RADIATION FROM HYDROGEN JET FIRES INVESTIGATED BY TIME-RESOLVED SPECTROSCOPY

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ABSTRACT

Jet fires develop on release of hydrogen from pressurized storage depending on orifice, pressures and volumes. Risks arise from flame contact, dispersion of hot gases and heat radiation. The latter varies strongly in time at short scales down to milliseconds caused by turbulent air entrainment and fluctuations. These jets emit bands of OH in the UV and water in the NIR and IR spectral range. These spectra enable the temperature measurement and the estimation of the air number of the measuring spot which can be used to estimate the total radiation at least from the bright combustion zones. Compared to video and IR camera frames the radiation enables to estimate species and temperatures distributions and total emissions. Impurities generate continuum radiation and the emission of CO_2 in the IR indicates air entrainment which can be compared to CHEMKIN II calculation of the reaction with air.

1.0 INTRODUCTION

Hydrogen release on accidents might generate hot flame jets or explosions on ignition, which is likely at nearly all conditions [1-3]. Depending on the properties of releases the mixture with air or oxygen will determine the subsequent effects. The explosive reactions occur in wide ranges of fuel/oxidizer compositions with flame velocities up to more than 100 meter per second, which are strongly enhanced by turbulence especially in spherical explosions [4-6].

Hydrogen combustion in air emits heat mainly by broad H_2O bands in NIR and IR spectral range and the UV emission is generated by the dominant radical O-H [7-10]. Especially, in the case of large cloud explosion, the risk of heat radiation is commonly underestimated due to the non-visible flame of hydrogen-air combustion. In realistic industrial cases explosion accidents will occur accompanied by the entrainment of contaminants inorganic and organic substances. These may produce soot and carbon oxide and increase the total heat radiation, substantially. When pure hydrogen burns in air the air content at spot observed might be estimated by the CO_2 which is present normally in the air. The UV and the NIR/IR spectra measured are normally used for determining the temperature. The used fast scanning spectrometers enable a time resolution in the 1 - 10 ms range and have been often applied to the transient combustion of propellants and pyrotechnics (see e.g [11]) but was already applied to hydrogen combustion and flame jets [8-10, 12]. Turbulent hydrogen/air diffusion flames were investigated by Gore et al. [7] and the relevance to turbulence mechanism shown [13]. The radiation from flame jets was also investigated in some detail [14-16] and analysed with RADCAL [17].

The purpose of this study was to estimate the heat radiation emitted from a highly transient hydrogen flame jet depending on the initial storage pressure in reservoir explosions. These experiments were also investigated by high speed cameras and IR camera, the results together with the experimental set-up of which are published in a separate paper [18]. The evaluation concerned the temperature and the species concentration especially also carbon dioxide to estimate the air entrainment at the measuring

spot by analysis of the H_2O/CO_2 ratio which was already proposed [12]. In addition, the total radiation should be estimated.

2.0 EXPERIMENTS AND DATA EVALUATION

The experimental set-up is described already in a separate paper presented in this conference [18] including the positions of the measurement systems and the spectrometer as well. The release of hydrogen from 5 l reservoir was to be studied using high speed and IR camera technics which have to be compared to spectroscopic measurements. The reservoir could be operated up to 400 bar and be opened by a rupture disc to release the stored hydrogen with an opening of a diameter of 10 mm. The experiments evaluated were run with storage pressures of 100, 180 and 260 bar. The high pressure storage means that transient hydrogen jets of high momentum are generated deploying into flame jets close to the nozzle of release. It is clear that such jets are strongly fluctuating by the induced turbulence. An analysis of such jets requires time resolved spectroscopy.

Time resolved spectroscopy can be provide from available equipment which consists of fast scanning UV-spectrometer to analyse the OH band in the spectral range of 280 to 325 nm which is commercially produced. The used spectrometer is a UV/VIS grating imaging spectrometer in Czerny-Turner-arrangement with a focal length of 498 mm (Andor Shamrock A-SR500i B2). Six different gratings are available with different resolutions. Gratings with 1200 l/mm and different blaze angles were used to cover the wavelength range from 200 to 900 nm. The spectrometer is coupled to an Si-CCD-camera with 256 x 1024 pixels and a maximum speed of 1.000 spectra / s in full vertical binning mode (Andor CCD DU920P-UV-BR-DD). Mercury-argon and neon lamps were used to calibrate the wavelengths of the spectra. To correct the intensity distribution for the different sensitivities of the gratings and the CCD-camera pixels for different wavelengths a tungsten strip lamp with a defined radiation capacity was used for a relative intensity calibration.
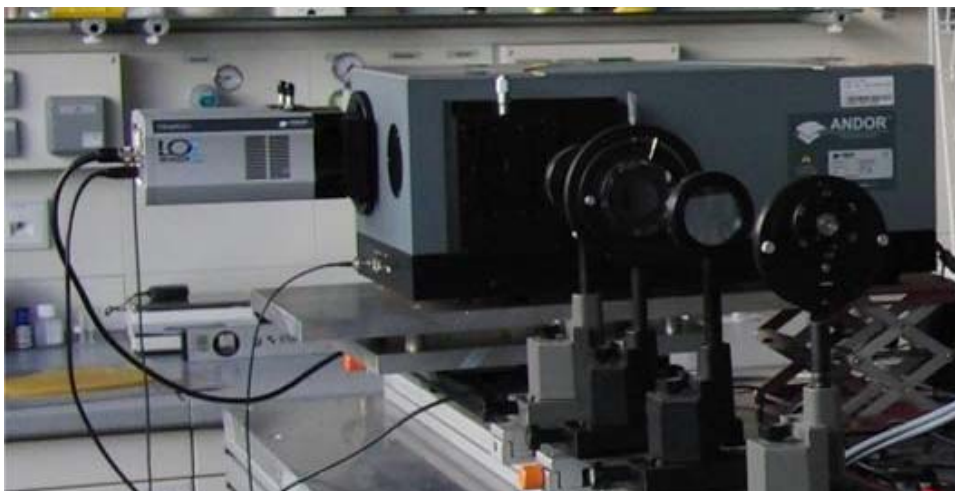

Figure 1: UV/Vis spectrometer to record the OH band at 309 nm.

This spectrometer (fig. 1) partially resolves the OH band between 280 nm and 325 nm into its rotational lines or line groups. The temperature is derived by fitting a calculated spectrum to the measured spectrum whereas an adequate peak profile with the temperature as fitting parameter. Such spectra might be important to the integration of reaction mechanisms into combustion calculations. The fitting procedure was outlined in earlier publications and has been applied to various combustion processes [23-25]. In the experiments this spectrometer was used with scan rates of 10 and 15 ms. It observed the flame in its full deployment.

Own developments of fast scanning spectrometers were used in the NIR and the IR spectral range, as well. For the NIR spectral range an AOTF (acusto-optical tunable filter) spectrometer was used [19, 20]. It scans a wavelength range of 1.25 to 2.6 µm with a resolution of 2.5 nm at scan rates up to 1500

Hz of a full spectrum. This device was earlier used for both fast plastic identification [21] and for combustion and explosions [8, 19, 22].
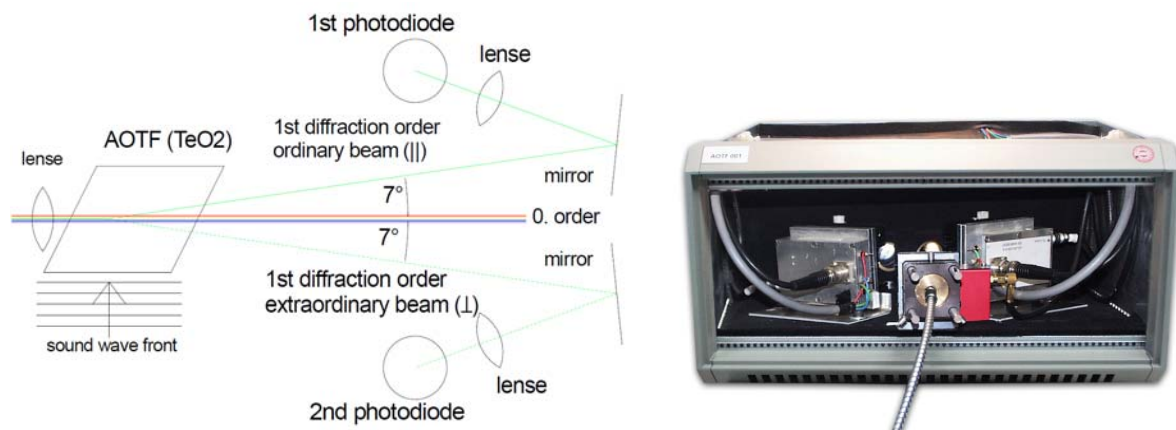

Figure 2: NIR spectrometer based an AOTF (acusto-optical tunable filter) to record the OH band at 309 nm, principle and used equipment.

The radiative emission in the IR spectral range was recorded by an own developed IR-filterwheel spectrometer covering the spectral range of 2.4 to 14 μm [19]. It changes spectral transparency depending on wavelength enables a full spectrum resolved in time with a rate of 100-150 spectra/s to obtain the transient time structure of the jet emission. This spectrometer was applied to many transient combustion processes in the past (see e. g. [11, 12, 19]).
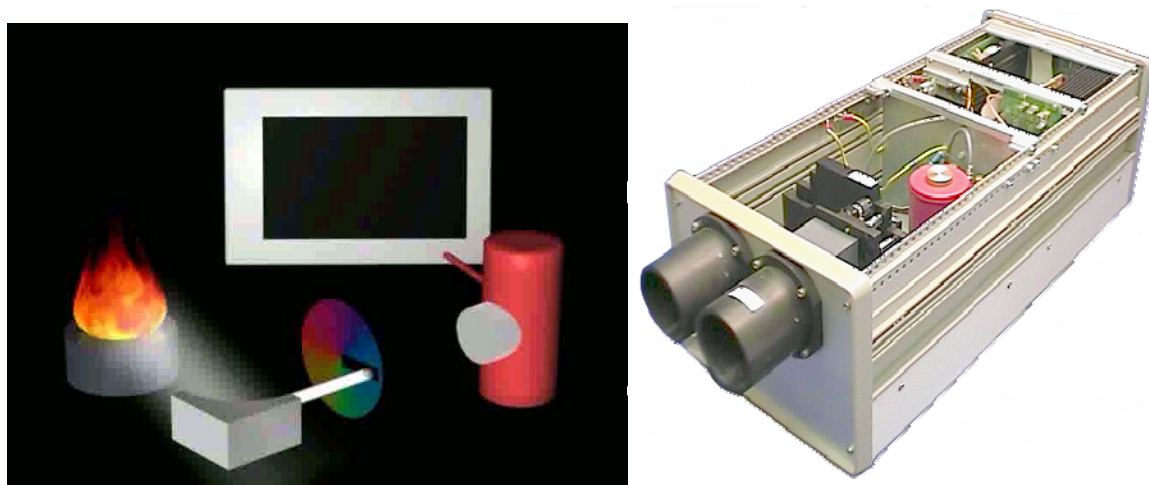

Figure 3: IR spectrometer based on a filter wheel varying continuously the wavelength transparency to record the range from 2.5 to 14 μm.

The spectra series were analysed by numerical comparison to theoretical intensity distributions calculated by single line group modelling [10, 11]. The applied methods including diagnostic equipment as well as evaluation methods are described in more detail in other publications

A quantitative spectral analysis of the measured NIR and IR spectra from flame jets applies molecular band modelling of the involved species. An adequate code BAM was developed at Fraunhofer ICT which calculates these spectra. In addition, it enables a least squares fit to experimental spectra whereas temperature and concentrations are the parameters to fit (see the detailed description in ref. [11]). The computer code uses as basis the data from the Handbook of Infrared Radiation of Combustion Gases [14, 15] which cover the temperature interval from 600 to 3000 K. The BAM code can calculate NIR/IR-spectra (1-10 μm) of gas mixtures of H_2O (bands are at 1.3, 1.8, 2.7 and 6.2 μm),

CO_2 (bands close to 2.7 and 4.3 µm), CO (4.65 µm), NO (5.3 µm) and HCl (3.5 µm). It can include soot particle emission, as well as self-absorption, and pressure line broadening. The spectral bands of three-atomic molecules consist of thousands of single lines, e.g. HITRAN [27, 28] lists nearly 50,000 lines for H_2O and 60,000 for CO_2 and simplified models to quickly obtain line positions and strengths are currently not available. The HITRAN code was designed for atmospheric absorption which can be here also used to correct the recorded spectra. Therefore it accounts the distance between emitter and spectrometer. A fast scanning IR-spectrometer and the BAM data evaluation were already applied to transient large hydrogen jet flames from 75 l cryogenic hydrogen tanks [9]. Recent published results on hydrogen flame jets [14-16] are based on calculations with the RADCAL code [17]. This code uses the same principles as the BAM code, but does not enable least squares fit procedures of spectra to obtain temperatures and species.

All spectrometers have the possibility to be up-graded to imaging spectrometer, if the detectors are substitutes by cameras which can record the related wavelength ranges. In future experiments imaging spectroscopy would enable to record spectra of the complete flame or at least substantial parts of it. Evaluation could then prepare distributions of species and temperatures.

3.0 RESULTS AND DISCUSSION

A result of a the UV/Vis spectrometer record is shown in fig. 4, obtained at a scan rate of 10 ms at 0.02 s after opening of the reservoir. The spectrum exhibits strong self-absorption, especially of the prominent peak at 309 nm. This effect proves the strong interaction of the flame jet radiation with this key radical OH in the flame kinetics mainly present in the reaction front. For the fit only the part of the spectrum between 306 and 308.8 nm was used because self-absorption is difficult to account for and which is currently not done. However, rotational temperature are often found to be high as the equilibrium temperatures and indicate involvement into the flame kinetics.
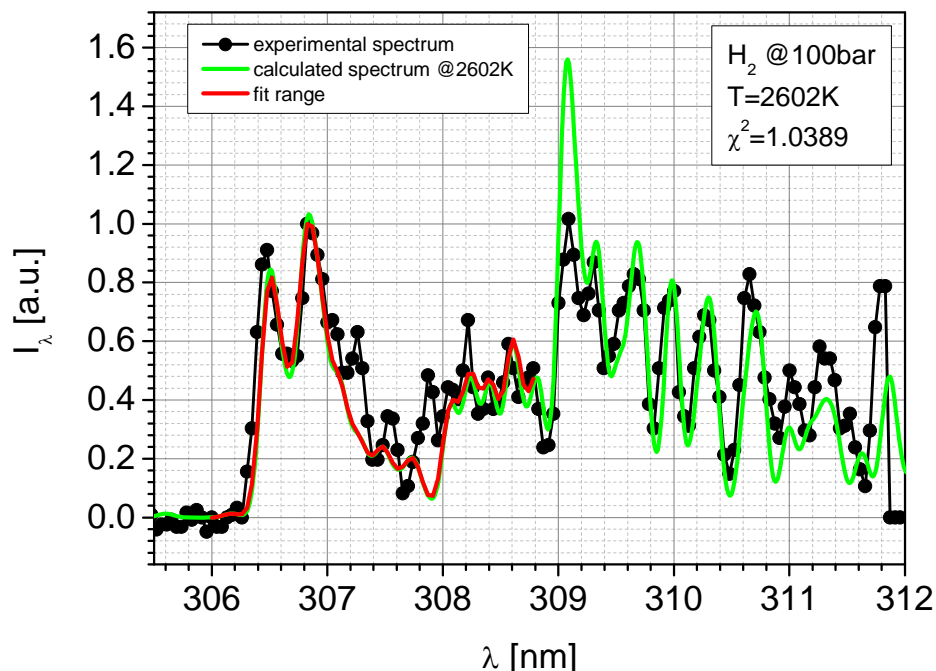

Figure 4: UV spectrum of the OH band at 309 nm with fit (red) and calculated one (green) of a jet starting at 100 bar initial pressure

Similar spectra are also obtained for the other experiments. The obtained temperatures are high an effect often found for OH rotational temperature due to the strong self-absorption. It indicates involvement of OH into the flame kinetics where it plays a key role. Considering self-absorption the "missing" peak at 309 nm would give the concentration of OH bands

within the viewing angle. High initial pressures increase the hot zone volume with bright emission in the IR increasing the amount of total OH species. The 309 nm peak is therefore reduced with respect to the peak of the 100 bar jet (see fig. 5). Further evaluation will take this effect into account to estimate overall OH concentrations..
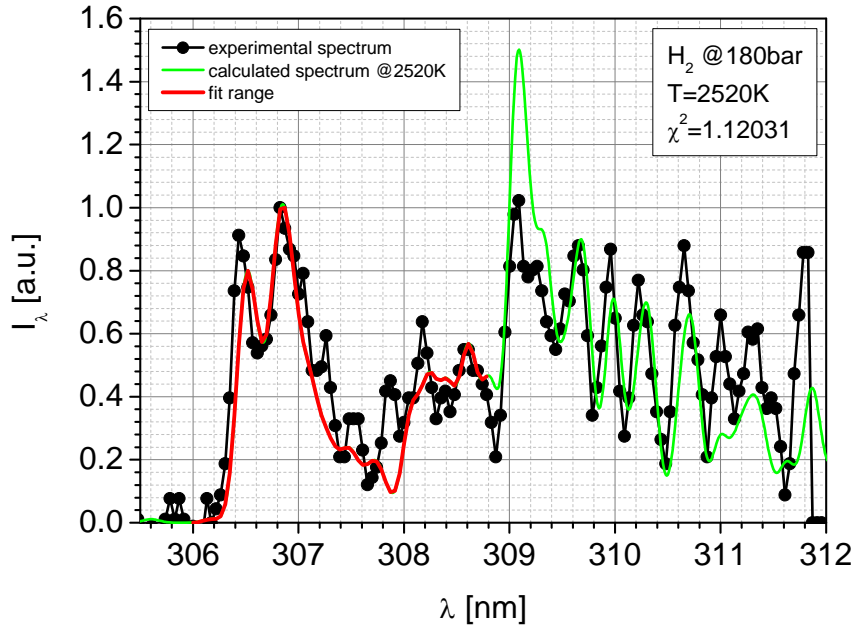

Figure 5: UV spectrum of the OH band at 309 nm with fit (red) and calculated one (green) of a jet starting at 180 bar initial pressure

The AOTF spectrometer was also used to observe the bright flame jet region with a scan time interval of 5.3 ms/spectrum. A series of spectra within the spectral range of 1.25 and 2.2 µm from a flame jet of 180 bar is plotted in fig. 6. Within more than 0.5 s the intensity slightly decreases with a high intensity at the beginning when the flame front reaches the field of view.
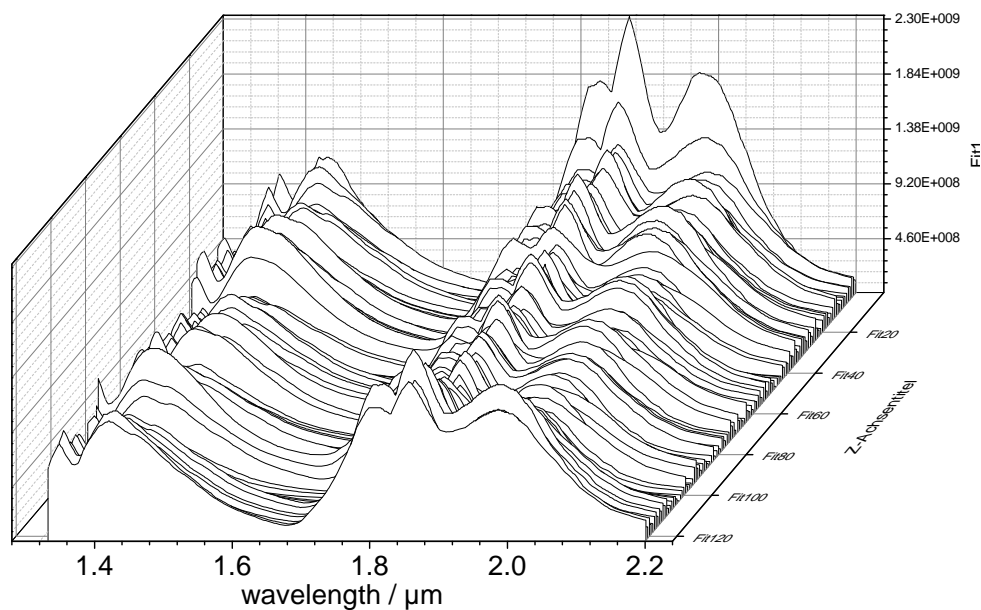

Figure 6: Series of NIR spectra showing the water bands between 1.25 and 2.2 µm of a jet starting at 180 bar initial pressure, progressing time from background to foreground

A selected spectrum is plotted in fig. 7. The least squares fit with BAM code delivers a temperature of 2168 K. Figure 8 shows the temperature obtained throughout the experiment with a jet emitted with initially 180 bar. They scatter between 2150 and 2500 K with an average value close to 2200 K after an increase at the beginning. A dependence on the initial pressure of the jet release is not evident (fig. 8).
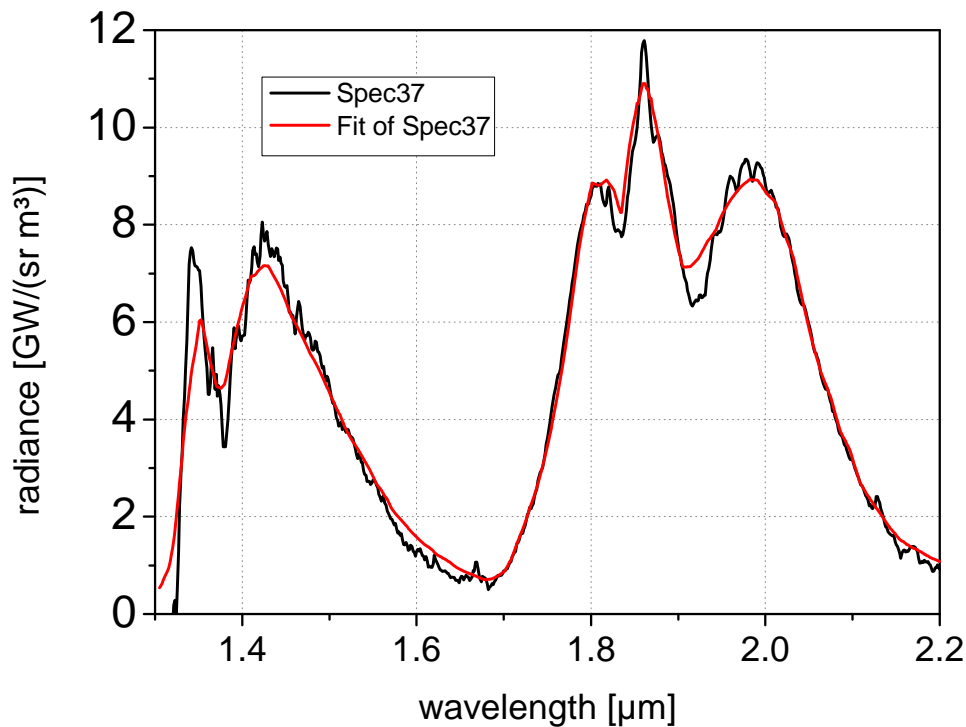

Figure 7: NIR spectrum of the water bands between 1.25 and 2.2 μm of a jet starting at 180 bar initial pressure recorded 2.5 m from the nozzle in the center, T= 2168 K, 0.085 s

Similar IR spectra were obtained by the filter wheel spectrometer. The series are similar to those obtained by the AOTF spectrometer, however with an extended wavelength range to 10 μm. Least squares fit run quite well (see fig. 9) and a stable temperatures with low deviation are obtained throughout the experiments (fig. 10) which very close to 2200K if initial scattering is ignored.

The CO_2 peak is small in the spectra this is due to the limited air entrainment and also to the beginning decomposition into CO at the measured temperatures. This results in a strong scattering of the CO_2/H_2O ratio (see fig. 10). The ratio is in average close to 0.0025 for all initial pressures. Might be the ratio is slightly higher for jets with higher initial pressure.

When a hydrogen jet entrains ambient air also a noteworthy amount of CO_2 is mixed in. Close to the ground a typical air composition includes 0.035 %.
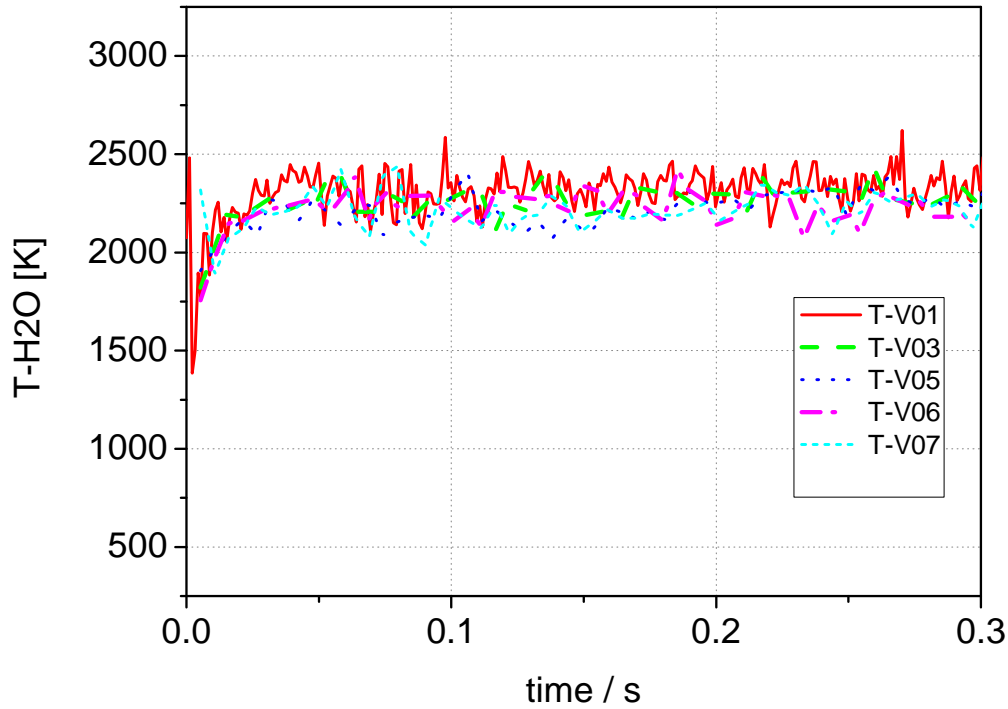
Figure 8: Temperature obtained by analysing the series of NIR spectra of the water bands between 1.25 and 2.2 µm for 5 experiments recorded 2.5 m from the nozzle in the center, temperature scatter between 2100 and 2500 K
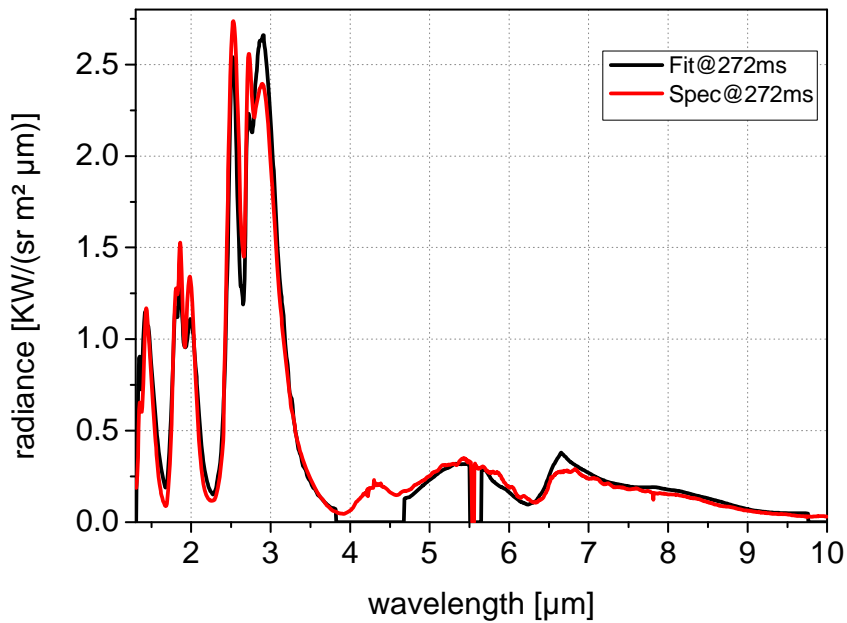

Figure 9: IR spectrum of the water bands between 1.4 and 10 µm of a jet starting at 180 bar initial pressure recorded 2.5 m from the nozzle in the center, T= 2200 K, 0.272 s
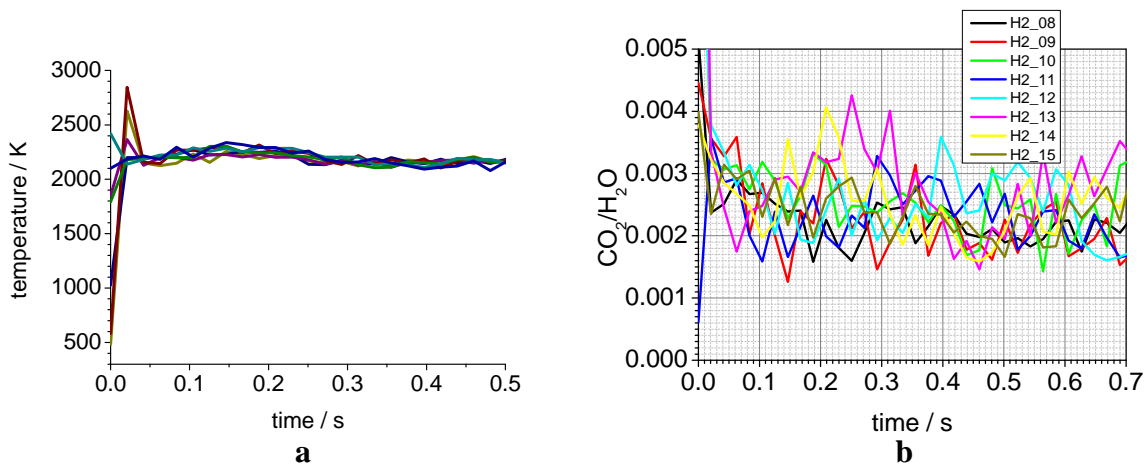
Figure 10: a: Temperature obtained by analysing the series of IR spectra of jets starting at the 3 initial pressures, b: CO_2/H_2O obtained by analysing the series of IR spectra

Component		N2	O2	CO2	Ar
Concentration	Vol%	77.1	20.7	1.3	0.9

Table 1: Composition of air used for CHEMKIN calculations.

For hydrogen combustion air is the only source for CO_2 and may be used as a tracer for the air concentration in the flame. But for temperatures >2000 K, CO_2 also decomposes depending on temperature and flame composition. The decomposition of CO_2 is well investigated and understood and can be predicted with thermodynamic calculations of the chemical equilibrium or better in combination with complex elementary reaction kinetics like e.g. given in the well proved and established GRI-Mechanism 3.0 [29]. Multiple calculations were performed at 2200 K for the reaction of hydrogen with air using the composition of Tab. 1. The hydrogen/air ratio was varied over the complete ignition limits from 4% to 80% H_2 in air. That corresponds to an air ratio (defined as the quotient of available air to stoichiometric air concentration) of 0.1 to 10. Each run results in the time history of the concentrations of all involved components starting with the initial mixture up to the final equilibrium concentration in molar fractions that are identical to volume fractions for non-pressurized gases. Fig. 11 presents a characteristic example for an air ratio of 0.5.

The final equilibrium concentration is achieved at the latest after 1 ms. The equilibrium of CO_2 and CO is achieved even one magnitude earlier. Fig. 12 presents the resulting CO_2/H_2O-ratios as a function of the mixture ratio referenced as air number. It is obvious that this ratio is more important than the original mixture ratio because it will be found in the measurement. Quantitative spectra are then calculated for the bright zone (defined as a volume at the head of the flame jet which emits strongly [28]) of the flame zone (see fig. 13).

4.0 CONCLUSION

Fast scanning time resolved spectroscopy shows that the radiation from the bulk hot gas interacts with the OH expressed by self-absorption and tentative higher rotational temperatures than equilibrium estimates. Evaluation in the NIR and IR spectral ranges results in temperatures around 2200 K with a remarkable stability and does not depend on the conditions of the jet or position. At the temperature found the CO_2 entrained by air undergoes substantial decomposition. Considering this effect the CO_2 peak in the spectra indicates the main combustion occurs at air ratios close to 0.5 at the positions. A bright zone at the head of the transient flame jet contributes the major component to the radiation emission. The results of the volume separation of this bright zone enable the estimated of the total emission.
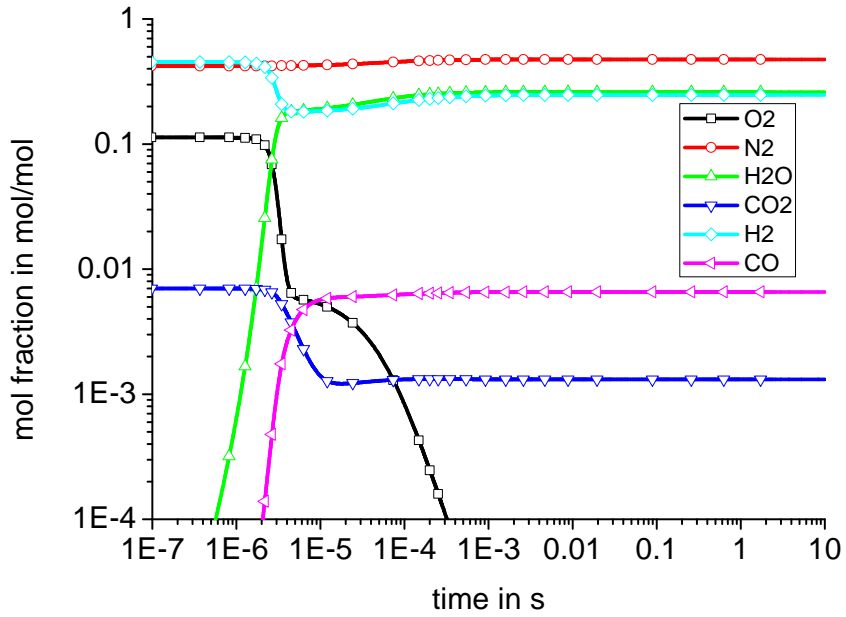
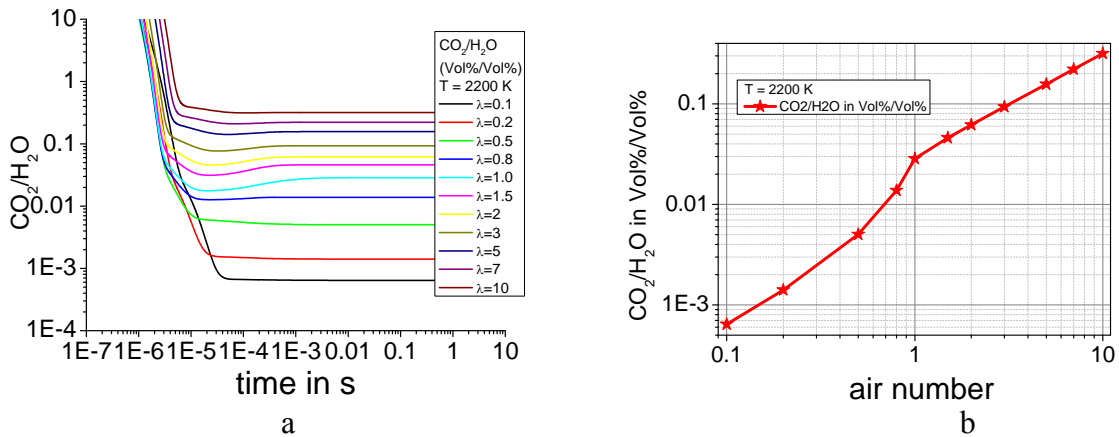**Figure 11: Decomposition of CO_2 starting with an air ratio of 0.5**

a

b

Figure 12: (a) decay of CO_2/H_2O on air ratio, (b): resulting volume concentrations
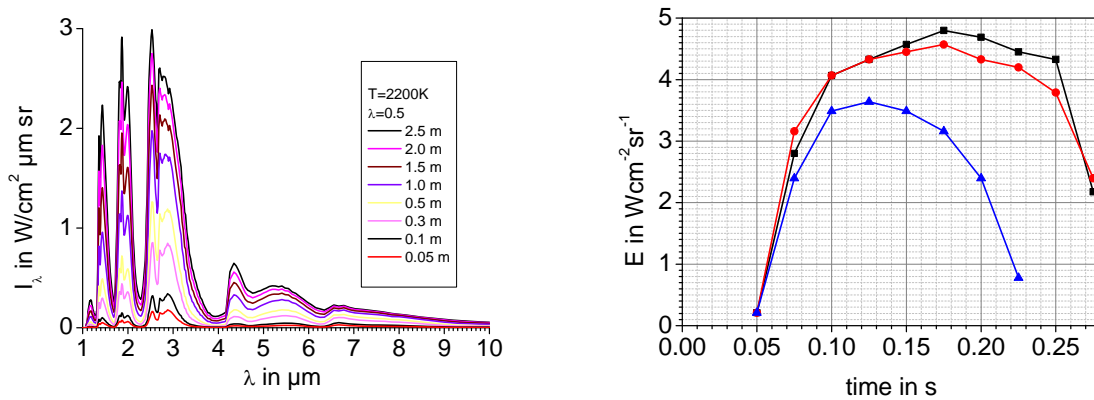

Figure 13: Emission spectra calculated for a volume with referenced diameters (left) and the emission from the bright zone of the jet for the initial pressures 100, 180 and 260 bar.

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