

***AERODYNE RESEARCH, Inc.***

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# **Atmospheric Trace Gas Measurements With Pulsed- Quantum Cascade Lasers: sub-ppb Ammonia Detection**

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Fraunhofer IPM QC Laser Workshop  
February 2001

- Technique
  - Pulsed-QC Detection Method
  - Advances in Hardware and Software
- Open Path Ammonia Measurements
  - Automobile Emissions
- Closed Path Indoor Air Ammonia
- Applications to Other Gases

# TILDAS APPLICATIONS

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## ■ Atmospheric Fluxes

- $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ,  
 $\text{HNO}_3$ ,  $\text{NH}_3$

## ■ Urban Air Pollutants

- $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{CO}$ ,  
 $\text{HONO}$ ,  $\text{NO}$ ,  $\text{NO}_2$

## ■ Tracer Studies

- $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$

## ■ Combustion Exhausts

- $\text{NO}_x$ ,  $\text{HONO}$ ,  $\text{NH}_3$   
 $\text{SO}_2$ ,  $\text{SO}_3$

## ■ Plasma Processing

- $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  
 $\text{CH}_3$ ,  $\text{HO}_2$

## ■ Petroleum Exploration

- $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$

## ■ Cigarette Smoke

- $\text{NH}_3$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  
 $\text{C}_2\text{H}_4$ ,  $\text{H}_4\text{C}_3\text{O}$

# Cryogen-Free Pulsed QC Lasers

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## ADVANTAGES:

- Decreased Instrument Size and Weight
- Reduced Transport Logistics
- Unattended Remote Monitoring
- “Turn-Key” Operation
- Improved Safety

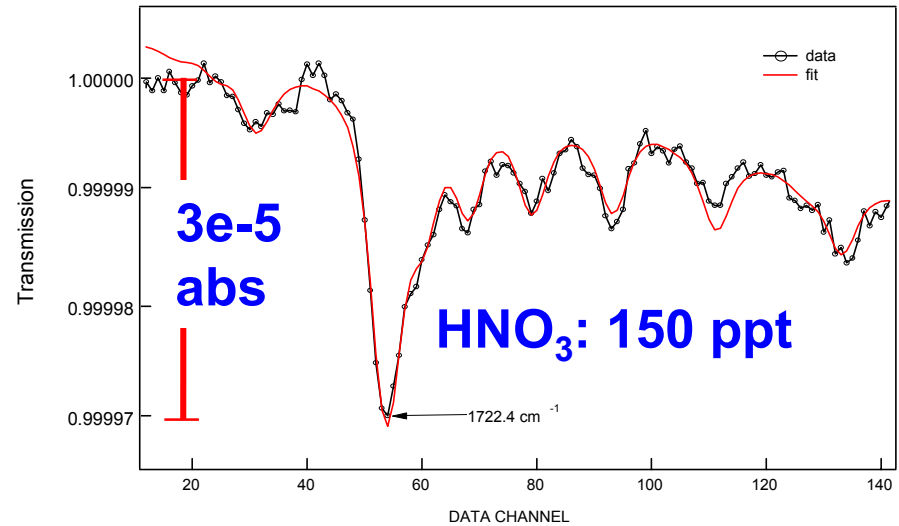
## DISADVANTAGE:

- Increased Laser Line Width

# DIRECT ABSORPTION SPECTRA ANALYSIS

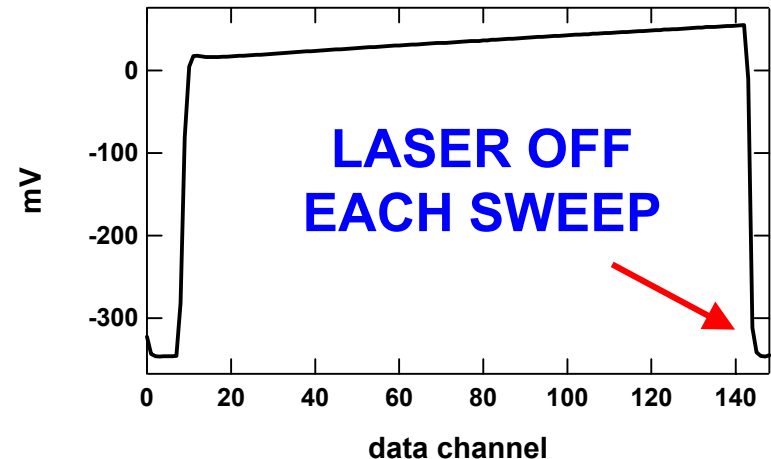
## RAPID SCAN SWEEP INTEGRATION

- Laser Intensity at each sweep
- 3 MHz acquisition rate
- Nonlinear fits to HITRAN  $f(T,P)$
- Multiple Species, Multiple Lines

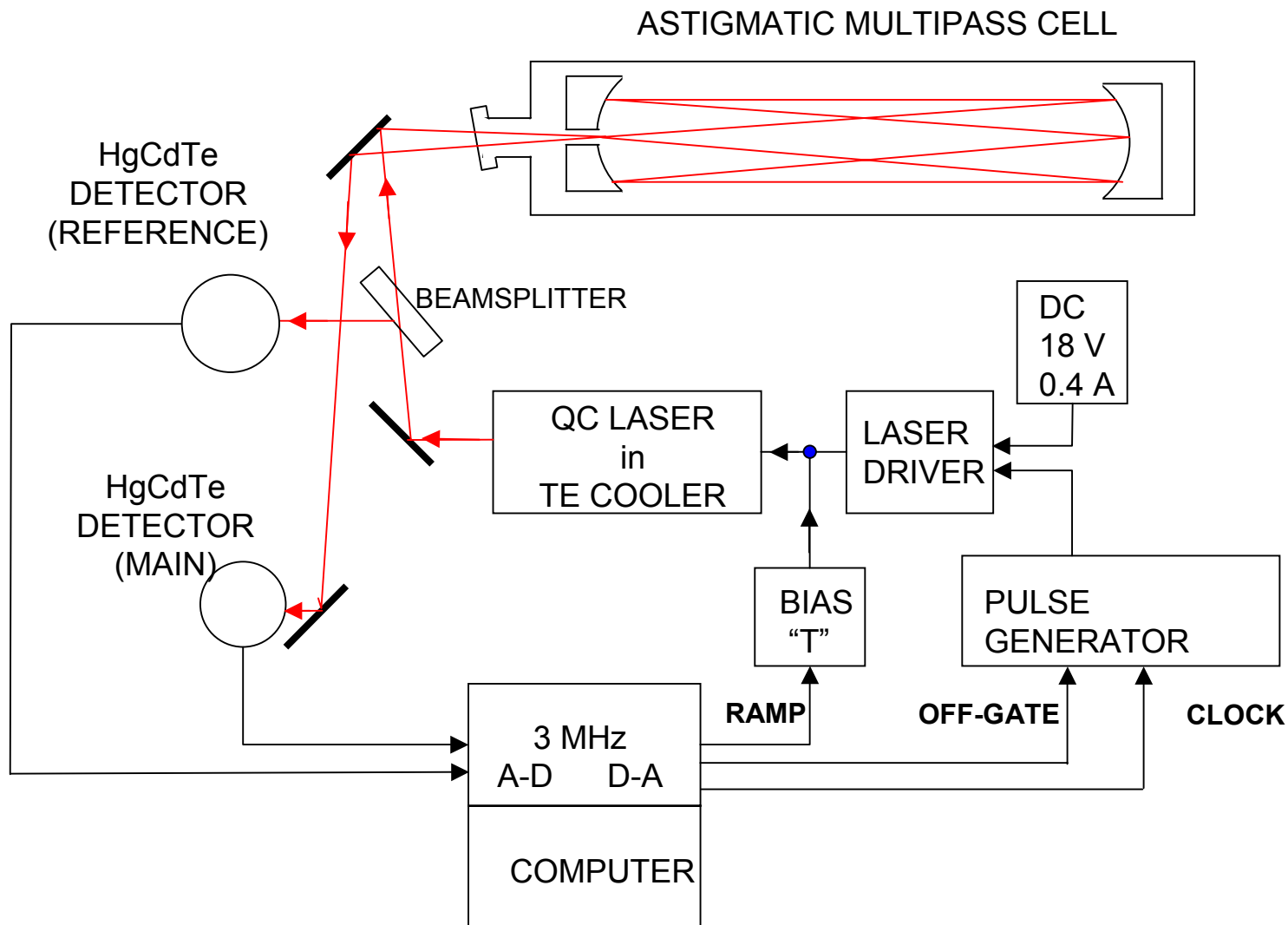


## BENEFITS:

- Absolute concentrations
- Higher resolution than FM
- Ability to use unresolved lines
- Fingerprint identification



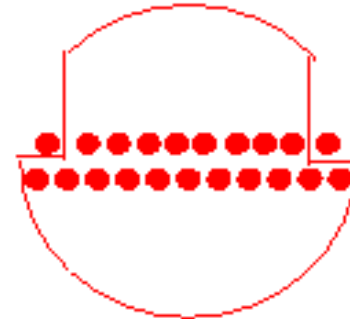
# QCLAS Schematic



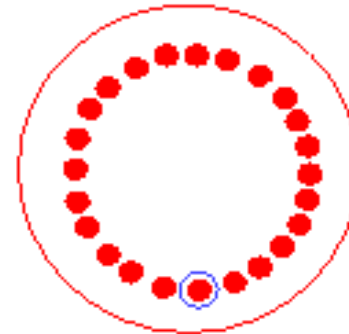
# Comparison of Multipass Cell Designs

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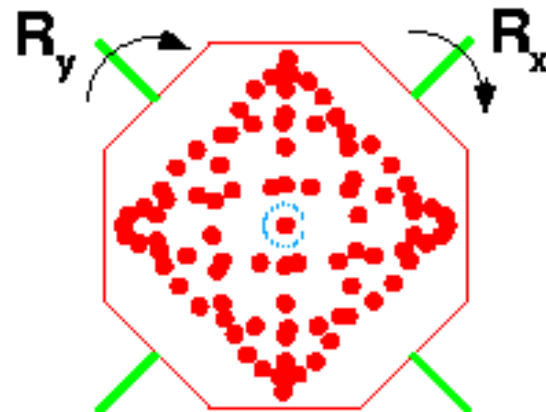
**“WHITE” CELL**



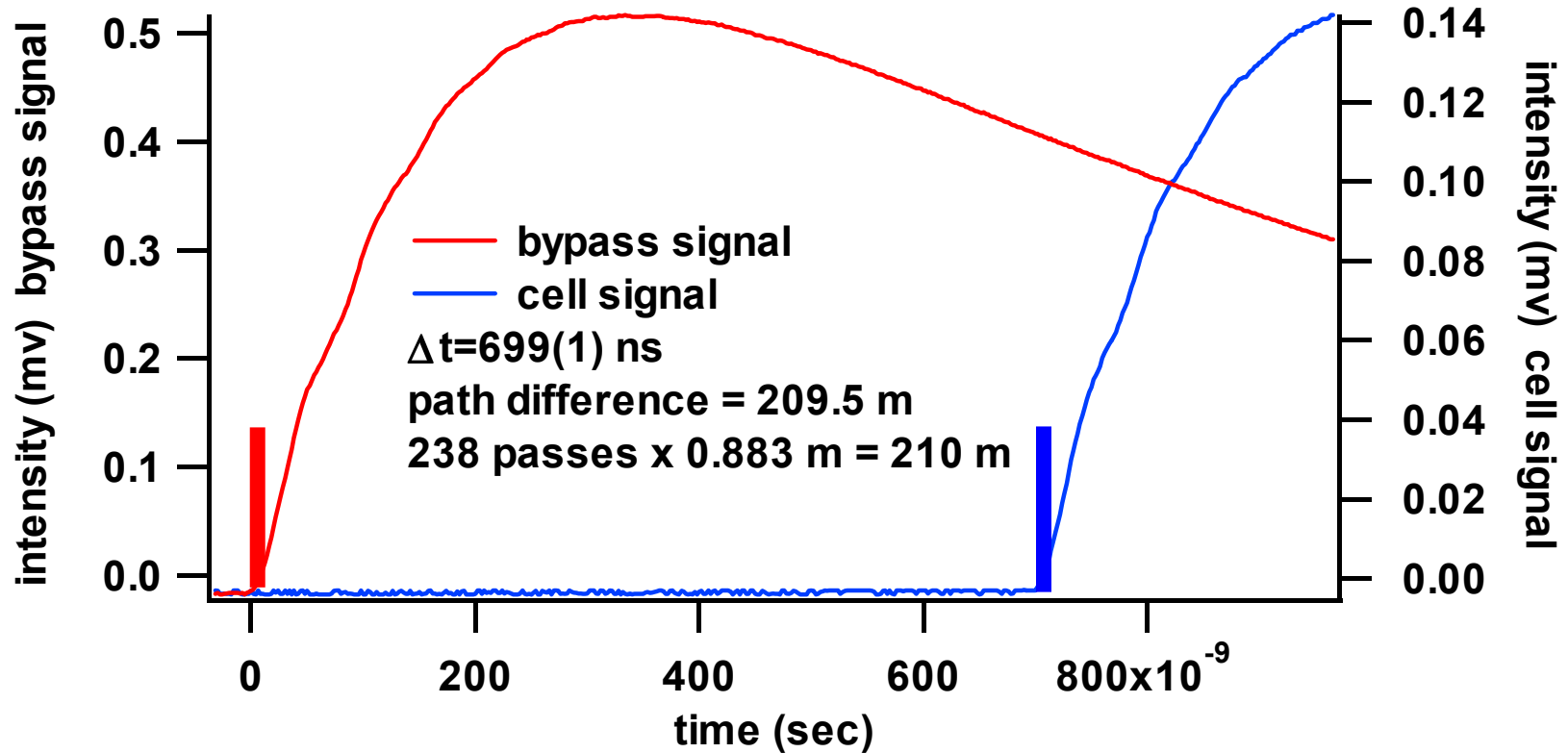
**SPHERICAL  
HERRIOTT  
CELL**



**ASTIGMATIC  
HERRIOTT CELL**



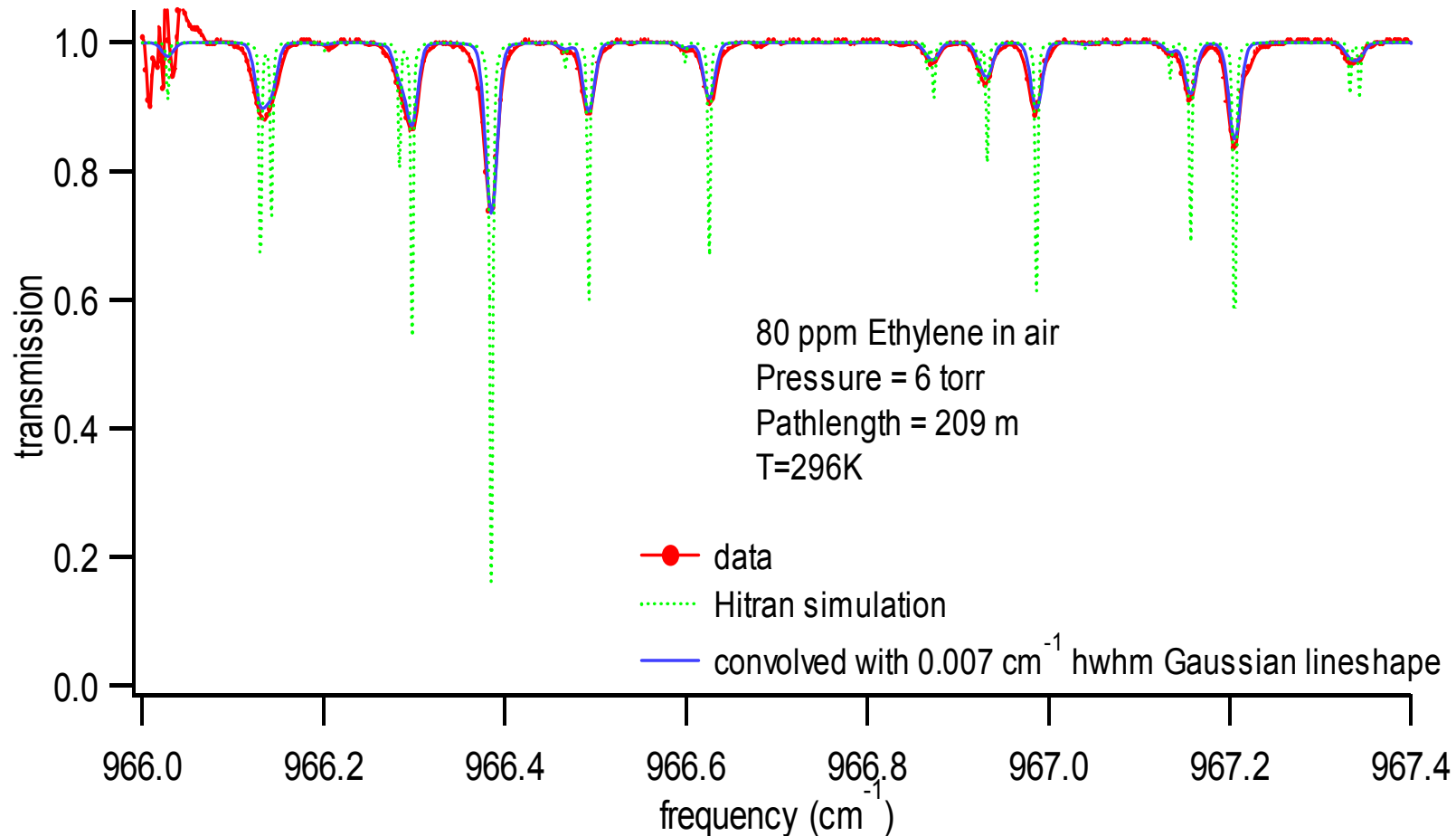
# Optical Delay with Multiple Pass Cell



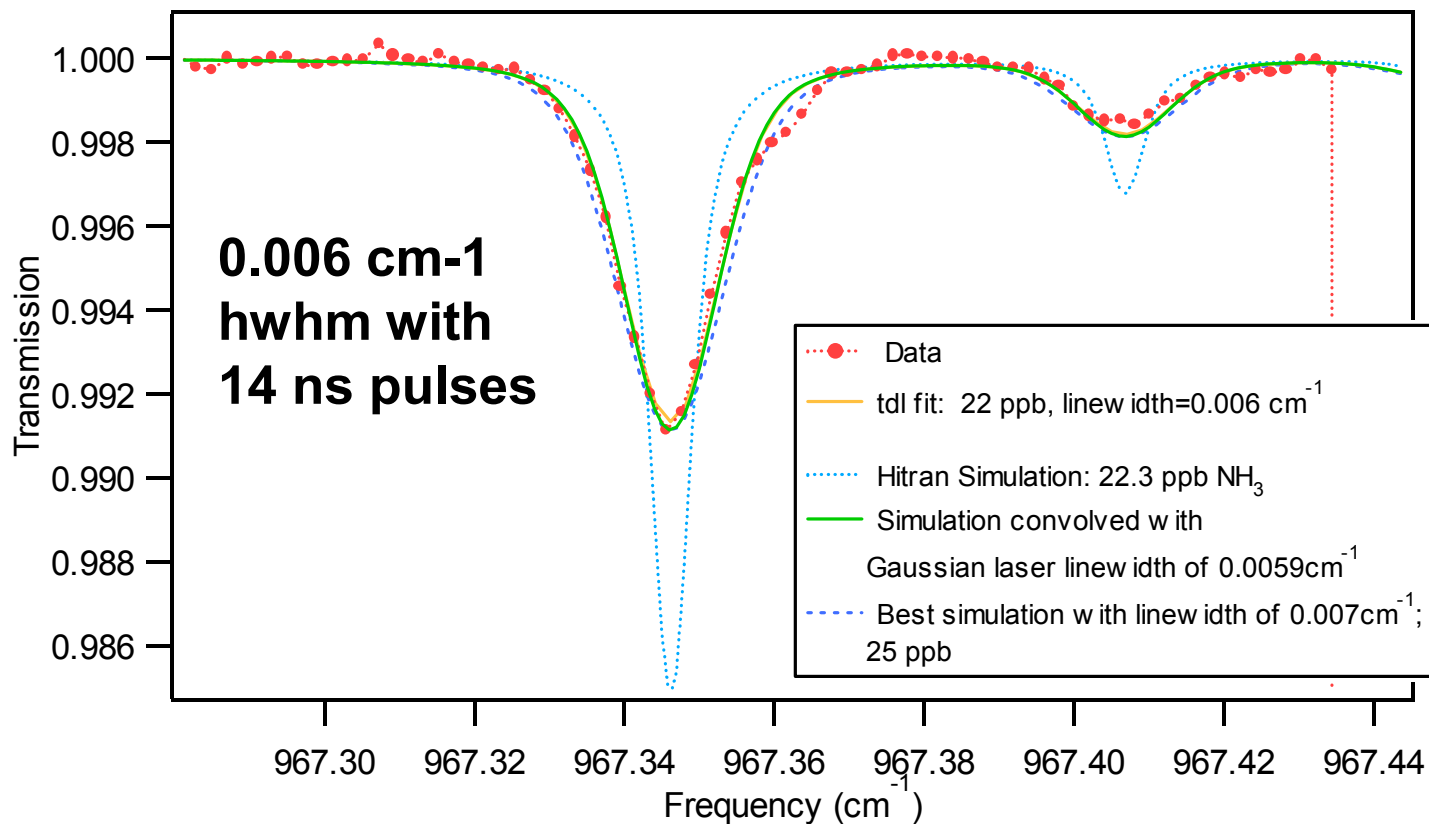
**POTENTIAL FRINGE SUPPRESSION**

# TUNING RANGE OF QC LASER

## Ethylene in Low Pressure Multipass Cell

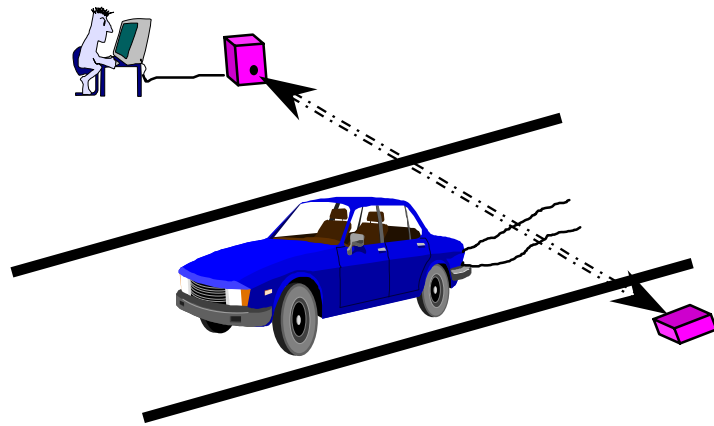


# QC Laser Linewidth



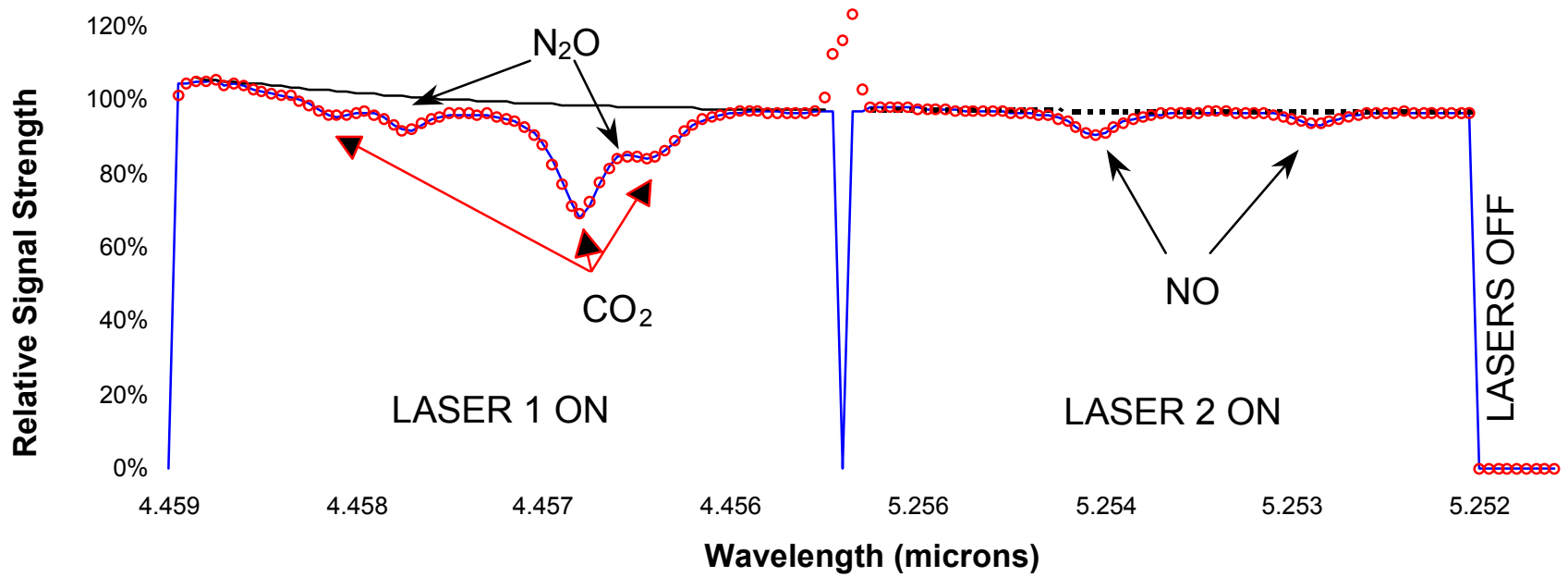
**20 ppb NH<sub>3</sub> in room air  
Pressure 20 torr  
Pathlength 209 m**

# TILDAS Remote Sensing



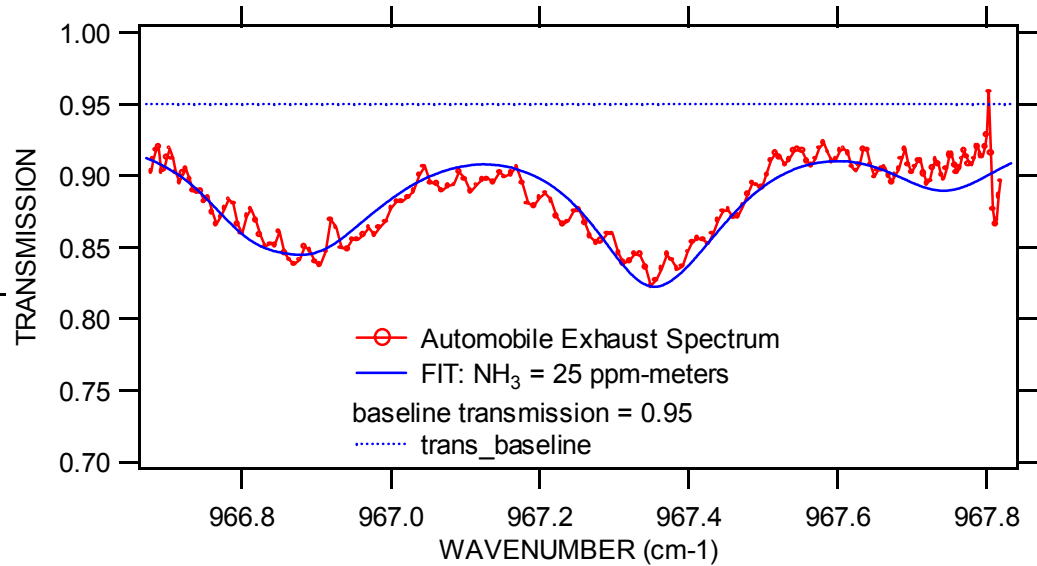
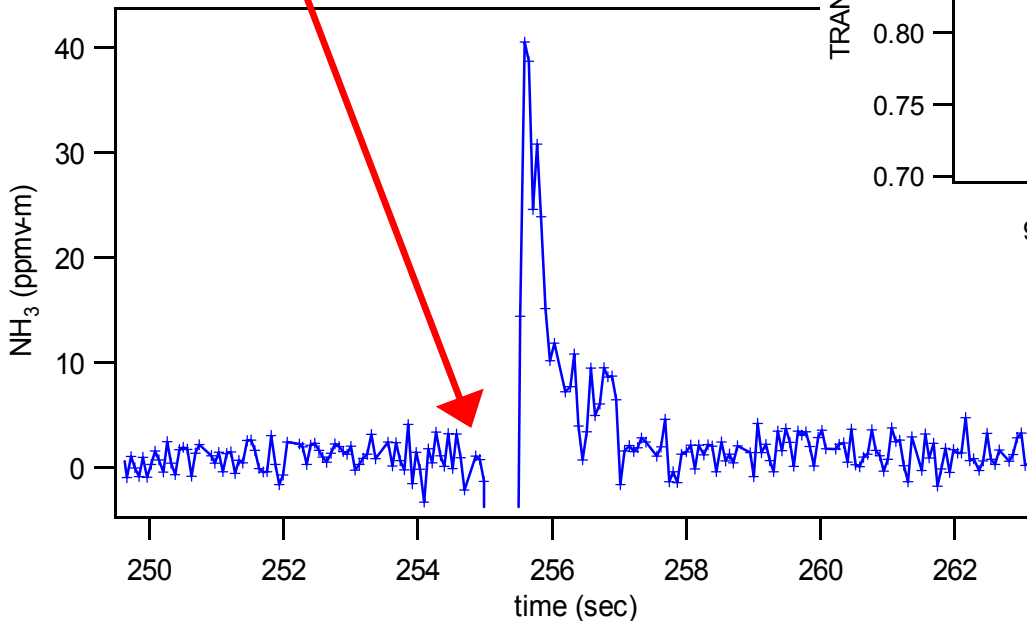
$$\frac{\Delta I}{I_0} = \exp(-\sigma(\nu)NL)$$

Frequency      Path Length  
Absorption Cross-Section      Molecular Density



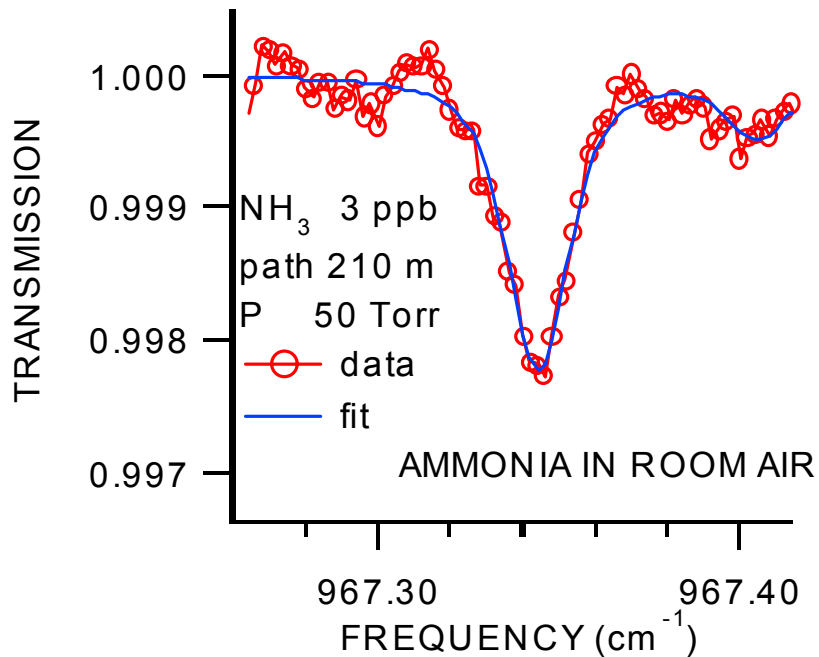
# NH<sub>3</sub> in Automobile Exhaust

**CAR CROSSES  
LASER BEAM**

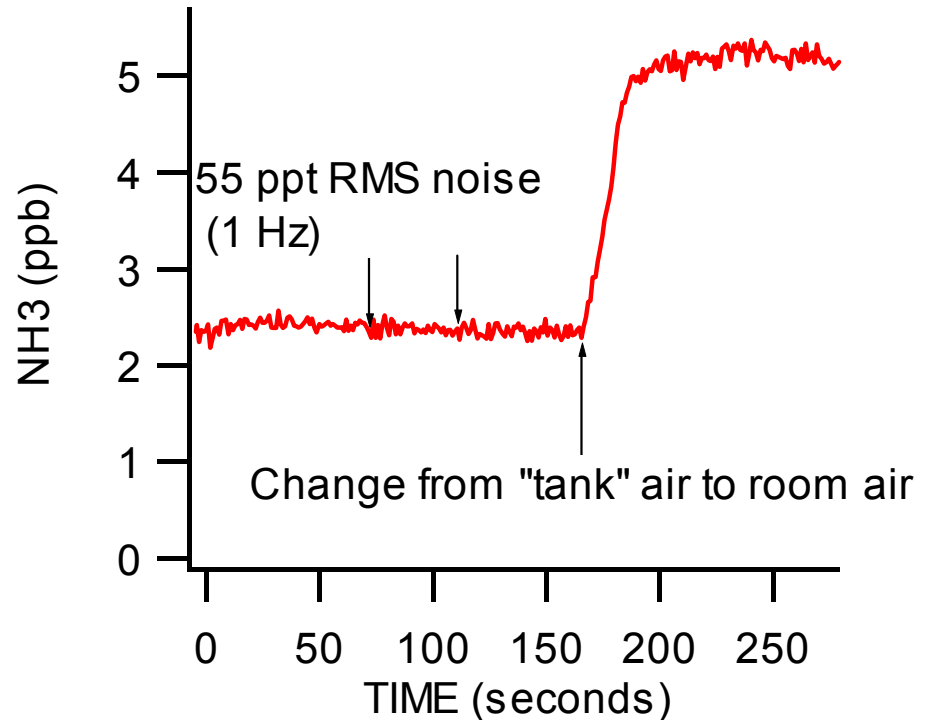


**EXHAUST NH<sub>3</sub>  
~200 ppm**

# AMMONIA DETECTION in ROOM AIR



**Path Length 210 m**  
**Line Width 0.006 cm<sup>-1</sup>**  
**(180 MHz)**



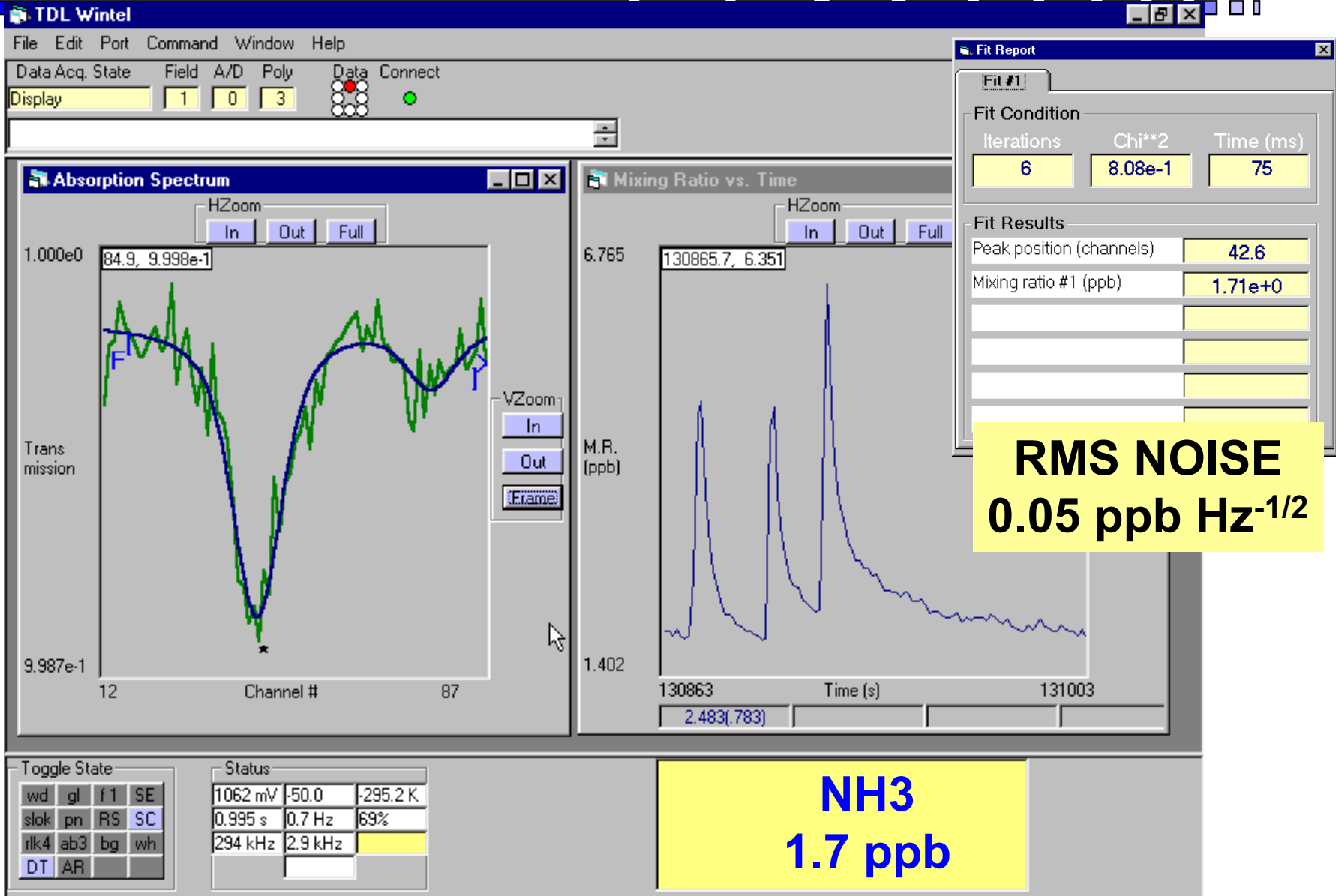
**PRECISION**  
**55 ppt Hz<sup>-1/2</sup>**  
**3x10<sup>-5</sup> absorbance**

# Signal Processing Software

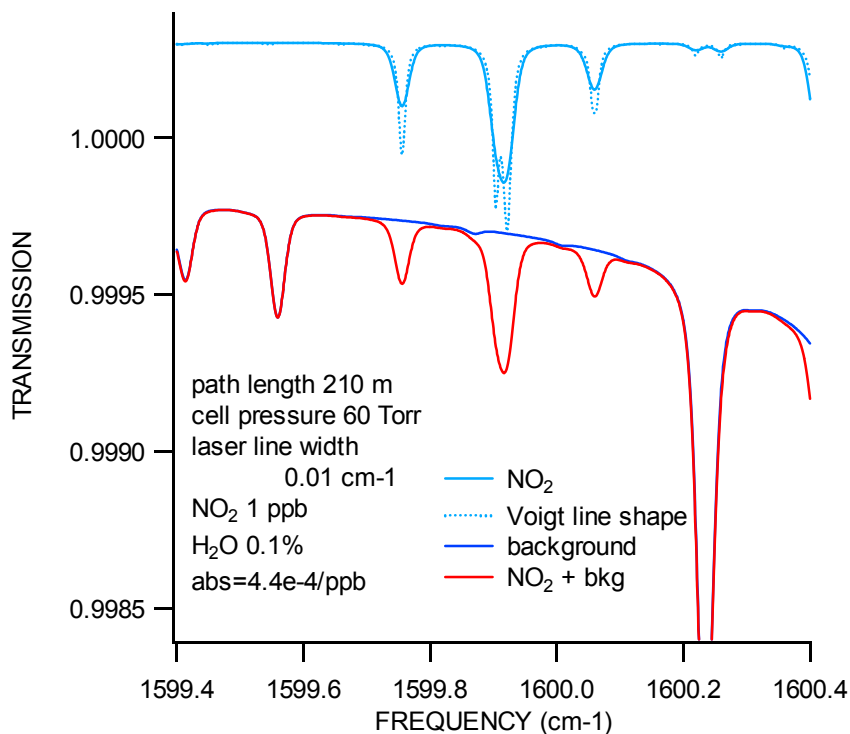
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- Sweep integration with 100% duty cycle
- CW or Pulsed Laser
- Pulse height normalization
- Spectral scans two lasers
- Automatic background subtraction
- Absolute species concentrations determined by nonlinear least squares fit
- Interfaced with HITRAN spectral database
- Steady state data rate: 20 Hz
- Burst mode data rate: > 10 kHz

# SIGNAL PROCESSING SOFTWARE



# PROJECTED DETECTION LIMITS



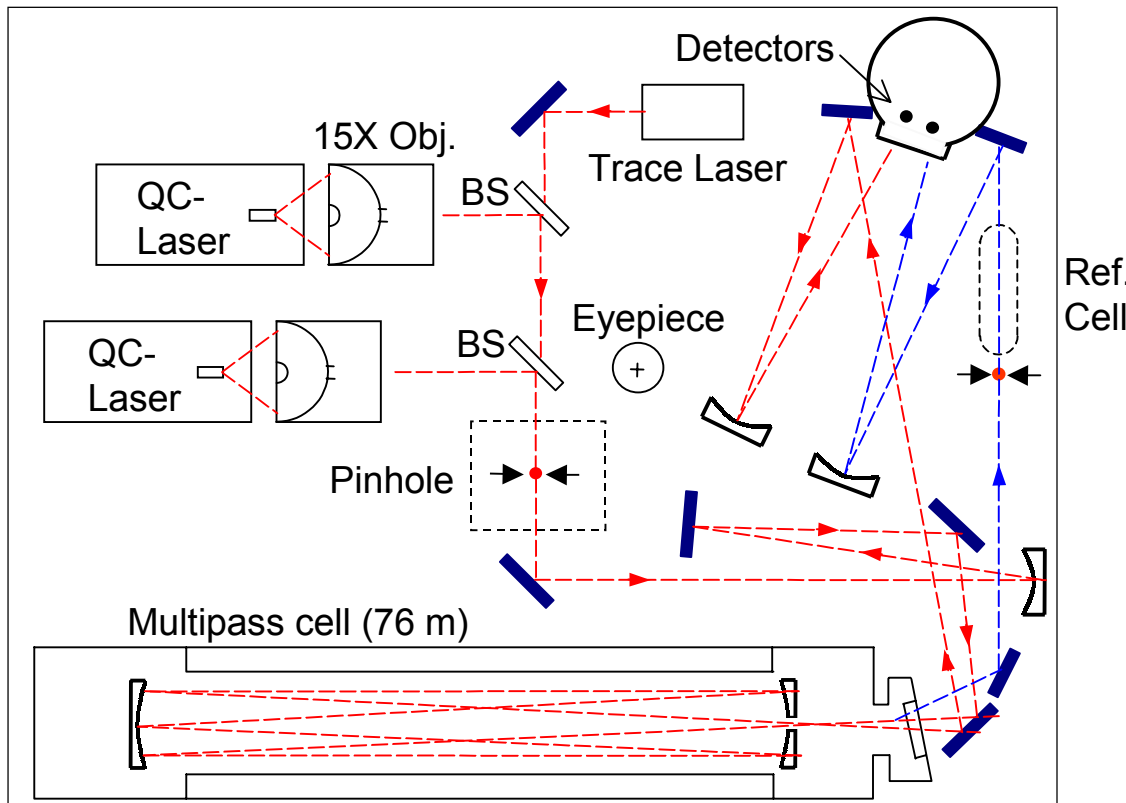
**HITRAN TRANSMISSION  
SIMULATION for NO<sub>2</sub>**

Species	cm <sup>-1</sup>	Precision 1 s RMS	LOD 100 s
NH <sub>3</sub>	967	50	20
NO <sub>2</sub>	1600	80	40
OCS	2060	100	40
CO	2190	120	50
N <sub>2</sub> O	1306	180	70
HNO <sub>3</sub>	1720	200	80
C <sub>2</sub> H <sub>2</sub>	1365	230	90
NO	1905	270	110
CH <sub>4</sub>	1306	290	115
SO <sub>2</sub>	1370	310	120
C <sub>2</sub> H <sub>4</sub>	950	360	140
HCHO	1764	350	140
H <sub>2</sub> O <sub>2</sub>	1267	1000	400

**10<sup>-12</sup> v/v (ppt)  
Limits of Detection for S/N=2  
Path Length 210 m**

# COMPACT DUAL-QCLAS

40 x 50 cm



Cell 76 m; 0.5 liters

Precision  
ppb Hz<sup>-1/2</sup>

CH <sub>4</sub>	0.8
N <sub>2</sub> O	0.5
CO	0.5

Applications:  
Eddy Fluxes  
Atmospheric Tracers  
Pollution Monitors

# Pulsed-QC vs TDL

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- No Cryogenics
  - Good mode quality
  - Excellent stability
  - High power  $>1$  mW
  - Reduced fringes
    - lower drift
    - longer paths
    - lower volume
  - Off-gate for zero
- Narrow line widths
    - $<.001$  vs  $.006$   $\text{cm}^{-1}$
  - Wide tunability
    - $200$  vs  $2$   $\text{cm}^{-1}$
  - Established user base
  - Proven longevity with continuous operation

# CONCLUSIONS

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- **PULSED QC LASERS CAN PROVIDE CRYOGEN-FREE ATMOSPHERIC TRACE GAS DETECTION WITH BOTH OPEN AND CLOSED PATH SAMPLING**
- **DETECTION SENSITIVITY WITH PULSED-QC LASERS CAN BE COMPARABLE TO *cw* TDLs**
- **TECHNIQUES DEVELOPED FOR TDLs ARE DIRECTLY APPLICABLE TO QCLS**
- **IMPROVEMENTS ARE EXPECTED WITH NARROWER LINEWIDTHS AND IMPROVED PULSE NORMALIZATION**
- **POTENTIAL FOR COMPACT INSTRUMENTATION AND REMOTE OPERATION FOR ATMOSPHERIC AND INDUSTRIAL PROCESS MONITORING**

# Acknowledgments

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- Daniel Hofstetter

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- ◆ Purdue University
- ◆ Institute for Low Temperature Plasma Physics, Greifswald
- ◆ Philip Morris Inc. USA
- ◆ Shell Research Ltd. UK

- ◆ **US EPA, NSF, NASA, DOE**

**Small Business Innovation Research Programs**