

Fast Emission Spectroscopy for a Better Understanding of Pyrotechnic Combustion Behavior

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Abstract

Pyrotechnic mixtures react mostly fast and under a high release of thermal energy and heat radiation. A spectral analysis of this emission allows deep insight into the reaction process by the non-intrusive determination of the reaction temperatures and observation of the main reaction species and their concentrations. In the presentation various pyrometric and spectroscopic measurement techniques and data analysis and interpretation procedures are introduced using the spectral range from the ultraviolet, visible and near to medium infrared in combination with image processing of video and IR-camera signals. The available scan rate of several hundred spectra per second is sufficient to investigate:

- flame structure of high pressure strand burners from rocket propellants, gun powders and gas generators
- reaction processes in bulk pyrotechnic mixtures like igniter mixtures, flares, incendiary compositions, etc.
- moving and burning of single particles
- ignition processes of gun powders
- propagation of gas explosions
- in-situ observations of reactions in closed burning chambers via fiber optics

The quantitative intensity calibration of the recorded spectra series is carried out by relation to reference spectra of a black body radiator in units of power per wavelength, area and steradian. The evaluation uses the BAM code of ICT to model bands of reaction products. The code calculates NIR/IR-spectra (1–10 μm) of non homogenous gas mixtures of H_2O (with bands around 1.3, 1.8, 2.7 and 6.2 μm), CO_2 (with bands near 2.7 and 4.3 μm), CO (4.65 μm), NO (5.3 μm) and HCl (3.5 μm) taking into consideration also emission of soot particles. It is based on the single line group model and makes also use of tabulated data of H_2O and CO_2 . Rotationally resolved emission spectra of diatomic flame radicals in UV/Vis-range like OH , CH , C_2 , NH correlate directly to the energies regarding electronic, vibrational and rotational energy transitions and therefore enable the estimation of flame temperatures. Taking into account that there are many unknown parameters influencing the emission spectrum of an inhomogenous gas mixture, only a simplified model can be applied. Therefore, it was assumed that the flame consists only of one hot emitting layer of undefined thickness, constant temperature, constant concentration of the various gases and soot particles in thermal equilibrium. These assumptions lead to a reasonable number of parameters, which can be determined by a least squares fit procedure fitting calculated spectra to experimental data. With this restriction, temperature and concentration * length of major combustion products can be determined. Additionally, it is found that many pyrotechnic reactions emit a

nearly grey continuum in the NIR spectral range that can be used for temperature determination.

For spatial allocation of the spectroscopic emission signals the intensity distribution of simultaneously recorded video or IR-camera frames were used.

Keywords: Fast Emission Spectroscopy, Filter Wheel Spectrometer, Hot Gas Sensor, AOTF-Spectrometer, NIR/IR-Spectroscopy, Modeling of Emission Spectra

1 Introduction

Reacting plumes of pyrotechnics consist of hot gases and particles produced by the conversion of the energetic materials in a burning chamber and/or the surrounding atmosphere [1, 2]. In addition, secondary interactions with the environment after the main reaction might strongly influence the radiative properties of the exhaust by completing conversion and condensation of constituents [3]. Therefore the signatures contain detailed information about the composition burnt. In general, the spectroscopic investigation of pyrotechnics will on the one hand give a detailed insight into the reaction mechanisms and leading parameters like temperature which control the intensity and spectral characteristics. On the other hand the spectroscopic results might enable the design of information to be generated by pyrotechnics for identification and decoying. In the future, it might be required to even better simulate the light emission of rocket or jet plumes to account for improved spectrally resolving sensors.

In principle, it would be possible to obtain all data needed from theoretical calculations. The chemical composition in a reaction plume can be estimated from thermodynamic codes and the light emission can be derived from models describing the radiative properties of the species and the temperatures. However, the conditions of the plumes are more complicated to be described with sufficient accuracy by models based on equilibrium calculations.

- Final products of combustion expand after the reaction. So non-equilibrium distribution of temperatures has to be taken into account which reduces the applicability of codes for species and radiance.
- The particle density which is responsible for the strong continuous radiation cannot exactly be predicted.
- Partially reacted species lead to further conversion, e.g. those not completely oxidized. This effect increases the

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temperature depending on air entrainment which is a phenomenon of the flow field established close to the reaction.

Therefore, experimental data have to be acquired and compared to theoretical calculations. For measurement of radiation from pyrotechnic plumes and propellant flames, spectroscopic equipment is available to cover the wavelength regions of interest from the UV to the mid-infrared with sufficient sensitivity and time resolution.

It is the objective of the reported work to describe an experimental set up for spectroscopic measurements, theoretical models to predict the radiance of hot gases including particles, two and three atomic molecules and to illustrate by examples. The most important types of propellants are taken into account by using simplified compositions with the main components which might be a guiding concept of pyrotechnic development.

- Emission spectra in the UV/Vis [3]
- A filter wheel spectrometer consists of fast rotating wheels with continuously dispersing interference filter segments for the wavelengths region of 1.2 to 14 μm [4].
- A fast scanning hot gas sensor (HGS) based on a Zeiss MCS 511 NIR for mainly analyzing water bands and grey body radiation from particles [5].
- An AOTF-spectrometer system enabling the acquisition of spectra in the NIR range 1000–2500 nm at rates up to 1000 scans/s at a wavelength resolution of 2–3 nm [4].

Adequate data models analyze the obtained spectra covering grey body radiation of particles, the emission of diatomic radicals in the UV/Vis-range and combustion gases in the IR spectral range. These models enable the estimation of temperatures and species concentrations.

2 Experimental Devices

The investigations of pyrotechnic mixtures or charges are in a similar way performed as igniter mixtures, propellants and energetic materials, in general. The experiments are performed in open cups (pools), in closed bombs with windows or with the plumes from burning chambers or real rockets. A typical setup for the investigation of the burning of a propellant, a mixture of energetic materials or a metal powder is shown in Fig. 1. Simultaneously to the spectroscopic studies video techniques give a visual impression of the experiment.

Flames, consisting of hot gases and particles emit radiation in a broad spectral range from the UV to the far infrared with substantial intensity, and spectrometer to analyze this radiation should cover this range. Maximum intensities lie in the NIR spectral region due to the expected temperatures from 1000 to 4000 K.

Normally spectrometer observes only one spot of an event which focused from the flame to a pinhole or directly to the entrance slit of the spectrometer. The spatial profiles of the observed flame volume might be obtained by scanning with a moving mirror or if a flame propagation passes the imaged spot. Imaging spectrometers are currently under development. E.g. an AOTF spectrometer would allow the development of fast scanning and imaging one if a detector array is used.

2.1 Emission Spectroscopy in the UV/Vis-Range

For the acquisition of emission spectra in the UV/Vis-range commercial diode array spectrometers are available [3]. The examples described here were obtained using a Tracor Northern grating spectrometer and a Jarrel Ash monochromator (focal length 275 mm, entrance slit 50 μm). To get rotationally resolved spectra, a grating with 2400 lines/mm has been chosen (wavelength resolution 20 cm^{-1}).

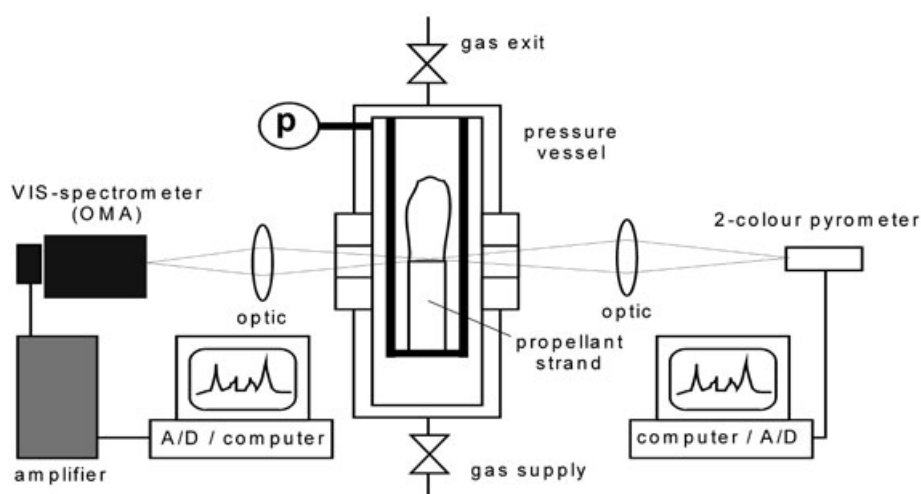


Figure 1. Experimental set-up for simultaneous spectroscopic and pyrometric investigation of propellant (see [3]).

The detector is equipped with a 1024 element diode array. Minimum time resolution of the system is 10 ms. Considering assumed steady-state conditions, experimental spectra were recorded with 100 ms per scan and averaged over 10 scans. If no rotational resolution was needed, a grating with 300 lines/mm has been used. Wavelength calibration is performed by standard lamps of Hg and Ne and the intensity calibration by black body radiators or tungsten strip lamps.

2.2 NIR/IR-Range

A filter wheel spectrometer consists of fast rotating wheels with interference filter segments. They continuously vary the transparency in the wavelength regions from 1200 to 2500 nm (InSb-detector) and 2450 to 14000 nm (InSb/HgCdTe-sandwich-detector) [4]. Investigations included an AOTF-spectrometer system enabling the acquisition of spectra in the NIR range 1000–2500 nm at rates up to 1000 scans/s at a wavelength resolution of 2–3 nm. The intensity calibration was carried out by recording reference spectra of a black body radiator.

2.3 Hot Gas Sensor

The fast scanning hot gas sensor (HGS) based on a Zeiss MCS 511 NIR spectrometer [5] is a grating spectrometer with an InGaAs diode array as detector (spectral range 0.9 to 1.7 μm). The spectral resolution is about 15 nm at a scan rate of 300 spectra per second. Currently, a spectrometer is available using the same spectrometer type with the wavelength sensitivity extended to 2.2 μm .

2.4 Pyrometers

In case of Grey Body radiation 2-colour pyrometers can be applied to obtain temperatures. Sandwich detectors of various semi-conductor diode combinations are available [3]. The combination of Si/Ge covers the NIR spectral region appropriate for pyrotechnics and a version was used here. Such pyrometers can measure temperatures with rates of more than 1 MHz, and single particles can be resolved on movement.

3 Evaluation of Spectra

Emitted radiation depends strongly on the temperature and the chemical composition of the flame. In principle, three types appear:

- Continuous radiation from particles
- molecular bands from hot gases
- lines from vaporized metals

3.1 Grey Body Radiation

The description of continuous emission or absorption from particles is based on the radiance L describing black body radiation:

$$L_{\lambda B}(\lambda, T) = \frac{c_1}{\lambda^5 (\exp(\frac{c_2}{\lambda T}) - 1)} \quad (1)$$

$$c_1 = 2\pi hc^2 = 3.7415 \cdot 10^{-12} \text{ W cm}^2$$

$$c_2 = hc/k_B = 1.43879 \text{ cm K}$$

For real samples it has to be modified by an emissivity ε depending on wavelength λ and temperature T :

$$L_\lambda(\lambda, T) = \varepsilon(\lambda, T) \cdot L_{\lambda B}(\lambda, T) \quad (2)$$

In the case that a grey body radiation is assumed emissivity ε does not depend on wavelength and temperature.

$$L_\lambda(\lambda, T) = \varepsilon \cdot L_{\lambda B}(\lambda, T) \quad (3)$$

For example, sooty flames can be described by a grey body radiator. The integration of $L_{\lambda B}$ results in Stefan-Boltzmann law of radiation which relates the total radiance to the 4th power of temperature.

$$E = \varepsilon \sigma T^4 \quad (4)$$

ε depends on the particle concentration and on the volume of the emitting body, σ being the Stefan-Boltzmann constant. ε is very small for lean and small flames (≈ 0.0001) and close to 1 for large fires especially when containing many particles. To derive temperatures from 2-colour pyrometers ε is assumed to be independent of wavelength and temperature.

3.2 Radiation in the UV/Vis from Diatomic Molecules

In the spectral range of the UV/Vis diatomic molecules emit specific bands the rotational structure of which is partially resolved by the spectrometer types described above. Determination of rotational and vibrational temperatures of various diatomic molecules and transitions from UV/Vis emission spectra is based on the calculation of line intensities and profiles [6]. The intensity of a spectral line is given by [6]:

$$I_{em} = N_n h c \nu_{nm} A_{nm} \quad (5)$$

where I_{em} is the emission of a rotational line, N_n are the atoms in the initial state, $h c \nu_{nm}$ is the energy of each emitted photon of the transition and A_{nm} is the Einstein transition probability of spontaneous emission. Taking into account thermal equilibrium, Born-Oppenheimer approximation

and the explicit expression for Einstein coefficients, Equation (5) can be written as:

$$I_{em} = C \cdot q_{j'j''} \cdot S_{j'j''} \cdot \nu^4 \cdot \exp(-E_{vib}/kT_{vib} - E_{rot}/kT_{rot}) \quad (6)$$

where $q_{j'j''}$ and $S_{j'j''}$ are the vibrational and rotational line strength, E_{vib} and E_{rot} are the vibrational and rotational energies of the upper level, k is the Boltzmann constant and T_{vib} and T_{rot} are the vibrational and rotational temperatures. The constants and parameters for the different molecules and transitions are taken from literature [6–9].

Temperatures have been determined comparing calculated line profiles to experimental data [10–13]. Therefore, a line profile must be taken into account. In case of a spectral resolution of about 0.1 nm, the line profile is dominated by the slit function of the spectrometer and can be approximated by a single Lorentzian. The broadened lines are overlapped by adding the contribution of each line at a given wavelength.

3.3 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 [14]. The calculations use the data from the *Handbook of Infrared Radiation from Combustion Gases* [15] 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 [16, 17] 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 UV/Vis spectral range [3] for band modeling.

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 [18]. Line

shapes, half widths and positions of lines contribute to the models. 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 Curti-Godson approximation was used. Benefits, shortcomings and possible errors of this model are discussed in the *Handbook of Infrared Radiation from Combustion Gases* [15].

The optical path through an inhomogeneous medium is approximated by L consecutive homogeneous layers, with temperature T_l , pressure p_l , thickness s_l and concentrations $c_{l,n}$ of considered N molecule types and the absorption coefficient being given by $\bar{k}_n(\omega, T_l)$.

The temperature and pressure conditions are related to standard conditions for layer $u_{l,n}$ (temperature $T = 273$ K, partial pressure $p = 1013$ hPa):

$$u_{l,n} = s_l \left(\frac{273\text{K}}{T_l} \right) \left(\frac{1013\text{hPa}}{c_{l,n} p_l} \right) \quad (7)$$

The total layer thickness $U_{l,n}$ from layer 1 to layer l is given by:

$$U_{l,n} = \sum_{j=1}^l u_{j,n} \quad (8)$$

For optical thin media the optical depth results:

$$X_{l,n}^* = \int_0^{U_{l,n}} \bar{k}_n(\omega, T_l) du = \sum_{j=1}^l u_{j,n} \bar{k}_n(\omega, T_l) \quad (9)$$

The Curtis-Godson-Approximation delivers the “true” optical path $X_{l,n}$:

$$X_{l,n} = X_{l,n}^* \sqrt{1 - Y_{l,n}^{-1/2}} \quad (10)$$

including the collision- and Doppler-Optical depth $Y_{l,n}$:

$$Y_{l,n} = \left[1 - \left(\frac{X_{l,n}^C}{X_{l,n}^*} \right) \right]^{-2} + \left[1 - \left(\frac{X_{l,n}^D}{X_{l,n}^*} \right) \right]^{-2} - 1 \quad (11)$$

which is composed of the optical depth for the pure collision “Curve of Growth” $X_{l,n}^C$:

$$X_{l,n}^C = X_{l,n}^* \left(1 + \frac{X_{l,n}^*}{4a_{l,n}^C} \right)^{-1/2} \quad (12)$$

using the collision-parameter $a_{l,n}^C$:

$$a_{l,n}^C = \frac{1}{X_{l,n}^*} \int_0^{U_{l,n}} \frac{\gamma_C}{\bar{d}_n(\omega, T)} \bar{k}_n(\omega, T) du \quad (13)$$

and the optical depth for the pure Doppler-“Curve of Growth”

$$X_{l,n}^D = 1.7 a_{l,n}^D \sqrt{\ln \left[1 + \left(\frac{X_{l,n}^*}{1.7 a_{l,n}^D} \right)^2 \right]} \quad (14)$$

using the Doppler-broadening-fine structure parameter

$$a_{l,n}^D = \frac{1}{X_{l,n}^*} \int_0^{U_{l,n}} \frac{\gamma_D}{d_n(\omega, T)} \bar{k}_n(\omega, T) du \quad (15)$$

γ_C are the collision half-widths specific for the molecule type and γ_D the Doppler half-width, obtained by standard procedures.

$\bar{k}_n(\omega, T)$ and line density $\bar{d}_n(\omega, T)$ are tabulated for H₂O and CO₂ in [15]. Diatomic molecule spectra can be calculated a priori. In the NIR/IR case, absorption coefficients and line densities are averaged for the spectral interval $\Delta\omega = 25 \text{ cm}^{-1}$:

$$\bar{k}_n(\omega, T) = \frac{1}{\Delta\omega} \int_{\omega - \frac{1}{2}\Delta\omega}^{\omega + \frac{1}{2}\Delta\omega} k_n(\omega, T) \text{ bzw.} \quad (16)$$

$$\bar{d}_n(\omega, T) = \frac{1}{\Delta\omega} \int_{\omega - \frac{1}{2}\Delta\omega}^{\omega + \frac{1}{2}\Delta\omega} d_n(\omega, T)$$

For the total optical path it results:

$$X_{total} = \sum_{n=1}^N X_{l,n} \quad (17)$$

with a transmission coefficient $\tau_l(\omega)$:

$$\tau_l(\omega) = \exp \left(- \sum_{n=1}^N X_{l,n} \right) \quad (18)$$

for the total path:

$$\tau_{total}(\omega) = - \exp(-X_{total}) \quad (19)$$

The total radiance is derived by using the radiance of the black body radiator

$$I(\omega) = - \int_0^s I_s(\omega, T(l)) \left(\frac{d\tau(\omega, l)}{dl} \right) dl$$

$$= \sum_{l=1}^L I_s(\omega, T_l) \Delta\tau_l(\omega) \quad (20)$$

with $\Delta\tau_l(\omega) = \tau_l(\omega) - \tau_{l-1}(\omega)$ and $\tau_l(\omega) = 1$

For analyzing soot it is assumed that the particle size is small compared to the wavelength which enables to write down the absorption coefficient as [4]:

$$k_{soot}(\lambda) = \frac{36\pi\rho F(\lambda)}{\rho_0\lambda} \quad (21)$$

particle mass density ρ in g/cm³, density of solid soot ρ_0 and wavelength λ . $F(\lambda)$ depends on the complex refractive index and was analyzed by Boynton et al. [19].

This absorption coefficient can be used as one of gases resulting in an optical depth X

$$X = k_{soot}(\omega, T) \rho s \quad (22)$$

allowing a summation on many layers as for the case of gases.

The molecules consisting of C, N, O and H are quite well documented and analyzed [14, 15, 18, 20–26]. 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 [27]
- CuH, CuCl, CuOH in propellants with copper catalysts
- BO, HBO₂ and especially BO₂ in the visible range [27–29]
- BaCl, CuCl, CuOH, CuO, Sr_xO_y and SrOH for pyrotechnic mixtures [1, 2]

These bands were not studied in detail by fundamental research therefore the use for temperature measurement is rather limited.

3.4 Metal Lines

In addition, many metal lines can be found in flames of pyrotechnics. Resonance lines are strongly present, often in full self absorption. They will not be considered here in detail.

4 Results and Discussion

In pyrotechnic mixtures or charges similar components as in rocket propellants can be found.

The combustion products of some model propellant formulations were calculated to get an overview of constituents by using a thermodynamic code developed at ICT [30]. Results and compositions of the basic formulations are shown in Table 1. Reaction products and temperatures were obtained assuming

- an inert atmosphere at 10 MPa
- a combustion in air after expanding to 0.1 MPa.

The latter data should account for after burning of the species in the rocket plume.

Table 1. Temperatures and main reaction products calculated from ICT thermodynamic code for different propellant formulations at 10 and 0.1 MPa simulating a rocket exhaust plume including secondary combustion with air

Propellant	Nitramine		Double Base		Composite	
Composition	85% HMX 15% binder		50% NC (13.3% N) 35% NGI 11% Triacetine 2% Centralite 2% CuO		80% AP 10% Al 10% binder	
Atmosphere	inert	air	inert	air	inert	air
Pressure in MPa	10	0.1	10	0.1	10	0.1
Temperature in K	2293	1227	2508	1317	3470	1909
Main reaction products in wt%						
CO ₂	5.931	27.700	21.790	37.832	8.362	19.647
H ₂ O	9.132	10.111	17.215	10.746	20.720	18.089
N ₂	32.551	62.168	13.332	50.743	9.509	34.100
CO	49.946	0.001	45.021	0.013	14.724	0.228
H ₂	2.421	0.000	1.008	0.000		
OH					1.487	0.034
Cl					2.332	0.261
HCl					22.166	15.492

For experimental investigations model propellant samples were investigated, like RDX/Estane or nitromethane pool fires. The spectra exhibit diatomic molecule bands in the UV/Vis-range and the combustion products in the NIR/IR-range.

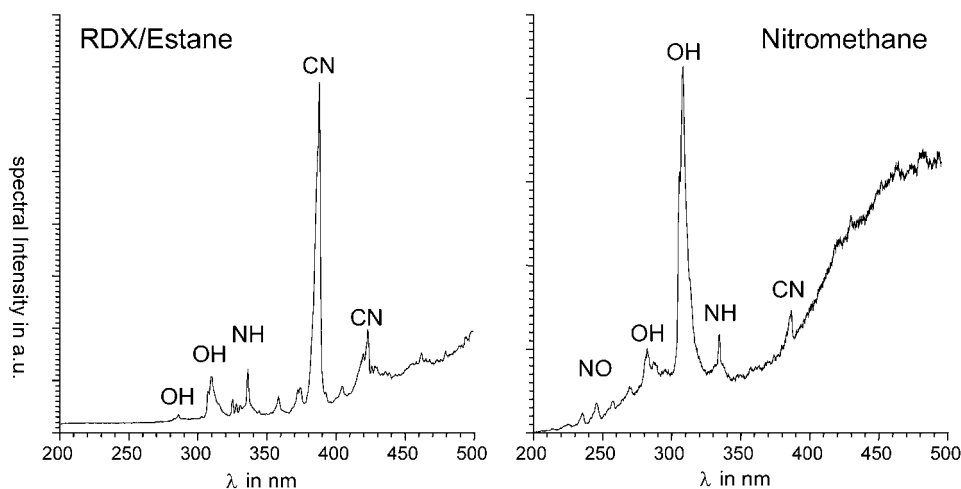
A medium resolved UV/Vis-spectrum (≈ 1 nm wavelength resolution) of a 95/5 RDX/Estane flame at a pressure of 0.5 MPa in nitrogen atmosphere is shown in Fig. 2. Besides the metal lines of Cu, Na and K, the emission bands of the decomposition products OH, CN and NH are observable.

The focus of the spectroscopic investigations was to record an intensity development at moderate pressures of the intermediate combustion products. Resulting profiles in flames for example show the influence of the hydrocarbon binder on the decomposition of RDX. The CN and NH radicals are observed only in the reaction zone. Also the

intensity of the OH molecule decreases with increasing height above the burning surface. This is in contrast to the finding that OH continues to emit with constant intensity also in upper flame regions of neat RDX [31–35]. With increasing binder, the hydroxyl radical is also limited to the reaction zone of the propellant flame following the profile of CN and NH.

From a composite rocket plume an example of an OH band analyzed for temperature is given in Fig. 3. More results are to be found in Ref. [36].

The band profile of OH has been rotationally resolved by using a 2400 lines/mm grating. The 0–0 band of OH has been compared to calculated intensity distribution for temperature determination (see Fig. 2). Average rotational temperatures 15 cm behind the nozzle were about 2500 to 3000 K. The calculated adiabatic temperature at a pressure of 10 MPa (pressure in the burning chamber) is 3500 K.

**Figure 2.** UV spectra of burning RDX model propellant and a nitromethane pool flame.

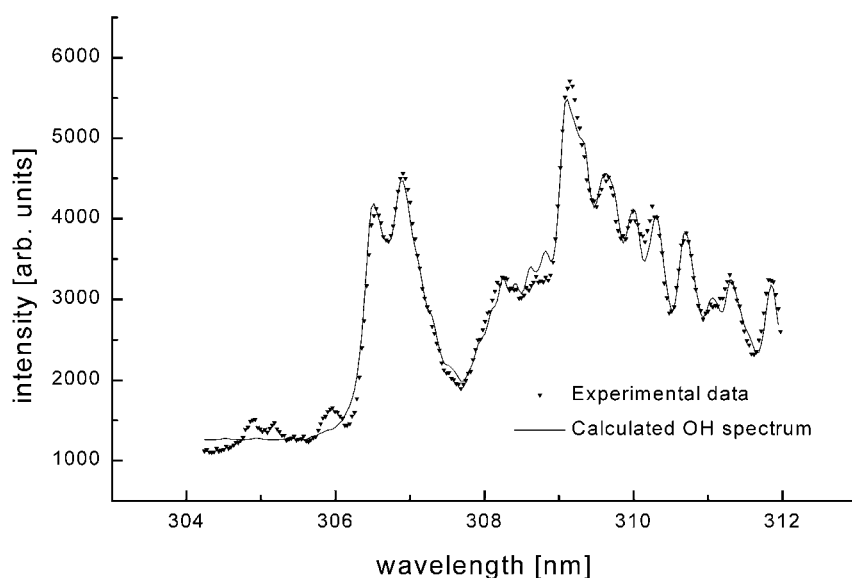


Figure 3. Rotationally resolved OH 0–0 band for temperature determination in a composite propellant exhaust plume.

Table 2. Molecules in a nitromethane pool fire and their temperatures from a fit to the emitted bands

Molecule	Transition	T_{rot}	T_{vib}
OH	$X^2\Pi - A^2\Sigma$	2380 (± 120) K	$= T_{rot}$
NH	$X^3\Pi - A^3\Pi$	2300 (± 170) K	$= T_{rot}$
CN	$X^2\Sigma - A^2\Pi$	2100 (± 110) K	4300 (± 210) K

Taking into account expansion to 0.1 MPa, temperatures of 2000 K are expected (see Table 1).

Pool fires of nitromethane deliver also interesting molecular flame bands (see Fig. 2 and Fig. 4). The resolved CN band in Fig. 4 is analyzed to obtain a rotational and a vibrational temperature.

Table 2 shows the different temperatures which might be obtained from an analysis of emitted molecular bands. It has to be taken into account if chemo luminescence might contribute to the emission band. In addition, self absorption might modify the band shape and make an analysis quite difficult.

Diffusion flames often emit a continuous spectrum [14]. The radiation from an isooctane pool fire generates a grey body spectrum an example of which is plotted in Fig. 5.

Profiles of molecule emissions of H_2O , CO_2 , CO , NO and NO_2 representing combustion products are obtained in the NIR and IR spectral range from various fires containing hydrocarbons using the fast scanning spectrometers described above. The analysis by the BAM code gives temperature

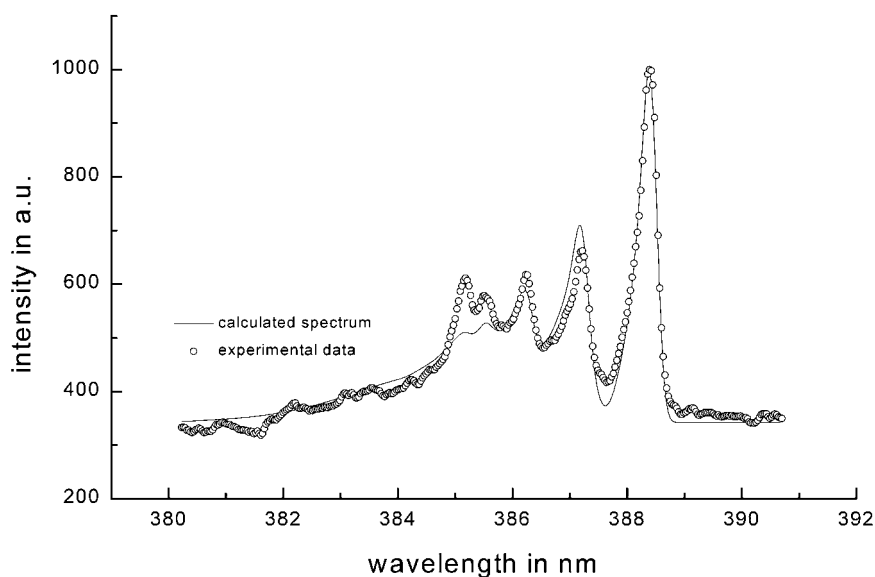


Figure 4. Comparison of an experimental and a calculated CN spectrum from the reaction cone of the nitromethane pool fire.

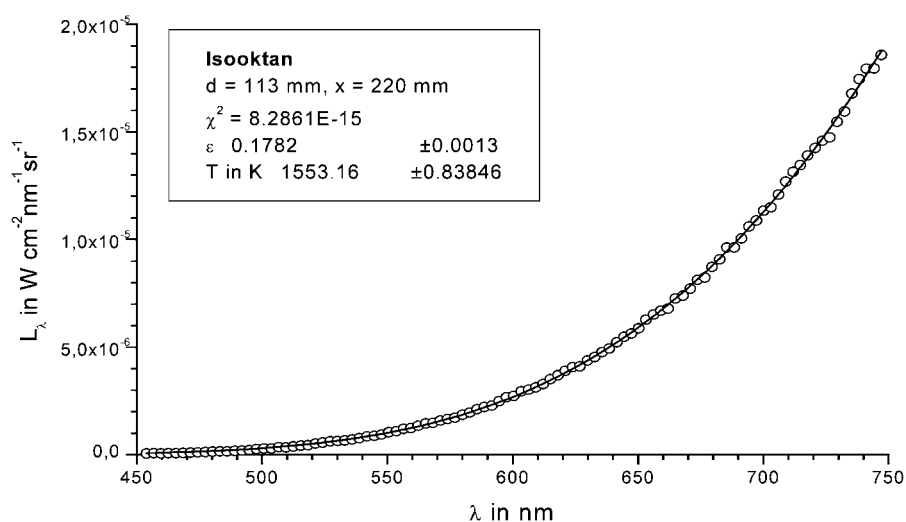


Figure 5. Continuous spectrum of an isooctane pool flame and its least squares fit by Grey Body radiation.

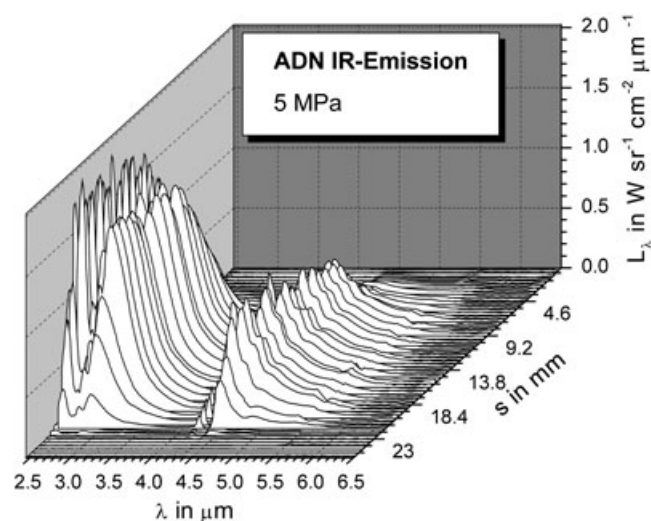


Figure 6. A series of IR spectra from the flame of ADN and an organic model binder.

profiles and relative concentrations of these compounds. A profile of bands in the IR is plotted in Fig. 6 measured from a flame of a sample of ADN with paraffin as an organic model binder. Details are published in Ref. [39].

Least squares fit of spectra using the BAM code are given in Fig. 7 for the nitramine model sample and for a nitromethane pool flame in Fig. 8. A nitramine model propellant sample burns generating the main reaction products H_2O , CO_2 and soot. In a nitromethane flame also NO and CO emit strong bands whereas soot particles are not present at remarkable amounts. More data are published elsewhere [26, 35, 38].

The spectroscopic methods are also useful for the investigation of droplets. An example is the behavior of nitromethane in a high-pressure high-temperature cell on heating shown in Fig. 9. The sequence of evaporation and decomposition is observed by the absorption bands of

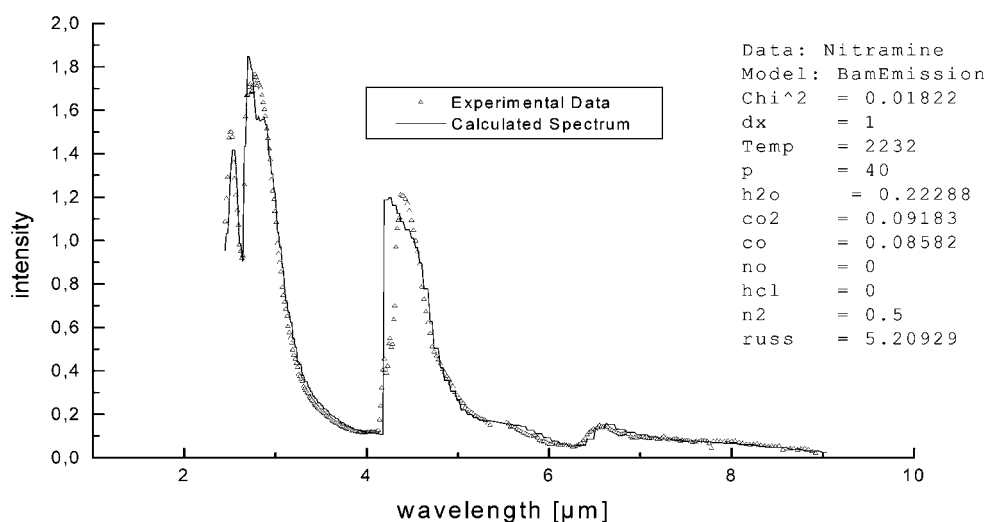


Figure 7. Comparison of a calculated and experimental spectrum of a nitramine model propellant flame ($T = 2200 \text{ K}$).

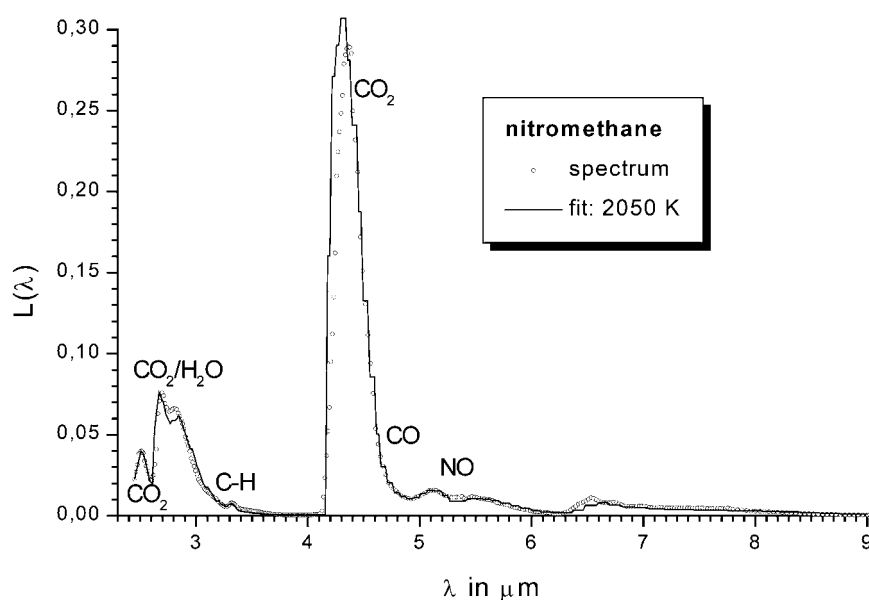


Figure 8. IR spectrum of a nitromethane pool flame and the least squares fit by the BAM code to obtain temperatures and relative concentrations.

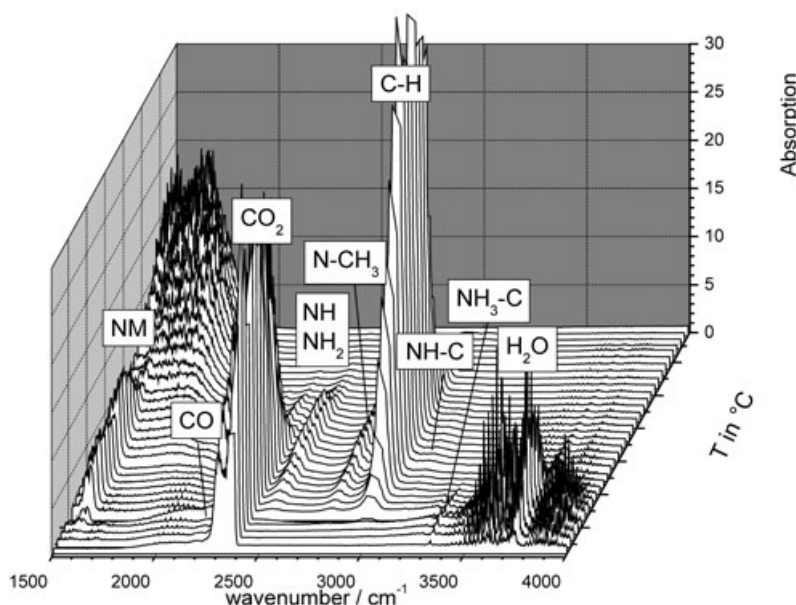


Figure 9. Evaporation and decomposition of nitromethane in a high pressure cell on heating.

initially nitromethane and at elevated temperature of degradation products and oxidation products.

A falling droplet (see Fig. 10) of a gelled propellant mixture of nitromethane/H₂O₂ was investigated by high speed video techniques, IR-cameras and the fast scanning NIR techniques [40, 42]. Application of the Hot Gas Sensor and evaluation of the results gives profiles of temperature and water concentration around these droplets (see Fig. 11 and 12). At the front end, the stagnation flow point, an immediate temperature increase is found, whereas temperature decreases slowly and water spreads out in the wake of the droplet.

During the burning of metal powders MeO and MeOH or MeH bands are often emitted [20, 21, 41]. An example of a burning Mg powder is shown in Fig. 13.

5 Conclusion

Time resolved spectroscopy can contribute to the understanding of the combustion of energetic materials. Temperatures and concentration profiles can be obtained from flames of propellant samples, pyrotechnic mixtures, metal powders and droplets. Measurements at distances for rocket

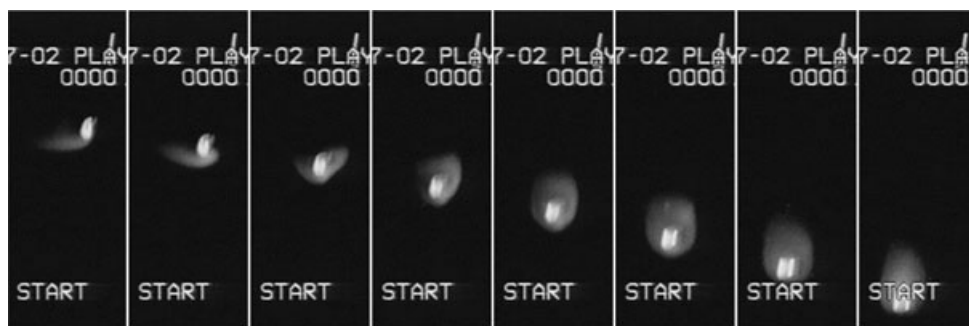


Figure 10. A falling droplet of a gelled nitromethan/H₂O₂ mixture.

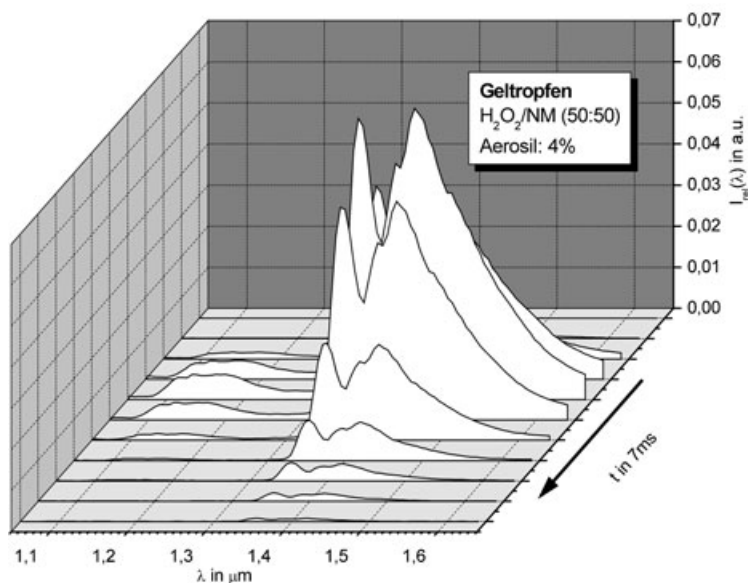


Figure 11. Hot Gas Sensor measurement of the water band at 1.4 μm .

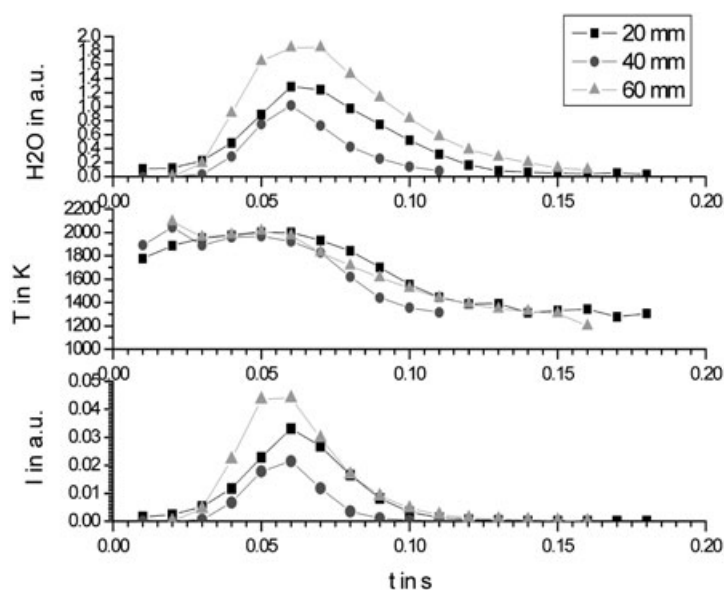


Figure 12. Measurement and evaluation of the Hot Gas Sensor when the falling droplet passes the spot of observation at various positions from the top.

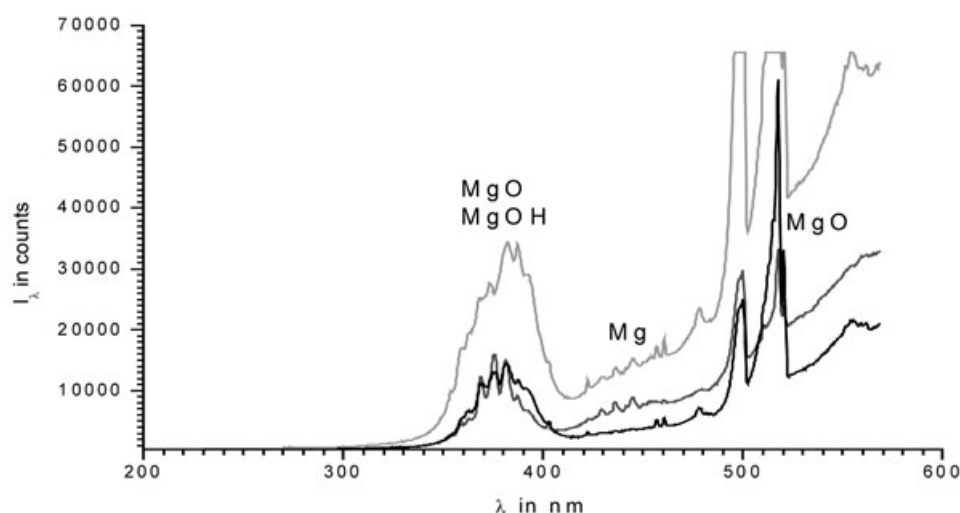


Figure 13. Spectrum in UV/Vis-range of a Mg powder flame.

plumes or flares are possible to enable the understanding of mechanisms and the progress of reactions self sustained or supported by environmental air.

6 Literature

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