Recent Developments of Chemical Sensors based on Quartz Enhanced Photoacoustic Spectroscopy

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OUTLINE

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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of QE Photoacoustic Spectroscopy
- Selected Applications of QEPAS
  - 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 Detection with 4.6 µm LN_2 cw DFB quantum cascade laser
- Merits, Summary and Outlook for QEPAS

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Gas sensing: wide range of 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**
- **Law enforcement**
- **Fundamental Science and Photochemistry**

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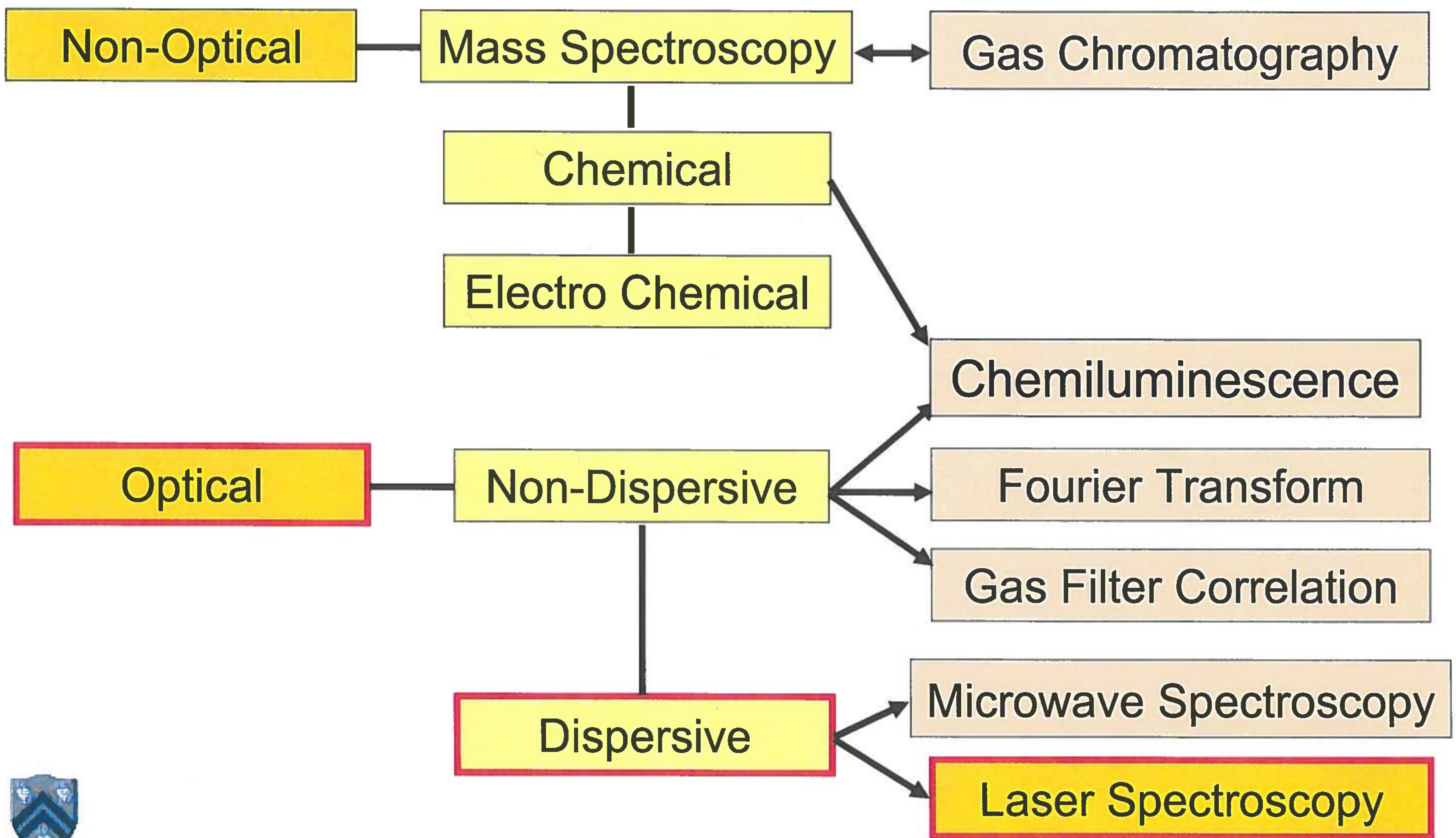
Existing Methods for Trace Gas Detection



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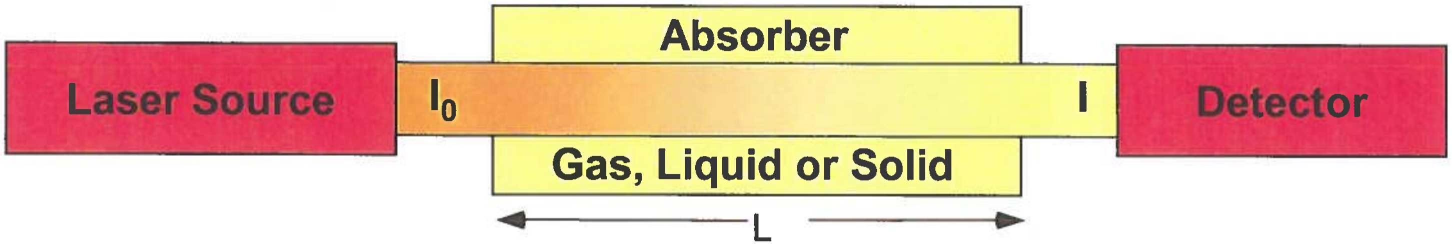
Direct Laser Absorption Spectroscopy

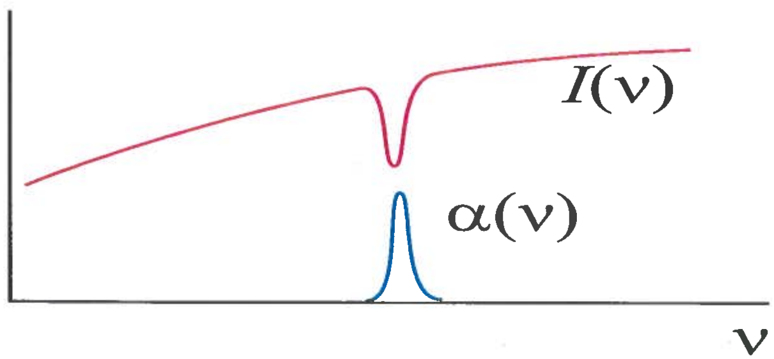


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - 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 [$molecule \cdot cm^{-3} \cdot atm^{1}$]

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

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

Sensitivity Enhancement Techniques

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriott)
  - 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**
  - **N**oise **I**mmune **C**avity **E**nhanced-**O**ptical **H**eterodyne **M**olecular **S**pectroscopy (NICE-OHMS)

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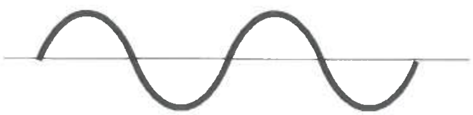
Resonant photoacoustic spectroscopy

Q>>1000

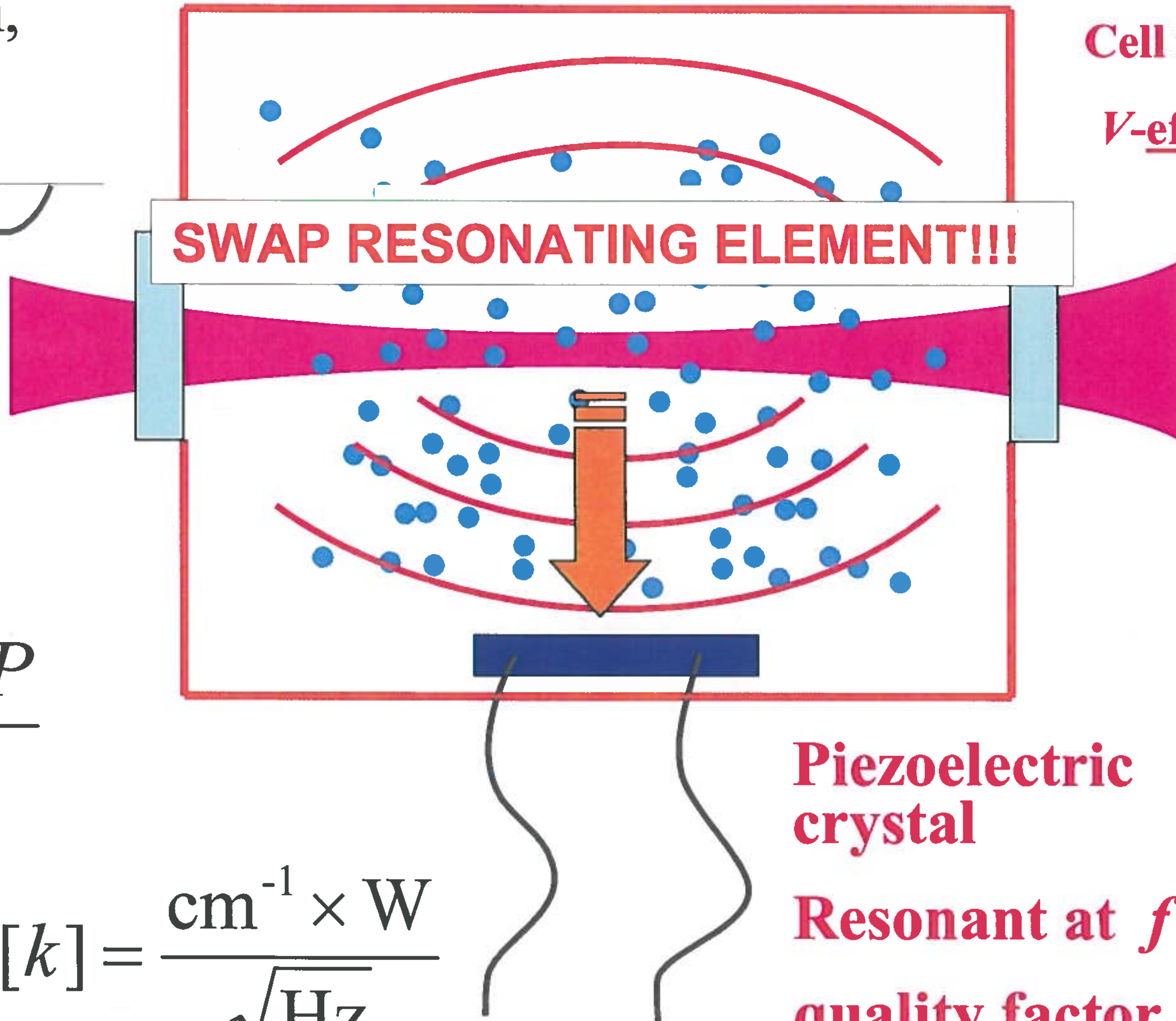
Cell is OPTIONAL!

V-effective volume

Laser beam,
power *P*



Modulated
(*P* or λ) at *f*
or *f*/2



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

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

Piezoelectric crystal

Resonant at *f*

quality factor *Q*

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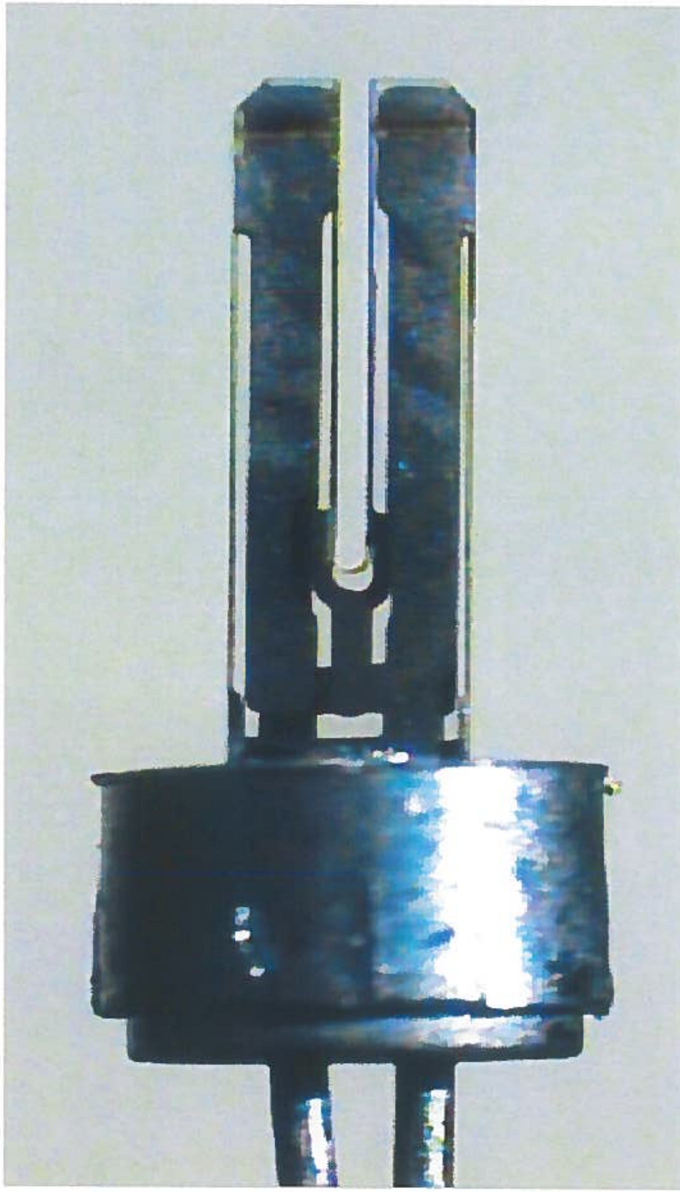
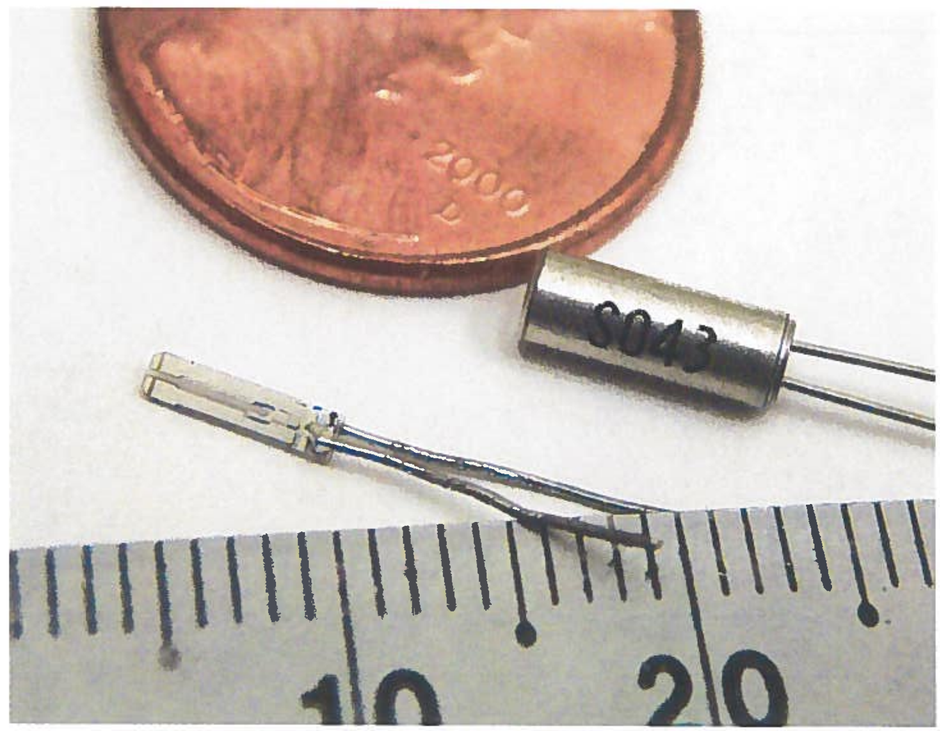
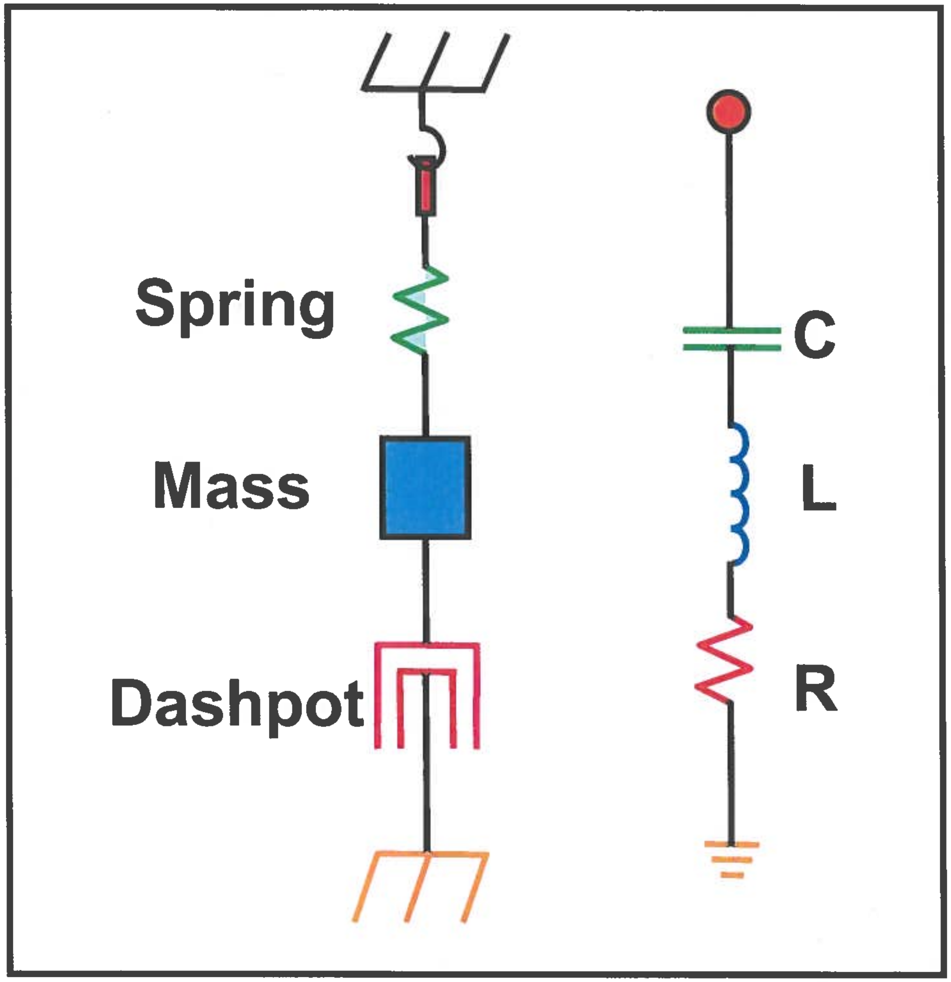
Quartz Tuning Fork as a Resonant Microphone



- 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 circuit of a quartz TF



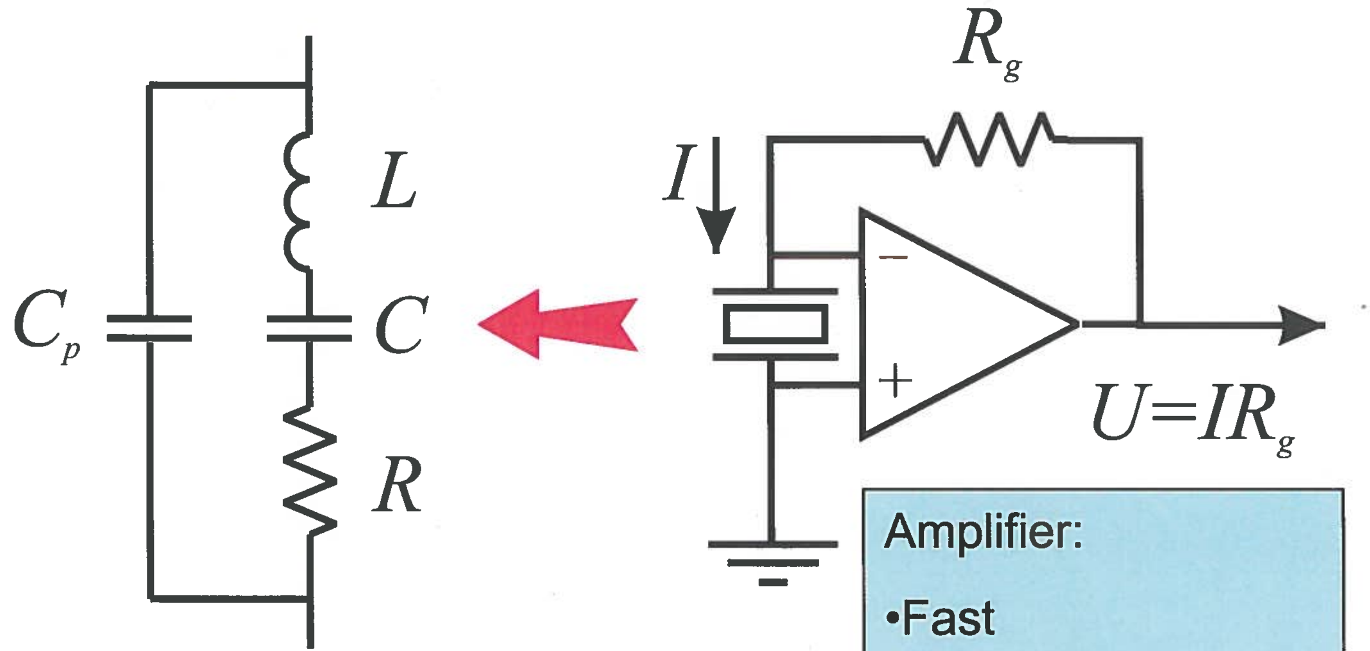
$$\omega_0 = \sqrt{\frac{1}{LC}}$$

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

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

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

Noise analysis



Amplifier:

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

$S_1 = \sqrt{4k_B T R_g}$; $\quad R_g = 10\ \mathrm{M\Omega} \Rightarrow S_1 = 4.1\cdot 1$

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

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

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

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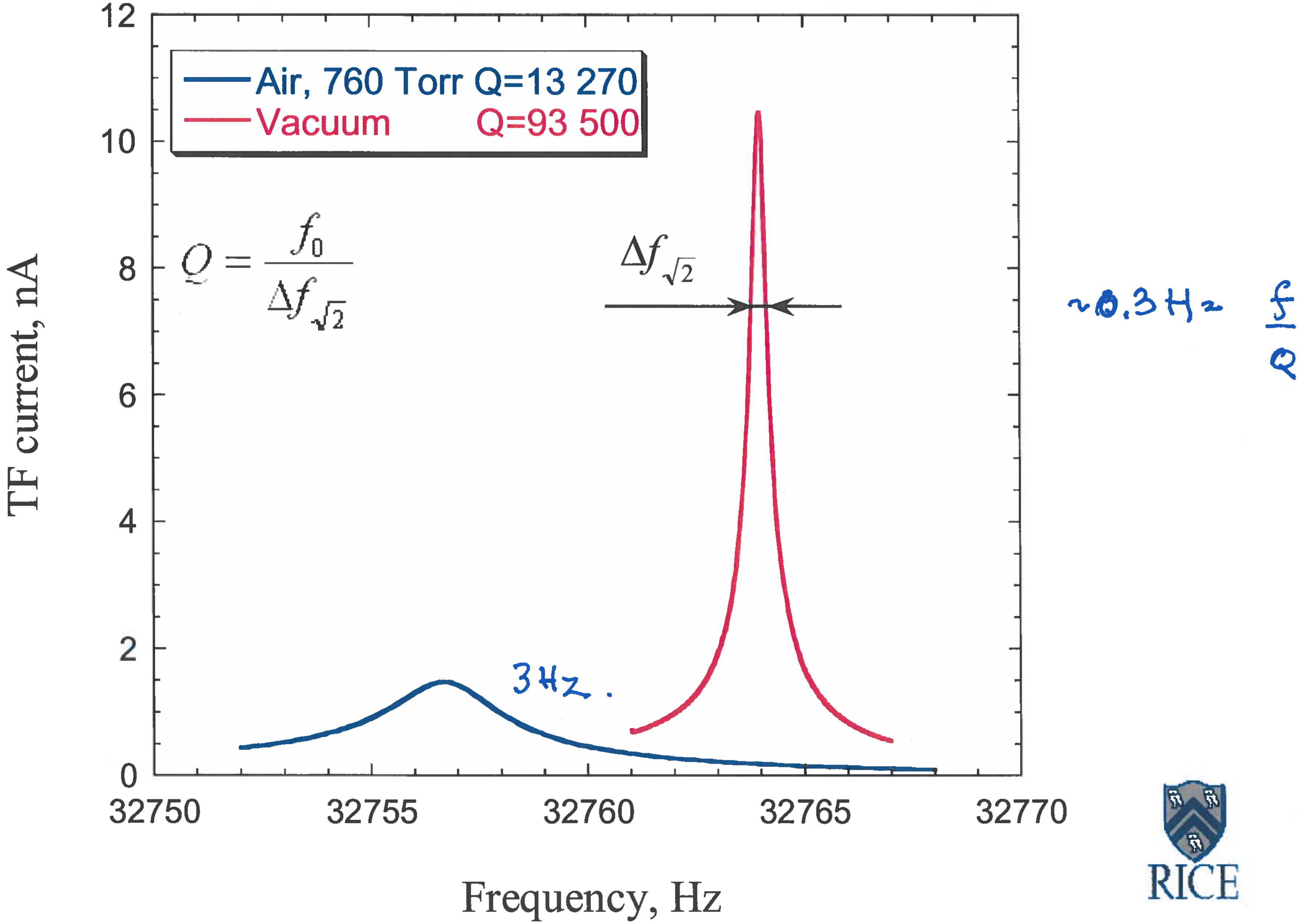
Typical QTF resonance curves



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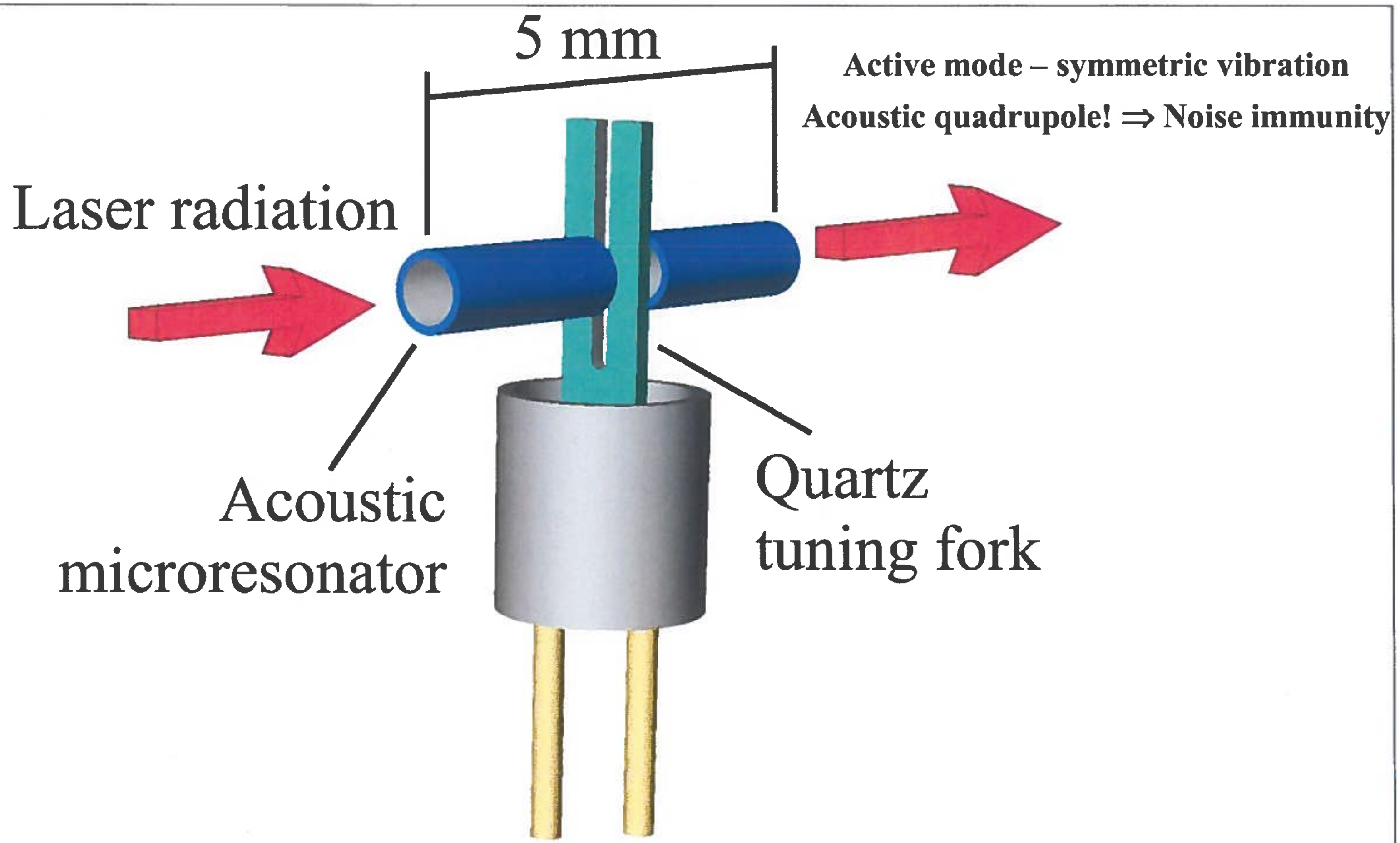
Quartz Enhanced PAS ADM



Acoustic micro-cavity is added to enhance sensitivity

NASA Target Gas Opportunity Matrix

Molecule	Detection Limit (ppb)	QEPAS detectable?	
		1.3-1.7 μm	2-5 μm
Formaldehyde	10	No	X (red)
Acetaldehyde	20	Experiments required	
Ammonia	100	X (green)	X (blue)
Carbon monoxide	1000	Probably not	X (green)
Hydrogen cyanide	100	X (blue)	X (blue)
Carbon dioxide	<2%	X (green)	X (blue)
Nitrogen dioxide	100	Probably not	X (blue)
HF	100	Experiments required	
Acrolein (2-Propenal)	5	Unlikely	
Water vapor	10-90%	X (green)	X (blue)

X – Demonstrated (green)

X – Highly expected based on the existing technology level (blue)

X – Expected with the technology advance (red)

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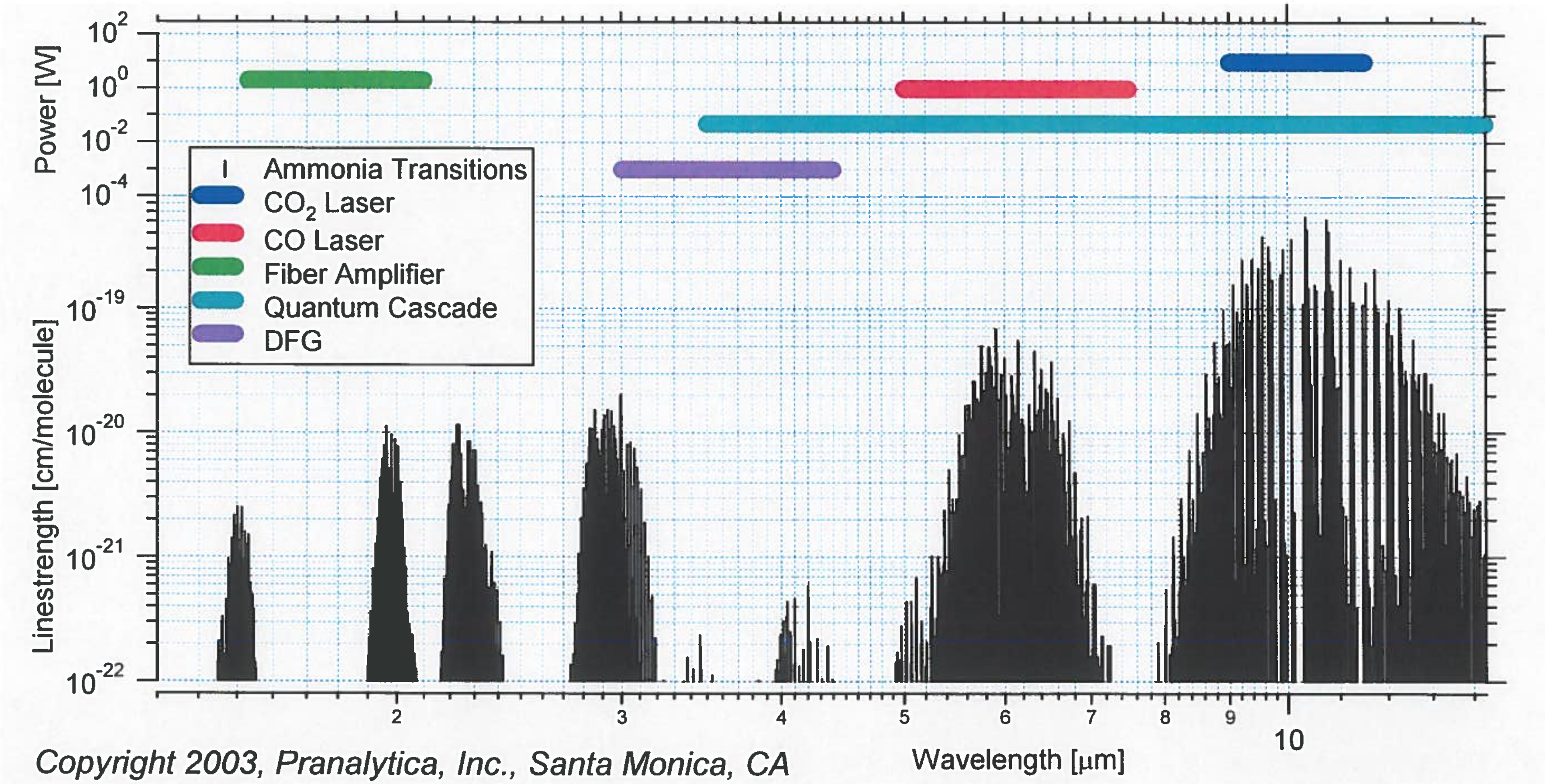
Motivation for NH_3 Detection

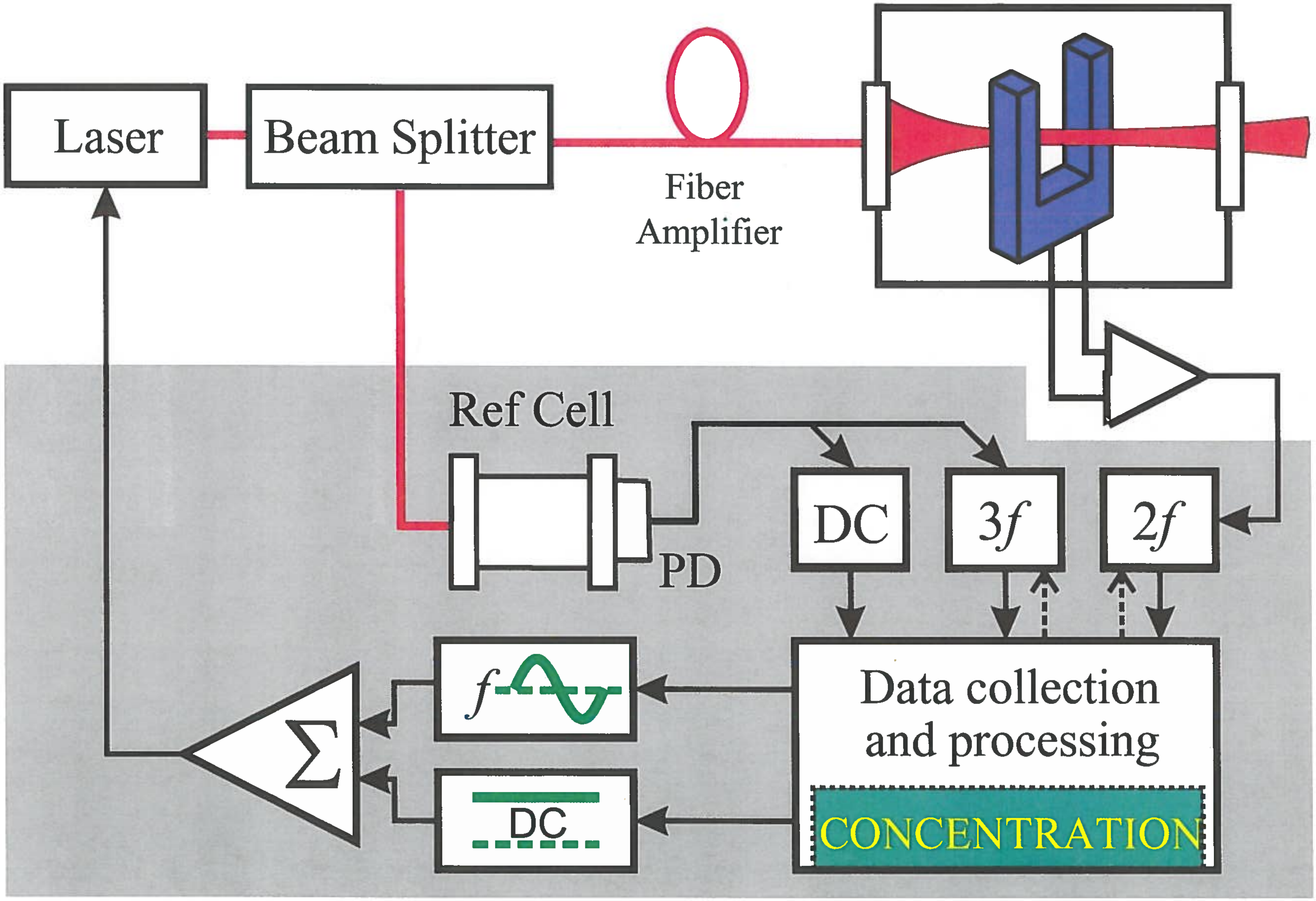
- Spacecraft related gas monitoring
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric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

Molecular absorption spectra: NH_3



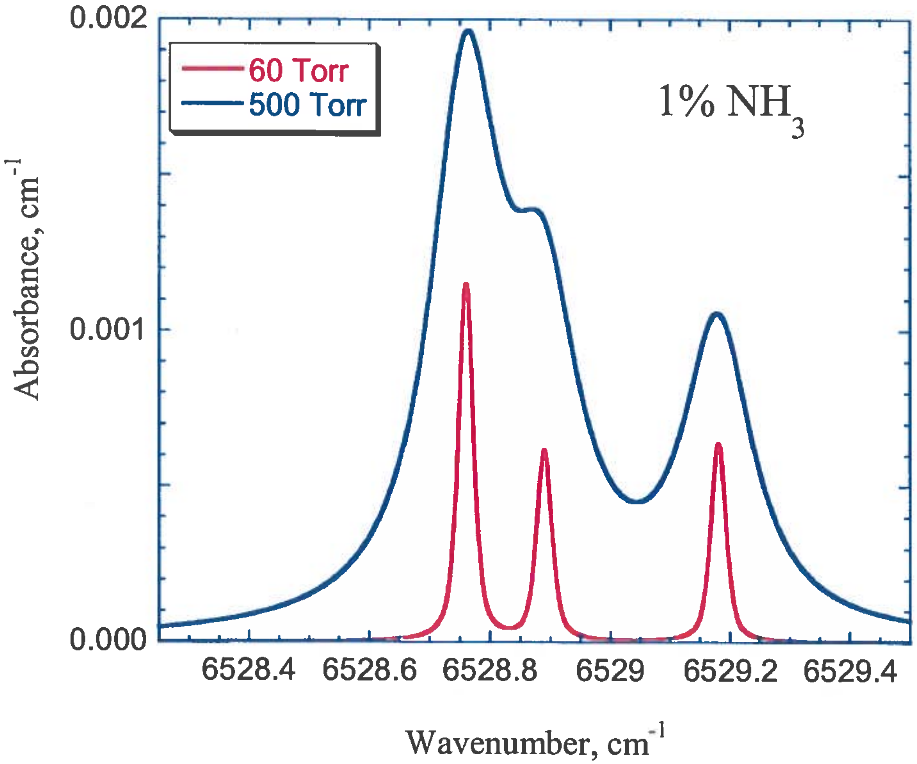
M. Webber et al. 2003, Pranalytica

QEPAS fiber based gas sensor architecture

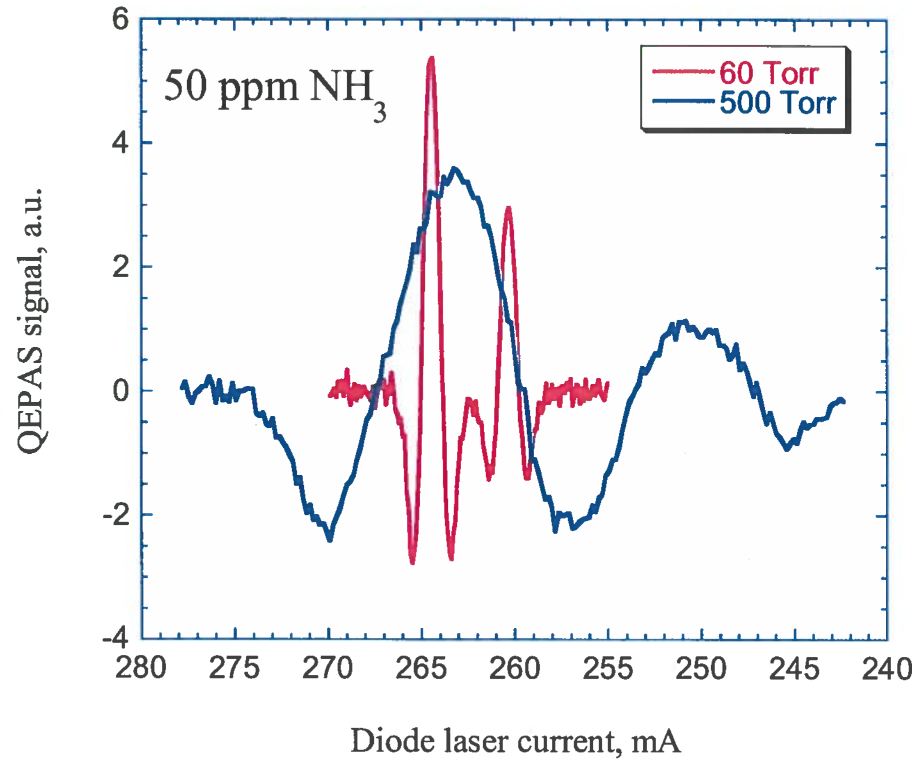


Fiber Connection — Electrical Connection

Ammonia Detection using a 1.53 μm Telecom Diode Laser



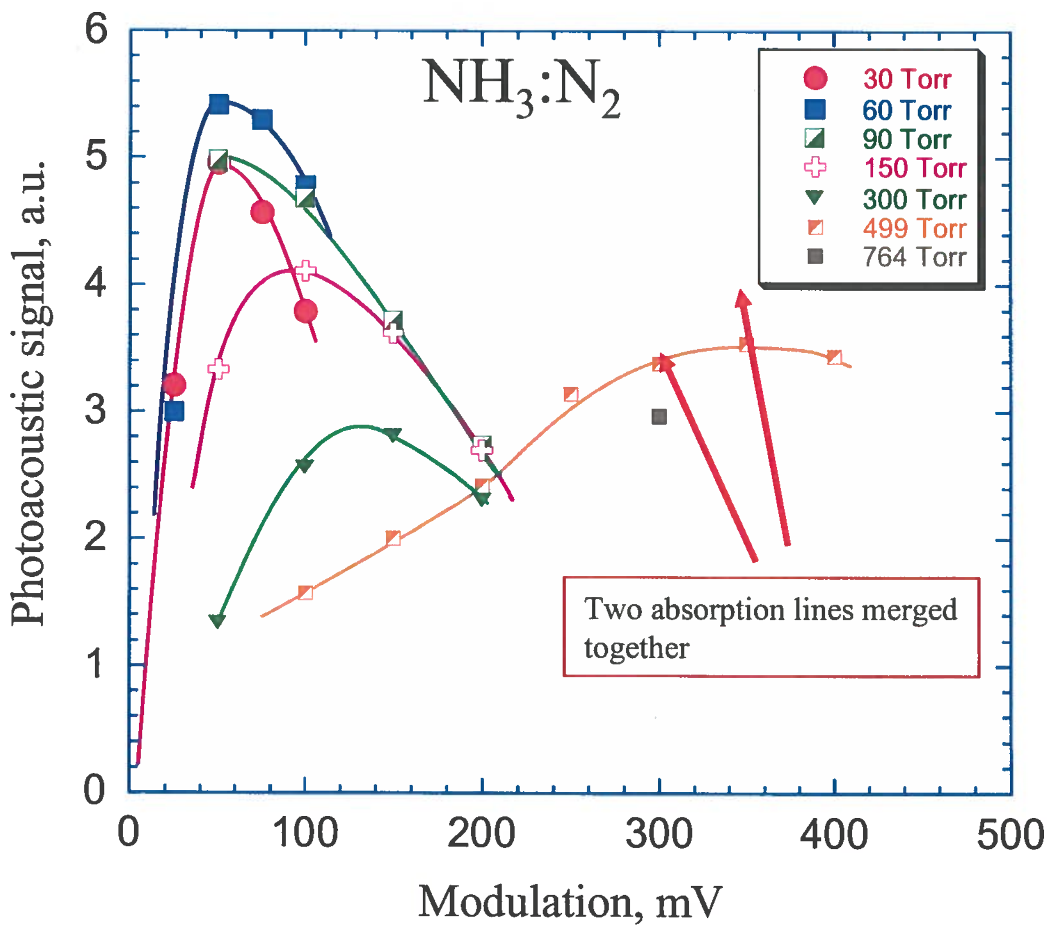
Spectral simulations based on data from Webber et al., APPLIED OPTICS 40, 2031-2042 (2001)]



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 relaxion is faster at higher pressure
- Acoustic resonator enhancement factor changes with pressure

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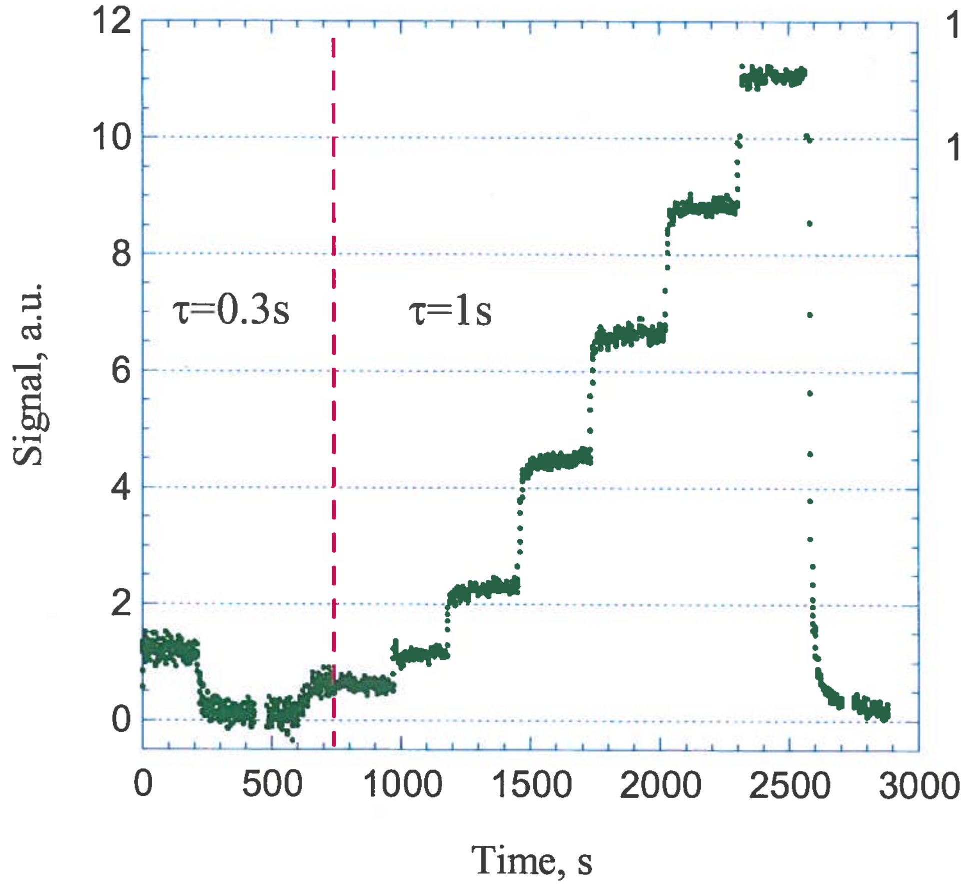
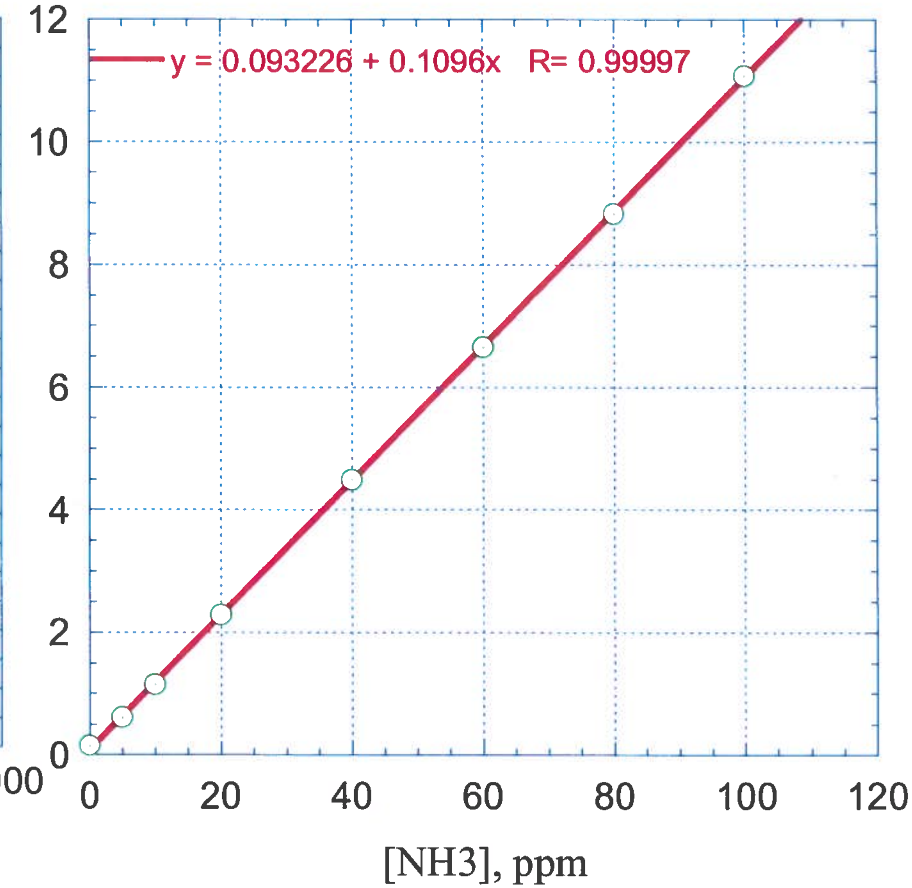
Calibration and Linearity of QEPAS based NH_3 Sensor





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^{-9} $cm^{-1}W/\sqrt{Hz}$)

***Webber et al., APPLIED OPTICS April 2003 Vol. 42, No. 12, p.2119**

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

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) ~1W.

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Motivation for Precision Monitoring of H_2CO

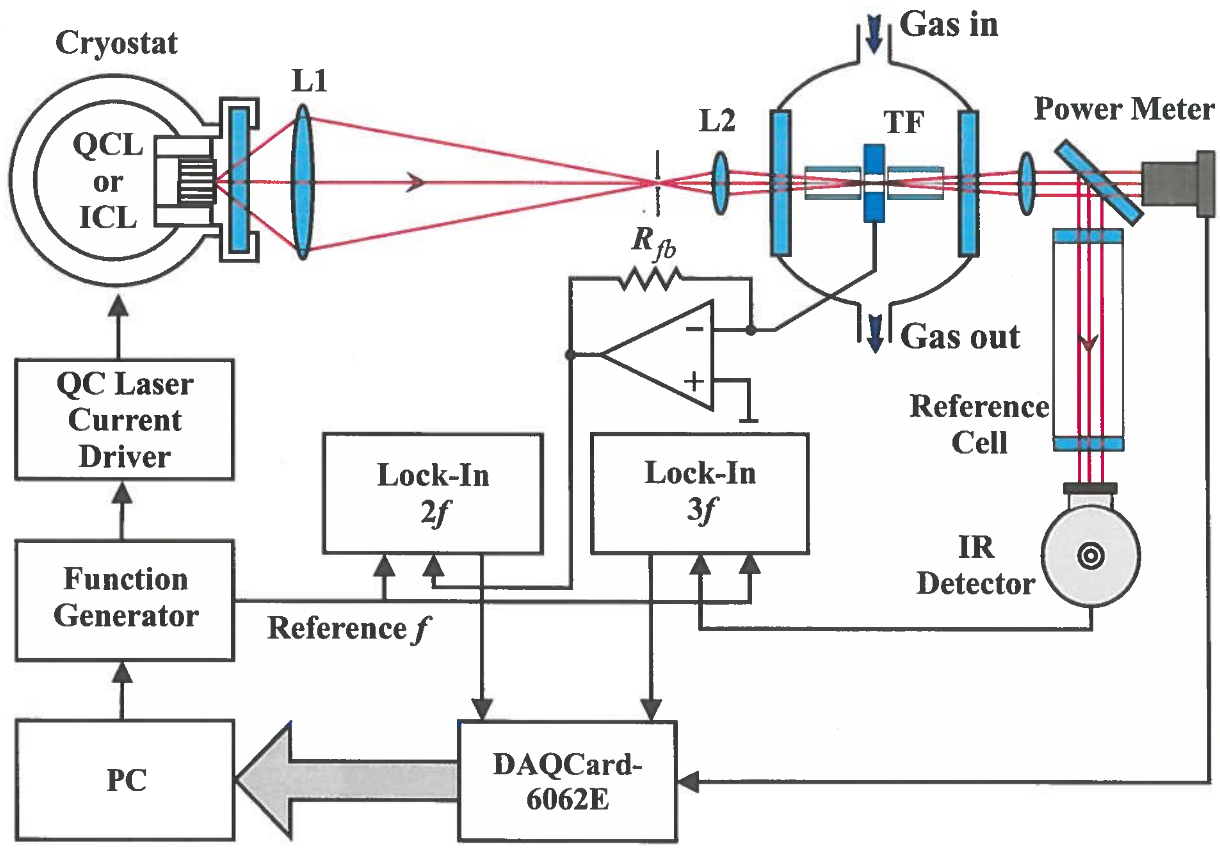
- Potential trace contaminant in industrial manufactured products

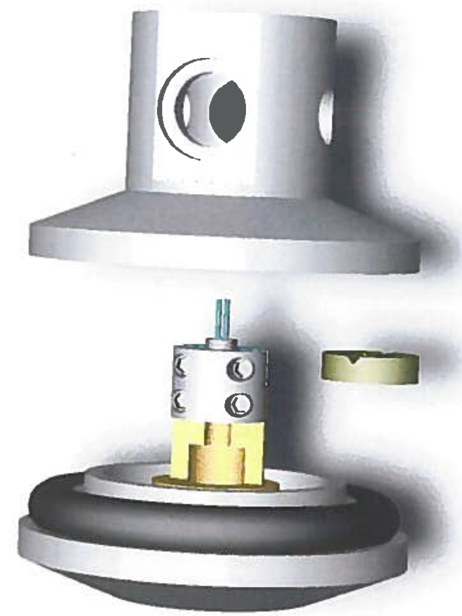
- Precursor to atmospheric O_3 production

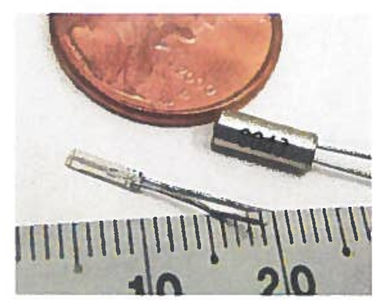
- Pollutant due to incomplete fuel combustion processes

- Medically important gas

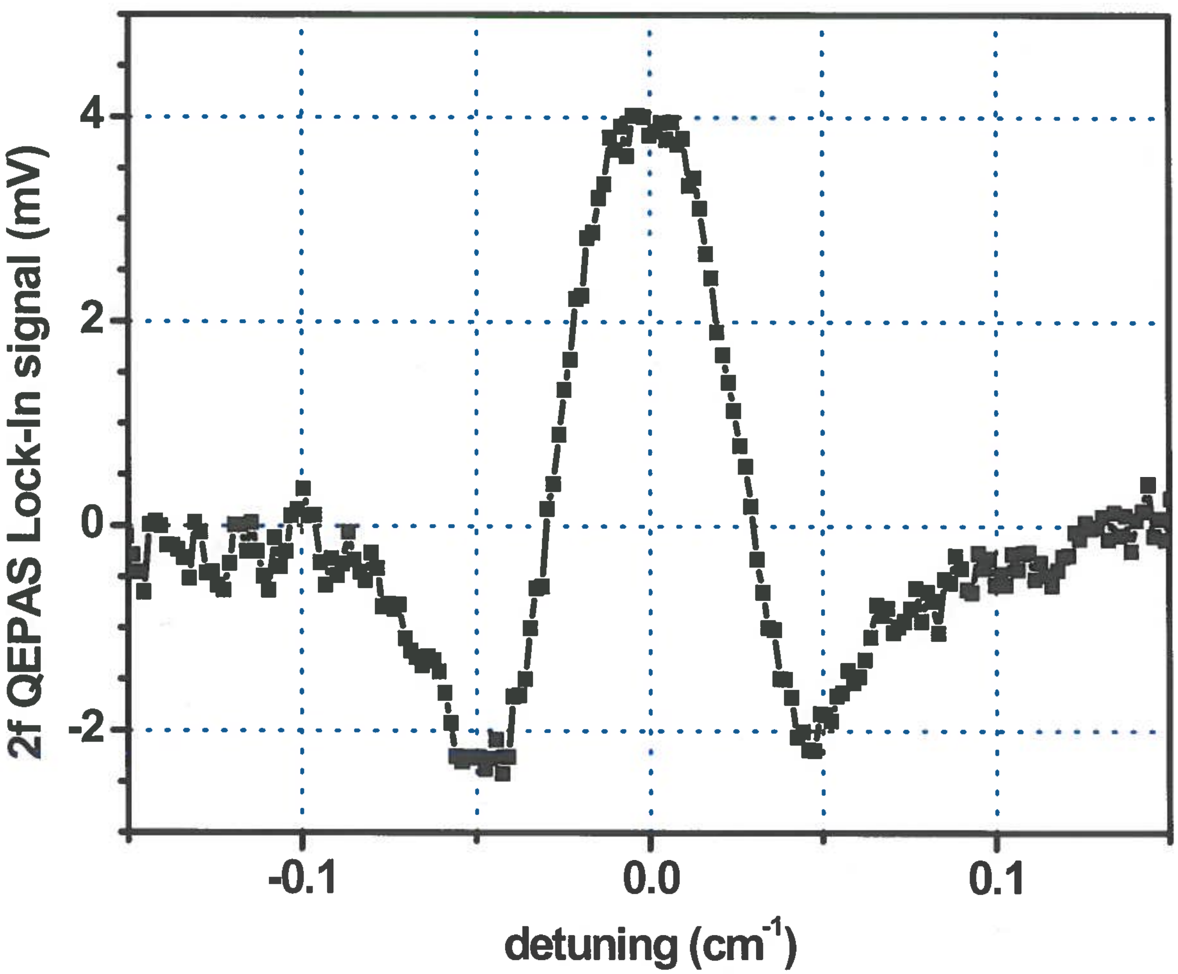
QCL based Quartz-Enhanced Photoacoustic Sensor







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:
  $7.2\times10^{-9} cm^{-1} W/ \sqrt{Hz}$

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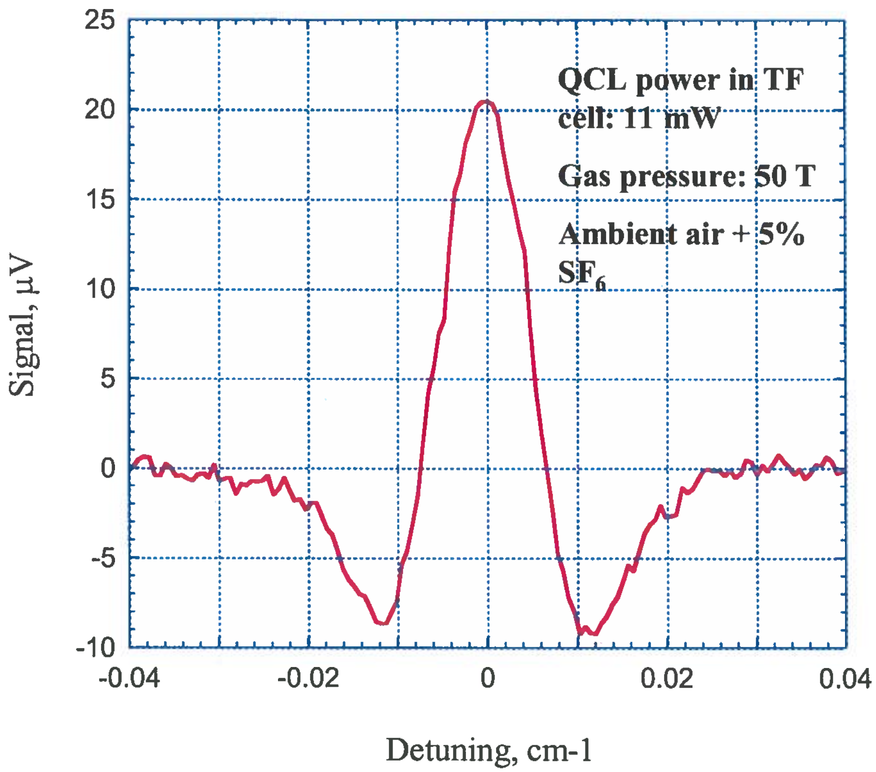
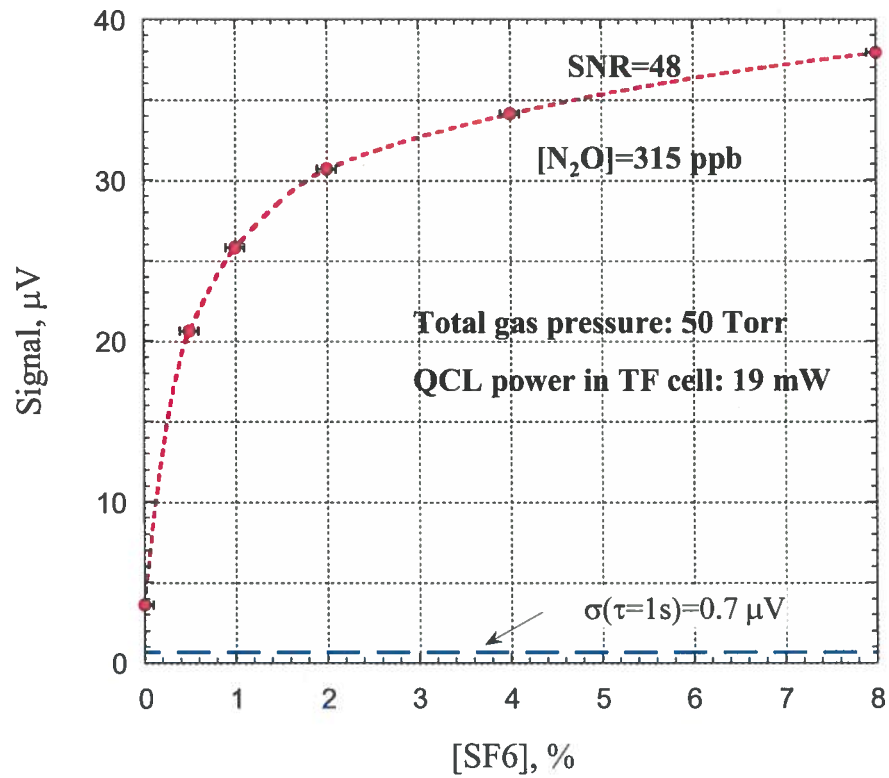
N_2O Detection in Ambient Air at 4.55 μm (2195.6 cm^{-1})

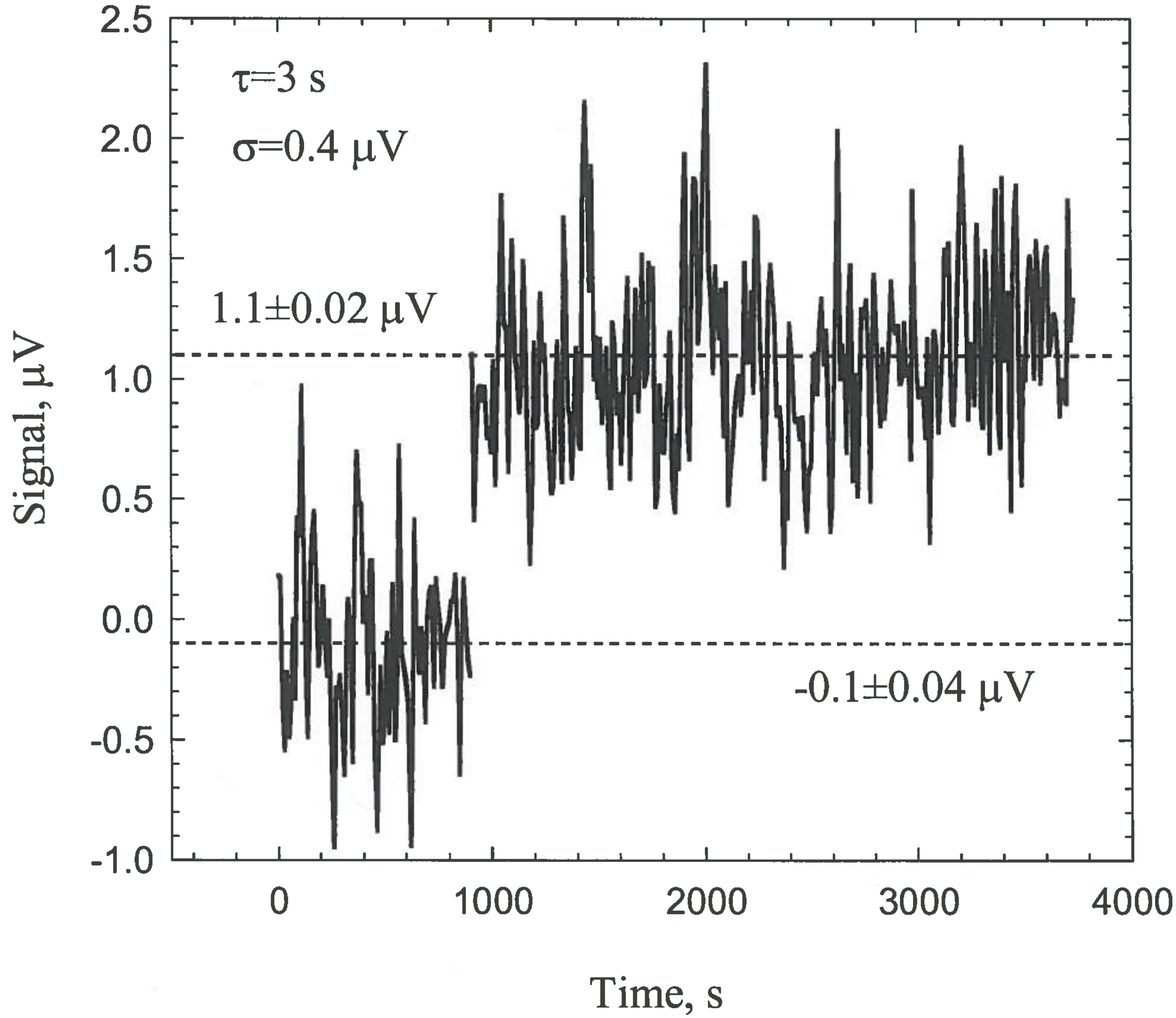




Noise-equivalent absorption coefficient *is* 1.5×10^{-8} $cm^{-1}W/Hz^{1/2}$ for 5% SF_6 with a noise equivalent concentration of 4 ppbv for τ = 3 sec

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 various 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	7.4×10^{-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} $cm^{-1}W/\sqrt{Hz}$ (32,760 Hz)

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)

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