

**Recent Advances of Trace Gas Sensors based on Infrared Semiconductor Lasers: Global Opportunities and Challenges**

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

- Motivation: Wide-range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sources and Sensing Technologies
- Selected Applications of Trace Gas Detection
  - Environmental Monitoring ( $H_2CO$  and  $C_2H_4$ )
  - Detection of nitric oxide and ethanol
  - QEPAS based monitoring of broadband absorbers
- Future Directions and Summary

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**Wide Range of Trace Gas Sensing Applications**

- Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, 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 Industries
- Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- Applications in Medicine and Life Sciences**
- Technologies for Law Enforcement and National Security**
- Fundamental Science and Photochemistry**

UDLA 2

**Existing Methods for Trace Gas Detection**

**Direct Laser Absorption Spectroscopy**

**Beer-Lambert's Law of Linear Absorption**

$$I(\nu) = I_0 \cdot e^{-\alpha(\nu) \cdot P_p \cdot L}$$

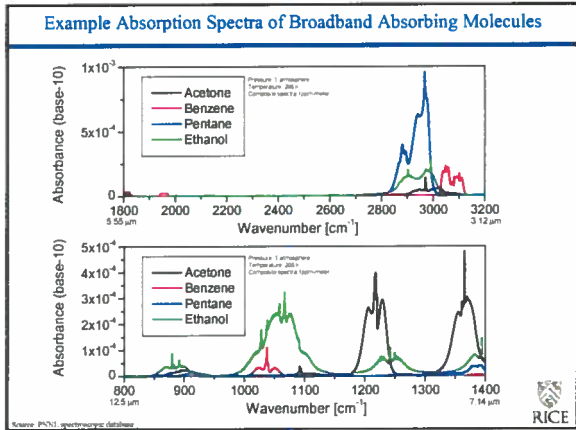
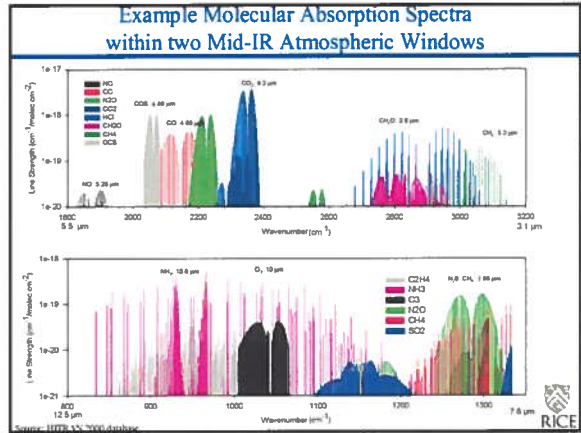
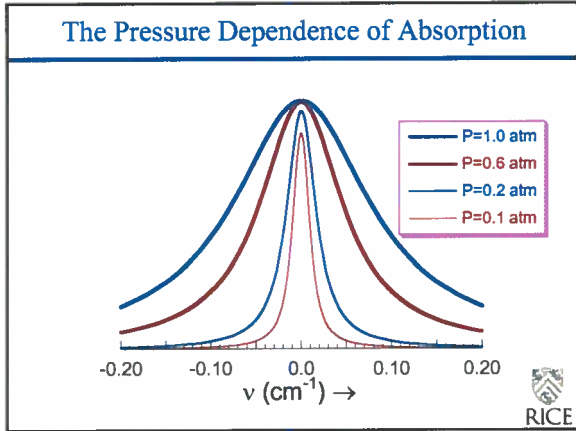
$\alpha(\nu)$  - absorption coefficient [ $cm^{-1} \cdot atm^{-1}$ ];  $L$  - path length [cm]  
 $\nu$  - frequency [ $cm^{-1}$ ];  $P_p$  - partial pressure [atm]

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

$C$  - total number of molecules of absorbing gas/atm/cm<sup>2</sup> [molecule cm<sup>-2</sup> · atm<sup>-1</sup>]  
 $S$  - molecular line intensity [cm · molecule<sup>-1</sup>]  
 $g(\nu - \nu_0)$  - normalized lineshape function [cm], (Gaussian, Lorentzian, Voigt)

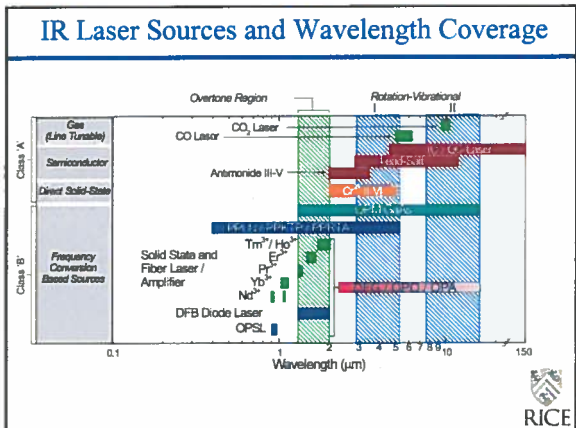
**Sensitivity Enhancement Techniques**

- Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- Long Optical Pathlengths**
  - Multipass Absorption Cell (White, Herriot)
  - Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
  - Open Path Monitoring (with retro-reflector)
  - Evanescent Wave Spectroscopy (Fibers & Waveguides)
- Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy
  - Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)



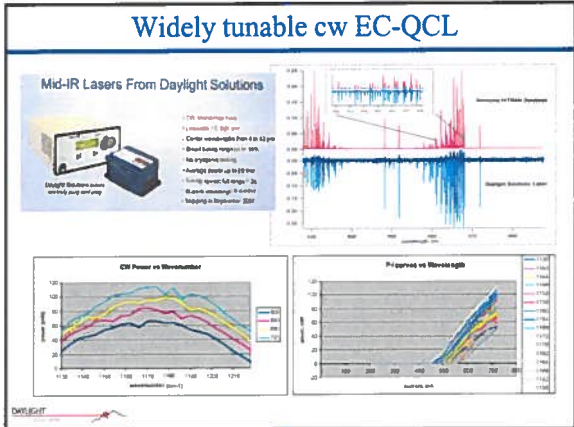
### Mid-IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	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



- ### Key Characteristics of Mid-IR Quantum Cascade Lasers for Spectroscopy
- Laser wavelengths cover the entire Mid-IR range from 3 to 24 μm
  - High power (>500 mW cw, >5W peak for pulsed)
  - High spectral purity - single frequency with DFB structure or external cavity: < kHz to 33 MHz
  - Continuous tuning by temperature (~10 cm<sup>-1</sup>), current (~1 cm<sup>-1</sup>) or external cavity (>200 cm<sup>-1</sup> → pulsed mode)
  - High reliability: low failure rate, long lifetime and robust
  - Capable of room temperature operation
    - Pulsed: up to +150°C
    - CW: up to RT
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## Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

### First Report of PAS in 1881

Alexander Graham Bell in 1876

Alexander Graham Bell's *spectrophone* "for the purpose of the examination of the absorption spectra of bodies in those portions of the spectrum that are invisible" *Philosophical Magazine* Series 5, Vol. 11, 510 (1881)

recognize the fact that the spectrophon must ever remain a mere adjunct to the spectroscope; but anticipate that it has wide and independent field of usefulness in the investigation of absorption-spectra in the ultra-red.

### Resonant photoacoustic spectroscopy

Laser beam, power  $P$

Modulated ( $P$  or  $\lambda$ ) at  $f$  or  $f/2$

Absorption:  $\alpha(\lambda)$

Cavity, resonant at  $f$ , volume  $V$ , quality factor  $Q$

Microphone

$$S_{PAS} \sim \frac{Q\alpha P}{fV}$$

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

### Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

Laser beam, power  $P$

Modulated ( $P$  or  $\lambda$ ) at  $f$  or  $f/2$

Absorption  $\alpha$

$Q \gg 1000$   
Cell is **OPTIONAL!**  
 $V$ -effective volume

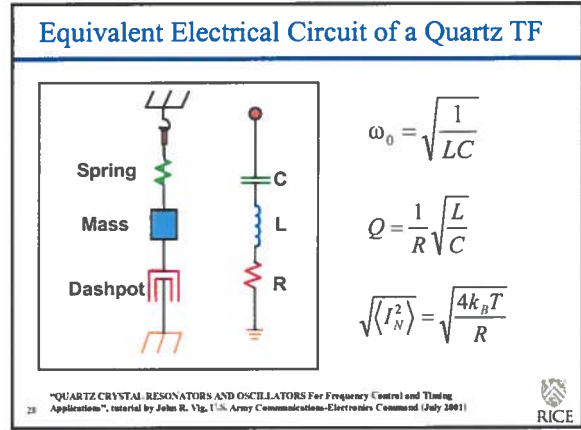
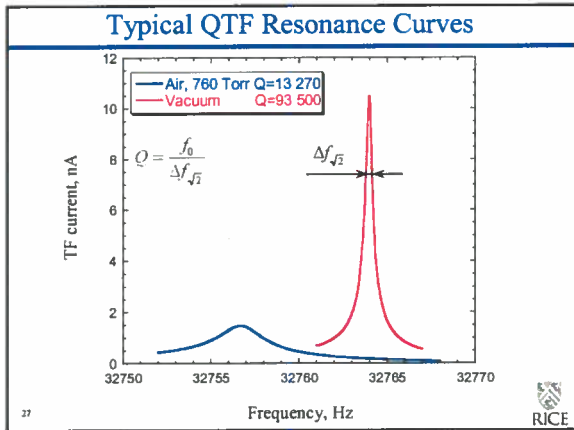
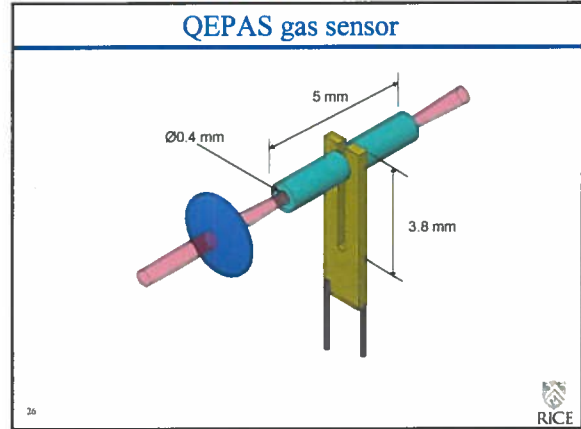
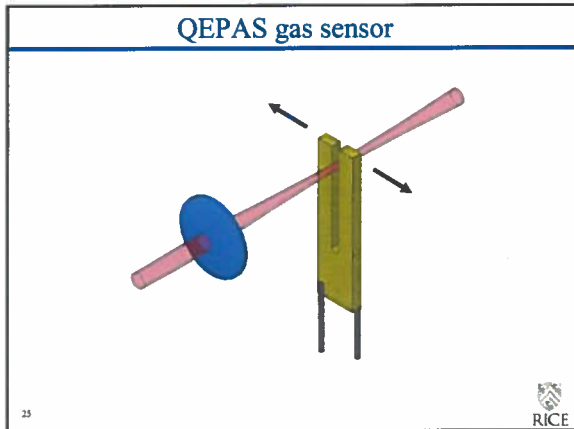
Piezoelectric crystal  
Resonant at  $f$   
quality factor  $Q$

$$S \sim \frac{Q\alpha P}{fV}$$

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

### Quartz Tuning Fork (TF) as a Resonant Microphone

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



### Comparative Size of Absorption Detection Modules (ADM)

- Resonant frequency  $f = 32.8$  kHz
- Intrinsically high Q factor:  $Q_{\text{max}} = 125\,000$   
 $Q_{\text{a}} = 10\,000$  for ambient conditions
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for watches & clocks – low cost

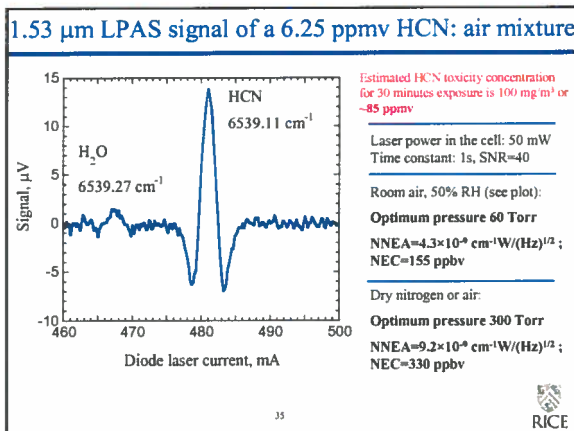
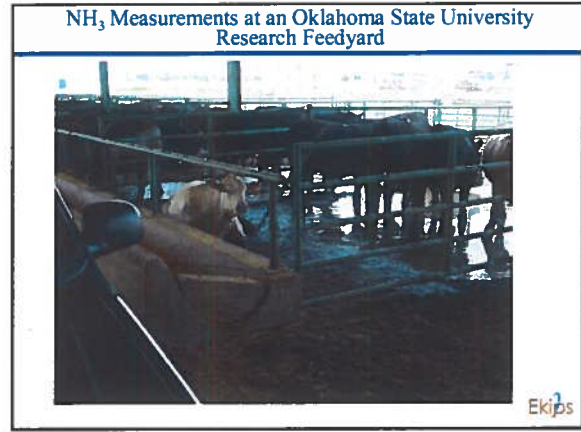
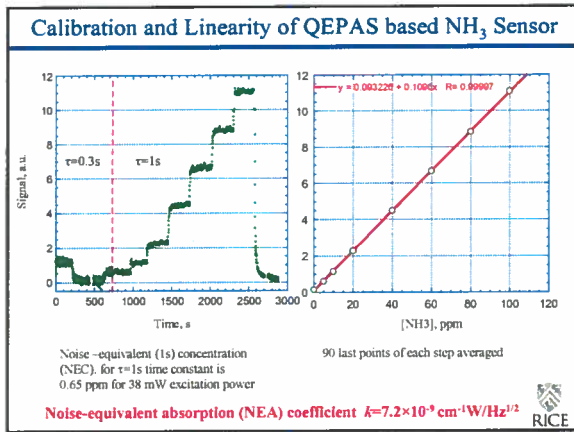
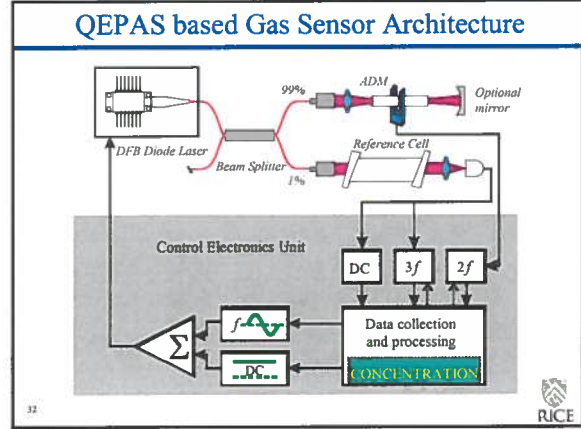
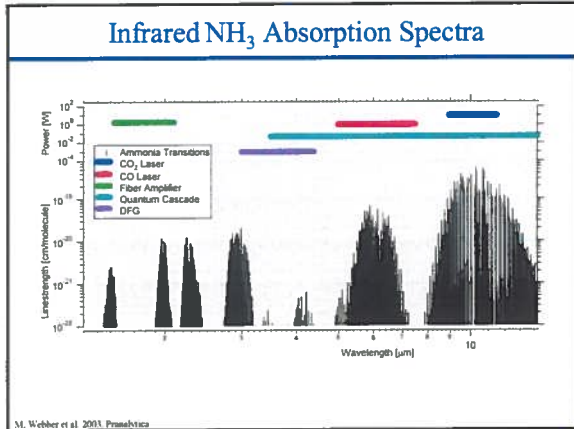
Optical multipass cell (100 m):  
 $l \sim 70$  cm,  $V \sim 3000$  cm<sup>3</sup>

Resonant photoacoustic cell (1000 Hz):  
 $l \sim 60$  cm,  $V \sim 50$  cm<sup>3</sup>

QEPAS spectrophone:  
 $l \sim 1$  cm,  $V \sim 0.05$  cm<sup>3</sup>

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- ### 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<sup>3</sup>)
  - Applicable over a wide range of pressures
  - Temperature, pressure and humidity insensitive
  - Rugged and low cost (compared to other optical sensor architectures)
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### QEPAS Performance for 13 Trace Gas Species (Oct.'07)

Molecule (Host)	Frequency, cm <sup>-1</sup>	Pressure, Torr	NNEA, cm <sup>-1</sup> W/Hz <sup>1/2</sup>	Power, mW	NEC (τ=1s), ppmv
H <sub>2</sub> O (N <sub>2</sub> )**	7508.75	60	1.9×10 <sup>-8</sup>	9.5	0.69
HCN (air; 50% RH)**	6539.11	60	4.3×10 <sup>-8</sup>	50	0.16
CaH <sub>2</sub> (N <sub>2</sub> )**	6529.17	75	2.5×10 <sup>-8</sup>	40	0.06
NH <sub>3</sub> (N <sub>2</sub> )*	6528.76	575	3.1×10 <sup>-8</sup>	60	0.06
CH <sub>4</sub> (N <sub>2</sub> )*	6037.09	950	2.9×10 <sup>-8</sup>	13.7	2.1
CO <sub>2</sub> (breath ~100% RH)	6361.23	90	1.6×10 <sup>-8</sup>	26	410
H <sub>2</sub> S (N <sub>2</sub> )*	6357.63	780	5.6×10 <sup>-8</sup>	45	0.30
CO <sub>2</sub> (N <sub>2</sub> +1.5% H <sub>2</sub> O)*	4991.26	50	1.4×10 <sup>-8</sup>	4.4	18
CH <sub>2</sub> O (N <sub>2</sub> ; 75% RH)**	2804.90	75	8.7×10 <sup>-8</sup>	7.2	0.12
CO (N <sub>2</sub> )	2196.66	50	5.3×10 <sup>-8</sup>	1.3	0.5
CO (propylene)	2196.66	50	7.4×10 <sup>-8</sup>	6.5	0.14
N <sub>2</sub> O (air+5%SK <sub>2</sub> )	2193.63	50	1.5×10 <sup>-8</sup>	19	0.007
C <sub>2</sub> H <sub>5</sub> OH (N <sub>2</sub> )**	1934.2	770	2.2×10 <sup>-8</sup>	10	90
C <sub>2</sub> H <sub>2</sub> (N <sub>2</sub> )**	1208.62	770	7.8×10 <sup>-8</sup>	6.6	0.009
NH <sub>3</sub> (N <sub>2</sub> )*	1046.39	110	7.8×10 <sup>-8</sup>	15	0.04

\* - 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

For comparison: conventional PAS 2.2 (2.6)×10<sup>-8</sup> cm<sup>-1</sup>W/Hz (1,800; 10,300 Hz) for NH<sub>3</sub> (10<sup>-10</sup>)  
\* M. F. Webber et al. Appl. Opt. 42, 2119-2126 (2003); \*\* J. S. Pilgreen et al. SPIE Proc. 8775-2007-01, 2122

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## Sensor Areas Explored at Rice

- Methods employed
  - Extended pathlengths
  - Cavity ringdown
  - Integrated Off-Axis Spectroscopy
  - Wavelength Modulation
  - Pulse-to-pulse fluctuation removal by comparing the same pulse on the same or another detector
  - Tuning fork photoacoustic spectroscopy
- 16 gases detected: NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>S, N<sub>2</sub>O, CO<sub>2</sub>, CO, NO, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>O, OCS, C<sub>2</sub>H<sub>4</sub>, SO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>HF<sub>5</sub>, H<sub>2</sub>CO, C<sub>2</sub>H<sub>6</sub>, HCN
- Practical applications
  - Crew Health Maintenance & Life Support - H<sub>2</sub>CO, NH<sub>3</sub>
  - Radioactive site remediation
  - Medical breath analysis - OCS, NO, CO<sub>2</sub>, acetone
  - Industry catalyst poison - CO
  - Urban air smog - H<sub>2</sub>CO



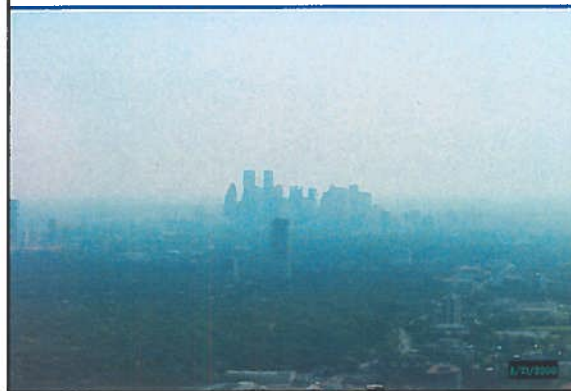
## Trace Gas Sensing Examples

## Motivation for Precision Monitoring of H<sub>2</sub>CO

- Precursor to atmospheric O<sub>3</sub> production
- Pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products
- Medically important gas



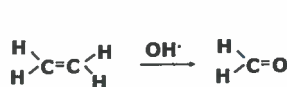
## Megacity Air Pollution: Houston, TX



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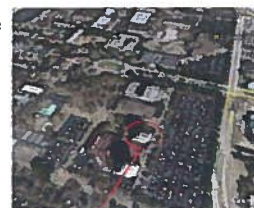
## Houston Ozone Chemistry

- Rapid oxidation of highly reactive VOCs leads to ozone formation in urban areas
- As a major petrochemical center, the Houston region produces ~30 billion pounds of ethylene annually



## TexAQ5 II Field Campaign Summer 2006

- To study ozone formation and transport, a coordinated field study was conducted during August to September 2006 in the Greater Houston area
- 5 aircraft, one ship, two ground chemistry sites, ~20 periphery and meteorological sites were employed during TexAQ5 II
- Participation by ~300 scientists from academia, national laboratories, industry and government agencies

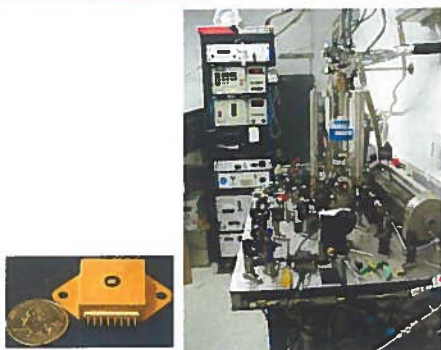


Moody Tower, UH Campus



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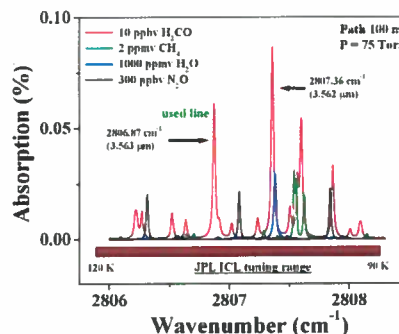
### ICL based H<sub>2</sub>CO Sensor for studying Urban Air Pollution



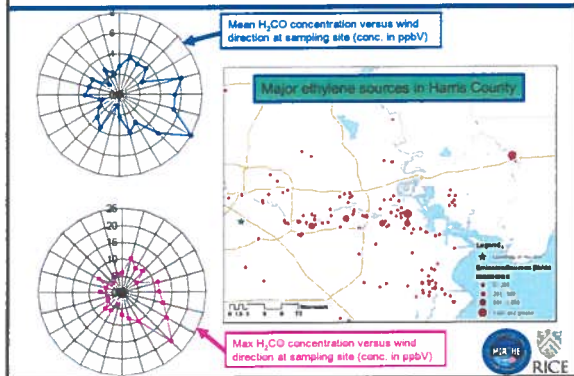
JPL 3.3 μm cw,TEC cooled ICL Rice dual ICL system



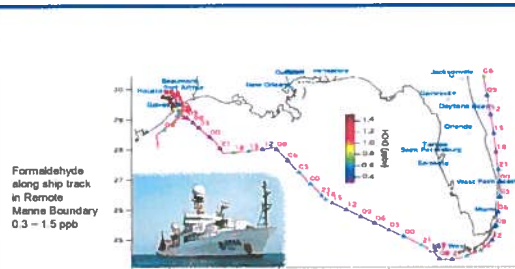
### HITRAN Based Simulation of a H<sub>2</sub>CO Spectrum in Tuning Range of a 3.56μm IC Laser



### H<sub>2</sub>CO Concentration (ppb) Versus Wind Direction



### LAS based Formaldehyde Measurements from the R/V Brown during TexAQS 2006



46 Provided by Dr. M. Zahniser, Aerodyne Research Inc.

### Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO<sub>x</sub> monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection



### NO as a Biomarker

- NO is biochemically involved in most tissues and physiological processes in the human body
- NO excretion increases in exhaled breath in lung diseases such as :
  - ✓ Asthma<sup>1</sup>
  - ✓ Chronic Obstructive Pulmonary Disease<sup>2</sup>
  - ✓ Acute lung rejection<sup>3</sup>
  - ✓ Acute respiratory distress syndrome<sup>4</sup>
  - ✓ Pneumonia (useful for intubated patients)<sup>5</sup>

<sup>1</sup>Alving K, E Weitzberg, JM Lundberg. Increased amount of NO in exhaled air of asthmatics. Eur Respir J 1991; 4: 1368-1370  
<sup>2</sup>Kawanishi M, S Lankford, S Calvert, P Salzman, S Kawanishi, P Barnes. Exhaled NO in COPD. Am J Respir Crit Care Med 1998; 157: pp 996-1002  
<sup>3</sup>Schoff PE et al. Exhaled NO in human lung transplantation: A noninvasive marker of acute rejection. Am J Respir Crit Care Med 1999; 159(8): 1822-1829  
<sup>4</sup>West MJ, Evans TW. Measurement of endogenous NO in the lungs of patients with the ARDS. Am J Respir Crit Care Med 1998; 157(3 Pt 1): 993-7  
<sup>5</sup>Ahne C et al. Exhaled and nasal NO as a marker of pneumonia in ventilated patients. Am J Respir Crit Care Med 2001; 163(5):1143-9



## Why is Breath so Useful ?

- Breath can be analyzed non-invasively from spontaneously breathing human subjects (neonate to the elderly), laboratory animals (from mice to horses), or from intubated patients (in ORs or ICUs).
- Breath can be sampled in the clinic, the home, the field, at the patient bedside, or in the physician's office by nurses, technicians, physicians and by the patient themselves.
- Breath analysis can be used for nutritional studies, exercise studies, to detect disease, stage disease, to monitor therapy or to monitor treatment

Terence Rieby, Johns Hopkins University

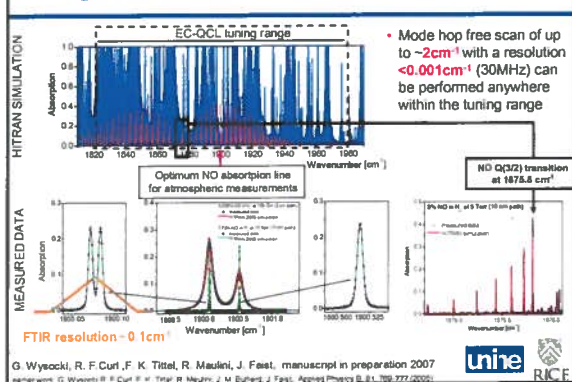
## Biomarkers Present in Exhaled Human Breath

As many as 400 different molecules in breath; many with well defined biochemical pathways

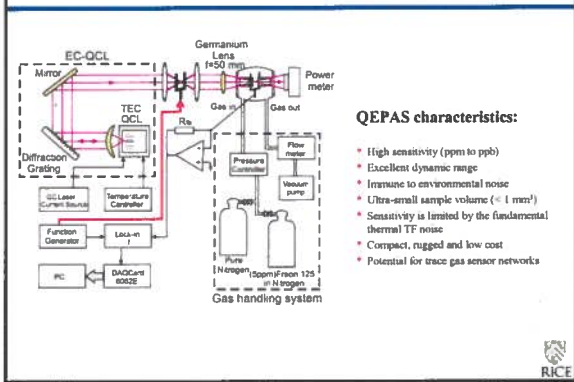
BROADBAND ABSORBERS	Compound	Concentration	Physiological basis/Pathology Indication
	Acetaldehyde	ppb	Ethanol metabolism
	Acetone	ppm	Decarboxylation of acetoacetate, diabetes
	Ammonia	ppb	protein metabolism, liver and renal disease
	Carbon dioxide	%	Product of respiration, Helicobacter pylori
	Carbon disulfide	ppb	Gut bacteria, schizophrenia
	Carbon monoxide	ppm	Production catalyzed by heme oxygenase
	Carbonyl sulfide	ppb	Gut tract area, liver disease
	Ethane	ppb	Lipid peroxidation and oxidative stress
	Isoprene	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
	Oxetane	ppb	Lipid peroxidation, oxidative stress
	Water	%	Product of respiration

Terence Rieby, Johns Hopkins University

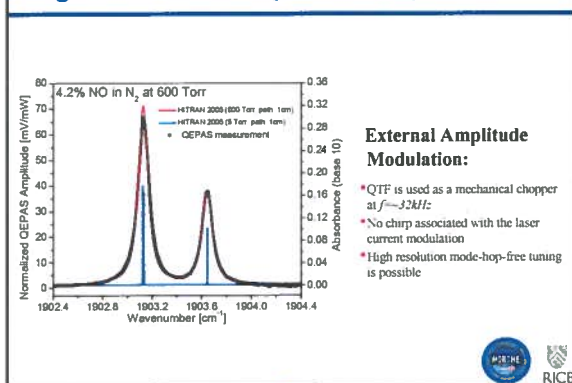
## High resolution spectroscopy with a 5.3μm EC-QCL



## QCL based Quartz-Enhanced Photoacoustic Gas Sensor



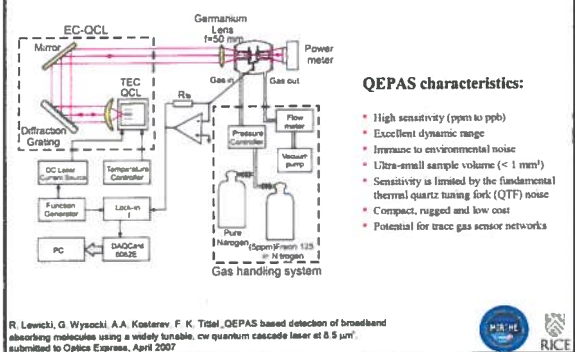
## High resolution EC-QCL based QEPAS of NO



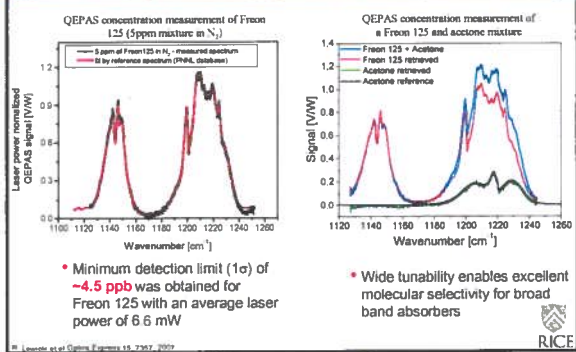
## Monitoring of two broadband absorbers

- Freon 125 ( $\text{C}_2\text{HF}_5$ )
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals e.g. chemical warfare agents
- Acetone ( $\text{CH}_3\text{COCH}_3$ )
  - Recognized biomarker for diabetes

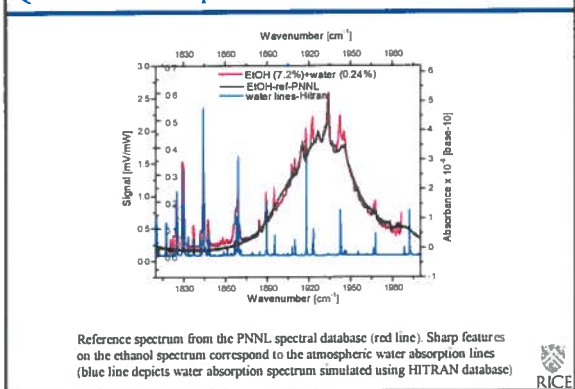
## QCL based Quartz-Enhanced Photoacoustic Gas Sensor



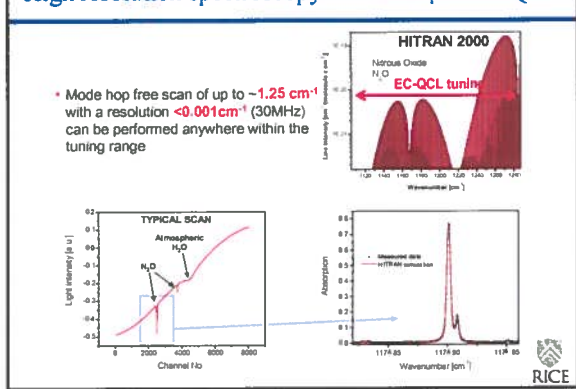
## Spectroscopy of Freon 125 and Acetone with a Widely Tunable 8.4 $\mu\text{m}$ CW EC-QCL



## QEPAS Ethanol Spectrum between 1825 & 1980 $\text{cm}^{-1}$



## High resolution spectroscopy with a 8.4 $\mu\text{m}$ EC-QCL



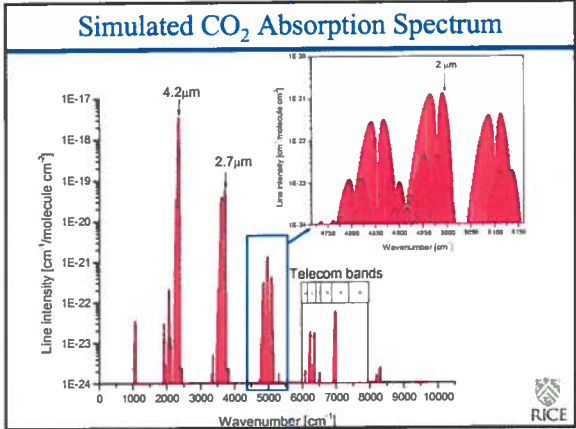
Future of Chemical Trace Gas Sensing

## 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

To Internet via base-station

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### Miniature QEPAS CO<sub>2</sub> sensor ( $\lambda=2\mu\text{m}$ ) boards

- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0.2W control system power consumption
- Projected sensitivity\* to CO<sub>2</sub> 110 ppm with 1sec. lock-in TC
- Over 10<sup>3</sup> improvement in sensitivity @4.2 $\mu\text{m}$

\*G. Wysocki, A. A. Kosterev, and F. K. Tittel "Influence of Molecular Relaxation Dynamics on Quartz-Enhanced Photoacoustic Detection of CO<sub>2</sub> at  $\lambda = 2 \mu\text{m}$ ", Applied Physics B 85, 301-308 (2006)

*new design*

### Existing Environmental Trace Gas Networks

- Fluxnet (pictured) (Oak Ridge National Laboratory) <http://www-esds.cml.gov/FLUXNET>
- Carbon tracker (National Oceanic and Atmospheric Administration) <http://www.cmdl.noaa.gov/carbontracker>
- National Ecological Observatory Network (NEON) (National Science Foundation) <http://www.neoninc.org/>
- Rely on sparse data (due to cost/size of sensors) or satellite data
- Deploy with other types of sensors (e.g. wind)

### Future Directions of Mid-IR Sensor Technology

- 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 (especially sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs)
- Development of optically multiplexed gas sensor networks based on QEPAS

### New Applications of Trace Gas Detection

- Distributed sensor networks for environmental monitoring (NH<sub>3</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>CO)
- Inexpensive and sensitive sensors for industrial process control and chemical analysis (HCN, NO, NH<sub>3</sub>, H<sub>2</sub>O)
- Wearable sensors for medical & biomedical diagnostics (NO, CO, COS, CO<sub>2</sub>, NH<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>)
- Hand-held sensors and sensor network technologies for law enforcement

### Summary and Future Directions

- **Near and Mid-Infrared Semiconductor Laser based Trace Gas Sensors**
  - Compact, robust sensor technology based on multipass cell absorption, cavity enhanced and quartz enhanced photoacoustic spectroscopy (QEPAS)
  - High sensitivity (<10<sup>-4</sup>) and selectivity (3 to 500 MHz)
  - Fast data acquisition and analysis
  - Detected 13 trace gases to date: NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>S, N<sub>2</sub>O, CO<sub>2</sub>, CO, NO, H<sub>2</sub>O, COS, C<sub>2</sub>H<sub>4</sub>, SO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>HF<sub>3</sub> and isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Distributed sensor networks for environmental monitoring (NH<sub>3</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>CO)
  - Inexpensive and sensitive sensors for industrial process control and chemical analysis (HCN, NO, NH<sub>3</sub>, H<sub>2</sub>O)
  - Sensors for medical & biomedical diagnostics (NO, CO, COS, CO<sub>2</sub>, NH<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>)
- **Future Directions and Collaborations**
  - Further improvements of the existing sensor technologies using novel, thermoelectrically cooled, cw, high power mid-IR interband and intersubband quantum cascade lasers and QEPAS
  - New applications enabled by novel widely tunable quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs)
  - Development of optically multiplexed gas sensor networks based on QEPAS

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