

MEASURING AND MODELLING UNSTEADY RADIATION OF HYDROGEN COMBUSTION

**Volker Weiser, Evelin Roth, Stefan Kelzenberg, Wilhelm Eckl, Norbert Eisenreich, Gesa Langer
Fraunhofer Institut für Chemische Technologie (ICT), Joseph-von-Fraunhofer-Str. 7, 76327
Pfinztal, Germany**

ABSTRACT

Burning hydrogen emits thermal radiation in UV, NIR and IR spectral range. 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 the case of a real explosion accident organic substances or inert dust might be entrained from outer sources to produce soot or heated solids to substantially increase the heat release by continuum radiation. To investigate the corresponding combustion phenomena, different hydrogen-air mixtures were ignited in a closed vessel and the combustion was observed with fast scanning spectrometers using a sampling rate up to 1000 spectra/s. In some experiments, to take into account the influence of organic co-combustion, a spray of a liquid glycol-ester and milk powder was added to the mixture. The spectra evaluation uses the BAM code of ICT to model bands of reaction products and thus to get the temperatures. The code calculates NIR/IR-spectra (1 - 10 μm) of non-homogenous gas mixtures of H_2O , CO_2 , CO , NO and HCl taking into consideration also emission of soot particles. It is based on a single line group model and makes also use of tabulated data of H_2O and CO_2 and a Least Squares Fit of calculated spectra to experimental ones enables the estimation of flame temperatures. During hydrogen combustion OH emits an intense spectrum at 306 nm. This intermediary radical allows monitoring the reaction progress. Intense water band systems between 1.2 and 3 μm emit remarkable amounts of heat radiation according to a measured flame temperature of 2000 K. At this temperature broad optically-thick water bands between 4.5 μm and 10 μm contribute only scarcely to the total heat output. In case of co-combustion of organic materials, additional emission bands of CO and CO_2 as well as a continuum radiation of soot and other particles occur and particularly increase the total thermal output drastically.

1.0 INTRODUCTION

In various branches of industry like chemical, pharmaceutical and food industry large quantities of fuel, flammable chemicals and explosive substances are produced and stored. To prevent disastrous impact on the environment in the case of a hazardous accident these materials have to be handled and stored under safe conditions. In order to prevent transfer between processing facilities and storage containers, buildings have to be separated by safety distances.

Pressure waves generated by gaseous explosions mainly endanger the environmental buildings. The power and impulse of these waves depend on the type of the explosive material the entrainment of air, the confinement, obstacles and induced turbulence and the volume of the gas cloud. These effects were thoroughly investigated by experimental and theoretical approaches in the past and reliable computer codes are developed which simulate the processes and interactions and their dependencies on given conditions with sufficient accuracy in many cases.

Beneath the pressure waves, radiation is the main effect to influence the surroundings and contribute to fire and explosion transfer and propagation. The radiative emission of hazardous fires and gas explosions is strongly variable in time at short scales down to milliseconds. In addition it includes fundamental information concerning the mechanisms and progress of burning. A scanning analysis of the spectral flame radiation must be fast enough to detect pre-reactions, transient phenomena, starting explosions, to enable the understanding of propagation mechanisms as well as quenching or extinguishing mechanisms. For fires and explosion hazards these investigations are able to provide safety engineers with a basis to develop effective methods for:

- early detection,
- prevention or suppression and
- effective fire fighting.

In contrast to pressure effects, time resolved radiation of fires and explosions is not yet investigated in a sufficient extend, especially, concerning spectral resolution. There are only some publications on time resolved emission spectroscopy of gas explosions [1-4].

This paper presents equipment for time and spectrally resolved investigation down to the millisecond scale, methods of data evaluation to obtain temperatures and species as well as radiative power. These techniques, mainly using the NIR and IR spectral range, are applied to hydrogen explosions.

2.0 CALCULATION OF NIR/IR SPECTRA

2.1 Molecular Spectra of Flames from Hydrocarbons in the NIR/IR-Range

A quantitative data analysis of infrared spectra measured from flames and plumes of pyrotechnics has to be based on band modeling. An appropriate code BAM was developed by ICT which calculates NIR/IR-spectra and allows least squares fits to experimental ones with temperature and concentrations being the fitting parameters (see the summarizing reference [5]). The calculations use the data from the *Handbook of Infrared Radiation from Combustion Gases* [6, 7] which cover the temperature range from 600 to 3000 K. The computer program BAM can calculate NIR/IR-spectra (1-10 μm) of inhomogeneous gas mixtures of H_2O (with bands around 1.3, 1.8, 2.7 and 6.2 μm), CO_2 (with bands around 2.7 and 4.3 μm), CO (4.65 μm), NO (5.3 μm) and HCl (3.5 μm) and can take into account emission of soot particles. Self absorption and pressure line broadening can be taken into account.

The calculation of an emission or transmission spectrum along an optical path starts from the determination of the absorption coefficients resolved with respect to wavelength. The spectral bands of three-atomic molecules consist of thousands of single lines, e.g. for important flame constituents HITRAN [8, 9] lists nearly 50,000 lines for H_2O and 60,000 for CO_2 and simplified models to quickly obtain line positions and strength are currently not available. Therefore tabulated data are used. The calculation of a spectrum of diatomic molecules is based on the anharmonic oscillator and corrections for vibration-rotation interaction to end up with averaged absorption coefficients and line densities derived from the approach described above for spectra in the NIR/IR spectral range [10] for band modeling. The molecules, which emit in the UV/Vis, consisting of C, N, O and H are quite well documented and analyzed [10-12]. Calculated band profiles allow the calculation of temperature in case of time resolution also time profiles [13-18].

The band models enable an effective calculation of radiation transport in inhomogeneous media in order not to apply a transport equation for each single line [5-7]. Line shapes, half widths and positions of lines contribute to the model. At high temperatures a *Random Band Model* has proved to be appropriate using a Doppler-Lorentzian line shape. For the separated bands of the various molecules the individual lines were accumulated to a Single Line Group and for the *Curve of Growth* the Curtis-Godson approximation was used. Benefits, shortcomings and possible errors of this model are discussed in the *Handbook of Infrared Radiation from Combustion Gases* [6].

For analyzing soot it is assumed that the particle size is small compared to the wavelength.

If the energetic compositions contain larger amounts of metals various molecules with O, N, H or Cl or F from the oxidizer emit strongly. Examples are

- AlH and AlO bands in the composite propellants [10-12]

- CuH, CuCl, CuOH in propellants with copper catalysts [10-12]
- BO, HBO₂ and especially BO₂ in the visible range [10-12, 19]
- BaCl, CuCl, CuOH, CuO, Sr_xO_y and SrOH for pyrotechnic mixtures [10-12, 20, 21]

These bands were not studied in detail by fundamental research therefore the use for temperature measurement is rather limited. These bands might be observed if in addition to organic materials also metallic impurities are entrained into the hydrogen air mixture.

Hydrogen reacts with oxygen of air to water that is a well known strong emitter of bands in near and medium infrared spectral range. Co-combusting of hydrocarbons additionally produces emission active products like CO₂, CH, CO and soot. Thermodynamic equilibrium calculations of hydrogen/air and hydrogen/hydrocarbon/air mixtures in stoichiometric compositions of air numbers between 0.5 and 4 executed with the ICT-code [22] result in typical temperatures in the range of 2000 to 2800 K.

Fig. 1 shows the spectra of a BAM simulation of hot water emitted from layers of various thicknesses in comparison to a Black Body radiator. It is shown that the water bands become “black” – meaning band intensity and profile approaches the broad continuum of black body radiation at the band position - with increasing layer thickness the earlier the higher the wavelength is. At a thickness of 100 m the 1.3 μm has become black.

Fig. 2 shows that the intensities of the lower wavelength bands become stronger than those of higher wavelengths when temperature is increased at a constant layer thickness. The reason is that the maximum of temperature between 2000 and 3000 K lies between 1.5 and 1 μm and shift to lower wavelengths on temperature rise.

Fig. 3 shows that soot, which emits a continuous Gray Body radiation, adds a continuum radiation to the water bands. At smaller concentrations of soot both bands and continuum are clearly indicated. At higher soot concentrations the water bands degenerate to small modulations on the continuum.

The combination of water bands with soot and hydrocarbon combustion products CO and CO₂ modify the spectrum mainly at 2.3, 2.7 and 4.25 μm whereas the contribution of CO₂ dominates.

In a real explosion which might entrain dust and organics these bands are to be expected to combine in a similar way depending on the special constraints of the experiment or accident. The analysis of the spectra enables to derive the progress of reaction, reaction front, hot reaction products and their expansion and temperature profiles. Well defined experiments should be performed to verify the spectral characteristics predicted by the calculations.

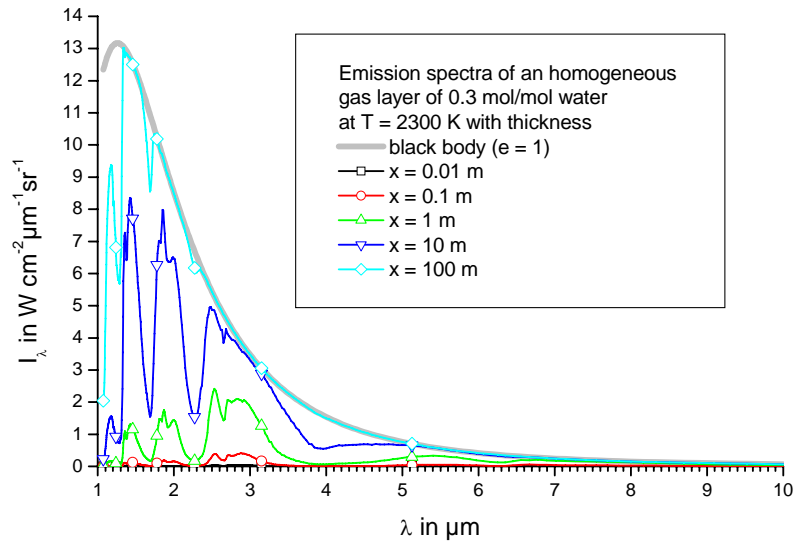


Figure 1. BAM simulation of emission spectra of differently thick homogeneous gas layers of 30 mol% water in air at 2300 K

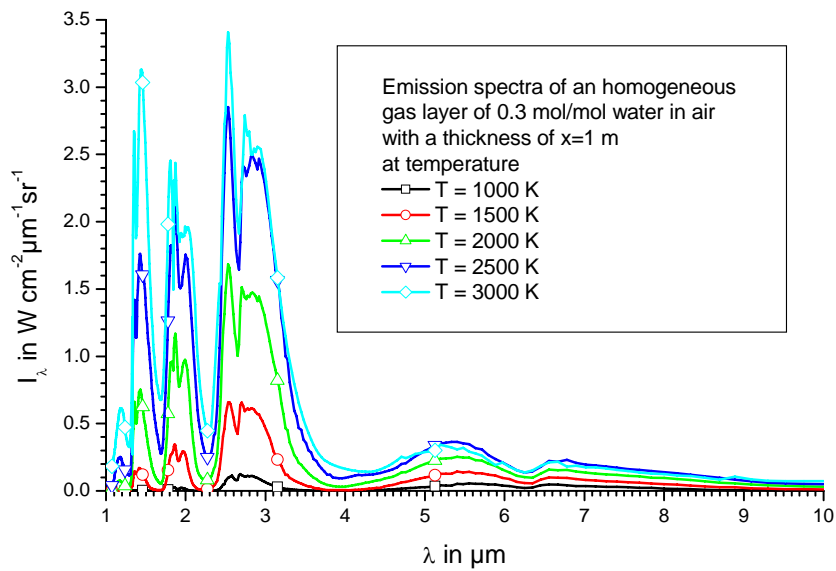


Figure 2. BAM simulation of emission spectra of homogeneous gas layers of 30 mol% water in air with an optical depth of 1 m at different temperatures

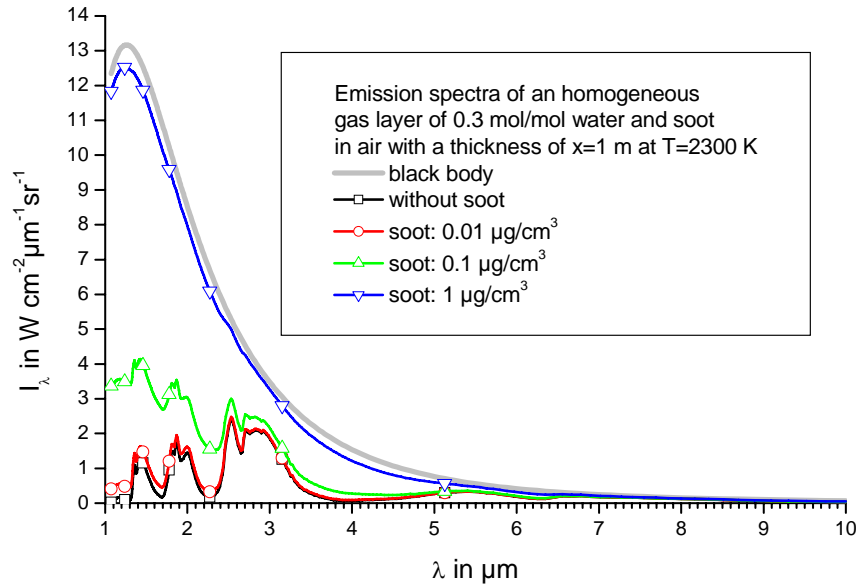


Figure 3. BAM simulation of emission spectra of homogeneous gas layers with 1 m thickness of 30 mol% water in air with additional emitting soot of different concentrations

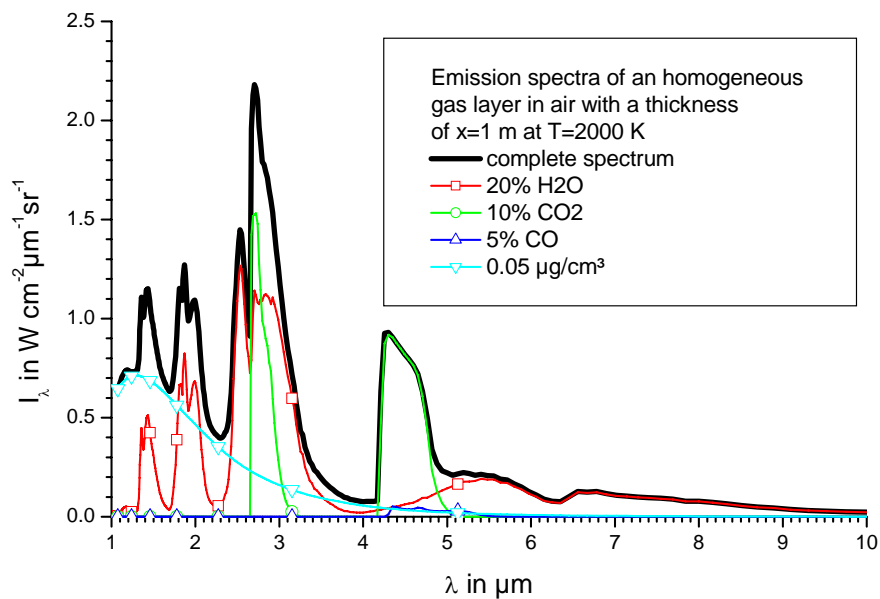


Figure 4. BAM simulation of emission spectra of a homogeneous gas layer with 1 m thickness of typical hydrogen, hydrocarbon air composition

3.0 EXPERIMENTAL SETUP

For detailed analysis of pure hydrogen/air explosions and explosions with additionally added inert dust agents (e.g. Aerosil) and liquid or solid reactive organic substances (e.g. milk powder, dimethylglycoether (DPM)) a special autoclave with a volume of 35 l was manufactured equipped with windows of a wide spectral transmittance. It is shown in Figure 5 including all instrumentation

for the observation of the reactions. It withstands pressures at least up to 6 MPa and enables input of different additives shortly before, during and after ignition of the gas explosion.

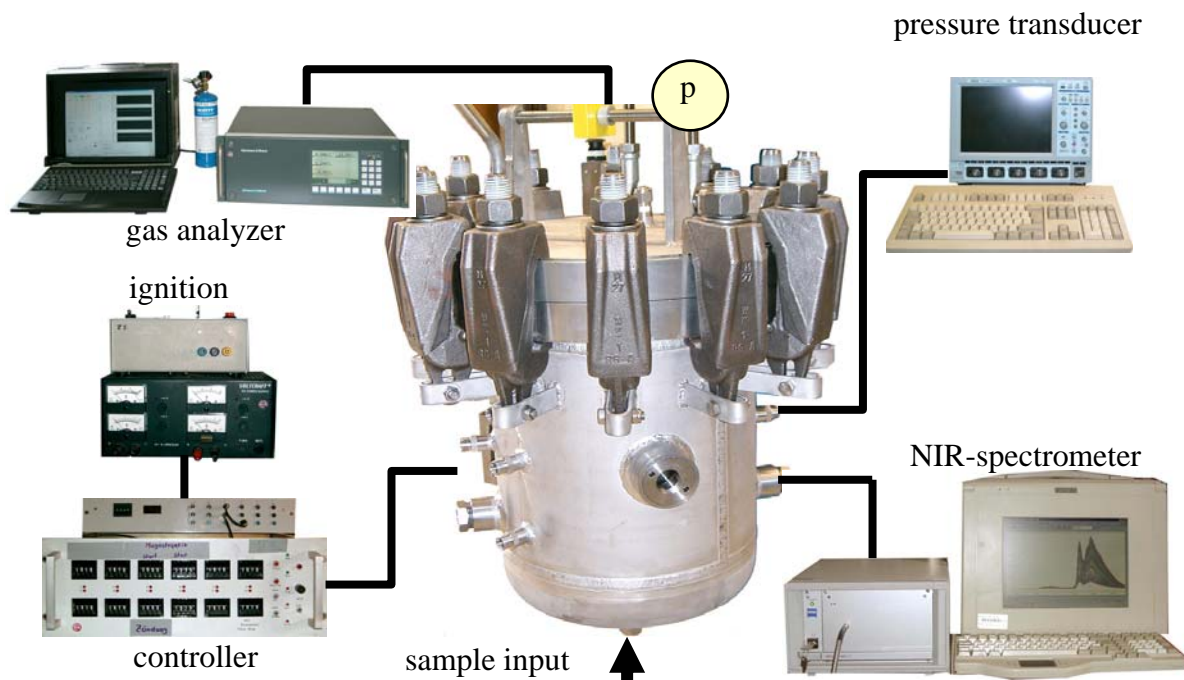


Figure 5. High pressure bomb (6 MPa) with window, ignition, in-situ measurement instrumentation and control

Hydrogen/air mixtures of air/numbers between 0.4 and 4 were produced using the partial pressure method at pressures of 0.1 to 0.2 MPa. For preliminary investigations of co-combustion agents 5 g of substance were injected into the vessel shortly after ignition of the mixture. As inert agent ultrafine SiO_2 (Aerosil 200) were used. As organic liquid spray agent DPM was used. Milk powder served as organic dust to be burnt.

4.0 RESULTS AND DISCUSSION

The results consisted of pressure time curves and spectra. The spectra were recorded according to the methods described in references [23-25]. One example is a series of experiments shown in Fig. 6. It is expected that the maximum pressure is highest for the stoichiometric hydrogen air mixture. After reaching a maximum the hot combustion products cool down. However, also in this phase they might endanger the environment as the emitted radiation is quite high for some seconds. However, an unconfined hot gas volume expands, rises because of buoyancy and cools down earlier.

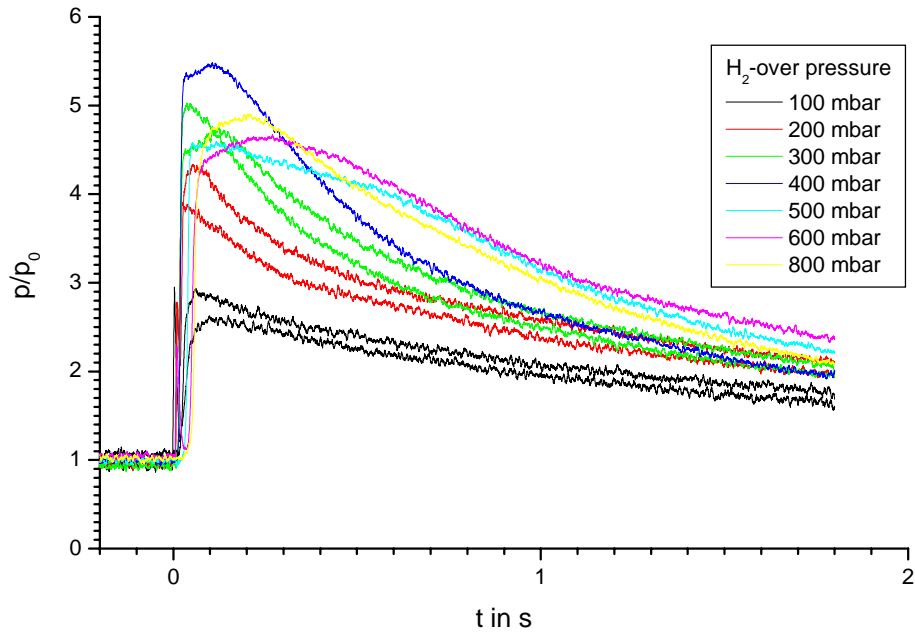


Figure 6. Pressure-time curves of explosion of different partial hydrogen pressures in air

A series of spectra in the NIR is plotted in Figs. 7 and 8.

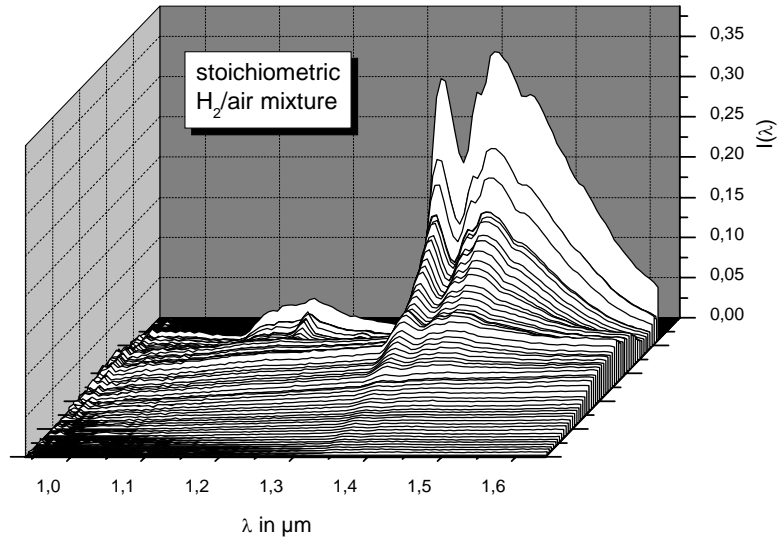


Figure 7. Series of NIR-spectra of a hydrogen/air explosion, the dominating 1.3 μm band is recorded at the rising phase.

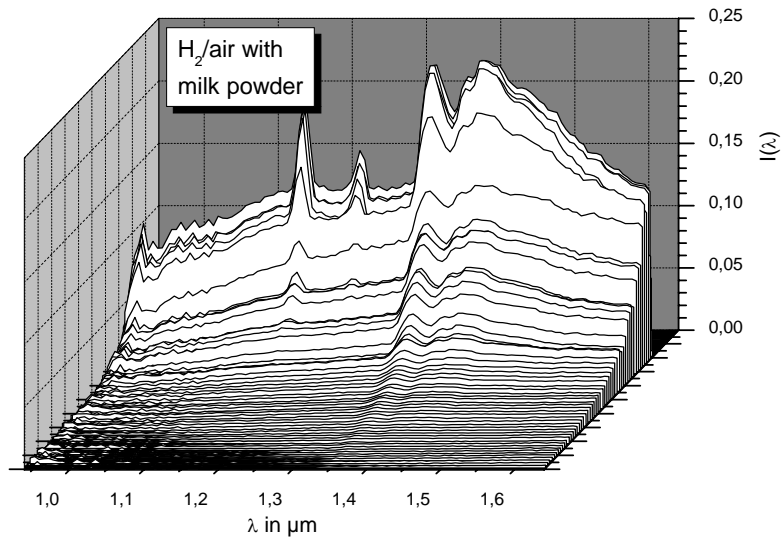


Figure 8. Series of NIR-spectra of a hydrogen/air explosion, the 1.3 μm band is recorded.

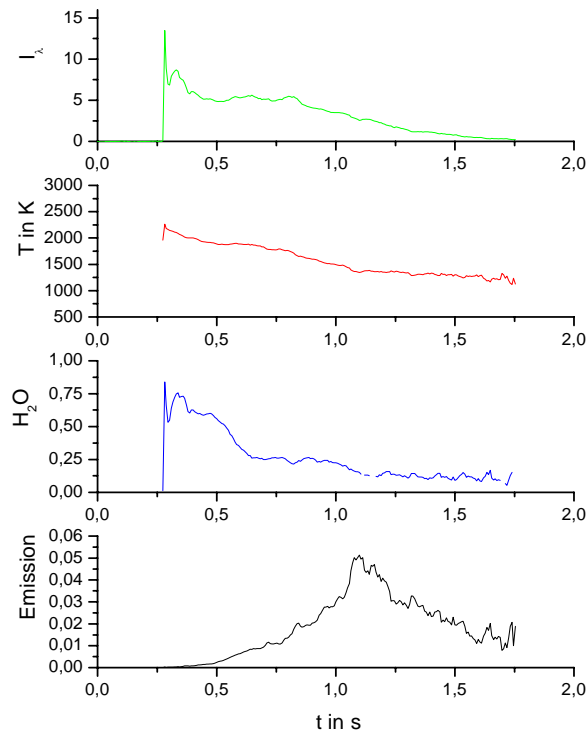


Figure 9. BAM evaluation of stoichiometric hydrogen-air mixture. Increase of emissivity after 0.5 s depends to surface heating of the vessel walls

The evaluation of the spectra as described above gave in addition to the pressure profiles the radiation intensity, the temperature, the water concentration and the emissivity (see Fig. 9). The latter might indicate solid particles or solids. It increases when the reaction front reaches the autoclave wall.

The injection of additional material modifies strongly the radiation characteristics. In Fig. 10 the profiles of the evaluating procedure is plotted for an experiment with milk powder injected. It is remarkable that the emissivity rises fast after injection which indicates heating and degradation to soot.

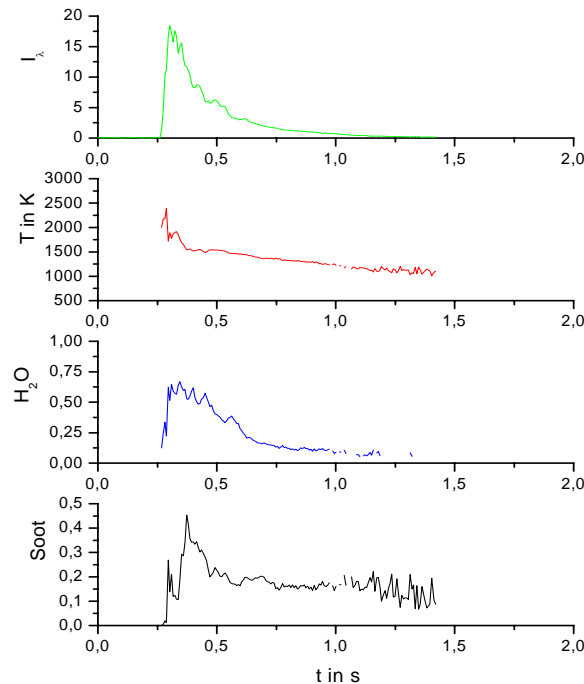


Figure 10. BAM evaluation of hydrogen-air mixture (1 : 5 vol%). Parallel to ignition 10 g milk powder was injected resulting in increase of emissivity.

5.0 CONCLUSIONS

Beneath pressure the radiation of hydrogen/air explosions might endanger the environment. Equipment has been presented for time-resolved spectroscopic investigation of this radiation in the relevant spectral range down to the millisecond scale. Methods of data evaluation are based on the analysis of molecular spectroscopy being demonstrated by hydrogen air explosions in a 35 l autoclave. Good agreement between experimental data and theoretical calculations was found. Least squares fit enables to obtain temperatures and species as well as radiative power. Mainly the NIR and IR spectral range was used mainly modeling bands of water and continuous radiation. In addition experiments confirmed that dust induces strong continuous radiation which might even dominate the emitted heat at higher concentrations.

6.0 REFERENCES

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