Sensing combustion intermediates by femtosecond filament excitation

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Simultaneous monitoring of multiple combustion intermediates using femtosecond filament-induced nonlinear spectroscopy is demonstrated. Clean fluorescence emissions from free radicals CH, CN, NH, OH, and C_2, as well as atomic C and H, are observed when a femtosecond filament is formed in the laminar ethanol/air flame on an alcohol burner. The fluorescence signals of these species are found to vary as functions of the position of interaction of the filament with the flame along the vertical axis of the central combusting flow, opening up a possibility for remote combustion diagnostic in engines by the excitation of femtosecond laser filament.   © 2013 Optical Society of America

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Mapping the concentration distributions of intermediate species in combustion is essential to rationalize the physical and chemical nature of combustion systems for efficient combustion with low-pollution products. So far, a large variety of methods for probing the intermediate species of a combustion process have been developed (see [1,2] and references therein). Among the techniques available, the laser-based techniques, such as laser-induced fluorescence, coherent anti-Stokes Raman scattering, and polarization spectroscopy have been extensively employed because of their noninvasive and high-sensitivity detection capabilities. For example, with these techniques, measurements of a large variety of intermediate species in combustion, such as OH, C_2, CN, CH, and CO have been demonstrated [1,2].

Because the laser wavelengths required for probing different species vary over wide spectral ranges, which are generally not achievable with only one laser source, most of the laser spectroscopic techniques have been limited to sensing one species at a time. It is desired that a large number of combustion intermediates could be detected simultaneously. Laser-induced breakdown spectroscopy (LIBS), which is based on the emission spectroscopy of materials ablated into a small plasma by a tightly focused laser beam, has been used in combustion to provide multiple elemental analysis [3], but LIBS involves detecting various atomic species thereby making it difficult to give a clear picture of the local concentration distribution of combustion intermediates.

Recent advances in high-power femtosecond laser technologies have enabled advances in practical applications, such as generation of energetic few-cycle pulses, remote sensing of atmospheric constituents, and micro/nano fabrication [4–6]. This results from the unique properties of femtosecond laser pulses; those properties being broadband, ultrafast, and high intensity. Only a few studies on combustion analysis using femtosecond laser pulses have been reported [7–10]. In this Letter, we experimentally demonstrate the feasibility of simultaneous detection and identification of multiple intermediate species in a flame using filament-induced nonlinear spectroscopy (FINS) [11].

A femtosecond filament appears as a dynamic balance between the optical Kerr-effect-induced self-focusing and the defocusing effect of the self-generated plasma during the intense ultrashort laser pulse propagation in optical media [12]. The intensity inside the filament is clamped to approximately 10^{13}–10^{14} W/cm^2 in gases, which is high enough to excite molecules into highly excited states by multiphoton excitation, resulting in characteristic fluorescence. In particular, it is worth stressing that femtosecond laser filamentation can be formed at a distance in adverse atmospheric environments [13], and is hardly disturbed by turbulence [14]. For this reason, we expect that the FINS technique could be applied to remote sensing of multiple intermediate species in combustion even for extreme environments associated with many real-world combustion flows. To demonstrate the proof of concept for the FINS technique in combustion diagnostics, we employed the laminar ethanol/air flame on an alcohol burner as the target, not only because of its simplicity and low cost, but also the similarity of its diffusion to other practical systems, such as rocket combustor and industrial stoves [15].

The experiment was conducted with a Ti:sapphire femtosecond laser system (Spectra Physics, Spitfire). Briefly, the laser pulses, characterized by a repetition rate of 1 kHz, a duration of 100 fs, an energy of 0.5 mJ/pulse, and a central wavelength at 800 nm, were focused by a fused silica lens of 200 mm into the ethanol/air flame on an alcohol burner to generate a single filament with a length of approximately 1 cm. The flame was surrounded by a top-opened black box to avoid the turbulence of air. A moving stage was used to lift or lower the alcohol burner to control the position of interaction of the flame with the short filament along the dashed–arrow line shown in inset (a) of Fig. 1.

The fluorescence induced by the filament was collected at a right angle to the laser propagation direction, and focused onto the entrance slit of a spectrometer
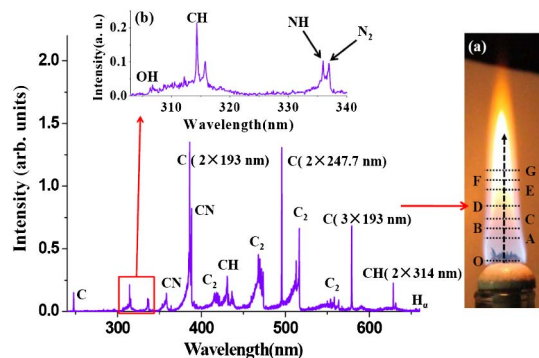
Fig. 1. (Color online) Spectrum of the ethanol/air flame on an alcohol burner by the excitation of a femtosecond filament. Insets: (a) flame and the filament positions marked by the dash lines, (b) zoomed-in spectrum in the range of 303–340 nm.

(Andor Shamrock SR-303i) by a $2f - 2f$ imaging system using a fused silica lens ($f = 60$ mm, diameter = 50.8 mm). The entrance slit width was set to 50 μm. Therefore, only the fluorescence emitted from a 50 μm length of filament in the central part of the flame as shown at the crossing spots in inset (a) of Fig. 1 was sent into the spectrometer. This will avoid the collective effect of fluorescence signals due to chemical variations along the horizontal axis of the flame, and give a meaningful comparison for the fluorescence signals measured at different positions along the vertical axis of the flame. The fluorescence was then dispersed by a grating of 1200 grooves/mm (blazed wavelength at 500 nm), and detected by a gated intensified charge coupled device (ICCD, Andor iStar). Using the measurement system, the spectrum in the range from 185 to 850 nm can be recorded.

Figure 1 shows a typical filament-induced nonlinear spectrum of the ethanol/air flame in ambient atmosphere in the UV–Vis range from 240 to 660 nm. The ICCD gate width and delay were set to $\Delta t = 210$ ns and $t = -2$ ns, respectively (note that the laser pulse arriving time at the interaction zone is $t = 0$). The data were accumulated over 1000 laser shots. The filament was formed at a height of 17 mm (dashed line D) above the burner wick (dashed line O), as shown by inset (a) of Fig. 1. The signal uncertainty is about 10%–20%, which mainly comes from the swing of the flame. It should be pointed out that the emission from the flame itself cannot be observed when the femtosecond laser pulse is blocked. Also, it is carefully checked that the observed spectra are not due to scattered/reflected light from the filament as the burner is raised or lowered. Analysis of the spectrum in Fig. 1 shows that the species in the alcohol burner flame are very rich, consisting of not only atoms but also molecules.

The three spectral bands at around 563, 516, and 416 nm are assigned to the Swan band ($d^3\Pi_g - a^3\Pi_u$) of the C_2 radical, and that at around 408 nm belongs to the Deslandres–D'azambuja band of the C_2 radical; the two spectral bands around 430 and 314 nm result from the $A^2\Delta - X^2\Pi$ and $C^2\Sigma - X^2\Pi$ transitions of the CH radical, respectively; the spectral bands around 388 and 358 nm originate from the $B^2\Sigma^+ - X^2\Sigma^+$ transition of the cyano radical, CN [16]. In addition, several weak band

emissions from the molecules, such as N_2 (337 nm), NH (336 nm), and OH (307 nm) can be observed in the spectrum. Besides the molecular bands, atomic lines of C(I) at 247.7 nm and H_α at 656 nm can be seen in Fig. 1. Note that the spectral line at 495.4 nm results from the second-order diffraction of C(I) at 247.7 nm, whereas the spectral lines at 386 and 579 nm come from the grating's second- and third-order diffractions of the atomic C(I) line at 193 nm (not shown). It should be noted that in Fig. 1 the N_2 signal at 337 nm is quite weak, which is contrast to those obtained in trace gas measurements [11], indicating the weakness of the N_2 concentration in the diffusion flame. The identification of these free radicals and atomic species in the flame confirms the potential of FINS for detecting the intermediate species in a combusting flow by the excitation of femtosecond filament.

It is noteworthy that the spectrum of Fig. 1 is very clean and free from plasma continuum. This is consistent with previous observations of filament-induced spectra in air and other gases [5]. In addition, it should be emphasized that, in Fig. 1, the spectral lines from atomic N and O, such as the emissions of N(I) at 744 nm and O(I) at 777 and 845 nm, which appear generally in laser-induced breakdown spectra [5], are not observable, indicating the absence of the breakdown processes in FINS.

To demonstrate the ability of FINS in mapping the concentration distribution of combustion intermediates in flames, we carried out the measurements of filament-induced spectra (Fig. 2) at different positions of the flame along the dashed–arrow line of inset (a) of Fig. 1. The distances above the burner wick were set to A, $d = 7$ mm; B, $d = 10$ mm; C, $d = 13$ mm; D, $d = 17$ mm; E, $d = 22$ mm; F, $d = 25$ mm; and G, $d = 28$ mm. It can be seen in Fig. 2 that the observed combustion intermediates are identical at different zones of the flame, but their signal intensities are quite different for different distances. To give a clear picture of the distribution characteristics of the intermediate species in the flame, we first plot the signal intensities of the four species, C_2, CH,
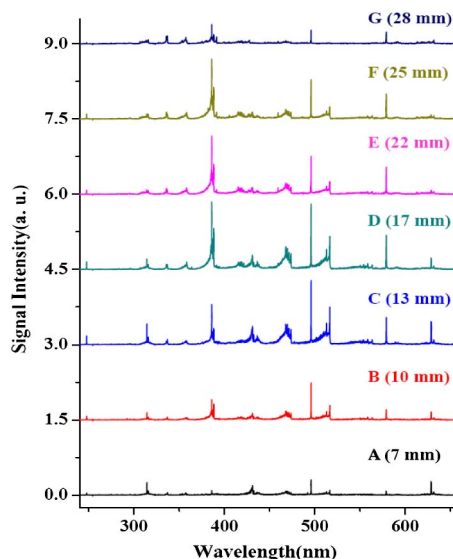

Fig. 2. (Color online) Filament-induced spectra recorded in different positions of the flame above the burner wick.
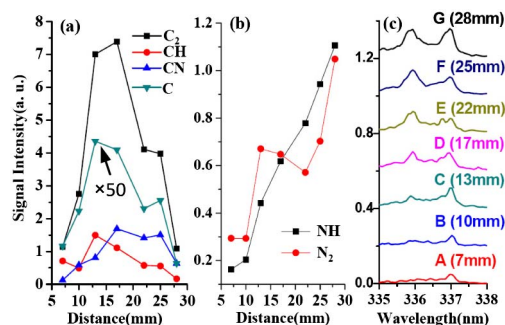
Fig. 3. (Color online) (a) Signal intensities of C_2, CN, C, and CH, obtained at different positions of the flame. (b) and (c) Signal intensities and spectra of NH and N_2.

CN, and C as a function of the distance d in Fig. 3(a). The signal intensities are obtained by summing up all the bands or lines emitted from the same species. For C_2, the signal intensity was accumulated from four bands in the ranges of 552.3–564.7 nm, 510.7–517.8 nm, 466.7–474.4 nm, and 414.3–420.5 nm. For CH, the signal intensity was from two bands in the ranges of 428.8–432.8 nm and 314.1–314.8 nm. For CN, the signal intensity resulted from two spectral bands in the ranges of 386.5–389.0 nm and 357.1–360.3 nm. For atomic C, the signal intensity was from the spectral line in the range of 247.4–248.0 nm.

As can be seen from Fig. 3(a), the signal intensities from all four species first increase and then decrease as the distance d increases. This observation may be related to the concentration distribution of the four intermediate species in the flame. When ethanol molecules are just ejected from the alcohol burner, the combustion has not been fully developed, leading to very weak signals of the four intermediates in the combustion zone close to the wick, which may reflect the less importance of direct ionization and dissociation of ethanol molecules in the fluorescence signals of combustion intermediates induced by the excitation of femtosecond filament. Subsequent development of the combustion enhances signal intensities of the intermediates. Finally, the combustion intermediates are consumed in the fully developed combustion zone far from the wick, and the final products, i.e., water and CO_2, are produced, making the signal intensities of the intermediate species decrease, as shown in Fig. 3(a). Moreover, it can be noted that the CH signal at the distance of 7 mm is a little stronger. This may reflect that part of the CH radical is generated from the fragmentation of ethanol molecules by the filament excitation when ethanol molecules are just ejected from the burner and have not been reactive yet. It can also be seen that the increasing slope of the CN signal is a little slower, which may reflect the rate of N_2 involved into the combustion flows from the ambient air because CN might come from the reaction of $C_2 + N_2 \rightarrow 2CN$. This point may be further confirmed from the signal variation of NH by plotting the signal intensity of N_2 and NH as a function of the distance d, as shown in Fig. 3(b). In this

case, the signal intensities of NH and N_2 are obtained by summing up the band signals in the ranges of 335.6–336.1 nm and 336.7–337.2 nm, respectively, as shown in Fig. 3(c). It can be seen in Fig. 3(b) that the NH signal increases linearly as the distance d increases. The linear dependence of NH on the distance may also reflect the concentrations of H atoms and N_2 molecules involved in the reactive flows. Further efforts are needed to give a deeper understanding of the luminescence mechanisms of atoms and molecules with the excitation of femtosecond filament in different air–hydrocarbon combustion systems.

In summary, we demonstrate the feasibility for combustion diagnostics of flames using femtosecond filament excitation. The fact that this spectroscopic technique requires an extremely simple optical geometry, and that femtosecond filament can be formed in an adverse turbulent environment, makes the excitation scheme potential practical for complex reactive-flow combustion systems. Moreover, a femtosecond laser system with a high repetition rate of 1–10 kHz is now available, providing the possibility for the FINS technique as an application for continuous monitoring of fuel contents in various combustion environments.

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