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Diode-laser absorption sensor system for measurements of combustion pollutants

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**Abstract (Maximum 200 Words)**
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**Subject Terms**
diode laser; external-cavity diode laser; sensors; absorption spectroscopy; combustion pollutants; SERDP; SERDP Collection

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ABSTRACT

A diode-laser sensor system has been applied to measure the concentrations of NO, N₂O, CO, and CO₂ in combustion gases using absorption spectroscopy and fast extraction-sampling techniques. Measured survey spectra of the NO 3ν band (R branch) and H₂O lines from the ν₂ + ν₃ band in the spectral region from 5556 cm⁻¹ to 5572 cm⁻¹ were recorded and compared to calculated spectra to select optimum transitions for NO detection. Similarly, measured survey spectra of the N₂O 3ν₁ band from 6535 cm⁻¹ to 6600 cm⁻¹ were used to identify optimum transitions for N₂O detection. High-resolution NO absorption measurements (R₁(7.5) and R₁(7.5) lines) were recorded in a fast-flow multipass cell containing probe-sampled combustion gases to determine NO concentrations in a laminar, premixed CH₄/air flame, seeded with NH₃. For fuel-lean conditions, the measured NO mole fractions corresponded to 68% of the injected NH₃. For fuel-rich conditions, the fraction of NH₃ converted to NO decreased with increasing equivalence ratio. In additional experiments, CO and CO₂ absorption measurements (R(13) line of the 3ν band and R(16) line of the 2ν₁ + 2ν₃ + ν₃ band, respectively) were determined to measure NO concentrations above a laminar, premixed CH₄/air flame. Good agreement was found between measured CO and CO₂ concentrations and calculated chemical equilibrium values.

Keywords: diode laser, external-cavity diode laser, sensors, absorption spectroscopy, combustion pollutants

1. INTRODUCTION

Recent developments in semiconductor diode-laser technology have extended the range of available laser wavelengths and, hence, the number of accessible species that may be probed using absorption spectroscopy techniques. For example, room-temperature, narrow-linewidth tunable sources near 1.8 μm enable absolute concentration measurements of NO (3ν band), an important combustion-generated pollutant.¹ Near-IR lasers operating near 1.34 μm–1.39 μm (H₂O), 1.56 μm (CO), 1.57 μm (CO₂), and 1.65 μm (CH₃, C₂H₆, CH₂Cl) have been successfully applied to measure species concentrations in a variety of environments.²⁵ Additionally, near-UV and visible diode lasers near 0.39 μm (frequency doubled) and 0.67 μm (NO₂), and 0.76 μm (O₂) enhance the variety of accessible species and, thus, the range of possible applications.³⁷

NO and CO are toxic substances and major combustion-generated pollutants that are facing increasingly strict emission regulations. Global increases in N₂O and CO₂ levels have been attributed to anthropogenic sources, in particular to increased combustion of biomass and fossil fuels. N₂O and CO₂ contribute to the greenhouse effect and are currently being discussed as candidates for future emission regulations.³ A diode-laser sensor system, capable of measuring these species, might be incorporated in combustion-control applications to reduce pollutant emissions and increase fuel efficiency.

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The aim of the present work is to develop a fiber-optic diode-laser system to measure NO, N₂O, CO, and CO₂ in combustion environments using absorption spectroscopy and fast-extraction sampling techniques. Initial experiments served to improve the spectroscopic database and to determine the optimum transitions for species detection. An on-line data reduction system was developed to convert measured absorption spectra automatically into species mole fraction values using the previously obtained spectroscopic parameters.

Measured NO survey spectra (3v band, R branch) in the spectral region from 5556–5572 cm⁻¹ were recorded in a multipass cell and compared with calculated values using published spectroscopic parameters and an existing expression for the electric dipole moment of the \( X^2\Pi \) ground state of NO. Additional measurements of H₂O in the same spectral region were performed to select optimum NO lines with maximum detectivity and minimum H₂O interference. Measured N₂O survey spectra in the spectral region from 6535–6600 cm⁻¹ were recorded and compared to calculated H₂O survey spectra to identify optimum transitions for N₂O measurements.

In the first set of sampling experiments, the diode laser absorption sensor system was applied to measure NO molefractions in a premixed CH₄/air flame, seeded with NH₃. In the second set of measurements, the system was used to measure CO and CO₂ concentrations in combustion gases from a non-seeded, premixed CH₄/air flame.

2. EXPERIMENTAL DETAILS AND THEORY

Figure 1 is a schematic of the experimental setup consisting of the burner, the fast-sampling apparatus, and the diode-laser system. A water-cooled, premixed, flat-flame burner (McKenna) with a 6-cm diameter served as the combustion test facility. Methane, air, and 30% NH₃/N₂ flows were metered with calibrated rotameters, premixed, and injected into the burner. The 30% NH₃ in N₂ mixture was supplied at flow rates of 0.24 l/min and 0.43 l/min. For the typical operating conditions (3.0 l/min CH₄ and 19.5–42.4 l/min air, no NH₃/N₂ injection), the stoichiometry was varied between equivalence ratios of \( \phi \) = 0.67 to 1.47.
Post-flame gas temperatures were measured with uncoated type-S thermocouples (3 mil wire diameter) and corrected for radiation losses. The measurement location was 2 cm above the burner and 1.5 cm from the sampling probe where no probe-induced combustion-gas cooling was observable. The estimated uncertainty in the measured temperatures, ± 20 K, was primarily due to uncertainty in bead size.

A water-cooled stainless steel probe (4.1-mm internal diameter) with four inlet holes of 0.50-mm diameter was used to continuously sample (choked flow) combustion gases 2 cm above the burner. The samples were drawn through an ice-bath-cooled water trap, a drying column, and a two-stage filter to reduce the water molecule fraction and to remove particles. Temperature and static pressure in the absorption cell were monitored using a type-S thermocouple and an MKS Baratron pressure gauge with a full scale range of 1 atm and accuracy of ±1%. The cell temperature remained within 1 K above ambient levels during all measurements, confirming that the sampled gas had been effectively cooled. The sampled flow entered the cell on the same end as the optical beam and exited on the opposite end through 1/2-inch diameter ports before being drawn through a two-stage rotary pump and vented into the exhaust stack.

The diode-laser system consisted of a distributed feedback (DFB) InGaAsP diode laser operating between 5556 cm⁻¹ and 5572 cm⁻¹ (case temperature between 50 and 5°C) and an external cavity InGaAsP diode laser (ECDL) with a spectral tuning range between 6321–6680 cm⁻¹. Individual lineshape measurements with the DFB laser were recorded over a 0.8 cm⁻¹–1.0 cm⁻¹ spectral window by varying the injection current using a sawtooth waveform at 1.25 Hz. H₂O survey spectra between 5556 cm⁻¹ and 5572 cm⁻¹ were measured by temperature tuning the DFB laser. N₂O survey spectra were recorded with the ECDL by using the internal wavelength ramp function of the ECDL controller. Measurements of individual transitions of CO, CO₂, and N₂O (1.0-cm⁻¹ scans) were made by adjusting the internal grating of the ECDL to the respective center wavelengths and by applying a 6-volt sawtooth voltage waveform at a 1.25-Hz repetition rate to the wavelength modulation input. A Burleigh wavemeter was used for absolute wavelength measurements.

Each laser output was passed through an optical isolator to prevent reflections into the laser cavity and split into two beams using 30-min wedged beam splitters. The reflected beams were directed through solid étalons, with free spectral ranges of 2.0 GHz, to monitor the wavelength tuning of the laser. The transmitted beams were focused into optical fibers (8-μm core diameter) and guided to a 1×2 fiber splitter. One output from the splitter was used to measure the reference intensity, I₀. The other output was directed into the multipass absorption cell and focused at the exit onto a detector to measure the transmitted intensity, I. Germanium and InGaAs detectors (300 kHz bandwidth (-3dB)) were used to measure signals near 1.8 μm and 1.5 μm, respectively.

The multipass cell (0.3-liter-volume) consisted of two astigmatic mirrors (20-cm separation) that allowed for a high absorption path to volume ratio, ideal for fast-flow applications. In sampling experiments, the pumping speed was approximately 0.4 l/s and the resulting cell response time (0 to 90% of the final value) was ~1s. The effective absorption path was determined from absorption measurements of CH₄ and O₂, and known line strengths for various cell pressures between 0–760 torr. The measured effective absorption path was 3276 cm. The estimated pathlength uncertainty (2%) was primarily due to uncertainty in linestrength. The total measurement uncertainty of individual transitions probed was estimated to be ~4% owing to mixture fraction uncertainty (2%), pathlength uncertainty (2%), uncertainty in pressure measurements (1%), and uncertainty in the computed area under each Voigt profile (1%).

An on-line data analysis system (Figure 2) was developed for the sampling experiments to calculate species mole fractions from the measured transmission, reference, and étalon signals. A 200-MHz Pentium MMX personal computer served as a computational platform using LabVIEW® as the graphical programming language. Transmission and reference signals, I and I₀, were analog low-pass filtered (200-Hz passband) to avoid aliasing and subtracted to cancel common mode noise. The difference, reference, and étalon signals, were then digitized using a 12-bit A/D converter and transferred to the computer. Additional digital signal processing (FIR filter, 20-Hz passband) further reduced noise without introducing phase distortion. For typical operating conditions, signal-to-noise levels of ~40 dB were achieved. The étalon signal was used to convert the difference and reference signals from the time domain into the optical frequency domain.
The spectral absorbance $\alpha_v$ is related to measured difference and reference signals, $I_d$ and $I_r$, via Beer-Lambert's relation

$$\alpha_v = -\ln \left( 1 - \frac{I_d - I_r}{I_r} \right).$$  \hspace{1cm} (1)

The spectral absorbance is linearly dependent on the mole fraction $X_i$ of species $i$ with $M$ overlapping absorption lines by

$$\alpha_v = P X_i L \sum_{j} S_{ij}(T) \Phi_{ij}(\nu - \nu_{0,ij}, a_{ij}),$$  \hspace{1cm} (2)

where $P$ is the total pressure (atm), $L$ is the absorption pathlength (cm), $S_{ij}$ is the temperature-dependent linestrength of line $j$ and species $i$ (cm$^2$/atm), and $\Phi$ is the lineshape function (cm). Mole fractions of species $i$, $X_i$, were determined by iteratively fitting the measured absorbance to a previously established spectroscopic model containing relative line positions and linestrengths, and to a third-order polynomial that accounted for the unbalanced response between the reference and the transmission detector. The least-squares fitting procedure incorporated the nonlinear Levenberg-Marquardt algorithm and converged within two iterations to best-fit multi-line Voigt profiles. Integration of the fitted Voigt profiles over a 2 cm$^{-1}$ spectral window and application of Equation (2) yielded reliable mole fraction values.

### 3. RESULTS

#### 3.1 Spectroscopic Studies

The lack of spectroscopic data for the NO 3v band (not included in HITRAN96) and the need to predict line positions and intensities for the selection of appropriate laser wavelengths motivated the fundamental spectroscopic computations.

The coupling of rotation and electronic motion of the NO $X^3\Pi$ ground state represents an intermediate case between Hund's case (a) and (b) with transition from case (a) to (b) with increasing nuclear rotation. For the $J^\nu$ of interest, Hund's case (a) was a good approximation and the selection rules were chosen accordingly. As a result, the $3\Pi \leftarrow 2\Pi$ band splits into two sub-bands, $3\Pi_{\kappa'} \leftarrow 2\Pi_{\kappa}$ and $3\Pi_{\kappa} \leftarrow 2\Pi_{\kappa}$, corresponding to an $F_2$ and an $F_1$ manifold, respectively. The energy
levels for the $X^1\Pi$ ground state of NO were calculated, neglecting $A$-type doubling, by numerical diagonalization of the Hamiltonian matrix using published matrix elements.\textsuperscript{10} Einstein $A$ coefficients were calculated using

$$A_{\nu', \nu, J' \rightarrow \nu, J} = \frac{64\pi^4v^3}{3hc^2} \frac{\rho^2}{2J' + 1} q_{\nu', \nu} S_{\nu},$$

where $R$ is the transition moment integral, $q_{\nu', \nu}$ is the Franck-Condon factor, and $S_{\nu}$ is the Hönl-London factor. The transition moment integral was calculated on the basis of a rotationless transition by

$$R = \langle \nu' | \mu(r) | \nu \rangle,$$

for $\nu' = 3$ and $\nu'' = 0$ using an existing expression for the electronic dipole moment $\mu(r)$ and previously published spectroscopic constants.\textsuperscript{10-12}

Figure 3 shows the calculated absorption spectra for the NO 3v band (1 atm and 296 K). A universal broadening coefficient of $2\gamma = 0.13$ cm$^{-1}$/atm was used to model the collisional contribution to the linewidth. The spectra exhibits a P-Q-R structure with a weak Q-branch. The strongest transitions occur in the R branch in the spectral region between 5562 cm$^{-1}$ and 5580 cm$^{-1}$ with approximately 60% higher values than the strongest P branch transitions.

Fig. 3 Calculated absorption spectra of the NO 3v band for 296 K and 1 atm. A universal broadening coefficient of $2\gamma = 0.13$ cm$^{-1}$/atm was used to model the collisional contribution to each individual linewidth.

In addition to identifying strong transitions it is important to analyze interfering absorption from other species for the successful selection of laser wavelengths. In room air, the major interference arises from H$_2$O absorption. Figure 4 compares the calculated NO and H$_2$O spectra (using the HITRAN96 database) for conditions of 296 K and 1 atm. H$_2$O lines are more than 40 times stronger than NO transitions (5460–5550 cm$^{-1}$) and decrease in intensity with increasing frequency. The spectral region between 5556 cm$^{-1}$ and 5578 cm$^{-1}$ (R branch of NO) seems most promising since it contains strong NO transitions and relatively weak and sparse H$_2$O lines.

Figure 5 is a plot of the measured NO survey spectra within the DFB laser tuning range (5556–5572 cm$^{-1}$) obtained at 296 K, 240 torr, and 5020 ppm NO in N$_2$. The spectra were constructed by recording several 0.8–1.0 cm$^{-1}$ interval scans. The $^3\Pi_K ^-\!^1\Pi_G$ and $^1\Pi_K ^-\!^1\Pi_G$ subbands are clearly distinguishable for $J'' < 8.5$.\textsuperscript{13}

Fig. 4 Comparison of the calculated NO (3v band) and H$_2$O spectra in the spectral region between 5460 cm$^{-1}$–5600 cm$^{-1}$ (296 K, 1 atm).
Figure 6 is a plot of the measured Λ-doubled line pairs $R_u(7.5)+R_u(7.5)$ and $R_u(7.5)+R_u(7.5)$ (296 K, 240 torr, 5020 ppm NO in $N_2$). Contributions from the $^4\Pi_u^+\leftrightarrow^2\Pi_u^-$ and $^4\Pi_u^+\leftrightarrow^2\Pi_u^-$ subbands are illustrated as broken lines. The residual corresponds to the normalized difference between the data and the 2-line best-fit Voigt profile. Λ-type doubling was not resolved since its magnitude was approximately one order of magnitude lower than the Doppler contribution to the linewidth ($\Delta V_D = 1.25\times10^3$ cm$^{-1}$ at 296 K and 5568.3 cm$^{-1}$). A comparison of the measured and calculated line positions and intensities of the $R_u(7.5)+R_u(7.5)$ and $R_u(7.5)+R_u(7.5)$ line pairs is shown in Table 1. Good agreement was found between calculated and measured line intensities.

![Figure 5](image_url)  
Fig. 5 Measured NO survey spectra (3v band, R branch) between 5556 cm$^{-1}$ and 5572 cm$^{-1}$ (296 K, 240 torr, 5020 ppm NO in $N_2$).

![Figure 6](image_url)  
Fig. 6 Single-sweep measurement of the spectral absorption coefficient obtained by tuning the DFB laser over the Λ-doubled line pairs $R_u(7.5)+R_u(7.5)$ and $R_u(7.5)+R_u(7.5)$ of NO near 5568.3 cm$^{-1}$ (296 K, 240 torr, 5020 ppm NO in $N_2$).

<table>
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<tr>
<th>Transition</th>
<th>measured [cm$^{-1}$]</th>
<th>calculated [cm$^{-1}$]</th>
<th>difference measured-calculated [cm$^{-1}$]</th>
<th>measured [cm$^2$/atm]</th>
<th>calculated [cm$^2$/atm]</th>
<th>diff. rel. to calculated [%]</th>
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<td>5568.25</td>
<td>-0.02</td>
<td>6.91×10$^4$</td>
<td>6.81×10$^4$</td>
<td>1.5</td>
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<tr>
<td>$R_u(7.5)+R_u(7.5)$</td>
<td>5568.30</td>
<td>5568.32</td>
<td>-0.02</td>
<td>1.19×10$^3$</td>
<td>1.27×10$^3$</td>
<td>-6.0</td>
</tr>
</tbody>
</table>

Table 1 Comparison of measured and calculated line positions and line strengths of the $R_u(7.5)+R_u(7.5)$ and $R_u(7.5)+R_u(7.5)$ Λ-doubled line pairs at 296 K.

Figure 7 shows a) the measured and b) the calculated (HITRAN96) spectral absorption coefficient of H$_2$O between 5556–5571 cm$^{-1}$ (297 K, 114 torr, 1.15% H$_2$O in air). All measured strong lines are also predicted by HITRAN96. Measured peak heights are (on average) 10% lower than calculated values. Measured line strengths, however, are within ±7% of HITRAN96 values, suggesting that broadening coefficients may be inaccurate. Measured line positions generally agree with the HITRAN96 database to within the wavemeter reading accuracy of ±0.01 cm$^{-1}$. 

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Figure 8 shows the comparison of a) measured and b) calculated (HITRAN96) spectral features of H₂O in a 0.2 cm⁻¹ spectral window near 5567.75 cm⁻¹ (297 K, 114 torr, 1.15% H₂O in air). The measurements indicate that the actual spectral separation between the overlapping lineshapes is 0.02 cm⁻¹ and not 0.011 cm⁻¹ as listed in HITRAN96. The measured sum linestrength of both features is within 1% of the tabulated value in the HITRAN96 database.

A comparison of measured NO and H₂O survey spectra showed that most NO lines in the region between 5556–5572 cm⁻¹ are free of H₂O spectral interference. For maximum detectivity and minimum H₂O interference, the R₉(7.5)+R₉(7.5) and R₈(7.5)+R₈(7.5) Λ-doubled line pair was chosen to determine NO mole fractions in sampling experiments.

![Figure 7](image)

**Fig. 7** Comparison of the a) measured and b) calculated (HITRAN96) spectral absorption coefficient of H₂O between 5556 cm⁻¹ and 5571 cm⁻¹ for cell conditions of 297 K, 114 torr, 1.15% H₂O in air.

![Figure 8](image)

**Fig. 8** Comparison of the a) measured and b) calculated (HITRAN96) spectral absorption coefficient of H₂O in a 0.2 cm⁻¹ spectral window near 5567.75 cm⁻¹ (297 K, 114 torr, 1.15% H₂O in air).

Although N₂O has been studied in the near-IR using Fourier transform spectroscopy, no line strength data are available.¹⁴ Figure 9 shows the measured survey spectra of the N₂O 3ν₁ band and line assignments in the spectral range from 6535

![Figure 9](image)

**Fig. 9** Measured survey spectra of the N₂O 3ν₁ band in the spectral range from 6535–6600 cm⁻¹ (297 K, 272 torr, 5.0% N₂O in air). Indicated is the P(14) line that was used for sampling experiments.
cm<sup>-1</sup>–6600 cm<sup>-1</sup> (297 K, 272 torr, 5.0% N<sub>2</sub>O in air). Comparison of the measured N<sub>2</sub>O survey spectra with calculated H<sub>2</sub>O spectra (HITRAN96) were performed to select optimum transitions for N<sub>2</sub>O measurements. The indicated P(14) transition was well isolated from spectral H<sub>2</sub>O interference (v<sub>1</sub>+2v<sub>2</sub> and 2v<sub>2</sub>−v<sub>3</sub> bands) and was chosen for N<sub>2</sub>O detection. Line position and line strength values are listed in Table 2.

Fig. 10 Calculated survey spectra (HITRAN96) of CO, CO<sub>2</sub>, and H<sub>2</sub>O in the spectral range from 6250 cm<sup>-1</sup> to 6666 cm<sup>-1</sup> for 296 K and 1 atm. Indicated are the R(13) line of the CO 3v band and the R(16) line of the CO<sub>2</sub> 2v<sub>1</sub>−v<sub>3</sub>−v<sub>4</sub> band that were used to determine species mole fractions.

Fig. 11 Single-sweep measurement of the R(13) line of CO (296 K, 214 torr, 230-ppm CO). The residual represents the normalized difference between the best-fit Voigt profile and the data.

Figure 10 is a plot of the calculated survey spectra (HITRAN96) of CO, CO<sub>2</sub>, and H<sub>2</sub>O in the spectral range from 6250 cm<sup>-1</sup> to 6666 cm<sup>-1</sup> for 296 K and 1 atm. Indicated are the R(13) line of the CO 3v band and the R(16) line of the CO<sub>2</sub> 2v<sub>1</sub>−v<sub>3</sub>−v<sub>4</sub> band that were used to determine species specific mole fractions. These lines were chosen to avoid mutual interference between CO and CO<sub>2</sub> absorption and to maximize species detectivity. Measured survey spectra and line strengths of CO, CO<sub>2</sub>, and H<sub>2</sub>O have been published previously.<sup>4</sup>

<table>
<thead>
<tr>
<th>Species</th>
<th>Transition</th>
<th>Position [cm&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>Strength (296K) [cm&lt;sup&gt;2&lt;/sup&gt;/atm]</th>
<th>min. Absorbance</th>
<th>Detectivity [ppm]</th>
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<td>NO</td>
<td>R&lt;sub&gt;2&lt;/sub&gt;(7.5)+R&lt;sub&gt;3&lt;/sub&gt;(7.5)</td>
<td>5568.23</td>
<td>6.81×10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>4.24×10&lt;sup&gt;4&lt;/sup&gt;</td>
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<td></td>
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<td>5568.30</td>
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<tr>
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<td>P(14)</td>
<td>6567.29</td>
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<td>CO</td>
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<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>6359.97</td>
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<td>4.50×10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>7</td>
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</table>

Table 2 Transitions, line positions, and line strengths used for the sampling experiments. The calculated detectivities are based on the measured minimum absorbances in a 20-Hz bandwidth and a 1-sec measurement time.
Figure 11 shows a single-sweep measurement of the CO R(13) line (296 K, 214 torr, 230 ppm CO). The residual represents the normalized difference between the best-fit Voigt profile and the data. The minimum measured detectable absorbance was 4.5×10⁻⁵ (20-Hz noise bandwidth, 1-sec measurement time) and corresponded to a CO detectivity of 9 ppm.

Table 2 lists the transitions, line positions and strengths that were used for the sampling experiments. The calculated species detectivities of the diode-laser sensor system are based on the measured minimum detectable absorbance for a 20-Hz noise bandwidth and a 1-sec measurement time. Measurements of NO were limited by etaloning from the fiber couplers and from (Ge) detector noise. Properly coated optical components could enhance the detectivity of NO to 2 ppm (calculation based on min. detectable absorbance of 4.5×10⁻⁵ in a 20-Hz noise bandwidth and 1-sec measurement time). Measurements of N₂O, CO, and CO₂ were limited by interference effects in the absorption cell, optical components, and laser cavity.

3.2 Sampling Experiments

As the first set of sampling experiments, calibrated flows of 30% NH₃/N₂ (NH₃ injection of 0.13 l/min and 0.07 l/min) were added to the premixed gases of CH₄ and air. NO mole fractions in the post flame region of the premixed, laminar, flat flame were determined from measured absorption of probe-sampled combustion gases in the multipass cell. Measured NO mole fractions of the dried samples were converted to wet-basis mole fractions by assuming that water vapor equal to the equilibrium value at the metered equivalence ratio and measured temperature had been removed.

![Fig. 12](image1.png)

**Fig. 12** Measured temperatures and NO molefractions (wet basis) as a function of equivalence ratio and injected NH₃ flow rate in a premixed, NH₃ seeded CH₄/air flame.

![Fig. 13](image2.png)

**Fig. 13** Fraction of NH₃ converted to NO as a function of equivalence ratio and injected NH₃ flow rates.

Figure 12 shows the measured temperatures and NO concentrations (wet basis) as a function of equivalence ratio and injected NH₃ flow rate. Temperature measurements were on average 15 K higher for the higher NH₃ flow rate. The measured NO molefractions increased for both injected NH₃ flow rates with equivalence ratio from Φ=0.7 to 1.0 by ~11% (0.13 l/min NH₃ injection) and ~19% (0.07 l/min NH₃ injection). For fuel rich conditions, the measured NO molefractions decreased with increasing equivalence ratio (Φ=1.02 to 1.33) by ~68% (0.13 l/min NH₃ injection) and ~54% (0.07 l/min NH₃ injection).
Figure 13 provides a plot of converted NH$_3$ to NO as a function of equivalence ratio and injected NH$_3$ flow rate. For fuel-lean conditions, the measured average fractions of NO converted to NH$_3$ (68%) compared well with previously published results (70%). For fuel rich conditions, the average NH$_3$ to NO conversion decreases from 68% to approximately 20% at $\phi$=1.33. The NH$_3$ conversion is ~35% higher for the lower NH$_3$ injection rate (0.07 l/min) compared to the higher NH$_3$ injection rate (0.13 l/min) at $\phi$=1.3.

A second set of sampling experiments were performed to measure CO and CO$_2$ concentrations in the post-flame gases above a premixed CH$_4$/air flame. Species mole fractions were calculated from measured absorption in probe-sampled combustion gases, measured cell pressure and temperature, and known line strengths. The measured CO and CO$_2$ mole fractions (dry basis) are shown as a function of equivalence ratio in Figure 14. The solid lines represent chemical-equilibrium calculations of the respective species mole fractions at measured temperatures (top half of Figure 14). The vertical bars represent the uncertainty in measured species mole fractions due to line strength and measurement uncertainty.

![Graph showing temperature and mole fraction vs equivalence ratio](image)

**Fig. 14** Comparison of measured CO and CO$_2$ mole fractions (dry basis) to calculated equilibrium values at measured temperatures.

The CO$_2$ data agree to within 3% with calculated equilibrium values in the fuel-lean region. For $\phi$>1 the measured CO$_2$ mole fractions are slightly higher and the measured CO mole fractions are slightly lower than the calculated equilibrium values, suggesting a partial conversion of CO to CO$_2$ in the sampling probe. The partial conversion is likely due to surface kinetics effects and the finite residence time in the probe. NO and N$_2$O were not detected in the post-flame gases, indicating that concentrations were below the respective detection limits.

4. CONCLUSIONS

A fiber-optic diode-laser absorption sensor system has been developed to measure NO, N$_2$O, CO, CO$_2$ concentrations using absorption spectroscopy and fast-extraction probe sampling techniques. The system was applied to measure NO mole fractions in the post-flame gases of a premixed CH$_4$/air flame seeded with NH$_3$. In addition, CO and CO$_2$ molefractions were measured in the combustion products of a non-seeded, premixed CH$_4$/air flame.
Measured room-temperature survey spectra of NO in the spectral region from 5556–5572 cm\(^{-1}\) (1.8 \(\mu m\)) compared favorably with calculated values. In addition, measurements of \(\text{H}_2\text{O}\) survey spectra were recorded in this spectral region to select optimum NO lines with maximum detectivity and minimum \(\text{H}_2\text{O}\) interference for NO concentration measurements. Measured survey spectra of the \(\text{N}_2\text{O}\) \(3v_3\) band (6535–6600 cm\(^{-1}\)) were used to select appropriate transitions for \(\text{N}_2\text{O}\) measurements.

Sampling experiments with a \(\text{CH}_4/\text{air}\) flame seeded with \(\text{NH}_3\) showed that for fuel-lean conditions approximately 70\% of the injected \(\text{NH}_3\) was converted to NO. For fuel-rich conditions, the fraction of \(\text{NH}_3\) converted to NO decreased from 68\% (\(\Phi\leq1\)) to approximately 20\% (\(\Phi=1.33\)). In sampling experiments in a non-seeded, premixed \(\text{CH}_4/\text{air}\) flame, measured CO concentrations were slightly lower and measured \(\text{CO}_2\) concentration were slightly higher than calculated equilibrium values for fuel-rich conditions indicating partial conversion of CO to \(\text{CO}_2\) in the sampling probe. This system may be applied for continuous measurements of NO, \(\text{N}_2\text{O},\text{ CO and }\text{CO}_2\) in stack gases of combustion systems for open- and closed-loop applications.

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