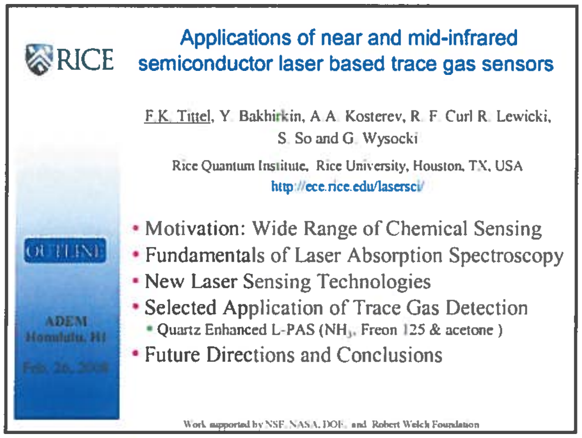


Applications of near and mid-infrared semiconductor laser based trace gas sensors

F.K. Tittel, Y. Bakhirkin, A.A. Kosterev, R. F. Curl R. Lewicki,
S. So and G. Wysocki

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

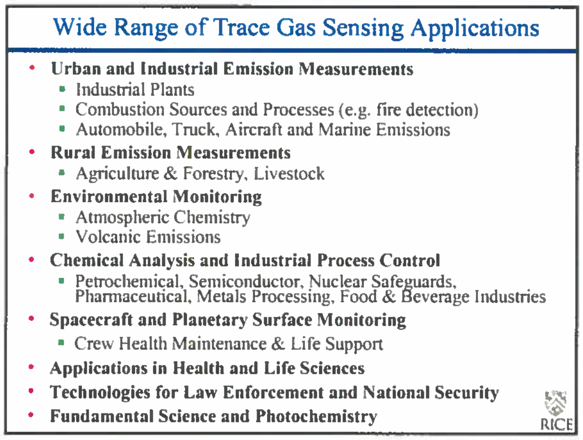
OUTLINE

- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sensing Technologies
- Selected Application of Trace Gas Detection
  - Quartz Enhanced L-PAS (NH_3, Freon 125 & acetone)
- Future Directions and Conclusions

ADEM
Honolulu, HI
Feb. 26, 2008

Work supported by NSF, NASA, DOE, and Robert Welch Foundation

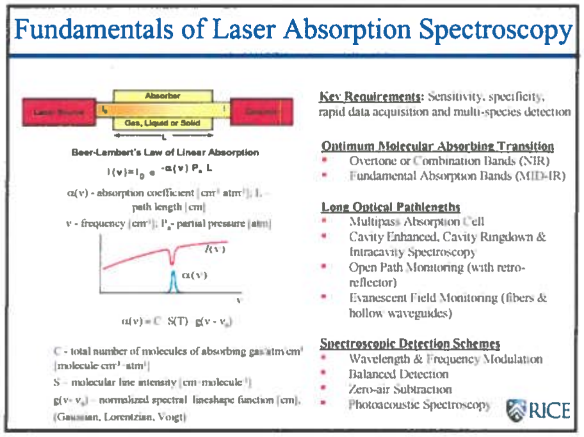
①



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 Health and Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

②



Fundamentals of Laser Absorption Spectroscopy

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]

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

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)

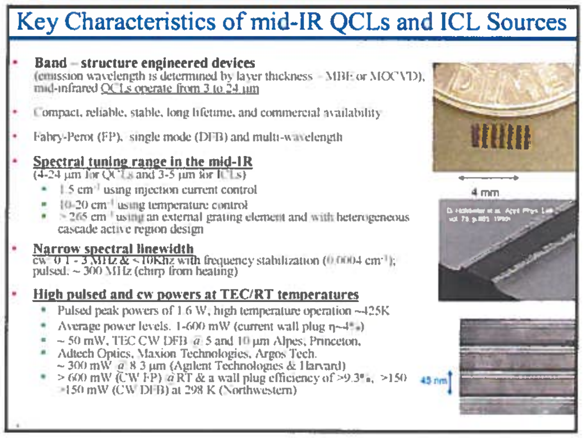
Key Requirements: Sensitivity, specificity, rapid data acquisition and multi-species detection

Optimum Molecular Absorbing Transition
- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

Long Optical Pathlengths
- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Evanescent Field Monitoring (fibers & hollow waveguides)

Spectroscopic Detection Schemes
- Wavelength & Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy

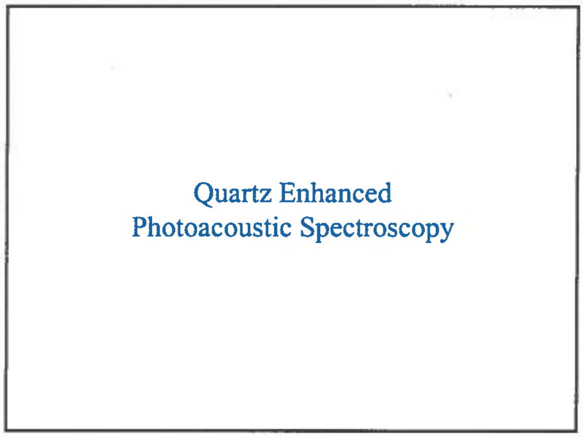
③



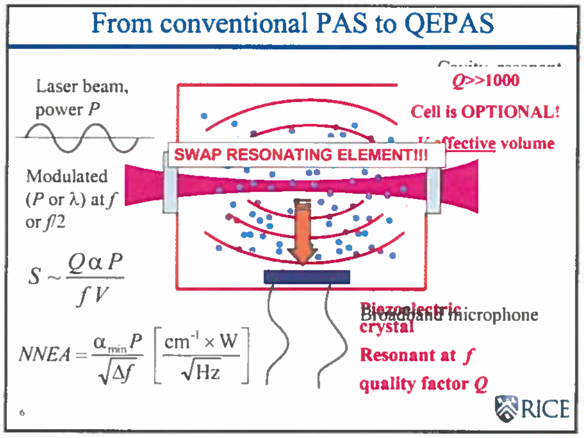
Key Characteristics of mid-IR QCLs and ICL Sources

- **Band – structure engineered devices**
  (emission wavelength is determined by layer thickness – MBE or MOCVD), mid-infrared QCLs operate from 3 to 24 µm
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- **Spectral tuning range in the mid-IR**
  (4-24 µm for QCLs and 3-5 µm for ICLs)
  - 1.5 cm^{-1} using injection current control
  - 10-20 cm^{-1} using temperature control
  - > 265 cm^{-1} using an external grating element and with heterogeneous cascade active region design
- **Narrow spectral linewidth**
  cw: 0.1 - 3 MHz & <10Khz with frequency stabilization (0.0004 cm^{-1}); pulsed: ~ 300 MHz (chirp from heating)
- **High pulsed and cw powers at TEC/RT temperatures**
  - Pulsed peak powers of 1.6 W, high temperature operation ~425K
  - Average power levels: 1-600 mW (current wall plug η~4%)
  - ~ 50 mW, TEC CW DFB @ 5 and 10 µm Alpes, Princeton,
  - Adtech Optics, Maxion Technologies, Argos Tech.
    ~ 300 mW @ 8.3 µm (Agilent Technologies & Harvard)
  - > 600 mW (CW FP) @RT & a wall plug efficiency of >9.3%, >150
    >150 mW (CW DFB) at 298 K (Northwestern)

④



Quartz Enhanced Photoacoustic Spectroscopy



From conventional PAS to QEPAS

Laser beam, power P

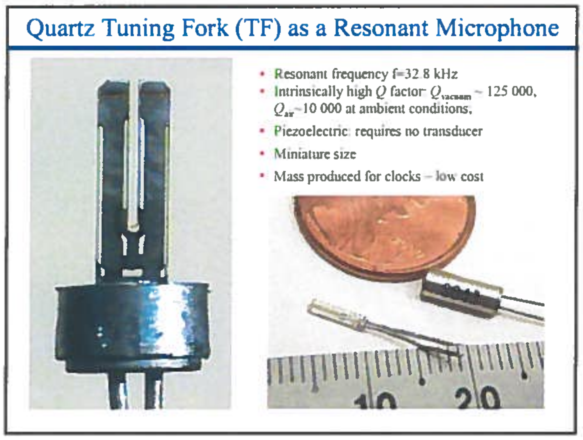
Modulated (P or λ) at f or $f/2$

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

$$NNEA = \frac{\alpha_{min} P}{\sqrt{\Delta f}} \left[\frac{cm^{-1} \times W}{\sqrt{Hz}}\right]$$

6

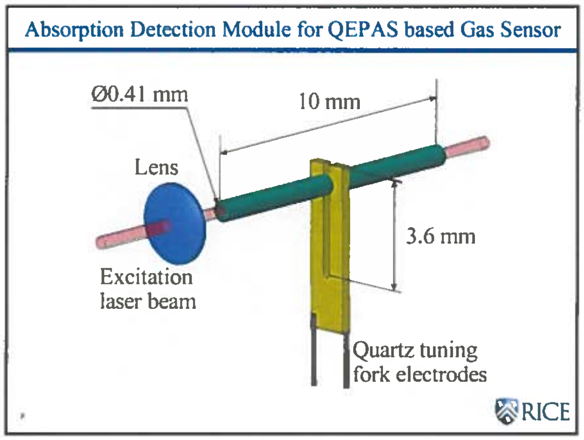
5



Quartz Tuning Fork (TF) as a Resonant Microphone

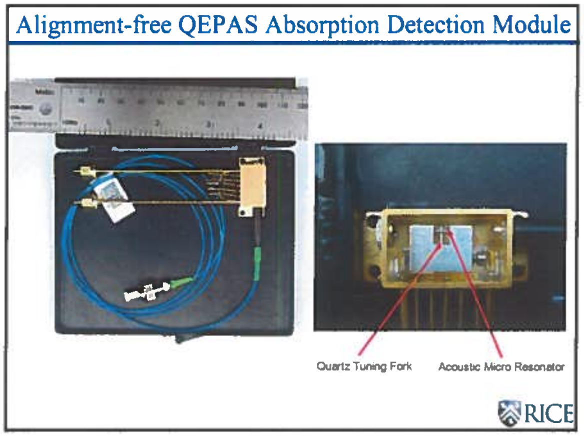
- Resonant frequency f=32.8 kHz
- Intrinsically high Q factor: Q_{vacuum} ~ 125 000, Q_{air}~10 000 at ambient conditions;
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for clocks – low cost

6



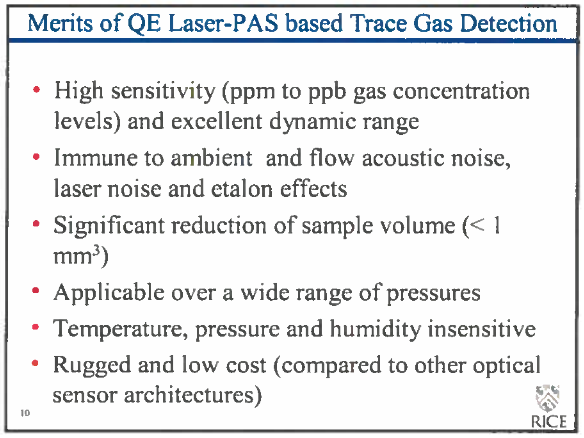
Absorption Detection Module for QEPAS based Gas Sensor

7



Alignment-free QEPAS Absorption Detection Module

8



Merits of QE Laser-PAS based Trace Gas Detection

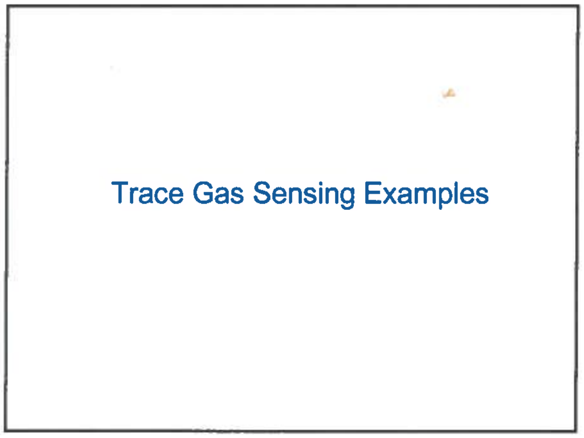
- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to ambient and flow acoustic noise, laser noise and etalon effects
- Significant reduction of sample volume (< 1 mm^3)
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive
- Rugged and low cost (compared to other optical sensor architectures)

10

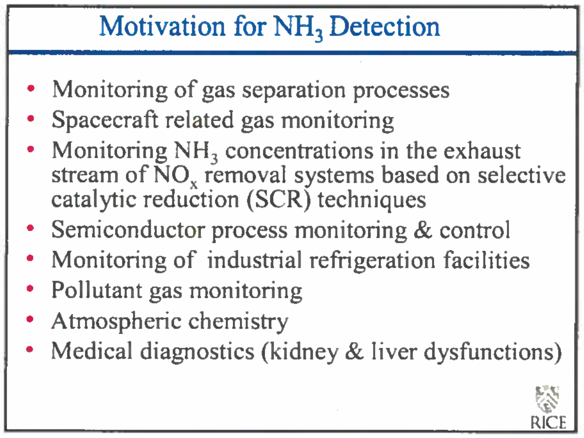
RICE

9

1/2



Trace Gas Sensing Examples

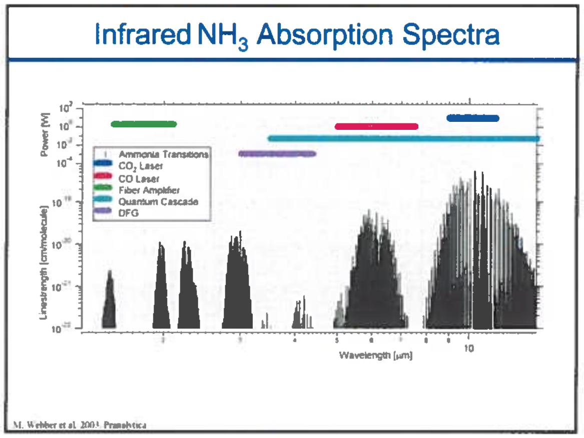


Motivation for NH_3 Detection

- Monitoring of gas separation processes
- 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)

RICE

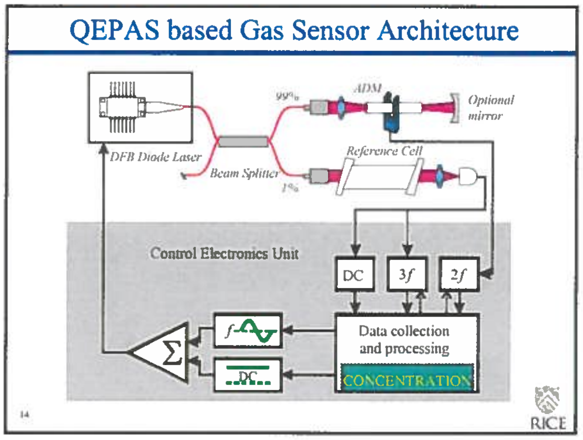
10



Infrared NH_3 Absorption Spectra

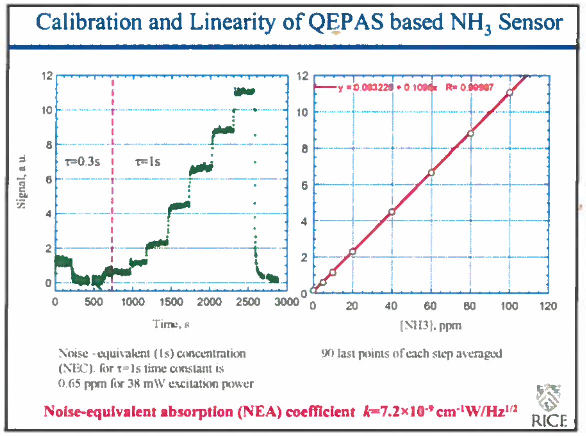
M. Webber et al. 2003, Pranalytica

11



QEPAS based Gas Sensor Architecture

12



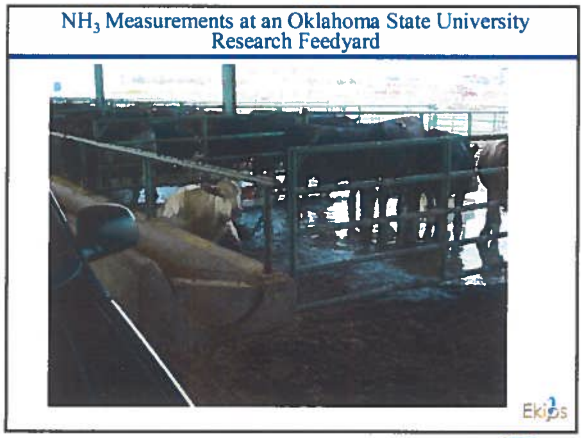
Calibration and Linearity of QEPAS based NH_3 Sensor

Noise -equivalent (1s) concentration (NEC). for τ=1s time constant is 0.65 ppm for 38 mW excitation power

90 last points of each step averaged

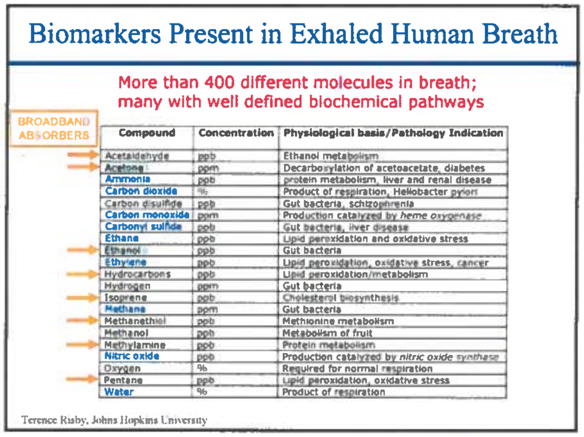
Noise-equivalent absorption (NEA) coefficient k=7.2×10^{-9} $cm^{-1}W/Hz^{1/2}$

13



NH_3 Measurements at an Oklahoma State University Research Feedyard

14



Biomarkers Present in Exhaled Human Breath

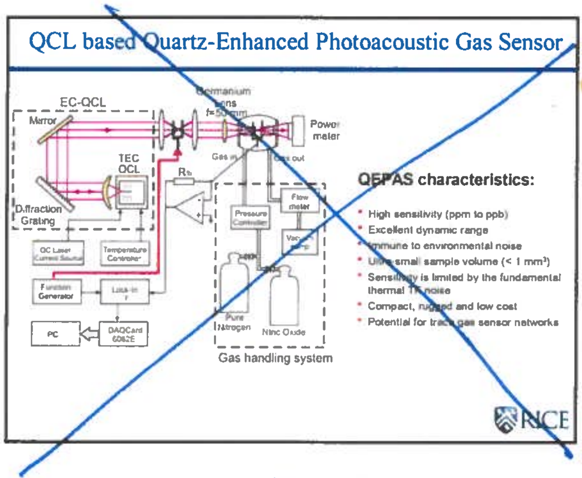
More than 400 different molecules in breath;
many with well defined biochemical pathways

BROADBAND ABSORBERS

Compound	Concentration	Physiological basis/Pathology Indication
Acetaldehyde	ppb	Ethanol metabolism
Acetone	ppm	Decarboxylation of acetoacetate, diabetes
Ammonia	ppb	protein metabolism, liver and renal disease
Carbon dioxide	%	Product of respiration, Helicobacter pylori
Carbon disulfide	ppb	Gut bacteria, schizophrenia
Carbon monoxide	ppm	Production catalyzed by *heme oxygenase*
Carbonyl sulfide	ppb	Gut bacteria, liver disease
Ethane	ppb	Lipid peroxidation and oxidative stress
Ethanol	ppb	Gut bacteria
Ethylene	ppb	Lipid peroxidation, oxidative stress, cancer
Hydrocarbons	ppb	Lipid peroxidation/metabolism
Hydrogen	ppm	Gut bacteria
Isoprene	ppb	Cholesterol biosynthesis
Methane	ppm	Gut bacteria
Methanethiol	ppb	Methionine metabolism
Methanol	ppb	Metabolism of fruit
Methylamine	ppb	Protein metabolism
Nitric oxide	ppb	Production catalyzed by *nitric oxide synthase*
Oxygen	%	Required for normal respiration
Pentane	ppb	Lipid peroxidation, oxidative stress
Water	%	Product of respiration

Terence Risby, Johns Hopkins University

15



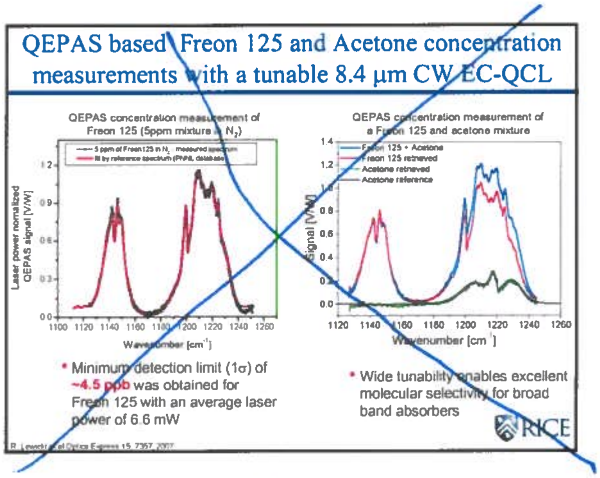
~~QCL based Quartz-Enhanced Photoacoustic Gas Sensor~~

~~**QEPAS characteristics:**~~

- ~~High sensitivity (ppm to ppb)~~
- ~~Excellent dynamic range~~
- ~~Immune to environmental noise~~
- ~~Ultra-small sample volume (< 1 mm³)~~
- ~~Sensitivity is limited by the fundamental thermal TF noise~~
- ~~Compact, rugged and low cost~~
- ~~Potential for trace gas sensor networks~~

NO (Wysocki)

explosives



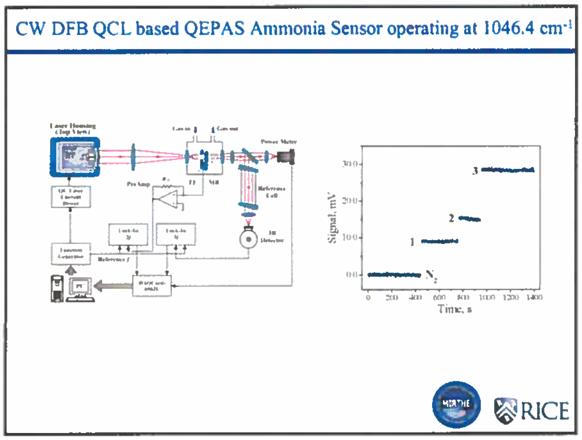
~~QEPAS based Freon 125 and Acetone concentration measurements with a tunable 8.4 µm CW EC-QCL~~

- ~~Minimum detection limit (1σ) of ~4.5 ppb was obtained for Freon 125 with an average laser power of 6.6 mW~~
- ~~Wide tunability enables excellent molecular selectivity for broad band absorbers~~

~~R. Lewicki et al Optics Express 15, 7357, 2007~~

RICE

X



CW DFB QCL based QEPAS Ammonia Sensor operating at 1046.4 cm^{-1}

RICE

16

QEPAS Performance for 14 Trace Gas Species (Feb.'08)

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	$<4.3\times10^{-9}$	50	0.16
C_2H_2 (N_2)**	6529.17	75	2.5×10^{-9}	40	0.06
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 + 0.3% H_2O)*	6057.09	950	1.0×10^{-8}	13.7	0.8
CO_2 (breath ~100% RH)	6361.25	90	1.6×10^{-8}	26	410
H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	0.30
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 (1,800; 10,300 Hz) for NH_3 (*,)**

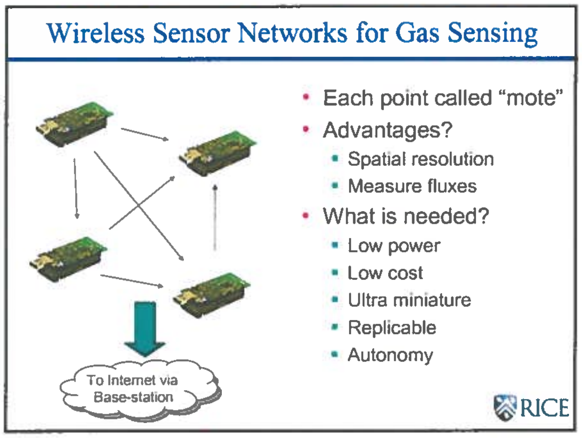
* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003); ** J. S. Pilgrim et al, SAE Intl. ICES 2007-01-3152

RICE

17

Future of Chemical Trace Gas Sensing

4

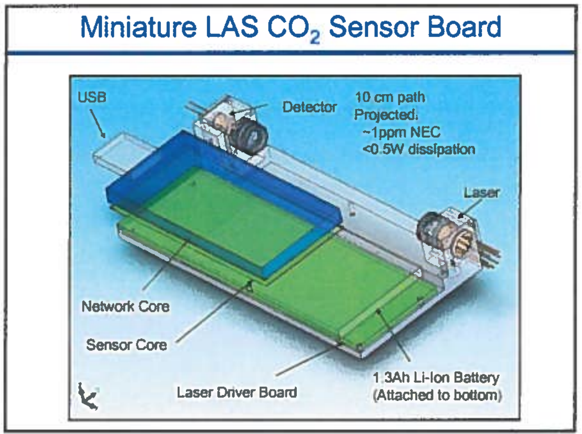


Wireless Sensor Networks for Gas Sensing

- Each point called "mote"
- Advantages?
  - Spatial resolution
  - Measure fluxes
- What is needed?
  - Low power
  - Low cost
  - Ultra miniature
  - Replicable
  - Autonomy

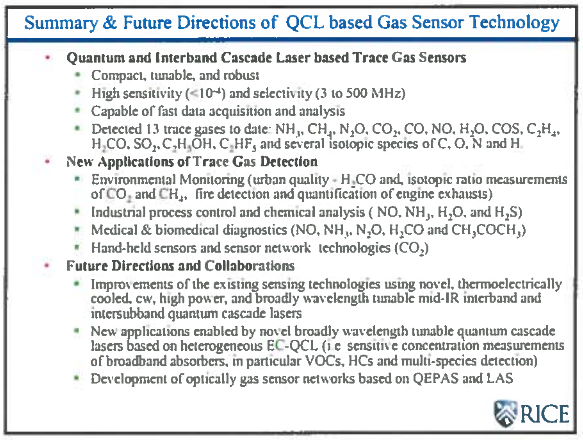
RICE

18



Miniature LAS CO_2 Sensor Board

19



Summary & Future Directions of QCL based Gas Sensor Technology

- **Quantum and Interband Cascade Laser based 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 13 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, H_2CO, SO_2, C_2H_5OH, C_2HF_5 and several isotopic species of C, O, N and H
- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality - H_2CO and, isotopic ratio measurements of CO_2 and CH_4, fire detection and quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH_3, H_2O, and H_2S)
  - Medical & biomedical diagnostics (NO, NH_3, N_2O, H_2CO and CH_3COCH_3)
  - Hand-held sensors and sensor network technologies (CO_2)
- **Future Directions and Collaborations**
  - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR interband and intersubband quantum cascade lasers
  - New applications enabled by novel broadly wavelength tunable quantum cascade lasers based on heterogeneous EC-QCL (i.e. sensitive concentration measurements of broadband absorbers, in particular VOCs, HCs and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS

RICE

20