Ultrasensitive Gas Detection by Quartz-Enhanced Photoacoustic Spectroscopy

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OUTLINE

GRC
Trieste, Italy
June 26-July 1, 2005

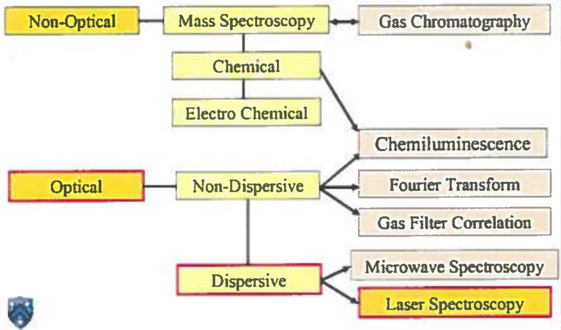
- Motivation: Wide Range of Chemical Sensing Applications
- Fundamentals of QE-Photoacoustic Spectroscopy
  - Comparison of QEPAS to L-PAS
- Selected Applications of QE-PAS
  - NH_3 Detection with 1.5 μm RT cw DFB Diode Laser
  - H_2CO Detection with 3.5 μm LN_2 CW DFB Interband Cascade Laser
  - N_2O & CO Detection with a 4.6 μm LN_2 CW DFB Quantum Cascade Laser
- Conclusions and Outlook

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 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 & Human Life Support Technology
- **Biomedical and Clinical Diagnostics** (eg. breath analysis)
- **Forensic Science and Security**
- **Fundamental Science and Photochemistry**

Existing Methods for Trace Gas Detection


Non-Optical
Mass Spectroscopy
Gas Chromatography
Chemical
Electro Chemical
Chemiluminescence
Optical
Non-Dispersive
Fourier Transform
Gas Filter Correlation
Dispersive
Microwave Spectroscopy
Laser Spectroscopy

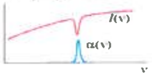
Fundamentals of Laser Absorption Spectroscopy

Beer-Lambert's Law of Linear Absorption

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

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

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



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

C - total number of molecules of absorbing gas/atm/cm³ [$molecule\, cm^{-3}\, atm^{-1}$]

S - molecular line intensity [cm/molecule]

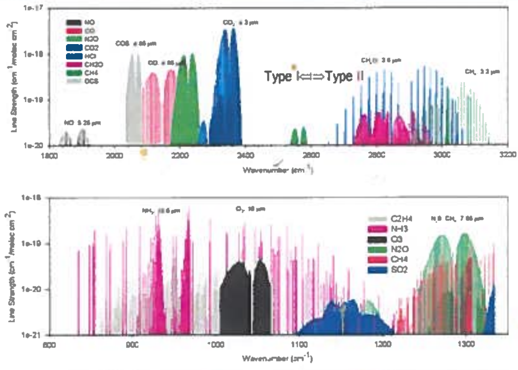
$g(\nu - \nu_0)$ - normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

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

Long Optical Pathlengths
- Multipass Absorption Cell
- Cavity Enhanced and Cavity Ringdown Spectroscopy
- Open Path Monitoring (with retro-reflector)

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

HITRAN Simulation of Absorption Spectra (3.1-5.5 & 7.6-12.5 μm)



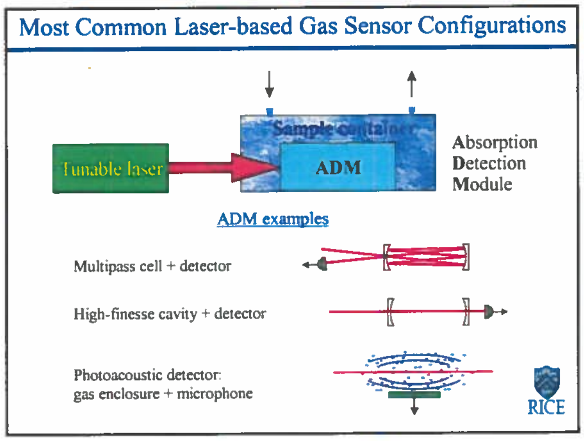
Representative Trace Gas Detection Limits

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

LOD for S/N = 2

Pathlength: 210 m

Mark S. Zahniser, SIRIS 2004, September 2004

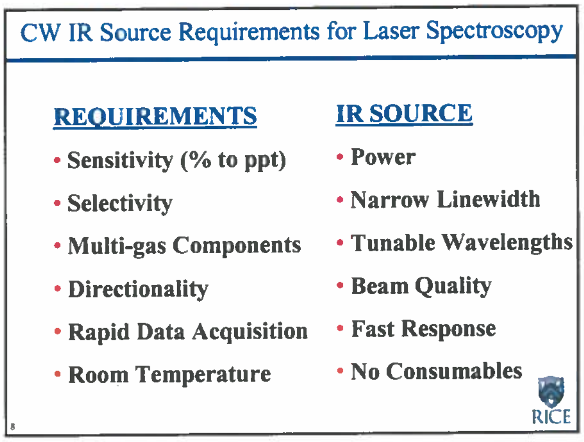


Most Common Laser-based Gas Sensor Configurations

Absorption Detection Module

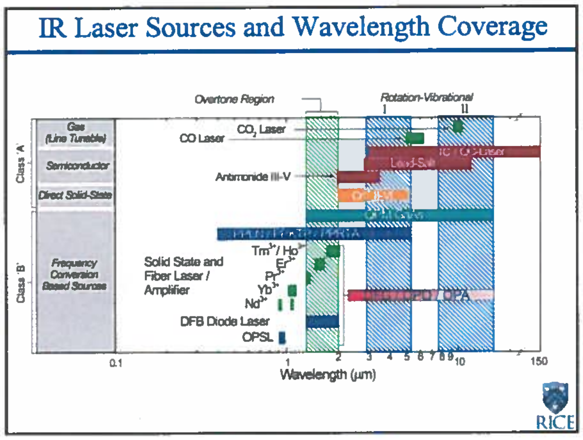
ADM examples

- Multipass cell + detector
- High-finesse cavity + detector
- Photoacoustic detector: gas enclosure + microphone

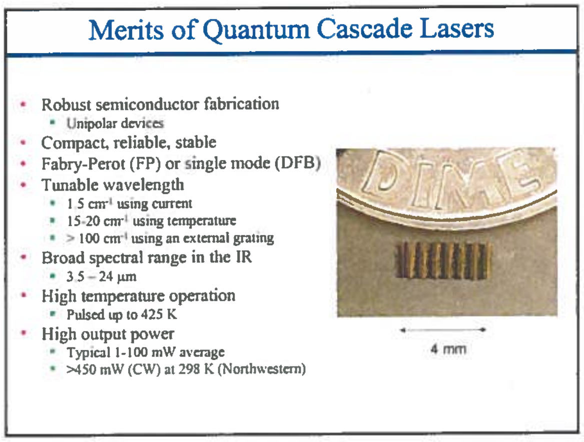


CW IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR SOURCE
• Sensitivity (% to ppt)	• Power
• Selectivity	• Narrow Linewidth
• Multi-gas Components	• Tunable Wavelengths
• Directionality	• Beam Quality
• Rapid Data Acquisition	• Fast Response
• Room Temperature	• No Consumables

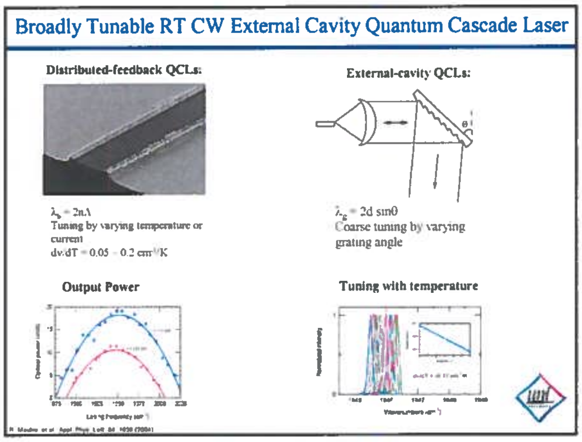


IR Laser Sources and Wavelength Coverage



Merits of Quantum Cascade Lasers

- Robust semiconductor fabrication
  - Unipolar devices
- Compact, reliable, stable
- Fabry-Perot (FP) or single mode (DFB)
- Tunable wavelength
  - 1.5 cm^{-1} using current
  - 15-20 cm^{-1} using temperature
  - > 100 cm^{-1} using an external grating
- Broad spectral range in the IR
  - 3.5 – 24 µm
- High temperature operation
  - Pulsed up to 425 K
- High output power
  - Typical 1-100 mW average
  - >450 mW (CW) at 298 K (Northwestern)



Broadly Tunable RT CW External Cavity Quantum Cascade Laser

Distributed-feedback QCLs:

$\lambda_B = 2n\Lambda$
Tuning by varying temperature or current
$d\nu/dT = 0.05 - 0.2$ cm^{-1}/K

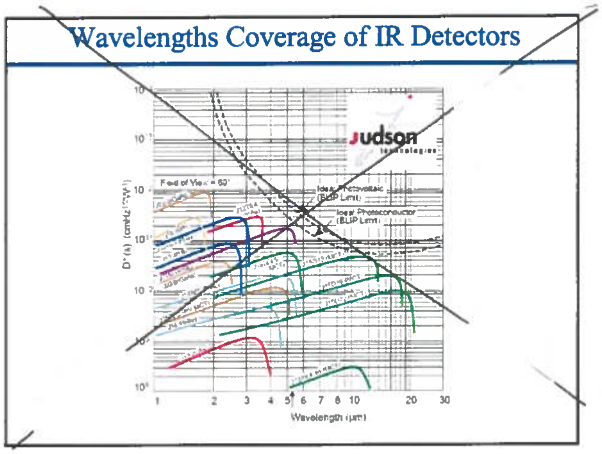
External-cavity QCLs:

$\lambda_g = 2d \sin\theta$
Coarse tuning by varying grating angle

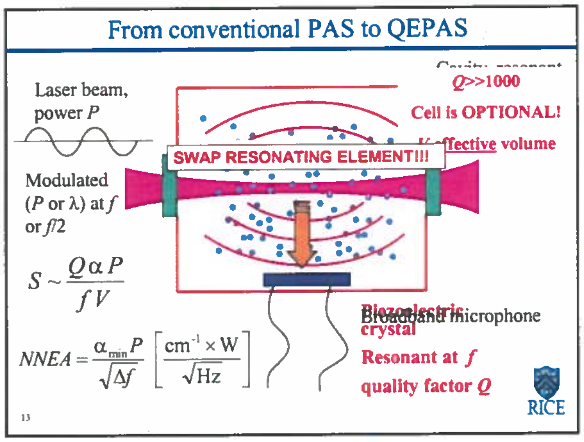
Output Power

Tuning with temperature

R. Maulini et al., Appl. Phys. Lett. 84, 1659 (2004)



Wavelengths Coverage of IR Detectors



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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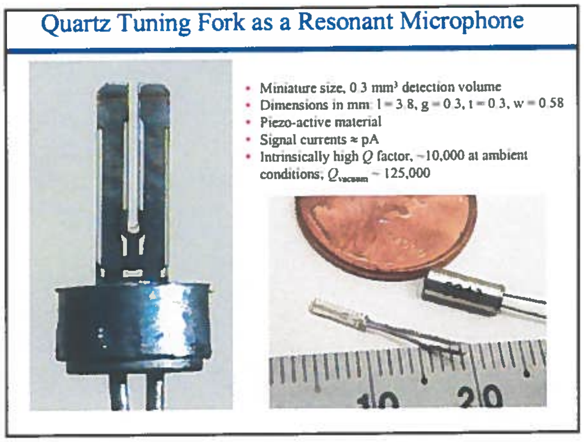
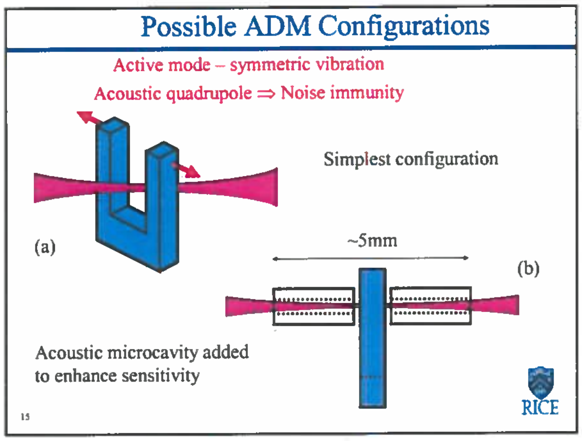


Quartz Tuning Fork as a Resonant Microphone

- Miniature size, 0.3 mm³ detection volume
- Dimensions in mm: l = 3.8, g = 0.3, t = 0.3, w = 0.58
- Piezo-active material
- Signal currents ≈ pA
- Intrinsically high *Q* factor, ~10,000 at ambient conditions; Q_{vacuum} ~ 125,000



Possible ADM Configurations

Active mode – symmetric vibration

Acoustic quadrupole ⇒ Noise immunity

Simplest configuration

(a)

~5mm

(b)

Acoustic microcavity added to enhance sensitivity

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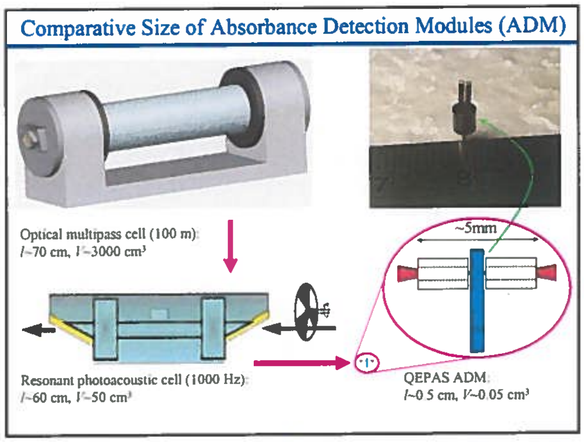


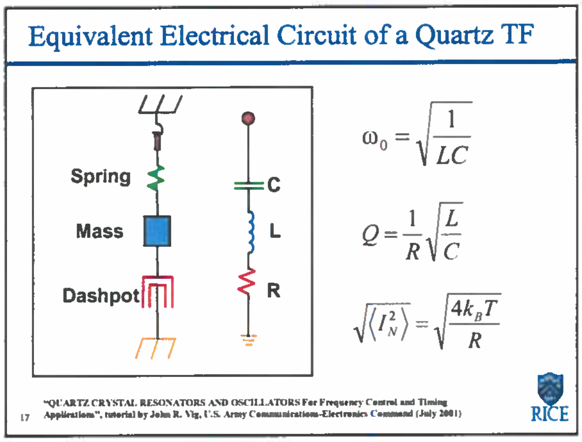
Comparative Size of Absorbance Detection Modules (ADM)

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

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

~5mm

QEPAS ADM: *l*~0.5 cm, *V*~0.05 cm³



Equivalent Electrical Circuit of a Quartz TF

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

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

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

"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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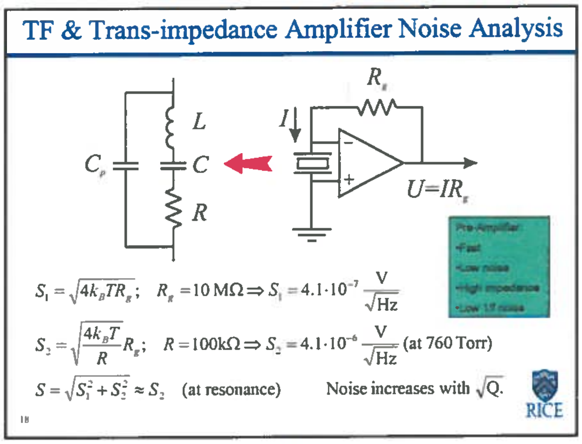

TF & Trans-impedance Amplifier Noise Analysis

$$S_1 = \sqrt{4k_B T R_g};\quad R_g = 10\,\text{M}\Omega \Rightarrow S_1 = 4.1\cdot 10^{-7}\,\frac{\text{V}}{\sqrt{\text{Hz}}}$$

$$S_2 = \sqrt{\frac{4k_B T}{R}} R_g;\quad R = 100\text{k}\Omega \Rightarrow S_2 = 4.1\cdot 10^{-6}\,\frac{\text{V}}{\sqrt{\text{Hz}}} \text{ (at 760 Torr)}$$

$$S = \sqrt{S_1^2 + S_2^2} \approx S_2 \quad \text{(at resonance)}$$

Noise increases with $\sqrt{\text{Q}}$.

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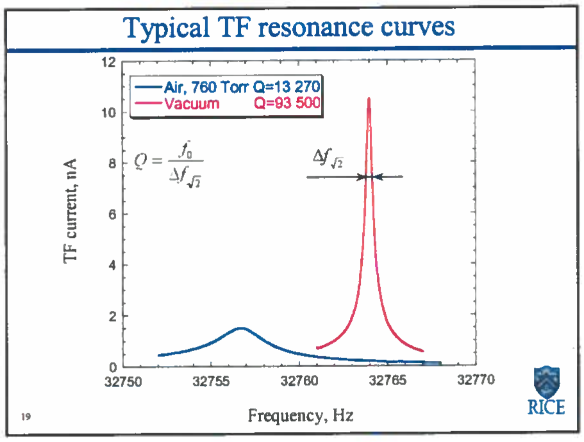
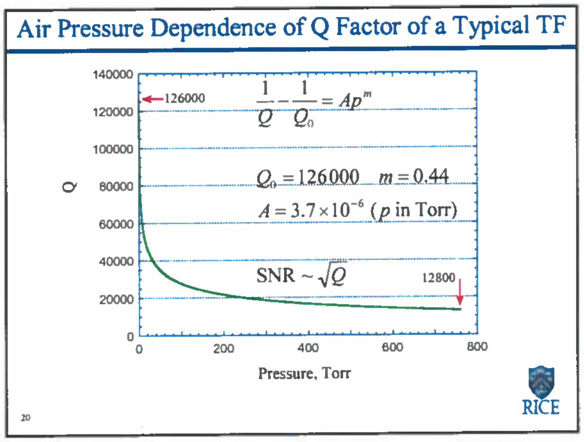


Typical TF resonance curves



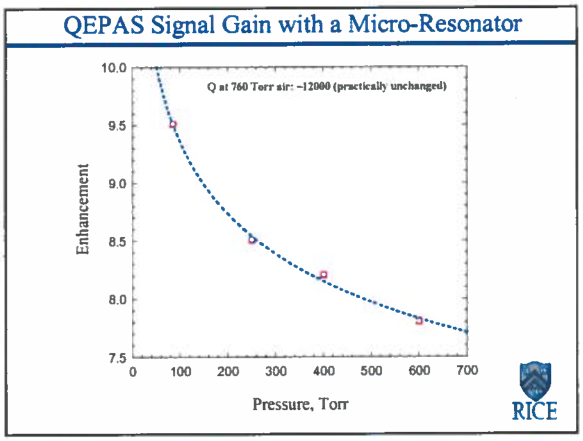
Air Pressure Dependence of Q Factor of a Typical TF

$$\frac{1}{Q} - \frac{1}{Q_0} = Ap^m$$

$Q_0 = 126000 \quad m = 0.44$

$A = 3.7 \times 10^{-6}$ (p in Torr)

SNR ~ $\sqrt{Q}$



QEPAS Signal Gain with a Micro-Resonator

Q at 760 Torr air: ~12000 (practically unchanged)

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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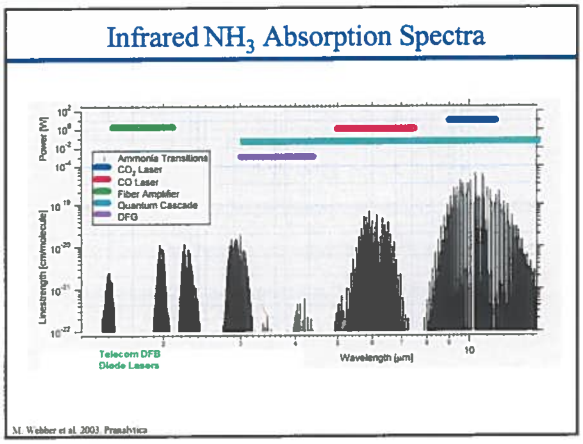
Motivation for NH_3 Detection

- Monitoring 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

Case study: NH_3 (100 ppb target)

Presently demonstrated sensitivity – NIR: 490 ppb

Parameter	Now	Modified	Scaling	Expected sensitivity, ppb
τ	1s	10s	3.2	155
W	38 mW	60 mW	1.6	100
f	32.7 kHz	10 kHz	3.2	35

Conclusion: QEPAS provides adequate sensitivity to NH_3 with NIR telecom lasers. Power consumption by the 63 mW JDS-Uniphase laser is (only) ~1 W.

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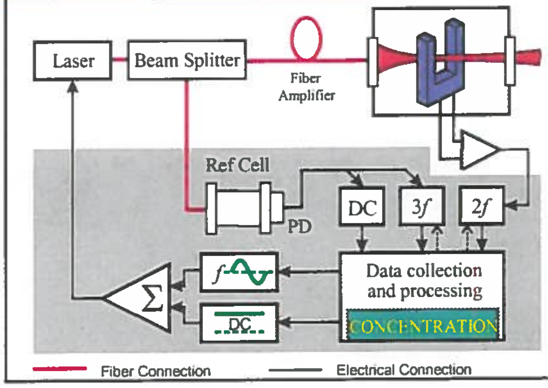
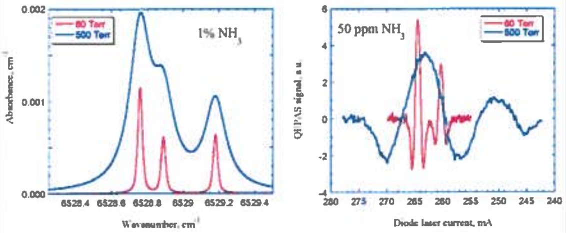
QEPAS fiber based gas sensor architecture



Ammonia Detection using a 1.53 μm Telecom Diode Laser

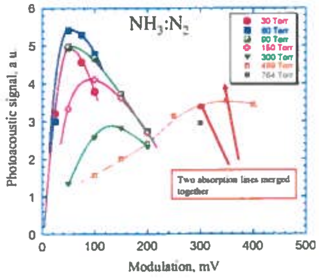


Spectral simulations based on data from Webber et al., APPLIED OPTICS 40, 2031-2042 (2001)]

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

Pressure Dependence of QEPAS Sensitivity



- **Peak optical absorption varies with pressure**
- **Q-factor decreases at higher pressure**
- **V-T relaxation is faster at higher pressure**
- **Acoustic resonator enhancement factor changes with pressure**

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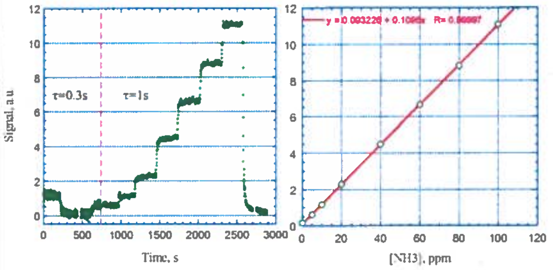
Calibration and Linearity of QEPAS based NH_3 Sensor



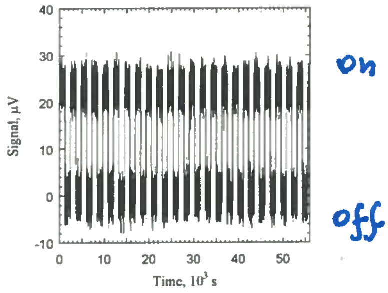
Noise –equivalent (1s) concentration (NEC). for τ=1s time constant is 0.65 ppmv for 38 mW excitation power

90 last points of each step averaged

(Traditional) PAS* – 1.5×10^{-8} $cm^{-1}W/\sqrt{Hz}$)
*Webber et al., APPLIED OPTICS April 2003 Vol. 42, No. 12, p.2119

Noise-equivalent absorption (NEA) coefficient $k=7.2\times10^{-9}$ $cm^{-1}W/Hz^{1/2}$

Consecutive QEPAS readings acquired over a period of ~16 hours



on

off

30

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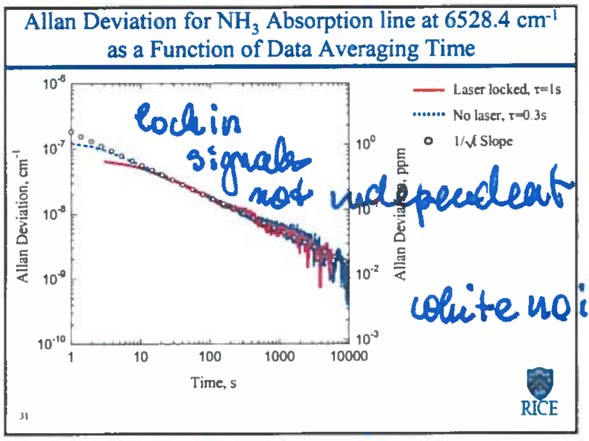
Allan Deviation for NH$_3$ Absorption line at 6528.4 cm^{-1} as a Function of Data Averaging Time



lock in signals not independent

white noise

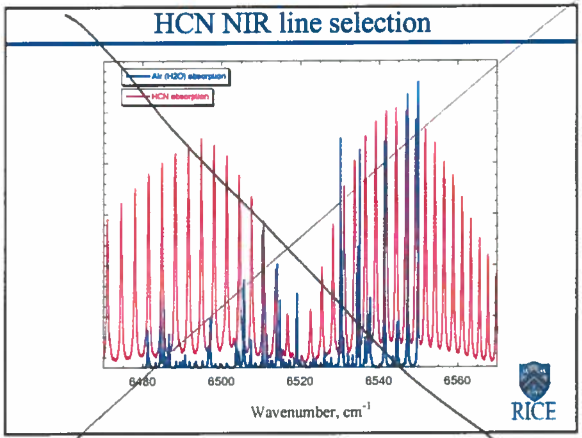
Merits of QE Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to ambient and flow acoustic noise, laser noise and etalon effects
- Significant reduction of sample volume (< 1 mm^3)
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive
- Compact, rugged and low cost compared to LAS that requires a multipass absorption cell and infrared detector(s)
- Potential for optically multiplexed concentration measurements

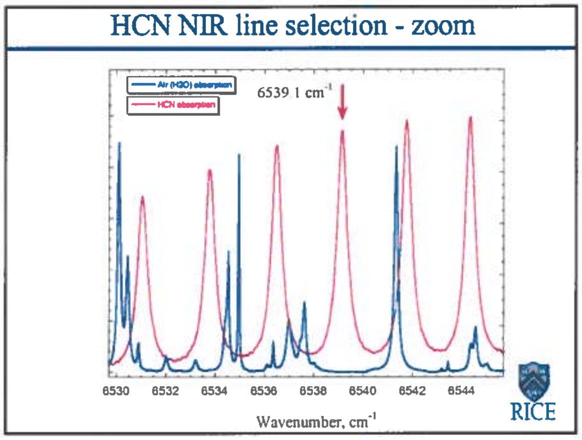
QEPAS versus Traditional PAS

Parameter	Traditional PAS	QEPAS
f, Hz	100 to 4000	Presently ~32 760
Q	20 to 200	10 000 to 30 000
Q vs. pressure	INCREASES (high spectral resolution is problematic)	DECREASES (high spectral resolution is achievable)
Sample volume	>10 cm^3	<1 mm^3
Sensitivity to ambient acoustic and flow noise	Usually high	None observed
Pathlength involved	~10 cm	(a) 0.3mm, (b) 5mm

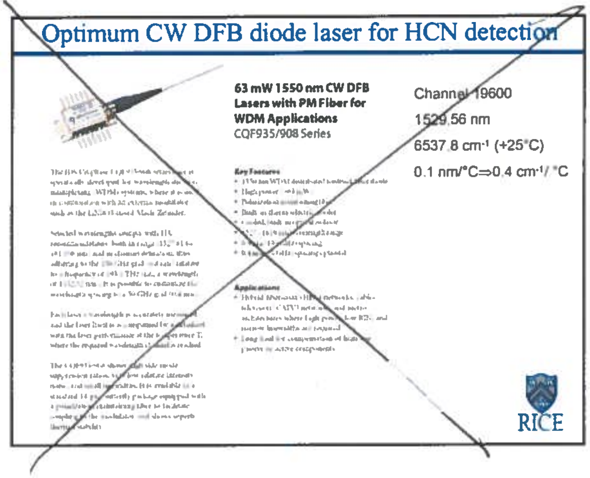
~~HCN NIR line selection~~



HCN NIR line selection - zoom



~~Optimum CW DFB diode laser for HCN detection~~

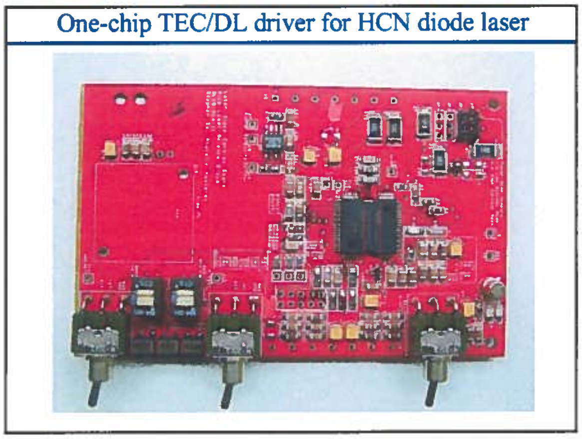


~~**63 mW 1550 nm CW DFB Lasers with PM Fiber for WDM Applications**~~
~~CQF935/908 Series~~

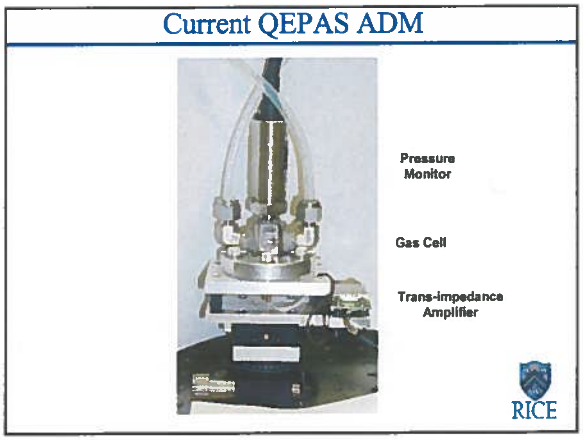
~~**Key Features**~~

~~**Applications**~~

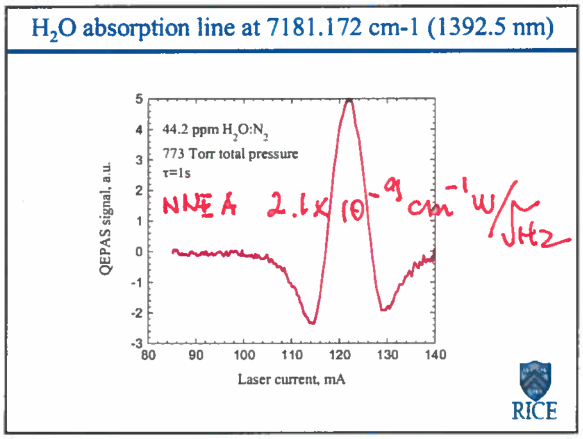
~~Channel 19600~~
~~1529.56 nm~~
~~6537.8 cm^{-1} (+25°C)~~
~~0.1 nm/°C⇒0.4 cm^{-1}/ °C~~



One-chip TEC/DL driver for HCN diode laser



Current QEPAS ADM



H_2O absorption line at 7181.172 cm-1 (1392.5 nm)

NNEA 2.1×10^{-9} cm^{-1} $W/\sqrt{Hz}$

Motivation for Precision Monitoring of H_2CO

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

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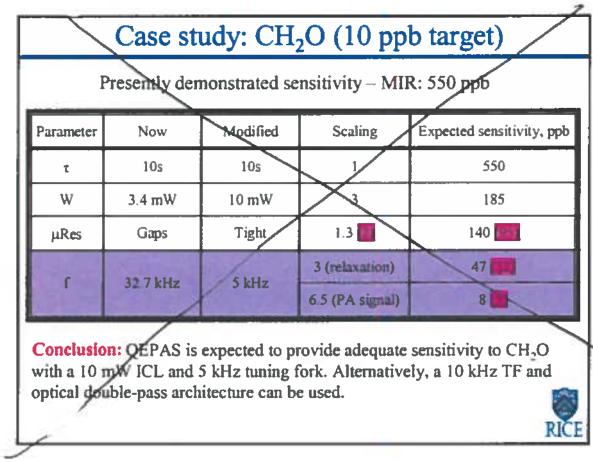

~~Case study: CH_2O (10 ppb target)~~

~~Presently demonstrated sensitivity – MIR: 550 ppb~~

~~Parameter~~	~~Now~~	~~Modified~~	~~Scaling~~	~~Expected sensitivity, ppb~~
~~τ~~	~~10s~~	~~10s~~	~~1~~	~~550~~
~~W~~	~~3.4 mW~~	~~10 mW~~	~~3~~	~~185~~
~~μRes~~	~~Gaps~~	~~Tight~~	~~1.3~~ [redacted]	~~140~~ [redacted]
~~f~~	~~32.7 kHz~~	~~5 kHz~~	~~3 (relaxation)~~	~~47~~ [redacted]
			~~6.5 (PA signal)~~	~~8~~ [redacted]

~~**Conclusion:** QEPAS is expected to provide adequate sensitivity to CH_2O with a 10 mW ICL and 5 kHz tuning fork. Alternatively, a 10 kHz TF and optical double-pass architecture can be used.~~

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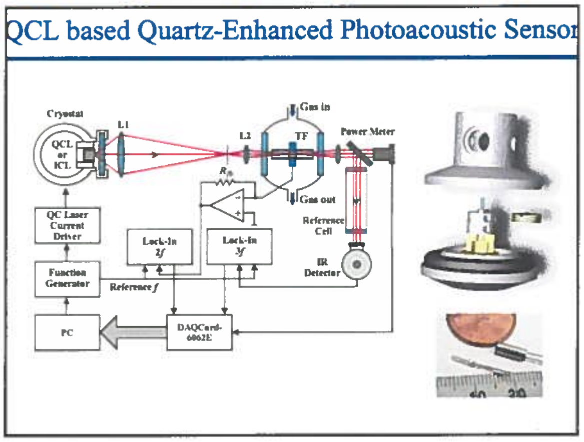
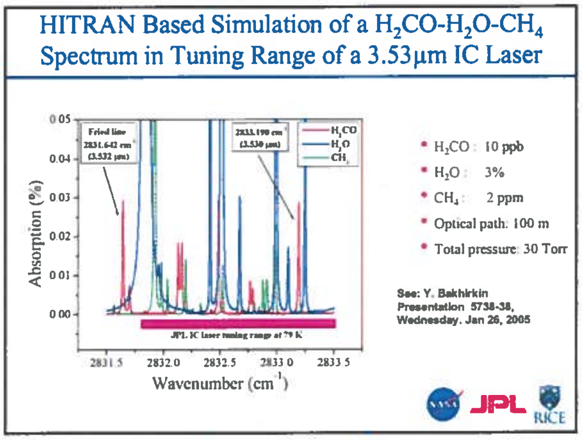


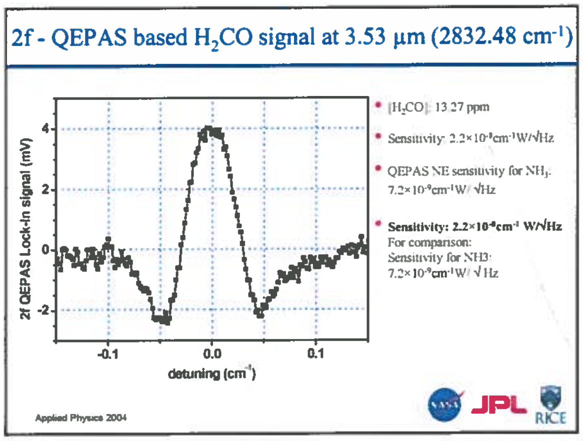
QCL based Quartz-Enhanced Photoacoustic Sensor



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

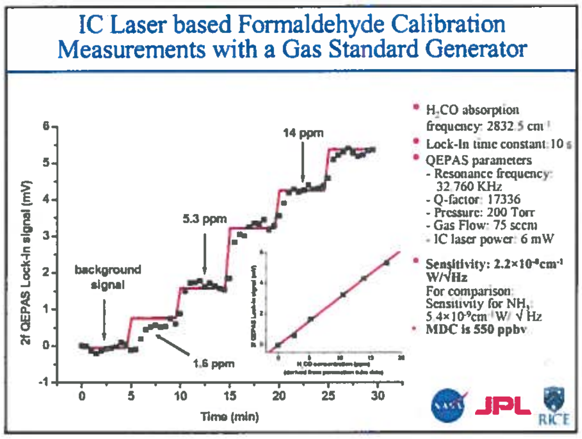
See: Y. Bakhirkin
Presentation 5738-38,
Wednesday, Jan 26, 2005



2f - QEPAS based H_2CO signal at 3.53 μm (2832.48 cm^{-1})

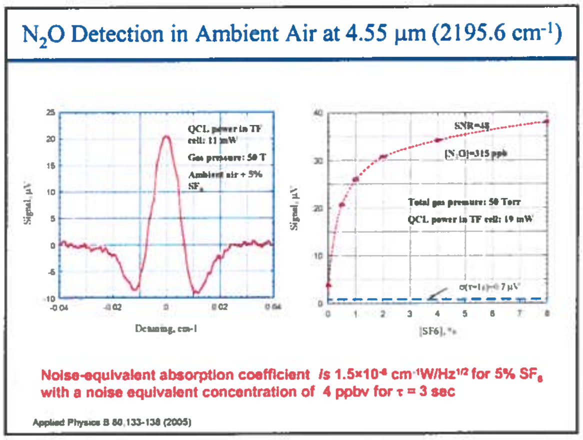
- $[H_2CO]$: 13.27 ppm
- Sensitivity: $2.2\times10^{-8}cm^{-1}W/\sqrt{Hz}$
- QEPAS NE sensitivity for NH_3: $7.2\times10^{-9}cm^{-1}W/\sqrt{Hz}$
- **Sensitivity: $2.2\times10^{-8}cm^{-1}$ W/√Hz**
  For comparison:
  Sensitivity for NH3:
  $7.2\times10^{-9}cm^{-1}W/\sqrt{Hz}$

Applied Physics 2004



IC Laser based Formaldehyde Calibration Measurements with a Gas Standard Generator

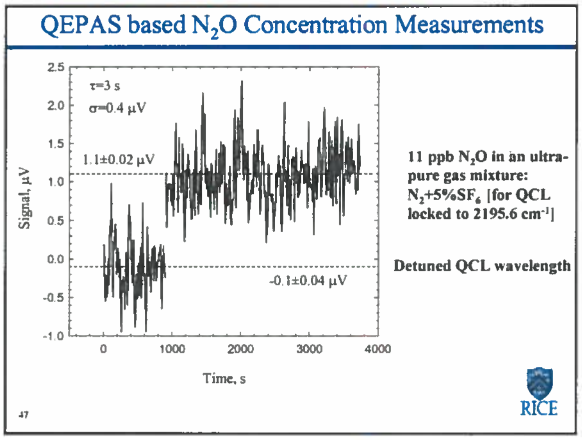
- H_2CO absorption frequency: 2832.5 cm^{-1}
- Lock-In time constant: 10 s
- QEPAS parameters
  - Resonance frequency: 32.760 KHz
  - Q-factor: 17336
  - Pressure: 200 Torr
  - Gas Flow: 75 sccm
  - IC laser power: 6 mW
- **Sensitivity: $2.2\times10^{-8}cm^{-1}$ W/√Hz**
  For comparison:
  Sensitivity for NH_3:
  $5.4\times10^{-9}cm^{-1}W/\sqrt{Hz}$
- **MDC is 550 ppbv**



N_2O Detection in Ambient Air at 4.55 μm (2195.6 cm^{-1})

Noise-equivalent absorption coefficient *is* 1.5×10^{-8} $cm^{-1}W/Hz^{1/2}$ for 5% SF_6 with a noise equivalent concentration of 4 ppbv for τ = 3 sec

Applied Physics B 80,133-138 (2005)



QEPAS based N_2O Concentration Measurements

11 ppb N_2O in an ultra-pure gas mixture: N_2+5%SF_6 [for QCL locked to 2195.6 cm^{-1}]

Detuned QCL wavelength

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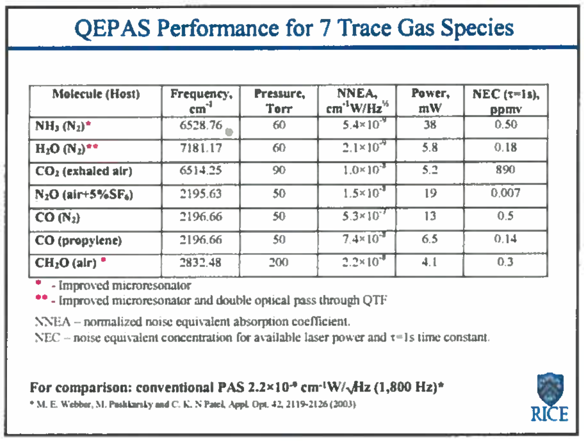


QEPAS Performance for 7 Trace Gas Species

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{1/2}$	Power, mW	NEC (τ=1s), ppmv
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	0.50
H_2O (N_2)**	7181.17	60	2.1×10^{-9}	5.8	0.18
CO_2 (exhaled air)	6514.25	90	1.0×10^{-8}	5.2	890
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007
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
CH_2O (air) *	2832.48	200	2.2×10^{-8}	4.1	0.3

* - Improved microresonator
** - Improved microresonator and double optical pass through QTF

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

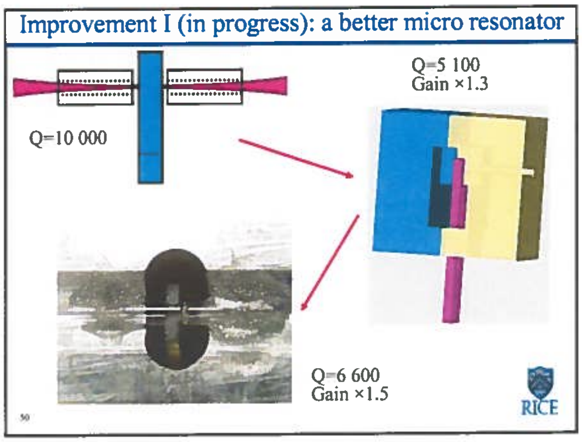
For comparison: conventional PAS 2.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (1,800 Hz)*

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

Current QEPAS Design R&D Activities

- Micro-resonator
- Lower frequency TF
- Better Coupling (Collimation)
- Intra-cavity
- New Target Gases: H_2O, HCN and C_2H_6
- Integrated, ultra-compact design
- Potential for optically multiplexed concentration measurements

RICE



Improvement I (in progress): a better micro resonator

Quest for a low-frequency TF: Why?

$$S = k\frac{\alpha lCPQ}{fV} = k\frac{\alpha CPQ}{fA}$$

$$m' = nm$$

$$f_0' = \frac{f_0}{\sqrt{n}}, \quad Q' = Q\sqrt{n}$$

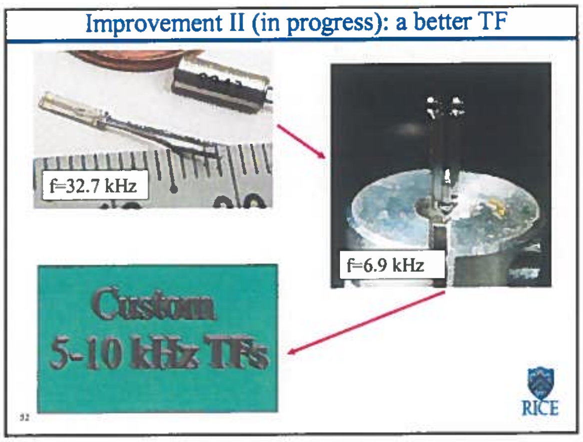
$$f_0 = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$$

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

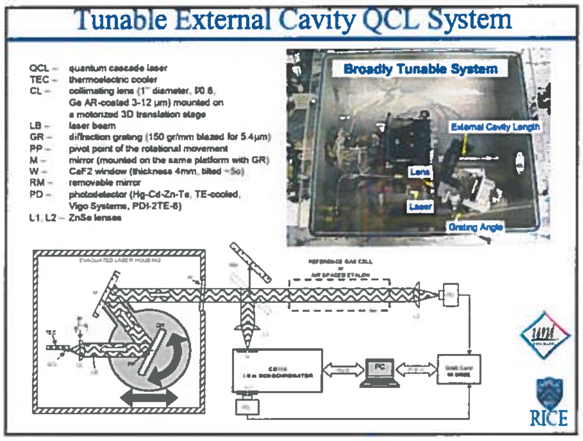
$$\frac{\sqrt{\langle V_N^2 \rangle}}{\sqrt{\Delta f}} = R_g\sqrt{\frac{4k_B T}{R}}$$

$$\boxed{S' = nS = \left(\frac{f_0}{f_0'}\right)^2}$$

RICE

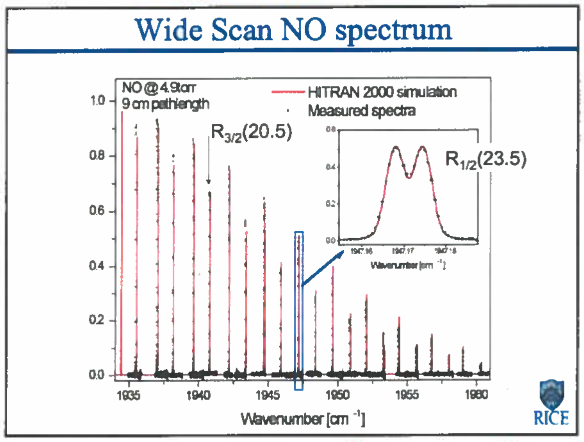


Improvement II (in progress): a better TF



Tunable External Cavity QCL System

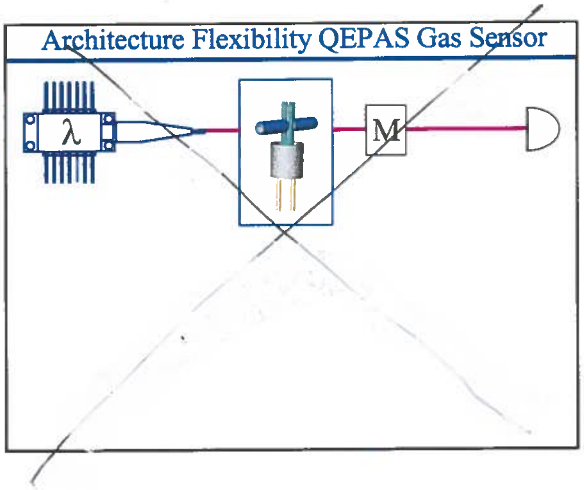
QCL – quantum cascade laser
TEC – thermoelectric cooler
CL – collimating lens (1" diameter, f/0.6, Ge AR-coated 3-12 μm) mounted on a motorized 3D translation stage
LB – laser beam
GR – diffraction grating (150 gr/mm blazed for 5.4μm)
PP – pivot point of the rotational movement
M – mirror (mounted on the same platform with GR)
W – CaF2 window (thickness 4mm, tilted ~5o)
RM – removable mirror
PD – photodetector (Hg-Cd-Zn-Te, TE-cooled, Vigo Systems, PDI-2TE-6)
L1, L2 – ZnSe lenses



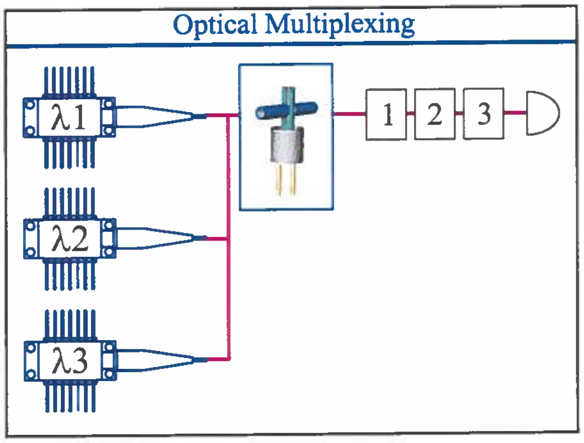
Wide Scan NO spectrum

1000 [illegible]

100ppb [illegible]



~~Architecture Flexibility QEPAS Gas Sensor~~



Optical Multiplexing

~~Summary of QEPAS advantages~~

- ~~Ultra-compact, simple and rugged ADM, small sample volume~~
- ~~No spectrally selective elements~~
  - ~~Easy change of the target species (only laser & reference cell need to be replaced)~~
  - ~~Potential for multiplexing (many lasers or , mixture of target species in the reference cell)~~
- ~~Adequate sensitivity; proportional to laser power~~
  - ~~Will improve with progress of semiconductor laser excitation sources~~
- ~~Wide dynamic range~~
- ~~Applicable over a wide range of sampled gas pressures, including ambient atmospheric pressure~~
- ~~Stable calibration – zero drift in 1 year verified~~
- ~~Immune to acoustic noise~~

RICE

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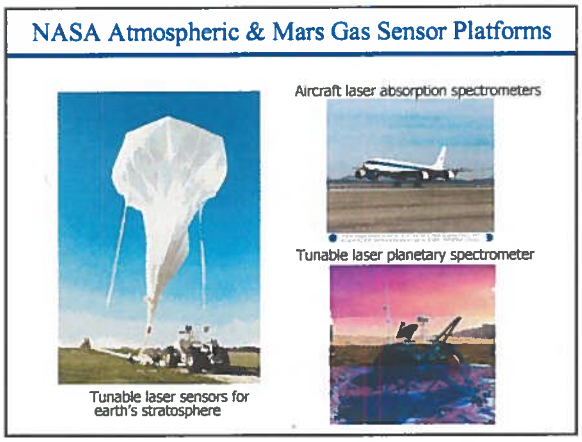
Conclusions and Future Directions

- **Laser based Trace Gas Sensors**
  - Ultra compact (~0.2 mm^3) , robust and low cost sensors based on QE L-PAS and QC-LAS
  - QEL-PAS is immune to ambient noise.
  - High detection sensitivity (limited by thermal excitation of symmetric mode)
  - Best demonstrated minimum detectable absorption coefficient is 5.4 x 10^{-9} $cm^{-1}W/\sqrt{Hz}$
  - Detected trace gases: **NH_3, CH_4, N_2O, CO_2, CO,** NO, **H_2O**, COS, 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, C_2H_4)
  - Industrial process control and chemical analysis (NO, NH_3)
- **Future Directions and Collaborations**
  - QE L-PAS and cavity enhanced (ICOS) spectroscopy based applications using novel thermoelectrically cooled cw and broadly wavelength tunable quantum cascade lasers
  - Applications using interband and quantum cascade lasers
  - New target gases, in particular VOCs and HCs
  - Development of optically multiplexed gas sensor networks



NASA Atmospheric & Mars Gas Sensor Platforms

Aircraft laser absorption spectrometers

Tunable laser planetary spectrometer

Tunable laser sensors for earth's stratosphere