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Environmental Sentinels 2002

September 2002

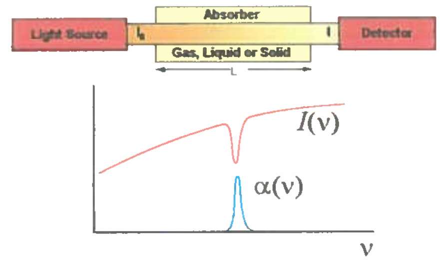
Laser Spectroscopy for Chemical Sensing Applications

A.A Kosterev, Yu.A. Bakhirkin, C. Roller, R.F. Curl, and F.K. Tittel
Rice University
Houston, TX

OUTLINE

- Basics of spectroscopic detection
- Gas sensors based on pulsed QC-DFB lasers
- QEPAS – a new photoacoustic method
- Summary

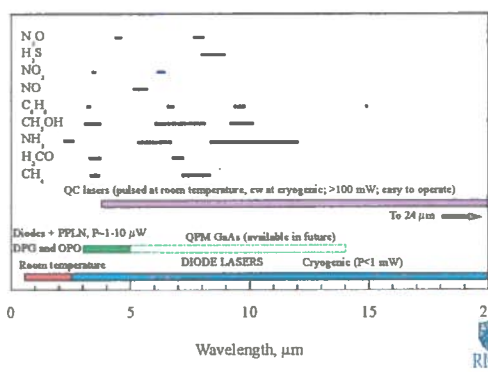
Absorption Spectroscopy



$$I(\nu) = I_0(\nu)\times\exp[-\alpha(\nu)\cdot nL] \Rightarrow n = -\ln\left(\frac{I(\nu)}{I_0(\nu)}\right)\cdot\frac{1}{\alpha(\nu)L}$$

IR Source Requirements for Spectroscopy

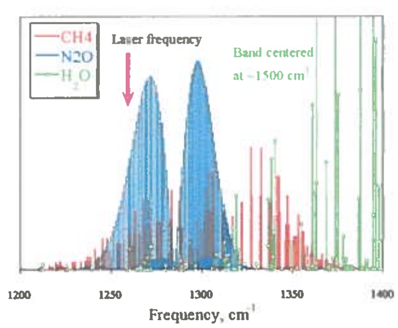
REQUIREMENTS	SOURCE
Sensitivity	Power
Specificity	Line Width
Multi-gas Components	Tunable
Directionality	Beam Quality
Rapid Data Acquisition	Response
Room Temperature	



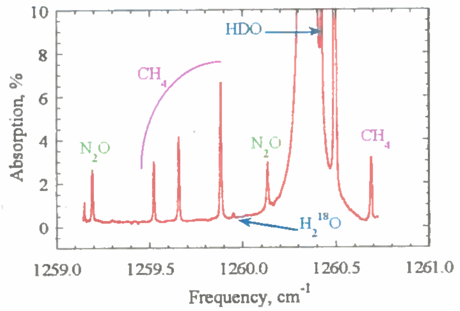
Key Characteristics of Quantum Cascade Lasers

- 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
- Wavelength tuning by current or temperature scanning
- High reliability: low failure rate, long lifetime, robust operation and reproducible emission wavelengths

Multiple species can be detected even with a short wavelength scan



Absorption Spectrum of Room Air



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QC-DFB Laser: Pulsed vs. CW

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

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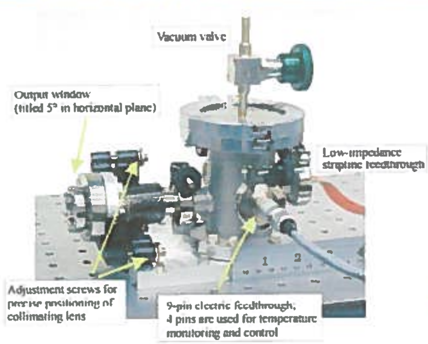
QC Laser Housing



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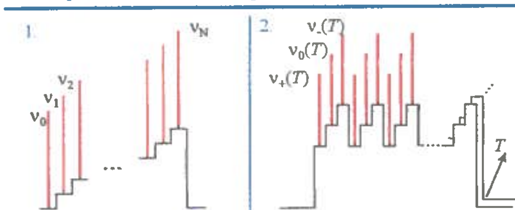
Synchronous Frequency Manipulation



Synchronous digitally synthesized steps of tuning current (enables linearization of scan)

Fast cycling of the laser frequency with a subthreshold current and slow scanning with temperature (wavelength modulation)

A. A. Kosterev, F. K. Tittel, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, and A. Y. Cho, "Trace-gas detection in ambient air with a thermoelectrically cooled, pulsed quantum-cascade distributed feedback laser", *Appl. Opt.* 39, 6866-6872 (2000)

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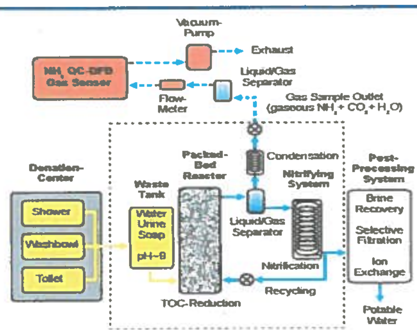
NASA Water Recovery System



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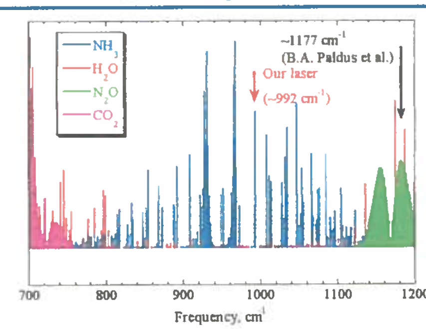
Ammonia Absorption Spectrum



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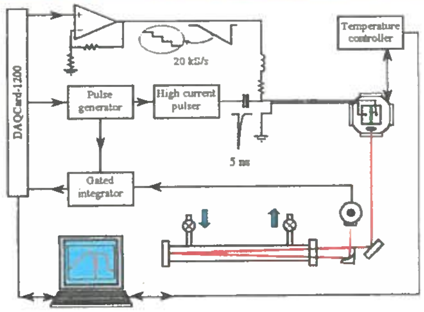
Single-Channel Gas Sensor



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NH_3 Sensor Based on Pulsed 10.05 μm laser

One IR detector

Sensitivity ~0.3 ppm

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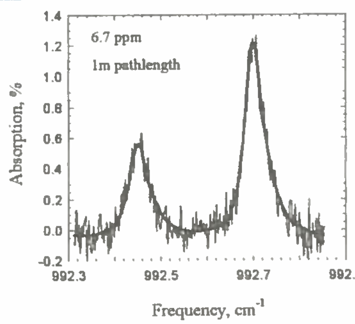
Ammonia Absorption near 993 cm^{-1}



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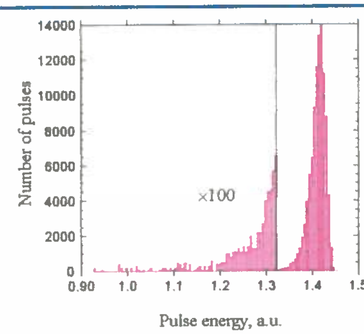
Energy Distribution of the QC Laser Pulses



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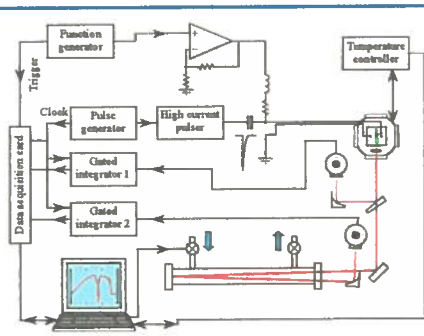
Two-Channel Data Acquisition



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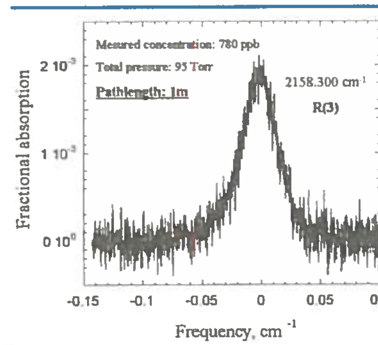
CO Absorption: Ambient Air Sample



Two IR detectors

Sensitivity ~10 ppb

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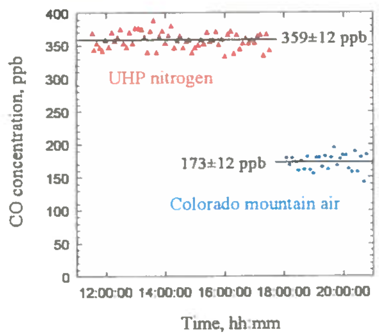
CO Concentration in Two Gas Cylinders



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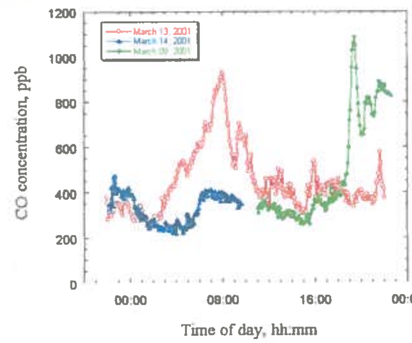
CO Concentration in the Laboratory



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Molecules detected with QC Lasers at Rice

Molecule	Wavelength and method
$^{13}CH_4$ and $^{12}CH_4$, N_2O, H_2O and HDO	8 μm, CW and pulsed, ambient air, 100 m pathlength, Voigt fit and linear regression analysis
C_2H_5OH	8 μm, CW, 100 m pathlength, linear regression analysis
NO	5.2 μm, CW, ICOS and CRDS
NH_3	10 μm, pulsed, 1 m pathlength
CO	4.6 μm, pulsed, ambient air, 1 m pathlength, reference channel
CO_2	15.5 μm, pulsed, ambient air, 1 m pathlength

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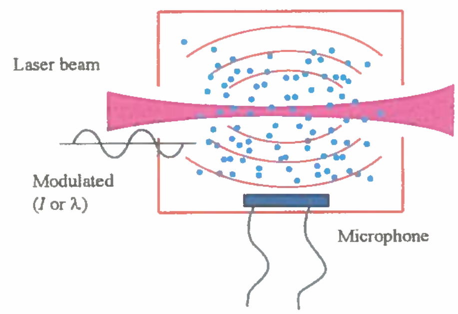
Resonant Photoacoustic Spectroscopy



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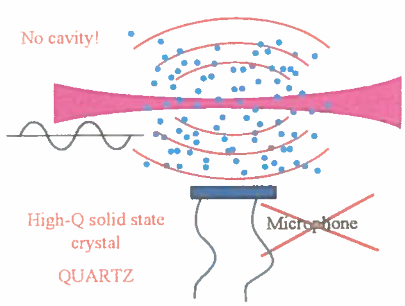
Quartz-Enhanced PAS (QEPAS)



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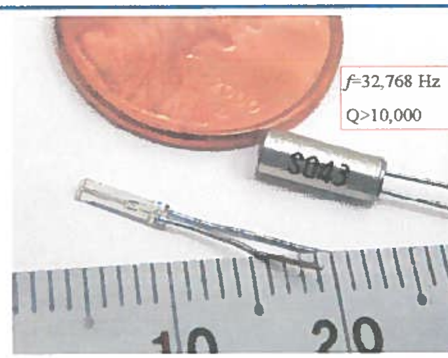
Quartz Watch Tuning Fork



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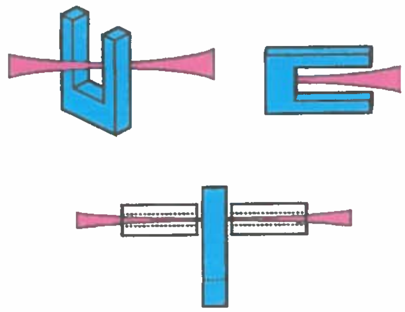
Possible Configurations



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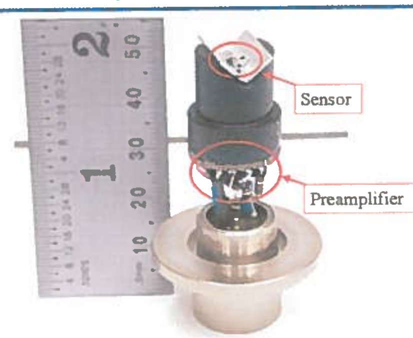
QEPAS Module



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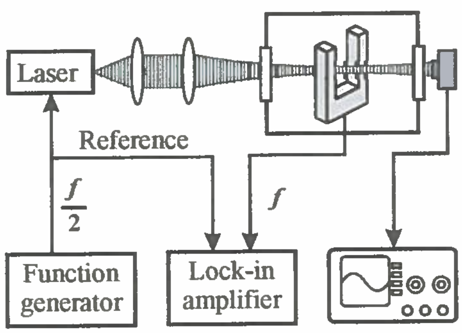
QEPAS Setup



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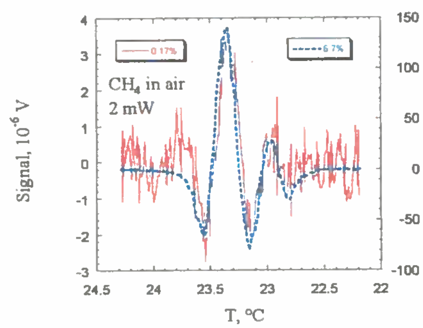
First Results



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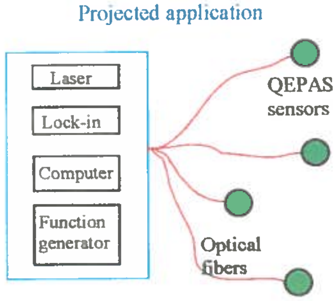
Projected application



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Summary

- Pulsed QC-DFB lasers can be used to create portable (ultra)sensitive chemical detectors for gas phase monitoring based on direct absorption or wavelength modulation spectroscopy.
- CW QC-DFB lasers offer additional opportunities but presently require cryogenic cooling, thus limiting the applications.
- Recently invented QEPAS technique is a promising approach to multipoint sensing. It can be combined either with readily available near-IR diode lasers for moderate sensitivity, or with non-cryogenic mid-IR CW QC-DFB lasers (which are expected to become available soon) for high sensitivity.

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