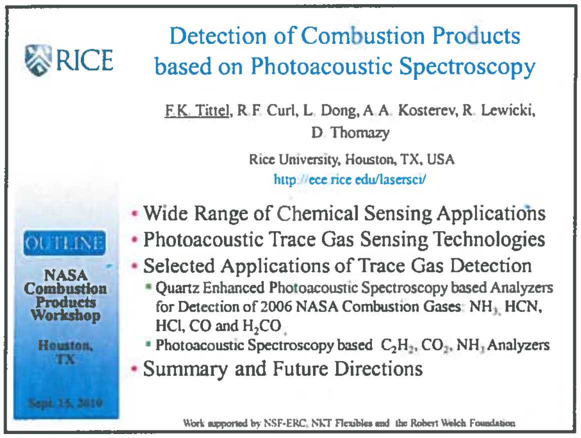


Detection of Combustion Products based on Photoacoustic Spectroscopy

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

Rice University, Houston, TX, USA
http://ece.rice.edu/lasersci/

OUTLINE

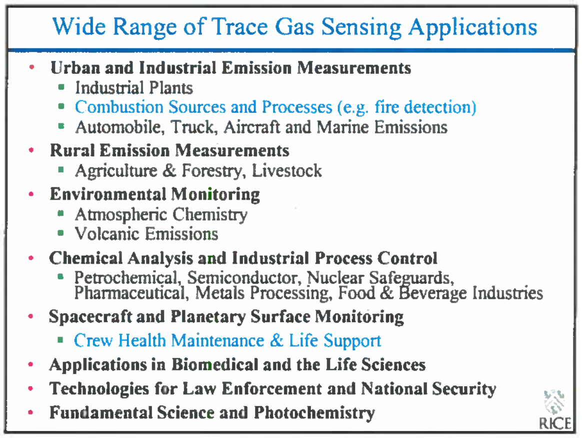
NASA Combustion Products Workshop

Houston, TX

Sept. 15, 2010

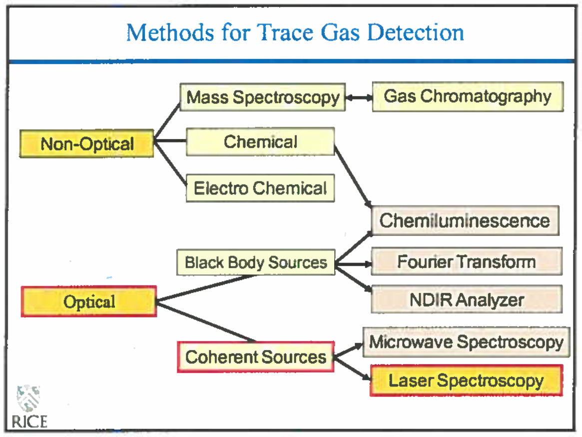
- Wide Range of Chemical Sensing Applications
- Photoacoustic Trace Gas Sensing Technologies
- Selected Applications of Trace Gas Detection
  - Quartz Enhanced Photoacoustic Spectroscopy based Analyzers for Detection of 2006 NASA Combustion Gases: NH_3, HCN, HCl, CO and H_2CO
  - Photoacoustic Spectroscopy based C_2H_2, CO_2, NH_3 Analyzers
- Summary and Future Directions

Work supported by NSF-ERC, NKT Flexibles and the Robert Welch Foundation

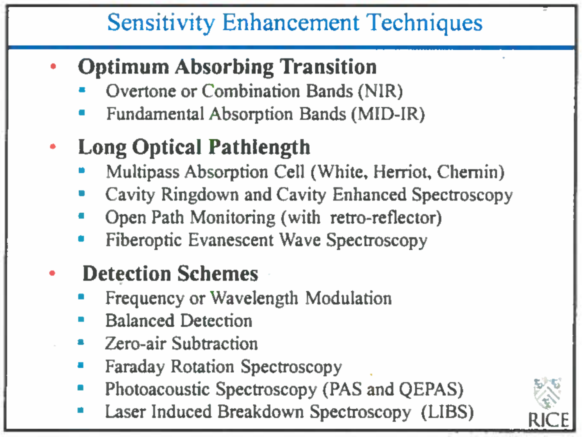


Wide Range of Trace Gas Sensing Applications

- **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**

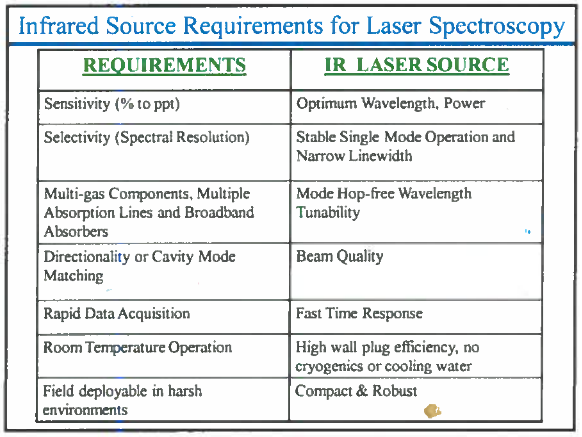


Methods for Trace Gas Detection



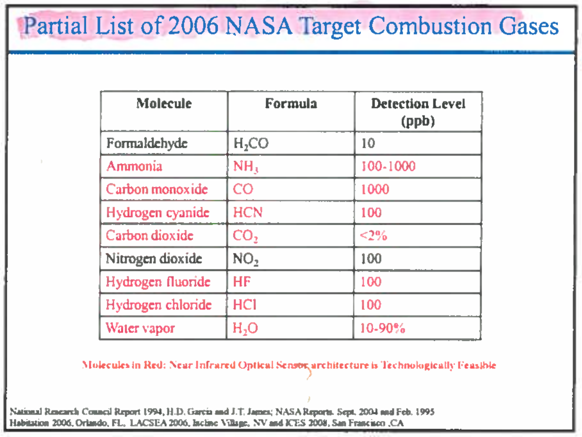
Sensitivity Enhancement Techniques

- **Optimum Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot, Chernin)
  - Cavity Ringdown and Cavity Enhanced Spectroscopy
  - Open Path Monitoring (with retro-reflector)
  - Fiberoptic Evanescent Wave Spectroscopy
- **Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Faraday Rotation Spectroscopy
  - Photoacoustic Spectroscopy (PAS and QEPAS)
  - Laser Induced Breakdown Spectroscopy (LIBS)



Infrared Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Optimum Wavelength, Power
Selectivity (Spectral Resolution)	Stable Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Mode Hop-free Wavelength Tunability
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	High wall plug efficiency, no cryogenics or cooling water
Field deployable in harsh environments	Compact & Robust

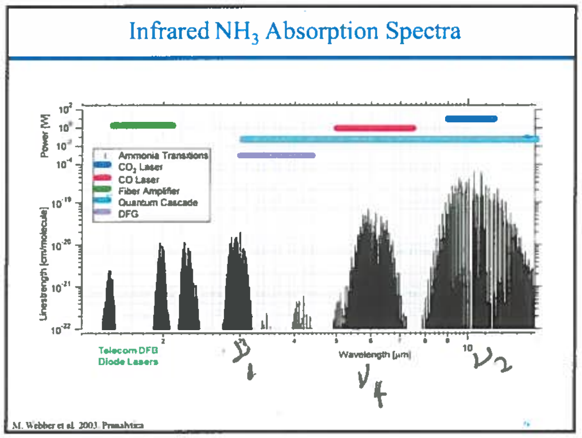


Partial List of 2006 NASA Target Combustion Gases

Molecule	Formula	Detection Level (ppb)
Formaldehyde	H_2CO	10
Ammonia	NH_3	100-1000
Carbon monoxide	CO	1000
Hydrogen cyanide	HCN	100
Carbon dioxide	CO_2	<2%
Nitrogen dioxide	NO_2	100
Hydrogen fluoride	HF	100
Hydrogen chloride	HCl	100
Water vapor	H_2O	10-90%

Molecules in Red: Near Infrared Optical Sensor architecture is Technologically Feasible

National Research Council Report 1994, H.D. Garcia and J.T. James; NASA Reports. Sept. 2004 and Feb. 1995 Habitation 2006, Orlando, FL, LACSEA 2006, Incline Village, NV and ICES 2008, San Francisco ,CA

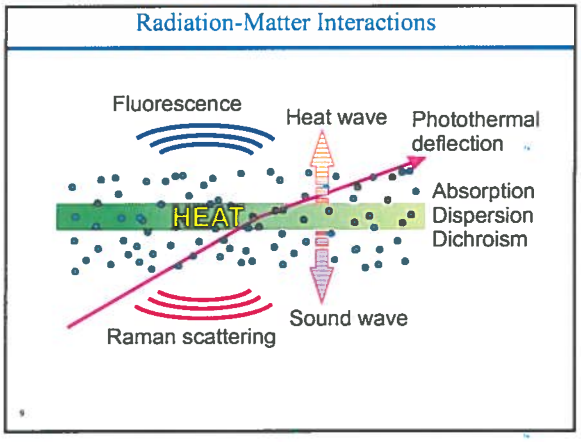


Infrared NH_3 Absorption Spectra

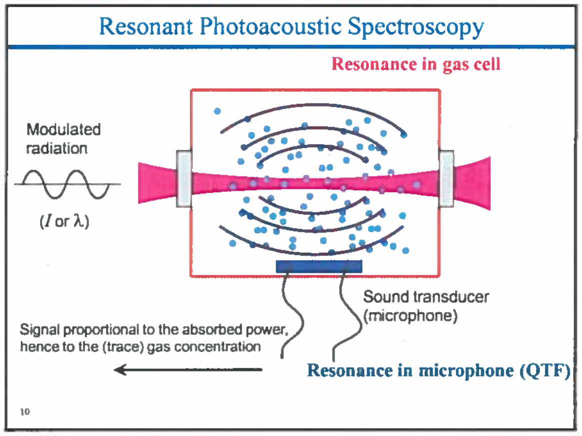
ν_1 ν_4 ν_2

M. Webber et al. 2003, Pranalytica

Photoacoustic Spectroscopy



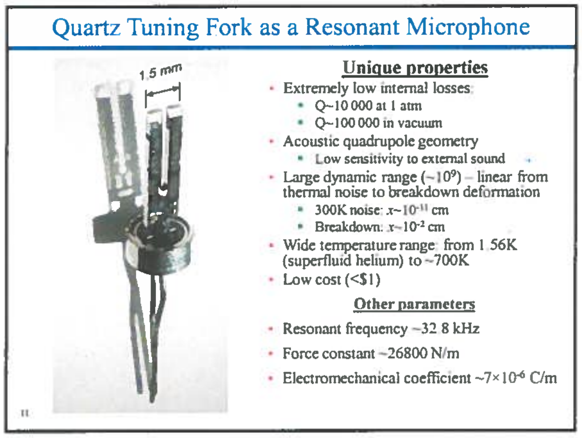
Radiation-Matter Interactions



Resonant Photoacoustic Spectroscopy

Signal proportional to the absorbed power, hence to the (trace) gas concentration

Resonance in microphone (QTF)



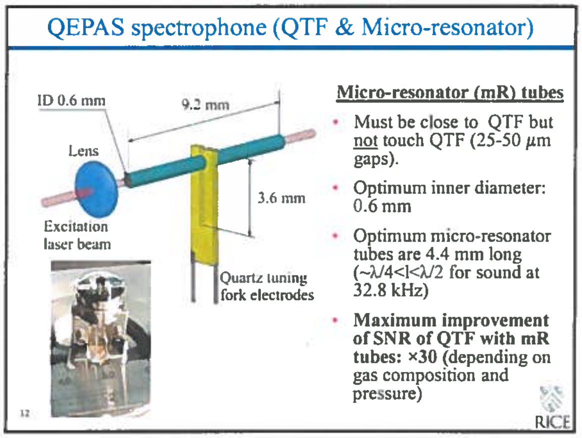
Quartz Tuning Fork as a Resonant Microphone

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 (~10^{9}) – 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



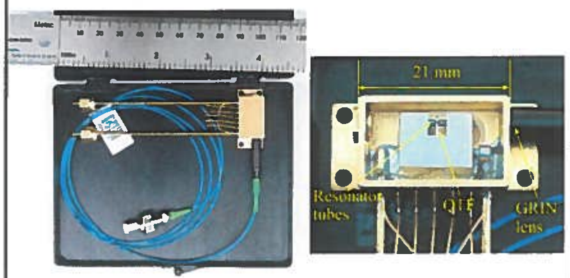
QEPAS spectrophone (QTF & Micro-resonator)

Micro-resonator (mR) tubes

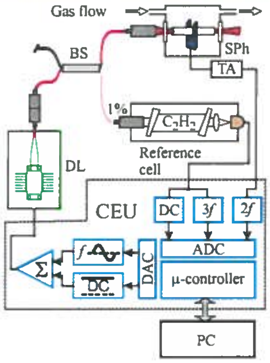
- Must be close to QTF but not touch QTF (25-50 µm gaps).
- Optimum inner diameter: 0.6 mm
- Optimum micro-resonator tubes are 4.4 mm long (~λ/4<l<λ/2 for sound at 32.8 kHz)
- **Maximum improvement of SNR of QTF with mR tubes: ×30 (depending on gas composition and pressure)**

RICE

Alignment-free QEPAS Absorption Detection Module

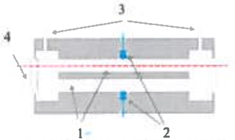


Principal Architecture of a QEPAS Gas Sensor



Comparison of State-of-the-Art CPAS & QEPAS Detection Modules

CPAS



1. Acoustic resonator;2 Microphone;3 Gas inlet-outlet; 4. Windows

l=136 mm, Ø56.5 mm
Resonator: 4500 mm³
Optical pathlength: 90 mm
f_0=1790 Hz in N_2
Q=49 in N_2

C.-M. Lee, K. V. Bychkov, V. A. Kapitanov, A. I. Karapuzikov, Y. N. Ponomarev, I. V. Sherstov, V. A. Vasiliev, High-sensitivity laser photoacoustic leak detector, Opt. Eng. 46, 064302 (2007)

QEPAS

21×12.7×8.5 mm
Resonator: 2 mm³
Optical pathlength: 9 mm
f_0=32735 Hz in N_2
Q=3630 in N_2

CPAS vs. QEPAS: C_2H_2 and CO_2 Sensitivity Comparison

C_2H_2 : absorption line at 6529.17cm⁻¹, 10 ppmv

CO_2: 6361.25 cm⁻¹ , 100%

	10 ppm C_2H_2 in N_2		Pure CO_2	
	QEPAS	CPAS	QEPAS	CPAS
Signal, μV	6280	46	13880	413
Noise, μV	53	0.49	74	0.91
SNR	119	94	188	455
Laser Power, mW	37.2	39.0	21.1	24.3
NNEA, cm⁻¹W/√Hz	4.1×10^{-9}	5.4×10^{-9}	16.0×10^{-9}	7.6×10^{-9}

NNEA: normalized noise-equivalent absorption coefficient
(lower NNEA means better sensitivity)
Equivalent noise detection bandwidth is 0.833 Hz

QEPAS Performance for 16 Trace Gas Species (Sept. '10)

Molecule (Host)	Frequency, cm⁻¹	Pressure, Torr	NNEA, cm⁻¹W/Hz^½	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	4.6×10^{-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 ~60% RH)	6361.25	150	8.2×10^{-9}	45	40
H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	5
HCl (N_2 dry)	5739.26	760	5.2×10^{-8}	15	0.7
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
NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	0.003
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⁻¹W/√Hz (1,800; 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

Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm³)
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range
- Frequency and spatial selectivity of acoustic signals
- 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
- Absence of low-frequency noise: SNR scales as √*t*, up to *t*=3 hours as experimentally verified

QEPAS: some technical challenges

- Responsivity depends on the speed of sound and molecular energy transfer processes
- Sensitivity scales with laser power
- Effect of H_2O
- Cross sensitivity issues
- Alignment cost

|| add table on pg 9
of instructions.
current and future

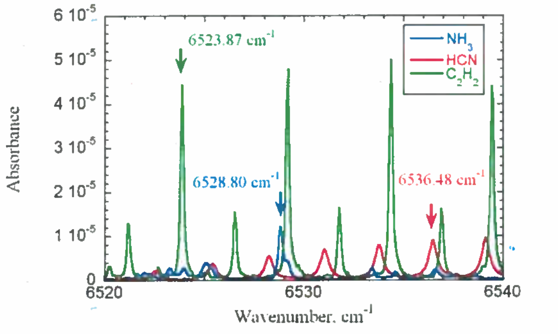
Recent Applications of mid-infrared Laser based Trace Gas Sensors

Motivation for NH_3 Detection

- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- 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 diseases)

RICE

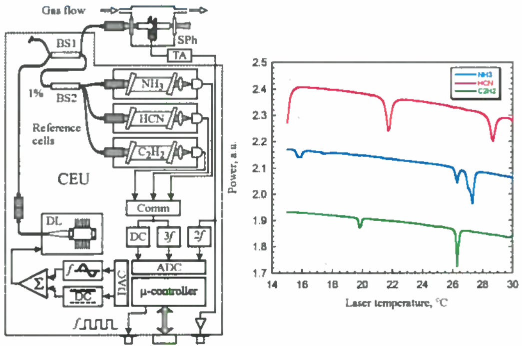
Simulated Spectra of 3 Target molecules: NH_3, HCN & C_2H_2



FTIR spectra from PNNL database, 1 atm pressure, 1 ppmv

RICE

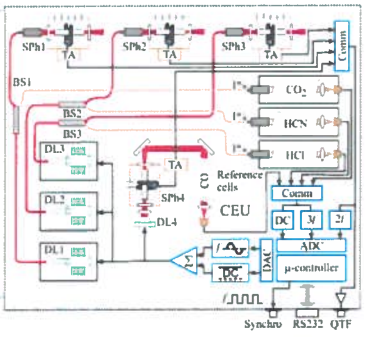
Multispecies QEPAS trace gas sensor



A.Kosterev, F.K.Tittel & G. Bearman., *SAE Intl J. Aerosp* 1, 331-336, 2008

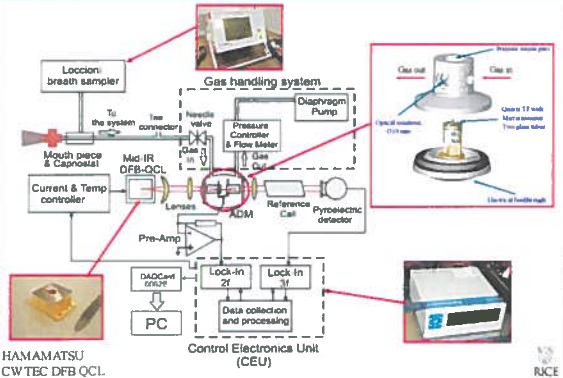
RICE

QEPAS based sensor for CO, CO_2, HCN & HCl detection



RICE

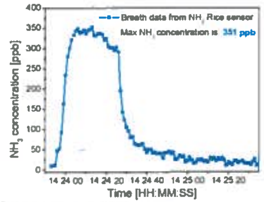
QEPAS based NH_3 Gas Sensor Architecture

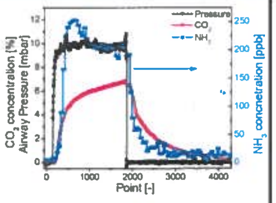


HAMAMATSU
CW TEC DFB QCL

RICE

Real-time exhaled human NH_3 Breath Data





For each patient, a separate folder is created on the Loccioni memory stick.

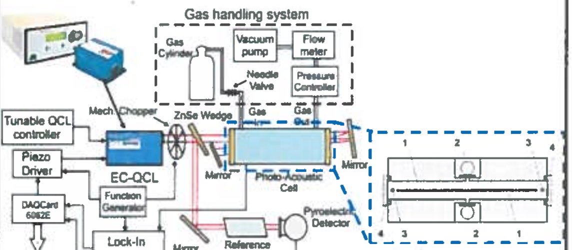
Each folder contains:

- Excel worksheet with 3 columns data: CO_2 [%],
- Airway pressure [mbar] and Ammonia [ppb]
- CO_2 [%] plot
- Airway pressure [mbar] plot

The Ammonia [ppb] data is not saved as a plot

RICE

Mid-IR EC-QCL based AM-PAS Sensor for atmospheric NH_3 Detection



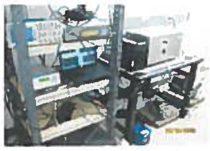
A ring differential resonance Photo-Acoustic Cell:

1. Acoustic resonator,
2. Microphone,
3. Gas input and output,
4. Window

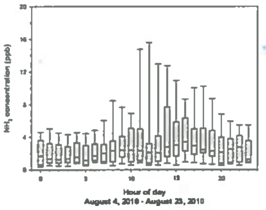
RICE

NH_3 Data after Sensor Installation on the 60 m high Moody Tower Roof (UH campus)

Moody Tower at the UH campus, Houston, TX



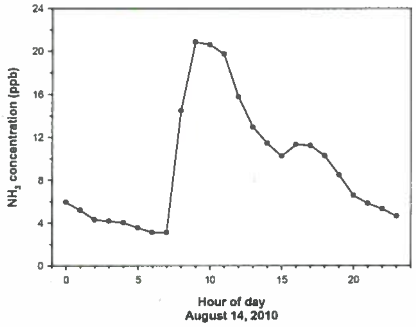
Ammonia sensor and electronics installed on Moody Tower roof



Diurnal trend of atmospheric NH_3 concentration

RICE

Accidental NH_3 release on I-45 (Aug 14,2010)



Groups working on Quartz Enhanced Photoacoustic Spectroscopy

- Rice University
- UMBC, Baltimore, MD
- Savannah River National Laboratory, Aikin, SC
- Pacific Northwest National Laboratory, Richland, WA
- NASA- JSC, Houston, TX
- JPL, Pasadena, CA
- Woods Hole Oceanographic Institution, MA
- United States Naval Academy, Annapolis, MD
- Daylight Solutions Inc., San Diego, CA
- NKT Flexibles, Copenhagen, Denmark
- University of Bari, Italy
- Anhui Institute of Optics and Fine Mechanics, Heifei, China
- Zhejiang University, Hangzhou, China
- TU Clausthal, Germany
- University of Montpellier, France
- University of Littoral, Dunkerque, France
- Institute of Spectroscopy, Troitsk, Russia
- And others

Summary & Future Directions of QEPAS based Gas Sensor Technology

- **Semiconductor Laser based QEPAS Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity ($<10^{-4}$) and selectivity (3 to 500 MHz)
  - Capable of fast data acquisition and analysis
  - Detected 17 trace gases using QEPAS to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, H_2S, HCN, HCl, H_2CO, SO_2, C_2H_5OH, C_2HF_5 ,TATP and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality – NH_3, H_2CO, NO, isotopic ratio measurements of CO_2 and CH_4, fire and post fire detection; quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH_3, H_2O, and H_2S)
  - Medical & biomedical non-invasive diagnostics (NH_3, NO, N_2O and CH_3COCH_3)
  - Ultra-compact, low cost, robust sensors
- **Future Directions and Collaborations**
  - Improvements of existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR intersubband and interband quantum cascade lasers
  - Further development of spectrophone technology
  - New applications enabled by novel broadly wavelength tunable quantum cascade lasers based on EC-QCLs (e.g. sensitive concentration measurements of broadband absorbers, in particular Hydrazine, NO_2, C_2H_4O, VOCs, and HCs
  - Development of optically gas sensor networks based on QEPAS and LAS