

SIMULTANEOUS DIODE-LASER-BASED *IN SITU* DETECTION OF MULTIPLE SPECIES AND TEMPERATURE IN A GAS-FIRED POWER PLANT

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We have developed a diode-laser (DL)-based spectrometer and demonstrated, to our knowledge, the first simultaneous *in situ* detection of all major combustion species and the temperature in the same measurement volume for active combustion control purposes and to ensure a safe ignition procedure of large-scale multi-burner gas-fired combustion systems. Two distributed-feedback DLs at 760 nm and 1.65 μm were used to detect O_2 , CH_4 , and CO_2 , while a Fabry-Perot DL at 812 nm served to extract absolute H_2O concentrations and the temperature from multiline water spectra. Permanent alignment of the laser beams could be ensured, despite strong wall deformation, with a new active alignment control loop. We analyzed the stationary ignition procedure of a full-scale gas-fired power plant with a 10 m furnace diameter using the spectrometer. A time resolution of 1.6 s and a minimum detectable absorption better than 10^{-3} OD could be achieved. CH_4 could be detected with a dynamic range of more than two orders of magnitude and a detectivity in the 100 ppm range. A strong dependence of the CH_4 signal on the burner height was found. This spectrometer is well suited to enable an on-line control of the furnace atmosphere and a rapid detection of ignition delays by unburned CH_4 .

Introduction

Natural gas combustion in combination with combined-cycle processes is playing an increasingly important role in energy production. This is due to the high conversion efficiency of the process, its low emission of pollutants such as NO_x or SO_x and especially its low overall costs, which even compete with nuclear energy production. To adapt the total power production to the public demand, it is common for most energy production processes to require the ability for rapid load variations. Consequently, there is a need for power plants that have to be turned on and off very frequently and rapidly to cover the peak power variations of the distributing net. In principle, gas-fired power plants are well suited for this purpose, but there is a proven risk of severe ignition delays. Such delays result in a large amount of premixed gas being injected in the combustion chamber, so that the next successful ignition in the multiburner system will cause a so-called puff. Severe damage to the combustion chamber, often in the multimillion-dollar range, can be the consequence of such an event. The cause for these ignition delays is still under investigation, but they may be partly attributed to flame quenching by excess humidity and hence the high heat capacity of the primary air. The response time of suction-probe extractive sensors is too slow to avoid puff events. In

addition, such sensors do not obtain a methane signal representative of the large combustion chamber. In order to maintain optimum operating conditions for large-scale natural gas combustion systems under all process conditions, that is, under frequent and strong variations in total power, and to enable secure ignition and precise active control of the multiburner systems, it would be most helpful to have a versatile, *in situ* sensor with fast response time for gaseous species, especially CH_4 , and temperature.

Over the past 15 years, we have developed several laser-based *in situ* sensors, including a CO_2 -laser-based NH_3 sensor, among others [1,2]. Diode-laser-based absorption spectrometers in the MIR and NIR spectral range have proven to be versatile instruments in research and small-scale industrial applications [3–8]. The application to full-size industrial combustion processes has been realized only in a few instances due to the severe problems of obtaining an *in situ* measurement under such conditions. However, we have successfully demonstrated an *in situ* sensor for active combustion control applications measuring simultaneously the oxygen and water concentration in a full-scale waste incinerator [9,10].

The quantity of interest for the avoidance of puffs in gas-fired power plants is the methane concentration, which can indicate an ignition failure. Most interesting are the methane data during start-up conditions right after the ignition of the first few

burners. Due to the very steep temperature gradients that are present during this time period, it is mandatory to correct the absorption signal for temperature-dependent variations in line strength and density in order to gain quantitative signals. However, in many technical applications, permanent temperature sensors in the hot reaction zone are either not available, due to problems with long-term stability, or have thick protective ceramic covers that make them rather slow and unsuitable for correcting a rapidly changing optical signal. In our application, it is therefore necessary—and advantageous—to perform a simultaneous optical temperature measurement. This has been demonstrated in small combustion systems by detection of suitable water absorption lines [3–5].

As proposed in Ref. [9], the usefulness of a DL spectrometer for active control purposes can be enhanced greatly if more than one or two species are detected simultaneously. A real multipurpose device would be a sensor that is capable of measuring all main educt and product species (CH_4 , O_2 , H_2O , CO_2) and the temperature: oxygen and methane concentrations would provide a fuel-to-air ratio measurement, the water content can be used to extract gas temperatures and flame quenching properties by excess humidity, and CO_2 and water could be used to monitor fuel quality, namely the C/H ratio [9]. To probe the local chemistry without being excessively sensitive to inhomogeneities in the combustion chamber or to drift between different species sensors, it is necessary to probe all species in the same detection volume. To our knowledge, no such simultaneous measurement of the four species of interest and temperature has been reported in a full-scale industrial environment.

We started the development of such a multipurpose *in situ* absorption spectrometer based upon room-temperature near-infrared diode lasers. This device is able to determine simultaneously, within a single absorption path, multiple species concentrations of the major combustion educts and products (CH_4 , H_2O , CO_2 , and O_2) and the temperature. To make this possible it was mandatory to develop techniques for an efficient and complete correction of the complex disturbances that bury the molecular absorption signals. The most important disturbances are strong and rapid fluctuations of the transmission of the *in situ* path and of the thermal background emission. In addition, dynamic changes in the optical alignment of the spectrometer caused by wall deformations due to the large temperature gradients during the start-up procedure have to be removed. To maintain permanent alignment during the ignition period, we developed an active alignment control loop. We applied this spectrometer successfully during the ignition and turn-off cycle of a full-scale gas-fired power plant with a thermal gross power of 1

GW and an inner diameter of the combustion chamber of 10 m. Here, we report the first results regarding *in situ* species and temperature detection under ignition conditions.

Experimental

In situ measurements are often plagued by rather broadband spectral disturbances, which are sometimes up to 100 to 1000 times larger than the molecular signal. Thermal background radiation, $E(t)$, from particles or furnace walls increases the detector photo current, while dust, soot particles, or beam steering due to refractive index fluctuations lead to time-dependent variations in the background transmission, T , of the measurement path. The detected optical power is described by Beer's law and is expressed as

$$I(\lambda, t) = I_0(\lambda) \cdot e^{(-S(T) \cdot g(\lambda - \lambda_0) \cdot N \cdot L)} \cdot T(t) + E(t)$$

where N is the number density of the molecular absorbers, $I_0(\lambda)$ is the initial laser intensity, and $I(\lambda)$ is the intensity detected after passage through the absorbing medium of thickness L (here assumed to be homogenous). The absorption line is characterized by $S(T)$, the temperature dependent spectrally integrated line strength, and $g(\lambda, \lambda_0)$, which describes the shape of the absorption line centered at wavelength λ_0 . On-line suppression or correction of these effects and efficient noise reduction methods as described in Refs. [9,10] are indispensable to extract the small molecular losses.

In this work, we used tunable near-infrared diode lasers (NIR-DLs) as light sources. In contrast to many other lasers, NIR-DLs are most suitable for industrial applications since they are inexpensive, compact, rugged, and relatively simple to operate. Their excellent coverage of the spectral range between 630 and 1650 nm, fast tunability, high spectral resolution, and spectral power density offer many interesting opportunities from non-intrusive, fast-response-time multispecies sensors with high sensitivity and specificity [3–10] to optical temperature measurements by two-line absorption techniques [3–5,8,11].

In our case, three lasers were required to detect the four species of interest. One prototype distributed feedback laser (DFB) at $1.65 \mu\text{m}$ (10 mW) detected methane via the R5 line group of the first overtone of the asymmetric stretch ($2\nu_3$) at 6067.08 cm^{-1} [11] and CO_2 via a line group that belongs presumably to the P21 line in the $(11111) \leftarrow (00000)$ combination and the R66 line in the $(31114) \leftarrow (01101)$ hot band. A second DFB (5 mW), which could access any line within the R branch of the A-band of oxygen, a rotationally resolved vibrational subtransition ($0 \leftarrow 0$) of the $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ electronic transition [12], detected O_2 via the R15Q16 and R17R17 transitions. Finally, we measured up to

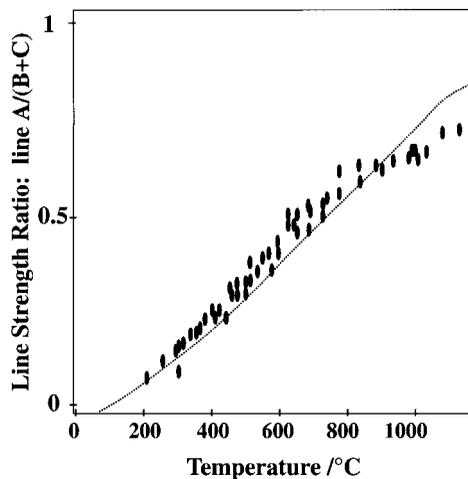


FIG. 1. Temperature dependence of the line strength ratio of the A, B, and C lines of water (see Fig. 5 and text) used for *in situ* temperature determination. Experimental data (dots); calculation based on HITRAN92 data (line). These absorption lines at about 12295 cm^{-1} belong to (211) and $(112) \leftarrow (000)$ vibrational combination bands [11] (see text). Despite severe discrepancies for line B in the individual line data between HITRAN and the experimental spectra, we achieved good agreement in the line strength *ratio* if we evaluated the area of line A divided by the *sum* of line B and C (see text).

five rotationally resolved water lines via the vibrational combination band $(1,1,2)$ and $(2,1,1) \leftarrow (0,0,0)$ with a 35 mW high-power Fabry-Perot DL (FP) at 812 nm. Due to its discontinuous tuning behavior, the FP laser had to be carefully selected for coincidences with water absorption lines [9]. Not only did we desire absolute water number densities, we also wanted to extract *in situ* temperatures from the line ratios of the three strongest lines of this spectrum (designated A, B, and C in Fig. 5).

Strong discrepancies between the HITRAN databases [13] and experimental data can be found [14–17]. According to HITRAN96, line D is more than 10 times stronger than C. Therefore, we experimentally verified the temperature dependence of the line ratio in a high-temperature absorption cell at temperatures from 300°C to 1100°C [14]. In contradiction to HITRAN96, neither the position nor the ground state energy of line B is identical to C ($E_c'' = 649\text{ cm}^{-1}$). B appears to be red-shifted and has a ground state energy similar to line A ($E_A'' = 1807\text{ cm}^{-1}$) [18]. However, we find good agreement between our experiment and HITRAN96-based data up to 1200 K if we ignore these errors and evaluate the strength ratio between line A and the *sum* of B and C (Fig. 1). HITEMP [19] did not contain significant new data in this spectral range.

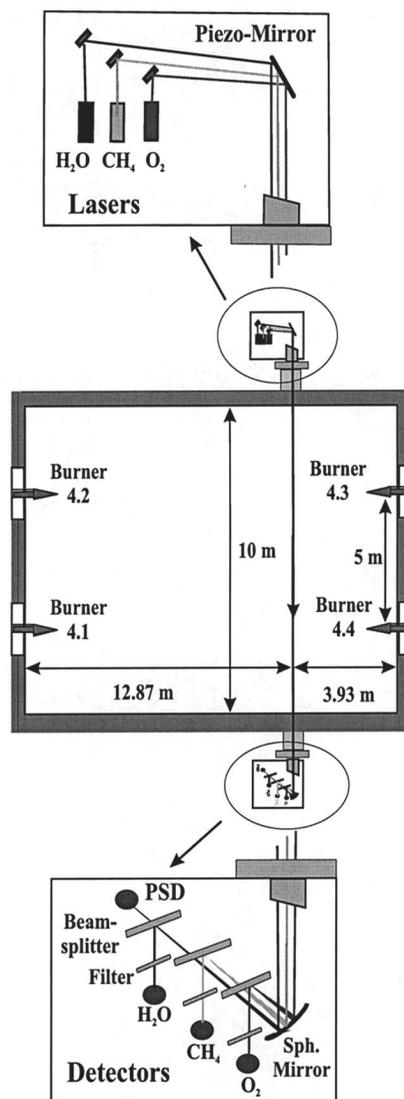


FIG. 2. Experimental setup of the diode-laser-based multispecies *in situ* spectrometer. Cross section in the measurement plane through the gas-fired 1 GW power plant. Only the four burners of level 4 located in the plane of measurement are indicated. The optical setup containing lasers, optics, and detectors has been enlarged for clarity.

In situ measurements were performed at a full-scale gas-fired power plant with a thermal gross power of 1 GW. The combustion chamber, with a cross section of 10 by 16.5 m and a height of 37 m, was fired by twenty 50 MW burners. Four burners are arranged in each of five height levels with a vertical separation of 5 m between each level. The schematic of the laser *in situ* spectrometer is depicted in Fig. 2. The measurement plane was about 21 m

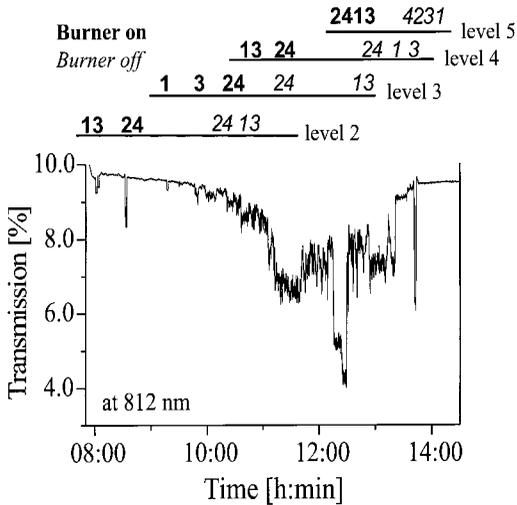


FIG. 3. Top: Burner ignition sequence during the multi-species measurements at the power plant. The burner height is indicated by levels 1 to 5, which are vertically separated by 5 m. Each burner in each level is identified by a one-digit number. The counting order (1 to 4) can be derived from Fig. 2. The placement of the numbers along the horizontal time axis indicates the approximate ignition or turn-off time. Bottom: Time evolution of the amount of laser light at 812 nm reaching the detector, indicating the overall transmission of the *in situ* path (including all optical elements) at this wavelength. In the worst case, only 4% of the light can be used to extract the absorption signal.

above the furnace floor and coincided with level four of the burner arrangement. The laser beams were separated 3.9 m from the exits of burners 4.3 and 4.4. Diode lasers and receiving optics were mounted without any further vibrational damping on steel platforms and bolted to a 300 mm long and 100 mm inner diameter double-walled air-cooled flange. Since strong vertical thermal expansion movements of up to 20 cm were expected, the air-cooled flanges were mounted onto the furnace walls to ensure permanent alignment. All diode laser beams were collimated, carefully overlapped, and guided through air-purged Brewster windows (BK7, 50 mm).

A triangular modulation of the respective laser current by two independent but phase-locked function generators (one for $\text{H}_2\text{O} + \text{O}_2$ and another for $\text{CH}_4 + \text{CO}_2$) scanned the laser wavelengths at a 1 kHz repetition rate over the desired absorption lines. The light transmitted through the furnace was collected by a 3 inch gold-coated mirror, separated into the three wavelength components by dichroic beam-splitters, filtered on each channel by narrowband interference filters to minimize cross talk between wavelength channels and to suppress thermal background radiation, and then directed onto room-temperature silicon ($\text{Ø}10$ mm) and InGaAs ($\text{Ø}5$ mm)

detectors, respectively. The photocurrents were preamplified and digitized at 1.0 Msample/s by a 12-bit eight-channel simultaneously sampling A/D converter on a PCI-board (Imtec). Between 25 and 500 consecutive scans were averaged for further noise reduction. Concentrations values were extracted by a fitting procedure assuming up to five independent Lorentzian line shape functions and a background polynomial of maximum fourth order.

We found no problems in mounting the optics onto the furnace walls in other *in situ* applications [9]. However, during the two measurement campaigns described here, the continuous measurement time was limited to less than an hour due to misalignment of the laser beam, which we attributed to a deformation of the combustor walls caused by the strong temporal temperature gradients. In order to allow a permanent *in situ* measurement, we developed an active alignment control loop for the laser beams [20]. Requirements for the control loop were insensitivity to fluctuations in overall transmission and thermal background radiation and a control bandwidth of the order of 10 Hz. These conditions were ensured by combining a narrowband (10 nm) filtered 10×10 mm position sensitive silicon detector (PSD) as a sensor and a piezo-driven mirror as an actuator with all-analog evaluation electronics. The PSD signal was evaluated and corrected for intensity fluctuations by fast analog dividers and then fed into a multichannel piezo controller (PI), followed by high-power low-voltage piezo drivers (PI) driving the $42 \mu\text{m}$ range piezo-driven micrometers. An angular error of 3.23 mrad, corresponding to a 3.5 cm lateral beam displacement over an 11 m distance, could be corrected [18]. In the plant setup, we created a “guiding” laser using a 50% beam splitter to generate a secondary 812 nm beam for the PSD, thereby avoiding the complexity of an additional laser (Fig. 2). The robustness of this setup was successfully lab tested by irradiating the detector-filter combination with a 4-Hz-modulated 50 W tungsten lamp while simultaneously mimicking transmission fluctuations by inducing a 95% amplitude modulation on the laser output (8 to $180 \mu\text{W}$). Under these circumstances, the PSD signal changed by only 0.9%.

Results and Discussion

The following data were obtained during a single ignition and turn-off procedure over about 5 h. It should be noted that the ignition sequence of the burners (Fig. 3, top) started at level 2 and that two burners at level 4 were firing directly through the measurement plane. Also shown (Fig. 3, bottom) is the overall transmission of the measurement path recorded with the H_2O detector at 812 nm. Initial losses of 90% of the laser radiation are to a large

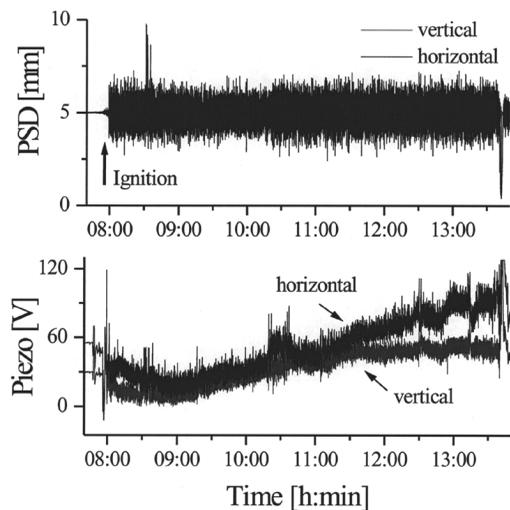


FIG. 4. Time evolution of the performance of the active alignment control setup. Top: Error signal of the control loop indicated by the position of the laser spot on the PSD. Bottom: Control voltages of the two piezo actuators. These signals represent the angular misalignment of the spectrometer (in two perpendicular directions) corrected by the control loop.

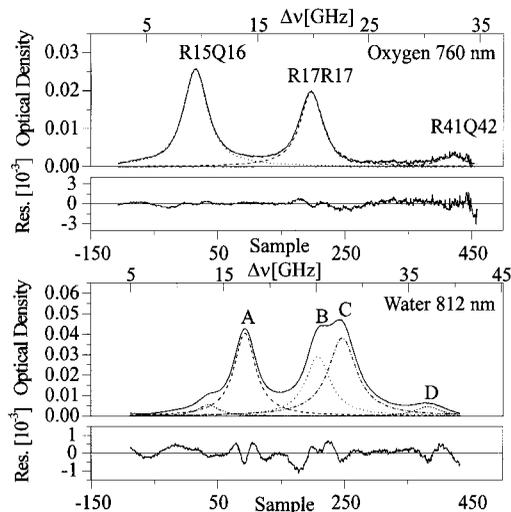


FIG. 5. *In situ* spectra at the power plant and calculated spectra with residuals. Top: Oxygen at 760 nm. The spectral lines have been assigned using the HITRAN92 database. Bottom: Water at 812 nm. Assignment of the spectral lines is indicated by letters and discussed in the text.

extent caused by optical elements in the beam path. Losses increase further to 96% by turbulence-induced gradient index fluctuations if the burners in the measurement plane are ignited. Spikelike features are often seen during burner ignition.

Nevertheless, we successfully demonstrated under industrial conditions the first active alignment control loop based on a PSD and a piezo-driven mirror. As seen in Fig. 4, the error signal of the PSD that mostly scatters around the detector center (5 mm) clearly indicates that the control loop was working perfectly. Immediately after the first ignition, a noiselike scatter on the error signal with 0.54 mm standard deviation is evident. We attribute this to the fast gradient index fluctuations for which the control loop was not intended to correct. The reaction time was determined to be about 0.2 s, corresponding to 5-Hz loop bandwidth. The compensated angular misalignment can be seen in the actuator signal in Fig. 4 (bottom). The complete range of the piezo was needed for correction at the end of the run. Even before the first ignition, relatively strong disturbances were found that we think were caused by flooding the furnace volume with preheated air, leading to thermal expansion movements and gradient index fluctuations.

Typical absorption spectra gained under combustion conditions are shown in Fig. 5 for the case of oxygen and water. Clean profiles of the oxygen R15Q16, R17R17, and even R41Q42 lines were gained, indicating a signal-to-noise ratio of about 100 and an excellent minimum detectable absorption in the 10^{-4} OD range, despite measuring the direct de-coupled signals. The noise increase at the R41Q42 line is caused by low laser power. The bottom trace shows the *in situ* signal of the water lines, again with good signal-to-noise ratio. The total area of line B and C served as an indicator for the water concentration, while the area ratio $A/(B + C)$ was used as a temperature indicator. *In situ* spectra at 1.65 μm and moderate temperatures (Fig. 6, top) contained only the $2\nu_3$ -R5 line of methane. Numerous new lines not mentioned in HITRAN92 or 96 could be measured (Fig. 6, bottom) at high temperatures. These lines were identified as water and CO_2 lines using HITEMP to correlate their relative position.

Figure 7 shows the time histories of the *in situ* signals of CO_2 and oxygen. This data clearly demonstrate the ability to monitor a complete ignition and turn-off event over the period of several hours. The *in situ* temperature that is necessary for the conversion of the spectra to absolute number densities and the absolute water content of the flue gas were determined with a temporal resolution of 1.6 s via the multiline water spectra at 812 nm, as depicted in Fig. 8. The standard deviation (1σ) of the short-term temperature fluctuations was determined to be

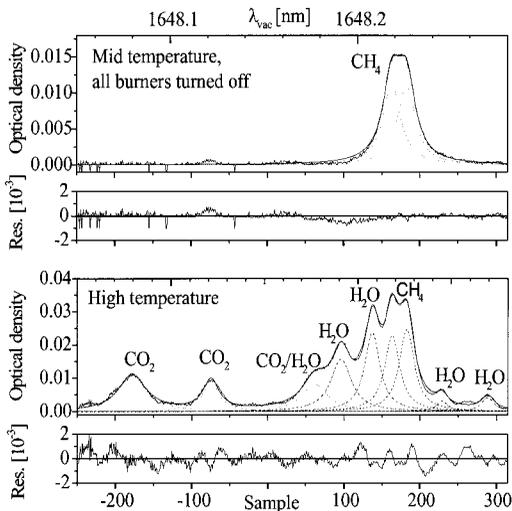


FIG. 6. *In situ* spectra at moderate combustion temperatures immediately after all burners are turned off (top) and at higher temperatures when level 4 burners were ignited (bottom), acquired with a current-tuned DFB laser in the $1.65\ \mu\text{m}$ spectral window. The top trace shows only the $2\nu_3$ -R5 line of methane. Numerous water and CO_2 transitions not tabulated in HITRAN92 or 96 show up in the bottom trace and belong to hot bands and overtone combination bands.

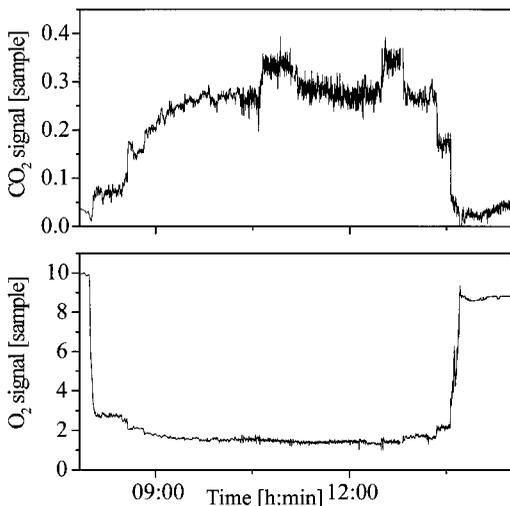


FIG. 7. Time history of the CO_2 (top) and the O_2 (bottom) *in situ* signal during the ignition procedure in the gas-fired power plant. The signals have not been corrected for temperature effects as indicated by the differences in the oxygen signal before ignition and after complete turn-off. Nevertheless a stepwise decrease and increase of the signals can be seen, which is correlated with the ignition and turn-off times of the individual burner levels (compare to Fig. 3 for the ignition schedule).

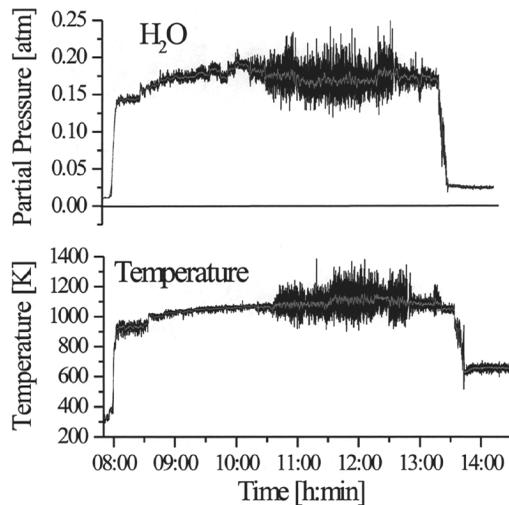


FIG. 8. *In situ* detection of the absolute H_2O concentration (top) and the gas temperature (bottom) determined in the gas-fired power plant during a full ignition and turn-off event. Strong turbulence-induced fluctuations appear in both signals as soon as the burners within the plane of measurement (level 4) are ignited. As expected, the data show a slight increase in humidity and a moderate increase in gas temperature after all burners are turned off (13:45).

$\pm 10\ \text{K}$ between 9:00 and 10:00, and $\pm 56\ \text{K}$ between 11:00 and 12:00 when the burners within the plane of measurement were firing. The temperature signal also reveals clearly that the air was preheated before ignition and cooled down to about 600 K after turn-off of all burners.

Figure 9 demonstrates the first successful *in situ* measurement of absolute CH_4 concentrations with ppm sensitivity in a full-scale power plant. More than two orders of magnitude dynamic range could be demonstrated over a time period of 4 h. A direct comparison of the methane signal, which has been averaged by a 40-point moving average, with ignition times and burner positions also reveals a close correlation of the CH_4 concentration with the height level of the ignited burners. We attribute the strong increase in CH_4 at 10:40 to a large recirculation zone created by the diagonally fired burners, which gradually disappears as more burners on level 4 fire.

Conclusions

We have demonstrated the first simultaneous *in situ* detection, to our knowledge, of all major combustion species (CH_4 , H_2O , O_2 , and CO_2) and temperature in the same measurement volume using a multidiode laser spectrometer. We applied this technique successfully to a full-scale, gas-fired power plant with 1 GW thermal power. Close coupling between species and temperature signals and strong

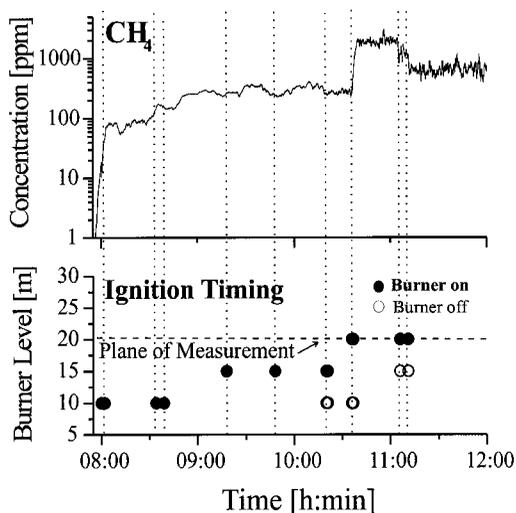


FIG. 9. Time history of the ignition procedure (bottom) and the absolute *in situ* CH₄ concentration (top) determined in the gas-fired power plant. A close correlation between burner level and the CH₄ signal can be found. The increase of methane with decreasing distance between burner and measurement plane indicates the decreasing burnout of the gases. The strong increase in CH₄ when the first two opposing burners in the measurement plane are ignited may be attributed to the creation of a large recirculation zone with low oxygen concentration that disappears as soon as all burners in the measurement plane are ignited.

dependence of the CH₄ signal on burner location were found. The spectrometer was capable of a time resolution of about 1.6 s and a minimum detectable absorption better than 10^{-3} OD. This device should allow on-line control of the furnace atmosphere humidity and provide for the rapid and reliable detection of ignition delays by unburned CH₄.

Acknowledgments

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REFERENCES

- Meienburg, W., and Wolfrum, J., *Proc. Combust. Inst.* 23:231–236 (1990).
- Schuler, F., Rampp, F., Martin, J., and Wolfrum, J., *Combust. Flame* 99:431–439 (1994).
- Baer, D. S., Hanson, R. K., Newfield, M. E., and Gopaul, N. K. J. M., *Opt. Lett.* 19:1900–1902 (1994).
- Furlong, E. R., Baer, D. S., and Hanson, R. K., *Proc. Combust. Inst.* 26:2851–2858 (1996).
- Allen, M. G., *Meas. Sci. Technol.* 9(4):545–562 (1998).
- Hemberger, R., Muris, S., Pleban, K.-U., and Wolfrum, J., *Combust. Flame* 99:660–668 (1994).
- Werle, P., *Infrared Phys. Technol.* 37:59–66 (1996).
- Silver, J. A., and Kane, D. J., *Meas. Sci. Technol.* 10:845–852 (1999).
- Ebert, V., Fitzer, J., Gerstenberg, I., Pleban, K.-U., Pitz, H., Wolfrum, J., Jochem, M., and Martin, J., *Proc. Combust. Inst.* 27:1301–1308 (1998).
- Ebert, V., Schulz, C., Volpp, H. R., Wolfrum, J., and Monkhouse, P., *Isr. J. Chem.* 39:1–24 (1999).
- Nagali, V., Chou, S. I., Baer, D. S., Hanson, R. K., and Segall, J., *Appl. Opt.* 35(21):4026–4032 (1996).
- Ritter, K. I., and Wilkerson, T. D., *J. Mol. Spec.* 121:1 (1987).
- Rothman, L. S., Gamache, R. R., Tipping, R. H., Rinsland, C. P., Smith, M. A. H., Benner, D. C., Devi, V. M., Flaud, J.-M., Camy-Peyret, C., Perrin, A., Goldman, A., Massie, S. T., Brown, L. R., and Toth, R. A., *J. Quant. Spectrosc. Radiat. Transfer* 48(5/6):469–508 (1992); Rothman, L. S., Rinsland, C. P., Goldman, A., Massie, S. T., Edwards, D. P., Flaud, J.-M., Perrin, A., Camy-Peyret, C., Dana, V., Mandin, J.-Y., Schroeder, J., McCann, A., Gamache, R. R., Wattson, R. B., Yoshino, K., Chance, K. V., Jucks, K. W., Brown, L. R., Nemtchinov, V., and Varanasi, P., *J. Quant. Spectrosc. Radiat. Transfer* 60:665–710 (1998); www.hitran.com.
- Fitzer, J., “In-situ Nachweis von Methan in einem 1 GW_{th} Gaskraftwerk mit Hilfe der NIR-Diodenlasern,” Dissertation, Universität Heidelberg, Heidelberg, Germany, 1997 (in German).
- Adler-Golden, S., Lee, J., and Goldstein, N., *J. Quant. Spectrosc. Radiat. Transfer* 48(5/6):527–535 (1992).
- Arroyo, M. P., and Hanson, R. K., *Appl. Opt.* 32:6104–6116 (1993).
- Langlois, S., Birbeck, T. P., and Hanson, R. K., *J. Mol. Spec.* 163:27–42 (1994).
- Pitz, H., “Empfindlicher In-situ Nachweis von Methan in einem 1 GW_{th} Gaskraftwerk mit Hilfe der NIR-Diodenlaserspektroskopie,” Dissertation, Universität Heidelberg, Heidelberg, Germany, 2000 (in German).
- Rothman, L. S., Wattson, R. B., Gamache, R. R., Goorvitch, D., Hawkins, R. L., Selby, J. E. A., Camy-Peyret, C., Flaud, J. M., Schroeder, J., and McCann, A., “HITEMP, the High-Temperature Molecular Spectroscopic Database,” unpublished manuscript (2000).
- Giesemann, C., “Entwicklung eines Strahlführungssystems für In-situ Absorptionsmessungen mit NIR-Diodenlasern in einem 1 GW_{th} Gaskraftwerk,” diploma thesis, Universität Heidelberg, Heidelberg, Germany, 1999 (in German).

COMMENTS

Jay Jeffries, Stanford University, USA. If you wish to use this sensor as part of a safety system to prevent puffs, what sensor and what activation time response is required?

Author's Reply. Due to the omission of gas transport, our *in situ* gas detection system is much faster than any standard extractive sampling technique. So far, we used an overall response time of the sensor of 1.6 s (which is satisfactory according to the safety engineers). This value could be reduced to a few milliseconds by evaluating single scans. In any case, compared to the extractive sensors which would have to be used otherwise, we save a few seconds to tens of seconds by measuring *in situ* (depending on the location and speed of the extractive sensor). This time savings should allow the use of the standard valves used so far to switch off the fuel lines.

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Christopher Shaddix, Sandia National Laboratories, USA. Did you consider the use of wavelength modulation spectroscopy (WMS) to improve the sensitivity and time response of the diode laser measurement? If time response of the sensor is critical, this would seem to be the preferable detection methodology, although the spectral overlap of the absorption features that you probed would complicate quantification of the concentrations. Also, what level of error do you anticipate in your deduced methane concentrations once burner ignition has occurred and most of the probed water is presumably at much higher temperatures than the natural gas fuel?

Author's Reply. We did not use WMS because we wanted to be able to infer the concentration of the detected species directly from the scan without the need for a further calibration procedure. Since the WMS signal is strongly influenced by the temperature-, pressure-, and composition-dependent pressure broadening of the absorption line, it is more difficult to evaluate than the direct absorption signal and mostly requires a calibration measurement. Regarding the time response, I disagree that WMS is more suitable if a fast response is needed. To detect an absorption profile within less than a millisecond you need a fast modulation frequency in the order of a 1 MHz, which on the other hand requires much faster detectors (which then have to have a much smaller diameter) and lock-ins which can demodulate signals in the MHz range. (These are hardly commercially available and rather expensive.) Our setup is much more simple and thus less expensive. Despite that, the sensitivity which we achieved, being the direct detection of the signal, was sufficient for the intended purpose.

The system is not intended to be used to detect ignition failures by measuring through the flames of the burners, but at a certain distance to the burner. Because of that, we would avoid the error you mentioned. However, to extend the use of the system to the mentioned situation, we are preparing to measure simultaneously the temperature of the educts and the products via the absorption signal of oxygen and water, respectively. This way we should be able to evaluate a possible temperature difference between educts and products and to deduce an error in the methane signal.