SPACE PROPULSION 2016

LASER-INDUCED BREAKDOWN SPECTROSCOPY ON GAS COMPOSITIONS FOR EQUIVALENCE RATIO DETERMINATION IN SPACE PROPULSION

Robert Stützer[(1)], Michael Börner[(2)], Manuel Kuchelmeister[(3)], Michael Oschwald[(4)]

[(1)]*DLR – German Aerospace Center, Im Langen Grund, 74239 Hardthausen, Germany,*
Email: robert.stuetzer@dlr.de

[(2)]*DLR – German Aerospace Center, Im Langen Grund, 74239 Hardthausen, Germany,*
Email: michael.boerner@dlr.de

[(3)]*Technical University Munich, Arcisstr. 21, 80333 Munich, Germany,*
Email: m.kuchelmeister@mytum.de

[(4)]*DLR – German Aerospace Center, Im Langen Grund, 74239 Hardthausen, Germany,*
Email: michael.oschwald@dlr.de

KEYWORDS: Laser-induced Breakdown Spectroscopy, LIBS, Plasma Spectroscopy, Gas Composition, Equivalence Ratio, ROF, Laser Ignition

ABSTRACT:

Laser-induced breakdown spectroscopy (LIBS) was applied for local ROF measurements in rocket propulsion. Atomic hydrogen and oxygen spectral lines, emitted during laser-ignition of a LOx/GH$_2$ injection, are compared with the plasma emission of gases under well-defined conditions regarding equivalence ratio, pressure and temperature.

1. INTRODUCTION

Injection of multi-phase propellant compositions into a rocket combustion chamber results in inhomogeneous conditions. In particular, the critical shear layer between oxidizer and fuel is subjected to distinct turbulences. Hence, the determination of equivalence ratios for a narrow volume at a short period of time is challenging, whereas the overall ROF within the combustion chamber may be well-known. However, using the plasma emission of the laser-induced ignition breakdown, information from the critical volume of ignition can be obtained.

Laser-ignition is a reliable and reproducible method to start combustion under harsh conditions. Furthermore, the laser-induced ignition spark reveals important information of the conditions within the volume of its decay. As laser ignition is a highly localized ignition method the local ratio of oxidizer and fuel (ROF) is decisive for the success of the ignition process. Therefore, the plasma emission is used to determine the ROF exactly within the volume of ignition. Since atomic plasma emission depends on transition probabilities and other limiting factors, the intensities of the oxygen and hydrogen plasma lines are calibrated using LIBS on known gas mixtures in a lab-scale cavity.

A pulsed Nd:YAG laser is focused on the shear layer between liquid oxygen (Lox) and gaseous hydrogen (gH$_2$), resulting in a hot plasma that extends over a volume in the order of 1 mm^3. While decaying the plasma emits characteristic photons, carrying information of the constituents and therefore a spectral analysis of the plasma gives information about the equivalence ratio at the point of ignition. Furthermore, the hydrogen atom

delivers with its emission lines of the Balmer series a tool to calculate the plasma temperature when measuring during the state of local thermal equilibrium (LTE).

Using dynamic data acquisition methods for the intensity measurement of optical emission and pressure values, it is possible to determine the time of ignition to about 10 µs. The exact size and position of the plasma is monitored by an upstream oriented nozzle camera in order to control the ignition and flame anchoring on the multi-injector face plate (see Fig. 5).

2. EXPERIMENTAL

Two settings for LIBS measurements have been used for the comparison between cryogenic rocket combustion and experiments on gaseous compositions. A research rocket combustion chamber was laser-ignited with the opportunity to evaluate the ignition spark, and on the other hand, well-defined gas mixtures within a laboratory-scale cavity were analyzed using plasma spectroscopy.

2.1. Research combustor *BKA*

The model research combustor A (BKA) is a cylindrical, segmented rocket combustion chamber with an inner diameter of 50 mm and a nozzle diameter of 33 mm. Relevant optical and pressure probes as well as optical access for the laser-igniter are located in the diagnostic segment which is mounted directly on the same level with the multi-injector faceplate (Fig. 1). The centered injector serves as an arbitrary igniter but was disabled for this study.

In order to monitor the laser-induced plasma highly time-resolved, photo-multipliers were mounted to probe ports pointing onto the plasma volume. A breakdown control probe was equipped with an optical band pass filter for (306±5) nm in order to collect the OH* emission. The probe port opposite to the plasma control port was used for LIBS measurements and pointed also to the plasma volume. Furthermore, two opposite mounted ports for dynamic pressure sensors are applied perpendicularly to the laser beam. Further description of the combustion chamber and the test run setup can be found elsewhere [2].

Hot firing tests with two different propellants have been carried out on the European Research and Technology Test Bench P8 [1] at the DLR Institute of Space Propulsion in Lampoldshausen, Germany. Hydrogen or methane were applied in the gas phase, oxygen was injected as liquid. Pre-set injection parameters are depicted in Table 1. In total, more than 40 test runs were carried out during the campaign. In general a test run lasted 30 minutes and involved 60 ignition tests. The ignition itself was triggered using a laser burst of 20 single laser pulses, fired with a frequency of 50 Hz, a pulse width of 1—2 ns, and a peak energy of 30 mJ. The applied laser ignition system was a Q-switched HiPoLas® laser made by CTR (Carinthian Tech Research AG) directly mounted to the combustion chamber via a lens tube containing optics for optimal focusing and precise focal point placing within the combustor. This system allowed the radial displacement of the focal point position on the shear layer between LOx and the gaseous fuel for best ignition. The laser-induced ignition spark and the flame emission of the hot exhaust gas during a firing test using GCH4 and LOx is shown in Fig. 2.

Table 1. Preset injection conditions for laser-ignition tests on cryogenic propellants using rocket combustor "BKA".

	max. mass flow [g/s]	calc. injection velocity [m/s]	Temp. at ignition [K]
oxygen	600	10.6	110; 280
hydrogen	150	1300	120—280
methane	200	450	279—290

Furthermore, a Dalsa® Genie-HM 1024 surveillance camera was mounted in front of the nozzle with unobstructed view to the place of ignition. The camera possesses a monochromatic 2/3" CMOS sensor with global shutter and 1024X768 pixels. The sequence of interest was recorded with the maximum frame rate of 117 frames per second. A LED light source was installed behind the camera to illuminate the combustion chamber face plate. Both camera and light source were encased by a steel housing with a 2 cm thick quartz glass window on its front end. Convective cooling with gaseous nitrogen prevented the system from overheating when exposed to hot gases of the exhaust plume.

Laser-induced breakdown spectroscopy (LIBS) on the ignition spark was conducted using two spectroscopic systems for simultaneous recordings of highly spectral resolved data as well as overall pictures ranging from UV to NIR. As depicted in Fig. 3 the plasma signal was split via fibre switch and both ends connected to the spectrographs.

Using a control voltage signal of the laser diode the pulse generator and therefore both spectrographs were triggered simultaneously.
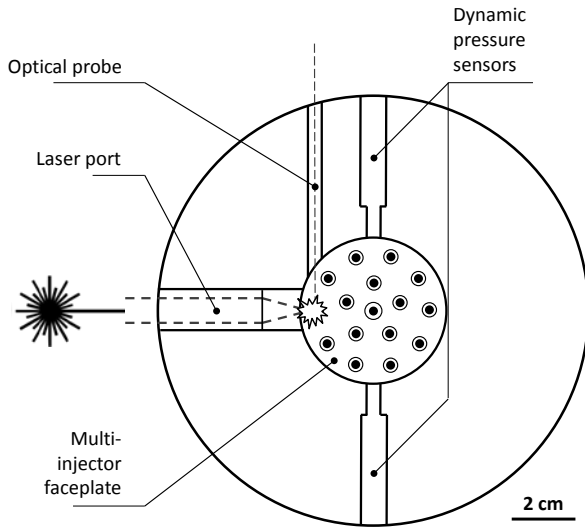

Figure 1. Diagnostic segment (front view) as used in combustion chamber "BKA" for optical and pressure measurements. The laser-induced ignition spark is located at an outer coaxial injector with the possibility for plasma spectroscopy (LIBS).

The Acton spectrograph SP2750 from Princeton Instruments[TM] was used for the requirement of higher spectral resolution. It has a focal length of 750 mm, a scan range of 0-1400 nm, and is arranged in a Czerny-Turner design. Optical signals were recorded via the intensified camera PI-MAX: 1024 (PI[TM]) with a front illuminated, Peltier-cooled, 1012 x 256 imaging array (pixel size: 26µm x 26µm). All measurements were conducted in gated mode for short exposure times and to avoid outshining by the laser intensity. All spectra were recorded using a grating with 150 gr/mm and a center wavelength of 720 nm in order to depict emission of the Hα-line at 656.3 nm and of oxygen at 777.2 nm on a single frame.
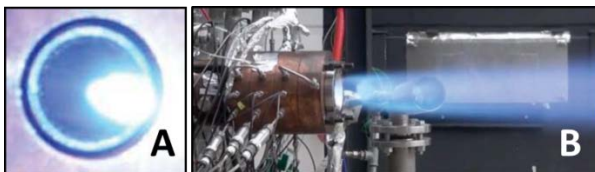

Figure 2. Ignition spark on one of the 15 coaxial injectors (A), and the exhaust plume of a LOx/GCH4 combustion at test bench P8 (DLR Inst. of Space Propulsion) after laser ignition.

Wider range LIBS measurements were carried out using the Czerny-Turner designed Andor[TM] Shamrock SR-163 spectrograph with a focal length of 163 mm. A diffraction grating, blazed for 350 nm and 150 gr/mm was applied in order to obtain the entire spectrum from 250 nm to 900 nm wavelength in a single exposure.

The optical equipment was connected to the combustion chamber using sapphire rods, installed inside patent pending stainless steel probes (design: S. Gröning (DLR Institute of Space Propulsion)), described in more detail in [3]. These connections ensured line-of-sight measurements for a wide range of optical wavelengths in high-pressure and high-temperature environment.
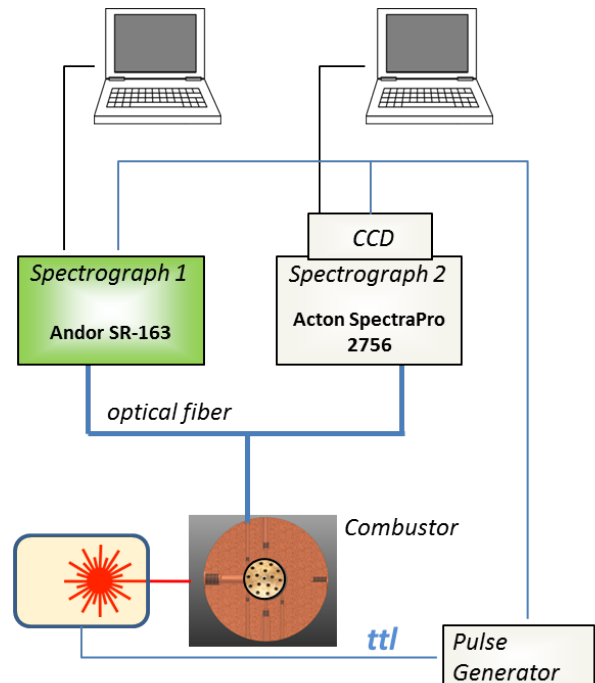

Figure 3. Measurement setup for laser-induced breakdown spectroscopy (LIBS). The collected signal is simultaneously recorded by two spectrographs.

2.2. LIBS on gas mixtures

LIBS measurements on defined gas compositions were carried out at the DLR Institute of Space Propulsion. A small stainless-steel chamber with a cavity of the size of ca. 10 cm^3 was used to retain the gas mixture. The ratio of the components was controlled via pressure sensors in order to adjust

correct partial pressure values. A sketched figure is shown in Fig. 4. Besides air, 4 gases have been used solely and composed in defined mixtures: hydrogen, oxygen, helium and argon.
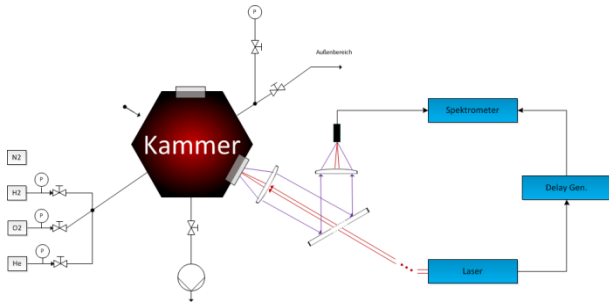

Figure 4. LIBS setup for gas mixture measurements [14].

The chamber, designed for pressures up to 15 bar, has several gas connections and is optically accessible using quartz glass windows. The laser beam was focused into the cavity by a lens with $f=$ 150 mm in order to create a volume for breakdown of 1 mm^3 in the gas phase (non-ablative). A dichroic mirror (Thorlabs®) with a cutoff wavelength of 950 nm, filtering the laser wavelength of 1064 nm, allowed coaxial application of the laser beam and the plasma emission. The latter was focused on the optical fiber by a $f=$ 40 mm plano-concave lens. Using the spectrograph SP2750 of Princeton Instruments^{TM}, described in section 2.1., the plasma emission was spectrally analyzed.

A water-cooled Nd:YAG Quantel^{TM} laser system was applied in order to induce the ignition plasma in the gas chamber (non-ablative) using its fundamental wavelength of 1064 nm and pulse energies between 30 mJ and 60 mJ. For hydrogen/oxygen gas compositions only one breakdown could be induced in order to obtain emission of the virgin mixture. Inert gas mixtures were pulsed with a frequency of 10 Hz. Accumulations of 50 up to 100 plasma emissions were used to analyze one measurement point (mixture ratio). The pulse width of the laser was in the range of 10 ns (FWHM) and the primary beam diameter was less than 10 mm. The dichroic mirror enabled coaxial access into the cavity and quartz glass lenses focused the laser beam on the location of breakdown. The Gaussian line-shape of the applied laser beam was evaluated using time-resolved calorimetric measurements.

3. RESULTS AND DISCUSSION

Both setups use optical elements in order to increase the energy density of the laser beam within a volume of ca. 1 mm^3. For plasma spectroscopy on the cryogenic propellants, ignition-laser and optical probe were spatially separated (Fig. 3). The setup for reference measurements on well-defined gas mixtures was equipped with a coaxial access for laser-beam and plasma emission signal for analysis. However, results of both setups are separately described but compared in order to validate a potential calibration tool.

3.1. Laser-ignition on cryogenic propellants

Using the research combustor BKA laser-ignition was carried out on the shear layer between liquid oxygen (LOx) and gaseous hydrogen (GH2) or LOx and gaseous methane (GCH4). The plasma cloud as well as the stabilized flame can be seen in Fig. 5 for hydrogen combustion, viewing directly on the multi-injector face plate in counter-flow direction.
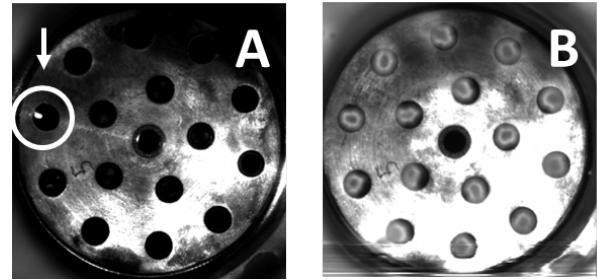

Figure 5. View into the combustion chamber during laser-ignition. A: Plasma cloud on the LOx/GH2 shear layer (white circle) of one of the 15 coaxial injectors at time t_0. B: stable combustion 720 ms after t_0.

The 117 fps and the exposure time of 8 ms of the Dalsa Genie camera are sufficient to resolve the image of several integrated breakdown events. The volume of the plasma is in the order of one cubic millimeter. After 720 ms, however, the stable combustion phase is reached. Since hydrogen/oxygen as well as methane/oxygen flames emit mainly in the UV and only slightly in the visible optical regime [4] the flame appears transparent. However, due to a pressure dependency of the intensity in the visible regime [5] the anchoring of the flame on the injectors

becomes visible due to emission of the typical blue radiation. Over the entire combustion process the flame structures remained constant though deviating from an ideal circular form.

A typical response of optical and pressure data is shown in Fig. 6. The laser-induced plasma emission is clearly visible in the photo-multiplier data during the first 500 ms. The first laser pulses do not lead to ignition of the LOx/GH2 mixture indicated by the flame emission, which lasts until combustions shutdown at 2.2 s. Therefore, the radiation source mainly is the emission of the OH* radical. The corresponding pressure data are shown in the red graph, revealing a distinctive match between both optical and pressure data sets. This is in excellent agreement with results of further investigation on hydrogen flames [6]. A FFT analysis also showed identical behavior for optical and pressure responses. Hydrogen flames exhibit a dominant frequency at 950 Hz. On the other hand, methane flames show 4 distinct frequencies at 950 Hz, 1750 Hz, 3600 Hz, and 5450 Hz [7] for this experimental set-up.
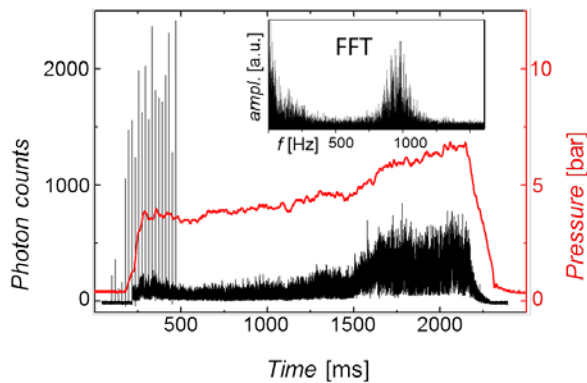

Figure 6. Typical sequence of a laser-ignited LOx/GH2 combustion in BKA. The black line depicts the optical signal with the clearly visible laser-induced plasma emission peaks during the first 500 ms. The red line is the corresponding chamber pressure. Inlay: both optical and pressure data show a dominant frequency at 950 Hz.

Using the setup depicted in Fig. 3, laser-induced breakdown spectroscopy was carried out on a narrow spectral regime from 650 nm up to 800 nm and on a wider regime from UV to NIR. As depicted in Fig. 7 (A) and (B), a center wavelength of 725 nm was used to collect data of the hydrogen alpha line (656.3 nm) and the transition triplet of oxygen (777.2 nm, 777.4nm, 777.5 nm) [8], though the latter appears in the spectrogram only as a single band due to the used spectral resolution of about 1 nm. The peak intensity of both emission bands shows a linear dependence on the laser pulse energy. However, the ratio between Hα and the O I triplet is nearly constant over a wide range of laser pulse energy values [9]. On the other hand, an increase in the single-shot deviance has been shown for increased laser pulse energy [10].
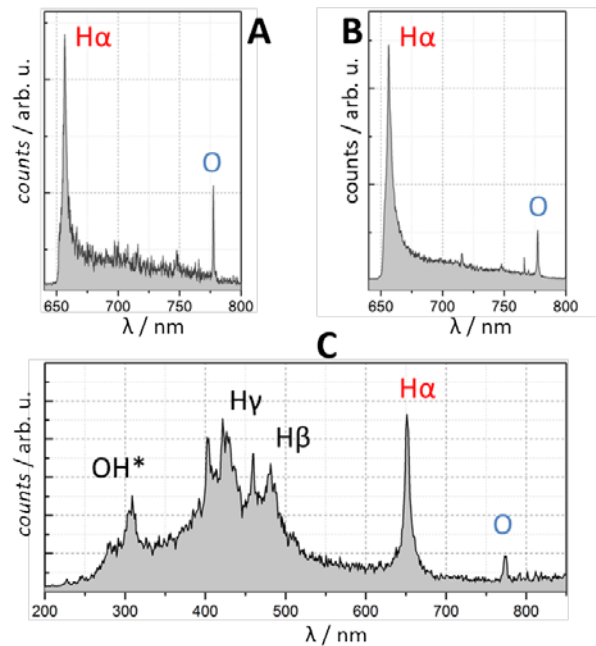

Figure 7. LIBS on ignition sparks of cryogenic propellants. A: LOx/GH2 combustion. B and C show the plasma emission of LOx/GCH4 mixtures. Graph C depicts the overall emission with the equivalence-ratio dependent H and O lines together with 2 other lines of the Balmer-series and the flame emission indicated by the OH band around 306 nm.*

LIBS measurements on the Hα/O ratio were carried out in gated mode operating with a gate width of 2 μs, and the wider range spectra ungated. The latter showed not only atomic plasma decay lines but also signals of flame emission as the OH* band around 306 nm. Furthermore, several other lines of the Balmer-series such as Hβ and Hγ are resolved in the spectra.

Due to prolonged read-out times and trigger adjustment it was only possible to collect data of every second laser-induced breakdown spark. The

first recorded spectrum shows no signal indicating therefore the absence of plasma at that time. The second spectrum 40 ms later shows a distinct peak at 656.3 nm for the Hα-line [7]. However, no oxygen emission is visible. As seen in Fig. 2(A) and Fig. 5(A), the introduced plasma breakdown is located well within the shear layer between the two constituents. Moreover, injection velocity of circa 20 m/s for liquid oxygen and the gate width of 2 μs preclude the possibility of turbulence effects to explain the absence of oxygen. At a time of 120 ms after the first laser pulse, oxygen emission at 777 nm becomes visible and is recorded in the spectrum [7].
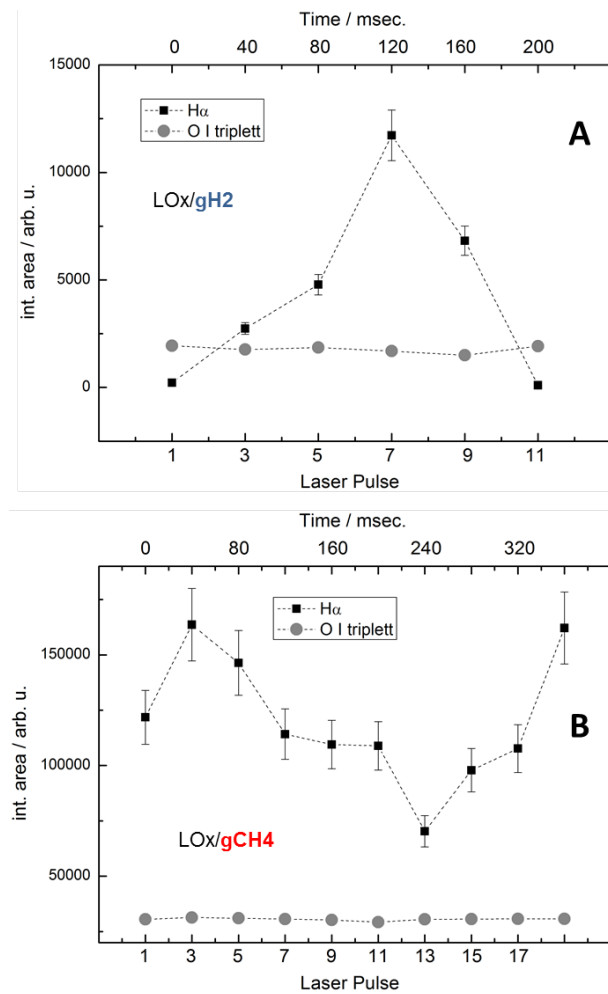
Figure 8. Integral intensities of plasma decay lines as a function of time (number of laser pulse) for an ignition of LOx/gH2 (A) and LOx/gCH4 (B).

Inhomogeneous propellant feeding across the injector faceplate can be caused by the injector geometry. Time series of relevant plasma decay lines are depicted in Fig. 8. As expected, the Hα

line dominates the spectral recordings at the ignition phase. Hα at 656.28 nm is the brightest spectral line of excited hydrogen and origins from the $3 \rightarrow 2$ transition with a probability of 4.41e+07 s^{-1} [8]. Oxygen at 777 nm on the other hand, is a triplet of the $^5P \rightarrow ^5S$ transition with a probability of 3.69e+07 s^{-1} [8]. However, after 250 ms plasma decay signals decrease drastically. Flame emission can be measured from ca. 0.5 ms after triggering the first ignition laser pulse with a significantly increasing intensity (Fig. 6).

3.2. LIBS on Gaseous Mixtures

Unlike measurements under real rocket combustor conditions described in the previous subsection, plasma spectroscopy in a laboratory scale cavity delivered results for known composition ratios, pressure and temperature.

Propagation and decay of laser-induced plasma sparks are determined several aspects such as laser pulse shape, degree of ionization, and specific ionization energy. Therefore, a superposition of a variety of approaches describes the time and spatial distribution of the plasma emission [11], [12]. The time frame for signal recording is thus a crucial parameter and has to be examined carefully. A time series of the intensity-background ratio of nitrogen and oxygen plasma emission lines as depicted in Fig. 9 delivered an optimal delay time of about 2000 ns.
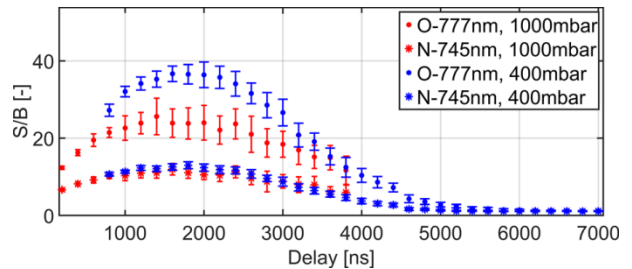
Figure 9. Signal/background ratio (S/B) as a function of delay time (time between initial laser trigger and spectrograph shutter opening). Medium: Air.

The oxygen triplet around 777 nm and the nitrogen emission line at 745 nm where examined at low pressure and ambient temperature. The signal to noise ratio reaches its maximum also at a delay time of about 2000 ns. Using the optimal delay time for measurements, pressure dependent recordings where carried out for several gases. As seen in Fig. 10 for oxygen and hydrogen under low pressure and ambient temperature conditions, the

intensity of atomic plasma emission lines of oxygen increases with a sigmoidal shape for increasing pressure. Hydrogen intensities grow exponentially with increasing pressure. It is assumed, that hydrogen as well shows sigmoidal behavior, yet the depicted range is not wide enough to show the saturation. Both oxygen and hydrogen where investigated using two lines that are close enough for an exposure on the same measurement. Nevertheless, the intensity ratio between both corresponding lines over the same pressure range remains nearly constant. Only the data point for the lowest pressure depicts an outlier.
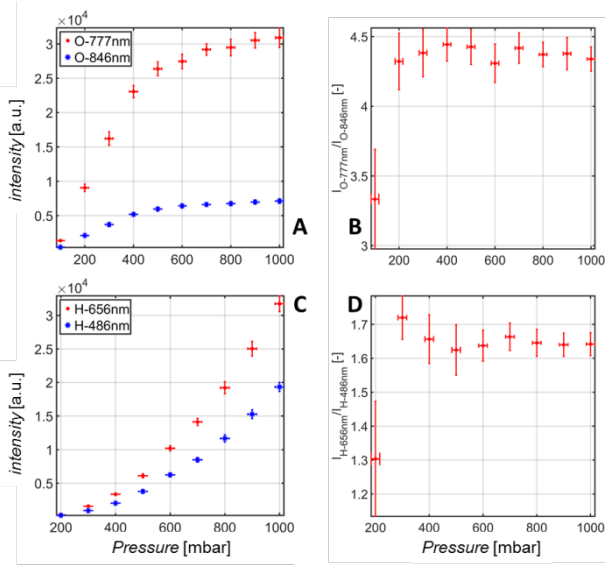

Figure 10. Pressure dependent line intensities of oxygen (A) and hydrogen (C). Corresponding line intensity ratios are shown in (B) and (D).

Moreover, other gases such as helium and nitrogen reveal similar behavior regarding their line intensities in the investigated pressure regime. Furthermore, it was shown that laser pulse energy of 30 mJ is sufficient to induce a breakdown in the gas phase for all pressure values under investigation. The apparent saturation effect of the emission intensity for higher pressure values in gases is explained by an increasing energy of the free electrons accompanied by a preference for second order collisions [13].

In order to characterize oxygen and hydrogen containing gas mixtures with improved reproducibility, these propellants were first combined with inert gases that resemble the absent constituent.

Oxygen/Helium

Helium with its very low spectral background noise and its emission lines which do not interfere with those of O_2 makes it the ideal surrogate for hydrogen. While pressure within the cavity was kept constant the mixture ratio was determined by the partial pressure. The development of the oxygen emission line at 777 nm and the helium emission line at 586 nm as well as their intensity ratios are depicted in Fig. 11 as functions of the constituent's partial pressure. A typically sigmoidal shape characterizes their pressure dependence.
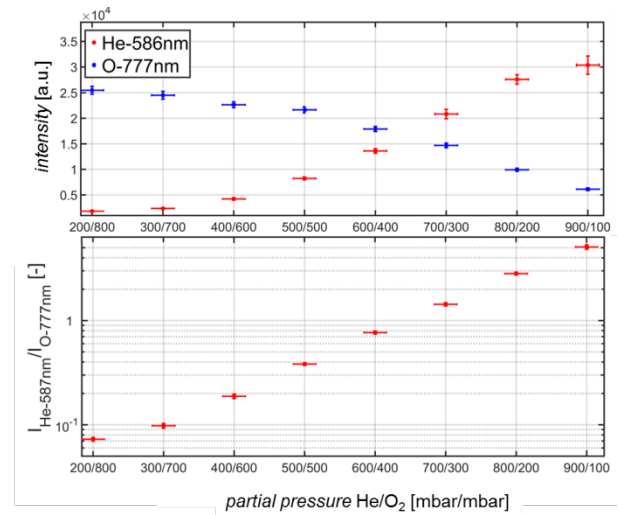

Figure 11. LIBS on oxygen/helium compositions. The upper graph shows integral intensities of specific emission lines for a series of partial pressures (mixture ratios). The lower graph shows the development of the intensity ratio of both lines for the considered partial pressure range.

Hydrogen/Helium

In order to obtain reproducible data for hydrogen in a gas mixture, helium is used as the oxygen surrogate to prevent ignition of the gas mixture to be investigated. The total pressure is kept constant at 1 bar. Corresponding mass ratios are listed in Tab. 2. The measurements were carried out in steps of 100 mbar under ambient temperature conditions. An absent combustion enables extensive series of laser-induced breakdowns without to alter chemically and physically the state

of the propellants. Hence, recording rates of 10 spectra per seconds are possible.

Table 2. Partial pressure ratios of He and O_2 with corresponding mass ratios.

p_{He}/p_{O2} [mbar/mbar]	m_{He}/m_{O2} [g/g]
200/800	0.03
300/700	0.05
400/600	0.08
500/500	0.13
600/400	0.19
700/300	0.29
900/100	1.13

However, LIBS on H/He compositions revealed clearly a dominant hydrogen emission for a broad regime of partial pressure ratios. Even mixtures with the highest helium proportion showed only evanescent traces of the characteristic emission line at 586 nm compared to the emission lines of the hydrogen Balmer series as depicted exemplified in Fig 12.
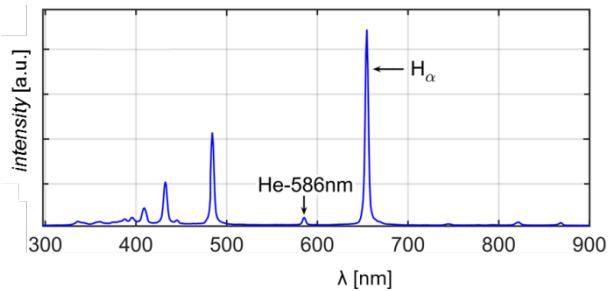

Figure 12. Plasma emission spectrum of a helium/hydrogen gas mixture. The partial pressure ratio is 4:1 (He:H).

Moreover, the absolute intensities of both helium and hydrogen increase with higher values of He partial pressure. This remarkable result is in considerable contrast to measurements of all other gas compositions. The overall plasma emission therefore increases with a higher helium portion, yet hydrogen outshines the total recording. For a concluding explanation of this phenomenon further studies have to be conducted. Nevertheless, the dominant hydrogen emission can only be described under the assumption of differences in the mean free path of both particle species. This

may result in an outer hydrogen layer encasing the plasma cloud. Since plasma absorbs radiation of all wavelengths, radiation from decay processes of the inner core of the plasma is prevented from reaching the outer zones of the spark. Therefore, only the lighter hydrogen can emit its characteristic light from the outer sphere.

Hydrogen/Nitrogen

With nitrogen as the inert gas of the periodic table of the ements main group V, H_2 is mixed with a diatomic partner in order to evaluate a second non-ignitable gas composition using LIBS. At equalized partial pressure conditions, only minor nitrogen emission is visible in the plasma spectrum compared to the overwhelming Hα line. The intensity ratio between Hα and the nitrogen line at 745 nm is 44.36. When increasing the nitrogen partial pressure to 800 mbar and decreasing P_{H2} to 200 mbar the total plasma emission increases significantly. However, the Hα/N-745 line ratio is 22.9. Even the continuous emission background noise of the nitrogen plasma is negligible. However, with P_{N2} = 900 mbar and P_{H2} = 100 mbar the line ratio is reaches 11.64.

The amount of plasma emission seems to benefit from the presence of inert gases such as helium and nitrogen. Elevated electron density and temperature can result in a sustained local thermal equilibrium (LTE) and therefore the recombination of hydrogen is delayed.

Hydrogen/Oxygen

The ignitable mixture H_2/O_2 is used to reproduce equivalence ratios of the previously described rocket combustor. Experiments with two total pressures were conducted, 1000 mbar and 500 mbar. Though the used pressure values are lower than those during the cryogenic combustion at test bench P8, the used ROF value series applied within the lab-scale cavity resembles the mixture ratios in the BKA rocket combustion chamber.
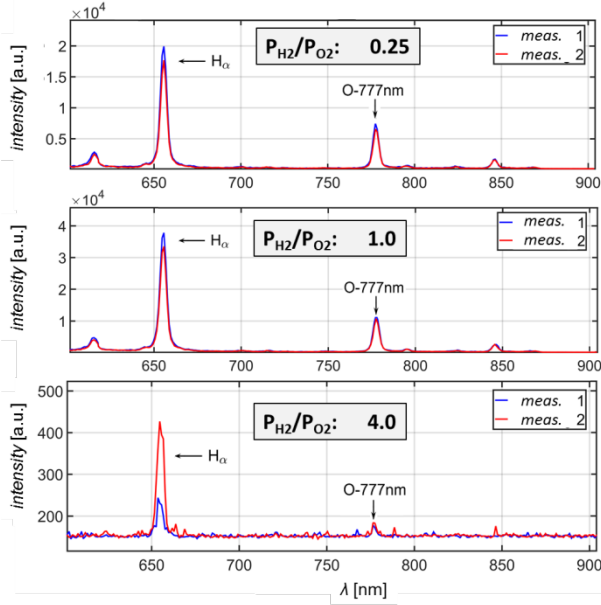
Figure 13. LIBS measurements of three hydrogen/oxygen gas compositions. Upper graph: high amount of oxygen. Lower graph: high amount of hydrogen.

Plasma emission spectra of three different equivalence ratios are depicted in Fig. 13. The total pressure was measured 500 mbar before ignition. Corresponding mass ratios are listed in Table 3. Regarding the recorded spectra the signal of the gas mixture of partial pressure ratio 1:4 appears intense whereas the signal of the gas mixture with the reverse partial pressure ratio of 4:1 appears weak and relatively noisy. However, hydrogen absorbs less laser energy than oxygen and exhibits a significantly shorter plasma life time when solely existing in the excited volume [14].

Table 3. Partial pressure ratios of H_2 and O_2 with corresponding mass ratios.

p_{H2}/p_{O2} [mbar/mbar]	m_{H2}/m_{O2} [g/g]
400/100	3.97
250/250	15.87
100/400	63.49

Moreover, a minor hydrogen percentage results in intensified emission for delayed measurements, e.g. 2000 ns after peak emission. With increasing proportion of hydrogen the life time of the plasma decreases considerably. The deviation of line intensities for higher amounts of H_2 implies strong

background noise and a variation in the plasma life time.

In order to obtain ideal signal to noise ratios, plasma measurements were carried out 250 ns after triggering of the laser pulse.
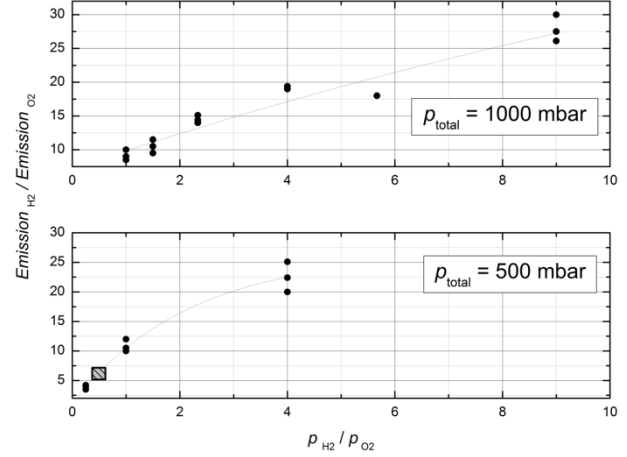

Figure 14. Results of LIBS-measurements on H_2/O_2 compositions for two total pressure values. The rectangle in the lower graph assigns the plasma line ratio of Hα and O(777nm), emitted from the ignition spark, analyzed in Fig. 8.

A series of plasma line ratios (Hα/O-777nm) as a function of the partial pressure ratio between hydrogen and oxygen is depicted in Fig. 14. Two different total pressure values are considered, 1000 mbar, and 500 mbar. Measurements for all pressure settings were repeated severally. However, the measured dependency between partial pressure value and plasma emission slightly deviates from the expected linearity when the total pressure is 1 bar, but differs more significantly when pressurized to 500 mbar.

Table 4. Density (ρ) and molar masses (M) of gaseous hydrogen and gaseous oxygen at ambient conditions as well as liquid oxygen at p= 1 bar and T= 90K. The number of particles (n) within the considered volume (1 mm^3) refers to the molecules H_2 and O_2 for gaseous media and O_1 for liquid oxygen.

	ρ [mg/mm³]	M [g/mol]	n / mm³
gH2	0.0899×10^{-3}	2.016	2.685×10^{16}
gO2	1.43×10^{-3}	32.0	2.689×10^{16}
lOx	1.141	16.0	4.295×10^{19}

The ignition spark is considered to be extended over a volume of 1 mm^3. With the density and molar mass values listed in Tab. 4 a total number of n molecules can be derived for the constituents within the excited volume.

Therefore, the measured plasma emission, recorded at the laser-ignition analyzed in Fig. 8 and depicted in Fig. 14 refers to an equivalent gaseous partial pressure value of 0.45, which in turn indicates a number of 2.96×10^{16} excited oxygen atoms within the volume of the ignition spark. Thus, the measured emission ratio correlates with a volume proportion of 6.9×10^{-4} of liquid oxygen inside the considered volume. Moreover, when taking the molar masses of the constituents into account, a local ROF inside the ignition spark of 35.3 is derived.

4. CONCLUSION

Laser-induced breakdown spectroscopy on ignition sparks was carried out. In order to derive local values for the equivalence ratio within the volume of the plasma, two studies were conducted. On the one hand a laser-ignited cryogenic combustion study at the European research test bench P8, and, on the other hand, ignition experiments on well-defined gas mixtures in a lab-scale cavity for comparative measurements regarding reliable and reproducible calibration values were realized.

Using the ratio between characteristic plasma emission lines of hydrogen and oxygen, the mixture ratio between both constituents can be calibrated on known compositions. Thus, estimations can be made on the spectral data of the LOx/gH2 combustion regarding the local ROF within the plasma volume. The relatively high value of 35.3 for the mass fraction between H_2 and O_2 is due to the used gaseous hydrogen and the relatively dense liquid oxygen in the volume of ignition. With respect to the optically non-transparent plasma, only emission from the outer plasma layers can be recorded. Thus, information from inner plasma areas is shielded and can attain the surface only indirectly.

Moreover, the synchronism of optical emission and pressure in the combustor *BKA* could be shown. Emission intensities as a function of time as well as their underlying frequencies are in good agreement with the measured pressure data.

6. REFERENCES

1. Haberzettl, A. *et al.* (2000). European research and technology test bench P8 for high-pressure liquid rocket propellants. In: *36th AIAA/SAE/ASME/ASEE Joint Propulsion Conference*.

2. Börner, M., Manfletti, C., Grebe, A., Hardi, J., Stützer, R., Suslov, D. & Oschwald, M. (2015). Experimental Study of a Laser-Ignited Liquid Cryogenic Rocket Engine. In: *Laser Ignition Conference (LIC)*.

3. Gröning, S. *et al.* (2015). Analysis of Phase Shift Between Oscillations of Pressure and Flame Radiation Intensity of Combustion Instabilities. In: *6th European Conference for Aeronautics and Space Sciences (EUCASS)*.

4. Fdida, N., Vingert, L. Ordonneau, Ristori, A., Brossard, C., Stützer, R. & Sender, J. (2013). Characterization of a Double Swirl Injector in a LOx/LCH4 Fueled Combustor on Mascotte Test Bench. In: *5th European Conference for Aeronautics and Space Sciences (EUCASS)*.

5. Fiala, T. & Sattelmayer, T. (2015). Heat Release and UV-Vis Radiation in Non-Premixed Hydrogen-Oxygen Flames. *Exp Fluids* **56**(144), 1-15.

6. Fiala, T., Sattelmayer, T., Gröning, S., Hardi, J., Stützer, R., Webster, S. & Oschwald, M. (2016). Comparison Between OH* and Blue Radiation from Hydrogen Rocket Combustion. *To be published*.

7. Stützer, R.G., Börner, M. & Oschwald, M. (2015). Optical Investigation of a Laser-Ignited Cryogenic Rocket Combustion. In: *6th European Conference for Aeronautics and Space Sciences (EUCASS)*.

8. NIST *Atomic Spectra Database 5.2*. National Institute of Standards and Technology, Gaithsburg, MD.

9. Phuoc, T. & White, F. (2002). Laser-Induced Spark for Measurements of the Fuel-to-Air Ratio of a Combustive Mixture. *Fuel* **81**, 1761-1765.

10. Zimmerer, L. & Tachibana, S. (2007). Laser Induced Plasma Spectroscopy for Local Equivalence Ratio Measurements in an Oscillating Combustion Environment. In *Proceedings of the Combustion Institute* **31**, 737-745.

11. Harilal, S.S., Brumfield, B.E. & Phillips, M.C. (2015). Lifecycle of Laser-Produced Air Sparks. *Physics of Plasmas* **22**, 063301.

12. Braithwaite, N.St.J. (2000). Introduction to Gas Discharges. *Plasma Sources Sci. Technol.* **9**, 517-527.

13. Hanafi, M., Omar, M.M. & Gamal, Y.E.E-D. (2000). Study of LIBS of Gases. *Radiation Physics and Chemistry* **57**, 11-20.

14. Kuchelmeister, M. (2015). LIBS an Wasserstoff und Sauerstoff als Charakterisierungs-methode für Mischungsverhältnisse von Treibstoffen in Raketenbrennkammern. *Master Thesis*, Technical University of Munich, Germany.