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Significance of ambient conditions in uranium absorption and emission features of laser ablation plasmas

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ABSTRACT

This study employs laser ablation (LA) to investigate mechanisms for U optical signal variation under various environmental conditions during laser absorption spectroscopy (LAS) and optical emission spectroscopy (OES). Potential mechanisms explored for signal quenching related to ambient conditions include plasma chemistry (e.g., uranium oxide formation), ambient gas confinement effects, and other collisional interactions between plasma constituents and the ambient gas. LA-LAS studies show that the persistence of the U ground state population is significantly reduced in the presence of air ambient compared to nitrogen. LA-OES yields congested spectra from which the U I 356.18 nm transition is prominent and serves as the basis for signal tracking. LA-OES signal and persistence vary negligibly between the test gases (air and N_2), unlike the LA-LAS results. The plume hydrodynamic features and plume fundamental properties showed similar results in both air and nitrogen ambient. Investigation of U oxide formation in the laser-produced plasma suggests that low U concentration in a sample hinders consistent detection of UO molecular spectra.

1. Introduction

Laser ablation (LA) has a growing range of applications related to spectrometry, propulsion, micro-machining, thin film deposition, etc. [1–4]. Popular LA spectrometric techniques include LA-inductively coupled plasma-mass spectrometry (LA-ICP-MS) [5–7], LA-laser absorption spectroscopy (LA-LAS) [2,8–10], LA-optical emission spectroscopy (LA-OES, commonly called laser-induced breakdown spectroscopy or LIBS) [1,11], and LA-laser induced fluorescence (LA-LIF) [12]. Such analytical techniques provide elemental and isotopic information about target materials. Arguably the most robust technique is LA-OES when considering its simplicity, practicality, near-instantaneous in-situ remote detection capability [1,13,14], and portability [15]. LA-OES analyzes emission from the laser-produced plasma (LPP). Optical emission spectra act as fingerprints for specific plasma constituents. However, inherent disadvantages exist with LA-OES such as higher limits of detection in comparison to the other spectrometric techniques [16,17] and potentially detrimental matrix effects in multi-constituent targets [18]. Nevertheless, LA-OES is practical for numerous applications including nuclear forensics. LA-LAS measures the inverse phenomenon to LA-OES. A continuous wave (CW) probe laser is transmitted through the LPP, and plasma constituents absorb at a particular wavelength that corresponds to the excitation energy of a transition. Changing the wavelength of the probe laser allows an absorption spectrum to be measured. Compared to LA-OES, LA-LAS provides higher sensitivity and is capable of probing both ground and excited state populations in a laser-plasma system. Furthermore, since LA-LAS can probe ground state transitions, plasma fundamental information may be gathered at very late times (≥100 μs) during the plasma evolution when emission is too weak to detect because of lower plasma temperatures [2].

Nuclear forensic sciences require innovative approaches for the purpose of industrial safeguard certification, nuclear fuel prospecting, nuclear fuel cycle analysis, non-proliferation, treaty verification, etc. Additionally, nuclear forensic techniques must be safe, portable, and practical. LA-OES (or LIBS) meets most of these criteria (rapid analysis, fieldable, no sample preparation), albeit with some challenges with regard to characterization and identification of nuclear materials (e.g., U). The electronic complexity of high-Z elements, or elements with high partition functions, such as U, generates congested spectra in which specific emission features are challenging to discern without high-resolution spectroscopic equipment [2,3,5,15,19,20]. Furthermore, samples may only contain trace amounts of U in a multi-constituent matrix, allowing emission features of more abundant target constituents to

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obfuscate those of U [13,18]. Consequently, further investigation into the practicality of LA-OES for usage in the nuclear forensics field is paramount.

Limited studies exist on the practicality of LA-OES for U identification [3,13,16,19]. Notably, LA-OES proves practical in detecting isotopic shifts of elements including U [21–27]. Reported U detection limits employing LA-OES are on the order of parts per million (ppm) [20,28,29]. However, previous investigations also suggest that the U signal varies significantly with ambient conditions using different LA spectrometric techniques [30]. Moreover, U emission as well as absorption persistence vary significantly with respect to environment, i.e., the nature of the ambient gas and system pressure [2,13].

Typically, all LA-based standoff detection tools are operated in air ambient; however, the presence of oxygen in the air can alter the plasma chemistry and hence the emission/absorption features. This study investigates absorption and emission spectroscopy of U species in a laser-plasma system and explores various mechanisms leading to U signal quenching. The relevant plasma diagnostic techniques include LA-LAS, LA-OES, optical time-of-flight (OTOF) emission spectroscopy, and shadowgraphy. Ablation and plasma formation occurs in a vacuum chamber with varying ambient conditions. Plasma features within two different gases (N_2 and air) at different pressures are investigated. Plasma chemistry (oxide formation), plasma confinement effects, and changes in plasma fundamental properties are investigated as plausible mechanisms for variation in U signal in emission and absorption.

2. Experimental details

A schematic of the experimental setup for LA-LAS, LA-OES, and OTOF is given in Fig. 1, while an example schematic for shadowgraphy can be found in ref. [31]. For LA, 1064 nm pulses from a Q-switched Nd:YAG laser are used. The pulse energy is varied using a half-wave plate and cube polarizer. The laser beam is focused by a plano-convex lens onto a glass sample containing 1.3% depleted UO_2 by weight. The target (3 mm thickness and 25 mm diameter) is mounted on a motorized translation stage which is moved to avoid target cratering effects. Experiments are performed at different background pressures. Two different gases (N_2 and air) are used to study confinement and plasma chemistry.

Methods for U detection in this study include LA-LAS, LA-OES, and OTOF. The LA-LAS measurements use a differential CW-tunable diode laser setup to probe the ^{238}U I 860.795 nm transition. Two spatially overlapped and co-propagating diode lasers with linewidths of approximately 5 MHz pass through the plasma, with the reference laser (DL1 in Fig. 1(a)) being a distributed feedback (DFB) diode laser that remains fixed at a wavelength ~20 GHz detuned from the transition and the probe laser (DL2 in Fig. 1(a)) is an external cavity diode laser (ECDL) that scans its wavelength over the desired atomic transition. A scanning confocal interferometer ensures the probe laser remains single-mode while scanning the wavelength and acquiring spectra. The wavelength of the probe laser is measured using a wavemeter with 10 MHz resolution. The reference and probe beams were polarized orthogonally and combined using a polarizing beam splitter cube and pass through a spatial filter to improve the beam quality. The beams were then focused using a 25 cm lens and pass through the plasma 0.6 mm above the target surface, yielding a focused spot size in the LPP of ~200 μm. After propagation through the plasma, the beams are separated using a polarizing beam splitter cube and detected with two silicon photodiodes with gain of + 50 mV/μA and bandwidth of 3 MHz. This signal is transferred into a 16-bit ADC at a 1 μs sampling rate. The reference beam was used to remove noise from particle ejection and beam steering within the plasma. More information regarding experimental details and data processing can be found in Taylor and Phillips [2].

Emission spectroscopy involves imaging the plasma plume onto the slit of a 0.5 m spectrograph with an intensified CCD (ICCD) camera and a photomultiplier tube (PMT) occupying the two exit slits. The

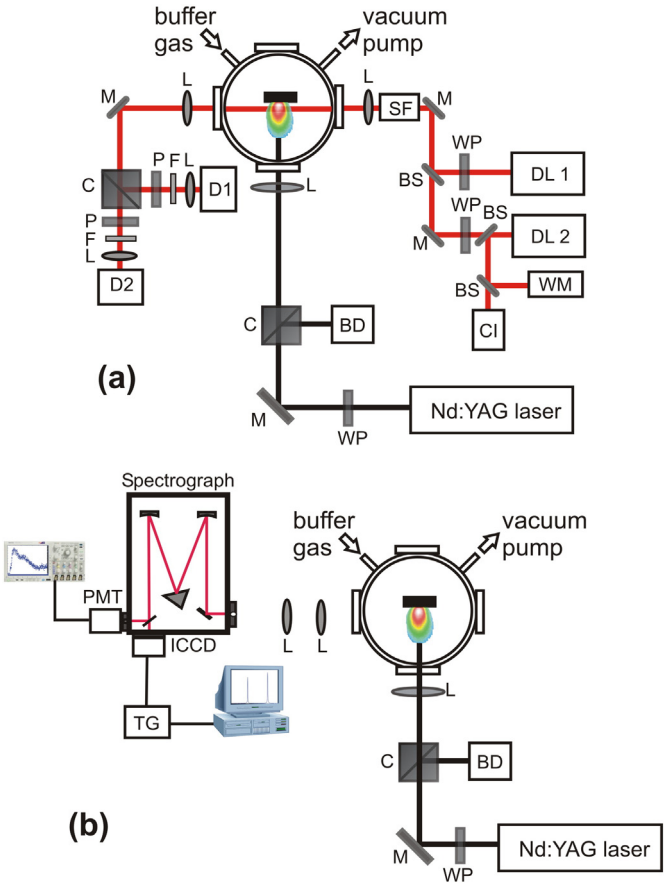

Fig. 1. Experimental schematic for (a) LA-LAS and (b) LA-OES (BD: beam dump, BS: beam splitter, C: polarizing beam splitter cube, CI: confocal interferometer, D: detector, DL: diode laser, F: filter, ICCD: intensified charge-coupled device, L: lens, M: mirror, P: polarizer, PMT: photomultiplier tube, SF: spatial filter, TG: timing generator, WM: wavemeter, WP: wave plate).

spectrograph has a 3-grating capability (300 g/mm, 1200 g/mm, and 2400 g/mm), with a maximum resolution of ~0.03 nm when using the 2400 g/mm grating. The slit width during the experiment is kept constant at 20 μm. Spectroscopic data is collected at a distance 1.5 mm above the target surface. OTOF data is obtained using a monochromator-PMT configuration, and signal features are recorded using a 1 GHz bandwidth oscilloscope. Additionally, emission spectroscopy of a U pure metal target was carried out at Penn State University under similar LA conditions (laser fluence ~ 80 J/cm^2, air at atmospheric pressure).

Focused shadowgraphy tracks shockwave propagation in each of the two gases at ~700 Torr pressure. The experimental parameters were similar to the ones used for emission spectroscopy. In this setup, a relay lens images the plasma plume onto a CMOS detector (1280 × 960 pixels) [32]. 532 nm, 4 ns pulses from an Nd:YAG laser provide backlight. A timing generator synchronizes the arrival of the backlight pulse to that of the ablation laser pulse.

3. Results & analysis

LA for analytical techniques has a vast parametric space. Absorption and emission signals are transient in nature, vary with location in LPP, and vary with ablation parameters (i.e. ablation wavelength, nature of the ambient gas, ambient gas pressure) [13]. LA-LAS, despite requiring a more complex experimental setup, is more sensitive than standard LIBS and is able to measure ground state populations, which is useful in understanding the properties of the plasma at later times. LA-OES, on the other hand, has lower sensitivity and exhibits congested spectra for high-Z elements, but is a more simple and robust experimental