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Femtosecond laser induced breakdown for combustion diagnostics

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The focused beam of a 100 fs, 800 nm laser is used to induce a spark in some laminar premixed air-methane flames operating with variable fuel content (equivalence ratio). The analysis of the light escaping from the plasma revealed that the Balmer hydrogen lines, H\textsubscript{a} and H\textsubscript{b}, and some molecular origin emissions were the most prominent spectral features, while the CN (\textit{B}\textsuperscript{2}\Sigma\textsuperscript{+}-\textit{X}\textsuperscript{2}\Sigma\textsuperscript{+}) band intensity was found to depend linearly with methane content, suggesting that femtosecond laser induced breakdown spectroscopy can be a useful tool for the \textit{in-situ} determination and local mapping of fuel content in hydrocarbon-air combustible mixtures. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4731781]

Laser induced breakdown spectroscopy (LIBS) has attracted a lot of scientific interest during the last two decades as it is generally considered as an experimentally simple and efficient laser-based technique which can perform real time, qualitative, and quantitative elemental analyses.\textsuperscript{1-3} Furthermore, LIBS can operate \textit{in situ}, remotely and in dangerous and harsh environments, being capable of providing useful information about the elemental composition of all kinds of matter, such as solids, liquids, gases, conducting and dielectric materials. All these reasons can explain the increasing number of proposed potential applications of LIBS and why it has become one of the most popular laser-based techniques in relatively short time since it emerged. The most attractive aspects of LIBS, however, remain its experimental simplicity and its real time operation coupled with the fact that it does not require any previous treatment or preparation of the sample prior to its irradiation.

The basic idea of LIBS is the creation of spark/plasma through tight focusing of a laser beam on the surface or into a sample, the subsequent atomization of a tiny amount of the sample (which is found where the spark occurred) and also the excitation of the atomized sample atoms. It is important to notice that with LIBS technique, the atomization and excitation processes occur simultaneously in one single step in contrast to other elemental analysis techniques where these processes constitute two different steps.

In most of the LIBS-related work published so far, nanosecond lasers, in particular, Nd\textsuperscript{3+}:YAG lasers operating at their fundamental wavelength at 1064 nm have been employed, while some ICCD (Intensified Charge Coupled Device) device, connected to a spectrometer, was used for obtaining time resolved measurements of the plasma emitted light.\textsuperscript{4,5} However, the availability of reliable, tabletop ultra-fast lasers nowadays has allowed the study of laser matter interactions under ultra-short, ultra-intense laser pulses. The interaction of such laser pulses with matter opened new ways that can be advantageous for the LIBS community. For example, the plasma produced from such laser–matter interactions resulting, e.g., from field ionization of both the outer and inner electrons of a sample has higher electronic density and therefore higher collision rates than the plasma produced using nanosecond lasers.\textsuperscript{9} A direct consequence is the more intense and richer emission spectra while intense femtosecond (fs) laser pulse can be employed for remote LIBS application based on laser filamentation effects.\textsuperscript{10,11} Besides, under some conditions, fs pulses can dissociate a sample more efficiently than nanosecond pulses. In all these cases, the result is that fs-LIBS has the potential to provide higher signal to noise ratios and higher accuracy than ns-LIBS.

Recently, LIBS has been proposed as a tool for combustion diagnostics, in particular, for the determination of equivalence ratio in various air-hydrocarbon flames.\textsuperscript{12-21} In most of these studies, the intensities of atomic lines or ratios of intensities of atomic lines have been used.

In the present work, femtosecond laser induced breakdown (i.e., fs-LIBS) is used for elemental analysis of some gaseous reactive mixtures. In particular, fs-LIBS is used to create plasma in the reaction zone of some laminar premixed air-methane flames, operating with variable fuel content, in order to perform combustion diagnostics. More specifically, the possibility of using fs-LIBS and simple spectroscopic measurements for the determination of the fuel content (i.e., equivalence ratio) is investigated.

During the experiments, the focused beam of a 100 fs Ti:sapphire laser system, operating at 800 nm, at a repetition rate of 10 Hz has been employed for the creation of the plasma within the reaction zone of an axi-symmetric laminar premixed air-methane flame stabilized on a stainless steel Bunsen burner having 9 and 11.5 mm inner and outer diameters, respectively, and 350 mm length in order to ensure fully mixed and developed flow. High purity (99.95\%) methane and synthetic air (21\% oxygen, 79\% nitrogen, 30–35 ppm humidity) were supplied from bottles while ambient air was also used in most of the experiments. The flow of the gases was regulated by calibrated flow meters, while the

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The equivalence ratio of the flame, defined as the fuel-to-oxidizer mass fraction divided by the stoichiometric fuel-to-oxidizer mass fraction for the particular mixture, could be easily calculated from their indications.\textsuperscript{11} The equivalence ratio defined this way is a spatially and temporally averaged quantity which provides an effective way to characterize the fuel/hydrocarbon content.

The light emitted from the plasma was collected by means of a quartz fiber bundle, connected to a 75 mm focal length portable spectrometer (AvaSpec-2048), having a 50 $\mu$m fixed width entrance slit and equipped with a 300 lines/mm grating blazed at 300 nm, covering the spectral range 175–1100 nm. The dispersed light was detected by a 2048 pixels CCD linear array, each pixel being 14 $\mu$m wide. Since only the 1624 pixels were active, the pixel dispersion was calculated to be 0.57 nm/pixel, while the reciprocal dispersion has been calculated to be 40.68 nm/mm. The CCD detector of the spectrometer could operate using an integration time (i.e., a time window) $t_i$ for signal acquisition of 1.1 ms minimum and up to several seconds. The time interval between the trigger needed to activate the CCD electronics to be ready for acquisition and the actual taking of the measurement, i.e., the instrumental time delay, was 1.28 $\mu$s. In other words, for the measurement of the plasma emission during the initial moments of the plasma creation, e.g., at time $t = 0$ (corresponding to the moment that laser induced breakdown occurs), the spectrometer should have been triggered 1.28 $\mu$s in advance. Furthermore, the minimum integration time $t_i$ of a signal can be further delayed in a continuous way, beyond the 1.28 $\mu$s instrumental delay, allowing the study of the temporal evolution of an emitted light with a limited temporal resolution but still capable of providing useful information. This way, the temporal development of the phenomenon can be captured by triggering the spectrometer appropriately and measuring the plasma emitted light with a minimum integration time $t_i$ of 1.1 ms and shifting it in time.\textsuperscript{22}

Some typical emission spectra corresponding at laser induced plasma created in atmospheric air using laser pulses of an energy of 5.2 mJ, measured at three different delay times $t_d$, namely, for $t_d = 0$, 200 and 300 ns and using an integration time $t_i$ of 1.1 ms are presented in Figure 1(a). As can be seen from these emission spectra, at early stages, they are dominated by an intense broad continuum extending over the 300 to 700 nm spectral region and some strong spectral features, overlapping with the continuum, not well resolved because of the limited spectral resolution of the spectrometer and their broadening.

On the other hand, towards the longer wavelengths side of the spectrum (i.e., above 700 nm), where the continuum has significantly reduced, some better resolved, relatively intense spectral lines have been observed assigned to atomic nitrogen (N(I)) and oxygen (O(I)). In fact, the following spectral lines have been identified: N(I)-744.2 nm (triplet, consisting of the 742.4, 744.2, 746.8 nm lines), N(I)-821.6 nm, N(I)-871.2 nm, O(I)-777 nm (triplet, consisting of the 777.2, 777.4, and 777.5 nm lines, often reported as oxygen 777 nm line), and the O(I)-844.6 (triplet, consisting of the 844.62, 844.64, 844.68 nm).\textsuperscript{12} Because of the limited resolution of the apparatus, the triplets could not be resolved. These atomic species originated from the dissociation of molecular nitrogen (N$_2$) and oxygen (O$_2$) present in air, under the intense laser field during the breakdown. The measurement of the atmospheric air plasma emission at longer times, as for example after a delay time of 300 ns, has shown an almost completely extinguished continuum spectrum, while the atomic nitrogen and oxygen spectral lines have been observed still to exist although significantly weaker than at earlier times.

When the laser beam was focused into the reaction zone of the air-methane flame, three additional spectral features have been observed to emerge prominently from the intense broad continuum, as shown in the top spectrum of Figure 1(b).\textsuperscript{19,23–25} These new features have been attributed to the atomic hydrogen Balmer lines H$_\alpha$ at 656.3 and H$_\beta$ at 486.1 nm, and the CN molecular emission at about 388.3 nm, corresponding to the (0,0) band head of the violet CN system corresponding to the transition B$^2\Sigma^+ - X^2\Sigma^+$. In addition to these prominent features, several other spectral features, exhibiting however a weaker intensity have been clearly observed in these emission spectra. So, the spectral lines appearing at 359.0 and 421.6 nm have been assigned to the vibrational transitions (1,0) and (0,1) of the CN-(B$^2\Sigma^+ - X^2\Sigma^+$) system, suggesting that a considerable amount of excited CN molecules was formed.\textsuperscript{26–28} Moreover, the OH (A$^3\Pi - X^2\Sigma^+$) emission at 307.8 nm has been also clearly observed, even after some delay time, while the weak bands appearing at the spectral regions 564–550 nm, 517–510 nm, and 474–465 nm belong to the C$_2$ (d$^3$P$_g$–a$^3$P$_u$) Swan band system.\textsuperscript{25,26} These spectral features are better resolved in Figure 2 measured with a delay time of 230 ns. Finally, the spectral lines of atomic nitrogen at 744.2, 821.6, and 871.2 nm and of atomic oxygen at 777 and 844.6 nm, which have been previously observed in the atmospheric air LIBS spectra, have also been found to appear in the LIBS spectra of the flame although significantly weaker.

Subsequently, the temporal evolution of the observed spectral lines was measured using different delay times and the minimum possible integration time $t_i$ of the spectrometer’s detector, i.e., 1.1 ms. Figures 1(a) and 1(b) depict some

![Image](https://via.placeholder.com/150.png?text=FIG.1. Emission+spectra+of+laser+induced+plasma+taking+place+(a)+in+atmospheric+air+and+(b)+in+the+reaction+zone+of+a+premixed+laminar+stochiometric+($\phi=1$)+air-methane+flame+measured+at+three+different+delay+times+$t_d=0$,+200+and+300+ns.+The+detector+integration+time+was+1.1+ms+and+the+laser+energy+was+5.2+mJ.)
representative emission spectra of the laser induced plasma created in atmospheric air and in the reaction zone of a laminar premixed air-methane stoichiometric flame for three different delay times, i.e., at 0, 200 and 300 ns. As can be seen, as the plasma becomes colder, e.g., 200 ns after its creation, the CN-388.3 nm and the Hα-656.3 nm lines remain the most prominent features, as the continuum decreases significantly, while 300 ns after the plasma creation, the CN-388.3 nm line was observed to be the only spectral feature, persisting with significant intensity compared to the intensity of the atomic hydrogen line.

The effect of the laser energy on the plasma emission was studied afterwards. In Figure 2, the emission spectra of laser induced plasma produced in the reaction zone of a premixed laminar stoichiometric (\( \phi = 1 \)) air-methane flame, using different laser energies, and 1.1 ms integration time and 230 ns delay time are presented. As shown, the H\(_2\) and the CN-388.3 nm features were observed to be the most prominent spectral features, for all laser energies employed, while some other weaker features belonging to the (1,0) and (0,1) transitions of the CN (\( B^2\Sigma^+ - X^2\Sigma^+ \)) system, some transitions from the C\(_2\) Swan system together with the OH (A-X) band head were also observed clearly. However, the CN-388.3 nm band was the only remaining feature at lower energies. The variation of the total intensity of the CN-388.3 nm band is presented in Figure 3, as calculated from the emission spectra obtained using different laser energies and for different delay times, e.g., 0, 40, 140, and 230 ns for a stoichiometric (\( \phi = 1 \)) air-methane flame. All presented results were obtained from spectra measured with an integration time of 1.1 ms. As shown, the variation of the intensity of the CN-388.3 nm band was much more important at shorter delay times and at higher laser energies, than at later times and for lower energies. For incident laser energy higher than 4 mJ, saturation was observed to occur and these measurements have not been included here.

In the following, fs-LIBS spectra have been measured while the flame was operating with various air-methane mixtures, corresponding to lean, stoichiometric, and rich in fuel conditions, or equivalently, for equivalence ratio \( \phi : \phi < 1, \phi = 1 \) and \( \phi > 1 \), respectively. Figure 4 presents some representative emission spectra of the plasma created in the flame reaction zone obtained while the flame was operating in each...

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**FIG. 2.** Emission spectra of laser induced plasma occurring in a premixed laminar stoichiometric (\( \phi = 1 \)) air-methane flame, using different laser energies, integration time \( t_w = 1.1 \) ms, and delay time \( t_d = 230 \) ns.

**FIG. 3.** Intensity variation of the CN-388.3 nm band as a function of the incident laser energy (\( E_{\text{laser}} \)) at different delay times.

**FIG. 4.** fs-LIBS spectra obtained in a premixed laminar air-methane flame operating under lean (\( \phi < 1 \)), stoichiometric (\( \phi = 1 \)), and rich (\( \phi > 1 \)) conditions.
one of the three previously mentioned situations. The integration time used for these measurements was 1.1 ms, while the delay time was chosen to be 1 µs in order that the obtain spectra being free of continuum background, facilitating the observation of the CN-388.3 nm variations. As shown, the CN-388.3 nm band was observed to be the most prominent feature of the fs-LIBS spectra, under all operation conditions of the flame, while its intensity was noticeably varying with fuel content. In order to further validate this observation, the effect of the composition of the air-methane mixture on the total intensity of the CN-388.3 nm band was studied operating the flame at several different equivalence ratio values and measuring the plasma light at different time delays as well. The obtained results are summarized in Figure 5.

The straight lines correspond to the linear best fits of the experimental data points for each time delay used respectively. As shown, the intensity of the CN-388.3 nm band was found to vary linearly upon methane concentration, suggesting that it can be employed for the determination and/or the continuous monitoring of the fuel content in combustion environments from simple spectroscopic measurements. Furthermore, due to the local character and the time resolution of such LIBS measurements, a spatial and temporal cartography of the fuel content within the flame can be easily obtained, providing useful information about the combustion evolution. Further work is actually in progress in order to illuminate the mechanisms of formation of the CN molecules under fs-LIBS conditions and also investigating other air-hydrocarbon flames.

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