

Self-channeling of Femtosecond Laser Pulses for Rapid and Efficient Standoff Detection of Energetic Materials

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Abstract — *Self-channeling properties of high intensity laser pulses are used to extend spectroscopic methods as LIBS to standoff. This work shows the advantages of using self-channeled femtosecond pulses in Laser-Induced Breakdown Spectroscopy of polymeric micrometer-size thin films in a standoff configuration at 12 meters. We show the possibility of trace analysis on surfaces and the importance of molecular signal as a signature for carbon-based samples.*

I. INTRODUCTION

The ability to detect organic compounds, as energetic materials, in the field under air atmosphere and at a distance has been an issue for homeland security purposes [1]. As the unlawful use of energetic materials continues to evolve, so too must the detection and regulation of these dangerous chemicals. Furthermore, the need of standoff techniques to provide decision at a distance in real-time gives an advantage to the optical spectroscopy techniques since they don't need mechanical assistance on the target.

To provide the excitation energy at several hundreds of meters, the use of the nonlinear propagation properties of ultra-intense femtosecond pulses is a good candidate for such standoff optical techniques. By shaping the laser pulses, they can propagate against diffraction law over kilometers to provide high intensities up to 10^{14} W.cm⁻² [2].

Laser Induced Breakdown Spectroscopy (LIBS) is a field of intense study due to the vast amount of available applications [3,4]. LIBS provides a means of conducting real-time analysis and multi-elemental spectroscopy on samples that require minimal to no sample preparation. LIBS is used in the detection of trace compounds, ranges data are collected ordinarily a few centimeters from the sample. To use LIBS in a stand-off detection scenario, we use the properties of self-channeling of high-intensity laser pulses. The combination of LIBS and self-channeling (or filamentation) leads to what is called Filament-Induced Breakdown Spectroscopy (FIBS) [5]. Several previous studies have shown how useful can be FIBS for remote detection of metallic, organic and biological targets up to 180 meters [5-11].

Our motivation for this research is to provide a means for stand-off detection of trace organic materials. For the purpose of this experiment, we use a CPA femtosecond laser system as a laser source to produce the filaments. The light is collected by a parabolic mirror (diameter 316 mm, focal length 1900mm) and is analyzed by an imaging spectrometer coupled to an iCCD camera. Tests have been performed on copper and graphite and then detection of an organic compound was done.

II. SELF CHANNELED LIBS

A. Self-channeling of High Intensity Laser Pulses

Linear propagation of laser pulses in air obeys the laws of diffraction. For example, if the laser beam has a Gaussian spatial mode of radius w_0 and wavelength λ , the beam radius along the z axis will be defined by the Gaussian beam propagation equation (Eq. 1.1)

$$w(z) = w_0 \sqrt{1 + \left(\frac{z\lambda}{\pi w_0^2} \right)^2} \quad (1.1)$$

When the intensity $I(r,t)$ of the laser pulse increases, nonlinearities of the refraction index n of the air become non-negligible and show an intensity-dependent behavior (Equation 1.2)

$$n = n_0 + n_2 I(r,t) \quad (1.2)$$

with n_0 the linear refractive index and n_2 the nonlinear Kerr index coefficient, positive in the air. The intensity on the axis being more intense the refractive index of the air is higher on the axis. As a consequence, the wavefront is curved as by the effect of a positive lens, and along the propagation this effect is amplified and leads to the collapse of the beam on itself [2].

As the intensity of the self-focused pulse increases, multiphoton ionization of the air occurs and plasma is created. The generation of this plasma (with an electronic density $\rho(r,t)$) induced a local reduction in the refraction index according to Equation 1.3

$$n \approx n_0 - \frac{\rho(r,t)}{2\rho_c} \quad (1.3)$$

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with ρ_c the critical plasma density above which it becomes opaque. This local reduction of refractive index on the axis acts like a negative lens and so the laser pulse doesn't collapse.

By a dynamic balance between the two processes of self-focusing and plasma defocusing, the beam self-propagates in the medium, the air in our case, against the diffraction laws as long as the pulse has enough intensity to produce these processes. The self-channeling of ultra-short pulses is also characterized by the presence of plasma channels, called *filaments*, where the intensity is clamped to approximately 10^{14} W.cm⁻² around which the full beam (called *photon reservoir*) continues its propagation (Fig. 1). This composed entity "*filament + photon reservoir*" is stable along its propagation in turbulent conditions and even scattering media.

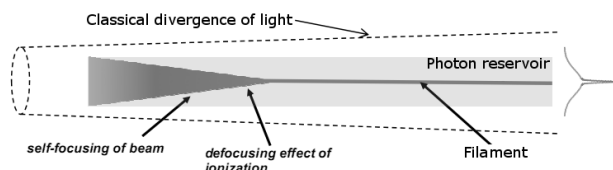


Figure 1. Schematic of the self-channeling process

By shaping the temporal, spatial and phase profiles of the laser pulses, it's possible to control the filaments themselves: the distance where they begin, their length and the spectral content of the beam.

B. Filament-Induced Breakdown Spectroscopy

The intensity contained in a self-channeled beam, as mentioned above, is high enough to overcome the breakdown threshold of most materials (between 10^{12} and 10^{13} W.cm⁻² for metal [12] and polymer [13] ablation with femtosecond pulses). Thus, this property can be used to apply Laser-Induced Breakdown Spectroscopy (LIBS) of the sample at distance.

LIBS is a spectroscopic technique consisting of ablating and exciting material from a material to create a plasma that relaxes and produces characteristic emission of its chemical composition. The spectroscopic signal can then be analyzed to determine a signature for the analyzed sample. The use of self-channeled laser pulses and LIBS is called Filament-Induced Breakdown Spectroscopy (FIBS).

Analysis of organic samples by FIBS has been investigated in few previous studies [7]. They show that the plasma emission can be related to the sample composition. Other studies show that intrinsically the creation of the plasma from the sample by the filament, which is characterized by a plasma channel in the atmosphere above the sample, can lead to issues in the determination of either or not a plasma emitter is native from the sample or not. This is seen more especially when carbon-based samples, as graphite or polymers, are analyzed. Even if the sample is just made of carbon (and hydrogen for polymers), signal from CN molecular emitter is observed. The main explanation of this phenomenon is the recombination between native carbon from the sample and excited nitrogen

from the air [14]. As a consequence, detection of organic compounds by FIBS has to be done with careful understanding of plasma chemistry.

III. EXPERIMENTAL SETUP

The experimental setup of our standoff detection of organic samples at a distance is shown in Figure 2.

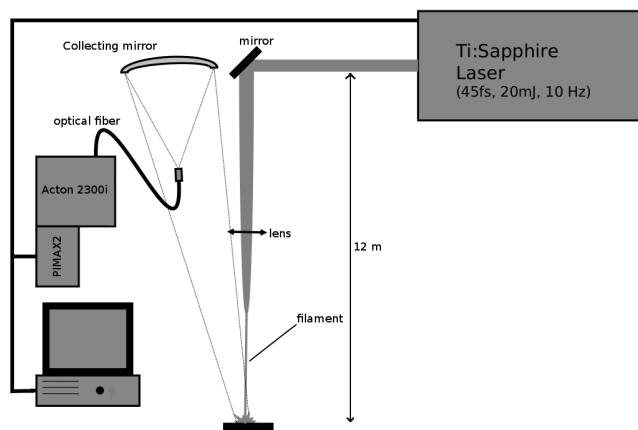


Figure 2. Experimental setup of standoff detection.

A. Laser

Filaments are produced by pulses from a Chirped Pulsed Amplified Ti:Sapphire laser. It delivers 45 fs pulses centered at 800 nm at a 10 Hz repetition rate. The oscillator (Tsunami – Spectra Physics), pumped by a doubled Nd:YVO₄ laser (Millenia – Spectra Physics), delivers sub-35 fs pulses with a spectrum centered at 800 nm. After being shaped by an acousto-optical programmable dispersion filter (Dazzler – Fastlite) to pre-compensate the dispersion inside the amplifying chain, the pulses are stretched and seed a regenerative amplifier pumped by an Nd:YLF laser (Evolution – Spectra Physics). The amplified pulses are then amplified in a double-pass amplifier pumped by an Nd:YAG laser (Quanta-Ray – Spectra Physics) at 10 Hz. Then the pulses are compressed to 45 fs with an energy of 20 mJ centered around 800 nm.

We force the self-focusing process of the self-channeling by a 1 meter focal length lens to better stabilize the spatial position of the filament inside the beam. The plasma is created by the formed filament on the target 2 meters away from the lens, 12 meters from the detection telescope.

B. Detection

The plasma emission is collected by a 316 mm diameter, 1900 mm focal length UV-coated parabolic mirror. This latter was extracted from a Newtonian designed telescope to

decrease the obstruction due to the secondary mirror in the tube assembly.

The signal is then focused on a round-to-line UV-transmissive fiber bundle connected to a 0.3 meter spectrometer (2300i – Acton Princeton Instruments). The spectrum is then recorded on an iCCD 512x512 camera (PIMAX2 – Princeton Instruments) to allow fast triggering of the detection time after the laser pulse.

C. Samples

For this experiment, we used three different samples: a copper plate, a graphite disk and a thin film of polyisobutylene (PIB). This latter was prepared by spin coating a solution of PIB on a silicon wafer to a thickness of 3 μm .

IV. RESULTS AND DISCUSSION

A. Copper sample

The spectra obtained by five consecutive single shot plasma on a single spot (detection delay time = 94 ns, integration time = 1 μs) are displayed in Figure 3. We observed the expected atomic copper lines at 510.6 nm, 515.3 nm, 521.8 nm, 570 nm and 578.2 nm, in addition to atomic sodium at 589 nm. Sodium is known to be common pollutant that is adsorbed onto the surface.

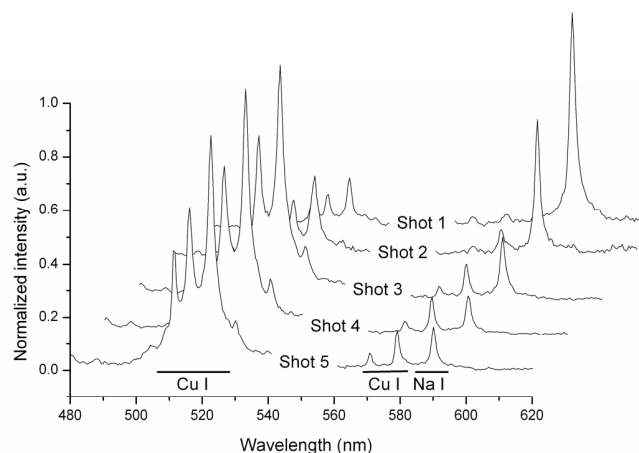


Figure 3. Single-shot spectra of copper obtained by drilling into the sample

By ablating the sample without moving it we drill into it and so we are able to monitor one shot after another the spectrum for each ablated depth. We notice that copper lines remain at a relatively stable intensity throughout the drilling after the first two shots where the sodium signal is prominent; however, after those initial two shots, the surface pollutant emission at 589 nm become less intense in comparison with the copper line at 521.8 nm. This observation proved that filament-induced breakdown spectroscopy is able to give a

spectral signature in a single shot basis of an adsorbed compound at the surface of a metallic sample.

B. Graphite Sample

The aim of this study is to show the possibility of using self-channeled femtosecond pulses to obtain a spectral signature of trace organic materials. Moving towards that goal, we analyzed graphite as a carbon-based sample. Figure 4 shows the molecular spectrum we obtained from graphite: the visible region where the emission of C_2 (Swan System) and CN Violet System) molecules occur.

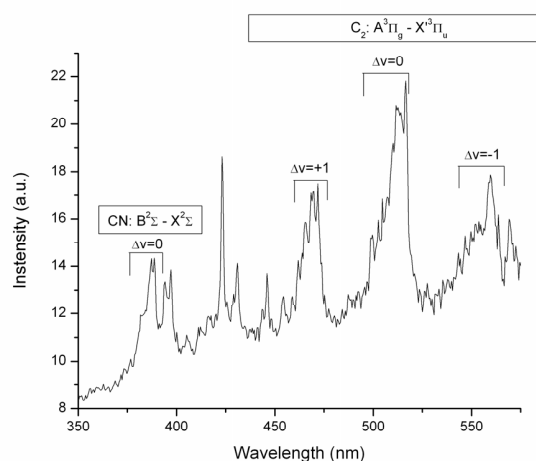


Figure 4. Single-shot spectrum of graphite

We were unable to observe any atomic carbon at 247.9 nm in our spectra; however, we were able to detect molecular signals from CN and C_2 . C_2 is expected from the graphite sample, since this material is composed of carbon only. But CN is certainly formed by recombination between the carbon (atomic and/or molecular) ablated from the sample and the nitrogen in the surrounding atmosphere (air in our experiment) [14]. As a conclusion at this point, this examination shows the molecular signal can be a signature for carbon-based samples in FIBS while being careful on the interpretation of the molecular CN signal.

C. Organic sample

In the final part of this study, we analyze a polymeric film on a non-metallic substrate. Polyisobutylene (PIB) was chosen as it is a common polymer as well as a stimulant of a residual organic material. Furthermore, the spin-coated format allows us to have a uniform sample in order to have reproducible conditions one plasma after another. Its chemical composition ($\text{[CH}_2\text{-C(CH}_3\text{)}_2\text{]}_n$) shows that there is only carbon and hydrogen in its structure, so no CN bonds that can emit as a

signature of the. An excerpt of the spectrum obtained by FIBS after one single-shot on the surface is shown in Figure 5.

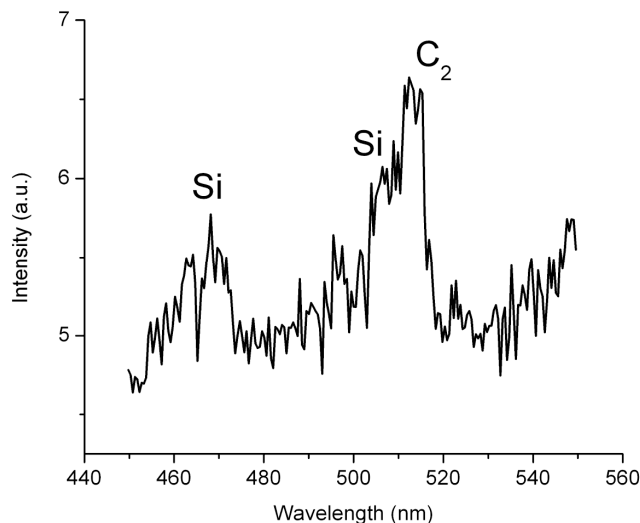


Figure 5. Single-shot spectrum of polyisobutylene centered on C_2 and Si emissions

We observe molecular carbon signal centered at 516.5 nm from the organic film, but we also see the singly-ionized and atomic silicon emission respectively around 462 nm and 505 nm ablated from the substrate. This proves that the pulse passes through the film on the first shot and, as a consequence, creates plasma composed of both constituents of the sample. We didn't observe any atomic carbon as in the analysis of graphite. However, this also shows that Filament-Induced Breakdown Spectroscopy is efficient at detecting the signature of an organic sample on the first shot with the molecular signal.

This situation is very comparable to the case of copper polluted by the adsorption of sodium. So we decided to apply the "drilling method" to monitor the predominant emission along the depth in the sample. Figure 6 shows the single-shot-spectra of the six first shots on a single spot on the sample. It is very clear on these spectra that the emission of the initial shots is dominated by the molecular carbon signal from the organic film but then the signal is dominated by the atomic silicon emission from the substrate. This behavior is an other proof of the capability of FIBS to detect trace organic materials in a single shot basis is possible by monitoring the spectral emission of the plasma along the drilling.

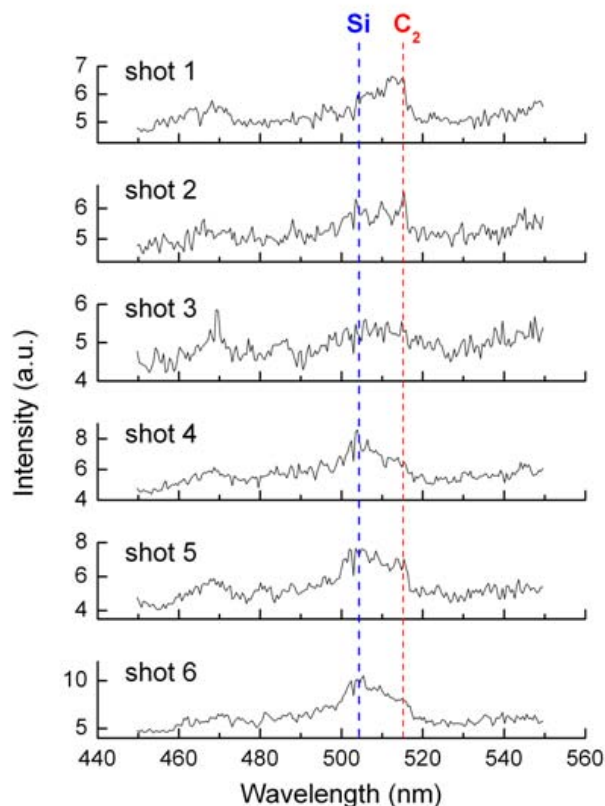


Figure 6. Six first single-shot-spectra of polyisobutylene on silicon wafer along the drilling of the sample on the same location

V. CONCLUSION

In this study, we show the potential of using self-channeling of femtosecond laser pulses to spectrally detect organic compounds on a non-metallic surface in a single-shot basis. Our results show that the use of filaments to create plasma at distance and monitor its spectral emission (Filament-Induced Breakdown Spectroscopy) is efficient for detecting molecular signal representative of the organic film and to detect its evolution shot after shot along the drilling of the sample by the filament. This technique, called Filament-Induced Spectral Depth Profiling (FISDEP), is promising for detecting any trace amounts on a surface.

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