Development of Advanced Mid-Infrared Laser Based Gas Sensor technology

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OUTLINE

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- Motivation and Technology Issues
- Development of Quartz-Enhanced Photoacoustic Spectroscopy
- Photonic Technologies for Early Detection of Human Disease

Photonic Technologies for Early Detection of Human Disease

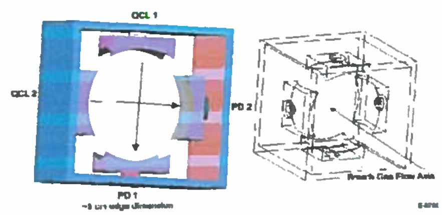
- Target Trace Gases and Pathologies
- Motivation and Background for Physiological Monitors based on Expired Human Breath
- Ultra-Sensitive Gas Detection based Quantum Cascade Laser (QCL) Absorption
- Examples of QCL-based Breath Measurements

Trace Reactive Gases As Physiological Messengers

- NO production is tied to numerous physiological processes in humans:
  - vasorelaxation, inflammation, thrombosis, immunity
  - reduced NO production associated with atherosclerosis and ulcers
  - enhanced NO production associated with asthma, endotoxin shock, diabetes, and edema
- CO production is important in vascular muscle cell physiology and platelet aggregation
- Trace levels of these and other breath species are associated with numerous physiological pathologies
- Typical endogenous production rates are~ 10 pmol/min requiring trace gas detection levels in the range of 1to 10 ppbv.

Overall Project Goal

To develop and demonstrate a prototype sensor for multi-gas analysis in exhaled human breath based on a Quantum-Cascade Laser Sensor with Cavity Enhanced Spectroscopy



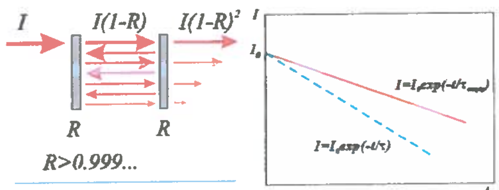
Multi-Gas QCL-Based Breath Analyzer

- Cavity-enhanced optical cells can provide ~100 m of optical pathlength in 2 cm of physical pathlength
- Each cell capable of ppb-level detection of trace breath radicals (NO, CO), organic biomarkers (pentane, ethane, formaldehyde, acetone, isoprene), and other breath species (ammonia, isotopic CO_2, etc.)
- Configurable array of stacked optical cells arranged along a common breath flow axis should permit rapid, non-invasive assay of basic biological functions with no consumables

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	COS	100 – 1000	Liver disease & acute rejection in lung transplant recipients
Formaldehyde	HCHO	400 - 1500	Cancerous tumors, breast cancer

Cavity ring-down spectroscopy

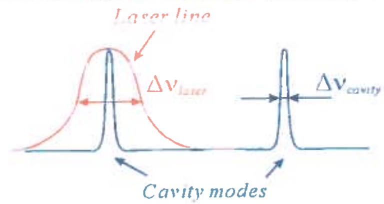


$$I = I_0 \exp\left(-\frac{t}{\tau}\right)$$

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

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

Optical Cavity Transmission Considerations



$$T \approx \frac{\Delta\nu_{cavity}}{\Delta\nu_{laser}} \qquad \Delta\nu_{cavity} = \frac{c(1-R)}{2\pi d} = \frac{1}{2\pi\tau}$$

$$\tau = 3.5\mu s \quad \Rightarrow \quad \Delta\nu_{cavity} = 45\,\text{kHz};\ T = \frac{45\,\text{kHz}}{3\,\text{MHz}} = 1.5\%$$

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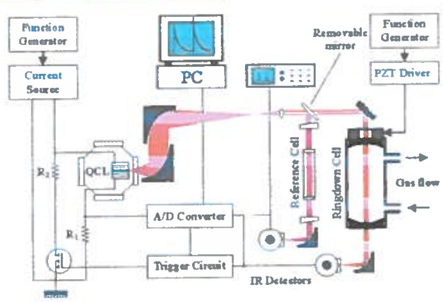
CRDS Based Gas Sensor



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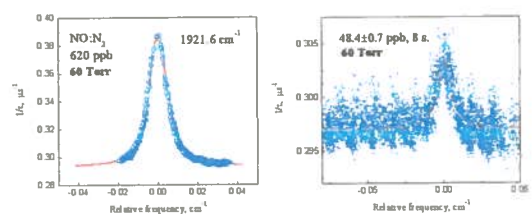
NO absorption in Nitrogen @ 1921.6 cm^{-1}



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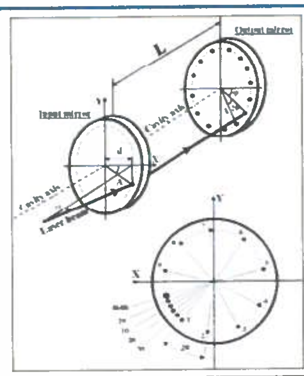
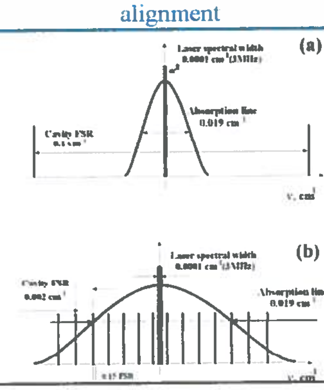
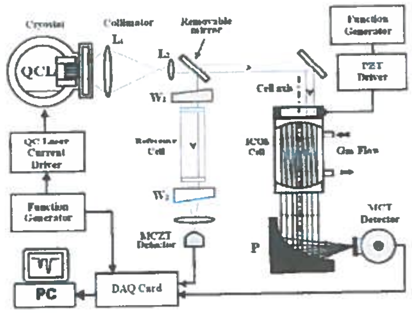
Off-Axis alignment of laser beams inside cavity



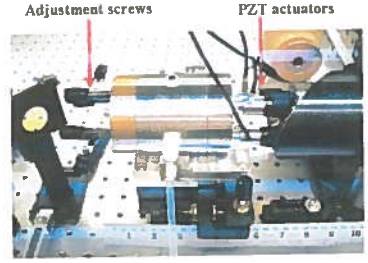
Frequency hierarchy for On-Axis laser-cavity alignment



Off-Axis ICOS experimental arrangement



Novel compact gas cell design for Off-Axis ICOS



Adjustment screws are utilized to make spherical mirror astigmatic

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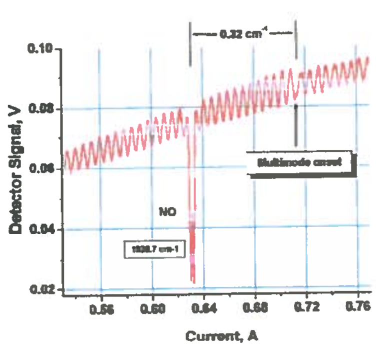
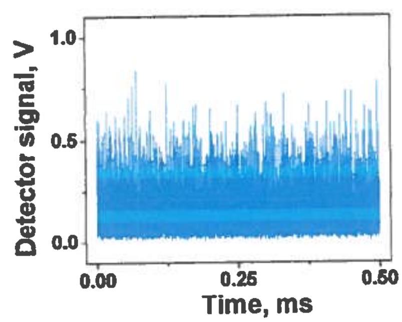
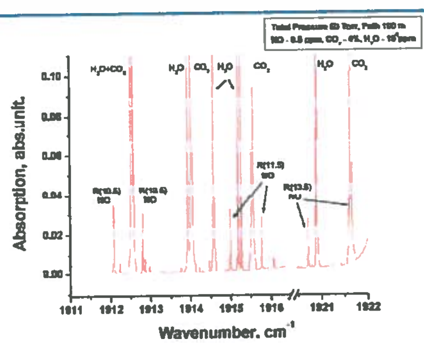


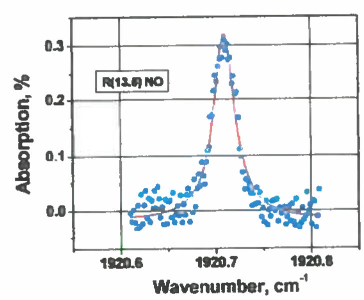
Time Integrated OA-ICOS Cavity Output



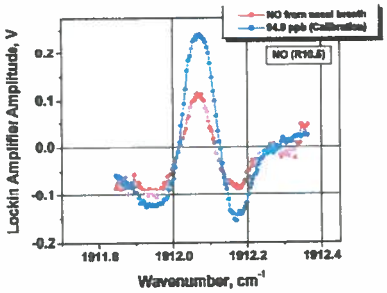
Simulation of mid-IR Absorption Spectrum @ 1950 cm^{-1}



Voigt fit of the measured R(13.5) NO absorption line at 1920.7 cm^{-1}



eNO concentration measurement from nasal breath using wavelength modulation applied to OA-ICOS



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, COS, C_2H_4, C_2H_5OH and isotopic species
- **Applications in Trace Gas Detection**
  - Industrial process control and chemical analysis (NO)
  - Environmental monitoring (HCHO, CO_2)
  - Medical Diagnostics (NO, CO, COS, CO_2)
- **Future Directions**
  - Cavity ring down and QE-PAS spectroscopy based applications
  - Applications using thermoelectrically cooled, cw quantum cascade lasers and amplifiers
  - Applications using near IR interband and far-IR intersub-band quantum cascade lasers

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QC-DFB Laser: Pulsed vs. CW operation

ADVANTAGES	SPECIFIC DEVICE ISSUES
• Laser can be operated at near-room temperature (TE cooling)	• Broad asymmetric linewidth (>170 MHz FWHM) related to heating during excitation pulse
• Facilitates temperature control	• Reduced average power
• No consumables (liquid N_2)	• Optimum frequency tuning
• Unattended remote monitoring	• More sophisticated electronics for driving QC laser and data acquisition system are required
• Decreased instrument size & weight	

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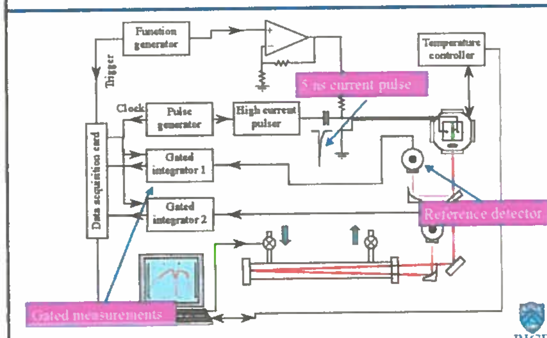
Pulsed QC Laser Based CO Gas Sensor



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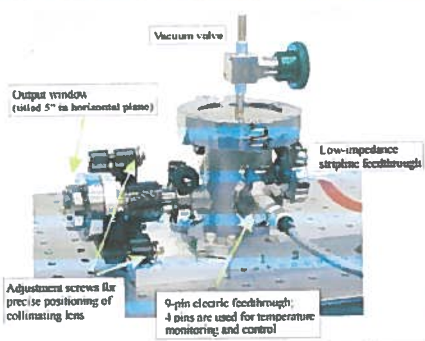
A. Kosterev et al, Applied Optics 41, 1170 2002

TEC cooled QC Laser Housing



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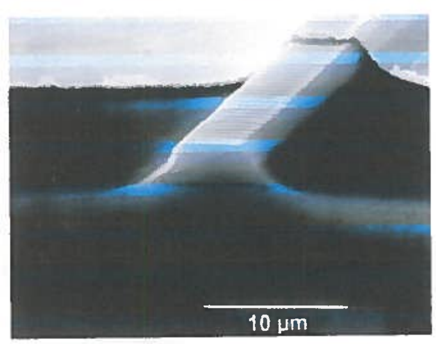
DFB QC Laser - SEM picture



Provided by C.Gmachl, Lucent Technology

Key Characteristics of Mid-IR Quantum Cascade Lasers

- QC laser wavelengths cover entire mid-IR range from 3.5 to 24 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 frequency:<kHz - 330MHz)
- Wavelength tunable by current (~1cm^{-1}) or temperature scanning (~10cm^{-1})
- High reliability: long lifetime, robust operation and reproducible emission wavelengths

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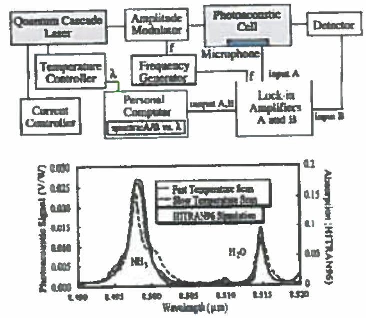
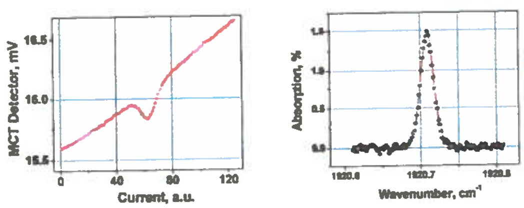
QC Laser Based Photoacoustic Sensor



B. A. Paldus, et. al., Optics Letter 24, 178, 1999

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*10^{-7} cm^{-1} Hz$^{-1/2}$ (NE sensitivity: 9 ppb)

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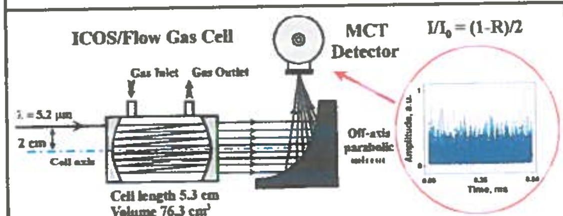
Off-Axis CW Integrated Cavity Output Spectroscopy (ICOS)



Typical single scan pattern of cell throughput

- 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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