Infrared Technologies for Environmental Sensing: Present and Future Opportunities and Challenges

RICE

F.K. Tittel, R.F. Curl, L. Dong, J. Doty, A.A. Kosterev, R. Lewicki, and D. Thomazy

Rice Quantum Institute, Rice University, Houston, TX, USA

http://ece.rice.edu/lasersci/

OUTLINE

MEMS Alliance Symposium

Washington, D.C.

Nov 30, 2009

- Motivation: Chemical Sensing Applications
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sensing Technologies (QEPAS)
- Selected Applications of Trace Gas Detection
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
  - NH_3 Detection for Environmental Applications
  - Nitric Oxide Detection (LAS & Faraday Rotation Spectroscopy)
  - Monitoring of Broadband Absorbers
- Future Directions of Laser based Gas Sensor Technology

Work supported by NSF ERC MIRTHE, NASA-JSC, DoE STTR and the Welch Foundation

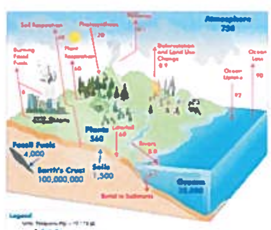
Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, Truck, Aircraft and Marine Emissions
- **Rural Emission Measurements**
  - Agriculture & Forestry, Livestock
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Nuclear Safeguards, Pharmaceutical, Metals Processing, Food & Beverage Industries
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Biomedical and the Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

RICE

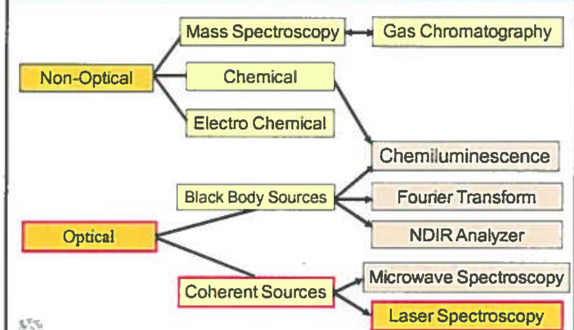
Greenhouse Gases and Climate Change

- Kyoto Protocol Dec. 1997 and Copenhagen Dec. 2009)
  - Carbon credit and carbon trading
- Need to measure and locate all sources and sinks
  - Must be in real time and continuous
- Multiple greenhouse gases
  - Carbon dioxide
  - Methane
  - Nitrous oxide



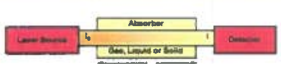
3

Existing Methods for Trace Gas Detection



RICE

Basics of Optical Trace Gas Analyzers

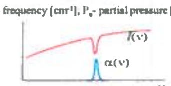


Beer-Lambert's Law of Linear Absorption

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

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

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



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

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)

Key Requirements: Sensitivity, specificity, rapid data acquisition and multi-species detection

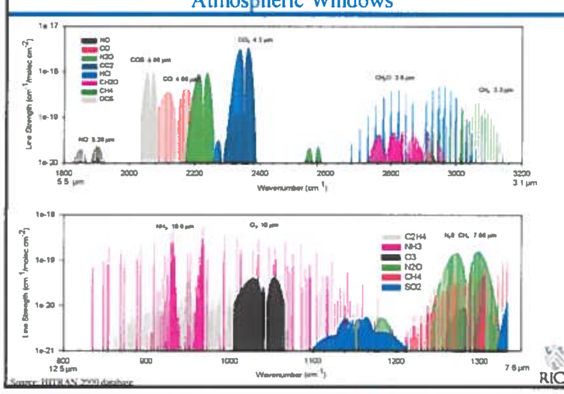
Optimum Molecular Absorbing Transition
- NIR Overtone or Combination Bands
- **MIR Fundamental Absorption Bands**

Long Optical Pathlengths
- Multipass Absorption Cell White, Herriott)
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector); Standoff and Remote Detection
- Fiberoptic evanescent wave Spectroscopy

Spectroscopic Detection Schemes
- Wavelength or Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy (PAS or QEPAS
- NICE-OHMS, LIBS and LIF

5

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



RICE

6

Mid-IR Source Requirements for Laser Spectroscopy

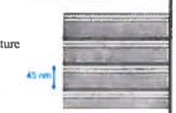
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Optimum Wavelength, Power
Selectivity (Spectral Resolution)	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelength
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

7

Key Characteristics of mid-IR QCL and ICL Sources - Nov 2009

- **Band – structure engineered devices**
  (Emission wavelength is determined by layer thickness – MBE or MOCVD); mid-infrared QCLs operate from 3 to 24 µm (AlInAs/GaInAs)
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- **Broad spectral tuning range in the mid-IR**
  (4-24 µm for QCLs and 3-5 µm for ICLs and GaSb diodes)
  - 1.5 cm^{-1} using injection current control for DFB devices
  - 10-20 cm^{-1} using temperature control for DFB devices
  - > 430 cm^{-1} using an external grating element and FP chips with heterogeneous cascade active region design; also QCL DFB Array
- **Narrow spectral linewidth**
  - CW: 0.1 - 3 MHz & <10Khz with frequency stabilization (0.0004 cm^{-1})
  - Pulsed: ~ 300 MHz
- **High pulsed and cw powers of QCLs at TEC/RT temperatures**
  - Pulsed and CW powers of 34 W and 3 W respectively; high temperature operation ~300K
  - >280 mW, TEC CW DFB @ 5 µm
  - > 600 mW (CW FP) @ RT, wall plug efficiency of ~17 % at 4.6µm;

4 mm



8

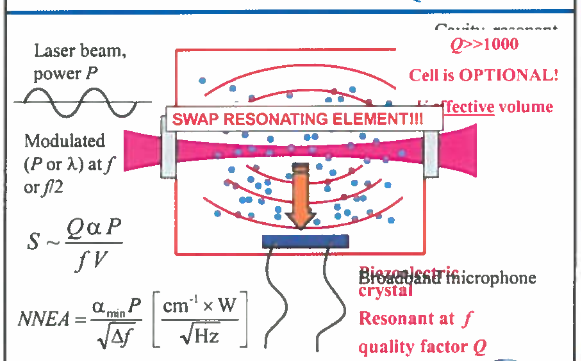
Quantum Cascade (QC), Interband (IC) and GaSb Laser Availability in November 2009

- Commercial Sources
  - Adtech, CA
  - Alpes Lasers, Switzerland & Germany
  - Alcatel-Thales, France
  - Hamamatsu, USA & Japan
  - Maxion Technologies, Inc (Physical Sciences, Inc), MD
  - Nanoplus, Germany
  - Pranalytica, CA
- Research Groups
  - Harvard University
  - Fraunhofer-IAF, Freiburg, Germany
  - NASA-JPL, Pasadena, CA
  - Naval Research Laboratories, Washington, DC
  - Northwestern University, Evanston, IL
  - Princeton University (MIRTHE), NJ
  - State University of New York
  - Technical University, Zuerich, CH
  - University of Montpelier, France
  - UK: Sheffield

9

Quartz Enhanced Photoacoustic Spectroscopy

From conventional PAS to QEPAS



11 RICE

Quartz Tuning Fork as a Resonant Microphone

Unique properties

- Extremely low internal losses:
  - Q~10 000 at 1 atm
  - Q~100 000 in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range – linear from thermal noise to breakdown deformation
  - 300K noise: $x \sim 10^{-11}$ cm
  - Breakdown: $x \sim 10^{-2}$ cm
- Wide temperature range: from 1.56K (superfluid helium) to ~700K
- Low cost (<$1)

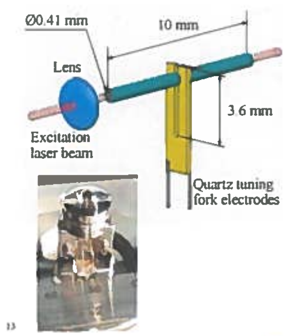
Other parameters

- Resonant frequency ~32.8 kHz
- Force constant ~26800 N/m
- Electromechanical coefficient ~7×10^{-6} C/m

12 RICE

12

QEPAS spectrophone



Micro-resonator tubes

- Must be close to QTF but not touch TF (30-50 mm gaps).
- Optimum inner diameter 0.41 mm (10% lower signal with 0.6 mm diameter tubes).
- Each micro-resonator tube ~5mm long (~λ/2 for sound at 32.8 kHz)

Gain: ×10 to ×20

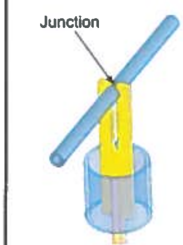
Windows

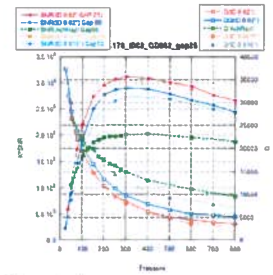
- Must be tilted to prevent reflected light from entering micro-resonator tubes.
- Exact positioning is not important, to the best of our current knowledge.

13 RICE

13

QEPAS SNR Enhancement of Acoustic Microresonator



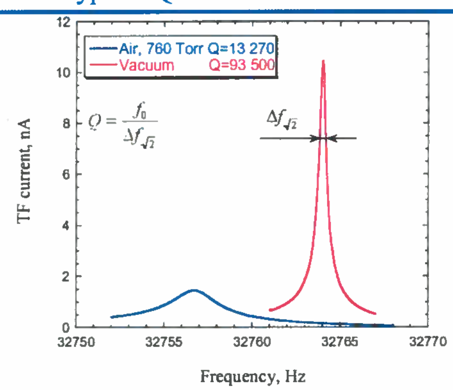


Microresonator tubes
Must be close to QTF but not touching (i.e. 30-50μm gaps).
Each tube is ~ 5mm long (~λ/2 for sound at 32.8 kHz)

QEPAS Signal Gain: × 8 to ×20 depending on pressure & gas

RICE

Typical QTF Resonance Curves

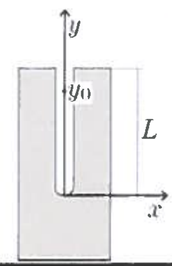


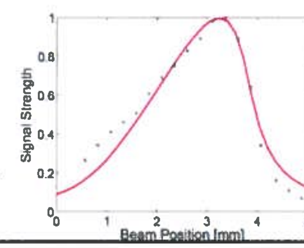
15 RICE

What about QEPAS Modeling ?

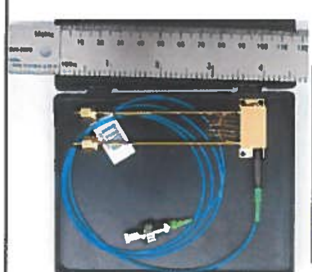
MIRTHE UMBC team :N. Petra, J. Zweck, A. A. Kosterev, S. E. Minkoff and D. Thomazy, "Theoretical Analysis of a Quartz-Enhanced Photoacoustic Spectroscopy Sensor", Appl. Phys B 94, 673-680 (2009)

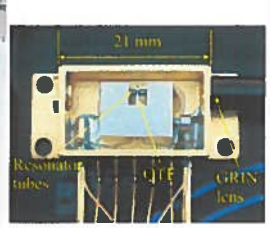
Also: S. L. Firebaugh, F. Roignant & E A. Terray, "Modelling the Response of Photoacoustic Gas Sensors", Comsol Conf, Boston, MA ; Oct 8-10,2009





Alignment-free QEPAS Absorption Detection Module

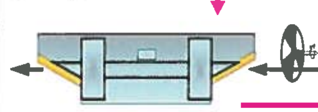




RICE

Comparative Sizes of QEPAS & PAS ADMs

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



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

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

RICE

18

Merits of QEPAS based Trace Gas Detection

- Very small sensing module and the sample volume (a few mm^3)
- Optical detector is not required
- Wide dynamic range
- Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
- Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise: k_BT energy in the TF symmetric mode, directly observed
- Absence of low-frequency noise: SNR scales as $\sqrt{t}$, up to t=3 hours experimentally verified

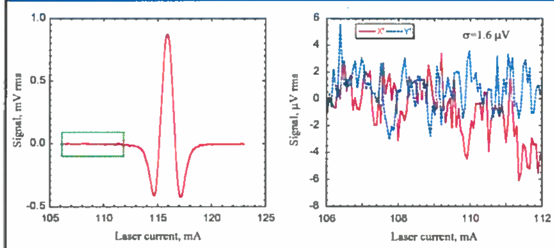
QEPAS: some challenges

- Responsivity depends on the speed of sound and molecular energy transfer processes
- Sensitivity scales with laser power

19

19

WM QEPAS signal for H_2O line @ 7306.75 cm^{-1}, 48 ppmv



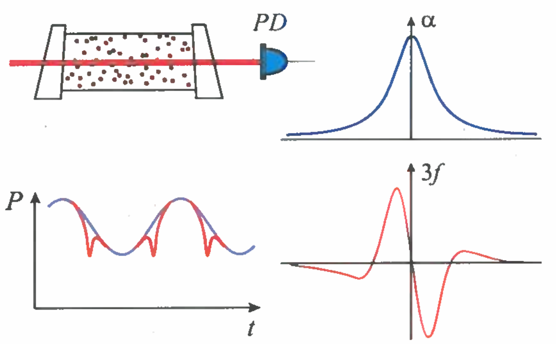
Laser power in cell: 9.5 mW; Time constant: 1s; SNR=550

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

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

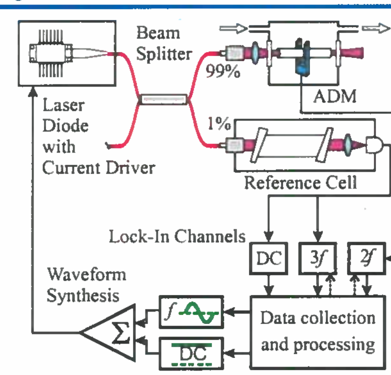
20

Line locking based on 3f detection



21

Principal Architecture of a QEPAS Gas Sensor

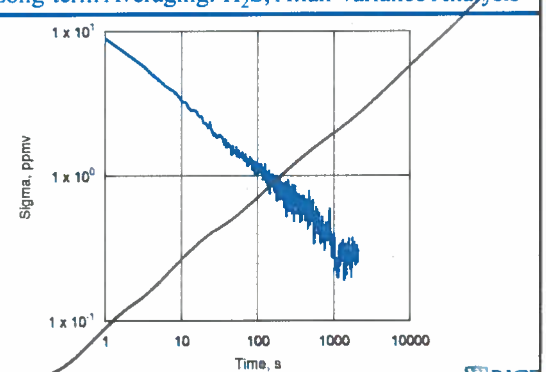


22

RICE

22

Long-term Averaging: H_2S, Allan Variance Analysis



23

RICE

QEPAS Performance for 13 Trace Gas Species (Nov. '09)

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% RH)*	6539.11	60	< 4.3×10^{-9}	50	0.16
C_2H_2 (N_2)*	6523.88	720	4.1×10^{-9}	57	0.03
NH_3 (N_2)*	6528.76	575	3.1×10^{-9}	60	0.06
C_2H_4 (N_2)*	6177.07	715	5.4×10^{-9}	15	1.7
CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10^{-9}	16	0.24
CO_2 (breath ~100% RH)	6361.25	150	8.2×10^{-9}	45	40
H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	5
CO_2 (N_2+1.5% H2O)*	4991.26	50	1.4×10^{-8}	4.4	18
CH_2O (N_2: 75% RH)*	2804.90	75	8.7×10^{-9}	7.2	0.12
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
C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	90
C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	0.009
NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	0.006

* - Improved microresonator
** - Improved microresonator and double optical pass through ADM
*** - With amplitude modulation and metal microresonator

NNEA – normalized noise equivalent absorption coefficient
NEC – noise equivalent concentration for available laser power and τ=1s time constant, 18 dB/oct filter slope

For comparison: conventional PAS 2.2 (2.6)×10^{-9} cm^{-1}W/√Hz (1,000; 10,300 Hz) for NH_3*,**

* M. E. Webber et al, Appl Opt 42, 2119-2126 (2003); ** J. S. Pilgrim et al, SAE Intl ICES 2007-01-3152

RICE

24