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# Combustion Diagnostics with Femtosecond Laser Radiation

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**Abstract.** In the present work, the potential of Laser Induced Breakdown Spectroscopy employing femtosecond laser pulses (fs-LIBS) for fuel-air equivalence ratio measurements in premixed methane-air and propane-air flames is presented. A Ti-Sapphire laser system (100 fs, 10 Hz, 800 nm) was used as an excitation source for the plasma creation, while a spectrometer was employed to record the plasma emission spectra. The concentration of the investigated methane-air and propane-air mixtures were expressed by the fuel mole fraction  $X_{\text{fuel}}$  and varied from only air –  $X_{\text{fuel}}=0$  ( $\phi=0$ ) to only fuel –  $X_{\text{fuel}}=1$  ( $\phi=\infty$ ). The spectral characteristics of the fs-LIBS spectra are discussed, while the time and energy dependence of the main spectral features are presented. Moreover, from the analysis of fs-LIBS spectra collected at different fuel mole fractions  $X_{\text{fuel}}$ , it was found that the fuel variations could be very well correlated with the variation of the intensity of some spectral lines and/or their ratios. The prepared calibration curves of the fuel mole fraction  $X_{\text{fuel}}$  versus the atomic line total intensity ratios ( $H_{\alpha}$  656.3 nm and O (I) 777 nm) and molecular lines total intensity ratios ( $C_2$  516.5 nm and CN 388.3 nm) suggest the high potential of using fs-LIBS for the determination of the local fuel concentration and its temporal variations.

## 1. Introduction

Over the years, Laser Induced Breakdown Spectroscopy (LIBS) has been established as a versatile laser based diagnostic technique in the field of combustion diagnostics [1-5]. So far, LIBS has been used to perform measurements of the equivalence ratio [6], determine the employed hydrocarbon among various hydrocarbons of a fuel [7], measure the flame temperature [8] and describe the fuel distribution within the flame volume [9]. However, all these studies have been focused on fuel lean combustible mixtures since energy saving and reduction of soot emission were targeted. Nevertheless, an overall fuel lean mixture can be also accompanied by severe changes of fuel concentration locally in the flame. Seeing this, Kotzagianni et al [10] and Yuan et al [11] have developed a new calibration scheme able to determine all potential fuel concentrations in methane-air and heptane droplets-air spray flames.

Simultaneously, in the majority of LIBS experiments related to combustion, nanosecond lasers have been used, while only few publications using femtosecond lasers have been reported up to now [12, 13]. Despite the limited published works so far, the use of fs-laser pulses in the field of combustion could hold great advantages especially for the mapping of the fuel distribution within the



flame volume. In more detail, the high energetic content of the fs laser pulses leads to the breakdown of the gases even in the case of the hot products allowing the determination of the concentration of fuel everywhere in the flame, while the reduced volume of the laser plasma in comparison to the plasma induced by ns laser source offers the opportunity to perform more accurate local measurements of the amount of fuel with higher spatial resolution. Thus, deeper understanding of fundamental aspects of plasma emission induced by fs pulses in flames is required, while the prospects and limitations of fs-LIBS for combustion diagnostics need further study and evaluation. In order to achieve these goals, fs-LIBS has been applied in combustible mixtures of air with hydrocarbons, namely methane ( $\text{CH}_4$ ) and propane ( $\text{C}_3\text{H}_8$ ), with variable fuel concentrations ranging from only air to only fuel. Thus from the acquired emission spectra, the most significant spectral features are assigned and the influence of the laser energy and of the detection time on their shape (FWHM) and duration (lifetime,  $\tau$ ) are examined. Finally, the potential of the quantitative correlation of the intensity or the ratio of intensities of atomic and/or molecular origin spectral lines to the fuel mole fraction is investigated for combustion diagnostics.

## 2. Experimental arrangement

For the needs of the present study, the laser employed was a 100 fs Ti-sapphire laser system operating at 800 nm and at repetition rate of 10 Hz. The laser beam passed through a  $\lambda/2$  polarizer to adjust its energetic content and was then expanded  $\times 2$  by means of a telescope. The expanded laser beam was reflected by a dichroic mirror onto a 100 mm focal length parabolic mirror in order to create plasma in the centreline of the flame whilst the plasma emission was transmitted through the mirror which was then coupled into an optical fibre. The optical fibre was attached to a 75 mm focal length Czerny-Turner type spectrometer (AvaSpec-2048-USB2), equipped with a 300 lines/mm grating and a 2048 pixel CCD detector array. The spectrometer was able to acquire emission spectra extended from 175 to 1100 nm, while the minimum integration time of its CCD detector was 1.1 ms.

The flames used were stabilized on the rim of a stainless steel Bunsen burner having 9 and 11.5 mm inner and outer diameters respectively, and 350 mm length in order to ensure uniform mixtures. The fuels methane and propane, were supplied from bottles of 99.90 % purity while synthetic air was employed (20.5 % oxygen, 79.5 % nitrogen, 5 ppmv humidity). The flow of the gases was regulated by calibrated flow meters. Although often in LIBS experiments the amount of fuel in a flame is expressed by the equivalence ratio ( $\phi$ ), in the present work the fuel mole fraction ( $X_{\text{fuel}}$ ) is used since it is considered to be more suitable for the interpretation of the results. The values of  $X_{\text{fuel}}$  were varied from 0, which corresponds to only air, up to 1, which corresponds to only fuel. For stoichiometric methane- and propane-air flames, the corresponding mole fractions  $X_{\text{CH}_4}$  and  $X_{\text{C}_3\text{H}_8}$  are 0.1 and 0.04, respectively. Mixtures with lower fuel mole fraction are characterized as fuel-lean, while in the opposite case are fuel-rich ones.

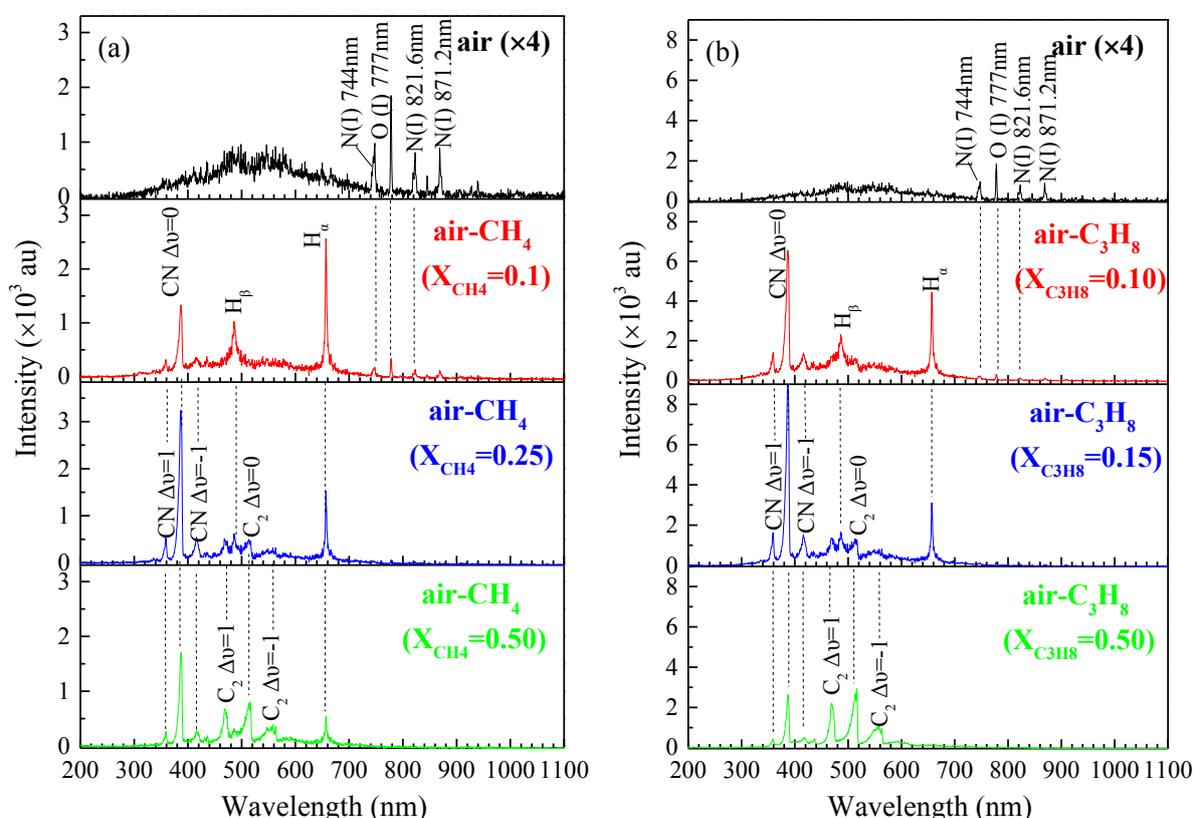
## 3. Results and discussion

### 3.1. fs-LIBS Emission Spectra in different hydrocarbons

Typical emission spectra arising from the fs laser induced spark in air and in various fuel-air mixtures with different mole fractions are shown in Figure 1. Each spectrum is the average of 100 laser shots detected with a time delay of 170 ns after the plasma creation, while the laser energy was 2 mJ. In the case of fs-LIBS in air, the spectrum is dominated by atomic lines arising from fragments of the constituent molecules of air, namely  $\text{N}_2$  and  $\text{O}_2$ , and are peaked at N (I) 744 nm, N (I) 821.6 nm, N (I) 871.2 nm, and O (I) 777 nm. These atomic lines were also observable in the spectra of stoichiometric fuel-air mixtures (i.e. at  $X_{\text{fuel}}=0.1$ ). However, in this case, they were weaker in intensity, while some new spectral features assigned to atomic hydrogen ( $\text{H}_\alpha$  656.3 nm and  $\text{H}_\beta$  486.1 nm) and to cyanogen molecular band  $\text{CN B}^2\text{X}^+-\Sigma^2\text{X}^+$  ( $\Delta v=1, 0, -1$  at 359.0 nm, 388.3 nm and 421.6 nm respectively) were also presented. The formation and appearance of these spectral features in the spark emission spectra

are directly linked to the presence of fuel ( $\text{CH}_4$  or  $\text{C}_3\text{H}_8$ ) which is atomized and excited/ionized under the intense laser radiation at the focus.

Shown next in Figure 1 are the fs-LIBS spectra in the case of laser spark formed in fuel-air mixtures with increasing fuel concentration. From the analysis of the spectra, it was found that at  $X_{\text{CH}_4}=0.25$  for methane and at  $X_{\text{C}_3\text{H}_8}=0.15$  for propane, the  $\text{C}_2$   $d^3\Pi_g-a^3\Pi_u$  ( $\Delta v=1, 0, -1$  at 473.7 nm, 516.5 nm and 563.5 nm, respectively) molecular band started to appear in the fs-LIBS spectra. The presence of the  $\text{C}_2$  band at lower mole fraction in the case of propane is most probably related to the larger number of carbon atoms of this hydrocarbon in comparison to methane. In addition, the atomic lines of nitrogen and oxygen were found to decrease significantly and finally disappear completely at richer mixtures, i.e. for fuel mole fractions higher than 0.5 for methane and 0.2 for propane.

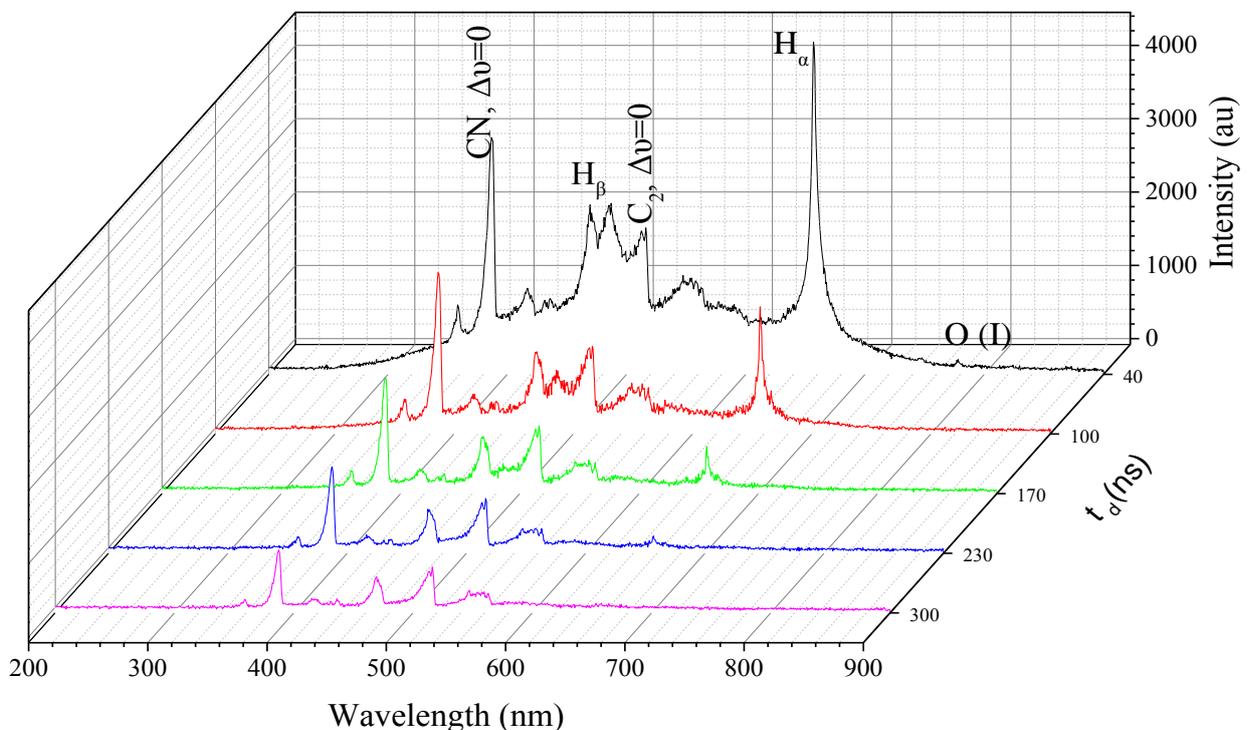


**Figure 1.** fs-LIBS spectra in various a)  $\text{CH}_4$ -air and b)  $\text{C}_3\text{H}_8$ -air fuel mole fraction flames.

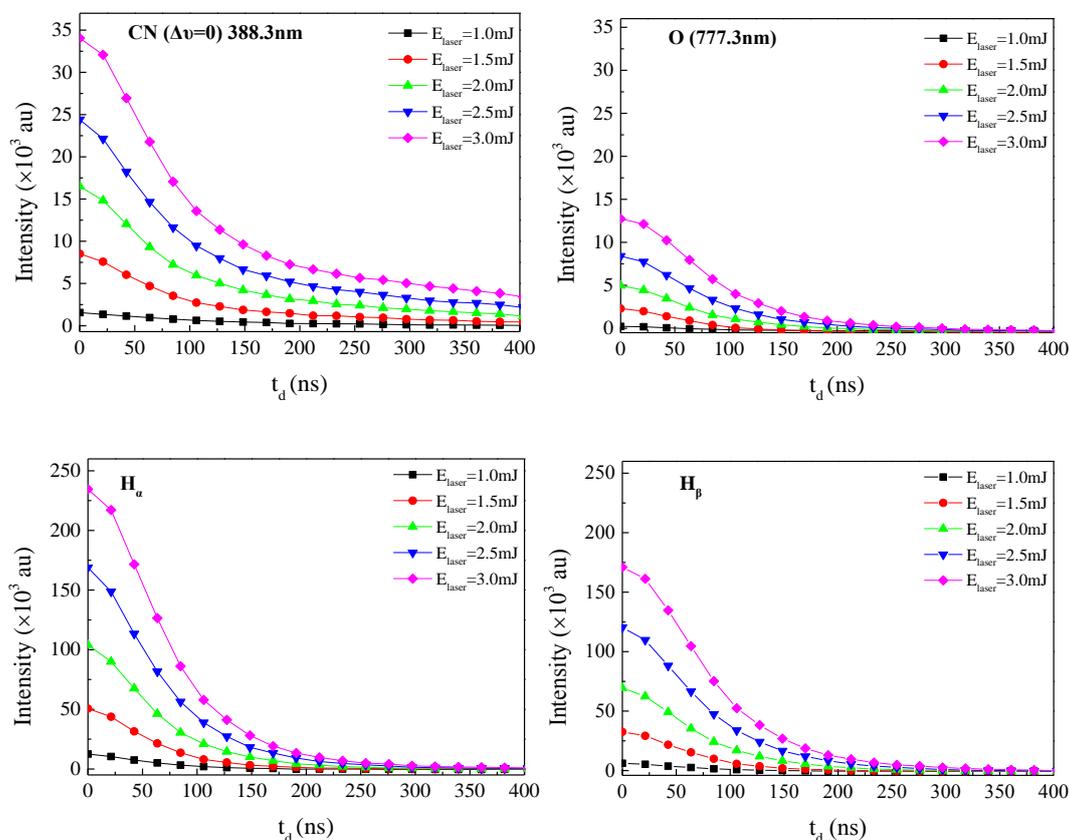
### 3.2. Temporal evolution and energy dependence of fs-LIBS spectra

In this section, the temporal evolution of the plasma emission is discussed. The emission spectra shown in Figure 2 correspond to the formation of plasma in a methane-air mixture with a fuel mole fraction  $X_{\text{CH}_4}$  of 0.3 while the acquisition parameters were:  $t_w=1.1$  ms and  $t_d=40, 100, 170, 230$  and 300 ns. As can be seen from this Figure, at the initial stages of the plasma formation ( $t_d=40$  ns), a strong continuum corresponding to the Bremsstrahlung radiation is extended through the visible region of the spectrum, whilst some spectral lines which appear are superimposed on the continuum and severely broadened.

It is obvious that by increasing the delay of the detection time, the intensity of the continuum drops significantly, and at about 170 ns after the laser spark it is extinguished completely. At the same time, the broadening has been reduced significantly while the intensity of the spectral lines follows this also decrease, as expected. The atomic lines of hydrogen remain significant up to 230 ns while the molecular bands of CN and C<sub>2</sub> remain clearly observable up to 300 ns after the plasma formation. The full width at half maximum (FWHM) and the lifetime of the most important spectral features observed in the fs-LIBS spectra were obtained from the quantitative analysis of the spectra shown in Figure 3. Presented in more detail in Figure 3 are the variation of the total intensity of the 383.3 nm CN band, and of the lines H<sub>α</sub> (656.3 nm) and H<sub>β</sub> (486.1 nm) of hydrogen and O (777.3 nm) of oxygen as a function of the delay time. For all excitation energies used, ranging from 1 to 3 mJ, all emission lines were found to exhibit an exponential decay, their intensity becoming negligible after 200 ns, whereas the intensity of the molecular band remains observable up to 400 ns. The FWHM of the lines together with the lifetimes are presented in Table 1.



**Figure 2.** fs-LIBS spectra in a CH<sub>4</sub>-air flame with X<sub>CH<sub>4</sub></sub>=0.3, measured at different time delays  $t_d$ : 40, 100, 170, 230 and 300 ns. The integration time was 1.1 ms and the energy of the laser was 2 mJ.



**Figure 3.** Temporal evolution of the intensity of the: CN (388.3 nm) band, the  $H_{\alpha}$  (656.3 nm) and  $H_{\beta}$  (486.1 nm) and the O (777.3 nm) atomic lines obtained from fs-LIBS spectra occurring in  $CH_4$ -air flame ( $X_{CH_4}=0.3$ ) at different laser excitation energies.

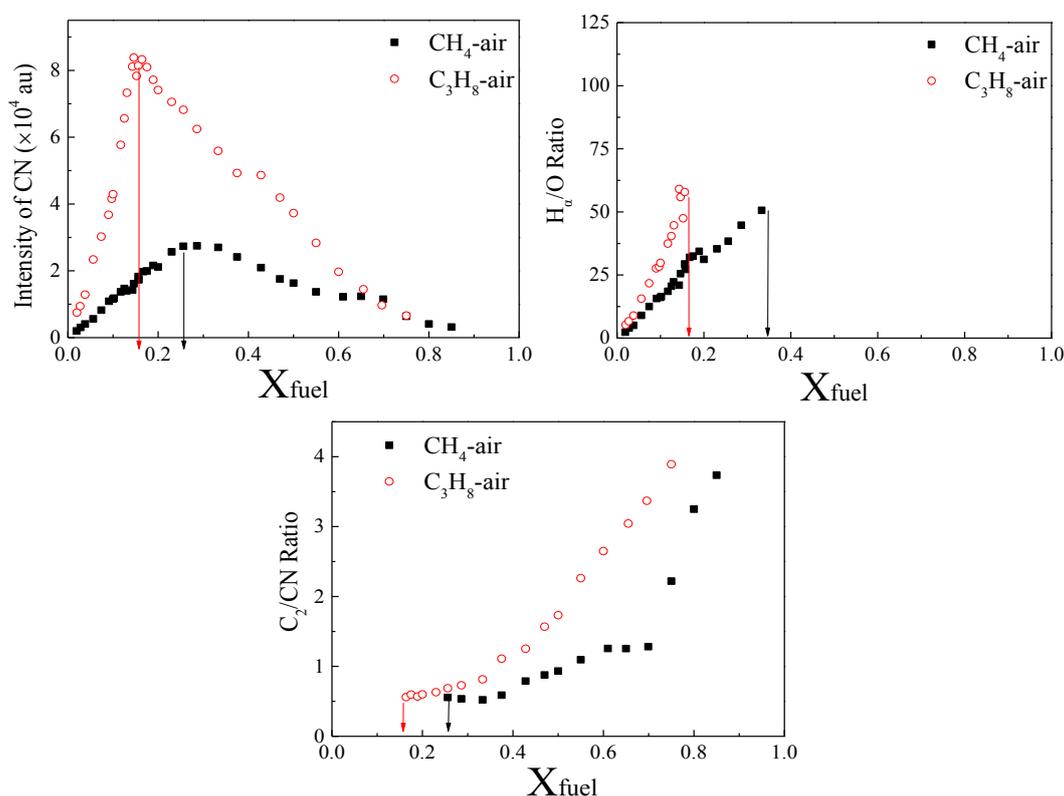
**Table 1.** The lifetime and the FWHM of CN,  $H_{\alpha}$ ,  $H_{\beta}$  and O lines as a function of  $E_{laser}$

$E_{laser}$ (mJ)	$\tau$ (ns)				FWHM (nm)			
	CN	$H_{\beta}$	$H_{\alpha}$	O	CN	$H_{\beta}$	$H_{\alpha}$	O
1	70	55	54	34	6.8	17.7	4.5	2.9
1.5	72	60	55	52	6.3	19.9	4.7	2.6
2	74	65	58	63	7.2	19.6	4.6	2.6
2.5	81	71	62	73	6.5	19.3	4.6	2.8
3	85	77	69	77	6.5	19.7	4.8	2.6

### 3.3. Dependence of the CN intensity and of the $H_{\alpha}/O$ and $C_2/CN$ ratios upon the fuel mole fraction in $CH_4$ - and $C_3H_8$ -air flames

Finally, the dependence of the intensity of CN (388.3 nm) and the ratios  $H_{\alpha}/O$  (777 nm) and  $C_2$  (516.5 nm)/CN (388.3 nm) are presented in Figure 4. These choices have been recently suggested [10-13] and in the present work it is intended to investigate if they can be used in fs-LIBS spectra in very rich fuel

mixtures. As can be easily observed, the intensity of CN is increasing up to  $X_{\text{CH}_4}=0.25$  and of  $X_{\text{C}_3\text{H}_8}=0.17$  for methane and propane-air flames respectively, while the same linear increase is also observed in the case of  $H_\alpha/O$  (777 nm) ratio. Further increase of fuel leads to formation of  $\text{C}_2$  and decrease of the CN band intensity, which seems to be related to the decrease of  $\text{N}_2$  molecules in the mixture. Therefore, the  $\text{C}_2/\text{CN}$  ratio exhibiting a monotonic increase with the fuel mole fraction can be a useful tool for diagnostics in fs-LIBS.



**Figure 4.** Dependence of the: a) CN intensity, b)  $H_\alpha/O$  ratio and c)  $\text{C}_2/\text{CN}$  ratio versus the fuel mole fraction  $X_{\text{fuel}}$  in some  $\text{CH}_4$ -air and  $\text{C}_3\text{H}_8$ -air flames.

#### 4. Conclusions

Femtosecond Laser Induced Breakdown Spectroscopy (fs-LIBS) has been successfully employed in hydrocarbon-air flames of different compositions in order to use the light emitted from the plasma to obtain useful information about the fuel content and its distribution within the flame and demonstrate the potential of fs-LIBS for combustion diagnostics as well. Moreover, the temporal evolution of the plasma emission was used to derive valuable information about the conditions of formation of species like  $\text{C}_2$ , CN, etc., while the influence of the laser energy on the spectral lines intensity was also studied. Finally, the  $H_\alpha/O$  ratio was found to vary linearly with the fuel mole fraction for values up to 0.17 for  $\text{C}_3\text{H}_8$ -air mixtures and up to 0.35 for  $\text{CH}_4$ -air ones while the ratio of  $\text{C}_2/\text{CN}$  was found to increase monotonically with  $X_{\text{fuel}}$  for values greater than 0.17 and 0.35 for  $\text{C}_3\text{H}_8$  and  $\text{CH}_4$  mixtures respectively. The present results can be applied to prepare appropriate calibration curves for  $\text{CH}_4$ - and  $\text{C}_3\text{H}_8$ -air mixture allowing for the fast determination of fuel concentration in such flammable hydrocarbon-air mixtures and providing a spectroscopic tool for *in situ* diagnostics.

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