



Short communication

Femtosecond laser filamentation for sensing combustion intermediates: A comparative study



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ABSTRACT

We demonstrate experimental evidences that femtosecond filament-induced clean fingerprint fluorescence can indeed be employed to characterize the combustion intermediates in flames. By comparing the emission spectra obtained from an ethanol–air flame by femtosecond filament excitation, nanosecond laser-breakdown excitation, as well as without any laser excitation, it is found that the filament-induced fluorescence in the combustion flame mainly results from the interaction of femtosecond laser pulses with the combustion intermediates such as OH, CH, and C₂ existing in the combustion, but not from the fragmentation of parent ethanol molecules.

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1. Introduction

The measurement of local compositions in combustion flames is of particular importance in development of the engines for improving combustion efficiency and reducing pollutant products. Among the methods available, laser spectroscopy techniques, such as laser-induced fluorescence (LIF), infrared spectroscopy and polarization spectroscopy, have been extensively employed for combustion diagnostics because of their non-invasive, real-time and high-sensitivity properties [1–3]. However, most of such laser-based techniques require the laser to be resonant with the species to be probed, and thus can only be used to detect one specific species at a time. On the other hand, multiple elemental analyses in combustion have also been demonstrated by the techniques such as laser-induced breakdown spectroscopy (LIBS), which is based on optical emissions of a tightly confined plasma spark induced by laser pulses in flames [4]. However, conventional LIBS using nanosecond laser pulses in general leads to the formation of atomic compositions in the plasma zone, and could not provide the information on the

combustion intermediates, which are more desirable in the combustion diagnostics.

Recently, it was demonstrated that femtosecond laser pulses have the high potential for simultaneous monitoring of multiple combustion intermediates [5], which is based on femtosecond laser filamentation in flames, resulting from the dynamic balance between optical Kerr self-focusing and defocusing effect of the self-generated low-density plasma [6]. With filament-induced nonlinear spectroscopy (FINS) [7], clean fluorescence emissions from free radicals CH, CN, NH, OH, and C₂, as well as atomic C and H, were observed in a plasma filament in an ethanol–air flame, which were suggested as fingerprints for sensing combustion intermediates [5]. Most recently, it was found that the filament-induced fluorescence emission from the specific species can be amplified by observing the backward fluorescence intensity as a function of the plasma length in the flame, providing a possibility to improve the signal-to-noise ratio in combustion diagnosis by using the FINS technique [8].

Since femtosecond laser filamentation can be formed without perturbation in adverse atmospheric conditions [9], it would be greatly advantageous to combustion diagnostics in the highly turbulent combustion environment. However, it is questioned for such studies whether the fingerprint emissions result from the combustion intermediates by the combustion flame itself when interacting with femtosecond laser filament or from the fragments resulted from the dissociation of parent molecules by the intense

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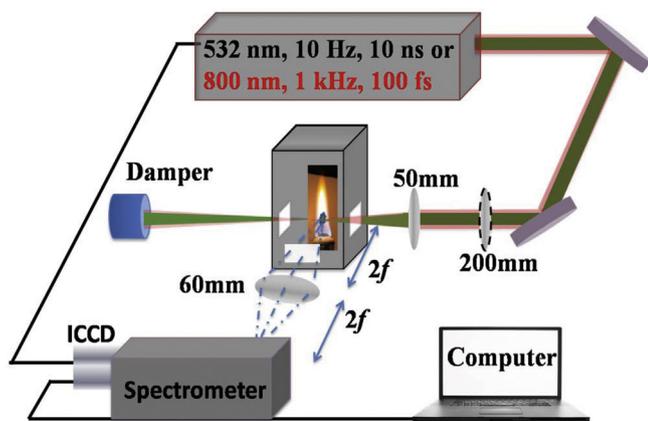


Fig. 1. The experimental setup.

femtosecond laser field, because the laser peak intensity is extremely high in the plasma filament due to intensity clamping [6]. In this letter, we measure the emission spectra of an ethanol–air flame induced by femtosecond laser filamentation, nanosecond laser breakdown as well as that from the flame itself without any laser excitation, and compare their differences, based on which we demonstrate that the filament-induced fluorescence can be used for characterizing the intermediate species in the combustion flame.

2. Experiments

The schematic of the experimental setup is illustrated in Fig. 1. The experiments were first conducted using a Ti:sapphire femtosecond laser system (Spectra Physics, Spitfire), which produced laser pulses with a central wavelength of 800 nm, a pulse duration of 100 fs, a pulse energy of 0.7 mJ and a repetition rate of 1 kHz. The laser pulses from the Ti:sapphire laser were focused by a fused silica lens of 200 mm into an ethanol–air flame on an alcohol burner to generate a plasma filament with the length of ~ 1 cm. Alternatively, the laser pulses from a frequency-doubled Nd:YAG laser system, characterized with a laser wavelength of 532 nm, a repetition rate of 10 Hz, a pulse duration of 10 ns and a pulse energy of 100 mJ, were focused by a fused silica lens of 50 mm into the flame to induce the breakdown plasma spark. The interaction position of both the nanosecond and femtosecond laser pulses at the focus and the flame is approximately 18 mm above the wick (note that the total length of the flame is ~ 50 mm). The flame was surrounded by a top-opened box, which is used to avoid the wind from the laboratory air conditioner that may lead to a strong swing of the flame. Two holes (rectangle) along the laser propagation direction were drilled on the box to permit the laser beam passing through, and one hole (rectangle) was opened on the box from the side of the laser propagation direction to allow the collection of fluorescence light, respectively.

Optical emissions from the femtosecond and nanosecond laser-induced plasmas as well as from the flame itself were collected perpendicularly to the laser propagation direction using a fused silica lens (60 mm focal length; 50.8 mm diameter) in a $2f$ – $2f$ imaging scheme. The emission spectra were measured by a spectrometer (Andor Shamrock SR-303i) coupled with a gated intensified charge coupled device (ICCD, Andor iStar). The entrance slit width of the spectrometer was fixed to be 50 μm . It is worth stressing that because of the use of $2f$ – $2f$ imaging system an aperture slot with a diameter of 1 mm was attached to the entrance slit of the spectrometer to permit only the emissions from a small part of the flame itself in the vertical direction around the interaction zone to be recorded,

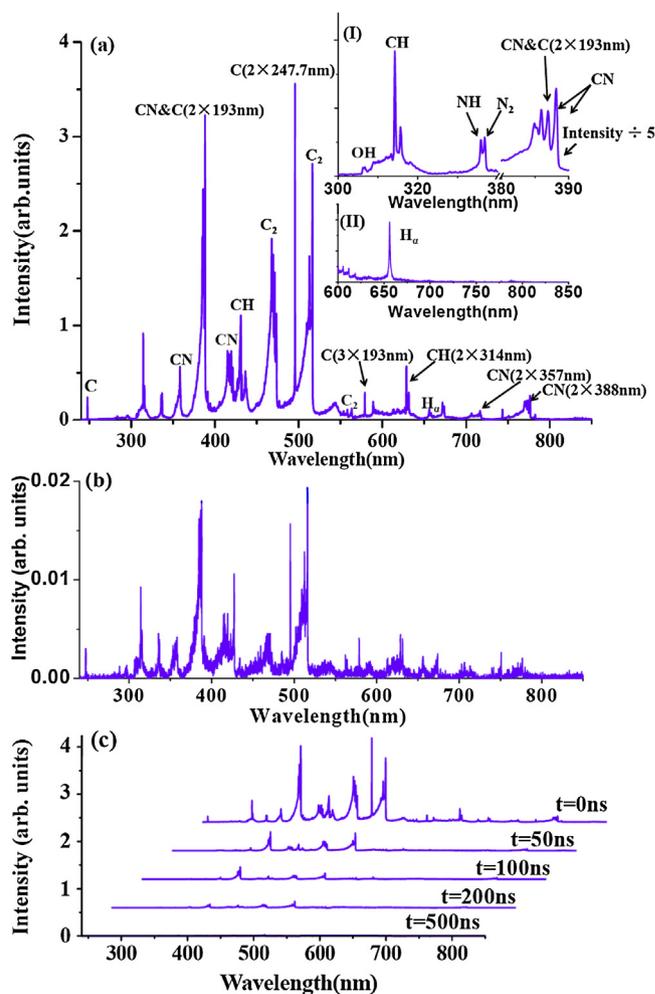


Fig. 2. (a) Filament-induced nonlinear spectrum of the laminar ethanol–air flame. Insets: (I) zoomed-in spectrum in the range of 300–345 nm, and (II) spectrum obtained with a highpass filter. (b) A single-shot filament-induced nonlinear spectrum with the gate width of 20 ns. (c) Time-resolved spectra obtained with different temporal delays.

in order to compare all the results from the same combustion area of the flame.

3. Results and discussion

Fig. 2(a) shows a typical filament-induced nonlinear spectrum of the laminar ethanol–air flame in the spectral range of 240–850 nm with an ICCD gate width of $\Delta t = 2 \mu\text{s}$ and a gate delay time of $t = 0$ ns. The inset (I) of Fig. 2(a) presents a higher-resolution spectrum in the spectral range of 300–345 nm. Note that the laser pulse arrives at the interaction zone at $t = 0$ ns. The data were accumulated over 200 laser shots to increase the signal-to-noise ratio. The ICCD gate width of $2 \mu\text{s}$ can confirm all the fluorescence being integrated. It should be pointed out that the FINS technique has a high time resolution, depending on the used detector (in our case, the time resolution of ICCD is a few nanoseconds). As an example, Fig. 2(b) shows a filament-induced spectrum by a single shot pulse with an ICCD gate width of 20 ns, which still shows clear spectral signals. The filament-induced spectrum shown in Fig. 2(a) is very clean (i.e. free of plasma continuum), and the spectral bands can be assigned to free radicals CH, CN, NH, OH, and C_2 , as well as to C and H atoms, which show the same feature as that reported previously in Ref. [5]. Moreover, it should be pointed out that except for the hydrogen atomic line at 656 nm, all the spectral lines/bands in the

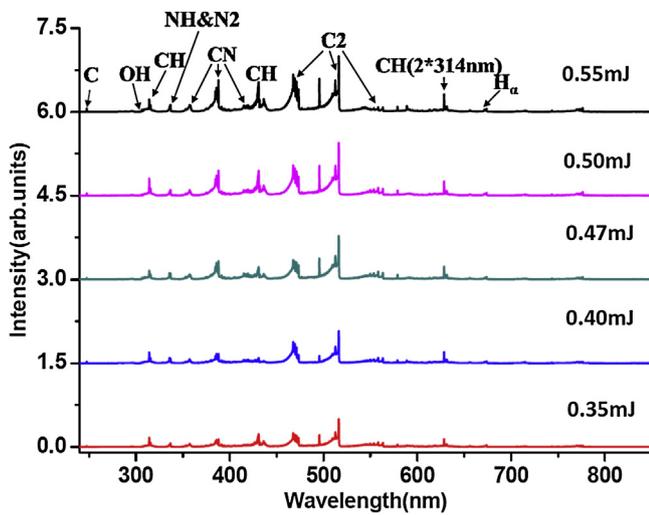


Fig. 3. The FINS spectra obtained with different laser energies.

range of 600–850 nm can be assigned to the second- or third-order diffraction of the shorter wavelength signals, which is confirmed by inserting a highpass filter before the entrance slit to block the signal below 450 nm (as shown in the inset (II) of Fig. 2(a)). This indicates the absence of the laser-induced breakdown in the FINS process. In addition, we performed the measurement of the FINS spectra with different time delays, as shown in Fig. 2(c), while the gate width was kept to be 2 μ s. It can be seen from Fig. 2(c) that all the signal intensities of different species dramatically decrease when the delay time increases, indicating that all the spectral bands indeed result from the interaction of femtosecond laser pulse with the flame, rather than from the flame itself.

We also examined the dependence of the laser energy on the fluorescence spectrum, as shown in Fig. 3. In this case, because the higher energy would not lead to a higher intensity in the filament due to the intensity clamping [6], we only measured the FS laser-induced emission spectra of the flame with lower laser energies. It can be seen from Fig. 3 that these spectra show identical spectral bands of OH, CN, CH and C₂, but the spectral intensities of different species become stronger as the laser energy increases. The fact that the FINS spectra show the similar spectral feature to those obtained with the lower laser energies further confirms the absence of breakdown in the FINS process.

In order to further examine the difference of spectral characteristics between FINS and conventional ns-LIBS in analyzing the combustion flame, an ns-LIBS spectrum of the laminar ethanol–air flame was measured, as presented in Fig. 4. The ICCD gate width and gate delay were set to be the same as those in the FINS measurement, while the ICCD gain is reduced. In contrast to that observed in Fig. 2, the spectrum in Fig. 4 exhibits typical narrow line-width atomic lines superposed on a broadband continuum, which exhibits the most prominent characteristics in the ns-LIBS scheme. Intense spectral lines on the plasma continuum are assigned to the Balmer hydrogen lines H α , H β , H γ , and C(I) at 247.7 nm. In addition, two spectral bands at 388 and 358 nm resulting from the B² Σ^+ –X² Σ^+ transition of CN radical are observed. Meanwhile, the spectrum in the longer wavelength side was measured by inserting the same highpass filter before the entrance slit of the spectrometer as that used in FINS, as shown in the inset of Fig. 4, from which it can be seen that the atomic lines from C(I) at 711 nm, N(I) at 746 and 818 nm and O(I) at 715, 777 and 795 nm exist. These atomic lines clearly show the main atomic compositions of C, H, O and N in the flame. However, although some spectral lines from combustion intermediates can still be observed in Fig. 4, but they are strongly masked by

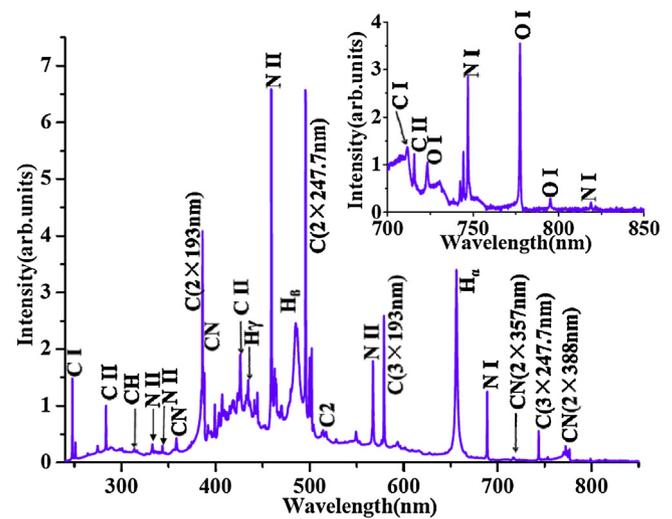


Fig. 4. A typical ns-LIBS spectrum of the ethanol–air flame. Inset: spectrum obtained with a highpass filter.

the continuum emissions, showing the advantages of femtosecond laser pulses in application to combustion diagnostics.

To further demonstrate the ability of FINS in the application for sensing combustion intermediates, the emission spectrum of the laminar ethanol–air flame without laser excitation (defined as non-laser-ES) was also measured, as shown in Fig. 5. In this case, the total ICCD accumulation time was set to be 450 ms. As can be seen in Fig. 5, a broad low-intensity continuum resulting from the blackbody radiation and the molecular emission bands can clearly be observed. The spectral bands are assigned to the combustion intermediates of OH, CH, and C₂, which come from the combustion processes [10]. In addition, the spectral lines of atomic sodium at 588.9 and 589.6 nm can be observed, which may result from the contamination of the wick.

By comparing the spectra shown in Figs. 2 and 5, it can be seen that all of the free radicals, such as C₂ at 562, 516 and 466 nm, CH at 431 nm and OH at 308 nm can be observed in both cases. This indicates that FINS can carry the molecular information in combustion flames. However, it can also be observed that the ratios of the signal intensities of OH, CH, CN and C₂ with respect to each other are different for the two cases, for example, CH (431 nm):C₂ (516 nm)=0.32, C₂ (516 nm):CN (388.3 nm)=0.87, and OH (308.9 nm):CH (431 nm)=0.11 for the spectral bands in Fig. 2, and CH (431 nm):C₂ (516 nm)=3.02 and OH (308.9 nm):CH (388.3 nm)=0.18 for those in Fig. 5, respectively. It can be noted

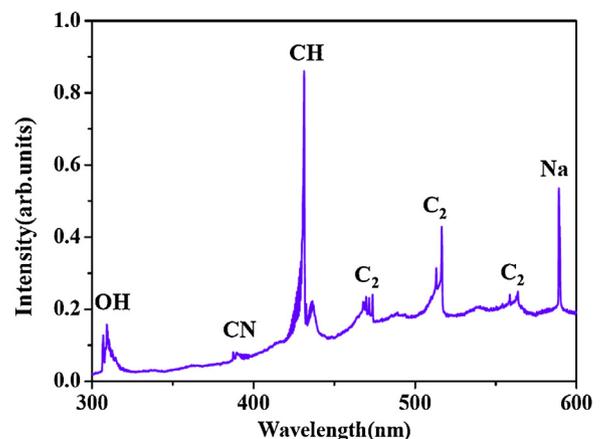


Fig. 5. Emission spectrum of the laminar ethanol–air flame without laser excitation.

that the signal of CN at 389 nm is relatively strong in FINS than that in non-laser-ES. Since CN mainly results from the interaction of C₂ and N₂ through C₂ + N₂ → 2CN [5,11], the strong CN signal in FINS implies that laser-induced plasma may enhance the collisional reaction of C₂ and N₂ in the flame. This can be confirmed by the observation of CN signal in ns-LIBS in Fig. 4, in which CN would be mainly generated after the avalanche ionization and inversed Bremsstrahlung process. Furthermore, it should be noted that the atomic sodium line could not be observed in Fig. 2. This is because the transition of Na I at 589 nm cannot be matched by one photon or multi-photon frequency of femtosecond laser pulses.

It can also be seen that the ratio of the signal intensity of CH at 431 nm to that of the strongest C₂ band at 516 nm is much smaller in Fig. 2 than that in Fig. 5. It is well known that the dissociation of parent ethanol molecule in intense femtosecond laser fields prefers to form CH than C₂ [12], which would give a stronger signal ratio of CH to C₂ in Fig. 2, in contrast to our observation. Therefore, the plasma-assisted collision, which could make a contribution to the formation of C₂, would be one of the reasons for understanding the relative high intensity of C₂ than that of CH in Fig. 2. Nevertheless, the very weak C₂ signal in Fig. 4 (i.e., the ratio of the signal of C₂ to that of CN is much smaller in Fig. 4 than in Fig. 2) indicates that the femtosecond filament excitation of C₂ existing in the combustion flame plays a significant role in populating the excited C₂. It should be pointed out that the population-inverted CN could be built up by femtosecond laser-induced filament in the flame, but this is not the case for C₂ [6]. This implies that the plasma-assisted collision may dominate the formation of the B²Σ excited state of CN, in a similar manner as the C³Π_u excited state of N₂ in air [13,14], while the excited C₂ is mainly dominated by multiphoton excitation of C₂ existing in the combustion flame. In addition, in the FINS scheme, the signal of OH radical may result from the flame itself and the dissociation of H₂O or the parent ethanol molecule inside the filament [15]. However, it is worth stressing that the intensity of OH radical in FINS process is relatively weak, and the ratio of its intensity to that of CH is much weaker in Fig. 2 than in Fig. 5. This may indicate that the OH radical generated in the filament mainly results from the multiphoton excitation rather than from the dissociation of parent molecules.

4. Conclusions

We compared femtosecond laser filament-induced spectrum of the ethanol–air flame with those obtained from ns-LIBS and the flame itself and found that the filament-induced fingerprint fluorescence from the intermediates including CH, C₂ and OH in the combustion flame mainly results from the interaction or direct excitation of some specific species existing in the combustion. The observation that the filament-induced clean spectrum consists of rich molecular information provides a possibility of using femtosecond laser pulses for combustion diagnostics.

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References

- [1] A.C. Eckbreth, *Laser Diagnostics for Combustion Temperature and Species*, 2nd ed., Gordon & Breach, UK, 1996.
- [2] K. Kohse-Höinghaus, R.S. Barlow, M. Aldén, J. Wolfrum, *Combustion at the focus: laser diagnostics and control*, Proc. Combust. Inst. 30 (2005) 89–123.
- [3] M. Aldén, J. Bood, Z.S. Li, M. Richter, Visualization and understanding of combustion processes using spatially and temporally resolved laser diagnostic techniques, Proc. Combust. Inst. 33 (2011) 69–97.
- [4] D.A. Cremers, L.J. Radziemski, *Handbook of Laser-Induced Breakdown Spectroscopy*, John Wiley and Sons, Ltd., Chichester, 2006.
- [5] H. Li, H.L. Xu, B. Yang, Q. Chen, T. Zhang, H. Sun, Sensing combustion intermediates by femtosecond filament excitation, Opt. Lett. 38 (8) (2013) 1250–1252.
- [6] S.L. Chin, *Femtosecond Laser Filamentation*, Springer, New York, 2010.
- [7] H.L. Xu, Y. Kamali, C. Marceau, P.T. Simard, W. Liu, J. Bernhardt, G. Méjean, P. Mathieu, G. Roy, J.R. Simard, S.L. Chin, Simultaneous detection and identification of multigas pollutants using filament-induced nonlinear spectroscopy, Appl. Phys. Lett. 90 (10) (2007), 101106 (1–3).
- [8] W. Chu, H. Li, J. Ni, B. Zeng, J. Yao, H. Zhang, G. Li, C. Jing, H. Xie, H.L. Xu, K. Yamanouchi, Y. Cheng, Lasing action induced by femtosecond laser filamentation in ethanol flame for combustion diagnosis, Appl. Phys. Lett. 104 (2014) 091106.
- [9] R. Ackermann, G. Méjean, J. Kasparian, J. Yu, E. Salmon, J.-P. Wolf, Laser filaments generated and transmitted in highly turbulent air, Opt. Lett. 31 (1) (2006) 86–88.
- [10] S. Mahesh, D.P. Mishra, Flame structure of LPG-air inverse diffusion flame in a backstep burner, Fuel 89 (8) (2010) 2145–2148.
- [11] M. Kotzagianni, S. Couris, Femtosecond laser induced breakdown spectroscopy of air–methane mixtures, Chem. Phys. Lett. 561 (2013) 36–41.
- [12] J. Chen, R. Ma, H. Ren, X. Li, H. Yang, Q. Gong, Femtosecond laser-induced dissociative ionization and Coulomb explosion of ethanol, Int. J. Mass Spectrom. 241 (2005) 25–29.
- [13] H.L. Xu, A. Azarm, J. Bernhardt, Y. Kamali, S.L. Chin, The mechanism of nitrogen fluorescence inside a femtosecond laser filament in air, Chem. Phys. 360 (2009) 171–175.
- [14] Q. Luo, W. Liu, S.L. Chin, Lasing action in air induced by ultra-fast laser filamentation, Appl. Phys. B 76 (2003) 337–340.
- [15] Q. Luo, H.L. Xu, S.A. Hosseini, J.F. Daigle, F. Théberge, M. Sharifi, S.L. Chin, Remote sensing of pollutants using femtosecond laser pulse fluorescence spectroscopy, Appl. Phys. B 82 (2006) 105–109.

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