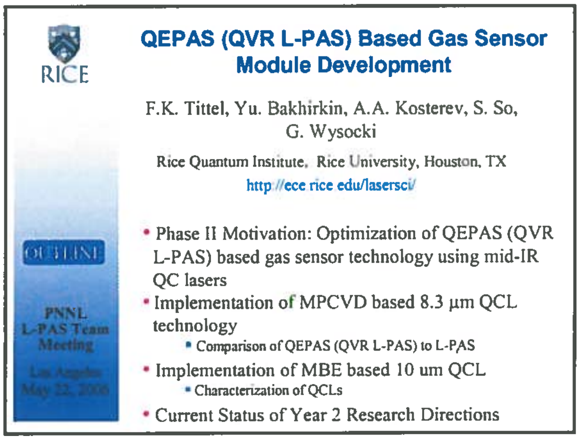

## QEPAS (QVR L-PAS) Based Gas Sensor Module Development

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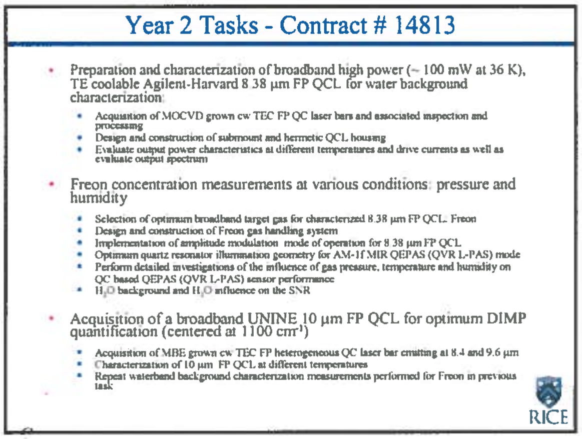
OUTLINE

PNNL
L-PAS Team
Meeting

Los Angeles
May 22, 2006

- Phase II Motivation: Optimization of QEPAS (QVR L-PAS) based gas sensor technology using mid-IR QC lasers
- Implementation of MPCVD based 8.3 μm QCL technology
  - Comparison of QEPAS (QVR L-PAS) to L-PAS
- Implementation of MBE based 10 um QCL
  - Characterization of QCLs
- Current Status of Year 2 Research Directions



## Year 2 Tasks - Contract # 14813

- Preparation and characterization of broadband high power (~ 100 mW at 36 K), TE coolable Agilent-Harvard 8.38 μm FP QCL for water background characterization
  - Acquisition of MOCVD grown cw TEC FP QC laser bars and associated inspection and processing
  - Design and construction of submount and hermetic QCL housing
  - Evaluate output power characteristics at different temperatures and drive currents as well as evaluate output spectrum
- Freon concentration measurements at various conditions: pressure and humidity
  - Selection of optimum broadband target gas for characterized 8.38 μm FP QCL: Freon
  - Design and construction of Freon gas handling system
  - Implementation of amplitude modulation mode of operation for 8.38 μm FP QCL
  - Optimum quartz resonator illumination geometry for AM-1f MIR QEPAS (QVR L-PAS) mode
  - Perform detailed investigations of the influence of gas pressure, temperature and humidity on QC based QEPAS (QVR L-PAS) sensor performance
  - $H_2O$ background and $H_2O$ influence on the SNR
- Acquisition of a broadband UNINE 10 μm FP QCL for optimum DIMP quantification (centered at 1100 $cm^{-1}$)
  - Acquisition of MBE grown cw TEC FP heterogeneous QC laser bar emitting at 8.4 and 9.6 μm
  - Characterization of 10 μm FP QCL at different temperatures
  - Repeat waterband background characterization measurements performed for Freon in previous task

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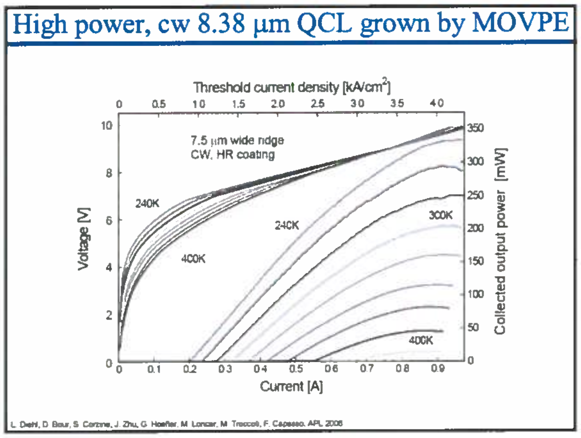
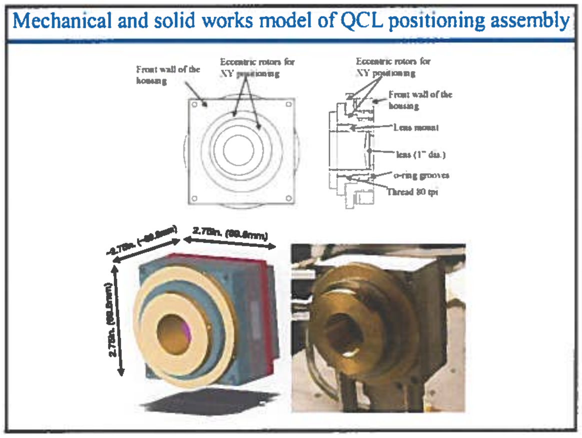
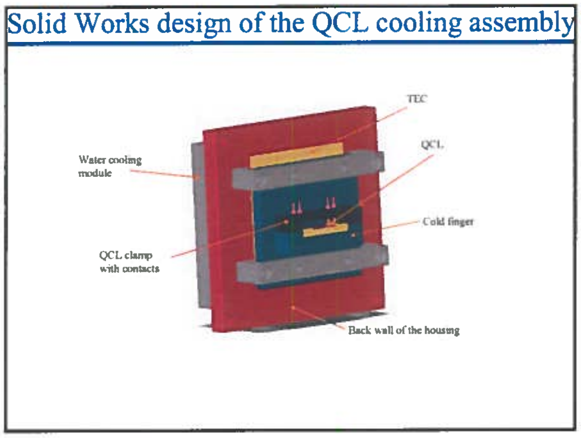


## High power, cw 8.38 μm QCL grown by MOVPE

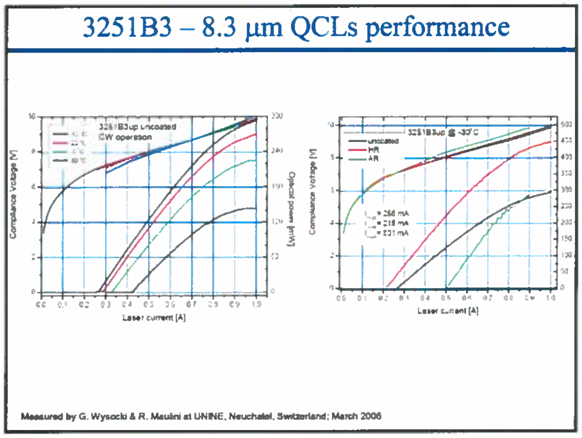
L. Diehl, D. Bour, S. Corzine, J. Zhu, G. Hoefler, M. Loncar, M. Troccoli, F. Capasso, APL 2006



## Mechanical and solid works model of QCL positioning assembly

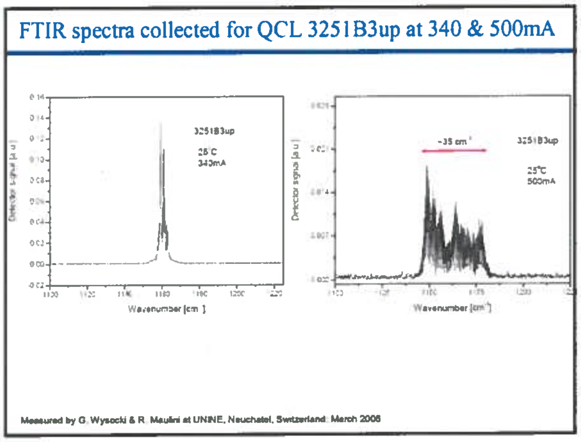


## Solid Works design of the QCL cooling assembly



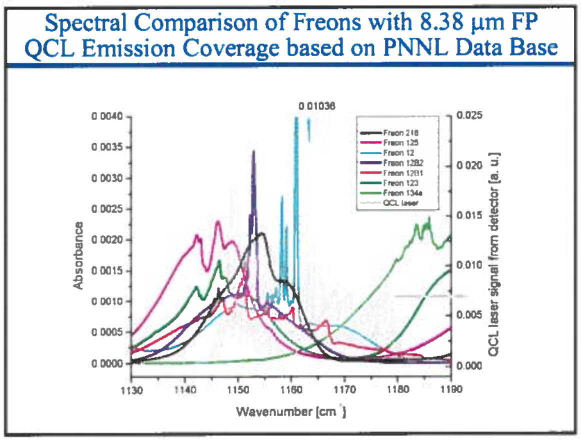
## 3251B3 – 8.3 μm QCLs performance

Measured by G. Wysocki & R. Maulini at UNINE, Neuchatel, Switzerland; March 2006



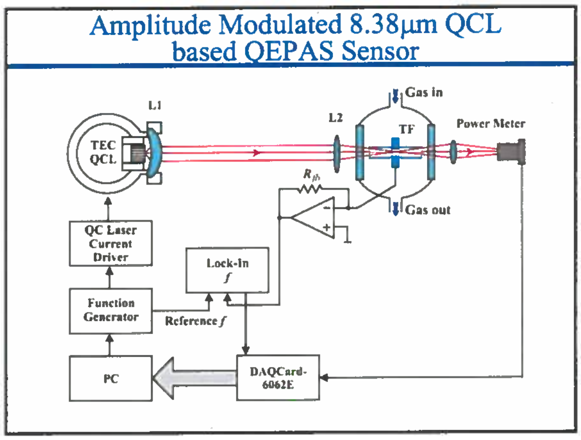
## FTIR spectra collected for QCL 3251B3up at 340 & 500mA

Measured by G. Wysocki & R. Maulini at UNINE, Neuchatel, Switzerland: March 2006



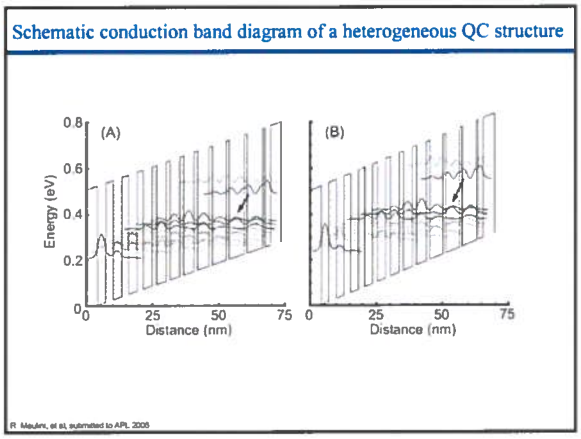
## Spectral Comparison of Freons with 8.38 µm FP QCL Emission Coverage based on PNNL Data Base

8



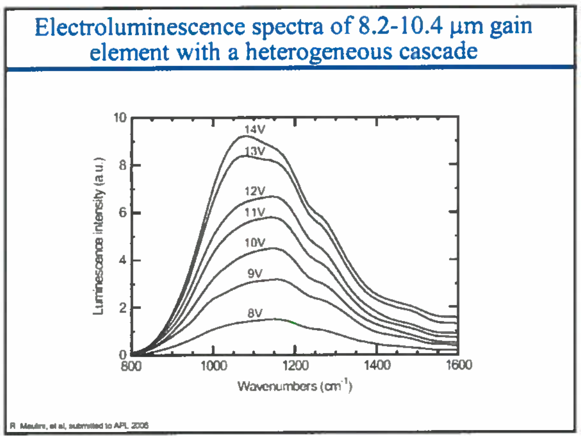
## Amplitude Modulated 8.38µm QCL based QEPAS Sensor

9



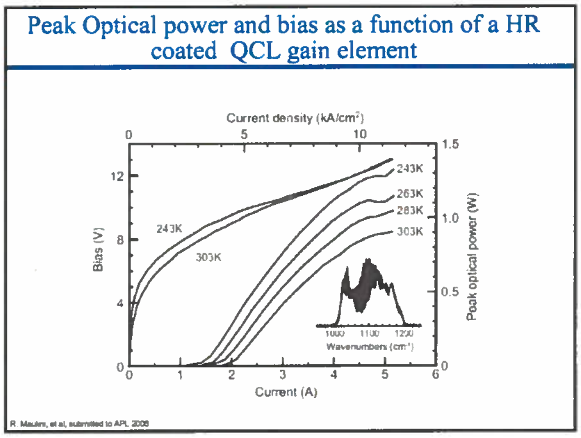
## Schematic conduction band diagram of a heterogeneous QC structure

R. Maulini, et al, submitted to APL 2006



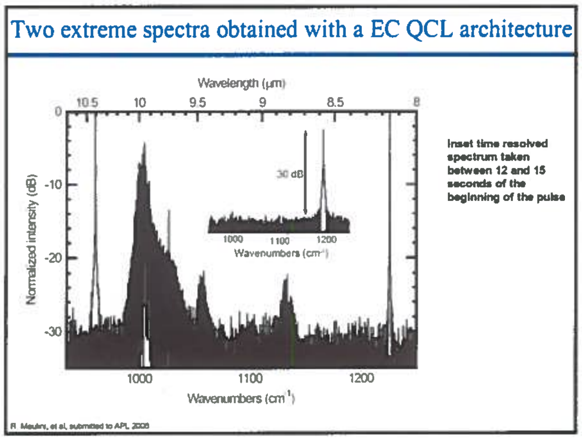
## Electroluminescence spectra of 8.2-10.4 µm gain element with a heterogeneous cascade

R. Maulini, et al, submitted to APL 2006



## Peak Optical power and bias as a function of a HR coated QCL gain element

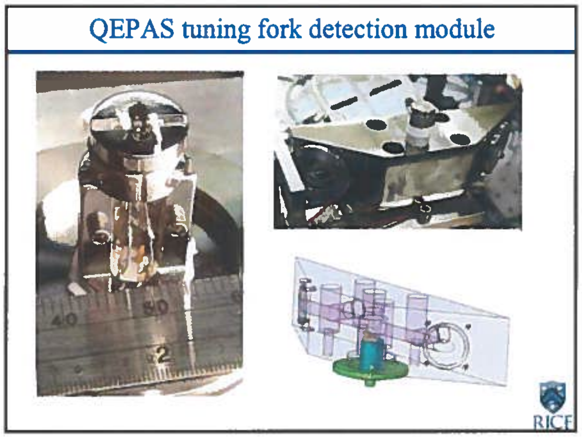
R. Maulini, et al, submitted to APL 2006



## Two extreme spectra obtained with a EC QCL architecture

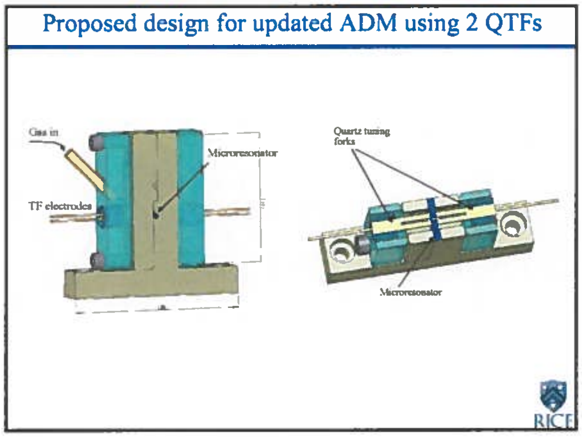
Inset time resolved spectrum taken between 12 and 15 seconds of the beginning of the pulse

R. Maulini, et al, submitted to APL 2005

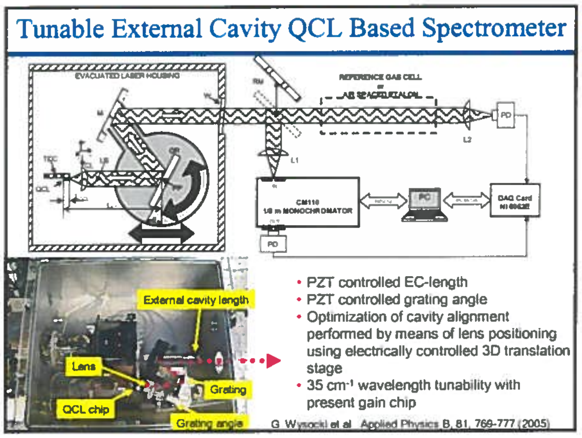


## QEPAS tuning fork detection module

## Other QTFs



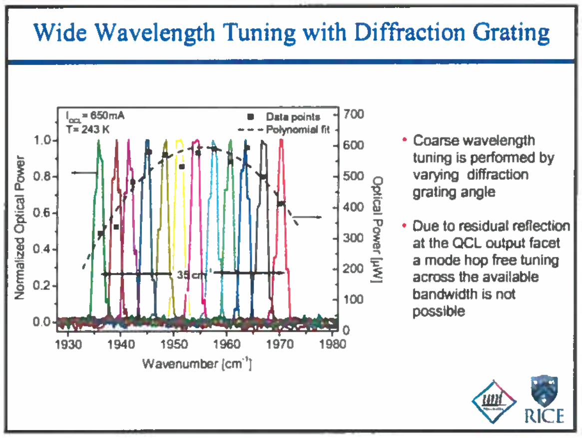
## Proposed design for updated ADM using 2 QTFs



## Tunable External Cavity QCL Based Spectrometer

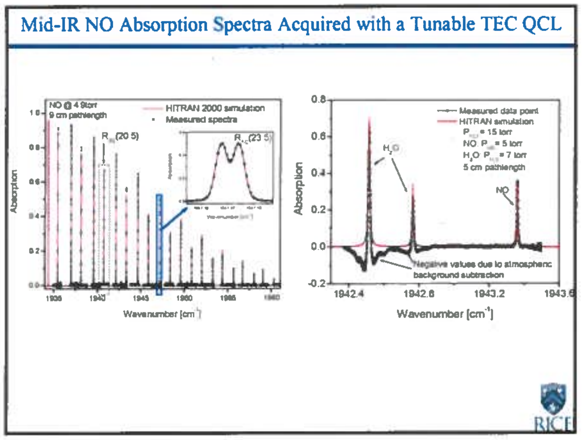
- PZT controlled EC-length
- PZT controlled grating angle
- Optimization of cavity alignment performed by means of lens positioning using electrically controlled 3D translation stage
- 35 $cm^{-1}$ wavelength tunability with present gain chip

G. Wysocki et al. Applied Physics B, 81, 769-777 (2005)

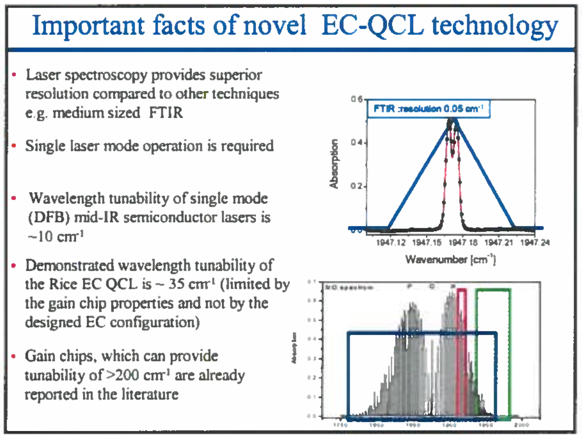


## Wide Wavelength Tuning with Diffraction Grating

- Coarse wavelength tuning is performed by varying diffraction grating angle
- Due to residual reflection at the QCL output facet a mode hop free tuning across the available bandwidth is not possible



## Mid-IR NO Absorption Spectra Acquired with a Tunable TEC QCL



## Important facts of novel EC-QCL technology

- Laser spectroscopy provides superior resolution compared to other techniques e.g. medium sized FTIR
- Single laser mode operation is required
- Wavelength tunability of single mode (DFB) mid-IR semiconductor lasers is ~10 $cm^{-1}$
- Demonstrated wavelength tunability of the Rice EC QCL is ~ 35 $cm^{-1}$ (limited by the gain chip properties and not by the designed EC configuration)
- Gain chips, which can provide tunability of >200 $cm^{-1}$ are already reported in the literature

## Merits of QE Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to ambient and flow acoustic noise, laser noise and etalon effects
- Significant reduction of sample volume (< 1 $mm^3$)
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive
- Rugged and low cost compared to LAS that requires a multipass absorption cell and infrared detector(s)
- Potential for optically multiplexed concentration measurements

## QEPAS Performance for 11 Trace Gas Species (May'06)

| Molecule (Host) | Frequency, $cm^{-1}$ | Pressure, Torr | NNEA, $cm^{-1}W/Hz^{½}$ | Power, mW | NEC (τ=1s), ppmv |
|---|---|---|---|---|---|
| $H_2O$ ($N_2$)** | 7181.17 | 60 | $2.1\times10^{-9}$ | 5.8 | 0.18 |
| HCN (air: 50% hum) ** | 6539.11 | 60 | $<2.6\times10^{-9}$ | 50 | 0.1 |
| $C_2H_2$ (($N_2$)** | 6529.17 | 75 | $\sim2.5\times10^{-9}$ | ~40 | 0.06 |
| $NH_3$ ($N_2$)* | 6528.76 | 60 | $5.4\times10^{-9}$ | 38 | 0.50 |
| $C_2H_2$ | 6528.76 |  |  | 38 | 0.1 |
| $CO_2$ (exhaled air) | 6514.25 | 90 | $1.0\times10^{-8}$ | 5.2 | 890 |
| $CO_2$ ($N_2$) *** | 4990.00 | 300 | $1.5\times10^{-7}$ | 4.6 | 130 |
| $CH_2O$ ($N_2$) * | 2832.48 | 100 | $1.1\times10^{-8}$ | 4.6 | 0.28 |
| CO ($N_2$) | 2196.66 | 50 | $5.3\times10^{-7}$ | 13 | 0.5 |
| CO (propylene) | 2196.66 | 50 | $7.4\times10^{-8}$ | 6.5 | 0.14 |
| $N_2O$ (air+5%$SF_6$) | 2195.63 | 50 | $1.5\times10^{-8}$ | 19 | 0.007 |

* - Improved microresonator
** - Improved microresonator and double optical pass through QTF
*** - Without microresonator

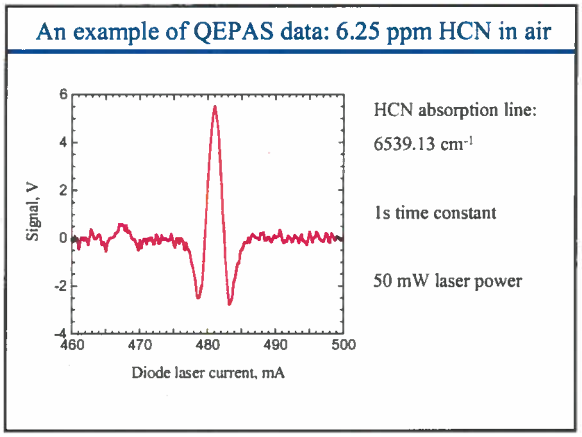
NNEA – normalized noise equivalent absorption coefficient.
NEC – noise equivalent concentration for available laser power and τ=1s time constant.

**For comparison: conventional PAS $2.2\times10^{-9}$ $cm^{-1}W/\sqrt{Hz}$ (1,800 Hz) for $NH_3$***

* M. E. Webber, M. Pushkarsky and C. K. N Patel, Appl. Opt. 42, 2119-2126 (2003)

## QEPAS versus Traditional PAS

| Parameter | Traditional PAS | QEPAS |
|---|---|---|
| *f*, Hz | 100 to 4000 | Presently ~32 760 |
| Q | 20 to 200 | 10 000 to 30 000 |
| Q vs. pressure | INCREASES (high spectral resolution is problematic) | DECREASES (high spectral resolution is achievable) |
| Sample volume | >10 $cm^3$ | <1 $mm^3$ |
| Sensitivity to ambient acoustic and flow noise | Usually high | None observed |
| Pathlength involved | ~10 cm | (a) 0.3mm, (b) 5mm |

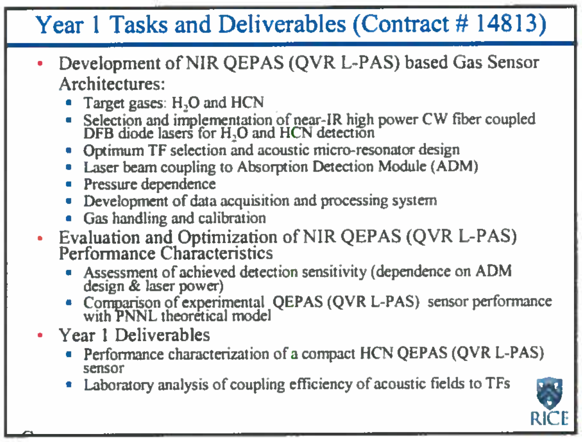


## An example of QEPAS data: 6.25 ppm HCN in air

HCN absorption line:
6539.13 $cm^{-1}$

1s time constant

50 mW laser power



## Year 1 Tasks and Deliverables (Contract # 14813)

- Development of NIR QEPAS (QVR L-PAS) based Gas Sensor Architectures:
  - Target gases: $H_2O$ and HCN
  - Selection and implementation of near-IR high power CW fiber coupled DFB diode lasers for $H_2O$ and HCN detection
  - Optimum TF selection and acoustic micro-resonator design
  - Laser beam coupling to Absorption Detection Module (ADM)
  - Pressure dependence
  - Development of data acquisition and processing system
  - Gas handling and calibration
- Evaluation and Optimization of NIR QEPAS (QVR L-PAS) Performance Characteristics
  - Assessment of achieved detection sensitivity (dependence on ADM design & laser power)
  - Comparison of experimental QEPAS (QVR L-PAS) sensor performance with PNNL theoretical model
- Year 1 Deliverables
  - Performance characterization of a compact HCN QEPAS (QVR L-PAS) sensor
  - Laboratory analysis of coupling efficiency of acoustic fields to TFs

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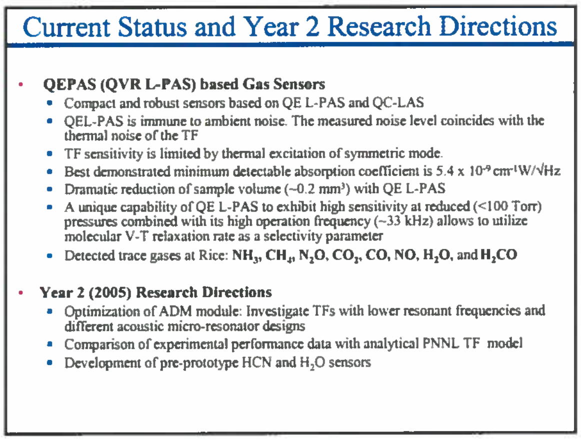
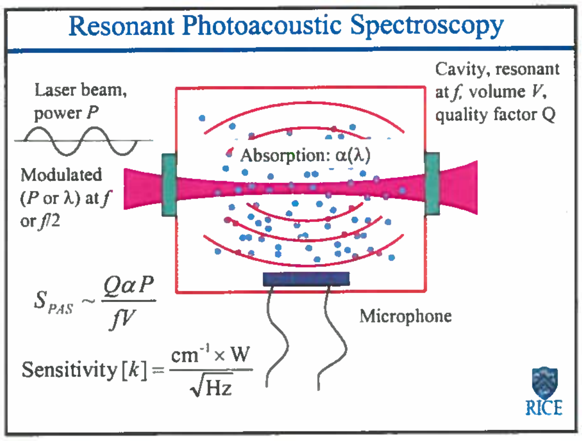


## Current Status and Year 2 Research Directions

- **QEPAS (QVR L-PAS) based Gas Sensors**
  - Compact and robust sensors based on QE L-PAS and QC-LAS
  - QEL-PAS is immune to ambient noise. The measured noise level coincides with the thermal noise of the TF
  - TF sensitivity is limited by thermal excitation of symmetric mode.
  - Best demonstrated minimum detectable absorption coefficient is $5.4 \times 10^{-9}$ $cm^{-1}W/\sqrt{Hz}$
  - Dramatic reduction of sample volume (~0.2 $mm^3$) with QE L-PAS
  - A unique capability of QE L-PAS to exhibit high sensitivity at reduced (<100 Torr) pressures combined with its high operation frequency (~33 kHz) allows to utilize molecular V-T relaxation rate as a selectivity parameter
  - Detected trace gases at Rice: **$NH_3$, $CH_4$, $N_2O$, $CO_2$, CO, NO, $H_2O$**, and **$H_2CO$**
- **Year 2 (2005) Research Directions**
  - Optimization of ADM module: Investigate TFs with lower resonant frequencies and different acoustic micro-resonator designs
  - Comparison of experimental performance data with analytical PNNL TF model
  - Development of pre-prototype HCN and $H_2O$ sensors



## Resonant Photoacoustic Spectroscopy

$$S_{PAS} \sim \frac{Q\alpha P}{fV}$$

$$\text{Sensitivity}\,[k] = \frac{cm^{-1} \times W}{\sqrt{Hz}}$$

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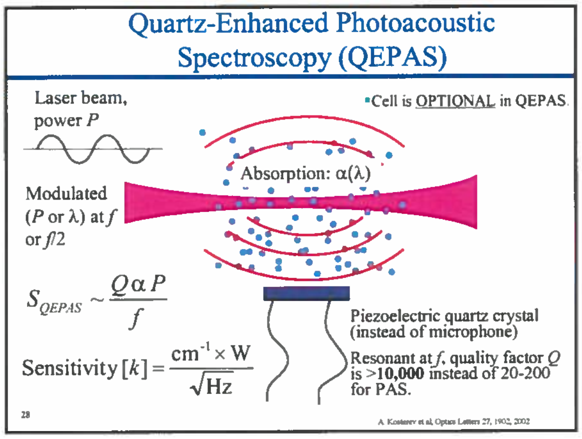

## Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)

- Cell is <u>OPTIONAL</u> in QEPAS.

$$S_{QEPAS} \sim \frac{Q\alpha P}{f}$$

$$\text{Sensitivity}\,[k] = \frac{cm^{-1} \times W}{\sqrt{Hz}}$$

Piezoelectric quartz crystal (instead of microphone)

Resonant at *f*, quality factor *Q* is >**10,000** instead of 20-200 for PAS.

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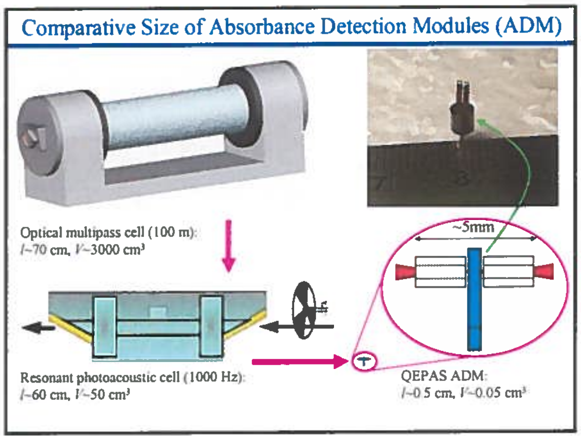
A. Kosterev et al, Optics Letters 27, 1902, 2002

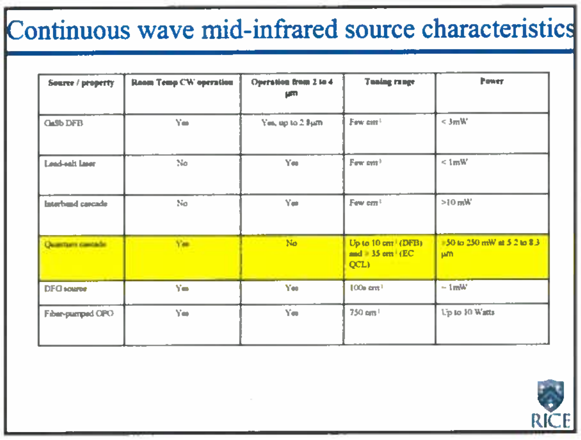


## Comparative Size of Absorbance Detection Modules (ADM)

Optical multipass cell (100 m): *l*~70 cm, *V*~3000 $cm^3$

Resonant photoacoustic cell (1000 Hz): *l*~60 cm, *V*~50 $cm^3$

QEPAS ADM: *l*~0.5 cm, *V*~0.05 $cm^3$



## Continuous wave mid-infrared source characteristics

| Source / property | Room Temp CW operation | Operation from 2 to 4 μm | Tuning range | Power |
|---|---|---|---|---|
| GaSb DFB | Yes | Yes, up to 2.8μm | Few $cm^{-1}$ | < 3mW |
| Lead-salt laser | No | Yes | Few $cm^{-1}$ | < 1mW |
| Interband cascade | No | Yes | Few $cm^{-1}$ | >10 mW |
| Quantum cascade | Yes | No | Up to 10 $cm^{-1}$ (DFB) and > 35 $cm^{-1}$ (EC QCL) | >50 to 250 mW at 5.2 to 8.3 μm |
| DFG source | Yes | Yes | 100s $cm^{-1}$ | ~ 1mW |
| Fiber-pumped OPO | Yes | Yes | 750 $cm^{-1}$ | Up to 10 Watts |

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## Performances vs ridge width

| | 3 microns | 5 microns | 7.5 microns |
|---|---|---|---|
| **$J_{th}$ pulsed @ 300K** | 2.05 kA/cm² | 1.62 kA/cm² | 1.38 kA/cm² |
| **Slope efficiency (cw):** | 252 mW/A | 300 mW/A | 305 mW/A |
| **$T_0$:** | 180K (pulsed)<br>163K (cw) | 159.9K (pulsed)<br>158.4K (cw) | 170.5K (pulsed)<br>140.7K (cw) |
| **Thermal resistance:** | 10.53 K/W | 8.91 K/W | 11.79 K/W |
| **Thermal conductance:** | 1055 K/Wcm² | 748 K/Wcm² | 377 K/Wcm² |

## Prototype control electronics unit (CEU) for a diode laser based QEPAS gas sensor.

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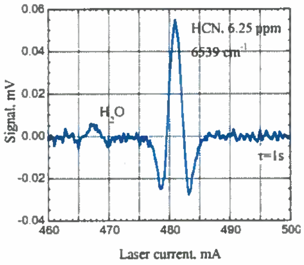
## Required chemical sensor features

- Chemical selectivity
- Sensitivity at ppb level (ppm-ppt)
- No calibration (or as little as possible)
- Immunity to environmental changes and interferences (temperature and pressure variations, vibrations, electrical noise)
- Compact size, low weight and power consumption, no consumables

## QEPAS Based HCN overtone spectrum



- Zero background
- Noise determined by the thermal TF motion
- High sensitivity – sub-ppm in overtone region
- Much higher sensitivity in terms of concentration is feasible exploiting MIR – fundamental absorption bands

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