Analysis of Radicals in Combustion Processes

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Abstract. This work reports on a variety of radical analysis applications in combustion that are performed in the laboratories of the Paul Scherrer Institute. Planar Laser-Induced Fluorescence and Resonant Holographic Interferometry is applied to the two-dimensional imaging of radicals in flames. The potential of Four-Wave Mixing Spectroscopy for non-perturbing combustion diagnostics is investigated and the method is applied to radicals in flames. Phase-Conjugation and the use of two different input frequencies are utilized to address typical problems in a combustion environment, *i.e.*, lensing effects due to temperature and density gradients and congested spectra of the analyte due to significant thermal population of the ground state.
More fundamentally, experiments are aimed to obtain detailed knowledge on the spectroscopy of many important radicals that are not yet characterized sufficiently for diagnostic purposes. A molecular beam apparatus has been set up where the collisionless and cold environment provides well defined experimental conditions to produce and investigate the relevant radicals. Finally, temporally and spectrally resolved fluorescence decays in the picosecond time domain are measured in an atmospheric pressure flame. These experiments yield results on vibrational and rotational energy transfer that are required for quantitative laser-induced fluorescence measurements.

1. Introduction

Free radicals are significant as intermediates in the chemical reactions of combustion processes. H, O, and OH are of eminent influence on ignition, heat release, flame propagation, and flame quenching. For example, the reaction OH + CO → H + CO_2 is the dominant source of CO_2 in the oxidation of hydrocarbons. Likewise, nitrogen and sulfur containing radicals are involved in NO_x and SO_x formation. Measurements of the location and concentration of such radicals are, therefore, useful for inferring the intensity and location of important chemical processes. Furthermore, these measurements are necessary to validate computer simulations of combustion processes. However, free radicals require highly sensitive detection methods due to their ephemeral nature as intermediates.

We report on the development of laser diagnostic techniques and their applications to the analysis of radical species in flames. The methods are generally non-perturbing, sensitive and capable of simultaneous high spatial and temporal res-

olution. Spatial resolution on the order of 50–500 μm are typically realized and are sufficient to resolve unsteady and turbulent phenomena in practical flames. Temporal resolution from the sub-picosecond time scale up to microseconds is routinely achievable nowadays and allows the *in situ* observation of inter- and intramolecular dynamics besides the flow processes occurring in combustion systems. In addition, laser detection techniques may provide special features like two-dimensional images or laser-like signal beams that ensures collection of the entire signal and permit the suppression of stray light by remote probing. Therefore, disturbing effects of luminous or scattering environments that are frequently encountered in combustion research are reduced.

2. Radical Analysis Applications in Combustion

2.1. *Qualitative Analysis of the OH Radical to Localize the Reaction Zone in a Commercial Burner*

The development of a new generation of oil-burning furnaces with high efficiency and low pollutant emission is stimulated by environmental concerns and more stringent regulatory constraints. Up to now, engineering efforts have been based to a considerable amount on empirical methods. But further improvements are increasingly more difficult to achieve. Non-intrusive laser-diagnostic methods provide a new tool for the characterization of a combustion device and open new ways for
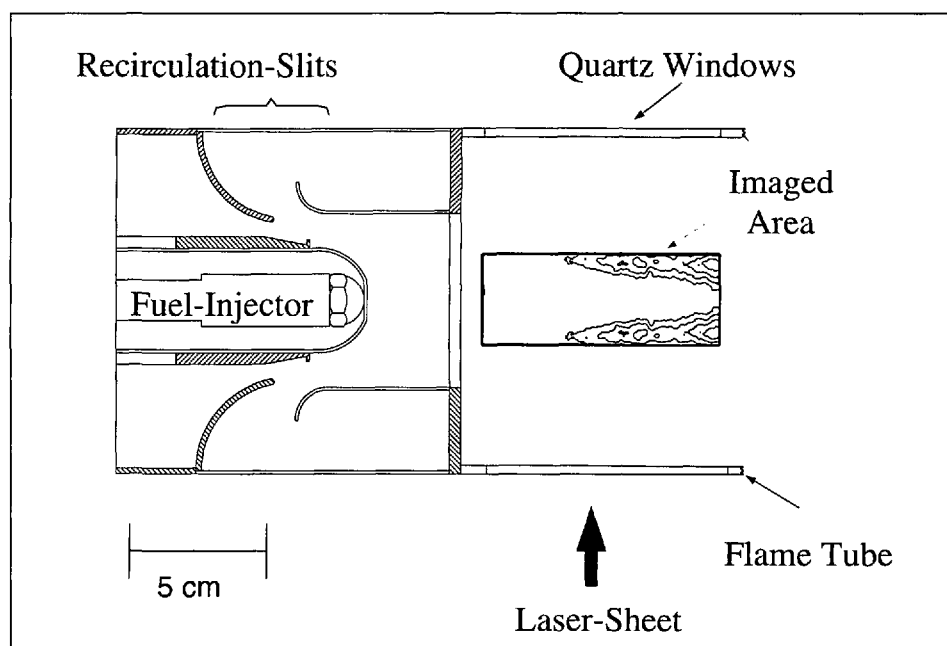
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Fig. 1. *Geometry of the fuel/air mixing device and the imaged area in a 100 kW oil-burning furnace.* See text for details.

optimization. Of particular interest is the imaging of the reaction zone by Planar Laser-Induced Fluorescence (PLIF). Most commonly, the hydroxyl radical is mapped since it serves as an indicator of the chemical reaction front of the flame and the subsequent effect of fluid motion on the state of the burned gases. Such investigations in a 100 kW *natural gas flame* have been reported [1]. However, for the application of PLIF of OH to *liquid-fueled spray flames* additional problems have to be addressed. Difficulties arise from intense interfering emissions caused by liquid and gaseous fuel. We have suggested recently a relatively simple method for the particular case where OH-radical concentrations are not required and only the localization of the reaction zone is of interest [2].

Fig. 1 shows the optically accessed area (30×100 mm^2) of a 100 kW oil-burning furnace and the fuel/air mixing device. The output of a broad-band XeCl excimer laser is formed into a sheet (0.5×50 mm^2) by a cylindrical lens of 300 mm focal length. Typical laser pulse energies are ≈ 100 mJ/pulse. The laser sheet enters the combustion chamber perpendicular to the flow axis through two quartz windows. The sheet leaves the furnace on the opposite side through a second set of two quartz windows. The laser-induced fluorescence is observed at a right angle through a third set of windows. A gated, image-intensified CCD camera images the entire optically accessible region by utilizing a quartz objective.

Observation of the OH radical is performed by applying a special fluorescence filtering method [2]. Briefly, the OH *and* the broadband emission from large hydrocarbons present in the unburned fuel are imaged by using a narrow band interference filter centered at 320 nm (FWHM of 10 nm). A second image is obtained by

applying a broadband transmission filter passing light from 350 to 500 nm. Since the OH fluorescence is significantly suppressed above 345 nm, the second image contains the hydrocarbon fluorescence only. A subsequent subtraction of the two images yield the OH distribution. A contour plot of a typical hydroxyl map is reproduced as an inset on the imaged area shown on *Fig. 1*. Several burner configurations have been measured and a good agreement with numerical simulations is found [3][4]. The observation of a slightly asymmetric spray with respect to the central axis of the burner is an additional, unexpected result. Such information is of importance to the engineering and development work.

2.2. Quantitative Analysis of Combustion Processes

2.2.1. *Absolute Concentration Measurements by Multiplex Spectroscopy (DFWM and Absorption) of OH and S$_2$*

In the outgoing century low sulfur fuels have been available minimizing the problems due to toxic and corrosive sulfur compounds formed in combustion processes. Due to declining natural resources, low sulfur oil is increasingly limited and fuels containing large quantities of sulfur oil (1–10% by wt.) are being used. Such a high abundance of sulfur in fuels significantly affects the combustion process (*i.e.*, flame temperature, flame speed, sooting limits, NO$_x$ emissions). Consequently, greater attention is required to study sulfur reactions and the resulting distribution of sulfur species in combustion environments.

To verify the sulfur chemistry mechanisms assumed in numerical simulations, degenerate four-wave mixing (DFWM) is applied to the measurement of S$_2$ and OH concentration profiles in a model flame. In fact, DFWM has received renewed attention during the past several years because

of its potential role as an optical diagnostic method. The wave-mixing process used in DFWM produces a coherent, highly collimated, and spectrally bright signal beam. These properties permit efficient rejection of interfering radiation, allow measurements to be obtained remotely, and permit the use of small optical ports for input and output beams. These features are in contrast to those of linear processes such as laser-induced fluorescence (LIF), for which the signal radiates nearly isotropically in space, making signal collection and background discrimination more difficult. Although nonlinear processes are generally considered to be weak, DFWM is a completely resonant process and has high sensitivity for detecting trace molecular species.

The arrangement of a typical four-wave mixing experiment is shown in *Fig. 2*. The output of the laser system is split by a 50% beam splitter (BS1). The reflected part of the beam is directed by a 10% reflectivity beam splitter (BS2) and two mirrors toward the interaction zone (probe beam). The beam transmitted by BS1 is reflected by a turning mirror into the flame (first pump beam). The counter-propagating pump beam (second pump) is conventionally produced by reflecting the first pump beam back onto itself by a mirror (M1). Alternatively, it can be produced by Stimulated Brillouin Scattering (SBS) in hexane (see below).

Substantial signal to noise ratios are achieved by DFWM since a coherent signal beam is generated that is essentially background free. Therefore, accurate relative profile measurements of OH and S$_2$ above the flat-flame burner are achieved in a straightforward manner. However, difficulties arise in obtaining absolute concentrations by using DFWM, mainly because an accurate measurement of the interaction volume of the overlapping input beams is difficult to achieve.

Complementary to DFWM, absorption spectroscopy is being used extensively in combustion for absolute concentration measurements where a sufficient decrease of transmission is observed. At positions of high OH occurrence, absorption measurements of the OH radical are feasible and performed simultaneously to obtain absolute hydroxyl concentrations. These results are subsequently used to calibrate the DFWM signals of OH and S$_2$. Thus, two spectroscopic methods, DFWM and absorption, are used in tandem in order to observe two different trace species simultaneously (Multiplex Spectroscopy). The specific advantages of each technique is exploited to yield absolute
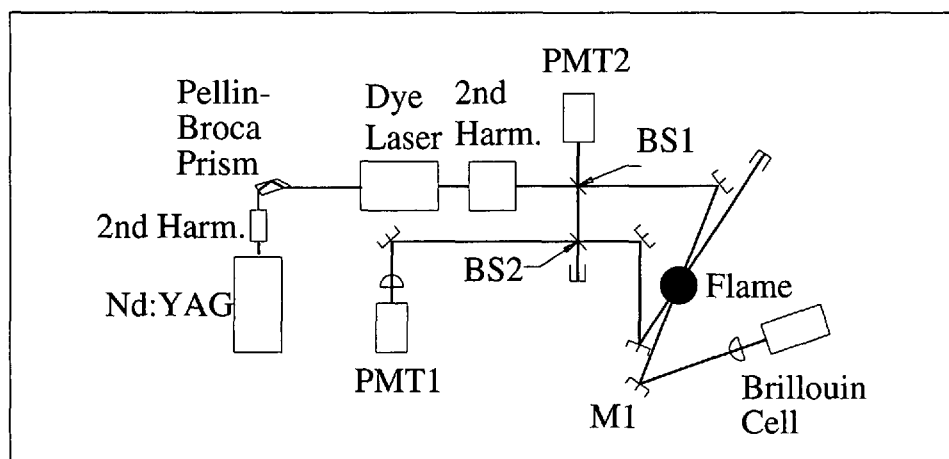

Fig. 2. *DFWM Experiment.* See text for details.

number densities as well as a high sensitivity. It must be emphasized, that the low sensitivity of absorption spectroscopy makes direct concentration measurements of S_2 impractical for the investigated combustion process.

Shown in *Fig. 3* are absolute spatial concentration profiles for OH and S_2 as a function of height above the surface of a flat-flame burner [5]. The premixed propane/air flame is run at a fuel/air ratio of 1.4 and a SO_2 mole fraction of ≈ 0.01. The peak concentration of OH is observed at a height of ≈ 2 mm indicating the flame front region. Downstream of the peak radical concentration, recombination reactions take place and are reducing the OH concentration to ≈ 100 ppm. On the other hand, S_2 is formed preferably in the post-flame region. An increase of the S_2 concentration from (273 ± 162) ppm at a height of 2.5 mm to (689 ± 419) ppm at 6.5 mm is observed in the present experiment.

The main features observed in this experiments are in qualitative agreement with the proposed reaction mechanism for the sulfur chemistry in $H_2/O_2/SO_2$ flames [6]. S_2 and other reduced sulfur species (SH and H_2S) are formed downstream of the OH radical peak. In this region of the flame the temperature and the major radicals are decreasing and S_2 is formed in the presence of S_2O. After formation, the diatomic sulfur species diffuse back toward the burner and undergo exothermic reactions to form the oxidized species. The species profiles computed in the simulation show a similar increase of the S_2 concentration in the post-flame region. Even though a qualitative agreement of the profiles is found, the model calculations underestimate the absolute S_2 concentrations by two orders of magnitude [7], indicating that important intermediates and reactions could have been omitted.

2.2.2. *Temperature and Relative Concentration of OH and NH in Combustion Environments by Four-Wave Mixing Spectroscopy*

As mentioned above, DFWM has been shown to be a technique with excellent selectivity and a sensitivity for minority species approaching that of laser-induced fluorescence. Concentration measurements and temperature determinations by observing the rotational state distribution have been demonstrated. However, in practical devices like internal combustion engines, furnaces and coal gasifiers, temperature- and density-gradients as well as turbulence cause spatial fluctuations of the refractive index l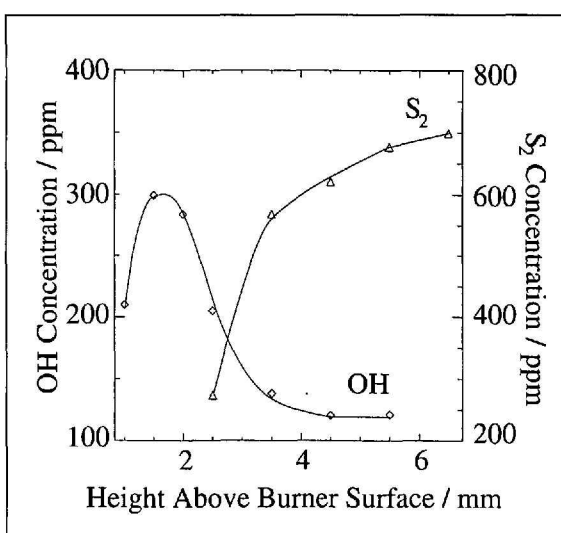eading to lensing effects. The overlap of the signal generating beams is, therefore, disturbed and is leading to a significant reduction of the efficiency of the DFWM technique.

Our research group at the PSI in conjunction with colleagues from United Technologies Research Center (UTRC) have developed a novel configuration for four-wave mixing experiments that circumvent the problems of incident beam distortion that affect the overlap volume by optical phase-conjugation [8] (*Fig. 4*). As mentioned above, the mirror M1 (*Fig. 2*) is conventionally used to back reflect the first pump beam into itself to produce the second pump beam. Alternatively, the mirror is tilted to turn the first pump into a quartz cuvette containing hexane. The counter-propagating, phase-conjugate beam produced by SBS serves then as second pump beam. Because of the phase-conjugate properties of the DFWM signal in respect to the probe beam and the phase-conjugate pump beams produced by SBS,

we refer to this new technique as Double Phase-Conjugate Four-Wave Mixing (DPCFWM).

The novel technique simplifies conventional DFWM by relaxing alignment constraints and sensitivities to index-of-refraction gradients in typical combustion experiments. Furthermore, by replacing the PMT1 by an intensified CCD camera and forming the pump beams into a sheet using telescopic optics, two-dimensional images of an analyte species can be obtained. A turbulent non-premixed methane jet flame emerging from a nozzle has been imaged [9]. Comparing DPCFWM using SBS to the conventional DFWM shows significantly better signal-to-noise using the double phase-conjugate geometry. The data from the conventional DFWM show much larger fluctuations. Often, no signal can be recorded which we attribute to misalignment of the sheets due to thermal gradients in the flow. In contrast, the

Fig. 3. *OH and S_2 concentration vs. height above a propane/air/SO_2 flat-flame.* Total errors for OH and S_2 concentrations are ± 30 and $\pm 60\%$, respectively.
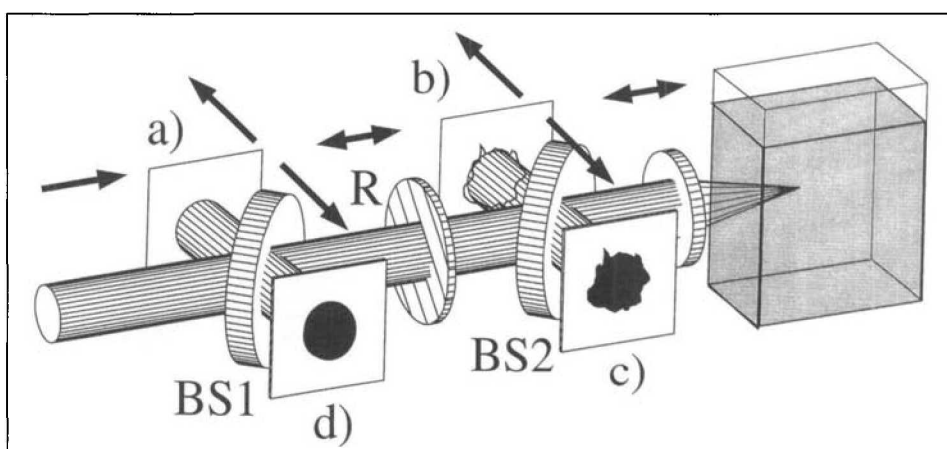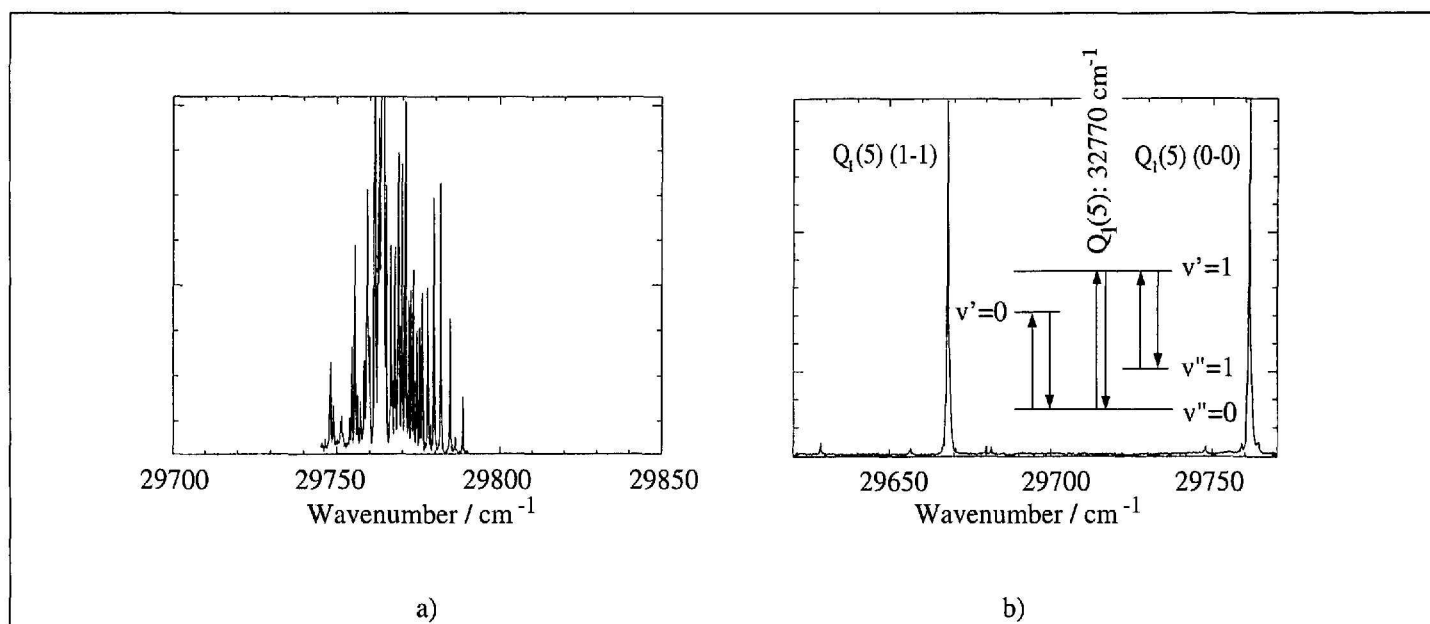

Fig. 4. *Phase-conjugation by SBS.* A laser beam passes through a beam splitter (BS1) and its profile can be monitored (*a*). The beam then passes through a randomizing medium (R), *i.e.* a flame. The sampled image (*b*) displays a distorted beam. The beam is focused into the *Brillouin* cell and a backward going wave is generated which still possesses the distortions (*c*). However, the beam will identically follow the incident beam. When this backward going wave passes through the medium (R) the second time, the original distortions are completely removed which can be verified at (*d*).

Fig. 5. *Spectral simplification of the NH spectrum by intermediate level labeling. a)* Congested one-color DFWM spectrum and *b)* simplified two-color RFWM by tuning the PUMP laser to the $Q_1(5)$ transition and scanning the frequency of the DUMP laser.
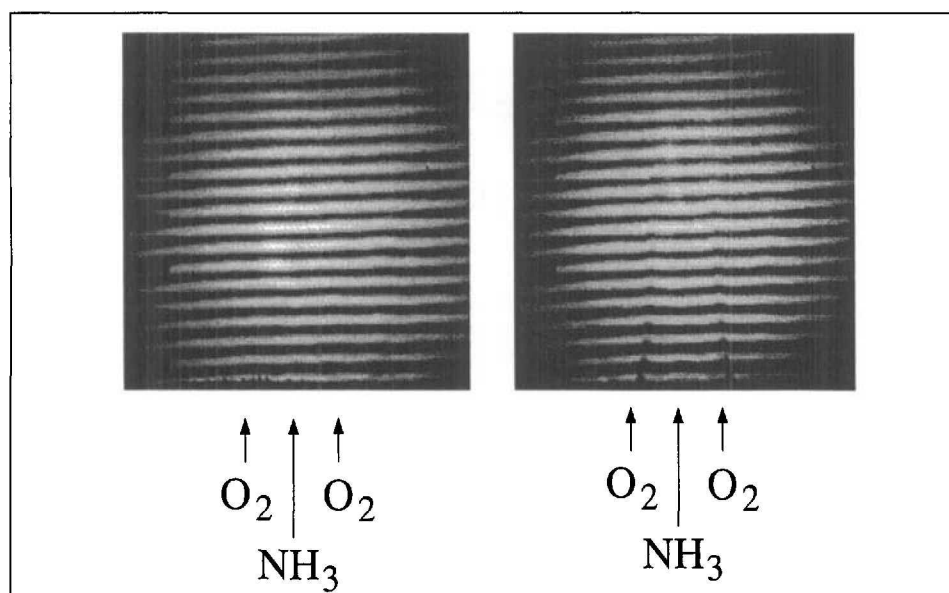

Fig. 6. *Holographic interferometry. a)* OFF and *b)* ON resonant. See text for details.

double phase-conjugate geometry provide reliable and consistent data even in the presence of the turbulent flame.

A further development for the application of four-wave mixing processes for combustion has been pioneered at the PSI [10]. The use of two separate input frequencies provides an added advantage because a signal is obtained only when both frequencies interact with distinct molecular transitions simultaneously. As a consequence of the increased selectivity, congested one-color spectra are simplified dramatically. *Fig. 5* demonstrates the simplification of the rotational DFWM spectrum of the NH radical in the Q-branch region in the (0–0) band of the $A^3\Pi$-$X^3\Sigma^-$ electronic transition. Shown in

Fig. 5, a is the conventional one-color DFWM spectrum. In contrast, *Fig. 5, b* depicts the two-color resonant four-wave mixing (RFWM) spectrum on the same frequency scale. The pump laser is tuned to overlap with the $Q_1(5)$ transition in the (1–0) band at 32770 cm^{-1}. Scanning the frequency of the dump laser in the vicinity of 337 nm (29674 cm^{-1}) reveals two strong transitions only, originating from the $Q_1(5)$ rotational transitions in the (1–1) and (0–0) vibrational bands as shown on the inset of *Fig. 5, b*. The signal-to-noise ratio of ~ 100:1 is typical for the two-color RFWM experiments performed on NH.

The method has the potential to monitor trace species that do not fluoresce or have poor fluorescent quantum yields (*e.g.*

radicals like CH_3, C_2H, C_2H_3, and C_6H_5). In particular, we believe that the technique is advantageous for the detection of polyatomic molecules displaying a congested one-photon spectra due to thermal population of many ro-vibrational levels in the ground state. The resulting one-color broad-band spectra prevent selective detection of specific levels and are, therefore, not useful for diagnostic purposes. Intermediate level labeling by using two input frequencies that interact with two distinct molecular transitions can simplify such spectra significantly, enabling the selective detection of such molecules.

2.2.3. *Two-Dimensional Concentration Profiles of OH and NH by RHI*

Resonant Holographic Interferometry (RHI) has gained attention as a non-intrusive technique in reacting gaseous flows since it combines the species selectivity of spectroscopy with the high sensitivity and the substantial spatial resolution capabilities of interferometry.

Near an electronic transition of a molecule, a light wave will experience an attenuation of its intensity due to absorption, originating from the imaginary part of the complex refractive index. In parallel, the substantial gradient in the real part of the refractive index gives rise to a relative phase shift between two waves of slightly different frequencies, within the absorption width, as they pass through the flame. The bulk refractive index of the flame is eliminated by holographic interferometric subtraction, yielding the net contribution of the resonance effect to the refractive index. For a typical experimen-

tal setup, the two waves are recorded on the same holographic plate and then reconstructed simultaneously to interfere. Fringe shifts are observed in areas where the resonant species have introduced a refractive index difference for the two exposure frequencies.

In order to provide the two frequencies required for RHI, we apply optical phase-conjugation by Stimulated *Brillouin* scattering (SBS) [11] (see *Fig. 4*). The resulting beam is phase-conjugate to the incoming light yielding a second 'laser beam' of high temporal and spatial quality. In fact, the presence of a time varying electric field in a liquid (or crystal or even a gas) gives rise to a time-varying electrostrictive strain and is thus capable of driving acoustic waves in the medium. The acoustic wave modulates the optical dielectric constant and causes an exchange of energy between electromagnetic waves whose frequencies differ by an amount equal to the acoustic frequency. The effect is analogous to stimulated *Raman* scattering with the acoustic waves playing the role of the molecular vibrations. Thus, SBS introduces a shift towards lower frequency, due to the diffraction of the beam on the acoustic wave. The frequency shift of ~8.5 GHz introduced by the phase-conjugation matches approximately the linewidth of many molecular transitions at typical flame temperatures.

For the experiment, a slot burner is used to stabilize a NH_3/O_2 flame. The object beam passes parallel to the slot axis and samples a two-dimensional flame and consequently a two-dimensional refractive index field. The two following figures show the resonant effect. In *Fig. 6, a* both wavelengths are OFF resonance, and only reference fringes are seen, since the two wavefronts are slightly tilted in respect to each other. The bulk refractive index of the flame has been eliminated. In *Fig. 6b* the two wavelengths are tuned into resonance of NH and fringe shifts appear where the two wavefronts interact with the NH radicals. Applying a computation of the complex refractive index, quantitative information on the NH concentration distribution is obtained.

2.3. *Picosecond Analysis of the Collisional Deactivation of OH in Flames*

As shown above, laser based methods such as LIF, PLIF and four wave-mixing spectroscopy are widely used as diagnostic tools in combustion. However, a detailed knowledge of the collisional deactivation of the excited electronic state is required to obtain quantitative results. Quenching, vibrational (VET) and rotational energy transfer (RET) cross sections of OH with important collision partners (such as H_2O, N_2, CO_2, CO, O_2, H_2, H) have been measured with different

techniques and for temperatures ranging from 300 to 2300 K. Despite the large number of experimental rates published in the literature, the final aim of these studies which is the accurate prediction of the temporal evolution of the state population upon excitation has yet to be accomplished.

Unfortunately, quenching, VET and RET are acting on a similar time scale and are, therefore, difficult to separate. Most of the rates have been measured in low pressure flames where nanosecond pulses are adequate. However, time resolved experiments in atmospheric pressure flames require picosecond resolution. In this work, we obtain detailed information on the inter- and intra-vibrational relaxation on the picosecond time scale. Measurements of temporally and spectrally resolved fluorescence of the OH $A^2\Sigma^+(v' = 0, 1) \rightarrow X^2\Pi(v'' = 1, 0)$ bands upon picosecond excitation of the OH $A^2\Sigma^+(v' = 1, N' = 4, 12)$ states are presented. These measurements permit a comprehensive investigation of the collisional deactivation of the excited molecule, *e.g.*, the study of LIF quenching, VET and RET.

A Ti: Sapphire laser system is utilized that produces pulses of 1.5 ps duration. The UV beam is focused into the burned gas region of a premixed laminar methane/air flame. The laser induced OH fluorescence is imaged through a monochromator onto the entrance slit of a streak
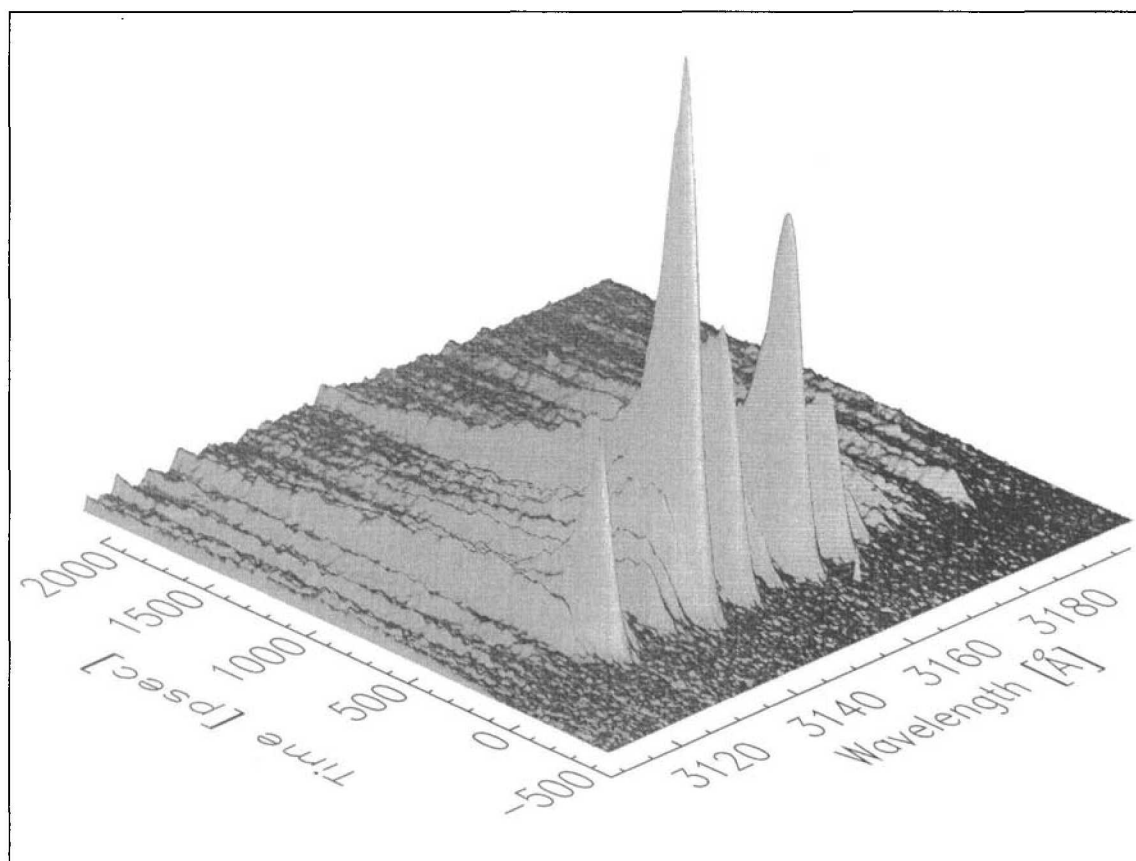

Fig. 7. *Temporally and spectrally resolved fluorescence of OH upon excitation of the* $Q_1(4)$. See text for details.
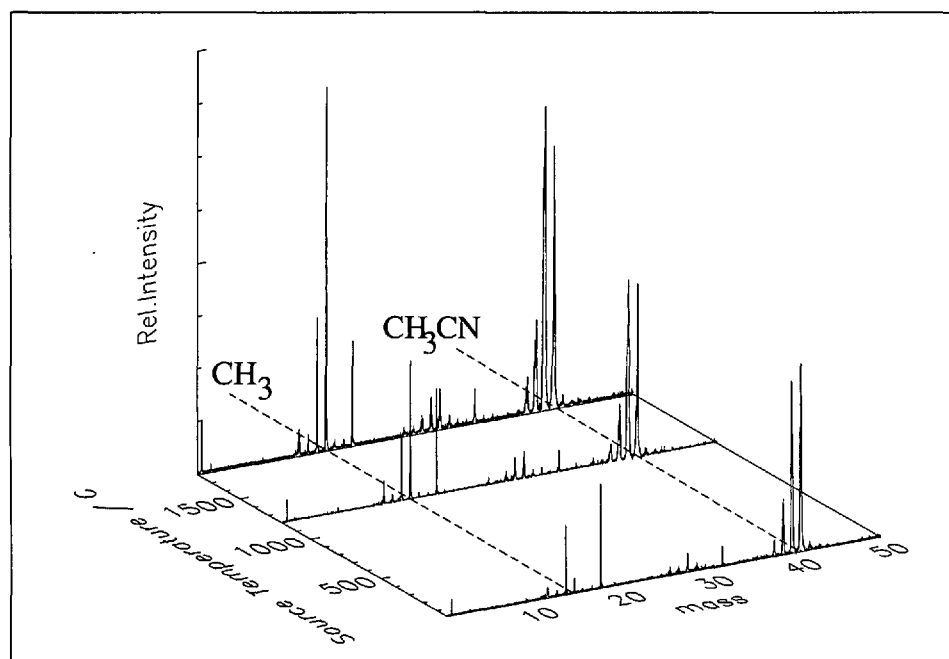
Fig. 8. *Pyrolytic production of the methyl radical in a molecular beam*

camera and stored on a slow scan CCD. The streak camera is set to record a time window of 7 ns.

The temporally and spectrally resolved fluorescence emission upon excitation of the $Q_1 4$ transition in the OH $A^2\Sigma^+(v' = 1)$ $\leftarrow X^2\Pi(v'' = 0)$ band is shown in *Fig. 7*. We have proposed an empirical model to describe the time dependence of quenching and VET, where the time dependency emerges from the thermalization process of the rotational state population upon excitation of a single state [12]. This model permits the determination of state specific rates for quenching and VET. We have also shown, that RET within the excited vibronic state can be reasonably well described by using the energy corrected sudden approximation (ECS) theory [13] in combination with a power gap law. Within the model, RET is described using three parameters only: the cross section, the collision length and the exponent of the power gap law. Finally, we want to point out, that such time and spectrally resolved measurements are very useful to validate LIF simulation codes.

2.4. Production and Characterization of Flame Species in the Controlled Environment of a Molecular Beam

A variety of radicals, in particular diatomic species, have been characterized sufficiently for diagnostic purposes. Some examples are OH, CH, C_2, CN. However, the detailed spectroscopy of many important radicals relevant to combustion is unknown. As a consequence, experimental and theoretical work is required to obtain fundamental spectroscopic data.

Unfortunately, a flame consists of a large number of different molecules that interact in regions of high temperature and density gradients. Such an environment obstructs the development of detection methods and the characterization of the flame radicals.

In order to provide a controlled environment for the investigation of radical species a molecular beam apparatus has been set up. As an alternative to the more conventional photolytic production of radicals [14] a pyrolytic source has been built following the original design of *Chen* [15]. A neon gas pulse with an appropriately designed organic precursor is expanded through a silicon carbide tube that is resistively heated to 1800°. The residence time in the hot zone is on the order of μs and produces specific radical species by unimolecular thermal dissociation. Immediately after the reaction zone the species are expanded into high vacuum to form a supersonic molecular beam. The collision free environment inhibits recombination or further decomposition reactions.

For example, *Fig. 8* shows the production of the methyl radical from CH_3CN precursor molecules by the pyrolysis source. Photoionization and mass spectrometry is utilized to characterize the radicals emerging from the pyrolytic source. Since femtosecond laser pulses are used, little or no fragmentation of the molecular ions take place. Consequently, the radicals emerging from the pyrolysis source are detected unambiguously in the mass spectrum. At 1800°, the CH_3 radical is most abundant in the beam. Typical number densities of these radicals are ≈

10^{14} cm^{-3}, sufficient for further analysis by the spectroscopic methods applied in this laboratory: LIF, one and two color four-wave mixing, MULTIPLEX spectroscopy, multiphoton ionization and mass spectrometry. In addition, work is under way to investigate combustion relevant reactions of radicals by using femtosecond pump/probe techniques.

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