Multiplexed Sensor for Synthesis Gas Composition and Temperature

DOE University Coal Research Project

Initiated September 2004

Steven G. Buckley, Reza Gharavi, Marco Leon, and Ariel Schuger

Department of Mechanical and Aerospace Engineering

University of California, San Diego

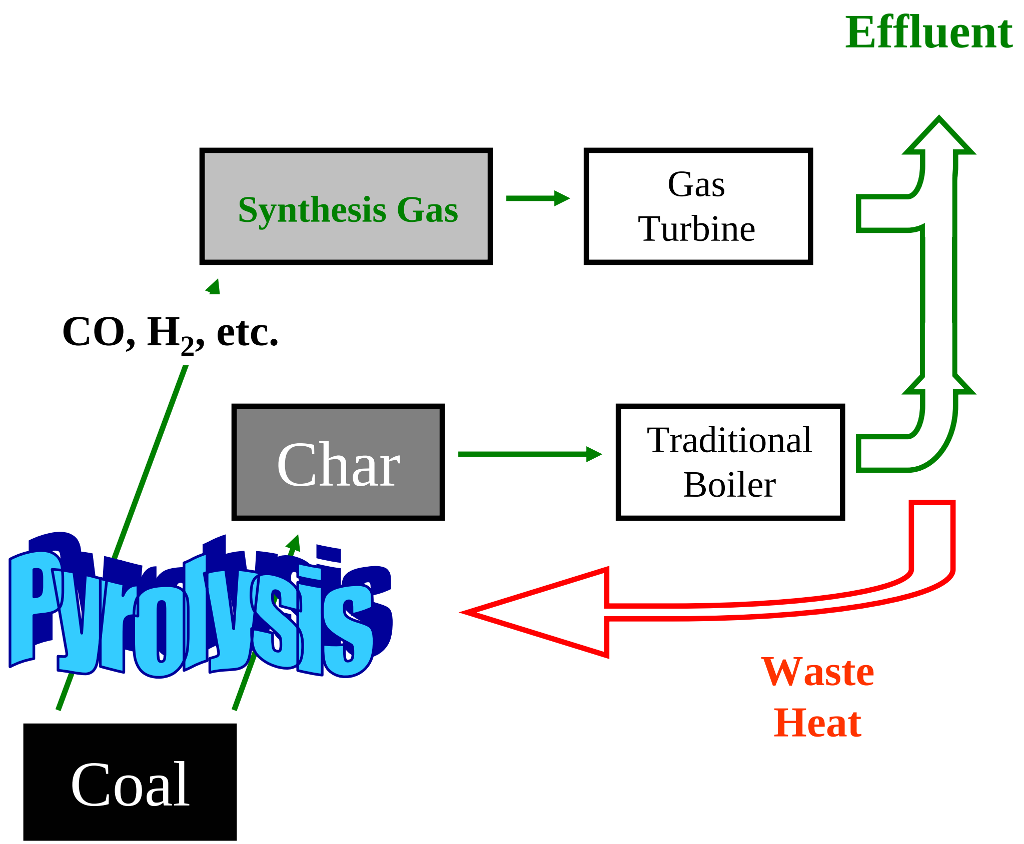
Contractors Meeting June 7-8, 2005

Outline of talk

- Introduction and motivation
- Description of the sensing technique
- Special challenges for high-pressure, high temperature measurements
- Design of sensor
- Progress on measurements
- Upcoming work

The promise of gasification

- "Baseline" coal plants are ~ 33-35% thermal efficiency
- Integrated combined-cycle plants may exceed 50% thermal efficiency
- May aid in CO_2 sequestration



The goals of this project

- **Integrated high-speed sensor that can measure composition of important major and minor species in real time and *in situ*.**
- ***<u>Targeted species</u>*: CH_4, H_2O, CO, CO_2, NH_3, H_2S**

➔ **Challenges**

- High, variable temperature
- High, variable pressure
- Sensitivity with short pathlength
- Rugged design

Benefits to tunable diode laser approach

- **Near-infrared tunable diode lasers have been developed by large telecommunications investment**
  - Relatively inexpensive hardware
  - Durable hardware
- **Direct optical measurements are obtained in real-time without perturbations to concentrations that might occur in a sampling system**
- **Measurements can easily be performed at several hundred Hz**
- **Laser light can be multiplexed and fiber-coupled**
- **Multiple species can be simultaneously measured with one detection system**

Familiar ground: Absorption spectroscopy

- **Beer's law**

$$\frac{dI(\bar{\nu})}{I_0(\bar{\nu})} = -k(\bar{\nu}) \cdot C \cdot dx$$

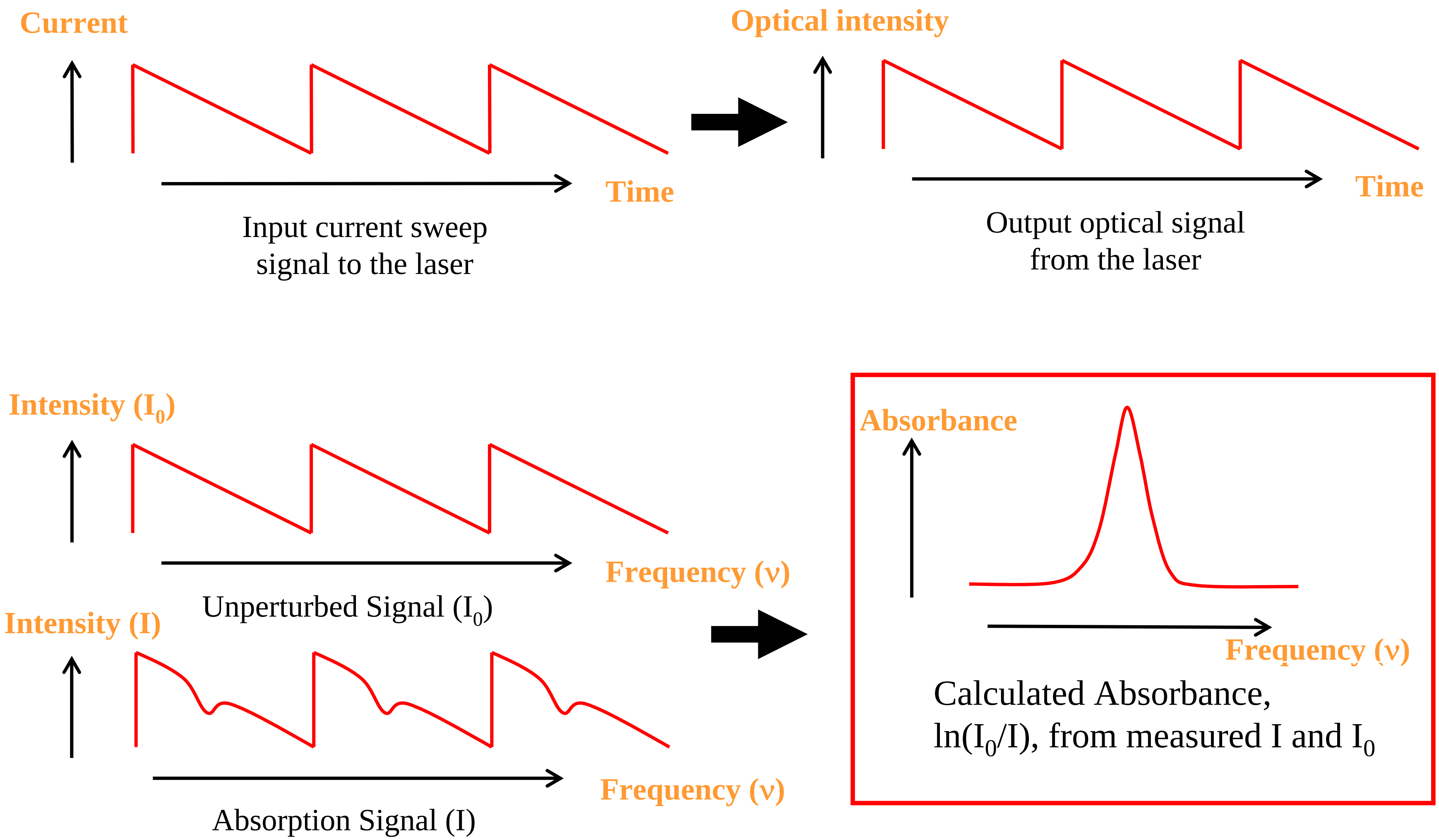
- **Concentration measurements**
  - Integrated absorption of spectral line

$$\bar{A} = \int_{line} k(\bar{\nu}) C L d\bar{\nu} = \bar{k} C L$$

  - Calibration

$$C_{sample} = \frac{\bar{A}_{sample}}{\bar{A}_{calibration}} \cdot C_{calibration} \cdot r_{path}$$

Theory of absorption spectroscopy



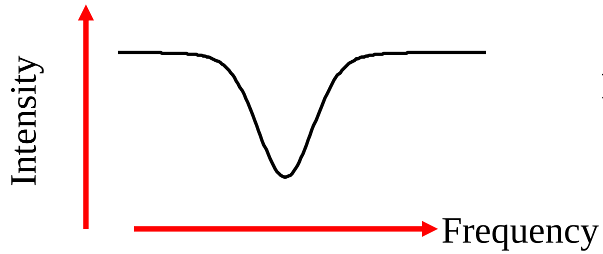
Key: Wavelength Modulation Spectroscopy (WMS)

Problem: difficulty in detecting a small dip in a large signal, particularly with a fluctuating background

- **Attributes of WMS**
  - Increases sensitivity by 2-3 orders of magnitude
  - Eliminates most flow-related sources of noise
  - Allows frequency-domain multiplexing and demodulation

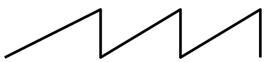
Direct absorption vs. "Wavelength modulation"

Typical absorption line shape



Function of collisional and Doppler broadening (Lorentzian shape) + (Gaussian shape)

Direct absorption



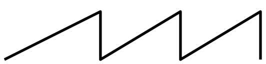
50 - 1000 Hz sweep of laser current

$$I / I_0 = \exp(- S_T g(\nu - \nu_0) L P_{abs})$$

Beer's law absorption

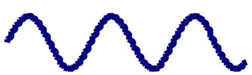
Problem: measurement of small signal on large background

Wavelength modulation



50 - 1000 Hz sweep of laser current

+



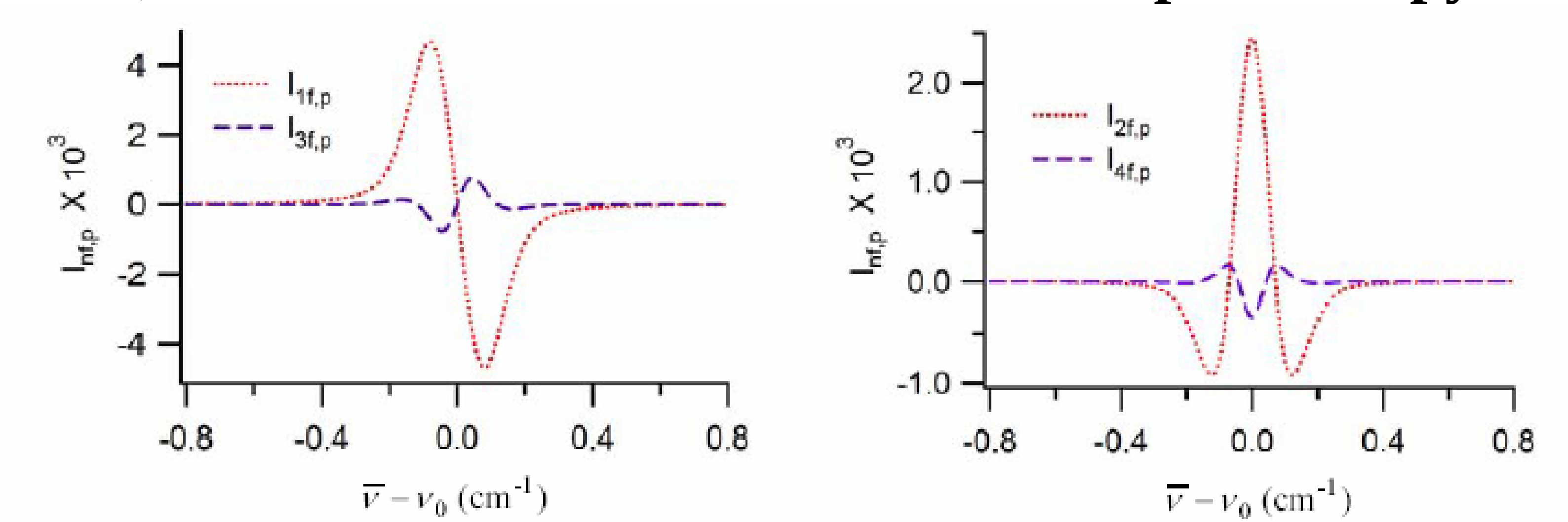
kHz rates modulation

- Modulation rejects flow-related noise, electrical noise, etc., typically 1/*f*
- Detection of 1*f*, 2*f*, etc. signals with lock-in amplifier

How WMS works

Generate driver signal → Laser controller modulates laser drive current → Laser frequency is modulated → Light is absorbed → Detector catches light → A lock-in amplifier compares detected signal with driver signal

- **Harmonic signals look like derivatives of the absorption line, hence sometimes called “derivative spectroscopy”**



How is the signal processed?

$$I_{2f} = I_0 \cdot H_2(\nu-\nu_0) \cdot S_T \cdot g(\nu-\nu_0) \cdot L \cdot P_{abs}$$

Measured signal

Initial intensity

Fourier coefficient (known function of amplitude of modulation and line width)

Absorption coefficient has two parts – a temperature-dependent line strength S_T, and a line shape function g

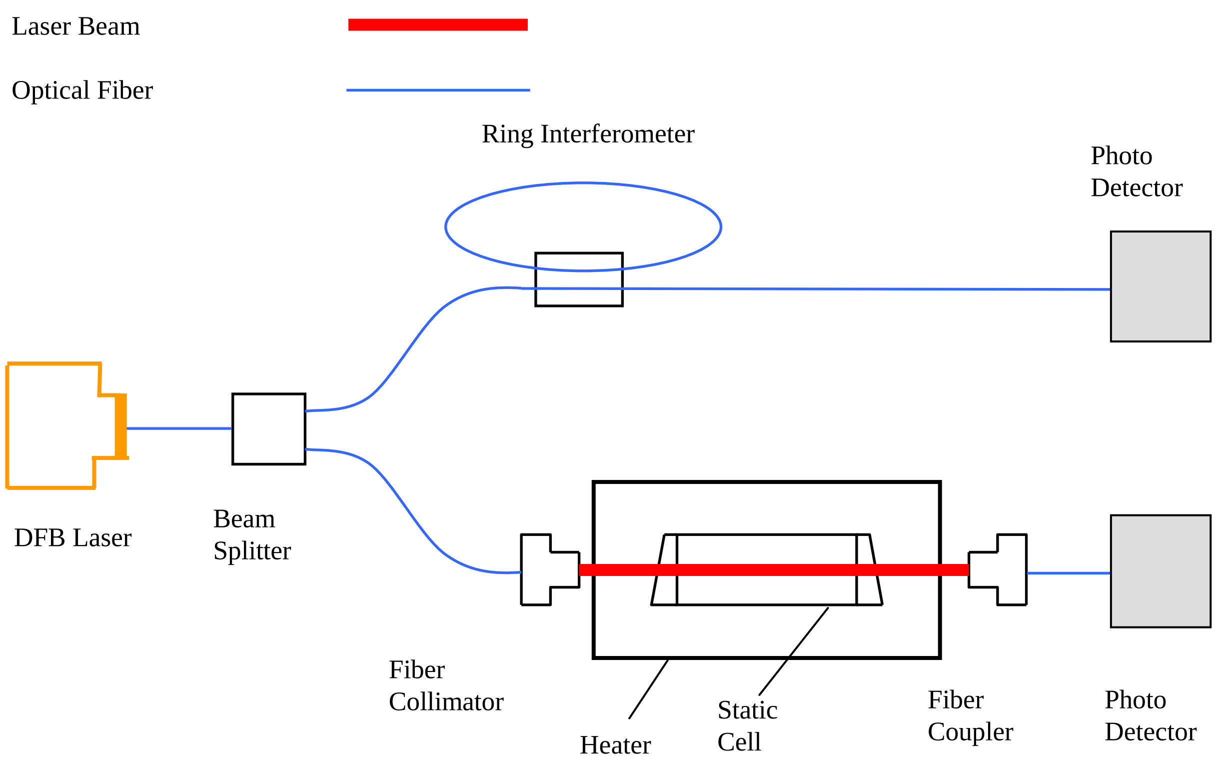
Path length (known)

Pressure of the absorbing species – what we want to find out

Line strength and line shape are functions of T and P, must be known to quantify WMS signal…

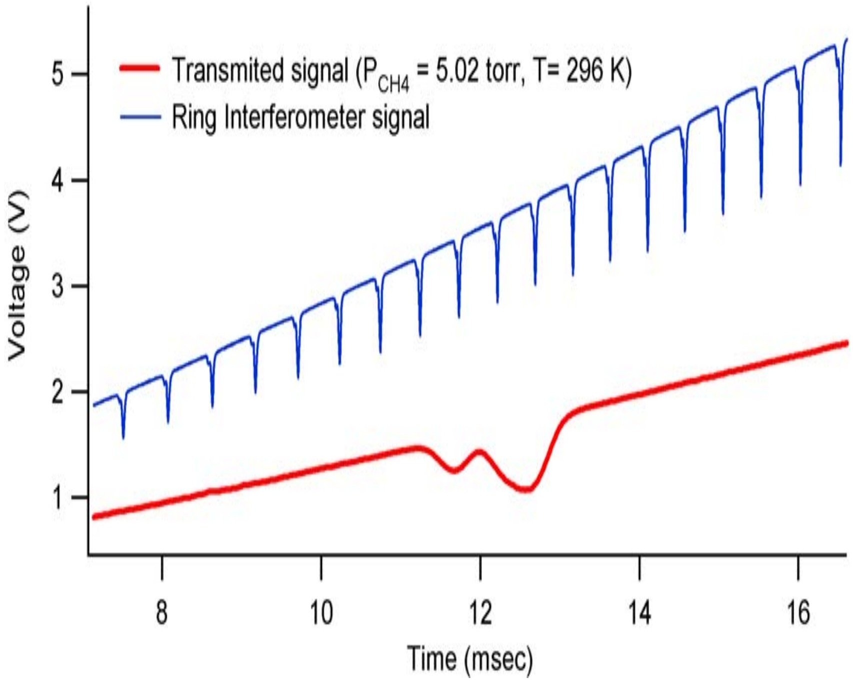
Experiments measure the temperature and pressure broadening characteristics of each absorption line

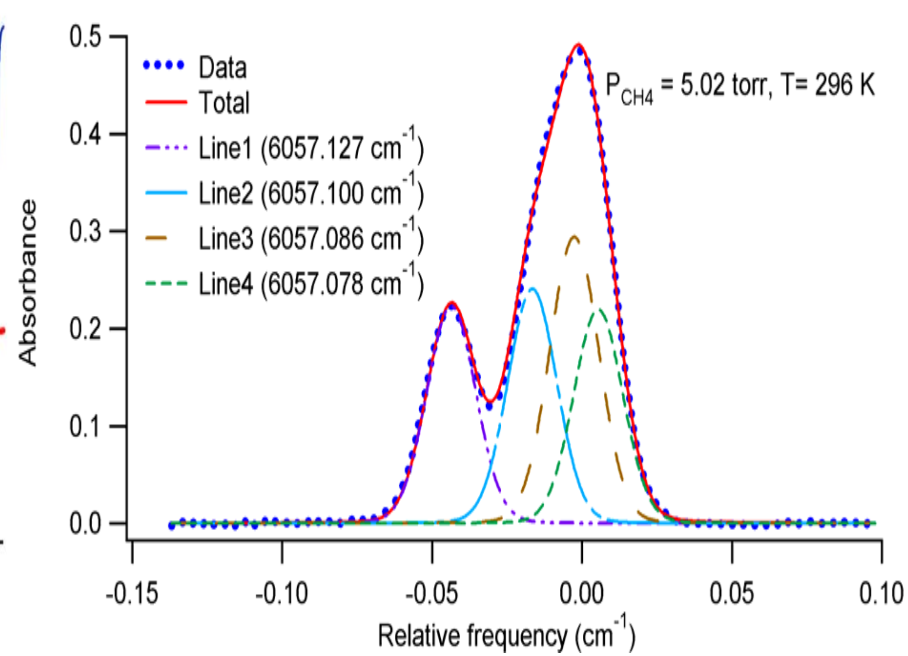
- **Schematic of the experimental apparatus for line strength and pressure broadening measurements (at different temperatures) is shown below**



Example: Line strength measurements as a function of temperature

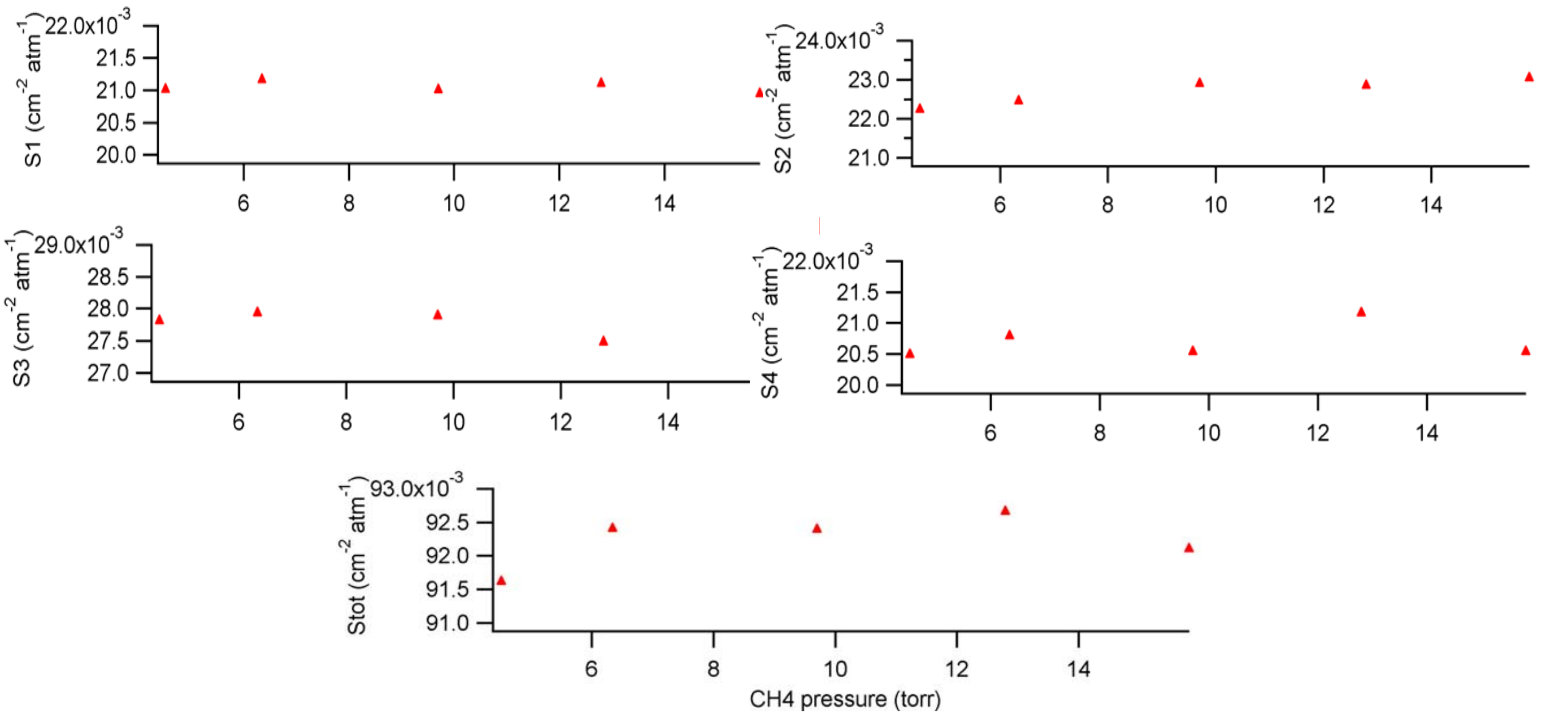
- **Measurements of R(4) CH_4 transition are fit to model to derive line strengths as a function of temperature**





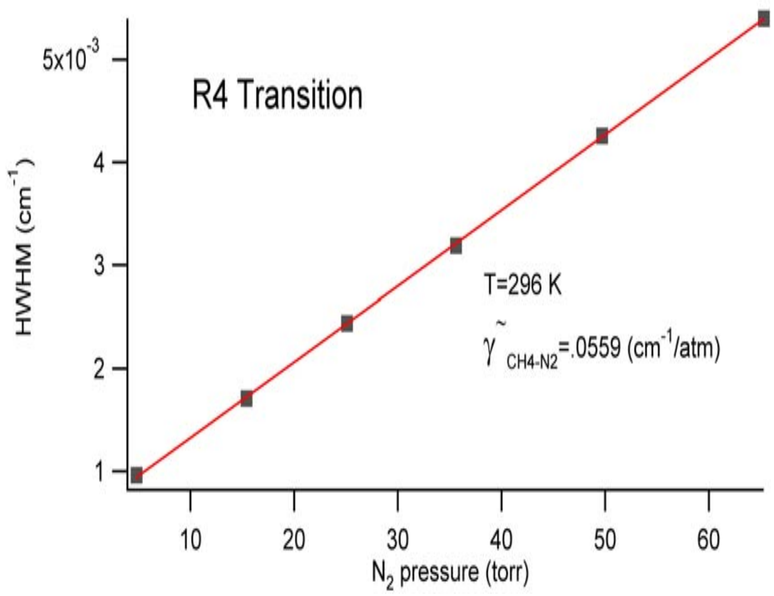
Example: Line strength measurements as a function of temperature

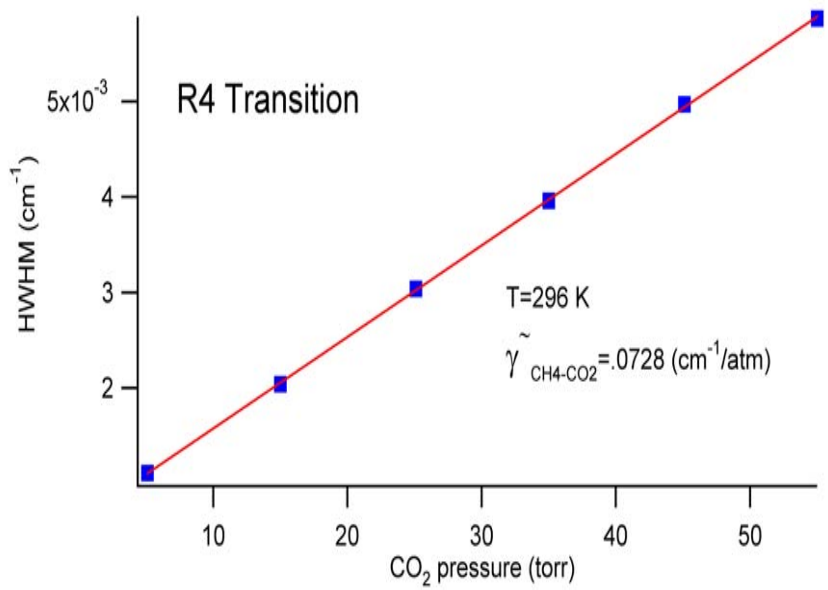
- **Measured individual line strengths of CH_4 R(4) manifold at T=296 K (Should be pressure-independent)**



Example: Pressure broadening measurement for CH_4 transitions

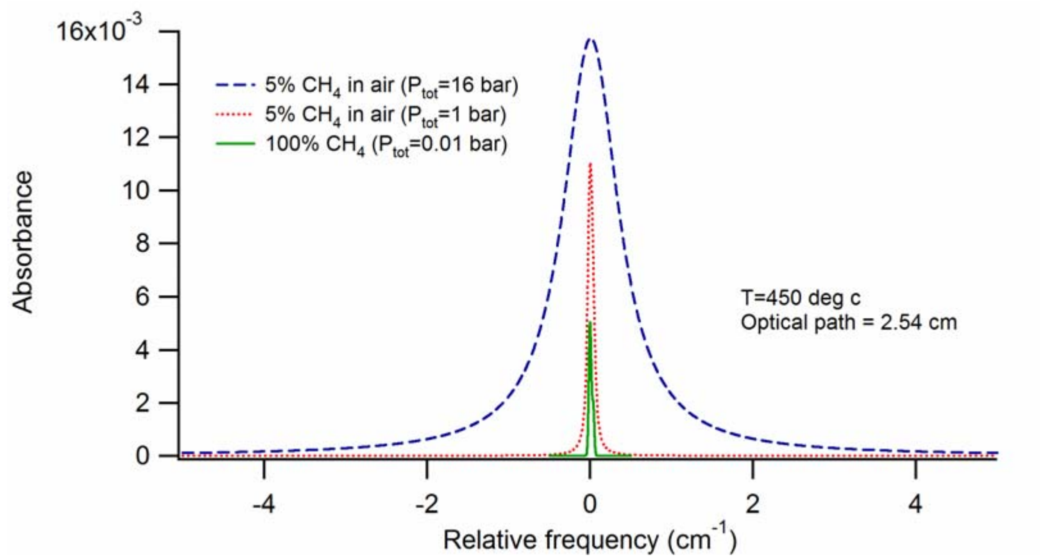
- **Each gas component in the mixture contributes independently to line broadening – must be measured**





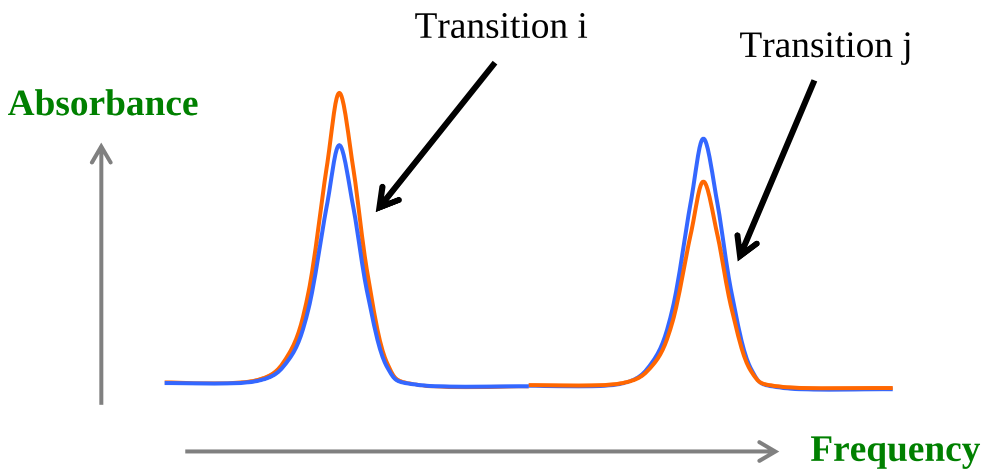
WMS at high pressure: Line-locked measurements

- **Increased broadening dramatically increases line width at high pressures**
- **Most near-infrared TDLs only tune 1-2 cm^{-1}**



- **Solution – eliminate the "sweep" signal, only modulate the laser about the line center**
- **Relies on having very accurate models of the line for interpretation of the signal**

TDL-based temperature measurements

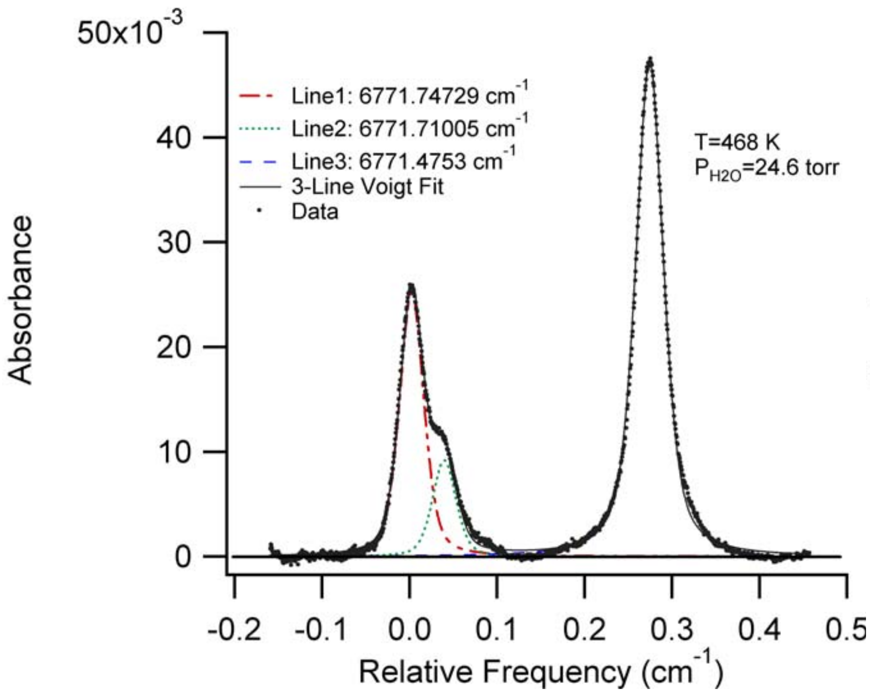


Schematic variation of line strength of two absorption lines with temperature

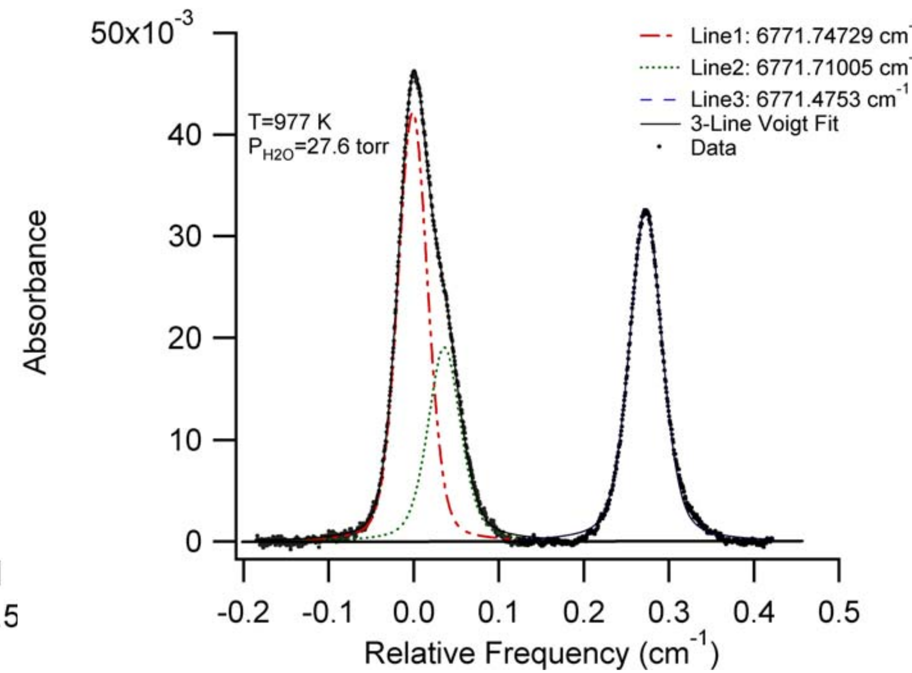
$$R_{abs}(T) = \frac{S_i(T)}{S_j(T)}$$

TDL H_2O / Temperature measurement

Measured absorbance of selected H_2O transitions (near 1478 nm) at two different temperatures



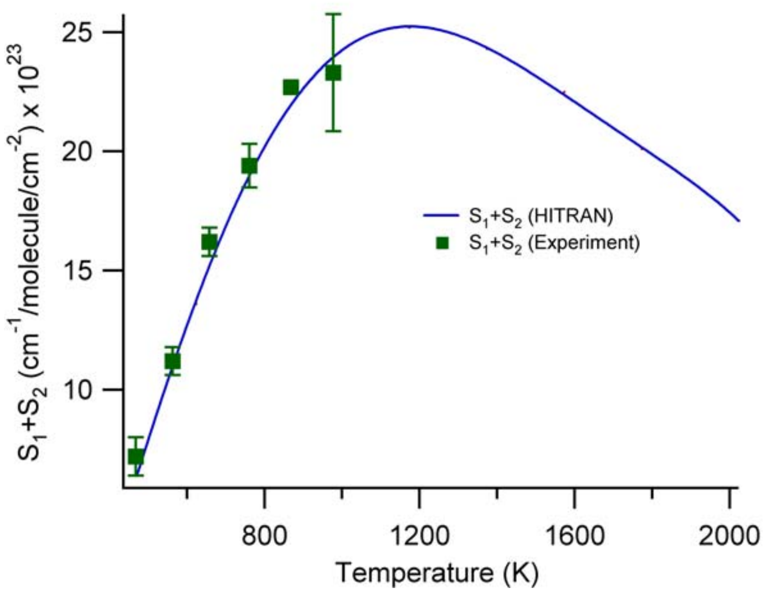
At T1=468 K

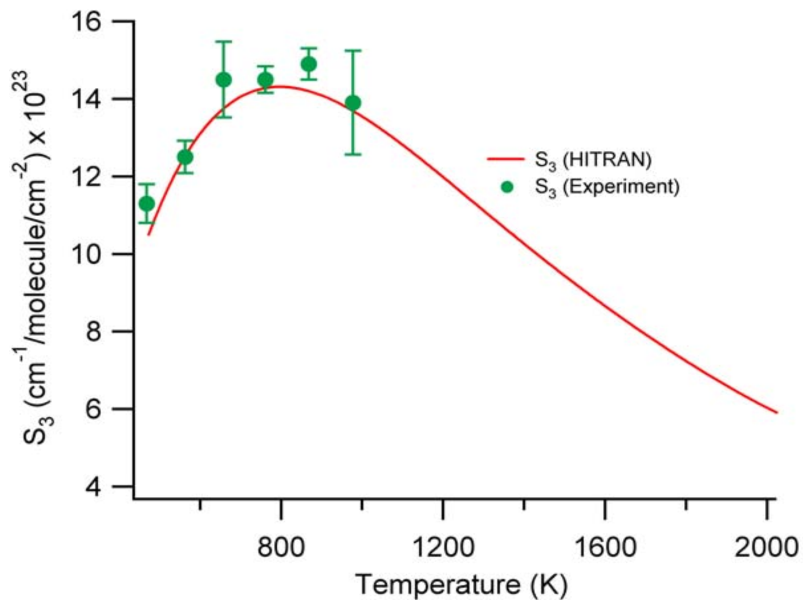


At T2=997 K

TDL H_2O / Temperature measurement

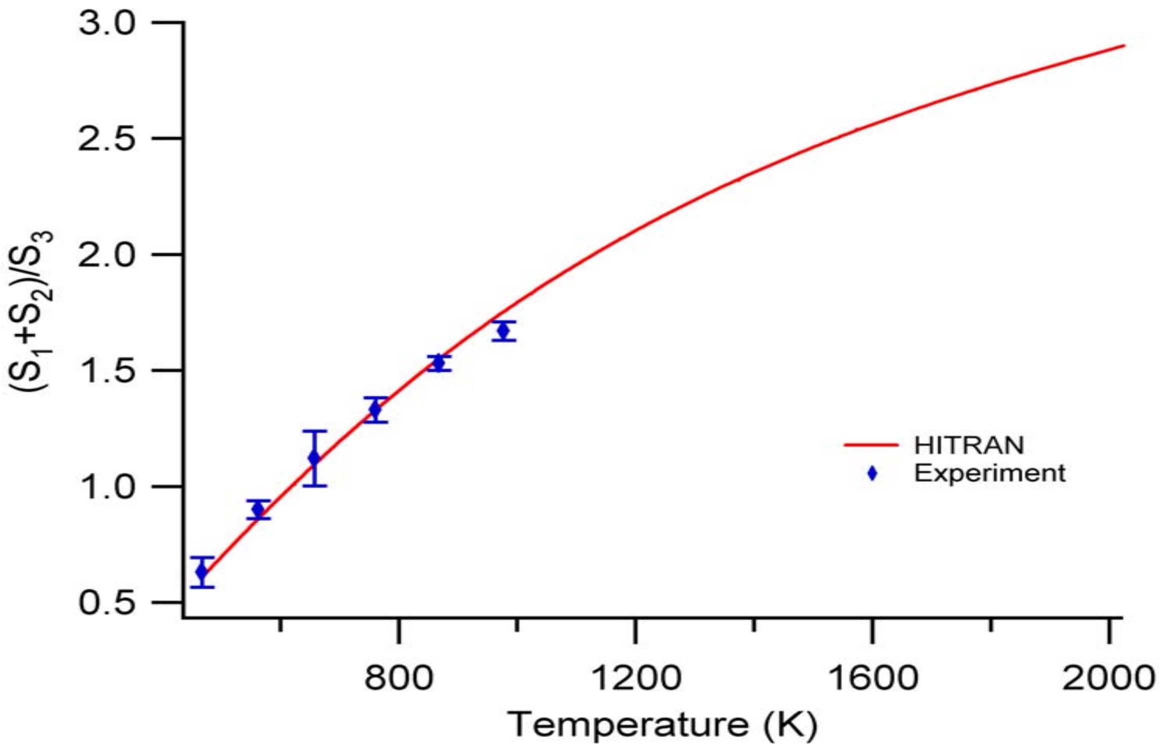
Measured absorption line strengths of the selected H_2O transitions vs. temperature



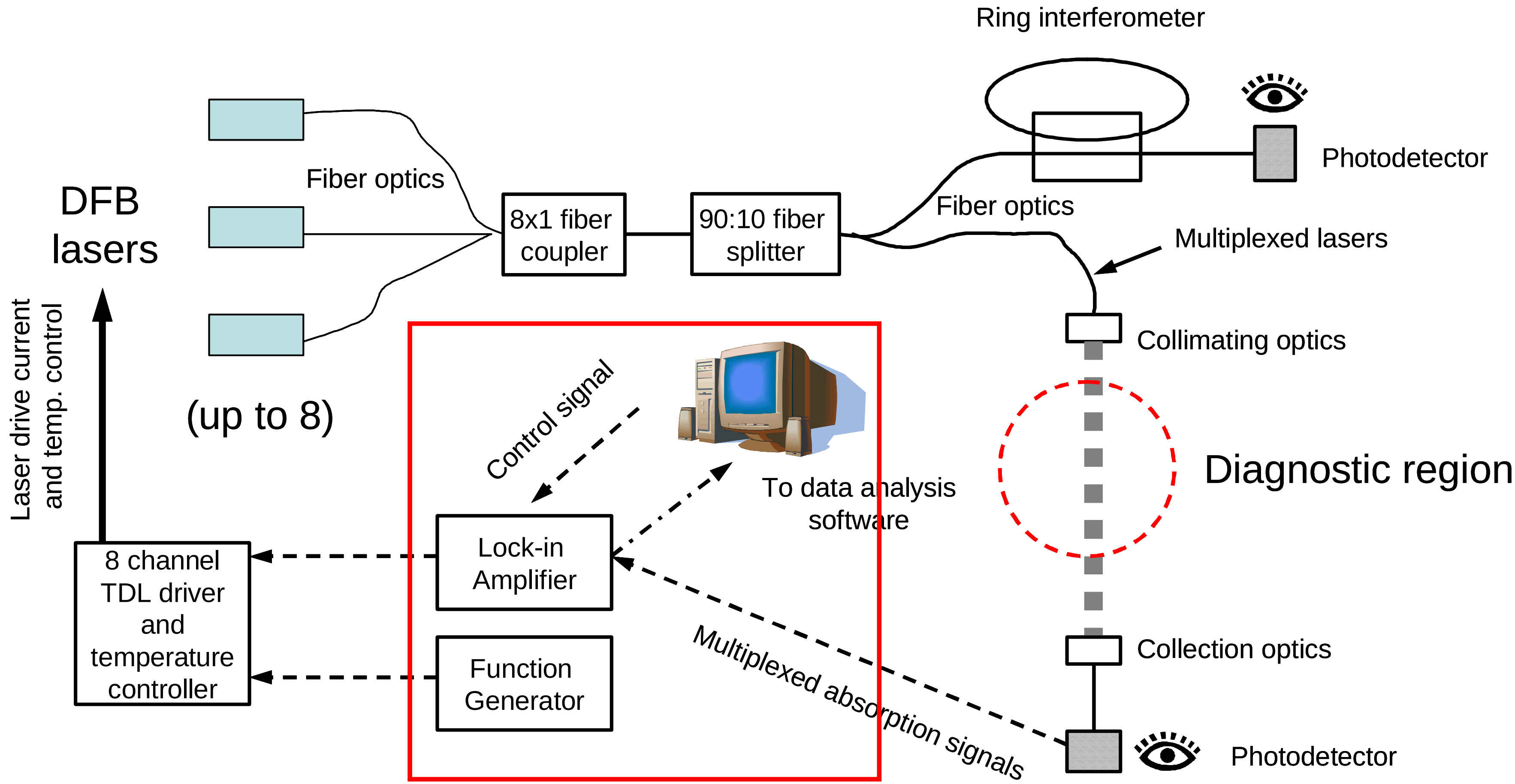


TDL H_2O / Temperature measurement

Variation of absorption ratio vs. temperature



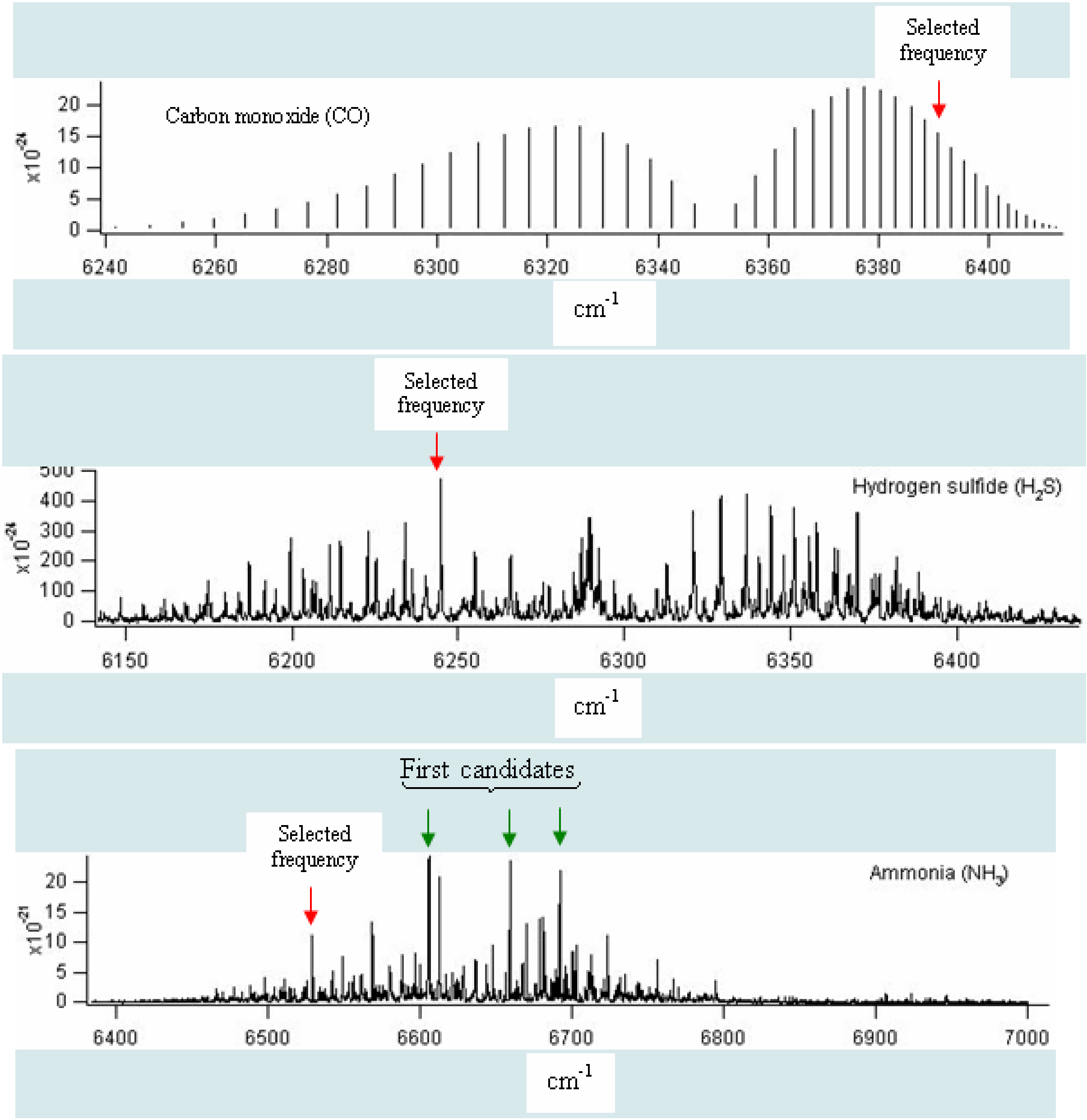
Overall sensor architecture



All to be done in Labview™

Progress to date in sensor development

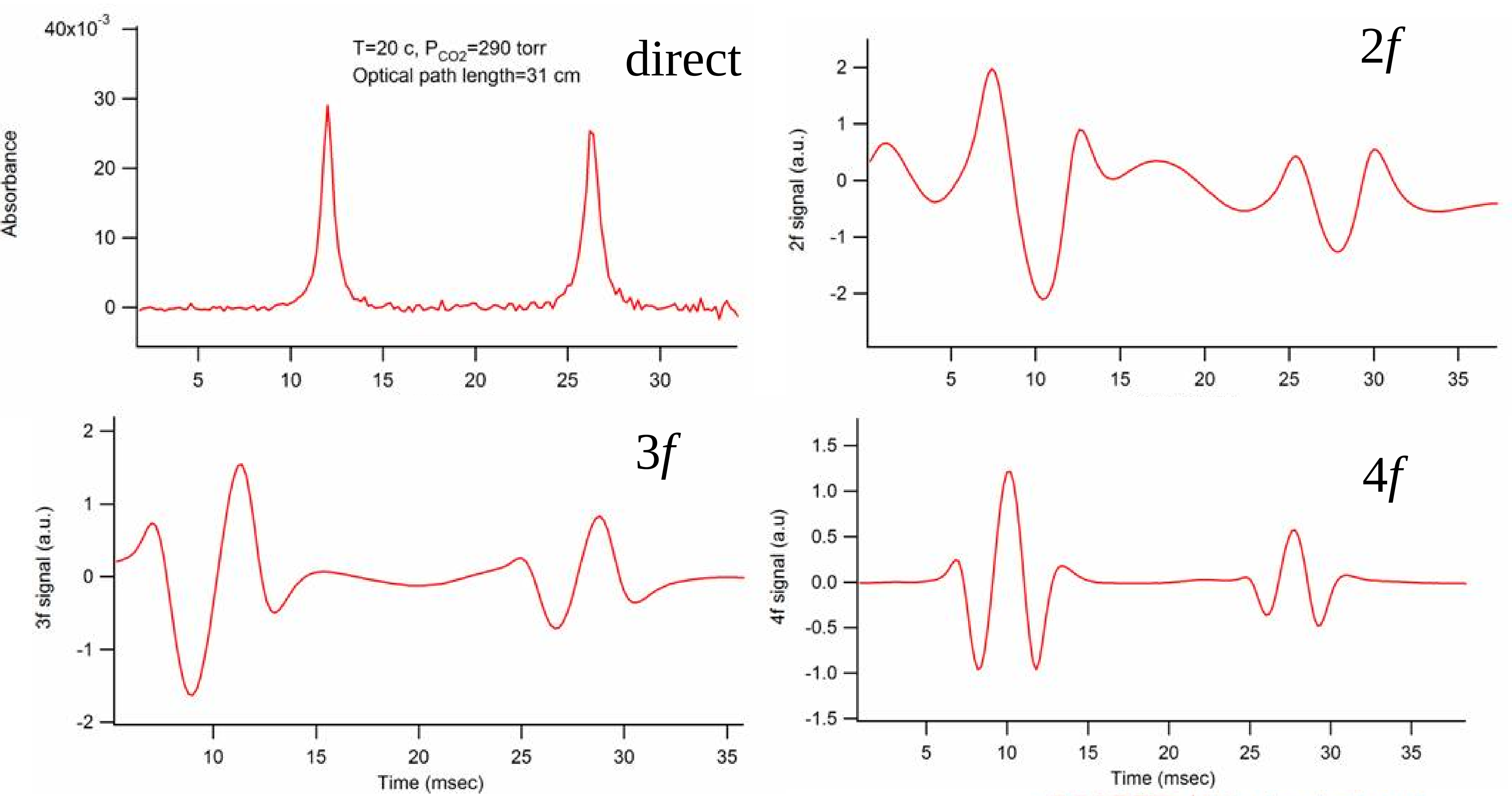
- **Lasers for H_2O and CH_4 have been in-house**
  - We have complete pressure broadening and temperature data for these species
- **New lasers for CO and CO_2 have arrived**
  - Initial spectra have been acquired, characterization of pressure broadening and temperature data is proceeding
  - A new high-pressure cell is being constructed for high pressure measurements
- **Lasers for H_2S and NH_3 have been ordered**
  - A cell and flow system for these toxic gases that will fit inside our chemical fume hood is being constructed



Laser selection

- Modeled and experimental spectra are consulted to find best lines in near infrared
- Lines are checked for interferences from H_2O and other gases
- Laser manufacturers are contacted to determine laser availability

Comparison of direct absorption, 2f, 3f, and 4f signals of 200 torr CO_2 with new laser

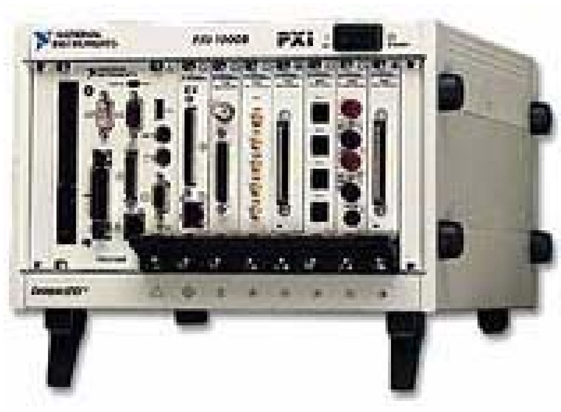


Progress to date: Design and construction

- **Two electronic boxes have been designed, built, and tested**
  - a modulation box that takes a single sweep input and superimposes 4 modulation signals of fixed frequency and variable amplitude
  - a reference box that normalizes the detector signal by the input laser power to correct for fluctuations and nonlinearities in the laser signal
- **Laser driver modules have been ordered and received**
- **Optical components (splitters, etc.) have been ordered and received**

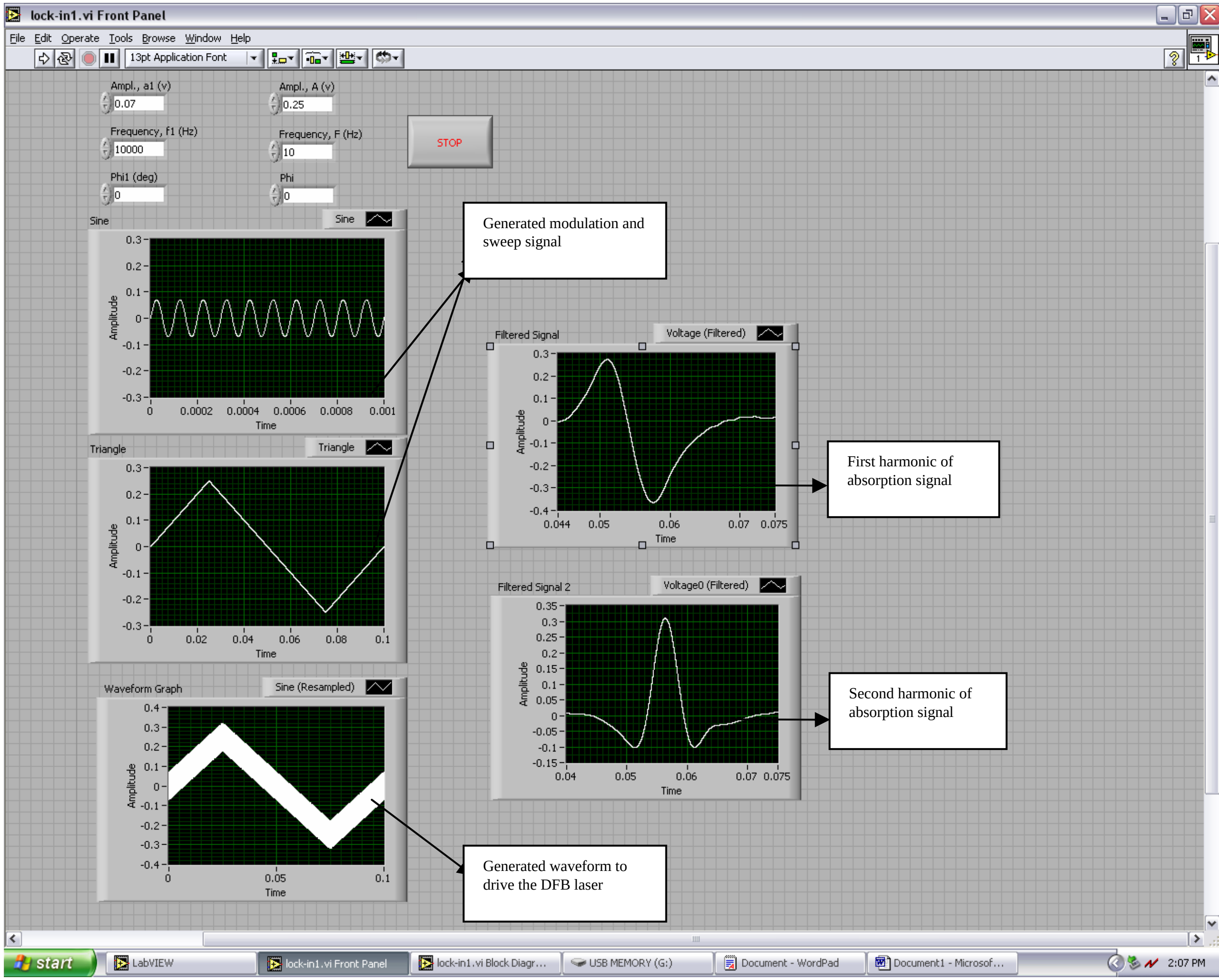
New National Instruments data acquisition system has been received and is being configured

- **PXI system has integrated Windows™-based microprocessor, 6 channels of 500 kHz analog input and 2 channels of analog output**
- **Completely configurable using Labview™ graphical programming language designed for data acquisition**
- **Enough horsepower to do some real-time computations**
- **Rugged and portable**



Labview™ code for generation of driver signals and detection of harmonic signals

- **Generates sweep plus sinusoid**
- **Performs lock-in detection on detected signal**



Key results

- **H_2O, temperature, and CH_4 have been simultaneously measured and quantified at high temperature using collisional broadening and line strengths measured in the laboratory**
- **CO_2 and CO spectra have been obtained, measurements of parameters is proceeding**
- **Architecture is set, hardware components are being designed and are coming together well**
- **Labview™ lock-in program coupled with new data acquisition system has been successfully tested**
  - This has the potential for eliminating many (expensive and large) lock-in amplifiers

Upcoming milestones

- **High temperature / pressure measurements for CO and CO_2**
- **Initial H_2S and NH_3 spectra, limited temperature and pressure-broadening information for these (toxic) molecules**
- **Labview™ program designed to accommodate all of the species / lasers**
- **Field trial on campus gas turbine**
- **Final – measurements on an operating gasifier**
  - Have been in touch with Dr. Tom Gale at the Southern Company gasifier about the potential for measurements there

Field Trial in August

- The UCSD campus (~23,000 students, 1,200 acres) generates most of its own power using 2 Solar Turbines Titan 130, 13 MW gas turbines
- UCSD internal funding will support real-time measurements on the turbines for emissions monitoring and oscillation detection
- Tentatively planned for August, 2005
- CO, CO_2, CH_4, H_2O, temperature, and possibly NH_3 will be monitored

Summary and Conclusions

- First 9 months of project are on track with respect to research and development goals
- Hardware development and spectroscopy development anticipated to be hard work but with no major hurdles
- New Labview™ data acquisition will replace a lot of hardware and make the system much more versatile and compact

Thanks for your attention!

We appreciate the kind assistance of our program manager Robie Lewis and the support of DOE on this project!