RICE

Semiconductor Laser based Trace Gas Sensor Technology: Advances and Challenges

F.K. Tittel, A.A. Kosterev, Yu. Bakhirkin, G. Wysocki, S. So & R.F.Curl

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

OUTLINE

Optics & Optoelectronics Conf. 5958

Warsaw, Poland

Aug 28-Sept 2, 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
- Conclusions and Outlook

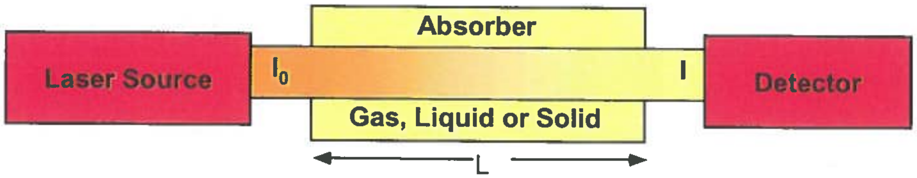
Work supported by NASA, PNNL, NSF, NIH and Welch Foundation

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 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**

RICE

Fundamentals of Laser Absorption Spectroscopy

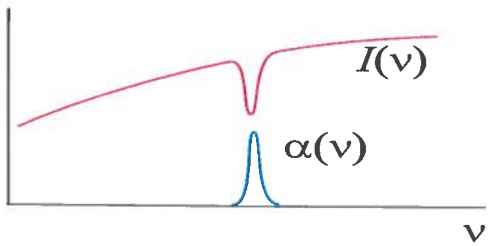


Beer-Lambert's Law of Linear Absorption

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

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

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



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

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

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

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

Optimum Molecular Absorbing Transition

- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

Long Optical Pathlengths

- Multipass Absorption Cell
- Cavity Enhanced and Cavity Ringdown Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Evanescent Wave Spectroscopy

Spectroscopic Detection Schemes

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

IR Source Requirements for Laser Spectroscopy

REQUIREMENTS

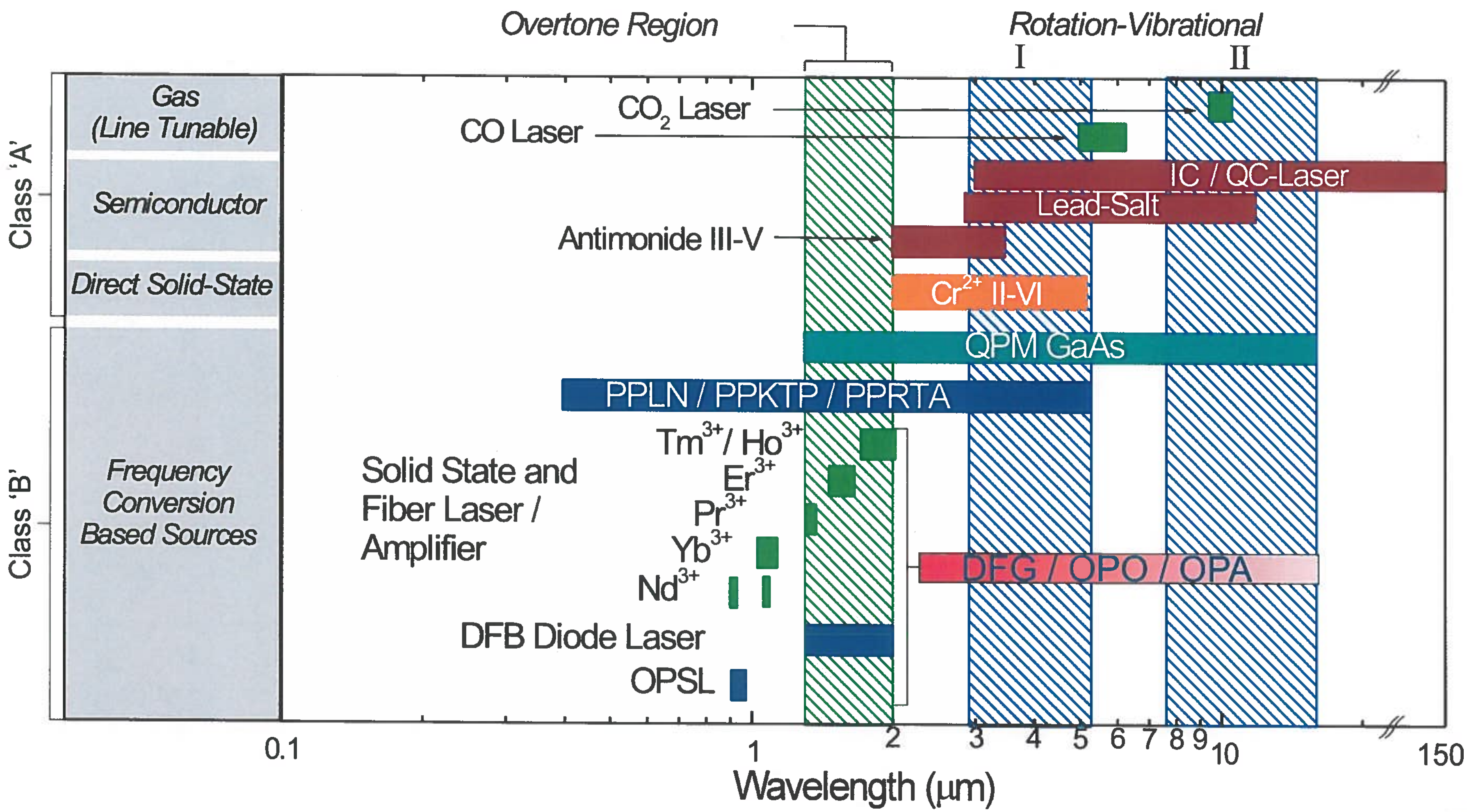
- Sensitivity (% to ppt)
- Selectivity
- Multi-gas Components
- Directionality
- Rapid Data Acquisition
- Room Temperature

IR SOURCE

- Power
- Narrow Linewidth
- Tunable Wavelengths
- Beam Quality
- Fast Response Time
- No Consumables

RICE

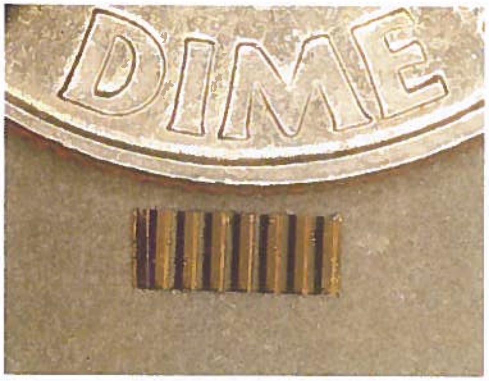
CW IR Laser Sources and Wavelength Coverage



RICE

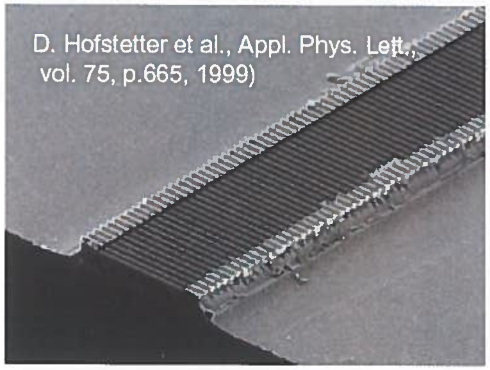
Quantum Cascade Laser: Basic Facts

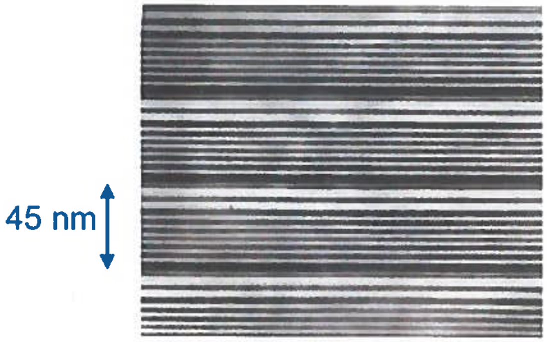
- Band – structure engineered devices (emission wavelength is defined by layer thickness – MBE or MOCVD) 3.5-160 μm
  - Unipolar devices
  - Cascading (each electron creates N laser photons and number of periods N determines laser power)
- Compact, reliable, stable, long life time
- Fabry-Perot (FP) or single mode (DFB)
- Tunable wavelengths
  - 1.5 cm^{-1} using current
  - 15-20 cm^{-1} using temperature
  - > 150 cm^{-1} using an external grating element
- Broad spectral range in the mid-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)



4 mm

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





ADM comparison

Technique	Sensitivity: Power dependent?	Pros	Cons
Multipass cell	No	• Does not require calibration • Works well with low-power sources	• Large volume • Critical alignment • Expensive optics • Small change of large signal
CRDS	No	• Does not require calibration • Not sensitive to laser power fluctuations	• Expensive and contamination-sensitive optics • Critical alignment • Cavity mode structure
Photoacoustic (PAS)	**Yes**	• No optical elements • Alignment is not critical • Background-free • Not sensitive to laser power fluctuations • Small sample volume	• Requires calibration • Sensitive t[illegible]tic noise Solved by QEPAS

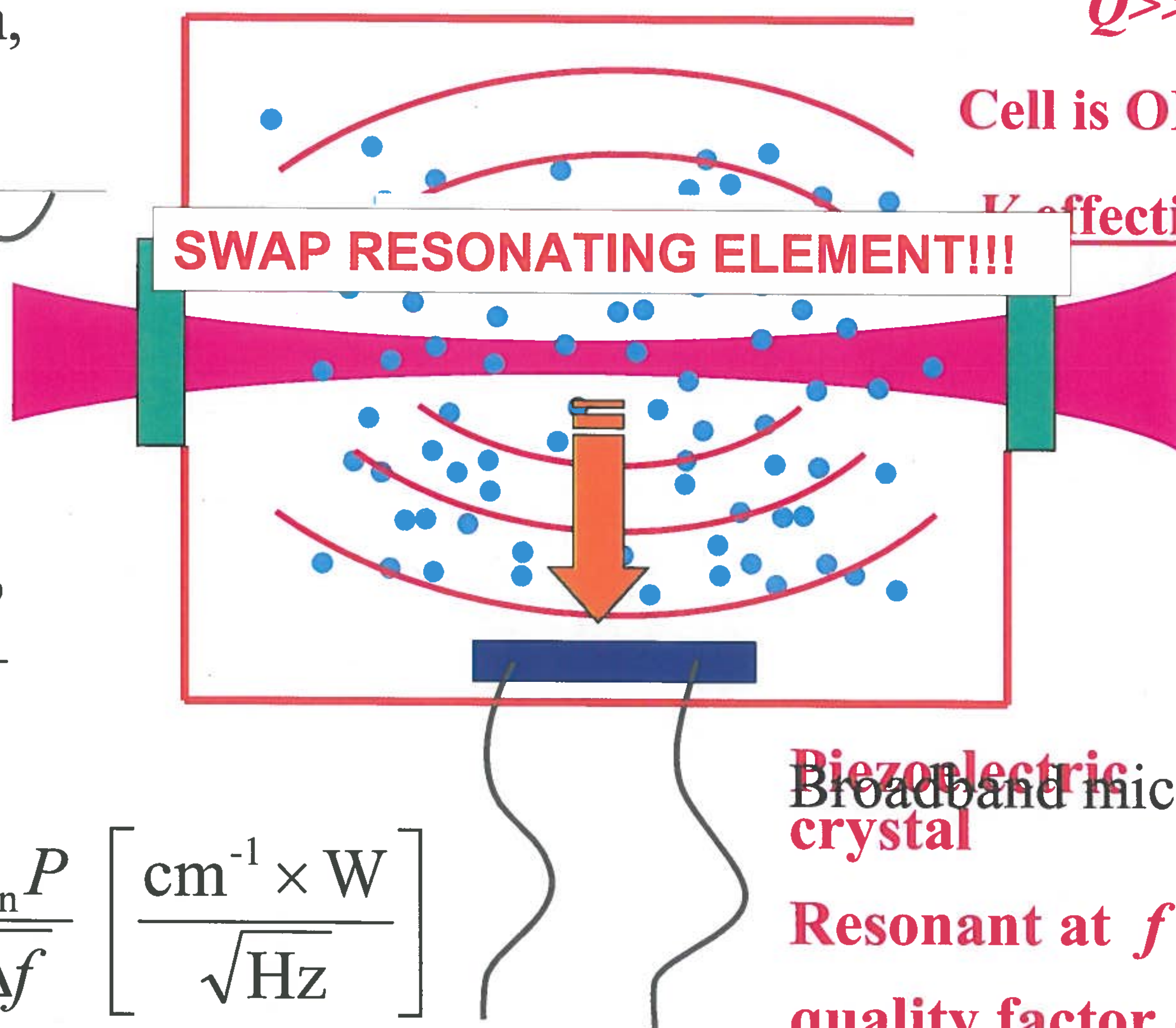
From conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$

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

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



Cavity resonant

Q>>1,000

Cell is OPTIONAL!

V effective volume

Piezoelectric crystal

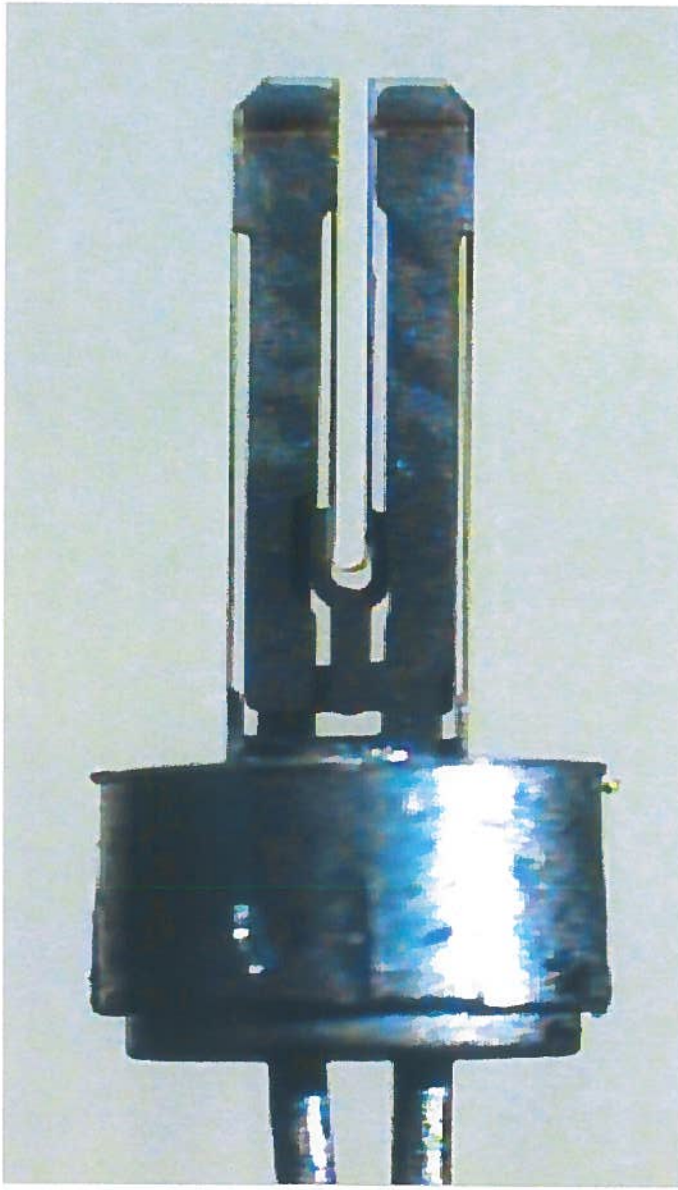
Broadband microphone

Resonant at f

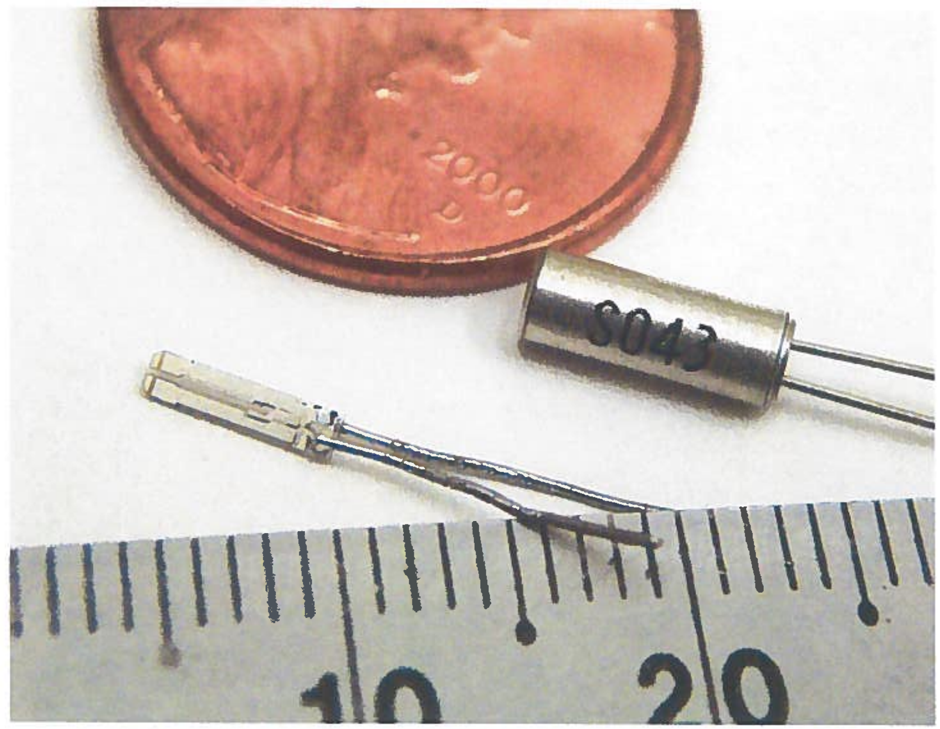
quality factor Q

RICE

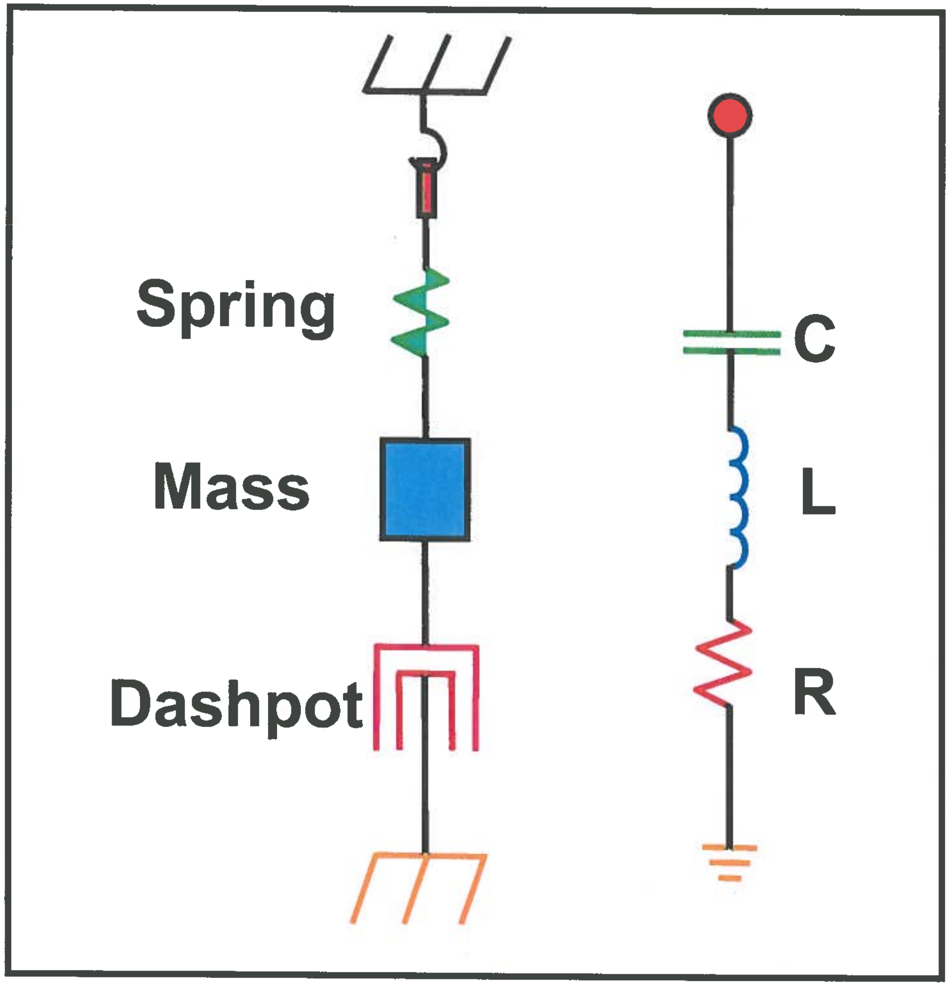
Quartz Tuning Fork as a Resonant Microphone



- Miniature size, 0.3 mm^3 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



Equivalent Electrical Circuit of a Quartz TF



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

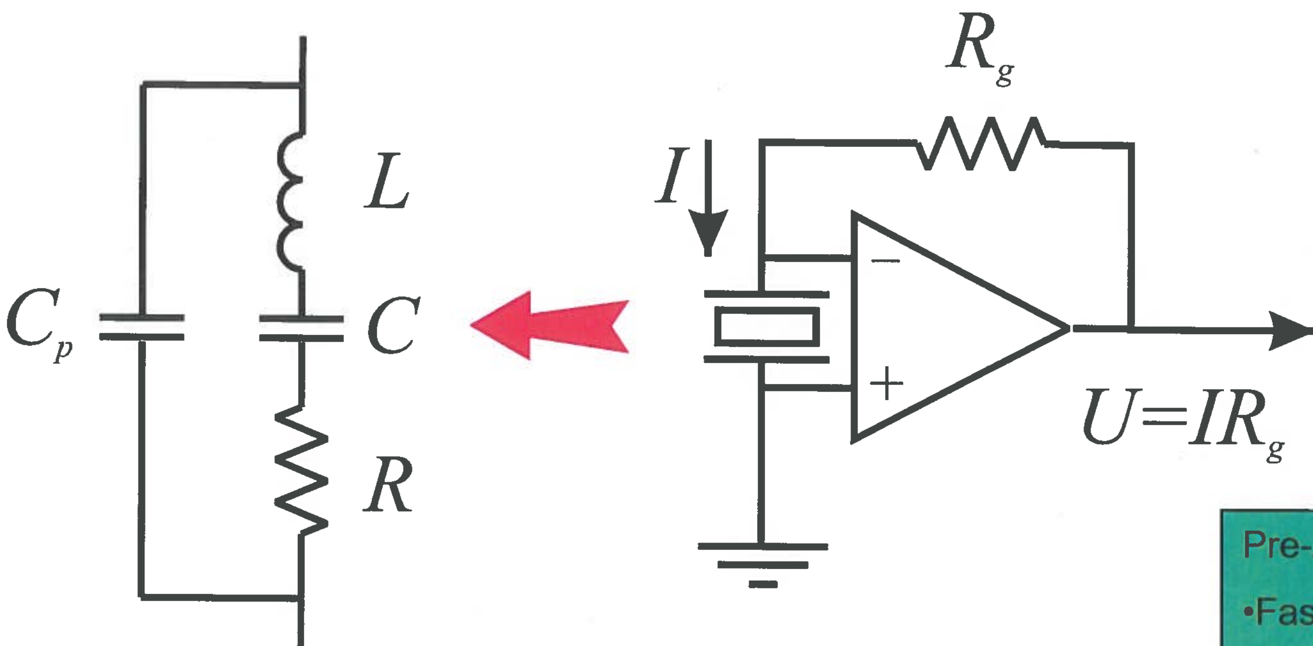
$$Q = \frac{1}{R}\sqrt{\frac{L}{C}}$$

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

"QUARTZ CRYSTAL RESONATORS AND OSCILLATORS For Frequency Control and Timing Applications", tutorial by John R. Vig, U.S. Army Communications-Electronics Command (July 2001)

RICE

TF & Trans-impedance Amplifier Noise Analysis



Pre-Amplifier:

- Fast
- Low noise
- High impedance
- Low 1/f noise

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

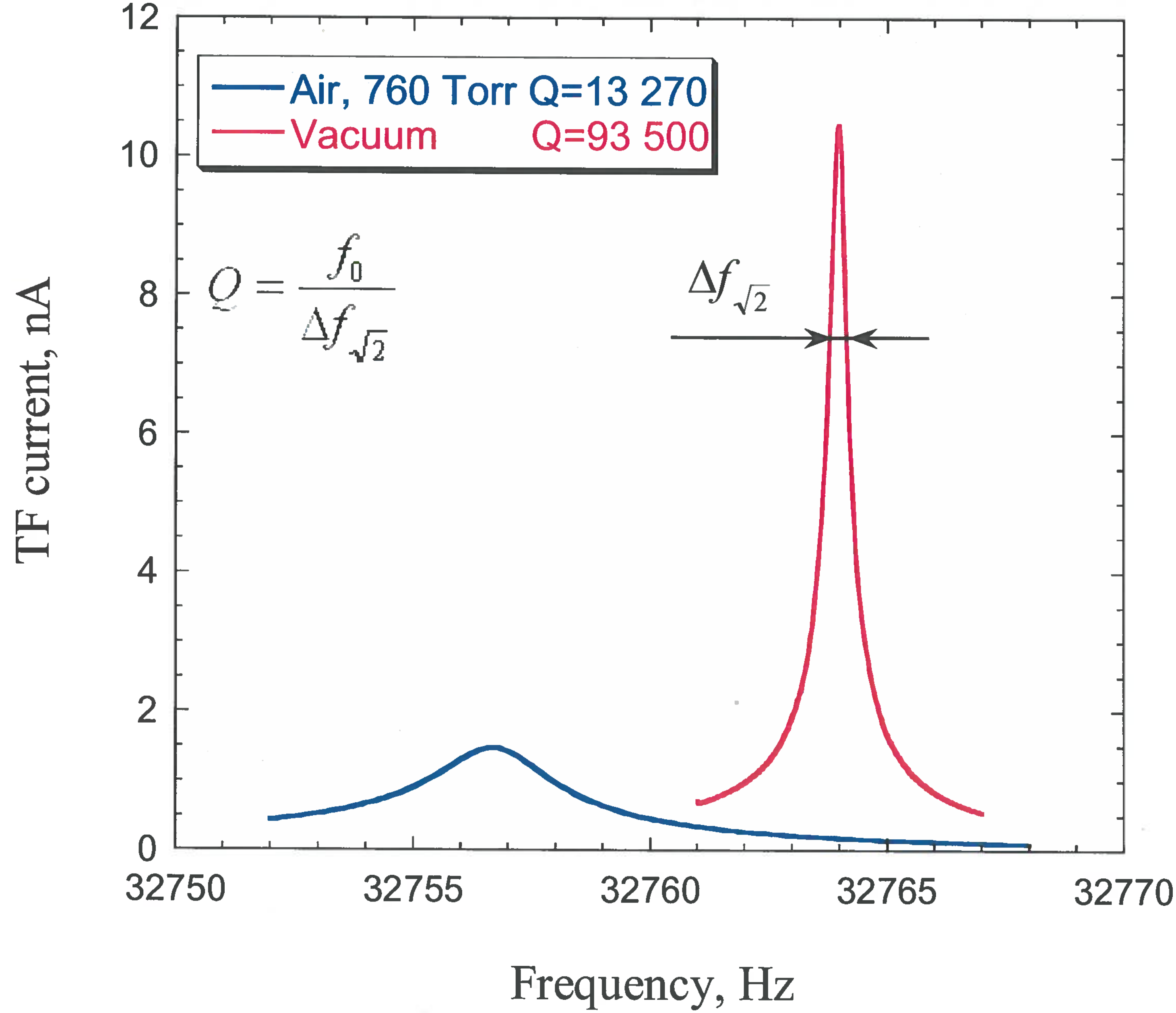
$$S_2 = \sqrt{\frac{4k_B T}{R} R_g}; \quad R = 100\mathrm{k\Omega} \Rightarrow S_2 = 4.1 \cdot 10^{-6} \frac{\mathrm{V}}{\sqrt{\mathrm{Hz}}} \text{ (at 760 Torr)}$$

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

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

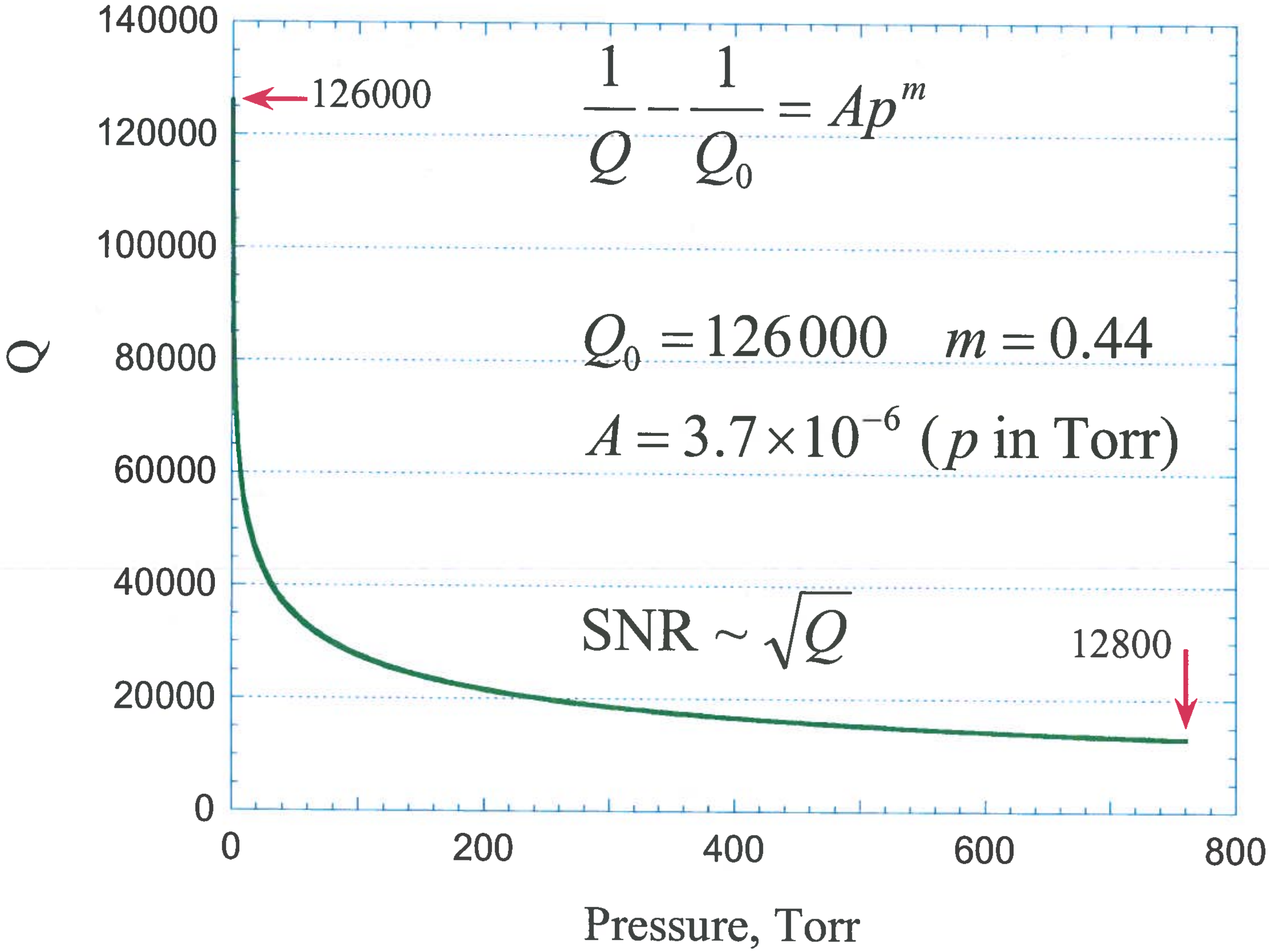
RICE

Typical QTF resonance curves



RICE

Air Pressure Dependence of Q Factor of a Typical TF

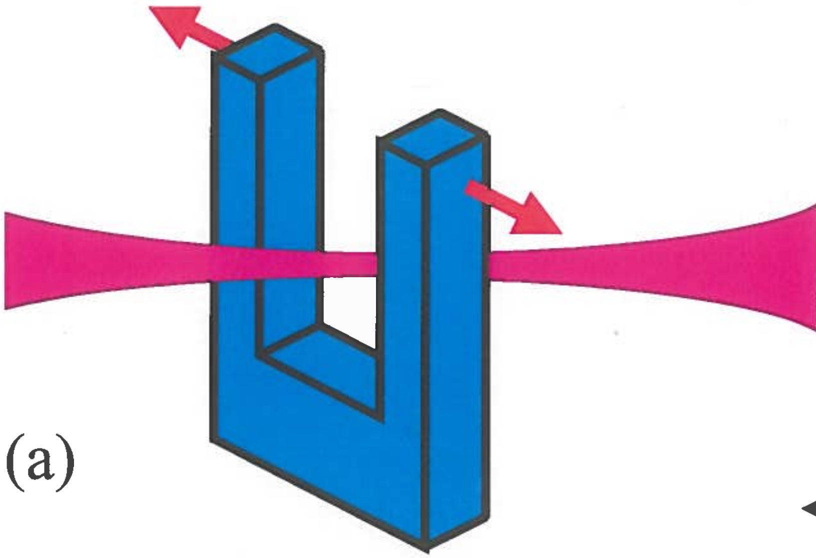


RICE

Possible ADM Configurations

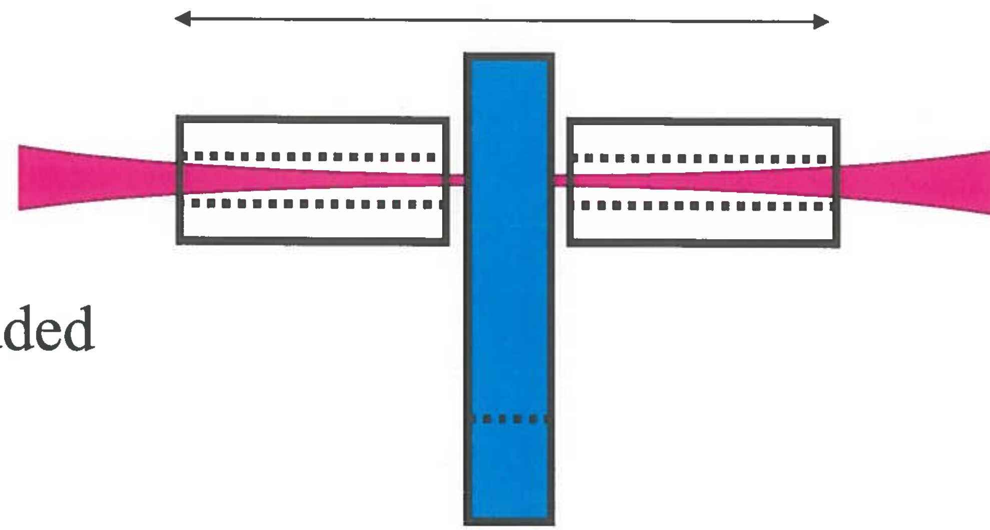
Active mode – symmetric vibration

Acoustic quadrupole ⇒ Noise immunity



(a)

Simplest configuration

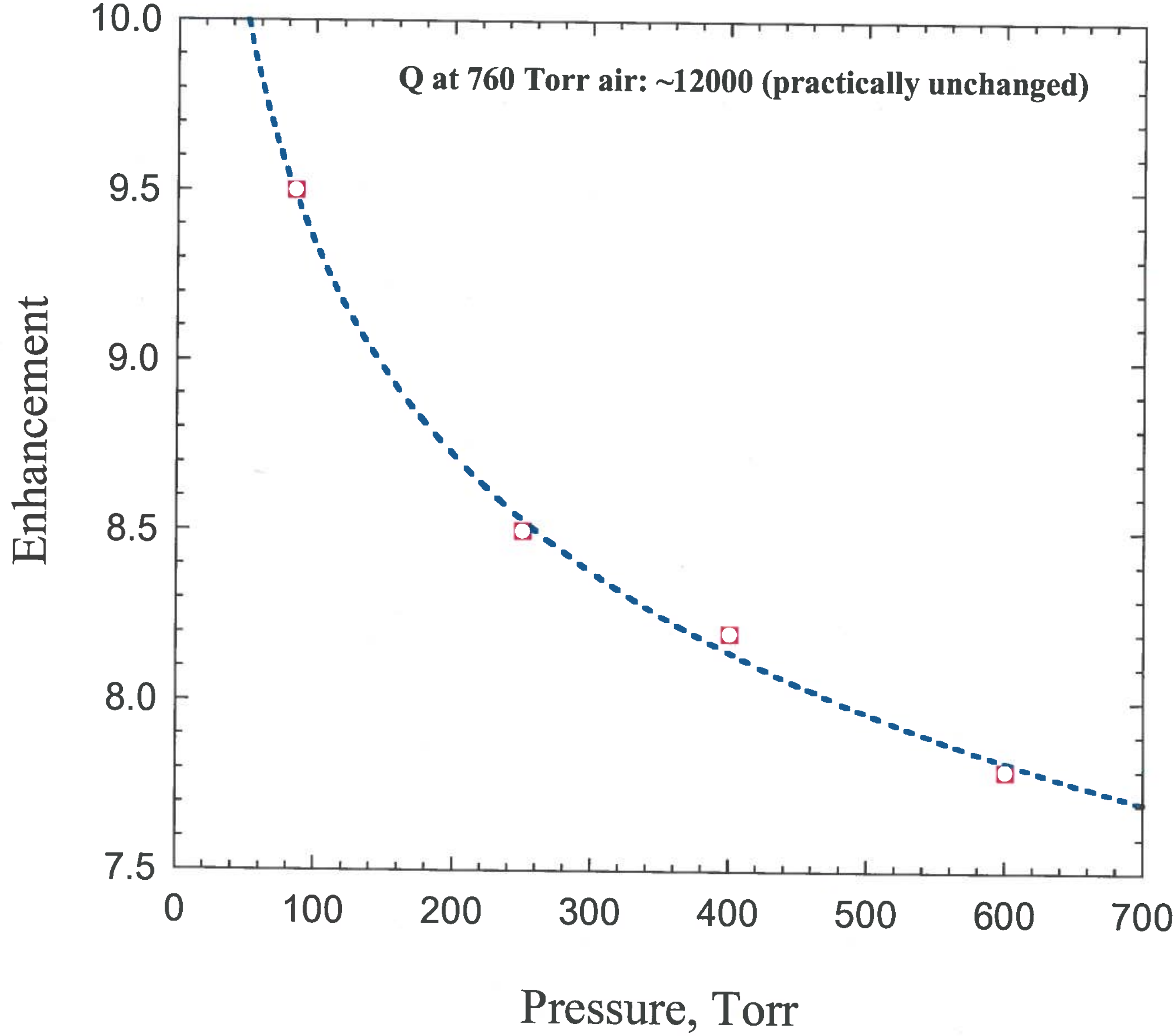


(b)

Acoustic microcavity added
to enhance sensitivity

RICE

QEPAS Signal Gain with a Micro-Resonator



Motivation for NH_3 Detection

- 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)

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

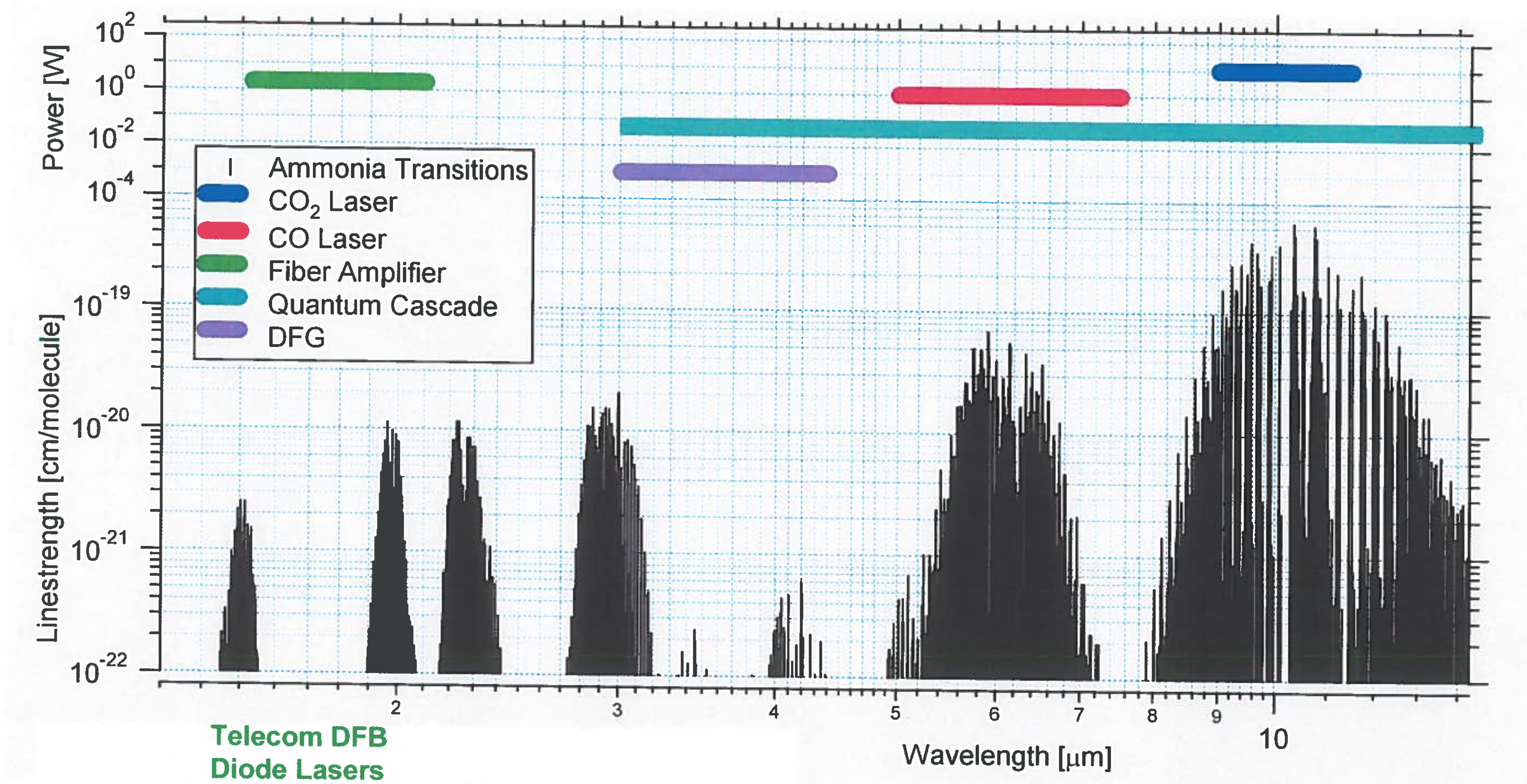
X – Demonstrated

X – Highly expected based on the existing technology level

X – Expected with the technology advance

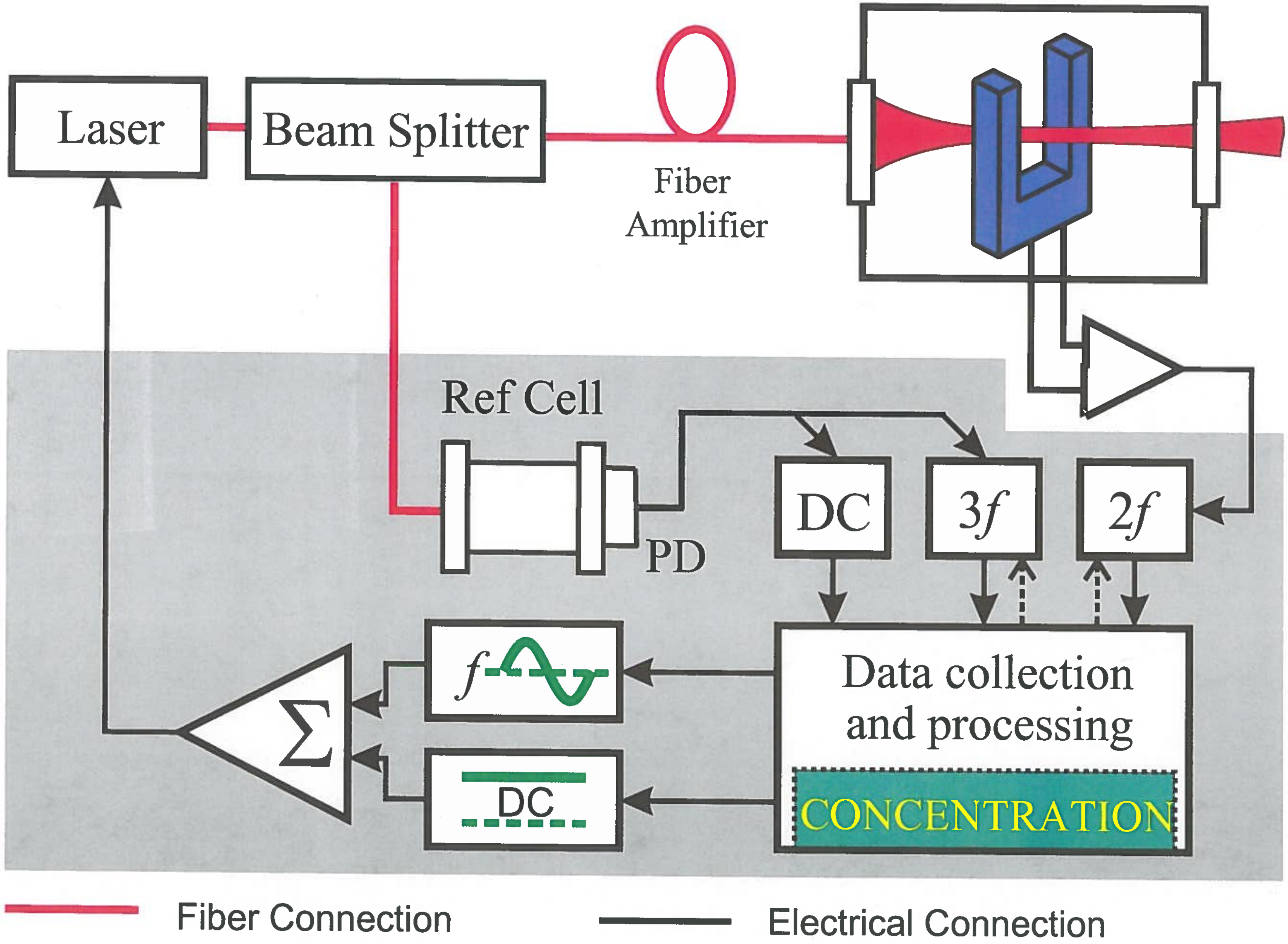
RICE

Infrared NH_3 Absorption Spectra

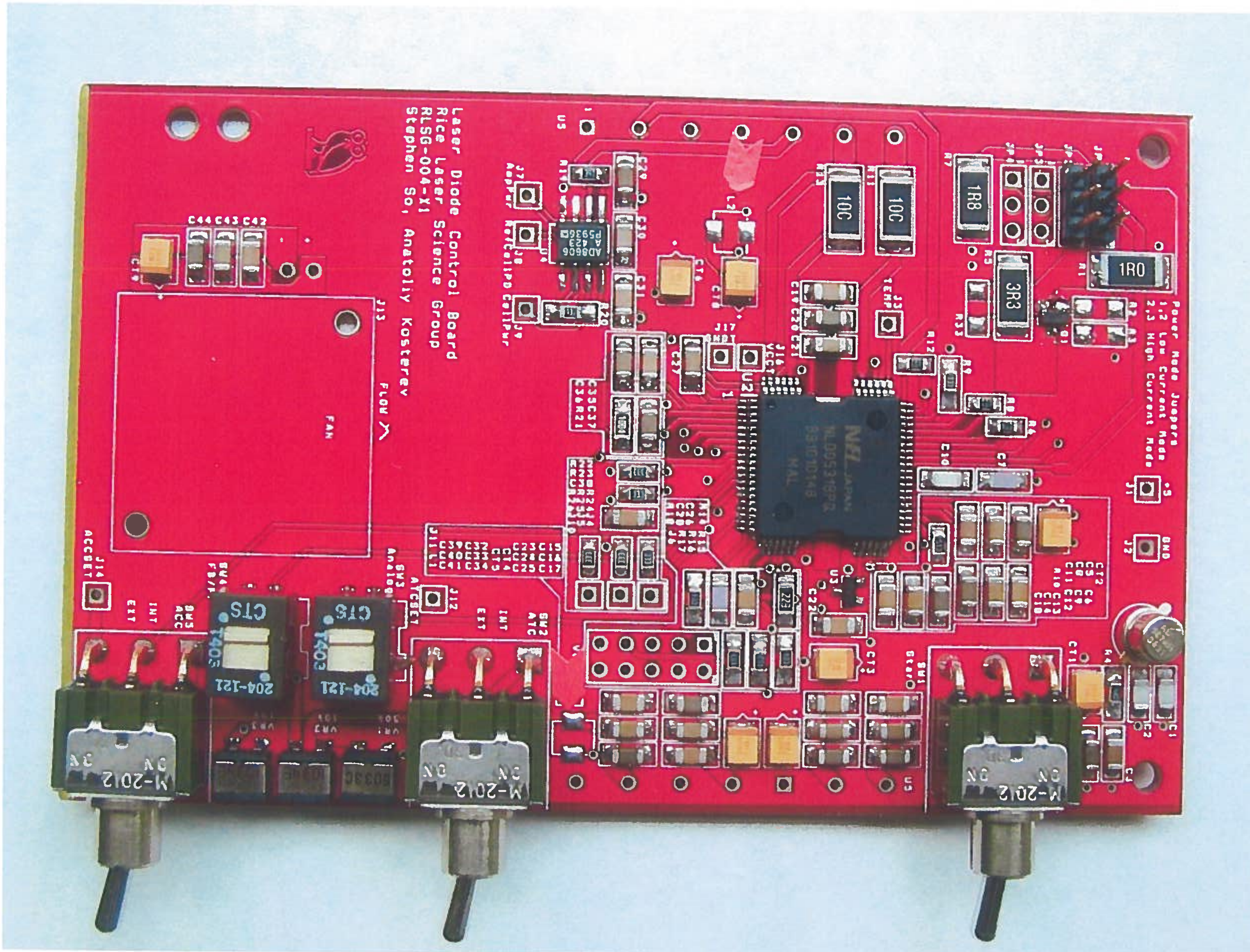


M. Webber et al. 2003, Pranalytica

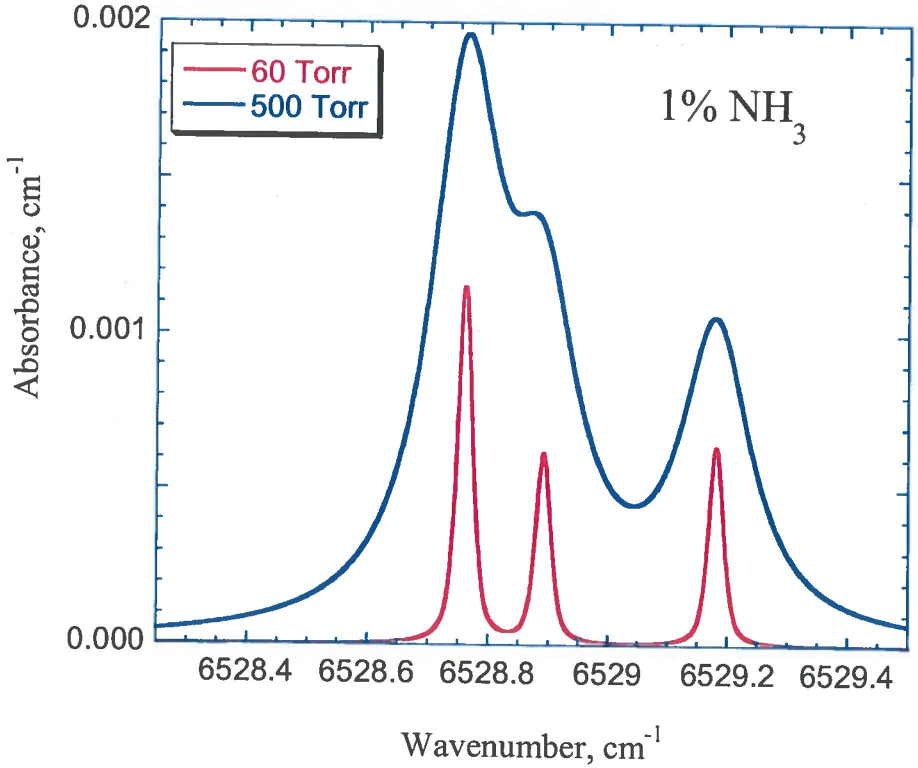
QEPAS fiber based gas sensor architecture



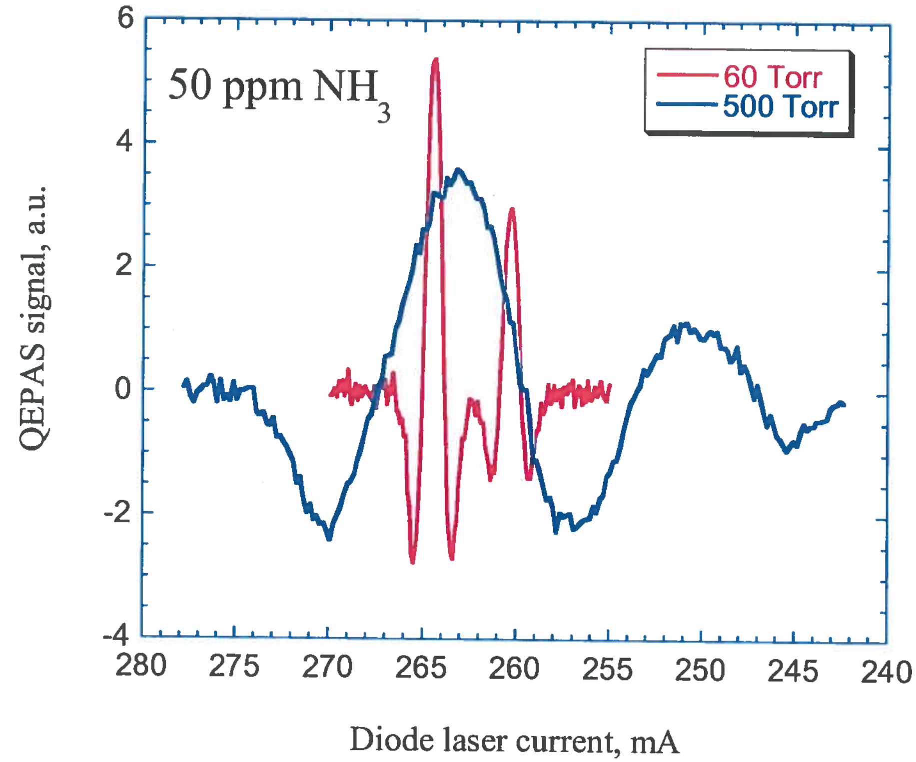
One-chip TEC/DL Driver for Telecom Diode Lasers



Ammonia Detection using a 1.53 μm Telecom Diode Laser



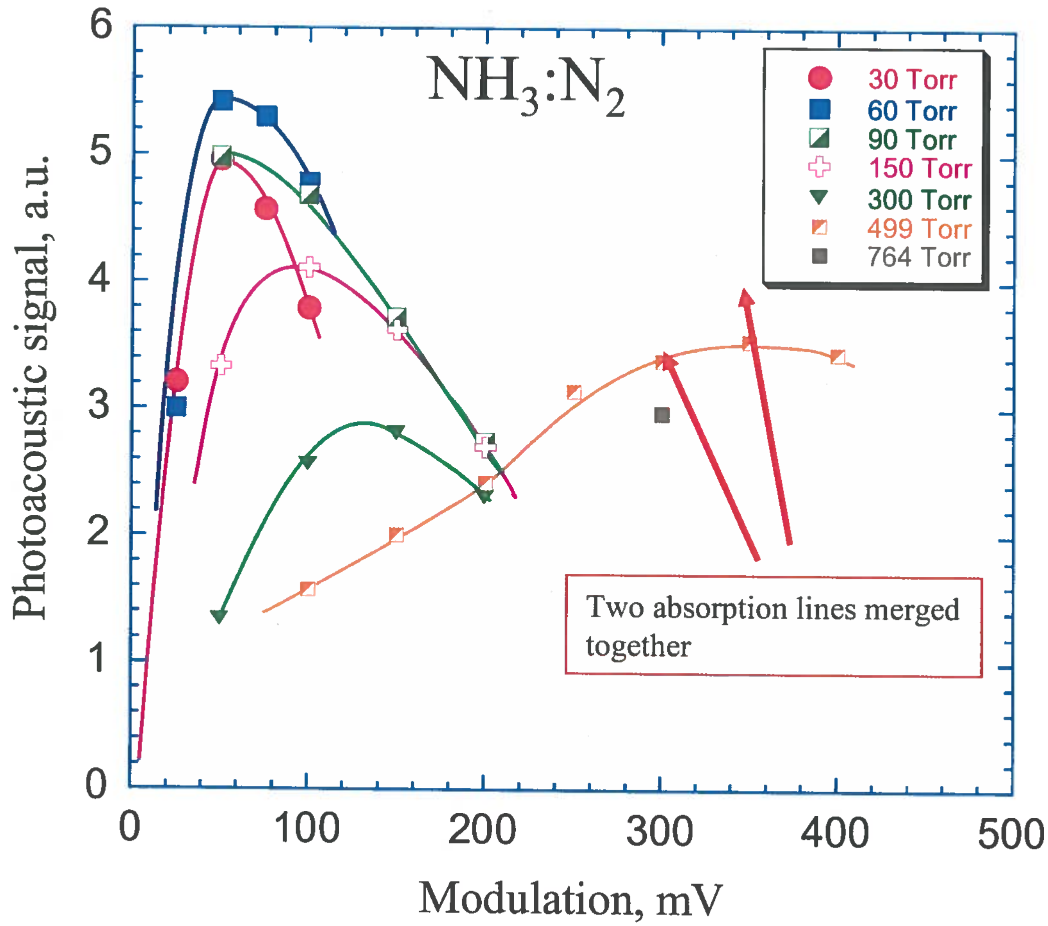
Spectral simulations based on data from Webber et al., APPLIED OPTICS 40, 2031-2042 (2001)]



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

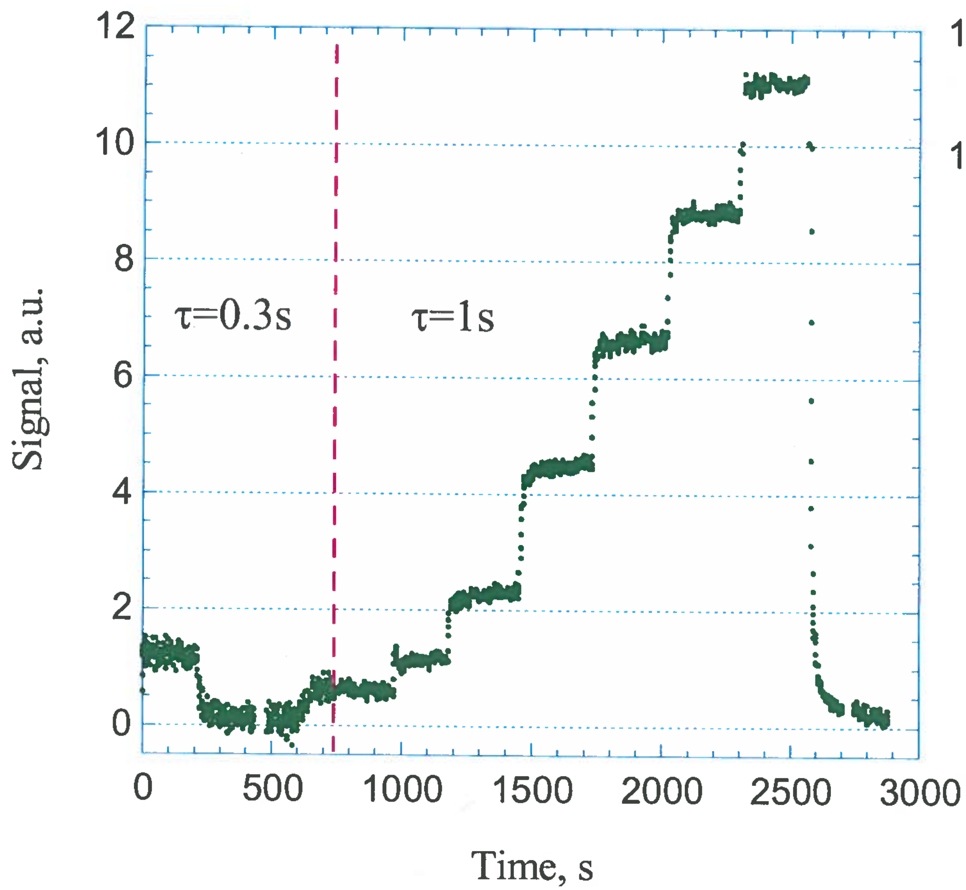
Pressure Dependence of QEPAS Sensitivity

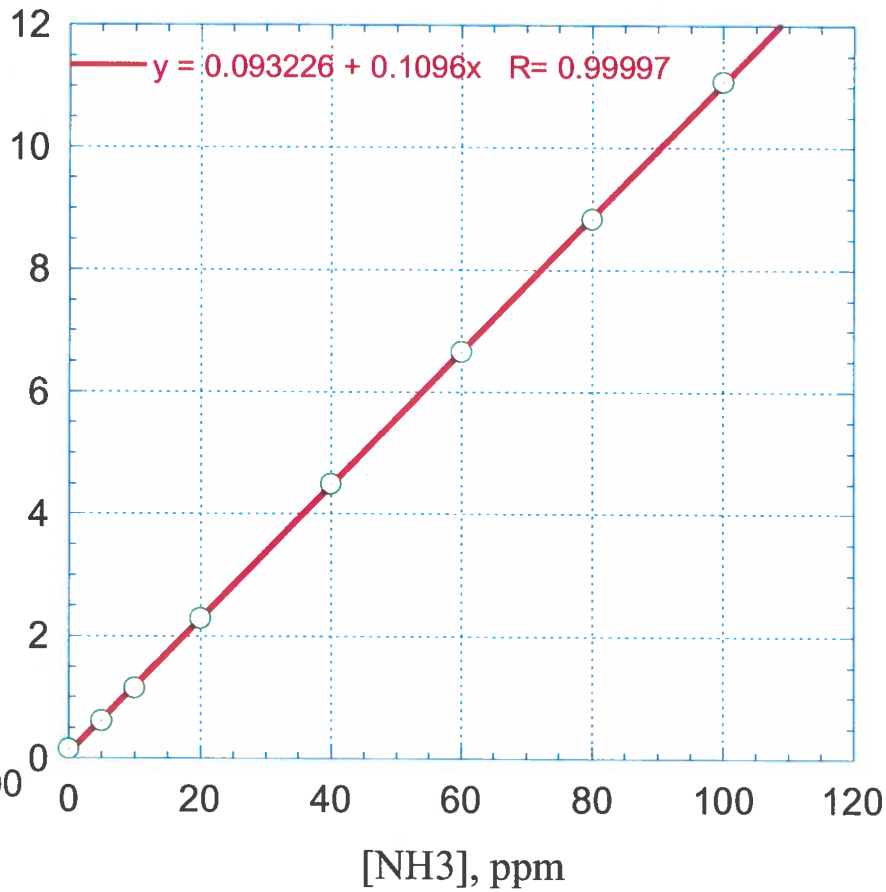


- Peak optical absorption varies with pressure
- Q-factor decreases at higher pressure
- V-T relaxation is faster at higher pressure
- Acoustic resonator enhancement factor changes with pressure

RICE

Calibration and Linearity of QEPAS based NH_3 Sensor





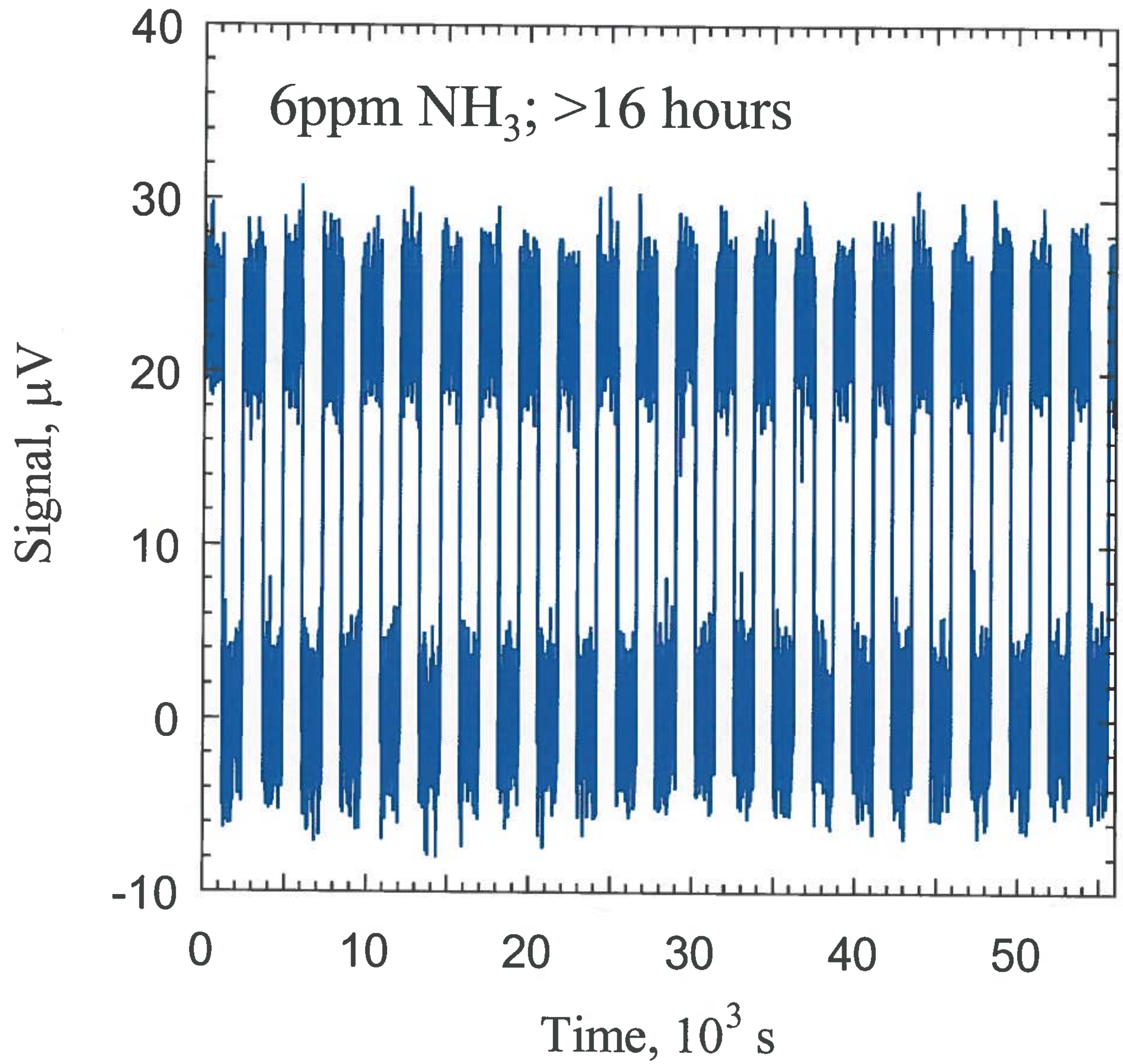
Noise –equivalent (1s) concentration (NEC). for τ=1s time constant is 0.65 ppmv for 38 mW excitation power

90 last points of each step averaged

(Traditional PAS* – 2.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$)
***Webber et al., APPLIED OPTICS 42, 2119, 2003**

To Date Noise-equivalent Absorption (NEA) Coefficient $k=5.4\times10^{-9}$ $cm^{-1}W/Hz^{1/2}$

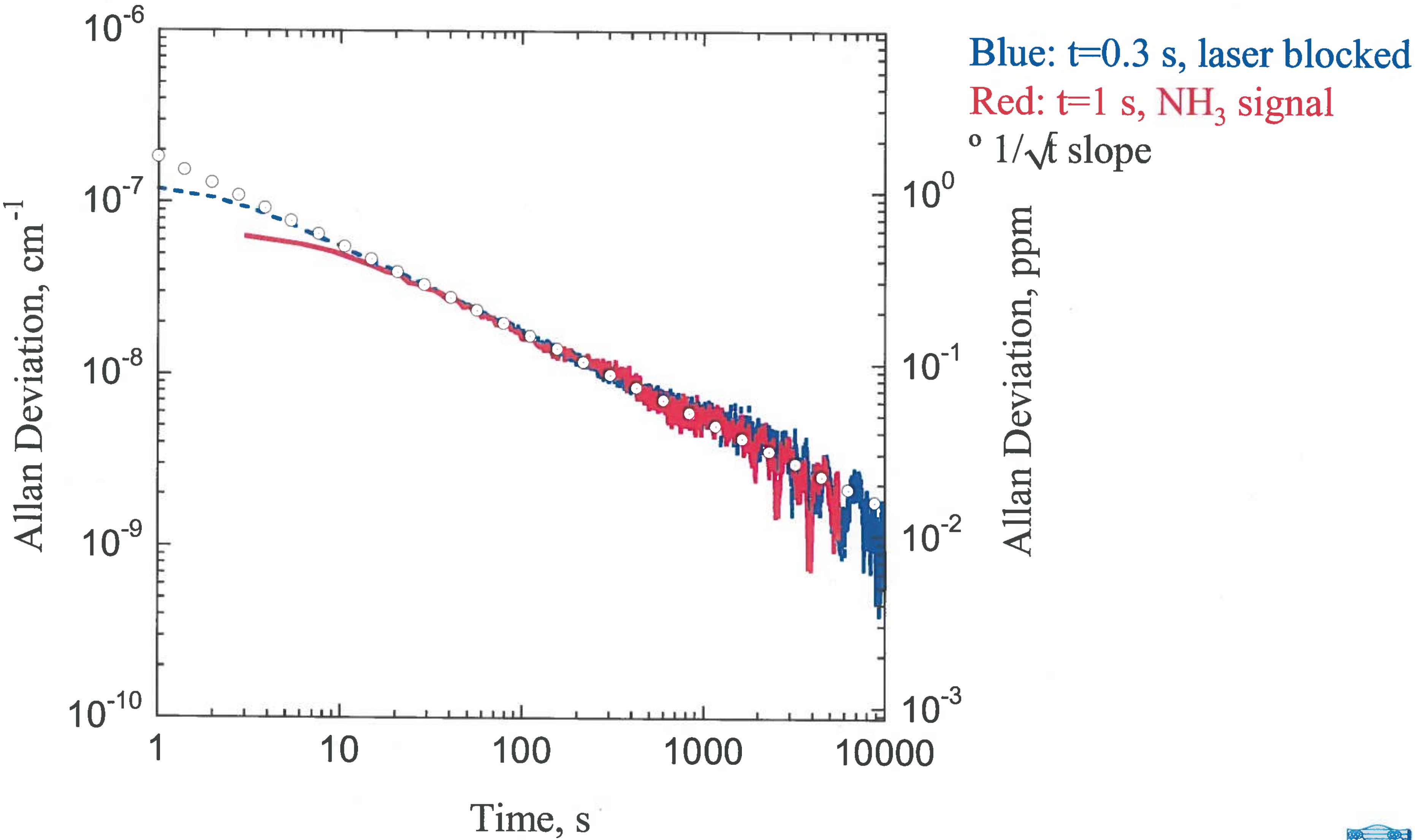
Low-frequency noise study



6528.76 cm^{-1}
38 mW

RICE

Low-frequency noise study (continued)



RICE

Merits of QE Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels); proportional to laser power and excellent dynamic range
- Immune to ambient and flow acoustic noise, laser noise and etalon effects, which allows applications that involve a harsh operating environment
- Required sample volume is very small. The volume is ultimately limited by the gap size between the TF prongs, which is 0.34 mm^3 for the presently used QTF.
- No spectrally selective elements
- Applicable over a wide range of pressures, including atmospheric pressure
- Temperature, pressure and humidity insensitive
- Finite time of the energy transfer rate from vibrational to translational degrees of freedom strongly influences amplitude and phase of the photoacoustic response, and hence the sensitivity of photoacoustic gas sensing.
- 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

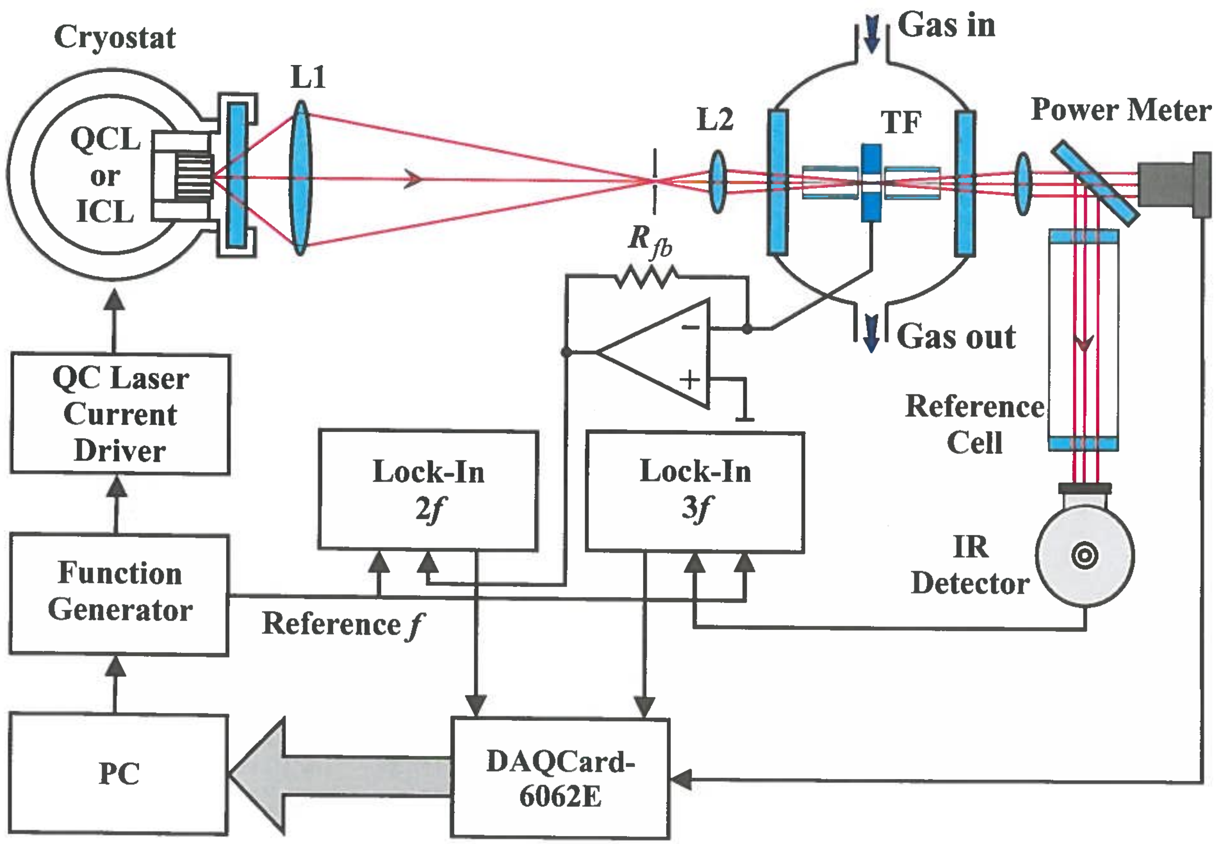
RICE

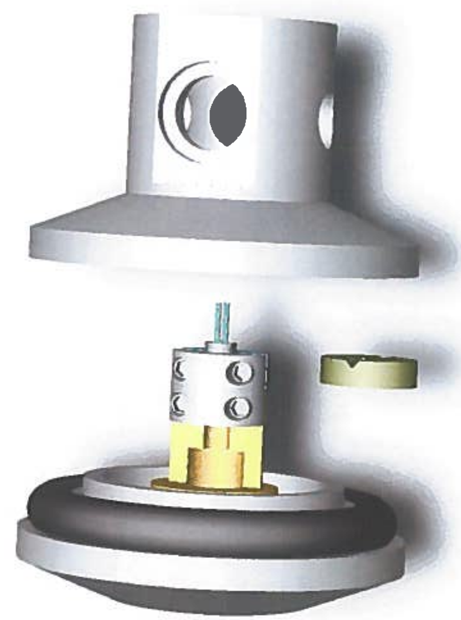
Motivation for Precision Monitoring of H_2CO

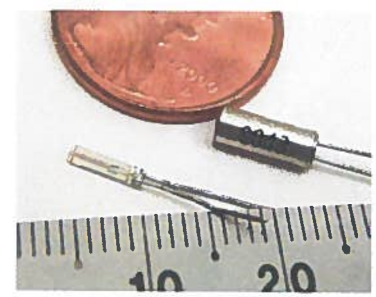
- Precursor to atmospheric O_3 production
- Pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products
- Medically important gas

RICE

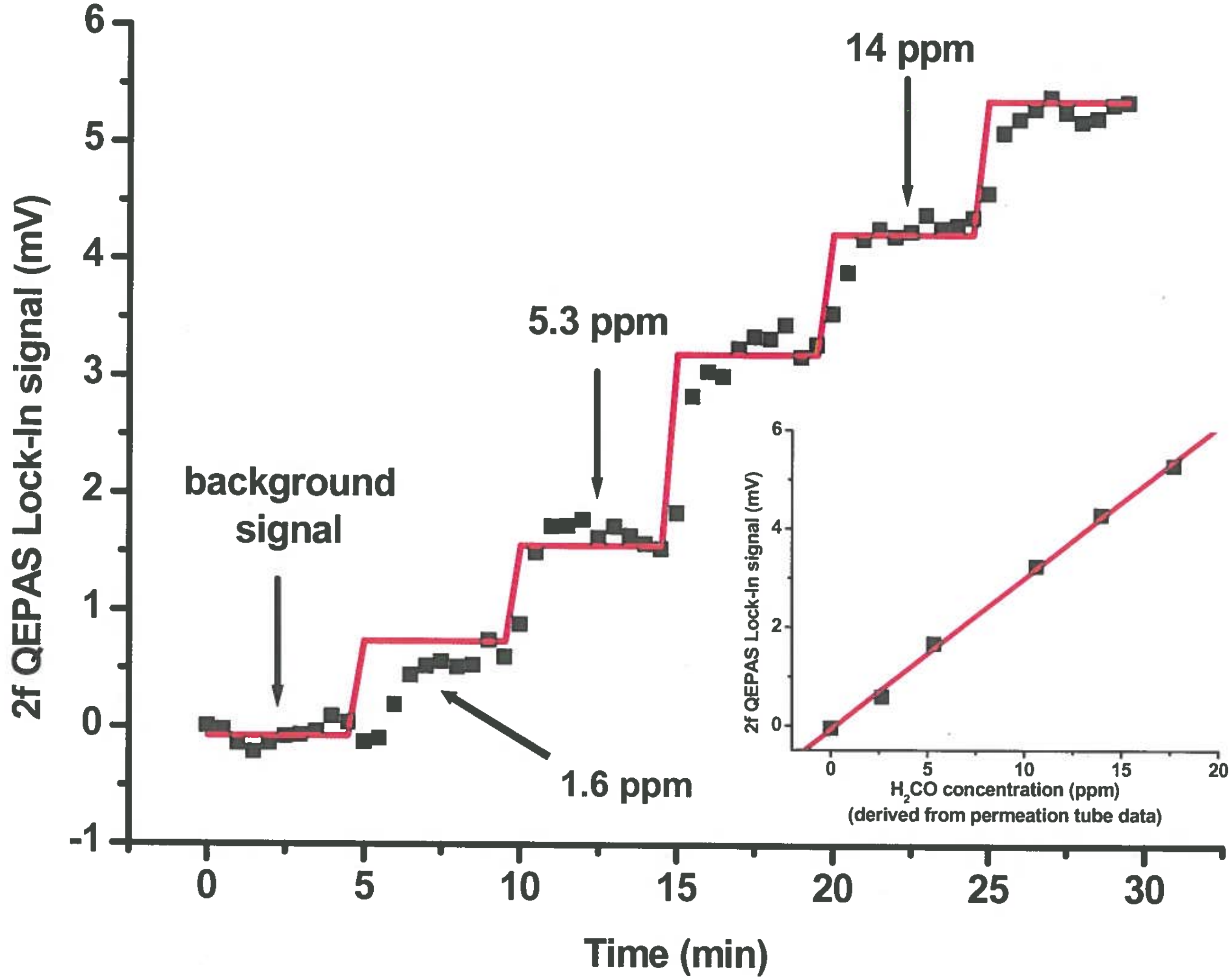
QCL based Quartz-Enhanced Photoacoustic Sensor







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
- **NNEA: 2.2×10^{-8}cm^{-1} W/√Hz**
- **NEC is 550 ppbv**
- **Recently MDC is 175 ppbv (3 sec) & NNEA is 4.6×10^{-9}cm^{-1} W/√Hz**

QEPAS Performance for 7 Trace Gas Species (June '05)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	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	100	4.6×10^{-9}	4.9	0.28

* - Improved microresonator

** - Improved microresonator and double optical pass through QTF

NNEA – normalized noise equivalent absorption coefficient.

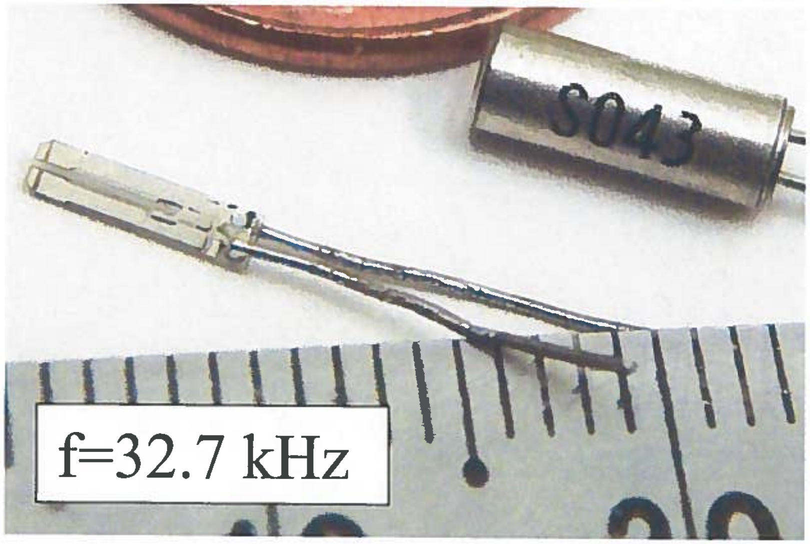
NEC – noise equivalent concentration for available laser power and τ=1s time constant.

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)

RICE

Improvement II (in progress): a better TF



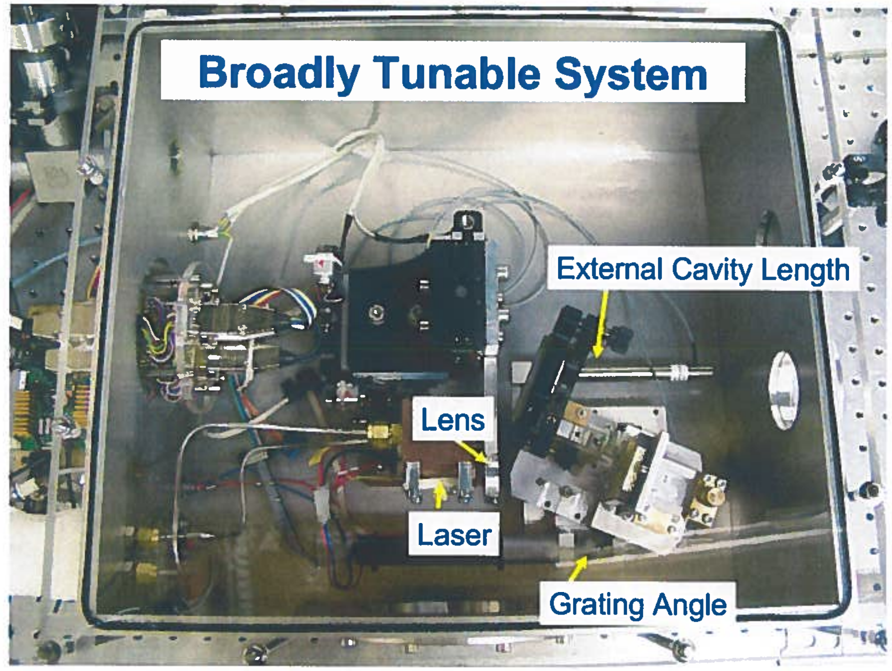
Custom
5-10 kHz TFs

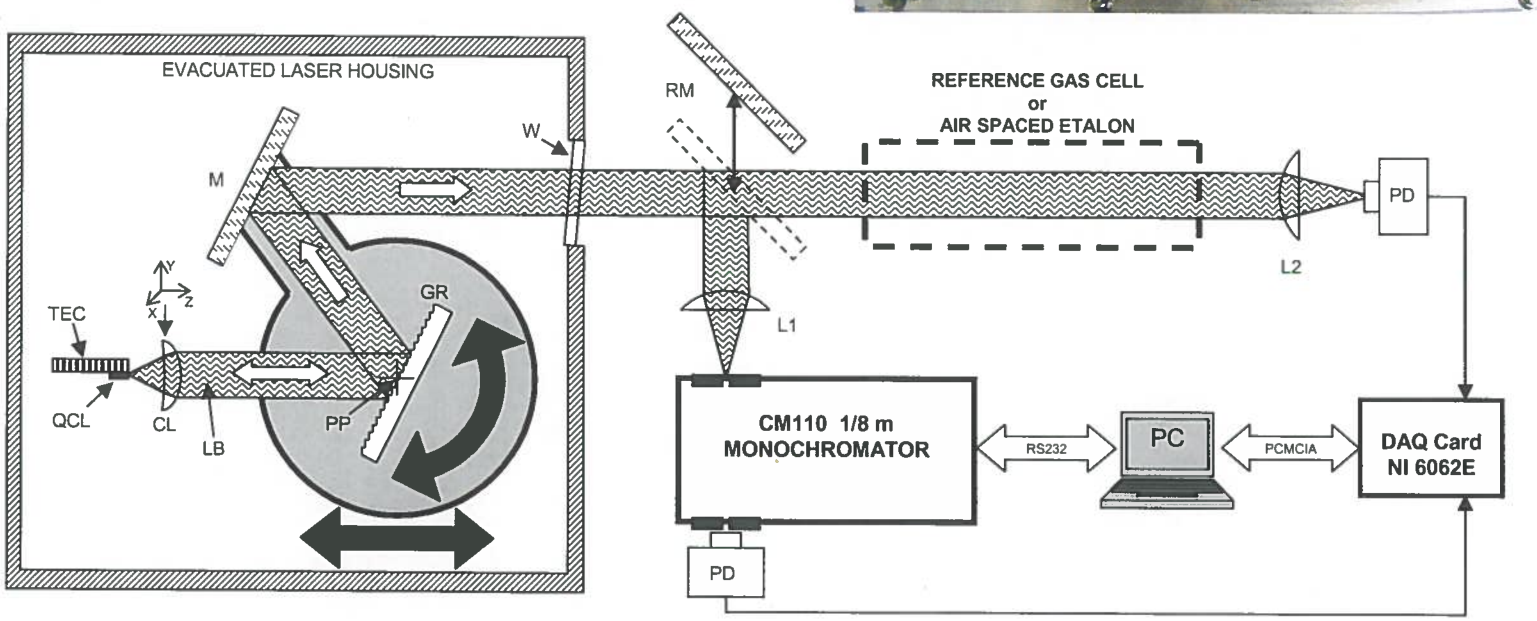
RICE

Tunable External Cavity QCL System

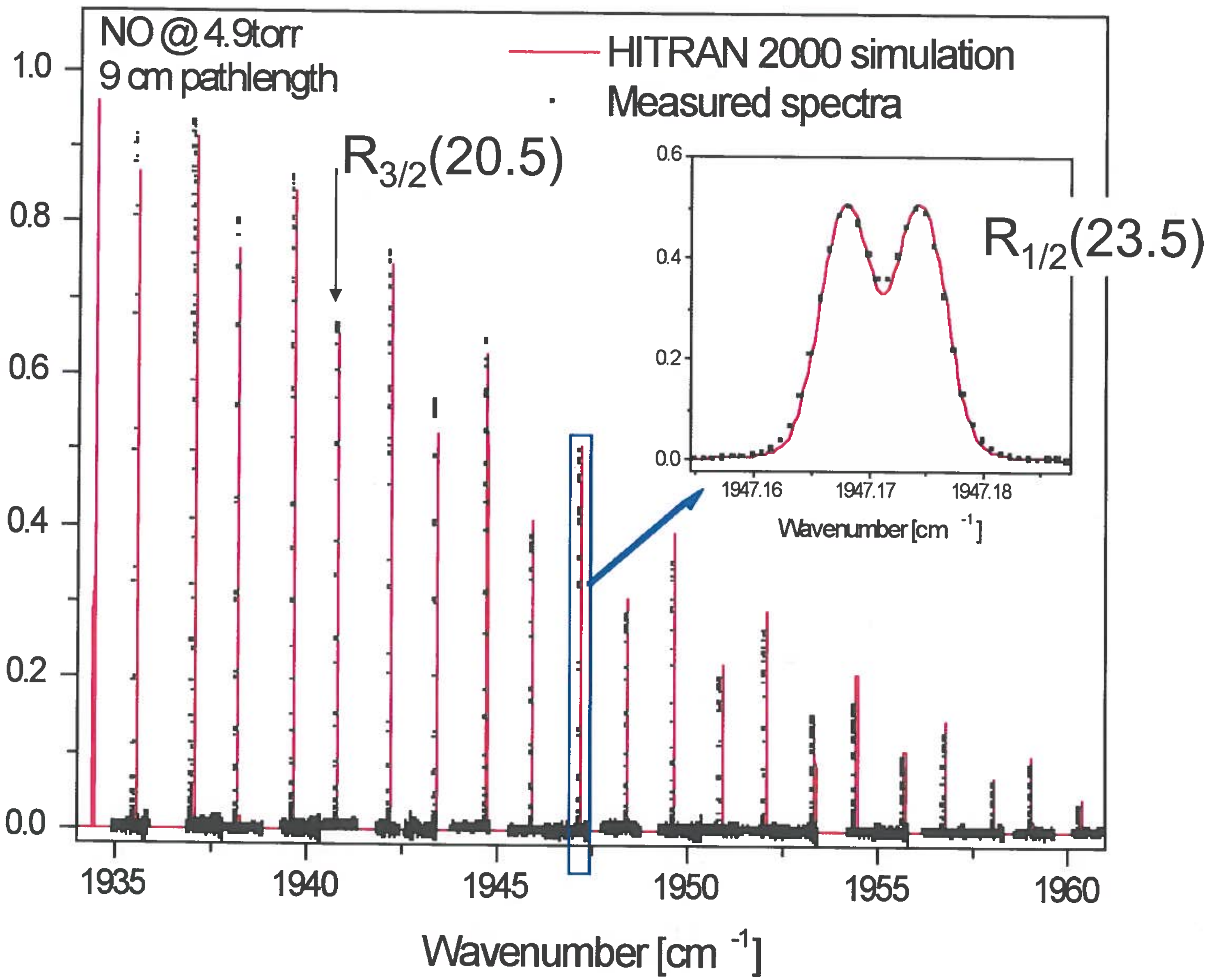
QCL – quantum cascade laser
TEC – thermoelectric cooler
CL – collimating lens (1" diameter, f/0.6, Ge AR-coated 3-12 μm) mounted on a motorized 3D translation stage
LB – laser beam
GR – diffraction grating (150 gr/mm blazed for 5.4μm)
PP – pivot point of the rotational movement
M – mirror (mounted on 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

Coupled cavities:
Laser Chip ~ 15 GHz, External Cavity ~ 1.5 GHz





Wide Scan NO Spectrum



Conclusions and Future Directions

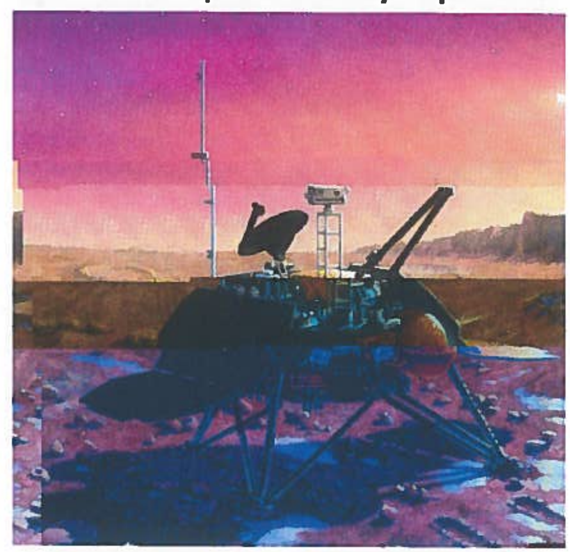
- **Laser based Trace Gas Sensors**
  - Ultra compact (~ 0.2 mm^3), robust & low cost sensors based on QE L-PAS
  - QEL-PAS is immune to ambient noise. The measured noise level coincides with the thermal noise of the QTF
  - Best to date demonstrated QEPAS sensitivity is 2.1 x 10^{-9} $cm^{-1}W/\sqrt{Hz}$ for H_2O:N_2
  - QEPAS exhibits a low 1/*f* noise level, allowing data averaging for more than 3 hours
  - Detected 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, 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 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

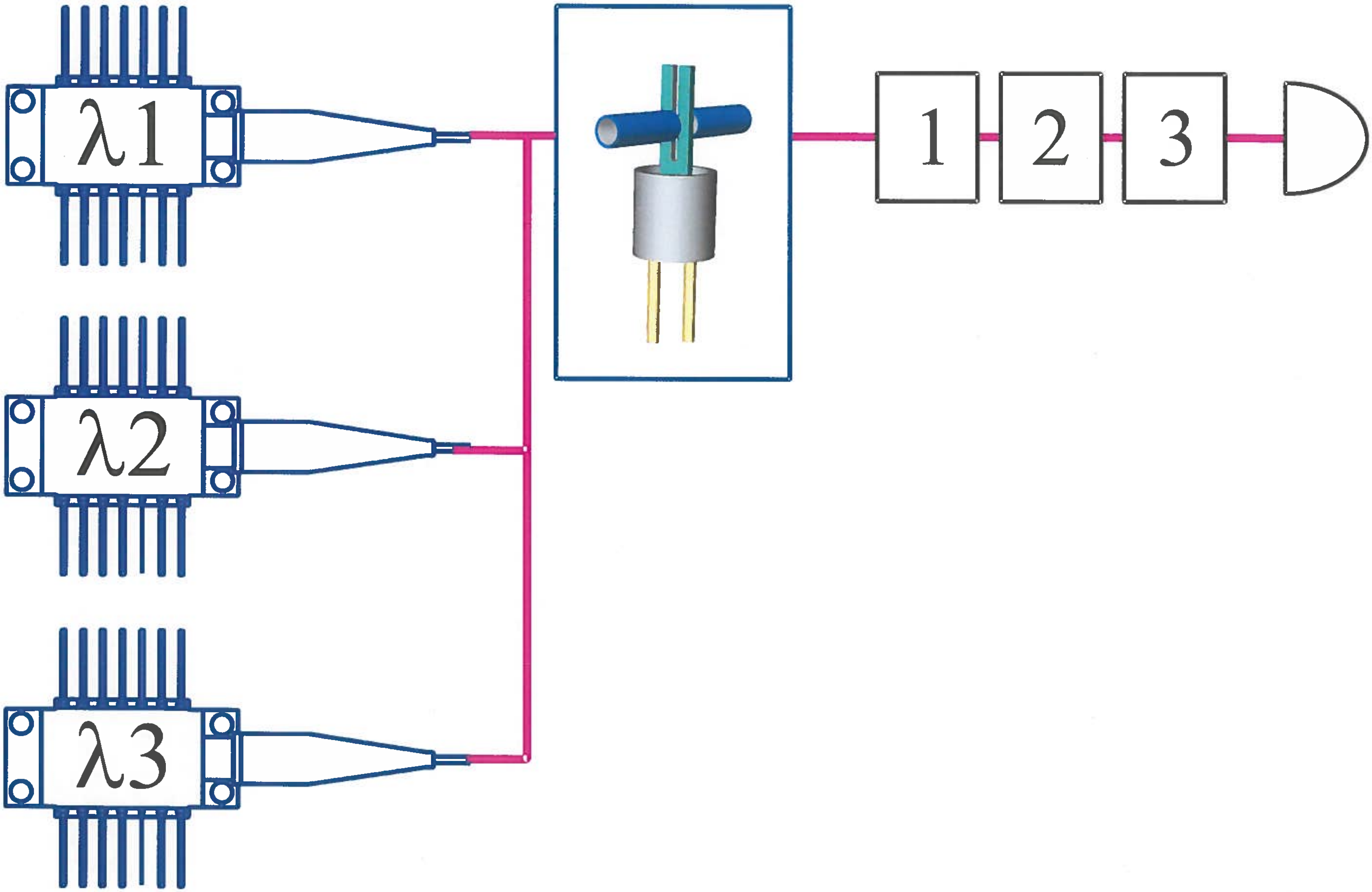
Tunable laser sensors for earth's stratosphere

Aircraft laser absorption spectrometers

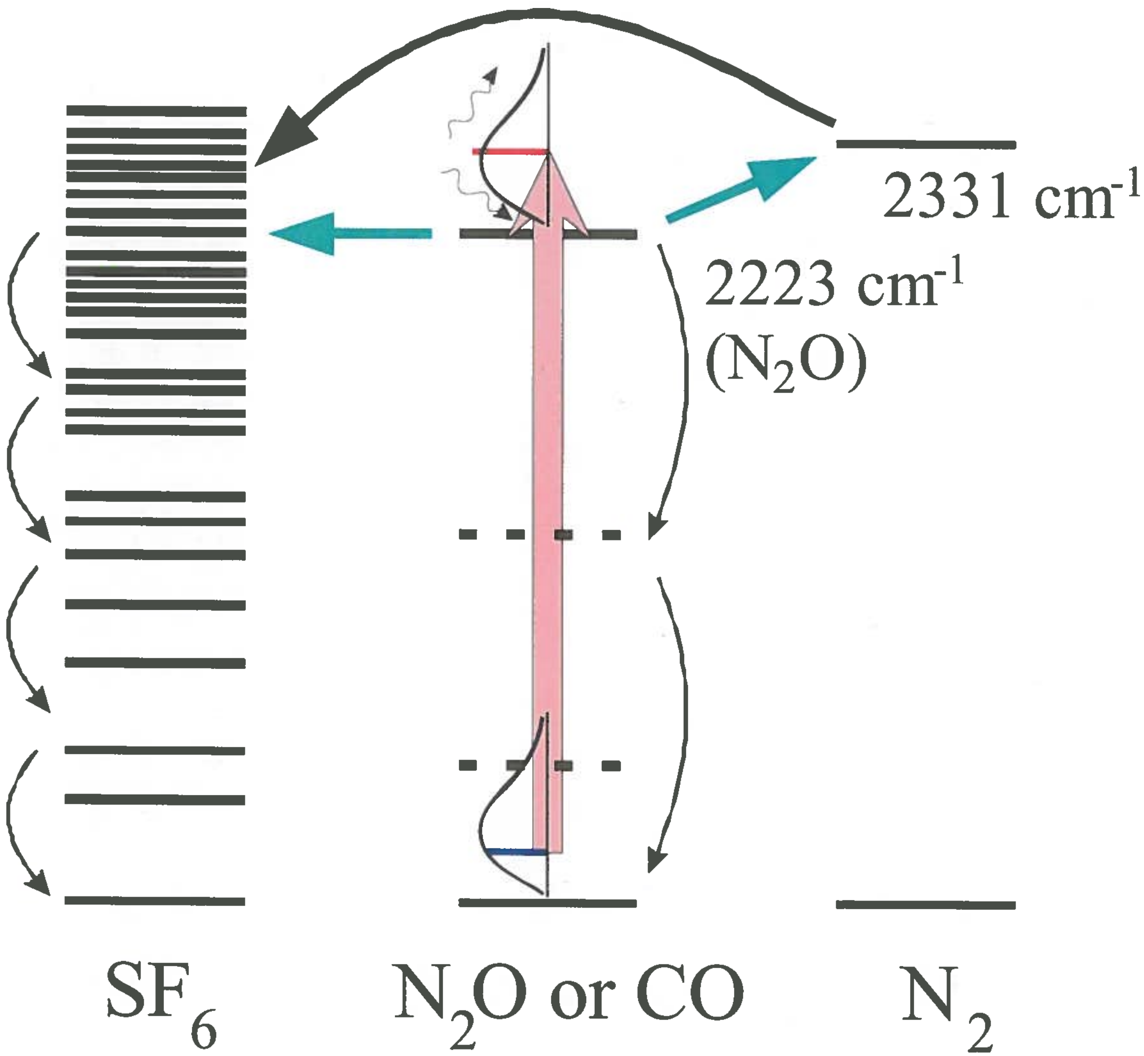
Tunable laser planetary spectrometer



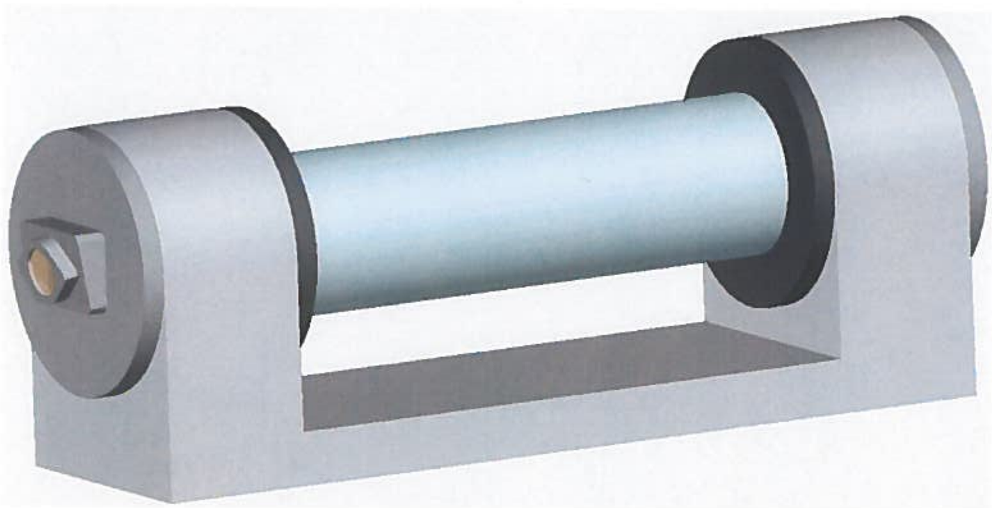
QEPAS Architecture Flexibility: Optical Multiplexing

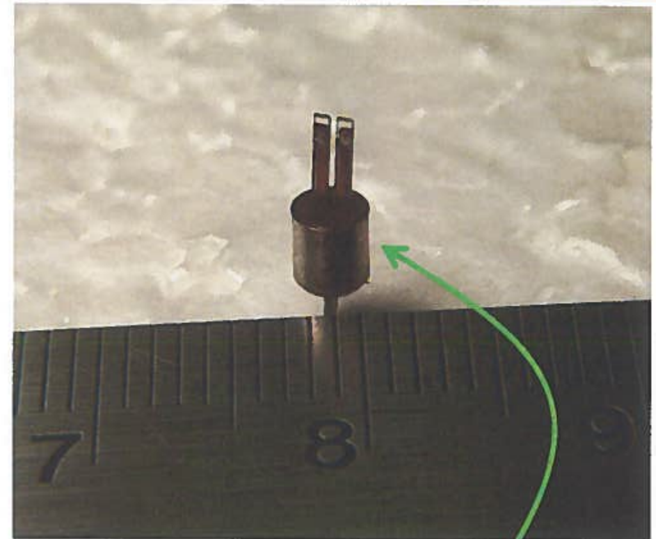


Relaxation pathways following optical excitation

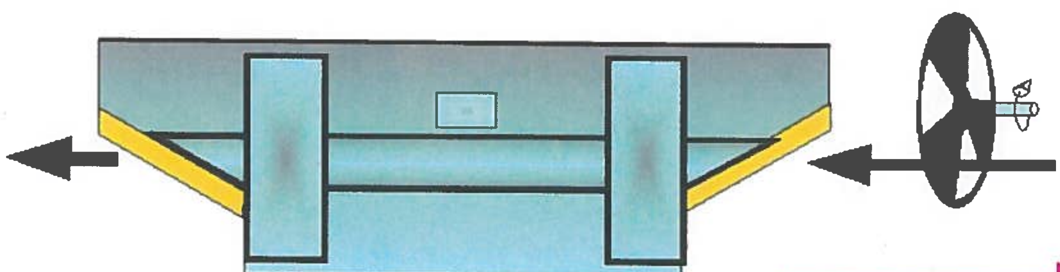


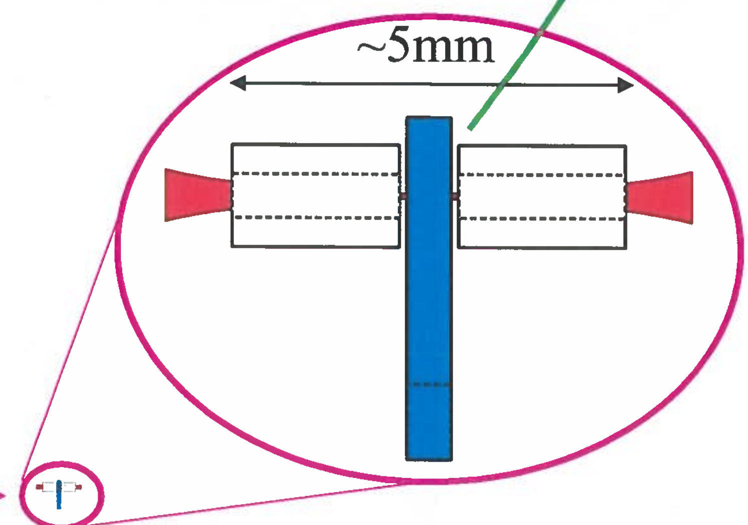
Comparative Size of Absorbance Detection Modules (ADM)





Optical multipass cell (100 m):
l~70 cm, V~3000 cm^3

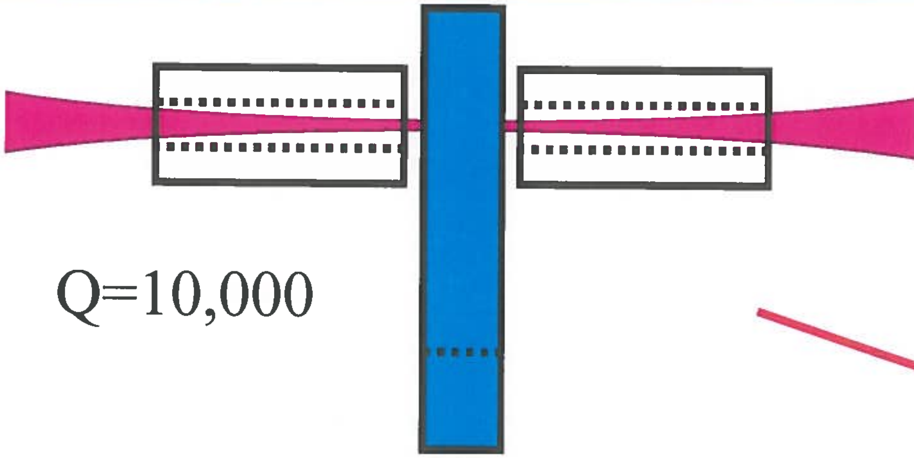




Resonant photoacoustic cell (1000 Hz):
l~60 cm, V~50 cm^3

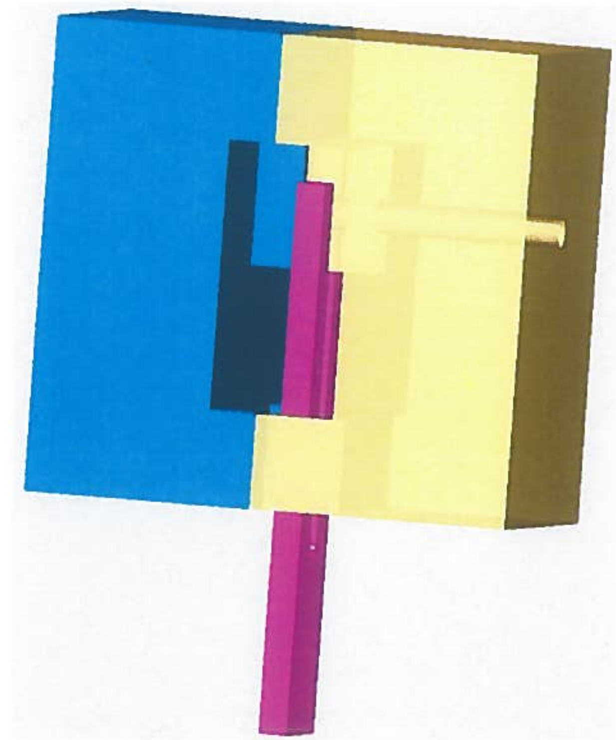
QEPAS ADM:
l~0.5 cm, V~0.05 cm^3

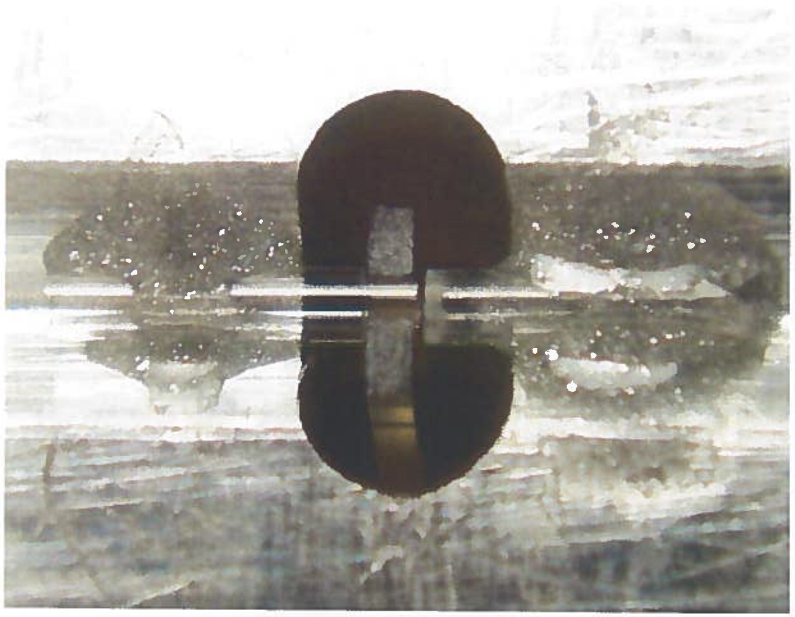
Improvements I (in progress): a better Micro-resonator



Q=10,000

Q=5,100
Gain ×1.3





Q=6 600
Gain ×1.5

RICE

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

Representative Trace Gas Detection Limits

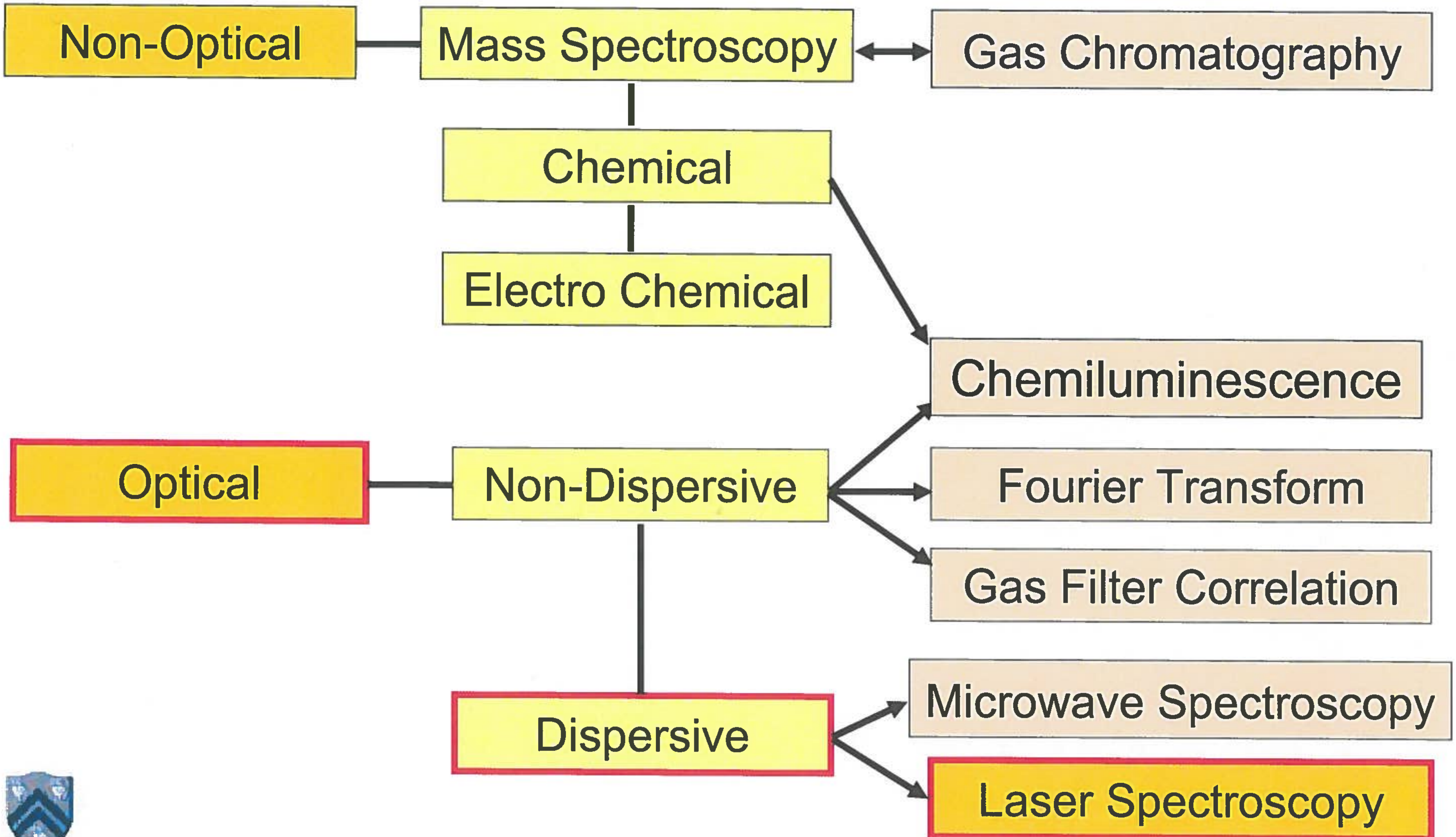
Species	cm^{-1}	Precision 1 s RMS (ppt)	LOD 100 s (ppt)
NH_3	967	50	20
NO_2	1600	80	40
HONO	1700	200	80
CO	2190	120	50
N_2O	2240	100	50
HNO_3	1720	200	80
O_3	1050	500	200
NO	1905	200	100
CH_4	1270	400	200
SO_2	1370	310	120
C_2H_4	960	360	140
HCHO	1765	350	100
H_2O_2	1267	1000	400

Limit of Detection (LOD) for S/N = 2

Pathlength: 210 m

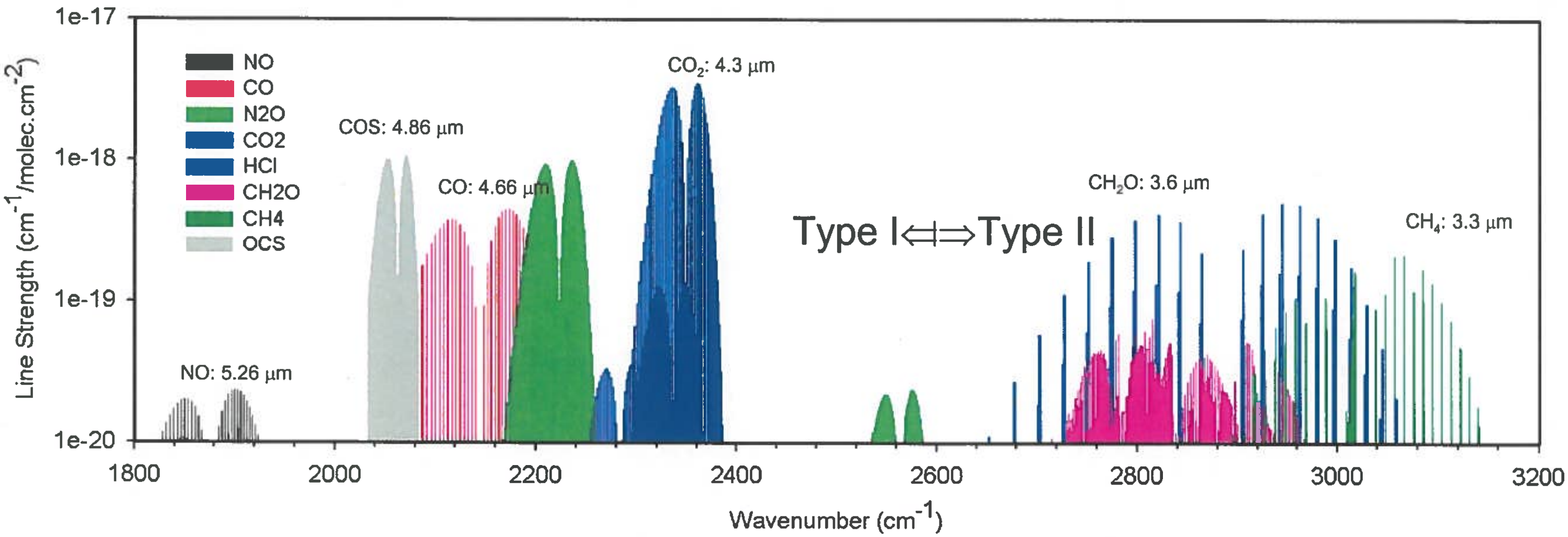
Mark S. Zahniser, SIRIS 2004, September 2004

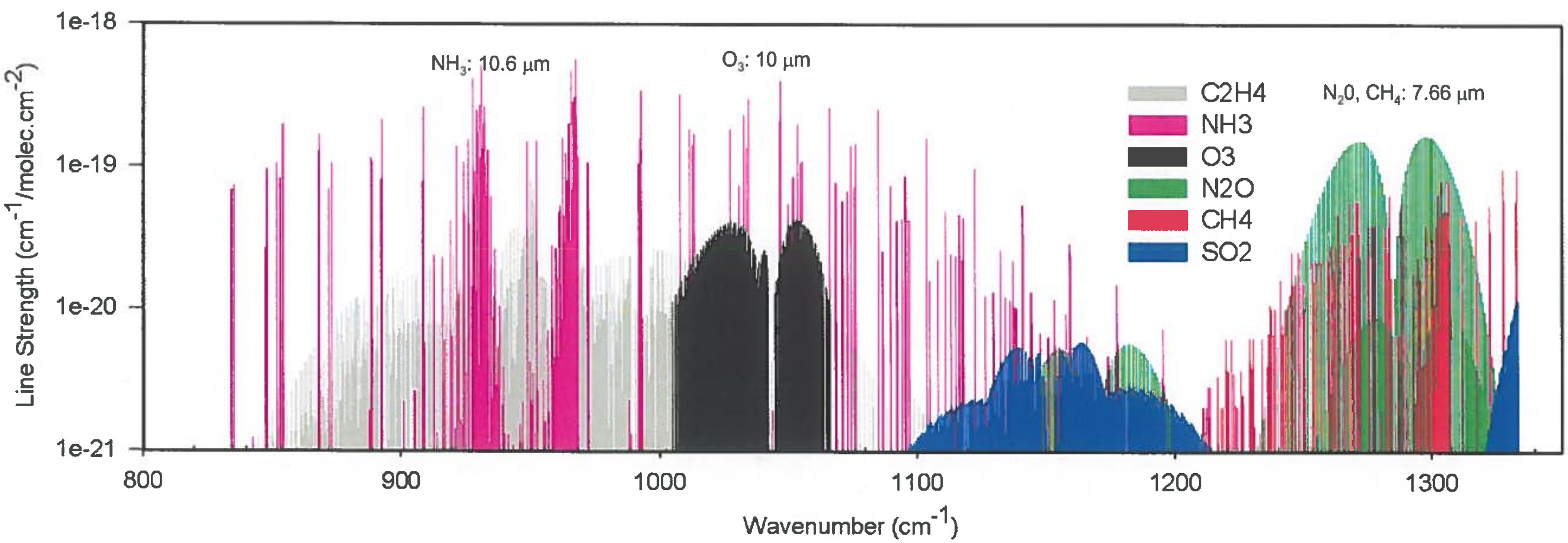
Existing Methods for Trace Gas Detection



RICE

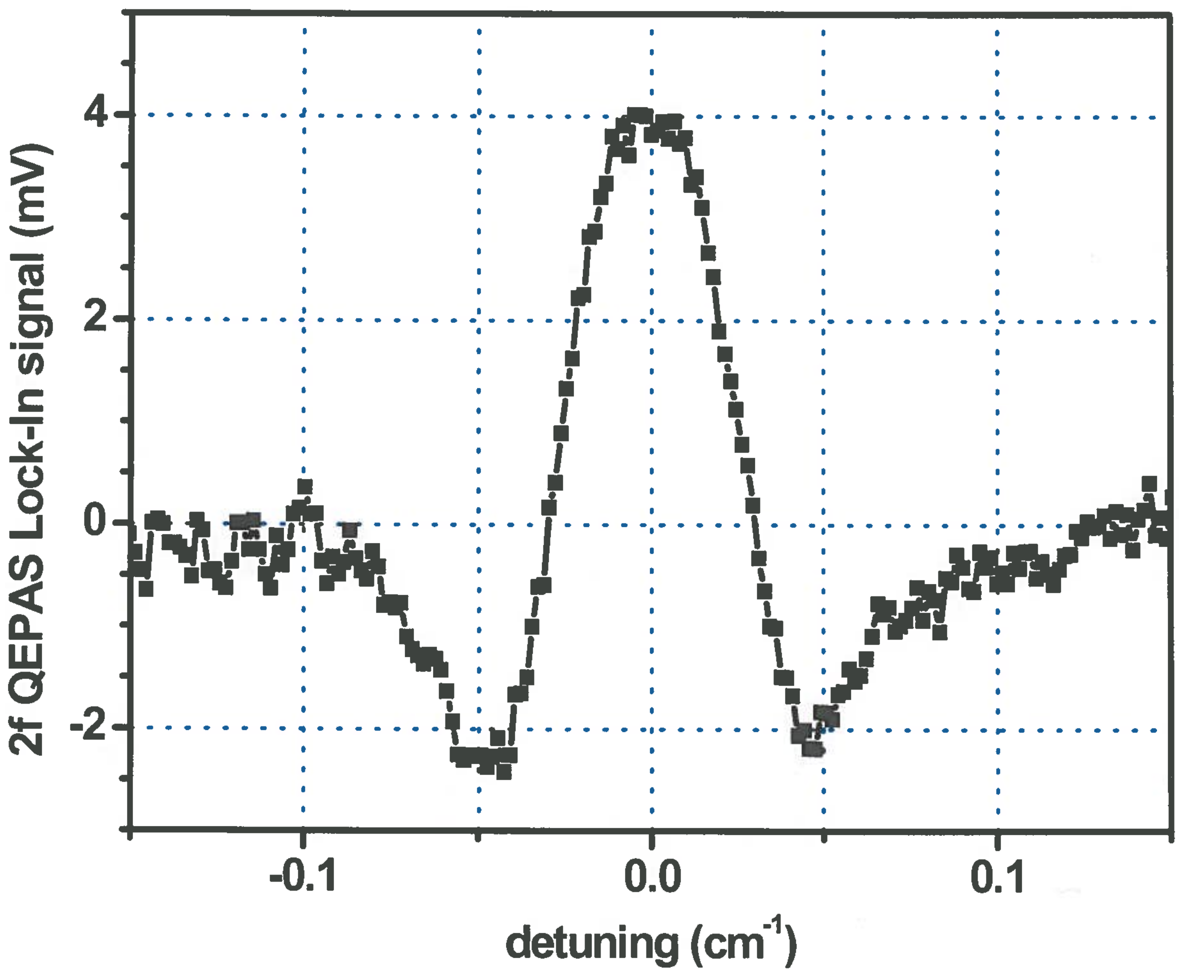
HITRAN Simulation of Absorption Spectra (3.1-5.5 & 7.6-12.5 μm)





RICE

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



- [H_2CO]: 13.27 ppm
- **QEPAS NNEA Sensitivity:** $2.2\times10^{-8}cm^{-1}$ W/√Hz;
- **4.6×10^{-9} cm^{-1} W/√Hz** as of June 10, 2005

For comparison:
QEPAS Sensitivity for NH_3 :
$5.4\times10^{-9}cm^{-1}$W/ √ Hz

Applied Physics 2004