Femtosecond laser induced breakdown spectroscopy of air–methane mixtures

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Femtosecond laser pulses are used in order to induce dielectric breakdown in gaseous mixtures, namely in some reactive air–methane mixtures. The light emitted from the laser induced plasma was analyzed while the main emission features are identified and assigned. From the analysis of the emission spectra, a linear relationship was found to hold between the intensity of some spectral features and methane content. Finally, the use of femtosecond laser induced breakdown as a tool for the in situ determination of the composition of gaseous mixtures (e.g., equivalence ratio) is also discussed.

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1. Introduction

Laser-induced breakdown phenomena are usually occurring when intense laser radiation is focused on/into a sample and the radiation intensity exceeds a certain threshold, depending in general on the wavelength, the pulse duration and the energetic content of the laser radiation and on the focusing conditions [1–3]. The breakdown phenomena are related with the plasma formation accompanied by emission which usually lasts longer than the initiating laser pulse and it contains valuable spectral information about the atomic, ionic, and molecular species of the sample. Similarly, when laser induced breakdown occurs in a gaseous environment (e.g., mixture), the emitted plasma light can provide in principle valuable qualitative and quantitative information about the mixture composition. So, in the case of reactive gases, information can be obtained while ignition by the laser pulse and combustion processes can occur. In fact, laser induced breakdown spectroscopy (LIBS) can be very useful in probing dangerous and hostile environments where physical access may not be possible or convenient, offering the possibility of performing real-time measurements, when it is necessary, without the need of any previous preparation or special treatment(s) of the sample. Some problems often met in LIBS experiments as e.g. the reproducibility of the LIBS signals in the case of solid samples, the detection limits for some species and the high cost equipment needed sometimes, are not enough to prevent LIBS technique to become a very popular technique for elemental analysis during the last years.

Recently, among the various applications proposed for LIBS, several reports have appeared suggesting the use of LIBS in flames and for combustion diagnostics, aiming to establish correlations between the LIBS resulting emission spectra and the various characteristics of the flame and/or the processes occurring, such as the fuel concentration (i.e., equivalence ratio), the fuel type, the ignition threshold, the mapping of the fuel concentration within the flame, etc. So, LIBS has been employed to ignite some air–methane mixtures and efforts have been put in establishing a correlation between the spark size and shape with the fuel content [4]. In another report, the relation between the H₂ and the O(I) – 777.3 nm lines with the equivalence ratio of some air–methane mixtures contained in an ignition cell has been investigated [5]. Similarly, the relation of the ratio of intensities of some atomic spectral lines, namely the C/N and C/O, with the equivalence ratio has been investigated in a spark ignited engine [6]. In the same study, the dependence of the intensity of a CN band located between 707 and 734 nm (most probably a part of the CN A2Π→X2Σ+ red band extended in the near infrared region) with the fuel content has been investigated. In another work, the relation between the composition of some gaseous mixtures of carbon containing molecules together with air/nitrogen (i.e., CO₂–air, C₂H₆–CO₂, C₃H₆–N₂) and the intensities of atomic lines of elements such as C, N, O and H resulting from LIBS experiments has been studied and calibration curves for these elements have been constructed [7]. Furthermore, the dependence of the ratio of the intensities of H₂ and O(I) – 777.3 nm lines (H₂/O) on the equivalence ratio in some laminar premixed air–methane flames stabilized on a Bunsen burner has been also studied using ns LIBS [8,9]. Similar experiments have been performed in air–methane, air–propane and air–carbon dioxide mixtures searching for a relation between the intensities of some atomic lines and the composition of the mixtures [10]. In that view, double pulsed laser LIBS has been used in flames and calibration curves for the H₂, H₂O, O(I) – 777.3 nm, N(I) – 745 nm and C(I) – 247 nm lines versus fuel concentration have been constructed [11]. In another study, LIBS has been applied in some air–methane and biodiesel diffusion flames in order to examine the possibility to
use a non-gated low cost detector instead of an expensive ICCD one for the equivalence ratio determination [12]. The determination of the equivalence ratio by means of LIBS has been also investigated in some laminar, premixed ethylene- and propane-air flames, aiming to prove the concept of the technique in the case of heavier hydrocarbons [13]. Very recently, LIBS has been proposed both for ignition and equivalence ratio determination in some dimethyl ether flames [14]. In all these LIBS related studies, nanosecond lasers have been almost exclusively employed. Simultaneously, the recent developments in femtosecond lasers have made them very attractive and promising, so considerable attention has been put in the applications of fs LIBS, as it offers greatly reduced thermal damage and minimal heat affected zone due to negligible heat conduction and hydrodynamic motion during the laser pulse duration.

In the present Letter, fs-LIBS has been used in gaseous mixtures, namely in some laminar premixed air–methane flames and in different methane–nitrogen mixtures as well, in order to obtain qualitative and quantitative information about the composition of these mixtures. The flames used were stabilized on Bunsen type burners and have been operated at various regimes (e.g., stoichiometric and fuel lean or rich conditions). The methane–nitrogen mixtures have been studied in a pressure controlled chamber at ambient temperature where no ignition of the mixture was possible to occur due to the absence of oxidizing medium (i.e. air, oxygen). LIBS spectra corresponding to various experimental conditions (e.g., mixture composition, laser energy, time delay, gate width, etc.) have been obtained and analyzed. The main finding of the present investigation was the linear relationship between the intensity of the cyanogen band (CN $2\Sigma_u^+ - \chi$) at 388.3 nm and methane content, indicating that this CN band can be a useful tool for the determination of the composition of reactive air–methane mixtures and for combustion diagnostics in general.

2. Experimental details

The laser employed was an amplified 100 fs Ti:sapphire based laser system operating at 800 nm, at a repetition rate of 10 Hz. The light emitted from the interaction of the laser beam with the gaseous samples was collected with a quartz fiber bundle and was driven into a 75 mm focal length portable Czerny-Turner type spectrometer (AvaSpec-2048-USB2), equipped with a 300 lines/mm grating and a 2048 pixel CCD detector array, covering the spectral region from 175 to 1100 nm. The CCD (and its associated electronics) had a minimum integration time of 1.1 ms while the minimum time required by the system to be ready to measure, after it has been triggered by a reference pulse, was 1.28 μs. For the synchronization of the CCD with the laser pulses a trigger signal delivered before every laser pulse, in a programmable way, by the laser system master clock has been used, allowing the CCD detector of the spectrometer to be ready for acquisition. So, the spectrometer was triggered 1.28 μs before the laser pulse arrival on the target, this time corresponding to zero time delay ($t_d = 0$ μs), while it was possible to be further adjusted/delayed. In this way, time resolved measurements have become possible and they were performed for different time delays, ranging from 0 to 3 μs, using different integration times from 1.1 to 9 ms in order to obtain good signal to noise ratio. A small jitter of few tenths of nanoseconds, due to the electronics of the spectrometer, was not critical for the purposes of the present investigation.

The laser beam was focused just above the rim and along the center line of a 9 mm inner diameter homemade Bunsen burner, using a 65 mm focal length lens, providing a short Rayleigh length ensuring the formation of the laser spark entirely into the ‘Bunsen cone’ zone and not in the diffusion zone of the flame. For the measurements in the various CH₄:N₂ mixtures, a four-arm cross-like chamber was used, equipped with four, 1-inch diameter, quartz windows allowing the entrance/exit of the laser beam and the collection and monitoring of the plasma emission at right angles as well. The laser beam was either focused with the 65 mm lens, as in the case of flames, at the geometrical center of this chamber or it was used unfocused. The chamber was connected to a vacuum pump for evacuation of its gaseous content and refilling with new un-irradiated gases while the pressure inside was measured by a calibrated pressure gauge.

The equivalence ratio $\phi$, for the particular mixture, is defined as the local fuel (i.e. CH₄) to oxidizer (i.e. air) mass fraction divided by the stoichiometric fuel to oxidizer mass fraction, and it can be expressed either on mass or on mole basis by the following relation:

$$\phi = \frac{m_{\text{CH}_4}/m_{\text{air}}}{(m_{\text{CH}_4}/m_{\text{air}})_\text{st}} = \frac{\eta_{\text{CH}_4}/\eta_{\text{air}}}{(\eta_{\text{CH}_4}/\eta_{\text{air}})_\text{st}}$$

For the needs of the present work the equivalence ratio $\phi$ was determined from the volumes of the reacting gases (i.e. CH₄ and air) which were controlled by calibrated mass flow meters. Methane, nitrogen and air were all supplied from bottles while ambient air from a laboratory compressor has been also used in some experiments. When the quantity of the oxidizer (i.e., the air) was just that amount needed to completely burn a quantity of methane, the mixture is characterized as stoichiometric with an equivalence ratio $\phi = 1$. If more than a stoichiometric quantity of oxidizer was supplied, then the mixture was characterized as fuel lean, with equivalence ratio $\phi < 1$, while in the opposite case the mixture was said to be fuel rich with equivalence ratio $\phi > 1$. In the present Letter, flames with equivalence ratios ranging from 0.6 to 1.55 have been investigated.

3. Results and discussion

Atmospheric air is basically a mixture of nitrogen (N₂) and oxygen (O₂), representing 78.084% and 20.946% v/v respectively, while several other gases (e.g. H₂, H₂O, CO₂, CH₄, N₂O, CO, NO₂, NH₃, etc.) are present at much smaller quantities. When laser induced breakdown occurs in air–methane mixture, excited atoms/ions and/or molecular fragments of the constituent gases are produced and they can contribute to the observed plasma emission. In order to account for the emissions resulting from the constituents of atmospheric air from those related with the presence of methane, fs-LIBS experiments were carried out separately in (ambient and dry-bottled) air and in air–methane mixtures under various experimental conditions. Under all experimental conditions tried, methane presence was manifested by some strong emissions, namely the H₂ and H₂ Balmer lines of hydrogen at 656.3 and 486.1 nm respectively and some molecular origin spectral features at 421.6, 388.3 and 359.0 nm, assigned to the CN violet band system $2\Sigma_u^+ - \chi^2\Sigma_u^+$ corresponding to the vibrational sequences $\Delta v = -1, 0, 1$ [15].

Besides the emissions associated to the methane, some atomic lines of nitrogen (i.e., N(I) – 744.2 nm, N(I) – 821.6 nm and N(I) – 871.1 nm) and oxygen (O(I) – 777.3 nm) molecules under the intense laser radiation conditions were also observed in the emission spectra. These spectral emissions have been also observed in ns-LIBS experiments [8]. The presence of O(I) and N(I) atomic lines can be explained by the atomization of the oxygen (O₂) and nitrogen (N₂) molecules of air, while the H₂ and H₂ Balmer atomic lines emission can be directly connected to the dissociation of methane (CH₄) molecules under the intense laser radiation conditions occurring at the focus.

In fact, it is well documented that such interactions, among the laser beam and the methane molecules, can lead to an efficient production of H atoms and a variety of other, small fragments, like...
CH, CH₂, C₃H₄ etc. resulting from various dissociation/fragmentation pathways and reactions pathways. Another possible source of H atoms, but rather of minor importance, can be water vapors (e.g. moisture) and hydrogen (H₂) molecules dissociation, both present in small quantities in air. However, LIBS experiments performed in dry air and in laboratory air containing moisture have revealed insignificant amounts of atomic hydrogen emissions. In the absence of methane, no hydrogen atomic lines have been observed. In general, emissions arising from the molecules being present in air (e.g. H₂, H₂O, CO₂, etc.) and/or their fragments were found to be insignificant and therefore they have been neglected. In fact, the H₂ and H₂ Balmer lines, together with the CN B²Σ⁺-X²Σ⁺, Δυ = 0 band were the most prominent spectral features in all the fs-LIBS spectra obtained in the air–methane mixtures during the present investigation.

Concerning the presence of CN emission, it can be explained by considering the dissociation of carbon-containing molecules, such as CH₄ and CO₂, resulting in the production of C, C' and C₂ species which together with the nitrogen atoms, also produced in the breakdown area, can result in the formation of electronically, vibrationally, and rotationally excited CN radicals, according e.g. to schemes such as: C₂ + N₂ → 2CN, C' + N₂ → N'+CN, C + N₂ → CN + N discussed in detail by Fuge et al. [16] and by Park et al. [17] and references therein.

Since CN emission is also observed in the chemiluminescence of air–hydrocarbon flames, resulting from various high temperature chemistry mechanisms [18–20], and in order to examine if it contributes to the CN emission observed under fs-LIBS conditions, measurements of the flame chemiluminescence have been performed under identical experimental conditions to those used for the LIBS experiments (i.e., integration time, fuel, etc.). However, the amount of CN chemiluminescence measured under LIBS conditions was found to be negligible.

In order to avoid the strong continuum present during the first few hundreds of ns after the plasma creation, not allowing for the accurate measurement of the spectral lines intensity, the measurements were performed with some time delay after the plasma creation, when the underlying continuum has been reduced significantly. So, in Figure 1, the emission spectra of the laser induced plasma formed in the 'Bunsen cone' region of a stoichiometric laminar premixed air–methane flame are presented for three different delay times, namely for tᵋ = 0, 0.2 and 0.3 μs. The integration time used was 1.1 ms, while the laser energy was 3.6 mJ. As shown, 0.2 μs after the plasma creation, the continuum has been drastically reduced, while the atomic lines and the molecular origin emissions have become background free and therefore their intensity could be accurately determined. At even longer delay times, e.g. for tᵋ = 0.3 μs, the observed atomic lines were found to decrease significantly while the only emission remaining clearly observable and relatively intense was the CN band B²Σ⁺-X²Σ⁺, Δυ = 0 at 388.3 nm. The graphs of Figure 2 show the temporal evolution of the intensity of the CN B²Σ⁺-X²Σ⁺, Δυ = 0 band and the H₂ line resulting from fs-LIBS experiments performed with different laser energies. The integration time used in these measurements was 1.1 ms. As can be seen, H₂ line was found to decay significantly faster than the CN B²Σ⁺-X²Σ⁺, Δυ = 0 band.

As it has been discussed previously, the CN molecules are most probably formed from C atoms/ions and/or C₂ stemming from carbon containing molecules. Consequently, the intensity of the CN B²Σ⁺-X²Σ⁺, Δυ = 0 band is expected to be correlated to the concentration of the carbon-containing molecules, i.e. methane in the present case. In that view, the emission spectra of fs laser induced breakdown taking place in an air–methane flame, operating with different methane contents (i.e. different equivalence ratios φ), are presented in Figure 3. All spectra shown in this figure have been measured using an integration time tᵋ = 1.1 ms and a delay time tᵋ = 1 μs, while the laser energy was 5.2 mJ.

As shown, the continuum has completely extinguished while the CN B²Σ⁺-X²Σ⁺, Δυ = 0 at 388.3 nm band visibly dominates...
the emission spectra. Some weaker emissions, at 656.3 and 307.8 nm, also present in the spectra, correspond to the H α line and to the \( \Delta v = 0 \) vibrational sequence of the OH \( A^2\Sigma^+ - X^2\Pi \) transition respectively. Thus, it becomes evident that the CN \( B^2\Sigma^+ - X^2\Sigma^+ \), \( \Delta v = 0 \) band intensity is very sensitive to the variations of methane content, i.e. the equivalence ratio \( \varphi \), demonstrating the close relationship between the CN emission and the fuel content.

In Figure 4, the variation of the CN \( B^2\Sigma^+ - X^2\Sigma^+ \), \( \Delta v = 0 \) band intensity versus the equivalence ratio \( \varphi \) is presented, as measured using an integration time \( t_w \) of 1.1 ms, a delay time \( t_d \) of 1 \( \mu \)s and a laser energy of 5.2 mJ. As shown, a very good linear correlation was found to hold between the band intensity and the equivalence ratio \( \varphi \). In addition, this linear relationship was found to remain valid independently of the delay time used for the recording of the emission spectra [21].

The formation of molecular species like CN and C\(_2\) has been reported previously by several authors studying laser induced plasmas on graphite targets [22–25], during laser ablation of organic compounds and polymers [26] and during the growth of carbon nitride (C\(_3\)N\(_x\)) films [27]. In these studies, CN and C\(_2\) molecules were readily formed during the interaction of ns laser radiation with carbon containing materials. In particular, the formation of CN and C\(_2\) was reported to occur both in the laser-material interaction zone and in the expansion zone of the plasma plume as well. The formation of CN and C\(_2\) have been also observed almost in all kinds of plasmas (as e.g. laser induced plasmas, microwave plasmas, in transient spark discharges) occurring in gaseous environments having carbon containing molecules (e.g., CO\(_2\)/N\(_2\) mixtures) [28–31]. Recently, fs laser induced breakdown has been employed for the detection of some nitrogen containing bacteria [32] and tri-nitrotoluene (TNT) based explosives [33]. In both of these studies strong emission of the CN \( B^2\Sigma^+ - X^2\Sigma^+ \), \( \Delta v = 0 \) band has been observed.

In order to further investigate the presence of CN, additional fs-LIBS experiments have been conducted in various compositions of
CH4–N2 mixtures using the air-tight (constant pressure) chamber. The laser beam was focused at the geometrical centre of the cross-like chamber with the same lens used in the flame experiments. However, in this case, the laser spark could not induce ignition because of the absence of oxidizer (i.e. air). In the next, similar experiments were performed using the fs laser beam unfocused. For both types of experiments, the resulted fluorescence was collected at right angle to the laser beam propagation direction using an optical fiber. The chamber was frequently refilled to avoid the accumulation of any unwanted photo-dissociation products. Similar experiments were performed with the chamber filled successively with nitrogen or methane at different pressures. The emission spectra resulted from the interaction of the unfocused fs laser beam with N2, CH4 and a mixture of CH4–N2 are presented in Figure 5a–c, while in Figure 5d the emission spectrum when laser induced breakdown was occurring (i.e. when the laser beam was focused) in the CH4–N2 mixture is shown. Each spectrum corresponds to the average of two hundreds single shot spectra, acquired using a time delay of 0 μs, an integration time of 9 ms and laser energy of 4.0 mJ.

It is interesting to notice the absence of continuum (background) from the spectra obtained using the unfocused laser, evidencing the absence of plasma formation; in fact, if plasma has been formed, a continuum should have been observable for measurements performed without 0 μs time delay. Moreover, comparing the spectra shown in Figure 5c and d, it becomes evident that they are very similar, suggesting that the observed CN emission is not a consequence of the laser induced breakdown, but of the interaction of laser beam with the constituent gases. Similar conclusion can be reached for the Hα and Hβ lines, and some (weaker) C2 emissions most probably resulting from the photodissociation of CH4 molecules as depicted by the spectrum of Figure 5b.

More in detail, in the case of Figure 5a, some weak N lines have been observed at 744.2, 821.6 and 871.2 nm, resulting from the photodissociation of molecular nitrogen, while in the case of Figure 5b, besides the Hα and Hβ lines, which were the most intense, some weaker features are observable, at 473.7, 516.5 and 563.5 nm, attributed to the well-known Swan band system (d1Πg–a1Πu) of C2 with Δv = 1, 0, –1 respectively. These C2 bands are usually observed in combustion processes of hydrocarbons [19].

Then, the time evolution and the laser beam energy dependence of the observed emission, resulting from the interaction of the unfocused laser with a 30 mbar methane and 225 mbar nitrogen mixture (corresponding to the volume ratio of these gases occurring in a stoichiometric air–methane flame) were also studied. So, in Figure 6, some emission spectra, measured at different time delays, t_d = 0, 0.2 and 0.3 μs and for an integration time of 9 ms, are presented, while Figure 7 compares the emission spectra resulting from the interaction of the mixture of gases with the unfocused laser beam with different pulse energies, namely E_laser = 0.50, 0.84 and 1.12 mJ. In the latter case, the integration time was set at 9 ms and no delay time was inserted.

As shown, the CN B^2Σ^+-X^2Σ^+, Δv = 0 band was found to decay significantly slower than the other spectral lines which have been observed to decay completely in less than 200 ns. Concerning the dependence of the intensity of the CN B^2Σ^+-X^2Σ^+, Δv = 0 band upon the laser energy, it was found to be reasonably intense at laser energies up to 0.5 mJ, as can be seen from the spectra presented in Figure 7.
Finally, the influence of nitrogen (N\textsubscript{2}) pressure on the intensity of the CN B^2\Sigma^-\textsuperscript{+}-X^2\Sigma^+, \Delta\nu = 0 emission has been examined, using mixtures consisting of 30 mbar CH\textsubscript{4} and different N\textsubscript{2} partial pressures. As can be seen in Figure 8, the intensity of the CN B^2\Sigma^-\textsuperscript{+}-X^2\Sigma^+, \Delta\nu = 0 band was found to reach a maximum (at about 330 mbars of N\textsubscript{2}), while higher N\textsubscript{2} partial pressure resulted to a monotonic decrease of the CN intensity.

Similar findings have been reported in various studies, investigating the processes occurring in the plume of laser induced plasmas on graphite or carbon targets in the presence of nitrogen [22,34–36]. A similar behavior has been predicted by a kinetic model developed to describe the relative intensities and the temporal variation of some atomic and molecular species such as C, H, N, O, C\textsubscript{2} and CN, often appearing in LIBS spectra a recent study [37].

4. Conclusions

In the present Letter, femtosecond laser induced breakdown spectroscopy (fs-LIBS) has been used to create plasma in some gaseous mixtures. In particular, fs-LIBS has been applied in some air–methane flames and also in some methane–nitrogen mixtures. From the analysis of the spectral emissions, the CN B^2\Sigma^-\textsuperscript{+}-X^2\Sigma^+, \Delta\nu = 0 band was found to be the most intense spectral feature and to depend linearly with the content of methane in the mixture allowing for the direct determination of the local equivalence ratio of the flame from simple spectroscopic measurements. In order to investigate more in detail the presence of the CN B^2\Sigma^-\textsuperscript{+}-X^2\Sigma^+, \Delta\nu = 0 band, further experiments were conducted in non-reactive CH\textsubscript{4}–N\textsubscript{2} mixtures using focused and unfocused laser beam. In all cases, strong CN B^2\Sigma^-\textsuperscript{+}-X^2\Sigma^+, \Delta\nu = 0 emission has been observed to result suggesting that CN was not formed under breakdown conditions. More work is currently in progress in order to get better understanding about the parameters which can affect the CN B^2\Sigma^-\textsuperscript{+}-X^2\Sigma^+, \Delta\nu = 0 emission.

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