Quantum Cascade Lasers for Trace Gas Sensing

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OUTLINE
LO'2003
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Russia
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2003

- Motivation and Technology Issues
- Mid-IR QC Laser based Gas Sensors
  - Pulsed quasi-room temperature sensors
  - CW cryogenically cooled sensors
- Selected Applications of Trace Gas Detection
- Outlook and Summary

Wide Range of Gas Sensor Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes
  - Automobile
- **Rural Emission Measurements**
  - Agriculture
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Chemical, Pharmaceutical, & Semiconductor Industry
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Medical Applications**
- **Fundamental Science and Photochemistry**

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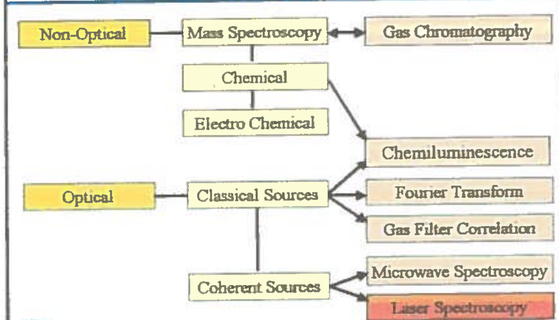
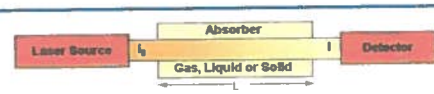
Existing Methods for Trace Gas Detection



Direct Laser Absorption Spectroscopy

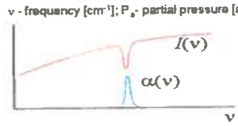


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - 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 lineshape function [cm], (Gaussian, Lorentzian, Voigt)

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Sensitivity Enhancement Techniques

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

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CW IR Source Requirements for Spectroscopy

REQUIREMENTS	SOURCE
• **Sensitivity**	• **Power**
• **Selectivity**	• **Line Width**
• **Multi-gas Components**	• **Tunable λ**
• **Directionality**	• **Beam Quality**
• **Rapid Data Acquisition**	• **Fast Response**
• **Room Temperature**	• **No Consumables**

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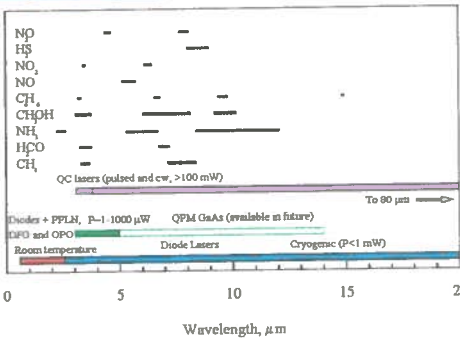
Spectral Coverage by Diode & QC Lasers



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Key Characteristics of Quantum Cascade Lasers

- QC laser wavelengths cover entire range from 3.5 to 66 μm determined by thickness of the quantum well and barrier layers of the active region
- Intrinsically high power lasers (determined by number of stages of injector-active quantum well gain regions)
  - CW:~100 mW @ 80°K, mWs @ 300 °K
  - Pulsed: 1 W peak at room temperature, ~50 mW avg. @ 0 °C (up to 80 % duty cycle)
- High Spectral purity (single mode: <kHz - 330MHz)
- Wavelength tunable by current or temperature scanning
- High reliability: long lifetime, robust operation and reproducible emission wavelengths

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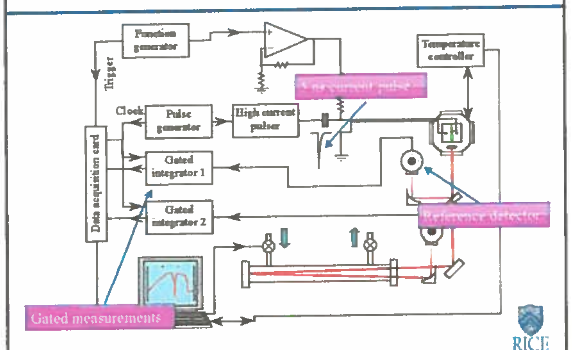
Pulsed QC Laser Based CO Gas Sensor



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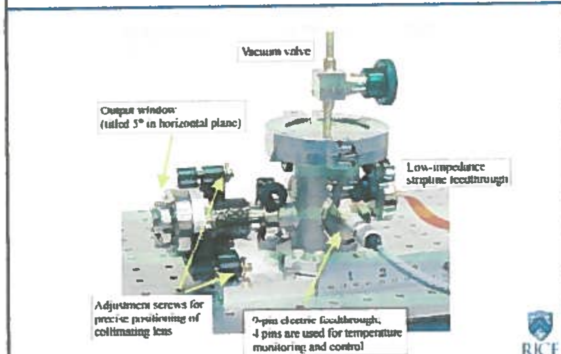
A. Kosterev et al, Applied Optics 41, 1170 2002

TEC cooled QC Laser Housing



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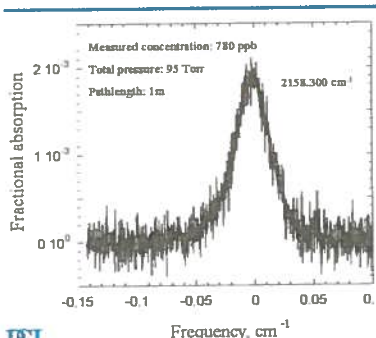
CO Absorption: Ambient Air Sample



Two IR detectors

Sensitivity ~7 ppb

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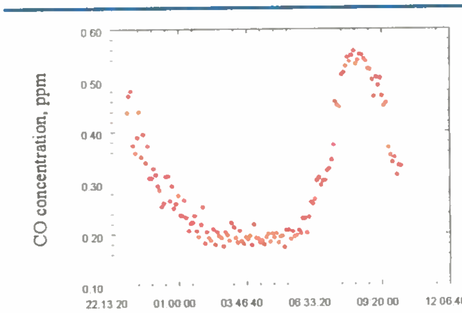
A. A. Kosterev et al, Applied Optics 41, 1169, 2002

CO Concentration Measurements



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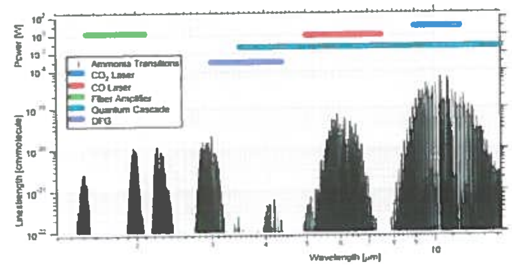
A. A. Kosterev et al, Applied Optics 41, 1169, 2002

Motivation for NH_3 Detection

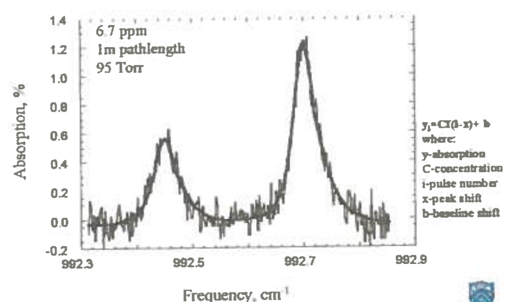
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Spacecraft related gas monitoring
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver dysfunctions)

Infrared NH_3 Absorption Spectra



M. Webber et al. 2003, Pranalytica

Ammonia Absorption Spectrum @ ~10µm

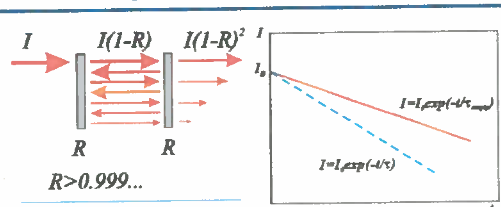


A. Kosterev et al, Applied Optics 41, 573 2002

Important Biomedical Target Gases

Molecule	Formula	Trace Concentration in Breath (ppb)	Biological/Pathology Indication
Nitric Oxide	NO	6 - 100	Inflammatory and immune responses (e.g., asthma) and vascular smooth muscle response
Carbon Monoxide	CO	400 - 3000	Smoking response, CO poisoning, vascular smooth muscle response, platelet aggregation
Hydrogen Peroxide	H_2O_2	1 - 5	Airway Inflammation, Oxidative stress
Carbonyl Sulfide	OCS	100 – 1000	Liver disease and acute allograft rejection in lung transplant recipients
Formaldehyde	HCHO	400 - 1500	Cancerous tumors, breast cancer

Cavity ring-down spectroscopy



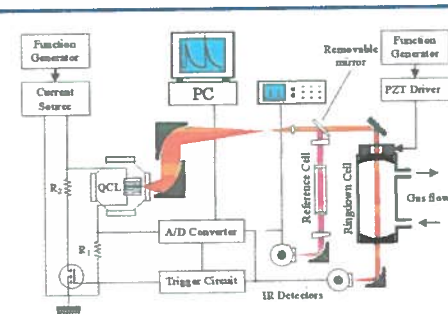
$R>0.999...$

$$I = I_0 \exp\left(-\frac{t}{\tau}\right)$$

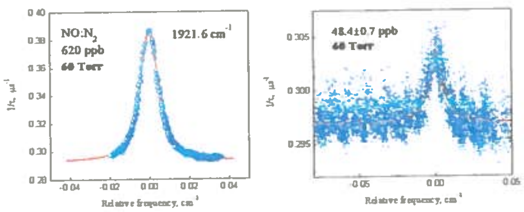
$$\tau = \frac{l}{c} \cdot \frac{1}{\alpha l - \ln\sqrt{R_1 R_2}}$$

$$\alpha = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_{empty}}\right)$$

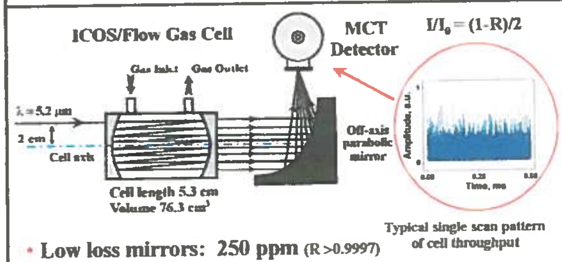
CRDS Based Gas Sensor



NO absorption in Nitrogen



Off-Axis CW Integrated Cavity Output Spectroscopy (ICOS)



- Low loss mirrors: 250 ppm (R >0.9997)
- Radius of curvature: 100 cm
- Mirrors diameter 5.08 cm; (effective diameter 4.27 cm)

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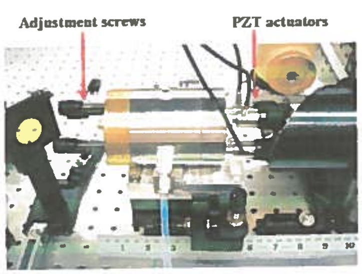
Novel compact gas cell design for Off-Axis ICOS



Adjustment screws are utilized to make spherical mirror astigmatic

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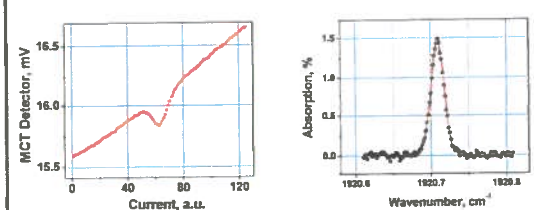
Absorption spectrum of NO in N_2 at 1920.7 cm^{-1}



Averaged ICOS cell throughput

- NO : N_2 Calibration mixture: 100 Torr
- NO concentration: 490 ppb
- Effective optical path ~ 70 m (1, 350 passes)
- Detection sensitivity: $1.0 \cdot 10^{-7}$ cm^{-1} $Hz^{-1/2}$ (NE sensitivity: 9 ppb)

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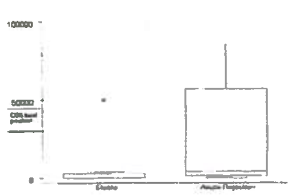
Exhaled Carbonyl Sulfide

- A 2001 study by the T. H. Risby group at John Hopkins University demonstrated that elevated levels of COS could have a diagnostic role in the detection of acute allograft rejection in lung transplant recipients
  - S. M. Studer, et. al., J. of Heart and Lung Transplantation, 20(11), 1158-66 (2001).

Measured with gas chromatography and flame ionization detection



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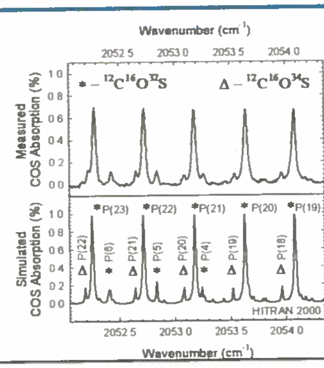
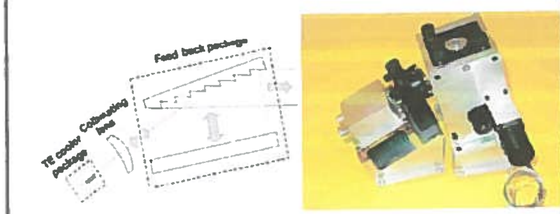
COS Spectra for 13-ppm

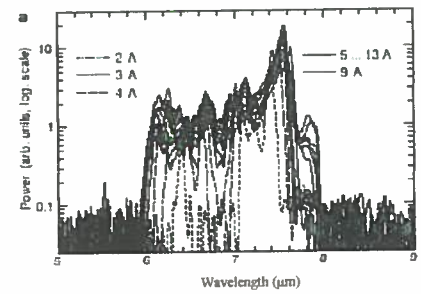


λ-Tunable Pulsed QC Laser GCEC Architecture



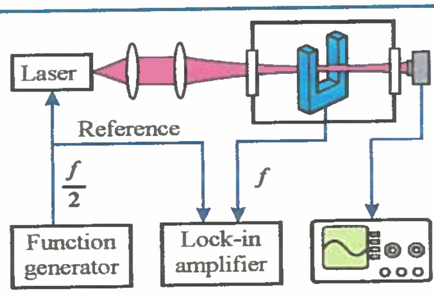
H. Le et al., Univ. of Houston

Laser Spectrum of Ultra-Broadband QC Laser



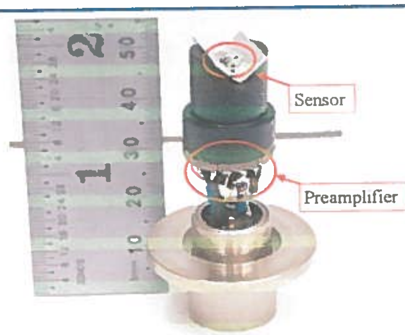
C. Gmachl et al. Nature 145, 883 (2002)

Photoacoustic Spectroscopy with a Solid State Resonator

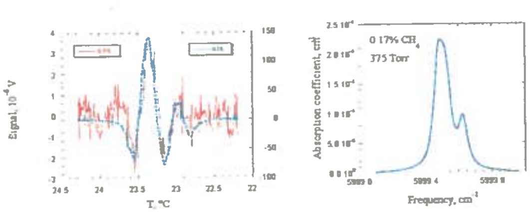


A. A. Kosterev, Y. A. Bakhirkin, R. F. Curl, F. K. Tittel, Optics Letters 27,1902-1904 (2002)

QEPAS based Gas Sensor Assembly



Measured and Simulated CH_4 Spectrum



A. A. Kosterev et al, Optics Letters 27, 1902 (2002)

Summary and Future Directions

- **Quantum Cascade Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity (<10^{-4}) and selectivity (3 to 300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, OCS, C_2H_4, C_2H_5OH and isotopic species
- **Applications in Trace Gas Detection**
  - Industrial process control and chemical analysis
  - Environmental monitoring (NASA, NCAR, NOAA, EPA)
  - Medical Diagnostics (NO, CO)
- **Future Directions**
  - Thermoelectrically cooled, cw quantum cascade lasers and amplifiers
  - Cavity ring down and QE-PAS spectroscopy
  - Near IR and Far-IR wavelengths quantum cascade lasers