



Gordon'01

July 2001

OUTLINE

# Gas sensing applications of quantum cascade lasers

A. A. Kosterev and F. K. Tittel

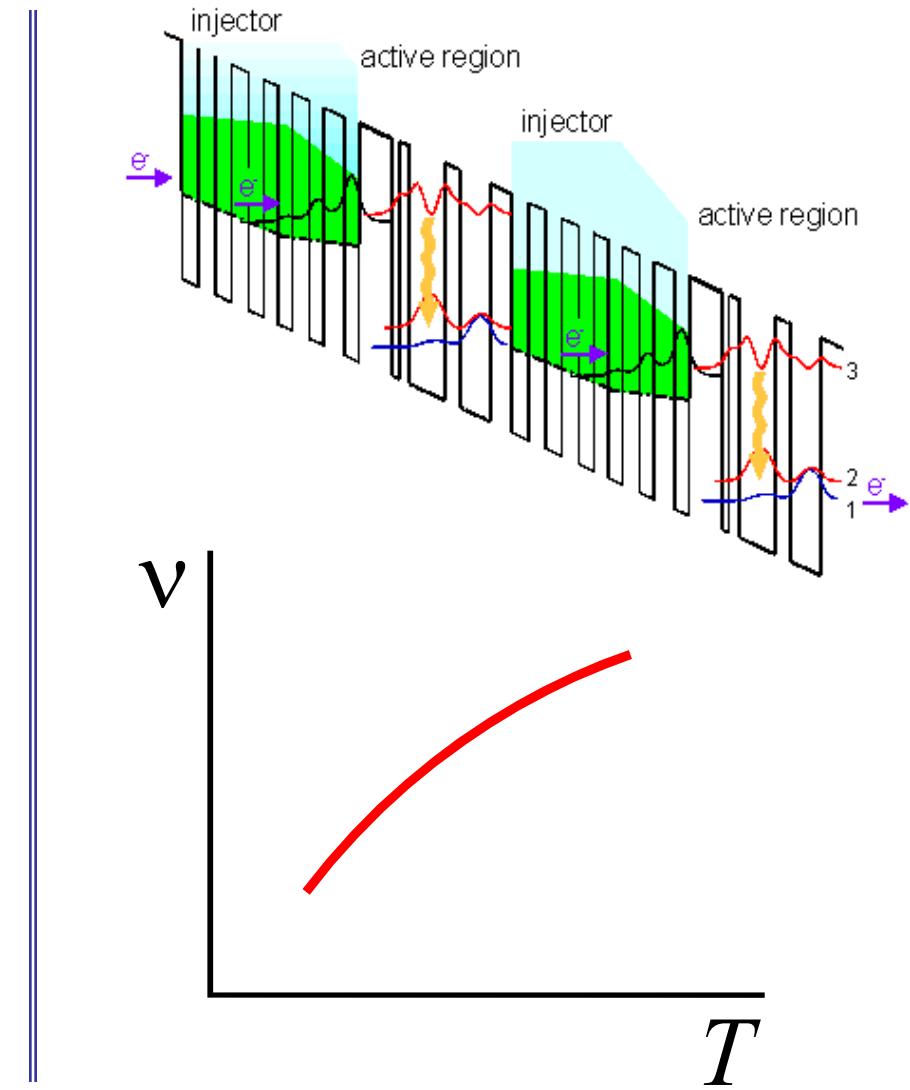
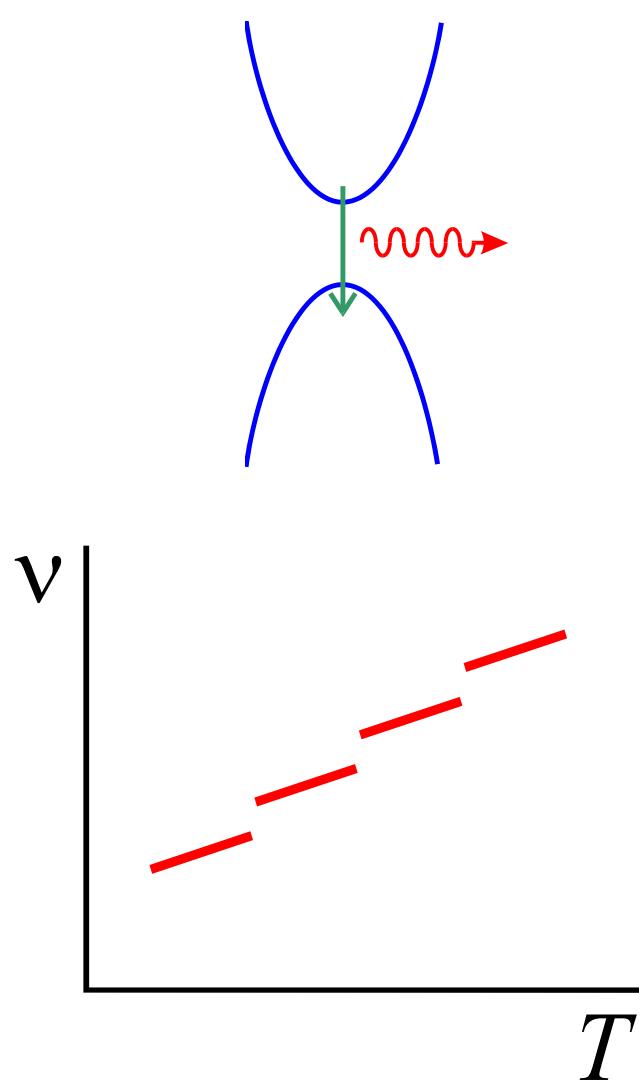
*Rice Quantum Institute, Rice University, Houston, TX 77251-1892*

C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, A.L.  
Hutchinson, and A.Y. Cho

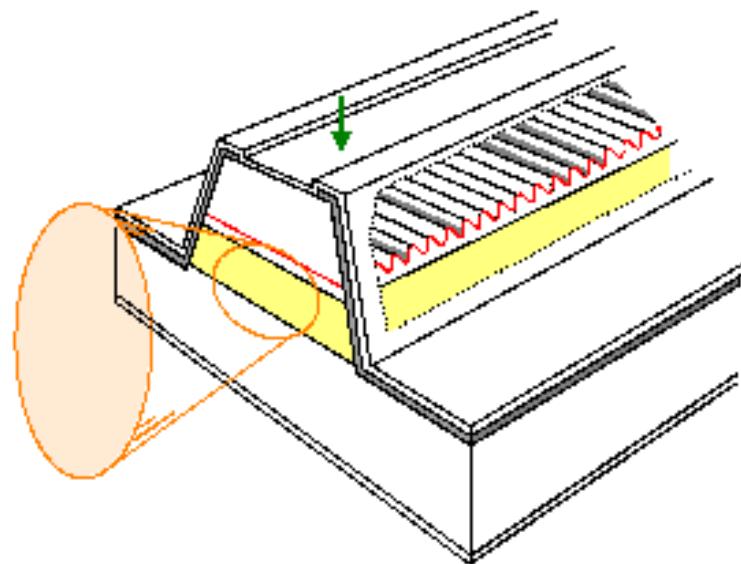
*Bell Laboratories, Lucent Technologies, 600 Mountain Avenue,  
Murray Hill, NJ 07974*

- ❖ Specific features of the QC lasers
- ❖ Spectroscopic detection of trace gases with CW QCs:
  - ❑ multipass cell
  - ❑ cavity ringdown
- ❖ Using pulsed QC lasers for trace gas detection

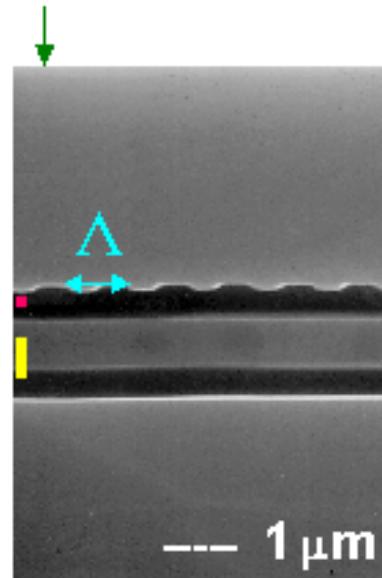
# QC-DFB Compared to Diode Lasers



# Distributed Feedback QC Laser-Schematic



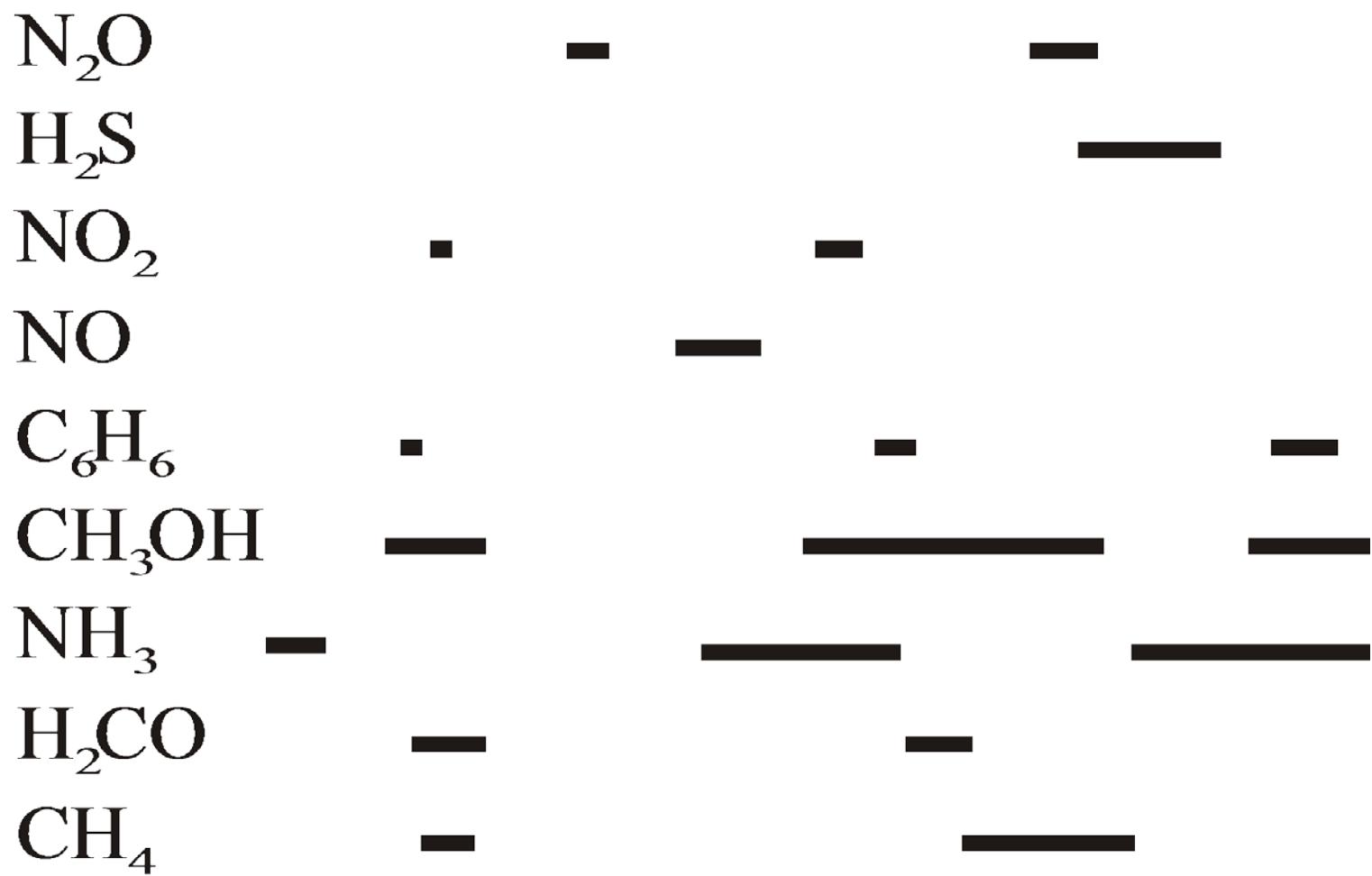
schematic



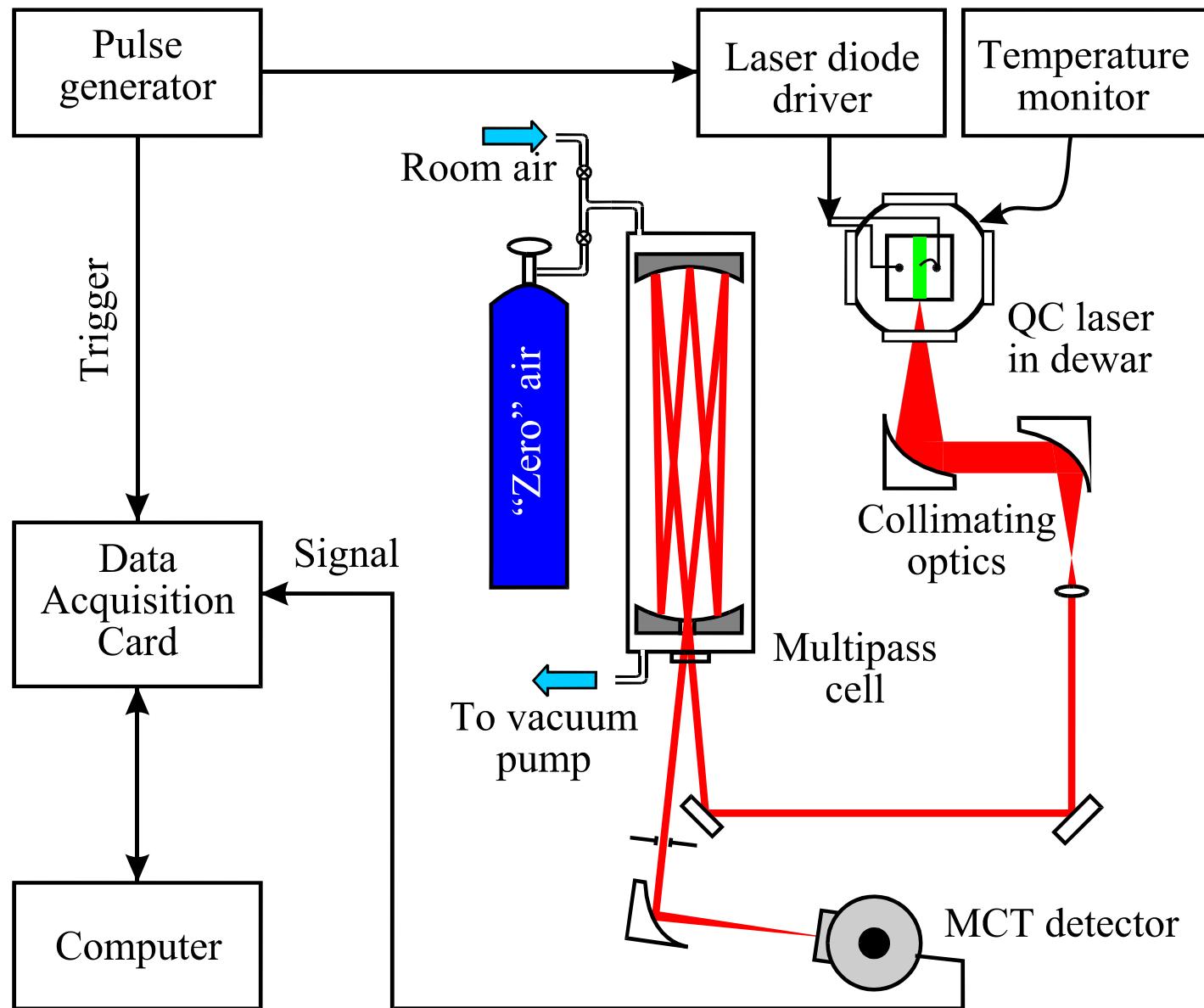
*cross-section micrograph*

- ❖ Grating selects well defined single wavelength
- ❖ Tunable with temperature

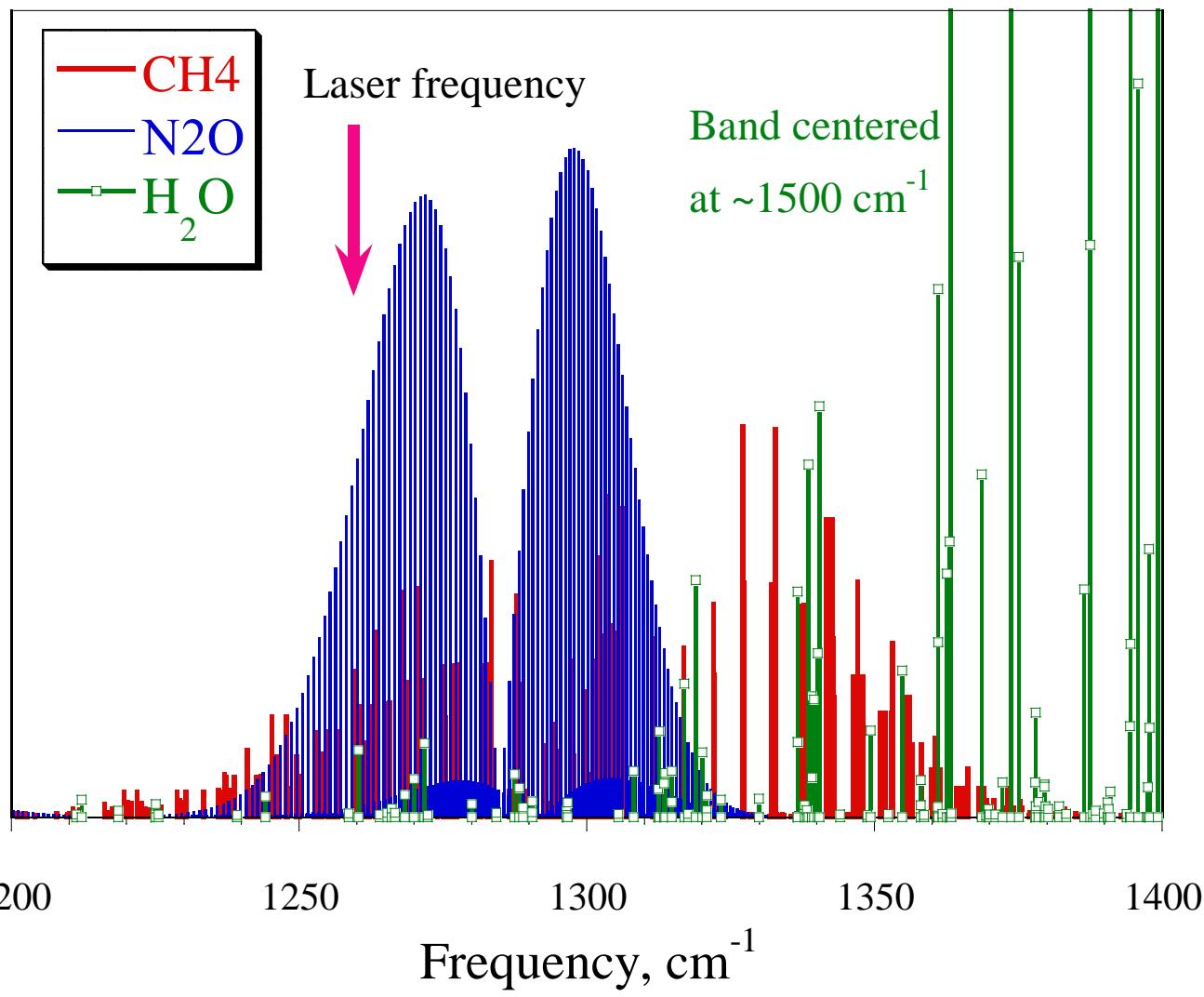
# Spectral Coverage by Diode/QC Lasers



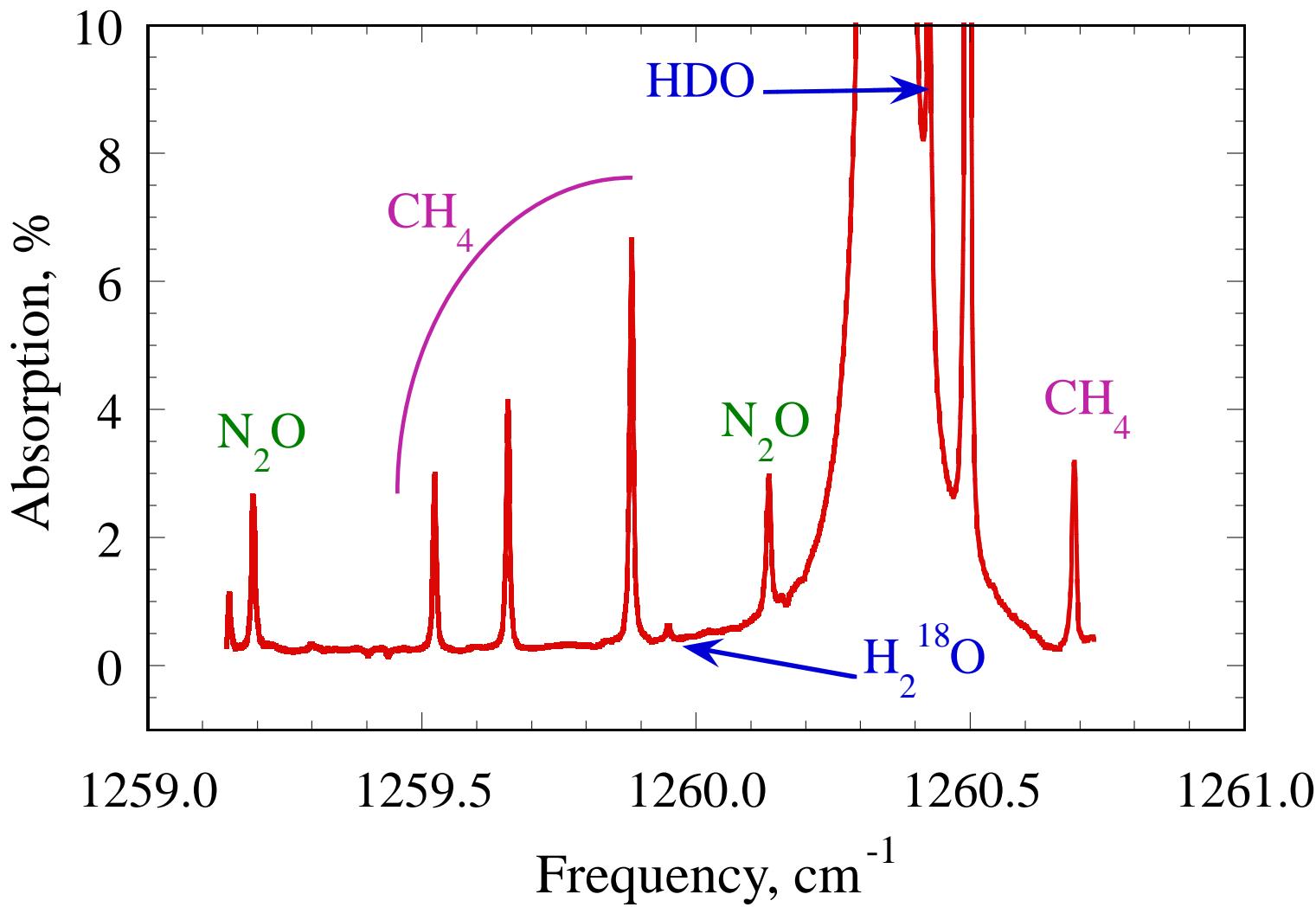
# Trace Gas Detection with a Multipass Cell



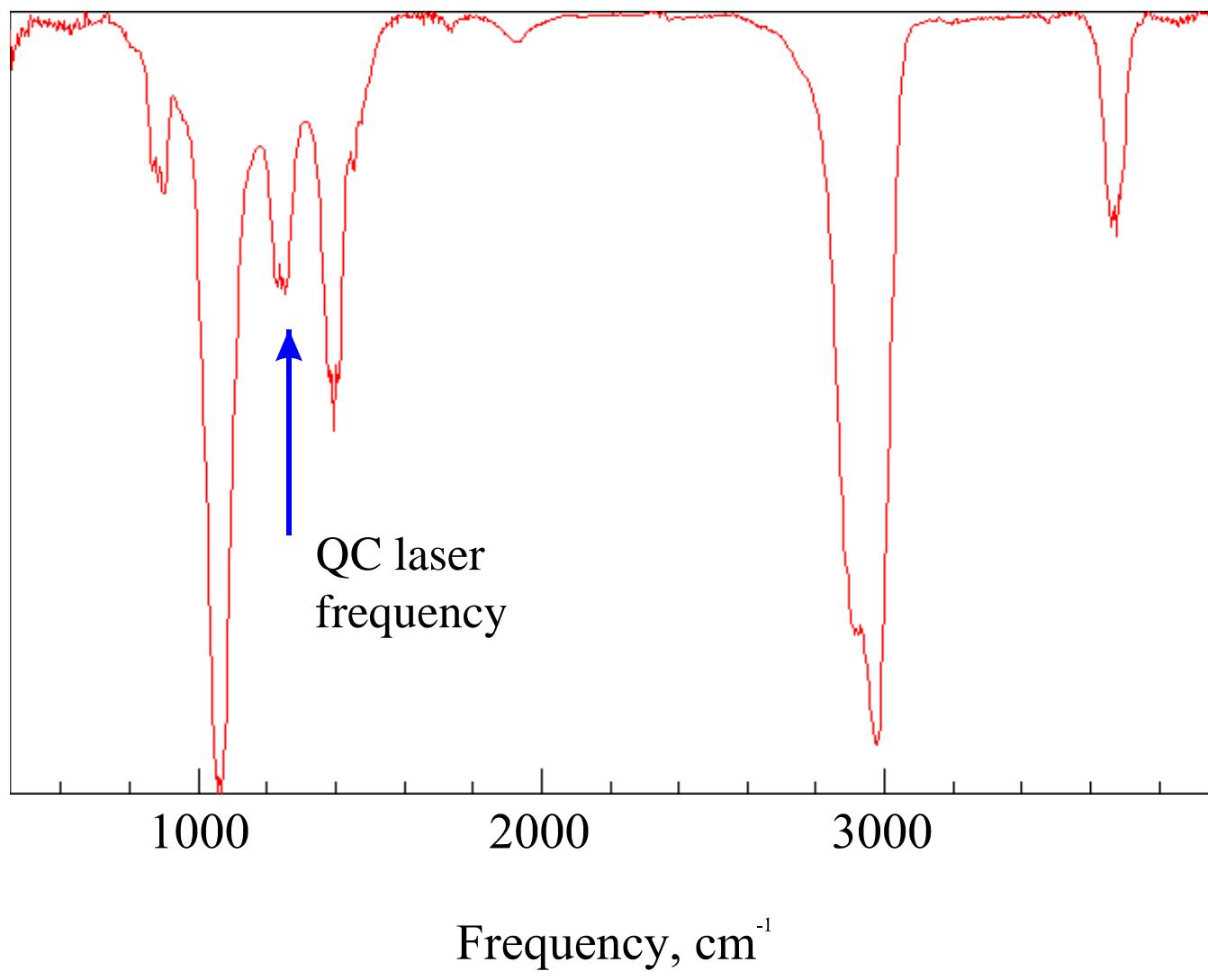
# $\text{CH}_4$ , $\text{H}_2\text{O}$ and $\text{N}_2\text{O}$ Absorption Spectra



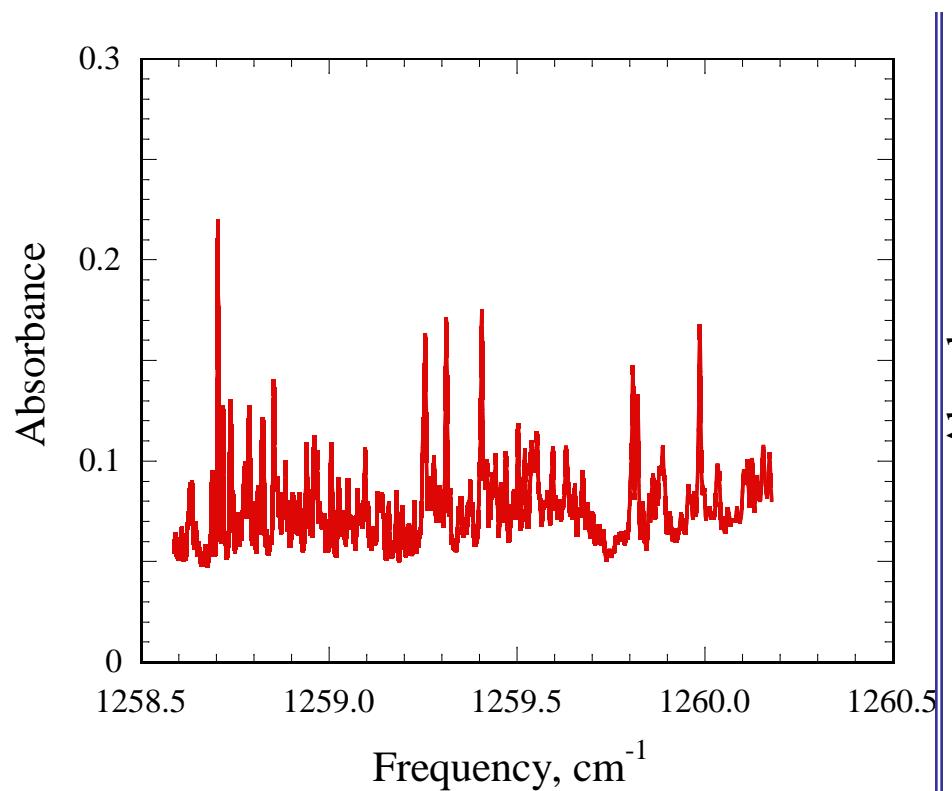
# Absorption Spectrum of Room Air



# IR Absorption Spectrum of Ethanol

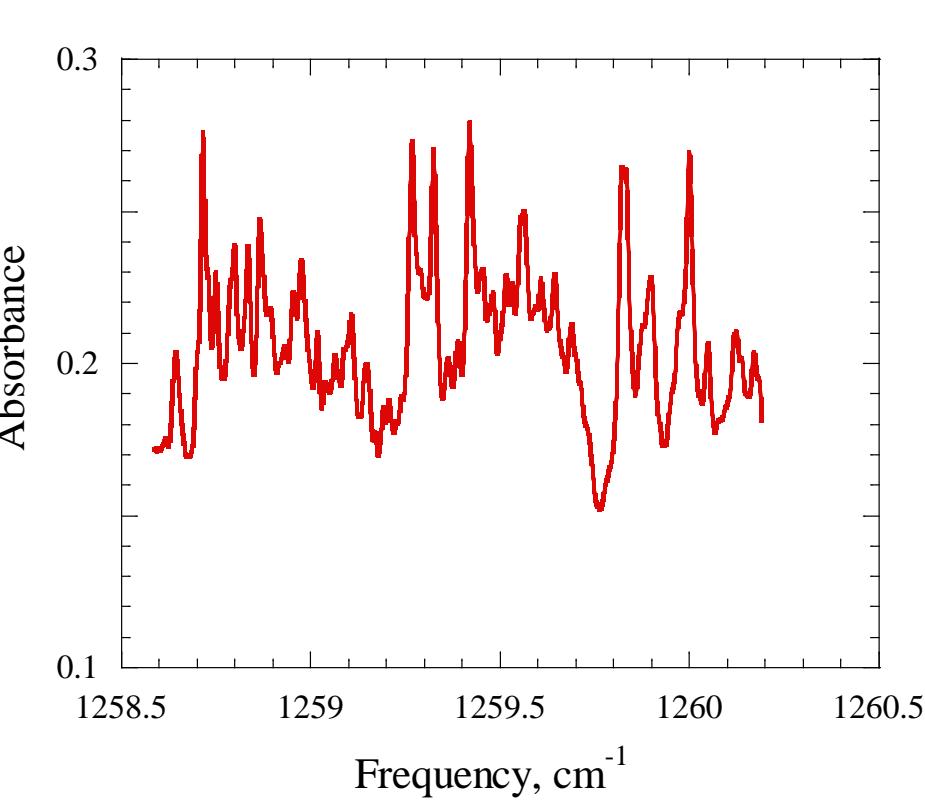


# High-resolution IR Ethanol Spectrum



Pure ethanol vapor

$P=1$  Torr

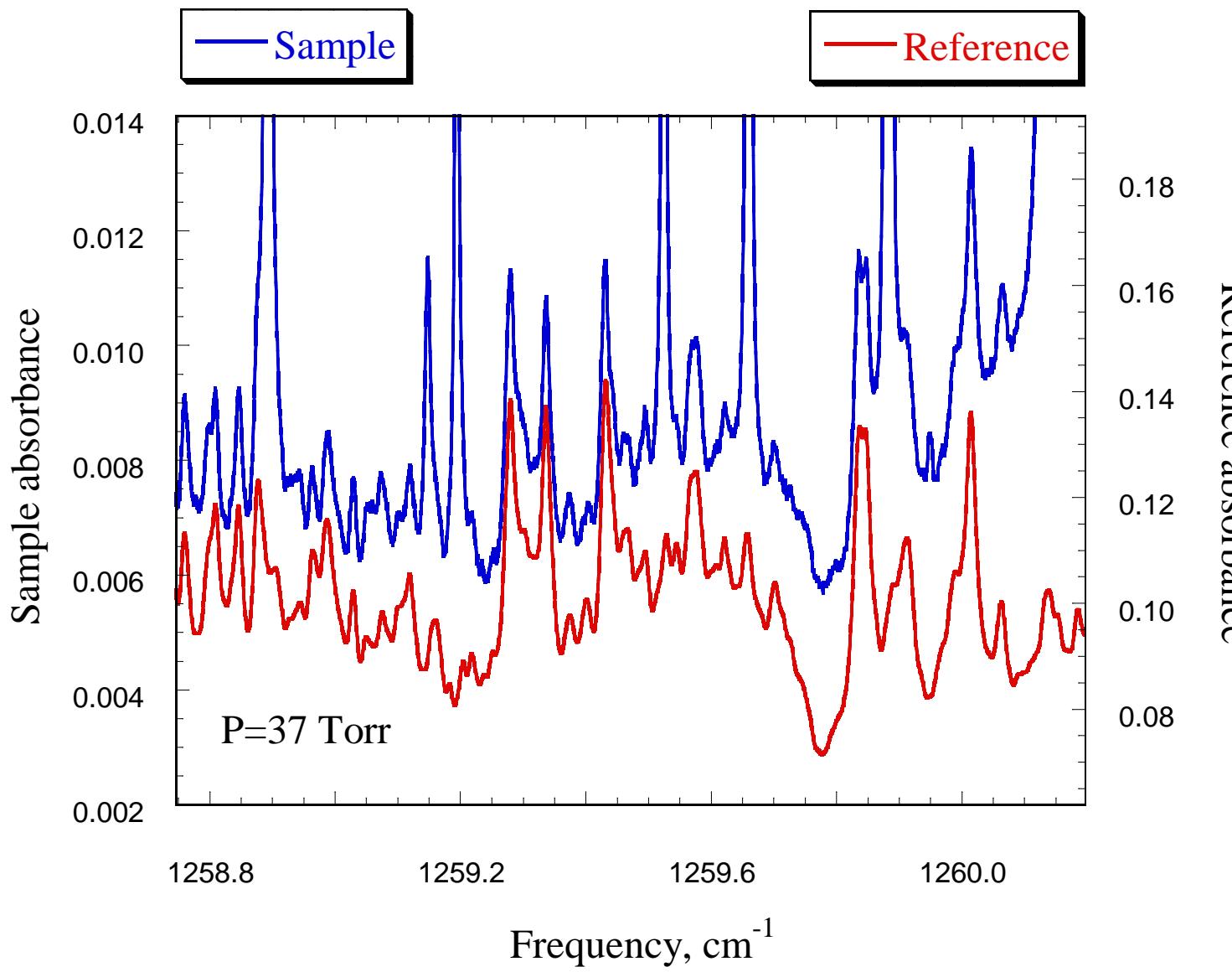


Ethanol vapor +air

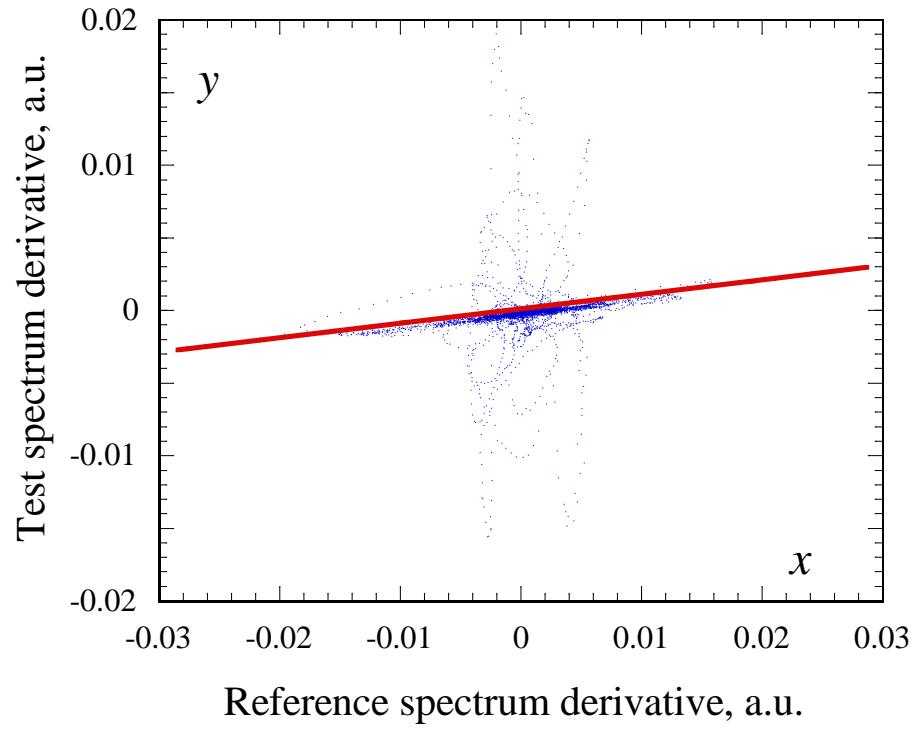
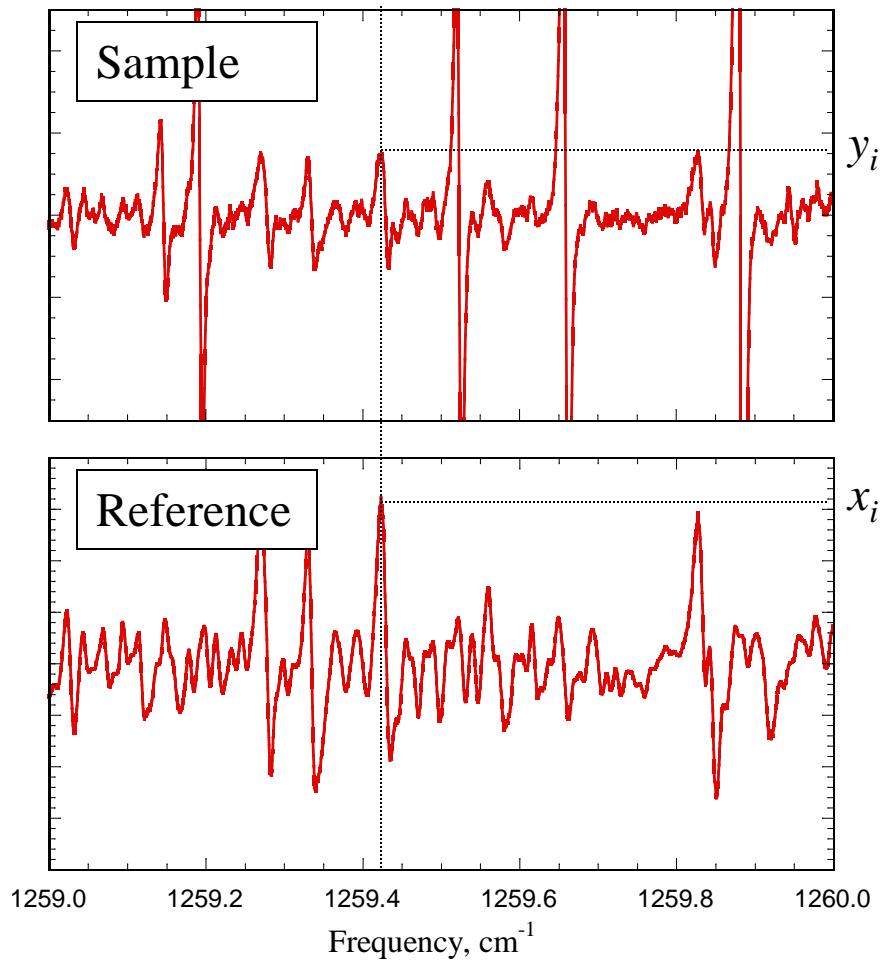
$P_{\text{eth}}=1$  Torr,  $P=36.6$  Torr



# Reference and Sample Spectra of Ethanol in Air



# Linear Regression Technique



$$1 - D : \quad y_i = ax_i$$

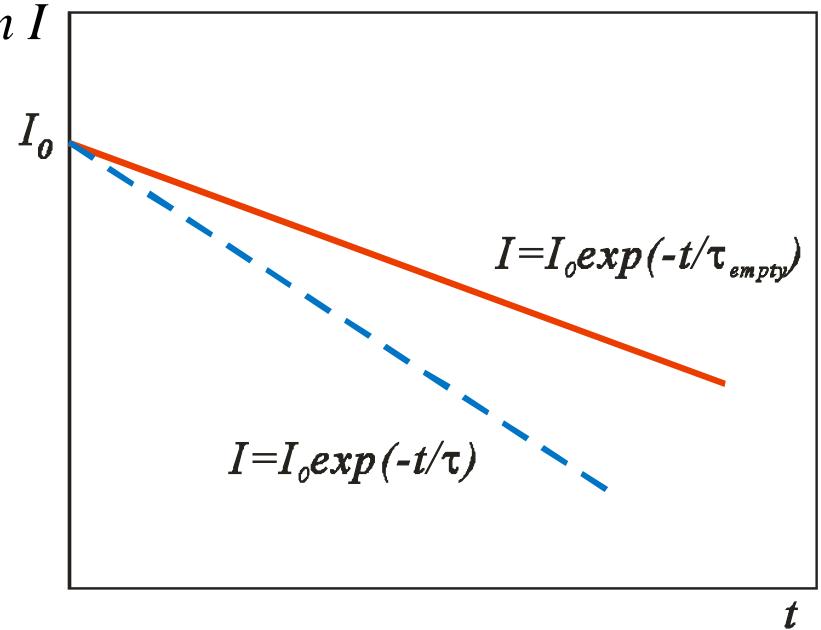
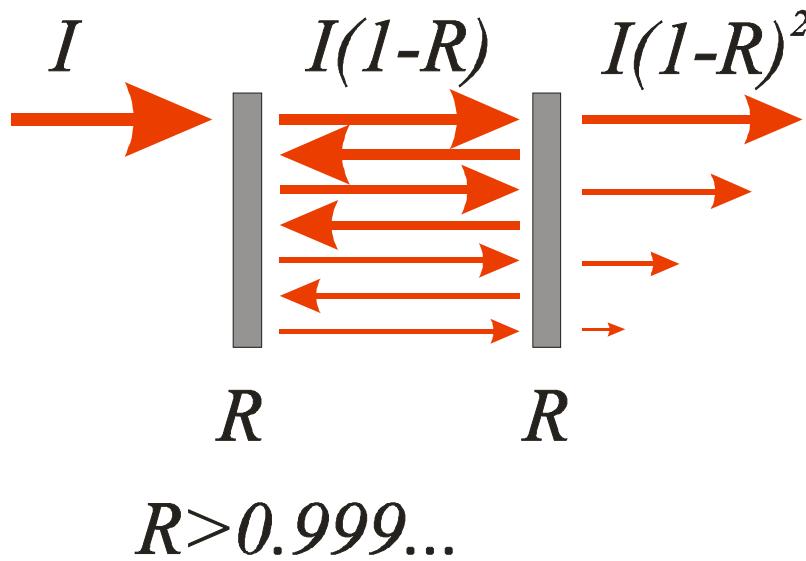
$$MLR : \quad y_i = \sum_{k=1}^N a_k x_{ki}$$

# Results of the Linear Regression Analysis

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Species	Measured concentration – sample 1		Measured concentration - sample 2	
	MLR	1-D regression	MLR	1-D regression
C <sub>2</sub> H <sub>5</sub> OH	$11.60 \times 10^{-6}$	$12.12 \times 10^{-6}$	$1.44 \times 10^{-6}$	$1.41 \times 10^{-6}$
CH <sub>4</sub>	$1.72 \times 10^{-6}$	-	$1.70 \times 10^{-6}$	-
N <sub>2</sub> O	$0.302 \times 10^{-6}$	-	$0.301 \times 10^{-6}$	-
H <sub>2</sub> O	$1.72 \times 10^{-3}$	-	$1.73 \times 10^{-3}$	-

# Cavity Ring-Down Spectroscopy

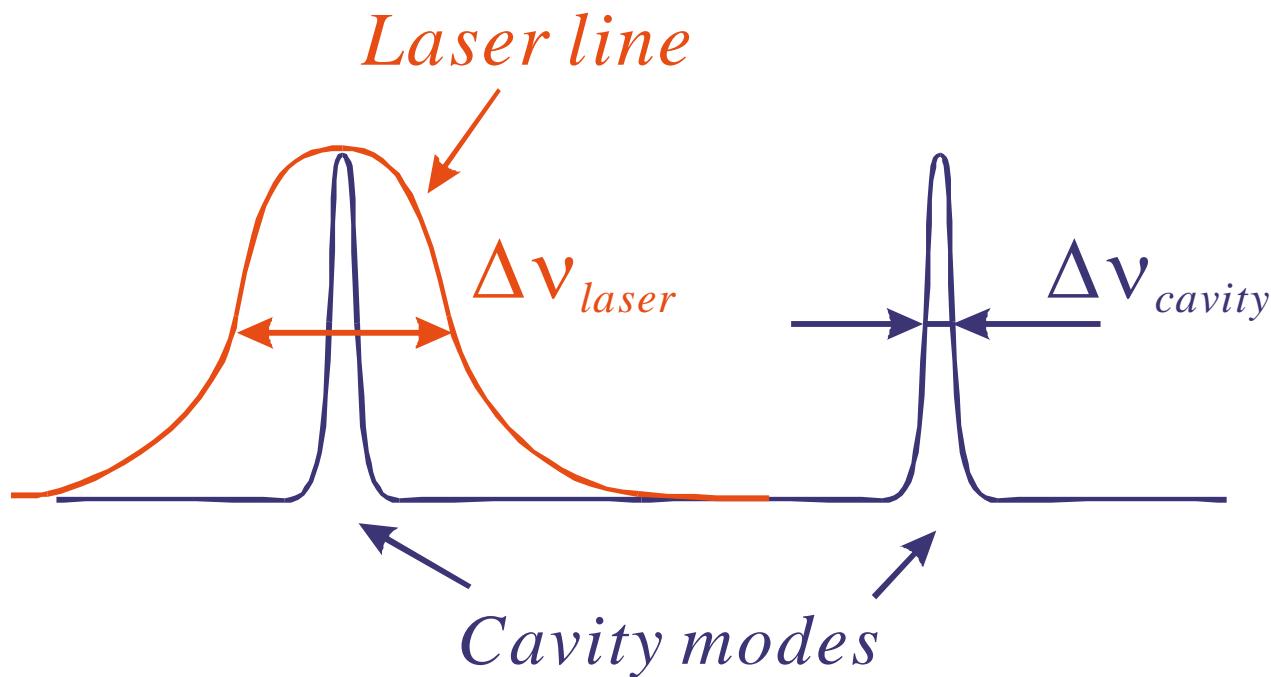


$$I = I_0 \exp\left(-\frac{t}{\tau}\right)$$

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

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

# Optical Cavity Transmission



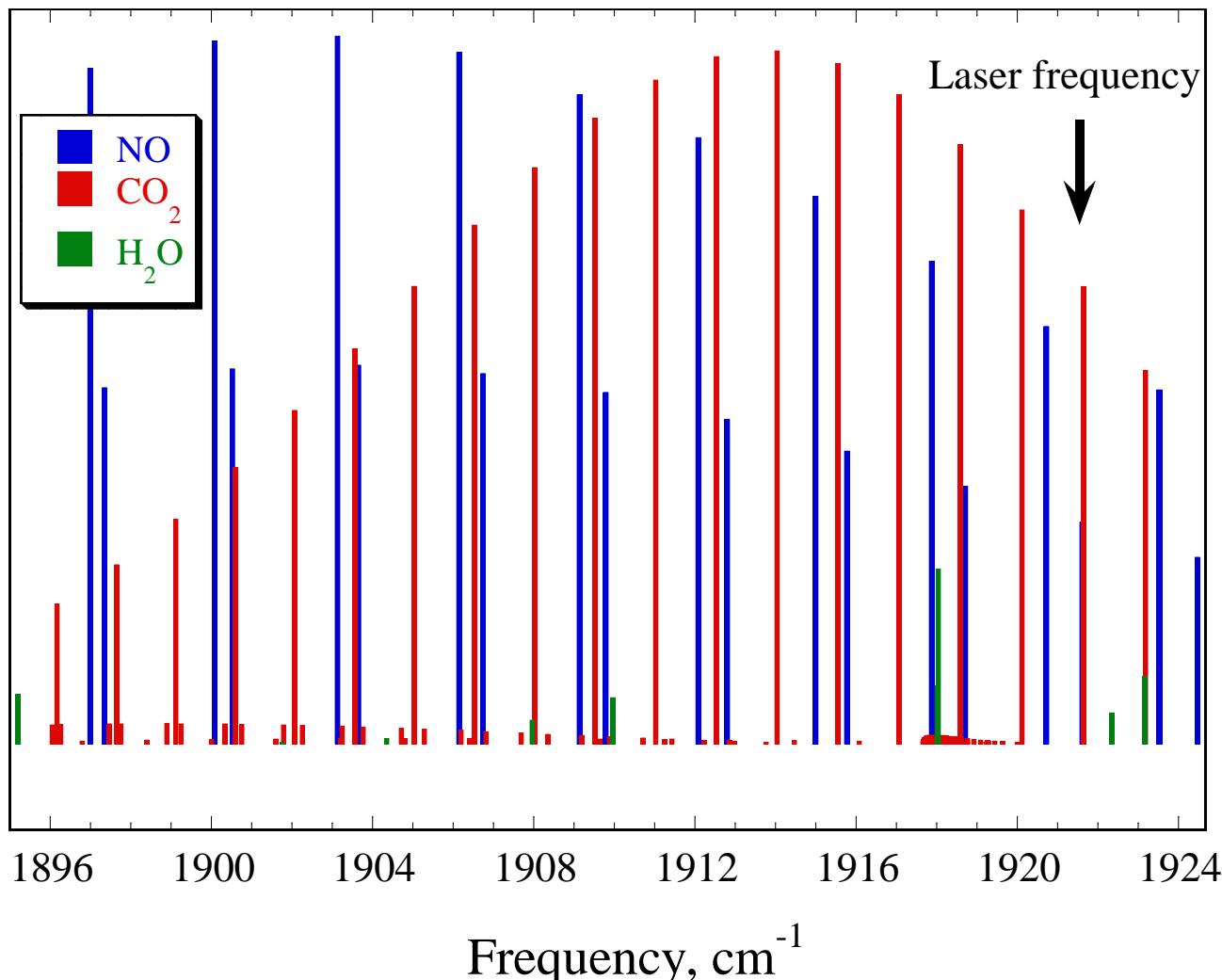
$$T \approx \frac{\Delta\nu_{cavity}}{\Delta\nu_{laser}}$$

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

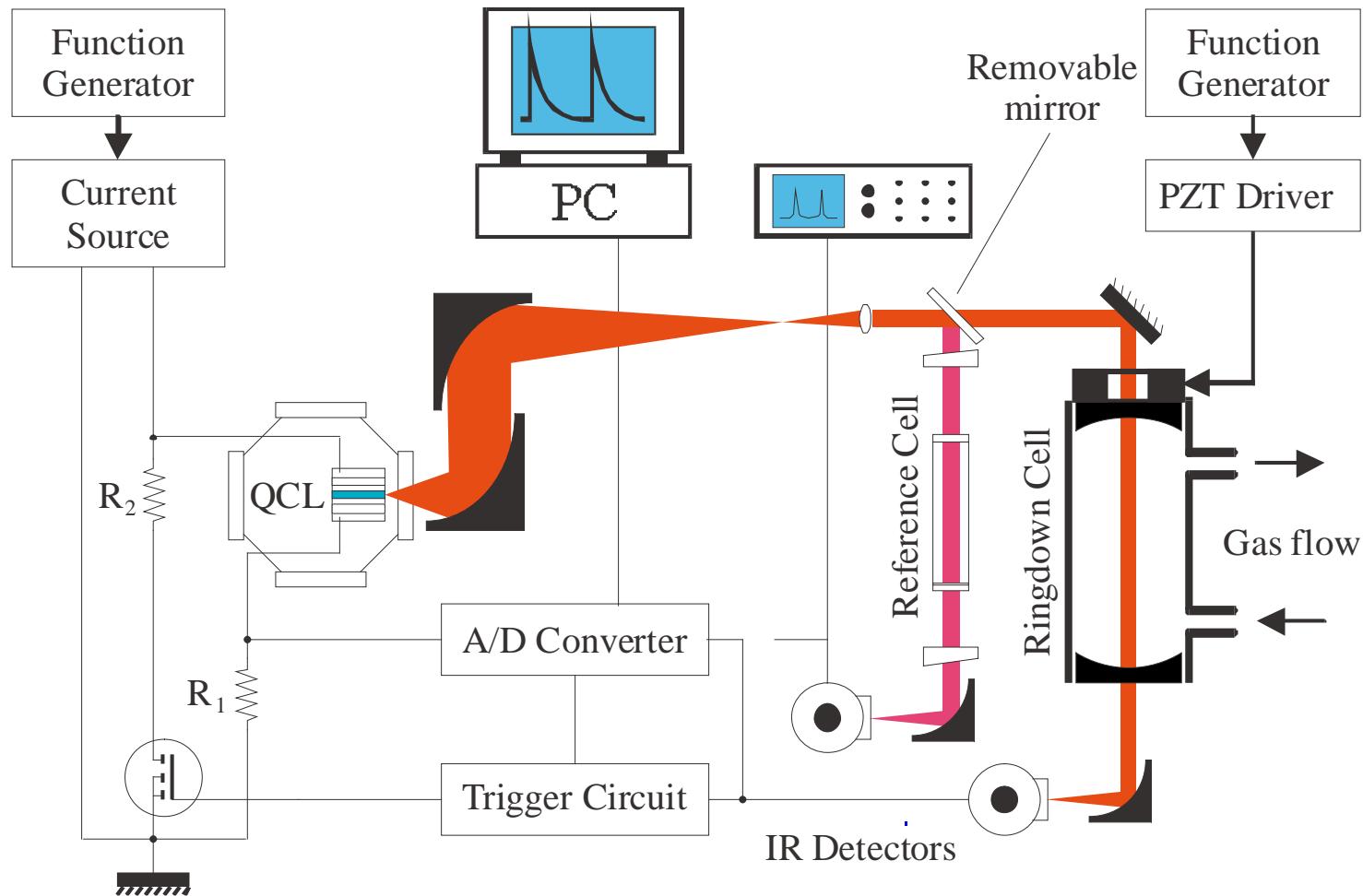
$$\tau = 3.5\mu\text{s} \quad \Rightarrow \quad \Delta\nu_{cavity} = 45\text{kHz}$$

# Absorption lines: NO, H<sub>2</sub>O and CO<sub>2</sub>

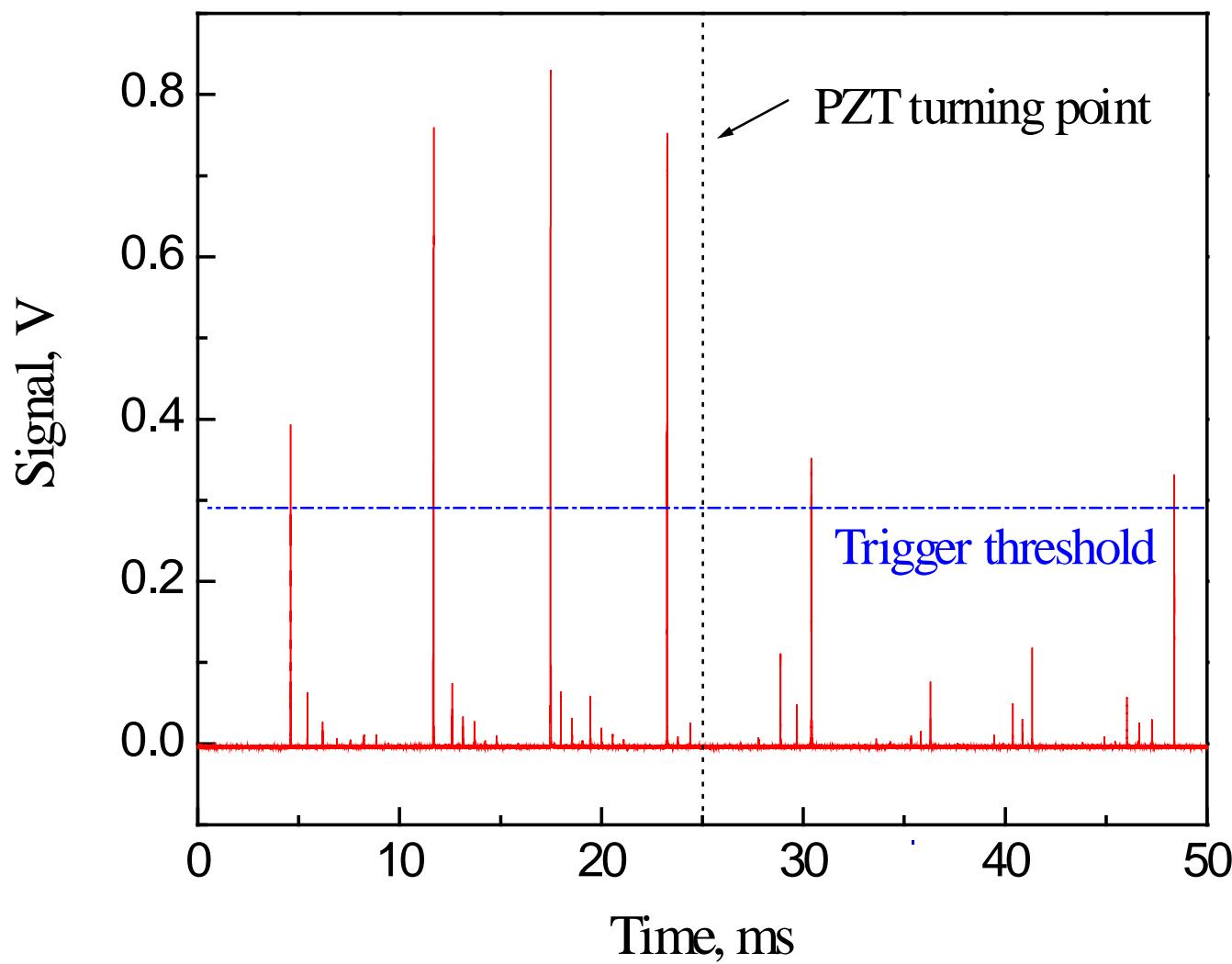
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# CRDS Gas Sensor

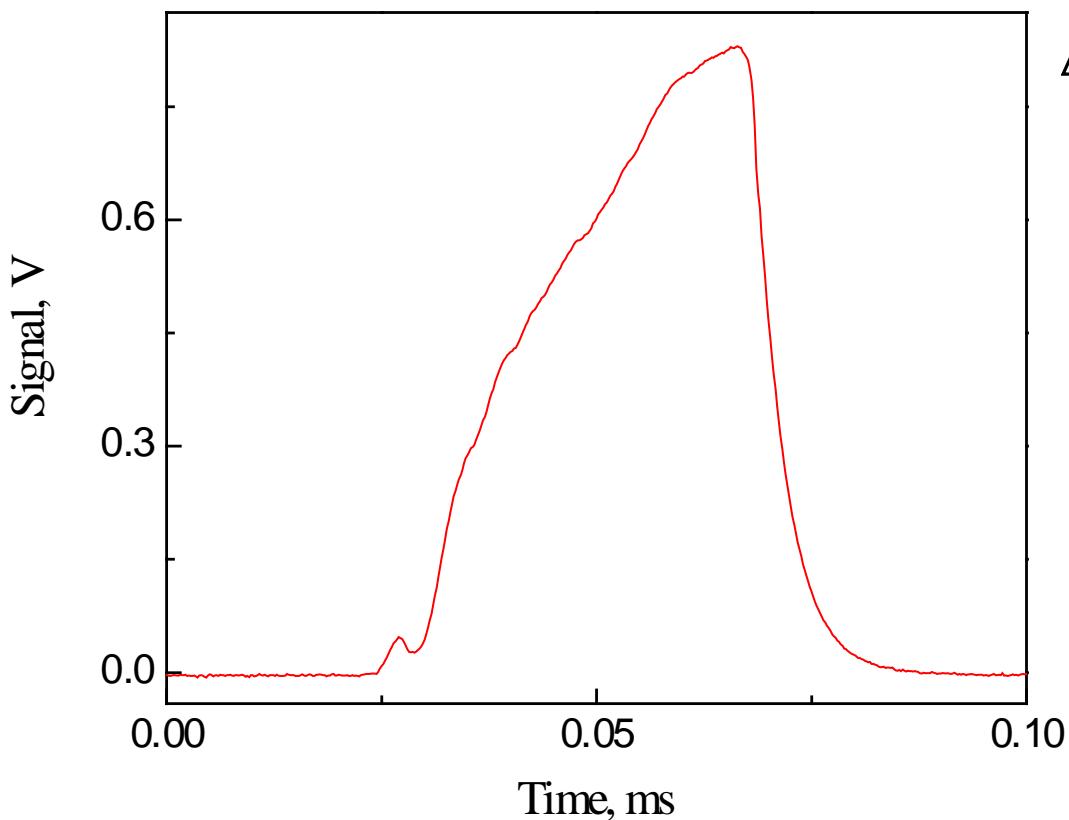


# $\text{TEM}_{00}$ and Higher Order Modes



# Laser Linewidth Estimate

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$$\Delta v_{QC}/\text{FSR} = \Delta t(\text{spike})/\Delta t(\text{FSR}) \approx 7.1 \times 10^{-3}$$

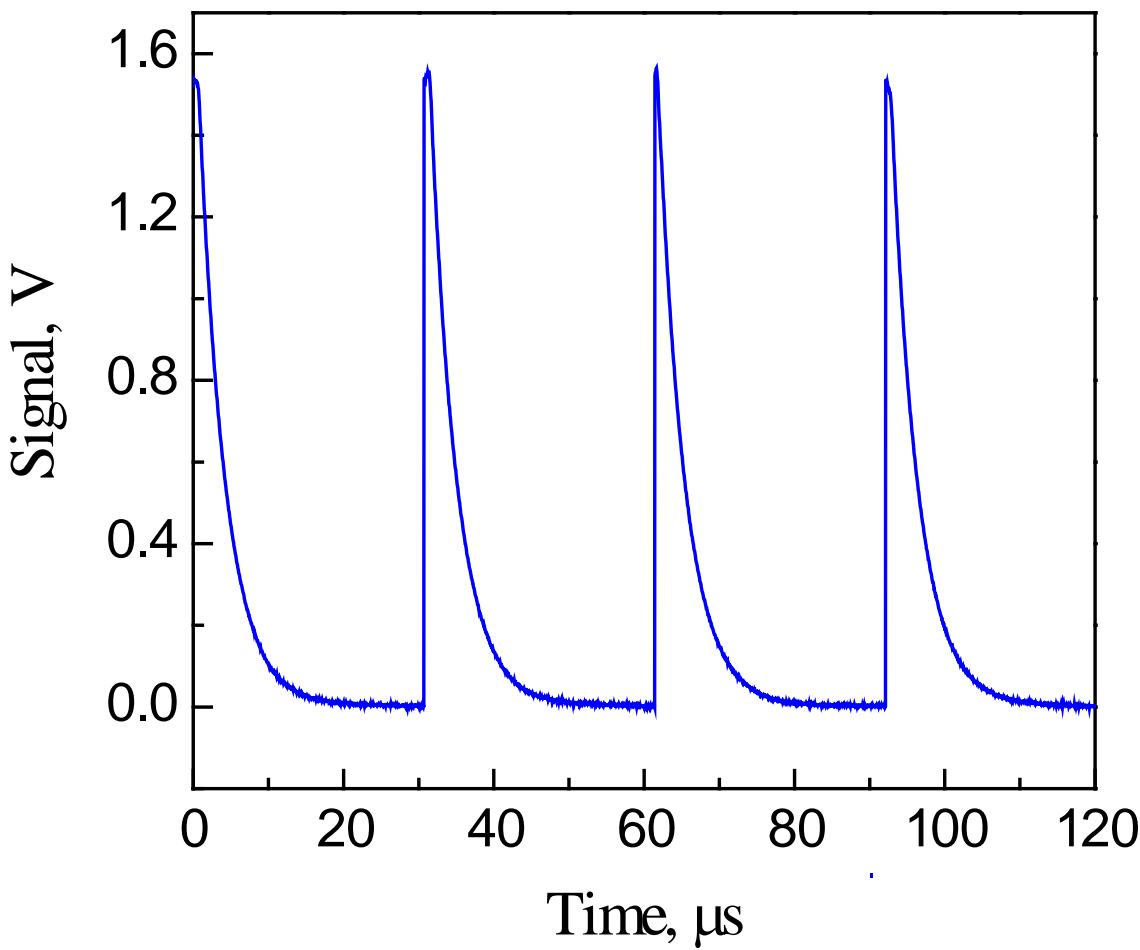
$$\text{FSR} = c/2l = 405 \text{ MHz}$$



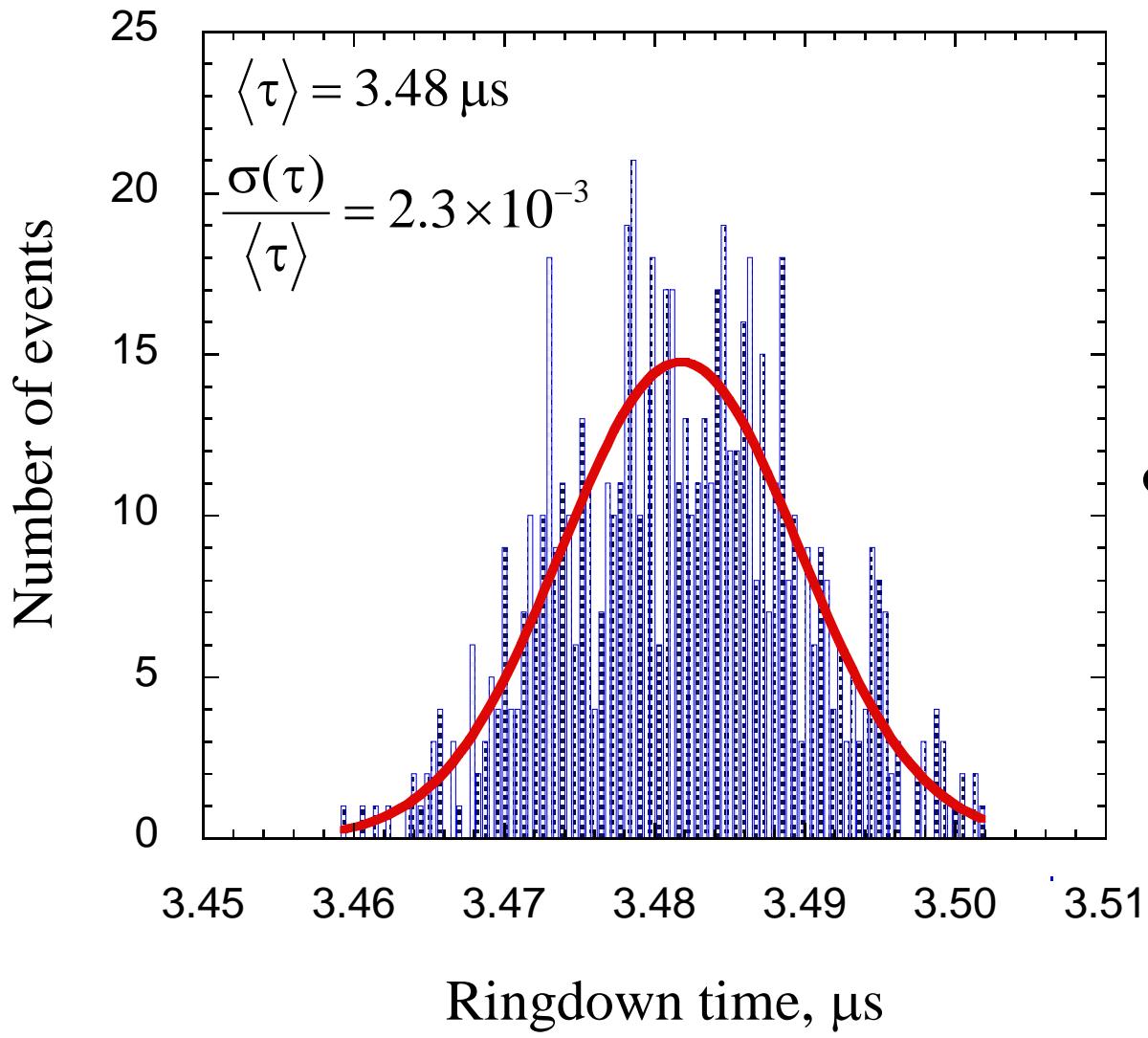
$$\Delta v_{QC} \approx 3 \text{ MHz}$$

# Recorded Ringdown Events

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# Distribution of Ringdown Times

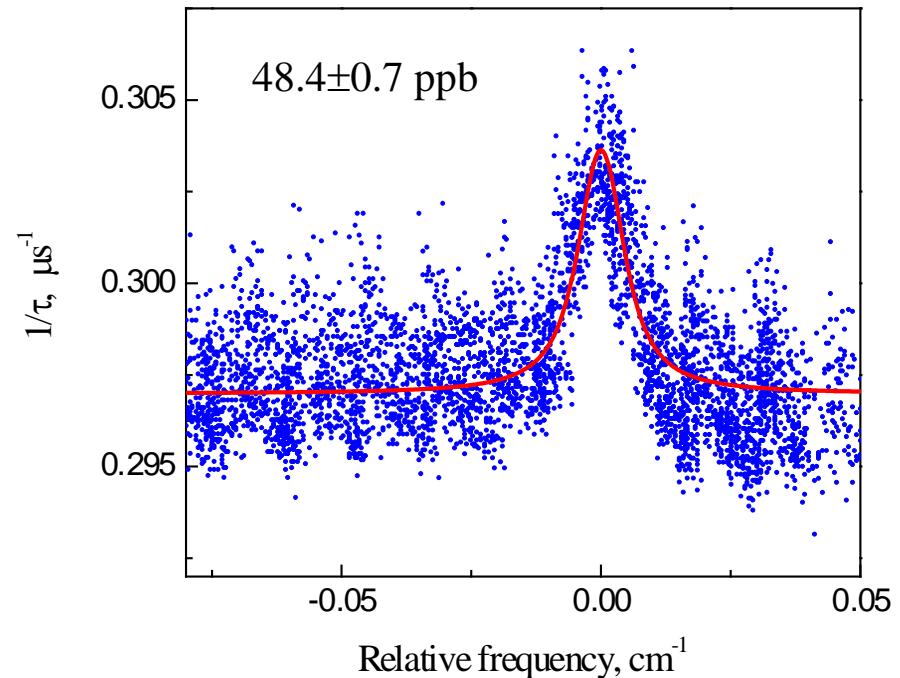
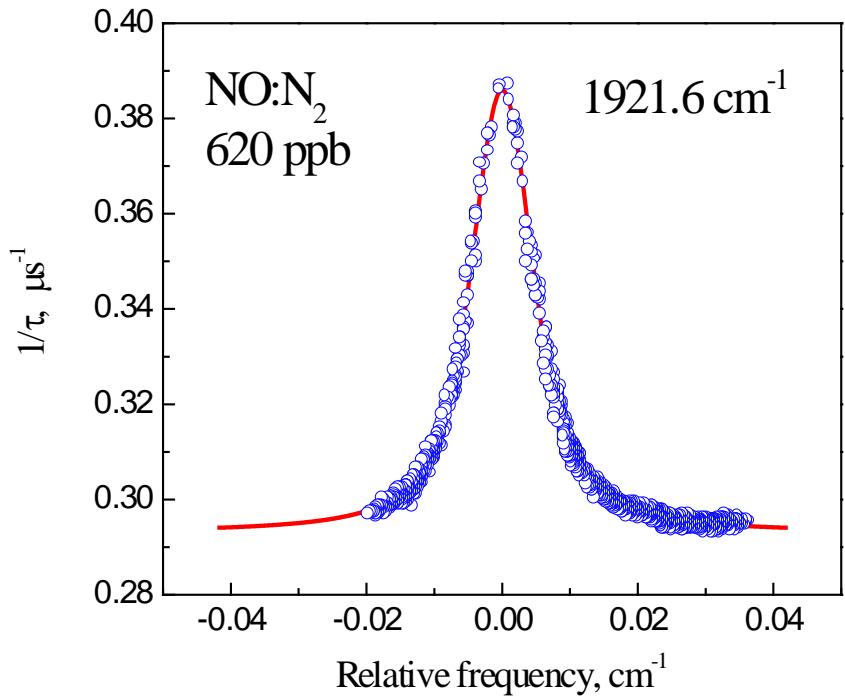


$$\sigma(\alpha) = \frac{1}{c\tau} \frac{\sigma(\tau)}{\langle \tau \rangle}$$

$$\sigma(\alpha) = 2.2 \times 10^{-8} \text{ cm}^{-1}$$

# NO absorption, 60 Torr Total Pressure

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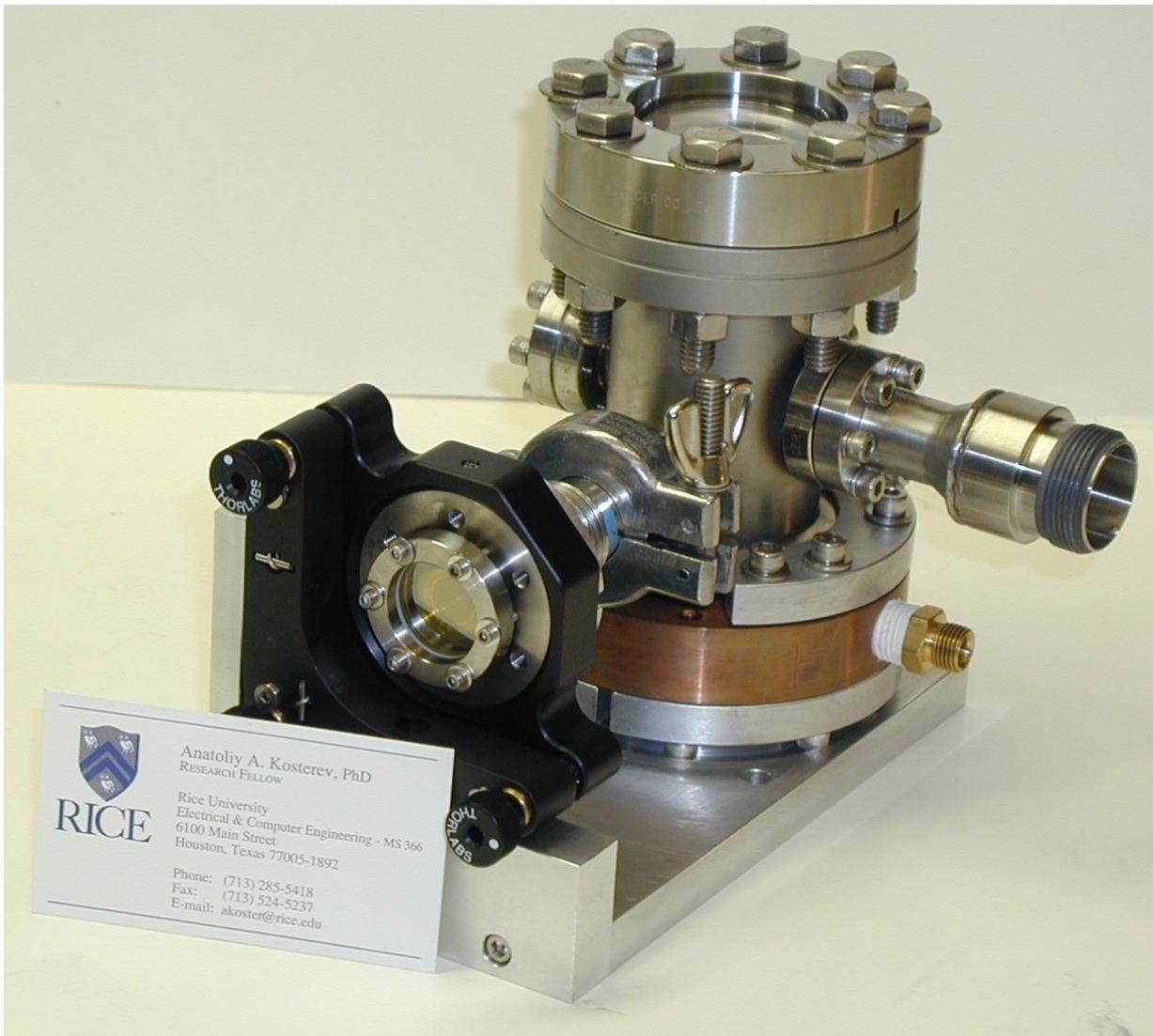
# Pulsed Operation of a QC-DFB Laser

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ADVANTAGES	DISADVANTAGES
<ul style="list-style-type: none"><li>◆ Laser can be operated at near-room temperature</li><li>◆ Facilitates temperature control</li><li>◆ No consumables (liquid N<sub>2</sub>)</li><li>◆ Compact</li></ul>	<ul style="list-style-type: none"><li>◆ Broader linewidth (~300 MHz)</li><li>◆ Reduced average power</li><li>◆ More sophisticated electronics for driving QC laser and data acquisition are required</li></ul>

# Pulsed QC-DFB Laser Housing

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RICE

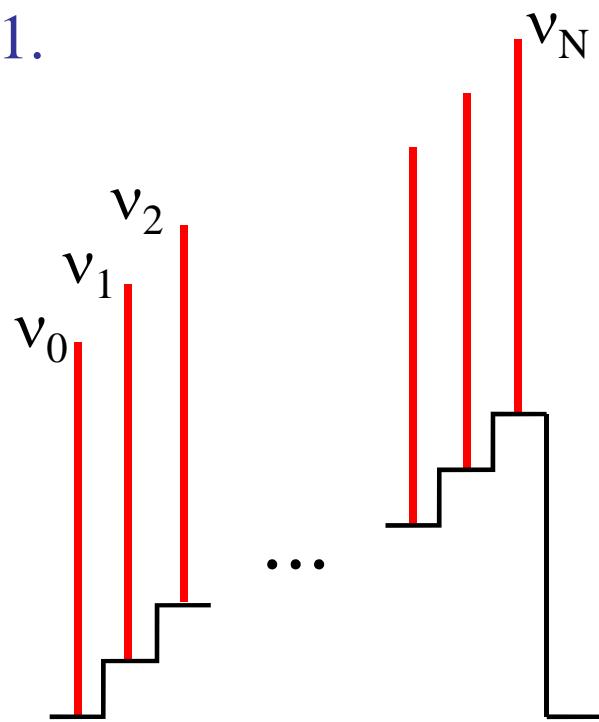
Anatoliy A. Kosterev, PhD  
RESEARCH FELLOW

Rice University  
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6100 Main Street  
Houston, Texas 77005-1892

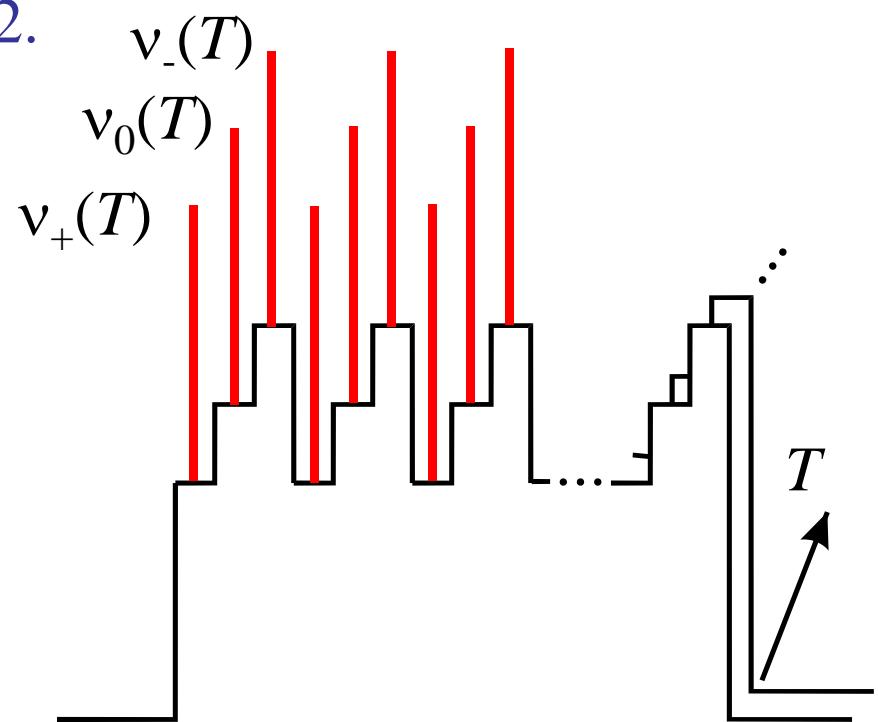
Phone: (713) 285-5418  
Fax: (713) 524-5237  
E-mail: akoster@rice.edu

# Manipulating the Pulsed QC Laser Frequency

1.



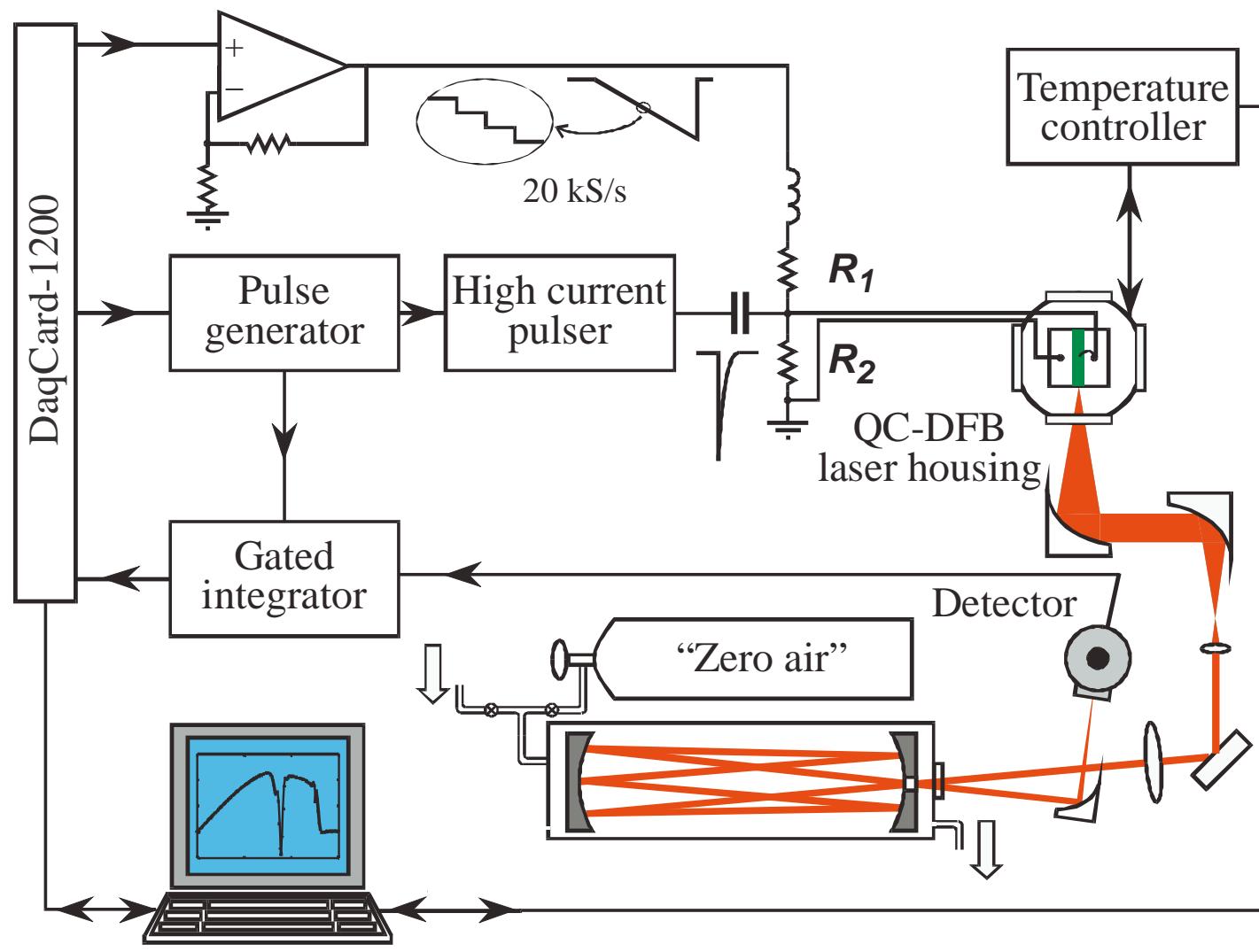
2.



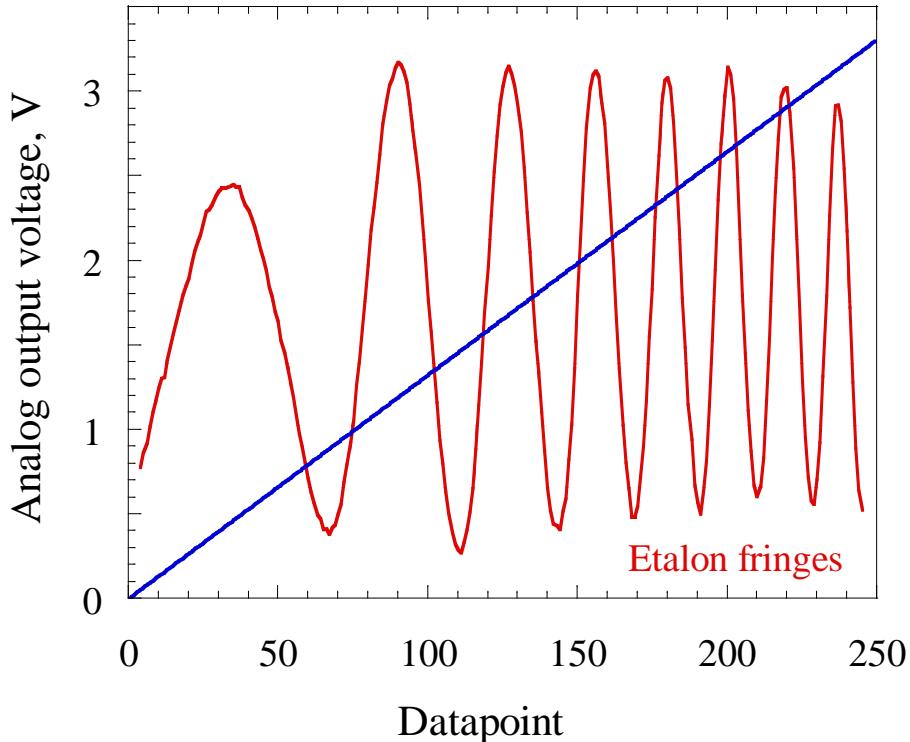
Fast scanning of the laser frequency with a subthreshold current

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

# Pulsed QC-DFB Spectrometer

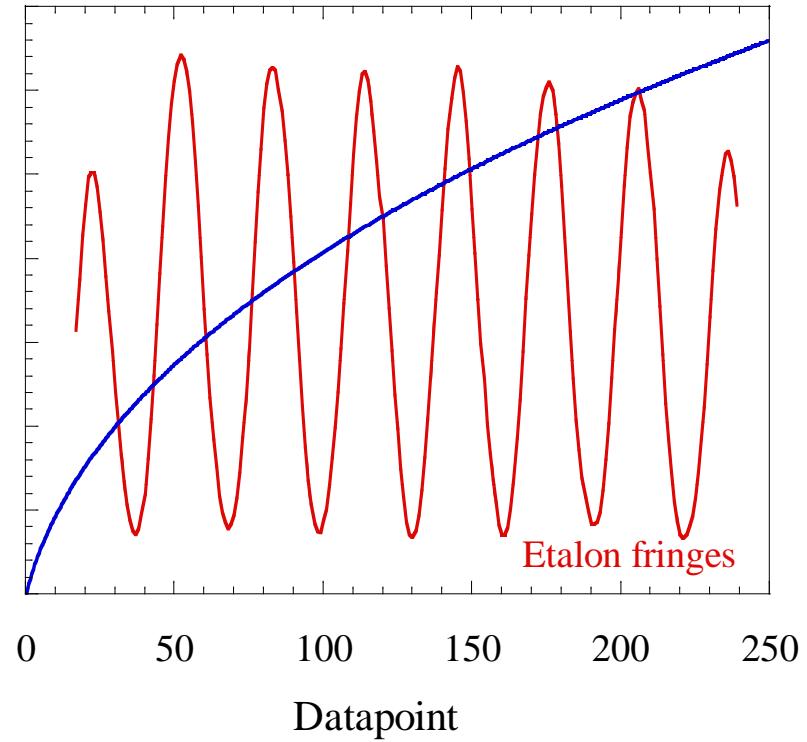


# Linearization of Fast Frequency Scan

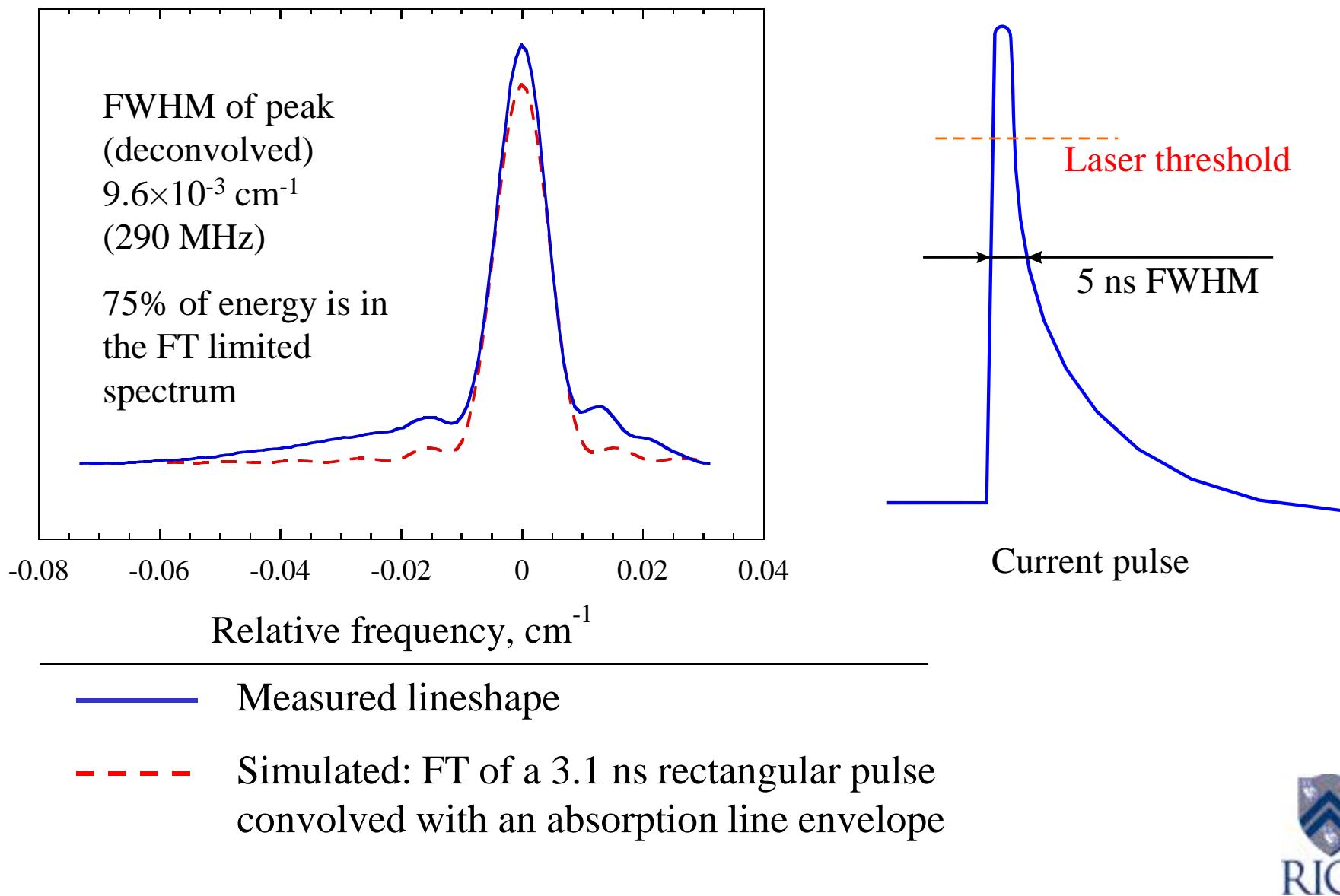


FSR=0.027 cm<sup>-1</sup>

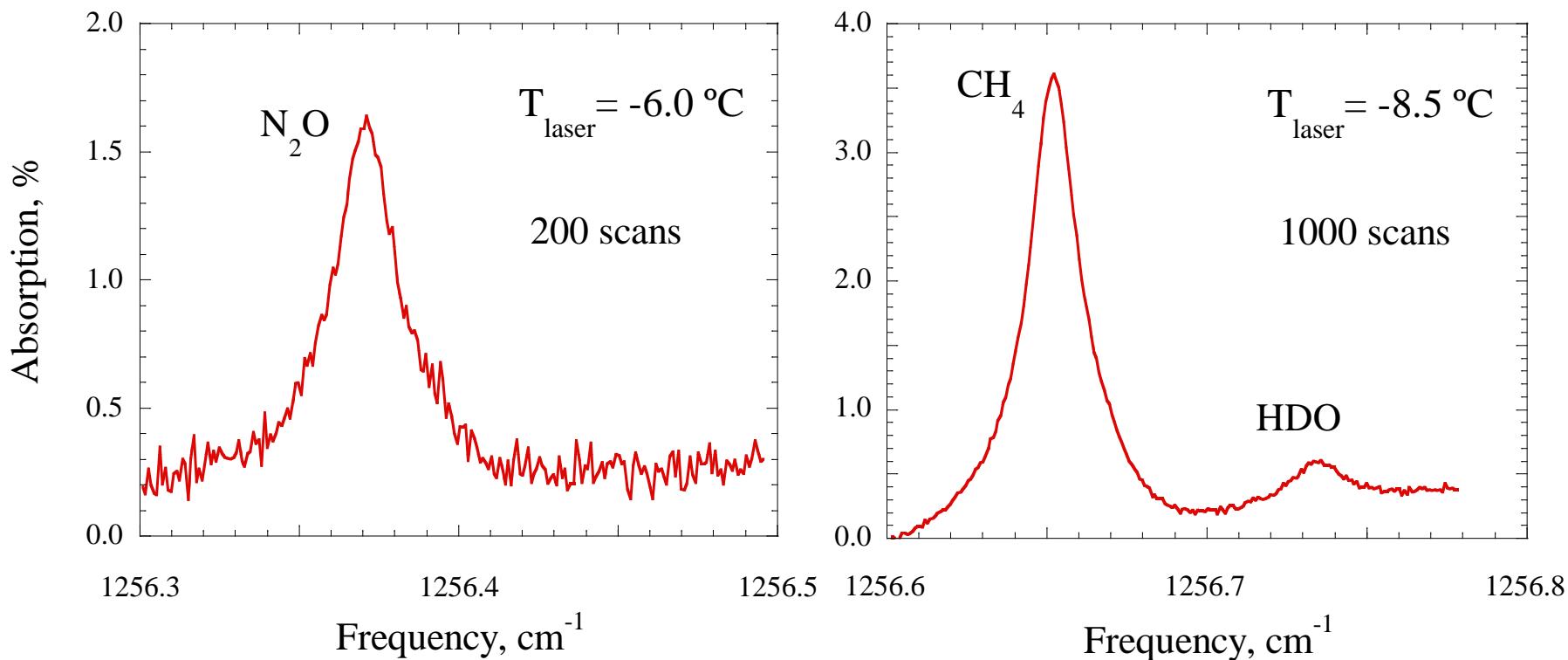
Acquisition rate  $\frac{1}{2} \times 20$  kS/s



# Spectral Shape of a Pulsed QC Laser Line



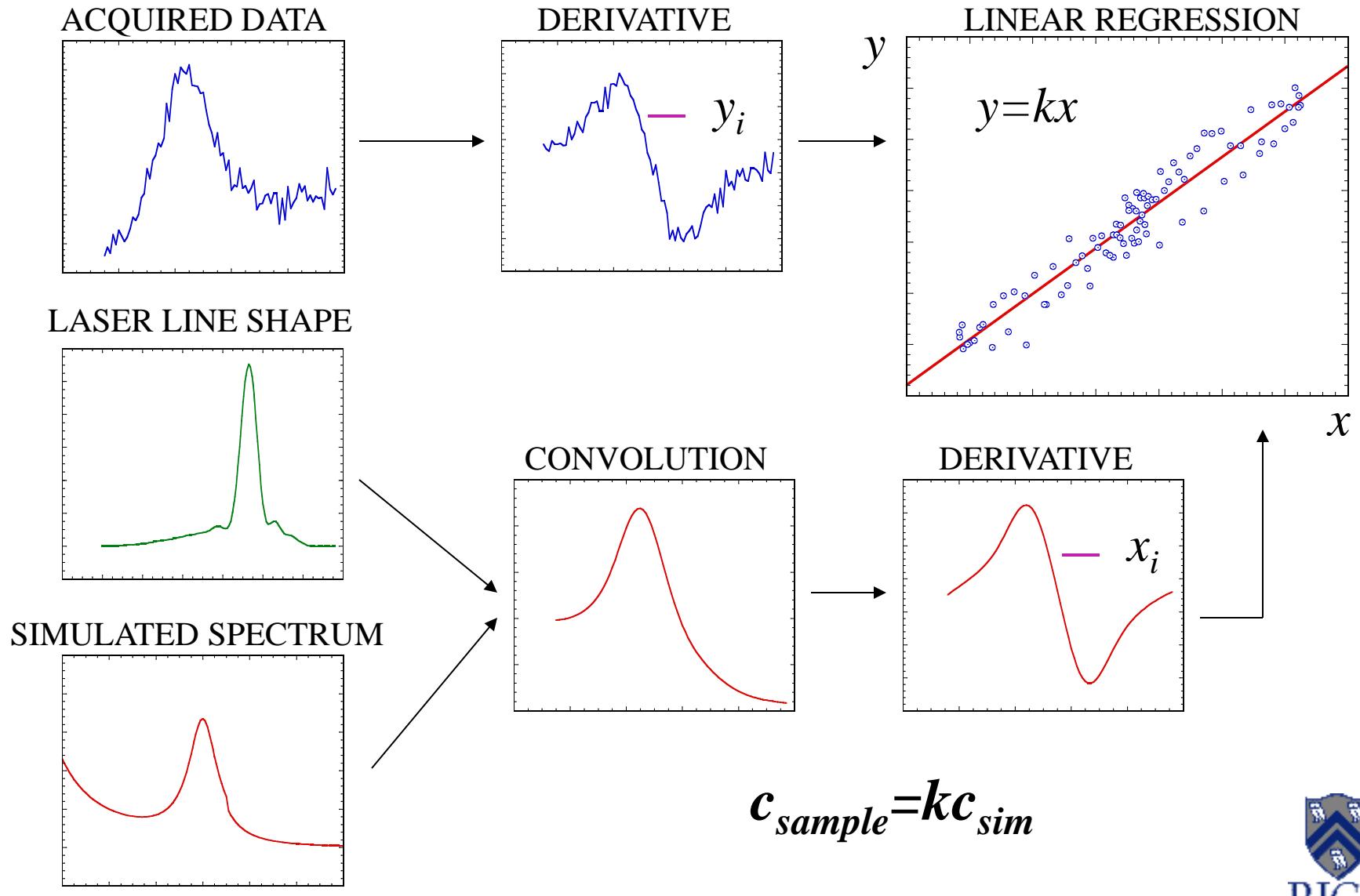
# “Fast Scan” Detection of Trace Gases in Air



Pathlength: 100 m (multipass cell)

Pressure: 85 Torr

# Extracting the Concentration



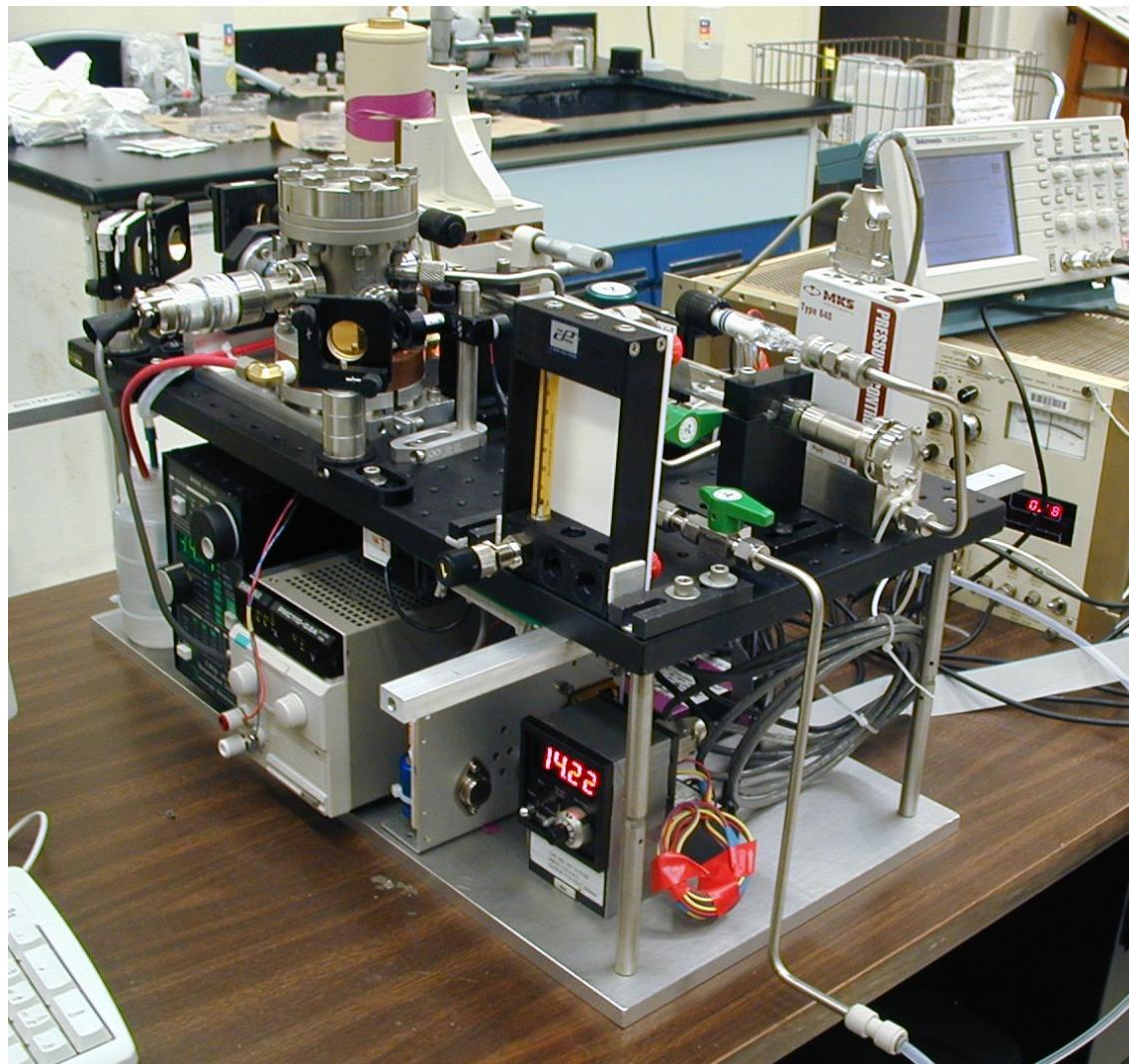
# Results of the Data Analysis

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Molecular species	CH <sub>4</sub>	HDO	N <sub>2</sub> O
Concentration assumed in simulations, ppm	1.7	2.408	0.32
Simulated peak absorption	4.58%	0.29%	2.15%
Number of scans	1000	1000	200
Linear regression slope	1.195±0.005	1.78±0.05	0.998±0.014
Resulting concentration, ppm	2.032±0.009	4.28±0.12	0.319±0.004

# NH<sub>3</sub> Sensor Based on Pulsed 10.05 μm laser

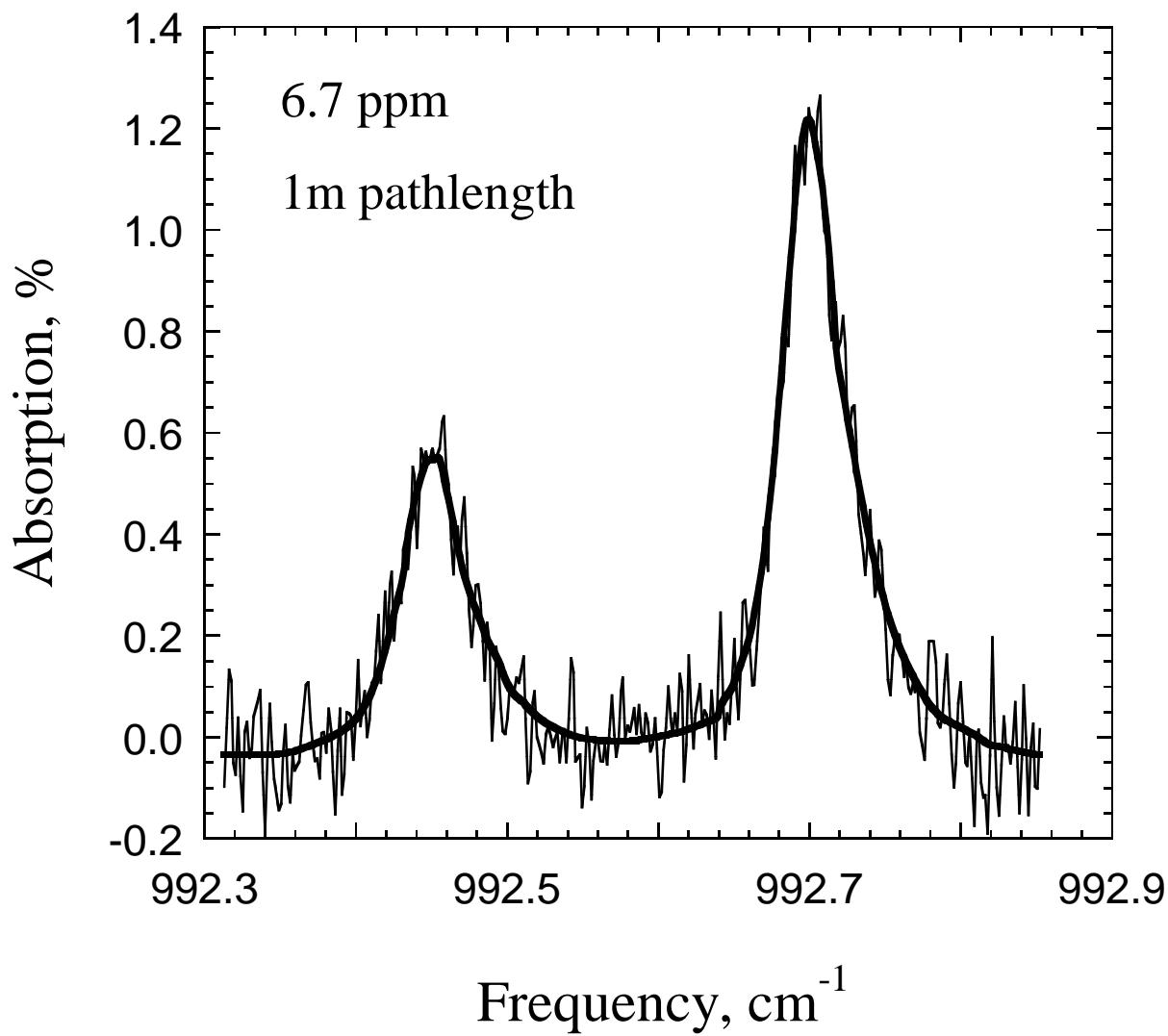
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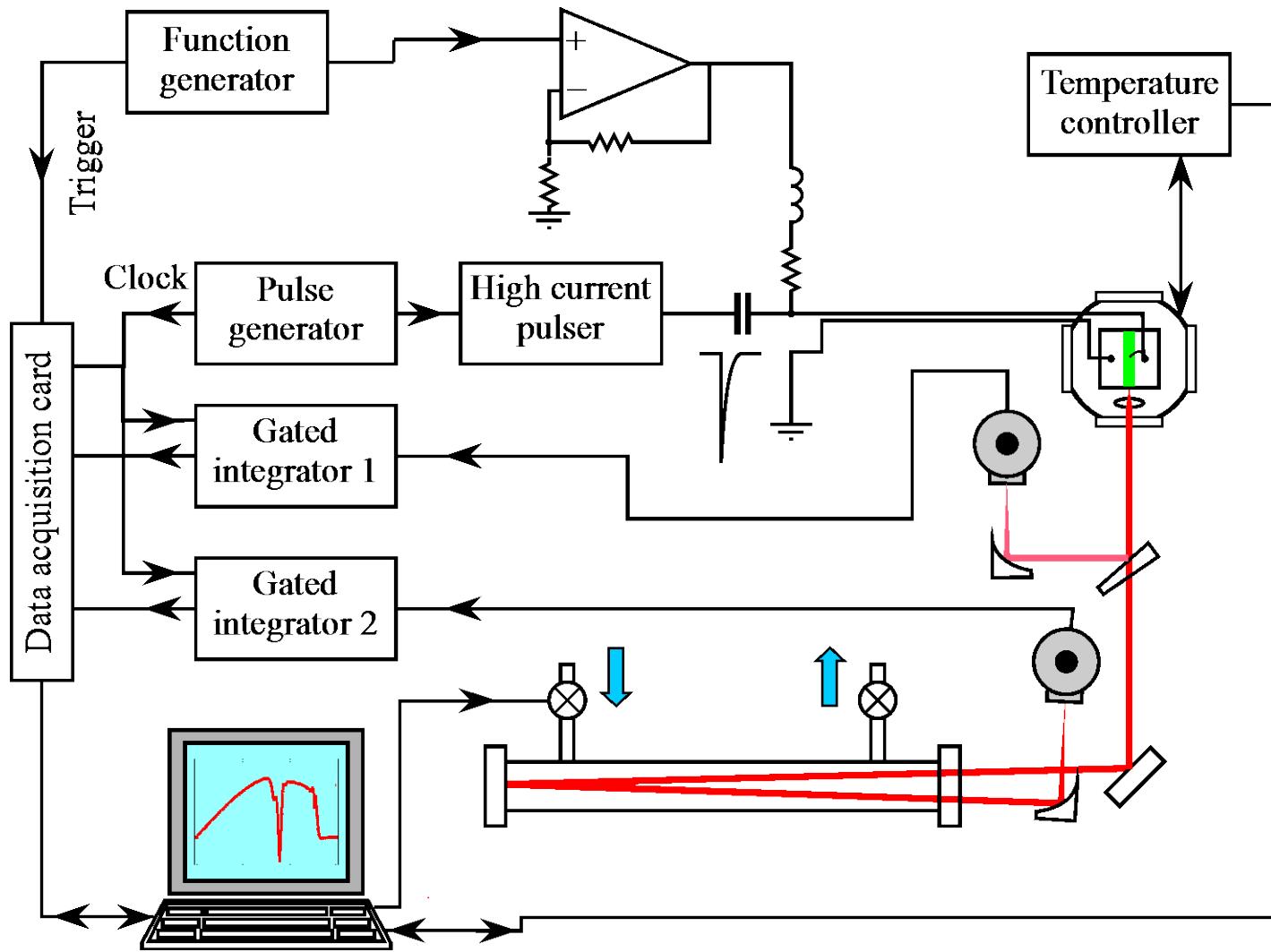
One IR detector  
Sensitivity ~0.3 ppm

# Ammonia Spectrum at 993 cm<sup>-1</sup>

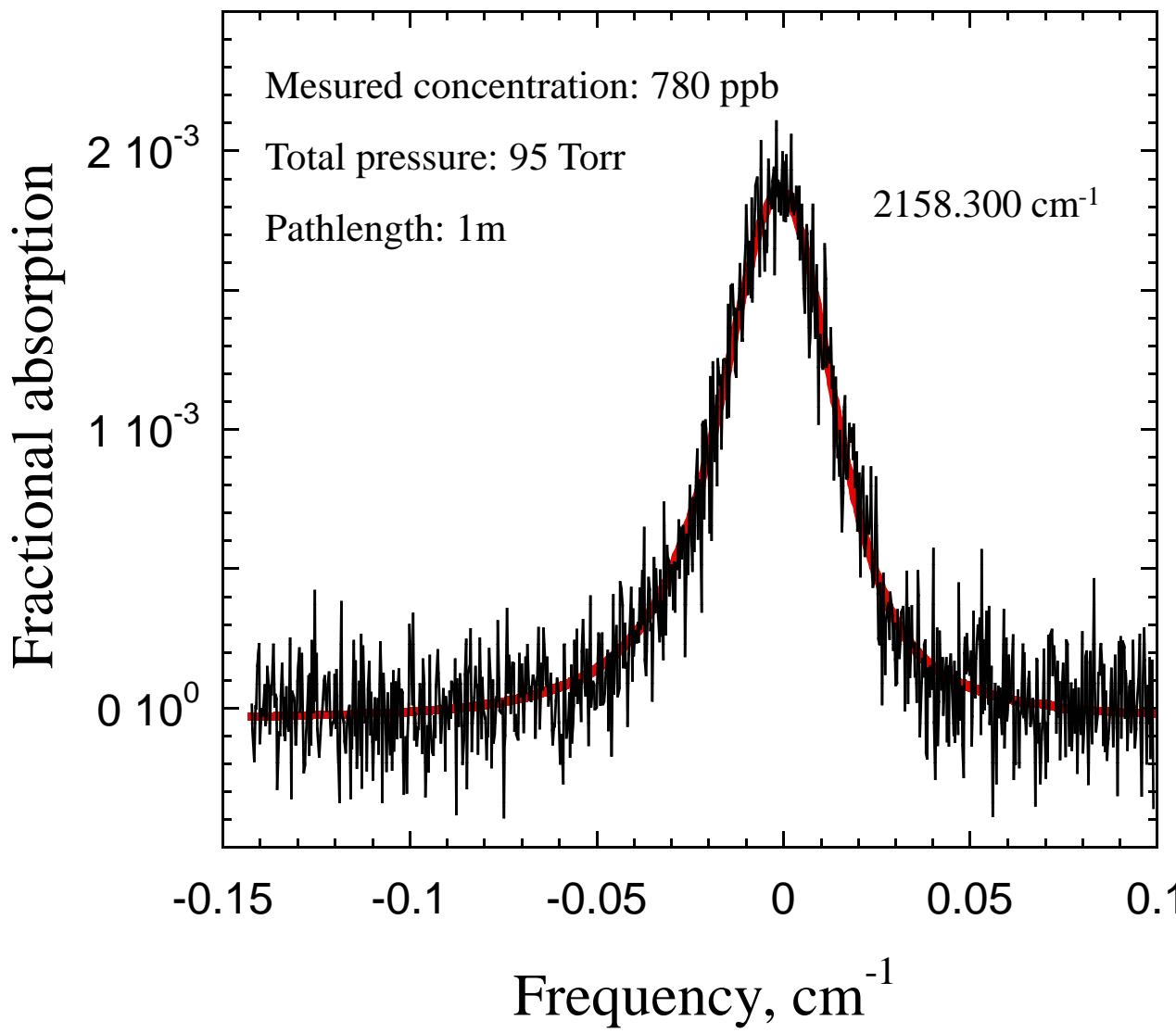
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# Two-Channel Data Acquisition

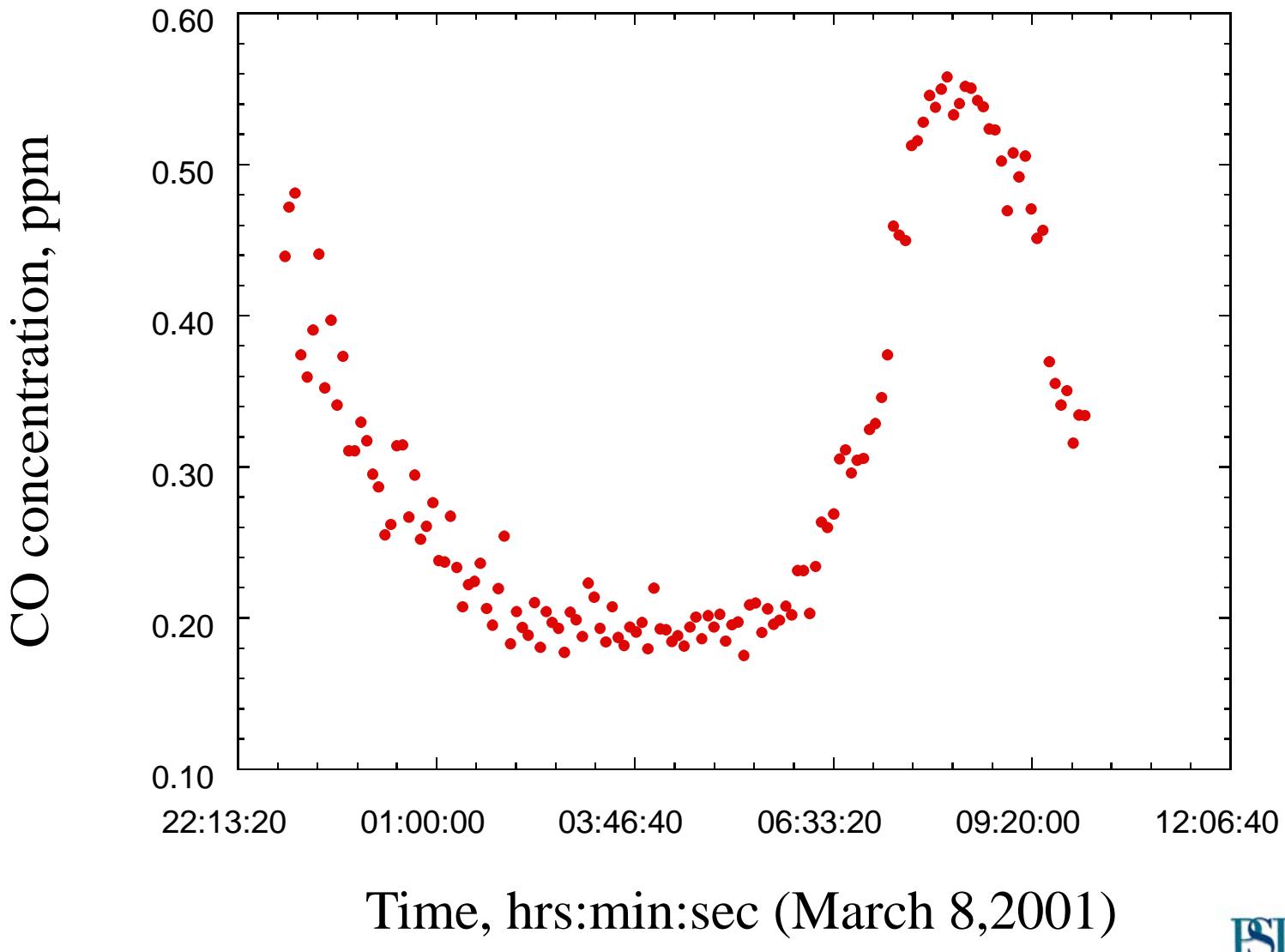


# CO Absorption: Ambient Air Sample



Two IR detectors  
Sensitivity  $\sim 10$  ppb

# CO Concentration Measurements



# Summary and Future Outlook

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- A variety of approaches can be used for QC-DFB laser based spectroscopic detection of trace species;
- Molecules detected with QC lasers at sub-ppm levels in the Rice Laser Science group:  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ , CO, NO,  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$

## Future developments

- ◆ Make compact gas sensors based on pulsed thermoelectrically cooled QC-DFB lasers, short optical path and two-channel detection
- ◆ Wider range of molecules, including bigger organic molecules
- ◆ Compact cavity ringdown sensors when thermoelectrically cooled CW QC lasers become available