Quartz Enhanced PhotoAcoustic Spectroscopyfor Trace Gas Sensing

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RICE

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QEPAS

- Motivation
- 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
  - Nuclear materials processing
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Medical Applications**
- **Fundamental Science and Photochemistry**

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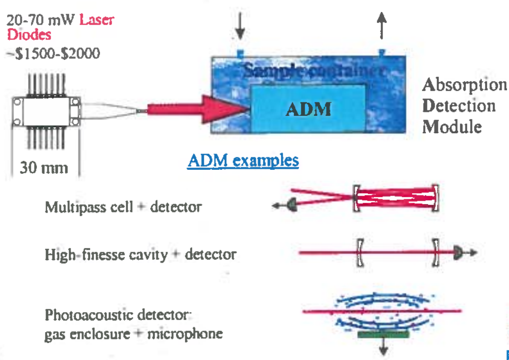
General laser-based gas sensor configurations



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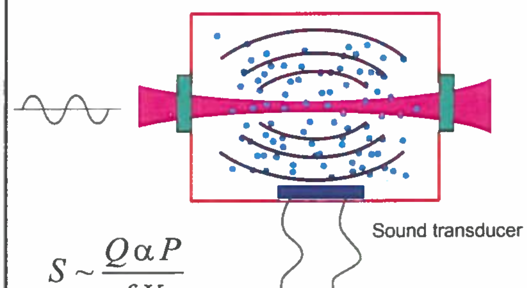
Conventional PAS: Resonating GAS SAMPLE



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

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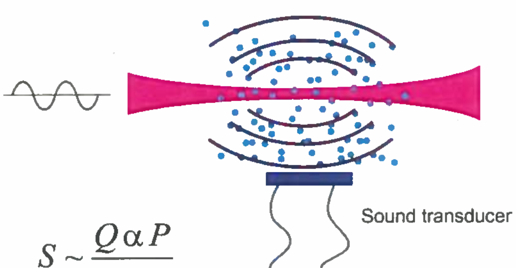
Quartz-Enhanced PAS: Resonating MICROPHONE



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

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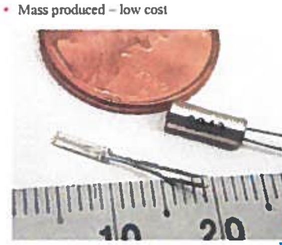
Quartz tuning fork (TF) as a resonant microphone

- Resonant frequency f=32.8 kHz
- Intrinsically high Q factor: Q_{vacuum} ~ 125 000, Q_{air} ~10 000 at ambient conditions;
- Piezoelectric: no additional transducer required
- Miniature size
- Mass produced – low cost



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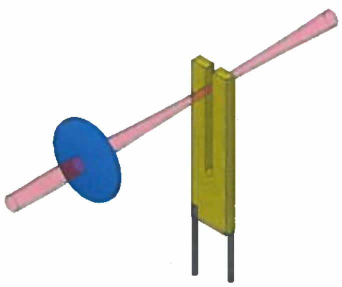
TF based spectrophone



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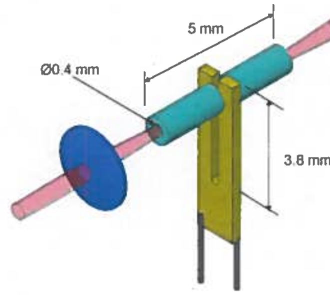
TF based spectrophone



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QEPAS advantages

- Very small absorption detection module (ADM; spectrophone)
- Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
- Ultrasmall sample volume - <1mm³
- Immune to environmental acoustic noise – acoustic quadrupole
- Sensitivity is limited by the fundamental thermal TF noise – $k_B T$ energy in the TF symmetric mode, directly observed
- White noise spectrum – SNR scales as $\sqrt{t}$, up to t=3 hours experimentally verified

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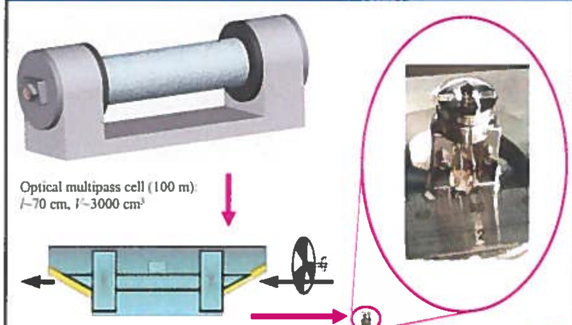
Comparative size of ADMs



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

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

QEPAS spectrophone: l~1 cm, V~0.05 cm³

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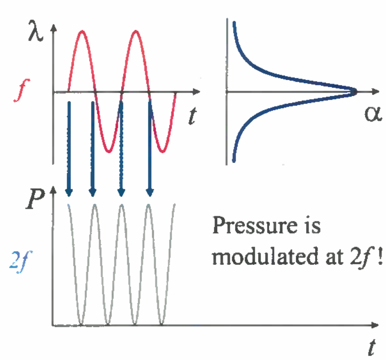
2*f* wavelength modulation PAS



Pressure is modulated at 2*f* !

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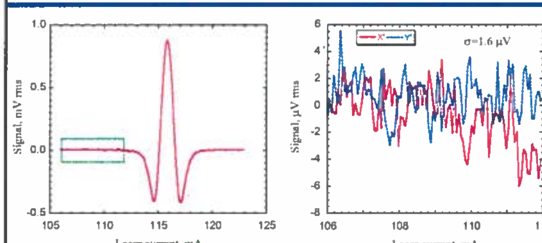
QEPAS signal: 7306.75 cm^{-1} H_2O line, 48 ppmv



Laser power after the cell window: 9.5 mW

Peak absorbance: 4.8×10^{-5} cm^{-1} (HITRAN)

Two passes (back-reflecting mirror)

Time constant: 1s, SNR=550

⇒ NNEA=1.9×10^{-9} cm^{-1}W/(Hz)$^{1/2}$; NEC=90 ppbv

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QEPAS performance for various chemical species

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{1/2}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10^{-9}	9.5	0.09
HCN (air: 50% hum) *	6539.11	60	4.3×10^{-9}	50	0.16
C_2H_2 (N_2)**	6529.17	75	$\sim2.5\times10^{-9}$	~40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	0.50
CO_2 (exhaled air)	6514.25	90	1.0×10^{-8}	5.2	890
CO_2 (N_2+1.5% H_2O)	4991.26	50	1.4×10^{-8}	4.4	18
CH_2O (air: 50% hum) *	2832.48	100	1.1×10^{-8}	4.6	0.28
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
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007

* - Improved microresonator

** - Improved microresonator and double optical pass through ADM

NNEA – normalized noise equivalent absorption coefficient.

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

Absolute sensitivity scales as a square root of the data acquisition time

QEPAS based gas sensor: main considerations

- Response is intrinsically slow – Qf_0>0.3s
- Real ZERO background (thermal noise only) if $2f$ wavelength modulation technique is used

Hence:

- The sensor must be operated in a **"locked to absorption line"** mode instead of a frequency-scan mode.

So:

- Use a reference cell and $3f$ component of the photodetector signal for line locking

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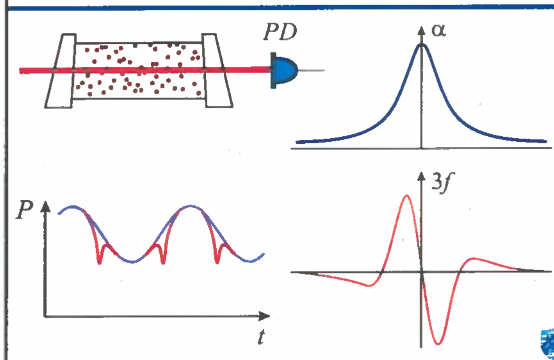
Line locking based on $3f$ detection



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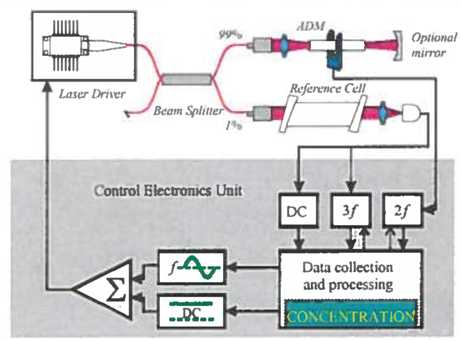
QEPAS based gas sensor architecture



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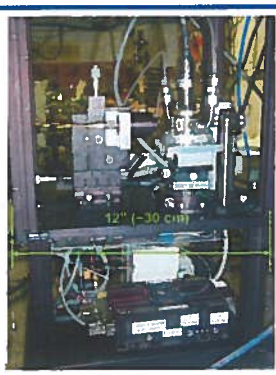
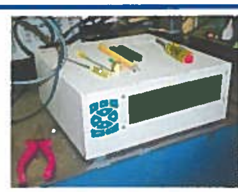
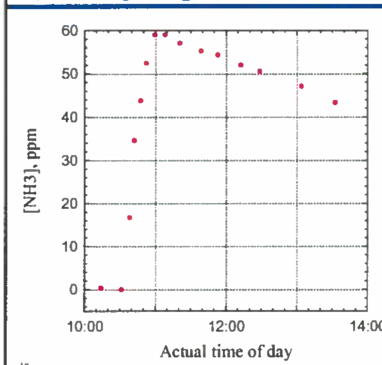
A prototype portable QEPAS NH_3 sensor





NH_3 in H_2: SRNL, reaction bed products



The spectrophone was not optimized for H_2 (different speed of sound), therefore the response was ~7 times weaker compared to N_2 as a carrier.

However, the sensitivity was still sufficient to monitor the NH_3 content in the post-reaction bed H_2 flow.

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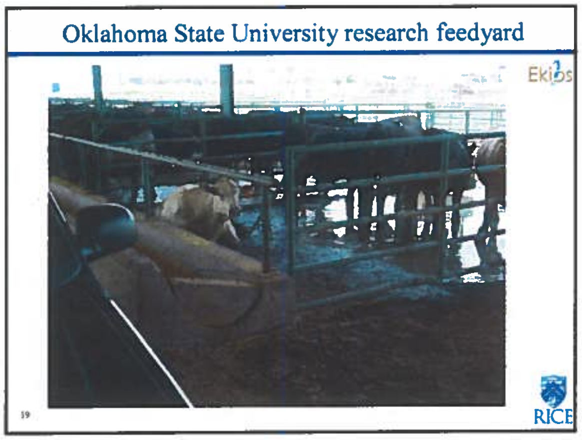
Oklahoma State University research feedyard
Ekips
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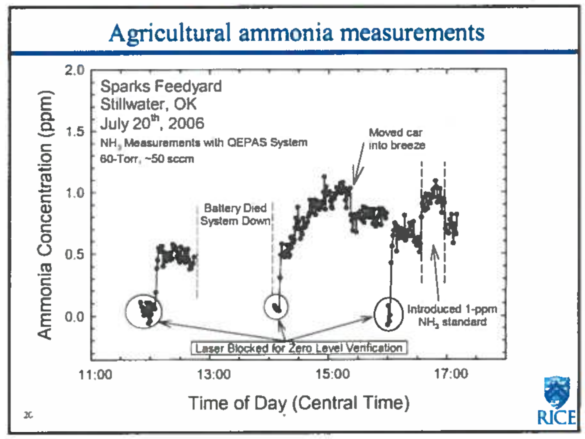
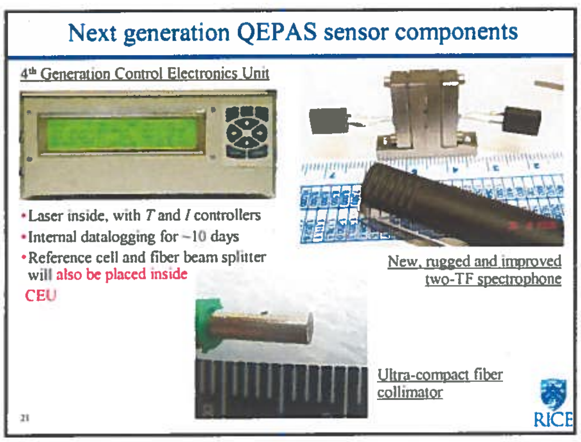

Agricultural ammonia measurements
Sparks Feedyard
Stillwater, OK
July 20th, 2006
NH3 Measurements with QEPAS System
60-Torr, ~50 sccm
Battery Died
System Down
Moved car
into breeze
Introduced 1-ppm
NH3 standard
Laser Blocked for Zero Level Verification
Ammonia Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
11:00
13:00
15:00
17:00
Time of Day (Central Time)
RICE


Next generation QEPAS sensor components
4th Generation Control Electronics Unit
•Laser inside, with T and I controllers
•Internal datalogging for ~10 days
•Reference cell and fiber beam splitter will also be placed inside CEU
New, rugged and improved two-TF spectrophone
Ultra-compact fiber collimator
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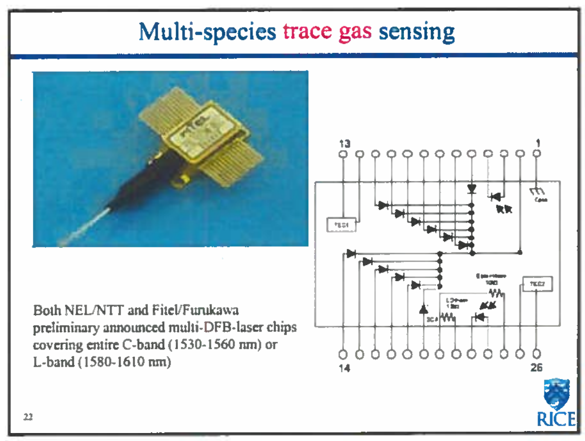
Multi-species trace gas sensing
Both NEL/NTT and Fitel/Furukawa preliminary announced multi-DFB-laser chips covering entire C-band (1530-1560 nm) or L-band (1580-1610 nm)
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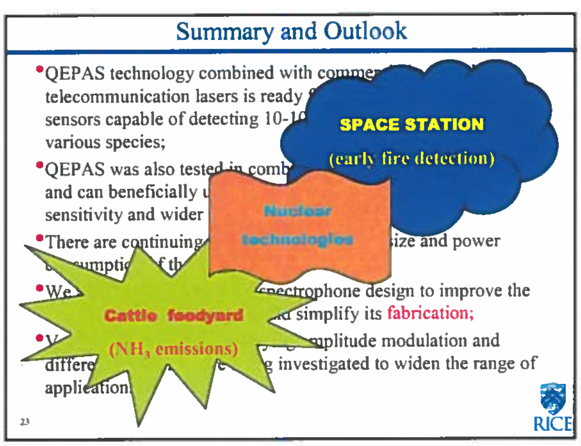
Summary and Outlook
•QEPAS technology combined with comme
telecommunication lasers is ready
sensors capable of detecting 10-10
various species;
•QEPAS was also tested in comb
and can beneficially
sensitivity and wider
•There are continuing
ize and power
•We
spectrophone design to improve the
simplify its fabrication;
mplitude modulation and
differe
investigated to widen the range of
application
SPACE STATION
(early fire detection)
Nuclear
technologies
Cattle feedyard
(NH3 emissions)
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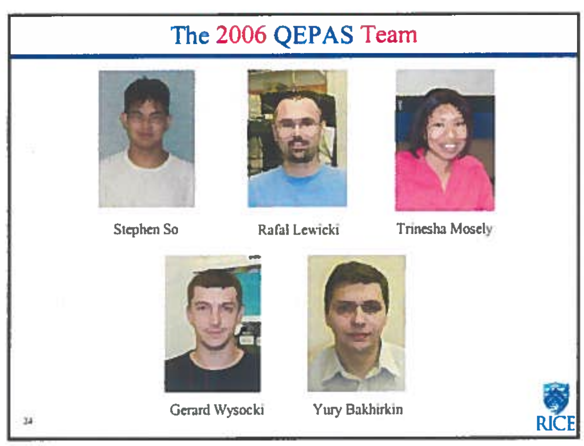
The 2006 QEPAS Team
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Gerard Wysocki
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