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Mid-IR enhanced laser ablation molecular isotopic spectrometry

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ABSTRACT

A double-pulsed laser-induced breakdown spectroscopy (DP-LIBS) technique utilizing wavelengths in the mid-infrared (MIR) for the second pulse, referred to as double-pulse LAMIS (DP-LAMIS), was examined for its effect on detection limits compared to single-pulse laser ablation molecular isotopic spectrometry (LAMIS). A MIR carbon dioxide (CO_2) laser pulse at 10.6 μm was employed to enhance spectral emissions from nanosecond-laser-induced plasma via mid-IR reheating and in turn, improve the determination of the relative abundance of isotopes in a sample. This technique was demonstrated on a collection of ^{10}BO and ^{11}BO molecular spectra created from enriched boric acid (H_3BO_3) isotopologues in varying concentrations. Effects on the overall ability of both LAMIS and DP-LAMIS to detect the relative abundance of boron isotopes in a starting sample were considered. Least-squares fitting to theoretical models was used to deduce plasma parameters and understand reproducibility of results. Furthermore, some optimization for conditions of the enhanced emission was achieved, along with a comparison of the overall emission intensity, plasma density, and plasma temperature generated by the two techniques.

1. Introduction

Recently, it has been proposed that isotopic information from a sample can be obtained via laser-induced breakdown spectroscopy (LIBS) by what is known as laser-ablation molecular isotopic spectrometry (LAMIS) [1–3]. In the LAMIS method, the rovibronic emission spectra of diatomic molecules produced in the LIBS plasma are shifted by the effect of the different isotopic masses on rovibronic energies [4,5]. Using these shifts, the relative abundance of isotopes in a normally solid sample can be determined [6,7].

While the original LAMIS research involved single-pulse LIBS, multi-pulse LIBS techniques for LAMIS have been suggested to lower limits of detection for a given element [2], and they could possibly offer more reliable determination of the isotopes of interest. The most common multi-pulse technique, which consists of two pulses separated in time, is termed double-pulse LIBS (DP-LIBS), as the second pulse is generally believed to be another breakdown and reheating of the first event [8–15]. Previous studies have shown that DP-LIBS techniques increase the overall emission from a plasma by about an order of magnitude, and thereby leading to better sensitivity for the detection of a given element [10,16–18]. Moreover, multi-pulse techniques have been shown to reduce the pulse-to-pulse variation inherent to single pulse LIBS, which improves the repeatability of LIBS experiments [19,20].

Multi-pulse LIBS can involve a variety of beam orientations and timings with their own designation, such as pre-ablative-spark LIBS [21,22], collinear DP-LIBS [23], and orthogonal DP-LIBS [24–26]. Any one of these techniques can potentially be used to enhance the LAMIS emission with the possibility of improving the ability to detect the relative abundance of isotopes (more specifically, those of lower abundance) by increasing their emission relative to the inherent noise in LIBS spectra. This concept was demonstrated by Mao et al. [2] with orthogonal DP-LIBS using two similar 355 nm lasers for LAMIS. Even so, the conditions that optimize the emission for a given species are not always apparent, principally because the exact experimental parameters, such as laser wavelengths, pulse energies, delay between pulses, offset of breakdown from the target surface, and other settings, are not absolute for these techniques [27–29]. The net result is that LAMIS acquires the same complexity as the LIBS method used to create the plasma, albeit the complexity allows for a great deal of customization that can improve the detection performance under controlled conditions.

One of these customizations is the signal-enhancing DP-LIBS technique denoted Townsend effect plasma spectroscopy (TEPS) [30]. TEPS is a double-pulse technique in which the second laser (the reheating pulse) has much longer wavelength and wider pulse length than the one producing the plasma. The TEPS method does not try to recreate a breakdown on the ablated material from the first LIBS pulse or cause a second LIBS event on the same surface as the first pulse of LIBS. Instead, a non-ablative, defocused or collimated, second laser pulse, in the mid-infrared (IR) region – typically a carbon dioxide (CO_2) transversely excited atmospheric (TEA) laser operating at 10.6 μm – is used to re-excite the plasma [30–32]. Whereas DP-LIBS

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routinely provides enhancements close to an order of magnitude, TEPS can create enhancements close to two orders of magnitude in some cases under long irradiance [33,34]. Though not certain, the larger enhancement is possibly due to plasma reheating in an air-rarefied region, as is common in DP-LIBS using only near-IR wavelengths [32,35–37]. It should be noted that TEPS likely does not rely on the electron scattering of the Townsend effect, as suggested by the acronym; however, the exact nature of the reheating process is not clear though it has been studied in the past [32,38]. Regardless, the long interaction time of the TEA laser that is associated with TEPS (commonly, 50% energy in a 100 to 200 ns peak with another 50% in a 1 to 10 μs tail), as well as the sustainment of the plasma for a longer period than for DP-LIBS with only near-IR wavelengths makes TEPS an alternative and potentially superior technique for creating ionic, atomic, and molecular species from a starting LIBS plasma [34,39]. Consequently, TEPS could provide even greater sensitivity over other DP-LIBS methods, making it useful for understanding its application to LAMIS. Nevertheless, the precise effect of double-pulse techniques such as TEPS on the emission from diatomics as desired for LAMIS is not widely available and is somewhat unclear. As an example, nanosecond-nanosecond (ns-ns) near-IR DP-LIBS of boron nitride shows increased emission from boron monoxide (BO) in a follow up paper to the original LAMIS work [2]. Others have seen similar enhancements for ns-ns DP-LIBS using two IR lasers applied to the detection of explosives and halide molecules [40,41]. On the contrary, a DP-LIBS investigation using femtosecond (fs) LIBS as the ablative pulse followed by a second fs pulse produced increased emission from neutrals and ions but not molecules [42]. These results suggest that the emission from molecules may depend on longer plasma-laser interaction, which would be advantageous for TEPS. In addition, the mid-IR wavelength of the second pulse of TEPS has the potential for more coronal and atmospheric plasma heating possibly leading to subsequent conduction of heat into the plasma [43,44]; though when the plasma density is high, it couples into the plasma less efficiently than the near-IR wavelengths of DP-LIBS more commonly used [44]. This conductive heating would maintain the plasma over an extended period, would further extend the plasma lifetime, and if molecular formation relates to plasma lifetime, would contribute to more molecule formation.

More specific to molecular emission is a recent study of polystyrene and TNT films where a CO_2 TEA laser was used as the second pulse in DP-LIBS after Nd^{3+}:YAG-laser LIBS [39]. The polystyrene films revealed an increase in emission of CN and C_2 under atmospheric conditions. However, the experiment on films of trinitrotoluene (TNT) showed no increase in C_2 emission, but trended to more intense CN features. These results suggest that chemical reactions with atmosphere initiated by the addition of the long IR pulse of DP-LIBS can create enhanced molecular emission [43,44], but enhancement may depend on the initial mechanisms of breakdown [39]. For the two cases here, a given IR power density likely facilitated the evaporation and explosive decomposition or burning of TNT, which has been personally observed by the current authors and others studying this effect [45–47], but polystyrene simply fragmented due to better chemical stability, as evidenced by the melting and boiling points of these two materials. Trinitrotoluene has an 80 °C melting point and a 240 °C explosive boiling point; polystyrene has a melting point greater than 100 °C m.p. but starts to decompose around 200 °C or greater. Though other factors such as reflectivity and thermal absorption are important [45–47], it is possible the limited amount of supplied energy enabled more energy transfer to the bulk TNT than bulk polystyrene, leading to more energized ablation products. It is the products of the initial reactions that likely reacted with the excited atmosphere to give some of the molecules that were observed. However, the conductive heating of the mid-IR laser should maintain the plasma over an extended period, as well as further extend the plasma lifetime. If molecular formation relates to plasma lifetime, the heating should additionally contribute to more molecule formation, including more molecular the oxides that are primarily used by LAMIS. However, a similar experiment on films of trinitrotoluene (TNT) showed no increase in C_2 emission, but trended to more intense CN features. These results suggest that chemical reactions with atmosphere initiated by the addition of the long IR pulse of TEPS can create enhanced molecular emission, but enhancement may depend on the initial mechanisms of breakdown [39]. For the two cases here, a given IR power density likely facilitated the explosive decomposition or burning of TNT, but polystyrene simply fragmented due to better chemical stability. It is the products of these initial reactions that reacted with the excited atmosphere to give some of the molecules that were observed.

The formation of larger amounts of molecules by atmospheric reaction in some cases would seem to make TEPS ideal for improving LAMIS, but this idea is not necessarily true. The increased number density of emitting molecules should improve the signal-to-noise over LIBS and

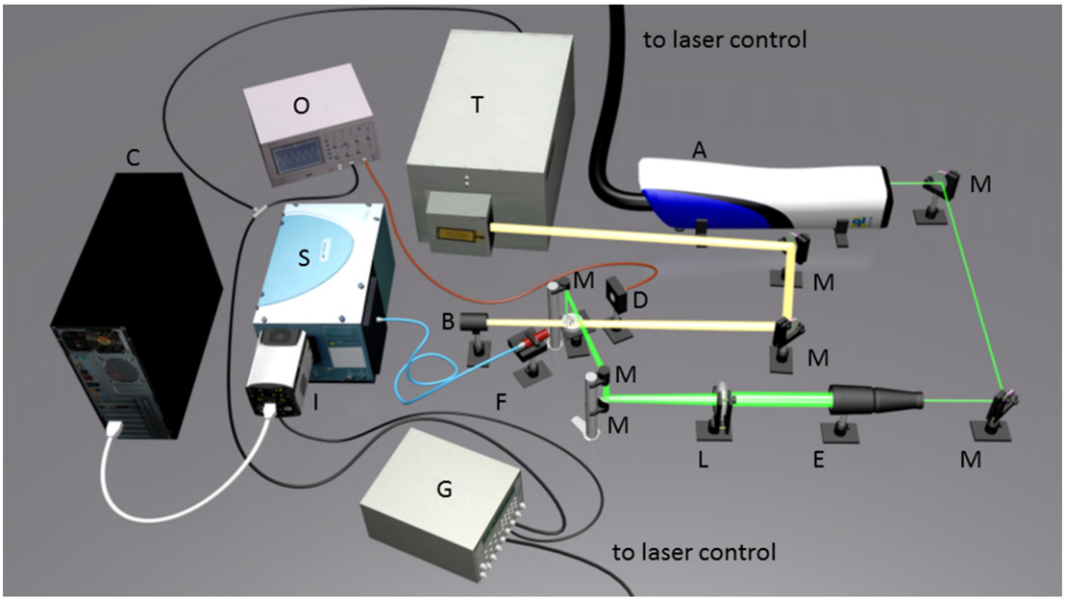

Fig. 1. Experimental setup for the LAMIS and DP-LAMIS analysis used in this work. In the figure, the symbols are as follows: A = laser, B = beam dump, C = computer, D = photodiode, E = beam expander, F = fiber optic collimating lens, G = digital-delay generator, I = iCCD camera, L = lens, M = mirror, O = oscilloscope, S = spectrometer, and T = CO_2 TEA laser. The digital-delay generator also times the laser through a laser-control box, which is not shown. This box is connected to the laser by an umbilical, part of which is detailed in the figure.