Optical Gas Sensing Based on Quartz Enhanced Photoacoustic Spectroscopy: Fundamentals and Applications

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http://www ece rice edu/lasersci

Pittcon
2005
Orlando, FL

- Basic principles
- Implementation details
- Observed performance
- Summary and outlook

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**
- **Fundamental Science and Photochemistry**

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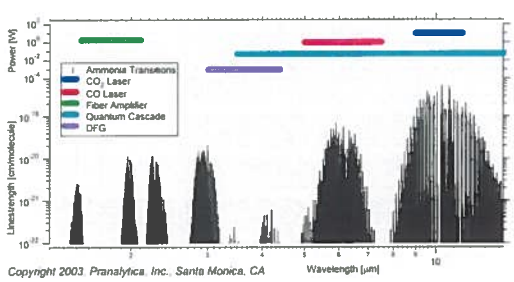
Molecular absorption spectra: NH_3



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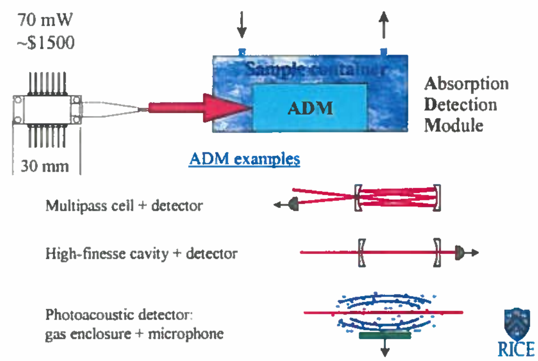
3 M. Webber et al. 2003, Pranalytica

General laser-based gas sensor configuration



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ADM comparison

Technique	Sensitivity: Power dependent?	Pros	Cons
Multipass cell	No	• Does not requre calibration • Works good with low-power sources	• Large volume • Critical alignment • Expensive optics • Small change of large signal
CRS	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 to acoustic noise

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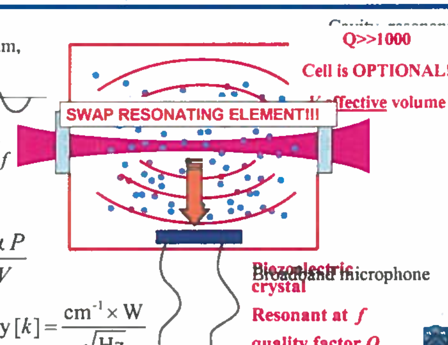
Resonant photoacoustic spectroscopy

Laser beam, power P

Modulated (P or λ) at f or $f/2$



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

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

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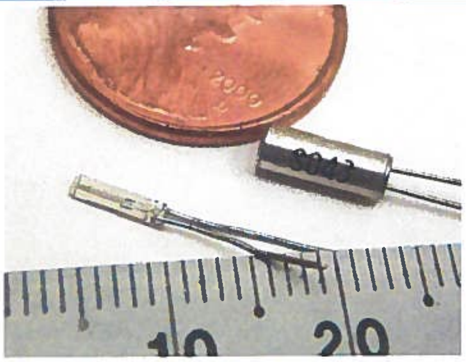
Quartz clock tuning fork (TF)



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Quartz clock tuning fork (TF)

RALTRON

WATCH CRYSTAL TUNING FORKS

R26

Frequency: 32.768kHz ±30ppm. **Operating temperature:** −10°C to +60°C
ESR: 35kohms max. **(R26)**, 50kohms max. **(R38)**

Retail price: $0.32 ea. (Newark Electronics)

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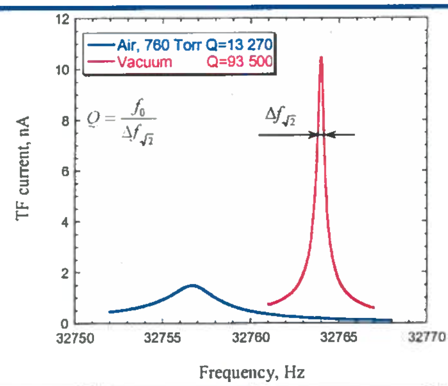
Typical TF resonance curves



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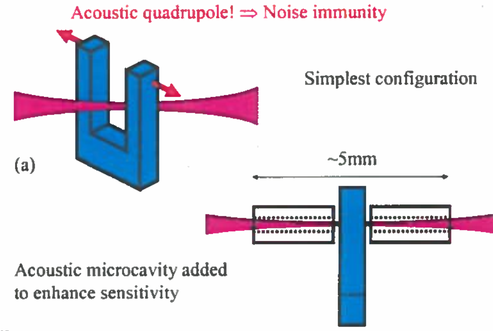
Possible ADM configurations

Active mode – symmetric vibration

Acoustic quadrupole! ⇒ Noise immunity



Acoustic microcavity added
to enhance sensitivity

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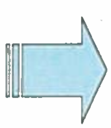
The name of the game

Quartz

Enhanced

Photo



QEPAS

Acoustic

Spectroscopy

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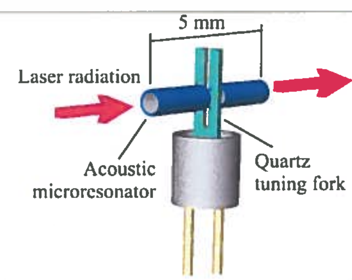
Quartz Enhanced PAS ADM



Architecture of the QEPAS ADM consisting
of a TF and acoustic micro-resonator.

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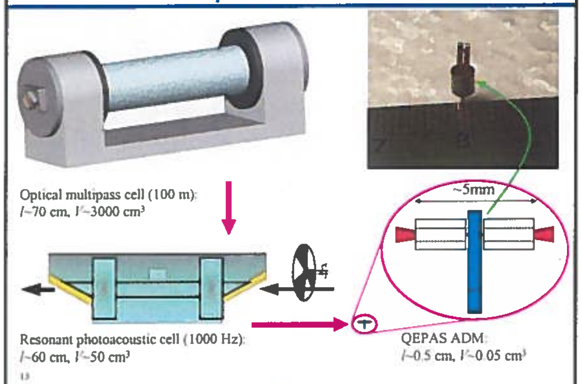
Comparative size of ADMs



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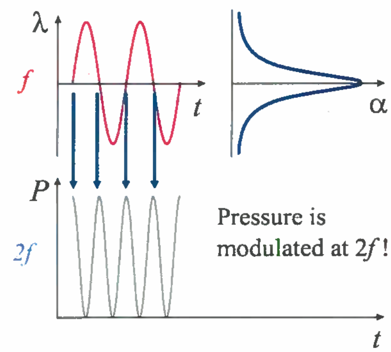
2*f* wavelength modulation PAS



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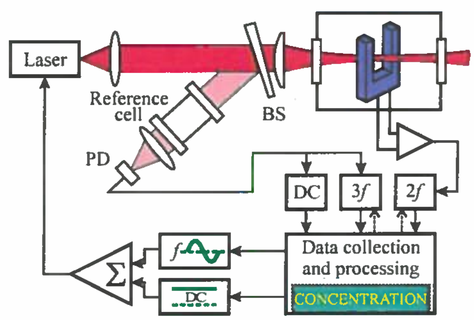
QEPAS based gas sensor architecture



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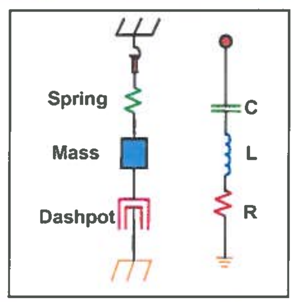
Equivalent circuit of a quartz TF



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

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

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

16 "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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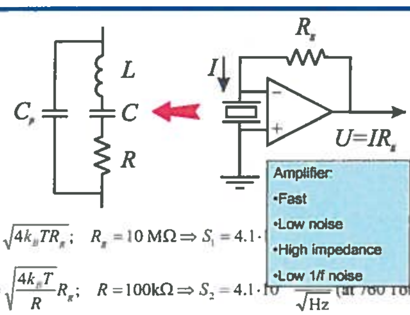
Noise analysis



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

$S_2 = \sqrt{\frac{4k_B T}{R}} R_g$; $R = 100\,\mathrm{k\Omega} \Rightarrow S_2 = 4.1 \cdot 10$ ... $\frac{}{\sqrt{\mathrm{Hz}}}$ (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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QEPAS vs. traditional PAS

Parameter	Traditional PAS	QEPAS
f, Hz	100 to 4000	Presently ~32 760
Q	20 to 200	10 000 to 30 000
Q/f, s	<0.025 s	>0.3 s
Q vs. pressure	INCREASES (high spectral resolution is problematic)	DECREASES (high spectral resolution is achievable)
Sample volume	>10 cm^3	<0.05 cm^3
Sensitivity to ambient acoustic and flow noise	Usually high	None observed

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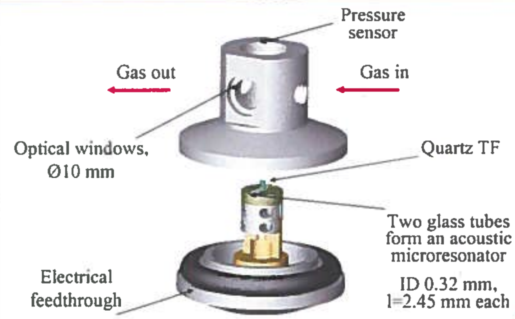
Gas cell for QEPAS experiments

Bottom part with a mounted TF

Assembled cell with a pressure sensor mounted on top

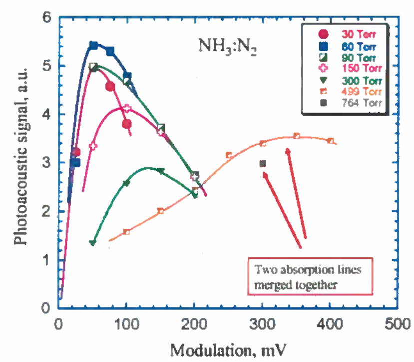
Gas cell for QEPAS experiments



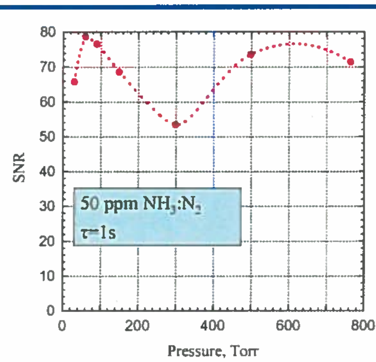
QEPAS sensitivity vs. pressure

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

QEPAS sensitivity vs. pressure



QEPAS sensitivity vs. pressure



QEPAS performance for various 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	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} $cm^{-1}W/\sqrt{Hz}$ (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)

QEPAS vs. conventional PAS: NH_3

Publication and comments	Resonant acoustic frequency, Hz	NNEA, $cm^{-1}W/\sqrt{Hz}$
[1] CO_2 laser, amplitude modulation	1840	1.1×10^{-8}
[2] Diode laser, amplitude modulation	4000	6.4×10^{-9} *
[3] Fiber-amplified diode laser, wavelength modulation	1800	2.2×10^{-9} *
QEPAS	**32760**	$\mathbf{5.4\times10^{-9}}$

1. M. B. Pushkarsky et all., *Appl. Phys. B* **77**, 381–385 (2003)
2. A. Schmohl et all., *Appl. Opt.* **41**, 1815-1823 (2002)
3. M. E. Webber et all., *Appl. Opt.* **42**, 2119-2126 (2003)

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Low-frequency (massive) TF: What to expect?

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

$$m' = nm$$

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

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

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

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

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

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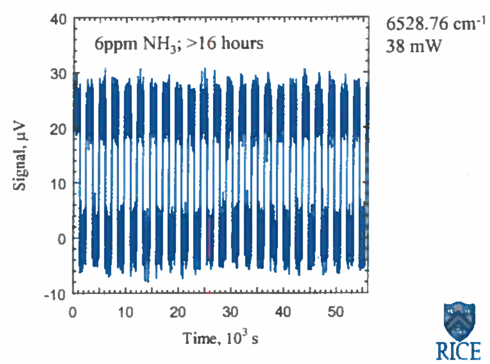
Low-frequency noise study



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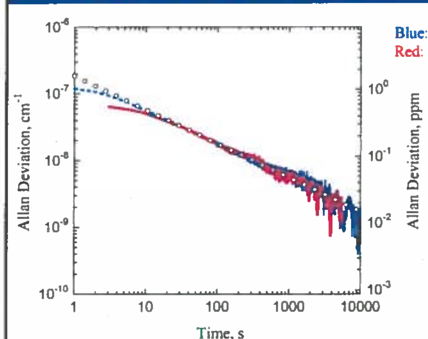
Low-frequency noise study



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Summary and Outlook

- QEPAS is immune to ambient noise. The experimentally measured noise level coincides with the thermal noise of the TF.
- 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 presently used TF.
- The best experimentally demonstrated sensitivity of QEPAS to date is $\mathbf{5.4\times10^{-9}}$ $\mathbf{cm^{-1}WHz^{-1/2}}$. This number was derived from the precision of NH_3 concentration measurements of 0.65 ppm, achieved with 38 mW power produced by a commercially available near-IR telecom diode laser.
- QEPAS exhibits an exceptionally low $1/f$ noise level, allowing data averaging for more than 3 hours

NEXT STEPS:

- Investigate TFs with lower resonant frequencies
- Optimize acoustic microresonator design (geometry and materials)
- Investigate amplitude modulation QEPAS potential and limitations

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