Advanced Laser Spectroscopy in Combustion Diagnostics

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ABSTRACT

In recent years, a large number of linear and nonlinear laser-based diagnostic techniques for non-intrusive measurements of species concentrations, temperatures, and gas velocities in a wide pressure and temperature range with high temporal and spatial resolution were developed and have become extremely valuable tools to study many aspects of combustion. Nonlinear laser spectroscopic techniques using infrared-visible sum-frequency generation can now bridge the pressure and materials gap to provide kinetic data for catalytic combustion. Laminar flames are ideal objects to develop the application of laser spectroscopic methods for practical combustion systems and to test and improve gas-phase reaction mechanism in combustion models. Non-intrusive laser point and field measurements, especially joint velocity-scalar data at the same point in space and time, are of basic importance in the validation and further development of turbulent combustion models. Finally, the potential of laser techniques for active combustion control in various devices from pressurized fluidized-bed reactors to gas fired power plants and municipal waste incinerators are illustrated.

Keywords:
Laser Diagnostics, catalytic combustion, combustion control, pollutant formation, laminar flames, turbulent flames
INTRODUCTION

Although it is well known that combustion of fossil fuels leads to the release of unwanted pollutants like e.g. carbon monoxide, unburned oxygenated hydrocarbons, sulfur and nitric oxides, and soot which affect our environment, it is still the most important technology providing the energy supply for our modern society. While during the first 1.6 million years of “combustion research”, which were characterized by the supposition of having an infinite reservoir of fuel, no systematic efforts were made to improve combustion efficiency and to preserve the environment nowadays considerable efforts are undertaken to optimize combustion processes to reduce pollutant formation while, at the same time, maintaining a high efficiency for the conversion of chemical to thermal, mechanical and electrical energy. However, even today the construction of technical combustion devices in general is still an essentially empirical process, calling to a large degree upon the experience of engineers and technicians employing methods based on cut and trial processes and global performance measurements. With the growing number of performance and environmental protection requirements that must be met, this kind of approach is reaching its limits. Combustion processes consist of a complex interaction of homogeneous and heterogeneous chemistry and transport processes [1]. As a consequence, the development of numerical simulation tools that can accurately predict combustion and its characteristics for practical applications has to be based on a detailed understanding of the underlying chemical reaction system and physical processes. New laser spectroscopic methods with high sensitivity which allow non-intrusive measurements of multidimensional temperature and species distributions in technical systems play an important role in the validation of the existing mathematical combustion models for laminar and turbulent reactive flows as well as in the development of active combustion control applications. As shown in Figure 1, the principle of stimulated emission has now been realized in all states of the matter.

This allows generation of coherent radiation from the far-infrared to the X-ray region. Particularly the introduction of tunable lasers and the development of non-linear optical techniques greatly expanded the possibilities of combustion spectroscopy using conventional light sources [2]. Even though higher order polarizations responsible for nonlinear optical phenomena are usually small, signal intensities in higher order wave mixing processes can be large, due to their strong dependence on laser intensities, concentration and interaction length.
Nonlinear susceptibilities are enhanced whenever one or more of the frequencies of the interacting laser beams are close to quantum mechanically allowed one- or multi-photon transitions. In microscopic terms the induced oscillating nonlinear polarization arises from the nonlinear mixing of the input waves to produce the same or new frequencies at various sum- and difference frequency combinations of the input frequencies. The spatial resolution of these techniques is determined by the intersection volume of the interacting beams. Another common feature is that all techniques need line-of-sight access to the combustion event, although large window openings, as are often necessary for incoherent methods, are not required. The direction of the emitted coherent signal beam is determined by the phase matching condition for efficient signal generation. The various linear and nonlinear coherent methods which have most successfully been used so far in combustion analysis are depicted in Figure 2. On the left, the relevant energy level diagrams are given. Upward-facing arrows indicate photon absorption (or conversion); down-ward-facing arrows depict photon emission; $\omega_i = 2 \pi \nu_i$ are the frequencies of the fields involved. The middle column depicts a simplified experimental setup for each method with corresponding beam and detection arrangements. The right column shows approximate analytic expressions for the signal intensity.

Figure 1: Wavelength range of Laser light sources
Figure 2: Survey of linear and nonlinear laser spectroscopic techniques applied in combustion diagnostics (See Ref. [4] for symbols).
Since laser spectroscopic techniques are now a normal working tool in combustion laboratories [3] around the world, a thorough review of the present status is clearly beyond the scope of this brief presentation. Therefore a number of representative examples, arranged in an increasing order of complexity ranging from the dynamics of elementary heterogeneous reactions to the incineration of municipal waste are selected for discussion in the following pages.

**LASER DIAGNOSTICS OF SURFACE SPECIES IN CATALYTIC COMBUSTION**

Catalytic combustion is a promising method for burning fuel in ultra lean mixtures which can lead to a significant reduction of pollutants formation, improved ignition, and enhanced stability of flames [5]. The heterogeneous combustion process is determined by a complex interaction of diffusion processes from and to the gas phase, by adsorption and desorption on the surface, and by surface diffusion and reaction kinetics [6]. As a consequence, the development of appropriate mathematical models for the numerical simulation of surface reactions and their coupling to the surrounding gas phase is essential for the detailed understanding of catalytic combustion under technical relevant conditions. Computational tools for the description of heterogeneous reaction systems have recently been developed [7], which include detailed surface chemistry as well as detailed models for molecular multi-species transport. However, so far only a few complete surface reaction mechanisms have been derived, which are mainly based on studies of elementary surface processes carried out under ultra-high vacuum (UHV) conditions on well-defined single surfaces [8]. The use of this kind of surface kinetics data in the modelling of technical processes which usually take place at high pressure (pressure gap) and on polycrystalline catalyst material (materials gap) emphasizes the importance to develop in-situ diagnostics techniques for molecular level studies of adsorbed species under practical catalytic combustion conditions. While laser spectroscopic techniques are now a normal working tool in gas-phase combustion diagnostics, methods for quantitative laser-based in situ diagnostics for the investigation of catalytic combustion are still under development. Infrared-visible sum-frequency generation (SFG) surface vibrational spectroscopy was used for CO detection during the high-pressure heterogeneous CO oxidation [9] and for the investigation of pressure [10] and temperature [11] dependent changes in the chemisorption of CO over a Pt(111) single crystal catalyst.
Only recently, it could be demonstrated that the SFG technique can also be used for "bridging the materials gap" in the Pt/CO system [12].

**Experimental**

The surface-species diagnostics experiments were carried out in a reaction chamber, which allows studies over a wide pressure range from UHV-conditions ($3 \times 10^{-10}$ mbar) up to atmospheric pressure. In the high pressure regime this experimental arrangement can be used to investigate reactive adsorption and desorption as well as processes of well-defined stagnation point flows of reactant mixtures on the catalyst surface. The reaction chamber was equipped with a quadrupole mass spectrometer for Thermal-Programmed Desorption (TPD) measurements, a Ar$^+$ sputter source, a retarding field analyser (RFA) for Auger Electron Spectroscopy (AES) and Low-Energy-Electron Diffraction (LEED) studies and CaF$_2$ and quartz windows serving as entrance and exit ports for the laser beams and the sum-frequency signal, respectively. A second differentially-pumped quadrupole mass spectrometer was connected to the vacuum line behind the reaction chamber which could be used for on-line monitoring of stable reaction products (in the present study e.g. CO$_2$) in the exhaust gas.

The Pt catalyst was mounted on a copper block and could be translated, tilted and rotated by means of a manipulator fitted with a differentially pumped rotary feedthrough. The Pt-foil (Advent, purity > 99.99%) could be resistively heated. The mounting allowed to work in the temperature range 300–1600 K using direct sample heating with a proportional-integral-derivative (PID) control unit. The temperature of the catalyst was measured by a Ni-NiCr thermocouple spot welded to the Pt-foil. Clean platinum surfaces could be obtained by applying several cycles of Ar$^+$ ion sputtering followed by oxidation at 1000 K. After the last sputter cycle, at 300 K with 3 keV Ar$^+$ ions for 45 min, the sample was heated to 750 K for 5 min. Then the sample was cooled down to 300 K. This procedure ensured reproducibility of the temperature dependent CO-SFG spectra measurements. During the CO oxidation measurements the premixed flows were 30 sccm O$_2$ (Messer Griesheim, 99.995%), 15 sccm CO (Messer Griesheim, 99.994%), and 105 sccm Ar (Messer Griesheim, 99.998%) at a total pressure of 20 mbar.

For the detection of chemisorbed CO a 40 ps mode-locked Nd:YAG laser system was used. A part of its output was frequency doubled to 532 nm and used as the visible input frequency
for the SFG process. The other part was used to pump an optical parametric system to generate infrared (IR) radiation tunable in the frequency range (1800–2200 cm\(^{-1}\)) with a pulse duration of 25 ps and a bandwidth of 7 ± 1 cm\(^{-1}\). The visible and the IR laser beam were p-polarized and overlapped at the surface. Incident angles were 55° for the visible and 35° for the infrared beam with energies of 400 µJ and 30 µJ per pulse, respectively. The spot size of the visible beam was 5 mm diameter and the infrared beam was slightly focussed to fall within the visible. The CO sum-frequency signal reflected from the Pt surface was detected after filtering of scattered light by a dielectric filter and a monochromator by a photomultiplier and a gated integrator and transferred to a laboratory computer. Every point of the CO SFG spectra shown in Figure 3 was obtained by averaging over 120 laser shots at a laser repetition rate of 10 Hz.

![Figure 3: Experimental setup for the in-situ detection of chemisorbed CO during CO oxidation on a polycrystalline Pt catalyst](image)

**CO Chemisorption Studies on a Polycrystalline Pt-Catalyst**

Chemisorption of CO on Pt surfaces is of importance in various catalytic processes, such as CO oxidation in car exhaust catalytic converters. In Figure 4, the relative coverage of chemisorbed CO measured during CO adsorption and desorption studies at a CO pressure of 1 mbar is plotted versus the Pt catalyst substrate temperature. The observed temperature
dependence of the CO coverage indicates the presence of two different adsorption/ desorption regimes. One in the temperature range $300 \, \text{K} < T < 580 \, \text{K}$ in which the equilibrium coverage decrease almost linearly with substrate temperature and a second one at $T > 600 \, \text{K}$ in which the equilibrium coverage decreases more rapidly with increasing substrate temperature. This behaviour could be explained by the presence of two distinct CO adsorption sites on the Pt foil (see Figure 5). The solid line depicted in Figure 4 represents the result of a numerical modelling calculation of a stagnation point flow of CO onto the Pt foil corresponding to the conditions of the experiment (CO flow rate: 30 sccm).
For the CO species correlated to the first kind of adsorption sites, a coverage-dependent activation energy for desorption increasing from 55 kJ/mol (at saturation coverage) to 110 kJ/mol with decreasing CO coverage was used. For the second adsorption site, the activation energy for desorption was 118 kJ/mol.

Detailed information about the nature of the different possible CO adsorption sites can be obtained from the analysis of the temperature dependence of the resonance frequency $\omega_{CO}$ (also depicted in Figure 4) and a comparison with results of SFG and infrared reflection-absorption spectroscopy (IRAS) experiments on well-defined Pt single crystal surfaces [14b]. In SFG studies on a Pt(111) single crystal at $T = 300$ K a value of $\omega_{CO} = (2093.3 \pm 1.6)$ cm$^{-1}$ was determined at saturation coverage [14c]. A comparable value of $\omega_{CO} = 2097$ cm$^{-1}$ was reported for a Pt-s[4(111) × (100)] surface [14a]. In both cases the frequencies were assigned to CO adsorbed on-top on (111) terrace sites. Within the experimental uncertainty the value $\omega_{CO} = (2096 \pm 4)$ cm$^{-1}$ observed in present study at $T = 300$ K is in good agreement with these values, indicating the presence of (111) terraces on the Pt-foil. In the low coverage regime (below 40% of saturation coverage) resonance frequencies in the range $\omega_{CO} = 2065$-2078 cm$^{-1}$ were determined in the IRAS studies on the Pt-s[4(111) × (100)] surface and assigned to CO linearly bound on step-sites [14a]. The values reported for $\omega_{CO}$ as well as their dependence on the CO coverage are in agreement with the results of the present SFG studies, suggesting a similarity in topology of the Pt-s[4(111) × (100)] and the polycrystalline Pt foil surface. Therefore the observed significant shift in the CO frequency from $(2096 \pm 4)$ cm$^{-1}$ to $(2057 \pm 5)$ cm$^{-1}$ coupled with the reduction of the CO coverage due to desorption can be explained as follows: At low temperature ($T \approx 300$ K) the center-frequency is dominated by CO species linearly bound at Pt terrace sites. With increasing temperature, desorption starts on the terraces with the weakest bound CO. Terrace-site desorption, which exhibits a coverage-dependent activation energy in the range $300$ K $< T < 580$ K, is followed (at $T > 600$ K) by the desorption of CO from step site where it is more strongly bound. Desorption from step site is characterized by a coverage-independent activation energy.

Investigation of CO Oxidation on a Polycrystalline Pt-Catalyst

In Figure 6, relative coverages of chemisorbed CO measured during CO oxidation studies at a pressure of 20 mbar are plotted versus the catalyst substrate temperature. Comparison with
the CO coverage measured during the CO adsorption/desorption studies (Figure 5) reveals that if O₂ is present in the stagnation-flow the CO surface coverage at T = 300 K is reduced.

However, as it can be seen in Figure 7, where the simultaneously measured absolute CO₂ formation rate is depicted, the observed decrease of the CO coverage at T = 300 K is not due to reaction but is the result of the competitive adsorption between CO and O₂. As it can also be seen in Figure 7, the following slight decrease in the CO surface coverage with
temperature in the range 300 K < T < 500 K is due to CO desorption (see Figure 5) rather than reaction. After the onset of reaction at T > 500 K, on the other hand, the CO coverage decreases rapidly with increasing substrate temperature. At T > 620 K no chemisorbed CO could be detected anymore indicating very small equilibrium CO surface concentrations under reaction conditions where CO is almost completely converted into CO₂. Over the whole temperature range (300 K ≤ T ≤ 620 K) where chemisorbed CO could be detected on the catalyst surface the resonance frequency $\omega_{CO}$ remained at values typical for CO terrace-site species. The experimental results are in agreement with the mechanism suggested by Xu and Yates, who found that the reaction occurs predominately between terrace-site CO and O atoms chemisorbed on step sites [15].

The solid lines shown in Figure 6 and Figure 7 represent the results of numerical simulations of a stagnation point flow of a CO/O₂/Ar-mixture onto the Pt foil corresponding to the conditions of the experiment. In the calculations detailed models for molecular transport and surface chemistry were used. Modelling of the surface chemistry was based on a mean field approach [13] with two different adsorption sites using the activation energies for desorption derived in the CO adsorption/desorption experimental studies. Kinetic data for the Lagmuir–Hinshelwood surface reaction mechanism was taken from Ref. [16], assuming competitive adsorption of CO and O₂ on both platinum adsorption sites. At present further theoretical and experimental studies are under way to investigate the influence of the catalysts surface structure, mixture composition and pressure on the ignition behaviour of the CO/O₂/Pt system in more detail.

**LAMINAR FLAMES**

Laminar premixed flames at low pressure on a flat-flame-burner constitute an ideal experimental arrangement for studying the interaction of elementary chemical combustion reactions, as first described by the Warnatz mechanism for hydrocarbon flames [17]. Experimental data on temperature as well as on concentration profiles for stable and unstable species are used to validate and further develop mathematical models which predict these profiles by numerical solution of the underlying conservation equations, including convection and molecular transport processes.
Figure 8 shows such an arrangement used for a low pressure CH$_4$/O$_2$/NO flame. Absolute concentration profiles of methyl and hydroxyl radicals as well as nitric oxide are measured by laser absorption spectroscopy. CH and CN radicals are followed by Laser induced Fluorescence (LIF). The quantitative application of LIF in such flames requires information on the dependence of the fluorescence quantum yield on pressure, temperature and chemical composition at the measurement location.

In low pressure flames, this can be done by direct measurement of the total fluorescence decay time as a function of the position in the flame with a time resolution in the nanosecond range. To obtain absolute number densities from the LIF signals, the remaining unknown factors such as excitation volume and optical collection and transmission efficiency can be determined from the slope of the Rayleigh scattering signal of known amounts of nitrogen in the burner, as described by Luque and Crosley [21]. As shown in Figure 9 the shape and absolute values of the concentration profiles for OH and CH$_3$ radicals as well as the initial reduction of nitric oxide are predicted well by the models. However, absolute CN radical concentration [20] are significantly overestimated by all models. More work has to be done on the details of the formation and destruction of CN during the reduction of nitric oxide in the reburn process. Further improvement in sensitive absorption spectroscopy in flames can
be obtained by using the cavity ring-down laser absorption spectroscopy (CRLAS) [22]. This technique circumvents the drawback of the two-dimensional multipass beam arrangements. In CRLAS, a laser beam is coupled into a linear cavity formed by two concave mirrors with high reflectivity at the species specific wavelength. The trapped light pulse is monitored in time via transmission through the output mirror. The decay time is a quantitative measure of the absorption strength, and hence the concentration of the species. Since only the decay time is relevant, the method also has the advantage of being insensitive to pulse-to-pulse energy fluctuations of the laser source. HCO radicals were detected in low-pressure flames by CRLAS by their weak electronic absorption [23] while CH₄, CH₃, H₂O and CO₂ were monitored quantitatively in a narrow range of their characteristic vibrational transitions in the infrared around 3 mm with high spectral resolution (0.007 cm⁻¹) using an optical parametric oscillator [24].

Until now, only few studies - experimentally and through modelling - have been conducted which address multidimensional, laminar and partially premixed flames with natural gas and realistic boundary conditions. Within a larger research and design consortium supported by the European Community (TOPDEC) a burner (Figure 10) was designed to mimic, on the one hand, the key features of practical appliances with a simplified flow field modelling (two-
Figure 10: Schematic of the 7-slot burner with heat exchanger for a domestic gas boiler with optical access to probe spatially resolved laser-induced fluorescence in premixed atmospheric pressure flames.
dimensional) and, on the other hand, to simultaneously perform detailed spatially resolved species concentration and temperature measurements within various test flames designed to represent typical burning situations in practical devices.

![Figure 11: Spatially resolved concentration profiles measured with laser induced fluorescence in the burner shown in Figure 10](image)

**Turbulent Flames**

Investigations of the interaction of an isolated vortex with a laminar flame provide the basic understanding necessary for modeling turbulence-chemistry interactions, introducing effects of strain, curvature and unsteadiness. Measurement of temporal evolution of the single-vortex flame interaction with a resolution in the kilohertz range is beyond the reach of conventional dye laser systems. However, these measurements are feasible in highly repeatable turbulent
systems by phase-sampling of a sequence which then provides the same time-resolved information. Furthermore, phase-locked averaging enables measurements of species with small abundancies and, thus, weak signal intensities. An experiment providing these advantages was set up by Nguyen and Paul [25] using a laminar V–flame and an acoustically driven vortex generator (Figure 12).

The exact position of the flame front, which is identified by the maximum heat release, is of major interest when investigating the turbulence-flame interaction. However, reactive radicals present close to the flame front, like OH and CH, have given ambiguous results in some cases. At high strain rate, the CH front breaks, whereas the OH front persists. From simulation calculations it has been shown that the formyl radical concentration closely matches the distribution of heat release, making it an ideal tracer for the flame front. However, due to the low abundancies and its fast pre-dissociation, LIF-imaging seems to be impossible in unsteady, non-reproducible turbulent systems. LIF measurements were performed in the experiment described above and showed a good correlation of HCO concentration distribution with model predictions [26]. However, comparable information can be obtained when the product of OH and CH₂O concentrations is assessed [27].

It has been shown from calculations that this product compares well with the local heat release rate. Since both quantities can be measured in unsteady systems on a single-shot base, this gives an opportunity to measure heat release and thus the exact position of the flame front in turbulent combustion processes.
Multi-scalar measurements of turbulence-chemistry interactions rely on a variety of Rayleigh, Raman and LIF techniques [28]. Flashlamp-pumped dye lasers, due to their long pulse length, provide high energy pulses ideal for Raman and Rayleigh measurements. Because of their low average power density, high signal levels can be obtained without inducing air breakdown. Spectral resolution of the signal yields simultaneous information about the concentration of the major species and the local temperature. These laser systems used in the intracavity configuration have also been applied successfully to two-dimensional Rayleigh and Raman imaging [29], which has been used to measure temperature and mixing ratio distributions. On the other hand, the long pulses produced by flashlamp pumped dye lasers may be disadvantageous when investigating highly turbulent flows. Other studies using KrF excimer lasers for excitation have been applied successfully to Raman measurements in hydrogen/air flames [30]. Due to the wavelength dependence of Raman cross sections, signal intensities are significantly higher. However, when applied to hydrocarbon flames, strong fluorescence may be induced, which interferes with several of the Raman signals. Thus polarization techniques [31] have been applied to separate the Raman signal, taking advantage of the fact that Raman scattered light, upon excitation with polarized laser light is not emitted isotropically, in contrast to the fluorescence signal. When using Nd:YAG lasers, due to the relatively short pulse duration, air break-down limits are rapidly met. Detailed multiscalar measurements are thus reported using pulse-stretching techniques [32]. A combination of this Raman/Rayleigh system with three different LIF systems was installed in the Sandia CRF, detecting OH, NO and CO. These fluorescence data can be evaluated quantitatively using temperature and species data derived from the Raman measurements, enabling corrections for temperature and quenching effects. Conditional statistics using these multiscalar point measurements in comparison to modeling results reveal significant differences in several cases yield an improvement of model

Figure 14: Images of mixture fraction ($\xi$), scalar dissipation rates ($\chi$) temperatures and OH concentrations in turbulent CH$_4$/air diffusion flames obtained by 2-D Raman, Rayleigh, and LIF spectroscopy [34]
assumptions. OH [33] and NO concentrations, e.g., have been shown to differ systematically from flamelet predictions. Revealing the structure of turbulent flames has found increasing interest and was addressed using laser imaging of temperature, mixture fraction and reactive radicals such as OH, CH and HCO. Simultaneous measurements of these quantities, yielding scalar dissipation rates, are critical for the validation of turbulent combustion models describing molecular mixing and extinction processes. Simultaneous measurements of Rayleigh scattering and fuel Raman imaging provides information about temperature distribution and mixing. Both can be used to further quantify e.g. OH LIF data by correcting for temperature and collisional quenching effects [34]. These measurements showed the correlation of reaction zone width and jet Reynolds numbers and addressed the influence of local dissipation rate on flame extinction.

Three-dimensional representations of concentration distributions [35, 36] yield additional information on the turbulent combustion system. Simultaneous flow field measurements using particle imaging velocimetry (PIV) and planar LIF measurements have been presented for a number of species. The concentration distributions of biacetyl, OH and CH have been measured together with the underlying flow fields using LIF [37] giving a localization of the instantaneous flame front position. The measurements of flame fronts embedded in the flow field gives valuable insight into the interaction of turbulence and chemistry. Flows seeded simultaneously with molecular tracers (biacetyl) and particles have been used for studying differential diffusion. Since particles have diffusion coefficients of essentially zero, particle distributions yield information about turbulent diffusion. On the other hand, the biacetyl distribution is affected by both turbulent and molecular diffusion. Differences in biacetyl and particle concentration can thus be attributed to molecular diffusion [38].

**Swirling Natural Gas Flames**

Swirling flames are widely applied in the field of technical combustion since they provide a high degree of stability at short flame lengths. An intensive turbulent mixing process which is originated by a curved free shear layer with large strain rates can be observed [39]. Earlier studies in similar flames [40, 41] relied on the application of intrusive measurement techniques to determine flow and temperature characteristics. Since these techniques bear major restrictions in highly strained recirculating flows, non-intrusive diagnostic techniques
prove to be clearly superior for the investigation of complex reactive flow systems. Up to now only a limited amount of temperature and species distribution data are available for swirling flames [42]. Especially the NO formation is difficult to observe due to the intrinsically low levels of NO produced in this flame type. Thus, the present study focuses on the experimental derivation of temperature and species concentration data by laser diagnostics within a confined strongly swirling standard flame with internal recirculation which is investigated within the TECFLAM project by different groups applying various experimental techniques [43, 44] which are used for the validation of simulation calculations performed within the project [45, 46, 47]. All investigations are focused on one standard operating condition (swirl number $S=0.9$, equivalence ratio $\phi=0.83$). Whereas for comparison with computational fluid dynamics (CFD) simulations temporally averaged information about temperature and species concentrations are sufficient, for probability density function (PDF) approaches especially correlations between different scalars are of interest. Two-dimensional measurements of these scalars by laser-based imaging techniques allow the assessment of the needed information.

For NO detection in atmospheric pressure combustion systems excitation in the NO A-X (0,0) band gives the best signal-to-background ratio. Furthermore, quantification of signal intensities is feasible, since data on collisional quenching [48] are available. Several rotational lines in the NO-A-X (0,0) band can be excited with KrF excimer laser radiation which is Raman-shifted ($\text{H}_2$, 10bar, 1$^{\text{st}}$ anti-Stokes) to 225nm. The $R_1(21.5)$ rotational line is
chosen to minimize influence of LIF of hot oxygen. For detecting OH, rotational transitions in the A-X(3,0) band can be excited [49] with 248nm readily available from tunable KrF excimer lasers.

For imaging of temperature distributions Rayleigh scattering techniques [50, 51] have shown to be helpful as long as the local Rayleigh cross-sections $\sigma_{Ray}$ are known. Then, at constant pressure, the local gas number density and thus the local temperature $T$ can be calculated from the scattering intensity $I_{Ray}$ by $T \sim \sigma_{Ray} / I_{Ray}$. In terms of Rayleigh-thermometry, premixed methane/air flames have the advantage that Rayleigh cross sections of fresh gas and burned gases are very similar (less than 2% variation for stoichiometric conditions) for premixed combustion. Mixing in the swirl flame which provides the homogeneous conditions necessary for Rayleigh thermometry can be observed by 2D-LIF as well. Tetrahydrothiophen (THT), which is added regularly to natural gas as an odorous component for safety reasons, fluoresces effectively after excitation at 248nm and can therefore be used as an fluorescing tracer.

Simultaneous measurements of temperature and concentration fields allow further quantification of NO-LIF signal intensities by correcting for temperature effects on ground state populations, line shape variations and quenching cross sections. Including temperature-induced variations in total number densities, concentrations (mole fractions) can be calculated from NO number densities obtained directly from the LIF measurements. Furthermore, correlations of temperature and species concentrations are obtained from the simultaneous measurements which are of major interest when comparing with PDF calculations.

Figure 16: Averaged temperature, NO- and OH- concentration distributions within a confined swirl flame. The complete field was measured in different positions.
In-situ Alkali Concentration Measurements in a Coal Combustor

The need for a significant reduction of CO\textsubscript{2} emission from coal combustion requires the development of new concepts to increase the conversion efficiency. An increase in efficiency – to 50% or more – is, in principle, feasible in a combined plant where an additional expansion turbine is included after the main combustion chamber. However, a major issue here is the removal of alkali metal compounds like e.g. NaCl, and KCl, because even at very low concentration levels (down to several ppb), the deposition of alkali vapours can lead to severe damage of reactor parts and the downstream equipment in gas turbines [52]. The in-situ measurement of such low concentrations with high time resolution (1 min or less) requires ultrahigh sensitivity. On the other hand, for coals with high alkali and chlorine content, and for high combustion temperatures (1300–1500°C), concentrations of alkalis in the flue gas may reach even ppm levels. Thus a dynamic range of several orders of magnitude is also needed.

A suitable optical on-line diagnostics method for detecting gas-phase alkali concentrations is the excimer laser induced fragmentation fluorescence (ELIF) technique [53, 54] where alkali compounds (MX) are photodissociated using e.g. 193 nm ArF excimer laser radiation. In the molecular fragmentation process electronically excited sodium Na(3\textsuperscript{2}P) and potassium K(4\textsuperscript{2}P) atoms (M*) can be formed via:

$$MX + h\nu_{\text{Laser}} \rightarrow M^* + X$$

Fluorescence emitted from the excited atoms ($M^* \rightarrow M + h\nu_{\text{ELIF}}$) can then be detected at wavelengths of $\lambda_{\text{ELIF}} = 589$ nm (Na) and $\lambda_{\text{ELIF}} = 768$ nm (K), respectively. The relationship between the fluorescence intensity $I_{\text{ELIF}}$ and the number density of excited atoms $N_{M^*}$ is given by:

$$I_{\text{ELIF}} = C \left( \tau_{\text{eff}} / \tau_{\text{rad}} \right) N_{M^*} \quad \text{(Eqn. 1)}$$

For $I_{\text{Laser}} \alpha(\lambda_{\text{Laser}}) \ll 1$, $N_{M^*}$ is related to the initial number density $N_{MX}$ of the parent MX molecules, their optical absorption cross section $\alpha(\lambda_{\text{Laser}})$, and the intensity of the photodissociation laser, $I_{\text{Laser}}$, by the following expression:
\[ N_{M^*} = N_{MX} \phi(M^*) \alpha(\lambda_{Laser})I_{laser} \quad (Eqn. 2) \]

\( \phi(M^*) \) is the quantum yield for \( M^* \) formation in the fragmentation process. Insertion of Eqn. 2 into Eqn. 1 leads to the final expression:

\[ I_{ELIF} = C \left( \frac{\tau_{eff}}{\tau_{rad}} \right) N_{MX} \phi(M^*) \alpha(\lambda_{Laser})I_{laser} \quad (Eqn. 3) \]

At this point it should be noted that only a small fraction of the alkali molecules (typically about 1%) is actually photodissociated during ELIF measurements leading to very low alkali atom concentrations. In test measurements no significant trapping of emitted fluorescence by alkali atoms was observed unless the concentration of the parent alkali molecules reached quite high values of about 20 ppm. Typical alkali concentrations during the ELIF measurements, where a hard coal was combusted, were in the range 1-65 ppb, depending on the conditions. In a previous investigation [55] the maximum concentration was nearly 800 ppb and was observed in a system without any hot gas filter and for the case were a low quality coal such as lignite was used as fuel. Eqn. 3 contains the ratio of the effective fluorescence lifetime \( \tau_{eff} \) to the radiative lifetime \( \tau_{rad} = 1/A \) (\( A \) is the Einstein coefficient of spontaneous emission) which accounts for fluorescence losses due to collision quenching of excited alkali atoms. In the flue gases of coal combustors, \( N_2, CO_2, O_2, \) and \( H_2O \) are the most important quenching partners with known mole fractions [55]. Therefore the value of \( \tau_{eff} = 1/(A + Q) \) can be determined by calculating the total quenching rate, \( Q = \Sigma_i q_i \), from the quenching rates \( q_i \) of the most important quenching partners. The photodissociation laser intensity, \( I_{Laser} \), could be determined from the measured laser pulse energies and the area of the laser beam. \( C \) describes a calibration factor which has to be determined in separate ELIF experiments using a heatable reference cell to produce well-defined alkali number densities. The ELIF technique was previously successfully applied during a series of measurements at the pressurized fluidised (PFB) bed reactor at the Deutsche Montan Technologie/Essen under industrial conditions (high temperature, high dust load). The reactor is depicted in Figure 17. It includes a lower, bubbling fluidized-bed combustion zone of 1.5 m bed depth and an upper, extended freeboard zone.

After leaving the reactor, part of the ash is removed from the flue gas in a cyclone located right in front of the optical access port for the alkali measurements. To allow operation at 10
bar, the reactor head, flue gas pipe, cyclone and optical access were designed using heat-resistant steel. Care had to be taken to optimize the $N_2$-flushing of the ELIF laser entrance/exit, and fluorescence exit windows in order to minimize dust deposition. By using two detection channels, Na and K could be monitored simultaneously and separately; a detection limit of 0.2 ppb was established for both alkalis at 10 bar total pressure and at a reactor temperature of 800°C [55].

Although, the geometry shown in Figure 17 is the most usual one for fluorescence experiments, it is not absolutely necessary to retain this arrangement. A single-port system has recently been designed [56], which is suitable for large flue gas ducts and conditions of high temperature and pressure. Under such conditions, absorption of the UV laser beam is so strong that typically more than 90% of the beam will be absorbed by the flue gases within 1 cm of entering the flue gas. The single-port arrangement (Figure 18), whereby laser access and fluorescence detection were achieved through the same window, was recently used for measurements in a pressurised circulating fluidised bed (PCFB) pilot plant (Foster Wheeler Energia [FWE], Karhula, Finland [57]). This geometry avoids the requirement for the laser beam to reach across the entire width of the flue gas pipe. In fact, it is only necessary for the beam to illuminate a small section (ca. 1 cm$^{-3}$) of the flue gas to generate an ELIF signal, which can be detected via the optical fibre, as mentioned above.

An alkali concentration history obtained over several hours using the setup depicted in Figure 18 is shown in Figure 19. Measurements were performed in the flue gas of the 10 MW FWE pilot plant after the hot gas filter at a total pressure of 10 bar using hard coal as a fuel. Alkali concentration profiles are shown together with the reactor temperature. As can be seen, the amount of alkali released follows the reactor temperature quite well. The ELIF alkali concentration measurements at the FWE plant could also be compared with measurements using plasma-excited alkali resonance line spectroscopy (PEARLS) [58].
complementary capabilities of the two methods, the PEARLS/ELIF signal ratio gives an indication of the proportions of alkali present in the gas-phase and on aerosols/particles. The ratio is variable, because the amount of aerosols and dust particles depends on the actual conditions in the flue gas.

Figure 18: ELIF setup for in situ alkali concentration measurements with single-port access for a larger scale flue gas duct

Figure 19: Alkali concentration time-history in flue gas of a pressurized circulating fluidised bed (PCFB) pilot plant (Foster Wheeler Energia in Karhula, Finland) measured with the ELIF method using the single-port access arrangement shown in Figure 18
The ongoing developments and refinements of the ELIF method will soon allow reliable and detailed investigations of alkali release and conversion in pressurised coal combustors in full-scale power plants. Furthermore, the development of the ELIF method to detect heavy metal compounds is under way.

**COMBUSTION CONTROL USING NIR-DIODE LASERS**

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 very low emission of pollutants like NO\textsubscript{x} or SO\textsubscript{x} and especially its low overall costs, which even compete with nuclear energy reactors. A common requirement for most energy production processes is the ability for rapid load variations to adapt the total power production of the plant to the public demand. As a consequence there is a need for power plants, which 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 very well suited for this purpose, but there is a proven risk of severe ignition delays. Then a large amount of premixed gas is injected in the combustion chamber, so that the next successful ignition in the multi-burner system will cause a so called “puff”. Severe damage to the combustion chamber often in the multi-10-million-dollar range can be the consequence of such an event. The cause for these ignition delays is still under investigation, but may be partly associated to flame quenching by excess humidity and hence high heat capacity of the primary air. Despite of the use of suction-probe-type extractive methane sensors these events could not be avoided because of the slow response time of these sensors and their lack to gain a methane signal which is representative for the large combustion chamber. In order to maintain the positive properties of large scale natural gas combustion systems under all process conditions, i.e. under frequent and strong variations in total power, and to enable secure ignition and precise active control of the huge multi-burner systems, it would be most helpful to have a versatile in-situ sensor with fast response time for gaseous species and the temperature. We have developed a multi-purpose in-situ absorption spectrometer based upon room temperature near infrared diode lasers, which is able to determine simultaneously multiple species concentrations, namely all major combustion gas constituents (CH\textsubscript{4}, H\textsubscript{2}O, CO\textsubscript{2} and O\textsubscript{2}) and the temperature on a single absorption path. To make this possible it was
mandatory to develop techniques for an efficient and complete correction of the complex disturbances which bury the molecular absorption signals as there are strong and rapid transmission and background emission fluctuations, which are known from other in-situ applications [58, 60], and dynamical changes in the optical alignment of the spectrometer caused by wall deformations due to the large temperature gradients during the start-up procedure. To assure a permanent alignment during the ignition period an active alignment control loop had to be developed. 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 by 16 meters (see Figure 20). Using our multi diode laser spectrometer we demonstrated to our knowledge the first simultaneous in-situ detection of all major combustion species (CH₄, H₂O, O₂, CO₂) and temperature in a the same measurement. The spectrometer was capable of a time resolution of about 1.6 s and a minimum detectable absorption below 10⁻³ OD.

Close coupling between species and temperature signal and strong dependence of the CH₄-signal on burner location could be found. This device should allow an on-line control of the humidity of the furnace atmosphere and a fast and secure detection of ignition delays by unburned CH₄.
Figure 21: In-situ spectra in the 1.65µm spectral window acquired with a current tuned DFB-laser at moderate temperatures immediately after all burners are turned off (Top) and at higher temperatures when level 4 burners were ignited. The top trace shows only the $2\nu_3$-R5 line of methane, while numerous water and CO$_2$-transitions not mentioned in HITRAN92 or 96 show up in the bottom trace which belong to hot bands and overtone combination bands.

Figure 22: Time history of the ignition procedure (Bottom) and the absolute in-situ CH$_4$-concentration (Top) determined in the 1 GWth gas-fired power plant. A close correlation between burner position and the CH$_4$-signal can be found. The increase of methane with decreasing distance between burner and measurement pane indicates the decreasing burn-out of the gases, while the strong increase in CH$_4$- 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, which is disappearing as soon as all burners in the measurement plane are ignited.
In-Situ Monitoring of O$_2$ and H$_2$O in a Full-Scale Waste Incinerator

Combustion of municipal waste can be a valuable source of energy which makes use of the relatively high energy content of the waste. Since fossil fuels are replaced, waste combustion has no negative effects on the CO$_2$ budget, whereas waste disposal in landfills, the most common disposal path in many countries, is responsible for long term emission of CH$_4$ into the atmosphere. CH$_4$ has a nearly 30-fold higher global warming potential than CO$_2$. To take advantage of the thermal conversion process, however, it is compelling to fulfill strict legal emission regulations by maximizing heat release and conversion efficiency of the overall combustion process. This can be achieved by ensuring homogeneous combustion throughout the entire furnace. Since waste shows very strong variations in its fuel parameters, e.g. calorific value and waste humidity, fast, in-situ species and temperature sensors and efficient combustion control strategies, are needed, to allow optimization of the primary process parameters. Over the last years two in-situ sensors were developed in our institute and tested under realistic conditions in a full scale industrial waste incinerator as depicted schematically in Figure 23.

The first sensor allows closed-loop control of the selective non-catalytic reduction (SNCR) process, commonly used on stationary combustion systems to control NO$_x$ emissions. Our...
laser in-situ ammonia monitor (LISA) which is based on a $^{13}\text{CO}_2$ laser allows precise control of the necessary additive injection (NH$_3$ or urea), minimized additive consumption and ensured up to 90% NO$_x$ removal [61]. A second combustion control sensor based on an infrared-scanner-camera for non-intrusive determination of the fuel bed surface temperature [62] allows closed-loop control of the primary air injection, the grate movement and the fuel feed. Meanwhile both sensors are commercialized and available on the market.

The current project, during which on-line sensors for waste incinerators will be developed, aims at the fast in-situ detection of fuel quality fluctuations, and at an active control of the homogeneous combustion process above the solid fuel bed. For this purpose near infrared diode lasers (NIRDL) and high resolution absorption spectroscopy are employed for simultaneous in-situ detection of O$_2$ and H$_2$O along a single absorption path at the end of the secondary combustion zone of a full-scale municipal waste-to-energy plant (see Figure 23). NIRDL are used because they offer a unique combination of advantages (low cost, size and power requirement; room temperature operation; high spectral resolution; long lifetime), which make them most suitable for industrial applications. Their versatile tuning properties – slow and coarse (range: several nm; speed: some GHz/s) by a change of laser temperature, and extremely fast fine tuning (range: tens of GHz; speed: $10^5$ GHz/s) by a modulation of the laser current – enable the detection of the complete profile of an absorption line and application of very efficient noise reduction strategies, so that excellent sensitivities down to the ppm-level could be demonstrated under well-controlled laboratory conditions. However, in particular the scale-up of these sensors to accommodate full-scale industrial processes has proven to be a tough task, since the weak molecular absorption signal can be affected by numerous disturbances. Depending on the used signal processing scheme it might be necessary e.g. to remove the strong thermal background radiation by appropriate narrow-band interference filters.

For the application in the incinerator it was most important to correct for any changes in the effective transmission of the complete light path between laser and detector. These changes can be caused by the quickly fluctuating dust load of the flue gases, window degradation by dust, heat, or chemical attack, vibrations or mechanical deformation of the boiler walls, and refractive index gradients or thermal lensing effects. For this purpose an all-analog electronic on-line transmission correction circuit was developed [63]. The circuit, which uses a double
divider configuration, corrects each individual scan in real time and has to be adapted to the results of a careful characterization of the absolute magnitude, frequency and temporal behaviour of the transmission fluctuations of the specific incinerator. The idea to correct these fluctuations makes use of the diode lasers high speed tuning capabilities, and requires that the scan frequency is chosen well above the fastest transmission variations. Since this way all interferences are frozen and only the molecular signal component changes within the scan time, an electronic correction by division through the quasi-static background transmission signal possible. An additional noise reduction is achieved by averaging consecutive absorption profiles and extracting the absorption signal i.e. the area underneath the absorption line by a fast fitting algorithm.

O₂ was detected via the well known atmospheric A-band \((b^1\Sigma^+ g; v' = 0 \leftrightarrow X^3 \Sigma^- g; v'' = 0)\), a magnetic dipole transition in the 759nm to 770nm region that shows line strengths in the order of \(2 \times 10^{-4} \text{ cm}^{-1} \text{ atm}^{-1}\). By using a continuously tuneable, distributed feedback diode laser, DFB-DL (Sensors Unlimited) we could access any line within the R-branch of the A-band. This minimizes the effect of the line-strength temperature dependence in the absorption signal by choice of an adequate absorption line. Water vapour, which shows numerous strong, rotationally resolved, vibrational overtone and combination bands in the near infrared, was monitored via the relatively weak \(((0,0,0) \rightarrow (1,1,2), (2,1,1))\) rovibrational transitions around 812 nm. This was possible since high power Fabry-Perot-type lasers (Mitsubishi, 30mW) are available for this spectral range. However, their discontinuous tuning behaviour made a careful search for coincidences with strong high-temperature H₂O absorption lines necessary. Theoretical absorption spectra based on the HITRAN 92 database were calculated and verified by laboratory measurements in a high temperature absorption cell in the temperature range 300–1000°C. The laboratory studies had to be performed because strong discrepancies between measurements and HITRAN 92 results were observed particularly at high temperatures.

The simultaneous single-path in-situ detection of O₂ and H₂O was performed in an incinerator with a boiler height of 18 m, a diameter of 4 m, with a thermal power of 40 MW. Combustion in such a waste incinerator takes place at atmospheric pressure with flue gas temperatures above 850°C, air ratios around 1.8, and O₂ or H₂O concentrations around 8 Vol.-% and 18 Vol.-%, respectively. The absorption path was separated one meter from the
furnace wall and located at the end of the secondary combustion zone (12.7 m above the fuel bed and 8.7 m above the secondary air injection nozzles). Lasers and detectors were mounted onto a flange on the furnace wall without water cooling or vibrational damping. Two opposing optical ports with 30 × 50 mm windows placed under the Brewster's-angle provided optical access to the furnace. Air purging of the windows was essential to prevent rapid condensation of opaque ammonia sulfates originating from the SNCR injection ports one meter below the windows. Both lasers were scanned independently over the selected absorption line pairs by a triangular phase locked current modulation of each laser at 1 kHz. A dichroic beamsplitter superimposed the two collimated laser beams, and a gold coated mirror directed them through the furnace. An identical dichroic beamsplitter separated the two wavelength components of the transmitted light. The two following interference filters minimized the cross talk between the two wavelength channels and suppressed thermal background radiation. The resulting detector signals were pre-amplified, transmission corrected, filtered by analog correction electronics and digitized with 1.2 M sample/s by a dual channel 12 Bit A/D converter plugged into a computer. 200 consecutive scans were averaged for additional noise reduction. A fitting procedure extracted the concentration value assuming a Lorentzian line shape function and a quadratic background polynomial. Both laser wavelengths were actively stabilized to increase system stability. The dual-species spectrometer was exposed to several weeks of testing under various load conditions. Typical results, which represent the first simultaneous, single-path in-situ measurements of oxygen and water using AlGaAs-diode-lasers in a full scale incinerator, are shown in Figure 24. The steep concentration changes are caused by grate agitation and fuel feed events. Comparing the two in-situ signals, the expected close temporal coupling between O₂ consumption and H₂O production [due to the overall reaction CₓHᵧ + (x + y/4) O₂ → y/2 H₂O + x CO₂] could be verified experimentally. Since no alternative in-situ species sensors are available so far, the laser signals were tested by comparison with standard gas sensors: an extractive ZrO²⁻ sensor for O₂ and an extractive non-dispersive infrared (NDIR) absorption sensor for H₂O. Both standard sensors analyse the gas at the relatively cold flue gas duct 45 m downstream of the laser measurement location (Figure 23), and are expected to show severe artifacts like signal time-delays due to the necessary gas transport to the sensor. However, after removal of these signal delays and low-pass filtering of the laser signals to compensate for the slower time response of the extractive sensors, the in-situ and reference signals show good agreement (Figure 24) indicating good linearity of the in-situ signals. The sensitivity was in
the order of 0.3 Vol.-% O₂ or H₂O. The major advantages of the in-situ measurement technique presented are the high time resolution of about 1 s, and especially the fact that the in-situ signals are much faster than the delayed reference signals (with a delay of 30 s for O₂ and 60 s for H₂O). This time gain can either be used to improve the bandwidth of a control loop significantly, or to setup a feedback system despite relatively slow actuators. These properties together with the complete absence of corrosion problems make a laser-based single-species measurement already very attractive for active combustion control purposes.

Even more interesting is the described possibility for simultaneous multi-species detection in a single-path, because all species are monitored in-situ with identical time response and within the same measurement volume, so that the local chemistry can be investigated directly without any errors due to different sensor response times and adsorption or chemical reaction effects in the probe lines. It should therefore be possible to monitor changes in the C/H-ratio of the waste (i.e. colorific value) on-line. On the other hand, if the C/H-ratio is constant, the combined in-situ O₂/H₂O signal allows to monitor non-combustion-related sources of water, like changes in waste humidity. In the next development step we will pursue a permanent installation in a full scale incinerator. In addition, we will extend our spectrometer to allow
simultaneous O₂, H₂O and CO₂ detection, so that calorific values and the waste humidity can be determined simultaneously.

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