Technical Progress Report

Project Number DE-FG26-02NT41535 Development of All-Solid-State Sensors for Measurement of Nitric Oxide and Ammonia Concentrations by Optical Absorption in Particle-Laden Combustion Exhaust Streams

October 1, 2003 – September 30, 2004

Jerald A. Caton, and Kalyan Annamalai, Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3123
Robert P. Lucht, School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907-2088

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.

In Year 1 of the research, the nitric oxide sensor was 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 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.

In Year 2 described in this progress report, the Toptica ECDL in the original system was replaced with a Sacher Lasers ECDL. The mode-hop-free tuning range and tuning rate of the Toptica ECDL were 25 GHz and a few Hz, respectively. The mode-hop-free tuning range and tuning rate of the Sacher Lasers ECDL were 90 GHz and a few hundred Hz, respectively. The Sacher Lasers ECDL thus allows us to scan over the entire NO absorption line and to determine the absorption baseline with increased accuracy and precision. The increased tuning rate is an advantage in that data can be acquired much more rapidly and the absorption measurements are less susceptible to the effects of transient fluctuations in the properties of the coal combustor exhaust stream. Gas cell measurements were performed using the NO sensor with the new ECDL, and a few spectra were acquired from the coal exhaust stream. However, the laser diode in the new ECDL failed during the coal combustor tests.

A series of spectral simulations was performed using the HITRAN code to investigate the potential sensitivity of absorption measurements of ammonia in different spectral regions. It was concluded that ammonia absorption features in the 3000-nm spectral region would be hard to measure due to water vapor interferences.

TABLE OF CONTENTS

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 progress 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. A new ECDL was incorporated into our NO sensor system to increase the accuracy and precision of the measurements and to make the measurements even less sensitive to the effects of broadband attenuation. Initial measurements with improved sensor were very encouraging, but the 395-nm laser diode failed during the course of the first set of measurements in the coal exhaust stream.

A theoretical study of ammonia spectroscopy was performed to evaluate the potential for using different spectral regions for absorption measurements. At this point, the spectral regions near 1.53 μm and 2.2 μm look more promising than the 3.0 μm spectral region.

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

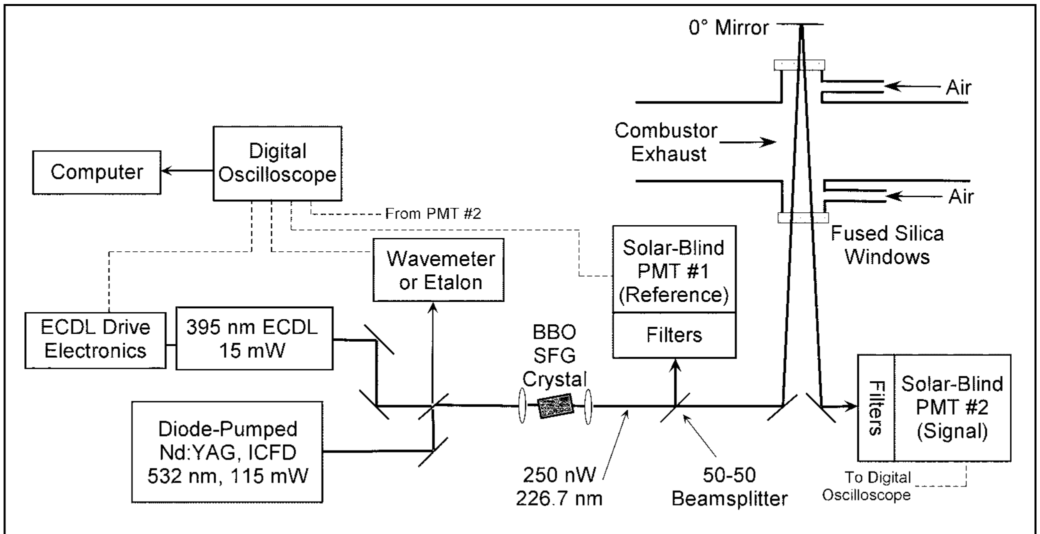

Fig. 1. Schematic diagram of the nitric oxide sensor measurements in the coal-particle-laden combustion exhaust stream.

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).

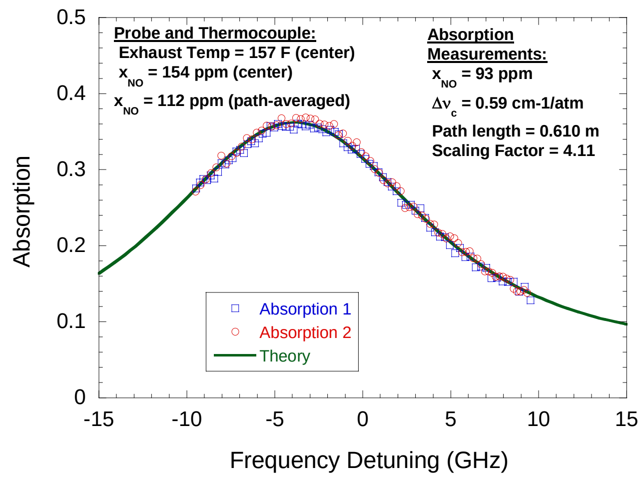

Fig. 2. NO absorption spectrum from the exhaust stream for combustion conditions of 10% excess air and a coal feed rate of 84.5 g/min. No water quenching to reduce particulate loading was used. The spectrum was averaged for 32 laser tuning ramp sweeps.

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. The signal and reference traces from the solar-blind photomultiplier tubes, the output of a 2-GHz free-spectral-range (FSR) spectrum analyzer, and the ramp voltage applied to the grating piezoelectric crystal are acquired as the ECDL frequency is scanned. The mode-hop-free tuning range of the 395-nm ECDL used in the Year 1 experiments was 25 GHz; a typical NO absorption spectrum from those experiments is shown in Fig. 2. By controlling the diode laser current as we tuned the ECDL grating, we were able to obtain a mode-hop-free tuning range of almost 90 GHz with the Sacher Lasers ECDL, over a factor of three better than with the Toptica ECDL. The mode-hop-free tuning of the Sacher Lasers ECDL is demonstrated in Fig. 3, where the output from the 2-GHz FSR spectrum analyzer is plotted. The increased mode-hop-free tuning range of the 395-nm ECDL will improve the accuracy and precision of our NO absorption measurements by minimizing any uncertainties in determining the unattenuated baseline for the NO spectral lines.

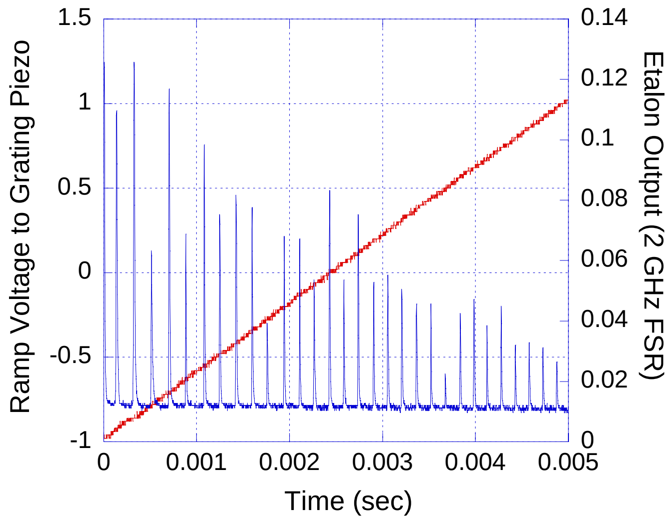

Fig. 3. Spectrum analyzer trace showing a mode-hop-free tuning range of > 60 GHz for the Sacher Lasers 395-nm ECDL. The laser ramp frequency is 100 Hz.

Coal Combustion Facility

A fully instrumented 100,000 BTU/hr (30 kW) boiler burner facility 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

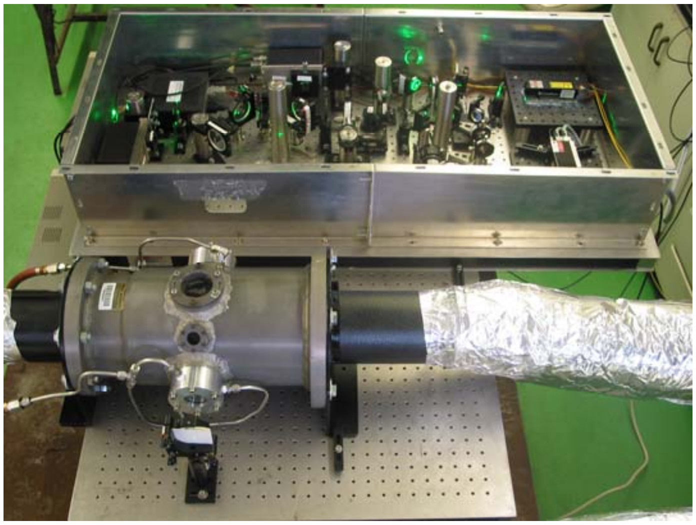

Fig. 4. Photograph of the NO sensor assembly (top) and the optical access chamber for the coal exhaust stream (bottom).

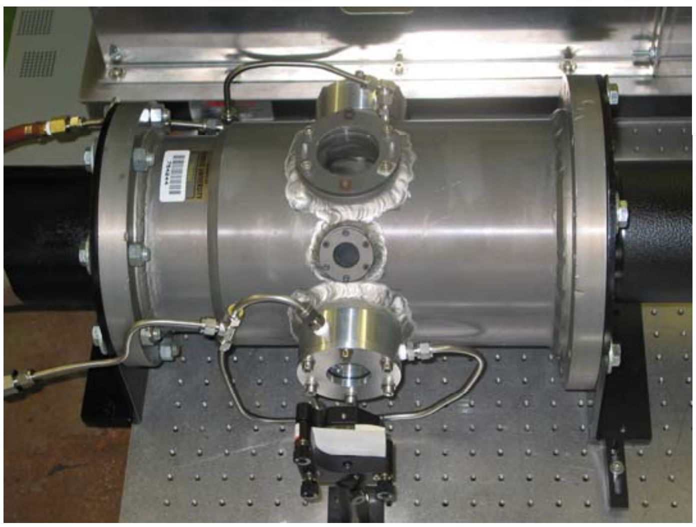

Fig. 5. Close-up photograph of the the optical access chamber for the coal exhaust stream (bottom).

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.

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 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.

A new optical chamber was fabricated and installed during Project Year 2 and is illustrated in Figs. 4 and 5. Window assemblies with air flow directed across the windows to prevent fouling were designed and installed. The optical chamber is fitted with holes for insertion of physical probes for extracting samples for NOx measurement. The NOx concentrations in ppm are measured on dry basis (with water vapor removed by desiccant) using ENERAC 3000 E gas analyzer which uses electrochemical cells for measuring NO and NO_2 separately; typically NO_2 is very low and of the order of 2 ppm. Thus NO_x (NO + NO_2) is reported as NO.

EXPERIMENTAL AND OPERATING DATA, DATA REDUCTION

Nitric oxide concentrations measurements were performed in a series of demonstration experiments at Texas A&M University in May-June, 2004. 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. A typical NO spectrum from a gas cell is shown in Fig. 6. This spectrum was acquired in preparation for a series of measurements planned in the coal exhaust stream in May-June 2004. As compared to the spectrum shown in Fig. 2, acquired in June 2003, the NO absorption spectrum shown in

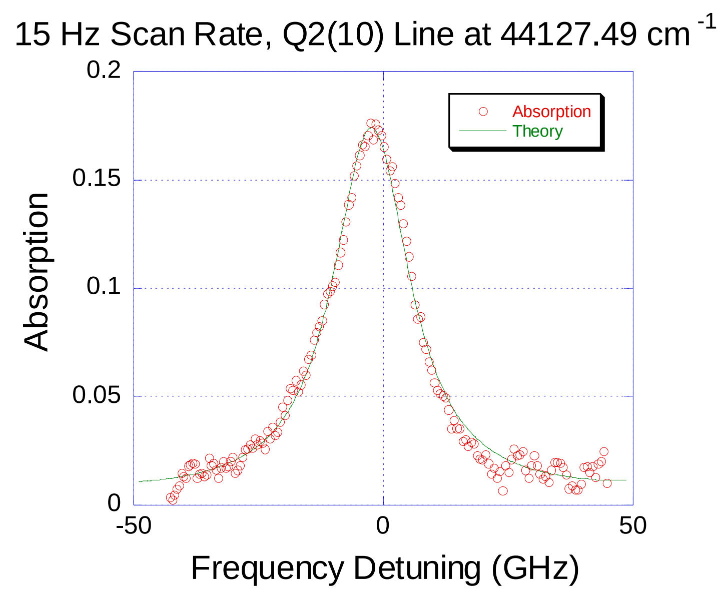

Fig. 6. NO absorption scan from room-temperature gas cell acquired using the new Sacher Lasers ECDL in the NO sensor system.

Fig. 6 exhibits a much larger mode-hop-free tuning range, allowing us to scan over the entire line and to determine the spectral baseline with more accuracy and precision.

After completing the gas cell measurements to test the performance of the new sensor, we moved the sensor into position next to the coal combustor exhaust line optical port. In preparation for measurements in the coal combustor exhaust, NO absorption measurements were performed as the coal combustor facility was being brought on line. Fig. 7 shows an NO spectrum obtained from the facility while a propane-air flame was being burned to warm the facility prior to coal injection. Unfortunately, the Sacher Lasers 395-nm diode laser failed shortly after the spectrum shown in Fig. 7 was acquired and we were not able to obtain the large set of exhaust stream NO measurements that we were planning to acquire.

We also performed a number of theoretical spectral simulations to determine the best spectral location for detecting the ammonia molecule. Because of our difference frequency mixing approach for our mid-infrared NH_3 sensor, our potential range of wavelengths is not limited by the availability of near-infrared diode lasers. At present, the most promising region for detection of NH3 seems to be the spectral region near 2.2 mm. A theoretical spectrum calculated using our absorption code and HITRAN data parameters is shown in Fig. 8.

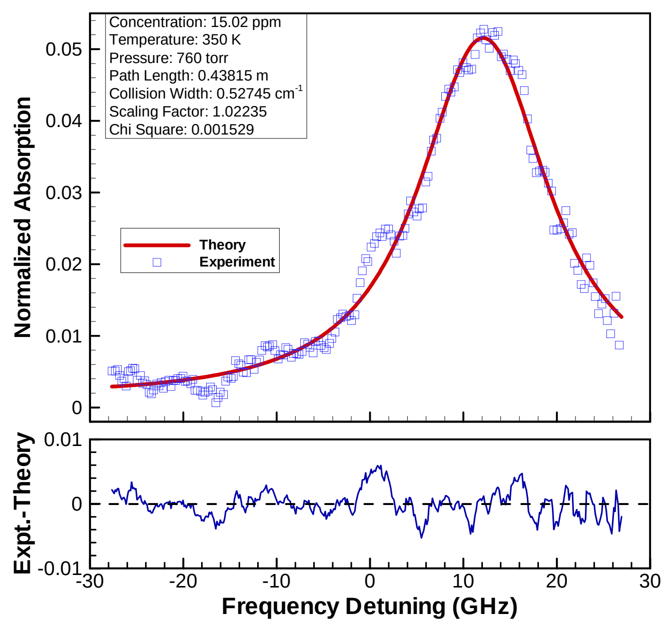

Fig. 7. NO absorption spectrum acquired from the combustor exhaust stream of the Texas A&M coal combustor facility. The combustor facility was operating with a propane/air flame at the time this spectrum was acquired. Note the low NO concentration of 15 ppm in the exhaust stream.

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 in Project Year 1. 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. In Project Year 2 discussed in this report, we replaced the Toptica ECDL in the original system was with a Sacher Lasers ECDL. The mode-hop-free tuning range and tuning rate of the Toptica ECDL were 25 GHz and a few Hz, respectively. The mode-hop-free tuning range and tuning rate of the Sacher Lasers ECDL were 90 GHz and a few hundred Hz,

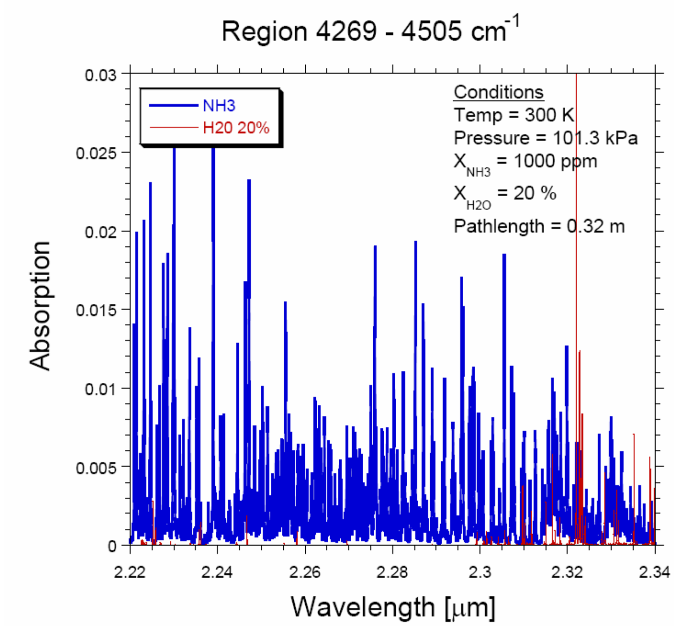

Fig. 3. Calculated ammonia spectrum with water vapor interferences in the spectral region between 2.22 and 2.34 μm.

respectively. The Sacher Lasers ECDL thus allowed us to scan over an entire NO absorption line and to determine the absorption baseline with increased accuracy and precision. Gas cell measurements were performed using the NO sensor with the new ECDL, and a few spectra were acquired from the coal combustor exhaust stream. However, the laser diode in the new ECDL failed during the coal combustor tests.

For future NO measurements in the exhaust stream, we have developed 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. Our diode-laser-based sensor for ammonia is under development and we will demonstrate that sensor both in gas cells and in the exhaust of the Texas A&M coal combustor in the third project year.

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.