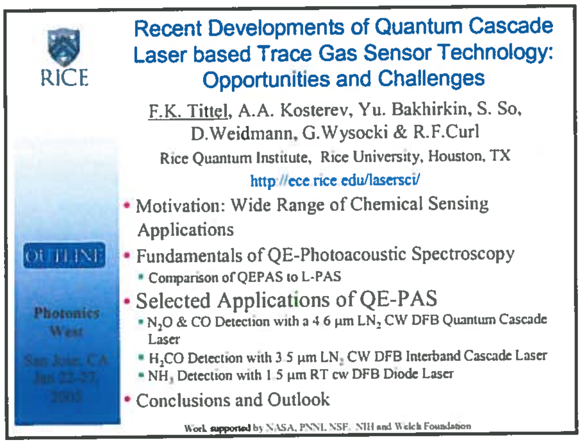
Photonics West



Recent Developments of Quantum Cascade Laser based Trace Gas Sensor Technology: Opportunities and Challenges

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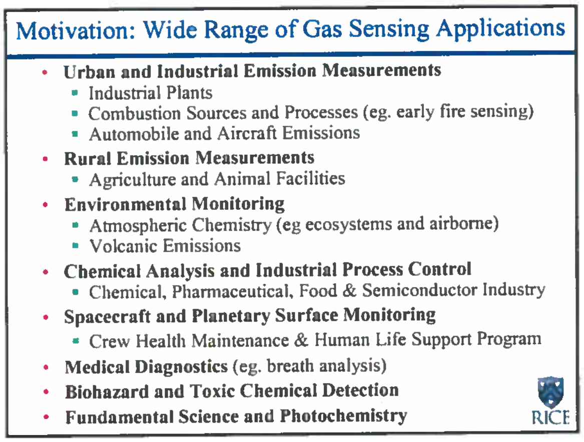
OUTLINE

Photonics West
San Jose, CA
Jan 22-27
2005

- Motivation: Wide Range of Chemical Sensing Applications
- Fundamentals of QE-Photoacoustic Spectroscopy
  - Comparison of QEPAS to L-PAS
- Selected Applications of QE-PAS
  - N_2O & CO Detection with a 4.6 μm LN_2 CW DFB Quantum Cascade Laser
  - H_2CO Detection with 3.5 μm LN_2 CW DFB Interband Cascade Laser
  - NH_3 Detection with 1.5 μm RT cw DFB Diode 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 sensing)
  - 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
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Human Life Support Program
- **Medical Diagnostics** (eg. breath analysis)
- **Biohazard and Toxic Chemical Detection**
- **Fundamental Science and Photochemistry**

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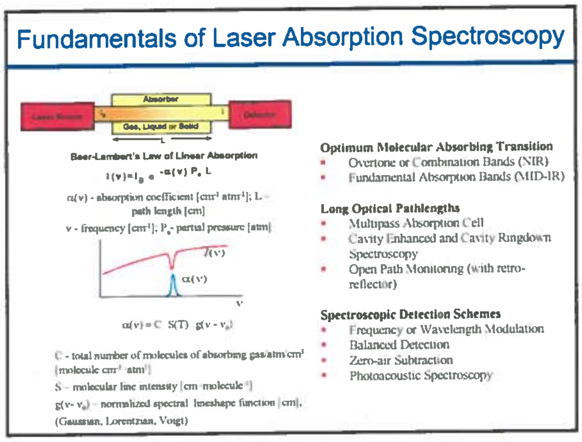


Fundamentals of Laser Absorption Spectroscopy

Beer-Lambert's Law of Linear Absorption

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

α(ν) - 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 $cm^{-3}\,atm^{-1}$]

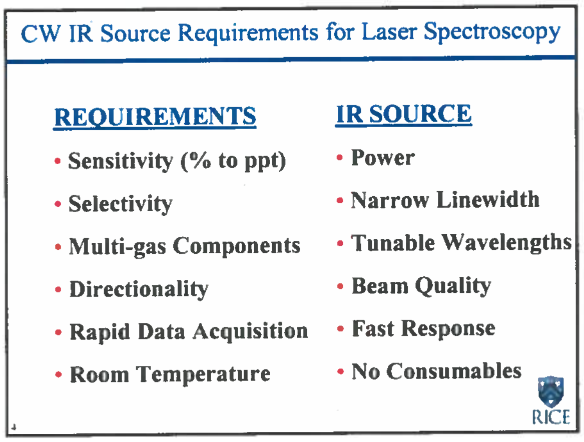
S – molecular line intensity [cm/molecule^{-1}]

g(ν- ν_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



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**

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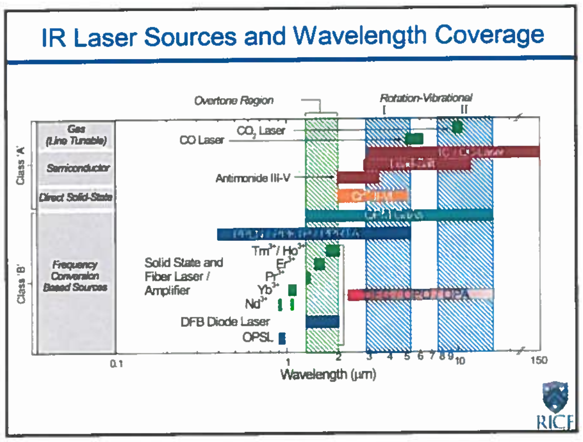

IR Laser Sources and Wavelength Coverage

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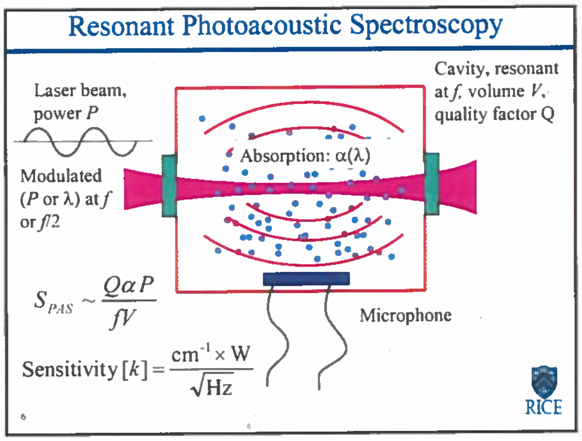

Resonant Photoacoustic Spectroscopy

$$S_{PAS} \sim \frac{Q\alpha P}{fV}$$

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

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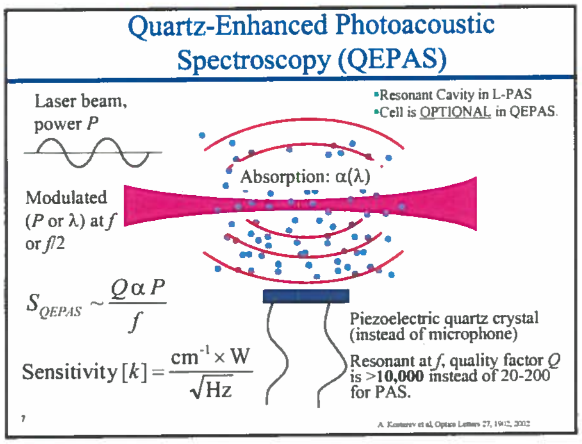

Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)

- Resonant Cavity in L-PAS
- Cell is <u>OPTIONAL</u> in QEPAS.

Laser beam, power *P*

Modulated (*P* or λ) at *f* or *f*/2

Absorption: $\alpha(\lambda)$

$$S_{QEPAS} \sim \frac{Q\alpha P}{f}$$

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

Piezoelectric quartz crystal (instead of microphone)

Resonant at *f*, quality factor *Q* is >**10,000** instead of 20-200 for PAS.

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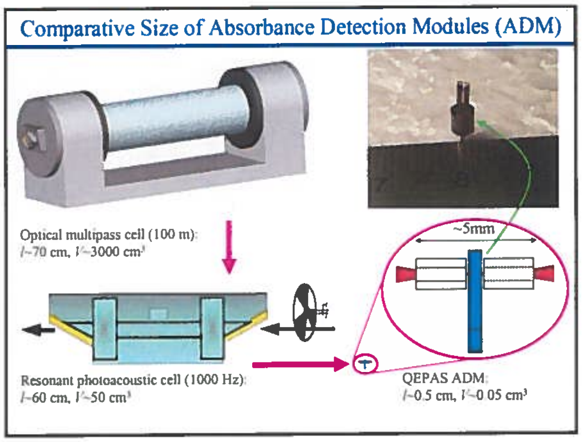
A. Kosterev et al, Optics Letters 27, 1902, 2002

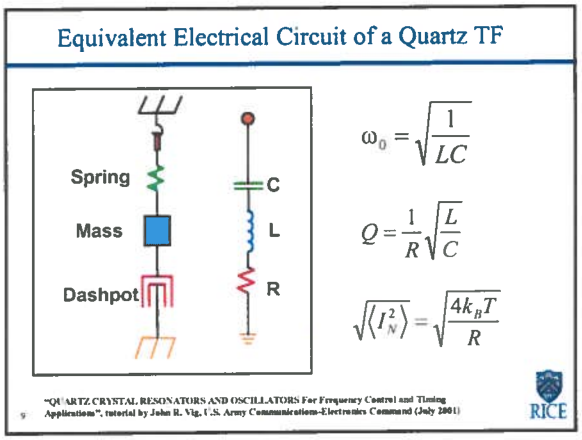


Comparative Size of Absorbance Detection Modules (ADM)

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



Equivalent Electrical Circuit of a Quartz TF

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

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

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

"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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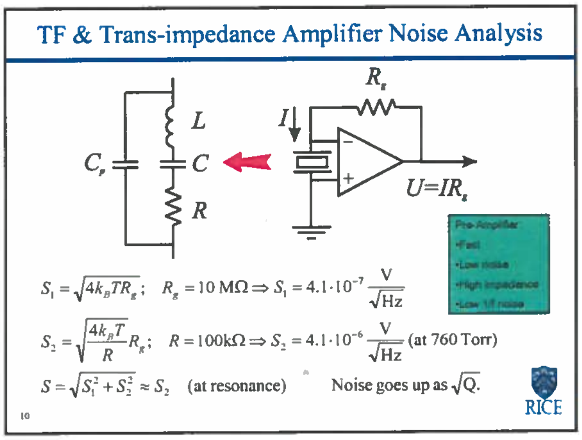

TF & Trans-impedance Amplifier Noise Analysis

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

$$S_1 = \sqrt{4k_BTR_g};\quad R_g = 10\,\text{M}\Omega \Rightarrow S_1 = 4.1\cdot10^{-7}\frac{\text{V}}{\sqrt{\text{Hz}}}$$

$$S_2 = \sqrt{\frac{4k_BT}{R}}R_g;\quad R = 100\text{k}\Omega \Rightarrow S_2 = 4.1\cdot10^{-6}\frac{\text{V}}{\sqrt{\text{Hz}}}\ \text{(at 760 Torr)}$$

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

Noise goes up as $\sqrt{\text{Q}}$.

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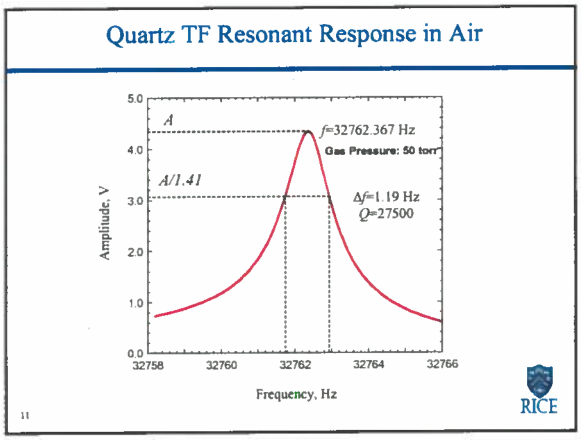

Quartz TF Resonant Response in Air

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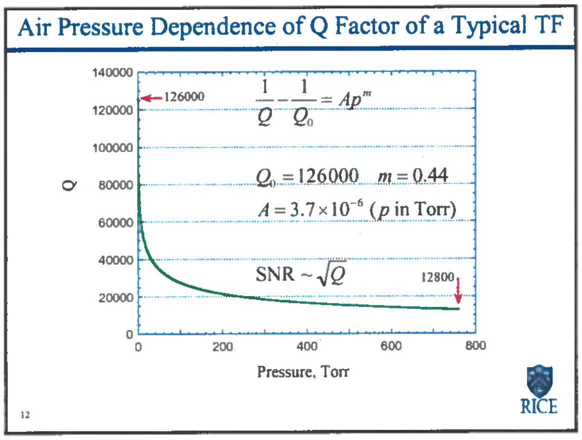

Air Pressure Dependence of Q Factor of a Typical TF

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

$Q_0 = 126000 \quad m = 0.44$

$A = 3.7\times10^{-6}$ (*p* in Torr)

SNR ~ $\sqrt{Q}$

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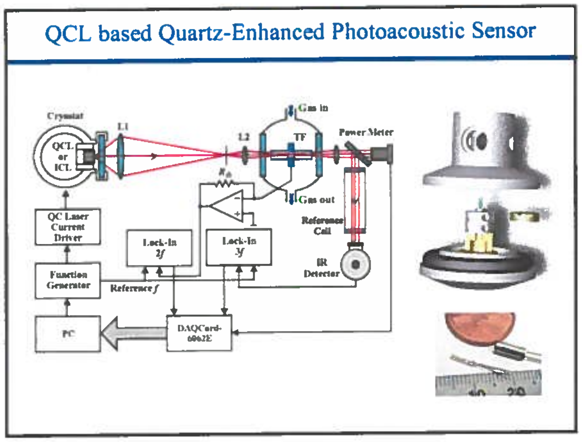
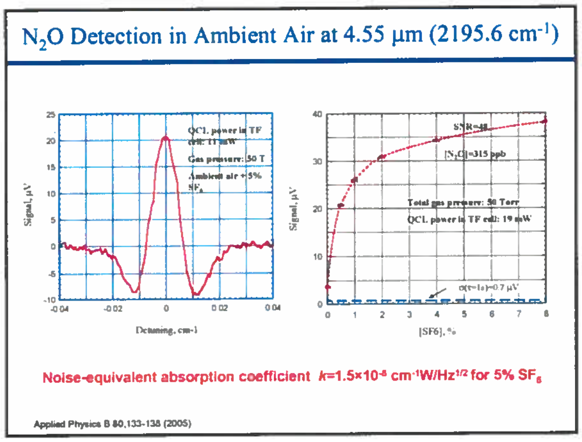


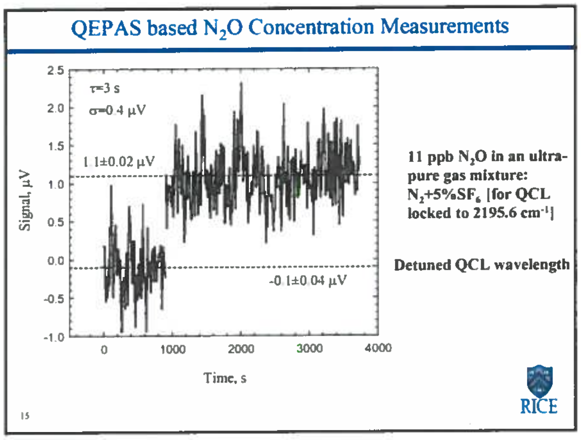
QCL based Quartz-Enhanced Photoacoustic Sensor



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

Noise-equivalent absorption coefficient $k=1.5\times10^{-8}$ $cm^{-1}W/Hz^{1/2}$ for 5% SF_6

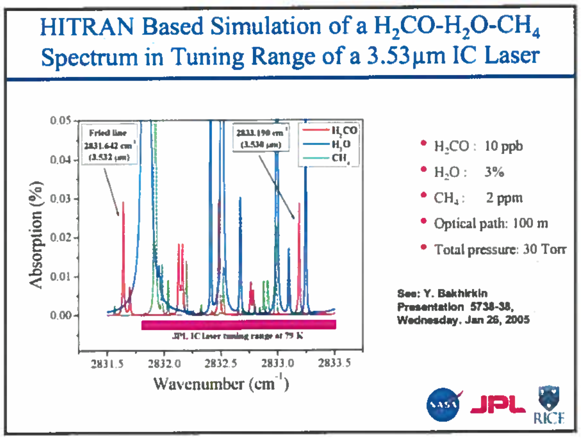
Applied Physics B 80,133-138 (2005)



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}]

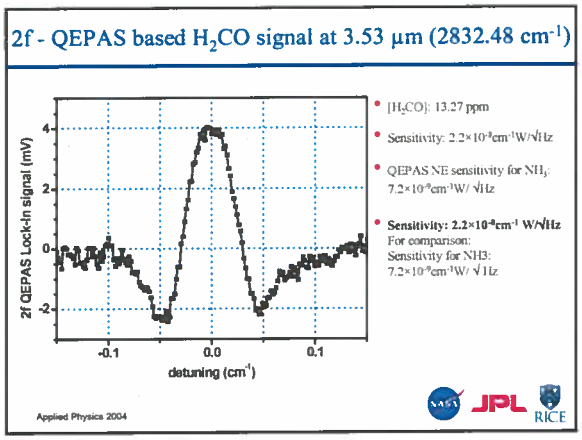
Detuned QCL wavelength



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

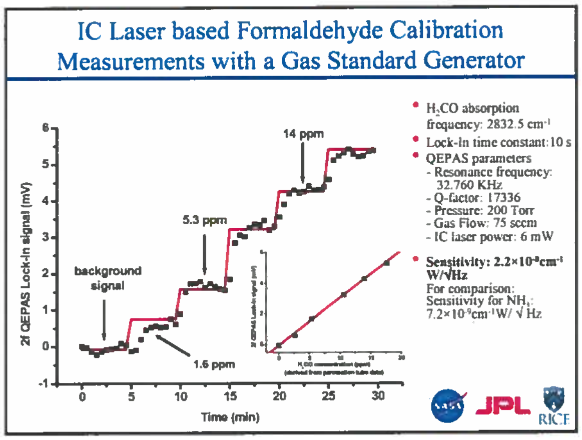
See: Y. Bakhirkin
Presentation 5738-38,
Wednesday, Jan 26, 2005



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

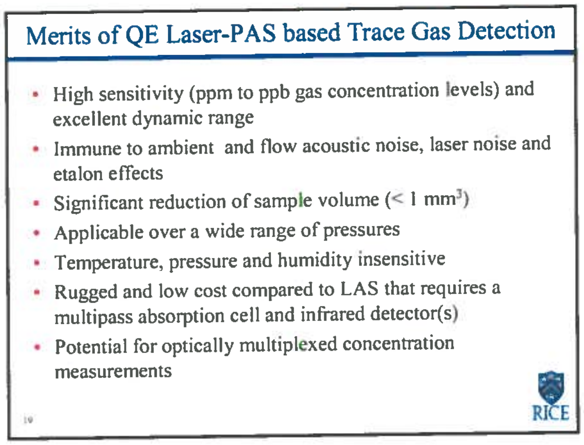
- $[H_2CO]$: 13.27 ppm
- Sensitivity: 2.2×10^{-8} $cm^{-1}W/\sqrt{Hz}$
- QEPAS NE sensitivity for NH_3: 7.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$
- **Sensitivity: 2.2×10^{-8} cm^{-1} $W/\sqrt{Hz}$**
  For comparison:
  Sensitivity for NH3:
  7.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$

Applied Physics 2004



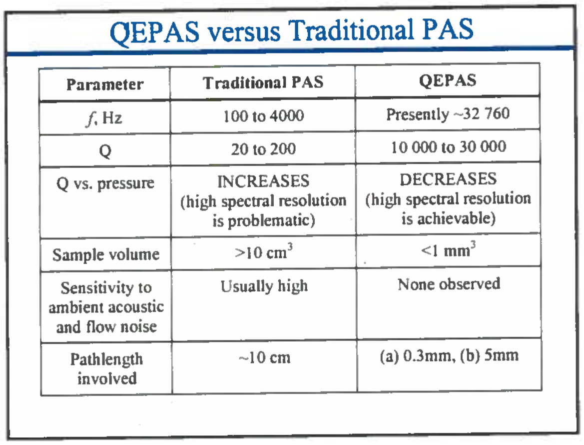
IC Laser based Formaldehyde Calibration Measurements with a Gas Standard Generator

- 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: 2.2×10^{-8} cm^{-1} $W/\sqrt{Hz}$**
  For comparison:
  Sensitivity for NH_3:
  7.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$



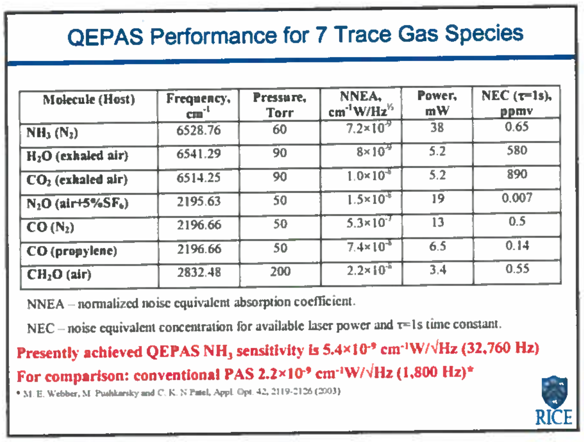
Merits of QE Laser-PAS based Trace Gas Detection

- 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
- 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



QEPAS Performance for 7 Trace Gas Species

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	7.2×10^{-9}	38	0.65
H_2O (exhaled air)	6541.29	90	8×10^{-9}	5.2	580
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}	3.4	0.55

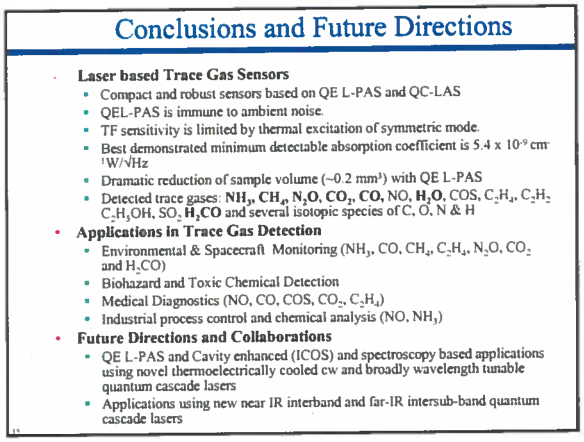
NNEA – normalized noise equivalent absorption coefficient.

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

Presently achieved QEPAS NH_3 sensitivity is 5.4×10^{-9} cm^{-1}W/√Hz (32,760 Hz)

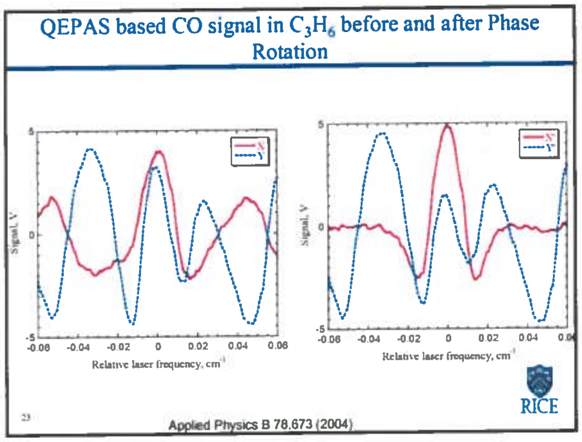
For comparison: conventional PAS 2.2×10^{-9} cm^{-1}W/√Hz (1,800 Hz)*

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



Conclusions and Future Directions

- **Laser based Trace Gas Sensors**
  - Compact and robust sensors based on QE L-PAS and QC-LAS
  - QEL-PAS is immune to ambient noise.
  - TF sensitivity is limited by thermal excitation of symmetric mode.
  - Best demonstrated minimum detectable absorption coefficient is 5.4 x 10^{-9} cm^{-1}W/√Hz
  - Dramatic reduction of sample volume (~0.2 mm^3) with QE L-PAS
  - 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)
  - Biohazard and Toxic Chemical Detection
  - 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) and spectroscopy based 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



QEPAS based CO signal in C_3H_6 before and after Phase Rotation

Applied Physics B 78,673 (2004)