ADVANCED DIODE LASER ABSORPTION SENSOR FOR *IN-SITU* COMBUSTION MEASUREMENTS OF CO$_2$, H$_2$O, AND GAS TEMPERATURE

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Abstract

A diode-laser sensor system based on absorption spectroscopy techniques has been developed to measure CO$_2$, H$_2$O, and temperature non-intrusively in high-temperature combustion environments. An external-cavity diode laser operating near 2.0 μm was used to scan over selected CO$_2$ ((12^01)–(00^00) band) and H$_2$O transitions ((011)–(000), (021)–(010) bands) near 1.996 μm and 1.992 μm for measurements of CO$_2$ and H$_2$O concentration and gas temperature. Gas temperature was determined from the ratio of integrated line intensities. Species concentration was determined from the integrated line intensity and the measured temperature. The system was applied to measure temperature and species concentrations in the combustion region of a premixed C$_2$H$_4$-air flat-flame burner operating at fuel-lean conditions. The laser-based temperature measurements were in agreement with values determined using a (type S) thermocouple to within 3%. In addition, the measured CO$_2$ and H$_2$O concentrations agreed to within 6% and 3%, respectively, with calculated equilibrium values at measured temperatures. The minimum CO$_2$ detectivity was 200 ppm (for $\Phi = 0.51$, 1470 K, a 1-m path length, 200-Hz detection bandwidth). These results represent the first *in situ* combustion measurements of CO$_2$ concentration using room-temperature near-IR diode lasers. Furthermore, the results demonstrate the utility of diode-laser absorption sensors, operating near 2.0 μm, as attractive diagnostic tools for *in-situ* combustion measurements of temperature and the concentrations of CO$_2$ and H$_2$O.

Introduction

Near-IR room-temperature diode lasers have been utilized for *in-situ* absolute measurements of species concentrations and gas temperature in a variety of combustion systems [1-7]. These lasers are very attractive for practical applications owing to their robustness, reasonable cost, compatibility with optical-fiber components, and relative ease-of-use. To date, multi-species sensor systems have been developed to probe multiple absorption transitions of H_2O and O_2, or H_2O and CH_4, simultaneously [3,4]. In addition, diode lasers have been employed as near real-time sensors of multiple combustion parameters for combustion-control applications [5].

Diode laser-based absorption diagnostics have generally been used to probe transitions of selected species corresponding to vibrational overtone and combination bands that overlap the spectral regions accessible with commercially available lasers (typically 0.63 – 1.8 μm). Consequently, detection sensitivity has been limited by the relatively weak transitions associated with these vibration-rotation bands. To improve sensitivity, high-frequency wavelength-modulation spectroscopy techniques have been developed to monitor combustion radicals (HCO, OH, and HO_2) [6] and fast extraction-sampling techniques have been employed for measurements of low levels of CO, CO_2, N_2O, and NO [7,8].

Recent developments in semiconductor diode-laser technology have extended the range of available wavelengths to 2.0 μm, allowing access to stronger ground-state vibrational overtones as well as stronger hot-band transitions of combustion species. Figure 1 shows the calculated survey spectra of CO_2 and H_2O at 296 K in the spectral region from 1–3 μm (HITRAN96 database [9]). CO_2 linestrengths near 2.0 μm ((12^01)–(00^00) band) are approximately 70 times stronger than those near 1.58 μm ((22^01)–(00^00) band).

Similarly, H_2O linestrengths in the 2.0-μm region ((011)-(000) band) are approximately one order of magnitude stronger than those near 1.4 μm ((200)-(000), ((101)-000) bands). As a result, the absorption measurements near 2.0 μm offer the potential for significantly increased sensitivity for CO_2 and H_2O detection compared with measurements recorded previously near 1.6 μm and 1.4 μm, respectively. In addition, compared with previous measurements near 1.4 μm, measurements of the relatively strong high-energy H_2O transitions near 2.0 μm are relatively insensitive to absorption due to cool room-air or boundary-layer gases and can thus be used to yield more accurate determinations of the flame temperature.

The aim of the present work is to apply a novel external cavity diode laser (ECDL) centered at 2.0 μm to measure CO_2, H_2O, and temperature in the post-flame region of a premixed, laminar flat-flame burner operating on C_2H_4-air at atmospheric conditions. This work extends the range of diode-laser applications and demonstrates the utility of 2.0-μm diode lasers for sensitive measurements of important combustion parameters. These results represent the first *in-situ* combustion measurements of CO_2 using a room-temperature near-IR diode laser.

Theory

The theoretical basis for determining gas temperature and species concentration (line-of-sight averaged) from measured absorption spectra in combustion flows has been described previously [3,4]. In brief, the Beer-Lambert relation [3] is used to determine the gas temperature from the ratio of measured H_2O absorbances obtained by tuning the narrow-linewidth laser across transitions near 5020.503 cm^{-1} ((011)–(000) band) and 5020.894 cm^{-1} ((021)–010) band). The CO_2 and H_2O concentration is then determined from the measured absorbance using the known linestrengths at the measured temperature.

Experimental Details

Figure 2 is a schematic of the experimental setup consisting of the burner and the diode-laser system. A water-cooled, premixed, flat-flame burner of rectangular shape (4×10 cm) served as the combustion test facility. Ethylene- and air-flows were metered with calibrated rotameters, premixed, and injected into the burner. For the typical operating conditions (1.4 l/min C_2H_4 and 26.2–39.1 l/min air), the equivalence ratio ranged from Φ= 0.51 to Φ= 0.76.

Post-flame gas temperatures were measured at the center of the burner at a height of 1 cm with an uncoated type-S thermocouple (3 mil wire diameter, corrected for radiation losses). The estimated uncertainty in the measured temperatures, ±30 K, was primarily due to uncertainty in bead size (~6 mil bead diameter) and uncertainty in the Nu number.

The diode-laser system consisted of an external-cavity diode laser (compressive-strained InGaAs/InP quantum wells with tensile-strained barrier regions) with a spectral tuning range between 4860 cm^{-1} and 5120 cm^{-1} (1.953 μm – 2.057 μm). Individual lineshape measurements (0.9-cm^{-1} scans) of CO_2 and H_2O were made by adjusting the internal grating of the external-cavity diode laser to the respective center wavelengths and by applying a 5-Volt sawtooth voltage waveform at a 12.5-Hz repetition rate to the wavelength modulation input (injection current: 129.8 mA, case temperature: 23 ℃). An IR wavelength meter was used for absolute wavelength measurements (0.01 cm^{-1} accuracy).

One part of the output from the ECDL was split off and directed through a solid étalon (free spectral range = 2.012 GHz) to monitor the wavelength variations as the laser was tuned. A second beam was separated from the main beam to measure the reference intensity I_0. The main beam was sent through a Glan-Thompson polarizer and passed through the combustion zone at a 1-cm height above the burner surface with a total pathlength of 50 cm (5 passes). The polarizer was adjusted to balance the measured transmitted (I) and reference intensity (I_0). The output signals I and I_0 of the extended InGaAs photodetectors (200-kHz bandwidth, -3dB) were analog low-pass filtered (10-kHz passband) to avoid aliasing and subtracted to cancel common-mode noise. The difference, reference, and étalon signals were then digitized (12-bit A/D converter) and transferred via GPIB to a Pentium-based personal computer for analysis. Additional digital low-pass filtering (200-Hz passband) was applied for further noise reduction.

Results

Extensive measurements of CO_2 and H_2O absorption spectra in the spectral range from 4860 cm^{-1} to 5120 cm^{-1} (1.953 μm – 2.057 μm) were performed in a heated static cell at various temperatures between 296 K – 1500 K in order to identify optimum transitions for accurate measurements of species concentrations and gas temperature [10]. Due to the relatively dense CO_2 and H_2O spectra near 2.0 μm at elevated temperatures, only few isolated CO_2 transitions are accessible for CO_2 detection in combustion flows. The spectral region between 5000 cm^{-1} –5015 cm^{-1} appears most promising since it contains relatively strong and isolated CO_2 transitions at elevated temperatures. The CO_2 R(56) transition at 5010.035 cm^{-1} ((12^01)–(00^00) band) was selected for optimum CO_2 detectivity at combustion temperatures (~1500 K) and for small H_2O interference in the neighborhood spectral region [10]. Other transitions may be more appropriate for measurements in flows with different characteristics (pressure, temperature, and composition) and absorption path lengths.

The H_2O transitions (denoted lines 1 and 2) were selected such that the ratio of absorbances yields a sensitive measurement of temperature within a 1-cm^{-1} scan. For example, a 1% uncertainty in the measured intensity ratio at 1500 K (50-cm absorption pathlength) leads to a relative temperature uncertainty of approximately 1.2% (18 K). Moreover, the selected H_2O transitions are relatively high-temperature transitions (linestrengths of lines 1 and 2 peak near 1220 K and 1510 K, respectively). The measured linestrengths of lines 1 and 2 at 296 K are 0.38% and 0.015% of the respective values at 1500 K. As a consequence, the contribution to the absorption from cold boundary-layer and room-air regions is small, allowing for representative measurements of the core combustion gas temperature. Table I lists the probed CO_2 and H_2O transitions, the measured linestrengths, line positions, and variations from the HITRAN96/HITEMP database.

Figure 3 shows the measured absorbance in the first spectral region (5009.67–5010.54 cm^{-1}) containing the CO_2 R(56) line ((12^01)–(00^00) band) that was used to measure the CO_2 concentrations for all equivalence ratios in the post-flame gases of a premixed C_2H_4-air burner (Φ=0.51, 50-cm path). The residual represents the normalized difference between the data and the 7-line best-fit Voigt profile. Individual interfering transitions are illustrated as dotted lines. The minimum detectable absorbance was 1.1×10^{-4} (200-Hz noise bandwidth, 80-ms measurement time) and corresponded to a CO_2 detectivity of approximately 210 ppm (normalized to a 1-m path, 1 atm, 1530 K thermocouple temperature) and was limited by beam steering on the detector surface and detector-amplifier noise.

Figure 4 shows the measured spectral absorbance in the second region from 5020.28–5021.16 cm^{-1} and the best-fit 5-line Voigt profile (Φ= 0.51, 50-cm path). The two highlighted H_2O lines (line 1 and line 2) were used to measure H_2O concentrations and temperature in a single sweep. Similar to the first spectral region (shown in Fig. 3), interferences from multiple hot-band H_2O transitions from the (120)-(010) and (041)-(030) bands (tabulated in the HTEMP database) are evident. The ratio of integrated H_2O intensities varies from 0.87 to 0.94 and corresponds to laser-based temperatures of 1470 K and 1630 K, respectively, as the equivalence ratio is increased from Φ= 0.51 to Φ= 0.76.

A comparison of laser-based (2-line) temperature, thermocouple measurements, and calculated adiabatic flame temperatures is illustrated in Fig. 5. The calculated radiation corrections for the thermocouple measurements (3-mil wire diameter) were in the range 43-46 K. Vertical error bars on the 2-line temperature measurements are due to uncertainty in H_2O linestrength (2%) and absorption measurement (2%). Horizontal error bars are due to uncertainties in stoichiometry from calibration errors. The measured temperatures were nearly independent of stoichiometry due to heat transfer to the burner. Flame temperatures from thermocouple measurements ranged from 1530 K to 1570 K. The good agreement of 2-line and thermocouple measurements (average variation <2.9%) confirms the ability to accurately measure temperature non-intrusively in a combustion flow.

The measured CO_2 (left axis) and H_2O mole fractions (right axis) at the measured 2-line temperatures are shown as a function of the equivalence ratio in Fig. 6. The solid lines illustrate calculated chemical equilibrium values of CO_2 and H_2O mole fractions at the measured (2-line) temperatures. Vertical error bars represent the uncertainty of measured CO_2 and H_2O mole fractions owing to uncertainties in measured linestrength (2%) and absorption measurement (2%). CO_2 and H_2O measurements agree to within 5.8% and 2.7%, respectively, with calculated equilibrium values. The lack of systematic errors demonstrates the validity of the experimental setup and the method of analysis. Measured and calculated CO_2 mole fractions agree to within 3.0% if the measured thermocouple temperatures are used to determine the CO_2 linestrength. The relatively better agreement is due to the high sensitivity of CO_2 linestrength to temperature (a 1% variation in temperature yields a 3.2% variation in measured CO_2 mole fraction at 1500 K). The accuracy of measured CO_2 mole fractions was limited by uncertainties in determining the (zero absorption) baseline signals due to the finite tuning range of the laser (0.9 cm^{-1}).

Figure 7 shows the calculated minimum CO_2 detectivity as a function of temperature (R(56) line, 1 atm, 1-m absorption pathlength) based on the measured minimum detectable absorbance of 1.1×10^{-4} (200-Hz noise bandwidth, 80-ms measurement time). The calculated CO_2 detectivity increases from 80 ppm to 600 ppm as the temperature increases from 1000 K to 2000 K due to the decreasing linestrength of the R(56) transition. At 1470 K (corresponding to the measured 2-line temperature at an equivalence ratio of Φ=0.51) the minimum CO_2 detectivity is approximately 200 ppm. Lower detection limits may be achieved using frequency-modulation or electronic common-mode noise-reduction techniques.

Conclusions

A diode-laser sensor system has been developed for non-intrusive measurements of CO_2, H_2O, and gas temperature in combustion systems using absorption spectroscopy techniques. The system was successfully applied to measure species concentrations and temperature in the post-flame region of a premixed, laminar, C_2H_4-air flat-flame burner operating fuel lean. Values of gas temperature determined using laser-based (2-line ratio) techniques were in agreement with values using a type-S thermocouple to within 3%. Measured CO_2 and H_2O concentrations agreed to within 6% and 3%, respectively, with equilibrium values calculated at measured (2-line ratio) temperatures. The minimum CO_2 detectivity was 200 ppm (1470 K, 1-m path, 200-Hz detection bandwidth) and was limited primarily by beam steering effects on the detector surface and secondarily by detector-amplifier noise. The results suggest that the sensor system may be applied for continuous, non-intrusive measurements of CO_2, H_2O, and temperature in high-temperature combustion environments for open- and closed-loop control applications. Anticipated availability of diode lasers operating near 2.3 μm and 2.6 μm will extend the capabilities of this sensor system and enable sensitive *in-situ* measurements of important combustion pollutants such as CO and NO.

to be presented at the 27th Symposium (International) on Combustion, Boulder (July 1998)

Acknowledgments

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Table I. Selected CO_2 and H_2O transitions used for the *in-situ* measurements

CO_2	Transition Frequency [cm^{-1}]	Var.* [cm^{-1}]	Linestrength (296 K) [cm^{-2}/atm]	Var.* [%]	Transition	Vibrational Band	Lower State Energy [cm^{-1}]
	5010.04	0.00	4.77E-04	12.2	R(56)	$(12^01)-(00^00)$	1244.22

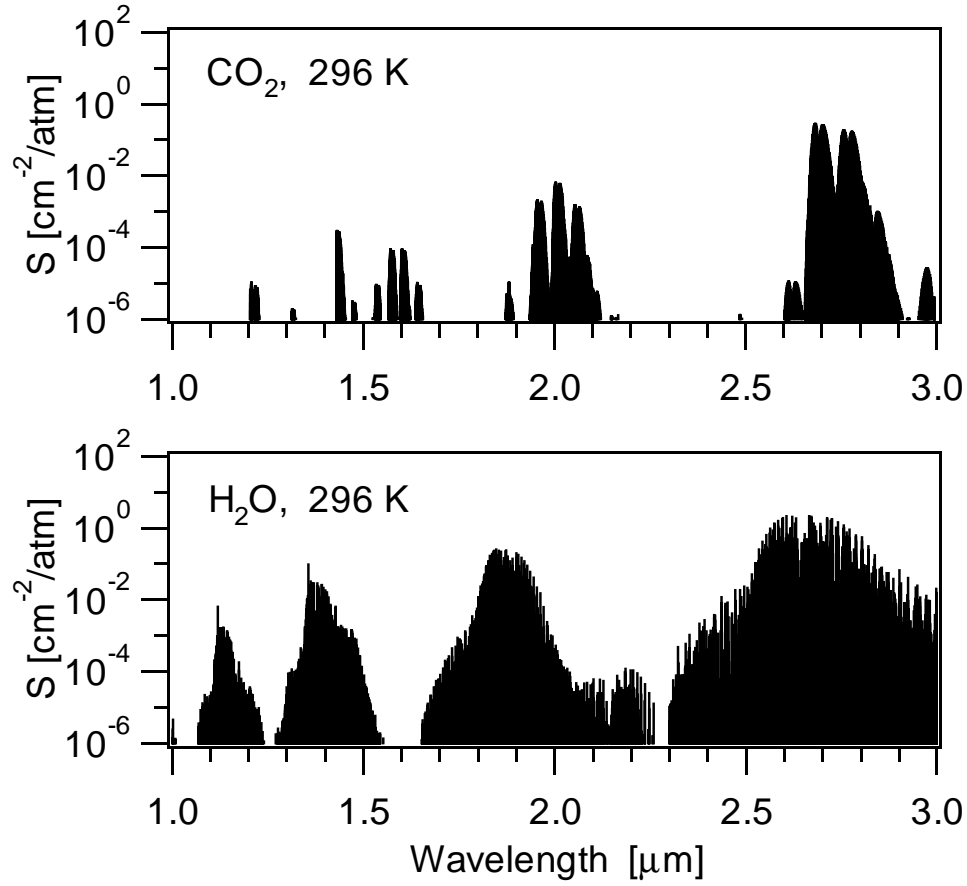| H_2O	Transition Frequency [cm^{-1}]	Var.* [cm^{-1}]	Linestrength (296 K) [cm^{-2}/atm]	Var.* [%]	J upper	K_a	K_c	J lower	K_a	K_c	Vibrational Band	Lower State Energy [cm^{-1}]
Line 1	5020.50	0.00	1.75E-05	5.0	12	4	8	13	4	9	(011)-(000)	2533.79
Line 2	5020.89	0.04	5.58E-07	-16.7	11	2	10	12	2	11	(021)-(010)	3386.42

* Variation from the HITRAN96/HITEMP database

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FIG. 1. Calculated survey spectra of CO_2 (top) and H_2O (bottom) between 1.0 μm – 3.0 μm at 296 K (HITRAN96 database)
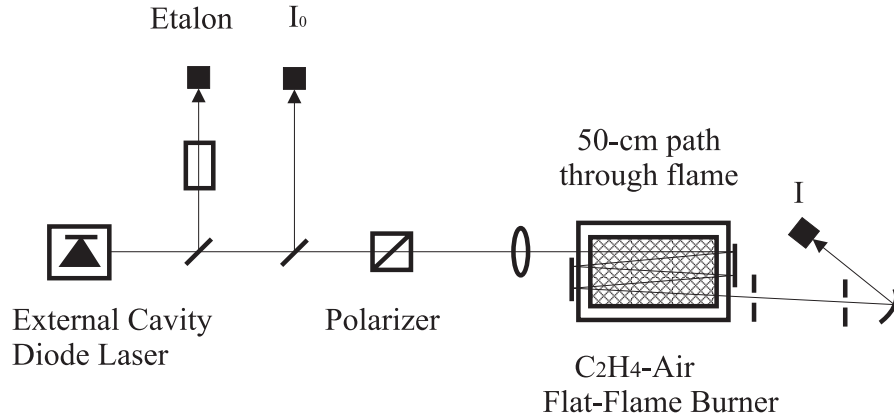

FIG. 2. Schematic diagram of the diode-laser sensor system with a folded path arrangement used to measure CO_2, H_2O, and temperature in the post-flame gases of a laminar, premixed C_2H_4-air flat-flame burner.
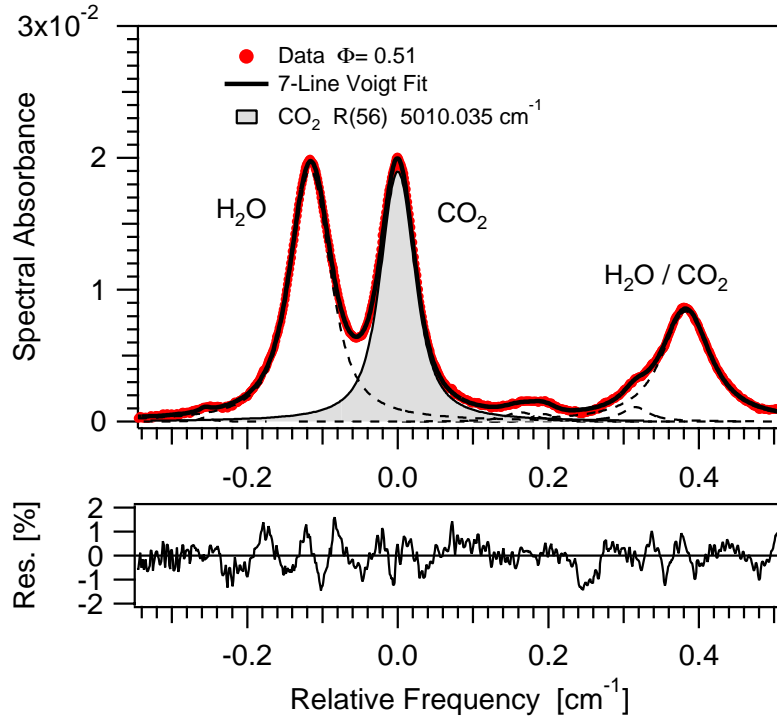
FIG. 3. Single-sweep measurements of CO_2 and H_2O absorption lineshapes recorded in a premixed C_2H_4-air flame (Φ= 0.51, 1470 K, 1 atm, X_{CO2}= 6.4%, X_{H2O}= 6.9%, 50-cm path). The CO_2 R(56) line ((12^01)–(00^00) band) was used to determine CO_2 concentrations. The residual represents the normalized difference between the data and the best-fit Voigt profile. Contributions from interfering CO_2 and H_2O transitions are illustrated as broken lines .
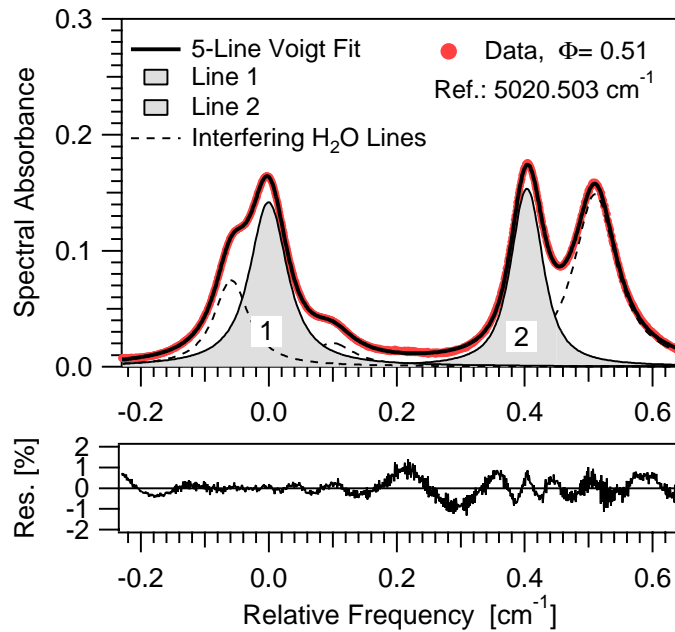

FIG. 4. Single-sweep measurements of H_2O absorption lineshapes recorded in a premixed C_2H_4-air flame (Φ= 0.51, 1470 K, 1 atm, X_{H2O}= 6.9%, 50-cm path). The selected H_2O transitions (line 1 and line 2) were used to determine gas temperature and H_2O mole fraction simultaneously. The dotted lines represent interfering H_2O transitions that were included in the 5-line Voigt fit.
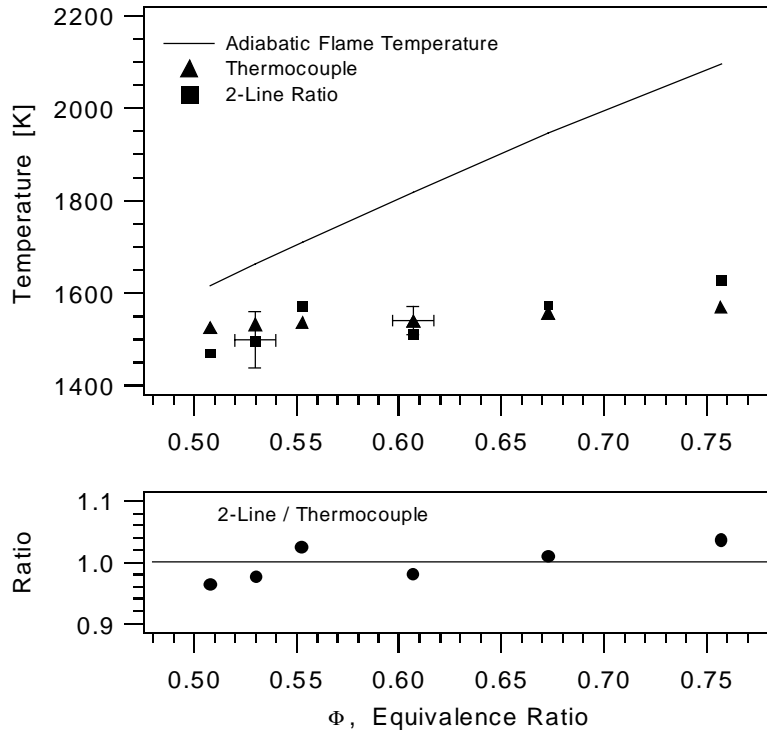
FIG. 5. Comparison of temperatures measured in the C_2H_4-air flame determined from H_2O line ratios (■) and type-S thermocouples (▲) as a function of equivalence ratio. The solid line represents the calculated adiabatic flame temperature.
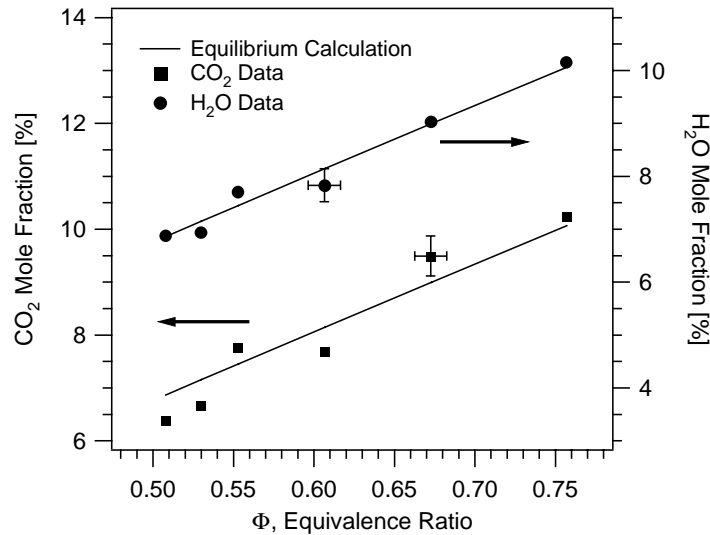

FIG. 6. Comparison of measured CO_2 (left axis) and H_2O mole fractions (right axis) in the C_2H_4-air flame to calculated equilibrium values at the measured (2-line) temperatures. The solid lines represent calculated chemical-equilibrium mole fractions using measured (2-line) temperatures.
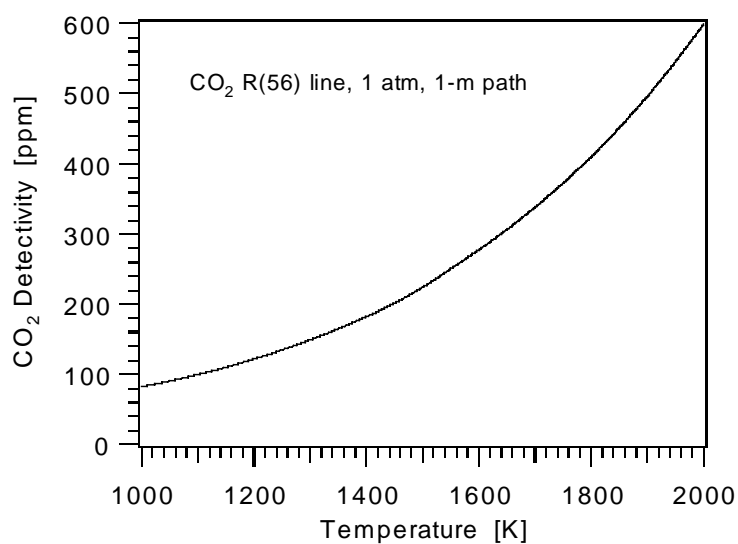
FIG. 7. Calculated CO_2 detectivity as a function of temperature (CO_2 R(56) line at 5010.035 cm^{-1}, 1 atm, 1-m pathlength) based on the measured minimum detectable absorbance of 1.1×10^{-4} (200-Hz noise bandwidth, 80-ms measurement time).

Figure Captions

FIG. 1. Calculated survey spectra of CO_2 (top) and H_2O (bottom) between 1.0 μm – 3.0 μm at 296 K (HITRAN96 database)

FIG. 2. Schematic diagram of the diode-laser sensor system with a folded path arrangement used to measure CO_2, H_2O, and temperature in the post-flame gases of a laminar, premixed C_2H_4-air flat-flame burner.

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FIG. 4. Single-sweep measurements of H_2O absorption lineshapes recorded in a premixed C_2H_4-air flame (Φ= 0.51, 1470 K, 1 atm, X_{H2O}= 6.9%, 50-cm path). The selected H_2O transitions (line 1 and line 2) were used to determine gas temperature and H_2O mole fraction simultaneously. The dotted lines represent interfering H_2O transitions that were included in the 5-line Voigt fit.

FIG. 5. Comparison of temperatures measured in the C_2H_4-air flame determined from H_2O line ratios (■) and type-S thermocouples (▲) as a function of equivalence ratio. The solid line represents the calculated adiabatic flame temperature.

FIG. 6. Comparison of measured CO_2 (left axis) and H_2O mole fractions (right axis) in the C_2H_4-air flame to calculated equilibrium values at the measured (2-line) temperatures. The solid lines represent calculated chemical-equilibrium mole fractions using measured (2-line) temperatures.

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