LPAS Based Gas Sensor Development at Rice: January 2005 – May 2006

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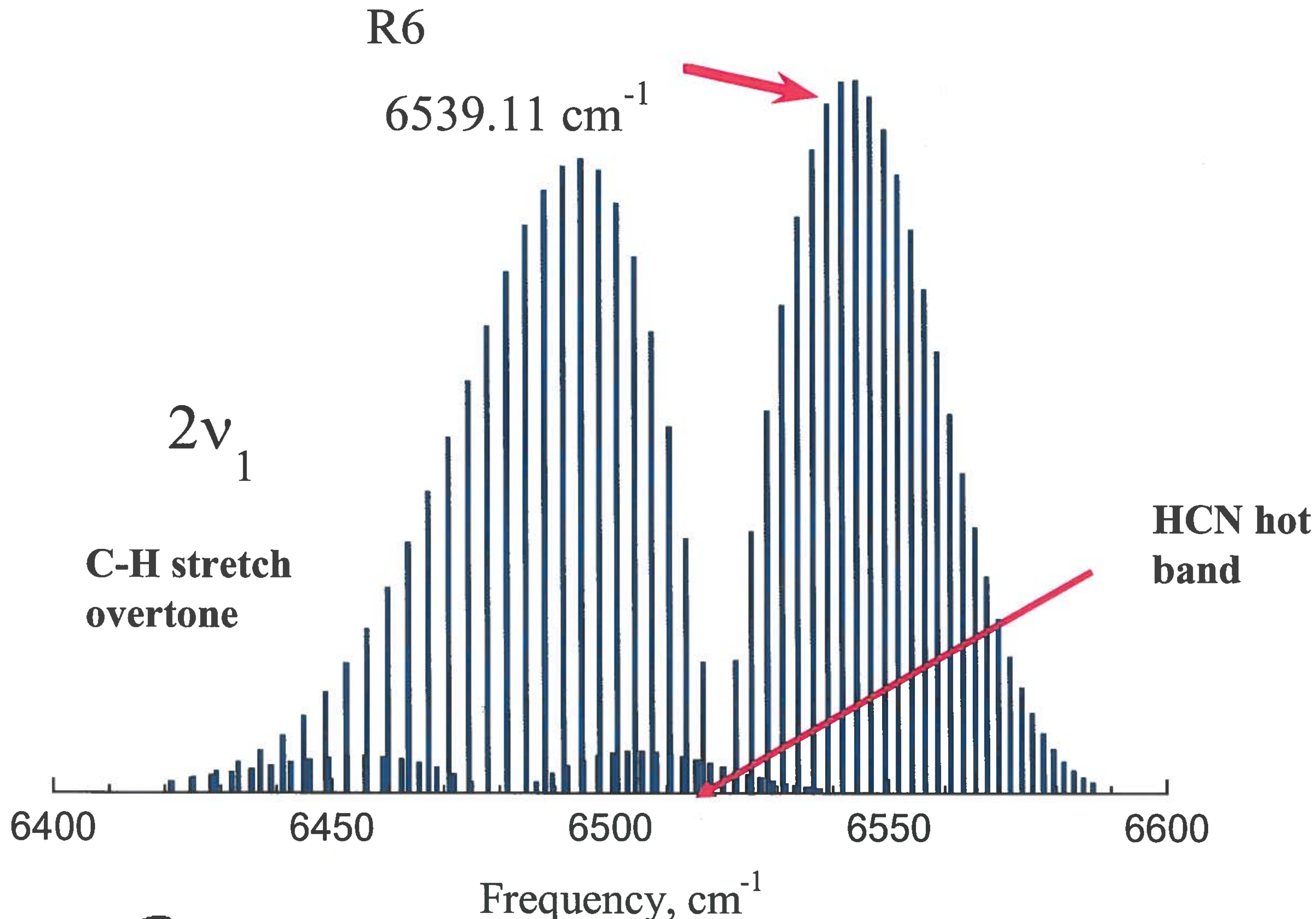
OUTLINE

PNNL LPAS Team Meeting

Laguna Beach June 12, 2006

- Phase I Motivation: Optimization of LPAS based near-IR gas sensor technology
  - Target Gas: HCN (blood agent)
- Phase II Motivation: Optimization of LPAS based mid-IR gas sensor technology for broadband absorbers
  - Implementation of MOVPE based 8.6 µm QC Laser technology
  - Target Gas: Freon 125 (simulant of a CWA)
- Summary and Future Phase II Research Directions

Simulated NIR absorption band of HCN centered at 1.53 μm



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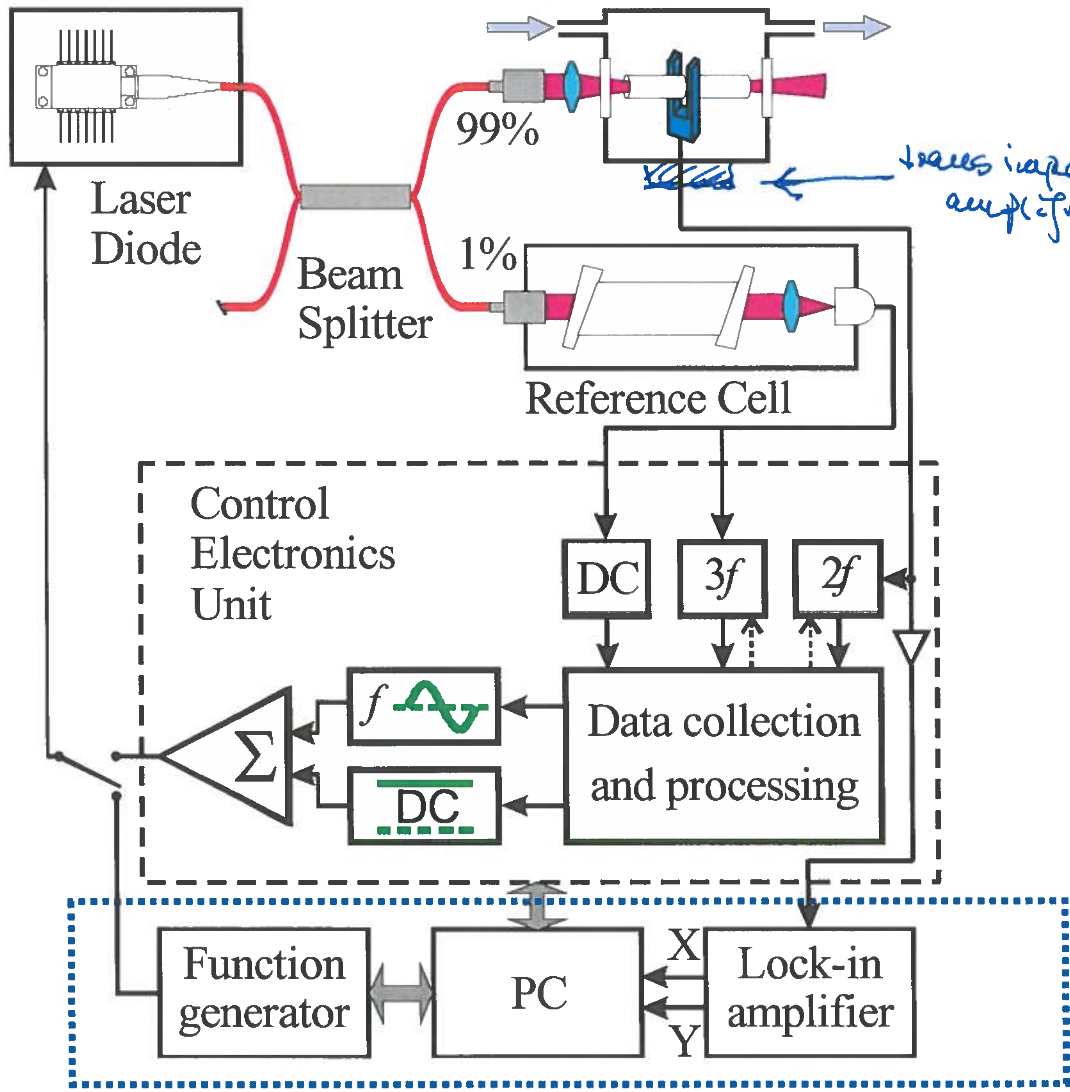
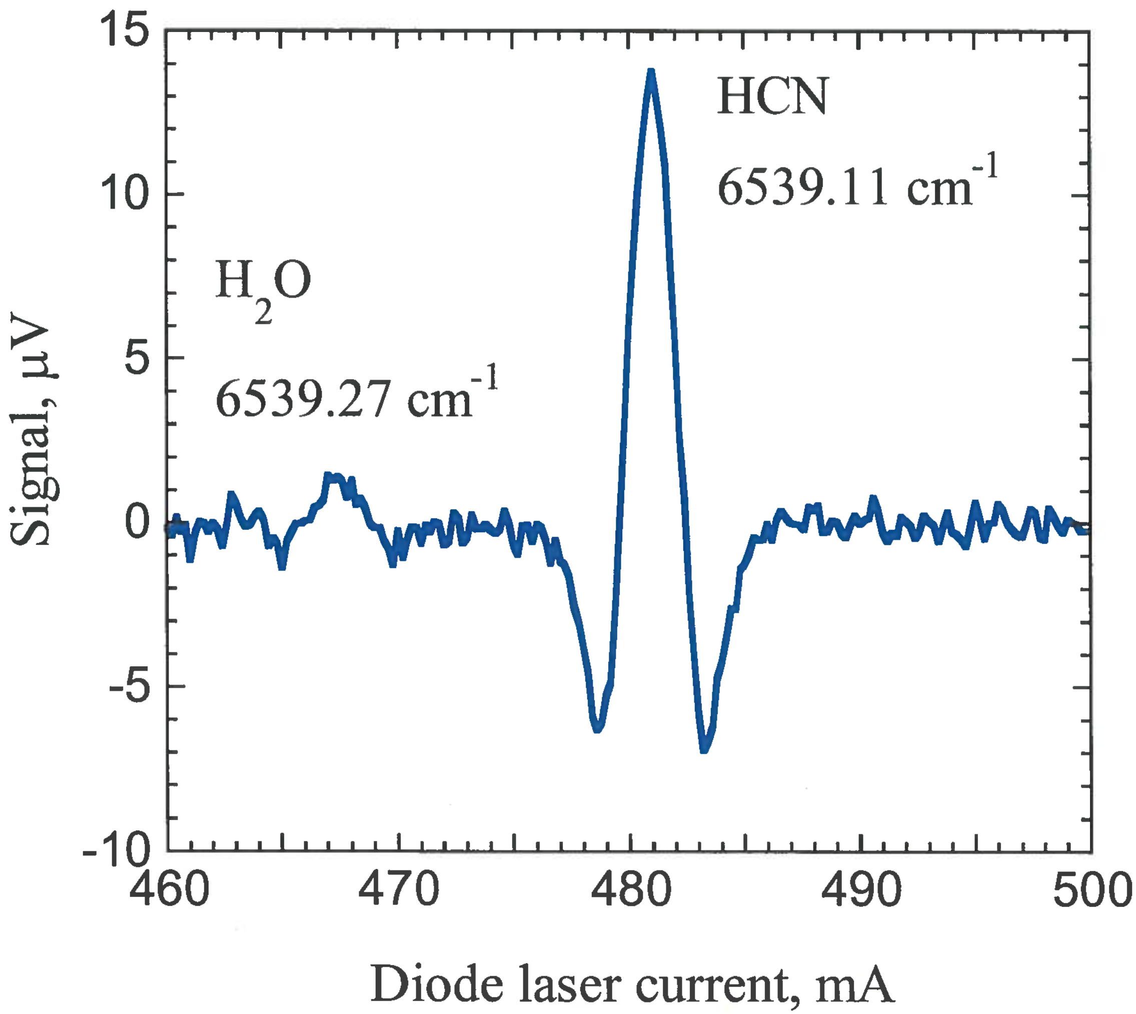
LPAS based gas sensor architecture



Optional, used only for initial sensor set-up

1.53 μm LPAS signal of a 6.25 ppmv HCN: air mixture



Estimated HCN toxicity concentration for 30 minutes exposure is 100 mg/m^3 or **~85 ppmv**

Laser power in the cell: 50 mW
Time constant: 1s, SNR=40

Room air, 50% RH (see plot):

Optimum pressure 60 Torr

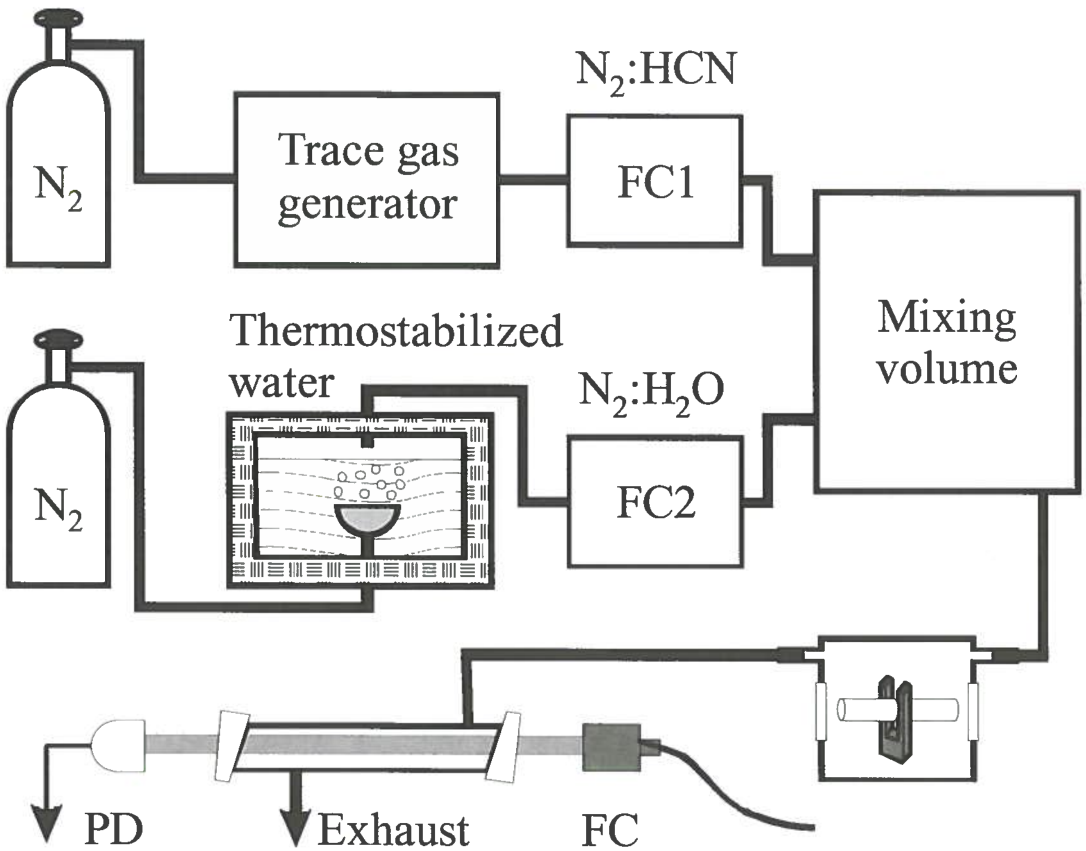
NNEA=4.3×10^{-9} cm^{-1}W/(Hz)$^{1/2}$; NEC=155 ppbv

Dry nitrogen or air:

Optimum pressure 300 Torr

NNEA=9.2×10^{-9} cm^{-1}W/(Hz)$^{1/2}$; NEC=330 ppbv

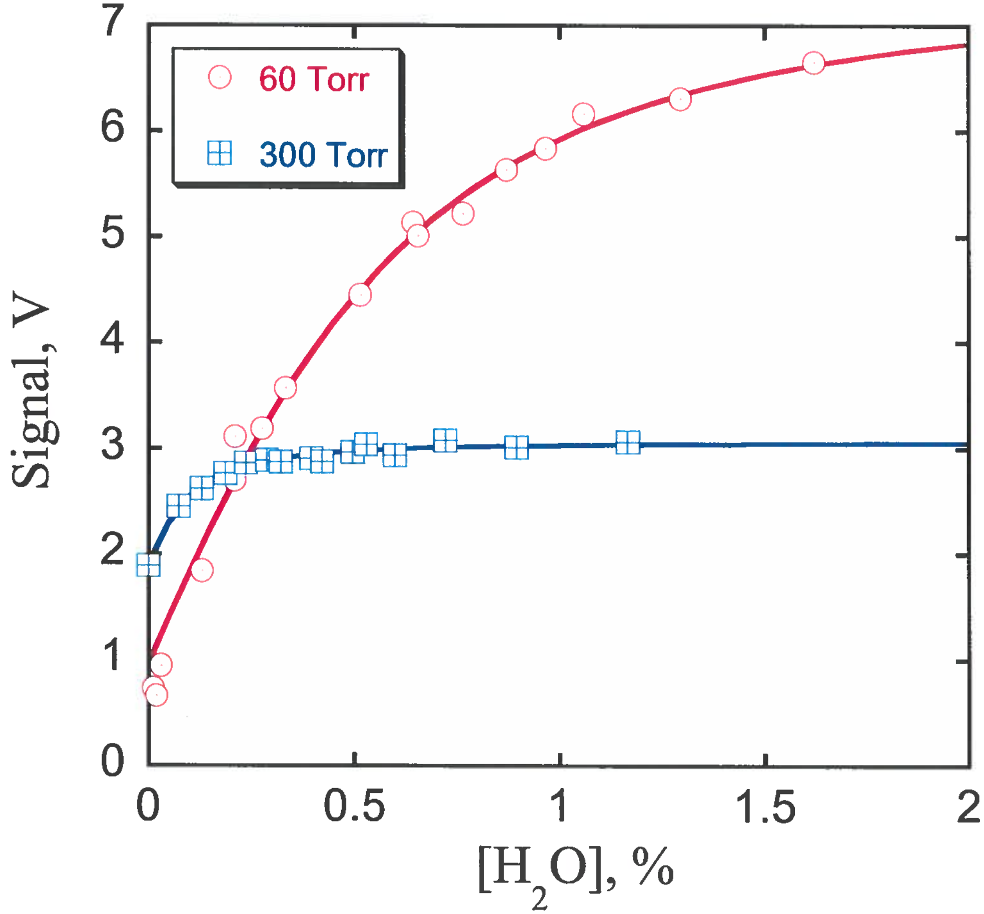
Generation of controlled H_2O concentrations in HCN gas flow



Humidifier was developed for HCN sensor characterization in Phase I and will be used in current Phase II project to study water interference and relaxation effects when targeting broadband absorbers, such as Freon 125.

FC1,2 – mass flow controllers, FC – fiber collimator to couple the diode laser radiation at 1.37 mm into the optical gas cell, PD – photodiode

LPAS HCN signal dependence on gas humidity



Addition of H_2O promotes V-T relaxation, resulting in a higher HCN detection sensitivity in humid air.

If the sensor is operated at 300 Torr, RH variations from 6% to 100% only change signal by 10%.

LPAS based performance for 8 trace gas species (June'06)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10^{-9}	9.5	0.09
HCN (air: 50% hum) *	6539.11	60	$< 4.3\times10^{-9}$	50	0.16
C_2H_2 (N_2)**	6529.17	75	$\sim2.5\times10^{-9}$	~40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	0.50
CO_2 (exhaled air)	6514.25	90	1.0×10^{-8}	5.2	890
CO_2 (N_2 + 1.5% H_2O) *	4991.26	50	1.4×10^{-8}	4.5	18
CH_2O (N_2) & *N_2:H_2O *	2832.48	100	1.1×10^{-8}	4.6	0.28
CO (N_2)	2196.66	50	5.3×10^{-7}	13	0.5
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007

* - Improved microresonator

** - Improved microresonator and double optical pass through QTF

NNEA – normalized noise equivalent absorption coefficient.

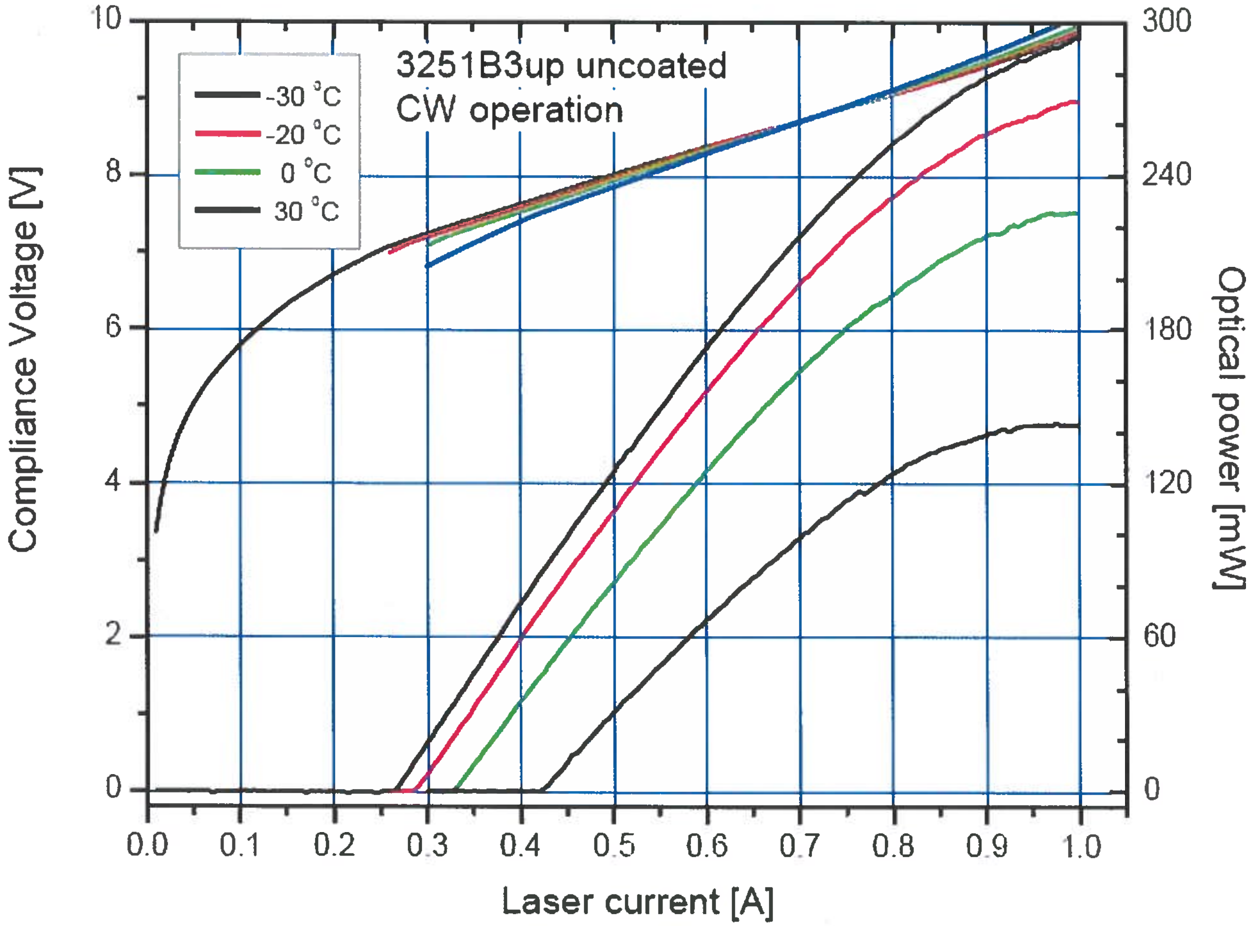
NEC – noise equivalent concentration for available laser power and τ=1s time constant.

QEPAS sensitivity matches the sensitivity of conventional PAS

Year 2 Tasks – PNNL Contract # 14813

- Preparation and characterization of broadband high power (~ 100 mW at 360 K), TE coolable Agilent Technologies-Harvard 8.6 μm FP QCL for water background characterization:
  - Acquisition of MOVPE 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 8.6 μm FP QCL: Freon 125
  - Design and construction of Freon gas handling system
  - Implementation of amplitude modulation mode of operation for 8.6 μm FP QCL
  - Optimum quartz resonator illumination geometry for AM-1f MIR QTF LPAS mode
  - Perform detailed investigations of the influence of gas pressure, temperature and humidity on QCL based QTF LPAS sensor performance
  - H_2O background and H_2O influence on LPAS Signal-to-Noise Ratio
- Acquisition of a broadband 10 μm FP QCL for optimum DIMP quantification (centered at 1100 cm^{-1})
  - Acquisition of MBE grown cw TEC FP heterogeneous QC laser bar with 2 active regions centered at 8.4 and 9.6 μm
  - Characterization of 10 μm FP QCL at different temperatures
  - Repeat H_2O background characterization measurements for DIMP

Performance characteristics of a high power cw 8.6 μm QCL grown by MOVPE



Measured by G. Wysocki (Rice) & R. Maulini at UNINE, Neuchatel, Switzerland; March 2006
based on a QCL design by L. Diehl et al APL 88, 201115 (2006)

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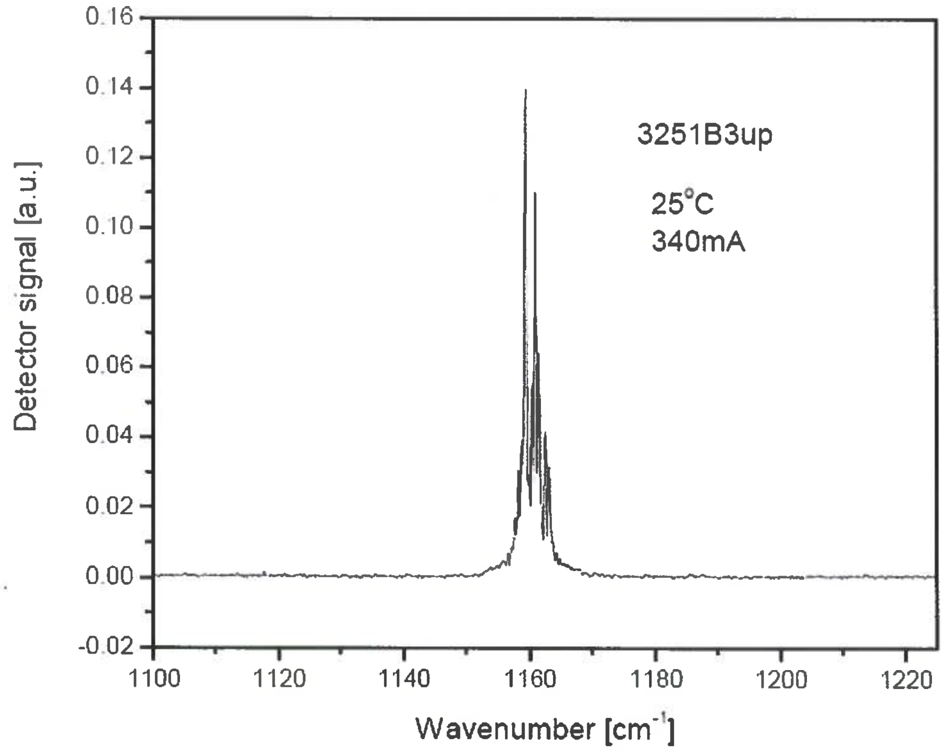
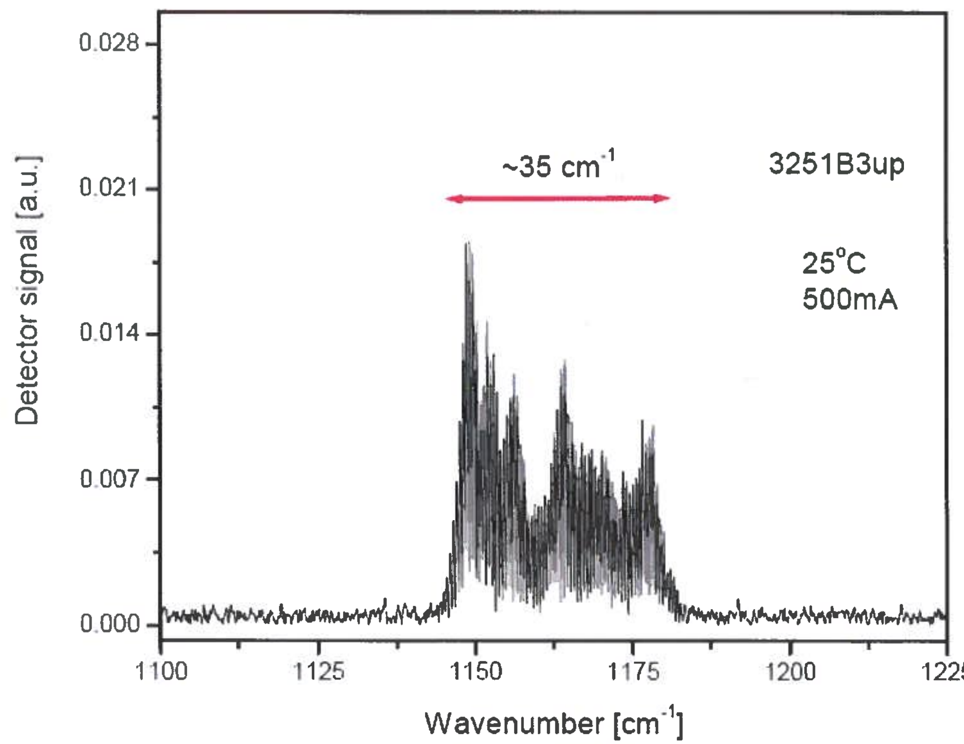
Measured FTIR spectra of cw 8.6 μm QCL at 340 & 500mA





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

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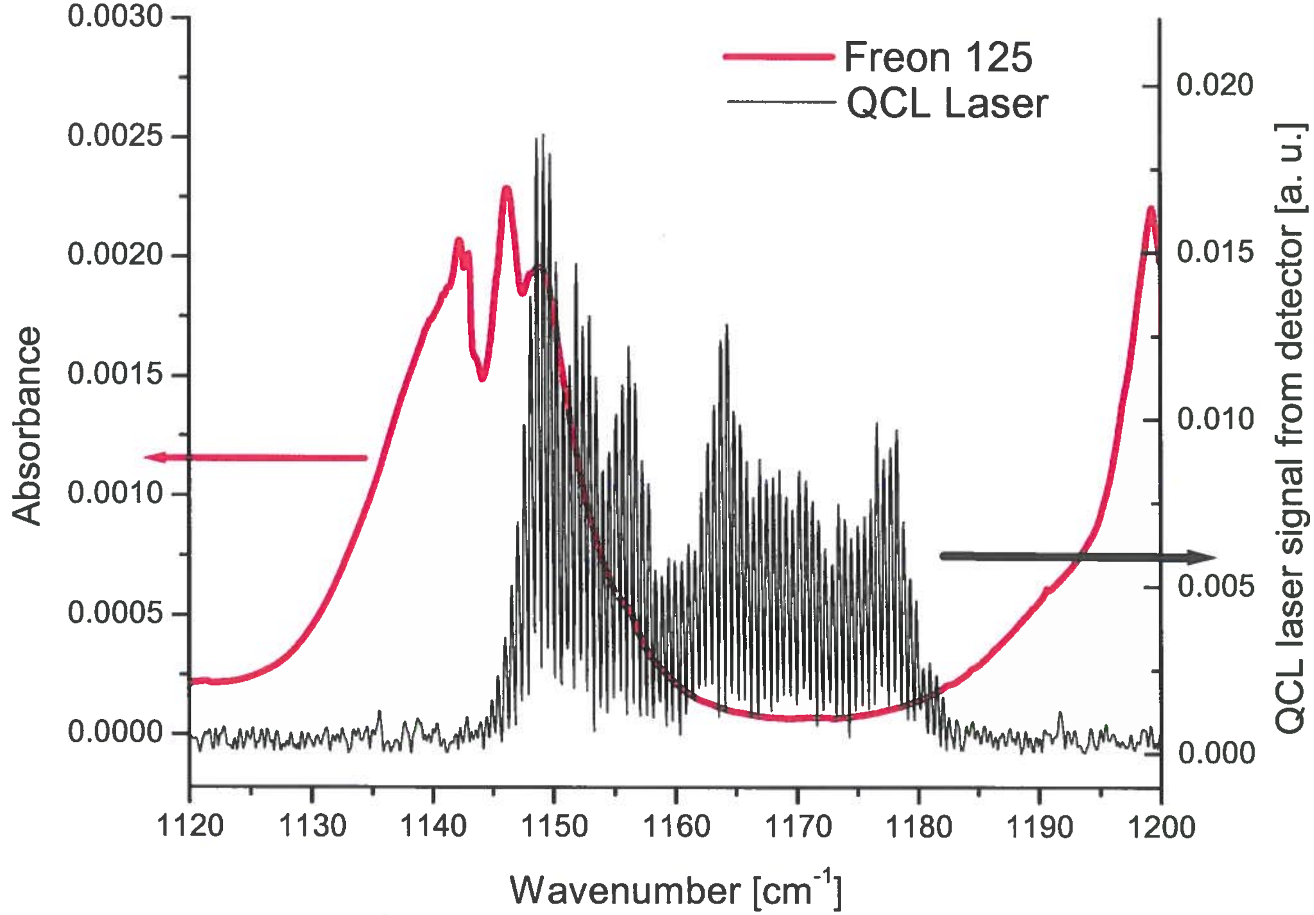
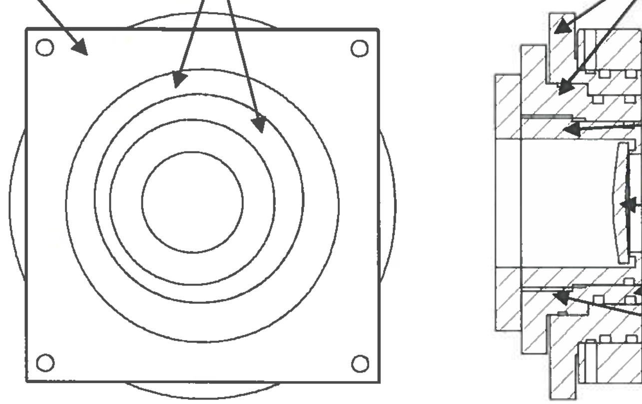
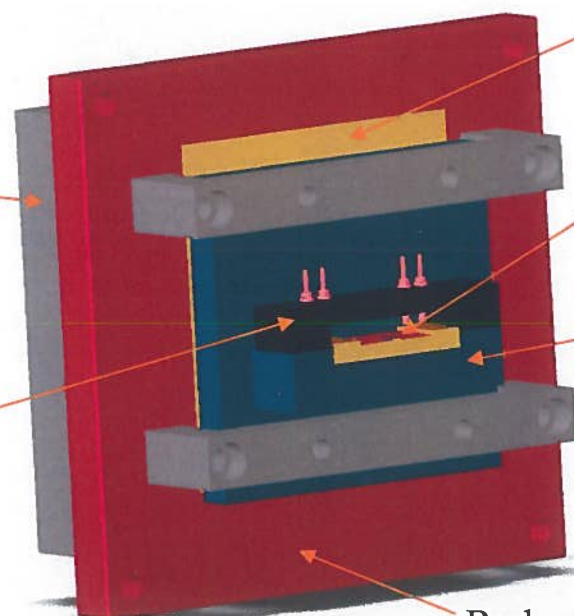
Spectral comparison of Freon 125 with emission coverage from a 8.6 μm FP QCL based on PNNL database



Design of QCL housing and lens positioning assembly





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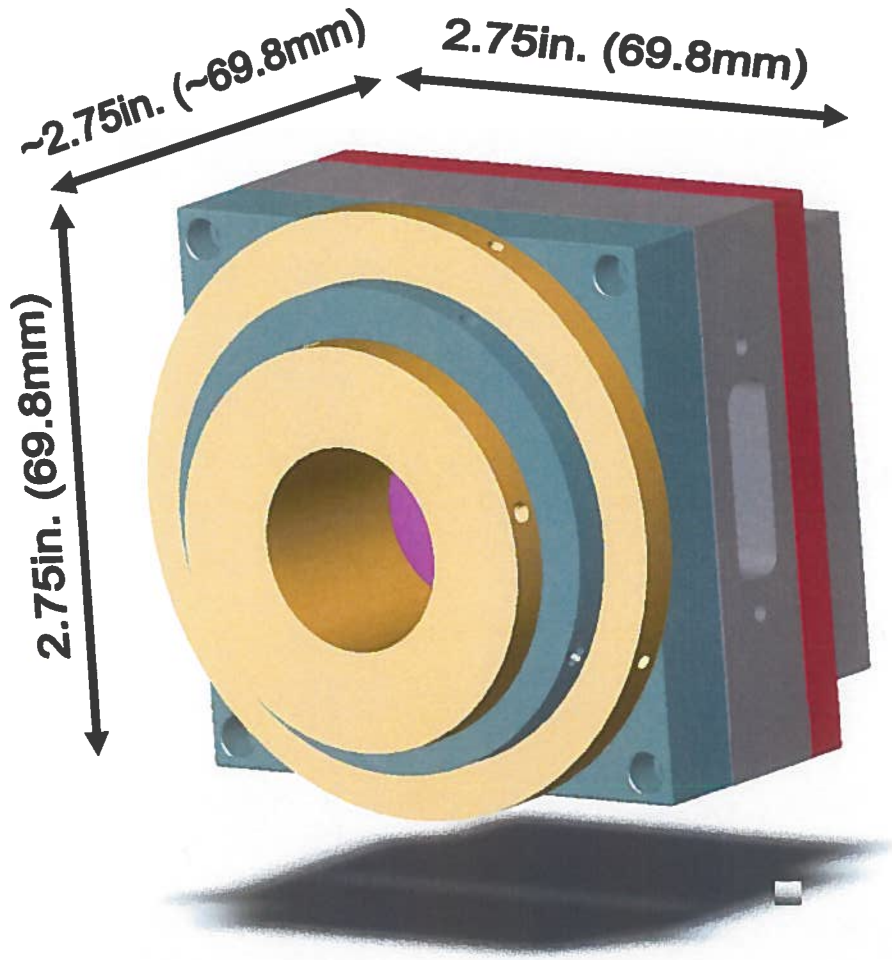
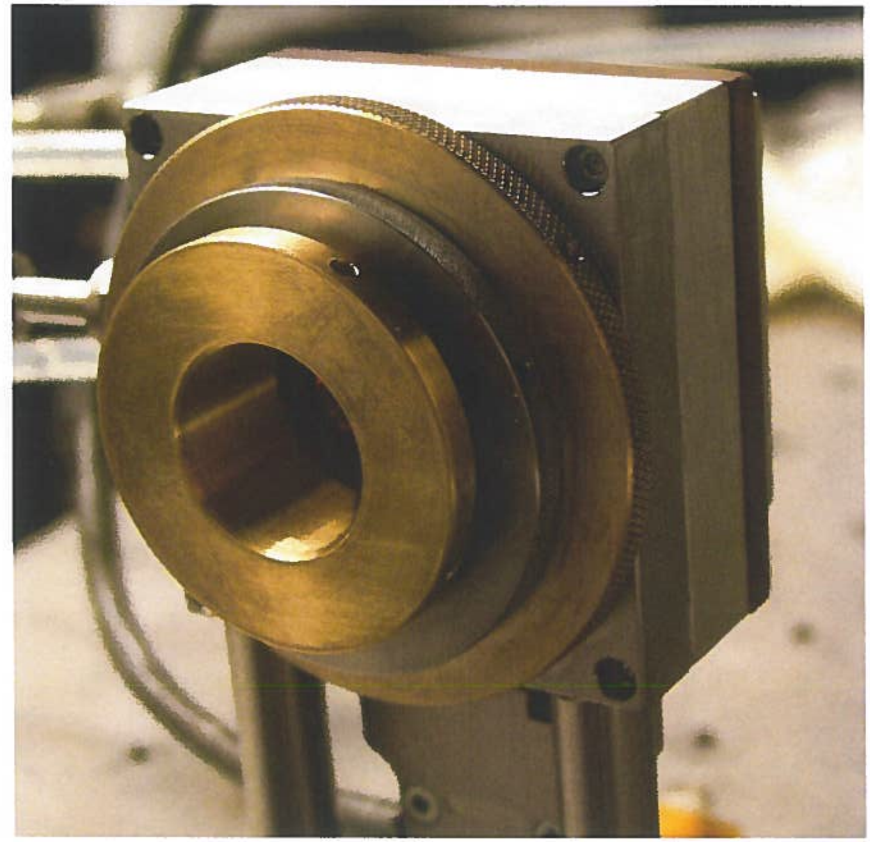
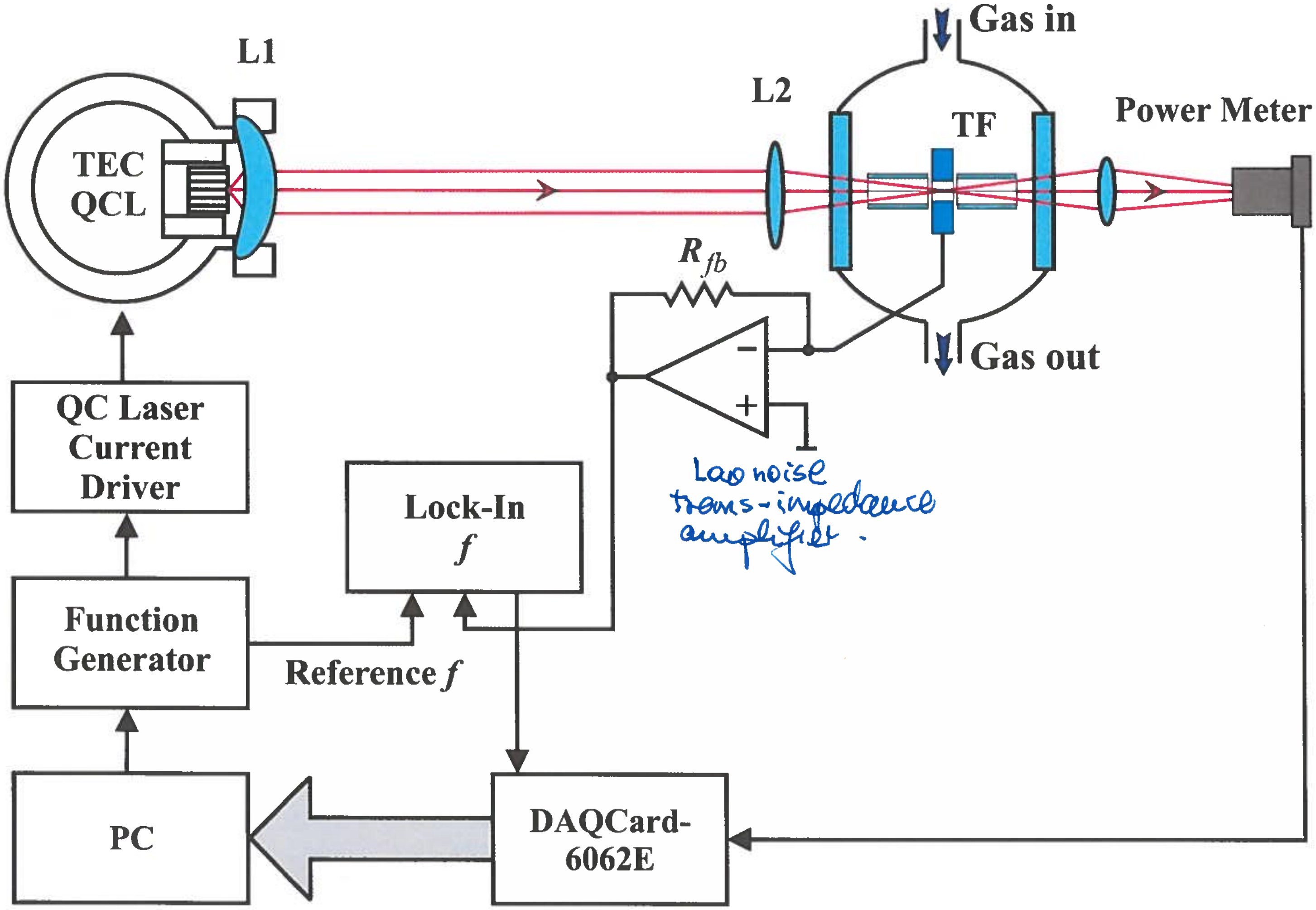
QCL housing and positioning assembly

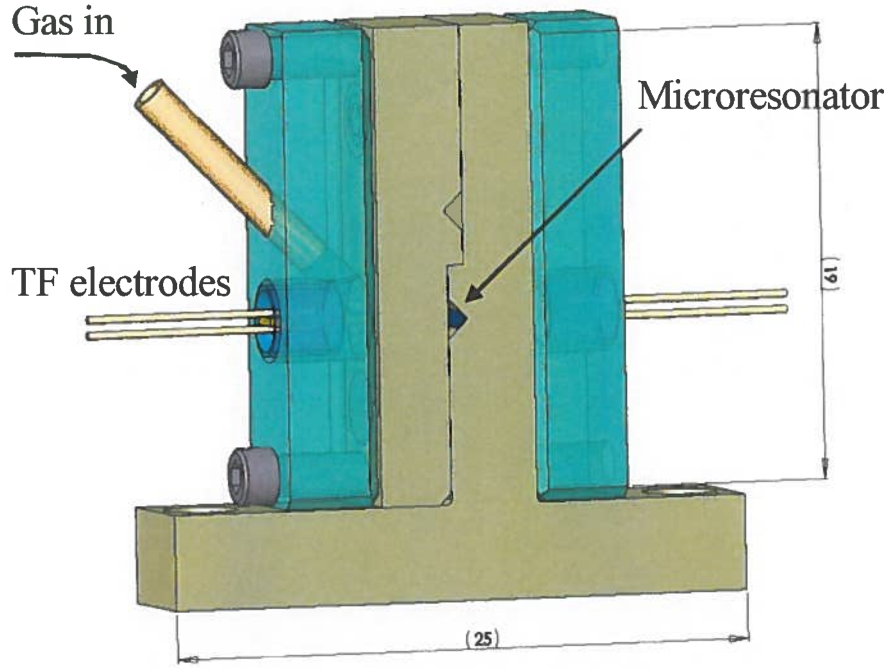


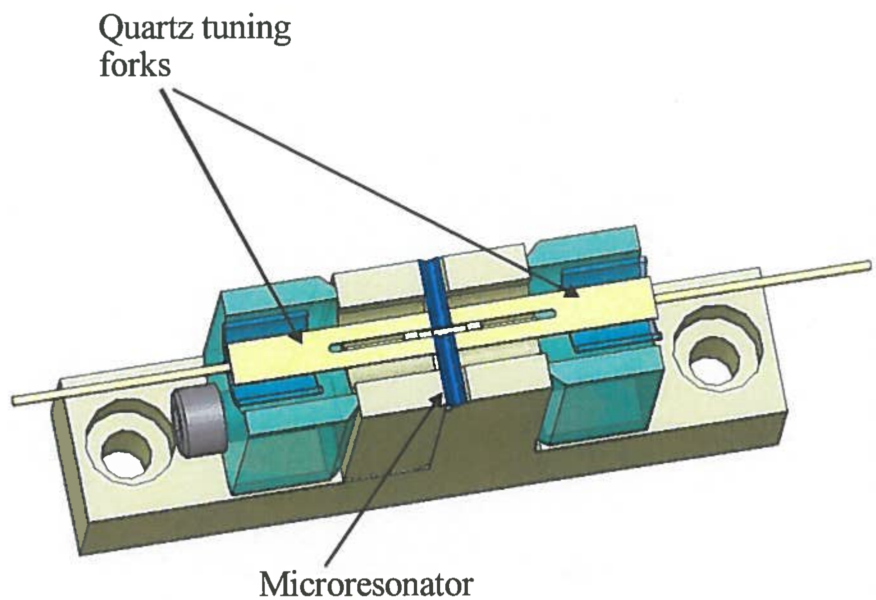


Amplitude Modulated 8.6 μm QCL based LPAS Sensor Platform



Design of a new QTF based absorption detection module





- •Compact & integrated design
- •Laser-induced background deduction
- •Machining precision of : +/- 10μm

- •Two QTFs connected in parallel results in enhanced √2 SNR
- •Minimum exposure of QTFs to QCL radiation
- •Efficient for gas flow to microresonator

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Current Status and Year 2 Research Directions

- **QTF LPAS based Gas Sensors**
  - Significant reduction in sensor size and weight is possible with LPAS
  - LPAS is immune to ambient acoustic noise. The measured noise level coincides with the thermal noise of the QTF. The sensitivity is limited by thermal excitation of the symmetric mode.
  - Demonstrated minimum normalized detectable absorption coefficient is 4.3×10^{-9} cm^{-1} W/√Hz (one pass configuration)

- **Year 2 (2006) Research Directions**
  - Implementation of Freon 125 (C_2HF_5) concentration measurements at 8.6 µm
  - Freon 125 sensor performance evaluation as a function of pressure and humidity
  - Characterization of a pulsed broadband heterogeneous 10 µm FP QCL gain chip for DIMP detection
  - Optimization of new LPAS based absorption detection module (spectraphone) designs

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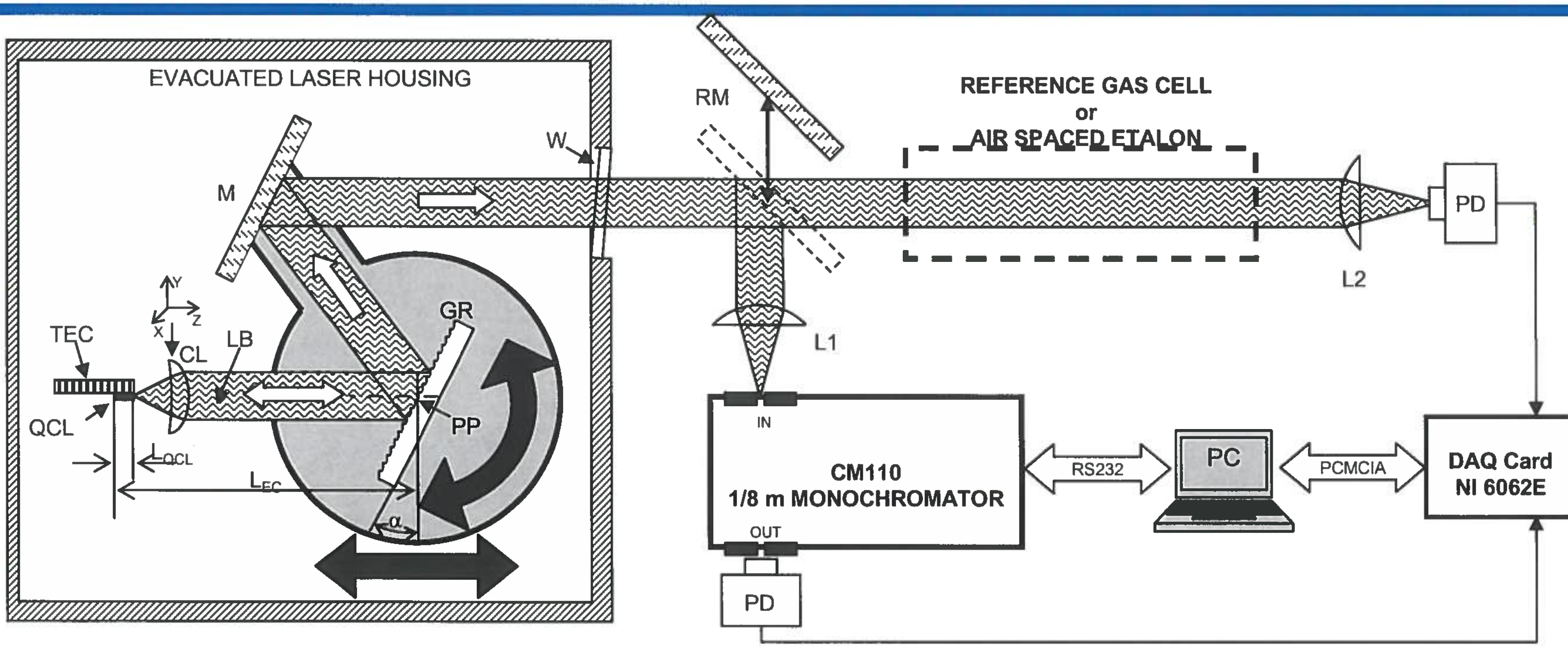
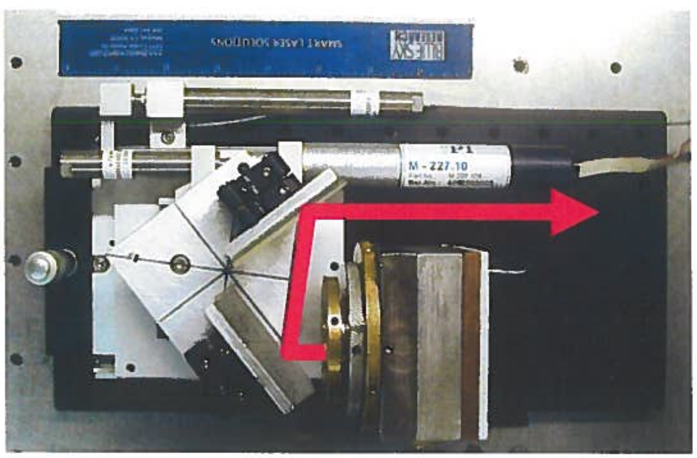
Tunable external cavity QCL based spectrometer



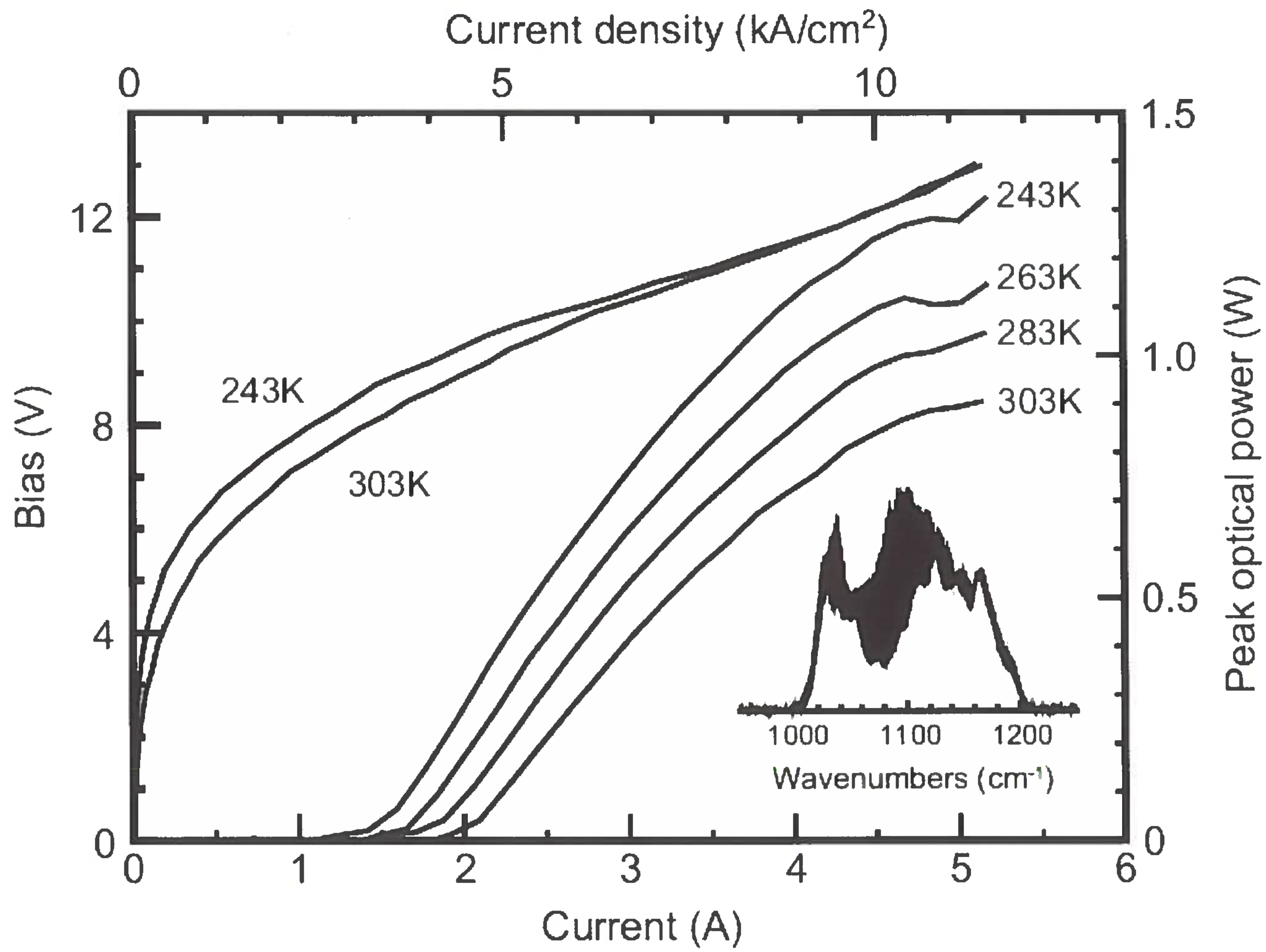
EC QCL, June 2006



- 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)

Peak optical power and bias of a 8.2-10.4 μm heterogeneous QCL gain element



R. Maulini, et al, APL 88, 201113 (2006)

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