

Final Technical Report for DOE Grant #DE-FG26-04NT42172

**Multiplexed Sensor for Synthesis Gas**  
**Composition and Temperature**

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## 1. Abstract

The overall goal of this project has been to develop a highly sensitive, multiplexed TDL-based sensor for CO<sub>2</sub>, CO, H<sub>2</sub>O (and temperature), CH<sub>4</sub>, H<sub>2</sub>S, and NH<sub>3</sub>. Such a sensor was designed with so-called “plug-and-play” characteristics to accommodate additional sensors, and provided *in situ* path-integrated measurements indicative of average concentrations at speeds suitable for direct gasifier control. The project developed the sensor and culminated in a real-world test of the underlying technology behind the sensor. During the project, new underlying measurements of spectroscopic constants for all of the gases of interest performed, in custom cells built for the project. The envisioned instrument was built from scratch from component lasers, fiber optics, amplifier blocks, detectors, etc. The sensor was tested for nearly a week in an operational power plant. The products of this research are expected to have a direct impact on gasifier technology and the production of high-quality syngas, with substantial broader application to coal and other energy systems. This report is the final technical report on project #DE-FG26-04NT42172. During the project we completed all of the milestones planned in the project, with a modification of milestone (7) required due to lack of funding and personnel.

## 2. Table of Contents

1. Abstract.....	3
2. Table of Contents.....	4
3. Executive Summary.....	5
4. Approach .....	6
4.1 Theoretical Basis for Wavelength Modulation Absorption Measurements ..	6
4.2 Experimental Setup and Instrument Design.....	9
4.2.1 Hardware .....	9
4.2.2 Development.....	10
5. Results.....	11
5.1 Task #1: Parameter selection .....	11
5.2 Task #2: Design .....	13
5.3 Task #3: Construction .....	15
5.4 Task #4: Software .....	16
5.5 Tasks #5 and #6: Temperature and Pressure Development.....	17
5.6 Task #7: Field Testing of the Instrument.....	20
6. Conclusions .....	21
7. Technology Transfer Activities .....	23
8. References .....	24
Appendix A: Spectroscopic data for H <sub>2</sub> O, CO, and CO <sub>2</sub> transitions .....	26
Appendix B: M.S. Thesis of Marco Leon.....	32
Appendix C: Presentation on NH <sub>3</sub> Spectroscopy to FACSS 2006 .....	122

### 3. Executive Summary

This project was to design, build, and test an integrated sensor that could be used to measure and control the products of coal gasification. The first milestone completed was the selection of experimental parameters, particularly the wavelengths for measurement of the desired species ( $H_2O$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ,  $H_2S$ , and  $NH_3$ ). This was accomplished using software databases, careful inspection for interferences, particularly from hot  $H_2O$  bands, and the availability of laser sources.

The design and construction milestones involved hardware design choices, followed by assembling and testing of hardware. The sensor design and construction milestones were completed in the first year of the project, as planned.

The measurement of temperature- and pressure-dependent spectroscopic parameters for the molecules and specific transitions of interest were monumental, time-consuming tasks. For these measurements, several long-path spectroscopic cells (one high pressure, one atmospheric and lower-pressure, two all-glass cells) were designed and built. Full spectroscopic understanding – measurement of all of the relevant pressure broadening and line strength parameters at a range of pressures from 0-10 bar and temperatures up to 800 K was achieved for the  $CO$ ,  $CO_2$ ,  $CH_4$ , and  $H_2O$  transitions selected for the sensor. Detailed and difficult similar measurements were also completed for  $NH_3$ . Based on these measurements, highly accurate concentration measurement of these five gases is possible. Based on a more limited set of parameter measurements, qualitative measurement of  $H_2S$  is also possible. The gas-handling requirements related to the toxicity of  $H_2S$ , plus difficulties in achieving a repeatable and stable  $H_2S$  concentration in the gas cell (due to the molecular polarity) ultimately hindered our ability to get exact spectroscopic data for  $H_2S$ .

A combination of real-world testing in the injector of an operating gas turbine and laboratory testing showed that the sensor can measure  $CH_4$  from 0 to 10 bar pressures, from room temperature to 600K, with a -3 dB bandwidth of 850 Hz. Real-world testing in the stack of the UCSD gas turbine power plant proved the long-term, unattended operation of the software and sensor. These measurements were compared with the performance of a Fourier Transform Infrared (FTIR) spectrometer sampling gases through the Continuous Emissions Monitoring (CEM) sample train at the power plant. Excellent performance was noted for temperature and  $H_2O$ , while moderately good performance was noted for  $CO_2$ . This field trial demonstrated multiplexed operation over a relatively long period, as might be expected in an actual application.

## 4. Approach

This project has had the primary objective to develop a “plug-and-play” style optical monitor to measure the concentrations of major and minor species in synthesis gas produced by flexible-fuel gasification systems. Targeted species include (but are not limited to) CO<sub>2</sub>, CO, H<sub>2</sub>O (and temperature), CH<sub>4</sub>, H<sub>2</sub>S, and NH<sub>3</sub>. This sensor system will work over a range of pressures and temperatures in potentially particulate-laden flow, with real-time data analysis suitable for direct system control applications. Phase I of the project was devoted to both the spectroscopic and mechanical design of the sensor. Following design, Phase II focused on construction and development of the probe for high temperature and high pressure measurements in a laboratory setting. Finally, Phase III of the project involved testing of the sensor in a real-world setting. Below we develop the underlying theoretical basis and methods for this work.

### 4.1 Theoretical Basis for Wavelength Modulation Absorption Measurements

The general theory of absorption spectroscopy is based on Beer-Lambert law, which relates the transmitted and incident light intensity in a weakly absorbing media by

$$\frac{I}{I_0} = \exp(-k_\nu L) \quad (1)$$

Here, I and I<sub>0</sub> represent transmitted and incident light intensity, L is the path length of the light through the absorbing media, and k<sub>ν</sub> is spectral absorption coefficient, given by:

$$k_\nu = P_{abs}S(T)\Phi(\nu - \nu_0) \quad (2)$$

where P<sub>abs</sub> is the partial pressure of the absorbing species, S(T) is the line strength which is only a function of temperature, and Φ is the line shape function, which is dependent on temperature and the partial pressure of all quenching gases in the probe region through the Doppler and collisional broadening effects.

As noted in the introduction, typical industrial measurements with TDLs measure the direct absorption as predicted by equation (1), scanning the laser over an entire molecular absorption line and integrating the line. This removes the influence of the wavelength-dependent line shape function Φ, which is shown in equation (2); the integrated value of Φ is always normalized to unity, and hence the absorption coefficient is only dependent on S(T) and P<sub>abs</sub>.

While this approach is conceptually simple, there are several limitations to direct absorption measurements. The two limitations that apply most directly to the measurement of high-pressure syngas composition are sensitivity and pressure broadening considerations. As shown in equation (1), direct absorption relies on the measurement of a small change in light intensity due to absorption in the sample. This change can be extremely difficult to detect, and generally in clean

systems limits sensitivity to  $10^{-3} - 10^{-4}$  for most molecules. A fluctuating thermal background and/or incandescent particles degrade this sensitivity further, rendering this approach unsuitable for minor species such as H<sub>2</sub>S or NH<sub>3</sub>, and very difficult to quantify for major species. Second, at high pressures absorption lines broaden due to energy transfer with colliding species. Typical pressure-broadened line widths are on the order of 0.02 – 0.08 cm<sup>-1</sup> / atm for most colliding species (Gharavi and Buckley 2004), as shown in the reference for CH<sub>4</sub>, with the lower broadening coefficients at high temperatures, in this case  $\sim 900$  K. Hence at pressures of 40 – 60 bar and high temperature conditions corresponding to gasifier exit conditions, a minimum line width of approximately 1 cm<sup>-1</sup> is expected, and conservatively a line width of 1.5 or even 2 cm<sup>-1</sup> might be anticipated. The typical tuning range of an inexpensive distributed feedback (DFB) TDL is between 0.5 and 1.5 cm<sup>-1</sup>. Hence these lasers are not able to make high pressure measurements using direct absorption. Other lasers are becoming available in the near IR and mid-IR, but following the discussion of Teichert et al., these do not yet have an array of wavelength choices and are not yet reliable or rugged enough for industrial scenarios (Teichert, Fernholz et al. 2003). In addition direct absorption requires the use of dispersive optics or beamsplitters to separate the various laser beams; for a system with 6-8 measurement components with closely spaced transitions, these can be cumbersome and highly inefficient.

Wavelength modulation spectroscopy (WMS), as briefly discussed in the introduction, provides advantages for sensitive measurements in environments with a high degree of temporal variability (Cassidy and Reid 1982). In WMS, a sinusoidal current modulation is added to the sweep variation employed in direct absorption, such that the drive current for the laser over one period of the sweep is described by:

$$i(t) = i_0 + \Delta i_{\text{sweep}}(t/t_p) + \Delta i_{\text{wms}} \cos \omega t \quad (3)$$

The changing current imposes a modulation on the frequency of the output light, as well as the intensity of the light. For WMS typically  $\omega \ll \Delta\nu$ , where  $\Delta\nu$  is the half-width of the absorption feature, typically  $\omega$  is in the range of tens of kHz. Lock-in detectors are then used to detect the signal or higher harmonics (2f, 3f, etc.) of the signal, with the advantage that higher frequency detection dramatically reduces noise, which is typically dominated by 1/f noise in the laser and detection system, turbulent fluctuations in fluids that follow power law decreasing in f before dissipating at the Kolomgorov scale, and incandescent particles crossing the detection region with an equivalent rate of a few hundred hertz. With the lock-in detector, only the noise that falls within the detection bandwidth is detected, enabling typically several orders of magnitude decrease in detection limits over direct absorption. Optimal modulation depths  $m = \Delta i_{\text{wms}} / \Delta\nu$  have been calculated for various harmonics by Silver, considering only frequency modulation of the light and neglecting the residual intensity modulation, using a Taylor series expansion of the absorption signal (Silver 1992).

The disadvantage for WMS is that the traditional Taylor series analysis for determination of the harmonics of the absorption signal yields an expression for the  $2f$  signal on the detector such as:

$$I_{2f} = I_0 \cdot H_2(v-v_0) \cdot S_T \cdot \Phi(v-v_0) \cdot L \cdot P_{abs} \quad (4)$$

Here,  $H_2(v-v_0)$  is the second Fourier coefficient in the expansion, which has been shown by Reid and Labrie (Reid and Labrie 1981) to depend on the modulation depth and the line shape function. The difficulty for measurements at high temperatures and pressures is that the line width  $\Delta v$  is a function of temperature, pressure, and gas composition, and hence the modulation depth changes dramatically with conditions. As discussed by Blevins and Peterson (Blevins and Peterson) as well as others, the decrease in line width as temperature increases can result in significant overmodulation ( $m > 2.2$ ) of the laser, which can result in both suboptimal signal-to-noise and incorrect quantification of the  $2f$  signal. Correct application and quantification of WMS in high temperature, high pressure processes using the traditional approach thus requires laborious measurement of the broadening coefficients *for each transition, for each bath gas*, as a function of temperature and pressure, as well as measurement of the line strength  $S(T)$  as a function of temperature. This has prevented broad practical application of WMS for such processes.

Recently a series of papers have emerged that provide a complete description of the harmonic signal (Kluczynski and Axner 1999; Kluczynski, Gustafsson et al. 2001; Kluczynski, Lindberg et al. 2001; Kluczynski, Lindberg et al. 2001; Schilt, Thevenaz et al. 2003). These papers rely on a direct Fourier analysis of the detected signal (rather than the Taylor series approximation which is strictly only applicable for  $m \ll \Delta v$ ), provide for both frequency modulation (FM) and residual intensity modulation (IM) of the laser, and have been shown to match experimental measurements essentially exactly (Schilt, Thevenaz et al. 2003). The mathematics is extremely cumbersome but the results are powerful. These exact theoretical descriptions provide the harmonic signals  $1f$ ,  $2f$ ,  $3f$ , etc. in terms of physically meaningful parameters  $m$  and  $\Delta v$ , plus easily measured parameters describing the laser power variation.

The exciting development in this project is that these models can be used to determine the direct absorption signal, and hence the concentration of the absorbing species, directly from the harmonic signal essentially exactly. Further, the entire line does not have to be swept, as the analytical function can be fit to the available WMS data to determine the entire WMS harmonic signal for severely broadened lines at high pressure. Using this concept to analytically determine the corresponding direct absorption signal from the harmonic signal, the advantages of high sensitivity, noise rejection, and frequency domain signal multiplexing inherent in WMS spectroscopy are preserved, with the advantage of easy quantification via equations (1) and (2), where  $\Phi$  is normalized to unity and only  $S(T)$  should be known. As demonstrated in recent and forthcoming papers from our group, determination of  $T$  is relatively straightforward using a single diode laser (Gharavi and Buckley 2003b) and accurate measurement of  $S(T)$  is

also very easy in a laboratory setting (Gharavi and Buckley 2003a; Gharavi and Buckley 2005). The detector signal processing method is shown schematically in Figure 1.

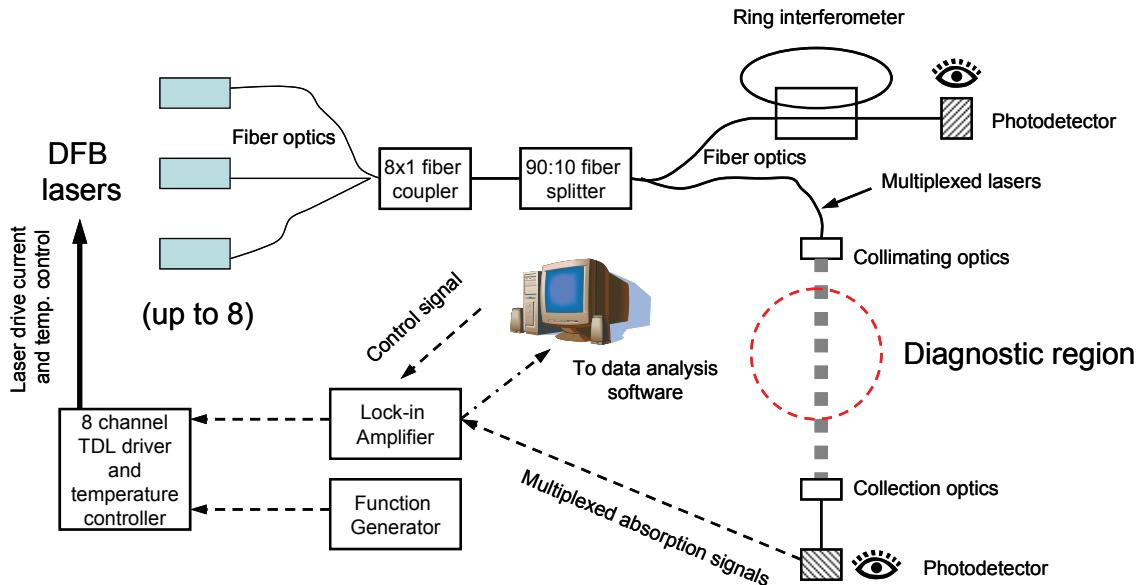


**Figure 1:** Measurement process based on application of theoretical developments to WMS for highly accurate, time-resolved concentration determination.

## 4.2 Experimental Setup and Instrument Design

### 4.2.1 Hardware

The instrument under development will be able to measure multiple species simultaneously. Targeted species include CO<sub>2</sub>, CO, H<sub>2</sub>O, CH<sub>4</sub>, H<sub>2</sub>S, and NH<sub>3</sub>; temperature is being determined via 2-line H<sub>2</sub>O measurement as described in Gharavi and Buckley (Gharavi and Buckley 2003b) and detailed below. Figure 2 shows a conceptual schematic of the sensor, which can accommodate several TDLs (only 3 are shown for simplicity), a ring interferometer for relative wavelength determination, the appropriate optics, a single broadband near-infrared detector, a temperature and current controller, modulation source(s) and lock-in detectors, and data acquisition and experimental control software.



**Figure 2:** Sensor schematic

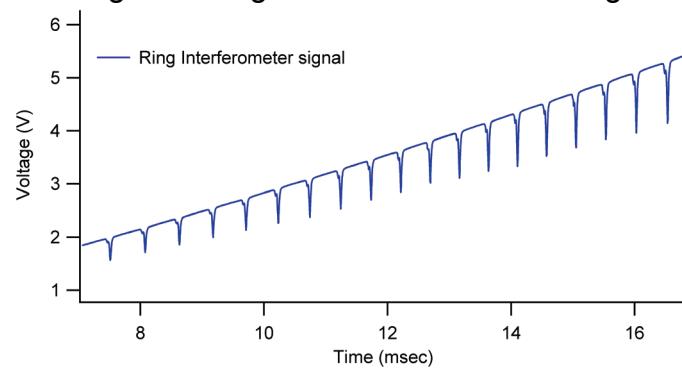
The DFB lasers are collimated in a fiber coupler into a multimode fiber optic. The light enters a fiber splitter, ~10% of the light is split off to enter a ring interferometer with a  $\sim 0.023 \text{ cm}^{-1}$  (actual value is precisely known) free spectral

range, while the main beam (90%) is collimated and launched into the diagnostic region. The ring interferometer allows conversion from the time domain to the frequency domain via measurement of interference fringe spacing; the ring interferometer is also used to reconstruct the incident light (unattenuated signal) entering the diagnostic region. An example of the signal from a ring interferometer is shown in Figure 3 (Buckley, Ferioli et al. 2003; Gharavi and Buckley 2003a).

The main beam enters the diagnostic region; in the laboratory this is a temperature and/or pressure-controlled cell, or a combustor, in field trials and deployment this will be a gasifier. Signals from both the ring interferometer and the diagnostic region are detected via large area broadband Ge photodetectors

such as New Focus model 2011.

Signals are collected and processed using the methodology outlined above, using Labview control software with Matlab mathematics modules written in-house. The software and instrument design are more fully covered in the Results section of this report.



**Figure 3:** Ring interferometer signal as a TDL is scanned.

#### 4.2.2 Development

For laboratory development of the sensor, a 32.1-cm-long quartz static cell and a 1-m-long metal cell, each with 1° wedged windows, are used for gas measurements at temperatures up to 900 °C. These windows are mounted to minimize the optical distortion associated with interference effects in the coherent light passing through the static cell. The cells are surrounded by a cylindrical ceramic fiber heater to heat the absorbing gas to a known temperature. Several type-K thermocouples measure the temperature along the cell axis. One of the thermocouples controls the cell temperature using a PID controller; measured temperature deviations along the cell axis are less than 2% during measurements. During typical experiments, the cell is evacuated to less than 1 torr, and is flushed and filled with gas several times before each measurement. An MKS Baraton pressure transducer with  $\pm 1\%$  reading accuracy measures the pressure in the cell.

The high temperature static cells are used for measurement of the line strength  $S(T)$ , which is independent of pressure, and also for measurement of specific collisional broadening parameters. However, the original cells in the laboratory were not designed for high pressures. For tests at moderate pressures (up to approximately 10 atm), a new cell with metal o-rings and fused silica windows

has been designed. The construction of the 1-m metal cell was quite involved and is documented in detail in the M.S. thesis of Marco Leon, which is included as Appendix A to this report. Without these cells, which include novel purge and seal sections, it would have been impossible to make the detailed measurements required for the instrument to be a success.

The metal cell was be used to determine the pressure broadening coefficients, and will be used to test the final sensor before deployment in the field. For pressures greater than approximately 10 atm we used a very small volume cell that has been developed for engine testing under separate funding. This cell was used to confirm line shapes expected in the gasifier and further test the measurement software under actual conditions.

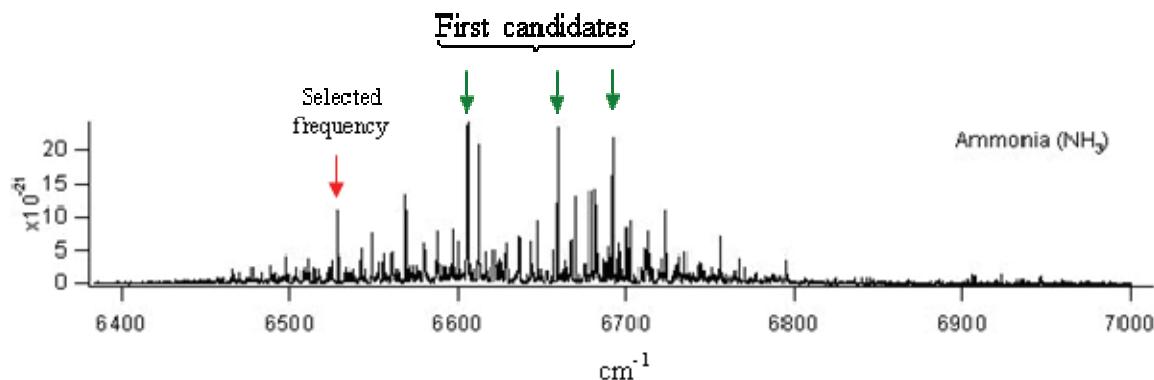
Some of the gases to be tested are hazardous in nature, particularly  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and  $\text{CO}$ , due to their toxicity. The OSHA permissible exposure limits for all three gases are below 40 parts-per-million by volume (Lewis 1994); all are acute toxins. The Combustion Laboratory at UCSD developed ventilated gas handling systems capable of storing these gases.

## 5. Results

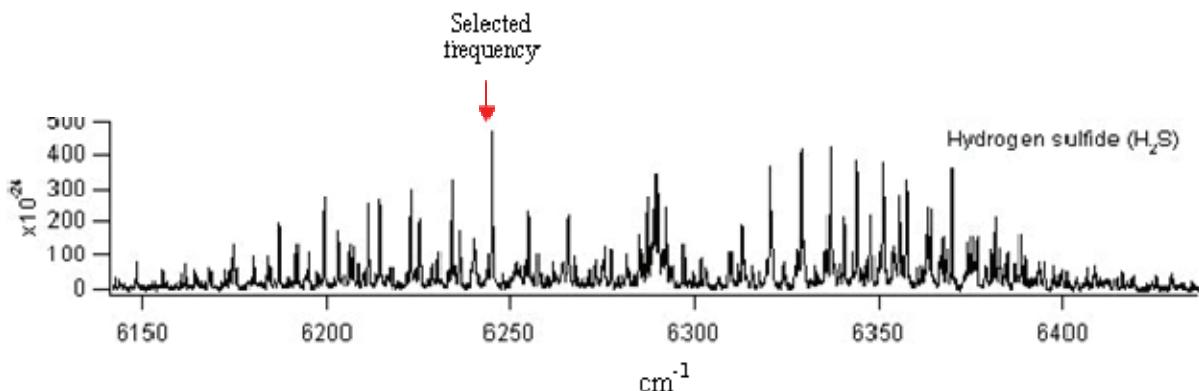
### 5.1 Task #1: Parameter selection

The HiTran spectroscopic database was used to select transitions for measurement of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$ ; we took the spectral data from HiTran and cross-referenced it to available lasers. In addition, a detailed investigation of potential interferences, particularly from  $\text{H}_2\text{O}$ , which is known to have very strong high temperature absorption bands throughout the near-infrared spectrum. We will use existing transitions and lasers for  $\text{CH}_4$  and  $\text{H}_2\text{O}$ .

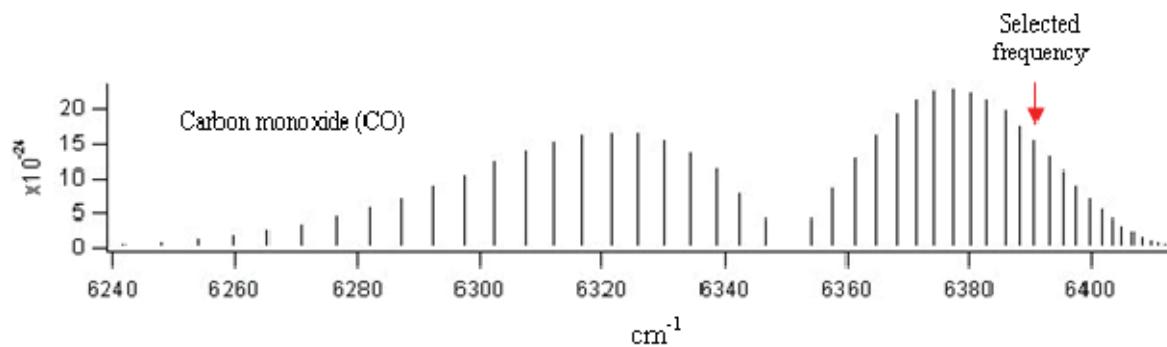
Figures 4-6 illustrate the spectral choices for  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{CO}$ , respectively, using pure spectral data from the Pacific Northwest National Laboratory data base. As you can see from the figures, the first candidates are not always the best, due to temperature sensitivity, availability of the lasers, or interferences.



**Figure 4:** Spectra of  $\text{NH}_3$  between 6400 to 7000  $\text{cm}^{-1}$  (from PNNL data base).



**Figure 5:** Spectra of  $\text{H}_2\text{S}$  between  $6400$  to  $7000\text{ cm}^{-1}$  (from PNNL data base).

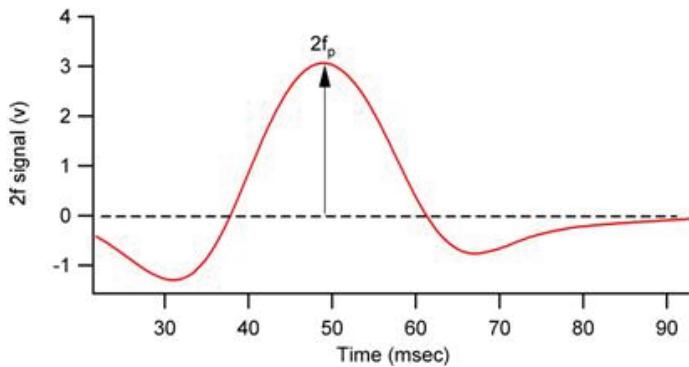


**Figure 6:** Spectra of CO between  $6240$  to  $6420\text{ cm}^{-1}$  (from PNNL data base).

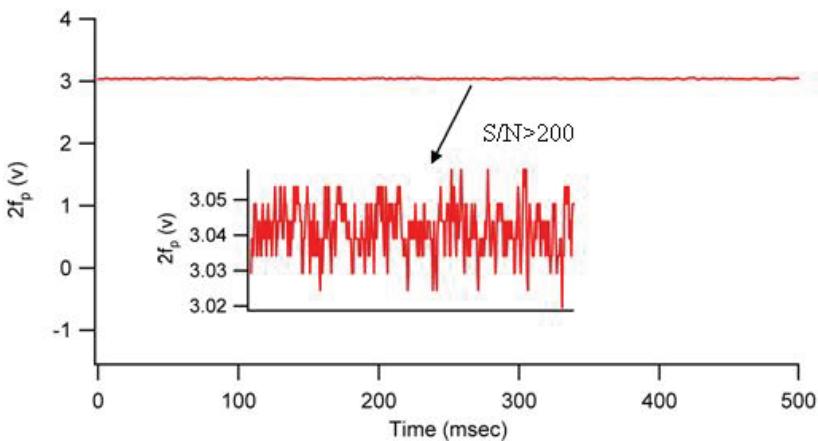
We calculated the effect of total pressure in the reaction zone on the spectra of  $\text{H}_2\text{O}$  for representative combustion conditions. These calculations showed that the total line broadening for the transitions used in this project is about  $3\text{-}4\text{ cm}^{-1}$  under worst-case conditions. Because we will not be able to scan any of the lasers over that range (most scan over only  $\sim 1\text{ cm}^{-1}$ ), we will need to lock the laser to the center of the absorption band and measure only a portion of the spectral feature, or temperature-tune the laser over a broader range. Comparison with the modeled spectrum will allow quantification.

As part of the design effort, one of the quantities that we measured is the sensitivity of the center line-locking technique and sensor response time. It is well known that the sensitivity of TDLAS is inversely proportional to root square of the detection bandwidth (a parameter which is proportional to response time). Based on measurement of second harmonic of one of the  $\text{H}_2\text{O}$  transitions with which we have experience (Figure 7) with a known absorbance (0.02), and for a detection bandwidth of 1.5 kHz, a signal-to-noise ratio of 200 was achieved (Figure 8).

Based on these results, the sensitivity of the sensor based on this measurement is expected to be  $2 \times 10^{-6}$  absorbance/Hz $^{0.5}$ . This sensitivity should be the same for all species using this method.



**Figure 7:** 2f spectra of one of the  $\text{H}_2\text{O}$  transitions around 1477 nm with the peak absorbance of 0.02.

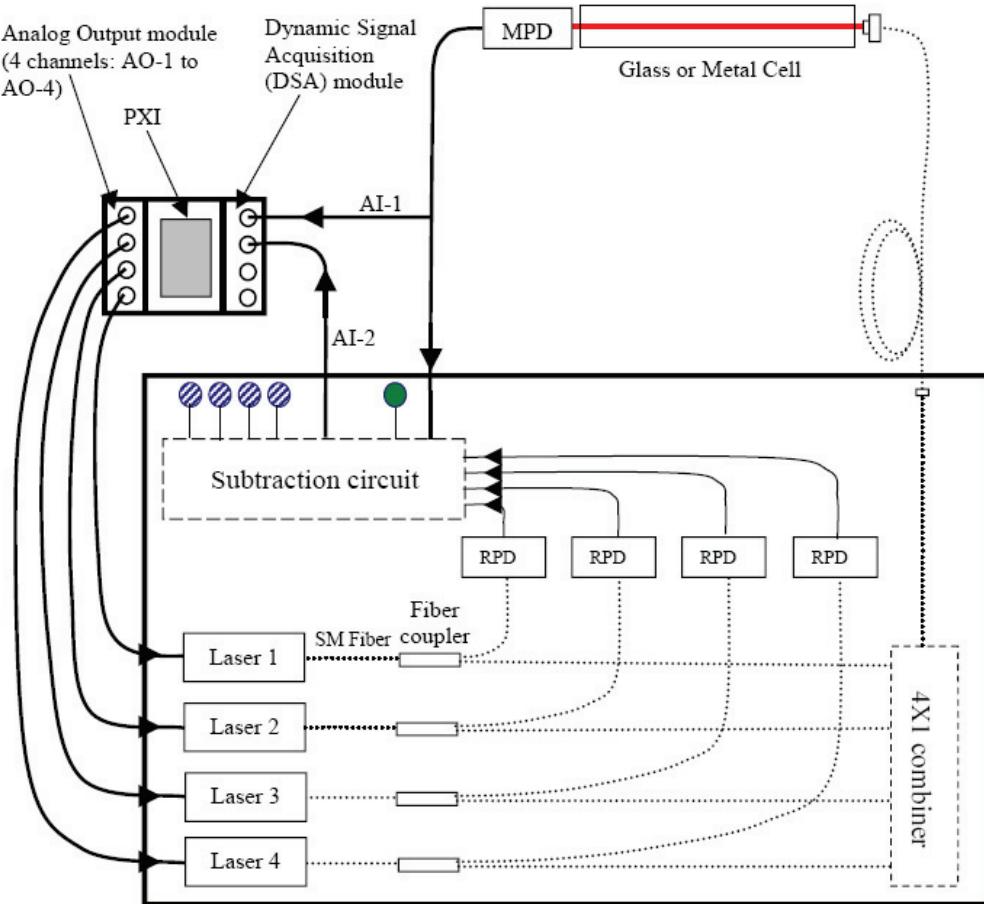


**Figure 8:** 2f signal at the peak of absorption frequency (with a peak absorbance of 0.02) when the laser frequency is manually (by adjusting the laser temperature) kept at

the peak absorption frequency. In this experiment the BW is 1.5 kHz and the modulation frequency is 30 kHz.

## 5.2 Task #2: Design

An overall view of the instrument is shown in Figure 9 on the following page. A balancing and amplification circuit was built to accommodate each of the lasers, and the lasers were multiplexed and integrated with the ring interferometer.



- Adjustment knob for adjusting the gain of the Reference Photodetector (RPD)
- Adjustment knob for adjusting the gain of the Main Photodetector (MPD)
- Optical signal
- Electrical signal

AI-1: This channel is used by the LabVIEW™ program to calculate first harmonic components of each absorption signal based on the MPD signal.

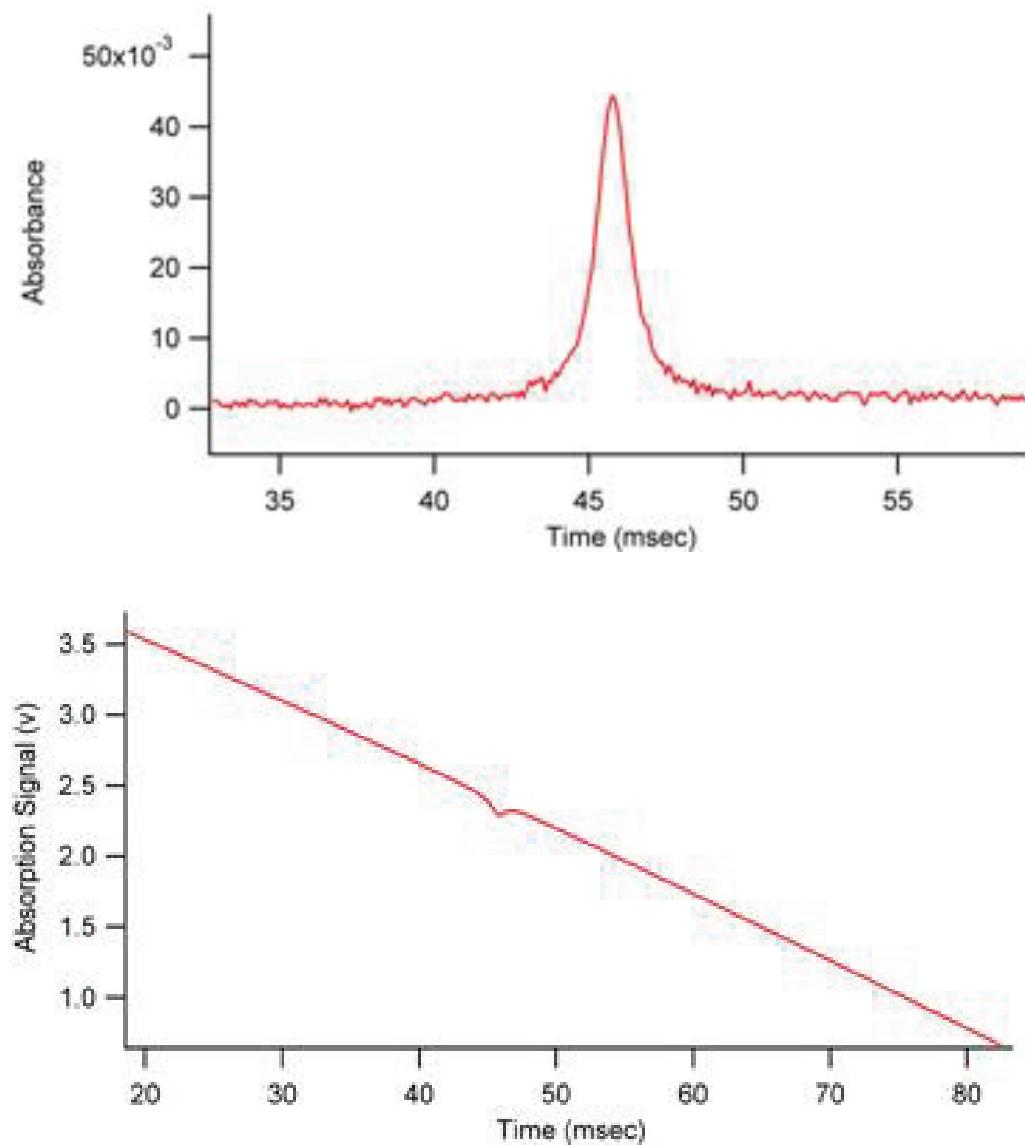
AI-2: This channel is used by the LabVIEW™ program to calculate second harmonic components of each absorption signal based on the subtracted signal.

AO-1 to 4: These channels are used by the LabVIEW™ program to generate four modulation signals, which drive the lasers.

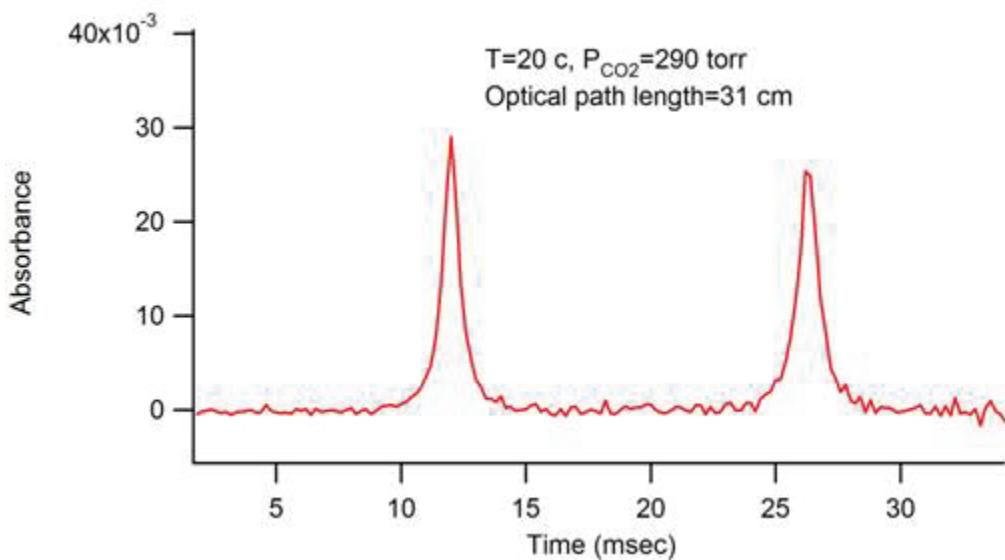
**Figure 9:** Schematic of instrument coupled with reference cell.

### 5.3 Task #3: Construction

Lasers for CO<sub>2</sub>, CO, NH<sub>3</sub>, and H<sub>2</sub>S were purchased, set up, and tested for operational characteristics. Before the start of the project we already had the CH<sub>4</sub> and H<sub>2</sub>O lasers needed for this project. Testing was accomplished in the static cells; for example, the CO laser was initially tested by measuring absorption spectra of CO in a static cell at room temperature, as shown in Figure 10. A CO<sub>2</sub> spectra is shown in Figure 11.



**Figure 10:** CO measurement in the gas cell. Upper trace shows the absorption spectra, bottom trace shows the raw absorption signal for the selected frequency.



**Figure 11:** Spectra of two CO<sub>2</sub> absorption transitions around 1600 nm.

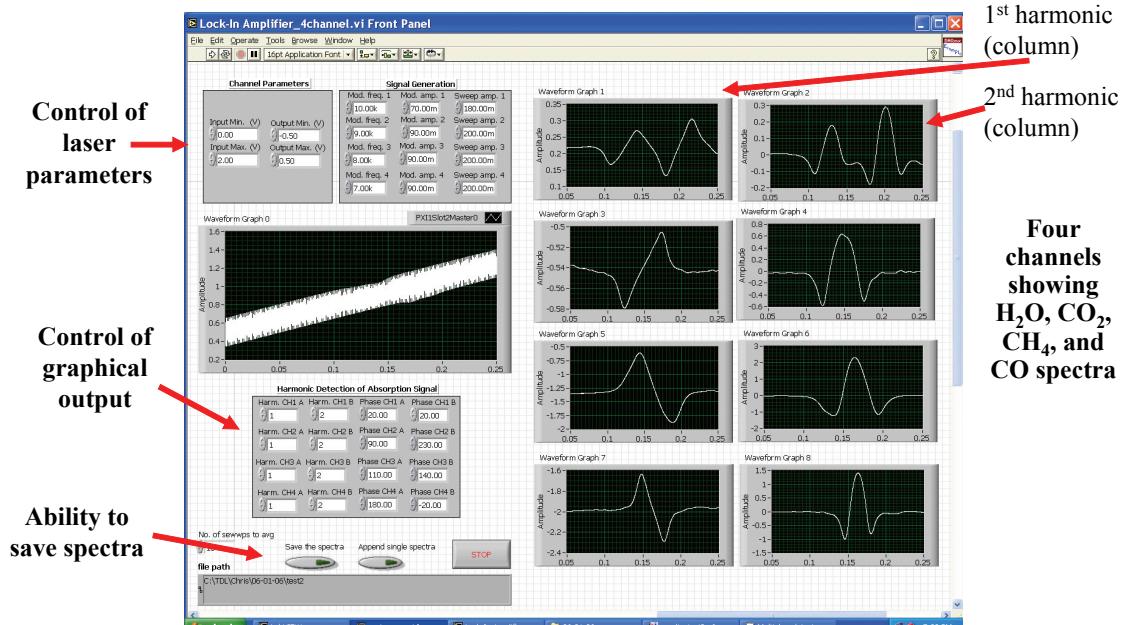
#### 5.4 Task #4: Software

The data acquisition software has been finalized and fully tested. Figure 12 illustrates the software configured for 4 gases, H<sub>2</sub>O, CO, CO<sub>2</sub>, and CH<sub>4</sub>. The screen shows all of the major features of the software. In the top left is a box that can control the laser parameters, including the minimum and maximum input/output voltages, and the modulation amplitude, modulation frequency, and sweep amplitude for each of the four channels. These parameters are all variable, and the result on the signal can be observed in the rightmost two columns.

The graph directly below the laser parameters shows the total signal on the detector. This is the integration (or summation) of light from all of the lasers hitting the single detector. Below the graph is the control of the graphical output that parses the integrated signal. These controls affect what is shown in the eight graphs (2 columns) on the right of the screen. In Figure 12, these are configured to show the 1<sup>st</sup> and 2<sup>nd</sup> harmonic signals for the 4 gases. However, based on the controls, they could also be configured to show any combination of harmonics for the 4 channels (e.g. 1<sup>st</sup> and 3<sup>rd</sup>, 2<sup>nd</sup> and 3<sup>rd</sup>, etc.). The phase is also controllable for each of the graphs.

Finally, the bottom controls allow continuous saving of spectra and/or single spectra to be saved. The path of the current save file is shown.

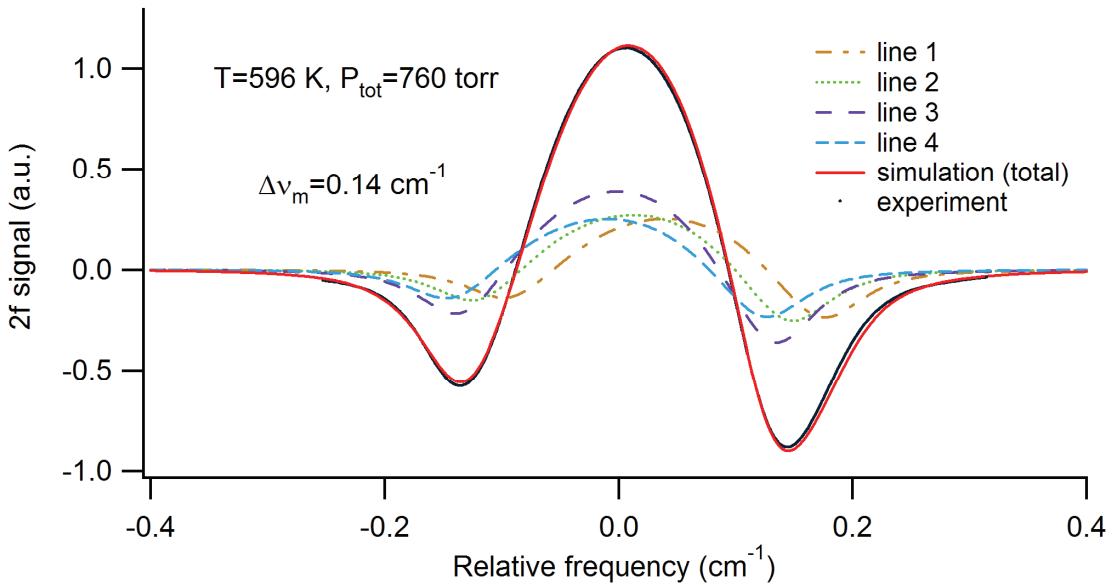
## Advanced Labview™ software controls system



**Figure 12:** Main screen of completed software, demonstrating 4-channel harmonic detection and signal control.

### 5.5 Tasks #5 and #6: Temperature and Pressure Development

The high pressure and low pressure 1-meter stainless steel cells were completed, as noted above, and high pressure data for CO, CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub> were obtained. These four gases were easily completed and can be fully modeled with WMS spectroscopy. An example of this is shown in Figure 13, which illustrates experiment and model overlap for a measurement of CH<sub>4</sub> at high temperature. The observed line is actually comprised of four overlapped transitions which must each be modeled correctly to properly quantify CH<sub>4</sub>. As shown in the figure, the sum of the four lines agrees essentially exactly with the data. To accomplish this, accurate measurements of the line strength and pressure broadening parameters were performed and these results applied to the model. Similar results have been obtained for a variety of temperatures and pressures, and for each of CO, CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub>. Data for CO, CO<sub>2</sub>, and H<sub>2</sub>O are included in Appendix A, while extensive data for CH<sub>4</sub> was published in Gharavi and Buckley, *Journal of Molecular Spectroscopy* 229 (2005) 78–88. Accurate models are important for quantification, particularly at high pressures at which the full transition may not be swept by the laser, and the model may only be able to address a portion of the entire line shape. Without an accurate model, quantification is not possible under these conditions.



**Figure 13:** Experimental (black line) measurement compared with a detailed model of 4 overlapped CH<sub>4</sub> transitions at high temperature.

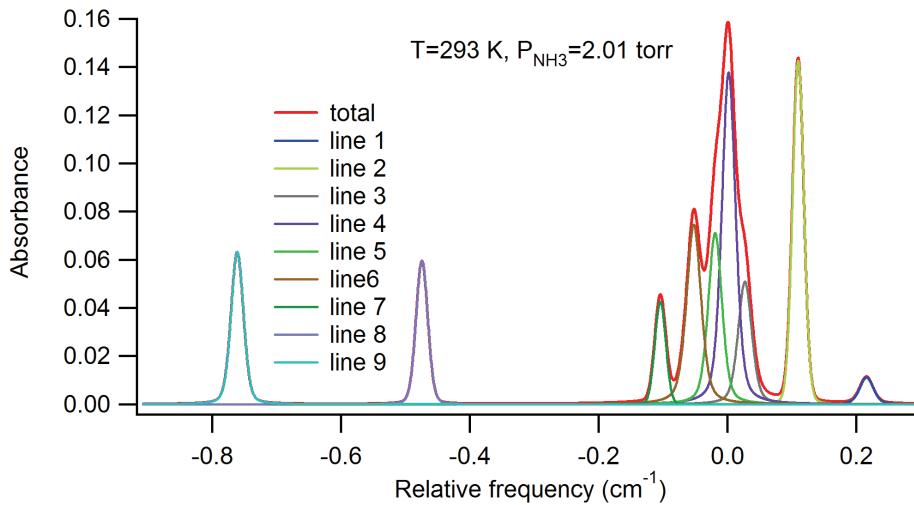
Ammonia and hydrogen sulfide are much more difficult to work with due to their toxicity and hydroscopic nature. Not only were special handling requirements necessary, but in a system with any appreciable amount of H<sub>2</sub>O, these gases will adsorb and the gas phase concentration will not necessarily reflect the volume of gas delivered to the sampling chamber. After several months of full-time work it was possible to accurately measure the parameters corresponding to a strong, isolated set of lines of NH<sub>3</sub> near 1512 nm. Table 1 shows the parameters measured for this project for the 9 overlapped lines of NH<sub>3</sub> in the spectral region.

Line	$v_0$ (cm <sup>-1</sup> )	$v_0$ (cm <sup>-1</sup> ) <sup>†</sup>	$v_0$ (cm <sup>-1</sup> ) <sup>‡</sup>	$S_0$ (cm <sup>-2</sup> atm <sup>-1</sup> )	$\sigma_{v0}$	$\sigma_{S0}$
1	6612.937	-	-	0.0031	0.001	0.0003
2	6612.831	6612.827	-	0.0386	0.000	0.0003
3	6612.748	-	6612.734	0.0194	0.000	0.0002
4	6612.723	6612.718	6612.723	0.0503	0.000	0.0010
5	6612.702	-	6612.695	0.0261	0.001	0.0006
6	6612.669	6612.667	-	0.0316	0.001	0.0009
7	6612.617	-	6612.615	0.0102	0.000	0.0006
8	6612.246	-	-	0.0173	0.000	0.0002
9	6611.961	-	-	0.0203	0.001	0.0002

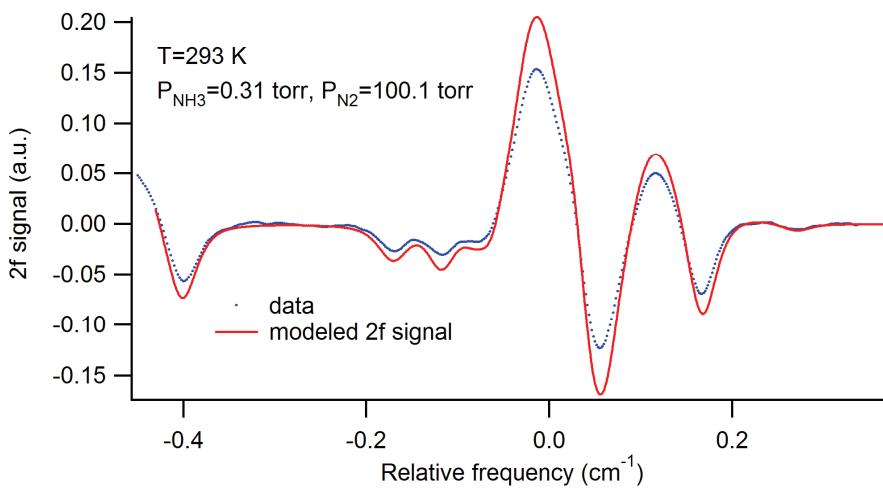
**Table 1:** Central frequencies, line strengths, and broadening coefficients for the nine lines of NH<sub>3</sub> measured for this project.

The parameters in Table 1 can be employed in a model to predict the spectrum of NH<sub>3</sub>, just as in Figure 13 a model predicted the WMS spectrum of CH<sub>4</sub>. Figure

14 shows all nine individual lines of  $\text{NH}_3$  at room temperature, and Figure 15 shows the measured spectrum and model at room temperature and slightly more than 100 torr total pressure. The  $\text{NH}_3$  modeled spectrum is based on an  $\text{NH}_3$  concentration from partial pressures of the gases introduced into the measurement cell. There is clear lack of agreement between the model and the experiment.



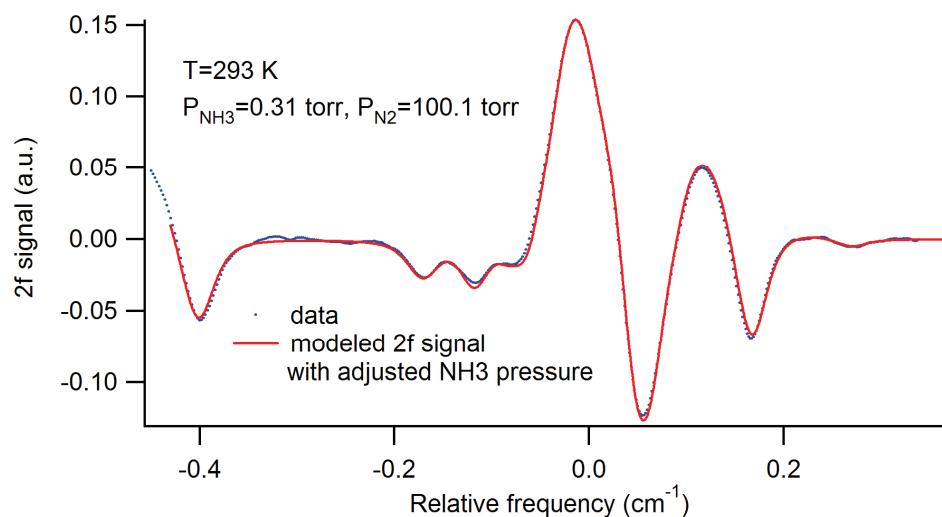
**Figure 14:** The 9  $\text{NH}_3$  lines in the measurement range.



**Figure 15:** Room-temperature, 100.1 torr total pressure measurement of 0.31 torr  $\text{NH}_3$  compared with model.

The disagreement between model and measurement in Figure 15 is caused by inaccuracy in the concentration of  $\text{NH}_3$ , despite the fact that the concentration of  $\text{NH}_3$  is determined by partial pressures using very accurate pressure transducers. We believe that substantial amounts of  $\text{NH}_3$  are lost to the walls of the cell. Evidence for this is in Figure 16, which shows essentially perfect agreement between the model and measurement of  $\text{NH}_3$  when the concentration of

ammonia in the model is decreased approximately 30%. Based on these results and the accuracy with which all of the spectral parameters capture the shape of the spectrum when the concentration is adjusted, we believe that there is substantial loss of  $\text{NH}_3$  to the walls of the measurement cell, and further that the WMS spectroscopy accurately measures the gas phase concentration. Extensive explanation of this issue is in a presentation at the Federation of Analytical Chemistry and Spectroscopy Societies meeting from early Fall 2006, which is included as Appendix C. Complete data for each of the other molecules of interest (except  $\text{H}_2\text{S}$ , as discussed below) were generated, similar to those shown in Appendix C.



**Figure 16:** Same as Figure 6, but with  $\text{NH}_3$  concentration decreased by ~30% in the model.

Given the complication and time involved in the  $\text{NH}_3$  measurement, it was decided to make semi-quantitative measurements of  $\text{H}_2\text{S}$ , based on approximate measurements of line strength and broadening parameters.  $\text{H}_2\text{S}$  is potentially even more toxic and more polar than  $\text{NH}_3$ , and thus possibly even more difficult to measure. It is expected that these measurements will be qualitatively correct, able to capture trends in the  $\text{H}_2\text{S}$  concentration. This should be sufficient for a first cut at control, where the objective would be to minimize  $\text{H}_2\text{S}$  emissions.

## 5.6 Task #7: Field Testing of the Instrument

The TDL system was initially field tested in September 2005, and successfully tested in April 2006. While the initial plan had been to test the sensor system in a gasifier environment, unexpected costs and turnover of personnel (specifically, the difficulties in getting  $\text{H}_2\text{S}$  and  $\text{NH}_3$  measurements, the sudden departure of Ph.D. student Geoff Rappoport, and the expected departure of post-doctoral scholar Reza Gharavi, none of which were under the PI's control) led to the test in April 2006 serving as the final test(s) in the gas turbine power plant stack at

UCSD. These tests were realistic and led to both validated data and suggestions for improvement of the instrument in the future. The tests, results, and recommendations are summarized here and are covered in full detail in the M.S. thesis of Marco Leon, which is included in this report as Appendix B.

In the initial test in September 2005, results were collected for 6 days on one of the two stacks of the UCSD power plant. Sights were set on measurement of temperature,  $H_2O$ , and  $CO_2$  in real time.  $CH_4$  and  $CO$  were also measured, but these were undetectable in the stack of the turbine. Results were compared with continuous FTIR emissions data as well as with continuous emissions data from the on-line CEMS (continuous emissions monitor) at the power plant. While some of the initial data from the test appeared good, it was apparent that a ground fault or similar error in the instrument had compromised the measurement, such that good temperatures could not be measured. Without temperature measurement, the spectroscopy of the molecules of interest could not be quantifiable. In addition, there were some serious problems with the software. This led the team back to the laboratory to fix and revise the instrument.

The second field attempt, in April 2006 was much more successful. As detailed in Appendix B, the  $CO_2$  content varied between 2 and 3.4%, while the  $H_2O$  content was very close to 7%. The TDL data fluctuated approximately  $\pm 1\%$  in absolute concentration for both measurements. This is compared with a 5% (absolute) fluctuation in the FTIR for the  $H_2O$  measurements, but only 0.2% for the FTIR  $CO_2$  measurements. Cyclical variations in  $H_2O$  and  $CO_2$  measured with the TDL could be correlated with the turbine load. A complete error analysis was performed, showing that the standard deviation of the  $H_2O$  measurement was 2.8% of the mean, while the standard deviation of the  $CO_2$  measurement was 9.4% of the mean. Suggestions were made in the thesis as to how these numbers could be improved. One other issue concerned the proper way to handle the incredible amount of data that is generated by the sensor, which recorded concentrations and temperatures at 10 Hz over a long period of time. This issue needs to be addressed if such an instrument is ever commercialized.

A no-cost extension was obtained on the grant from September 2006 – August 2007 to attempt to improve the instrument and also to conduct another field trial. However, the departure of Dr. Gharavi and imminent departure of Prof. Buckley on a leave of absence from the University prevented the recruitment of any new students and resulted in no significant progress. The time extension was requested in the hope that additional progress could have been made, but unfortunately, this was not the case.

## 6. Conclusions

This project has largely met the milestones it set out to meet. Among the accomplishments of the project:

- 1) Measurements of CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, and NH<sub>3</sub> with tunable diode lasers, and semiquantitative measurements of H<sub>2</sub>S.
- 2) Development of the spectroscopy of the molecules of interest, including pressure broadening coefficients and line strengths.
- 3) Multiplexed measurements of several species at one time using wavelength modulation spectroscopy in rugged, industrial environments.
- 4) Hardware and software development to facilitate the WMS measurements.

The quantification and data collection using WMS were both relatively successful in the laboratory and in the field trial. All of the molecules except H<sub>2</sub>S could be quantitatively measured. These measurements relied heavily on models for proper quantification, highlighting the fact that it is very important to have the spectroscopic data correct for the molecular transitions that are being measured.

Overall the software and hardware were acceptable, particularly considering that they were laboratory-built by student workers. Future work could include combination of measurement and quantification into a single software package. Throughout the project, quantification was only possible using stored data.

One issue that we had during this project was that we discovered that our planned scope was much too aggressive for the funding level. Once we began the project it became apparent that the spectroscopic measurements were much more difficult and time-consuming than originally expected, particularly for CO, H<sub>2</sub>S, and NH<sub>3</sub>. This caused delays in the schedule; we did our best to get the most important data with the time that we had. As a comment to any DOE program planners that may read this report, in the yearly funding for the UCR program it would have been helpful to have had funding for a full-time postdoctoral researcher and a full-time graduate student. As it was we had to work with a part-time post-doc, and this meant that we necessarily made less progress than we might have, as our key technical person was splitting his time among several projects.

Overall, this project has developed spectroscopy for measurement of small molecules with tunable diode lasers, and fielded an integrated system that shows promise for long-term measurements. We expect that this system will be useful in gasification systems and in other, similar industrial processes.

## 7. Technology Transfer Activities

A provisional patent disclosure was filed in March 2007; a patent was filed by UCSD on March 24, 2007 entitled "OPTICAL SENSING BASED ON WAVELENGTH MODULATION SPECTROSCOPY." This patent covers methods for calibration and operation of a tunable diode laser sensor that were in part developed during the course of this project. This pending patent technology has been licensed by Photon Machines, Inc. from Redmond, WA. The summary of the patent is reproduced here:

"This application includes examples of techniques, apparatus and systems for using Wavelength Modulation Spectroscopy measurements to optically monitor gas media such as gases in gas combustion chambers. In one aspect, a method for optically sensing a gas medium based on the Wavelength Modulation Spectroscopy is described to include modulating a laser wavelength of a tunable laser at a modulation frequency to produce a wavelength-modulated laser beam with a laser frequency range including an absorption band of molecules of a molecular species in the gas medium; directing the wavelength-modulated laser beam that transmits through the gas medium; measuring a transmission of the wavelength-modulated laser beam through the gas medium to obtain measurements of at least one signal at a harmonic frequency of the modulation frequency at different modulation depths in modulating the laser wavelength; and processing the measurements of the at least one signal at the harmonic frequency of the modulation frequency at different modulation depths to obtain a total broadening of absorption spectrum of the molecular species in the gas medium.

In another aspect, a method for performing Wavelength Modulation Spectroscopy measurements is described to include varying a modulation depth in modulating a laser wavelength of a laser used in the Wavelength Modulation Spectroscopy for measuring a gas medium to obtain measurements; and obtaining a total pressure broadening from the obtained measurements without prior knowledge of individual pressure broadening coefficients and gas composition.

In another aspect, a method for optically measuring a gas medium based on the Wavelength Modulation Spectroscopy is described to include directing a laser beam from a wavelength-modulated tunable diode laser through the gas medium; and measuring two different harmonic signals which have different responses to a total pressure in the gas medium to obtain both a gas concentration and a total pressure in the gas medium.

In another aspect, a method for optically measuring a gas medium based on the Wavelength Modulation Spectroscopy is described to include directing a first laser beam from a first wavelength-modulated tunable diode laser through the gas medium and a second laser beam from a second wavelength-modulated tunable diode laser through the gas medium, wherein the first wavelength-modulated tunable diode laser and the second

wavelength-modulated tunable diode laser are modulated at respective modulation frequencies; operating the first and the second tunable diode lasers differently with respect to a respective optimum modulation depth; and measuring a harmonic signal of the modulation frequency from the first laser beam and a second harmonic signal at a harmonic frequency of the second laser beam to obtain both a gas concentration and a total pressure in the gas medium.

In yet another aspect, a gas turbine system is described to include a gas turbine having a premixing gas chamber; a first input port to input air into the premixing gas chamber; a second input port to input a gas fuel into the premixing gas chamber to mix with the air; a wavelength modulation spectroscopy (WMS) optical monitoring device having at least one tunable laser to produce a wavelength-modulated laser beam and to direct the laser beam through at least a portion within the premixing gas chamber to interact with a mixture of the gas fuel and the air; and an optical detector to receive an optical transmission of the laser beam; a WMS processing device that processes an output of the optical detector to extract at least one signal at a harmonic frequency of the modulation frequency at different modulation depths; and a turbine control mechanism in communication with the WMS processing device and operable to control the gas fuel and the air input into the premixing gas chamber based on information in the at least one signal at the harmonic frequency of the modulation frequency.

These and other aspects, examples and implementations of techniques, apparatus and systems for using Wavelength Modulation Spectroscopy measurements to optically monitor gas media are described in detail in the drawings, the description and the claims.”

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## **Appendix A: Spectroscopic data for H<sub>2</sub>O, CO, and CO<sub>2</sub> transitions**

## H<sub>2</sub>O broadening

Table A1: Variation of collisional half-width with temperature for transitions 1 and 2.

Broadening Gas	$\gamma_{1,2}$ (cm <sup>-1</sup> atm <sup>-1</sup> )					
	483 K	584 K	723 K	770 K	860 K	999 K
N <sub>2</sub>	0.0334 ± 0.0005	0.0296 ± 0.0003	0.0264 ± 0.0005	---	---	0.0224 ± 0.0005
CO <sub>2</sub>	0.0462 ± 0.0005	0.0408 ± 0.0003	0.0373 ± 0.0006	---	0.0330 ± 0.0007	---
H <sub>2</sub> O	0.1574 ± 0.0014	0.1510 ± 0.0018	---	0.1300 ± 0.0019	0.1180 ± 0.0022	0.1142 ± 0.0000
O <sub>2</sub>	0.0152 ± 0.0002	0.0136 ± 0.0001	0.0125 ± 0.0003	---	0.0118 ± 0.0002	0.0106 ± 0.0001

Table A2: Variation of collisional half-width with temperature for transition 3.

Broadening Gas	$\gamma_3$ (cm <sup>-1</sup> atm <sup>-1</sup> )					
	483 K	584 K	723 K	770 K	860 K	999 K
N <sub>2</sub>	0.0572 ± 0.0006	0.0490 ± 0.0003	0.0424 ± 0.0004	---	---	0.0325 ± 0.0003
CO <sub>2</sub>	0.0742 ± 0.0007	0.0656 ± 0.0003	0.0611 ± 0.0004	---	0.0548 ± 0.0007	---
H <sub>2</sub> O	0.2346 ± 0.0011	0.2066 ± 0.0026	---	0.1648 ± 0.0019	0.1496 ± 0.0017	0.1363 ± 0.0000
O <sub>2</sub>	0.0239 ± 0.0001	0.0205 ± 0.0001	0.0179 ± 0.0002	---	0.0163 ± 0.0002	0.0149 ± 0.0001

Table A3: Temperature dependence of collisional broadening coefficient parameter  $n$  for different colliding gases.

Transition	<i>n</i>			
	N <sub>2</sub>	H <sub>2</sub> O	CO <sub>2</sub>	O <sub>2</sub>
1 and 2	0.552 ± 0.021	0.475 ± 0.049	0.563 ± 0.037	0.467 ± 0.030
3	0.768 ± 0.021	0.766 ± 0.020	0.505 ± 0.045	0.652 ± 0.030

Table A4: Collisional broadening coefficients for the H<sub>2</sub>O transitions at room temperature  $T_0=296$  K for different colliding gases.

Transition	$\gamma_0$ (cm <sup>-1</sup> /atm)			
	N <sub>2</sub>	H <sub>2</sub> O	CO <sub>2</sub>	O <sub>2</sub>
1 and 2	0.0435	0.2018	0.0606	0.0189
3	0.0830	0.3423	0.0940	0.0345

Table A5: Comparison of air collisional broadening coefficient between HITRAN2004 simulation and the measurements results at this study at room temperature ( $T_0=296$  K).

Transition	$\gamma_{0,H2O-air}$ (cm <sup>-1</sup> /atm)		<i>n</i>	
	This study	HITRAN2004	This study	HITRAN2004
1 and 2	0.0383	0.0418	0.539	0.53
3	0.0728	0.0737	0.757	0.59

Table A6: Collisional broadening parameters of CO<sub>2</sub> transition.

Broadening Gas		
	$\gamma_0$ (cm <sup>-1</sup> atm <sup>-1</sup> )	<i>n</i>
N <sub>2</sub>	0.0606	0.439
CO <sub>2</sub> (self)	0.0952	0.602
O <sub>2</sub>	0.0585	0.596

Table A7: Collisional broadening parameters of CO transition.

Broadening Gas		
	$\gamma_0$ (cm <sup>-1</sup> atm <sup>-1</sup> )	<i>n</i>
N <sub>2</sub>	0.0532	0.560
CO (self)	0.0533	0.839
O <sub>2</sub>	0.0405	---
CO <sub>2</sub>	0.0557	0.313

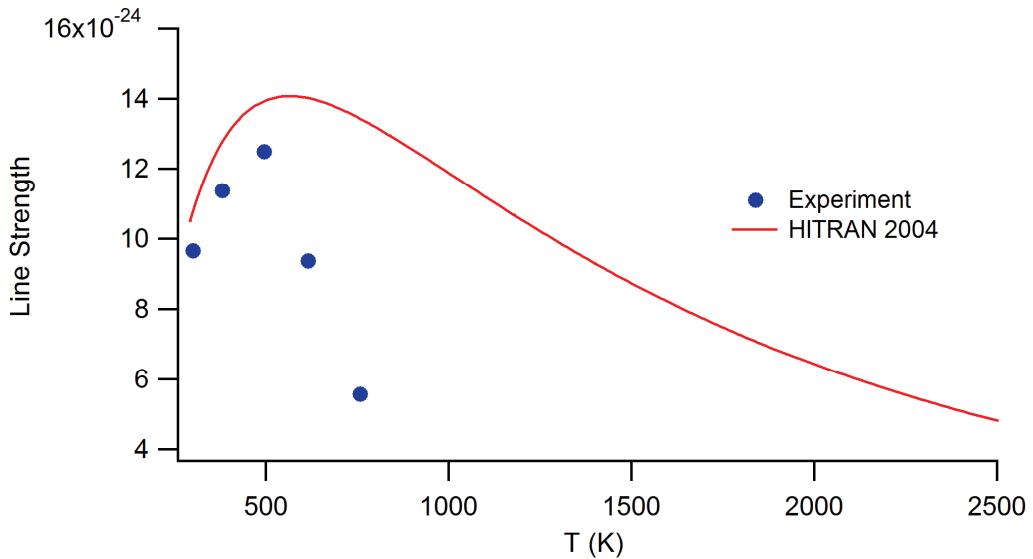


Fig. A1: Variation of Line Strength of the CO transition with temperature (we observed variation in the CO pressure in the static cell, pressure decrease, during experiments indicating dissociation of CO at elevated temperature especially at  $T=616$  and  $759$  K. Therefore we expect our measured S values have considerable error (especially above 500 K).

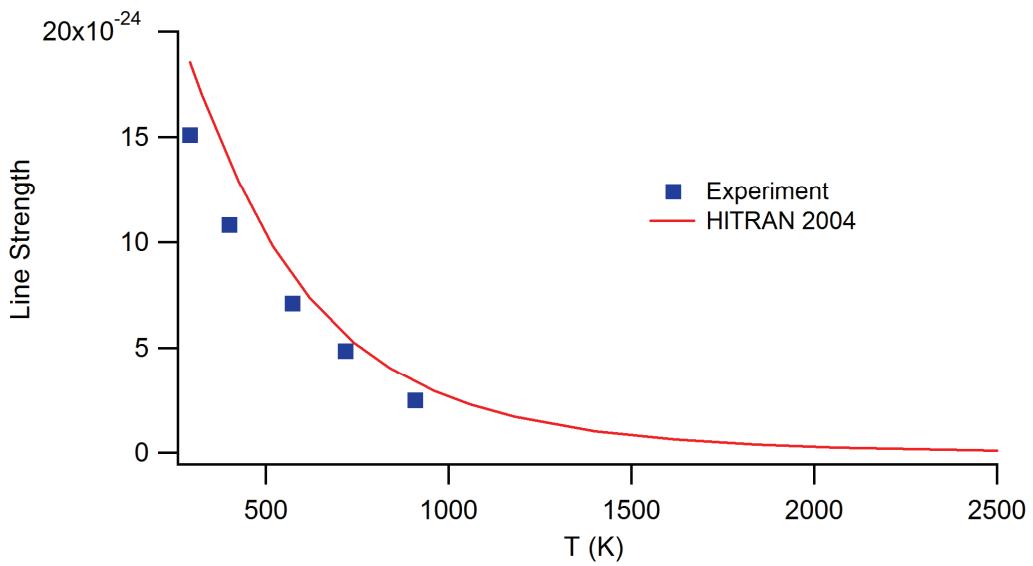


Fig. A2: Variation of Line Strength of the CO<sub>2</sub> transition with temperature.

## **Appendix B: M.S. Thesis of Marco Leon**

UNIVERSITY OF CALIFORNIA, SAN DIEGO

Diode Laser Measurement of H<sub>2</sub>O, CO<sub>2</sub>, and Temperature in Gas Turbine Exhaust  
through the Application of Wavelength Modulation Spectroscopy

A thesis submitted in partial satisfaction of the  
requirements for the degree Master of Science

in

Engineering Sciences (Mechanical Engineering)

by

Marco E. Leon

Committee in charge:

Professor Steven G. Buckley, Chair  
Professor Robert J. Cattolica  
Professor George R. Tynan

2007



The thesis of Marco E. Leon is approved:

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Chair

University of California, San Diego

2007

## DEDICATION

To my parents, Ralph Leon and Iren Schio, for always supporting my education.

## TABLE OF CONTENTS

Signature Page .....	iii
DEDICATION .....	iv
TABLE OF CONTENTS.....	v
LIST OF FIGURES .....	vii
LIST OF TABLES.....	xii
ACKNOWLEDGEMENTS.....	xiii
ABSTRACT OF THE THESIS .....	xiv
CHAPTER 1: Introduction .....	1
CHAPTER 2: Wavelength Modulation Spectroscopy.....	3
2.1 Introduction.....	3
2.2 Fundamentals of TDLAS.....	3
2.3 Development of TDLAS.....	5
2.4 Wavelength Modulation Spectroscopy Theory .....	8
CHAPTER 3: Experimental Setup.....	15
3.1 Introduction.....	15
3.2 TDL Laser Selection.....	15
3.3 Laboratory Setup.....	21
3.4 Field Setup .....	31
CHAPTER 4: Conversion of TDL Data .....	37
4.1 Introduction.....	37
4.2 H <sub>2</sub> O, CO <sub>2</sub> , and Temperature WMS Conversion .....	37
CHAPTER 5: Field Test Results .....	42
5.1 Introduction.....	42
5.2 FTIR Field Data .....	42
5.3 TDL Field Data.....	47
5.4 FTIR & TDL Field Data Comparison.....	65
5.5 Error Analysis .....	67
CHAPTER 6: Conclusion .....	71

Appendix.....	73
References.....	74

## LIST OF FIGURES

Figure 2.1: Typical experimental setup for direct absorption spectroscopy (from M. Gharavi) .....	6
Figure 2.2: Typical experimental setup for wavelength modulation spectroscopy (from M. Gharavi) .....	7
Figure 3.1: Line strength versus wavenumber for H <sub>2</sub> O, CO <sub>2</sub> , CO, CH <sub>4</sub> , NO, NO <sub>2</sub> taken from the Hitran 2004 database at 450 K .....	16
Figure 3.2: Hitran 2004 line strength versus wavenumber data from 300 to 900 K used to choose CO laser .....	18
Figure 3.3: Hitran 2004 line strength versus wavenumber data from 300 to 900 K used to choose the CO <sub>2</sub> laser .....	19
Figure 3.4: Line operating region of the lasers used in this research along with NO taken from Hitran 2004 at 450 K .....	20
Figure 3.5: Line strength as a function of temperature for the H <sub>2</sub> O, CO <sub>2</sub> , CO, and CH <sub>4</sub> lasers .....	20
Figure 3.6: Laser, cable, and laser controller wiring diagram (portion from A. Schuger) .....	22
Figure 3.7: Existing 30 cm core glass cell designed by M. Gharavi .....	23
Figure 3.8: Four-window 40 cm long core glass cell created for this project .....	24
Figure 3.9: Left: Low-pressure metal cell wedge window-flange interface (note outward facing C-Seal) .....	26
Figure 3.10: Right: High-pressure metal cell wedge window-flange interface (note inward facing C-Seal) .....	26
Figure 3.11: Wedge window machining drawing .....	26
Figure 3.12: Low-pressure metal cell assembly .....	28
Figure 3.13: High-pressure metal cell assembly .....	28
Figure 3.14: Metal cell & heater assembly modeled using Pro-E; the 30 cm long glass vacuum tubes are also shown on each end (note: actual heaters used were three .....	20

inch long sections, not two 12-inch and one 32-inch heater in the middle as shown)	28
Figure 3.15: Single species TDL testing setup using the glass or metal static cell .....	29
Figure 3.16: Pictures of the metal cell setup in the TDL laboratory.....	30
Figure 3.17: General top down view of UCSD power plant gas turbine systems .....	31
Figure 3.18: Side view of the systems downstream of each gas turbine (from J. Dilliot, UCSD power plant manager).....	32
Figure 3.19: Left: GT1 exhaust stack and CEMS shack; Right: TDL system on top of FTIR.....	33
Figure 3.20: Left: TDL collimating lens window assembly (note the CEMS sample hose in the background); Right: TDL photodetector window assembly .....	34
Figure 3.21: TDL system located inside the UCSD power plant CEMS shack .....	35
Figure 3.22: TDL box schematic (portion from A. Schuger) .....	36
Figure 4.1: Typical 2 <sup>nd</sup> harmonic signal of H <sub>2</sub> O at the selected H <sub>2</sub> O transitions (from Gharavi 2004) .....	39
Figure 4.2: Typical 2 <sup>nd</sup> harmonic signal of CO <sub>2</sub> at the selected CO <sub>2</sub> transition.....	40
Figure 4.3: Temperature versus $R_{I,II}$ (ratio) data for the selected H <sub>2</sub> O transitions from the HITRAN database.....	40
Figure 5.1: Complete FTIR data over a 1-hour time period noting that both exhaust stacks are sampled every 7.5 minutes (refer to Table 5.2 for FTIR species units).....	43
Figure 5.2: Overview of CO <sub>2</sub> , H <sub>2</sub> O, and CH <sub>4</sub> along with gas turbine percent load from FTIR data group A (9/16-9/18/05) (refer to Table 5.2 for FTIR species units).....	44
Figure 5.3: Overview of CO <sub>2</sub> , H <sub>2</sub> O, and CH <sub>4</sub> along with gas turbine percent load from FTIR data group D (9/20-9/22/05) (refer to Table 5.2 for FTIR species units).....	44
Figure 5.4: Overview of CO along with gas turbine percent load from FTIR data group A (9/16-9/18/05) (refer to Table 5.2 for FTIR species units) .....	45
Figure 5.5: Overview of CO along with gas turbine percent load from FTIR data group D (9/20-9/22/05) (refer to Table 5.2 for FTIR species units) .....	45

Figure 5.6: FTIR 1-hour time period from 9/17/05 showing CO, CO <sub>2</sub> , H <sub>2</sub> O, and CH <sub>4</sub> along with FTIR stack number; gas turbines operating close to 93% load (refer to Table 5.2 for FTIR species units) .....	46
Figure 5.7: FTIR 1-hour time period from 9/20/05 showing CO, CO <sub>2</sub> , H <sub>2</sub> O, and CH <sub>4</sub> along with FTIR stack number; gas turbines operating close to 93% load (refer to Table 5.2 for FTIR species units) .....	46
Figure 5.8: The first 14 hours of TDL field data collected in September 2005.....	47
Figure 5.9: April 2006 GT1 TDL H <sub>2</sub> O peak ratio raw data (entire data set).....	50
Figure 5.10: April 2006 GT1 TDL H <sub>2</sub> O peak ratio raw data (early 1-hour time period) .	50
Figure 5.11: April 2006 GT1 TDL H <sub>2</sub> O peak ratio filtered data (entire data set) .....	51
Figure 5.12: April 2006 GT1 TDL H <sub>2</sub> O peak ratio filtered & decimated (1-minute average) data (entire data set) .....	51
Figure 5.13: April 2006 GT1 TDL H <sub>2</sub> O peak ratio filtered & decimated (1-minute average) data (entire data set) along with GT1 hourly percent load data .....	52
Figure 5.14: April 2006 GT1 TDL calculated stack exhaust temperature data (entire data set).....	53
Figure 5.15: GT1 exhaust stack radial temperature measurement results .....	53
Figure 5.16: TDL exhaust stack and GT1 T7 temperature data over the April 2006 testing .....	54
Figure 5.17: Idealized T-s diagram for a Titan 130 gas turbine operating in SoLoNOx mode.....	56
Figure 5.18: April 2006 testing GT1 T7 average temperature vs percent load (hourly data) .....	56
Figure 5.19: TDL exhaust stack temperature and GT1 percent load data over the April 2006 testing.....	57
Figure 5.20: TDL raw H <sub>2</sub> O peak amplitude data over the entire April 2006 test period..	58
Figure 5.21: TDL raw H <sub>2</sub> O normalized peak amplitude data over the entire April 2006 test period.....	58

Figure 5.22: TDL H <sub>2</sub> O normalized peak amplitude filtered data over the entire April 2006 test period.....	59
Figure 5.23: TDL H <sub>2</sub> O normalized peak amplitude filtered & decimated (1-minute average) data over the entire April 2006 test period.....	59
Figure 5.24: TDL H <sub>2</sub> O mole fraction based on the filtered & decimated (1-minute average) H <sub>2</sub> O normalized peak data over the entire April 2006 test period .....	60
Figure 5.25: TDL H <sub>2</sub> O mole fraction based on the filtered & decimated (1-minute average) H <sub>2</sub> O normalized peak data along with GT1 percent load over the entire April 2006 test period .....	60
Figure 5.26: TDL raw CO <sub>2</sub> peak amplitude data over the entire April 2006 test period..	61
Figure 5.27: TDL raw normalized CO <sub>2</sub> peak amplitude data over the entire April 2006 test period.....	62
Figure 5.28: TDL raw normalized CO <sub>2</sub> peak amplitude data over the entire April 2006 test period showing the noisy data between 12 and 118 hours .....	62
Figure 5.29: TDL raw normalized CO <sub>2</sub> peak amplitude data after 120 hours.....	62
Figure 5.30: TDL normalized CO <sub>2</sub> peak amplitude filtered data over the entire April 2006 test period.....	63
Figure 5.31: TDL normalized CO <sub>2</sub> peak amplitude filtered & decimated (1-minute average) data over the entire April 2006 test period.....	63
Figure 5.32: TDL CO <sub>2</sub> mole fraction based on the filtered & decimated (1-minute average) CO <sub>2</sub> normalized peak data over the entire April 2006 test period .....	64
Figure 5.33: TDL CO <sub>2</sub> mole fraction based on the filtered & decimated (1-minute average) CO <sub>2</sub> normalized peak data along with GT1 percent load data over the entire April 2006 test period .....	64
Figure 5.34: GT1 exhaust stack H <sub>2</sub> O content as a function of percent load for the 9/05 FTIR and 4/06 TDL data.....	65
Figure 5.35: GT1 exhaust stack CO <sub>2</sub> content as a function of percent load for the 9/05 FTIR and 4/06 TDL data.....	66
Figure 5.36: Ratio of the standard deviation to the mean for the TDL and FTIR GT1 exhaust stack data .....	68

Figure 5.37: Ratio of  $H_2O$  and  $CO_2$  mole fractions versus time along with GT1 percent load..... 69

## LIST OF TABLES

Table 3.1: Detection limit at strongest absorption peaks in the mid- and near-infrared regions.....	17
Table 3.2: DFB lasers used for this research .....	19
Table 4.1: H <sub>2</sub> O and CO <sub>2</sub> spectroscopic data .....	39
Table 5.1: Table showing data collected from each gas turbine unit.....	42
Table 5.2: Table showing collected FTIR species and field data groups .....	43
Table 5.3: Table of TDL April 2006 field data from GT1 with data reduction summary	49

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## ABSTRACT OF THE THESIS

Diode Laser Measurement of H<sub>2</sub>O, CO<sub>2</sub>, and Temperature in Gas Turbine Exhaust  
through the Application of Wavelength Modulation Spectroscopy

by

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Tunable Diode Laser Absorption Spectroscopy (TDLAS) provides an accurate, fast, and non-intrusive solution for species and temperature measurement. The application of this technology to measure temperature, H<sub>2</sub>O, and CO<sub>2</sub> content from an industrial gas turbine has been demonstrated by this research. The multi-gas sensor system, consisting of inexpensive commercially available tunable diode lasers used in the telecommunications industry, uses Wavelength Modulation Spectroscopy (WMS) to quantify path-averaged temperature and concentrations. H<sub>2</sub>O and CO<sub>2</sub> spectroscopic information was first gathered in the laboratory and then the system was packaged for field use. The work culminated in an eight-day test in April 2006 where actual stationary gas turbine emissions data were captured. The results demonstrate the capability for measurement of temperature, H<sub>2</sub>O, and CO<sub>2</sub> in an industrial environment using two tunable diode lasers.

## CHAPTER 1: Introduction

Tunable Diode Laser Absorption Spectroscopy (TDLAS) provides an accurate, fast, and non-intrusive solution for species and temperature measurement. The application of this technology to measure temperature, H<sub>2</sub>O, and CO<sub>2</sub> content from an industrial gas turbine has been demonstrated by this research. The multi-gas sensor system, consisting of inexpensive commercially available tunable diode lasers used in the telecommunications industry, uses Wavelength Modulation Spectroscopy (WMS) to quantify path-averaged temperature and concentration. H<sub>2</sub>O and CO<sub>2</sub> spectroscopic information was first gathered in the laboratory and then the system was packaged for field use. The work culminated in an eight-day test in April 2006 where actual stationary gas turbine emissions data was measured.

Near-infrared tunable diode lasers have been used over the past two decades by laboratory researchers to measure many combustion-relevant species. The Beer-Lambert Law forms the theoretical framework for this work by relating the absorption of laser light by a molecule to its concentration. The development of WMS over the past decade has greatly increased the sensitivity of TDLAS. Research by Mohammadreza Gharavi and advisor Steven Buckley at UCSD laid the foundation for the field test data presented in this thesis by successfully using WMS to measure H<sub>2</sub>O and CH<sub>4</sub>. The capability to measure CO<sub>2</sub> in a portable multiplexed system with H<sub>2</sub>O makes this work novel.

The field-testing was performed on one of the gas turbines at the UCSD utility plant. A Fourier Transform Infrared (FTIR) system was also employed to gather data

along with the TDLAS system. In this thesis, both sets of data are compared against the gas turbine operating data.

TDLAS is promising for commercial use, because it is fast, non-intrusive, and accurate. It has the potential to be inexpensive and would be less maintenance-intensive compared to current Combustion Emissions Monitoring Systems (CEMS) that require calibration gases and frequent inspection. With data quantification capabilities on the millisecond time scale, TDLAS could also be used for active control of commercial power systems, like gas turbines.

The next chapter provides an overview of TDLAS fundamentals and WMS theory along with the historical background of these technologies. Chapter 3 covers the experimental setup used in the laboratory and field. The conversion of TDLAS data to temperature and concentration is presented in Chapter 4. Chapter 5 provides the field experimental data collected from the TDLAS, FTIR, and gas turbine systems. The final chapter summarizes the findings and outlines potential future work.

# CHAPTER 2: Wavelength Modulation Spectroscopy

## 2.1 Introduction

Distributed Feedback (DFB) lasers and infrared detectors have been widely used by the telecommunications industry, resulting in increased availability and low cost. Fiber-pigtailed tunable diode lasers, which fall in this category, are especially attractive for combustion diagnostics because of their small size and ability to be mounted away from harsh environments. Since the measurements are based on optical absorption, process intrusion is not an issue. An overview of the fundamentals, development, and techniques of TDLAS and WMS will be covered in this chapter.

## 2.2 Fundamentals of TDLAS

To understand TDLAS, it is necessary to begin with the physical phenomena of the absorption of electromagnetic waves by gas-phase molecules. Molecules only absorb or emit light at certain characteristic wavelengths; a scan across wavelength space showing absorption or emission lines is commonly referred to as the spectrum of the molecule. The spectrum can be measured in the laboratory and/or calculated using quantum mechanics. At infrared wavelengths, the spectrum is the result of particular rotational-vibrational effects of the atoms in the molecule. Observed spectroscopic transitions of molecules are results of the quantization of energy. A molecule may possess rotational energy (bodily rotation about its center of gravity), vibrational energy (periodic displacement of its atoms from their equilibrium positions), and electronic energy (continuous electron movement).

The key equation of absorption spectroscopy is the Beer-Lambert Law, which relates the transmission of light to molecular species absorption:

$$I(v) = I_0(v)e^{-k_v L}, \quad (2.1)$$

Here  $I(v)$  is the intensity of the laser light after it has passed through the region of interest (attenuated laser light intensity),  $I_0(v)$  is the initial intensity of the laser light (unattenuated laser light intensity),  $k_v$  is the absorption coefficient ( $\text{cm}^{-1}$ ), and  $L$  is the path length (cm) the light traverses through the region of interest. The amount of laser light at frequency  $v$  that is absorbed is the product  $k_v L$ . The absorbance,  $\alpha(v)$ , can be calculated from:

$$\alpha(v) \equiv -\ln\left(\frac{I(v)}{I_0(v)}\right) = k_v L = p_{abs} S(T) \phi(v - v_0) L, \quad (2.2)$$

where  $p_{abs}$  is the partial pressure (torr) of the absorbing molecule,  $S(T)$  is the absorption line strength ( $\text{cm}^{-2}\text{torr}^{-1}$ ) which is solely a function of temperature,  $T$ , and  $\phi(v - v_0)$  is the line shape function ( $1/\text{cm}^{-1}$ ).

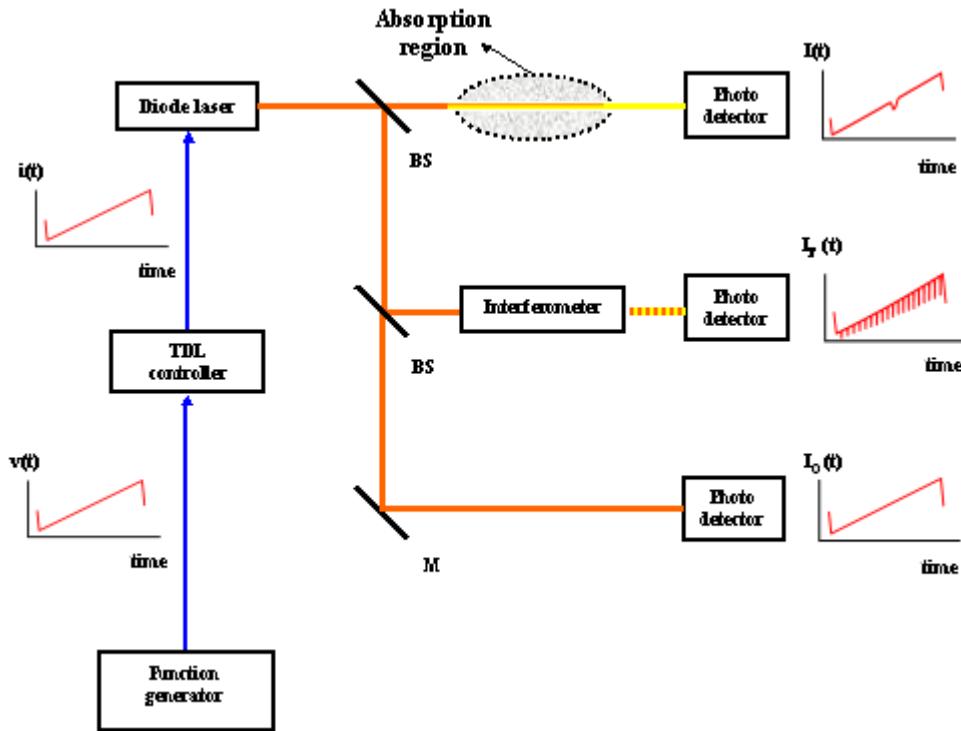
The line shape function is dependent on temperature by Doppler broadening effects and the partial pressure of all quenching gases in the laser region through collisional broadening effects. When the Doppler effect is dominant, the line shape function is normally represented by a Gaussian. In instances where only collisional effects are important, the line shape function is represented by a Lorentzian. However, in most combustion applications both Doppler and pressure broadening effects play a role and therefore a Voigt function is typically used to represent the line shape.

### 2.3 Development of TDLAS

In the late 1960's, direct current injection semiconductor lasers were used to measure species concentrations. By 1974, tunable mid-infrared diode lasers were used to measure CO from automobile traffic (Ku, Hinkley, and Sample 1975). Widespread use did not occur since the lasers had low output power (tens of  $\mu\text{W}$ ), multimode operation, and required cryogenic cooling. The development of near-infrared room temperature single mode diode lasers packaged with on-board thermoelectric cooling opened the door for widespread species measurements.

Tunable diode lasers may be used for spectroscopy as the laser optical frequency is tuned across a selected absorption transition of a particular species. The frequency can be tuned by changing the laser temperature or by changing the drive current. Several techniques exist for laser modulation and signal interpretation. In all cases, the laser frequency is kept near the center of the molecular transition of interest by adjusting the laser temperature. The frequency of the laser light is then tuned using injection current. The type of current modulation defines the different methods of absorption spectroscopy.

The most common method of injection current modulation is direct absorption, which uses a slow ramp modulation of the current over an entire absorption line. Species concentration is calculated by total integration of the measured absorption line. A typical experimental setup is shown in Figure 2.1.

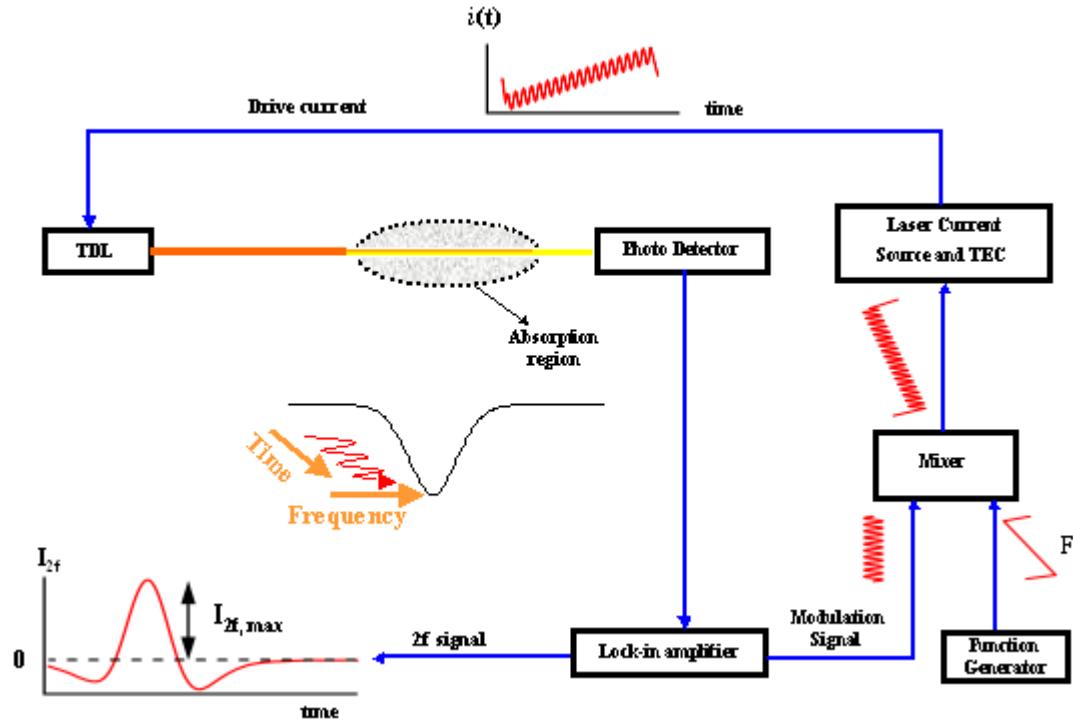


**Figure 2.1:** Typical experimental setup for direct absorption spectroscopy (from M. Gharavi)

There are several key drawbacks to the direct absorption technique. The primary disadvantage is the low sensitivity associated with direct absorption. In direct absorption the measurement is often a small change in a large signal (the laser), leading to relatively low sensitivity. In this mode, the signal can be very sensitive to fluctuating backgrounds common with high temperature measurements. Second, integration over the whole spectrum is not always possible due to interference between transitions or spectral broadening. And finally, the technique is heavily dependent on the measured reference signal.

The technique used for this research is Wavelength Modulation Spectroscopy (WMS). In WMS, the laser injection current is swept over a transition of interest (as in

direct absorption) at a frequency of 50 to 200 Hz with the addition of a small sinusoidal modulation of 10 to 50 kHz superimposed on the signal. A typical experimental setup is shown in Figure 2.2.



**Figure 2.2:** Typical experimental setup for wavelength modulation spectroscopy (from M. Gharavi)

The WMS technique allows for sensitivity improvement of 2-3 orders of magnitude over direct absorption (Reid and Labrie 1981). Other advantages include harmonic detection that nearly eliminates background, and frequency-domain multiplexing to minimize source noises (fluid, combustion, or electronic) and separate multiple laser signals. Multiplexed lasers can be carried to the diagnostic region on a single multimode fiber, launched, and detected on a single detector.

Tunable diode lasers have been employed in the laboratory using direct absorption and WMS to measure H<sub>2</sub>O (Arroyo and Hanson 1993; Gharavi and Buckley

2004), CH<sub>4</sub> (Nagali, Chou, Baer, Hanson, and Segall 1996; Gharavi and Buckley 2005), CO<sub>2</sub> (Mihalcea, Baer, and Handon 1998), and CO (Mihalcea, Baer, and Hanson 1997).

In industrial processes, multiplexed tunable diode lasers have successfully measured multiple species (typically CO and H<sub>2</sub>O) in high temperature atmospheric pressure environments. Examples include electric arc furnaces (Nikkari, Di Iorio, and Thomson 2002), basic oxygen furnaces (Alendorf, Ottesen, Hardesty, Goldstein, Smith, and Malcomson 1998), and coal fired power plants (Teichert, Fernholz, and Ebert 2003).

Xiang Liu at Stanford recently used a tunable diode laser sensor to measure gas turbine exhaust temperature (2006). The industrial studies have all used direct absorption with the exception of Nikkari. Liu's work is of particular interest since it is closely related to this research. He methodically designed, constructed, laboratory-validated, and demonstrated the use of a two TDL system to monitor two separate H<sub>2</sub>O transitions and calculate temperature in the exhaust of a 20 MW industrial gas turbine. Liu reported temperature accuracies of better than than 5 K from 350 to 1000 K and sensor response to changes in gas turbine load. A key improvement made by the research presented in this thesis is the use of a single TDL to monitor two H<sub>2</sub>O peaks for temperature and concentration calculation.

## 2.4 Wavelength Modulation Spectroscopy Theory

Several researchers have created theoretical models to quantify WMS. Wahlquist (1961) derived an analytical formula for the first three harmonic components of a modulated Lorentzian absorption line. Wilson (1963) used numerical integrations to obtain the first three harmonics for Lorentzian and Gaussian line shape functions. Using

a different mathematical approach, Arndt (1965) was able to generalize Wahlquist's formula for all harmonic components. Reid and Labrie (1981) were the first to validate these theoretical models with experimental data. Up until the 1990's, all the theoretical models were based on wavelength modulation and did not account for intensity modulation that results from the modulation of laser current in diode lasers. Philippe and Hanson (1993) included intensity modulation effects in WMS but did not account for the change in laser intensity as it is tuned across an absorption transition. A general theoretical model was presented by Shilt (2003) for diode laser WMS for Lorentzian line shape functions. In 2004, Gharavi formulated a general theoretical model for WMS quantification especially applicable for combustion measurements. His model, used for this research, can be used for any line shape function and includes all intensity modulation effects.

If injection current  $i$  of a diode laser is modulated at frequency  $f$  as shown in Equation 2.3:

$$i(t) = i_o + \Delta i \cos \omega t, \quad (2.3)$$

where  $i_o$  is the DC offset,  $\Delta i$  is the amplitude of the current modulation, and  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ) then the modulation in the incoming laser current simultaneously creates a modulation in the laser light intensity and in the optical frequency  $v$  as shown in Equation 2.4 and Equation 2.5:

$$I(t) = \bar{I} + \Delta I \cos \omega t, \quad (2.4)$$

$$v(t) = \bar{v} - \Delta v_m \cos(\omega t + \psi), \quad (2.5)$$

where  $I(t)$  is the laser light intensity as a function of time,  $\bar{I}$  is the average laser light intensity, and  $\Delta I$  is the amplitude of the intensity modulation, and where  $v(t)$  is the optical frequency as a function of time,  $\bar{v}$  is the laser center frequency,  $\Delta v_m$  is the wavelength modulation amplitude, and  $\psi$  is the phase difference between the intensity modulation and the frequency modulation.

The wavelength modulation amplitude is one-half of the peak-to-peak difference in frequency of the laser light from the lowest point to the highest point in the injection current driving the laser. Equations 2.3 to 2.5 are applicable when the wavelength modulation amplitude,  $\Delta v_m$ , is relatively small (less than  $0.12 \text{ cm}^{-1}$ ) since there is a linear relationship between laser intensity and optical frequency. This is the case when the high frequency sine wave modulation is the sole source of modulation of the laser drive current. However, in WMS where the laser is swept at a low frequency (typically up to  $1 \text{ cm}^{-1}$ ) in addition to the high frequency signal modulation, the nonlinearity in laser intensity becomes apparent. The low frequency current signal causes the laser intensity to vary parabolically as shown in Equation 2.6:

$$I_0(\bar{v}) = I_0 \left\{ 1 + s_{F1}(\bar{v} - v_0) + s_{F2}(\bar{v} - v_0)^2 \right\} \quad (2.6)$$

where  $I_0$  is the laser intensity at some particular reference frequency (molecular absorption frequency,  $v_0$ ) and  $s_{F1}$  and  $s_{F2}$  are coefficients with units of  $1/\text{cm}^{-1}$  and  $1/\text{cm}^{-2}$ , respectively.  $s_{F1}$  and  $s_{F2}$  are used to fit the observed interaction between intensity and frequency for a laser with sweep frequency,  $F$ . The superposition of the higher frequency sine wave current modulation adds another term and is expressed by:

$$I_0(\bar{v}) = I_0 \left\{ 1 + s_{F1}(\bar{v} - v_0) + s_{F2}(\bar{v} - v_0)^2 - s_f \Delta v_m \cos \omega t \right\} \quad (2.7)$$

where  $s_f$  is the laser intensity frequency parameter at modulation frequency  $f$  with units of  $1/\text{cm}^{-1}$ .  $s_{F1}$ ,  $s_{F2}$ , and  $s_f$  are highly dependent on the laser injection current frequency.

The Beer-Lambert Law is used to convert the laser intensity modulation to species concentration as expressed in Equations 2.1 and 2.2. Usually WMS is applied in situations with small absorbance ( $\alpha(v) < 0.1$ ). In this case a Taylor series expansion can be used to approximate the Beer-Lambert law. The first two terms in the Taylor series expansion of the exponential in Equation 2.1 give:

$$I(v) = I_0(v)[1 - \alpha(v)] \quad (2.8)$$

When the transmitted light  $I(v)$  is detected by a wide bandwidth photodetector, the photodetector generates a voltage signal proportional to  $I(v)$  given by Equation 2.9:

$$V_P(\bar{v}) = K_P \left[ 1 + s_{F1}(\bar{v} - v_0) + s_{F2}(\bar{v} - v_0)^2 - s_f \Delta v_m \cos \omega t \right] \times \{1 - \alpha[\bar{v} - \Delta v_m \cos(\omega t + \psi)]\} \quad (2.9)$$

where  $K_P$  is the electro-optical (or opto-electrical) gain of the photodetector in volts.

The electro-optical gain is the ratio of photodetector voltage to intensity. Expressing the photodetector signal in a Fourier series gives:

$$V_P(\bar{v}) = K_P \left[ \sum_{m=0}^{\infty} a_m(\bar{v}) \cos(m\omega t) + \sum_{m=0}^{\infty} b_m(\bar{v}) \sin(m\omega t) \right] \quad (2.10)$$

The  $n$ th harmonic component of the in-phase signal from the lock-in amplifier is given by:

$$I_{n,p}(\bar{v}) = K_{P,L} \int_{-\pi}^{\pi} \left\{ \left[ 1 + s_{F1}(\bar{v} - v_0) + s_{F2}(\bar{v} - v_0)^2 - s_f \Delta v_m \cos \omega t \right] \times \{1 - \alpha[\bar{v} - \Delta v_m \cos(\omega t + \psi)]\} \cos(n\omega t + \theta) \right\} d(\omega t) \quad (2.11)$$

The absorbance,  $\alpha(v)$  in Equation 2.11 is given by:

$$\alpha(\bar{v}) = \alpha[\bar{v} - \Delta v_m \cos(\omega t + \psi)] = S(T) g_v[\bar{v} - v_0 - \Delta v_m \cos(\omega t + \psi)] L p_{abs} \quad (2.12)$$

Equation 2.11 relates the measured  $I_{n,p}(\bar{v})$  to the absorbing species partial pressure,  $p_{abs}$ . The line shape can be represented by a Voigt function to account for the Doppler and pressure broadening effects common in combustion applications. The Voigt function  $g_v(v - v_0)$  is defined by the following equations:

$$g_v(v - v_0) = AB(x, y) \quad (2.13)$$

$$\text{where } A = \frac{1}{\Delta v_G} \sqrt{\ln(2) / \pi} \quad (2.14)$$

$$B(x, y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{y^2 + (x-t)^2} dt \quad (2.15)$$

$$x = \frac{v - v_0}{\Delta v_G} \sqrt{\ln(2)} \quad (2.16)$$

$$y = \frac{\Delta v_L}{\Delta v_G} \sqrt{\ln(2)}. \quad (2.17)$$

and  $g_v(v - v_0)$  has units of  $1/\text{cm}^{-1}$ ,  $\Delta v_L$  is the pressure broadening half-width in  $\text{cm}^{-1}$ ,  $\Delta v_G$  is the Doppler broadening half-width,  $v_0$  is the frequency of the absorption transition, and  $t$  is a variable of integration. The Doppler broadening half-width at half-maximum depends upon the temperature and the molecular weight as shown in Equation 2.18:

$$\Delta\nu_G = 3.581 \times 10^{-7} \nu_0 \sqrt{\frac{T}{M}} \quad (2.18)$$

where  $T$  is the temperature in Kelvin and  $M$  is the molecular weight.

The Voigt function is difficult to evaluate because of the integral in Equation 2.15 but can be approximated by Whiting's expression (Whiting 1968) as shown in Equation 2.19:

$$\sigma_V(v) = G(\nu_0) \left\{ (1-x)e^{-0.693y^2} + \frac{x}{1+y^2} + 0.016(1-x)x \left[ e^{-0.0841y^{2.25}} - \frac{1}{1+0.0210y^{2.25}} \right] \right\} \quad (2.19)$$

$$\text{where } x = \frac{\Delta\nu_L}{\Delta\nu_V} \quad (2.20)$$

$$y = \frac{|\nu - \nu_0|}{\Delta\nu_V} = \frac{|\bar{\nu} - \nu_0 - \Delta\nu_m \cos(\omega t + \psi)|}{\Delta\nu_V} \quad (2.21)$$

$\Delta\nu_V$  is the Voigt function half-width at half-maximum and can be calculated using the equation presented in (Olivero and Longbothum 1977):

$$\Delta\nu_V = 0.5346\Delta\nu_L + (0.2166\Delta\nu_L^2 + \Delta\nu_G^2)^{0.5} \quad (2.22)$$

where  $\Delta\nu_L$  is the pressure broadening half-width at half-maximum solved using:

$$\Delta\nu_{L,j} = P \sum_i \chi_i \gamma_{i-j}, \quad (2.23)$$

where  $\Delta\nu_{L,j}$  is the pressure broadening half-width of molecule  $j$ ,  $P$  is the total pressure in torr,  $\chi_i$  is the mole fraction of molecule  $i$ , and  $\gamma_{i-j}$  is the pressure broadening coefficient with units of  $\text{cm}^{-1}/\text{torr}$  for a collision between  $i$  and  $j$ . Equation 2.23 thus sums the pressure broadening caused by all collision partners.

$G(v_0)$  in Equation 2.19 is the cross-section at absorption line center given by Equation 2.24 as:

$$G(v_0) = \frac{S(T)}{2\Delta\nu_V (1.065 + 0.447x + 0.058x^2)} \quad (2.24)$$

with units of  $\text{cm}^2$ .

As the Lorentzian or Gaussian half-width approaches zero, the Voigt function is converted to a Gaussain or Lorentzian line shape respectively.

# CHAPTER 3: Experimental Setup

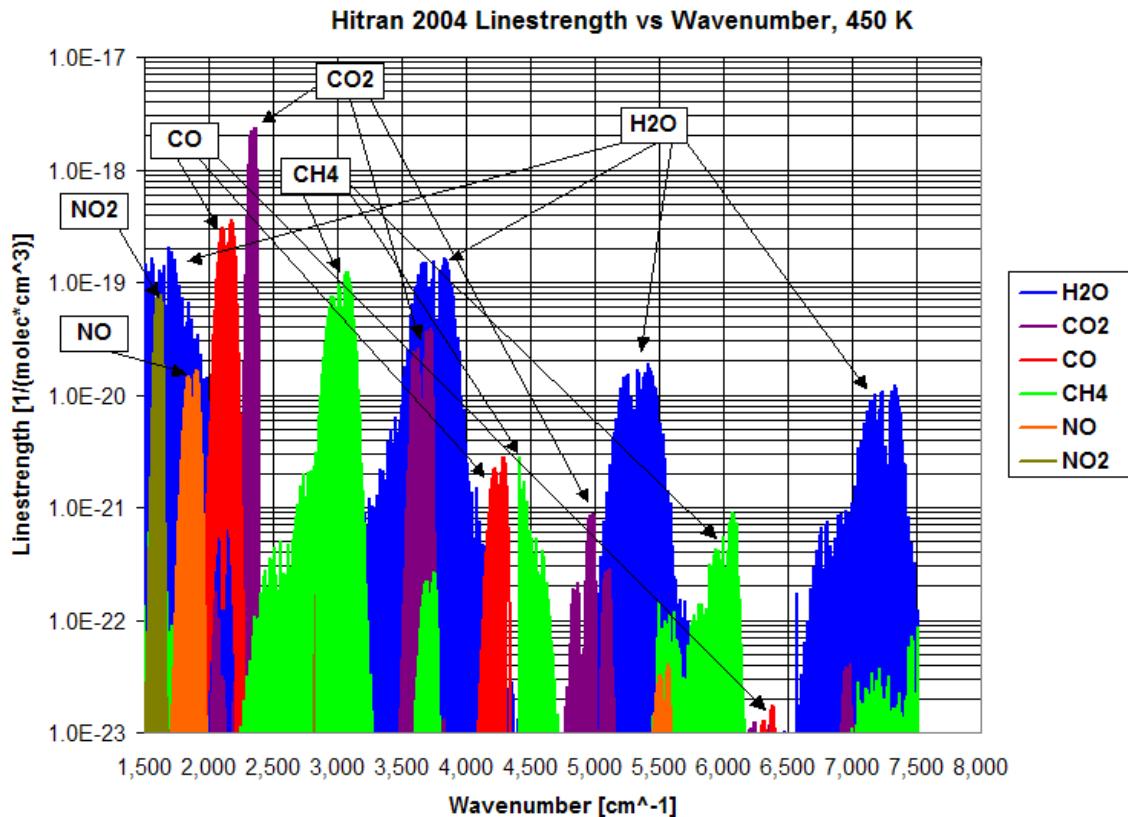
## 3.1 Introduction

This chapter covers the lab and field setup done to support the TDL system gas turbine exhaust flow testing. In the laboratory, support hardware for the TDL lasers was manufactured along with glass and metal calibration cells to provide the spectroscopic data necessary to quantify temperature, H<sub>2</sub>O, CO<sub>2</sub>, and CO concentrations. For field-testing, the TDL system was packaged for industrial use and window assemblies were created to sample exhaust stack data. The field-testing also included setup of an FTIR system to gather data in parallel to the TDL system.

## 3.2 TDL Laser Selection

The initial plan was to develop a high-speed multi-gas sensor for use in commercial energy generation applications such as stationary gas turbines. The sensor, based on commercially available tunable diode lasers, was envisioned to measure NO, CO, CH<sub>4</sub>, and H<sub>2</sub>O simultaneously. Laser path-averaged temperature would also be calculated using the H<sub>2</sub>O signal. Several researchers including Gharavi and Buckley (2005) had demonstrated H<sub>2</sub>O and CH<sub>4</sub> TDL measurements in the past. Research done for this thesis found that the NO signal was too weak for quantification given the spectral range of commercially available TDL technology. CO and CO<sub>2</sub> were developed instead for TDL measurements presented in this thesis. The TDL gas turbine exhaust data was taken using the H<sub>2</sub>O and CO<sub>2</sub> lasers since the CO concentrations present were too low to be quantifiable.

The line strengths of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{NO}$ , and  $\text{NO}_2$  transitions from 1500 to 8000 wavenumbers (6,667 to 1,250 nm) are shown in Figure 3.1. The data is from the Hitran 2004 database (Rothman et al. 2005) at 450 K, the gas turbine exhaust stack temperature.



**Figure 3.1:** Line strength versus wavenumber for  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{NO}$ ,  $\text{NO}_2$  taken from the Hitran 2004 database at 450 K.

Tunable diode InGaAsP communication lasers operate in the near-infrared region between 5000 to 8333 wavenumbers (2,000 to 1,200 nm).  $\text{H}_2\text{O}$  dominates the near IR region. In the mid-infrared region, between 833 to 2500 wavenumbers (12,000 to 4,000 nm)  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ , and  $\text{NO}$  are strong. Table 3.1 lists detection limits for the strongest absorption peaks present in the mid and near-infrared regions.

**Table 3.1:** Detection limit at strongest absorption peaks in the mid- and near-infrared regions

Species	Mid-Infrared:			Near-Infrared:		
	Detection Limit <sup>^</sup> (ppb)	Wavelength (nm)	Wavenumber (cm <sup>-1</sup> )	Detection Limit <sup>^</sup> (ppb)	Wavelength (nm)	Wavenumber (cm <sup>-1</sup> )
H <sub>2</sub> O	<b>2.0</b>	5,490	1821	<b>60</b>	1,390	7194
CH <sub>4</sub>	<b>1.7</b>	3,260	3067	<b>600</b>	1,650	6061
CO	<b>0.8</b>	4,600	2174	<b>30,000/500</b>	1,570/2,330	6369/4292
CO <sub>2</sub>	<b>0.1</b>	4,230	2364	<b>3,000</b>	1,960	5102
NO	<b>5.8</b>	5,250	1905	<b>60,000/1,000</b>	1,800/2,650	5556/3774
NO <sub>2</sub>	<b>3.0</b>	6,140	1629	<b>340</b>	680	14706

<sup>^</sup> Assuming 1e-5 absorbance, 1 Hz bandwidth & 1 meter path length

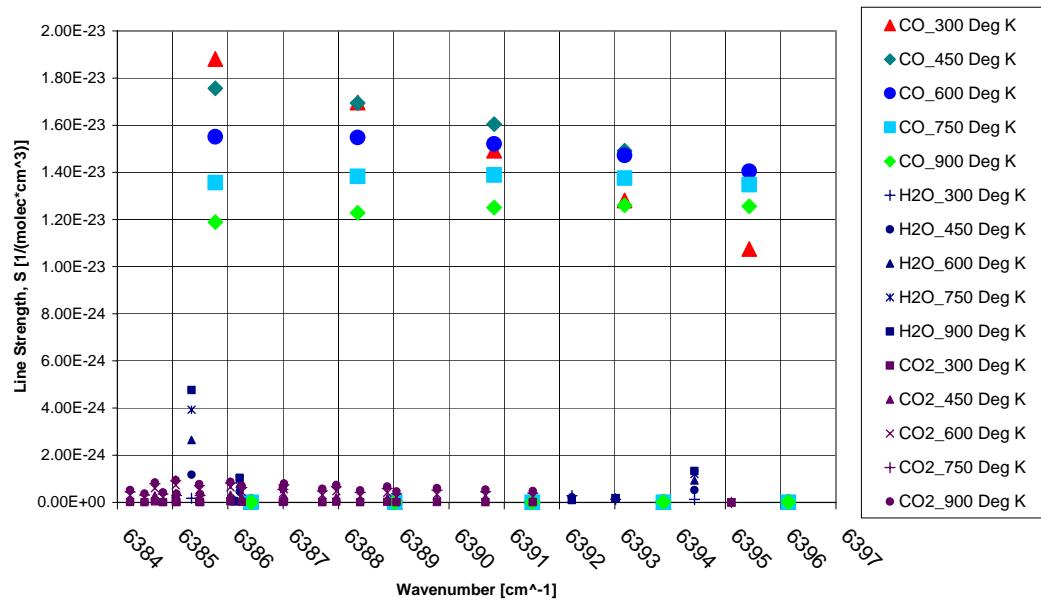
From Southwest Sciences website, <http://www.swsciences.com/technology/sensors.html>

For this research, TDL measurements were sought for NO, CO, and CO<sub>2</sub>, along with H<sub>2</sub>O and CH<sub>4</sub> which had already been proven. Multiple factors played a role in selecting the optimal TDL for a given species. The laser needed to be in a region where there was a strong absorption peak across the expected temperature range, which was free of interference from other species, and which was available as a low-cost commercial product. A target temperature of 450 K was chosen since this was the expected exhaust temperature from the stationary gas turbines at UCSD.

In the near-infrared region, where telecommunication TDLs exist, there is no strong absorption peak for NO. Strong NO features are present in the mid-infrared region, particularly at 1900 wavenumbers (5,250 nm), where Quantum Cascade (QC) lasers operate. Mann (2003) and Wehe (2003) have demonstrated promising results using these lasers. Unfortunately, QC lasers are not mass-produced and are currently quite costly. Some also require cryogenic cooling that adds significant complexity to the system. For these reasons NO was dropped from the experimental measurement plan.

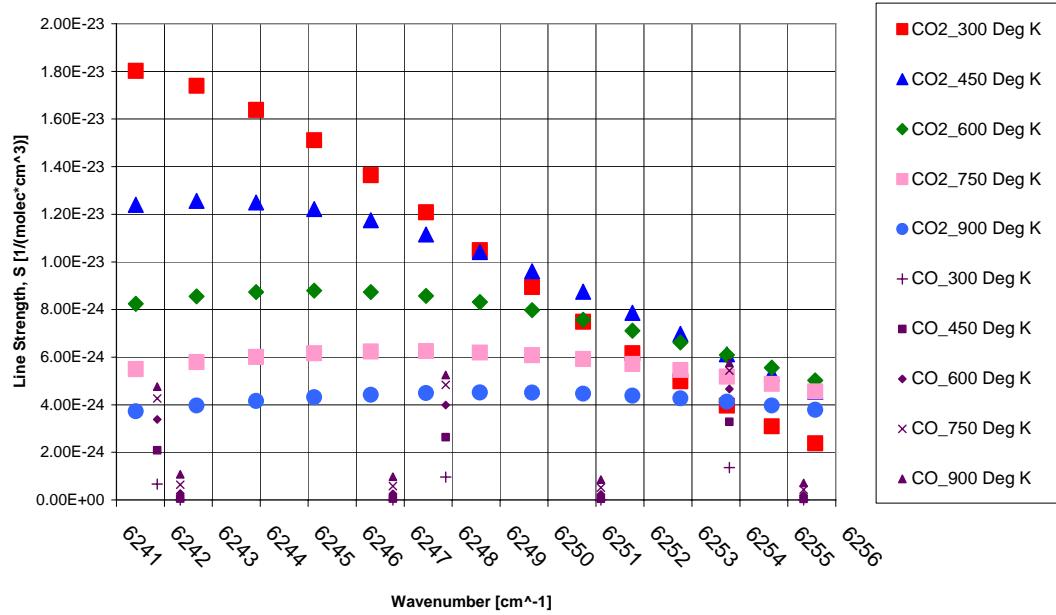
Evaluation of the Hitran 2004 database showed that the 6380 to 6400 wavenumber region was promising for CO measurement since this was the highest

absorption region in the near-infrared range. A distributed feedback (DFB) telecommunication TDL was obtained at 6391 wavenumber (1,565 nm). As shown in Figure 3.2, this spectral region is free of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  interference from 300 to 900 K.  $\text{CH}_4$  also has no spectral features in this region. The effects of temperature broadening were also investigated using Hitran data. The peak line strength at 6391 wavenumber was exhibited at 450 K, the target temperature.



**Figure 3.2:** Hitran 2004 line strength versus wavenumber data from 300 to 900 K used to choose CO laser

A similar study was completed using Hitran 2004 data for  $\text{CO}_2$ . A distributed feedback (DFB) telecommunication TDL was found at 6250 wavenumber (1,600 nm). As shown in Figure 3.3, this wavenumber is free of CO interference from 300 to 900 K.  $\text{H}_2\text{O}$  and  $\text{CH}_4$  also had no spectral features in this region. The effects of temperature broadening were also investigated using Hitran data. Like CO, the peak line strength at 6250 wavenumbers was exhibited at 450 K, the target temperature.



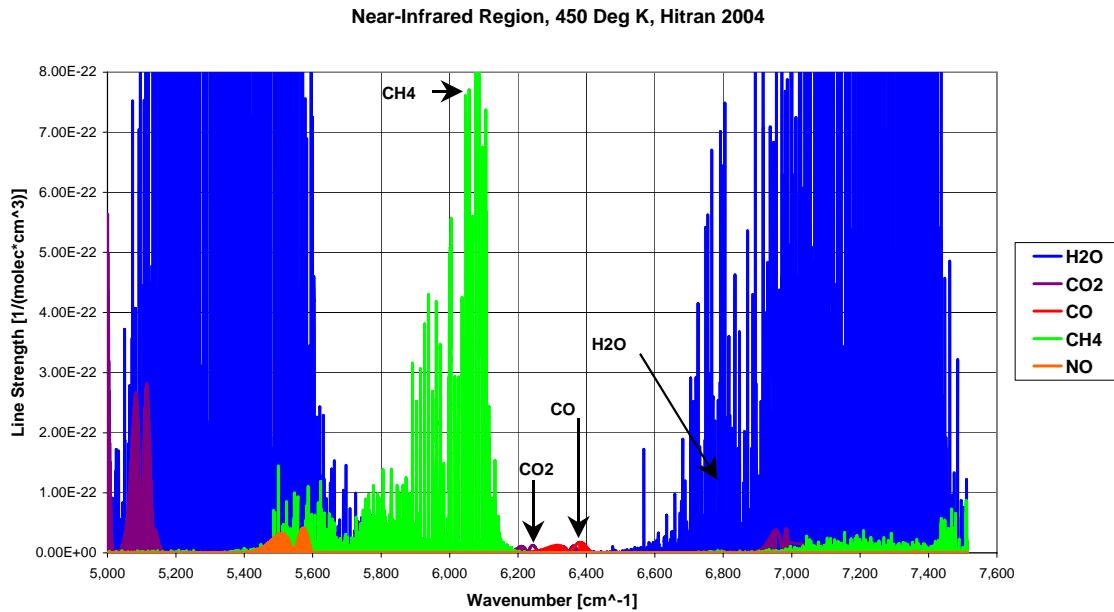
**Figure 3.3:** Hitran 2004 line strength versus wavenumber data from 300 to 900 K used to choose the CO<sub>2</sub> laser

Table 3.2 summarizes the DFB lasers used for this research. They are all 14 pin fiber-pigtailed telecommunication lasers with costs ranging from \$500 to \$1200 for a single laser.

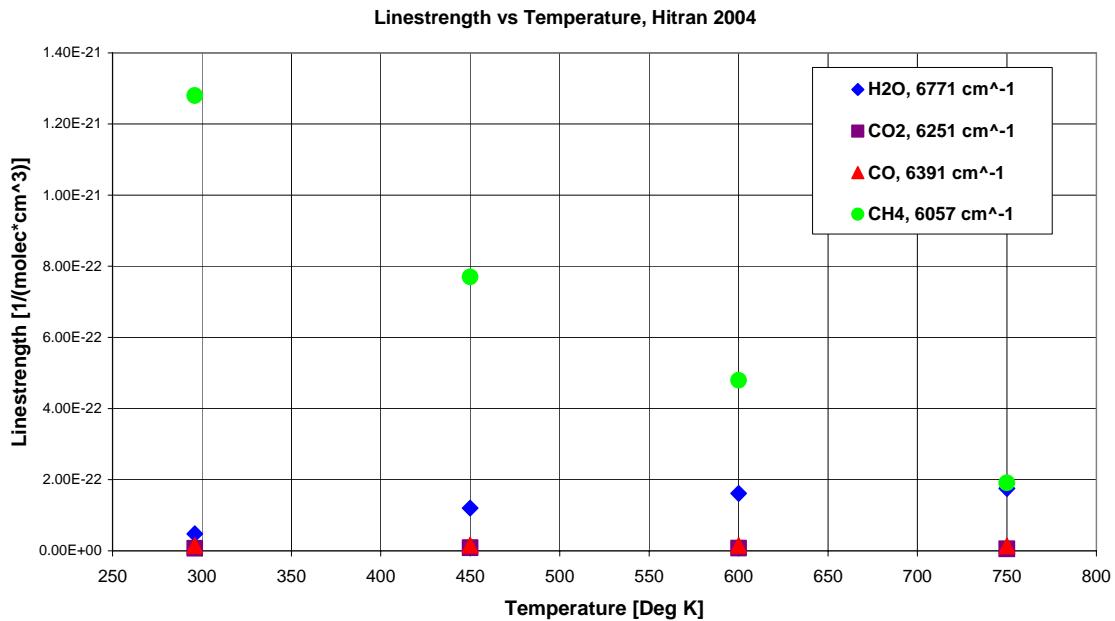
**Table 3.2:** DFB lasers used for this research

Species	Wavelength (nm)	Wavenumber (cm <sup>-1</sup> )	Manufacturer	Model Number	Power (mW)	Line Strength at 450 Deg K [1/(mole <sup>-1</sup> cm <sup>-3</sup> )]
H <sub>2</sub> O	1,477	6771	Corning Lasertron	QLM4S781-050	2	1.20E-22
CO	1,565	6391	Lucent Laser	D2570T916	40	1.60E-23
CO <sub>2</sub>	1,600	6250	NTT Electronics	P873	20	8.74E-24
CH <sub>4</sub>	1,651	6057	OKI	OL6109L-10B	10	7.70E-22

Figure 3.4 shows where the lasers operate in the near-infrared spectrum at 450 K based on the Hitran data. The line strength of CH<sub>4</sub> decreases with increasing temperature while the line strength of H<sub>2</sub>O increases. The line strengths of CO<sub>2</sub> and CO are not dependent on temperature (or exhibit very weak dependence) over this temperature range. This is shown in Figure 3.5.



**Figure 3.4:** Line operating region of the lasers used in this research along with NO taken from Hitran 2004 at 450 K



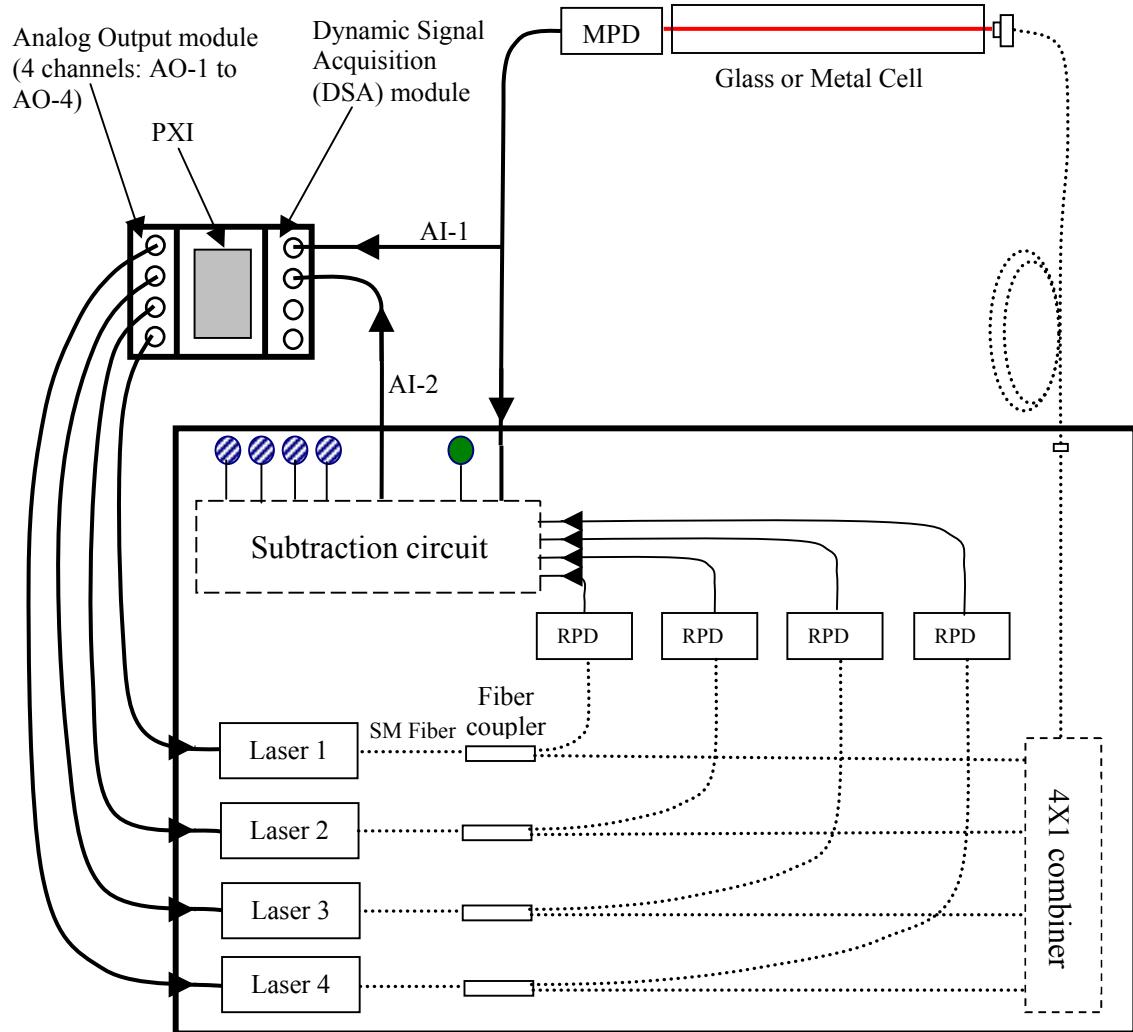
**Figure 3.5:** Line strength as a function of temperature for the H<sub>2</sub>O, CO<sub>2</sub>, CO, and CH<sub>4</sub> lasers

### 3.3 Laboratory Setup

Multiple devices were constructed to gather the necessary spectroscopic information required for quantification of H<sub>2</sub>O, CH<sub>4</sub>, CO, CO<sub>2</sub>, and temperature using TDL's. Electrical cables were made to control the lasers and a 4-laser mounting plate was created. The fiber optic cabling to and from the lasers was also arranged. In order to conduct the experiments, new glass and metal cells were designed and manufactured. The details of these assemblies will be presented in this section.

The four lasers are all room temperature, single mode, fiber pig-tailed DFB TDLs with 14 pin butterfly style pin-outs. These lasers have on-board thermoelectric cooling for temperature control. Four special cables were soldered to connect the lasers to the laser controllers (ILX Lightwave Model LDC-3900) using two-15 pin female connectors for the laser end and a 9-pin male connector to interface with the laser controller. A wiring diagram is shown in Figure 3.6. A metal base plate was also manufactured to situate up to four lasers.

To gather H<sub>2</sub>O-related data for the 2<sup>nd</sup> harmonic spectra model as well as the temperature-dependent line strength and pressure broadening parameters, a new longer glass cell was designed without the need for argon purging. The previously existing glass cell, shown in Figure 3.7, is 30 cm in length and uses argon purging to prevent atmospheric H<sub>2</sub>O from interfering with the laser beam before and after the cell in the transition zones outside of the ceramic heater.



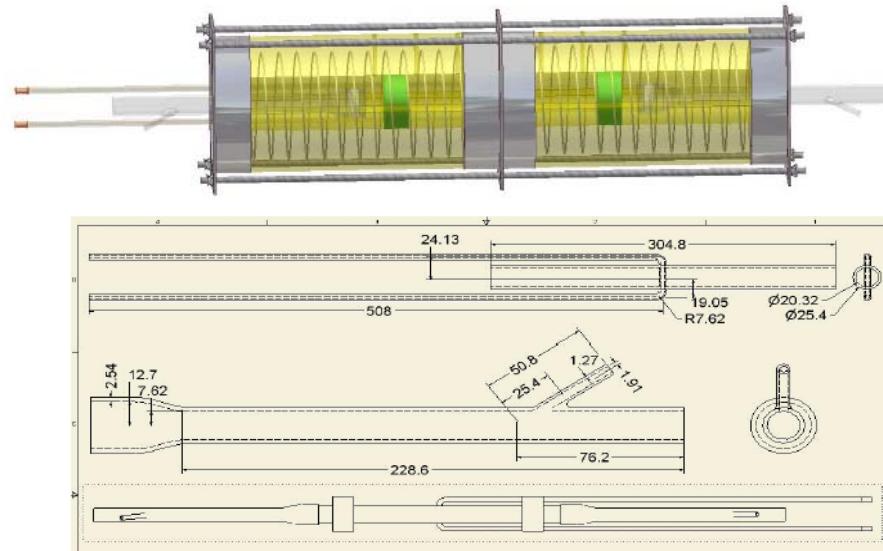
- ➊ Adjustment knob for adjusting the gain of the Reference Photodetector (RPD)
- ➋ Adjustment knob for adjusting the gain of the Main Photodetector (MPD)
- ..... Optical signal
- Electrical signal

AI-1: This channel is used by the LabVIEW™ program to calculate first harmonic components of each absorption signal based on the MPD signal.

AI-2: This channel is used by the LabVIEW™ program to calculate second harmonic components of each absorption signal based on the subtracted signal.

AO-1 to 4: These channels are used by the LabVIEW™ program to generate four modulation signals, which drive the lasers.

**Figure 3.6:** Laser, cable, and laser controller wiring diagram (portion from A. Schuger)



**Figure 3.7:** Existing 30 cm core glass cell designed by M. Gharavi

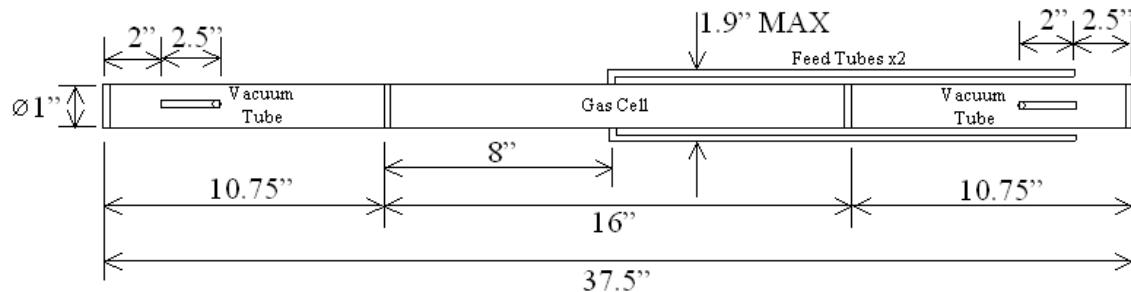
The new glass cell core is 40 cm long instead of 30 cm and utilizes a three-chamber design so that the outer two chambers can be brought to vacuum, which eliminates the need for argon purge. Four 1-inch diameter 1-degree fused silica wedge windows create the three sections and prevent back reflection of the laser light. The design drawing is shown in Figure 3.8. Two  $\frac{1}{4}$ -inch diameter tubes join the center chamber for species input/evacuation and pressure sensing. The new longer glass cell still mounts in the existing ceramic heater housing. Along with the new glass cell, two more 30 cm cells were made to support future testing. Curtis Technologies, a company located in Sorrento Valley, manufactured all of the glasswork.

## UCSD H<sub>2</sub>O GLASS CELL

M. LEON

4/15/05

### TOP VIEW



#### NOTES:

- Tube material: Quartz; Window material: Fused Silica
- 4 windows are  $\frac{1}{4}$ " thick with 1 degree wedge
- Window orientation defined by arrows at TDC
- Dimensions from outer face of windows
- Feed and vacuum tubes are  $\frac{1}{4}$ " diameter

**Figure 3.8:** Four-window 40 cm long core glass cell created for this project

To achieve the larger path length needed to detect CO and CO<sub>2</sub>, two 1-meter long 1.5-inch diameter metal cells were designed and constructed. Each 1-meter long stainless steel cell is housed within insulated ceramic heaters that extend 21 cm past either side of the cell. Two 30 cm long glass vacuum tubes eliminate interference from atmospheric water vapor allowing the laser-collimating lens and photo detector to be placed away from the high temperature inside the cell. Six K-type TC's measure the gas temperature along the axial length of the cell. A modular approach was taken to allow for access to the windows for cleaning. Metal C-Seals made by Perkin-Elmer were used to provide the seal between the metal flange and fused silica window. Two metal cells were constructed so that one could be used for low pressure testing and the other for high pressure flow-through testing.

The 1.5-inch diameter 1-meter long metal cell uses 2-inch diameter 1-degree wedge windows to prevent reflection interference (etaloning) along with the two 30 cm long vacuum tubes that have 1-inch diameter 1-degree wedged windows on each end. The laser beam must travel through 6 windows over 1.6 meters. Due to the wedged windows, while the laser passes through the 1-meter long metal cell, the beam could be offset up to 27.5% of the inner diameter of the metal cell. This is calculated from Equation 3.1 where  $q_d$  is the deviation of a ray incident on a wedged window with a wedge angle  $\alpha$ .

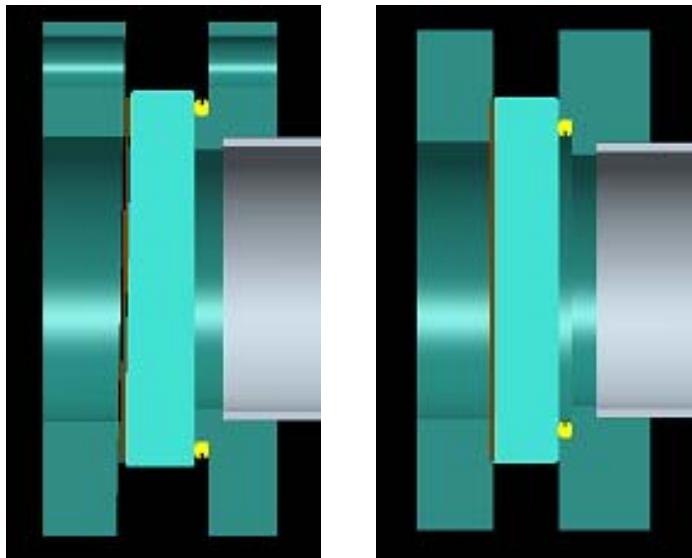
$$q_d = (n - 1)\alpha \quad (3.1)$$

A value of 1.5 was used as the refractive index,  $n$ . Additionally, to ensure that the beam passed through the entire path without interference, each 1-degree wedge window was oriented such that walk-off of the beam was avoided.

The C-Seals™ used in the seals are metal-to-metal seals able to create a gas-tight metal seal due to flexure of the seal under compression. These were required instead of elastomer-type seals due to the service temperature of the gas cell. For each application, the C-Seals are different due to their orientation; the positive curvature (convex) side is designed to go toward the lower pressure. Made of Inconel 718 with gold plating, they have a maximum operating temperature of 1400°F and can be used in ultra high vacuum ( $10^{-10}$  Torr) to high-pressure (200,000 psi) applications.

The crux of the metal cell design is the wedge window-to-flange interface. For the low-pressure metal cell, the C-Seal is oriented facing outward as shown in Figure 3.9. The wedge window was modified to have a flat rim, which allows for a parallel seal. The same methodology was used for the high-pressure metal cell but the flange was machined

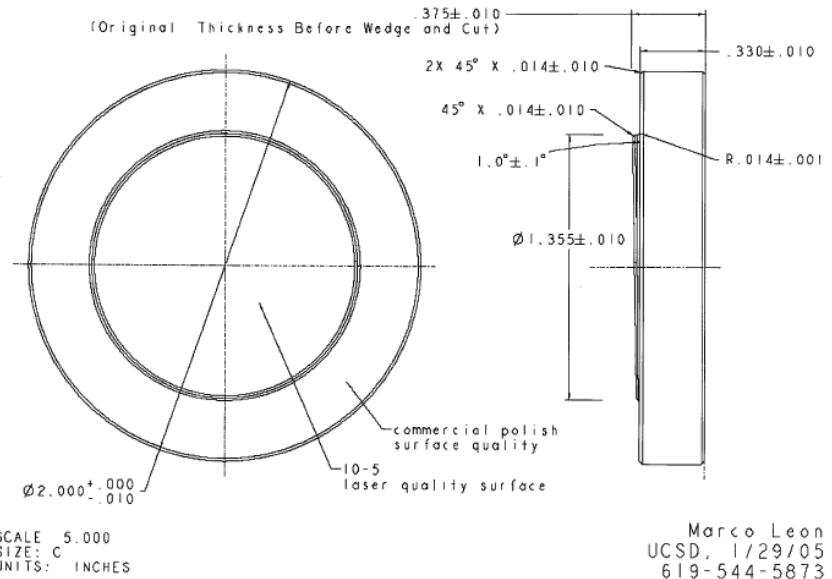
differently to account for the inward facing C-Seal as shown in Figure 3.10. The wedge window machining information is shown in Figure 3.11.



**Figure 3.9:** Left: Low-pressure metal cell wedge window-flange interface (note outward facing C-Seal)

**Figure 3.10:** Right: High-pressure metal cell wedge window-flange interface (note inward facing C-Seal)

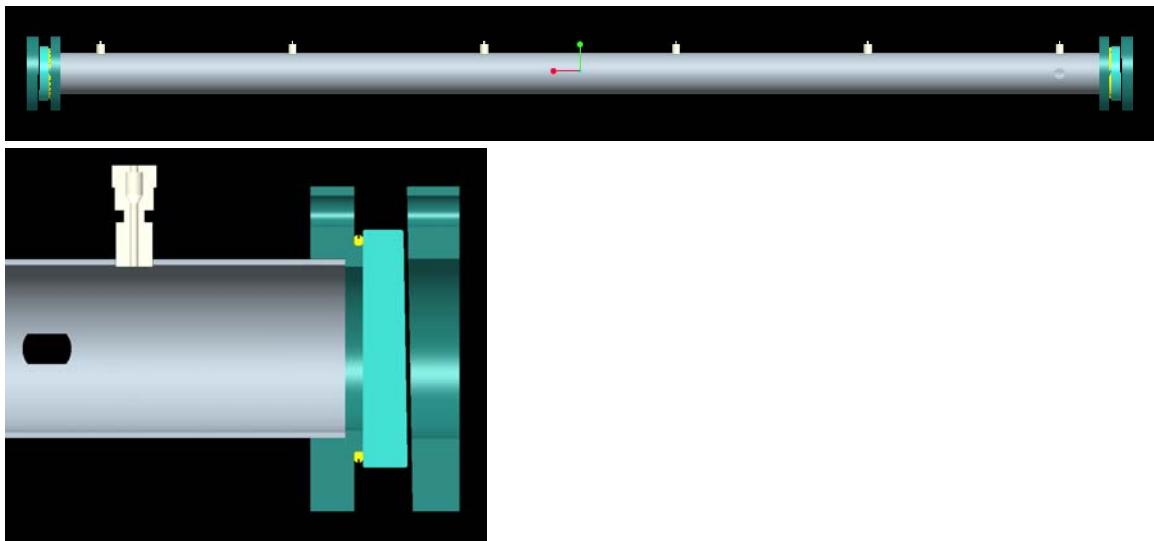
MODIFIED 2"Ø 1° WEDGE WINDOW, FUSED SILICA rev A



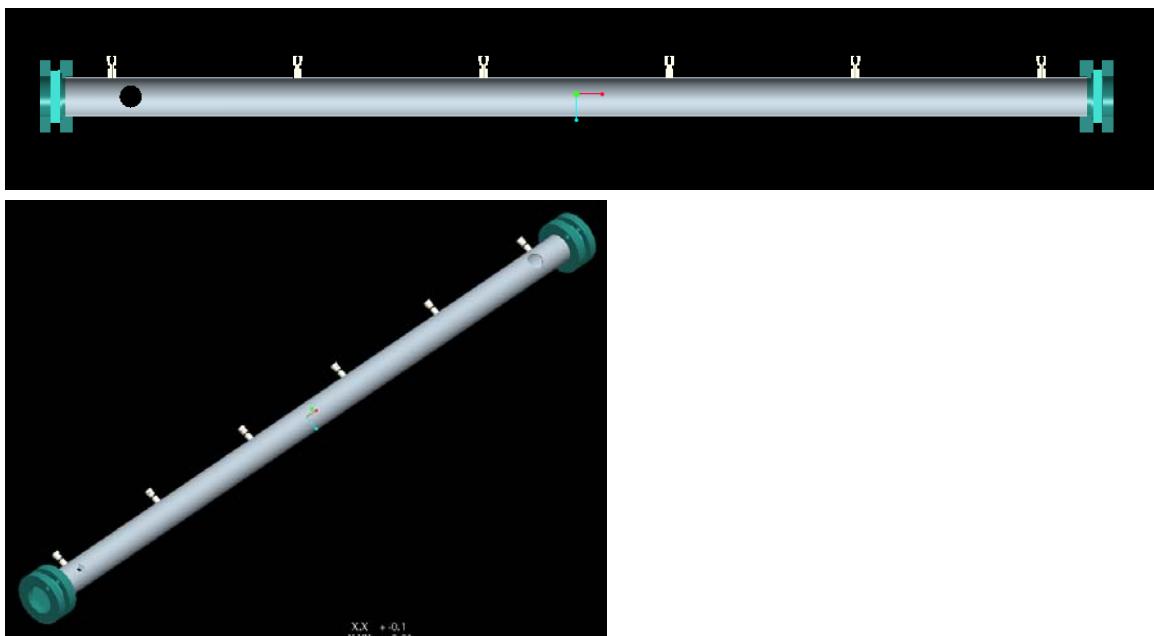
**Figure 3.11:** Wedge window machining drawing

The main body of the metal cell is seamless 1.5 inch outer diameter stainless steel 304 tubing (0.049 inch wall thickness). The inside window-to-window length is 1 meter. Six 0.062-inch diameter probe Conax fittings with graphoil seals good to 925°F are welded to the tube to seal and allow depth control of the K-type thermocouples (TCs). From the end of the tube, which has a total length of 39.072 inches, they are located at the following axial positions: 4.786, 11.536, 16.786, 22.036, 27.286, and 34.286 inches. The low-pressure metal cell has two  $\frac{1}{4}$ -inch Swagelok 90° fittings welded on for species feed/evacuation and pressure sensing. Along with one  $\frac{1}{4}$ -inch Swagelok 90° fitting for pressure sensing the high-pressure metal cell has two  $\frac{1}{2}$ -inch Swagelok 90° fittings on either end to support flow-through testing. Pro-E models of the low and high-pressure metal cells are shown in Figures 3.12 and 3.13.

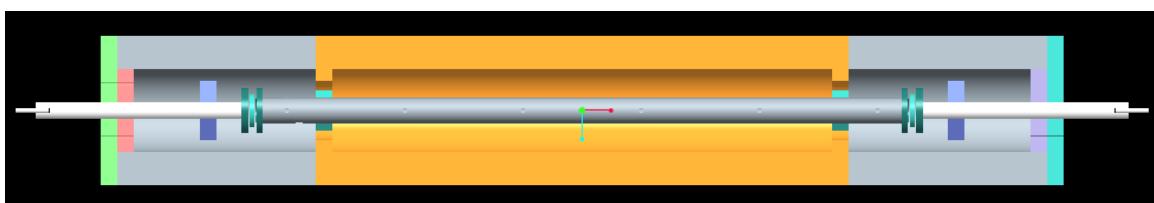
The thermocouples are K-type, inconel-sheathed, 6 feet long, and 0.063 inch diameter. The sensing side is sealed and the junction is ungrounded to provide electrical isolation. Mini male connectors were used on the opposite end. Three sets of 20-inch long 240V semi-cylindrical 5-inch ID Watlow ceramic fiber heaters encase the metal cell (9 inch OD). The heaters are covered with 1-inch thick mineral wool insulation and sheet metal. The feed/suction, pressure lines, and TCs all exit the ends of the heater assembly, which are enclosed with 1-inch thick silica insulation board. The entire metal cell/heater assembly was modeled using Pro-E and is shown in Figure 3.14. The bill of materials for the system, including vendor and part number information is listed in the Appendix. The glass and metal cell assemblies cost \$10,300. Bruce Thomas (Laboratory Engineer) and Alan Yang (Undergraduate Student) completed the majority of the fabrication in-house.



**Figure 3.12:** Low-pressure metal cell assembly

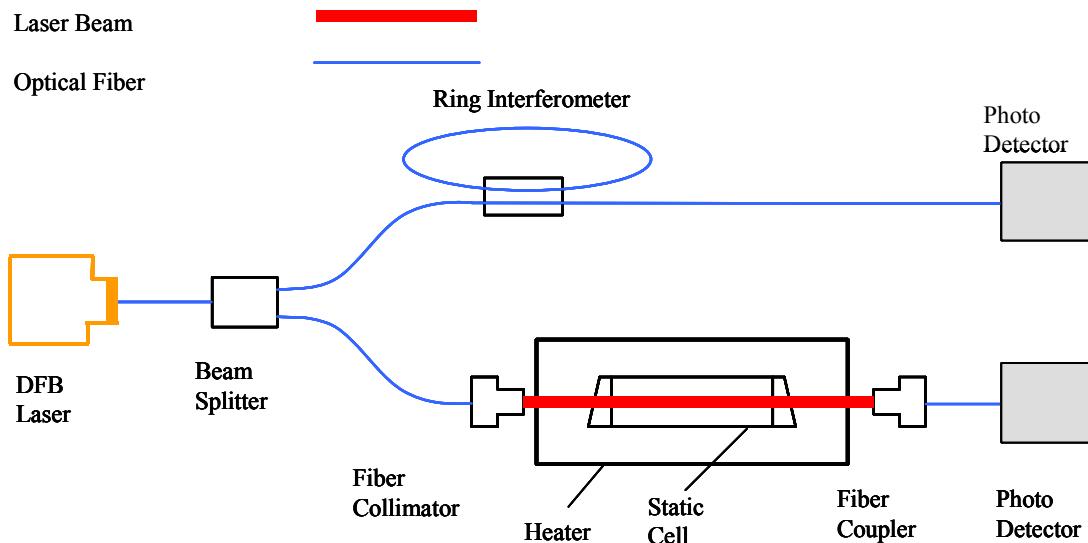


**Figure 3.13:** High-pressure metal cell assembly



**Figure 3.14:** Metal cell & heater assembly modeled using Pro-E; the 30 cm long glass vacuum tubes are also shown on each end (note: actual heaters used were three 20-inch long sections, not two 12-inch and one 32-inch heater in the middle as shown)

Testing with both the glass and metal cell is essentially the same; the metal cell is used for elevated pressure experiments. A diagram of the single-species measurement setup is shown in Figure 3.15 with the static cell being either the glass or metal version. Temperature regulation in the metal cell is done independently by the three sets of cylindrical heaters (zone heating). A TC from each section feeds three independent WATLOW series 93 DIN temperature controllers connected to three WATLOW DIN-A-MITE power controllers to regulate the current sent to the three sets of WATLOW cylindrical heaters. The glass cell system just uses one TC to control the single set of cylindrical heaters. A New Focus model 2033 large-area IR photodetector detects light passing through the cell. An MKS Baratron pressure transducer measures interior pressure.



**Figure 3.15:** Single species TDL testing setup using the glass or metal static cell

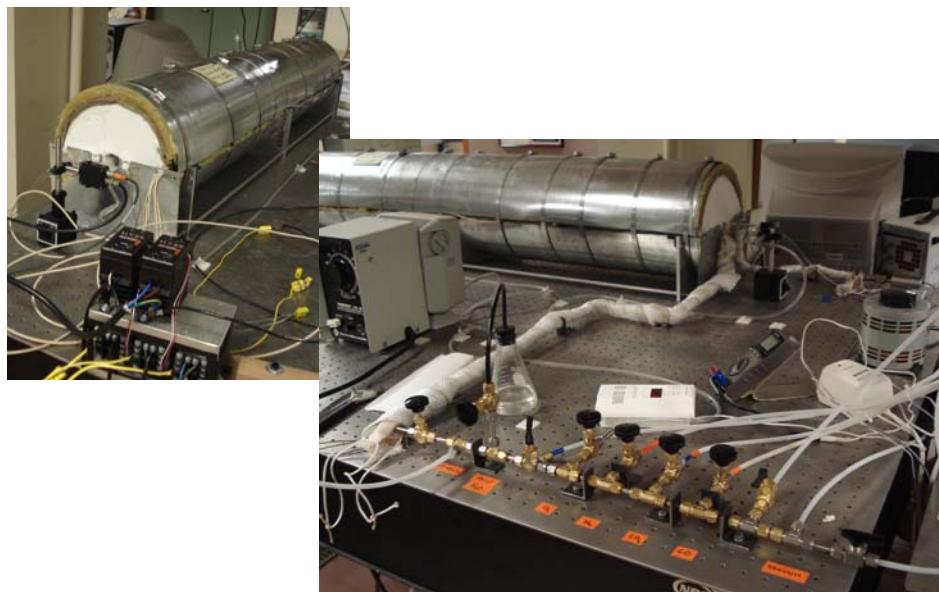
The ring interferometer was made by M. Gharavi using a spliced 95/5 single mode directional fiber optic coupler with an approximate circumference of 30 cm.

The Free Spectral Range (FSR) of the ring interferometer can be calculated by Equation 3.2 (Stokes, Chodorow, and Shaw 1982):

$$\text{Free Spectral Range} = \frac{1}{\eta L} \quad (3.2)$$

where  $\eta$  is the refractive index of the ring interferometer material and  $L$  is the optical path length (cm). Assuming a refractive index of 1.5 for infrared light, the FSR is 0.022  $\text{cm}^{-1}$ . Due to uncertainty of the exact length of the ring, the FSR was determined to be 0.022694  $\text{cm}^{-1}$  by comparing the spectra of the ring interferometer signal to the absorption spectra of two  $\text{H}_2\text{O}$  transitions whose frequencies are well known and documented in the HITRAN database.

A series of hand valves was used to control the evacuation and then species introduction to the cell. Up to four separate species could be added to the cell. Leakage rate testing showed that the metal cell holds an acceptable vacuum, with a leakage rate of 0.035 Torr/hour. Pictures of the metal cell and gas system are shown in Figure 3.16.



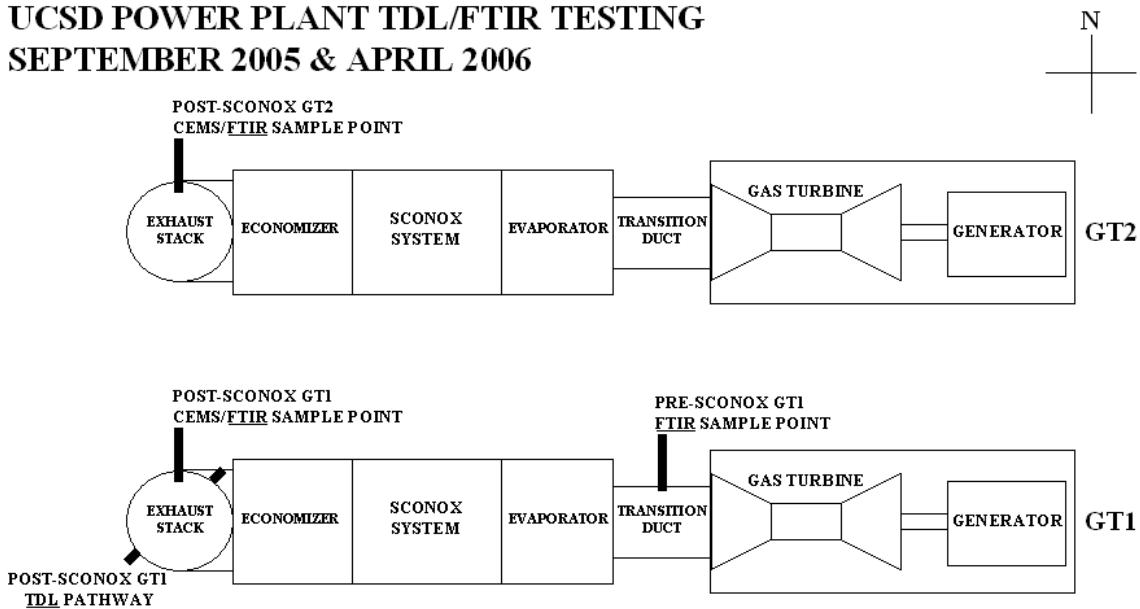
**Figure 3.16:** Pictures of the metal cell setup in the TDL laboratory

### 3.4 Field Setup

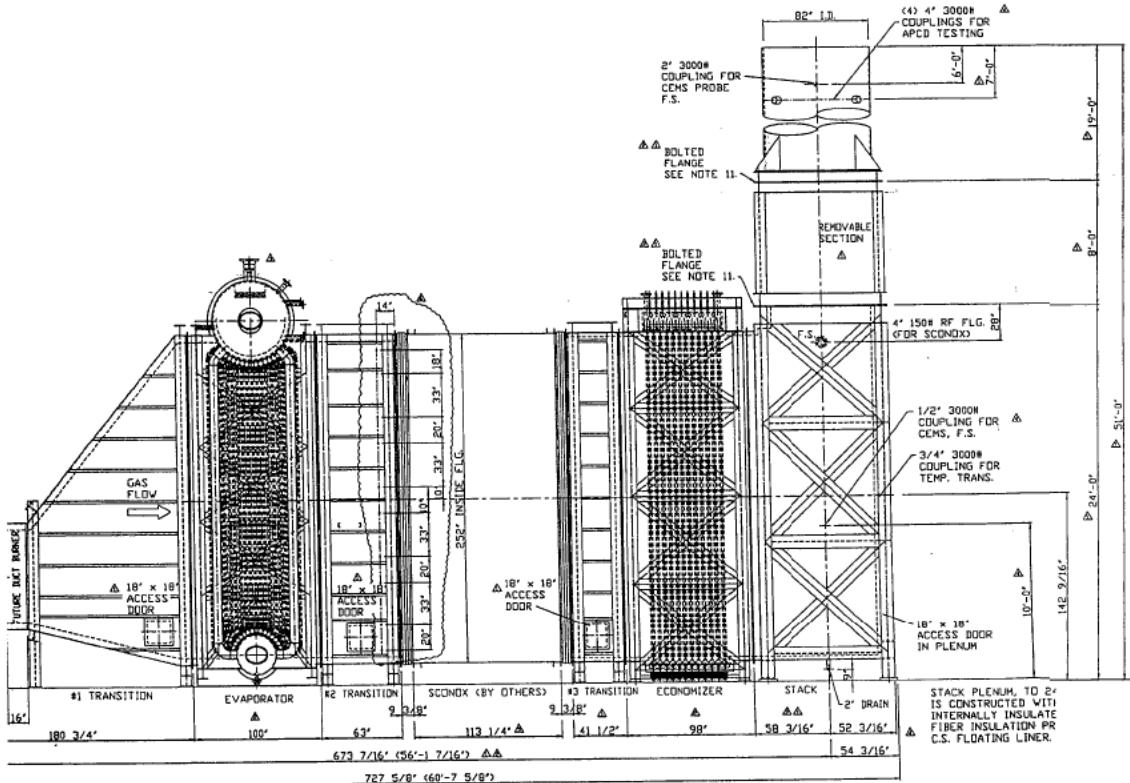
All of the laboratory work was aimed at demonstrating real-world monitoring of exhaust temperature, H<sub>2</sub>O, and CO<sub>2</sub> content using a TDL system at the UCSD power plant. The setup for this field-testing is documented in this section.

UCSD has a utility plant to provide electrical power, heating, and cooling to the campus. Two Solar Turbines Incorporated, 14 MWe Titan 130 stationary gas turbines provide about 90% of the electrical power for the UCSD campus. Both engines are equipped with heat recovery and Selective Catalytic Reduction (SCR) SCONOx systems. The SCONOx system brings the NOx emissions down from sub 25 ppm to less than 3 ppm, which is the concentration that the plant is permitted to emit. A schematic and plant drawings for the gas turbine systems are shown in Figures 3.17 and 3.18.

#### UCSD POWER PLANT TDL/FTIR TESTING SEPTEMBER 2005 & APRIL 2006



**Figure 3.17:** General top down view of UCSD power plant gas turbine systems



**Figure 3.18:** Side view of the systems downstream of each gas turbine (from J. Dilliot, UCSD power plant manager)

Field data was collected on two occasions. In September 2005, TDL and FTIR (Fourier-Transform InfraRed, discussed below) data was taken over a six-day period for data comparison purposes. After improving the TDL system, TDL data was collected again in April 2006 over an eight-day period. The TDL system was set up on the GT1 (Gas Turbine 1) exhaust stack using custom-made window fixtures mounted to the 4-inch coupling ports used for air emissions testing for regulatory purposes. The FTIR sampled exhaust stack gas from the sample lines used by the on-site Continuous Emissions Monitoring System (CEMS) at the power plant. The CEMS collects NOx and O<sub>2</sub> data from each stack downstream of the SCONOx systems, switching from stack to stack every 7.5 minutes. Post SCONOx FTIR data was collected through the CEMS heated

hoses, sampling from the stack exhaust not being analyzed by the CEMS. The FTIR and TDL systems were located in the temperature-controlled CEMS shack shown in Figure 3.19. The gas turbine operating data was collected every hour by Solar's Remote Monitoring & Diagnostics (RM&D) system.



**Figure 3.19:** Left: GT1 exhaust stack and CEMS shack; Right: TDL system on top of FTIR

The FTIR (MKS model 2030) operates by analyzing a gas sample in 5.1-meter long path length gas cell. The background and sample spectra are subtracted and then compared to a library of reference spectra to quantify concentration data for CO<sub>2</sub>, H<sub>2</sub>O, CO, NO, NO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>CO, CH<sub>4</sub>, and CF<sub>4</sub>. A separate analyzer was used to determine the concentration of O<sub>2</sub>, as the FTIR cannot measure homonuclear diatomic molecules

because they have no dipole. FTIR data was logged every minute with  $4\text{ cm}^{-1}$  resolution. A fresh fill of  $\text{LN}_2$  was required every 12 hours to provide cooling for the detector.

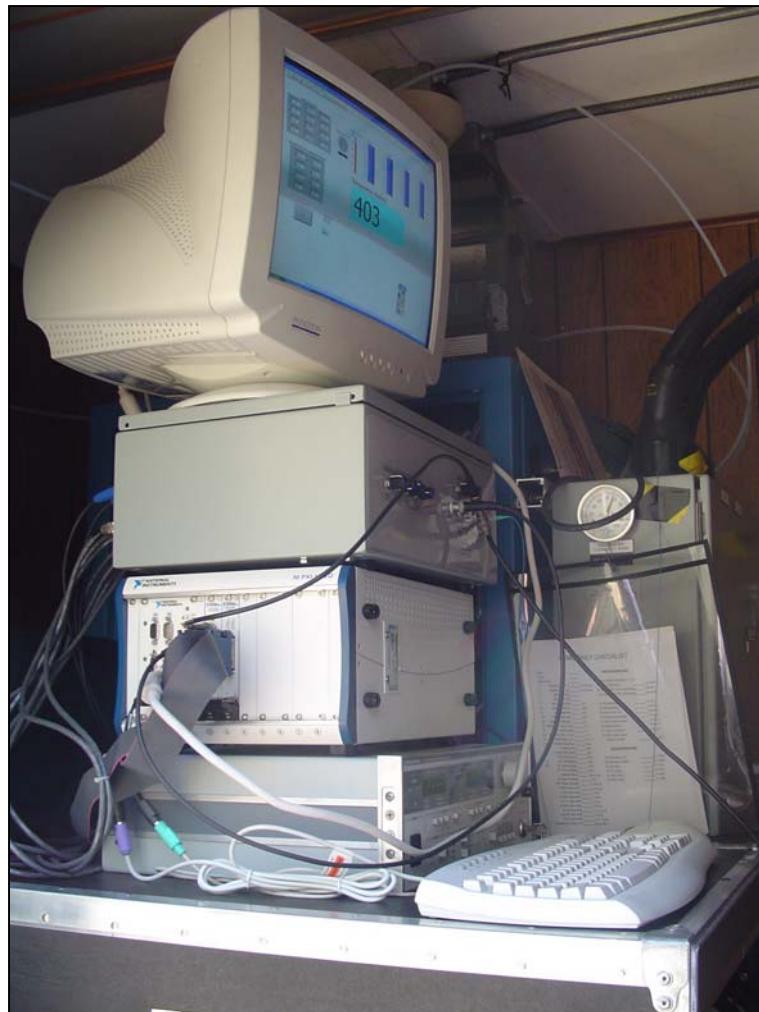
The TDL window assemblies located in the exhaust stack were constructed just like the high-pressure metal cell ends. A 2.5-inch long section of 1.5-inch diameter tubing was welded to a window assembly flange while the other side was welded to a 4-inch male NPT plug. Once installed, each assembly was wrapped with insulation. The insulation was necessary to prevent condensation buildup inside the wedge window. This approach avoided having to purge the windows. L-shaped brackets were mounted to each flange to support the TDL collimating lens or photodetector. Pictures of the two windows are shown in Figure 3.20.



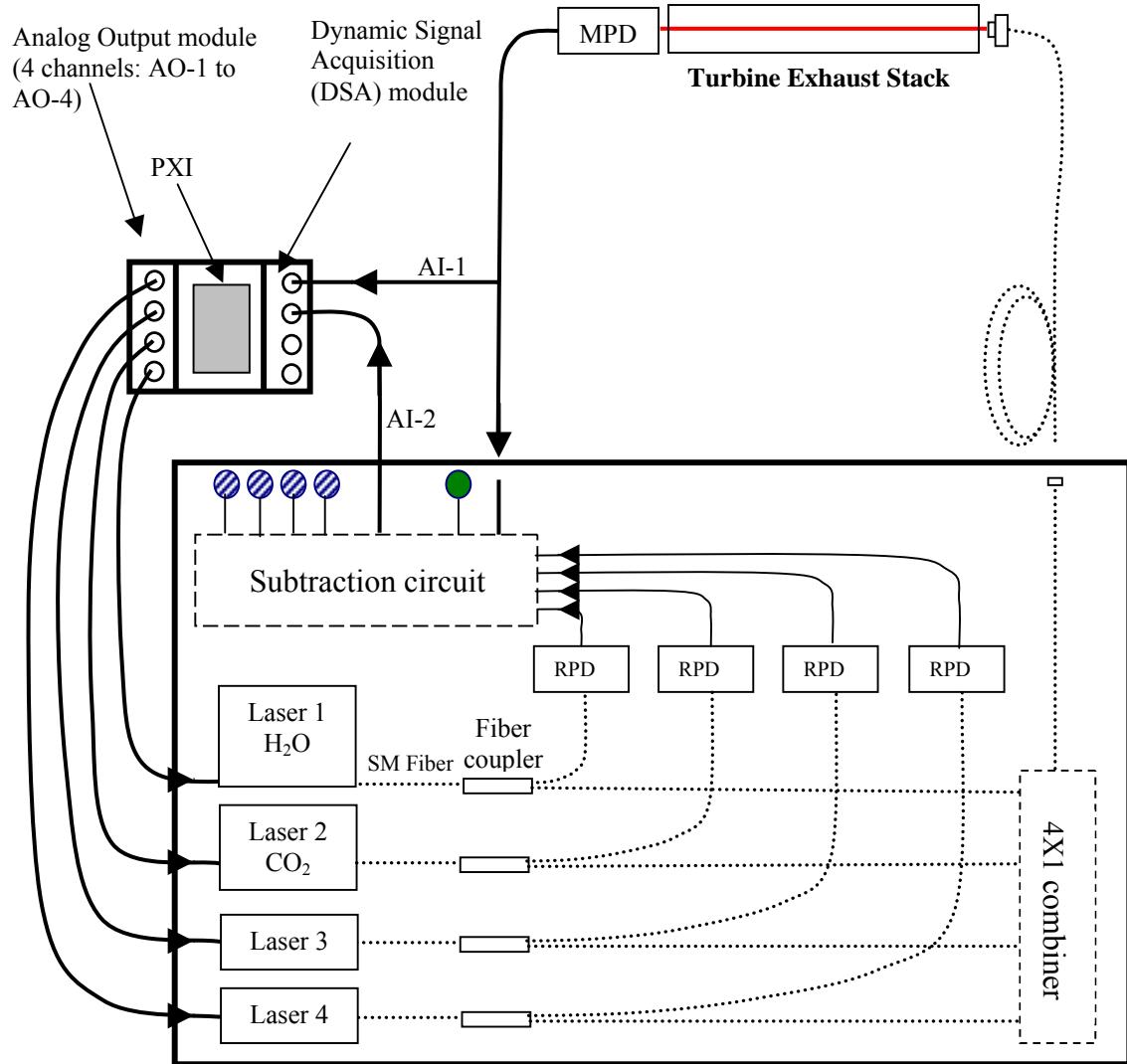
**Figure 3.20:** Left: TDL collimating lens window assembly (note the CEMS sample hose in the background); Right: TDL photodetector window assembly

The TDL system consists of a laser controller, a Labview PXI computer, portable TDL box housing the lasers, associated conditioning circuitry, and calibration

interferometer, and monitor/mouse/keyboard. The system is shown in Figure 3.21. A schematic of the TDL box is shown in Figure 3.22. For the field-testing only two of the available four channels were used ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ).



**Figure 3.21:** TDL system located inside the UCSD power plant CEMS shack



- ➊ Adjustment knob for adjusting the gain of the Reference Photodetector (RPD)
- ➋ Adjustment knob for adjusting the gain of the Main Photodetector (MPD)
- ..... Optical signal
- Electrical signal

AI-1: This channel is used by the LabVIEW™ program to calculate first harmonic components of each absorption signal based on the MPD signal.

AI-2: This channel is used by the LabVIEW™ program to calculate second harmonic components of each absorption signal based on the subtracted signal.

AO-1 to 4: These channels are used by the LabVIEW™ program to generate four modulation signals, which drive the lasers.

**Figure 3.22:** TDL box schematic (portion from A. Schuger)

# CHAPTER 4: Conversion of TDL Data

## 4.1 Introduction

This chapter will cover quantification of the WMS output signal for temperature and concentration measurements. The focus will be on temperature, H<sub>2</sub>O, and CO<sub>2</sub>, since these were the measurements made in the field. A summary of the procedure used for the concentration calculations will be presented.

## 4.2 H<sub>2</sub>O, CO<sub>2</sub>, and Temperature WMS Conversion

As explained in Section 2.4, the WMS output signal,  $I_{n,p}(\bar{v})$ , can be related to an absorbing species concentration by Equation 2.11. Even (rather than odd) harmonics are used since  $I_{n,p}(\bar{v})$  is maximum at the absorption center for the even harmonics. The main hurdle in quantification using this equation is that the line shape function must be known. This implies that the concentration of all of the important collisional species and the temperature are known. By characterizing all laser parameters and the spectroscopic parameters of the absorption transition, the  $I_{n,p}(\bar{v})$  per unit absorbing species concentration can be calculated through Equation 2.12. The concentration of the measured absorbing species is calculated by dividing the peak of the measured  $I_{n,p}(\bar{v})$  signal by the peak of the calculated  $I_{n,p}(\bar{v})$ . Since prediction of the electro-optical gain  $K_p$  is difficult, it can be determined by comparing a set of measured  $I_{n,p}(\bar{v})$  signals at known concentrations and temperatures with the corresponding calculated values from Equation 2.12. Temperature can be determined by the ratio of two integrated absorption

lines from a single species when the line strengths of the two transitions vary with temperature.

Gharavi's (2004) model simulates the WMS second harmonic spectra of the H<sub>2</sub>O and CO<sub>2</sub> lasers and is used to convert laser absorption data to temperature and concentration. The C++ code takes into account the changes in laser intensity that accompany WMS, the phase difference between intensity modulation and wavelength modulation, and the effects of pressure broadening and temperature broadening. The model requires the following inputs:

- Mole fraction of reactants;
- Laser operating parameters;
- Line strength fitting parameters; and,
- Broadening coefficient fitting parameters.

The mole fraction of reactants is determined from the flow rate of the reactants. The mole fraction of the combustion species in the application to gas turbine combustion is based on a complete combustion approximation. The laser operating parameters are measured and include: the modulation depth,  $\Delta\nu_m$ , intensity-frequency parameters ( $s_{F1}$ ,  $s_{F2}$ , and  $s_{f1}$ ), and electro-optical gain  $K_p$ . The modulation depth was calculated by the C++ code with an initial guess corresponding to the following expression,

$$\Delta\nu_m = \frac{\# \text{fringes} * FSR}{2} \quad (4.1)$$

where *# fringes* is the number of fringe points in the high-frequency signal from the modulation depth measurements and *FSR* is the free spectral range of the interferometer. A summary of the intensity-frequency parameters ( $s_{F1}$ ,  $s_{F2}$ , and  $s_{f1}$ ), and electro-optical gain  $K_p$  for the H<sub>2</sub>O and CO<sub>2</sub> lasers is shown in Table 4.1.

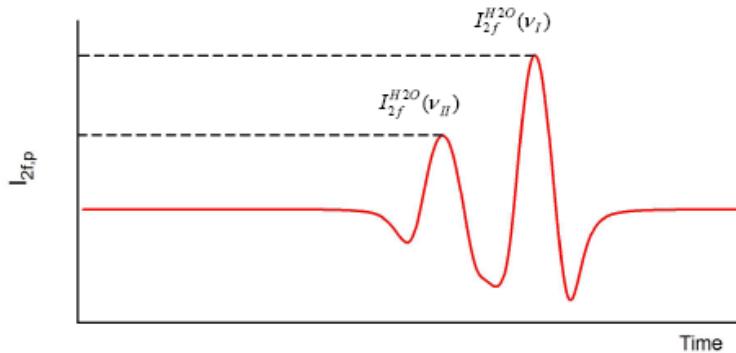
**Table 4.1:** H<sub>2</sub>O and CO<sub>2</sub> spectroscopic data

Laser	S <sub>F1</sub>	S <sub>F2</sub>	S <sub>f1</sub>	K <sub>p</sub>
H <sub>2</sub> O	-1.528	-0.017	-3.56	23.0
CO <sub>2</sub>	-1.078	-0.247	-1.941	87.0

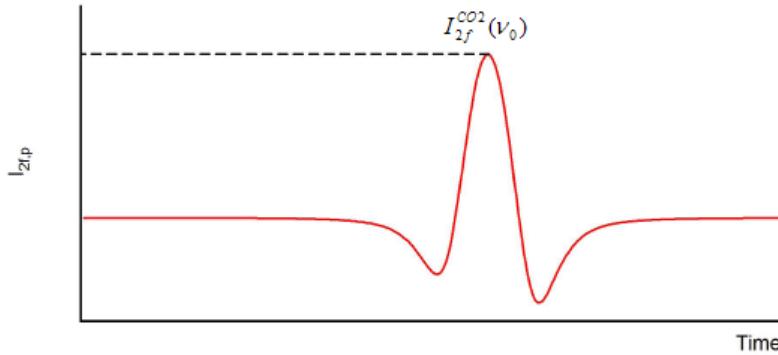
The line strength fitting parameters are obtained through least-squares fitting of the calculated line strengths versus temperature from the HITRAN database for all of the selected transitions. Pressure broadening measurements were done to calculate pressure-broadening coefficients for all of the quenching species. The glass cell was used in the laboratory to characterize the spectroscopic properties of H<sub>2</sub>O and CO<sub>2</sub> using the direct absorption technique. The metal cell was used to quantify pressure broadening using the WMS technique. A team of undergraduate students led by Alan Yang and Chris Hartley completed this work.

Given these inputs the following steps were necessary for quantification of temperature and concentration of H<sub>2</sub>O and CO<sub>2</sub>.

1. Measure the 2<sup>nd</sup> harmonic signal for H<sub>2</sub>O transitions and calculate the ratio of the two peaks,  $R_{I,II} = I_{2f}^{H2O}(\nu_I)/I_{2f}^{H2O}(\nu_{II})$  as illustrated in Figure 4.1.

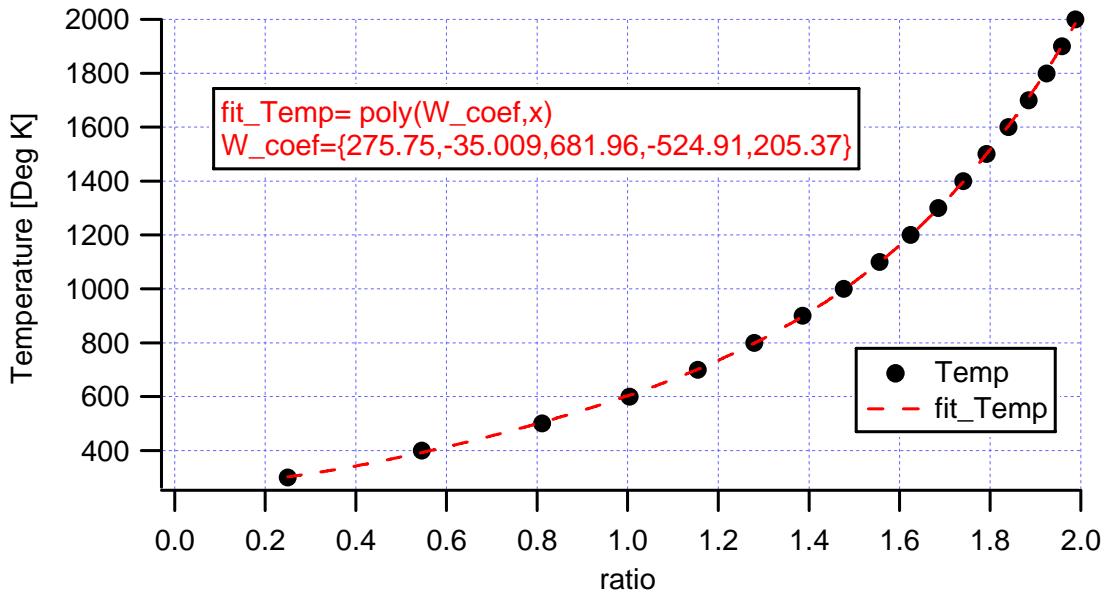
**Figure 4.1:** Typical 2<sup>nd</sup> harmonic signal of H<sub>2</sub>O at the selected H<sub>2</sub>O transitions (from Gharavi 2004)

- Measure the 2<sup>nd</sup> harmonic signal peak for the CO<sub>2</sub> transition,  $I_{2f}^{CO_2}(\nu_0)$



**Figure 4.2:** Typical 2<sup>nd</sup> harmonic signal of CO<sub>2</sub> at the selected CO<sub>2</sub> transition

- Use the measured  $R_{I,II}$  and pre-calculated HITRAN  $R_{I,II}$  versus temperature correlation to calculate temperature,  $T_m$ . The correlation is shown in Figure 4.3.



**Figure 4.3:** Temperature versus  $R_{I,II}$  (ratio) data for the selected H<sub>2</sub>O transitions from the HITRAN database

- Laboratory-generated metal cell data on the variation of one of the H<sub>2</sub>O peaks in the 2<sup>nd</sup> harmonic spectra  $\hat{I}_{2f}^{H_2O}(\nu_I)$  with temperature is used to calculate

$\hat{I}_{2f}^{H2O}(\nu_I)$  at  $T_m$ . Note that the  $\hat{I}_{2f}^{H2O}(\nu_I)$  versus temperature data is normalized by laser power and the partial pressure of H<sub>2</sub>O.

5. Laboratory-generated metal cell data on the variation of the CO<sub>2</sub> peak in the 2<sup>nd</sup> harmonic spectra  $\hat{I}_{2f}^{CO2}(\nu_0)$  with temperature is used to calculate  $\hat{I}_{2f}^{CO2}(\nu_0)$  at  $T_m$ .

Note that the  $\hat{I}_{2f}^{CO2}(\nu_0)$  versus temperature data is normalized by laser power and the partial pressure of CO<sub>2</sub>.

6. Calculate the partial pressure of H<sub>2</sub>O by  $P_{H2O} = K_p \frac{I_{2f}^{H2O}}{\hat{I}_{2f}^{H2O}(T_m)}$ , where  $I_{2f}^{H2O}$  is the field-measured WMS 2<sup>nd</sup> harmonic peak normalized by the laser power. The field gas turbine exhaust concentration data was calculated using the following

$$\text{equation: } \text{mole\_H2O} = \frac{I2f\_H2O\_norm\_filtered}{200 * 2.725e - 6 * 760 * 23.0}. \quad (4.2)$$

7. Calculate the partial pressure of CO<sub>2</sub> by  $P_{CO2} = K_p \frac{I_{2f}^{CO2}}{\hat{I}_{2f}^{CO2}(T_m)}$ , where  $I_{2f}^{CO2}$  is the field WMS measured 2<sup>nd</sup> harmonic peak normalized by the laser power. The field gas turbine exhaust concentration data was calculated using the following

$$\text{equation: } \text{mole\_CO2} = \frac{I2f\_CO2\_norm\_filtered}{200 * 6.050e - 7 * 760 * 87.0}. \quad (4.3)$$

$I2f\_H2O\_norm\_filtered$  and  $I2f\_CO2\_norm\_filtered$  in equations 4.2 and 4.3 are defined in Chapter 5. The numerical components of equations 4.2 and 4.3 correspond

to  $K_p \frac{1}{\hat{I}_{2f}^{H2O}(T_m)}$  and  $K_p \frac{1}{\hat{I}_{2f}^{CO2}(T_m)}$  respectively.

# CHAPTER 5: Field Test Results

## 5.1 Introduction

The results of the Gas Turbine, FTIR and TDL data gathered from the UCSD power plant will be presented in this chapter. The FTIR data was taken along with TDL data in September 2005 over a six-day period. After improving the TDL system, TDL data was collected again in April 2006 over an eight-day period. Temperature, H<sub>2</sub>O concentration, and CO<sub>2</sub> concentration will be compared along with the error analysis results.

## 5.2 FTIR Field Data

The FTIR system was set up as described in Chapter 3. The data presented in this section is focused on the post-ScoNOx system exhaust stream results taken near the TDL system ports. Since the FTIR gas sample was taken from the same heated hose system as used by the CEMS system, FTIR data from both gas turbine units was collected, switching between units every 7.5 minutes. An overview of the setup and FTIR data collected is presented in Table 5.1 and 5.2. There were two main groups of data collected from the exhaust stack port, each covering approximately 1.5 days (data groups A and D as shown in Table 5.2).

**Table 5.1:** Table showing data collected from each gas turbine unit

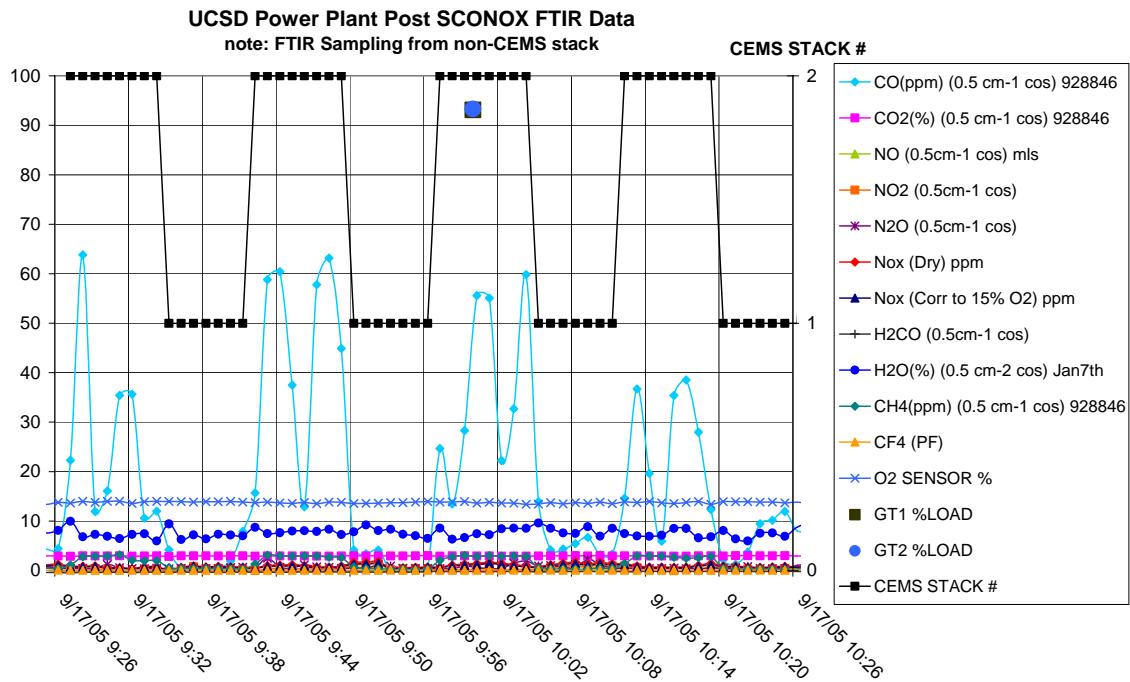
	<u>Stack:</u>	<u>Engine SN:</u>	<u>Notes:</u>
<b>South Unit (GT1)</b>	1	0012L	FTIR/TDL/GT Data
<b>North Unit (GT2)</b>	2	0019L	FTIR/GT Data

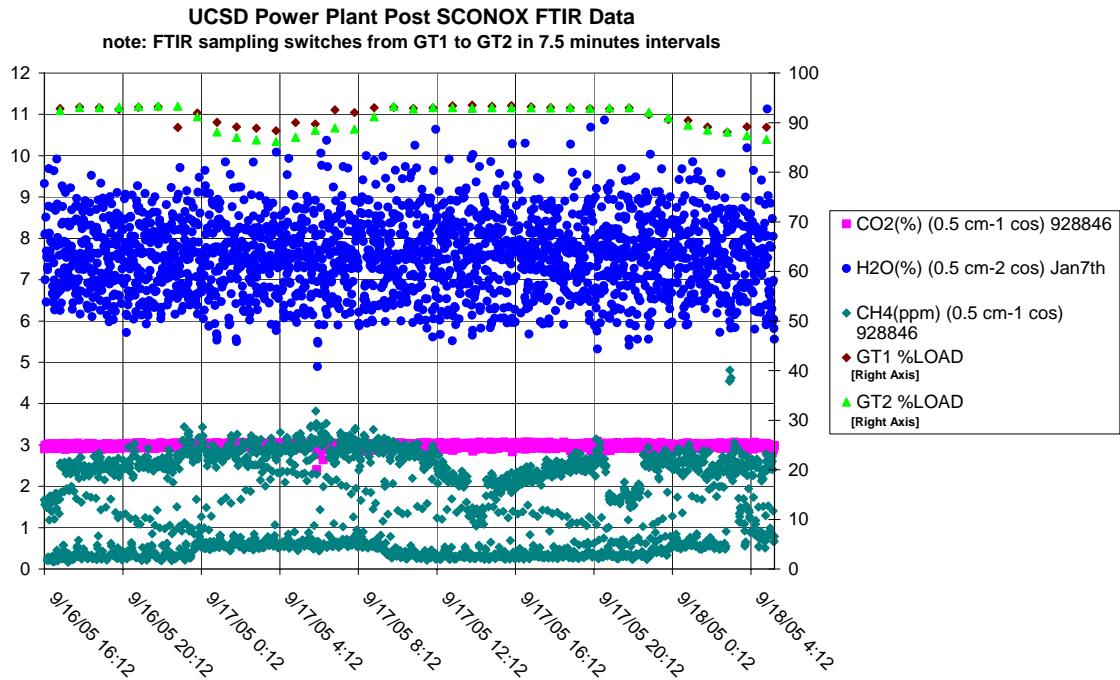
Note: FTIR sampling from non-CEMS stack (ie. When CEMS is on stack 1, FTIR is sampling from stack2)

**Table 5.2:** Table showing collected FTIR species and field data groups

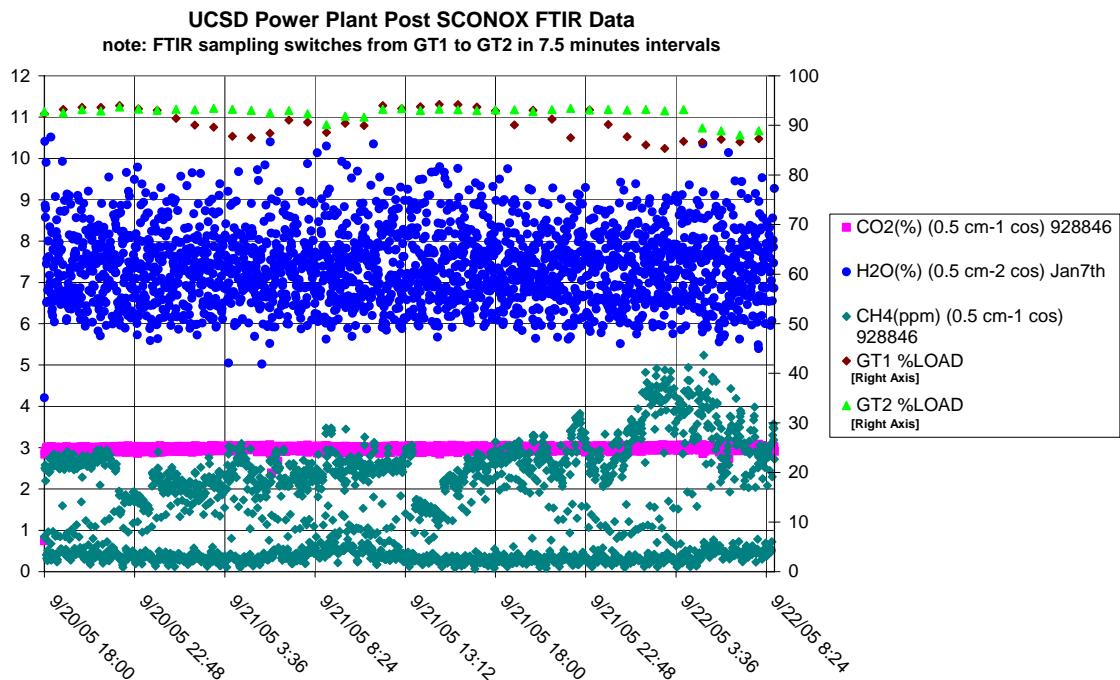
Species	Units	Start	End	Data Group
CO	ppm	9/16/05 16:12	9/18/05 5:24	A
CO <sub>2</sub>	%	9/19/05 16:53	9/19/05 16:57	B
NO	ppm	9/19/05 17:21	9/19/05 17:31	C
NO <sub>2</sub>	ppm	9/20/05 18:00	9/22/05 8:50	D
<b>Ambient Air</b>				
H <sub>2</sub> CO	ppm	9/19/05 16:27	9/19/05 16:53	
H <sub>2</sub> O	%	9/19/05 17:31	9/19/05 17:32	
NOx	ppm	9/19/05 17:33	9/19/05 17:48	
<b>Pre SCONOX DATA (GT1)</b>				
NOx corrected to 15% O <sub>2</sub>	ppm	9/19/05 17:49	9/19/05 17:53	A
H <sub>2</sub> CO	ppm	9/19/05 17:58	9/20/05 17:51	B
<b>Nitrogen</b>				
CH <sub>4</sub>	ppm	9/19/05 15:59	9/19/05 16:17	
CF <sub>4</sub>	ppm	9/19/05 17:07	9/19/05 17:07	
O <sub>2</sub>	%	9/22/05 8:53	9/22/05 8:56	
		9/22/05 9:17	9/22/05 9:27	

The exhaust stack FTIR data along with the gas turbine hourly percent load data over a one-hour period from data group A is shown in Figure 5.1. It is interesting to note that GT1 emits higher levels of CO and CH<sub>4</sub> than GT2.

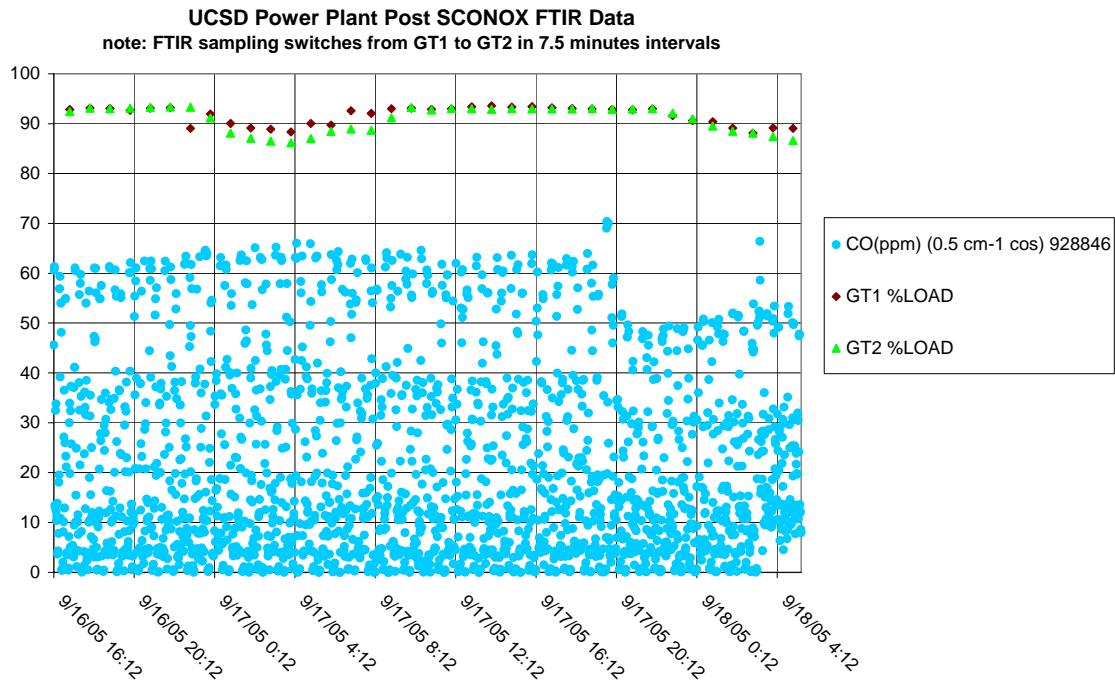
**Figure 5.1:** Complete FTIR data over a 1-hour time period noting that both exhaust stacks are sampled every 7.5 minutes (refer to Table 5.2 for FTIR species units)



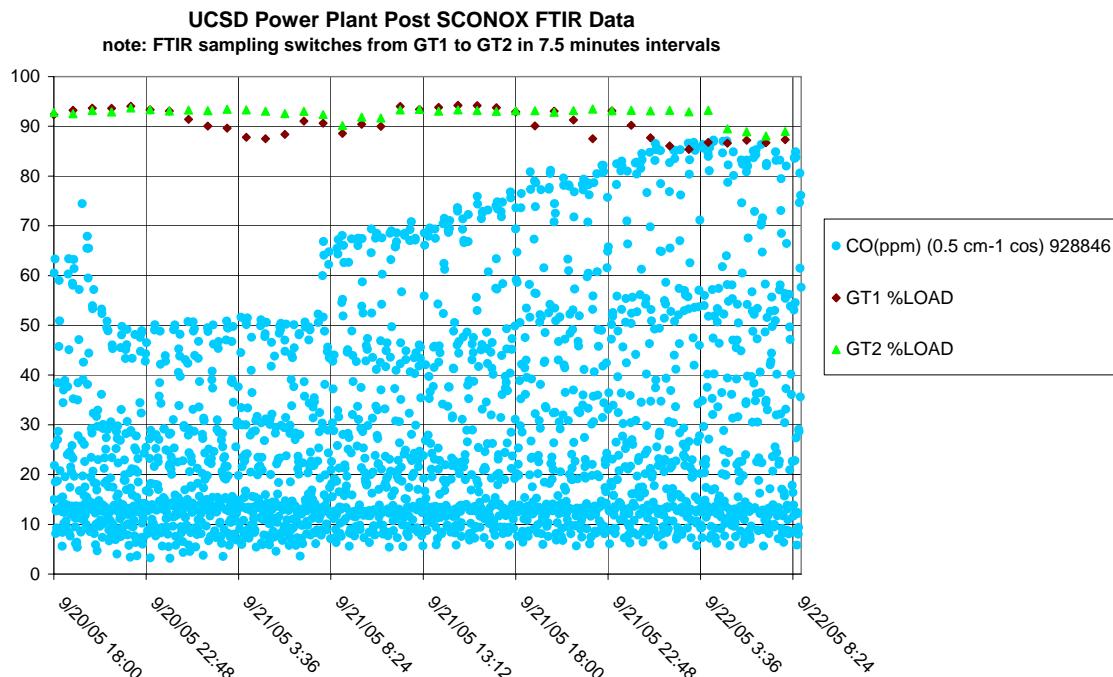
**Figure 5.2:** Overview of CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> along with gas turbine percent load from FTIR data group A (9/16-9/18/05) (refer to Table 5.2 for FTIR species units)



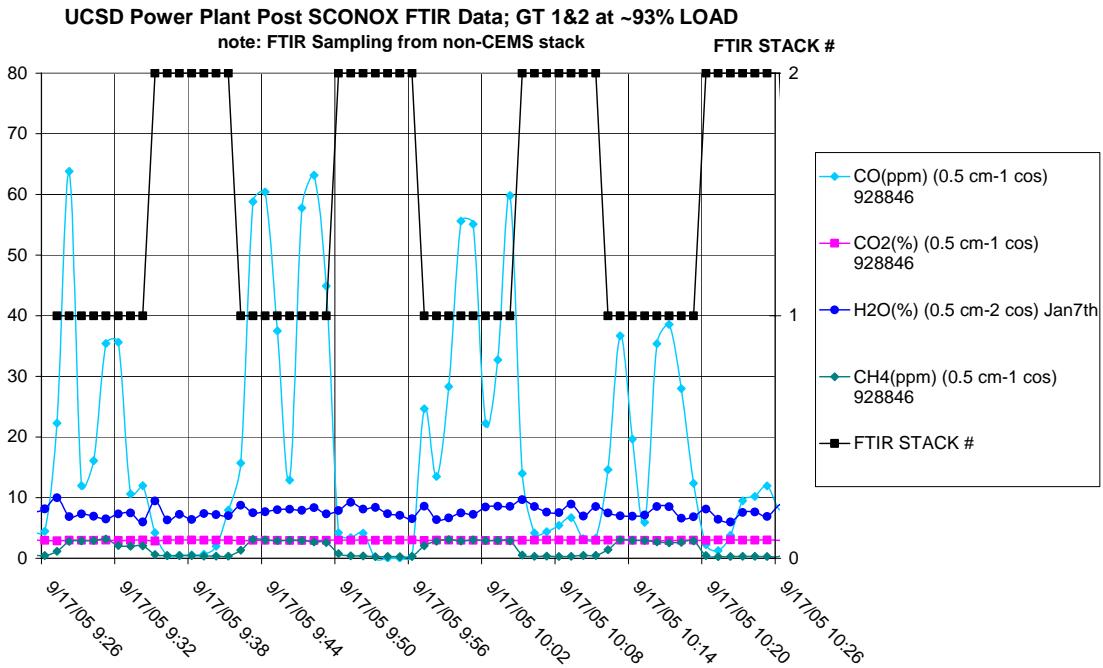
**Figure 5.3:** Overview of CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> along with gas turbine percent load from FTIR data group D (9/20-9/22/05) (refer to Table 5.2 for FTIR species units)



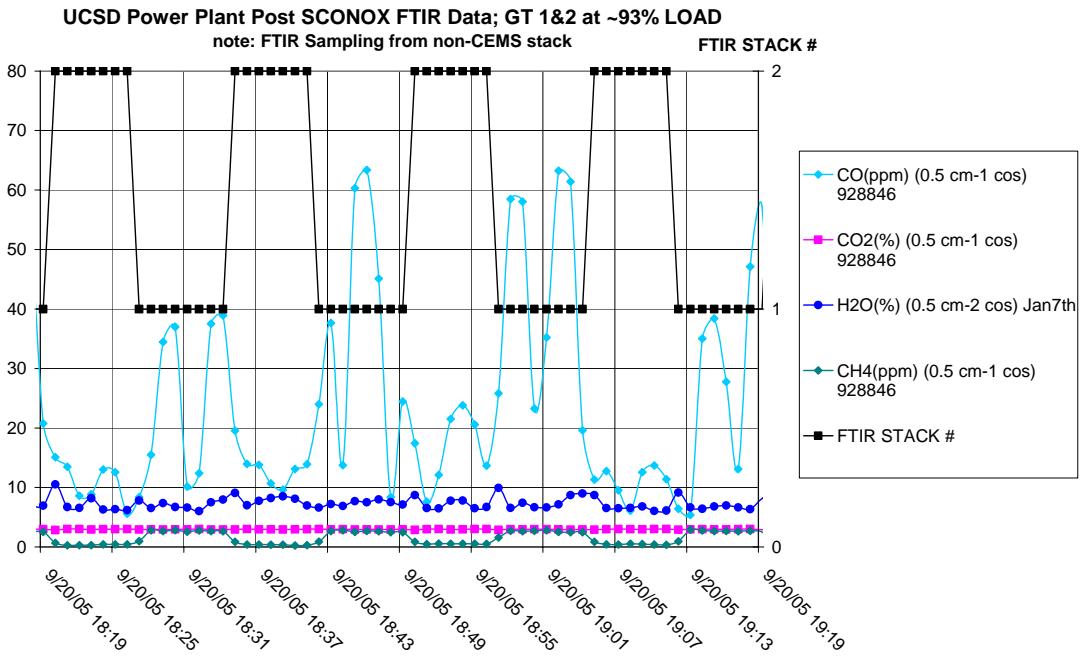
**Figure 5.4:** Overview of CO along with gas turbine percent load from FTIR data group A (9/16-9/18/05) (refer to Table 5.2 for FTIR species units)



**Figure 5.5:** Overview of CO along with gas turbine percent load from FTIR data group D (9/20-9/22/05) (refer to Table 5.2 for FTIR species units)



**Figure 5.6:** FTIR 1-hour time period from 9/17/05 showing CO, CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> along with FTIR stack number; gas turbines operating close to 93% load (refer to Table 5.2 for FTIR species units)

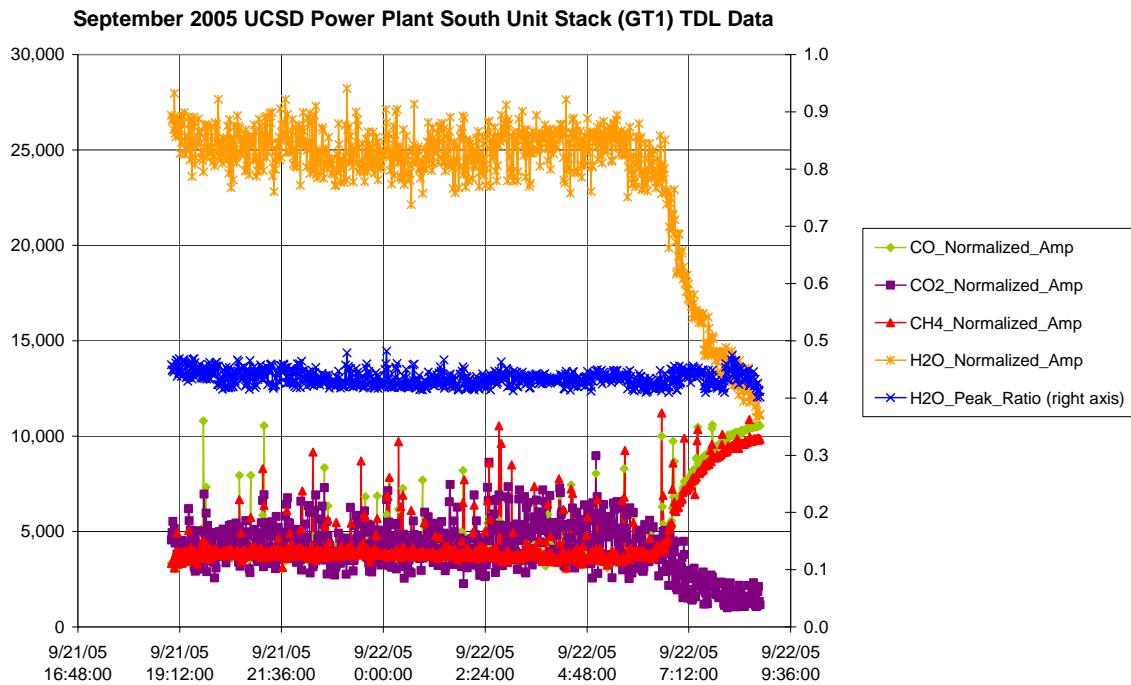


**Figure 5.7:** FTIR 1-hour time period from 9/20/05 showing CO, CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> along with FTIR stack number; gas turbines operating close to 93% load (refer to Table 5.2 for FTIR species units)

Figures 5.2 through 5.7 focused on H<sub>2</sub>O, CO<sub>2</sub>, CO, and CH<sub>4</sub> since they could also be measured using the TDL system. With the gas turbines operating between 85 to 94 percent load, the FTIR detected H<sub>2</sub>O content in the 5 to 10% range and CO<sub>2</sub> content around 2.9 to 3.1%. CO ranged from 0 to 90 ppm (0 to 20 ppm for GT2) and CH<sub>4</sub> was less than 5 ppm (less than 1 ppm for GT2).

### 5.3 TDL Field Data

TDL field data was collected from the UCSD power plant on two occasions. The first attempt was made along with the FTIR data collection in September 2005. The logged TDL data was not valid since the normalized H<sub>2</sub>O, CO<sub>2</sub>, CO, and CH<sub>4</sub> peak amplitude data was calculated incorrectly inside the Labview VI (program). An overview of the Round 1 data is shown in Figure 5.8.



**Figure 5.8:** The first 14 hours of TDL field data collected in September 2005

All of the normalized peak amplitudes shown in Figure 5.8 should be less than 1. Despite the poor results, we did prove that beam-steering and exhaust stack window condensation and fouling were not issues. We also learned that we were not able to detect the small concentrations of CO and CH<sub>4</sub> (less than 100 ppm) present in the exhaust. This experience prepared us for the second round of testing in April 2006 where we re-wired the TDL box optimized to take H<sub>2</sub>O and CO<sub>2</sub> data. The Labview VI used to capture the data was also corrected and upgraded. This data is the basis for this thesis and is presented in this chapter.

In April 2006, the TDL system was set up on the existing south unit stack window fixtures. Six parameters were recorded by the TDL Labview program: Time (sec), Ratio, 1<sup>st</sup> H<sub>2</sub>O normalized peak, CO<sub>2</sub> normalized peak, 1<sup>st</sup> H<sub>2</sub>O peak, and CO<sub>2</sub> peak amplitude. Snapshot data was captured every 0.5 seconds starting at 10:59 on 4/2/06 and ending at 15:00 on 4/10/06. The gas turbine ran continuously over this time period.

Over eight days worth of ½-second TDL data proved to be a data reduction challenge since 1,422,123 rows of data were captured. Since Excel can only handle 65,536 rows of data, Igor Pro version 3.1.4.0 was used to reduce and plot the data. In order to calculate and display meaningful temperature, H<sub>2</sub>O, and CO<sub>2</sub> concentration data, the following steps were taken. First, the data was filtered to remove outliers caused by noise in the laser. Second, the data was decimated (an Igor Pro function, explained below) to average the filtered ½ second data into 1-minute intervals. Third, in order to compare the TDL data to the FTIR data based on gas turbine percent load, hourly data was extracted. Table 5.3 summarizes the data from its raw to filtered and then decimated state. The outliers in the raw data set make up a small percentage of the overall data for

all of the parameters except for the normalized CO<sub>2</sub> peak amplitude as shown in the hard filter section of the table (calculated using statistical software MiniTab). Only 0.67% of the H<sub>2</sub>O peak ratio data and 1.12% of the normalized H<sub>2</sub>O peak amplitude was outside the hard filter bounds compared to 54% for the normalized CO<sub>2</sub> peak amplitude data.

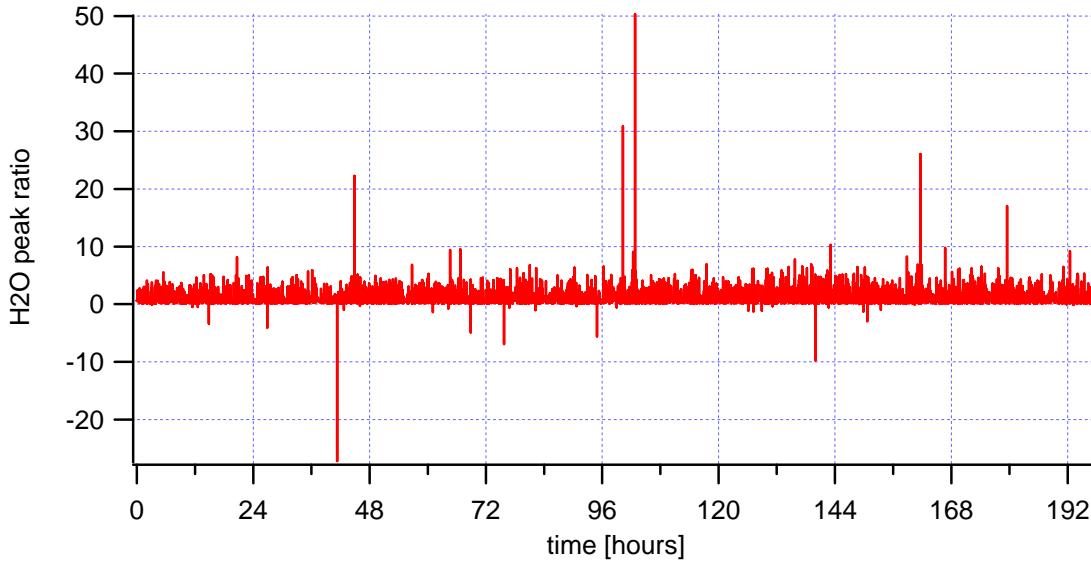
The first step in the data reduction and filtering was done using an Igor procedure written by Gharavi. The code checks if each data point is greater than the upper bound or less than the lower bound. If either case is true, a user-defined in-place average replaces the data point. The bounds and in-place averages used are listed in Table 5.3.

The second step in the data reduction was completed using an Igor function called Decimate that simply averages a user-defined number of data points into one. A decimation factor of 120 was used in order to turn the filtered ½ second data into 1-minute averages. A third data reduction step was taken in order to compare the FTIR and TDL data as a function of gas turbine percent load. Since the gas turbine data is hourly, the TDL data was reduced such that data each hour was retained. This was done with code in Igor.

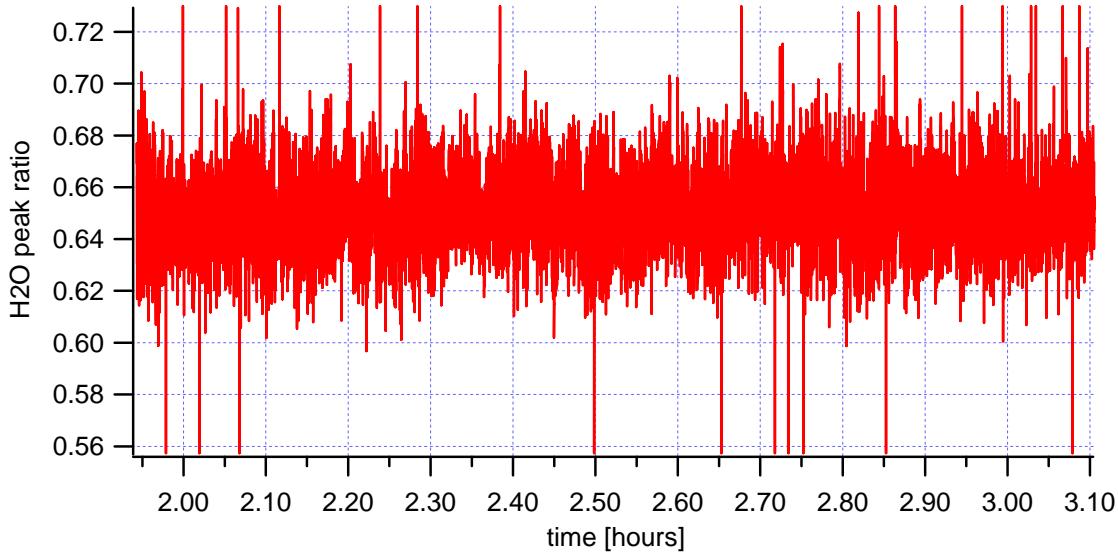
**Table 5.3:** Table of TDL April 2006 field data from GT1 with data reduction summary

	Ratio	First H2O Norm	CO2_Norm	First H2O Ampl	CO2 Ampl
<b>Raw Data</b>					
# of Datapoints	1,422,123	1,422,123	1,422,123	1,422,123	1,422,123
Minimum	-2.72E+01	-4.51E+00	-1.72E+06	-3.15E+00	7.31E+06
Maximum	5.03E+01	1.82E+01	6.03E+06	6.12E+00	5.68E+00
Average	6.50E-01	6.61E-01	6.40E+00	4.94E-01	2.71E-02
Standard Deviation	1.05E-01	9.07E-02	7.79E+03	6.50E-02	5.44E-02
% Standard Deviation	16.1%	13.7%	121725.0%	13.2%	200.8%
<b>Hard Filter</b>					
Lower Bound	0.60	0.60	0.10	0.40	0.02
Upper Bound	0.70	0.75	0.33	0.56	0.07
# of Datapoints	1,412,544	1,406,178	646,802	1,411,686	1,410,294
% Reduction	0.67%	1.12%	54.52%	0.73%	0.83%
<b>IGOR Filter</b>					
Lower Bound	0.58	0.58	0.00		
Upper Bound	0.72	0.86	1.00		
In Place Average	0.65	0.66	0.18		
# of Datapoints	1,422,123	1,422,123	1,422,123		
Minimum	0.58	0.58	0.01		
Maximum	0.72	0.86	1.00		
Average	0.65	0.66	0.19		
Standard Deviation	1.55E-02	2.53E-02	3.46E-02		
% Standard Deviation	2.4%	3.8%	17.9%		
<b>IGOR Decimation</b>					
Decimation Factor	120	120	120		
# of Datapoints	11,851	11,851	11,851		
Minimum	0.63	0.62	0.16		
Maximum	0.66	0.71	0.27		
Average	0.65	0.66	0.19		
Standard Deviation	5.04E-03	1.74E-02	1.79E-02		
% Standard Deviation	0.8%	2.6%	9.2%		

The raw H<sub>2</sub>O peak ratio data from April 2006 is shown in Figure 5.9. The noise is apparent but random. The cause is believed to be changes in laser power and fiber optic cable movement. By zooming in to a 1-hour time period it is clear that the majority of data falls into a much tighter band between 0.58 and 0.72 as shown in Figure 5.10.

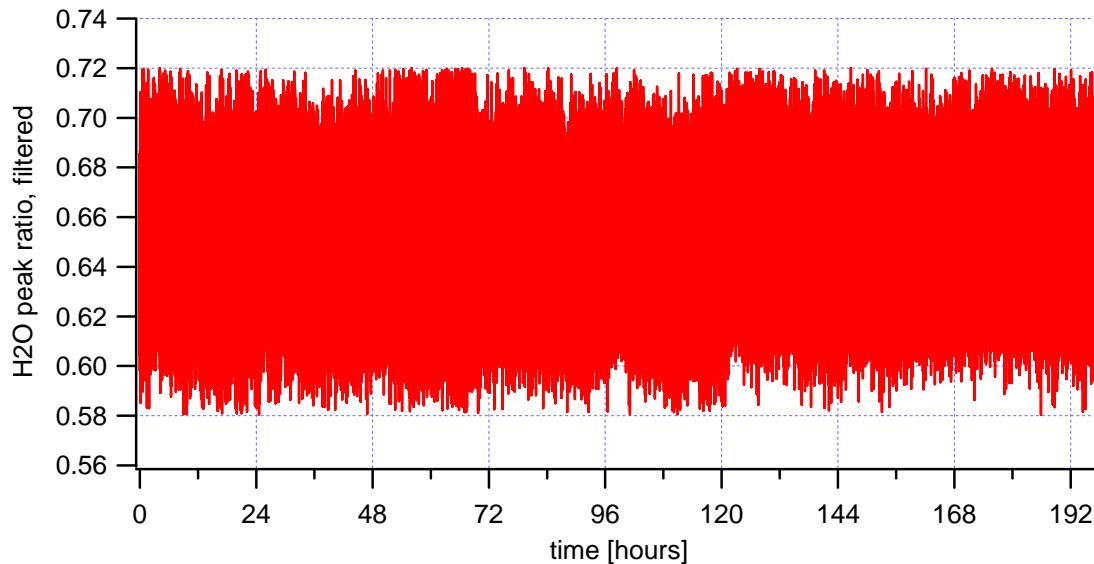


**Figure 5.9:** April 2006 GT1 TDL H<sub>2</sub>O peak ratio raw data (entire data set)

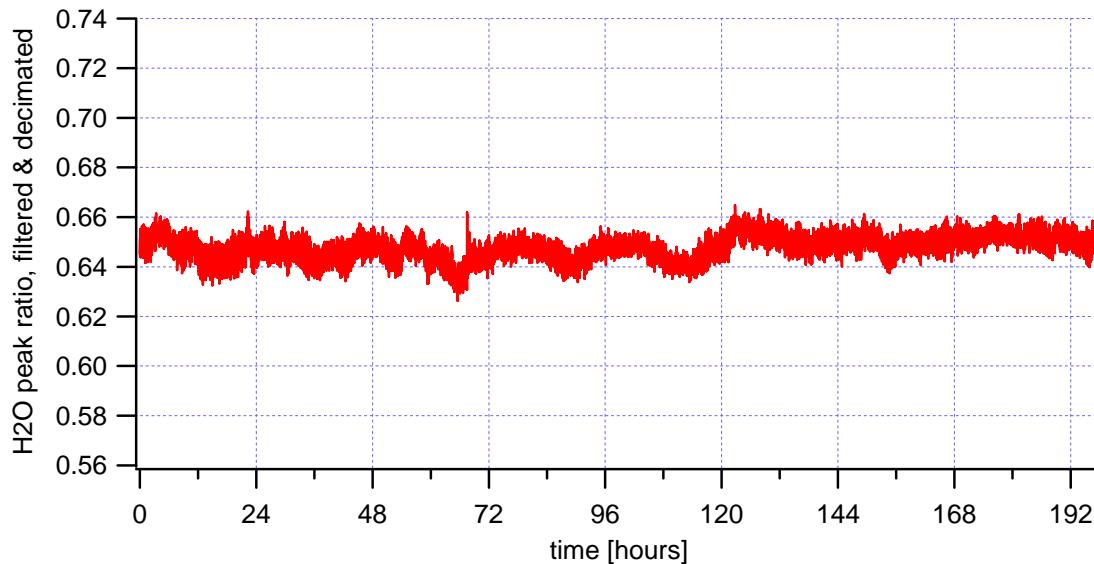


**Figure 5.10:** April 2006 GT1 TDL H<sub>2</sub>O peak ratio raw data (early 1-hour time period)

The filtering and then decimation of the raw H<sub>2</sub>O peak ratio data shows a clearer picture of the trend over the 196-hour test. These results are shown in Figures 5.11 and 5.12 below.

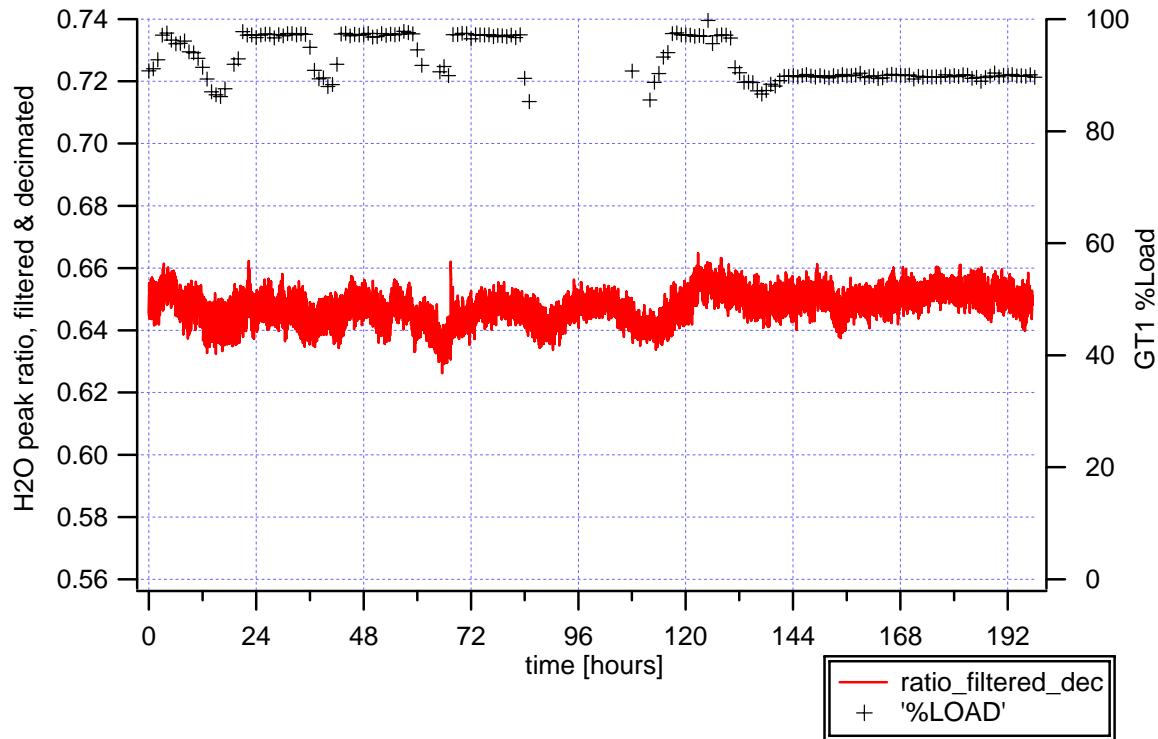


**Figure 5.11:** April 2006 GT1 TDL H<sub>2</sub>O peak ratio filtered data (entire data set)



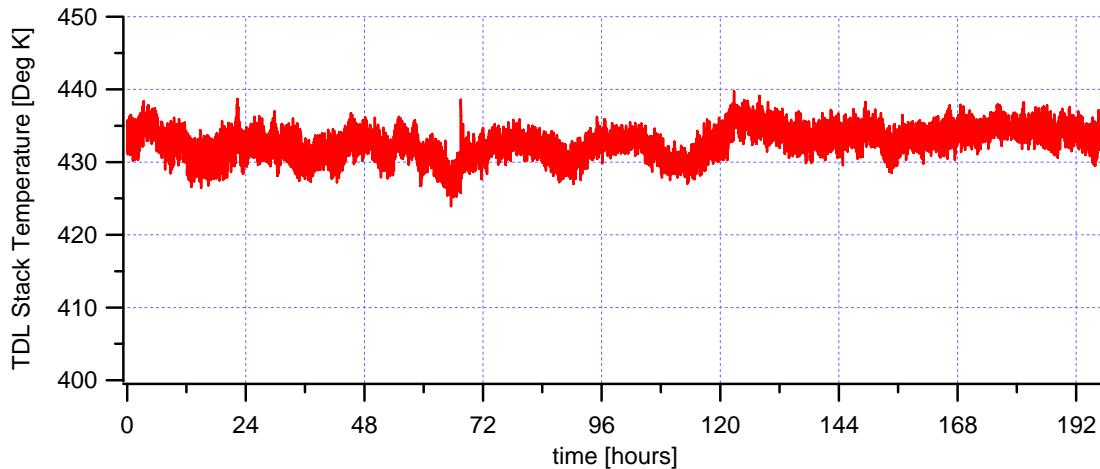
**Figure 5.12:** April 2006 GT1 TDL H<sub>2</sub>O peak ratio filtered & decimated (1-minute average) data (entire data set)

The next step was to determine if the changes in TDL H<sub>2</sub>O peak ratio correspond to actual temperature changes in the exhaust flow. To do this, H<sub>2</sub>O peak ratio was plotted along with the gas turbine (GT1) percent load in Figure 5.13. It does appear that the H<sub>2</sub>O peak ratio changes correspond to changes in gas turbine load.



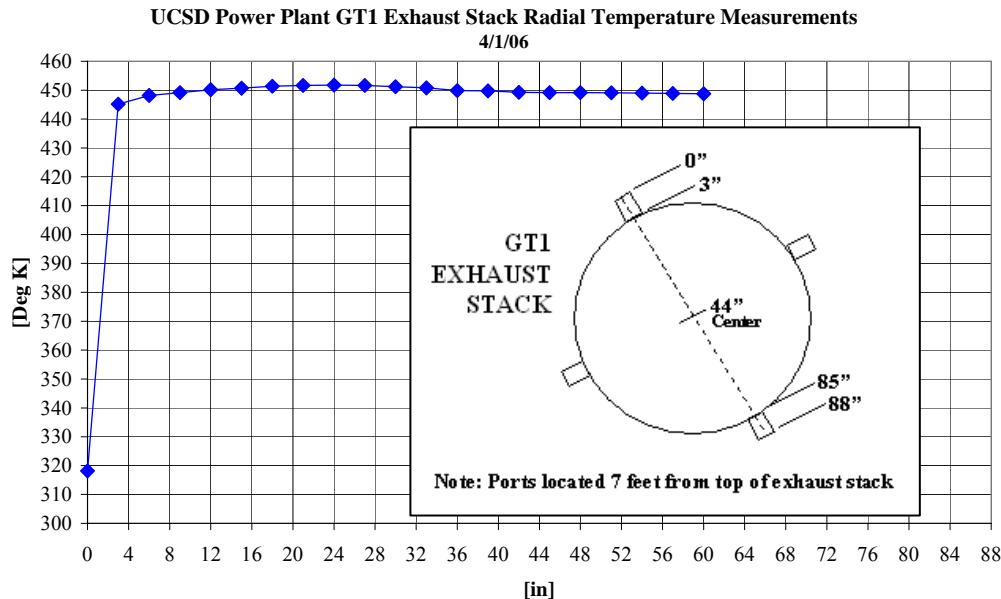
**Figure 5.13:** April 2006 GT1 TDL H<sub>2</sub>O peak ratio filtered & decimated (1-minute average) data (entire data set) along with GT1 hourly percent load data

Following the methodology outlined in Chapter Four, the filtered and decimated H<sub>2</sub>O peak ratio data was converted to temperature in Kelvin as shown in Figure 5.14. The temperature ranges between 424 and 440 K with an average of 433 K.



**Figure 5.14:** April 2006 GT1 TDL calculated stack exhaust temperature data (entire data set)

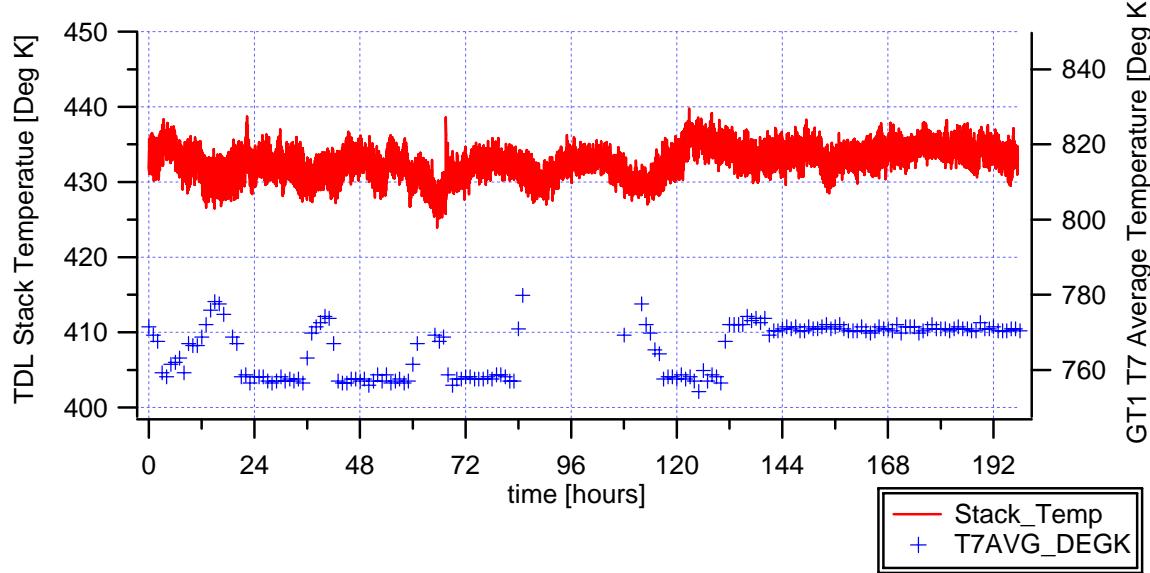
The TDL Labview computer did not have a TC input card so exhaust temperature data was not collected for the duration of the test. Future studies should collect this data. A stack exhaust temperature survey at the TDL measurement plane was completed the day before testing began however. The radial survey was done using a sealed Type K thermocouple connected to a Fluke TC reader. The results are shown in Figure 5.15.



**Figure 5.15:** GT1 exhaust stack radial temperature measurement results

Aside from the boundary layer measurement closest to the wall, the temperature profile was found to be flat with an average temperature of 450 K and a range of 7 K. These results are around 17 K higher than the TDL calculated exhaust temperature.

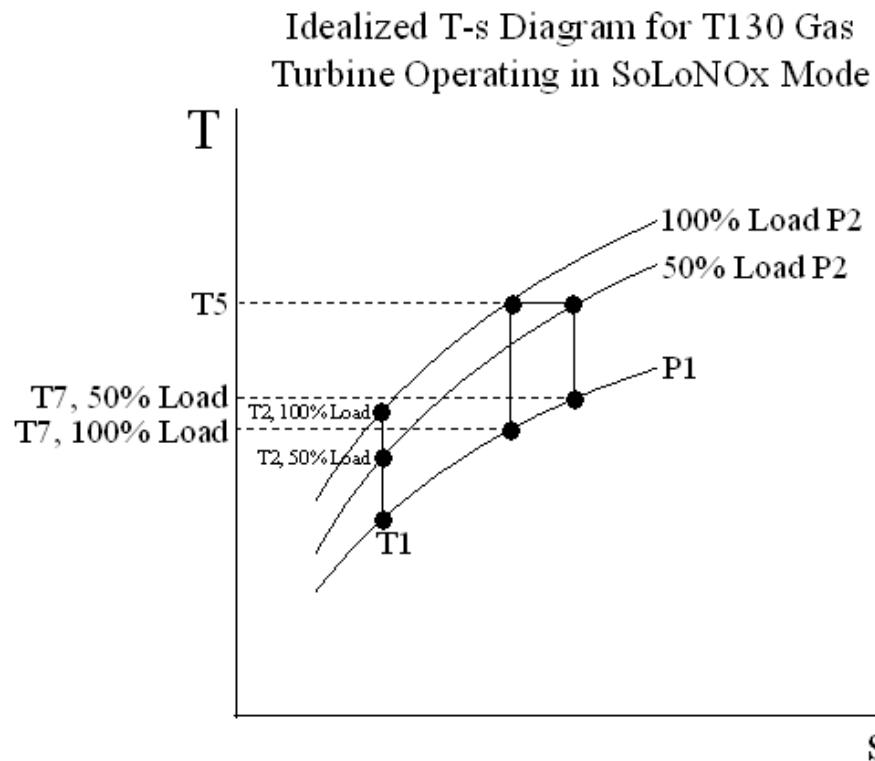
The TDL exhaust stack temperature can also be compared to the measured gas turbine exhaust temperature. Three N-Type TC's measure the exhaust temperature in the turbine exhaust collector downstream of the final turbine disk. This is referred to as the T7 plane. The exhaust flow then travels through the evaporator, ScoNOx system, and economizer before reaching the TDL measurement plane, which explains the roughly 330 K drop in temperature between the two points as shown in Figure 5.16.



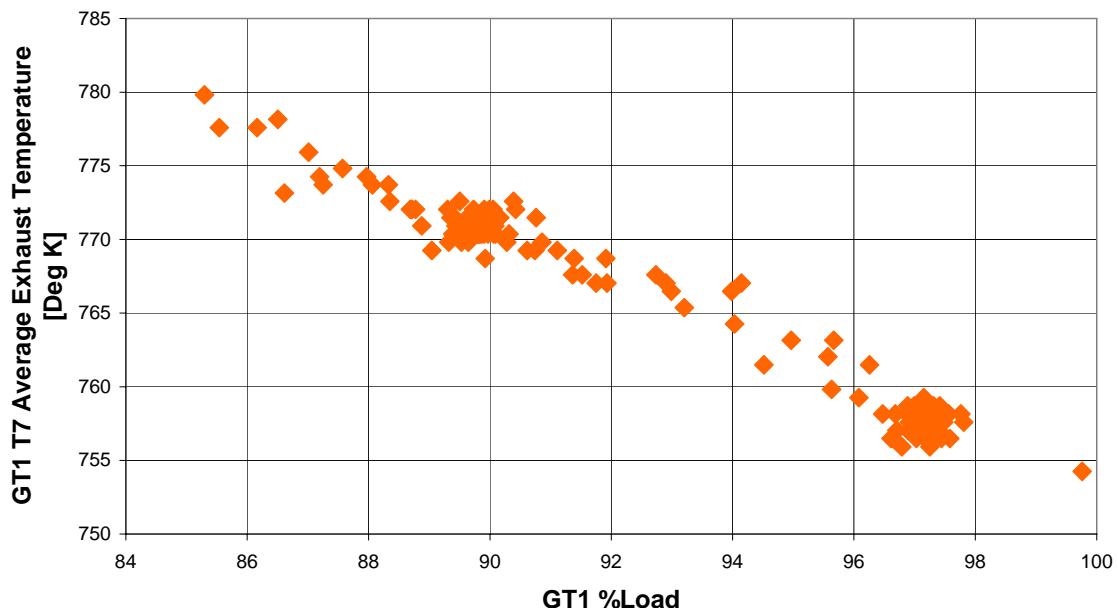
**Figure 5.16:** TDL exhaust stack and GT1 T7 temperature data over the April 2006 testing

The trends between the TDL and gas turbine exhaust temperatures seem to match but it is unclear why they are in opposite directions. When there is an increase in gas turbine measured T7 there is a corresponding decrease in TDL calculated exhaust temperature. Perhaps the heat recovery and/or ScoNOx systems account for this observation.

From the gas turbine perspective the T7 exhaust temperature decreases with load between 50 to 100% load, in which the turbine operates in dry lean pre-mixed low emissions mode (known as SoLoNOx by Solar Turbines Inc.). In SoLoNOx mode, electronic valves control the fuel and inlet guide vanes on the turbine axial compressor control the airflow to meet a desired third stage rotor inlet temperature (T5) in order to meet power and low emissions requirements. The T5 temperature remains constant while in SoLoNOx mode. An idealized T-s diagram shown in Figure 5.17 highlights why this scenario produces higher exhaust temperatures at part-load conditions. Figure 5.18 depicts this relationship by plotting measured T7 average exhaust temperature as a function of gas turbine percent load.

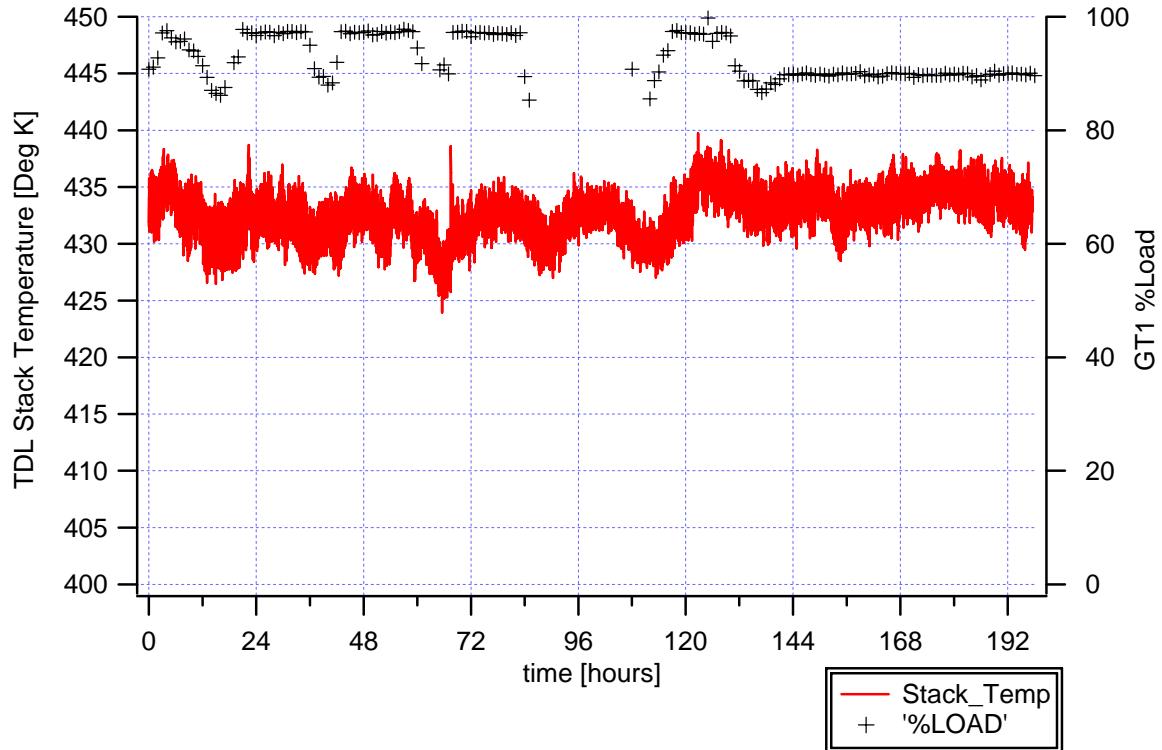


**Figure 5.17:** Idealized T-s diagram for a Titan 130 gas turbine operating in SoLoNOx mode



**Figure 5.18:** April 2006 testing GT1 T7 average temperature vs percent load (hourly data)

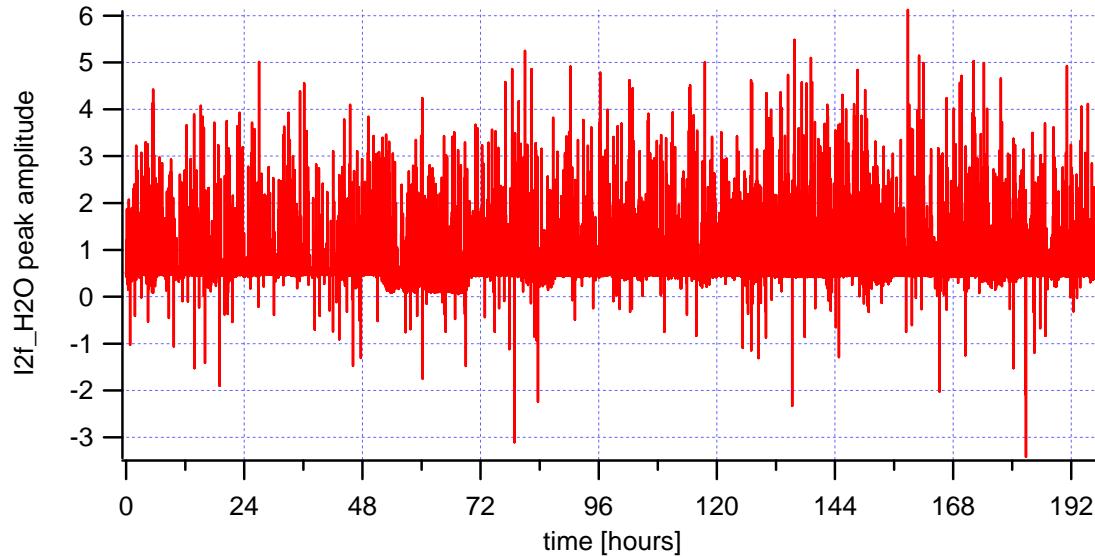
In Figure 5.19, the TDL exhaust stack temperature is plotted along with the gas turbine percent load. Opposite of the gas turbine exhaust temperature (T7) trend versus load, the TDL exhaust stack temperatures are highest at higher gas turbine loads.



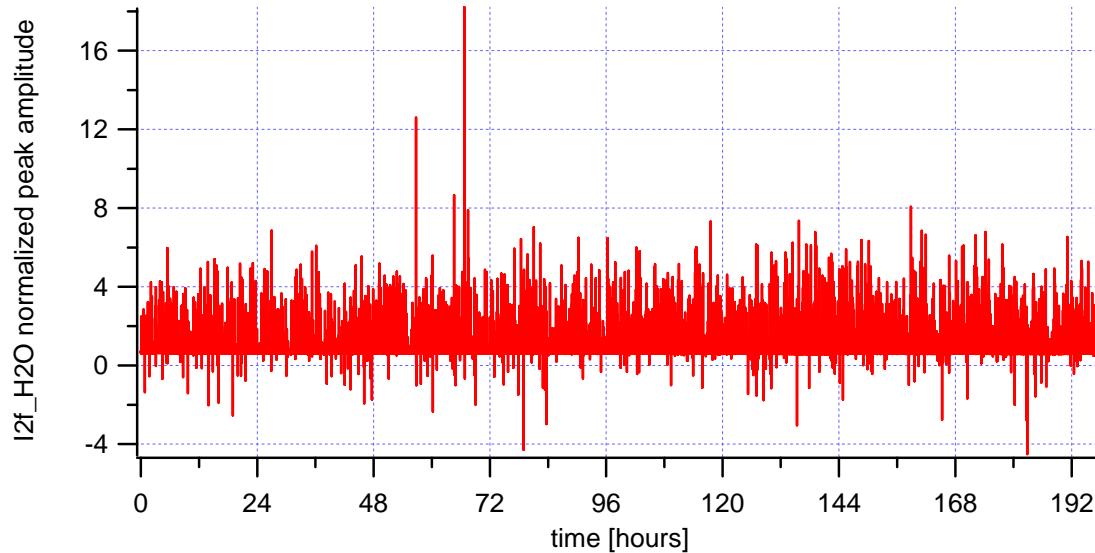
**Figure 5.19:** TDL exhaust stack temperature and GT1 percent load data over the April 2006 testing

$\text{H}_2\text{O}$  and  $\text{CO}_2$  content in the exhaust flow were also measured by the TDL system. Like the  $\text{H}_2\text{O}$  peak ratio data the same data reduction steps were taken. As defined in Chapter 4,  $\text{H}_2\text{O}$  content is calculated using the  $\text{H}_2\text{O}$  normalized peak amplitude TDL data. The raw peak amplitude and normalized peak amplitude  $\text{H}_2\text{O}$  data is shown in Figure 5.20 and 5.21. The filtering removed the noisy  $\frac{1}{2}$  second  $\text{H}_2\text{O}$  normalized peak amplitude data while the decimation allowed for a tighter trend to appear. These plots are shown in Figures 5.22 and 5.23. The filtered and decimated  $\text{H}_2\text{O}$  normalized peak

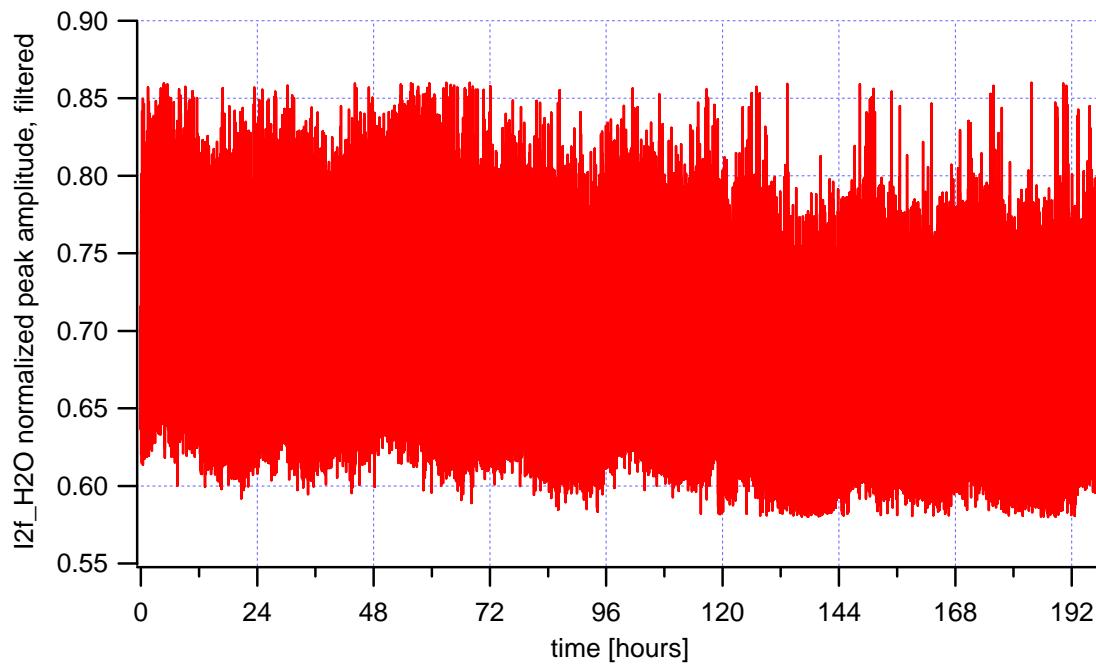
amplitude data was then used to calculate H<sub>2</sub>O mole fraction over the test period as shown in Figure 5.24.



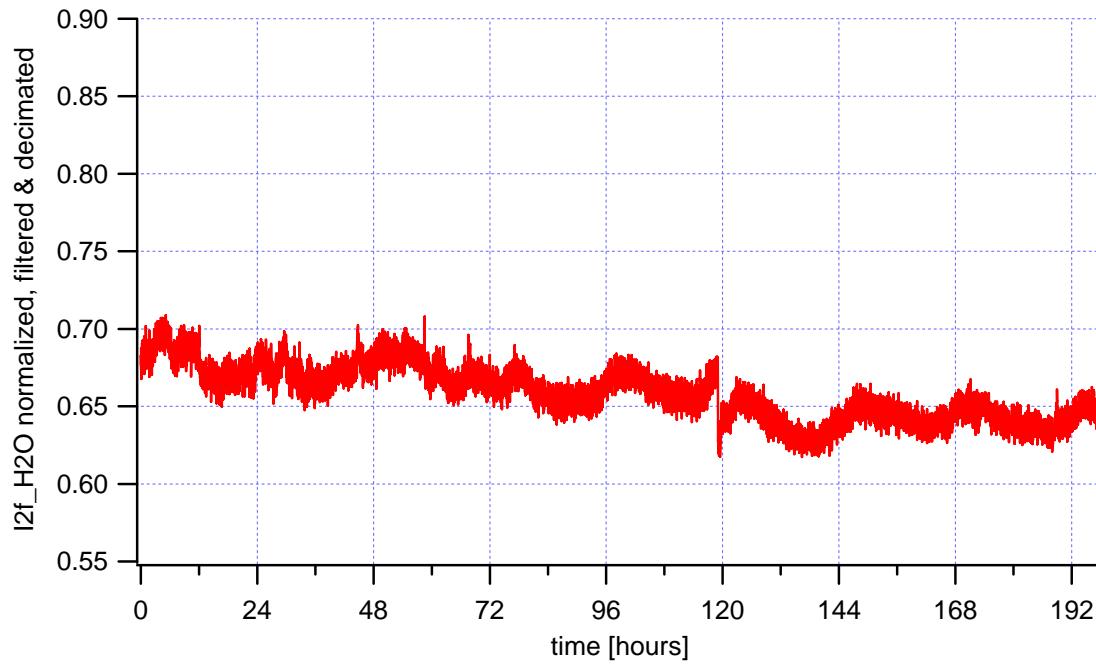
**Figure 5.20:** TDL raw H<sub>2</sub>O peak amplitude data over the entire April 2006 test period



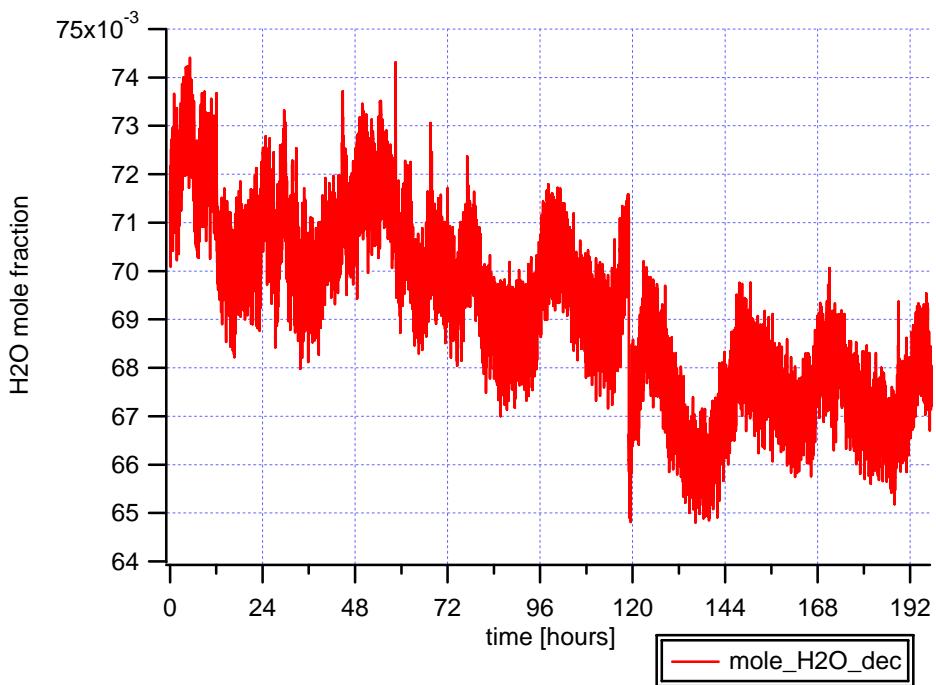
**Figure 5.21:** TDL raw H<sub>2</sub>O normalized peak amplitude data over the entire April 2006 test period



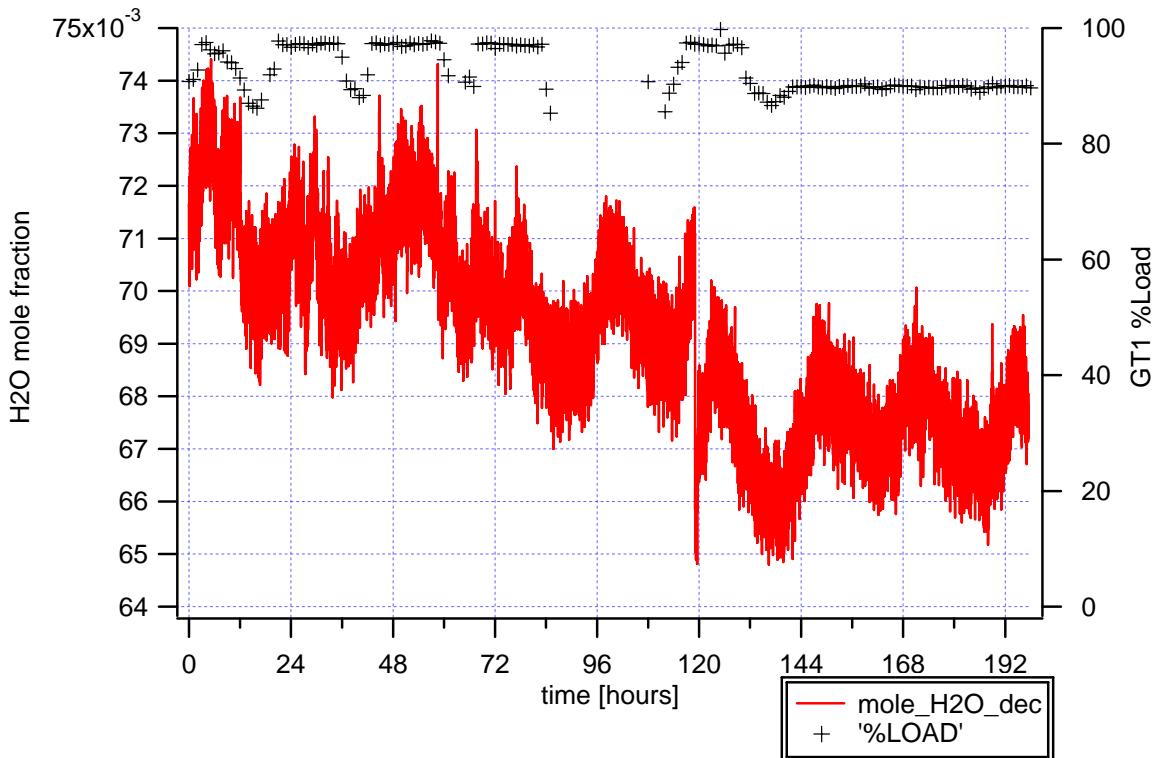
**Figure 5.22:** TDL H<sub>2</sub>O normalized peak amplitude filtered data over the entire April 2006 test period



**Figure 5.23:** TDL H<sub>2</sub>O normalized peak amplitude filtered & decimated (1-minute average) data over the entire April 2006 test period



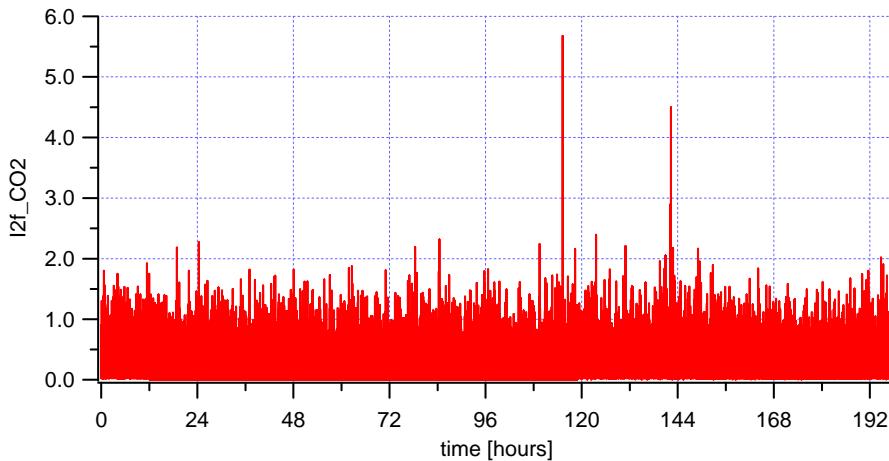
**Figure 5.24:** TDL H<sub>2</sub>O mole fraction based on the filtered & decimated (1-minute average) H<sub>2</sub>O normalized peak data over the entire April 2006 test period



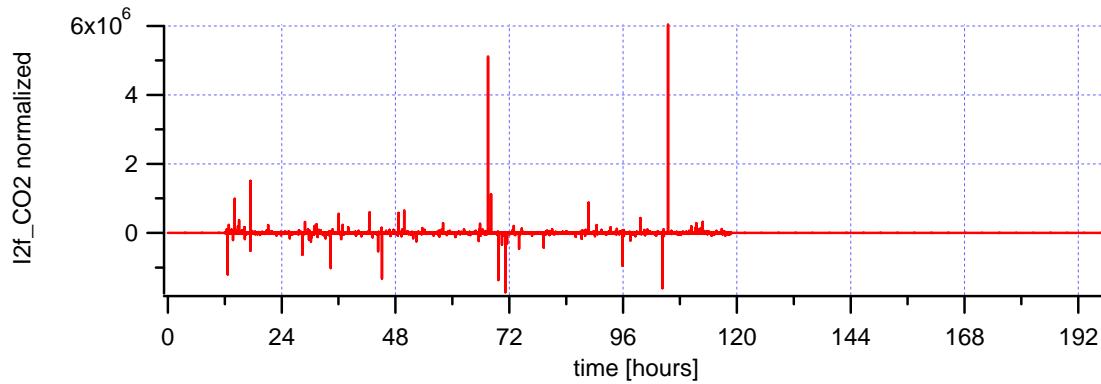
**Figure 5.25:** TDL H<sub>2</sub>O mole fraction based on the filtered & decimated (1-minute average) H<sub>2</sub>O normalized peak data along with GT1 percent load over the entire April 2006 test period

The filtered and decimated H<sub>2</sub>O content varied between 6.5 and 7.4 percent over the April 2006 test period. The downward trend can be explained by the shift in content just before the 120-hour mark. The H<sub>2</sub>O content appears to be cyclic, changing around 0.5% over each 24-hour period. Adding GT1 percent load over the test period is shown in Figure 5.25. This generally shows that H<sub>2</sub>O content is highest at full load.

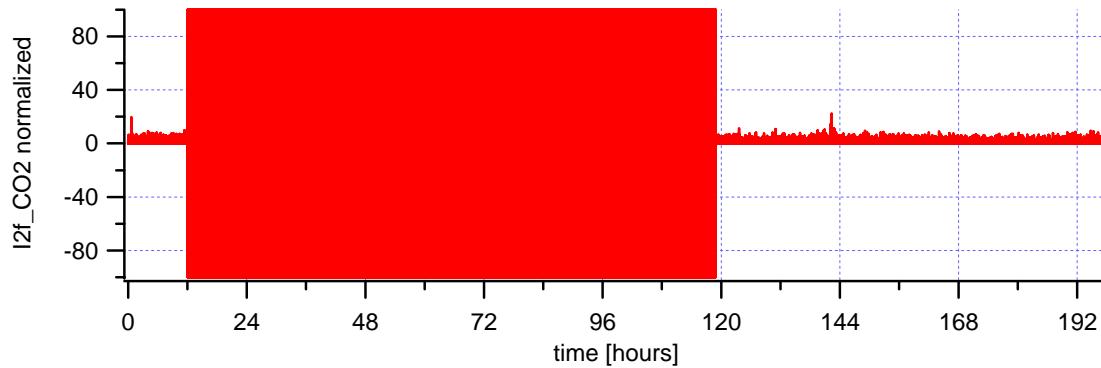
The CO<sub>2</sub> content over the test period was not as stable. This can be explained by the fact that the CO<sub>2</sub> peak signal is not as strong as H<sub>2</sub>O. As discussed in Chapter 4, CO<sub>2</sub> content is calculated using the CO<sub>2</sub> normalized peak amplitude TDL data. The raw peak amplitude and normalized peak amplitude CO<sub>2</sub> data is shown in Figures 5.26 through 5.29. The filtering removed the noisy ½ second CO<sub>2</sub> normalized peak amplitude data while the decimation allowed for a tighter trend to appear. The normalized peak CO<sub>2</sub> data is much cleaner up to the 12-hour and after the 118-hour points. These plots are shown in Figures 5.30 and 5.31. The filtered and decimated CO<sub>2</sub> normalized peak amplitude data is then used to calculate CO<sub>2</sub> mole fraction over the test period as shown in Figures 5.32 and 5.33.



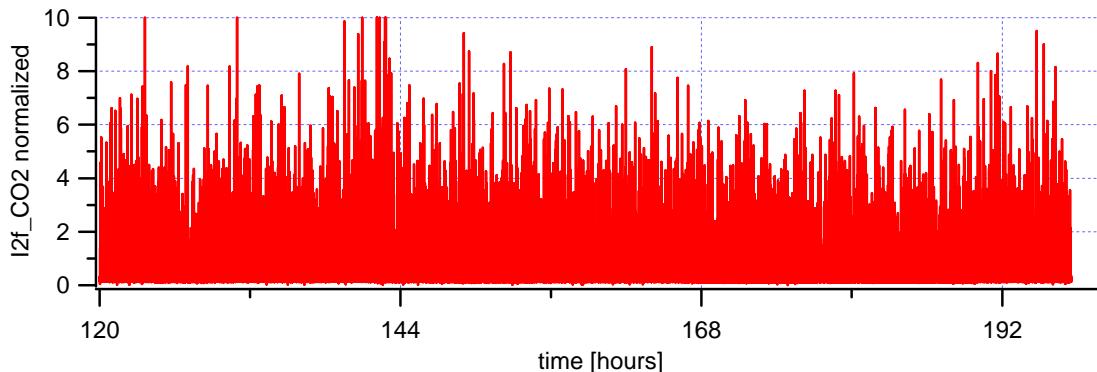
**Figure 5.26:** TDL raw CO<sub>2</sub> peak amplitude data over the entire April 2006 test period



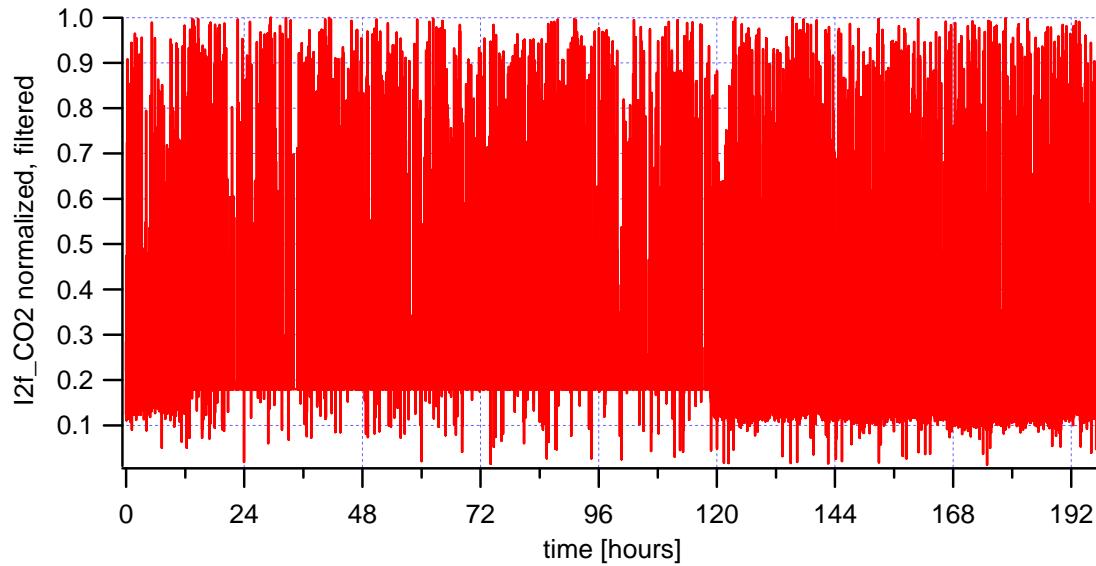
**Figure 5.27:** TDL raw normalized CO<sub>2</sub> peak amplitude data over the entire April 2006 test period



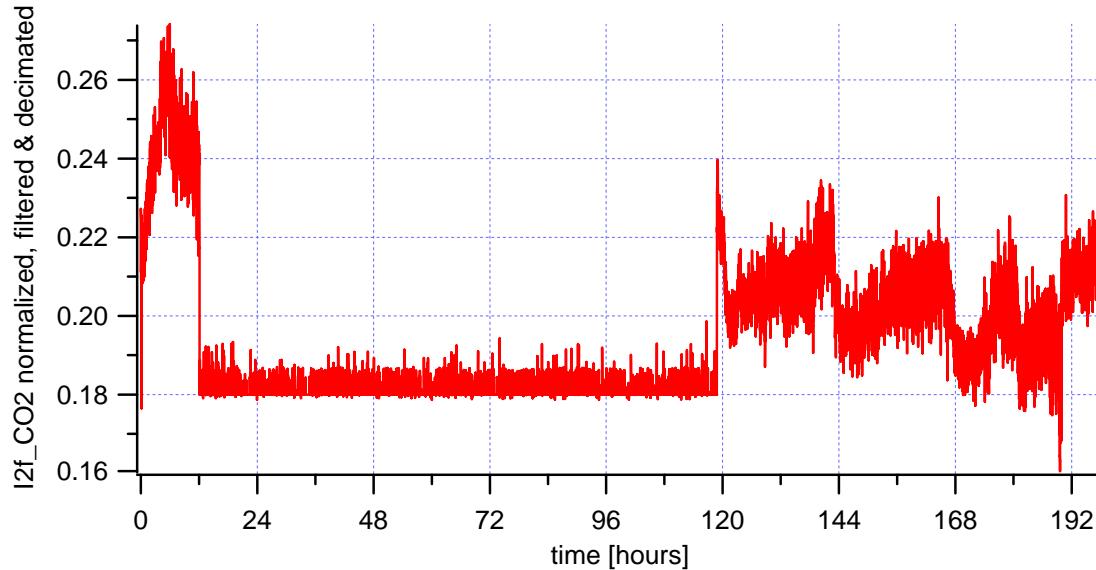
**Figure 5.28:** TDL raw normalized CO<sub>2</sub> peak amplitude data over the entire April 2006 test period showing the noisy data between 12 and 118 hours



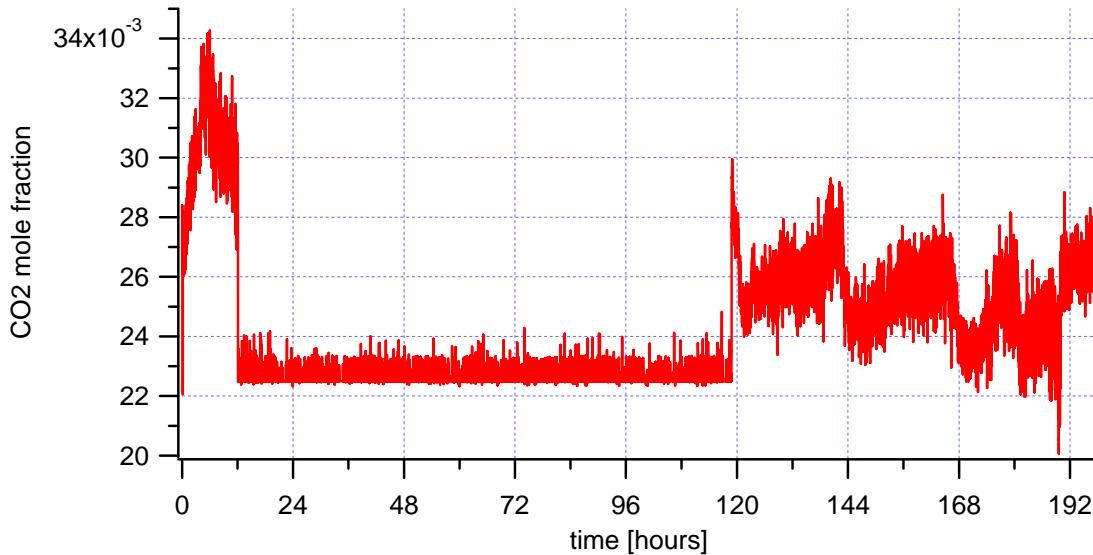
**Figure 5.29:** TDL raw normalized CO<sub>2</sub> peak amplitude data after 120 hours



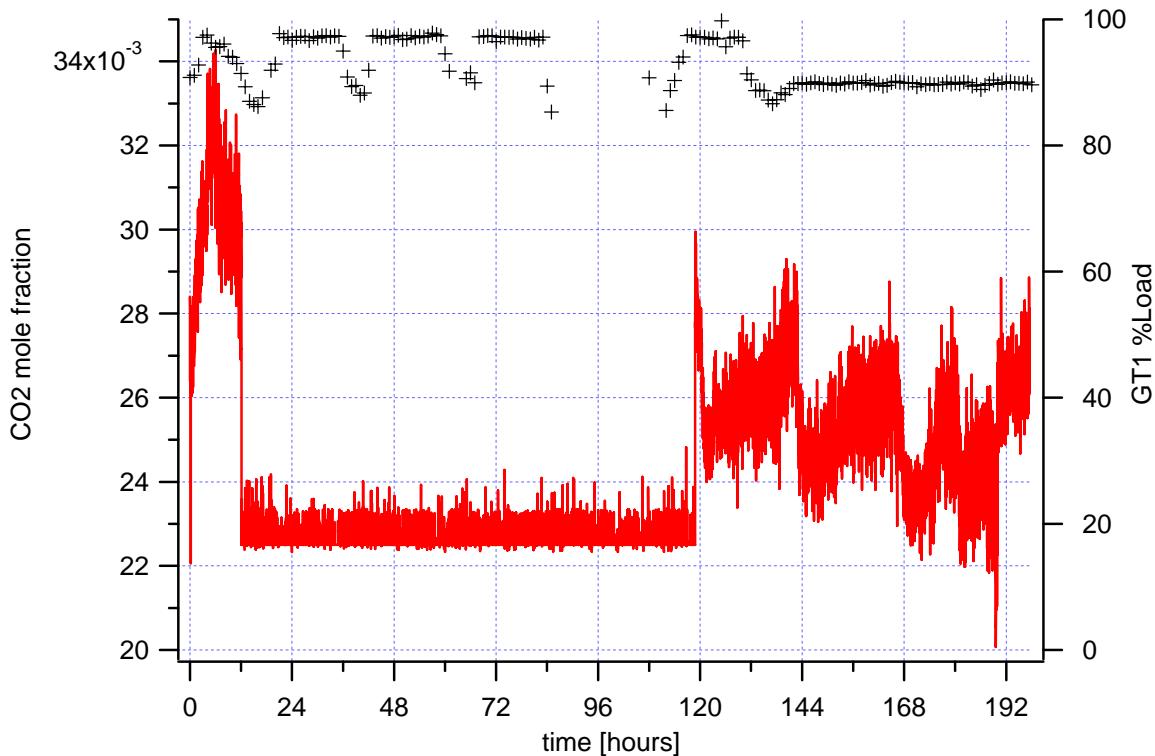
**Figure 5.30:** TDL normalized CO<sub>2</sub> peak amplitude filtered data over the entire April 2006 test period



**Figure 5.31:** TDL normalized CO<sub>2</sub> peak amplitude filtered & decimated (1-minute average) data over the entire April 2006 test period



**Figure 5.32:** TDL CO<sub>2</sub> mole fraction based on the filtered & decimated (1-minute average) CO<sub>2</sub> normalized peak data over the entire April 2006 test period

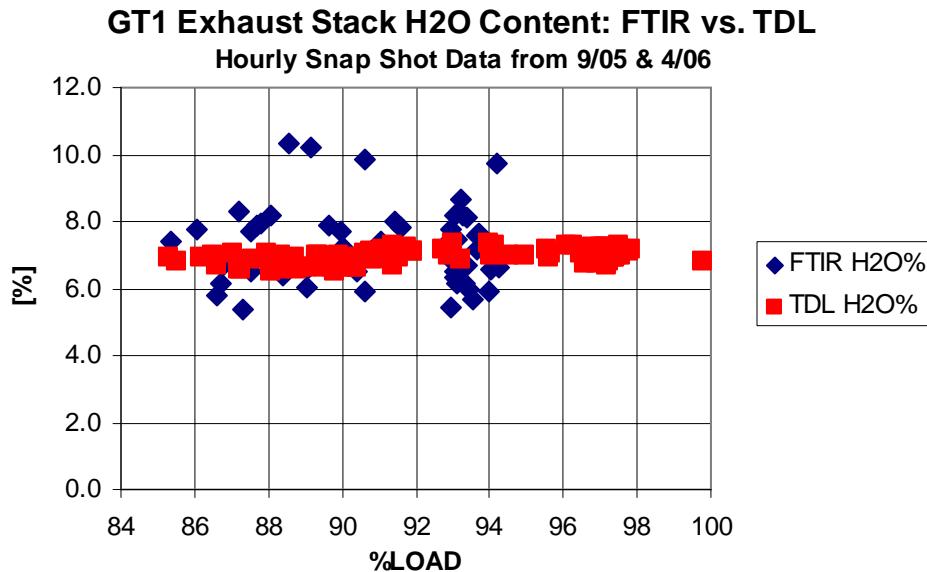


**Figure 5.33:** TDL CO<sub>2</sub> mole fraction based on the filtered & decimated (1-minute average) CO<sub>2</sub> normalized peak data along with GT1 percent load data over the entire April 2006 test period

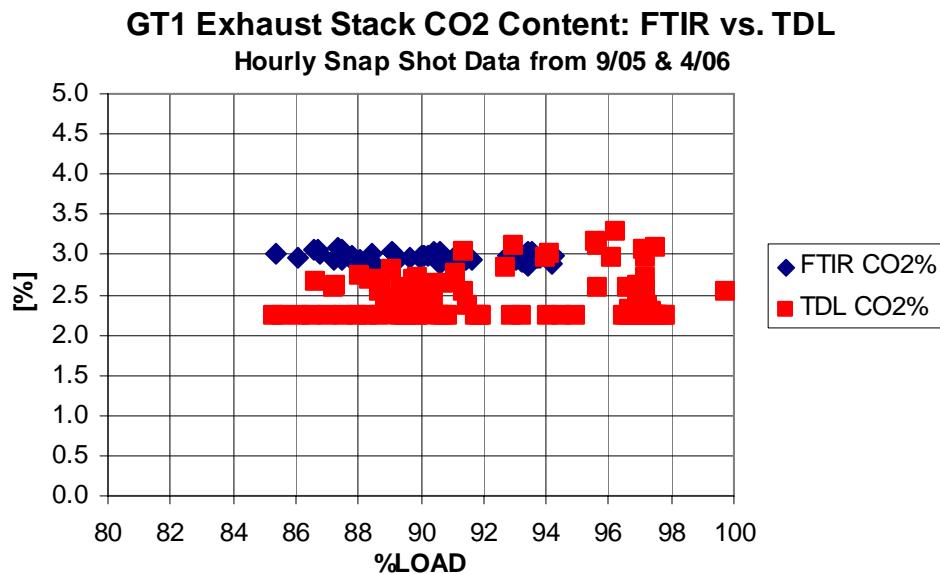
The CO<sub>2</sub> content varied between 2.0 and 3.4%. After the 120-hour mark the results were more reasonable and appeared to be cyclic like H<sub>2</sub>O. The data between 12 and 120 hours should be discounted as something was TDL setup was amiss. A strong relationship between CO<sub>2</sub> and GT1 percent load did not exist.

#### 5.4 FTIR & TDL Field Data Comparison

GT1 percent load can be used to compare the TDL results from the April 2006 testing and the FTIR data from September 2005. To do this, the data needed to be matched up in time to the hourly gas turbine data. This was done manually for the minute post-ScoNOx FTIR data. The decimated 1-minute average TDL data was resolved into hourly snapshot data using code written in Igor. Once the hourly FTIR and TDL data was linked to the gas turbine data, the following two plots of H<sub>2</sub>O and CO<sub>2</sub> content versus percent load were generated (Figures 5.34 & 5.35).



**Figure 5.34:** GT1 exhaust stack H<sub>2</sub>O content as a function of percent load for the 9/05 FTIR and 4/06 TDL data



**Figure 5.35:** GT1 exhaust stack CO<sub>2</sub> content as a function of percent load for the 9/05 FTIR and 4/06 TDL data

The TDL H<sub>2</sub>O content data was much tighter than that from the FTIR with only a 1% spread instead of 5%. The opposite is true for CO<sub>2</sub> where the FTIR showed a 0.2% spread while the TDL data exhibited over 1%. The latter may be explained by the fact that the mid-IR CO<sub>2</sub> peak measured by the FTIR is extremely strong, while as mentioned above, the TDL is measuring a relatively weak CO<sub>2</sub> absorption line in the near-IR.

## 5.5 Error Analysis

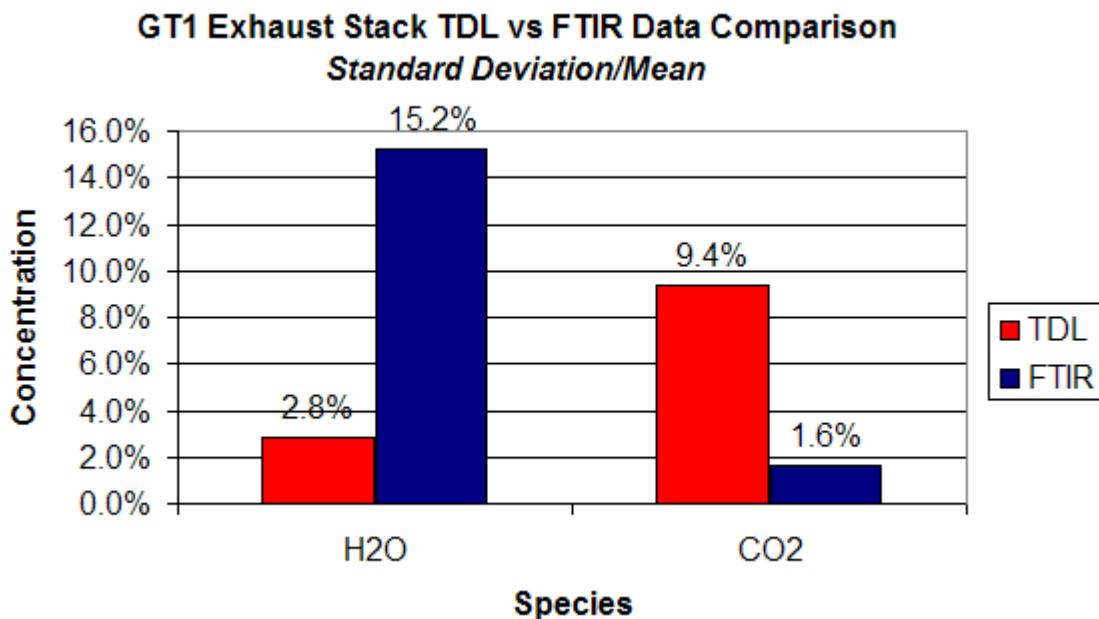
The TDLAS results presented in this research had the luxury of being benchmarked against secondary sources. Field TDL WMS concentration data was compared to a commercially available FTIR system while field gas turbine stack exhaust temperature measurements were taken at the same plane as the TDL line of sight. TDL-specific uncertainties will also be covered in this section.

Comparison of the average TDL WMS and TC gas turbine exhaust temperatures from Figures 5.14 and 5.15 showed that the TDL WMS system measured temperatures around 3.7% lower (433 K versus 450 K). The TDL temperature measurement corresponded to a path-averaged temperature that included colder boundary layer effects. The TDL versus TC exhaust temperature difference was also within the laboratory calculated TDL temperature uncertainty of  $\pm 24.9$  °C (Gharavi 2004).

Since the field FTIR and TDL concentration data were taken on different occasions, both sets of data were compared as a function of gas turbine load as shown in Figures 5.34 and 5.35. From Figure 5.34, it is clear that the TDL H<sub>2</sub>O measurements had much less variation compared to the FTIR data. While both averages were around 7% concentration, the TDL data range (minimum to maximum for the data set) was 0.8% percent concentration compared to 4.9% for the FTIR. The H<sub>2</sub>O TDL standard deviation was 0.19% compared to 1.10% for the FTIR data. This can be explained by the relatively strong H<sub>2</sub>O TDL WMS signal and the fact that water was most likely condensing somewhere inside the long heated FTIR feed lines. As shown in Figure 5.35, the TDL CO<sub>2</sub> data fluctuated more than the FTIR data, with a range of 1% concentration compared to a range of 0.2% for the FTIR data. The TDL CO<sub>2</sub> standard deviation was also worse at

0.23% compared to 0.05% for the FTIR. The TDL CO<sub>2</sub> concentration average was around 2.4% while the FTIR average concentration was a 3.0%. This difference is attributed to the weak TDL WMS CO<sub>2</sub> signal.

The results are summarized best by comparing the ratios of the standard deviation to the mean for the TDL and FTIR measurements.



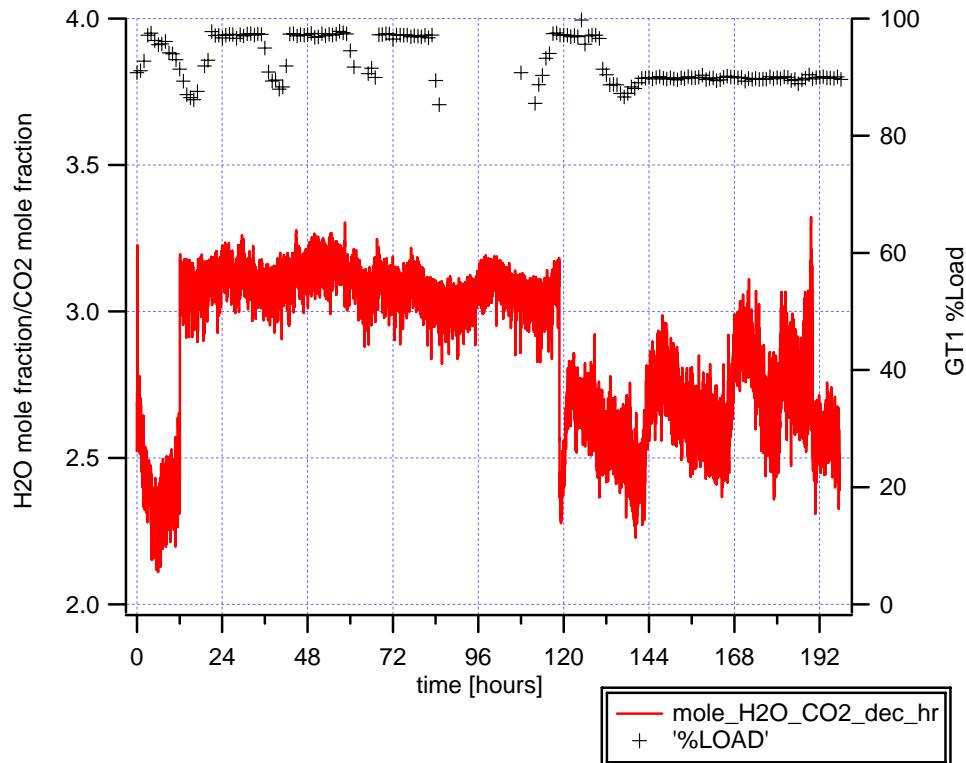
**Figure 5.36:** Ratio of the standard deviation to the mean for the TDL and FTIR GT1 exhaust stack data

Reviewing the TDL WMS H<sub>2</sub>O and CO<sub>2</sub> line strength and pressure-broadening uncertainties are worthwhile. Much effort was taken during the laboratory calibration of the sensors to minimize these errors. Each data point in the line strength measurement represented 3 or 4 measurements with 20 samples each at a different pressure.

The maximum uncertainty in the TDL H<sub>2</sub>O line strength measurement is approximately 11%, and most of the values are on the order of 3-4% (Gharavi 2004). These uncertainties take into account 1% error due to pressure measurement, 0.3% for

path length error, and 2% error for line strength function fitting. The primary uncertainty in the measured values of the line strengths is related to the background H<sub>2</sub>O absorption in the region outside the static cell. These errors were minimized by the vacuum tube transition zones utilized in the glass and metal cell designs. In atmospheric combustion systems where the pressure broadening is on the order of Doppler broadening the overall uncertainty is on the order of 15% (Gharavi 2004). For the CO<sub>2</sub> experiments, the signal measurement errors across multiple spectra were about 1% or less of the measured concentration (Hartley 2006).

Another method for analyzing the TDL WMS error is to track the ratio of H<sub>2</sub>O versus CO<sub>2</sub> concentration over the duration of the field-testing. This ratio is plotted against time in Figure 5.37.



**Figure 5.37:** Ratio of H<sub>2</sub>O and CO<sub>2</sub> mole fractions versus time along with GT1 percent load

Between hours 12 and 118, the CO2 signal was corrupted. Outside of this time period, the ratio was in the 2 to 3 range. The oscillation of the ratio does not appear to correspond to changes in turbine load, but rather may be indicative of something occurring within the instrument.

## CHAPTER 6: Conclusion

Tunable Diode Laser Absorption Spectroscopy (TDLAS) provides an accurate, fast, and non-intrusive solution for species and temperature measurement. The application of this technology to measure temperature, H<sub>2</sub>O, and CO<sub>2</sub> content from an industrial gas turbine has been demonstrated by this research. The multi-gas sensor system, consisting of inexpensive, commercially available, tunable diode lasers used in the telecommunications industry, uses Wavelength Modulation Spectroscopy (WMS) to quantify path-averaged temperature and concentrations.

H<sub>2</sub>O and CO<sub>2</sub> spectroscopic information was first gathered in the laboratory and then the system was packaged for field use. The work culminated in an eight-day test in April 2006 where actual stationary gas turbine emissions data were captured. The results demonstrate the capability to measure temperature, H<sub>2</sub>O, and CO<sub>2</sub> in an industrial environment using two tunable diode lasers. The results were compared against FTIR and Thermocouple (TC) data collected at the same site. The TDL WMS temperature measurements fell within the predicted accuracy of the sensor when compared with exhaust TC data. The TDL WMS H<sub>2</sub>O concentration results exhibited fewer fluctuations and the CO<sub>2</sub> measurements exhibited higher fluctuations when compared to the commercially available FTIR analyzer. Large amounts of TDL WMS data were handled by filtering and decimating.

Future work could integrate the algorithms derived in this research to the Labview program to eliminate the need for post-processing the data. Another improvement would

be to add a TC input to the TDL WMS box so that TDL versus TC temperature comparisons could be made for the duration of the testing.

Future research should focus on real time measurement of NOx and CO along with temperature and CO<sub>2</sub>. This data could be used for active control of gas turbines to optimize emissions performance. Quantum cascade laser technology is the most promising development for future species and temperature measurement of gas turbine exhaust, as there is a clear advantage to operating in the mid-infrared region. However, at this time quantum cascade lasers are still much more expensive than the telecommunication lasers used in this research.

# Appendix

## Bill of materials for the glass and metal cell assemblies:

M. Leon, UCSD TDL "Multiplexed Modulated Diode Laser System"  
12/30/2006

PURCHASED  
ALREADY IN LAB

CALC  
ESTIMATE

FAB#: 3219  
NRG5052

ITEM PART	VENDOR	PN	QTY PER CELL		# OF CELLS	TOTAL QTY	TOTAL COST
			COST	QTY			
1 2" OD Fused Silica 1 Degree Wedge Window for Metal Cells	CVI Laser	LW-2-2037-UV	\$195.00	2	4	4	\$780.00
2 1" OD Fused Silica 1 Degree Wedge Window for Glass Cell	CVI Laser	LW-1-1037-UV	\$105.00	4	12	12	\$1,140.00
3 Glass cell, 30 cm long, for use with existing heater	Curtis Technologies		\$390.00	1	2	2	\$780.00
4 New H2O glass cell; 4 windows	Curtis Technologies		\$650.00	1	1	1	\$650.00
5 Glass Vacuum Tubes, 30 cm long, for use with metal cell configuration	Curtis Technologies		\$310.00	2	2	2	\$620.00
6 Ceramic Fiber Heater, 5" ID, Semi-Cylinder, 20" total L, 240V	Watlow		\$800.00	2	2	2	\$1,600.00
7 0.063" TC's, K Type, Closed Ended, 6 ft long, Ungrounded, Mini Male Connectors	Durosense	KSU-063-72inch-I-MP	\$33.50	6	12	12	\$402.00
8 MDC FLANGE, 2.73" OD, 6 hole	MDC	110014	\$11.20	5	10	10	\$112.00
9 MDC FLANGE, 1.33x0.5 Bore Flanges	MDC	110003	\$9.60	4	8	8	\$76.80
10 MDC 1.33" Gaskets	MDC		\$13.30	1	2	2	\$26.60
11 MDC FLANGE, 2.73" OD, 6 hole	MDC	110014	\$11.20	1	2	2	\$22.40
12 C-SEAL, External Pressure	Perkin-Elmer	633R9Y-0028-C	\$78.41	2	12	12	\$940.92
13 C-SEAL, Internal Pressure	Perkin-Elmer	613R9Y-0025-C	\$78.41	2	12	12	\$940.92
14 Conax Fittings, 0.062" Probe, 1/16" NPT, Graphoil Sealant (925 Deg. F)	CONAX	MPG-062-A-G	\$27.00	6	12	12	\$324.00
15 Ss304 1.5" DIA. SEAMLESS TUBE, L=38.952", 0.049" Wall Thickness	McMaster-Carr	89895K783	\$105.00	1	2	2	\$210.00
16 1/4-28 Bolts, 1.75" long, 18-8 SST, Qty 50	McMaster-Carr	92198A112	\$0.51	12	24	24	\$12.18
17 1/4-28 Nuts, 18-8 SST, Qty 100	McMaster-Carr	91841A215	\$0.29	12	24	24	\$6.91
18 1/4" Washers, SST, Qty 100	McMaster-Carr	98017A660	\$0.15	24	48	48	\$7.08
19 1/4" Belleville Washers, SST	McMaster-Carr	9713K62	\$0.35	24	48	48	\$16.96
20 Silica insulation board for heater plugs and supports; 1" Thick; Max Temp 1925 Deg F	McMaster-Carr	6841K5	\$159.83	1	1	1	\$159.83
21 12" Dia Ducting to house heaters; 5' long	McMaster-Carr	1766K57	\$22.92	1	1	1	\$22.92
22 Mineral Wool Pipe Insulation to insulate heaters; 3' long	McMaster-Carr	9364K23	\$23.33	2	2	2	\$46.66
23 Band Clamps to hold heater support Structure together; 10 per pack	McMaster-Carr	45945K44	\$8.22	1	1	1	\$8.22
24 High Temp Refractory Cement; 2 quart	McMaster-Carr	9372K62	\$8.63	1	1	1	\$8.63
25 1/4" Elbow Weld On Fitting	Swagelok	SS-400-2-2W	\$11.00	3/1	4	4	\$44.00
26 1/4" Elbow Weld On Fitting	Swagelok	SS-400-2-4W	\$11.00	3/1	4	4	\$44.00
27 1/2" Elbow Weld On Fitting	Swagelok	SS-810-2-8W	\$20.00	2	1	2	\$40.00
28 1/2" to 1/4" Reducer	Swagelok	SS-400-R-8	\$15.00	2	1	2	\$30.00
29 1/4" Bellows Toggle Valve	Swagelok	SS-4BKT	\$140.00	2	1	2	\$280.00
30 1/4" Metering Needle Valve with Vernier	Swagelok	SS-SS4-VH	\$80.00	1	1	1	\$80.00
31 1/4" Metering Needle Valve	Swagelok	SS-SS4	\$80.00	1	1	1	\$80.00
32 1/4" Bellows Toggle Valve	Swagelok	SS-4BKT	\$140.00	4	1	4	\$560.00
33 1/4" Swagelok Tee	Swagelok	SS-400-3	\$15.00	10	1	10	\$150.00
34 1/4" Swagelok Port Connector	Swagelok	SS-401-PC	\$3.00	10	1	10	\$30.00
35 1.5" Tube by 1.5" Male NPT Swagelok Connector	Swagelok	SS-2400-1-24	\$20.00	1	2	2	\$40.00
36 Ceramic Fiber Heater, 5" ID, Semi-Cylinder, 20" total L, 240V	Watlow		\$800.00	4	1	4	
37 DIN-A-MITE "A" Power Controller	Watlow	DA10-24CO-0000	\$95.00	3	1	3	
38 Temperature Controller	Watlow	SD6C-HCAA-AARG	\$153.00	3	1	3	
39 Graphoil sheet for non-sealing window/flange interface			\$15.00	1	1	1	
40 1/4" Tubing for pressure and gas feeds			\$0.00	3	2	6	
41 Mixer (V=2XMetalCell/V)			\$100.00	1	1	1	
						<b>TOTAL</b>	<b>\$10,293.03</b>

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## **Appendix C: Presentation on NH<sub>3</sub> Spectroscopy to FACSS 2006**

# Appendix

Presented at FACSS 2006  
Reflects work June – August 2006



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# **Near-Infrared Optical Sensor for Monitoring NH<sub>3</sub> using Wavelength Modulation Spectroscopy**

**Mohammadreza Gharavi, Steven G. Buckley**

**Department of Mechanical and Aerospace Engineering  
University of California, San Diego**



*Center for Energy Research*

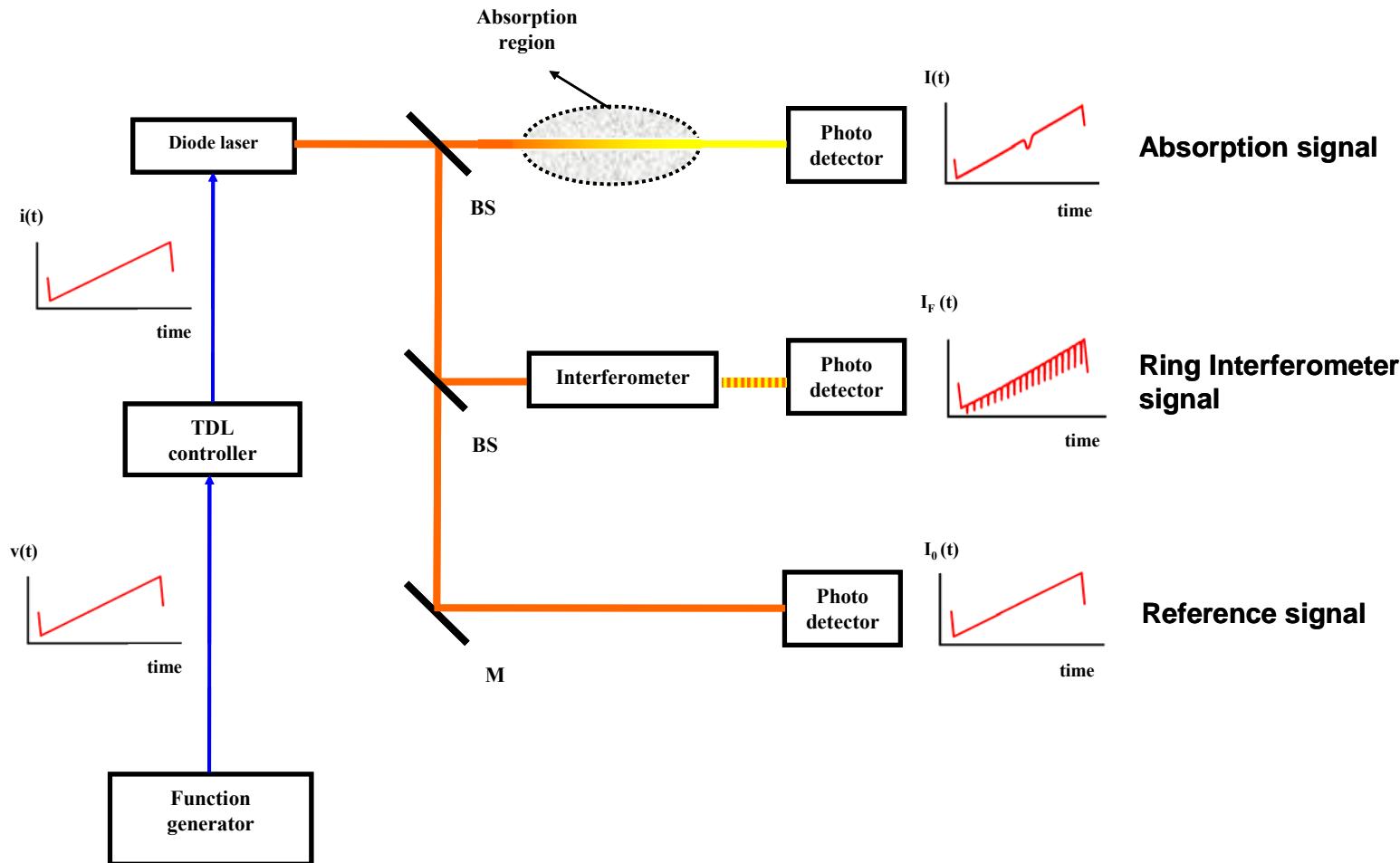
- **Main objective of this work**
- **Basic concept of diode laser absorption spectroscopy**
- **Techniques of diode laser absorption spectroscopy**
  - Direct Absorption
  - Wavelength Modulation Spectroscopy (WMS)
  - Advantages and disadvantages of WMS over direct absorption
- **NH<sub>3</sub> Absorption transitions**
  - Selected absorption transitions
  - Measurement of the spectroscopic properties of the transitions
  - Interference between H<sub>2</sub>O and NH<sub>3</sub> transitions
- **WMS measurement**
  - Schematic of the experimental setup
  - Modeling of the WMS signal
  - Evaluation of the accuracy of the WMS modeling
- **Conclusion**

## Main objective of this work

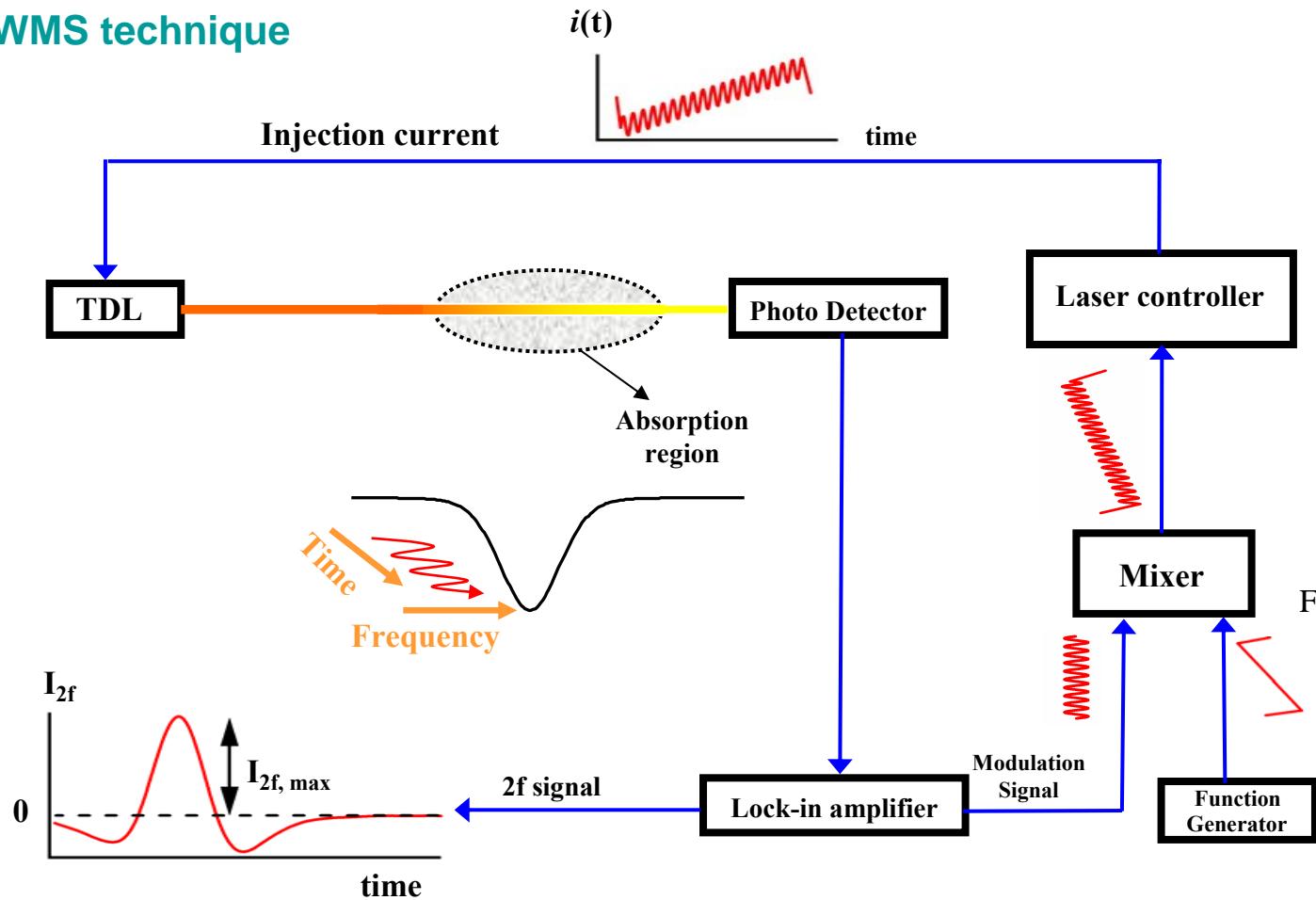
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- **Main objective:** Implementation of a **calibration-free optical sensor** for trace gas monitoring of  $\text{NH}_3$ , applicable in combustion systems, using **Wavelength Modulation Spectroscopy (WMS)**
  
- **Calibration-free WMS-based optical sensor?**  
**Meaning:** No experimental calibration is required → all sensor calibration information is determined solely from a simulation rather than from calibration experiments.  
**Advantage:**
  - Elimination of experimental setup for calibration
  - Improved safety in the measurement of toxic gases such as  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{S}$ , etc. with elimination of calibration step

## ➤ Direct Absorption method



➤ **WMS technique**





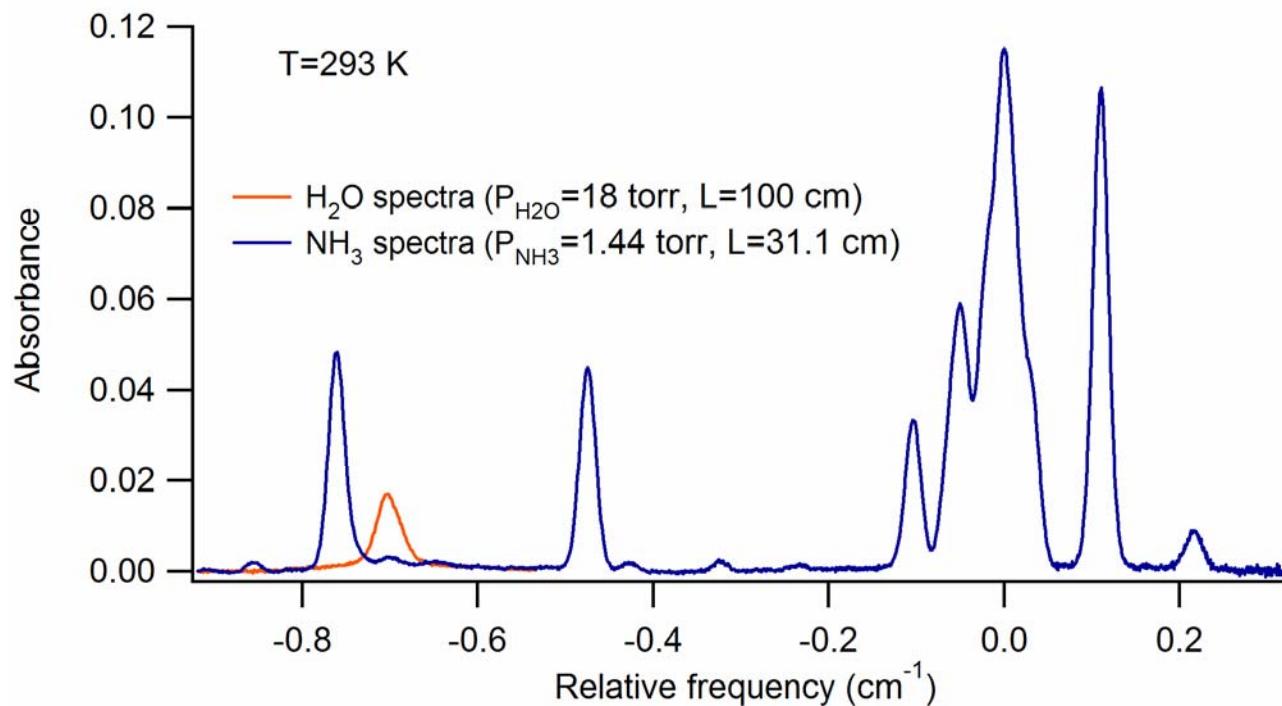
## Techniques of diode laser absorption spectroscopy

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- **Advantages and disadvantages of WMS with respect to direct absorption**
- **Advantage**
  - Significantly improves the S/N ratio
  - Does not rely on unattenuated signal for quantification
  - Does not require capture of the entire absorption region (only the peak value is used)
  - Much less susceptible to beam steering and intensity oscillation
  - Is a perfect technique for multiplexing several lasers for simultaneous multiple species measurement
  - Is perfect for high-speed measurements (real time measurements with a few kHz rate is possible)
- **Disadvantage**
  - Hard to quantify the signal (depends on many parameters such as pressure broadening coefficient of all major colliding species and their concentrations)
  - Extra equipment is required
  - Hard to extract spectroscopic information from WMS signal (sometimes impossible)

### ➤ Selected absorption transitions

- Located around 1512 nm (6612 cm<sup>-1</sup>)
- Spectroscopic parameters are not available in literature
- Fairly far from H<sub>2</sub>O and CO<sub>2</sub> transitions
- Strong line strengths

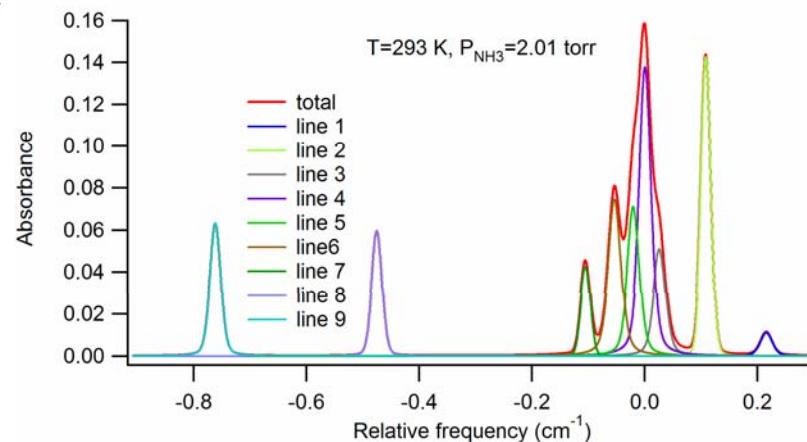
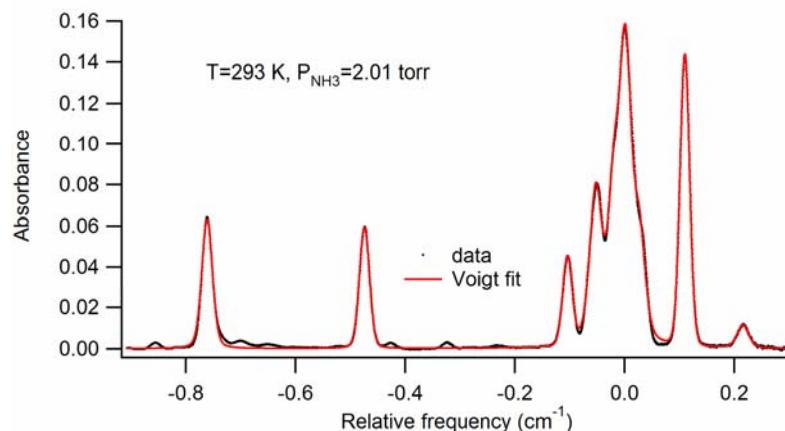


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## NH<sub>3</sub> Absorption Transitions

- **Measurement of the spectroscopic parameters: a) line locations and line strengths (at T=293 K)**
  - A model based on 27 fitting parameters which fits 9 Voigt functions to the overall measured absorption spectra is developed



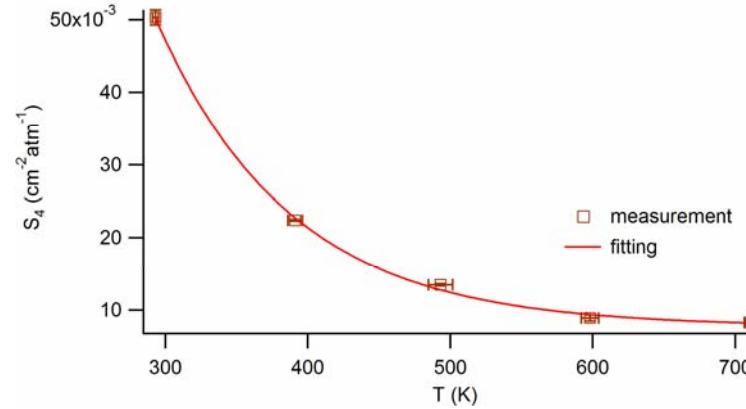
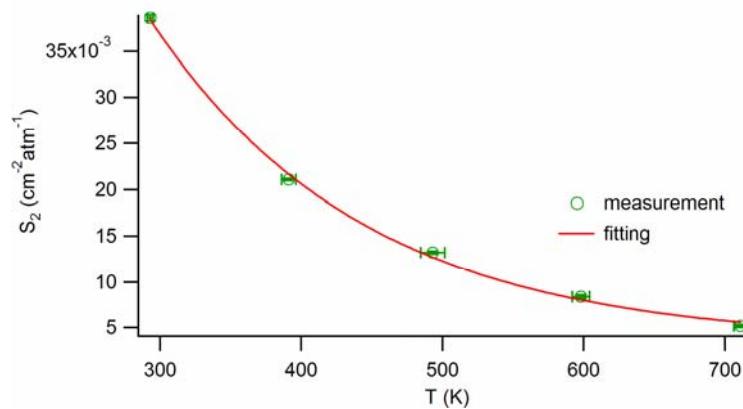
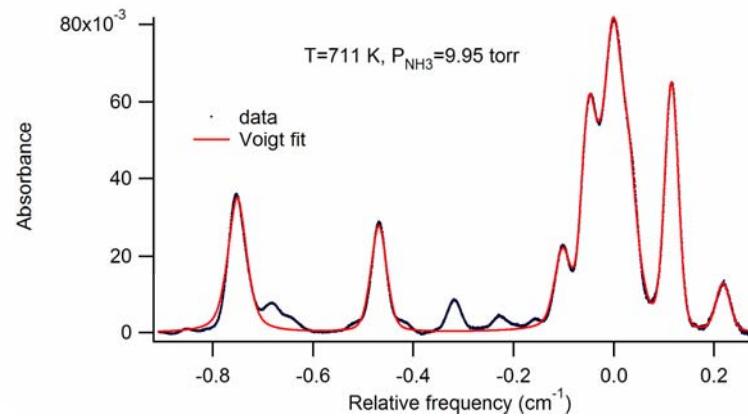
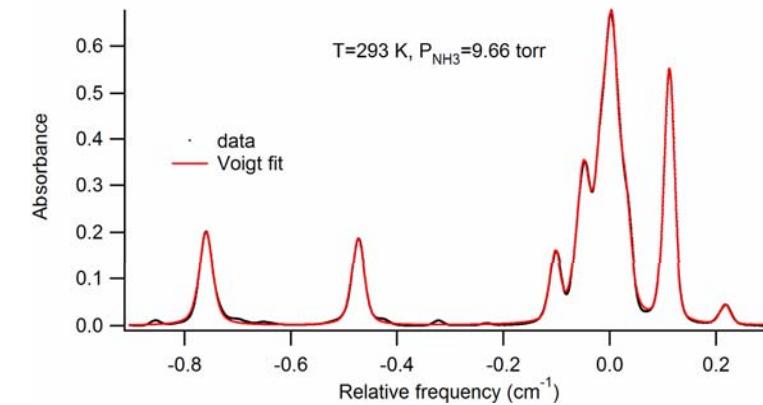
Line	$v_0$ ( $\text{cm}^{-1}$ )	$v_0$ ( $\text{cm}^{-1}$ ) <sup>†</sup>	$v_0$ ( $\text{cm}^{-1}$ ) <sup>‡</sup>	$S_0$ ( $\text{cm}^{-2} \text{ atm}^{-1}$ )	$\sigma_{v0}$	$\sigma_{S0}$
1	6612.937	-	-	0.0031	0.001	0.0003
2	6612.831	6612.827	-	0.0386	0.000	0.0003
3	6612.748	-	6612.734	0.0194	0.000	0.0002
4	6612.723	6612.718	6612.723	0.0503	0.000	0.0010
5	6612.702	-	6612.695	0.0261	0.001	0.0006
6	6612.669	6612.667	-	0.0316	0.001	0.0009
7	6612.617	-	6612.615	0.0102	0.000	0.0006
8	6612.246	-	-	0.0173	0.000	0.0002
9	6611.961	-	-	0.0203	0.001	0.0002

† L. Lundsberg et al. (J. Mol. Spect., 1993)

‡ G. Berden et al. (Chem. Phys. Lett., 1999)

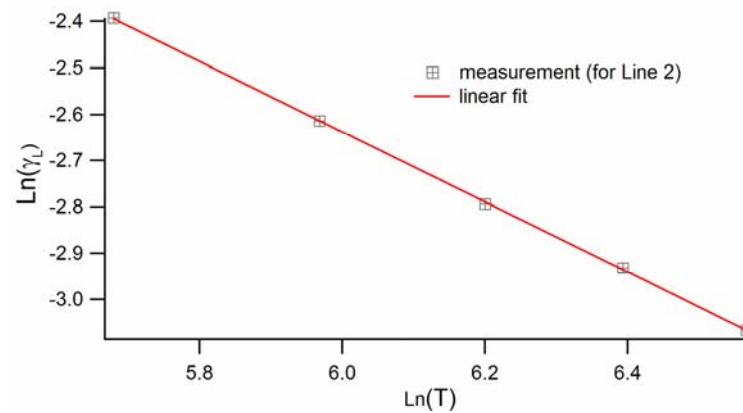
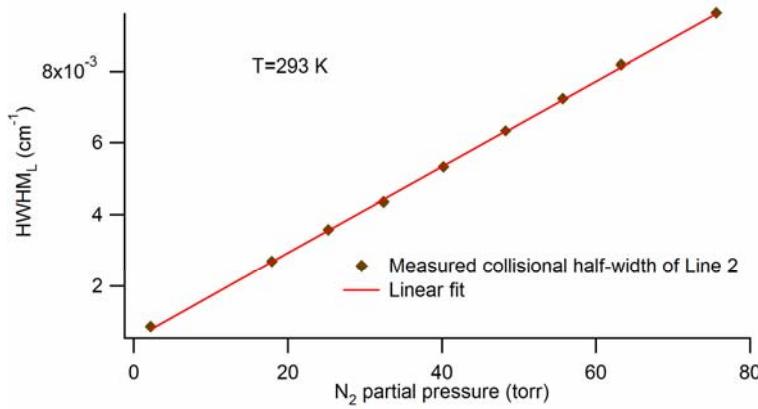
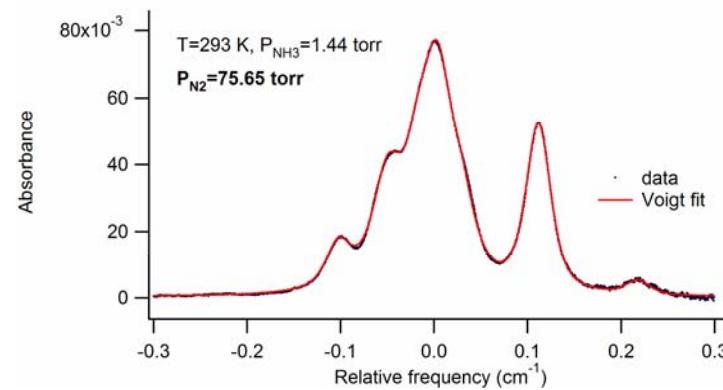
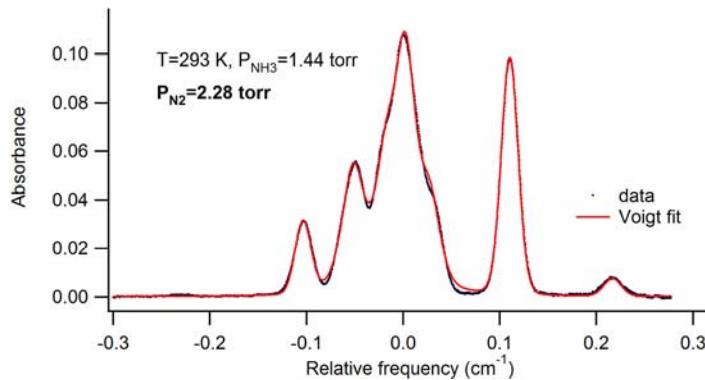
## NH<sub>3</sub> Absorption Transitions

- **Measurement of the spectroscopic parameters: b) line strengths at high temperature**
  - The 27-fitting-parameter model is used



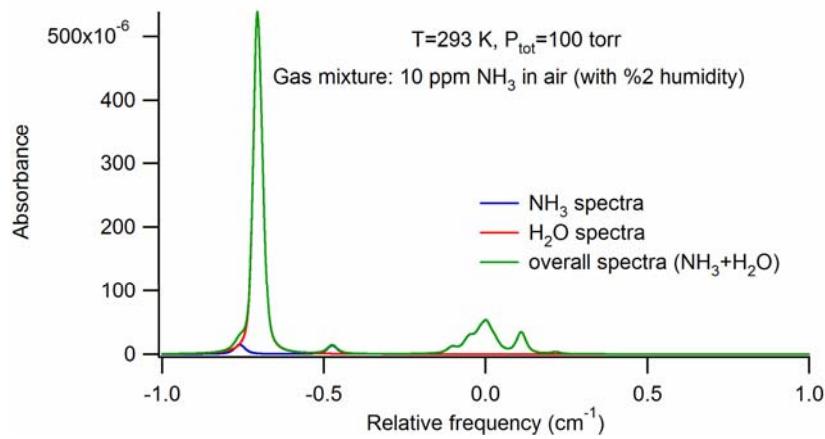
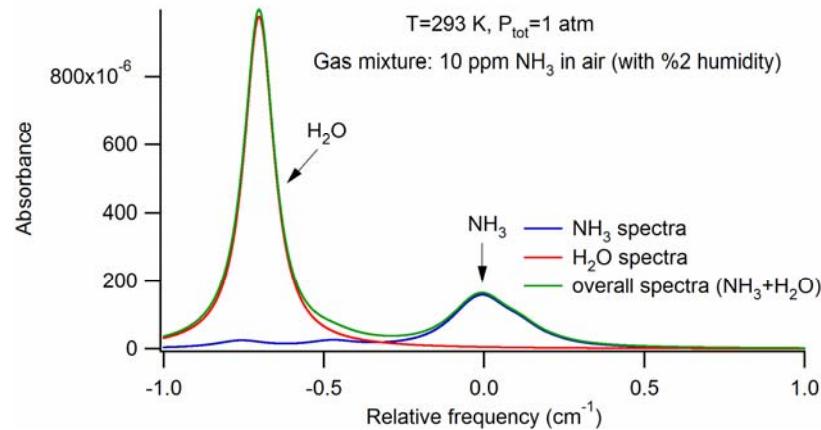
## NH<sub>3</sub> Absorption Transitions

- **Measurement of the spectroscopic parameters: c) pressure broadening coefficients**
  - A 9-fitting-parameter model is developed to measure the collisional width



## NH<sub>3</sub> Absorption Transitions

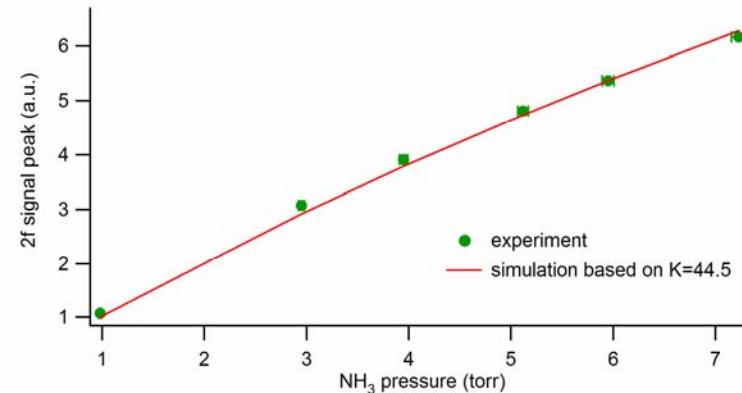
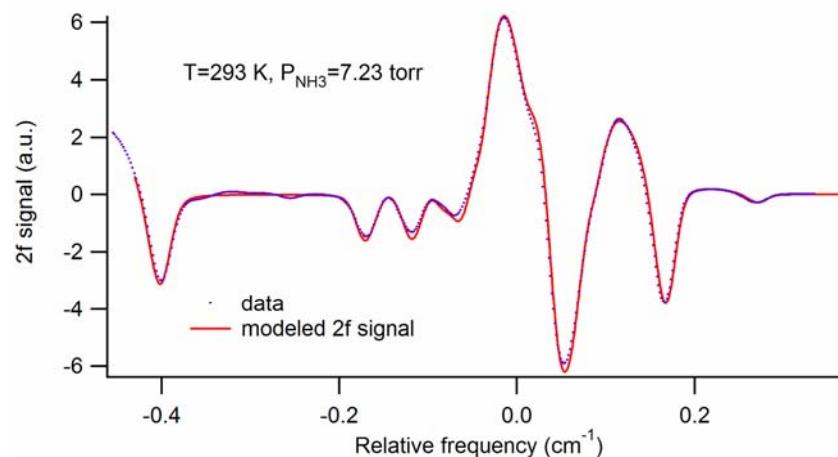
### ➤ Interference between H<sub>2</sub>O and NH<sub>3</sub> transitions



➤ Modeling of the WMS signal

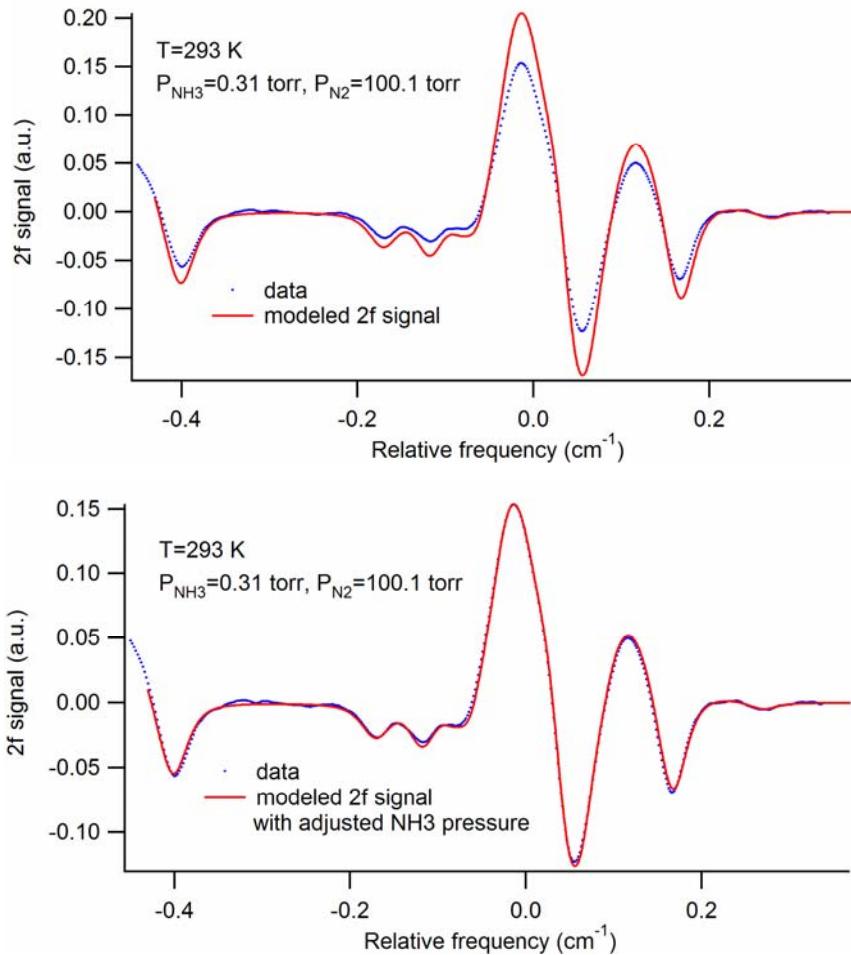
$$I_{2f}(\bar{v}_0) = K \cdot \sum_{i=1}^9 \int_{-\pi}^{+\pi} \left[ 1 + s_{F1}(\nu_{0,i} - \bar{v}_0) + s_{F2}(\nu_{0,i} - \bar{v}_0)^2 - p_f \cos \omega t \right] \times \left\{ 1 - \alpha_i [\nu_{0,i} - \Delta \nu_m(\bar{v}_0) \cos(\omega t + \psi)] \right\} \cos(2\omega t + \theta) d\omega t$$

$$= K \cdot f(T, S_i, P_k, \gamma_k, \Delta \nu_m(\bar{v}_0), p_f, s_{F1}, s_{F2}, \theta, \psi)$$



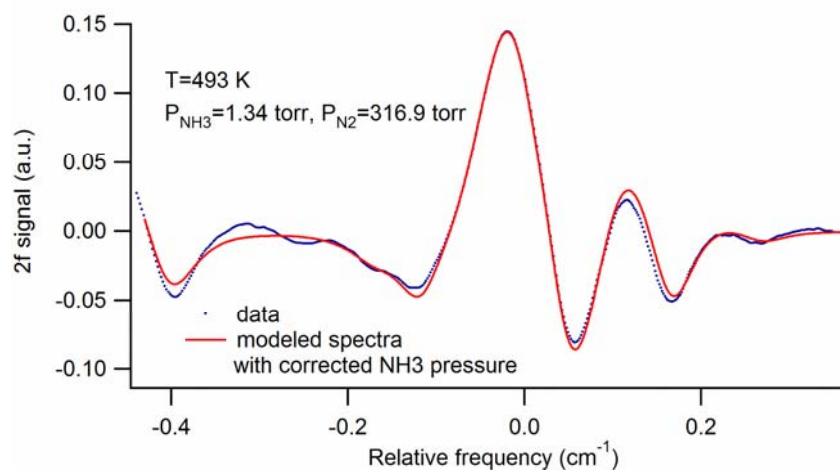
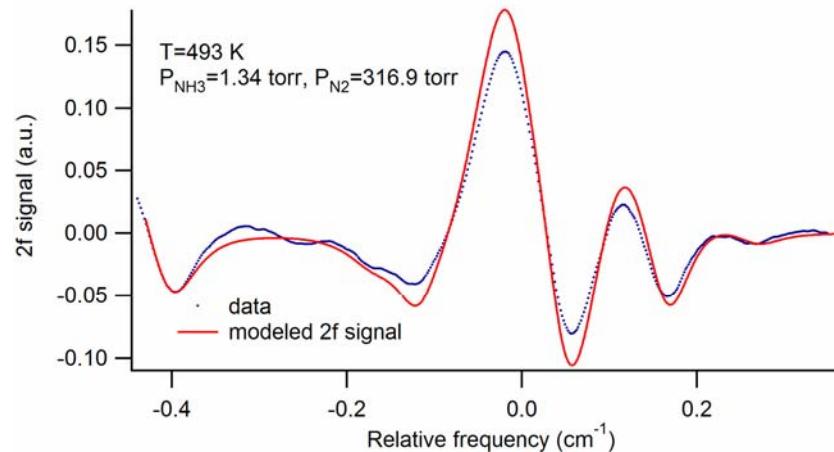
## WMS measurement

- Evaluation of the accuracy of the WMS modeling – room temperature, ~100 torr



## WMS measurement

- Evaluation of the accuracy of the WMS modeling, 493K, ~ 318 torr (total)



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## Conclusions

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- A set of  $\text{NH}_3$  absorption transitions fairly far from  $\text{H}_2\text{O}$  and  $\text{CO}_2$  absorption regions are selected for trace monitoring of  $\text{NH}_3$  in combustion systems.
- Spectroscopic parameters such as line strength, transitional frequencies, and pressure broadening coefficients of these transitions for colliding species such as  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  are measured.
- A mathematical model for simulation of the WMS signal (2f signal) of these transitions has been employed. This model can be used to directly quantify concentrations using the WMS-based optical sensor.
- An optical sensor based on WMS technique was implemented for measurement of the 2f signal of  $\text{NH}_3$ .
- Comparing the experimental data with the simulation results, it is observed that the model overestimates  $\text{NH}_3$  concentration (about 30%).
- Comparing the simulated and measured 2f spectra, it appears that the primary reason for the difference between the measured and simulated spectra is that some  $\text{NH}_3$  was adsorbed in the mixing chamber, and therefore the real concentration of  $\text{NH}_3$  in the gas cell was less than expected.
- A new method for comparing the simulation results with experiments must be devised, to precisely evaluate the accuracy of the simulation results.



## Acknowledgements

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# Questions?

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