Lock-in Amplifier
2f
DAQ Card

RICE

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)

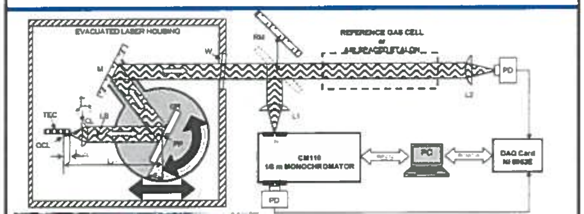
RICE

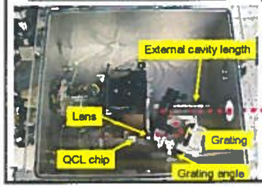
ICOS vs. CRDS

ICOS	CRDS
High sensitivity	Extremely high sensitivity possible – 10^{-11} cm⁻¹ demonstrated in NIR
High time resolution not required, slow detector is sufficient	Time resolved measurements, fast detector needed
Multiple high-order transverse modes, off-axis propagation	Single transverse mode, on-axis propagation – critical alignment
Relies on quasi-random mode structure, non-critical alignment	Laser must be locked to the cavity mode
Low throughput [(1-R)/2 max]	High throughput in resonance for a narrow line (~kHz) laser
No need for narrow line laser	
Sensitive to the source power fluctuations	Insensitive to the source power fluctuations

RICE

External Cavity QCL Based Spectrometer

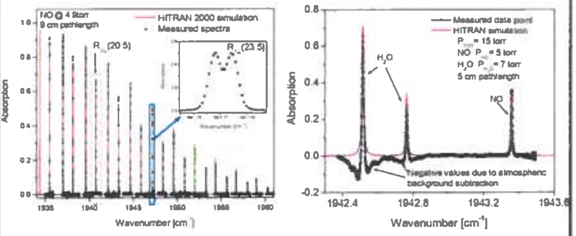


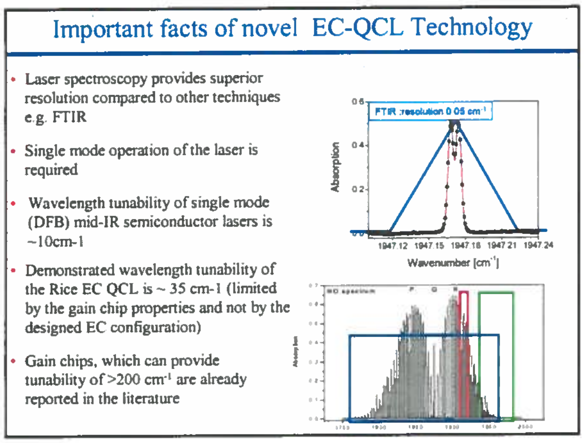


- PZT controlled EC-length
- PZT controlled grating angle
- Optimization of cavity alignment performed by means of lens positioning using electrically controlled 3D translation stage

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

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



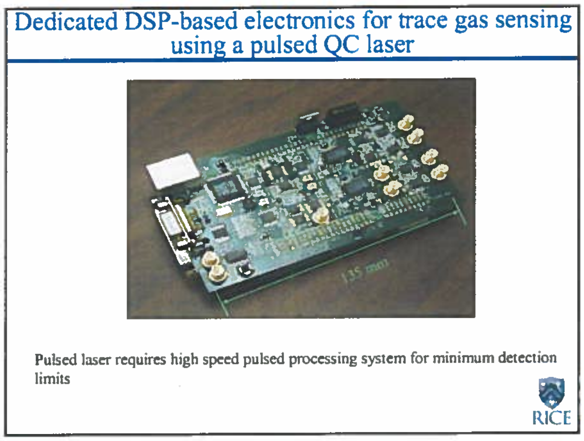


Important facts of novel EC-QCL Technology

- 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

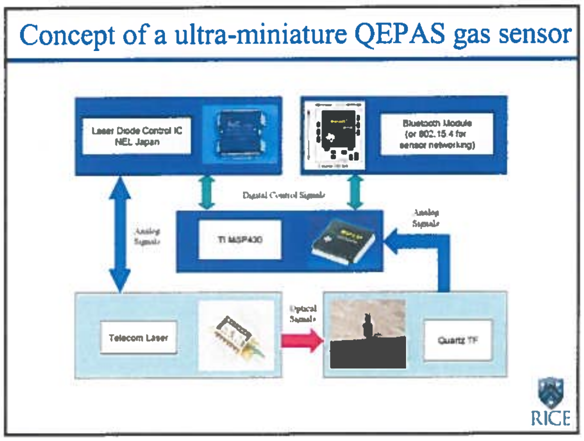
Sensor control and data processing

- 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



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

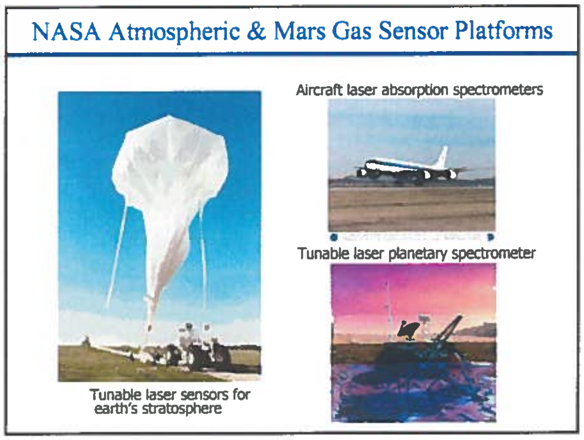
Pulsed laser requires high speed pulsed processing system for minimum detection limits



Concept of a ultra-miniature QEPAS gas sensor

Conclusions and Future Directions

- **Laser based Trace Gas Sensors**
  - Ultra compact (~ 0.2 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

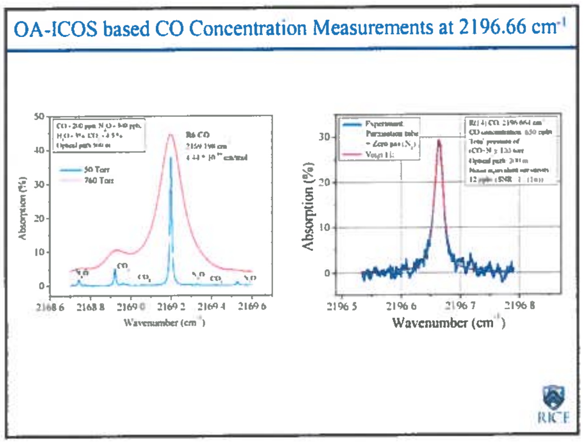


NASA Atmospheric & Mars Gas Sensor Platforms

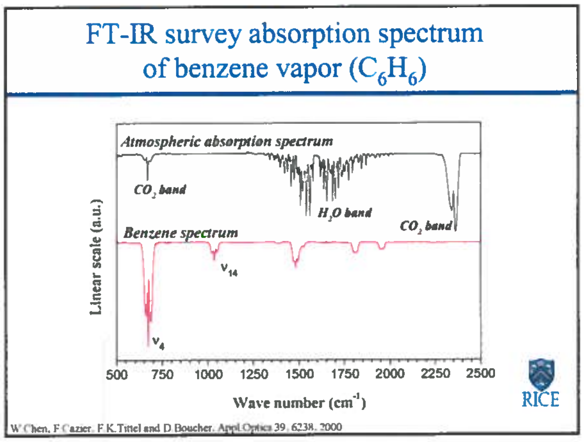
Aircraft laser absorption spectrometers

Tunable laser planetary spectrometer

Tunable laser sensors for earth's stratosphere



OA-ICOS based CO Concentration Measurements at 2196.66 cm^{-1}



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