Development of All-Solid-State Sensors for Measurement of Nitric Oxide and Ammonia Concentrations by Optical Absorption in Particle-Laden Combustion Exhaust Streams

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ABSTRACT

An all-solid-state continuous-wave (cw) laser system for ultraviolet absorption measurements of the nitric oxide (NO) molecule has been developed and demonstrated. For the NO sensor, 250 nW of tunable cw ultraviolet radiation is produced by sum-frequency-mixing of 532-nm radiation from a diode-pumped Nd:YAG laser and tunable 395-nm radiation from an external cavity diode laser (ECDL). The sum-frequency-mixing process occurs in a beta-barium borate crystal. The nitric oxide absorption measurements are performed by tuning the ECDL and scanning the sum-frequency-mixed radiation over strong nitric oxide absorption lines near 226 nm. The nitric oxide sensor has been used for measurements in the exhaust of a coal-fired laboratory combustion facility. The Texas A&M University boiler burner facility is a 30 kW (100,000 Btu/hr) downward-fired furnace with a steel shell encasing ceramic insulation. Measurements of nitric oxide concentration in the exhaust stream were performed after modification of the facility for laser based NOx diagnostics. The diode-laser-based sensor measurements showed good agreement with the results from physical probe sampling of the combustion exhaust. The diode-laser-based ultraviolet absorption measurements were successful even when the beam was severely attenuated by particulate in the exhaust stream and window fouling. Single-laser-sweep measurements were demonstrated with an effective time resolution of 100 msec, limited at this time by the scan rate of our mechanically tuned ECDL system. Future planned modifications will lead to even faster response times at sensitivity levels at or below 1 ppm.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

This report describes the application of a diode-laser-based sensor for ultraviolet absorption measurements of nitric oxide in a particle-laden exhaust flow from a laboratory-scale coal combustor. The primary objectives of the measurements were to test the performance of the sensor under conditions of severe attenuation of the absorption signal beam due to the particulate loading and/or window fouling, and to demonstrate the real-time data acquisition capabilities of the system. The ultraviolet absorption measurements are compared with the results of physical probe sampling followed by chemiluminescent analysis to determine the NO concentration.

Besides high sensitivity, diode-laser-based sensors also offer non-intrusive and potentially continuous, real-time measurements of these gases. With these attributes, diode-laser-based sensors are ideally suited to be incorporated into control systems to optimize combustion processes and minimize emissions. Much work has been done in developing these types of sensors, but much less work has been done to demonstrate that this technology can be applied in realistic combustion environments.

The nitric oxide sensor utilizes the absorption of ultraviolet (UV) radiation near 226.8 nm by NO. In the spectral region near 226 nm, the NO transitions are very strong and there is little interference from other molecules. UV radiation at this wavelength is generated by sum frequency mixing (SFM) the 10-mW output of an external-cavity diode laser (ECDL) at 395-nm with the 115-mW output of a frequency doubled, diode-pumped Nd:YAG laser at 532.299 nm (vacuum) in a beta-barium-borate (BBO) crystal. Approximately 250 nW of UV is generated in the SFM process. The UV beam is split into a signal and reference beam using a 50-50 beamsplitter. The reference beam is sent directly to a detector while the signal beam is directed through the combustion exhaust stream and then to a detector. Both beams are detected using solar blind photomultiplier tubes (PMTs). Interference filters centered at 228 nm are used to block the fundamental beams as well as any flame emission (which was not a problem in the experiments discussed here). Absorption spectra are acquired by tuning the wavelength of the 395-nm ECDL so that the wavelength of the ultraviolet beam is tuned over NO absorption lines to produce a fully resolved absorption spectrum. Typical data traces recorded by the digital oscilloscope are shown in the report for measurements in a gas cell using calibrated mixtures of NO in N_2 buffer gas.

The nitric oxide sensor has been used for measurements in the exhaust of a coal-fired laboratory combustion facility. The Texas A&M University boiler burner facility is a 30 kW (100,000 Btu/hr) downward-fired furnace with a steel shell encasing ceramic insulation. Measurements of nitric oxide concentration in the exhaust stream were performed after modification of the facility for laser based NOx diagnostics. The diode-laser-based sensor measurements showed good agreement with the results from physical probe sampling of the combustion exhaust. The diode-laser-based ultraviolet absorption measurements were successful even when the beam was severely attenuated by particulate in the exhaust stream and window fouling. Single-laser-sweep measurements were demonstrated with an effective time resolution of 100 msec, limited at this time by the scan rate of our mechanically tuned ECDL system. Future planned modifications will lead to even faster response times at sensitivity levels at or below 1 ppm.

INTRODUCTION

Increasing concern over the environmental impact of combustion emissions have brought about many new governmental regulations in recent years. Besides high sensitivity, diode-laser-based sensors also offer non-intrusive and potentially continuous, real-time measurements of these gases. With these attributes, diode-laser-based sensors are ideally suited to be incorporated into control systems to optimize combustion processes and minimize emissions. Much work has been done in developing these types of sensors, but much less work has been done to demonstrate that this technology can be applied in realistic combustion environments.

In this report, we discuss the application of a diode-laser-based sensor for ultraviolet absorption measurements of nitric oxide in a particle-laden exhaust flow from a laboratory-scale coal combustor. The primary objectives of the measurements were to test the performance of the sensor under conditions of severe attenuation of the absorption signal beam due to the particulate loading and/or window fouling, and to demonstrate the real-time data acquisition capabilities of the system. The ultraviolet absorption measurements are compared with the results of physical probe sampling followed by chemiluminescent analysis to determine the NO concentration.

EXPERIMENTAL APPARATUS

Diode-Laser-Based Nitric Oxide Sensor

The nitric oxide sensor utilizes the absorption of ultraviolet (UV) radiation near 226.8 nm by NO. A schematic diagram of the NO sensor is shown in Fig. 1. In the spectral region near 226 nm, the NO transitions are very strong and there is little interference from other molecules. UV radiation at this wavelength is generated by sum frequency mixing (SFM) the 10-mW output of an external-cavity diode laser (ECDL) at 395-nm with the 115-mW output of a frequency doubled, diode-pumped Nd:YAG laser at 532.299 nm (vacuum) in a beta-barium-borate (BBO) crystal. Approximately 250 nW of UV is generated in the SFM process. The UV beam is split into a signal and reference beam using a 50-50 beamsplitter. The reference beam is sent directly to a detector while the signal beam is directed through the combustion exhaust stream and then to

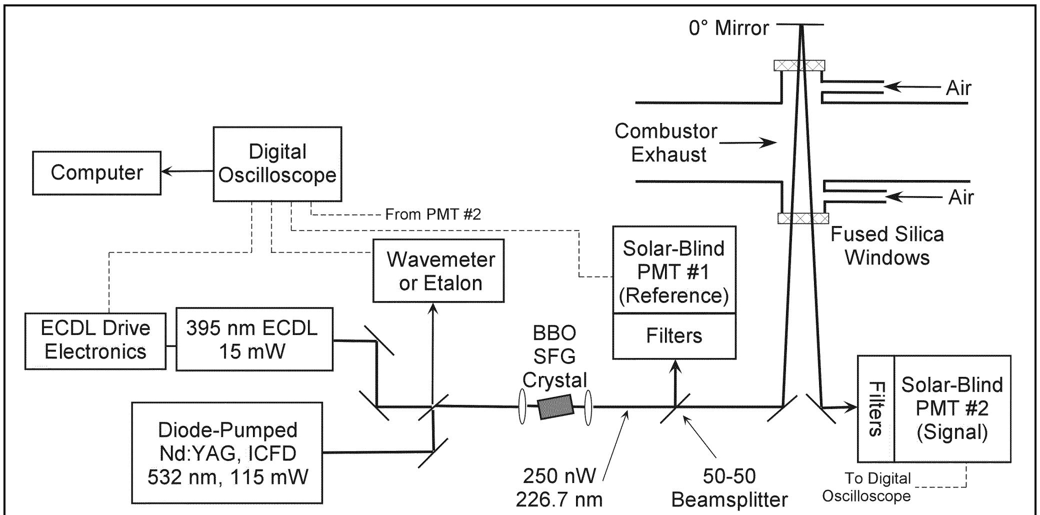

Fig. 1. Schematic diagram of the nitric oxide sensor measurements in the coal-particle-laden combustion exhaust stream.

a detector. Both beams are detected using solar blind photomultiplier tubes (PMTs). Interference filters centered at 228 nm are used to block the fundamental beams as well as any flame emission (which was not a problem in the experiments discussed here).

Absorption spectra are acquired by tuning the wavelength of the 395-nm ECDL so that the wavelength of the ultraviolet beam is tuned over NO absorption lines to produce a fully resolved absorption spectrum. Typical data traces recorded by the digital oscilloscope are shown in Fig. 2 for measurements in a gas cell using calibrated mixtures of NO in N_2 buffer gas. The signal and reference traces from the solar-blind photomultiplier tubes, the trace from the spectrum analyzer, and the ramp voltage applied to the grating piezoelectric crystal are plotted. The free spectral range (FSR) of the etalon in the spectrum analyzer is 2.0 GHz. The mode-hop-free tuning range of the 395-nm ECDL as shown in Fig. 2 is 25 GHz. The data traces acquired from the coal-particle-laden exhaust from the Texas A&M combustor look very similar, except that the particle-loading and window fouling result in a broadband absorption that decreases significantly the intensity of the signal trace.

Coal Combustion Facility

A fully instrumented 100,000 BTU/hr (30 kW) boiler burner facility, shown in Fig. 3, is available for sensor testing experiments. This facility can be fired with gaseous fuels, coal, biomass, and coal:biomass blends (Frazzitta et al., 1999; Annamalai et al., 2003; Sweeten et al., 2003). We have the capability of performing probe sampling emission measurements of NO, O_2, SO_2, and CO. The production of NO_x from coal:biomass combustion has been investigated extensively in previous experiments with this system.

The Texas A&M combustor provides an ideal device for development and testing of new sensor systems. The system is fairly small and inexpensive to operate but allows us to test the performance of the sensor under conditions very similar to those in an actual fossil fuel power plant. Parameters to be varied in the combustor for the sensor tests include equivalence ratio, furnace load, reburn fraction, and particulate loading in the exhaust stream.

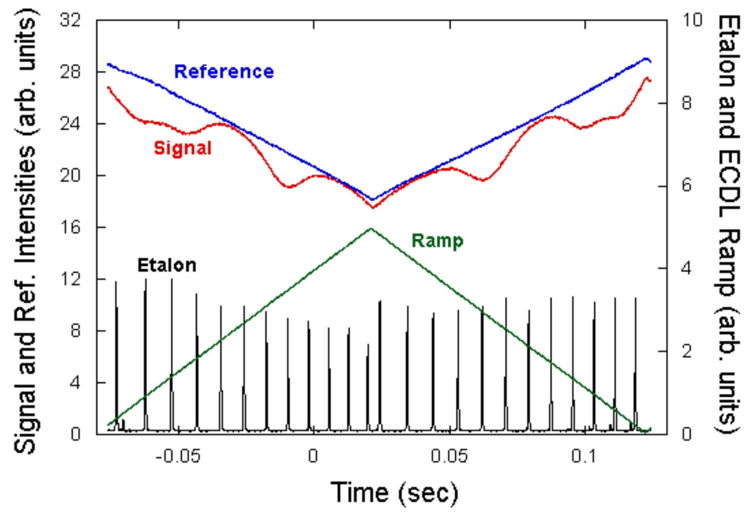

Fig. 2. Signal, reference, and etalon traces recorded for a typical NO absorption scan (Hanna et al., 2002). The ramp function applied to the piezoelectric crystal that moves the grating is also shown.

The laboratory room next to the combustor facility has been converted to a sensor laboratory as part of the research activities connected with the University Coal Research program grant. The exhaust from the coal/biomass facility is being redirected through the sensor laboratory as shown in Fig. 3 for measurements in the combustion exhaust. The level of particulate loading in the combustor exhaust stream can be controlled by varying the cooling water flow just upstream of the exhaust exit of the combustor (an additional water spray apparatus will be located downstream of the sensor to ensure that particulates are not exhausted to the atmosphere). The burner facility is built in sections. For future planned measurements in the primary combustion and reburn zones of the combustor, the appropriate sections of the combustor will be modified for optical access. For the measurements in the exhaust stream described in this report, window assemblies with air flow directed across the windows to prevent fouling were designed and installed. This window assembly is illustrated schematically in Fig. 1. A box with a width of 30 cm was installed in the exhaust stream, and window assemblies were attached to the sides of the box. The windows were purged with air to decrease window fouling from particulates and water vapor condensation. The purge tubes were approximately 4 cm long, and the window aperture was approximately 2.5 cm in diameter.

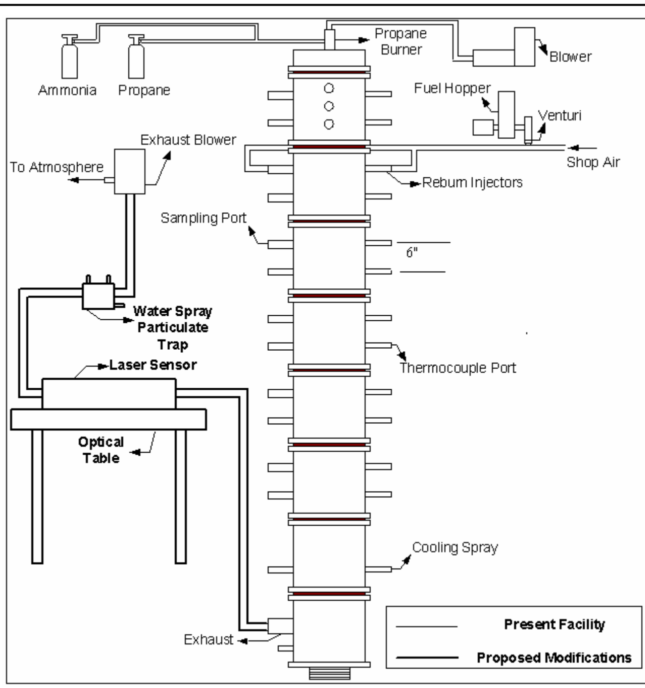

Fig. 3. Schematic diagram of the 30 kW (100,000 BTU /hr) TAMU Combustor Facility. The modifications for the sensor measurements in the exhaust are shown.

EXPERIMENTAL AND OPERATING DATA, DATA REDUCTION

Nitric oxide concentrations measurements were performed in a series of demonstration experiments at Texas A&M University in June, 2003. The objectives of the measurements were to test the performance of the sensor for measurements in the coal-particle-laden exhaust where significant attenuation of the ultraviolet laser radiation was expected, and to demonstrate the real-time response of the sensor. It was anticipated that the attenuation would result both from scattering and absorption by particulates in the exhaust stream and by window fouling. Window fouling, as expected, led to a gradual increase in beam attenuation during the course of the experiment. However, because we determine the NO concentration essentially from the shape of the signal beam absorption spectrum, we were able to perform accurate NO concentration measurements even at broadband attenuation levels of approximately 95%. In addition, the capability of acquiring NO absorption data in 0.1 sec was demonstrated.

An NO absorption scan for a combustion condition with 10% excess air, a coal feed rate of 84.5 g/min, and with no water quenching to reduce particulate loading is shown in Fig. 4. For the field tests, the center frequency of the ECDL was tuned to 395.237 nm (vacuum) to produce UV at 226.82 nm which is in resonance with the $P_2(10)$ and ${}^PQ_{12}(10)$ overlapped transitions at 44087.79 cm^{-1} and 44087.77 cm^{-1}, respectively (Luque and Crosley, 1999). The absorption spectrum shown in Fig. 4 was averaged for eight laser tuning ramp sweeps; this corresponds to a data acquisition time of 1.6 sec. At this condition the signal beam intensity had been attenuated by a factor of nearly ten due to particulate loading and window fouling. The raw data for this absorption scan is shown in Fig. 5. The laser tuning ramp, etalon trace, reference trace, and the signal trace (multiplied by a factor of 9.96) are shown. Prior to starting the combustion test, the signal and reference traces were overlapped on the digital oscilloscope. The scaling factor of 9.96 was used to get the best fit to the theoretical NO absorption line shape shown in Fig. 4. This scaling factor was one of the parameters that was adjusted to obtain the best fit between theoretical and experimental nitric oxide absorption spectra. The increased noise evident in the signal trace compared to the reference trace in Fig. 5 is the result of both the read noise in the digital oscilloscope, which is more evident because of the scaling, and of increased shot noise due to the lower signal intensity incident on the PMT. This noise is reduced substantially by av-

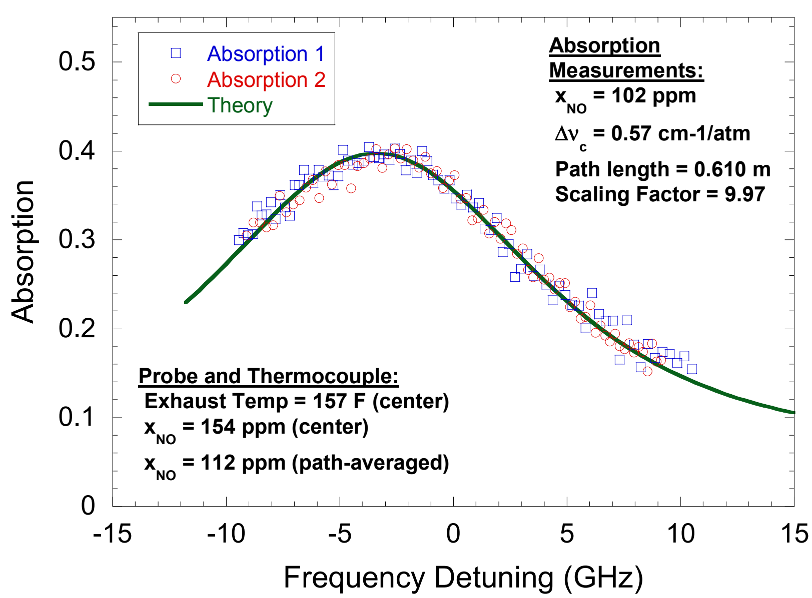

Fig. 4. NO absorption spectrum from the exhaust stream for combustion conditions of 10% excess air and a coal feed rate of 84.5 g/min. No water quenching to reduce particulate loading was used. The spectrum was averaged for 8 laser tuning ramp sweeps.

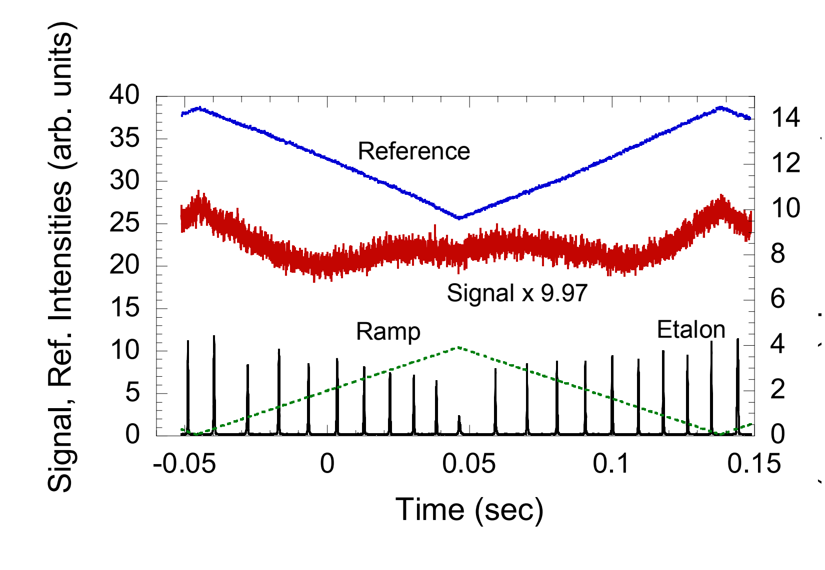

Fig. 5. Signal intensity, reference intensity, tuning ramp voltage, and etalon traces recorded for NO absorption scan shown in Fig. 4 recorded in the particle-laden exhaust. The traces were averaged for 8 tuning ramps.

eraging over 20 temporal channels on the digital oscilloscope; the digital oscilloscope has 10,000 temporal channels so averaging ten adjacent channels does not affect the spectral resolution. Despite the noise on the signal intensity trace shown in Fig. 5, the NO absorption feature is clearly evident even before the digital oscilloscope channels are averaged and the signal trace is divided by reference trace.

The best-fit measured NO concentration from the comparison of theoretical and experimental spectra shown in Fig. 4 was 102 ppm for a total path length of 0.610 m. This is two times the distance between the window port apertures shown in Fig. 1. It is assumed that with the purge air flow through the window port, there will be no exhaust flow in the window port. The NO concentration profile in the exhaust window assembly box was measured at three different spatial locations by chemiluminescent probe sampling. The results of this measurement are shown in Fig. 6. A fourth-order polynomial is fit to the sampling data assuming that the NO concentration goes to zero at the window purge flow aperture plane. This allows us to calculate the path-averaged NO concentration along the path length of the absorption beam through the exhaust stream. The ratio of the NO concentration at the center of the exhaust stream to the path-averaged concentration along the absorption beam path was determined to be 1.38 by integrating the profile shown in Fig. 6. This value was used for all combustion conditions that were investigated.

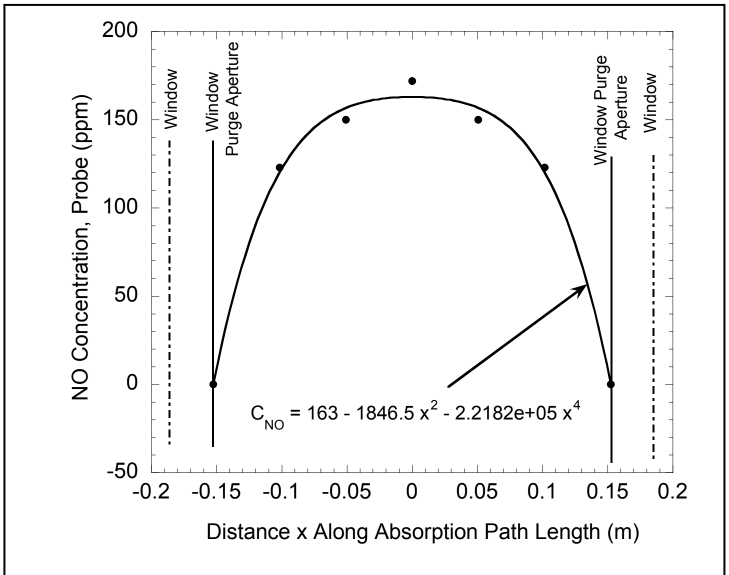

Fig. 6. NO profile in the exhaust stream for combustion conditions of 10% excess air and a coal feed rate of 84.5 g/min. The water quenching was used to reduce particulate loading for this condition..

Numerous NO absorption scans were conducted at the same combustion conditions as for the scan shown in Fig. 4. A single-laser-ramp scan is shown in Fig. 7, and a scan averaged over 32 laser ramps is shown in Fig. 8. Note that the NO concentrations determined from the scans in

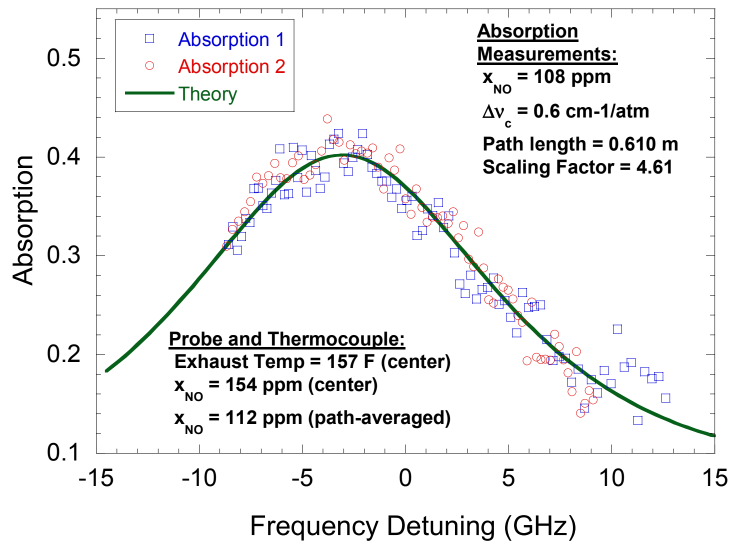

Fig. 7. NO absorption spectrum from the exhaust stream for combustion conditions of 10% excess air and a coal feed rate of 84.5 g/min. No water quenching to reduce particulate loading was used. The spectrum was acquired in a single laser tuning ramp sweep.

Figs. 4, 7, and 8 agree to within 10 ppm with each other. The scaling factors for the three scans differ by more than a factor of two because neutral density filters were removed from in front of the signal beam PMT as the scan proceeded to compensate for the slowly increasing attenuation of the signal beam due to window fouling. Despite the large variations in the overall signal intensity incident on the PMT, the concentrations that were determined from numerous NO spectra acquired for a given combustion condition were consistent to better than ±10%; that level of variation can also be attributed to drift in the combustion operating conditions. Note that the scaling factor is not an arbitrarily adjustable parameter, and that the NO absorption line shape is quite sensitive to the value of the scaling factor. There is obviously more noise in the single-sweep spectrum shown in Fig. 7 than in the scan shown in Fig. 8 which was averaged over 32 laser sweep. The increased noise in the single sweep scan is partly attributable to shot noise from our signal PMT. In general, it is necessary to attenuate the signal and reference beams by significant factors using neutral density filters to prevent PMT saturation. For the measurements in these particle-laden exhaust flows, this turns out to be an advantage because we can remove neutral density filters as the window fouling becomes a problem to increase the intensity in the signal channel.

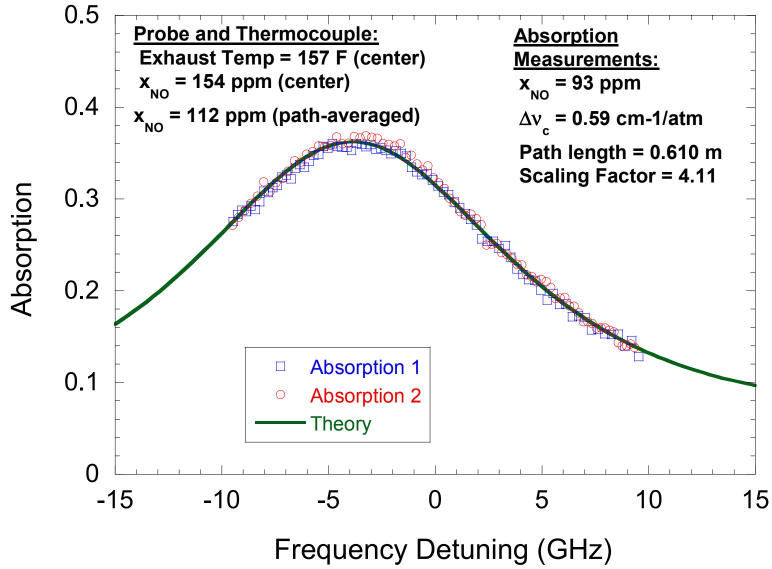

Fig. 8. NO absorption spectrum from the exhaust stream for combustion conditions of 10% excess air and a coal feed rate of 84.5 g/min. No water quenching to reduce particulate loading was used. The spectrum was averaged for 32 laser tuning ramp sweeps.

The NO concentrations that were measured with the ultraviolet absorption sensor tend to be approximately 10-20% lower than the path-averaged value determined using physical probe sampling. Part of this difference may be attributed to uncertainties in our assumed NO profile near the edges of the windowed box where the air was flowing past the windows and into the exhaust stream. Part of the difference may also be due to the fact that we were measuring only NO with the absorption measurement whereas total NO_x, NO and NO_2, was measured with the probe sampling.

CONCLUSIONS AND FUTURE WORK

A diode-laser-based ultraviolet absorption sensor was used to perform nitric oxide concentration measurements in the particle-laden exhaust stream of a laboratory-scale coal combustor. The measurements were successful even in the case of severe (>90%) attenuation of the ultraviolet absorption beam due to particulate loading and window fouling. Data acquisition times as short as 100 msec were demonstrated.

For future NO measurements in the exhaust stream, we will develop a second generation window assembly with more ports for probe sampling and a window design that minimizes the air flow required to prevent window fouling. We are presently developing a diode-laser-based sensor for ammonia and will demonstrate that sensor both in gas cells and in the exhaust of the Texas A&M coal combustor in 2004. We are also working on designs for electro-optically tuned ECDL cavities to increase our laser ramp tuning rate by a significant factor.

REFERENCES

K. Annamalai, B. Thien, and J. Sweeten (2003), "Co-Firing of Coal and Cattle Feedlot Biomass (FB) Fuels Part II: Performance Results from 100,000 BTU/Hr Laboratory Scale Boiler Burner," Fuel **82**, 1183-1193.

S. Frazzitta, K. Annamalai, and J. Sweeten (1999), "Performance of a Burner with Coal and Coal: Feedlot manure Blends," Journal of Propulsion and Power **15**, 181-186.

S. F. Hanna, R. Barron-Jimenez, T. N. Anderson, R. P. Lucht, J. A. Caton, and T. Walther (2002), "Diode-Laser-Based Ultraviolet Absorption Sensor for Nitric Oxide," Applied Physics B **75,** 113-117.

J. Luque and D. R. Crosley: "LIFBASE: Database and Spectral Simulation Program (Version 1.5)," SRI International Report MP 99-009 (1999).

J. M. Sweeten, K. Annamalai, B. Thien, and L. McDonald (2003), "Co-Firing of Coal and Cattle Feedlot Biomass (FB) Fuels, Part I: Feedlot Biomass (Cattle Manure) Fuel Quality and Characteristics," Fuel **82**, 1167-1182.