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Femtosecond filament-laser ablation molecular isotopic spectrometry

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ABSTRACT

A new remote sensing technology for real-time isotopic analysis is introduced: Femtosecond Filament-Induced Laser Ablation Molecular Isotopic Spectrometry (F^2-LAMIS). The technique combines femtosecond (fs) laser filamentation and ablation-based molecular isotopic spectroscopy, thereby enabling isotopic analysis of samples at a distance, in ambient air and at ambient pressure conditions. Isotopic analysis of zirconium (Zr) samples by F^2-LAMIS is demonstrated, and the molecular and atomic emission intensity, and properties of the filament-induced plasma generated at different filament propagation distances were investigated. Spectral fitting of F^2-LAMIS spectra enabled semi-quantitative isotopic analysis without the use of calibration standards, which was independent of the filament propagation distance for the studied range. This technology provides new capabilities for direct isotopic ratio measurements at remote distances.

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a powerful direct solid sampling analytical technique for rapid, all-optical elemental analysis of materials. The process involves a high-power pulsed laser beam directed and focused onto a sample surface to instantaneously convert a finite volume of the sample into plasma (laser ablation), and subsequent analysis of the resulting optical emission spectra. One of the advantages of LIBS is its all-optical nature, which enables stand-off elemental analysis. The most common configuration for creating the laser induced plasma at a distance is by focusing high energy nanosecond laser pulses with large open-truss telescope systems [1,2]. One of the challenges with using nanosecond (ns) lasers for stand-off LIBS is the limited operation range, associated with difficulty to tightly focus the laser beam at long distances. Classical optical diffraction causes the laser beam diameter at the focus to linearly increase with focusing distance, and as a result, delivering sufficient laser fluence for ablation at a distance is challenging. Today, conventional ns LIBS stand-off material analysis [1,2] is limited to a little over 100 m [3].

In contrast to nanosecond lasers, it is possible for femtosecond laser beams to propagate over long distances as a result of the non-linear process of laser filamentation [4]. Filamentation of an intense, ultrashort laser pulse arises from dynamic balance between beam Kerr self-focusing and defocusing action of free electrons produced by multi-photon ionization of air molecules [4–7]. Unlike ns lasers, self-sustained fs filaments do not require large telescope systems to focus the laser beam. Filaments have a central core (typical diameter: 10^2 μm) with high intensity (10^{13} W/cm^2 [8]) that is surrounded by an energy reservoir, which can replenish the filament core and support the filamentation process over long distances. The propagation distance before filament formation and the filament length depend on the laser parameters, and can be formed with pre-focused or freely propagating femtosecond laser beams [9]. Remote filament induced breakdown spectroscopy has been previously reported for elemental discrimination of composite graphite samples, [10] biological materials [11,12], metals [13] detection and sensing of explosives [14].

The ability to perform not just elemental analysis but also isotopic analysis at a distance is important for some remote sensing applications, including nuclear non-proliferation and forensics [15,16]. Despite all the research on LIBS, the ability to provide isotopic information is limited to only a few studies (e.g., H, Li and U) [17–19]. The recent development of Laser Ablation Molecular Isotopic Spectrometry (LAMIS) introduced a new way for direct isotopic analysis at atmospheric pressure. LAMIS uses radiative transitions from molecular species either directly vaporized from a sample or formed by associative mechanisms of atoms or ions in a laser ablation plume, [20,21] thereby expanding all the advantages of LIBS to isotopic analysis. LAMIS analysis of several isotope systems (H/D, $^{10/11}$B, $^{12/13}$C, $^{86/87/88}$Sr, $^{90/91/92/94}$Zr) has been reported [18,22–25] using conventional nanosecond and femtosecond laboratory instruments involving short focal length lenses.

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In this work, we introduce a new technology, Femtosecond Filament-Induced Laser Ablation Molecular Isotopic Spectrometry (F^2-LAMIS), which enables real-time isotopic analysis at remote distances. We demonstrate that the stable filaments generated by high-power, ultrashort laser pluses can be used for stand-off isotopic analysis of Zr, which contains five stable isotopes. The filament-induced plasma characteristics and F^2-LAMIS spectra were studied as a function of filament propagation distance. Spectral fitting of F^2-LAMIS spectra was incorporated for semi-quantitative isotopic ratio measurements of Zr as a function of distance.

2. Experimental system

A Ti:Sapphire (800 nm) femtosecond laser system (Mai-Tai oscillator coupled to a TSA-25 amplifier, Spectra Physics) was used for filament generation, delivering 100 fs, 7 mJ pulses at a repetition rate of 10 Hz. Filaments were generated by focusing the femtosecond laser beam with a plano convex lens ($f = 5$ m) (Fig. 1). The laser filaments propagated over several meters up to a distance of 7.8 m which was the limit of the available laboratory space. The filament propagation was clearly visible in reduced light conditions, extending over several meters, well beyond the calculated Rayleigh length of the focused laser beam (0.25 m). A schematic of the experimental system is shown in Fig. 1.

A zirconium (Zr) metal plate (99.2%, Alfa Aesar) was used as a sample. The Zr sample was placed on a motorized yz micrometric stage which was mounted on moveable carrier base along an optical rail, which was aligned parallel to the filament propagation direction. The distance between the lens and the sample (filament propagation distance-x) was controlled by translating the carrier on the rail. An iris with variable diameter was placed 5 cm in front the sample to ensure that the alignment was maintained for all sample positions along the rail. The iris remained open (diameter >1 cm) during the emission and acoustic measurements, ensuring that the energy reservoir surrounding the filament core was not blocked or influenced by the iris [26].

The filament-induced plasma from the Zr sample was imaged onto a collection fiber by using a plano-convex lens ($f = 5$ cm). The fiber was connected to the entrance slit of a Czerny–Turner spectrometer (focal length = 1.25 m, Horiba JY 1250 M) equipped with an intensified charge-coupled device (ICCD) (PI MAX 1024, Princeton Instruments) for spectral acquisition. The grating of the spectrometer had a groove density of 3600 per mm. The instrumental resolution of the spectrometer was determined as 11.8 pm at 435.8 nm, by using a mercury lamp. An acoustic signal sensor connected to an oscilloscope, was used to record acoustic signals in the filament-induced plasma vicinity. Both the spectral emission collection optics and fiber system, and the acoustic sensor were directly mounted on the sample carrier base, to ensure that the collection remained unaffected as a function of filament propagation distance.

The sample was translated along the vertical axis at a constant translation speed of 0.02 mm/s, thereby forming craters on the Zr plate surface. Following ablation, the three dimensional morphology of the ablated craters was measured by using a white light interferometer (Zygo NewView 6 K).

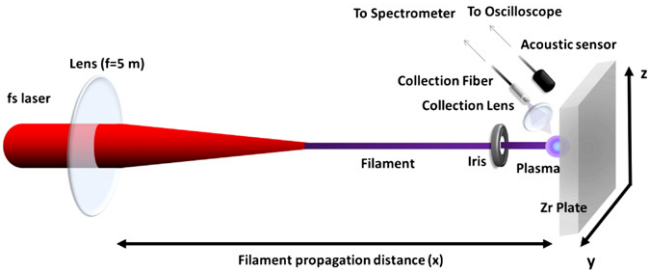

Fig. 1. Schematic diagram of the F^2-LAMIS experimental setup.

3. Results and discussion

3.1. F^2-LAMIS spectra and spectral deconvolution

The spectral range of 461.90 to 463.70 nm was selected for spectroscopic analysis of the filament-induced plasma, covering the α(0,0) band the of $d\,^3\Delta_3 - a\,^3\Delta_3$ system of ZrO and four zirconium atomic lines (Zr I 462.64 nm/462.77 nm/463.40 nm/463.46 nm) [25]. Fig. 2a shows the plasma spectral emission at a filament propagation distance of 6.8 m. In order to reconstruct the molecular and atomic emission from the acquired spectra, a fitting procedure was implemented (Fig. 2b). The observed transitions in diatomic molecules can be calculated by: $\Delta E = E(e', \nu', J') - E(e'', \nu'', J'')$, where $E(e, \nu, J) = E_{elc}(e) + E_{vib}(e, \nu) + E_{rot}(e, \nu, J)$. E_{elc}, E_{vib} and E_{rot} are the electronic, vibrational and rotational energies with corresponding quantum states denoted by e, ν, J, respectively. The intensity was determined by the transition probability and the population of the excited state $E(e', \nu', J')$. A detailed description of the fitting procedure can be found in our previous work [20,25]. For the simulation, molecular parameters

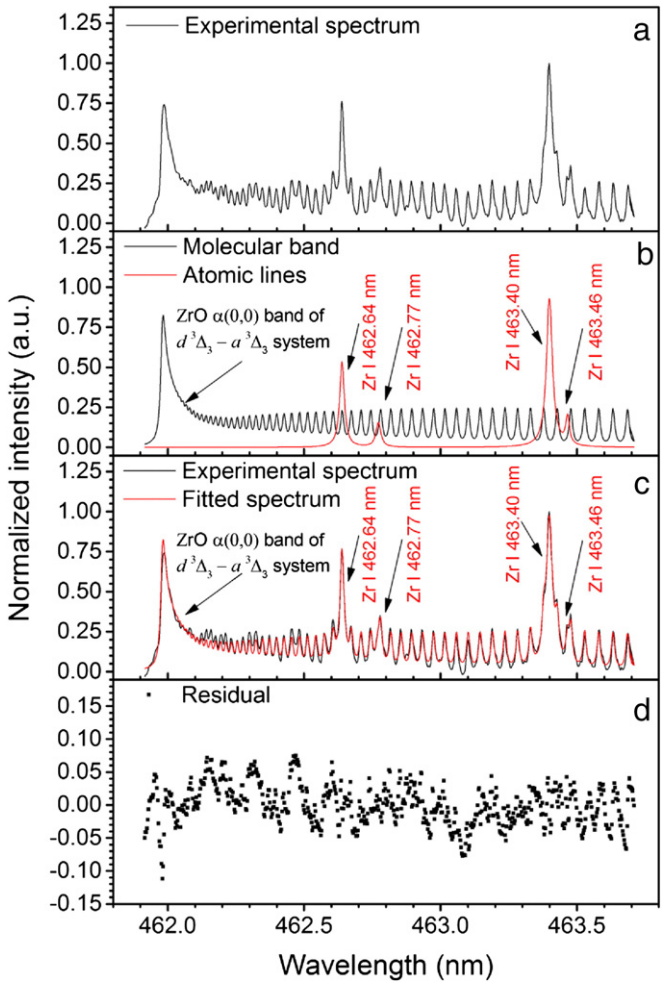

Fig. 2. (a) Typical F^2-LAMIS spectrum acquired from the Zr target at a filament propagation distance of 6.8 m. (b) The molecular band and atomic lines were re-constructed through a fitting procedure. (c) Fitted and experimental spectra. The fitting residual is shown in (d). The ICCD gate delay and gate width were set at 1.5 μs and 10 μs, respectively.