Chemical Sensors using Quantum Cascade Lasers

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

OUTLINE

3rd QCL Workshop
Freiburg Germany
Sept. 19, 2002

- Motivation and Technology Issues
- Infrared QC Laser-based Gas Sensors
  - Pulsed quasi-room temperature sensors
  - CW cryogenically cooled sensors
- Outlook and Summary

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Wide Range of Gas Sensor Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants – Fence-line perimeter monitoring
  - Combustion Diagnostics
  - Automobile
- Rural Emission Measurements
  - Agriculture
- Environmental Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
- Diagnostic and Industrial Process Control
  - Petrochemical and Semiconductor Industry
- Medical Diagnostics
- Fundamental Science-Kinetics and Photochemistry
- Law enforcement and military chemical sensing

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Air Composition

Main Components		Trace Components	
Nitrogen	78%	Methane	1.7 ppm
Oxygen	21%	CO	0.4 ppm
Water	0.8%	N_2O	0.3 ppm
CO_2	0.03 %	O_3	0.03 ppm
		H_2CO	0.001 ppm
		…	

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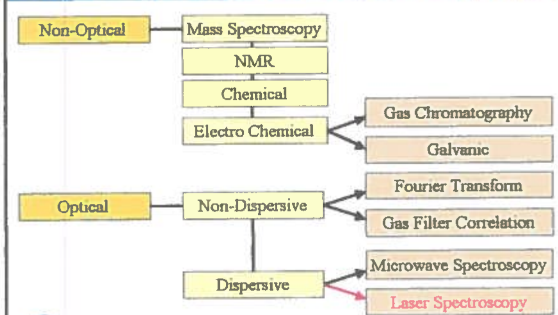
Existing Methods for Trace Gas Detection



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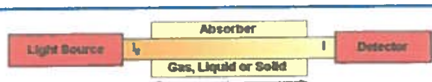
Absorption Spectroscopy



Beer-Lambert's Law

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

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

Molecular Absorption Coefficient

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

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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IR Source Requirements for Spectroscopy

REQUIREMENTS	SOURCE
Sensitivity	Power
Specificity	Line Width
Multi-gas Components	Tunable
Directionality	Beam Quality
Rapid Data Acquisition	Response
Room Temperature	

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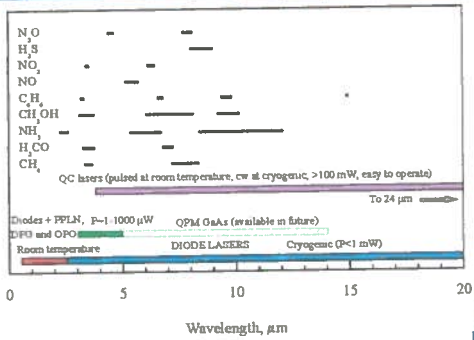
Spectral Coverage by Diode & QC Lasers



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Sensitivity Enhancement Techniques

- Optimum Absorbing Transition
  - Overtone or Combination Band
  - Fundamental Band
- Long Pathlength
  - Multipass Cell
  - Cavity Enhanced, Cavity Ringdown
  - Open Path [with retro-reflector]
  - Fiberoptic Evanescent Wave Spectroscopy
- Detection Schemes
  - Frequency Modulation, Wavelength Modulation, Two-tone frequency modulation
  - Balanced Detection
  - Zero-air Subtraction

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Key Characteristics of Quantum Cascade Lasers

- Laser wavelengths cover entire range from 3.5 to 66 μm determined by layer thickness of same material
- Intrinsically high power lasers (determined by number of stages)
  - 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: low failure rate, long lifetime, robust operation and reproducible emission wavelengths

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QC-DFB Laser: Pulsed vs. CW

ADVANTAGES	SPECIFIC ISSUES
• Laser can be operated at near-room temperature (TE cooling)	• Broad asymmetric linewidth (~200 MHz FWHM) related to heating during the pulse
• Facilitates temperature control	• How to tune the frequency
• No consumables (liquid N_2)	• Reduced average power
• Unattended remote monitoring	• More sophisticated electronics are required for driving QC laser and data acquisition are required
• Decreased instrument size & weight	

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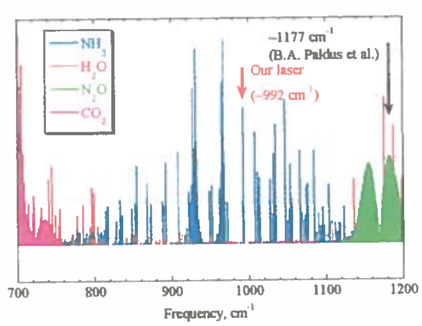
Simulated ν_2 NH_3 Absorption Spectrum



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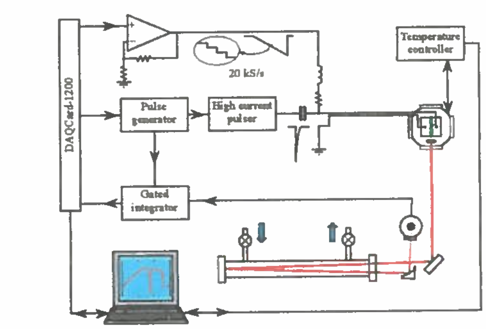
Pulsed QC Laser Based Gas Sensor



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

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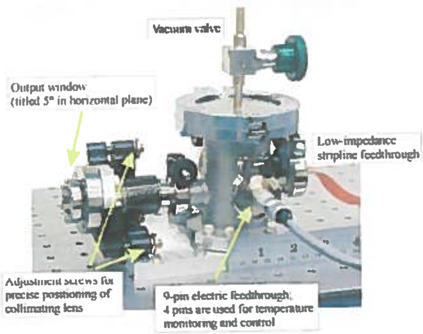
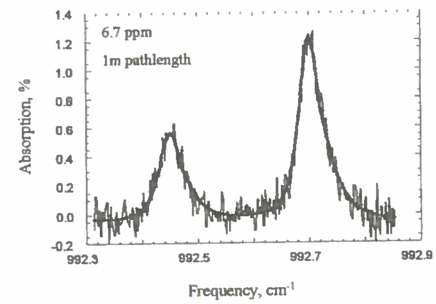
QC Laser Housing

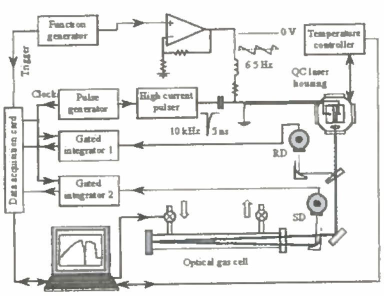


Detected Ammonia Absorption Spectrum



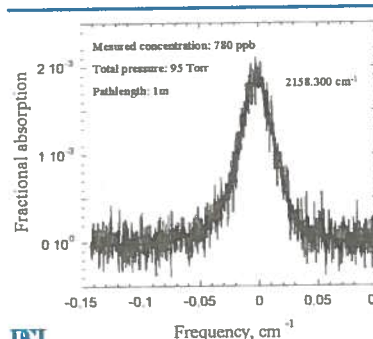
A. Kosterev et al, Applied Optics 41, 573 2002

Pulsed QC Laser Based CO Gas Sensor



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

CO Absorption: Ambient Air Sample

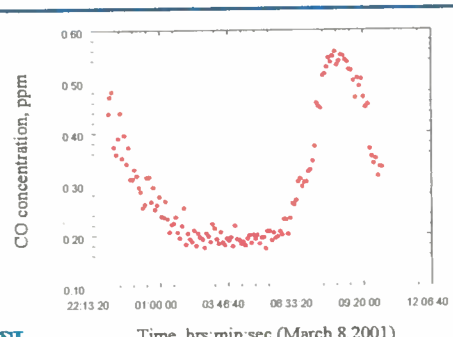


Two IR detectors

Sensitivity ~10 ppb

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

CO Concentration Measurements



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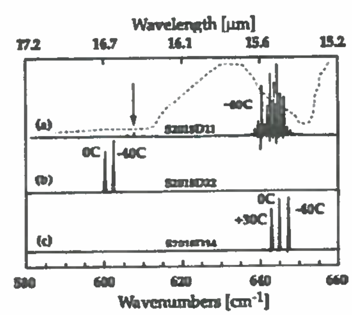
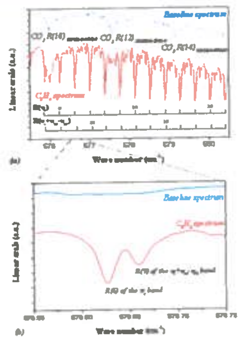
Spectral Emission from a 16 micron QC Laser



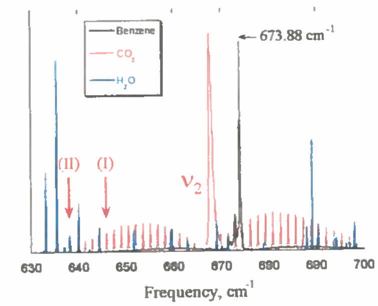
M. Rochat, D. Hofstetter, M. Beck, J. Faist, Appl. Phys. Lett. 79, p. 4271, 2001

C_6H_6 Absorption Line Selection

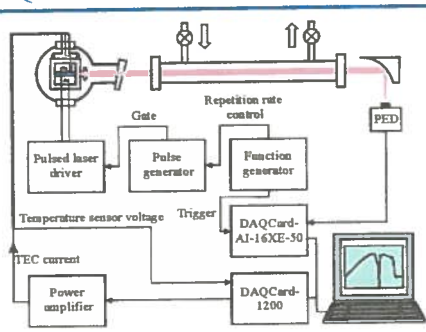


W Chen, F Cazier, F.K. Tittel and D Boucher, Appl Optics 39, 6238, 2000

Absorption Spectra of Benzene, CO_2 and H_2O



QC Laser based Chemical Sensor



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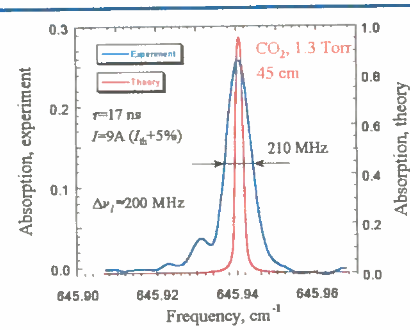
Record narrow Linewidth of pulsed QC Laser



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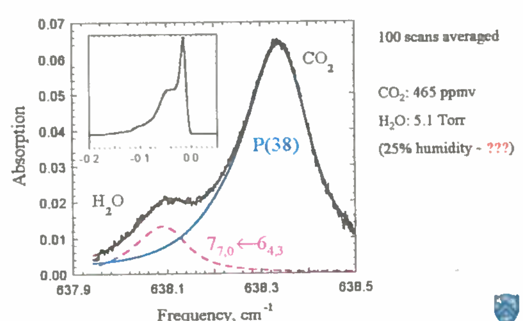
Ambient air absorption at 15.6 μm – 45 cm path



100 scans averaged

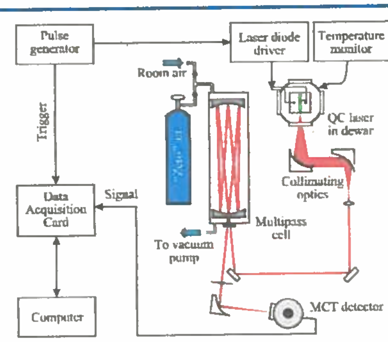
CO_2: 465 ppmv

H_2O: 5.1 Torr

(25% humidity - ???)

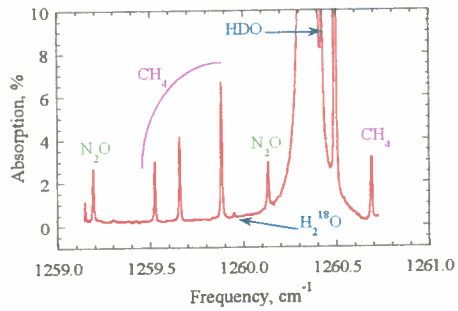
A. Kosterev et al, Applied Physics B, Sept 2002

Trace Gas Detection with a Multipass Cell



A. A. Kosterev, Applied Optics 39, 4425, 2000

Absorption Spectrum of Room Air



A. A. Kosterev, Applied Optics 39, 4425, 2000

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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

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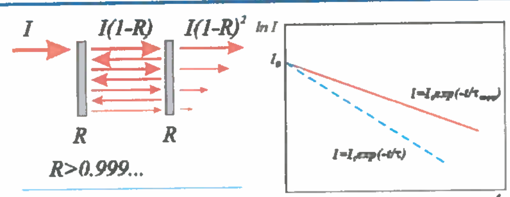
Cavity Ring-Down Spectroscopy

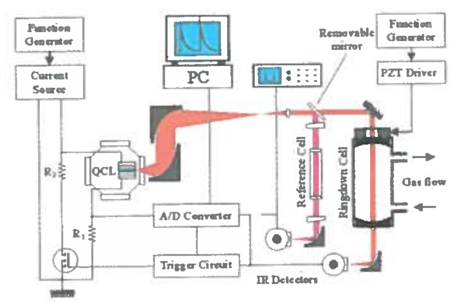


$$I = I_0 \exp\left(-\frac{t}{\tau}\right)$$

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

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

CRDS Based Gas Sensor



A. A. Kosterev, Applied Optics 40, 5522, 2001

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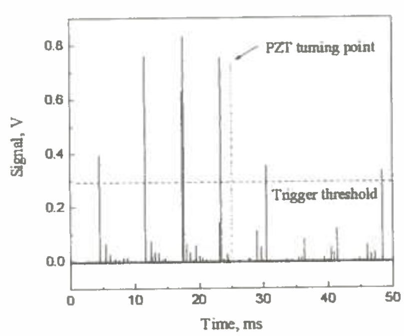
Laser-Cavity Resonances (spikes)



A. A. Kosterev, Applied Optics 40, 5522, 2001

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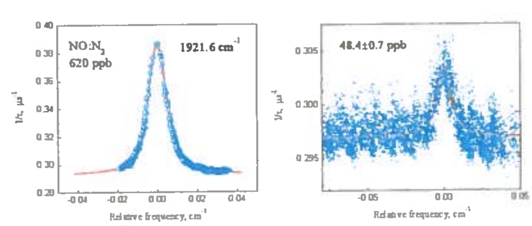
NO absorption, 60 Torr Total Pressure



A. A. Kosterev, Applied Optics 40, 5522, 2001

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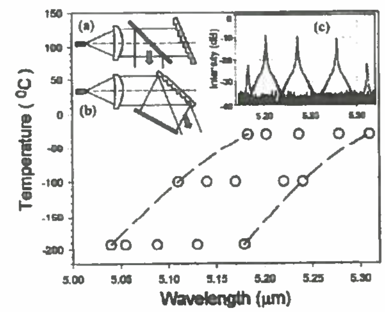
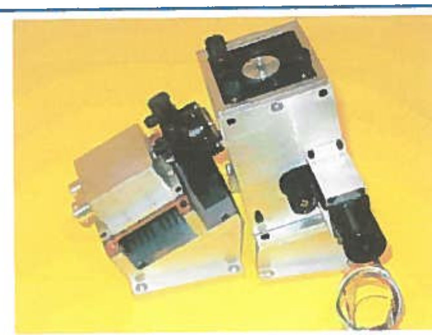
Tuning Range of Broadly λ-Tunable ECDL



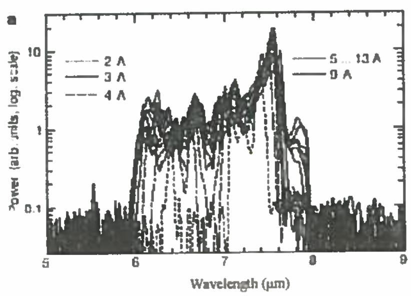
H. Le et al. Applied Physics Letters (2001)

ECDL Configuration for Pulsed QC Laser



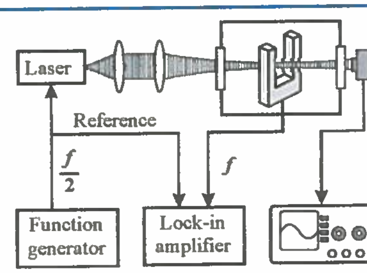
Design by H. Le, Univ. of Houston (2001)

Laser Spectrum of Ultra-Broadband QC Laser



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

Photoacoustic Spectroscopy with a Solid State Resonator



A. A. Kosterev, Y. A. Bakhirkin, R. F. Curl, F. K. Tittel, submitted to Optics Letters June 2002

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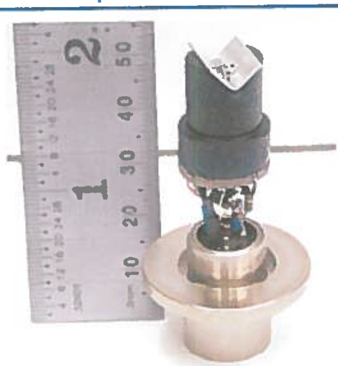
Close-up of QEPAS sensor



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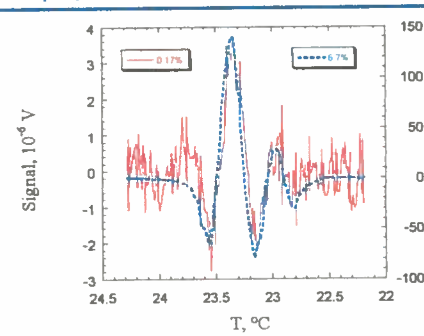
CH_4 Spectrum Acquired with QEPAS



A. A. Kosterev, Y. A. Bakhirkin, R. F. Curl, F. K. Tittel, accepted by Optics Letters August 2002

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Summary

- <u>Quantum Cascade and Diode Laser Based Trace Gas Sensors</u>
  - Compact, tunable, robust, fieldable
  - High sensitivity ($<2 \cdot 10^{-4}$ to 10^{-5}) and selectivity (10–300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: $\mathbf{NH_3}$, $\mathbf{CH_4}$, H_2CO, NO_2, $\mathbf{N_2O}$, $\mathbf{H_2O}$, $\mathbf{CO_2}$,
  - **CO**, **NO**, HCl, SO_2, $\mathbf{C_2H_5OH}$, isotopic species of ^{12,13}**C**, $^{16,17,18}O$, $^{35,37}Cl$
- <u>Applications in Trace Gas Detection</u>
  - Environmental monitoring and atmospheric chemistry: H_2CO, **CO**, $\mathbf{CO_2}$, $\mathbf{CH_4}$ (NASA, NCAR, NOAA, EPA)
  - Industrial process and chemical analysis: **NO**
  - Medical diagnostics: **NO, CO**, $\mathbf{CO_2}$
- <u>Future Directions</u>
  - Longer and shorter IR wavelengths with improved QC lasers
  - QC amplifiers and broadly tunable QC lasers
  - Cavity enhanced and cavity ringdown spectroscopy

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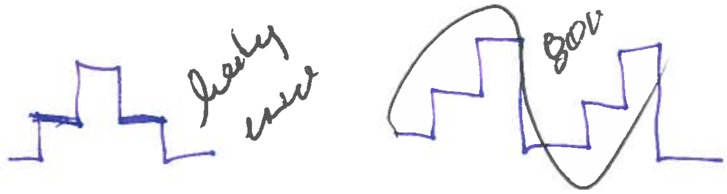

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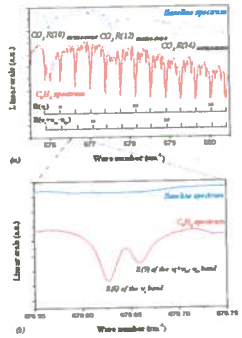

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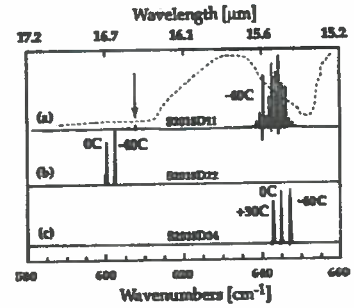

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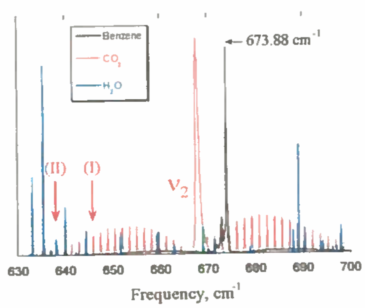
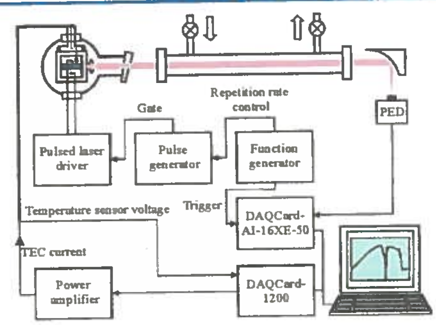


QC Laser based Chemical Sensor



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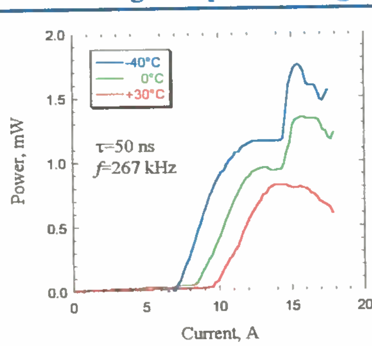
QC Laser Average Output Power @ 15.6 µm



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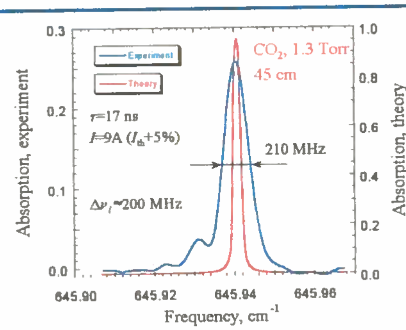

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