

Remote Sensing via Femtosecond Filament Based Technologies

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Abstract: *The use of laser-induced filaments for remote sensing is of interest due to unique capabilities, including: propagating unchanged over 1-100 m distances, the creation of high intensity (10^{13} W/cm²) and large spectral bandwidth, and the ability to control the position of filamentation in space by changing the spectral phase of the driving pulse. These characteristics are used here for remote detection of materials in two implementations. Filament induced breakdown spectroscopy (FIBS) was used to measure the carbon/clay ratios between three composites at a standoff distance greater than 5 meters. Filament induced stimulated Raman spectroscopy was demonstrated as a method for remote detection of gas-phase species. The impulsive Raman spectra of small molecules in air is reported.*

Keywords: filaments; remote sensing; stimulated Raman; nonlinear optics; remote chemical sensing

Introduction

Laser-induced filaments in the atmosphere represent a new source for remote detection schemes. Created by the high laser intensity available in regeneratively amplified femtosecond laser pulses, filaments produce coherent radiation extending from the terahertz to the ultraviolet. This continuum radiation can be used as a seed for nonlinear spectroscopy. Filaments can be formed at distances from tens to hundreds of meters by controlling the phase and spatial characteristics of the driving pulse. This allows spatially-selective probing of the atmosphere. Filaments self-regulate laser intensity to approximately 10^{13} watts/cm² in air. This allows laser-induced breakdown spectroscopy to be performed remotely, with enhanced

signal to noise. Filaments can propagate at high intensities for long distances (100 m), enabling nonlinear optical detection schemes for remote detection. In this paper we describe the use of two nonlinear optical detection schemes that utilize the unique properties of filaments: (i) filament-induced breakdown spectroscopy (FIBS) and (ii) filament-induced stimulated Raman spectroscopy (FISRS).

The phenomenon of filamentation occurs in any transparent medium when Kerr lensing dominates diffraction effects, causing the driving laser beam to self-focus to high intensity. Several nonlinear effects related to the optical Kerr effect (OKE) are observed in filamentation. In addition to the OKE-driven spatio-temporal focusing, self-steepening and self-phase modulation are present, causing strong spectral broadening and pulse self-compression in the filament [1-3]. Plasma generation also causes strong steepening at the back of the pulse and shortens the pulse duration [1-3]. Pulse durations as short as 8 fs have been predicted [4] and observed in a filament [5]. Ultrashort pulses generated in this fashion give rise to impulsive excitation of vibrations in the medium, provided that the temporal profile of the pulse is shorter than the vibrational period of the molecules under investigation. Under the conditions described above, impulsive excitation of high-energy vibrations (up to ~ 4167 cm⁻¹, corresponding to a vibrational period of 8 fs) is theoretically possible. Excitation of the H₂ fundamental vibrational mode with compressed filaments has recently been demonstrated [6]. Shorter temporal pulse sub-structures can lead to impulsive excitation of even shorter vibrations [7]. After impulsive excitation, the vibrational coherence can be detected using a long (ps to ns) probe pulse, yielding narrow gain features in the pulse spectrum.

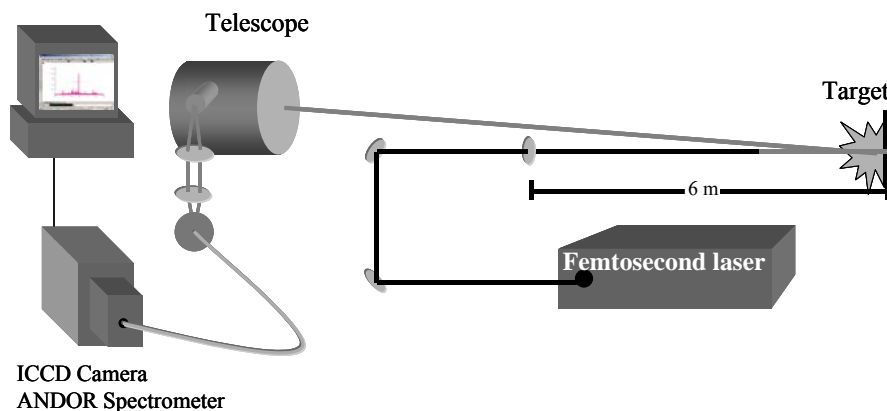


Figure 1. Filament induced breakdown spectroscopy setup.

Filament Induced Breakdown Spectroscopy

Remote filament-induced breakdown spectroscopy (R-FIBS) is an atomic emission spectroscopy technique that utilizes the intense core of a filament (10^{13} W/cm²), formed in a femtosecond laser pulse propagating through the atmosphere to ablate and interrogate the sample[8]. R-FIBS is an attractive analytic tool because it requires no sample preparation, provides virtually instantaneous identification of elemental composition, and is a technology providing facile remote detection capability because no focusing optics are required to induce plasma formation. Since the introduction of remote filament-induced breakdown spectroscopy, (R-FIBS) the method has been used successfully to detect atomic emission lines from copper and steel at a distance of 180 m from the laser system[9] and biological materials at distance of 3 meters[10].

Here, we describe the first investigation of complex composite materials using a high-resolution spectrometer to resolve atomic lines. In R-FIBS, the airborne filament resulting from self-focusing of an intense femtosecond laser beam is used as the excitation source to create a plasma on a target at a defined distance. Conversely, in LIBS, the plasma is generated by focusing the laser beam using a lens (geometric focusing). Filaments achieve intensities reaching 10^{13} W/cm² through self-focusing in air[11], which is well above the intensity threshold for ablation in all materials. This is above the 10^9 W/cm² threshold, which has been cited for stoichiometric ablation of a solid[12], suggesting that filaments should induce an emission signal that is representative of the elemental ratios found in the material.

The experimental setup for R-FIBS is shown in Figure 1. A Ti:sapphire laser system operating at 500 Hz, 800 nm central wavelength, 3 mJ per pulse with 60 femtosecond pulse duration, was used to ablate the samples. The target samples for these experiments were Dixon Ticonderoga pencils, #2, #2.5 and #3. These samples were chosen to investigate the discrimination power of R-FIBS for similar condensed phase solid samples. The laser beam is steered by two mirrors before being lightly focused by the lens, which induces filamentation. The sample was placed 6.1m

behind the 5.8m lens. This allowed for filament formation at 5.4m from the lens, and this filament was used to ablate the target, see Figure 1. A plasma was formed on the sample at this distance and induced emission from the targets. The backscatter from the emission was collected with a 14 inch Meade LX 200R telescope with Ritchey-Chretien optics, at a distance of approximately 10m from the target. The light collected from the telescope was focused into a 50 μ m i.d. fiber optic cable connected to an Andor Mechelle spectrometer with an iStar ICCD camera. Gating was used to eliminate the broad continuum and laser emission at 800nm.

Discrimination between the samples varying in graphite percent was performed by atomic ratio analysis. The spectra from three pencil types were analyzed to determine the line intensity of the C₂ Swan line at 516.5nm and the clay emission from Al I and K I peaks. The peak intensity was calculated by subtracting the baseline from the peak height. The peak intensity of Al I, K I, and C₂ at 516nm were then used to determine the C₂ emission to clay element ratio.

After confirming the graphite concentration is increasing as a function of pencil type (# 3, 2 1/2, 2 have 37.7%, 39% and 41.3% graphite respectively) using optical microscopy, electron microprobe spectroscopy was used to independently measure the atomic constituents of the clay composition. Both the FIBS and electron microprobe data revealed that the clay composition is changing between pencil types. The clay actually contains a mixture of two types of clay, Kaolin and Illite. The difference in the ratio of these two clays was causing the clay composition to change from pencil to pencil. The main difference between Illite and Kaolin, is the silicon to aluminum ratio, as seen in figure 2c, and Illite contains potassium. Therefore, the clay composition had to be measured and normalized before comparison of C₂/Al ratios between pencils was to be made. To normalize the clay, the plasma temperature had to be calculated in order determine the amount of each constituent in the material. A Boltzmann plot of the C₂ vibrational lines was used to determine the plasma temperature. Once the temperature was determined, the amount of Kaolin clay in each pencil was determined using the Al/K ratio and the stoichiometry of the clays. Finally,

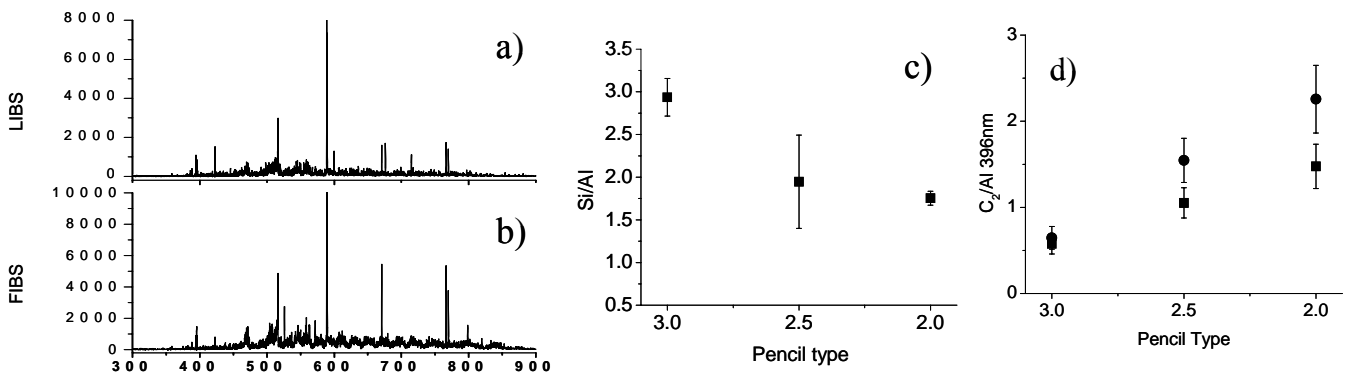


Figure 2. a) LIBS and b) FIBS emission spectra, c) Si/Al microprobe ratio and d) clay corrected ratios of FIBS C₂/Al

the clays for the three pencils were normalized and the C_2/Al ratio was compared. Figure 2a shows emission spectra of a pencil using both LIBS and FIBS techniques. Figure 2d shows the plot of FIBS C_2/Al which has the expected linear positive slope. These measurements reveal that FIBS can be used for standoff detection of atomic constituents.

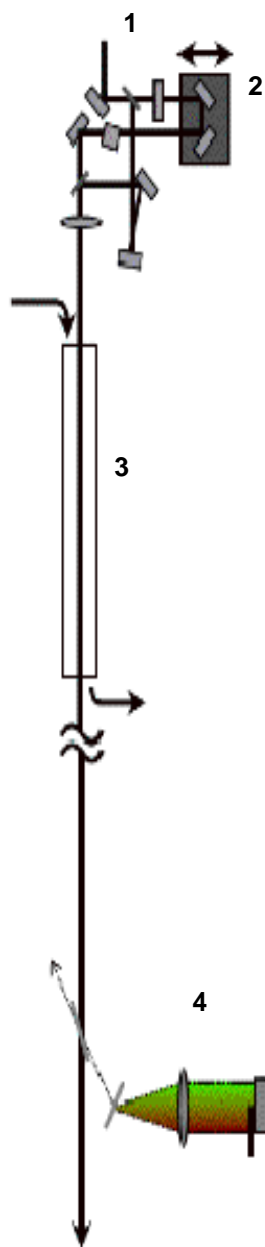


Figure 3. Experimental setup for Raman spectroscopy. The beam is split (1) into two and the weak beam is rotated with a half-wave plate, delayed, and frequency doubled (2). The filament is then generated in an open-ended tube (3), and spectrally filtered (4) before detection.

Filament-Induced Stimulated Raman Scattering

Vibrational spectroscopy offers the particular advantages of discrimination and nondestructive identification of molecular samples. Nonlinear signal enhancement through stimulated Raman scattering (SRS) can result in five orders of magnitude larger signal than for the spontaneous Raman process [13]. Both resonant enhancement and off-resonant fluorescence rejection schemes have also been designed and utilized for femtosecond SRS with good results [14-15]. In our experiments we have focused on vibrational Raman spectroscopy as a technique that can be coupled with filamentation to yield high-gain Raman spectra. At remote distance, SRS using pulsed lasers has the advantage of highly directional gain amplification, thus increasing the possible collection efficiency when compared to the spontaneous Raman process, where signal is distributed in all directions.

Our experimental setup for Raman spectroscopy is

shown in Figure 3. A Ti:sapphire regenerative amplifier (Legend, Coherent) delivers a 1 kHz train of 2.5 mJ, 60 fs pulses centered at 800 nm. The pulse is split 90:10 and the weaker portion is frequency doubled in a long BBO crystal, producing ~ 8 -10 μ J, relatively narrowband ~ 1 ps pulses at 400 nm. The 400 nm pulse is then collinearly recombined with the high-energy 800 nm pulse and focused in ambient air using a 2, 5, or 10 m lens. The 800 nm pulse undergoes filamentation, as revealed by an extended plasma channel (20-50 cm), refocusing, and strong white-light generation. A small portion of the beam is then selected from the combined beams (after the filament) and a grating and lens are used to resolve the spectrum into component frequencies. A hard edge is then used to remove the 400 nm beam from the spectrum and the spectrum is retro-reflected through the lens and grating and sent to a spectrometer (USB2000, Ocean Optics). Small amounts of gases can be injected into the filamentation region through the open-ended tube as depicted in Figure 3. A low vacuum maintains a steady flow of air through the tube to replenish atmospheric air and control turbulence.

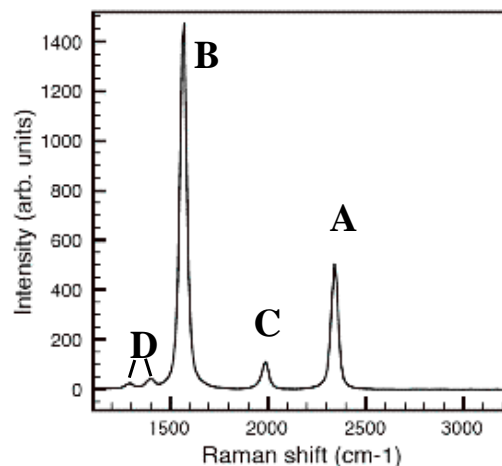


Figure 4. The Raman spectrum of air (A-oxygen, B-nitrogen), acetylene (C), and carbon dioxide (D), the latter two at $\sim 2\%$ and $\sim 0.3\%$ concentrations, respectively.

Preliminary experimental results are very promising. Figure 4 shows the spectrum of air containing acetylene and carbon dioxide obtained using our setup. No background subtraction was done on the spectrum shown in figure 4, which was taken with minimal integration and averaging (30 ms acquisition time). The resolution of the Raman peaks is limited primarily by the pump laser line-width (~ 55 cm^{-1}) and the resolution of the spectrometer. The signal intensity is limited primarily by the pump laser intensity. In a practical remote detection scheme, the use of a powerful narrowband ps laser would overcome these limitations easily. In liquid and solid phase experiments, the damage/boiling threshold of the medium limits the pump intensity, which in turn limits Raman gain. In the

gas-phase experiments presented here, ionization is the limiting factor for pump pulse energy, but the intensity required for ionization in the gas-phase is much higher than the maximum usable energy in condensed-phase experiments. Use of a LIDAR detection configuration with interference filters (to remove unwanted pump light) could be used to detect the Raman signal from surface scattering after the interaction region, or from the scattering after propagation in air after signal generation. An important advantage of using a collinear filament-pump Raman scheme is the increase in signal intensity due to the exponential dependence of Raman gain on the interaction path-length in the medium [16].

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In conclusion, we have presented a filament-based vibrational spectroscopy scheme that demonstrates good signal intensity and will be scalable to remote chemical detection over long distances with appropriate experimental modifications. FISRS also has the potential for simultaneous use with other filament-based remote detection schemes, which would provide complimentary molecular information to a LIBS or FIBS spectrum. This information would help to distinguish chemical isotopes and reduce the occurrence of false positives.