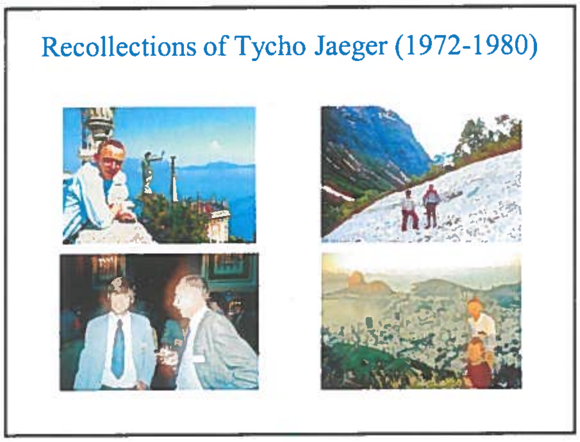

Recollections of Tycho Jaeger (1972-1980)

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

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

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

OUTLINE

Norsk Elektro Optikk

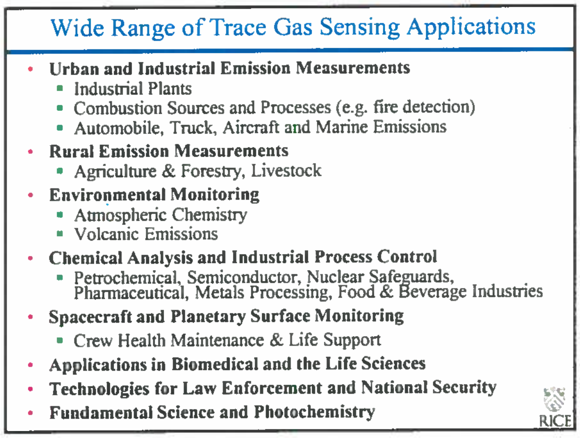
25th Anniversary Symposium

Oslo, Norway

June 11, 2010

- 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**

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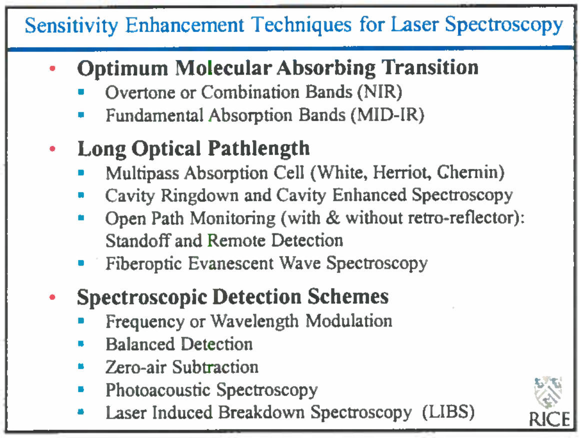

Sensitivity Enhancement Techniques for Laser Spectroscopy

- **Optimum Molecular 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 & without retro-reflector): Standoff and Remote Detection
  - Fiberoptic Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy
  - Laser Induced Breakdown Spectroscopy (LIBS)

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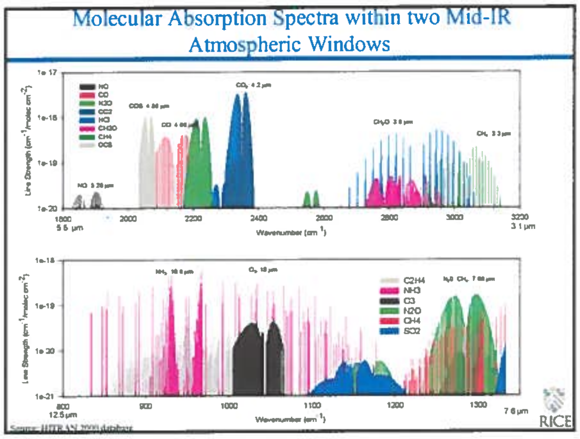
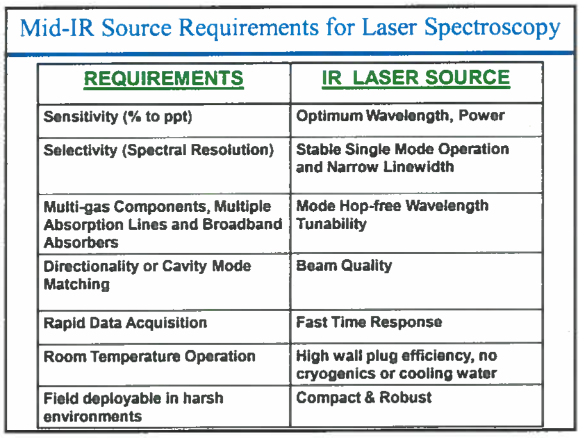


Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

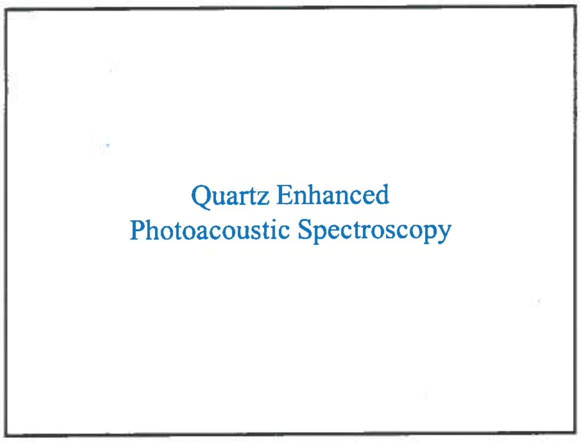
Source: HITRAN 2000 database

RICE

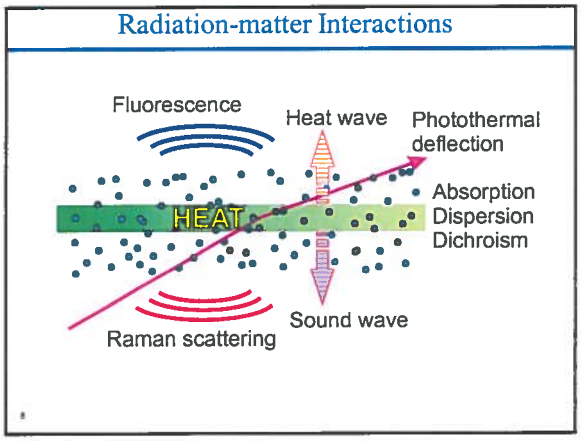


Mid-IR Source Requirements for Laser Spectroscopy

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



Quartz Enhanced Photoacoustic Spectroscopy



Radiation-matter Interactions

Fluorescence

Heat wave

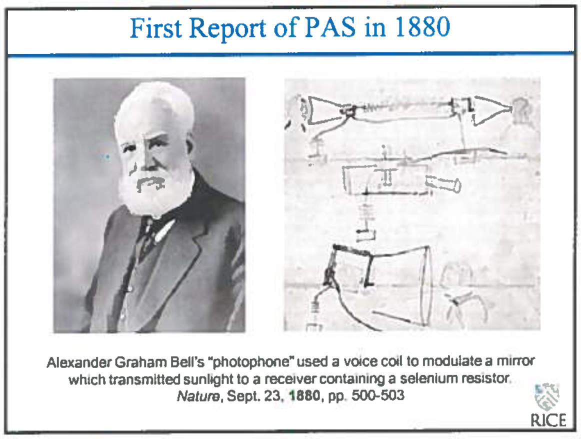
Photothermal deflection

HEAT

Absorption
Dispersion
Dichroism

Raman scattering

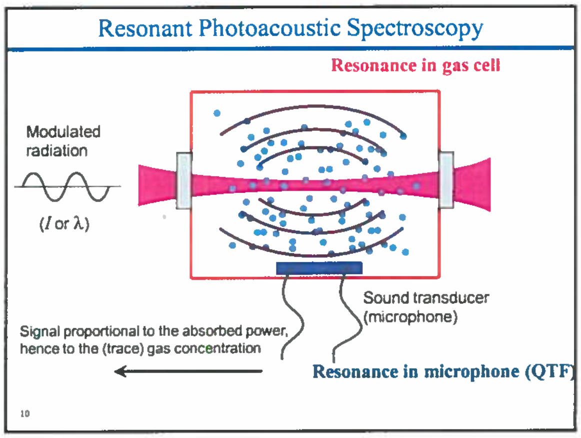
Sound wave



First Report of PAS in 1880

Alexander Graham Bell's "photophone" used a voice coil to modulate a mirror which transmitted sunlight to a receiver containing a selenium resistor.
Nature, Sept. 23, **1880**, pp. 500-503

RICE



Resonant Photoacoustic Spectroscopy

Resonance in gas cell

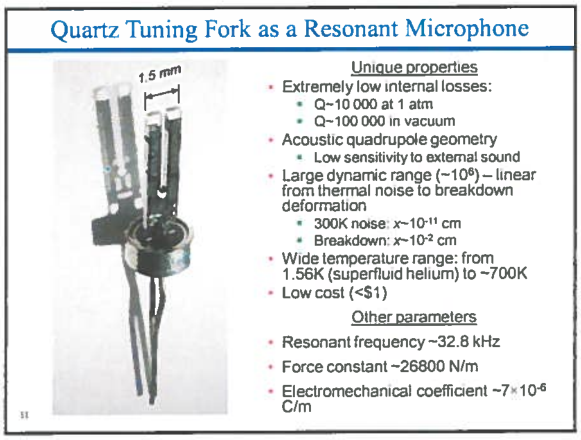
Modulated radiation

(*I* or λ)

Sound transducer (microphone)

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

Resonance in microphone (QTF)



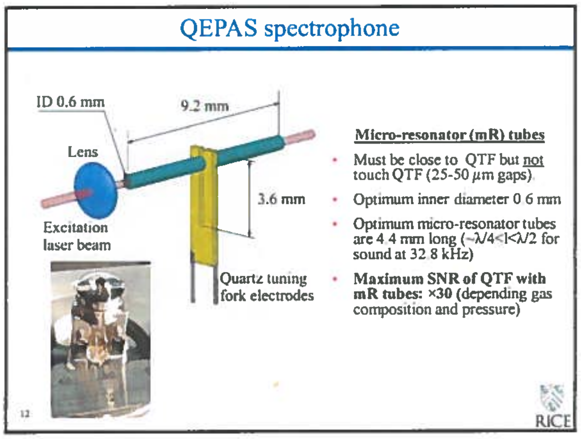
Quartz Tuning Fork as a Resonant Microphone

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 (~10^6) – linear from thermal noise to breakdown deformation
  - 300K noise: x~10^{-11} cm
  - Breakdown: x~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

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 SNR of QTF with mR tubes: ×30** (depending gas composition and pressure)

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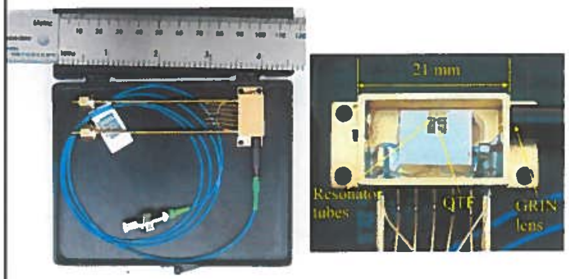
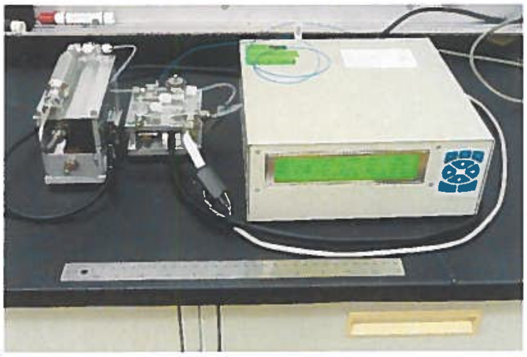
Alignment-free QEPAS Absorption Detection Module



NIR QEPAS based multi-species sensor system



Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm^3)
- 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 $\sqrt{t}$, up to t=3 hours as experimentally verified

QEPAS: some 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

QEPAS Performance for 15 Trace Gas Species (May '10)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, cm^{-1}W/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 ~50% 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

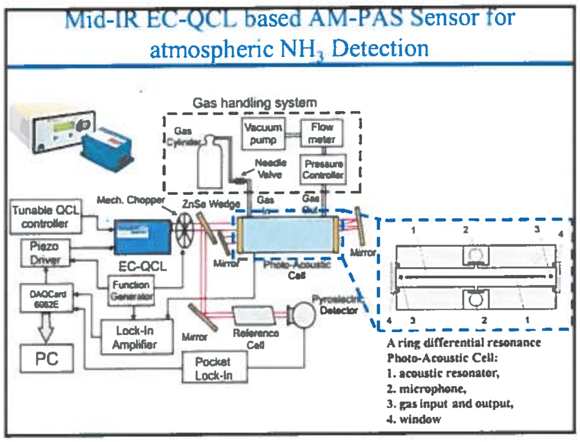
For comparison: conventional PAS 2.2 (2.6)×10^{-9} cm^{-1}W/√Hz (1,800; 10,300 Hz) for NH_3*, ***

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

Recent Applications of mid-infrared Laser based Trace Gas Sensors

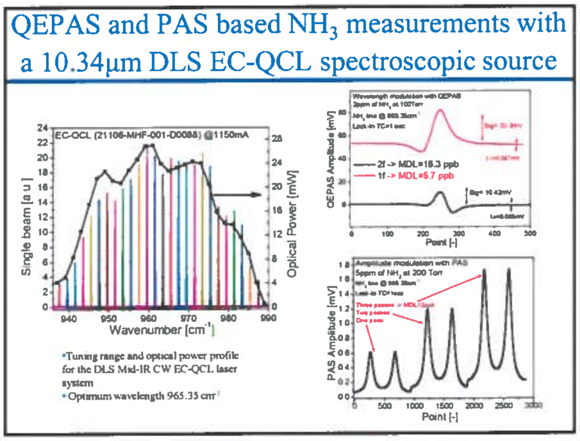
Motivation for NH_3 Detection

- 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)



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

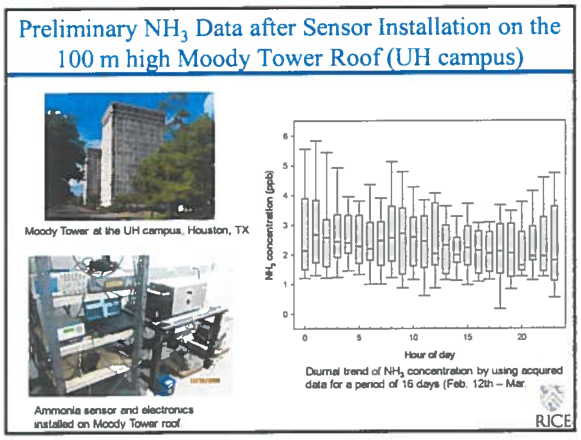
A ring differential resonance Photo-Acoustic Cell:
1. acoustic resonator,
2. microphone,
3. gas input and output,
4. window



QEPAS and PAS based NH_3 measurements with a 10.34µm DLS EC-QCL spectroscopic source

- Tuning range and optical power profile for the DLS Mid-IR CW EC-QCL laser system
- Optimum wavelength 965.35 cm⁻¹

new one RL, 965.35 cm⁻¹



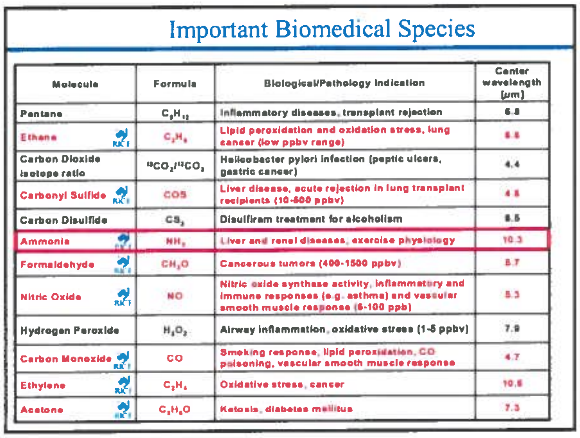
Preliminary NH_3 Data after Sensor Installation on the 100 m high Moody Tower Roof (UH campus)

Moody Tower at the UH campus, Houston, TX

Ammonia sensor and electronics installed on Moody Tower roof

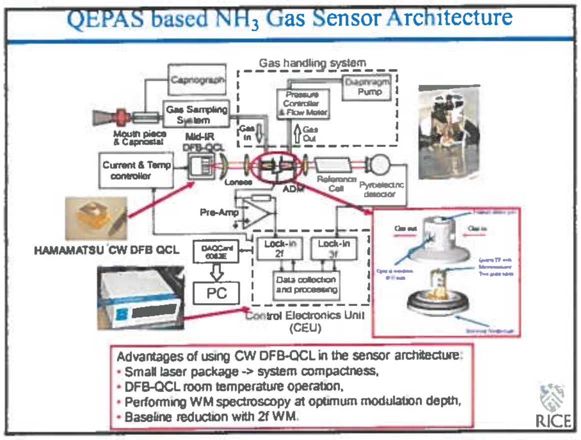
Diurnal trend of NH_3 concentration by using acquired data for a period of 16 days (Feb. 12th – Mar.

RICE



Important Biomedical Species

Molecule	Formula	Biological/Pathology Indication	Center wavelength [µm]
Pentane	C_5H_{12}	Inflammatory diseases, transplant rejection	6.8
Ethane	C_2H_6	Lipid peroxidation and oxidation stress, lung cancer (low ppbv range)	6.6
Carbon Dioxide isotope ratio	$^{13}CO_2/^{12}CO_2$	Helicobacter pylori infection (peptic ulcers, gastric cancer)	4.4
Carbonyl Sulfide	COS	Liver disease, acute rejection in lung transplant recipients (10-600 ppbv)	4.8
Carbon Disulfide	CS_2	Disulfiram treatment for alcoholism	6.5
Ammonia	NH_3	Liver and renal diseases, exercise physiology	10.3
Formaldehyde	CH_2O	Cancerous tumors (400-1500 ppbv)	5.7
Nitric Oxide	NO	Nitric oxide synthase activity, inflammatory and immune responses (e.g. asthma) and vascular smooth muscle response (6-100 ppb)	5.3
Hydrogen Peroxide	H_2O_2	Airway inflammation, oxidative stress (1-5 ppbv)	7.9
Carbon Monoxide	CO	Smoking response, lipid peroxidation, CO poisoning, vascular smooth muscle response	4.7
Ethylene	C_2H_4	Oxidative stress, cancer	10.6
Acetone	C_3H_6O	Ketosis, diabetes mellitus	7.3



QEPAS based NH_3 Gas Sensor Architecture

Advantages of using CW DFB-QCL in the sensor architecture:
- Small laser package -> system compactness,
- DFB-QCL room temperature operation,
- Performing WM spectroscopy at optimum modulation depth,
- Baseline reduction with 2f WM.

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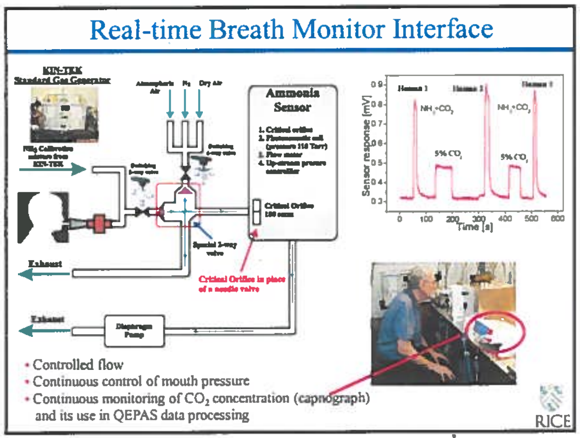


Real-time Breath Monitor Interface

- Controlled flow
- Continuous control of mouth pressure
- Continuous monitoring of CO_2 concentration (capnograph) and its use in QEPAS data processing

RICE

mw, tuning range, 9~~65~~.35 cm⁻¹
67

Middle reports, poster

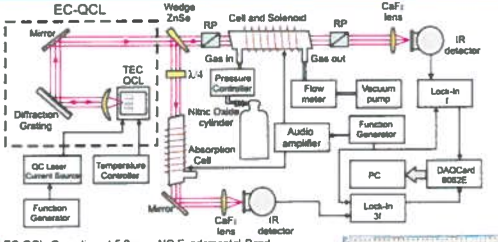
Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_x 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
- Photofragmentation of nitro-based explosives (TNT)

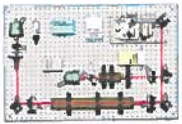
Motivation for Nitric Oxide Detection in Beijing 2008

- Environmental pollutant
  - Product of fossil fuel combustion process (automobile and power plant emissions)
  - Precursor of smog and acid rain

EC-QCL Based Faraday Rotation Spectrometer

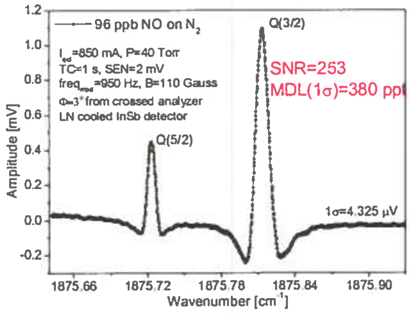


- EC-QCL Operating at 5.3μm – NO Fundamental Band
- 44cm effective optical pathlength
- Rochon Polarizer Extinction Ratio <10^{-5}
- Not sensitive to water interference
- Sensitivity Not Limited by Interference Fringes
- Gas Cell Volume (~ 250ml)
- Easy and Robust Optical Alignment
- Continuous NO Monitoring (Absorption Line Locking enabled with mode-hop free tuning using Zeeman Modulation at 3rd harmonic)



(3 x 2 ft.)

Faraday Rotation Spectroscopy of Nitric Oxide



Future Directions and Outlook of Chemical Trace Gas Sensing Technology

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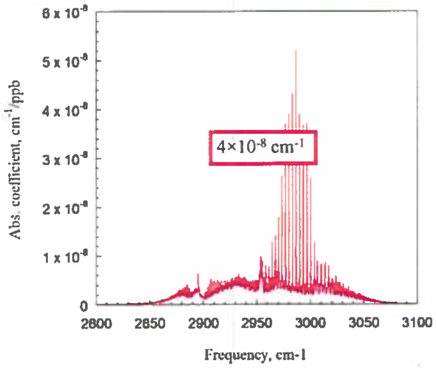
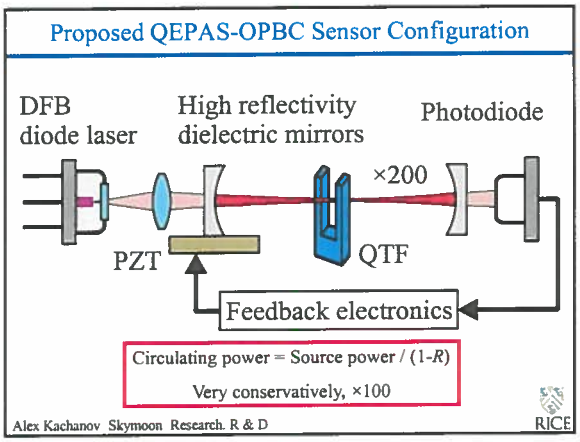
Ethane absorption spectrum





Proposed QEPAS-OPBC Sensor Configuration

DFB
diode laser

High reflectivity
dielectric mirrors

Photodiode

×200

PZT

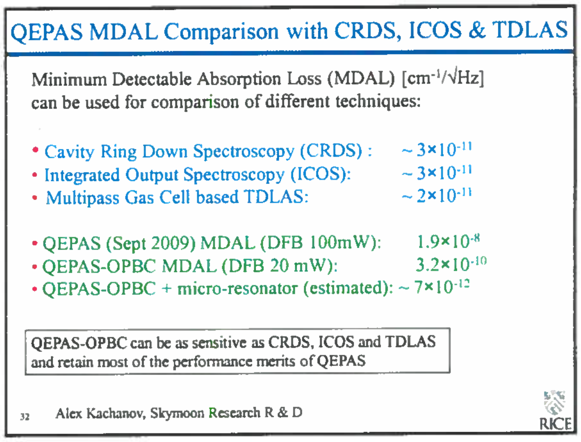
QTF

Feedback electronics

Circulating power = Source power / (1-*R*)

Very conservatively, ×100

Alex Kachanov Skymoon Research. R & D



QEPAS MDAL Comparison with CRDS, ICOS & TDLAS

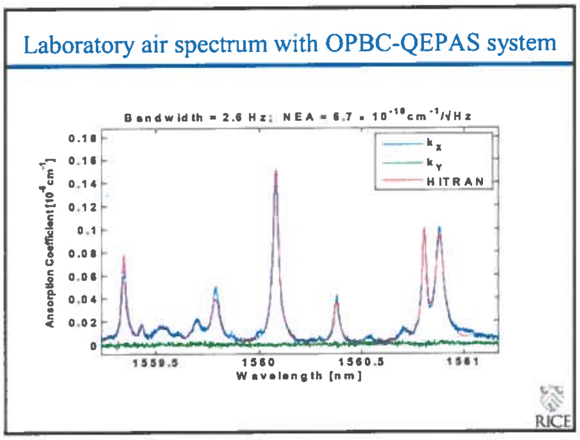
Minimum Detectable Absorption Loss (MDAL) [$\mathrm{cm}^{-1}/\sqrt{\mathrm{Hz}}$]
can be used for comparison of different techniques:

- Cavity Ring Down Spectroscopy (CRDS) : ~ 3×10^{-11}
- Integrated Output Spectroscopy (ICOS): ~ 3×10^{-11}
- Multipass Gas Cell based TDLAS: ~ 2×10^{-11}

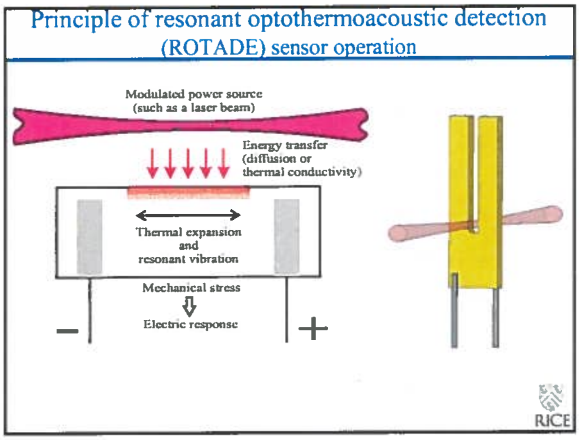
- QEPAS (Sept 2009) MDAL (DFB 100mW): 1.9×10^{-8}
- QEPAS-OPBC MDAL (DFB 20 mW): 3.2×10^{-10}
- QEPAS-OPBC + micro-resonator (estimated): ~ 7×10^{-12}

QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS
and retain most of the performance merits of QEPAS

32 Alex Kachanov, Skymoon Research R & D



Laboratory air spectrum with OPBC-QEPAS system



Principle of resonant optothermoacoustic detection (ROTADE) sensor operation

Modulated power source
(such as a laser beam)

Energy transfer
(diffusion or
thermal conductivity)

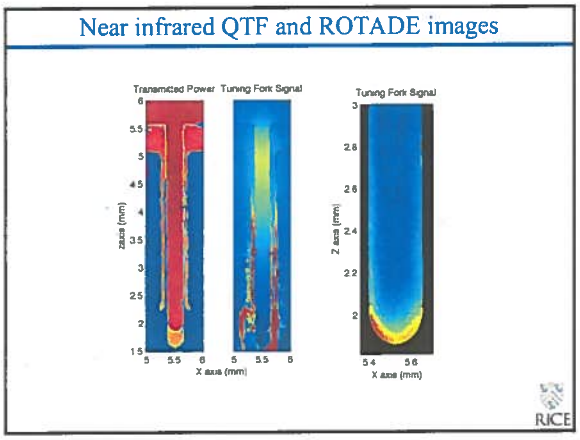
Thermal expansion
and
resonant vibration

Mechanical stress

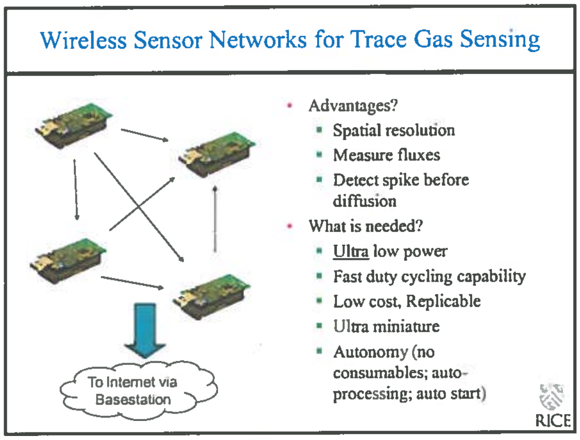
Electric response

−

+



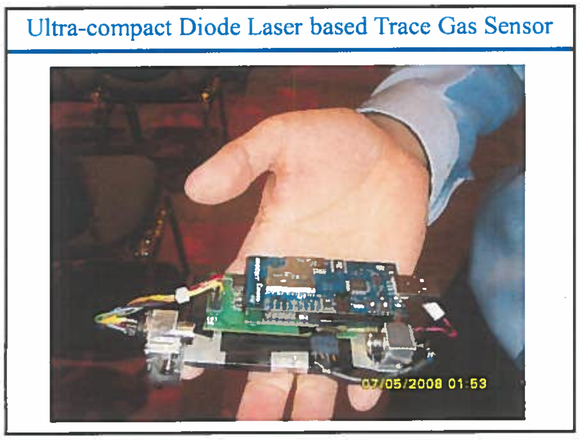
Near infrared QTF and ROTADE images



Wireless Sensor Networks for Trace Gas Sensing

To Internet via
Basestation

- Advantages?
  - Spatial resolution
  - Measure fluxes
  - Detect spike before diffusion
- What is needed?
  - Ultra low power
  - Fast duty cycling capability
  - Low cost, Replicable
  - Ultra miniature
  - Autonomy (no consumables; auto-processing; auto start)



Ultra-compact Diode Laser based Trace Gas Sensor

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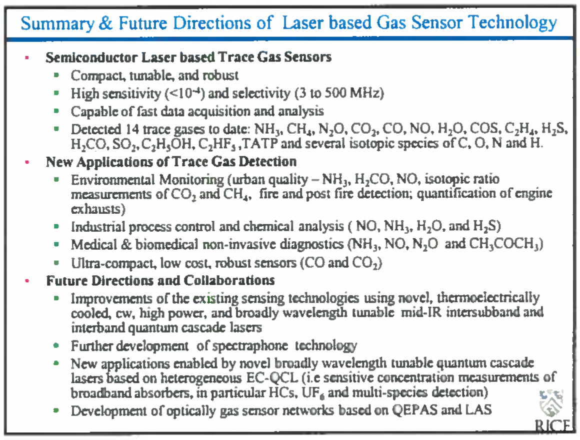
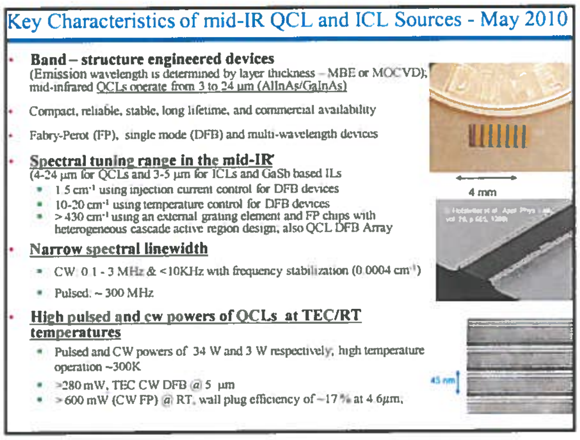


Summary & Future Directions of Laser based Gas Sensor Technology

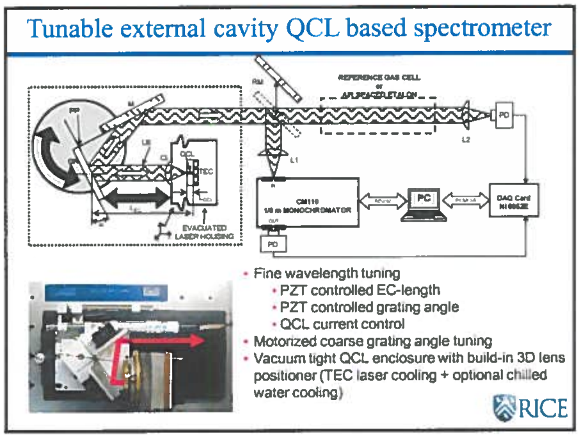
- **Semiconductor Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity ($<10^{-4}$) and selectivity (3 to 500 MHz)
  - Capable of fast data acquisition and analysis
  - Detected 14 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, H_2S, H_2CO, SO_2, 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 (CO and 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 intersubband and interband quantum cascade lasers
  - Further development of spectraphone technology
  - 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 HCs, UF_6 and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS

RICE



Key Characteristics of mid-IR QCL and ICL Sources - May 2010

- **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 devices
- **Spectral tuning range in the mid-IR**
  (4-24 μm for QCLs and 3-5 μm for ICLs and GaSb based ILs
  - 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;



Tunable external cavity QCL based spectrometer

- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + optional chilled water cooling)

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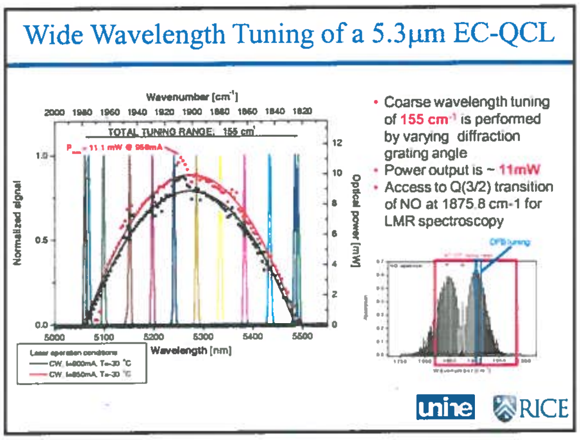

Wide Wavelength Tuning of a 5.3μm EC-QCL

- Coarse wavelength tuning of 155 cm^{-1} is performed by varying diffraction grating angle
- Power output is ~ 11mW
- Access to Q(3/2) transition of NO at 1875.8 cm-1 for LMR spectroscopy

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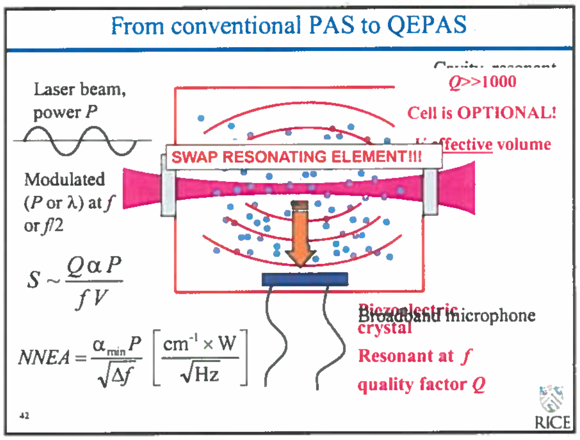

From conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$

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

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

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