

Technical Progress Report

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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.

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 NO_x 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, 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. In Year 3, however, we obtained a new GaN laser diode for our ECDL system, installed it, and completed an extensive series of measurements in the Texas A&M coal-fired laboratory combustion facility. The combustor was operated with coal and coal/biomass as fuels, with and without reburn, and with and without ammonia injection. Several different fuel equivalence ratios were investigated for each operating condition.

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. We will concentrate on the spectral region near 1530 nm, where other researchers have had some success in measuring ammonia.

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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. In Year 2, 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. In Year 3, the 395-nm laser diode was replaced and the NO sensor was used to perform an extensive series of measurements in the Texas A&M coal-fired combustion facility.

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 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. 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. 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. After the 395-nm diode was replaced in Year 3, we were able to obtain approximately 60 GHz of mode-hop-free tuning; the performance was degraded slightly because the diode was from a different vendor. The increased mode-hop-free tuning range of the 395-nm ECDL has improved the accuracy and precision of our NO absorption measurements by minimizing any uncertainties in determining the unattenuated baseline for the NO spectral lines.

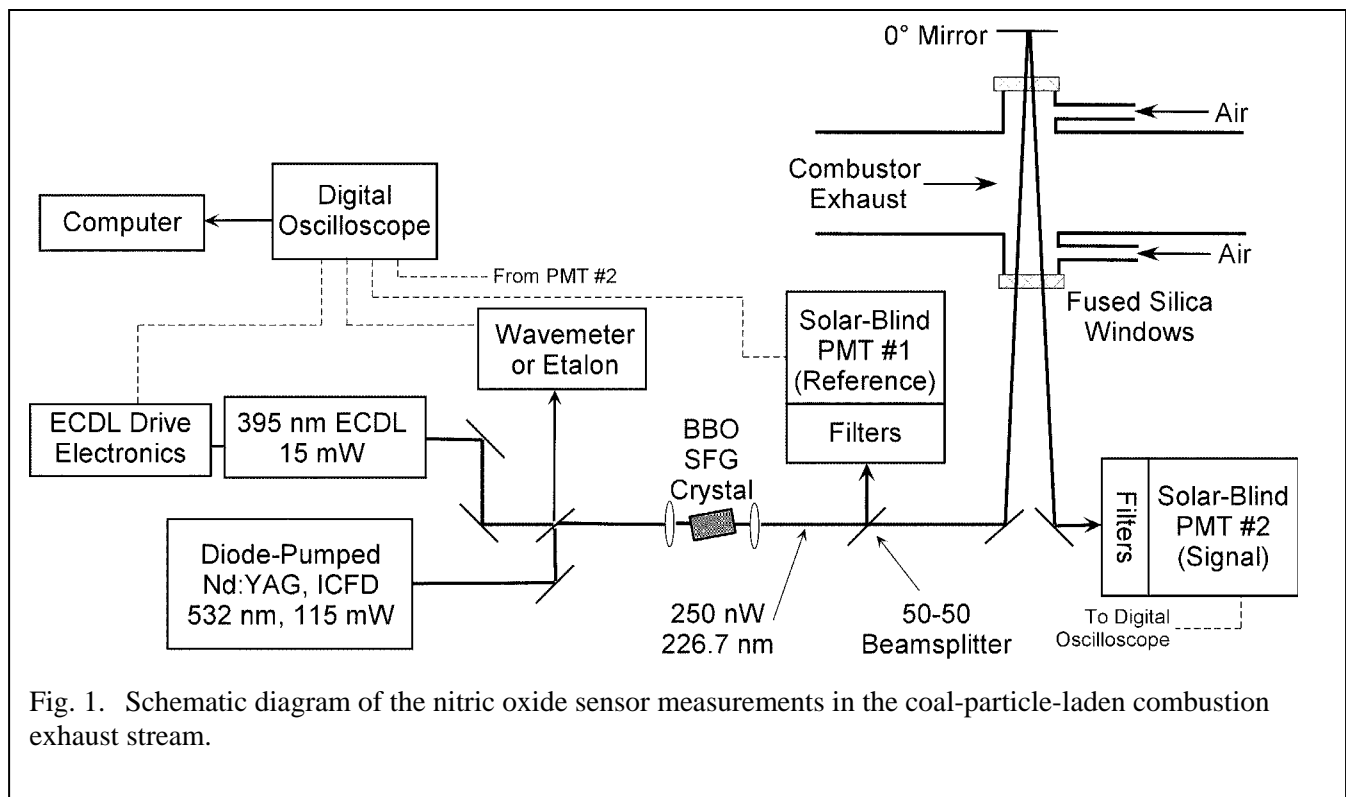


Fig. 1. Schematic diagram of the nitric oxide sensor measurements in the coal-particle-laden combustion exhaust stream.

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, O₂, SO₂, and CO. The production of NO_x from coal:biomass

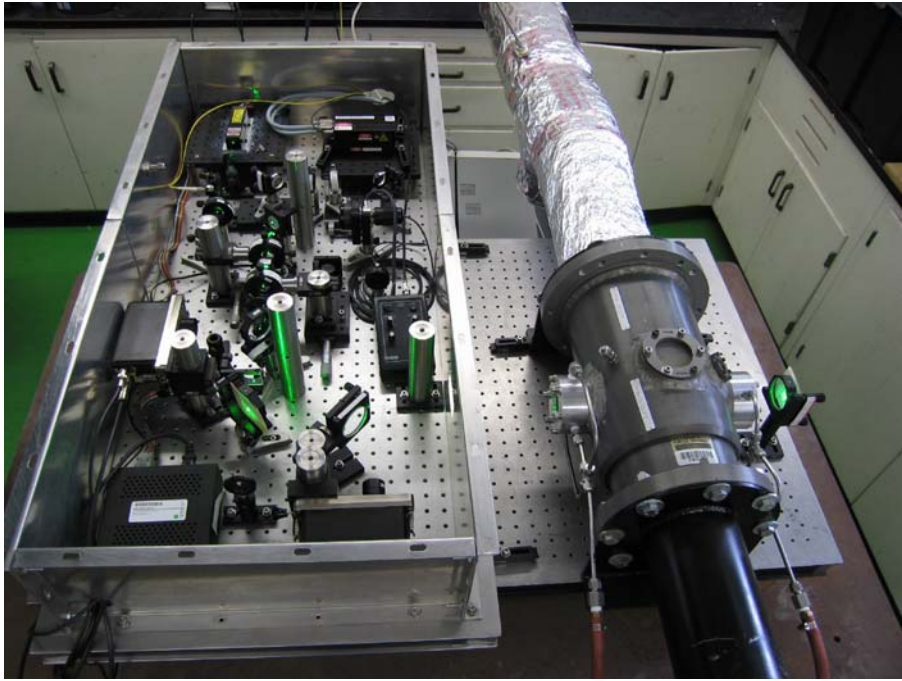


Fig. 4. Photograph of the NO sensor assembly (top) and the optical access chamber for the coal exhaust stream (bottom).

combustion has been investigated extensively in previous experiments with this system.

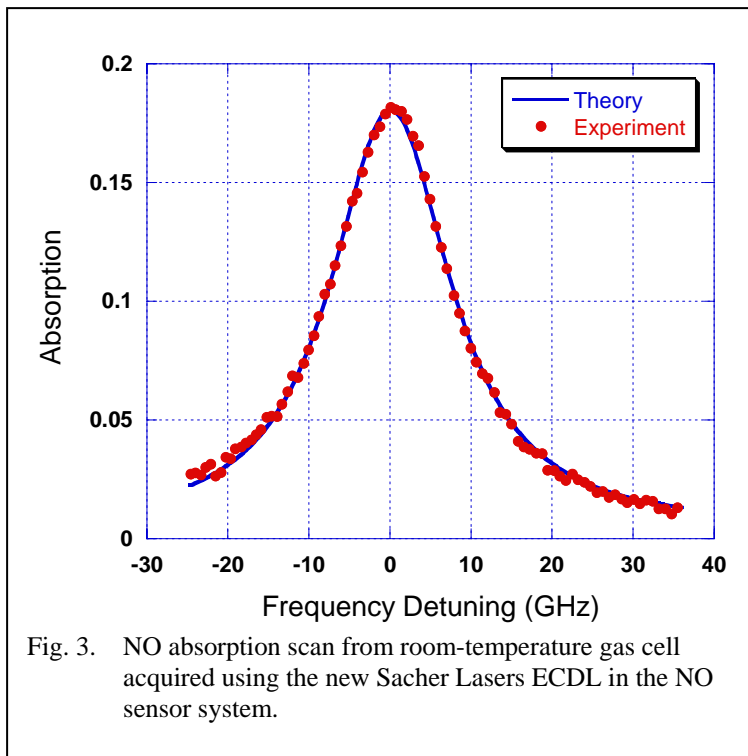
The Texas A&M combustor provides an ideal device for development and testing of new sensor systems. The system is fairly small and inexpensive to operate but allows us to test the performance of the sensor under conditions very similar to those in an actual fossil fuel power plant. Parameters to be varied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

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 Fig. 2. 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 NO_x measurement. The NO_x 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 NO₂ separately; typically NO₂ is very low and of the order of 2 ppm. Thus NO_x (NO + NO₂) 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, 2005. The objectives of the measurements were to



coal combustor tests began. In Year 3, however, we were able to complete an extensive series of measurements in the coal-fired combustion facility. NO absorption measurements were performed first of all with coal as the fuel. The combustor was first operated with no reburn. It was then operated with reburn, and then with ammonia injection combined with the reburn. This set of measurements was performed with 2-3 different fuel flow rates but with the same air flow rate. A typical spectrum

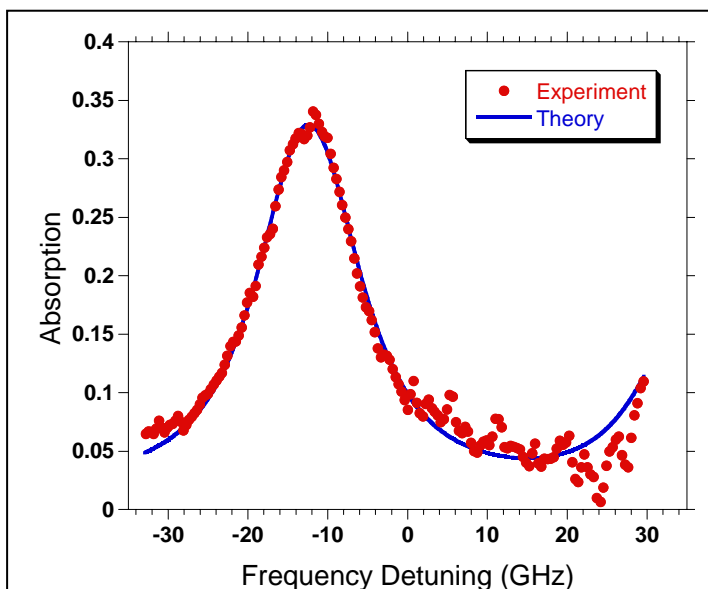


Fig. 4. NO absorption spectrum acquired from the combustor exhaust stream of the Texas A&M coal combustor facility in Year 3. The combustor facility was operating at the same nominal conditions as for the Year 1 measurements; see Figure 5. The ECDL was scanned over the NO line at 80 Hz, and the spectrum shown in the average of 39 sweeps (0.5 sec acquisition time).

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. 3. This spectrum was acquired in preparation for a series of measurements planned in the coal exhaust stream in May-June 2005. The NO absorption spectrum shown in Fig. 3 exhibits a 60 GHz 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 Year 2, the GaN diode in the 395-nm ECDL failed just after the

coal combustor tests began. In Year 3, however, we were able to complete an extensive series of measurements in the coal-fired combustion facility. NO absorption measurements were performed first of all with coal as the fuel. The combustor was first operated with no reburn. It was then operated with reburn, and then with ammonia injection combined with the reburn. This set of measurements was performed with 2-3 different fuel flow rates but with the same air flow rate. A typical spectrum acquired during these measurements is shown in Fig. 4. The spectrum shown in Fig. 4 was acquired in 0.5 sec. The mode-hop-free tuning range of 60 GHz is quite helpful in establishing a true baseline for the spectrum, as compared to the spectrum shown in Fig. 5 in Year 1 under similar combustor conditions.

The combustor facility was then operated with a fuel consisting of a mixture of coal and feedlot biomass. Again, the combustor was operated with and without reburn, and with and without ammonia injection.

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

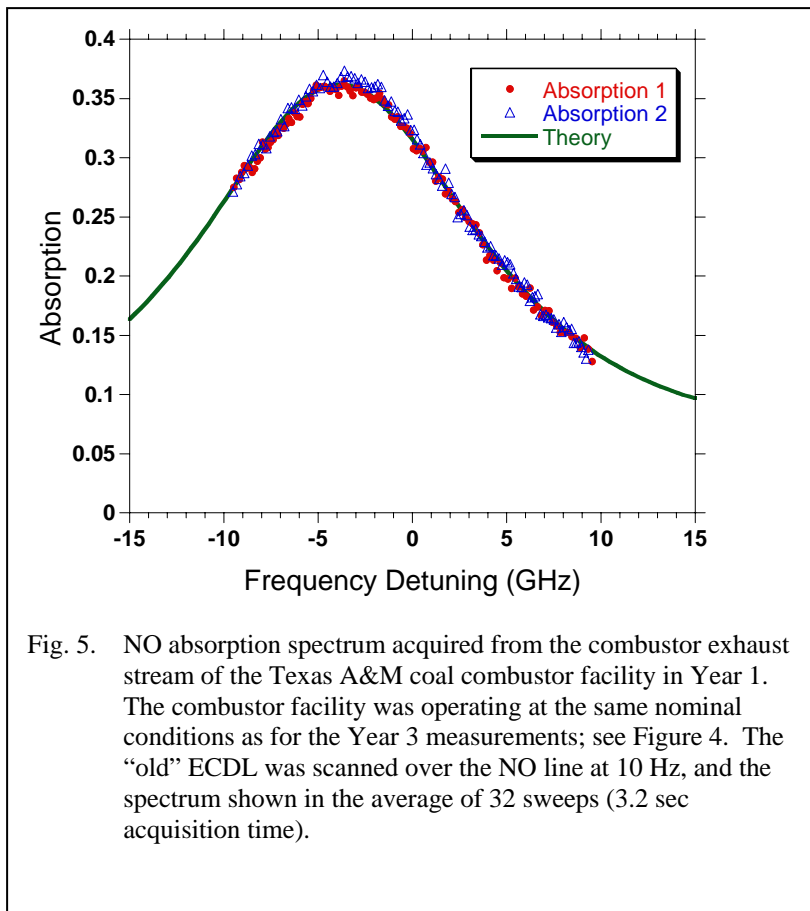


Fig. 5. NO absorption spectrum acquired from the combustor exhaust stream of the Texas A&M coal combustor facility in Year 1. The combustor facility was operating at the same nominal conditions as for the Year 3 measurements; see Figure 4. The “old” ECDL was scanned over the NO line at 10 Hz, and the spectrum shown in the average of 32 sweeps (3.2 sec acquisition time).

window fouling. Data acquisition times as short as 100 msec were demonstrated. In Project Year 2, we replaced the Toptica ECDL in the original system 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 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.

In Project Year 3, however, we used a Sacher Lasers ECDL with a

replacement diode and performed an extensive set of measurements in the coal combustion facility for a wide range of operating conditions. These data are still being analyzed and compared to electrochemical cell measurements; the data analysis and preparation of journal papers describing our experiments will be the main focus of our efforts in Project Year 4. The second generation window assembly with more ports for probe sampling and a window design that minimizes the air flow required to prevent window fouling was tested and worked very well during our Year 3 experiments. Our diode-laser-based sensor for ammonia is under development and we will attempt to demonstrate that sensor both in gas cells and in the exhaust of the Texas A&M coal combustor in the fourth project year.

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