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Proceedings of the Combustion Institute 33 (2011) 725–733

Proceedings of the Combustion Institute

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In situ absorption sensor for NO in combustion gases with a 5.2 μm quantum-cascade laser

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Abstract

A new mid-infrared absorption sensor for *in situ* detection of nitric oxide in combustion exhaust gases has been developed and demonstrated for temperatures up to 700 K. A novel external-cavity quantum-cascade diode laser, which can be wavelength-tuned over the R-branch of the fundamental absorption band near 5.2 μm, was utilized, enabling critical evaluation of the interference absorption by H_2O in combustion exhaust gases. The water vapor absorption spectrum was measured over the range 1880 cm^{-1} to 1951 cm^{-1} at 633 K (680 F), typical of conditions in the economizer region of coal-fired power plants. Based on the data for water vapor interference and laser performance, four candidate fundamental-band transitions (R10.5 (1/2, 3/2) and R15.5 (1/2, 3/2)) were selected as optimum and subsequently investigated in detail. A laboratory combustion exhaust rig with a 1.79 m constant-temperature line-of-sight path was then used to validate the sensor for NO concentrations between 20 and 95 ppm at 600 K; an NO detection limit of $<$60 ppb m $(Hz)^{-1/2}$ was obtained. The sensor was subsequently applied in successful real-time measurements of NO across a 3 m path in the exhaust of a pulverized-coal-fired power plant, including capture of a 30% transient change in NO concentration at the economizer exit that occurred during the shutdown and recovery of the SNCR NO_x control system. The sensor shows excellent promise for monitoring NO in practical combustion exhausts of coal-fired power plants at temperatures up to at least 700 K.

Keywords: Nitric oxide; Combustion exhaust; *In situ*; Quantum-cascade laser; Absorption spectroscopy

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1. Introduction

Nitric oxide (NO) is an important atmospheric constituent of the oxides of nitrogen (NO_x), and the majority of this pollutant is formed from the combustion of fossil fuels. NO contributes to ground-level ozone, acid rain, and a variety of adverse human health effects, which has led to increasingly stringent regulatory mandates on the emission of NO_x [1–3]. As a result, the electric-power industry has a growing need to develop reliable control systems to suppress the release of NO_x effluent from combustion-driven generation of electricity. Accurate and reliable real-time sensors are an important part of any control system, and measurements from a variety of locations in the power plant, ranging from the combustor to the atmospheric exit of the exhaust stack, could facilitate the needed NO_x control. The residence times in such power plants can be large, and thus,

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doi:10.1016/j.proci.2010.05.014

as NO is monitored closer to the combustion zone, the response time of a control system can become shorter.

Traditional extractive sampling methods suffer from long response time and have the potential for secondary chemistry in the sampling probes. There is thus strong motivation for developing sensors for *in situ* monitoring of NO in combustion exhaust streams. Optical absorption methods have the potential for fast, sensitive, accurate and species-selective*in situ* measurements in gas streams over a wide variety of conditions (e.g. temperature, pressure, gas composition) even in the presence of particulate such as fly ash, and owing to their high spectral intensity and potential for accessing strong absorption transitions, laser-based schemes show particular promise for practical applications, including power plants [4–11]. NO detection using laser absorption spectroscopy in the infrared has been one of the strategies extensively studied over the past few decades; see Fig. 1 for the NO absorption spectrum over the range 1–6 µm for a temperature of 600 K. Work has been reported using transitions in three different vibrational bands, the second overtone band ($\Delta v = 3$) near 1.8 µm [12,13], the first overtone band ($\Delta v = 2$) near 2.7 µm [14], and the fundamental band ($\Delta v = 1$) near 5.2 µm [15–17].

The absorption line strengths of CO, CO_2 and H_2O from the HITRAN database [18] are shown in Fig. 1 to illustrate the potential for interference absorption in hot combustion exhaust gases. The fundamental band holds the most promising candidate transitions in terms of their strong absorption (about 100-times stronger line strengths than in the first overtone band near 2.65 µm) and relatively weaker interference transitions of the other combustion species.

Refs. [15–17] illustrate the history of NO detection using transitions in the fundamental band. The first NO detection by tunable-diode-laser absorption in flames using fundamental-band transitions was conducted over twenty-five years ago by Falcone et al. at Stanford University [15]; unfortunately, the only lasers near 5.2 µm at that time were low-power, multimode, cryogenically cooled lead-salt devices. More recently, NO detection in the mid-infrared has benefitted from the improvement of room-temperature (thermoelectrically cooled) quantum-cascade (QC) laser technology, now available both in pulsed and continuous-wave devices. McManus et al. evaluated field instruments for atmospheric air quality that included absorption detection of NO at 1900 cm^{-1} using both pulsed and continuous-wave (CW) QC lasers [16]. With gas extraction at room temperature into an astigmatic multi-pass optical cell, detection precisions of 0.5 ppb $(\text{Hz})^{-1/2}$ and 0.1 ppb $(\text{Hz})^{-1/2}$ were reported, and long-term reliable use of QC laser technology was also demonstrated. Wysocki et al. [17] reported a 1σ noise-equivalent sensitivity of 100 ppb m $(\text{Hz})^{-1/2}$ at room temperature and 200 ppb m $(\text{Hz})^{-1/2}$ at 675 F (630 K) measured with a variety of gas mixtures in a heated cell, to illustrate the potential for a mid-IR absorption sensor for *in situ* sensing of NO in combustion exhaust gases.

Here we discuss the extension of QC-laser-based mid-IR absorption of NO to *in situ* detection in combustion exhausts. We first examine the fundamental band of NO and identify two pairs of promising transitions (R10.5 (1/2, 3/2)

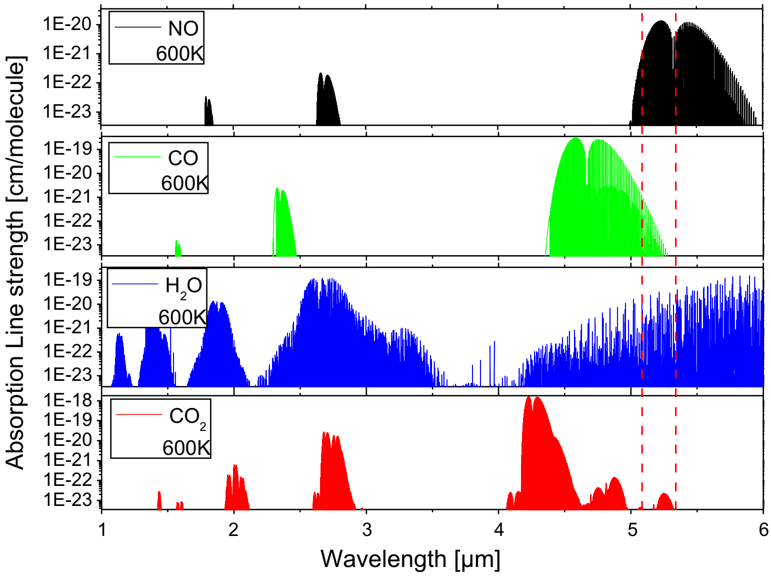

Fig. 1. Absorption line strengths in mid-IR region for NO, CO, H_2O and CO_2 at 600 K from HITRAN [18]. Transitions with line strengths less than 3.5×10^{-24} cm/molecule are not shown.