LASER-INDUCED BREAKDOWN SPECTROSCOPY WITH
IMPROVED DETECTION SENSITIVITY AND ISOTOPIC
DISCRIMINATION

A Dissertation in
Nuclear Engineering
by
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Abstract

Laser-induced breakdown spectroscopy (LIBS) could be used to perform rapid, real-time, elemental, and isotopic analysis of materials relevant to nuclear forensics, safeguards, and counterproliferation. The detection sensitivity of LIBS is element dependent and the limits of detection (LODs) are higher than competing techniques used in nuclear forensics like secondary ionization mass-spectroscopy or gamma spectroscopy. LIBS non-invasiveness, small sample size requirements, and a need for minimal or no sample preparation, are the main attributes and moderately responsible for the challenges encountered when identifying and quantifying elements with this technique. Secondly, interference of the individual spectral lines in the plasma emission spectrum limit the LIBS detection selectivity and reliability. Finally, the matrix effects also limit the performance of LIBS since the emission intensity from the target element depends on not only the concentration, but also the chemical and physical properties of the matrix.

In this dissertation, optimization of the characteristics of the laser pulse have been pursued and new analysis techniques were introduced to improve LIBS detection sensitivity and isotope selectivity. Optimization of the laser pulse shape through simple and more complex pulse shaping techniques was shown to influence the overall LIBS emission intensity, signal-to-background, and the ionization state of the plasma. Similarly, 2.05 μm femtosecond (fs) laser pulses were observed to produce a plasma of lower temperature and density compared to 800 nm fs laser pulses, resulting in an increased signal-to-background ratio (SBR). *Ab initio* modeling was applied to show that the reduced plasma temperature and density for longer wavelength laser pulses leads to the increased SBR.

As an extension of LIBS, laser ablation molecular isotopic spectrometry (LAMIS) was adapted for use with fs-laser pulses. Expansion of the LAMIS technique to isotopic analysis of uranium using fs-laser pulses and the capability to perform this analysis at remote distances through the combination of fs-filamentation
LAMIS (F2–LAMIS) was demonstrated. The molecular isotope shift for the UO emission band at 593.57 nm was measured to be $\sim 0.05 \pm 0.007$ nm, which is twice as large as the largest known atomic/ionic isotope shift of 0.025 nm for the 424.43 nm U II emission line. Spatio-temporally resolved spectral and shadowgraphic measurements showed that the UO species expanded at a slower rate compared to the uranium atomic species.

The bulk matrix composition of the sample was observed to affect the measured LIBS and LAMIS signal, and resulted in a reduced analytic capability of the technique for both elemental and isotopic measurement. In specific examples, the measured LIBS emission intensity for an analyte of interest was observed to increase with the presence of a second element of greater concentration, which is the inverse of what is expected for many other analytical techniques. The increase in the analyte emission intensity was studied via temporally resolved plasma and emission diagnostics and through the use of \textit{ab initio} modeling.

The results of this work provide new insights that will aid the development of LIBS/LAMIS as a technique capable of not just elemental analysis, but also isotopic analysis at standoff distances in real time, which is important to remote sensing applications in nuclear forensics, safeguards, and counterproliferation.
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List of Abbreviations and Initialisms

CF-LIBS  Calibration Free LIBS, p. 5
CCD  Charge Coupled Device, p. 28
DU  Depleted Uranium, p. 66
F2–LAMIS  Femtosecond Filamentation Laser Ablation Molecular Isotopic Spectrometry, p. 9
FWHM  Full Width at Half Maximum, p. 35
GDD  Group Delay Dispersion, p. 12
HEU  Highly Enriched Uranium, p. 5
ICP-AES  Inductively Couple Plasma Atomic Emission Spectroscopy, p. 11
ICP-MS  Inductively Couple Plasma Mass Spectroscopy, p. 25
IAEA  International Atomic Energy Agency, p. 4
ICCD  Intensified Charge Coupled Device, p. 28
IB  Inverse-Bremsstrahlung, p. 30
IP  Ionization Potential, p. 6
LA-ICP-MS  Laser Ablation Inductively Couple Plasma Mass Spectroscopy, p. 78
LAMIS  Laser Ablation Molecular Isotopic Spectrometry, p. 8
LANL  Los Alamos National Laboratory, p. 83
LIBS  Laser-Induced Breakdown Spectroscopy, p. 3
LIP  Laser-Induced Plasma, p. 3
LOD  Limit of Detection, p. 4
LSD  Laser Supported Detonation, p. 17
LTE  Local Thermodynamic Equilibrium, p. 6
MCP  Mult-Channel Plate, p. 69
NIST National Institute of Standards and Technology, p. 46
SBR  Signal-to-Background Ratio, p. 48
SDK  Software Development Kit, p. 69
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Dedication

To my family for all their love and support through my circuitous educational path and my many professional endeavors.

To my friends at the Department of Energy, International Atomic Energy Agency, Department of Defense, and Other Government Agencies who have repeatedly focussed, enhanced, and supported my research and professional career!
Chapter 1

Background and Significance of Work

1.1 Dissertation Outline

This dissertation consists of 8 chapters. Chapter 1 provides the motivation and the outline. Chapter 2 includes the introduction to the problem, the literature review, and background information. Chapters 3 and 4 introduce the physics involved with LIBS as well as the experimental design and characterization. Chapter 5 is dedicated entirely to the discussion of matrix effects and the elucidation of the origin of the matrix effect observed in binary aerosol samples from a theoretical and experimental perspective. Chapter 6 discusses the effect of laser pulse shape and wavelength on the measured LIBS spectrum. Chapter 7 introduces the LAMIS technique and its expansion here to fs laser pulses, laser filamentation, and to remote detection of uranium isotopics. Chapter 8 offers the conclusions and perspectives of this body of work.

1.2 Significance to Nuclear Forensics and Safeguards

Nuclear forensics is the technical means by which nuclear materials, whether interdicted intact material, parts of a intercepted nuclear device, effluent from a nuclear
proliferation or energy program, or retrieved from post-detonation debris are characterized (as to composition, physical condition, age, and history) [1]. The results of this characterization are interpreted by both scientists and analysts; after this interpretation an attribution decision can be made by government principals and policy makers. This characterization and interpretation is a result of field work to obtain representative samples of device components or nuclear materials (U.S. Nuclear Materials Identification Program), laboratory analysis (Air Force Technical Application Center (AFTAC) and associated labs), and comparison with both computer models and empirical databases. This effort requires a combination of technical data, relevant databases, and specialized skill and equipment.

Nuclear forensics, when combined with law enforcement and intelligence information, can suggest or exclude the origin of materials and nuclear devices. Therefore, nuclear forensics contributes to the attribution of materials or devices to its source [1, 2]. In short, nuclear forensics information is a necessary but not a sufficient criterion for the attribution process [3].

Nuclear forensics can play an important role in a number of counter weapons of mass destruction (C-WMD) scenarios. The first scenario is the interception of nuclear material and can consist of enriched uranium, plutonium, neptunium, device components, and non-radiological nuclear components (Zr lacking Hf contamination). The second scenario involves a radiological dispersal device (RDD), also known as a “dirty bomb” or an intact nuclear device. Additional scenarios exist but are beyond the scope of this introduction.

A number of technologies are involved in the C-WMD and nuclear forensics missions, which range from traditional nuclear detection and mass-spectroscopy to optical spectroscopy and radio frequency analysis. There is a need for analysts, inspectors, and first responders to be able to rapidly analyze samples of interest in the field [2]. The majority of technologies listed above fall into laboratory-based techniques and or require significant sample preparation that is not feasible in a theater environment or for quickly identifying interdicted material. LIBS currently has the capability to perform such an analysis on relevant material with matrix matched and calibration samples; however, a need exists to develop this technique for the analysis of uncharacterized/unknown samples. The IAEA and a number of U.S. Government Agencies have identified laser-induced breakdown spectroscopy
LIBS as a technology that could be used for identifying materials in the field during inspections or other on-the-ground activities for process monitoring and for nuclear forensics [2, 4, 5, 6].

1.3 Background and Motivation

When a powerful pulsed laser beam is focused to a small spot on a sample surface, optical breakdown may occur. The fundamental principle of laser plasma generation is quite simple and has been known since the first laser of sufficient power was focused to a small spot size on a sample [7]. By spectrally resolving and analyzing the optical emission from the laser induced plasma (LIP) that is a combination of characteristic line emission and continuum emission, the element composition of the sample can be deduced. This is the principal behind LIBS, and is also commonly referred to as laser-induced plasma spectroscopy (LIPS) [8].

LIBS has been successfully applied in many areas, such as on-line monitoring of hazardous elements, environmental monitoring, nuclear element detection, detection of aerosols, combustion analysis, depth profile analysis, detection of explosive composites, and analysis of biological samples [9, 10, 11, 12, 13, 14, 15]. There have been a number of commercial LIBS systems developed in the markets: ERCO, Ocean Optics LIBS 2000, and Applied Spectra for example. Recently, researchers have shown an increased interest in this novel technique due to significant attributes, including (1) real-time analysis, (2) no sample preparation, (3) high sensitivity, (4) high specificity for identifying or classifying unknown materials, (5) isotopic sensitivity, and (6) remote sensing applications [16, 14, 17].

LIBS is a real-time qualitative [18, 19] and quantitative [20, 21, 22, 23, 24] analysis technique for the determination of elemental composition, which has recently become a valuable analytical instrument in research laboratories and has been deployed in the field in the most extreme of the definition with the ChemCam instrument on the Mars Science Lab [25, 26, 27, 28]. LIBS measurements are dependent on the spectral acquisition and laser system used, which will be described more in Chapter 2. It is common for time-resolved spectra of atomic and ionic emission from the laser-induced plasma (LIP) to be reported due the possible presence of continuum emission that is dependent on the laser pulse du-
ration used in the measurement, which will be described more in Chapter 2 & 3. The material irradiated by the laser pulse within the focal volume on the sample surface undergoes near-instantaneous ablation and vaporization. The ablated material present in the vapor plume then undergoes rapid dissociation into excited atoms, excited ions, and free electrons [29, 30]. Two key processes related to the LIBS technique occur simultaneously as the plasma expands into the ambient atmosphere and cools: continuum emission and discrete line emission of the atoms and ions [31, 32]. The presence of characteristic atomic and ionic line emissions allows for the identification of the elements within the plasma, and the associated emission line intensities provides information on the relative abundance of the elements within the plasma.

However, as compared with other elemental analysis techniques, LIBS has some disadvantages, such as low detection sensitivity, poor selectivity, and low reliability [12, 33]. The poor selectivity is a result of the emission from the elements in the sample occurring at the same time, often with overlapping and interfering emission lines. The low reliability is a result of the poor selectability that leads to difficulty in identification. Due to the quick expansion and fast motion of the LIP, the lifetime of LIP is very short (typically \( \sim 2-5 \) µs). One reason why the detection sensitivity is low is that the expanding plasma tends to move away from the effective field of view of the detection optics in a short period of time. This is dependent on the system design and will be discussed further in Chapter 4. For example, the limit of detection (LOD) for uranium (U) is \( \approx 150 \) parts-per-million (PPM) [34, 35, 36, 37]. LIBS has poor selectivity and low reliability because of interference effects commonly referred to as “Matrix Effects” [38]. The interference effects are present because LIBS spectra are very complex, and many emission lines from different elements overlap with each other in wavelength. The interference can also occur due to the overlap of emission lines emanating from the same element due to the number of emission lines present or the amount of broadening occurring, as is the case for uranium and its estimated \( \sim 300,000 \) characteristic emission lines between 200 and 900 nm [39].

The non-destructive, expeditious, and in situ capabilities of LIBS have been identified by the International Atomic Energy Agency (IAEA) as promising for the use in detection of nuclear materials and for the use in the attribution process for
interdicted materials [34]. In order for a technique to stand-up to the unique levels of criticism and validation, as is given to technologies used for treaty verification, it is necessary to reduce the false identification rates as much as possible. Due to the interferences in LIBS spectra, sometimes false identifications can be made which makes LIBS currently unreliable in the material characterization community. Matrix effects also limit the detection sensitivity and reliability of LIBS. Due to the matrix effects, the emission intensity from the target element depends on not only the elemental concentration but also the physical and chemical properties of the elements in the sample. The latter effect is one of, if not the most challenging aspect in LIBS quantitative analysis and is characterized by the strong dependence of atomic emission spectra on relatively small variations in sample composition [40]. Matrix effects can be minimized by calibration with proper matrix-matched reference samples that have the same matrix composition or by normalization of the analyte signal by a reference signal (internal standard) [41]. However, in the case of highly variable or a lack of any *ab initio* knowledge of the matrix, which is the ultimate application of technologies for nuclear forensics and safeguards, these approaches would limit the method to semi-quantitative analysis [22, 4].

It should also be emphasized that in many applications it is difficult to find matrix-matched standards or a constant reference component in the system as is true for hard to get or restricted materials of specific interest to nuclear forensics like highly enriched uranium (HEU), plutonium (Pu), or neptunium (Np) [42, 43, 44]. Hence, methods which do not require the use of reference standards (standard-free) are highly desired.

Within the literature, a number of works have been conducted on the development of analytical procedures and theoretical models that can not only predict the observation of matrix effects but can also provide a means to invert the measured spectra and obtain quantitative information.

The Calibration-Free Laser-Induced Breakdown Spectroscopy (CF-LIBS) technique is an analytical procedure for multi-elemental quantitative analysis of LIBS spectra, based on the measurement of line intensities and plasma properties (plasma electron density and temperature) and on the assumption of a Maxwell-Boltzmann population of excited levels and an optically thin plasma (lacking self absorption and reversal of emission lines), which does not require the use of calibration curves
or matrix-matched standards. In close relation to the goal of quantitative analysis, several publications on theoretical modeling of laser-induced plasma expansion have an inherent yet untapped analytical significance [32]. Some models are capable of predicting the detailed spectral distribution of plasma radiation such as the model developed by Colgan et al. [32], which can produce simulated LIBS spectra for any element under a range of plasma conditions.

The model developed by Colgan et al. was able to predict the plasma spectrum not only in a wide spectral region but also in a narrow energy window under both local thermodynamic equilibrium (LTE) and non-LTE conditions with ab initio atomic structure and ionization cross section calculation. The ability to conduct modeling over a small spectral bandwidth has great significance in plasma spectroscopy measurements since observations are usually done in narrow spectral regions where the details of line profiles are more evident. Further work by the same group is being conducted to incorporate radiation transport effects and the capability to include multiple plasma regions within the model for both single elements and complex mixtures.

While these techniques have been shown to be successful in both the prediction of matrix effects, these techniques tend to be incomplete in their understanding of the fundamental quantum mechanics and plasma physics involved in the plasma that lead to such interferences. The use of CF-LIBS results in ad hoc factors to optimize the fitting parameters that are fundamental to CF-LIBS algorithm, which tend to be the temperature and density of the plasma. As alluded to earlier, and will be discussed further later in the dissertation, there are a number of processes and physical properties of the elements in the sample that lead to interferences in the observed LIBS spectra. The ionization potential (IP) and vaporization temperature of specific elements have been shown to cause a matrix effect in Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) [45] These processes have yet to be fully resolved or understood and are not included in current quantitative LIBS models or analysis.

Relevant to the nuclear forensics, safeguards, and counterproliferation missions is the ability to perform not just accurate quantitative analyses that phenomena like matrix effects hinder but to also determine the isotopic composition of an element or mixture of elements at standoff distances. The use of LIBS for isotopic
analysis was first conducted by Pietsch et al. in 1998 [46]. Smith et al. in reporting the detection of the isotope shift in Pu in 2002 [42] state that the observation of isotope shifts via optical emission spectroscopy is not a common application for LIBS.

The reasons for the LIBS technique not being a common tool for isotope identification are manifold. First, the atomic isotope shift for many lines is extremely small (on the order of $\sim$10’s pm or smaller). Second, the analysis commonly must be performed under rarefied atmospheric conditions to avoid broadening of spectral lines. Third, as was reported by Chan et al. in 2013 [35], elements for which isotopic information is of interest have $\sim$100,000’s emission lines, many of which interfere with each other. Last, in order to resolve the small isotope shifts, even when the other issues listed above have been addressed, large, cumbersome lab-based spectrometers are necessary, which removes a considerable amount of the utility of the LIBS technique. This is not a complete list of the many considerations which must be made when performing isotopic analysis if elements with LIBS as other issues like matrix effects can act to suppress emissions, and other phenomena not listed here may also impact the analysis under certain conditions.

Recently, work has been conducted on extending the application of LIBS to isotopic analysis by Ko et al. [47] and Chinni et al. [44]. In the first work, a novel hybrid interferometric-dispersive spectrometer was designed, built, and demonstrated to increase the resolution of a moderate-resolution (0.55 m spectrometer with a 1800 g/mm grating) Czerny-Turner spectrometer through the addition of a simple Fabry-Perot etalon to the system. The authors were able to resolve both the small (29 pm) separation in the 313 nm Hg doublet line as well as the smaller (25 pm) isotope shift in U I emission line at 424.43 nm under ambient atmospheric conditions [48]. In the second work, chemometric techniques were adapted for use in fitting two spectral lines to the two U lines present in the LIBS emission spectrum due to the isotope shift in a 50% enriched HEU sample under ambient atmospheric conditions. The success of these recent developments for LIBS isotope analysis in an ambient environment is important for the use of LIBS as a nuclear forensics tool. However, both of these methods depend on have close (3–5 cm) access to the sample and require $\sim$1000 laser shots on the sample.

From the previous work, it is evident that the LIBS technique would have to
be rethought if it was to be used in the field, as a remote sensing tool, or on small/micro-scale samples. Following ablation by a laser pulse a complex rapidly expanding plasma is produced that contains both atomic species (excited neutrals and ions) and excited diatomic molecular radicals. It was shown by Russo et al. [49] that the molecular spectra emitted by these excited diatomic molecules contain isotopic information which could be extracted through the use of known standards or semi-empirical modeling. The author defined this new technique as Laser Ablation Molecular Isotopic Spectrometry (LAMIS) [49, 50, 51]. These molecular isotope shifts are 4–100 times the atomic isotope shift for the element of interest allowing for the use of lower resolution spectrometers, and (due to the method in which these radicals are formed) this analysis can be conducted under ambient atmospheric conditions.

Of critical importance to national security is the ability to detect from remote distances the isotopic makeup of suspect or interdicted samples [2, 1]. The techniques and methods outlined above have to the best of our knowledge not addressed this need for isotopic analysis using LIBS or LAMIS at remote distances.

Extending LIBS to standoff distances greater than $\sim 10$ m poses practical challenges. The challenges stem from the implicit requirement imposed on LIBS, which is the delivery of laser pulses at high enough intensity, and thus focused to small enough size, such that the laser pulses are capable of creating a micro-plasma on the sample surface. Due to classical diffraction, prohibitively large diameter optics are required to deliver the laser pulse to a small enough focal spot at large standoff. Delivered focal spot intensity at a distance is further diminished by absorption and wavefront distortion in atmospheric propagation along with optical aberrations.

In contrast to nanosecond lasers, femtosecond lasers can circumvent this limitation by taking advantage of the complex but favorable nonlinear dynamics of femtosecond laser propagation in air. An initially collimated femtosecond laser pulse self-focuses in air. As the beam self-focuses, it can ionize air molecules, which in turn defocuses the beam through plasma induced diffraction. A favorable balance between the self-focusing and plasma defocusing creates intense light filaments with typical intensities of order $10^{13}$ W/cm$^2$, capable of propagating over long distances ($\sim 1$–4 km have been demonstrated) with beam diameters in the range 100–200 $\mu$m [52, 53, 54]. These unique features of the propagation
of high-power femtosecond pulses make them attractive for remote surface ablation and analysis, commonly known as filament-induced breakdown spectroscopy (FIBS) [55, 56]. Such laser pulses can be produced by laser systems sufficiently small to be mounted on vehicles, with a continued trend of miniaturization, reliability improvements, and reduction of cost. Materials in different states have been analyzed for their composition using the R-FIBS technique. These include the remote detection of NaCl in aqueous solution using R-FIBS at a distance of 16 m [57] and probing of solid metals such as copper at a distance of 90 m, which was limited only by the space available for the experiment [58].

The combination of FIBS and LAMIS for isotopic analysis of samples was recently shown in work by Hou et al. [55], and is known as Fs-Filamentation Laser Ablation Molecular Isotopic Spectrometry (F2-LAMIS). However, this work ignored the inherent remote detection capability of FIBS and placed the collection optics a few cm from the sample surface when a filament of $\sim$3 m was used in the study. Further, this work was limited to Sr where the molecular emission constants and spectra is well understood [59]. It is evident that a need exists to extend the F2-LAMIS technique to remote detection conditions and to nuclear forensics relevant materials like uranium.

To address these issues, the motivation of this dissertation is to improve the LIBS detection sensitivity, selectivity, and reliability at standoff distances. Specifically, this dissertation aims to address three areas related to the analysis of nuclear forensics relevant materials and their isotopics through the LIBS technique. First, LIBS signal enhancement to include the improvement of the LIBS signal-to-background ratio and the ionization state of the plasma. Second, the demonstration, combination, and expansion of R-FIBS and LAMIS to the analysis of uranium and its isotopics at standoff distances. Third, the origin of the matrix effect in binary elemental aerosol mixtures and the complication this poses to LIBS as an analytical technique. In order to study the improvement of the LIBS signal both radiological and non-radiological samples were studied. To elucidate the processes involved within the plasma that lead to the observation of matrix effects, simple non-radiological binary aerosol solutions were studied that have been previously reported to exhibit a matrix effect [60].
Overview of Laser-Induced Breakdown Spectroscopy

2.1 Introduction to Emission Spectroscopy

Optical emission spectroscopy (OES) is a spectroscopic technique which examines the wavelength of light emissions from atoms, ions, or molecules during their transition from an excited energy state to a lower energy state. Because each element or molecule has a unique electronic or molecular structure, the resulting emission spectrum is also unique to that element or molecule. Thus, examination of the spectrally resolved light emission can provide the chemical or molecular composition of the ablated sample.

The beginnings of OES can be traced back to 1860’s with Bunsen and Kirchhoff performed experiments in which the atomization and excitation source were provided by a flame. In flame emission spectroscopy, an analyte is introduced into the flame as a gas or aerosol solution. The heat from the flame vaporizes and atomizes the sample to produce free neutral and ionic atomic species. The thermal energy also excites the atomic and ionic species into excited states. Subsequently, light is emitted when the excited species undergoes radiative relaxation to lower electron energy states. By detecting and spectrally resolving the emitted light and generating calibration curves that relate the measured intensity to the analyte concentration (through known matrix matched samples), the elemental composition
can be determined and the quantitative analysis can be performed.

Following the development of flame emission spectroscopy, methods of excitation were developed using an electrical arc to interrogate the sample. The use of an electric arc allowed for a more controllable generation of sample breakdown and plasma formation. Inductively coupled plasma - atomic emission spectroscopy (ICP-AES) uses an inductively coupled plasma to produce excited atoms and ions. These OES methods typically require significant laboratory support facilities and sample preparations similar to mass spectroscopy techniques, and they have been used in limited and specific applications.

In the LIBS technique, a luminous plasma is formed when a high powered pulsed laser is focused onto small spot on the sample surface. The resulting laser irradiance on the sample surface or focal volume exceeds several megawatts per centimeter squared \((10^6 - 10^9 \text{ W cm}^{-2})\). LIBS is convenient and, at its basics, one of the simplest analytical methods for in-field analysis of samples at trace levels, because the LIP is an all inclusive source for the vaporization, dissociation, atomization, excitation, and ionization of the sample \([61, 62]\).

In this chapter, a summary of the development of LIBS is discussed, and a general overview of the basic principles and characteristics of LIBS is provided. In addition, a review of recent LIBS research and development for both fundamental research and analytic results of solids, liquids, and gases is presented below.

### 2.2 Introduction to LIBS

The research and development of LIBS technique has been summarized and discussed in great detail recently in many review articles \([12, 63, 64, 18, 12, 65]\) which cover different aspects of the LIBS technique. In light of these articles, only the most significant events in LIBS development are included in this document.

The first laser was developed in 1960 \([66]\); however, the first LIBS measurement had to wait until the development of a Q-switched ruby laser in 1963 \([67]\) when first LIP in gas was reported \([68]\). Since LIPs inherently exhibit a temporal evolution, the first temporally resolved LIBS was performed in 1964 using a simple fast photodiode detector. As the LIBS components (lasers, spectrographs, detectors) developed significantly, LIBS has been developed and used in a wide
range of applications. In 1992, the first portable LIBS system was developed [69]. In 1995, LIBS using fiber optics for delivery of laser pulses was demonstrated by Cremers et al [61]. Nowadays, there has been renewed interest in LIBS due to the emerging need to perform measurements under conditions not feasible with conventional analytical techniques such as measurements that require little to no sample preparation, in-field measurements, or near real-time information.

The first work on matrix effects in LIBS began in the late 1970s, and showed that physical properties of the elements, chemical composition, and surface of the sample play significant roles in the LIBS measurements [70, 71]. Moving into the 20th century, remote elemental analysis and portable instruments were demonstrated [61]. Shortly thereafter, analytic techniques were developed to account for the matrix effects in LIBS and obtain absolute concentrations of sample constituents from LIBS measurements. One such analytic technique for absolute concentration analysis is the CF-LIBS technique that was patented by the Palleschi research group in 1999. [72, 73].

Remote sensing applications commonly require standoff distances of \( \sim 1-5 \text{ km} \), and, although LIBS development had made great progress up to the early 1990’s, it appeared that the LIBS technique would not be suitable for remote measurements due to the limitation on focusing ns laser pulses at long distances [18, 58, 65]. In 1994, Mourou and his group at the University of Michigan were able to demonstrate the self-channeling of ultrashort laser pulses through 20 m of ambient air. The self-channeling of the ultrashort laser pulse was achieved through the favorable competition between the self-focusing of the originally uncollimated laser beam (due to the non-linear index of refraction of air) and the defocusing of the laser beam (due to the plasma induced index of refraction from the partial ionization of air within the channel). The authors observed an 80 \( \mu \text{m} \) diameter laser channel with 0.75 mJ of energy, which results in a laser pulse intensity of \( 7 \times 10^{13} \text{ W/cm}^2 \). The self-channeling of the ultrashort laser pulse is referred to as laser filamentation, and is readily extended to standoff distances greater than 100’s m.

To the best of the author’s knowledge, the only true remote LIBS measurements using laser filamentation have been performed by Rohwetter et al. [58, 65]. The authors were able to control the position at which filamentation occurred through the addition of positive group delay dispersion (GDD) to the originally transform
limited fs laser pulse.

Pietsch et al. [46] in 1998 performed what is believed to be the first uranium isotope sensitive LIBS measurement. The 25 pm shift in the 424.43 nm U II ionic emission line combined with the small amount of broadening present under the rarefied atmospheric conditions (0.02 Torr) allowed the authors to observe the uranium isotope shift. Smith et al. [42] in 2002 measured the isotope shift of plutonium (13 pm) under a 100 Torr He atmosphere. For both isotope selective LIBS measurements the sample was not maintained under ambient atmospheric conditions and required both high laser pulse energy (∼100’s mJ) and 1000’s of laser shots to be averaged.

Russo et al. [49] 2011 proposed a new method for isotope selective LIBS measurements through the analysis of the molecular isotope shift, which originates from diatomic molecules formed within the expanding plasma. The authors named this new technique Laser Ablation Molecular Isotopic Spectrometry (LAMIS). Since this initial work the authors have applied the technique to additional elements and have adapted the technique for use with fs laser filamentation [55, 50]. Additionally, work by Brown et al. [33] has shown that the matrix effects are present within the LAMIS measurement and result in an error in the calculated isotopic composition of the sample.

The LIBS technique has also been addressed in reviews of related laser applications like processing (micro-machining) and process monitoring for example. Many spectroscopic, interferometric, and shadowgraphic studies of laser plasmas have also appeared in physics journals. In this document, LIBS in analytical chemistry, plasma dynamics, and emission physics are included as they relate to matrix effects, the increase in the LIBS emission intensity, and to the measurement of nuclear materials by LIBS. The use of laser filamentation for the remote measurement of materials by the Rohwetter group ushered in a new epoch in LIBS development.

2.3 Review of LIBS Literature

Articles that relate to laser material processing and manufacturing have been, for the most part, omitted under the assumption that the laser, plasma, and material regimes are not typical of LIBS and beyond the scope of this work.
LIBS analysis of solid samples have been studied to a much greater extent than LIBS of liquids and gases. The section on LIBS of gases contains the first LIBS work that appeared in the literature. LIBS of liquid samples includes both bulk liquids and aerosols generated from liquid solutions that are nebulized to form an aerosol spray. By far, LIBS of liquids and aerosols has the smallest number of publications in the literature, and is primarily of interest to the medical and the geophysics community. The section on LIBS of solids also includes application of the LIBS technique to remote sensing and isotope sensitive measurements.

2.3.1 Solids

Many of the published works in LIBS arise from the need to more fully understand the LIBS plasma in order to obtain useful quantitative results. For example, one work is the 2009 publication by Hrdicka et al. [74], where the authors used the acoustic signal generated by a LIP and the correlation to the emission to correct for the fluctuation in the continuum background on wall tiles. The first study to notice such a correlation occurred in 1988 and was reported by Chen and Yeung who proposed to use the acoustic signal as an internal standard [75]. The authors observed that the measured acoustic signal was proportional to the emission lines in the plasma. Additionally, the authors found that the ratio of the measured acoustic signal to the emission line intensity was independent of the laser power, wavelength, and spot size.

Guo et al. [76] studied LIBS plasmas formed following ns laser ablation under magnetic and spatial confinement. The authors found that there was an enhancement of the emission due to the confinement of the plasma when the magnetic field was oriented normal to the direction of the laser propagation. Further, the authors found that both the presence of the magnetic confinement cavity and the magnetic field increased the emission intensity of each element in the sample. In the second part of the study, a temporal study was performed on the plasma emission for each case. It was reported that the emission intensity was at first similar for all three cases; however, after ~6 µs, the intensity increased drastically when a magnetic field was applied. The increase in the emission intensity is most likely due to Joule heating within the plasma evident by the fact that the increase was seen later in
time than the maximum applied electric field. It was noted that this increase was not observed for LIBS of silicon samples, which further justifies the conclusion of the presence of Joule heating within the plasma.

Lida et al. [77] in 1990 studied the effects that the ambient atmospheric pressure has on the laser vaporization and excitation process. Using a ruby laser (1.5 mJ, 20 ns), a plasma about 10 mm in height and more than 100 µs in duration was formed on Al samples. The plasma formed under an ambient Ar pressure of 50 Torr had a significantly increased line emission and background due to confinement by the ambient Ar compared to ablation in ambient air. The increase in plasma confinement and enhancement of the LIBS signal is expected due to the increased mass of the Ar atmosphere (40 amu) compared to air (∼30 amu). The plasma at a more rarefied Ar ambient pressure showed lower continuum and line emission that can be explained by the lack of shockwave production that produces additional ionization across the shockwave and acts to confine the plasma to a small volume against the sample surface at early stages in the plasma evolution.

The effects of buffer and ambient gases on the plasma produced by a Nd:YAG laser (1064 nm, 10 GW/cm², 5 ns) on a metal target was further studied by Ma et al. [78]. They observed that the ambient gas mixed into the core of the plasma, and acted to efficiently and softly (without producing a backwards propagating shockwave that is seen in physical or magnetic confinement [76, 79]) confined the plasma that resulted in a plasma core with uniform properties. The existence of such a plasma core with uniform distribution of plasma properties is attractive for applications like LIBS with the possibility to integrate the emission over a larger plasma region, thus, limiting the convolution of emissions from differing regimes within the plasma and increasing the amount of light collected.

Bogarerts et al. [31] developed a comprehensive model to describe the laser ablation of copper metal samples under different ambient gas environments like He, Ne, Ar, Kr, and N₂. The authors found that the background gas composition affected the target heating, melting, vaporization, and the plume dynamics. It was observed that under ambient gases of higher mass the confinement of the plume was increased that resulted in a slower expansion. Further, the ionization potential of the ambient gas was found to not significantly affect the plume dynamics.

Similarly, Dong et al. [80] studied the time-resolved analysis of laser-induced
coal plasmas in different gas environments (air, argon, and helium) and reported that by conducting LIBS measurements in an argon gas at atmospheric pressure, both the atomic and ionic emission of the plasma was increased for each constituent element compared to air. They further studied the effect of different ambient gases at atmospheric pressures and found that a He atmosphere resulted in the lowest observed emission intensity. It was postulated that the pre-ionization of the Ar atmosphere acted to increase the initial plasma density and, thus, the resulting overall measured emission. It is important to note at this point that the observed increase in emission trends with the first ionization potential for the primary element in the mixture, which will be discussed further in Chapter 6 as a type of matrix effect. They further noted that the molecular CN rotational emission band intensity was increased in air vs a He or Ar atmosphere due to the content of N in air; however, the band was still visible due to the N contained within the coal. However, in work by Bogarerts et al., described above, the authors predicted that the ambient gas composition would not affect the plasma temperature and density and, thus, the emission intensity, from their model. This result is of interest to the development of LIBS as an analytical technique, for it shows that plasma-assisted chemical reactions are possible, which further complicates the plasma evolution and emission but at the same time can contribute further information about the sample. Further, the discrepancy between modeling efforts and experimental results suggests a need to develop more robust models that take into account the possible pre-ablation of the ambient atmosphere above the sample as well as other complex plasma dynamics involved in the early plasma formation and vapor plume expansion.

Two research groups in 2011 reported on the lack of pre-ablation in the ambient gas surrounding a solid sample from femtosecond laser pulses, compared to longer ps or ns laser pulses [36, 81]. The lack of observed emission from the ambient gas under ultrashort laser ablation conditions contributes to the lower observed emission intensity and affects the early LIBS plasma dynamics. The lack of pre-ablation results in a lower observed plasma temperature and density. For molecular spectra, the lack of pre-ablation can result in a reduction in the intensity of the rotational spectra due to a reduced amount of ions being available to recombine and form excited diatomic radicals that are of interest to LIBS due to the recent
Ma et al. obtained full spectra at a number of axial distances away from the sample surface following laser ablation, as depicted in Fig. 2.1 [78]. They used this technique to create classification maps, which gave location of any species of interest within the plasma. Further, Bai et al. used narrowband filters centered on the emission from the ambient Ar atmosphere and Al sample to create temporally resolved images of the location of both neutral and ionized Ar and neutral Al within the plasma. The axial profiles show a zone of uniform plasma delimited in its expansion by the argon background gas. The authors observed a shell of ionized argon gas in the front of the plasma, which may also lead to the storage of laser energy in plasma through the Laser Supported Detonation (LSD) induced by the tail of the laser pulse. Their work provided a detailed description of the soft confinement of the plasma by the ambient argon atmosphere, which is argued to be the origin of the increased signal obtained in LIBS measurements performed in an argon gas. However, it still remains an open issue to understand how the interplay between the vapor plume and the argon gas leads to the observed effects.

Cristoforetti et al. studied the mass removal rates and thermodynamic equilibrium states of various metal samples from a theoretical and experimental perspective and determined relationships between laser energy and atomic/ionic yields [83]. Particular emphasis was given to the occurrence of LTE in LIBS plasmas, which
appears to be a key issue for the beneficial utilization of the technique. This issue is particularly crucial for methodologies, aimed at determining quantitatively the composition of the target, that rely on the so-called calibration-free or monte-carlo LIBS approach. The primary cause of deviation from LTE in LIBS plasmas namely radiative, transient and diffusive processes were discussed, both from a theoretical point of view and by referring to experimental results present in the literature. The theoretical investigation, based on the simplified approach of the LTE criteria and not on the utilization of complete kinetic codes, accounted only for the dominant processes in the plasma and was, therefore, subjected to some uncertainties. The results and suggestions are similar to that of Zhang et al. who reviewed the fundamental theories and calculation methods of LIP temperature, as well as its dependence on various experimental conditions, including laser parameters, ambient surroundings, sample characteristics, and sampling geometry, and temporal and spatial evolution. Most of the studies reviewed showed that plasma temperature increases with increasing laser wavelength, pulse width, and laser energy when fixing other parameters. Cristoforetti et al. further described a number of parameters that must be analyzed and considered to accurately claim the existence of LTE within a LIP; however, they show through an extensive review and theoretical analysis that a collisionally dominated LTE is commonly established within a LIP following the initial bremsstrahlung background [84].

In 2004, Capitelli et al. studied the emission of a LIBS plasma on graphite and other samples [85] and reviewed the theoretical and experimental efforts to describe the expansion of LIP plume. They used a Nd:YAG ns laser operating at 1064 nm and observed a multiple component plume as the plasma expanded in the normal direction to the sample surface. The authors claimed that these multiple regions or components existed due to the differing speeds of the expanding atoms and ions within the plasma. The fastest region was composed of ions from each element within the sample when the experiment was performed in air. The second region was composed of the compressed neutrals in the vicinity of the shockwave that was a mixture of ions and neutrals. The third region, and the slowest, was the target vapor composed of larger molecules and excited neutrals. The observations can be explained as arising from the acceleration of the positive ions in the rapidly expanding electron cloud (plasma) and the continuing ionization of the excited
Figure 2.2. Evolution of lines chosen for optimization with short pulse (SP) and optimized pulse (OP) [86].

Figure 2.3. Temporal shapes of short and optimized pulses (cross-correlation traces). Inset: Fitness behavior during the optimization for Al II 358.6 nm emission line. [86].

Gunaratne et al. in 2006, reported on the influence of pulse duration, bandwidth, and phase shaping on fs-LIBS [87]. They showed, as has been reported earlier, that fs pulses lead to lower laser breakdown thresholds. They determined that the reason for this enhancement was the additional bandwidth of ultrashort pulses, rather than their reduced pulse duration. A 40% increase in the LIBS emission was found for the addition of a significant positive linear chirp. This change in intensity reflects a shift from a highly localized excitation followed by fast Coulomb explosion on the sample surface to a slower process where electron phonon coupling leads to melting of the sample within the focal volume. Their
experiments showed that LIBS efficiency improves with bandwidth well beyond what is available using a typical short-pulse ps laser. This finding supports the use of broad bandwidth pulses for efficient LIBS. Further, through simple binary phase pulse shaping, an improvement in the LIBS emission for both Al and Cu was observed after a wide parameter space was mapped. This is an important experimental result, for it showed that there is now an ability to determine an optimum (even if simple) pulse shape that would lead to an enhancement of the characteristic emission for a specific element and even ionization state of interest.

Guillermin et al. in 2009 showed the possibility to achieve control of the plasma optical response by material irradiation with temporally shaped femtosecond pulses [86]. They applied an adaptive optimization loop to lock up temporal shapes, fulfilling user-designed constraints on plasma optical emission (through optimization of a defined figure-of-merit). The pulses that improved the ionic versus neutral emission showed a structured temporal form extending on several ps compared to the original fs transform limited pulse. It was shown (Fig. 2.2) that laser energy deposition with a series of femtosecond pulses leads to a reduction of the neutral species emission while energy deposition in the picosecond timescale augments the ionic emission and allows an enhancement of the global emission of the plasma plume. It was shown that by optimizing the pulse shape to ionize an aluminum sample, the Al II line intensity increased by 2 to 3 times that of the original transform limited pulse; at the same time, the Al I line decreased showing that the control of the ionization state of the plasma was controllable through pulsed-shaped LIBS. Further, through the implementation of a genetic algorithm, it was shown (Fig. 2.3) that the emission of the Al II line could be optimized within 40 iterations, starting with the transformed limited shape- following convergence the best optimum pulse shape was directly reported. The convergence on an optimized complex pulse shape within 40 iterations was a significant improvement over the simple pulse shapes used by Gunaratne et al. that required over a thousand different measurements to be conducted and further analyzed.

Harilal et al. in 2012 used a long pulse Nd:YAG laser to produce plasma on an aluminum target in a rarefied Ar atmosphere [88]. The hydrodynamics of the expanding plume in the presence of ambient Ar were studied using focused shadowgraphy and fast photography. The authors observed a secondary plasma
formed by compression in the vicinity of the shock wave. The authors observed that internal structures inside the plume-Ar interface are observed during the time window of 100–500 ns. A secondary shock observed behind the primary shock wave during this time window, which is also spherical through the part of the wave near to the laser cone angle, showed instabilities. The instabilities noticed in the secondary shock waves at the laser cone angle are caused by laser-plasma interaction. The authors were able to match experimental results to theoretical modeling using a continuum hydrodynamics model. The instabilities observed in the plasma around not only the laser interaction zone at early delay times but also at later times during secondary ionization across the expanding shockwave, complicate the collection and analysis of emission lines due to rapidly changing plasma dynamics. The success of the model and understanding of the shockwave is, however, limited to such narrow and specific LIBS cases and did not include any investigation on the interaction of a multiple component solid sample on the plume dynamics or emission.

A few studies will be highlighted here that have shown the success and capability of LIBS for analytical measurements, remote sensing applications, and for the analysis of nuclear materials. In addition, a short discussion on the current R&D need is provided. Hahn and his group at University of Florida published two reviews that comprehensively analyzed the current state-of-the-art LIBS systems and analytical capabilities [12, 89].

By using a 1064 nm ns-laser, Jedlinszki was able to show that the analytical performance of LIBS could be significantly improved if, instead of single or double pulse lasers, bursts of multiple collinear laser pulses are used for the plasma generation [90]. This improvement was documented for twenty spectral lines of a total of eleven elements. From their data analysis, it was suggested that the use of spatial and time integration of the plasma emission helps to realize not only enhanced sensitivities but also improved repeatability. Hahn was also able to elucidate from the vast amount of publications that plasma-particle interactions leading to repeatability and matrix effects could be reduced through multiple pulse LIBS and integration over the spatial distribution of the resulting LIBS plasma. The primary reason for this is an improved stability in the resulting ionization of the sample and the homogenization of the multiple spatial regimes within the
plasma plume during collection.

Bousquet et al. performed a quantitative analysis of chromium in soil samples [21]. It was demonstrated that the level of accuracy and repeatability when conducting a quantitative analysis of chromium samples was dependent on the chromium emission line studied. This observation is due to the inherent temporal evolution of the plasma plume and the emission spectra itself. As well, important matrix effects were observed to occur from one soil sample to the other, preventing any prediction of concentration in different soils on the basis of a univariate calibration curve that varied across observed emission lines as well.

Fantoni et al. published a review on the use of LIBS for the analysis of a number of elements in various matrices that highlights the success of LIBS for rapid quantitative analysis when careful methodologies are used to conduct the analysis [9]. The authors showed the importance of proper emission-line choice and LTE parameter definition, both in the case of calibration curve and calibration free approaches (especially in the latter where the assumption are used to directly derive the concentration). The authors further reviewed the effectiveness of correction for plasma parameters in relation to the problem of the need for matrix-matched samples with the same elemental composition for construction of reliable calibration curves. The authors further analyzed the use of modeling and simulation to understand the fractionation of elements and to address the experiments in order to minimize the related matrix effect problems.

Baudelet et al. in 2010 performed the first LIBS experiments that employed a thulium fiber laser at 2.0 μm and 100 μJ as the ablation source for LIBS of a copper sample. They reported that the low irradiance used in the experiment provided by the laser on the target surface generated a plasma in LTE, with a temperature of approximately 2.6 eV and electron density around 10^{21} \text{ e}^{-} \text{ cm}^{-3}. The resulting spectra showed both (i) a lack of continuum emission and (ii) no emission from atmospheric excitation. For ns-LIBS, this is an interesting result, for it could allow for the use of non-gated detectors due to the lack of continuum emission.

Russo et al. in 2011 introduced a new method of performing the optical isotopic analysis of condensed samples in ambient air and at ambient pressure: LAMIS. This technique uses radiative transitions from molecular species (rotational and vibrational transitions), either directly vaporized from a sample or formed by as-
sociative mechanisms of atoms or ions in a LIP plume. This method is an advanced modification of LIBS, which can determine not only chemical composition but also isotopic ratios of elements in the sample. Isotopic measurements are enabled by the increase in isotopic shift ranges of molecular emissions, compared to atomic emission that can range from 2–100 times that of the atomic shift, and is proportional to the reduced mass of the diatomic system. Analysis can be performed from a distance and in real time although this has not yet been proven beyond the laboratory seeing. Also, no sample preparation or pre-treatment is required, but the effects of contaminants on the precision or resolving power of the LAMIS technique were not studied due to the use of pure samples (i.e., matrix effects were not observed to exist with this technique initially).

Yee et al. in 2013 furthered developed the LAMIS technique by using a fs laser to generate the LIP, where the use of gated detector was shown to be unnecessary and the BO, CN, and C₂ diatomic excited radicals were clearly observed [91]. A multivariate regression was applied to two known and one unknown enriched boron samples, and an excellent agreement between the declared and measured enrichments was reported, using the LAMIS technique. The implementation of fs laser pulses for LAMIS measurements has lead directly to the development of the F2–LAMIS technique discussed earlier in Chapter 1. F2–LAMIS has been demonstrated for the measurement of Sr and its isotopes by Hou et al. [55]. Work by Rohwetter et al. [58] demonstrated the use of fs laser filaments for the remote measurement of a metallic sample (Cu) at distances of ~200 m. However, in the work by Hou et al. the authors did not perform a remote or standoff measurement of the Sr sample. Further, the filament produced in the previous work formed shortly after the geometric focus of the lens used to force focus the laser beam into a propagating filament, which has not been observed to occur in the work presented here in this dissertation. The standoff detection capability presented by fs filamentation combined with the isotope sensitivity of LAMIS could allow for the measurement of the isotope composition of nuclear forensics relevant materials at remote distances.

Brown et al. further showed that for the most recent advance in LIBS, analysis capabilities of interest to the nuclear forensics community (LAMIS) suffer from the same interference or matrix effect due to contaminant (trace) or bulk
Figure 2.4. Mean LIBS spectra for each of the pure compounds studied with 20 mJ ns pulse energy. Spectra have been offset for clarity. The apparent atomic transitions in the LaBO$_3$ spectrum have been clipped on the y-axis to focus on weaker BO emission that may have been present [33].

elements within the sample when performing an analysis [33]. The authors revealed some matrix effects on the determination of %$^{10}$B content when different pure compounds were used. It was reported that this was due to the difficulty and inaccuracy of matching theoretical molecular spectra to the experimentally measured spectra when there is a presence of a contaminant even when that contaminant is a boron containing molecule. It can be clearly seen from the results of Brown’s study in Fig. 2.4 that there is a matrix effect present within measured LAMIS spectra. It was also shown that different laser energies revealed a subtle matrix effect for different pure compounds. In addition it is also unclear what exact processes are involved in the observed matrix effect and whether the same degree of matrix effect would impact measurements for a real–in the field–sample.

2.3.2 Liquids

A majority of the publications also concern LIBS of aerosols vs bulk liquids where vastly different matrix, plasma, and spectral effects have been observed [60, 92, 41].

Single levitated aerosol droplets were examined by Biswas et al. in 1988 [93] to elucidate the effect of laser wavelength and power on the resulting LIBS spectra. Plasma spectra were obtained for single, optically levitated, micron-sized droplets composed of brine with glycerin solution mixture. Spectra of neutral and once-
ionized species were obtained, both below and above the air breakdown threshold, as a function of wavelength and energy. It was shown that the energy required for breakdown and the time of plasma emission increased with an increasing wavelength from 355–532 nm.

Matsumoto and Charfia used a Nd:YAG laser to produce and image laser-induced breakdown in water [94, 95]. The fundamental wavelength of 1064 nm was focused into the water to produce a breakdown. Charfia et al. axially resolved the water plasma emission and were able to show a simple spatial dependence of the emission of trace amounts of Mg and Na in the water. Matsumoto et al. observed that the spectral features varied considerably, depending on the detecting position, ranging from the self-reversed lines to the clear spectral lines.

Sacchi et al. in 1991 discussed the mechanisms of dielectric laser breakdown in water both theoretically and experimentally. The authors discussed the differences in the breakdown threshold for short pulse and long pulse lasers [96]. The authors claimed that physical mechanism responsible for the laser-induced breakdown of water is electron avalanche ionization.

Diwakar et al. in 2007, used a Nd:YAG laser (1064 nm, 260 mJ, 20 ns) to perform LIBS measurements on aerosols created from a bulk liquid, consisting of various Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) standard solutions. The authors studied the effect of aerosol mixtures on the measured LIBS spectra and reported that for Na- and Cu-mixed solutions the Na I emission intensity was increased over a pure Na solution when a 1:9 Na:Cu mixture was ablated. The result that the analyte emission intensity in an aerosol is affected by the presence of a contaminant or the bulk matrix is of significant importance to the LIBS community.

Recently, in 2015, Asgill et al. [97] studied the heat and mass diffusion rates within LIPs of aerosol samples and found that the resulting plasma is particle-rich with locally perturbed areas surrounded by a hot bulk plasma. The authors found that both the plasma surrounding the particle and the bulk liquid plasma were described by differing plasma parameters.

Sarkar et al. [98] implemented the LAMIS technique, described earlier in this chapter, to measure the deuterium and tritium concentrations in water. The authors observed a large molecular isotope shift for the OH and OD molecules, which
was expected due to the large change in the reduced mass for these diatomic molecules. Further, they observed that the measured spectrum for the two different isotopically enriched water samples exhibited significant differences that resulted in the partial least squares regression analysis quality to be degraded, which directly affected the measurement of the D/H isotope ratios. Last, the authors observed that the optimization of the spatial distribution, lens to sample distance, laser power, and pulse width affected the statistical quality of the regression model for the D/H isotope analysis.

2.3.3 Gases

Gaseous samples were the first materials to be measured and quantitatively analyzed through the use of LIBS in the 1960’s [99]. However, the number of published works on LIBS with gases is limited [100, 64, 101]. The majority of the discussion on the breakdown and analysis of the emission spectra from LIPs of gases are of a secondary nature, resulting from an analysis of a solid, liquid, aerosol, or particulate sample [64].

Parigger et al. used a ns Nd:YAG laser (1064 nm, 300 mJ, 7.5 ns) to produce a LIBS plasma in carbon monoxide [102]. They were able to observe the emission of the C$_2$ Swan band centered at 565 nm to determine the vibrational and rotational temperatures within the plasma. It is straightforward to create synthetic spectra through modeling, and the authors were able to fit the synthetic spectra to the measured spectra and obtain the rotational and vibrational temperature. Molecular C$_2$ Swan system and molecular CN violet system recombination spectra were observed to yield temperatures in excess of 6,000 K.

Cremers and Radziemski carried out early work on LIBS of gases and were able to detect chlorine and fluorine in air at trace levels [100]. Detection limits for these two gases were 8 and 38 ppm by weight, respectively. The experiments were carried out using a Nd:YAG laser (1064 nm, 100 mJ, 15 ns). The detection was achieved by monitoring the Cl I emission at 837.6 nm and F I emission at 685.6 nm, and the precision was reported to be 8% RSD for all measurements.

Yalcin et al. in 1996 investigated the sensitivity of LIBS measurements using a Nd:YAG at 532 nm under various atmospheric conditions to elucidate the ef-
fect that variable environment would have on in-field measurements. The authors studied the variation in background gas composition, presence of particles, and humidity for continuous in situ analysis of hazardous materials [103]. Of significant importance to LIBS measurements is the variation of the two dominant plasma parameters, plasma temperature and electron density, with ambient conditions. The authors used emission-based measurements to determine the two parameters, and found, of large significance, that the measurements show remarkably little variation in these parameters.

The primary interest in LIBS of gases recently has been in the observation of matrix effects arising from the presence of the gas around a solid or aerosol sample. The ionization potential, pressure, and purity of the gas has been shown to lead to variations in measurement through changes in the plasma properties and the resulting emission. It is important to note that beyond a few publications by Dong and Liu [80, 30, 104], very little has been done to determine whether similar effects are observed for fs-LIBS. This is of interest due to the fundamentally different laser material coupling and the early literature suggesting that there is a lack of pre-ablation of ambient gases around a solid sample from fs-lasers. Dacheng et al. [105] studied the effect that the ambient gas composition has on the measured uranium LIBS emission spectrum. The authors were able to show a dependence on both atomic and molecular emission lines on the composition of the ambient atmosphere. The diatomic uranium monoxide (UO) molecular emissions centered at $\sim$600 nm was shown to have an inverse relationship to the concentration of oxygen in the ambient atmosphere, and it was postulated that this effect is due to the formation of polyatomic $U_xO_y$ molecules.

### 2.4 Principles of LIBS

A typical laboratory LIBS system is shown in Fig. 2.5. The plasma emission is collected, using either a freely coupled lens system as shown in Fig. 2.5 or by a fiber optic cable. The collected plasma emission is spectrally resolved by a dispersive wavelength selection system that can consist of a Czerny Turner or Echelle spectrograph. Each type spectrometer has a number of unique benefits as well as drawbacks and must be chosen, based on the application or research prob-
lem to be addressed. The spectral information is recorded commonly, either by using a Charge Coupled Device (CCD) or a Intensified-Charge Coupled Device (ICCD). There are other possible detectors that can be used. For example, the Complementary Metal-Oxide-Semiconductor (CMOS), photodiodes, and the Electron Multiplying Charge Coupled Device (EMCCD) have all been implemented in LIBS experiments successfully. ICCDs have a unique capability to perform fast temporal gating due to the rapid switching on and off of the intensifier to an applied voltage gate. CCDs tend to have a greater sensitivity and are, by far, much cheaper than ICCDs and are easier to implement in a deployed system; however, CCDs will record the entire time-integrated spectrum of the LIBS emission.

When considering a LIBS set-up, it is common to consider a single laser shot either by the ns or fs laser to be a single LIBS measurement. However, for most LIBS measurements, multiple laser shots are typically accumulated into one acquisition, and a number of accumulations are averaged to produce the recorded LIBS
spectra. Depending on the spectrograph system implemented in the experimental setup it may be necessary to rotate the diffraction gratings to cover a wide wavelength range. It has been observed that by using this methodology, the precision in the LIBS measurement can be improved by removing the single-shot fluctuation in the signal due to the non-homogeneity of the sample and the stability of the laser source.

According to Russo \textit{et al.} [106], using short pulse lasers at irradiance higher than $10^9$ W cm$^{-2}$, will result in direct ionization or vaporization of the sample irradiated within the focal spot. Simple thermal heating of the sample within the focal spot leads to vaporization and subsequent plasma formation when the temperature of the sample surface is raised above the vaporization temperature. For fs laser pulses, the sample irradiated by the laser within the focal spot undergoes direct ionization, before any thermal heating can occur, which results plasma generation through a coulomb explosion process [65].

The ablation of the material from the sample has been considered to be stoichiometric for ns laser pulses by Chan \textit{et al.} [107]. As it is proposed that stoichiometric ablation occurs for ns laser ablation, this would suggest that the composition of the ns LIP is representative of the composition of the sample. For fs laser ablation, due to the ability to directly ionize the sample immediately through interaction with the intense laser field and the lack of uniform thermal heating, it is possible to see a deviation from stoichiometric ablation due to the selective multi-photon ionization of specific elements [108]. Further, the elemental fractionation effects observed in fs laser ablation increased when the laser fluence approached the ablation threshold of the sample.

Plasma formation will occur when the breakdown threshold is reached. The breakdown of the sample and the formation of the luminous plasma can be thought to occur in two processes. The initial process is primarily influenced by the ambient gas pressure surrounding the sample and the incident laser wavelength. At low pressures, where collision effects are negligible, the predominant mechanism leading to plasma formation is multiphoton ionization (MPI) that can be expressed as:

$$M + m\nu \rightarrow M^+ + e^-,$$
where m is the number of photons and M is the atom or ion of interest. Multpho-
ton ionization will result when the number of photons simultaneously absorbed is
greater than the ionization potential of the atom or the energy required to excite
a valence electron to the conduction band.

The second process involved in plasma initiation is electron avalanche ioniza-
tion, also referred to as cascade ionization or electron cascade growth. This process
occurs when a number of free electrons in a medium are subjected to strong accel-
eration by an electric field (laser pulse) and can impact ionize an atom or molecule
through the reaction

\[ e^- + M \rightarrow M^+ + 2e^- \]

Cascade ionization, as named, will lead to a cascade breakdown that results an
exponential increase in the number of free electrons. Following formation of the
initial plasma, inverse bremsstrahlung (IB) can enhance and sustain the plasma
formation when the laser pulse duration is long enough, and is further enhanced
when longer wavelength laser light is used.

Initially the LIBS plasma is observed first as a bright spark on the sample
surface followed rapidly by a prominent acoustic emission from the supersonic ex-
pending shockwaves. The magnitude of the acoustic emission has been shown to be
proportional to the electron density of the plasma [58]. As the high pressure vapor
and plasma rapidly expands and interacts with the surrounding ambient atmos-
phere or parts of the sample surface, it evolves through several different transient
regimes transferring energy through thermal conduction, radiative transfer, and
compression heating that drives the shockwave formation. The resulting ablation
crater which forms after the plasma has expanded from the sample surface is de-
pendent on the properties of the target material, the surrounding gas pressure, and
the experimental setup (laser energy and wavelength, focusing conditions, sample
orientation, etc.).
2.5 Plasma Optical Emission

2.5.1 Atomic Emission

The LIBS emission spectrum evolves rapidly in time primarily due to the initiation of the hot, dense plasma in a small volume on the sample surface. The primary differences between the emission spectrum observed for fs and ns laser pulse durations is the amount of bremsstrahlung or continuum emission present in the ns case that requires gating of the detector and the near immediate ionization, and, thus near immediate ionic emission observed in fs-LIBS. It has also been observed in the literature that fs-LIBS exhibits a shorter overall lifetime compared to ns-LIBS [109, 110, 111]. The increase in the amount of continuum emission observed in ns-LIBS measurements is due to the long pulse duration that is able to interact with the initial expanding plasma that is then heated through the inverse bremsstrahlung process.

Descriptively, during the onset of the plasma formation when ionization, temperature, and electron density are high, an intense broadband continuum (background emission) of light dominates the plasma emission until about 200–500 ns following irradiation of the sample by the focused laser pulse; however, large continuum emissions have been observed lasting as long as \( \sim 1 \mu s \) [111]. This continuum emission is a combination of bremsstrahlung or free-free (f-f) transitions and radiative recombination or free-bound (f-b) transitions. Characteristic line emissions are due to the radiative relaxation of excited atoms and ions within the plasma as the plasma expands and cools. The atomic line emission for a graphite sample following ablation by fs laser pulses using a non-gated detector is shown in Fig. 2.6. These transitions are commonly referred to as bound-bound transitions (b-b). In LIBS measurements, bremsstrahlung emission occurs when electrons decelerate around the electric field of atoms and ions in the plasma. When a free electron is captured into an atomic or ionic energy level, recombination (f-b) light is emitted due to the difference in the initial kinetic energy of the electron and the binding-energy of the electron in the atom or ion [112].

Atomic spectral lines that originate from the bound-bound (b-b) transitions are not just characteristic of the emitting elemental species but are also isotope dependent [112]. The energy difference in the emission originating from the same
electron transition for different isotopes of the same element is commonly referred to as an isotope shift. The origin of the isotope shift in atomic spectra can be thought of as a change in the mass of the nucleus affecting the orbit of the electrons for light nuclei or the change in the size of the nucleus and thus charge distribution affecting the orbit of the electrons for heavy nuclei [112]. The atomic isotope shift is different for every emission line as it is dependent of the electron configurations involved in the transition. The S electrons commonly exhibit the largest isotope shift due to the close orbit of these electrons around the nucleus.

### 2.5.2 Molecular Emission

Once the plasma is formed following laser ablation, a complex rapid cooling and expansion occurs where excited neutrals and ions can combine to form excited molecular radicals [49, 113]. The emission of excited molecular radicals commonly form bands due to the broadening of individual rotational and vibrational emission components that are closely spaced [49, 59, 91]. The CN molecular emission shown in Fig. 2.7 was collected following fs laser ablation of a graphite sample using a non-gated detector. The excited molecular radicals can form either from

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**Figure 2.6.** C atomic emission spectra following ablation of a graphite sample by fs-laser pulses under rarefied atmospheric conditions.
direct excitation of the preformed molecules on the sample surface or from plasma assisted chemical reactions with the ambient atmosphere [49, 51, 50, 113]. The exact origin of the excited molecular radicals has not yet been elucidated. However, current work is being conducted using isotopically enriched samples and spatially resolved LAMIS and LIBS spectral measurements to map the emission of specific elements, isotopes, and molecules over the plasma evolution, which will allow for the determination of the ambient atmosphere or the sample as being the source of the excited molecular radicals [114].

2.6 Summary

LIBS research has primarily been driven by either the laser and LIBS system available to the researcher or the specific analytical application. The number of studies varies greatly according to the type of sample, laser wavelength and pulse duration used to conduct the studies. Further, there has been a tendency for the LIBS community to “black-box” effects that are observed for complex mixed samples or non-ideal environments in which variations in the LIBS emission or plasma dynamics has been observed as “matrix effects”. LIBS matrix effects vary
from small changes in the plasma density and temperature to a complete lack of specific emission lines between a pure and mixed sample. Further, it has been shown that the emission intensity for an element can increase when it is mixed at a significantly reduced concentration with another element. Most results in the literature are based on a particular instrument and are not repeatable; it is a risk to make broad general claims about the fundamental mechanisms responsible for specific data under such situations. New studies based on both \textit{ab initio} modeling and a fundamental experimental understanding are needed to better define and predict the LIBS process including elucidation of the matrix effect. Additionally, a number of works have been reviewed that show the complexity of the LIBS ablation process for ns \& fs lasers that can affect the production of molecular radicals within the plasma, which are necessary for LAMIS measurements. Lastly, a number of studies have been reviewed that have shown the enhancement of the LIBS measurement technique through the manipulation of the laser pulse shape and wavelength for example.
Chapter 3

Fundamental Investigation of Laser Produced Plasmas

3.1 Spectral Line Profiles, Broadening Mechanisms, and Instrumental Function

As the LIBS plasma evolves, atoms, ions, and molecules emit characteristic emission lines through radiative relaxation. When the emitted light is collected and spectrally resolved using a spectrograph and detector system, emission lines are observed. There are a number of different broadening mechanisms that contribute to the measured emission line width, position, and absolute intensity.

A spectral line profile in discrete absorption or emission spectra are never purely monochromatic. Even when high resolution spectrometers or interferometers are used to resolve the spectral line profile a line profile of finite width is observed. The wavelength difference ($\Delta \lambda$) between the wavelength positions where the intensity is at half the maximum value for the line shape is referred to as the full width at half maximum (FWHM), which is also reported in the literature as the emission line width. The emission line profile has two main features: the line kernel and the line wings. The spectral region under the FWHM of the spectral line profile is referred to as the kernel of the line. The spectral region outside the FWHM of the spectral line profile are referred to as the wings of the spectral line.

The overall shape of the line profile depends on the broadening process or
processes that occur within the plasma. It is common to measure the impact of these different broadening processes by the change due to that process on the FWHM of the characteristic spectral line. Due to the possible presence of multiple broadening processes the FWHM does not, necessarily, impart information about the wings of the spectral line due to the convolution of different spectral line shapes (Lorentzian and Gaussian) associated with each broadening processes and possible additional optical aberrations.

In regards to quantitative analyses, the spectral line profile is a fundamental criterion in the selection of the spectral line used for an analysis. This is especially true when spectroscopic or quantitative information is desired, such as the plasma temperature and density or the concentration of an element within the plasma. The importance of understanding the broadening mechanisms and the degree to which the lines of interest are affected by broadening becomes even more important when interference between emission lines is present. This is especially true for complex elements like uranium, which has \( \sim 300,000 \) lines between 200 and 900 nm, where a majority of the observed background is actually due to the overlap of the spectral line shapes [35].

The major broadening phenomena that are routinely encountered in laser-induced plasmas (Doppler broadening, pressure broadening, and self-absorption) are described below. In addition to the broadening mechanisms that occur within the plasma, additional spectral line broadening occurs due to the instrument function of the detection system.

### 3.1.1 Line Broadening Mechanisms

#### 3.1.1.1 Doppler Broadening

Doppler broadening is the most common broadening mechanism observed in LIBS plasmas. Doppler broadening has been observed to be the dominant broadening mechanism several microseconds after the initial laser ablation and plasma formation [115]. Doppler broadening is the inhomogeneous broadening of the emission line profile of atomic transitions caused by the random movements of atoms. A source moving towards an observer causes the wavelength to decrease (blue shift), and a source moving away from an observer causes it to increase (red shift). Due
to the range of temperatures present in the evolving LIBS plasma the emission will be both blue and red shifted, and the emission line profile will be composed of a spread wavelengths. As Doppler broadening is a homogeneous process the intensity distribution will have a Gaussian profile, and the statistical distribution of velocities is described by Maxwell’s law if the atoms or ions are under a LTE condition. The full width at half maximum for Doppler broadening can be expressed as:

$$\Delta \lambda = \lambda_0 \sqrt{\frac{8k_B T \ln(2)}{mc^2}},$$  \hspace{1cm} (3.1)

where $T$ is the absolute temperature in kelvin, $k_B$ is Boltzmann constant ($J K^{-1}$), $m$ is the mass of radiating atom ($kg$), and $c$ is the speed of light ($m s^{-1}$). Eq. (3.1) can be simplified further through evaluation of the constants and substitution of the mass $m$ by the atomic or molecular weight $M = m N_A$ where $N_A$ is Avogadro’s number ($mol^{-1}$).

### 3.1.1.2 Pressure Broadening

Pressure broadening is a broad term applied to a number of interactions that is also commonly referred to as collisional broadening. This type of broadening is due to the interaction of the emitting species with another species within the plasma (atoms, ions, electrons, etc.). Pressure broadening can be expressed in terms of perturbation of energy levels, $V$, which varies with the inter-particle distance $R$ as given by Ref. [116, 117]

$$V(R) = \frac{C_x}{R^x},$$  \hspace{1cm} (3.2)

where the value of $x$ and the interaction constant $C_x$ depend on the type of interaction considered.

### 3.1.1.3 Van der Waals Broadening

Van der Waals broadening is attributed to the interaction between neutral species within the plasma. Specifically, this broadening mechanism occurs due the dipole interaction of an excited atom with the induced dipole of a ground state atom.
This dipole-induced interaction between neutral species can be expressed as [112]

\[ V(R) = \frac{-\alpha_p p^2}{4\pi\varepsilon_0} \frac{1}{R^6} = \frac{C_6}{R^6}, \tag{3.3} \]

where \( \varepsilon_0 \) is the permittivity of free space, \( \alpha_p \) is the polarizability of the perturber in \( m^3 \), \( p^2 \) is the mean square dipole moment, and the negative sign indicates that the Van der Waals force is attractive. Depending on the magnitude of the dipole moment and polarizability the shift can be observed towards the red or blue side of the emission center. According to the impact approximation, the corresponding broadening and shift (in m) due to van der Waals interaction are given by [117]

\[ \Delta\lambda_{VDW} = 2.71C_6^{2/5} \nu^{3/5} n_p \frac{\lambda^2}{c} \tag{3.4} \]

\[ \Delta\lambda_{VDW, shift} = 0.98C_6^{2/5} \nu^{5/5} n_p \frac{\lambda^2}{c} \tag{3.5} \]

where \( \lambda \) is the transition wavelength in m, \( \nu \) is the relative velocity in m s\(^{-1} \), \( n_p \) is the number density of perturbing particles (m\(^{-3} \)) and \( C_6 \) is the interaction constant in m\(^6 \) s\(^{-1} \), as given in Eq. (3.3).

### 3.1.1.4 Stark Broadening

The perturbation of the energy levels of an atom by an electric field induced by ions and/or electrons is a form of pressure broadening called the Stark effect, and it contributes significantly to line width broadening under typical LIBS plasma conditions. The result of linear Stark broadening for hydrogen like elements is a symmetrically broadened that is unshifted due to the symmetrical splitting of the energy levels from the electric field. In the case of linear Stark broadening, the FWHM (\( \Delta\lambda \)) of the spectral line is given by [118]

\[ \Delta\lambda_{FWHM} = [C(N_e, T_e)/N_e]^{2/3} \tag{3.6} \]

where \( C \) depends (weakly) on \( N_e \) and \( T_e \), and can be treated as constant.

For non-hydrogen like elements, the interaction is described by a quadratic Stark effect. The perturbation in this case is proportional to \( 1/R^4 \), and has the
effect to split the electron energy levels asymmetrically that also shifts the center of the emission line profile to longer wavelengths for both ions and electrons [119]. The FWHM of a Stark-broadened line and the emission line profile shift (in m) are given by [117, 119]

\[ \Delta \lambda_{\text{Stark}} = 2 \times 10^{-22} w_n e \left[ 1 + 5.53 \times 10^{-6} N_e \alpha_{\text{ion}} \times \left( 1 - 0.0068 n_e^{1/6} T^{-1/2} \right) \right] \tag{3.7} \]

and

\[ \Delta \lambda_{\text{Stark,shift}} = 1 \times 10^{-22} w_n e \left[ d/w + 6.32 \times 10^6 n_e^{1/4} \alpha_{\text{ion}} \times \left( 1 - 0.0068 n_e^{1/6} T^{-1/2} \right) \right], \tag{3.8} \]

where \( w \) is the electron impact half-width in m, \( d/w \) is the ratio of shift to width (dimensionless), \( n_e \) is the electron number density in m\(^{-3}\), and \( \alpha_{\text{ion}} \) is the ion-broadening parameter (dimensionless).

### 3.1.1.5 Resonance Broadening

Resonance broadening (self broadening) occurs only between identical species and is further limited to emission lines with the upper or lower electron energy levels having an electric dipole transition (resonance line) to the ground state electron energy level, and is described as a dipole-dipole interaction. This effect results in symmetrically broadened unshifted spectral line profiles [112, 116]. The FWHM in m can be expressed as [117]

\[ \Delta \lambda_{\text{res}} = \frac{3}{16} \left( \frac{g_i}{g_k} \right)^{1/2} \left( \frac{\lambda_0^3 e^2 f_{ik}}{\pi^2 \epsilon_0 m_e c^2} \right) n_e, \tag{3.9} \]

where \( g_i \) and \( g_k \) are the statistical weights (degeneracy) of the lower and upper states, respectively, \( f_{ik} \) is the transition oscillator strength (dimensionless), \( e \) and \( m_e \) are elementary charge (C) and mass (kg) of the electron, and the rest of the variables have been defined earlier.
3.1.1.6 Self-Absorption Broadening

Following the emission of light from the transition of an electron from an upper to lower level energy state, it is possible that this emission light is absorbed as it transports through the plasma to the detection system by a significant population of atoms in the lower level energy state of the original emission. This effect is commonly known as self-absorption, and is common for transitions involving the ground or near ground states (i.e., resonance or near-resonance transitions). Self-absorption broadening results in the distortion and broadening of the spectral line profile. If the population of atoms in the lower energy state are low, the entire line profile grows with concentration. However, as the population of atoms occupying the lower energy state are increased self absorption can occur and the line profile begins to increase non-linearly and attains a flattop shape, which is similar to simple Beer-Lambert absorption. It can be difficult to determine if a line suffers from self-absorption (without measurement of the emission from samples with a range of analyte concentrations) due to the small distortion in the spectral line profile from the broadening due to both Stark effect and the instrumental function [120].

3.1.1.7 Self-Reversal Broadening

Self-reversal is a related phenomenon to self-absorption that is observed in the measured LIBS emission spectrum as a dip at the center of the spectral line profile. If the plasma does not have a homogenous temperature and density distribution, which is common for LIBS plasma, self reversal can be observed. LIBS plasmas can be thought of as having a hot dense center surrounded by a cooler less dense layer. The cooler envelope will then absorb the emission from the hot center due to the increase in atoms occupying the lower level energy state of the transition in this region. An example of self reversal in LIBS of salt using a ns laser is shown in Fig. 3.1. Due to the prominent dip at the center of the emission line profile the presence of self-reversal is easily identified.
Figure 3.1. LIBS spectra of salt under atmospheric conditions using a 20 ns laser at 1064 nm and 10 mJ pulse energy showing self reversal for the two Na I lines at 588.99 and 589.59 nm.

3.1.2 Instrumental Function

If an emission spectrum consists of a single monochromatic emission ($\lambda_0$) and is spectrally resolved by an ideal spectrometer and detector, the output spectrum should be a single monochromatic emission at $\lambda_0$. The emission spectrum would then consist of a delta function centered at exactly $\lambda_0$. However, even with an ideal detection system, a finite line width matching the natural line width associated with the transition, due to the uncertainty principle, is observed. In practice, broadening of the spectral line profile occurs as spectrometers are not ideal optical systems. The spectral line profile now has a width due to both the natural line width of the emission line and the instrumental function. The natural line width of spectral lines is below the resolution of most moderate resolution spectrometers; thus, the difference between the known emission spectrum and the measured line profile is defined as the instrumental line profile or instrumental function.

It is possible to nearly eliminate the contribution of instrumental broadening in LIBS measurements by the use of high-resolution spectrometers, as it is possible for the instrumental broadening width of such instruments to be smaller than the spectral line width of the plasma emission. Due to the commensurate reduction of the measured emission intensity with a decrease in the amount of instrumental
broadening it is not possible in most cases to completely remove the instrumental profile. It is then necessary to de-convolve the true emission line profile from the measured LIBS emission line profile that requires an experimental determination of the instrumental function.

A number of parameters and optical components related to the detection system will effect the shape and magnitude of the instrumental broadening, such as width of the entrance slit, diffraction effects, ICCD/CCD pixel size, aberration effects, quality of the components, use of optical fibers, and alignment of the system.

3.1.2.1 Influence of Aberrations

The instrument function is further dependent on a number of optical aberrations. It is common that combinations of optical aberrations are observed simultaneously, which adds to the complexity of the determination of the instrumental function. The presence of aberrations leads to deviations of the optical elements from their ideal behavior and leads to broadening of the measured spectral line profile. The most common aberrations observed in LIBS measurements are astigmatism, spherical aberration, and coma.

An astigmatism is another type of aberration usually encountered with optical elements (especially lenses) where rays that propagate in two perpendicular planes have different foci in two different planes (tangential and sagittal).

Spherical aberration is an optical effect observed in an optical device as the result of rays emanating away from the surface of an optical element. For converging elements like lenses, off-axis or light rays emanating from the edge of a lens are focused closer to the lens than light rays close to the axis of the optical element. In the absence of spherical aberration, parallel rays incident on a spherical lens results in a circle in the focal plane. Spherical aberrations are dependent on the index of refraction of the optical element and is further dependent on the shape and the orientation of the optical element in relation to the incident light rays.

Similar to spherical aberration, a coma arises from differences in the optical path lengths of various rays to the focal plane in an optical system where the light rays are incident off-axis. Parallel rays that are incident on the lens at a small angle cause the image to develop a distorted image and/or tail (coma) similar to a comets tail. Broadening of the wing on one side of the spectral line profile occurs
due to the skewing of the light rays in the focal plane. This is commonly observed in LIBS measurements when the detector (ICCD/CCD) is being aligned on the spectrometer exit. Further, the presence of a coma can be an indication that the emission light coupled into the spectrometer is not oriented to the optical axis of the spectrometer.

3.1.2.2 Influence of Diffraction

Diffraction refers to various phenomena which occur when light encounters an obstacle, and is defined as the bending of light from rectilinear propagation around the edges of an obstacle. If the slit widths are infinitesimally small, aberrations are negligible, and the detector has infinitesimally small pixels/intensifier channels the resulting instrumental line profile is that of a classic diffraction pattern. The diffraction pattern increases the broadening $\Delta \lambda_d$ of the spectral line profile and adds to the broadening in the instrument function. $\Delta \lambda_d$ is the diffraction-limited spectral bandpass which can be expressed as

$$\Delta \lambda_d = R_d w_d = R_d \frac{2\lambda f}{\alpha},$$  \hspace{1cm} (3.10)

where $f$ is the focal length of the spectrometer, $w_d$ is the diffraction-limited slit width, and $\alpha$ is the width of the beam. The measured spectral intensity is primarily limited by the width of the entrance and exit slits of the detection system. Although an increase in the spectral resolution of the detection system can be realized by a reduction in the entrance slit width, the commensurate reduction of the emission line intensity with narrower slit widths will force a lower limit onto the slit width given by Eq. 3.10.

3.1.2.3 Overall Emission Line Profiles

Doppler and instrumental line profiles are homogenous broadening mechanisms and have a Gaussian distribution and collisional broadening processes are inhomogeneous broadening mechanism and have a Lorentzian distribution. When both pressure (Stark broadening) and Doppler broadening are observed with instrumental broadening (as is common with LIBS systems/measurements), and can be considered independent processes, the resulting line profile is a combination of
Lorentzian and Gaussian line shapes. It is important to point out that due to the strong temporal evolution of the LIBS plasma parameters the magnitude of the doppler broadening and pressure broadening can vary significantly. The result of this convolution is a Voigt profile with a FWHM given by

$$\Delta \lambda_v = \Delta \lambda_L^2 + \sqrt{\left(\frac{\Delta \lambda_L^2}{2}\right)^2 + \Delta \lambda_G^2}, \quad (3.11)$$

where $\Delta \lambda_G$ is the line width of the Lorentzian profile and $\Delta \lambda_L$ is the line width of the Gaussian profile.

The presence of both Doppler broadening and the instrumental function will result in a single Gaussian line profile that is a convolution of two or more Gaussian profiles, and the FWHM in this case is given by

$$\Delta \lambda_G = \sqrt{\Delta \lambda_D^2 + \Delta \lambda_I^2}, \quad (3.12)$$

where $\Delta \lambda_I$ is the line width of the instrumental profile.

### 3.2 Spatial and Temporal Dependence of Emission in LIBS

#### 3.2.1 Introduction

Measurement of the spatial and temporal development of the LIBS plasma have provided an insight into the complexity of LIBS plasma, and have the potential to considerably improve the analytical usefulness of LIBS results.

#### 3.2.1.1 Spectra

Since existing elemental spectral intensity tables are based mainly on sources such as electric arcs, sparks, and gas discharges, one often finds that they are not directly applicable to the observed laser-induced plasma intensities. Further, tabulated positions and intensities of molecular emission features were measured using a number of different experimental setups including rarefied gaseous sample conditions, arc
Figure 3.2. Full ns-LIBS spectrum of a depleted uranium oxide pellet with a 1 µs gate delay.

Figure 3.3. LIBS spectra of a uranium oxide pellet are shown between between 405 and 411 nm [37].
Figure 3.4. LIBS spectra of a uranium and thorium mixed oxide pellet are shown between 405 and 411 nm with a clear matrix effect compared to the pure uranium oxide pellet [37].

discharge, or supersonic cooled gaseous flows as examples. It is, therefore, necessary to capture and analyze the spectrum of the elements and molecules of interest, uranium, copper, silicon, etc., using a ns and fs LIBS instrument. As an example, spectra were accumulated from single laser shots on a solid uranium (DUO$_2$) and mixed uranium thorium (ThO$_2$–UO$_2$) target. Spectra were captured after a delay of 2 μs using an integration time of 15 μs, which was chosen to maximize the emission intensity and SBR after temporal analysis of the U LIBS emission. Each spectrum covered a wavelength window of 405–411 nm and successive sets (accumulations) of measurements were taken with an Echelle spectrometer. The resulting spectra are summarized in Figs. 3.3 and 3.4 from [37]. A full high-resolution spectrum using a Echelle spectrometer with 1.0 μs gate delay, 10 μs integration window, and 200 accumulations for ablation initiated by 15 mJ ns laser is shown in Fig. 3.2. Barefield and Judge analyzed the observed spectral lines for both uranium and thorium, and reported that a small, but analytically important difference in the line positions was observed compared to the National Institute of Standards and Technology (NIST) [121] values that highlights the need to measure and characterize the spectra under LIP conditions [37, 34, 122]. For the majority
of elements related to nuclear forensics (Pu, Np, Am, Pb, Zr, Hf, etc.) a similar study as that described and shown in the literature for U must be conducted to properly identify and characterize the relevant emission lines.

3.2.1.2 Angular Dependence

Since the plasma images observed in LIBS are not spherically symmetrical, the emission line intensity will be an anisotropic function [29]. This effect is strongest for fs ablation where an oblong plasma is observed following laser ablation [92]. The line of sight along which the emission intensity is maximized will also be the one providing the optimum sensitivity in a single parameter optimization. Experiments were carried out to determine if there was a dependence of the measured emission intensities on the angle of light collection when the whole volume of the LIBS plasma was observed experimentally by Castle et al. [123].

Ma et al. and Charfia et al. reported on the change in spatial distribution of the LIBS plasma for Al/Ar and Mg/Na mixtures respectively [78, 95]. Their results indicated that a breakdown in the gaseous atmosphere above the target occurred when laser energies of 200 mJ at 7 ns were used, which resulted in decreased ablation and emission from the target material due to a major portion of the laser radiation being absorbed in the plasma formed in the gas.

Multari and Cremers [124] reported on the spatial and temporal distribution of the Cr 425 nm line emitted by the LIBS plasma when a flat target was tilted at various angles with respect to the incident laser beam. They concluded that after the plasma formed on the solid target, it expanded upward along the path of the
incident laser pulse for the first \( \sim 0.25 \mu \text{s} \), but once the chromium line emission became dominant over the continuum background, the emission appeared symmetric about the normal to the surface rather than along the axis of the incident laser pulse. The initial plasma plasma formation along the axis of the incident laser light can be explained by the formation of pre-ablation above the sample surface in the ambient atmosphere. It was found that the plume was generated in the perpendicular direction regardless of the laser angle; however, the maximum emission signal was obtained with normal incidence.

Most recently, Merk et al. reported on the diagnostic of a laser-induced plasma, using Abel inversion reconstruction of the radial distribution of the plasma [125]. The authors presented a new method for precise reconstruction of temperature and density distributions inside a LIBS plasma. The plasma radiation was collected in parallel rays from a thin plasma slice cut perpendicularly to the plasma symmetry axis utilizing direct imaging of the plasma onto the slit of a Czery-Turner spectrometer. After preliminary processing of collected intensities via Abel integral inversion, the obtained spatially resolved emissivities were analyzed assuming plasma partial LTE conditions for a pure sample and are presented in Fig. 2.1.

It has been reported that the spatial and temporal behavior of the transient emission generated by a LIBS plasma is rather complicated [63]. The different spatial and temporal distributions for the ionic, atomic, and molecular lines is to be expected during the existence of the plasma considering the dynamic shift in ionization equilibrium and the formation of molecules as the plasma initially heats up and then cools down. It has been observed that different atomic lines for a specific element have different time and space dependencies within the plasma. Therefore, measured time resolved spectra, to establish the most appropriate time interval producing an optimum signal to background ratio (SBR) – or whatever parameter is optimized – will be dependent on the specific volume of plasma being observed and the line of sight of the detector due to the use of a lens for coupling of the plasma emission light to the spectrometer and detector system. These additional variables affecting the LIBS emission should be considered together with the well documented, independent variables, such as the laser pulse duration and shape in time, the laser wavelength and energy, the physical and chemical characteristics of the target material, and the composition and pressure of the
surrounding environment.

With homogeneous samples in solid phase and constant laser and spectral measurement parameters, the LIBS plasma is a robust, reproducible emission source, which is a promising characteristic for analytical applications. It is proposed, that time resolved, high-resolution spectral imaging, and combined spatial imaging has the potential to considerably improve LIBS results and leads to a better fundamental understanding of the LIBS plasma.

3.3 Level Populations in LIBS

The amount of ablated mass and the characteristic elemental emission intensity in LIBS vary between measurements due to the fluctuations in the laser energy and beam quality. The elemental composition and homogeneity of the sample, the physical, the properties of the sample surface (roughness), composition and density of the ambient atmosphere, and phase of the sample all influence the LIBS emission. The variation in the ablated mass leads directly to the population of the energy levels involved in the observed emission fluctuating due to the increase or decrease in the amount of atoms “sharing” the energy in the plasma. The observation of the dependence of the LIBS emission on the latter sample properties and measurement parameters suggest that a strong matrix effect exists in LIBS measurements.

3.3.1 Emission

The intensity of a spectral line for an atomic transition emitted from the plasma is determined by the temperature of the plasma and the population of the atomic species in the upper level of the transition. The intensity of an emission line, $I^{ki}_\lambda$, corresponding to the transition between upper energy level $E_k$ and lower energy level $E_i$ of an atomic species can be given by

$$I^{ki}_\lambda = n_s^s A_{ki} = n_{tot}^s A_{ki} \frac{g_k e^{-E_k/k_B T}}{U_s(T)} ,$$

(3.13)

where $T$ is the plasma temperature (K), $n_s$ is the number density (cm$^{-3}$) of species $s$ at level $k$, $\lambda$ is the transition wavelength (nm), $n_{tot}^s$ is the total number density
(cm$^{-3}$) of emitting atoms for each atomic species, $g_k$ is the upper level degeneracy, $A_{ki}$ is Einstein’s A coefficient for spontaneous emission probability (s$^{-1}$), $k_B$ is the Boltzmann’s constant (J K$^{-1}$), and $U_s(T)$ is the partition function for the emitting atomic species at the plasma temperature (dimensionless).

### 3.3.2 Temperature - Line Ratio Method

The following assumptions are required for the use of the line ratio method for plasma temperature measurement:

- The plasma volume under observation is in LTE, the plasma is homogenous, and the plasma can be assumed to be in a steady state condition during the measurement.
- The plasma is optically thin for the spectral lines measured.

From the absolute emission intensity of two spectral lines (indexed $i$ and $j$) from different upper excitation energy levels, $E_k^{ij}$, of the same element and ionization state, the temperature is given by

$$T = \frac{E_j - E_i}{k} \ln \left( \frac{I_{jg_iA_i\lambda_j}}{I_{ig_jA_j\lambda_i}} \right),$$  \hspace{1cm} (3.14)$$

with the degeneracy of the upper levels denoted by $g$, the emission transition probability by $A$, and the wavelength by $\lambda$. The two-line method has the advantage compared to a single line radiance measurement in that the value for the effective path-length through the plasma, the total particle number density in the plasma, the partition function (degree of ionization), and the need for absolute spectral intensity calibration of the detection system are not required. There are practical considerations that must be observed when selecting a pair of emission lines for the two line method. The first consideration is that the emission line pairs be in close wavelength proximity. The second consideration is that the difference in upper energies of the two transitions as large as possible. The first criterion is beneficial in the sense that the absolute calibration of the detection system is unnecessary due to the close proximity of the emission lines as well as being able to measure simultaneously both emission lines in a narrow band detector (as is the case with a high-resolution Czerny-Turner type spectrometer).
3.3.3 Temperature - Boltzmann Plot Method

The two-line ratio technique can be extended to a larger number of emission lines from the same element and ionization stage. The addition of multiple emission lines is similar to applying a linear regression to a larger number of points to determine the slope and intercept of a line instead of fitting a line of best fit from just two points. Thus, the Boltzmann plot method leads to increased accuracy in the plasma temperature measurement compared to the two line method. Rearranging the emission line intensity equation for multiple lines, indexed $i$, from the same element and ionization stage gives the expression:

$$
\ln \left( \frac{R_i \lambda_i}{g_i A_i} \right) = -\frac{1}{T} \left( \frac{E_i}{k_B} \right) + \ln \left( \frac{h c l n_s}{4 \pi Z} \right),
$$

(3.15)

where $l$ is the effective path-length through the radiation source, $n_s$, the particle number density, $Z$ the partition function (degree of ionization) and the other symbols have been defined above.

We can treat the quantity $\ln \left[ \left( \frac{R_i \lambda_i}{(g_i A_i)} \right) \right]$ as the dependent variable and $E_i/k$ as the independent variable for a set of emission lines from the same species and otherwise identical conditions. The result of this arrangement is a linear relationship with a slope of $-1/T$ and a constant offset or intercept of $\ln \left[ \left( \frac{h c l n_s}{4 \pi Z} \right) \right]$. The Boltzmann plot also requires the calibration of the spectral intensity at each of the wavelengths used in the Boltzmann plot. It is possible to avoid absolute spectral intensity calibration of the instrument if emission lines in close wavelength proximity are used; however, emission lines that tend to occur in close wavelength proximity tend to originate from similar electron energy levels, which reduces the accuracy of the Boltzmann plot method. By incorporation of a large number of upper level transition energies (from which the individual transition lines originate), the resulting Boltzmann plot can be fit by a straight line through a number of points, which increases the precision in the calculated plasma temperature. Therefore, absolute spectral intensity calibration of the experimental instrument must be performed.
3.3.4 Electron Density - Stark Broadening Method

One method to find the electron density of the plasma is through the width of Stark-broadened spectral lines. Both the linear and quadratic Stark broadening are encountered commonly in laser plasma spectroscopy, as described earlier in this chapter. It is only possible to observe the linear Stark effect in H like ions, for all other atoms exhibit the quadratic Stark effect. This is the reason that ideally information about electron density is inferred from the lines of H or H like ions, where the half-width or FWHM of the emission line can be easily calculated from a linear relationship with great accuracy. In the case of a linear Stark effect, the electron density is related to the line width and is given by a simple relation [126]

\[ N_e = C(N_e T_e) \Delta \lambda^{3/2}_{FWHM}, \]  

(3.16)

where \( \Delta \lambda \) is the natural FWHM and the parameter \( C \) depends (weakly) on \( N_e \) and \( T_e \). The constant \( C \) for the H Balmar lines is available in the literature and can be treated as constant for most LIBS measurements [127, 126, 128]. The presence of H in the ambient atmosphere results in the \( H_\beta \) emission line being easily observed in LIBS measurements. The \( H_\beta \) emission line broadening is well known (with an error of 5%) [127], and due to the large amount of line broadening present the change in the FWHM of the emission line is easily observed. Gigosos et al. [129] studied the broadening of the \( H_\alpha \) and \( H_\beta \) emission lines using computer simulations and showed that the broadening (in nm) of the prominent \( H_\alpha \) emission line in LIBS spectra can be described as

\[ FWHM = 0.549 \left( \frac{N_e}{10^{17}} \right)^{0.67965} \]  

(3.17)

where \( N_e \) is the plasma density in \( e^{-} cm^{-3} \).

To a good approximation the FWHM of neutral atoms and ions broadened by the Stark effect is the sum of the broadening contributions from electron-impact and ion-impact broadening terms given as

\[ \Delta \lambda_{1/2}(A) = 2\omega \left( \frac{N_e}{10^{16}} + 3.5A \left( \frac{N_e}{10^{16}} \right)^{1/4} \times \left[ 1 - \frac{3}{4} N_D^{-1/3} \right] \omega \left( \frac{N_2}{10^{16}} \right) \right) \]  

(3.18)
where $\omega$ is the electron impact width parameter, $N_D$ represents the number of particles in the Debye sphere, and $A$ is the ion-broadening parameter. It is common in LIBS measurements to assume that the contribution to the overall Stark broadening of an emission line due to ion-impact broadening is small and can be neglected.

### 3.3.5 Electron Density - Interferometry Method

The method of interferometry makes use of modulation of an electromagnetic wave due to the difference in phase of two or several superimposed waves in order to measure wavelengths or characteristic properties of a medium through which the beam passes. In a Mach-Zehnder Interferometer (Fig. 3.6), the phase difference between a reference arm and the probe arm (that passes through the plasma) is measured. If the phase difference is created by the plasma over the path length $z_1 - z_2$ of the probe arm inside the plasma: then the relation between phase shift $\Delta \phi$ and density $n_e$ is given by [126]

\[
\Delta \phi = r_e \int_L n_e dl,
\]

where $r_e = e^2/(4\pi\varepsilon_0 m_e) = 2.82 \times 10^{-15}$ m. The integration extends over the path length $L$. This means the phase change of the interferometric signal is proportional to the product of wavelength of the probe ray and the line integrated density along the plasma path.
the beam path. Dividing the phase change $\phi$ by $2\pi$ gives the number of the fringes $N_f$

$$N_f = \frac{\phi}{2\pi} = 4.49 \times 10^{-16} \int_{z_1}^{z_2} n_z \partial z.$$

(3.20)

To record the data, a CCD is used, in which the signal level is proportional to the strength of the electric field. As it is not possible for the detector to resolve the individual frequencies $\omega_1$ and $\omega_2$ of the light wave, a constant signal with a temporal change in amplitude modulation due to the resulting phase shift of the probe arm to the reference arm is obtained ($E_1, E_2$ are the electric field strengths of the two rays).

$$E^2 = \frac{1}{2}E_1^2 + \frac{1}{2}E_2^2 + E_1E_2\cos(\phi)$$

(3.21)

In the interferometric technique, it is not simple in practice to distinguish variations of amplitudes due to other causes (vibrations, absorption, diffraction [e.g. due to an asymmetric plasma density]). This technique has the ability to measure the plasma density regardless of the LTE or non-LTE condition within the plasma; however, it is much more complicated to initially set up and align.

In plasma physics, different interferometer setups are frequently used for plasma density measurement; Mach-Zehnder interferometers (Fig. 3.6) are preferable if there is enough space for the reference ray to be guided around the plasma apparatus. If there is not enough space, a Michelson type setup is used, where the probe ray is reflected back from a mirror, thus passing the plasma twice. Within the LIBS literature, the use of both of the mentioned interferometer designs have been previously applied [130, 131].
Chapter 4

Experimental Characterization and Equipment Integration

4.1 Introduction

For accurate quantitative information to be obtained from any analytic technique, complete characterization of the experimental setup and data acquisition system must be performed. Several parameters had to be optimized and calibrated in this research, which includes the instrumental function, detector spectral efficiency, spectral calibration, ICCD gate delay and gate timing, MCP gain, and the number of laser shots accumulated/averaged.

4.2 Instrument Design

The schematic diagram of the experimental system used for LIBS experiments performed under both atmospheric and vacuum conditions, using both ns and fs laser pulses, is depicted in Fig. 4.1. It consists of both a ns and fs laser system, a Czerny-Turner spectrometer with 1200, 1800, and 3600 g/mm gratings and an Echelle Spectrometer (~5,000 λ/Δλ resolving power over 200-780 nm), a delay generator, and a computer for control and data acquisition. The CT spectrometer has both a ICCD and CCD coupled to the axial and side exits, respectively. The Echelle spectrometer has a ICCD coupled to the exit of the spectrograph. The ns laser is a
Figure 4.1. Experimental LIBS setup used in this work. Not shown is the interferometer for plasma density and shadowgraphic measurements and the pulse shape diagnostic equipment (autocorrelator/SPIDER).

Q-switched Nd:YAG laser (Spectra Physics) delivering a maximum pulse energy of \( \sim 80 \) mJ at the fundamental wavelength of 1064 nm with a \( \sim 10\)-ns pulse duration and the repetition rate of 10 Hz. The fs laser is a Ti:sapphire chirped-amplification system (Amplitude Technologies), delivering a maximum energy of 15 mJ centered at 800 nm with a pulse duration of 42 fs. Ti:sapphire laser pulse shaping can be performed using an acousto-optic modulator (Fastlite Dazzler\textsuperscript{TM} [132, 133]). The pulsed laser beam is focused to a \( \sim 200 \) µm diameter spot on the target by using a 2.5 cm diameter, 35 cm focal length lens. For the present research, a pulse energy of \( \sim 8 \) mJ for the ns laser and \( \sim 2.0 \) mJ for the fs laser is used, which provides an incident laser irradiance several times higher than the breakdown threshold.

Movement of the sample is accomplished through the use of a custom designed 3-dimensional translation stage driven by three Newport Picomotor\textsuperscript{TM} Piezo Lin-
ear Actuators to accurately position the sample. For all measurements, the samples are translated to a new spot on the sample surface after a number of laser shots set for the measurement conducted. The laser ablation pulse can be transported delivered through either free space or an optical fiber. Free space propagation of a laser pulse reduces dispersion and non-linear effects and allows for higher pulse energies compared to fiber coupling [61]. In addition, smaller focal spots are possible by use of free space propagation since the fibers required for delivery of a high-power pulse have to be multi-mode, with large fiber area. Delivery of the short laser pulse from the Ti:sapphire laser is limited to free space.

Plasma emission is collected either by a 100 mm diameter lens with a focal length of 20 cm transported through free space to the spectrometer or by a 25 mm lens and fiber system that couples directly to the spectrometer. Transport of emission from the plasma through free space allows maximum flexibility while maintaining good transmission properties when studying emissions over a wide spectral range of interest. However, many LIBS experiments implement optical fibers for the collection of plasma emission due to the ease in alignment. The focal length and diameter of both lens systems were chosen and optimized to match the $f$ number ($f\#$) of the spectrometer and, for the fiber setup, the numerical aperture (NA) of the fiber for optimal light collection and coupling. Once the NA of the fiber is matched and all the optical components comprising the collection and fiber coupling setup are mounted into a fixed lens tube, the entire system can be aligned easily and referenced to the sample surface to achieve maximum collection by back transporting a light source through the fiber.

A schematic of the timing sequence is shown in Fig. 4.2. In this particular timing mode, the laser acts as the master oscillator and provides a trigger to the pulse generator to open the shutter and to begin the gated detection. An oscilloscope was used to measure the sequence of the acquisition, which began from the output trigger sent out by the boxcar to the laser flash lamp. Due to the close occurrence of the trigger signal from the laser to the arrival of the laser pulse at the LIBS chamber (∼660 µs), a custom TTL (AND) gate logic circuit had to be designed and built. This was necessary due to the slow (∼4 ms) mechanical response of the shutter opening, which allows the laser beam to propagate down the LIBS table to the chamber when an acquisition is desired. When an acquisition
Figure 4.2. Schematic diagram of (a) cable connections and the corresponding (b) timing sequence used in the experimental system.

trigger is sent to the delay generator from the computer, the shutter opens synced to the first laser pulse and remains open, which allows only the subsequent laser pulse to pass through the shutter. Following the shutter opening, the TTL circuit synchronizes the intensifier of the ICCD detector to the subsequent laser pulse and the open shutter signal. This results in a precise timing of the ICCD gate and delay to within 0.5 ns, determined from the standard deviation of the fluctuation present in the output of the logic circuit when referenced to the input laser trigger.

A LabVIEW program was custom written (described in more detail in Section 4.3) to control the experimental setup. This required accurate focusing and optimization of the ICCD position and rotation on the spectrometer and knowledge of the spectrometer design parameters. By use of the focal length, angle of incidence, angle of diffraction, and offset angle of the detector plane for the spectrometer, the pixel position was converted into wavelength and used as a part of
the LabVIEW script.

For experiments carried out in vacuum or with radiological materials the chamber was pumped down to $10^{-4}$ Torr. One end of the vacuum chamber was connected to a roughing pump, turbo molecular pump, and a pressure gauge and digital controller through a three-way valve, and the other end was connected to a needle valve for use of other gas mixtures following the evacuation of the chamber.

All LIBS measurements were acquired either in a time gated mode with a variable gate delay and width or time-integrated, depending on the requirements of the measurement conducted and plasma or emission property studied.

### 4.2.1 Optimization of the Slit Width

The slit width was optimized in order to determine to which maximum width it could be opened to maximize the collected light while not significantly affecting the spectral resolution of the collection system. The optimization was carried out by illuminating the entrance slit with a Hg hollow cathode lamp (Fisher Scientific Co.), coupled to the spectrometer using a UV-VIS fiber (Horiba Jobin-Yvon) that is terminated at the spectrometer end via a linear ferule aligned to the spectrometer slit and at the opposite end by a circular arrangement of the fiber bundle. The measurements were taken with the ICCD set to a 100 µs gate and internal triggering. The ICCD was set to record a spectrum (full vertical binning) for spectral calibration and was set to output an image in order to align the linear fiber ferule to the spectrometer slit. The MCP gain was varied, depending on the emission line under investigation, to avoid saturation of the ICCD. Fluctuations in the hollow cathode power supply current were observed in the emission spectrum as fluctuations in the emission intensity of the emission lines that required several acquisitions to be averaged. Several Hg (within an Ar buffer gas) lines were recorded at ten different slit widths, starting from 15 µm to 100 µm in 5 µm intervals. Single accumulations were acquired and averaged over 10 measurements to produce the recorded spectra.

One of the spectral lines used in the optimization of the slit width was the Hg I at 435.84 nm; this emission line at different slits widths is shown in Fig. 4.4. It can be observed that the FWHM increases in proportion to the slit width at values
greater than 20–25 µm. However, at slit widths less than 25 µm, the FWHM remains approximately constant and is larger than the calculated geometric spectral bandpass. This is because the spectral bandpass is controlled by aberrations and diffraction as well as dispersion. It is evident from the wavelength considered that the resolution can no longer be improved even if the slit width is further decreased to values lower than 25 µm; hence, the slit width was set to 25 µm for all succeeding measurements to maximize both the light throughput and the resolution. It should be noted that the optimal width of the entrance slit is the same as the pixel size of the intensifier on the ICCD; thus, this result was not unexpected from the consideration of the broadening due to the entrance and exit slit widths.

Using the expression given in Eq. (3.10) for the diffraction-limited spectral bandpass, ∆λ_d, can be calculated for Hg I at λ = 435.84 nm using the following instrumental parameters:

- reciprocal linear dispersion, \( R_d = 0.81-0.53 \text{ nm mm}^{-1} \)
- focal length, \( f = 550 \text{ mm} \)
- effective aperture width, \( a = 78 \text{ mm} \)

The result of the calculation of the diffraction-limited spectral bandpass given the above spectrograph parameters is \(~0.0034 \text{ nm}\). This value is much smaller than the measured experimental FWHM, which is \(~0.032 \text{ nm}\). The difference in the calculated minimum diffraction-limited spectral bandpass and the measured FWHM of the spectral line profile is due to the pixel size of the CCD/ICCD, which limits the resolution of the measurement. The resolution of the detection system must be measured over \(~2.5\) pixels due to Nyquist sampling theory, which implies that for a CCD/ICCD with a pixel size of 22.5 µm, the limiting resolution at 435.84 nm is 0.0298 nm, which is closer to the experimentally determined FWHM.

4.2.2 Determination of the Instrumental Function

The determination of the instrumental function is fundamental to successful LIBS measurements. The influence of the instrument function on the measured emission spectrum becomes even more important when the width of the spectral line
profile from the plasma emission is comparable to the magnitude of instrumental broadening.

A Hg hollow cathode pen lamp was used to measure the instrument function. The Hg I emission line at 435.84 nm was fitted with a Gaussian line shape and the FWHM was derived from the output of the fit for slit-widths of 5–105 µm. The spectra are shown in Fig. 4.3, and the overlaid emission line for the range of slit-width is shown in Fig. 4.4. It is of interest to note that with an improvement in resolution (decrease in FWHM of the emission line), there is a trade-off in the amount of light that is coupled into the spectrometer, which can be seen by the

**Figure 4.3.** Full Hg spectra taken using a Hg hollow cathode lamp in an Ar buffer gas taken with the Czerny-Turner spectrometer and CCD with 5 ms exposure time.

**Figure 4.4.** Overlayed Hg I 435.68 nm emission line as a function of slit-width (µm).
Figure 4.5. FWHM (nm) of Hg I 435 line vs slit-width (µm) of the Czerny-Turner spectrometer and 1800 g mm$^{-1}$ grating.

![Graph showing FWHM vs slit-width](image)

Figure 4.6. Calibrated emission curves for the deuterium (black) and halogen (red) lamps of the DH-2000 calibration source.

![Graph showing emission curves](image)

decreasing peak intensity of the emission line in Fig. 4.4. It was found that an optimum slit-width of 20–25 µm produced the smallest FWHM, while allowing more light into the spectrometer compared to the 5–15 µm slit-widths.
4.2.3 Determination of the Detector Spectral Efficiency

The absolute spectral efficiency of the grating, ICCD camera, collection optics, and fibers must be known over the entire spectral range of interest as their response is usually not flat with wavelength. A NIST traceable calibrated deuterium and halogen (tungsten) light source (DH-2000; Ocean Optics) was used to calibrate the detection system. The theoretical response curves of the deuterium and tungsten lamps are shown in Fig. 4.6, and the experimental response curves of the detection system are shown in Figs. 4.7 & 4.8 for the echelle spectrometer. The deuterium and tungsten calibrated light sources emit light over different spectral ranges and have different absolute emission intensities. Due to the differences in the emission spectra for each lamp, separate acquisitions had to be carried out for the two wavelength ranges covered by the lamps. Once the measured spectra for each lamp were acquired, the measured intensity at each wavelength was divided by the theoretical intensity at the same wavelength, which resulted in a correction factor for each measured wavelength normalized to a single wavelength of interest (in this work the correction factor was normalized to 450 nm). The resulting spectral emission intensity correction factor normalized to 450 nm for the complete LIBS detection system using the CT spectrometer is shown in Fig. 4.9. The saw-tooth
like pattern in the correction factor is due to the variation of spectral efficiency across the grating.

### 4.2.4 Determination of the MCP Gain Calibration Curve

The ICCD detector in the LIBS instrument has the capability for the MCP gain to be varied, allowing the measured LIBS signal amplification to be varied. The dependence of the measured emission signal on the MCP gain for the Ocean Optics DH-2000 calibration lamp was measured and is shown in Fig. 4.10. Through normalization of Fig. 4.10 to a single MCP set gain, it is possible to correct for the gain used in LIBS measurements. The MCP gain correction is especially important for LIBS measurements where a large emission intensity range is expected, such as trace level measurements and remote sensing applications.

### 4.2.5 Sample Types, Preparation, and Characterization

An important parameter, and a controllable one at that, in LIBS research that is often overlooked are the samples used for LIBS analysis. It has been shown by Tawfik et al. [134] and Diwakar et al. [60] that a small amount of a contaminant or minor element within a sample can have a large effect on the observed plasma tem-
Figure 4.9. Correction factor for the spectral intensity calibration of the CT spectrometer, optical fiber coupling, and achromat collection lenses normalized to 450 nm.

Figure 4.10. Dependence of the measured emission signal from the Ocean Optics DH-2000 calibration lamp on the magnitude of the MCP gain.
perature and density and emission intensity. This is a well-known effect; however, the LIBS literature typically assigns a low importance to the purity of samples in comparison to the characteristics of the laser system.

To elucidate the complex plasma dynamics and chemistry occurring in the LIBS process, it is necessary to properly characterize and prepare the samples used. The LIBS technique is versatile; it can be applied to any sample type under almost any condition (as long as a line of sight to the sample surface can be maintained); therefore, the type of sample utilized is dependent upon the effect to be studied or the analytical objective. Aerosols produced from bulk samples are the simplest to use in order to guarantee purity and allow for the simplicity in creating mixtures of different elements or molecules.

For the matrix effect studies performed in this work a Perkin-Elmer Mira Mist Nebulizer was implemented to aerosolize ICP-MS standard solutions. The use of liquid standard solutions allowed for the straightforward mixing of the different binary elemental mixtures used in this work. Further, the high purity standards reduced the probability that a contaminant would be present and affect the measurement. Of concern to this study was the precise mixture of the samples, which is a limitation of using pressed powders. With pressed powders it is not possible to guarantee that the sample is homogeneously mixed before the sample is pressed, nor is it possible to vary the amount of one element in the mixture without reducing the mass of another element present in the sample. Although the mixing of the liquid samples changes the concentration of the bulk water, it can be assumed that the concentration of the bulk water in the plasma does not vary significantly due to the low concentration of the analyte present compared to the bulk water.

For LIBS measurements of nuclear-relevant materials, uranium metal samples were attached to scanning electron microscope (SEM) mounts, which were then mounted to a custom sample holder inside the sample chamber. Legacy uranium metal samples from the Radiation Science and Engineering Center at the Pennsylvania State University were used, which was was possible by amending the radioactive use license int the laboratory space where the LIBS setup was located. Gamma spectroscopy was performed on the depleted uranium (DU) and HEU samples to confirm their $^{235}$U enrichment of 0.4$\pm$0.045 and 98$\pm$3.63, respectively. A Canberra liquid nitrogen cooled LEGe detector with a Canberra Inspector 2000
multi-channel analyzer and Genie 2000 software along with the Multi-group Uranium Analysis (MGAU Version 4.2) software package were used to carry out the independent uranium enrichment measurements.

### 4.3 Hardware Integration and LabVIEW Software Development

Due to the use of equipment from multiple vendors and the need to accurately control not just the position of the sample but the laser pulse-shape and triggering as well, it was necessary to develop a LabVIEW interface for the experiment control and data acquisition. LabVIEW sub VIs and DLL libraries were requested for the CCD, ICCD, spectrometer, picomotors, pulse shaper, shutter, and delay generator. Each sub VI was integrated into a master LabVIEW control panel and is shown in Fig. 4.12. The exact timing of the sub VIs and the laser triggering was determined in order for the acquisition to occur in the proper order and for the sub VIs to avoid a time-out situation if the wait time between commands was excessive.

The distance translated by the picomotors proved to be inconsistent between the positive (out) and negative (in) directions. It was determined that this inconsistency was due to the spring tension in the translation stage that the sample is mounted on. One of the two springs in the translation stage was removed in an attempt to reduce the force required by the picomotors to translate the sample stage. However, the difference in translation was still observed and the last spring was necessary to keep tension on the stage and could not be removed. It was determined that a simple multiplier could be applied within the LabVIEW code to the translation distance to correct for the spring tension acting on the picomotor, thus removing the inconsistency in one translation direction.

Since the ICCD and spectrometer were obtained from two different manufacturers, it was necessary for the LabVIEW control program to also calculate the wavelength abscissa for each acquired spectrum. The manufacturer of the Czerny-Turner spectrometer (Horiba Jobyn Yvon) provided its schematic, which allowed the dispersion calculations to be used to calculate the wavelength at every horizontal position across the ICCD array for a given grating and center wavelength.
Figure 4.11. Labview wire diagram for the calculation of the wavelength axis for any given central wavelength position for the three installed gratings within the spectrometer.

The LabVIEW wire diagram for this calculation and virtual instrument (VI) file is shown in Fig. 4.11. To facilitate the spectral calibration of the spectrometer, a separate VI was written that acquired a spectrum of a known light source (Hg in ambient room lights). The spectrum of the known light source combined with the known position of the spectral lines for the given emission source was feedback into the pixel to wavelength calculation to generate a numerical offset, which served as the calibration for the specific grating being used. This effort was required for the useful operation of the ICCD with the spectrometer, and has since been used to support all investigations using this setup, including those conducted by other researchers.

It was determined iteratively that the ICCD VI requires the trigger signal from the laser arrive within $\sim$1 s of the start of the acquisition executable being run within the VI. By placing the laser trigger sub VI within the actual ICCD acquire VI, the timeout could be avoided as the exact timing and flow of the two programs could be controlled through simple linear sequences and wait commands. Further, a wait command was included in the program to delay the readout of the data from the ICCD for 1 s in order to allow a complete acquisition of the data. The control of the ICCD gate and delay width is controlled from within the LabVIEW program. It was discovered that the supplied gate delay DLL contained an error and was not being read by the ICCD when the command was executed, which required a software patch in order to become functional. The manufacturer of
the ICCD (Andor) was able to provide this patch in the form of a new software development kit (SDK). The type of image, number of images, and acquisition type are also controlled from within the program, and the commands for these functions were found within the provided LabVIEW templates by Andor. Of special interest is the ability to control the multi-channel plate (MCP) and preamplifier gain. However, VIs for the control of these two gain settings were not provided in any of the Andor templates, and required editing of the actual DLL libraries that control the ICCD settings and creation of new VIs. This resulted in a LabVIEW control panel that could be easily automated for control of the ICCD gate width, gate delay, MCP gain, preamp gain, acquisition type, image type, and cooling of the camera.

This work on hardware integration and software development fulfilled a necessary requirement for complete experimental functionality and data acquisition and also enabled LIBS measurements to be performed by several other researchers using this setup.

4.4 Summary

In summary, to conduct a fundamental analysis of the physics involved in the LIBS process, it is necessary to properly characterize the experimental system and samples to be used. As it has been shown, the LIBS emission is very sensitive to
small changes in sample composition. This requires a complete characterization of the sample to elucidate the physical processes involved. It is also important to understand how certain factors, such as the change in atom density of ablated material when adjusting concentration of mixed samples, contribute to the results of measurements. This is because such effects will have to be deconvolved or understood to draw conclusions about the interaction of different elements or plasma parameters on the LIBS emission.
Matrix Effects in Atomic Emission Spectroscopy and Laser Ablation Techniques

5.1 Introduction

Two attributes of LIBS have made it attractive to researchers and analysts: non-invasiveness, requiring small amounts of a sample to be analyzed, and a need for minimal or no sample preparation. Those characteristics are also partially responsible for limited accuracy and precision in some circumstances. Since only a small amount of material is ablated and ionized/excited within the LIBS plasma, the accuracy and precision of the measurement can be dependent on the homogeneity of the sample and the fluctuations in the amount of the ablated material from the sample. Due to the limited sample preparation or lack thereof, the LIBS measurement can be dependent on the physical characteristics of the sample surface, such as the surface roughness. The surface roughness and shape can further affect the LIBS signal due to the distance between the laser focusing lens and the sample surface varying across the surface of the sample. A better understanding of the variables that affect the LIBS signal should improve the analytic capability of the LIBS technique for more complex samples, such as those used in nuclear forensics analysis.
Due to the variation in the mass removed by each laser pulse, the density of atoms in the plasma can fluctuate. If the ablated mass varies among laser pulses, both the temperature and density of the plasma can fluctuate. The fluctuation in the key plasma parameters leads directly to variation in the measured LIBS spectrum. The laser pulse stability, sample composition, sample phase, sample rigidity, and the laser focusing conditions can all affect the amount of mass ablated from the sample on each laser shot.

With recent advances in laser technology which resulted in more portable and reliable fs lasers, fs laser systems are becoming both more prevalent and preferred in LIBS measurements for both laboratory-based and in-field analyses [135, 136]. One consequence of using fs lasers in LIBS is the increase in complexity of the LIBS measurement due to the variation in laser parameters, not only within the set of measurements taken or on a day-to-day basis, but also when attempting to compare the results of measurements to previously reported results in the literature. This is especially the case for large, complex, research laboratory-based Ti:sapphire systems. The laser energy, stability, spectrum, beam quality, and pulse duration can vary greatly among various Ti:sapphire laser systems. A number of earlier publications (Chapters 1&2) have reported on the effect of the laser parameters on the measured LIBS signal.

5.2 Background

In the case of metallic samples, a stronger matrix effect has been observed for alloys with high Zn contents, like brass. Two main effects originate from the change of material composition and structure. One of them is the loss of the sample stoichiometry in the laser ablation process. Borisov et al. [137] studied laser ablation of Cu/Zn binary alloys using ICP-MS and observed an evolution from fractionation at low irradiances to stoichiometric ablation above certain irradiance. The threshold for stoichiometry was $\sim0.2$ GW cm$^{-2}$ for a 30 ns KrF excimer laser and $\sim10$ GW cm$^{-2}$ for a frequency doubled Nd:YAG laser emitting 30 ps pulses. It is common in analytic techniques to generate a calibration curve that directly relates the concentration of an analyte of interest to the magnitude of the measured signal. At irradiances at which stoichometric ablation is observed, non-
linear calibration curves for both Cu and Zn were obtained, which were explained by a change in mass ablation rate for samples with different composition. When the Zn signal was normalized to the Cu signal or to the crater volume, linear calibration curves were obtained. The variation of the ablation rate is a second type of matrix effect, and is related to the characteristics of the LIP, including the atom number densities, the temperature, and the electron density. Chaleard et al. [138] also observed different slopes of the calibration curves of Cu for brass samples with respect to Al and steel samples, which appeared on the same curve. A XeCl excimer laser emitting 28 ns pulses at 308 nm was used as the ablation source in air at atmospheric pressure. An efficient correction of the matrix effects was obtained by normalization of the emission signals by the acoustic signal emitted by the plasma, which is proportional to the vaporized mass and the excitation plasma temperature.

Matrix effects were also observed in samples without significant Zn content. Quentmeier et al. [139] measured significant changes in the plasma temperature and density in the LIP in samples with Cu, steel, and Al matrices using an infrared Nd:YAG laser of 8 ns pulse width under an argon atmosphere at 140 hPa pressure. The observation of variation in the plasma density and temperature for Al and steel alloys was also reported by Ismail et al. [140]. In spite of the different conditions for laser ablation in these experiments, which could partly explain the discrepancies, it is clear that a complete description of the phenomenon requires obtaining information about the atom number density, the other parameter that determines the calibration curves, in addition to temperature.

In some earlier work the characteristics of LIPs of Fe-based samples were compared. Leis et al. [141] obtained considerable differences in the temperatures of LIPs generated from binary Fe/Cr samples with Cr concentrations from 0 to 90%. The authors measured the crater volume and found that for higher concentrations of Cr within the sample, both a lower plasma temperature and increased mass removal were observed. Matrix effects in LIPs of high-alloy steels were investigated by Vrenegor et al. [38], where the authors compared the influence of single and double pulse laser ablation. The authors further showed that the use of inter-element corrections could be applied to reduce the standard deviation of the calibration curves. To investigate if the residuals could be explained with differences in the
plasma parameters, the temperature and electron density were determined for the plasmas produced from three to four samples. It was concluded that the changes in the plasma state may have existed, but could not be detected experimentally, since the relative errors of determination of the plasma parameters were of the same order of magnitude as the inter-element corrections. The results of this work indicate the need for accurate characterization techniques to investigate matrix effects, which may lead to smaller variations of the plasma parameters.

5.3 ICP-AES

Due to the similarity between ICP-AES and LIBS, it is of interest to perform a brief review of the literature on the observed matrix effects in ICP-AES. It is possible to draw similarities between the two spectroscopic techniques and, thus, the extensive work performed on elucidating the matrix effects in ICP-AES could lead to a description of the origins of and methods to mitigate matrix effects in LIBS.

In the ICP-AES technique, the matrix composition has been shown to affect the signal of the analyte of interest, as shown in Fig. 5.1. The presence of matrix effects in ICP-AES has been well observed [143, 107]. An example of such studies is the work by Todoli et al. [45], where the authors studied the effect that the concentration of acid in the ICP-MS standard solutions has on the measured
Figure 5.2. Influence of Na, Ca, Ba, and La on the measured ICP-AES ionic-to-neutral emission ratio [142].

The correction for this kind of matrix effect is straightforward, and involves the standardization of the acid and its concentration within the liquid samples introduced into the instrument.

Similarly, another type of matrix effect that is inherent in the ICP-AES technique is the dependence of the measured analyte signal on the presence of samples of different elemental composition. This type of matrix effect is not as easily addressed due to the inherent difference in the elemental composition of different samples and the fact that the absolute concentration of elements within the matrix is not known a priori.

Blades et al. [144] studied the effect that the spatial distribution of the elements within an ICP plasma has on the measured emission signal. The authors found that the ionization potential of the buffer gas plays a minimal role in the observation of the matrix effect in ICP-AES. The study, which dealt primarily with alkali metals, found that the increase in the alkali metal emission signal was observed primarily within the lower section of the ICP plasma channel, where the plasma density and temperature are highest. The authors proposed that this increase in the emission signal was due to the increase in the amount of collisional excitation that occurs in the lower section of the ICP plasma channel. Lastly, the authors found that matrix effects were observed when elements with low first ionization potentials were present in the sample matrix.

The first and second ionization potential of the elements within the sample
matrix has been considered within the literature as an important parameter that affects the observation of matrix effects [107, 145]. The ionic-to-atomic emission line intensity ratio for Zn, Mg, Cd, and Fe as a function of the elemental composition of the matrix is shown in Fig. 5.3. The effect of the ionization potential on the ionic-to-atomic emission line ratio for Zn is shown in Fig. 5.4. There is no obvious correlation of the ionic-to-atomic emission line ratio to the first ionization potential of the sample matrix; however, the first ionization potential of the element composing the matrix does have an effect on the AES emission.

**Figure 5.3.** Influence of 1st and 2nd ionization potential of the matrix on the ionic-to-atomic emission line ratio for Zn, Mg, Cd, and Fe ICP-AES analysis [145].
The mixture of different matrix compositions where a matrix effect is observed has not been observed to result in an additive increase in the matrix effect. Maessen et al. [146] studied mixtures of sodium, potassium, calcium, and magnesium in separate binary solutions with an analyte of interest to mixtures containing multiple combinations of these elemental solutions. The authors observed that binary combinations of sodium, potassium, and magnesium resulted in a more prominent matrix effect than the sum of the effect observed for the binary mixtures.

There have been a number of phenomena proposed in an attempt to explain the origin of the plasma-related matrix effects [107, 145, 144]: (i) energy consumption for the atomization of the matrix, (ii) shift of the ionization equilibrium, (iii) changes in the excitation conditions, (iv) Penning ionization, (v) ion-electron recombination, (vi) diffusion, vaporization, (vi) volatilization, and (vii) thermal conductivity.

Although work has been performed to evaluate the impact that those phenomena have on the observation of matrix effects in ICP-AES, the LIBS literature is lacking in similar studies of how the physical properties (specifically the ionization potential) of the matrix or contaminant elements effect the analyte signal.
Matrix effects have been observed in laser-ablation inductively coupled mass spectroscopy (LA-ICP-MS) for both ns and fs laser ablation systems [147], despite the fact that the laser is used only as a means of sample introduction and not excitation. Heino et al. in 2001 studied UV (266 nm) and IR (1064 nm) laser ablation of glass samples, and the fractionation effects associated with the two laser wavelengths. The authors observed that when all other laser parameters are maintained that the LA-ICP-MS elemental response was dependent on the chemical composition and also physical structure of the matrix, as shown in Fig. 5.5.
It was proposed that this dependence is due to the change in the amount of ablated material that occurs following irradiation of the sample by the UV or IR laser. Further, it was observed that the matrix effects were more prominent for the IR laser compared to the UV laser. The observation of the matrix effect between the different laser wavelengths suggested that fractionation occurs within the ablation process. Although fractionation was observed to be less prominent for the IR laser, the effect was not completely overcome. The authors concluded that the main source of fractionation within the ablation process was due to physical properties of the particulates and vapor phases following ablation.

This brief literature review concerning matrix effects in LA-ICP-MS is of interest to the consideration of the matrix effects associated with LIBS, due to the role of a laser in LIBS as a means for both sample introduction (ablation) and excitation.

5.5 LIBS

There are many ways to improve the reproducibility of LIBS, ICP-AES, LA-ICP-MS measurements. Chemometric techniques and correction of analytical signal, as reported in Ref. [75], are some possibilities, but a routine method for improving the reproducibility is the use of an internal standard.

A general thermodynamic criterion exists for choosing the emission line of the matrix element to be used as an internal standard, and that is the closeness of the upper level energy of the internal standard line to the line being measured. This is not a sufficient criterion for the choice of an internal standard as it implies plasma conditions (LTE) that may or may not exist during the measurement. In some cases, this criterion is sufficient and provides good results; however, it has been observed that the use of an internal standard can actually reduce accuracy. This is because factors such as fractionation, deviations from LTE, and the strong heterogeneity of the laser plasma and the strengthening of self-absorption lines of the matrix elements due to this heterogeneity additionally influence the LIBS signal. It is obvious that it is necessary to establish additional criteria to select an appropriate internal standard. The application of an internal standard means that the reference and the analytical line intensities are both related to the fluctuation
in parameters during the ablation and emission processes. To avoid the criteria for the choice of an internal standard being based solely on the model of the ablation process, the spectrum as a whole must be considered, and the correlation of the multiple matrix elements and their emission lines to the observed fluctuations in the analyte’s emission lines or an unknown minor contaminants emission lines must be considered [148].

The assumption of stoichiometric ablation forms the foundation of the LIBS technique and is necessary for the analysis of the measured emission spectra. The presence of non-stoichiometric ablation results in the measured LIBS signal not being representative of the composition of the irradiated sample. The occurrence of non-stoichiometric ablation in the LIBS measurement is referred to as fractionation and is another form of a matrix effect [106]. Fractionation has been studied and observed in other spectroscopic techniques like ICP-AES & ICP-MS discussed earlier [45].

Diwakar et al. studied the matrix effects observed in LIBS measurement of aerosols generated from binary mixtures of ICP-MS elemental solutions using a Nd:YAG laser (1064 nm, 260 mJ, 20 ns) [60]. The authors performed temporally resolved LIBS measurements of 1:1 and 1:9 binary mixtures of Na:Cu, Na:W, and Na:Zn. A 50% increase in sodium analyte emission was observed for the 1:9 binary mixtures. The enhancement in the emission was observed to initially increase in the first $\sim 15 \mu s$ and was greatly diminished by delay times of 60 $\mu s$. The authors suggested that the observed enhancement in the Na analyte emission was due to localized particle interactions within the larger aerosol plasma.

The same group studied the bulk and local plasma properties in order to elucidate the time scales under which heat and mass diffusion equilibrium exist, which was proposed by the authors as the driving force behind the observation of the analyte emission enhancement in binary aerosol particles [97]. However, the authors chose not to investigate the same binary aerosol mixtures that they reported on in earlier work [60]. The local plasma properties were derived from the analyte of interest, while the bulk plasma properties were derived from the Ar and H found in the aerosol spray. From the temporally resolved emission spectra and comparison of the bulk and local plasma properties the authors concluded that finite heat and mass diffusion rates exist, which is contrary to the assumption of
near instantaneous diffusion and dissociation of the sample in the LIBS plasma.

5.6 Elucidation of the Matrix Effect in Na Aerosol LIBS Measurements

5.6.1 Motivation

As a whole, the previous work on the presence of matrix effects in aerosol mixtures within the LIBS literature suggests that the rate of heat transfer from the bulk plasma to the particle, the mass diffusion rate, and the rate of plasma cooling are on the same time scale of the LIBS measurement. It is therefore necessary to understand the complex temporal behavior of the aerosol plasma that cannot be described as the result of near instantaneous dissociation of the aerosol particles. Further, the establishment of heat and mass diffusion equilibrium cannot be assumed to occur shortly after the formation of the aerosol plasma. In the previous work by Diwakar et al. [60], the authors reported on the observed matrix effect in Na:Cu and Mg: Cd binary mixtures. The authors showed that the plasma parameters (temperature and density) varied over the lifetime of the plasma, and postulated that the variation in the local (aerosol) and bulk plasma properties resulted in the enhancement of the Na emission in the presence of a bulk matrix component. The local plasma temperature was observed to increase at later plasma lifetimes, which is in contradiction with a vast number of LIBS work within the literature [97]. Further, the authors lacked evidence of the establishment of LTE within the aerosol plasma as neither the plasma density nor an example of the Boltzmann plot used to calculate the plasma temperature was provided within the work. For low density aerosol sprays the plasma density can be multiple orders of magnitude lower than plasma formed following laser ablation of a solid sample. Therefore, the increase in the plasma temperature at later plasma lifetimes could be the result of an error in the assumption of LTE being established. The bulk temperature was observed to decrease over time; however, similar to the local plasma temperature calculations, no evidence for the support of LTE being established was provided.

It is conjectured that the aerosol particle draws energy from the bulk plasma
(through heat diffusion) in order to dissociate and ionize. The existence of heat diffusion from the bulk plasma to the aerosol particle was observed by Diwakar et al. [60] through inflections observed in the ion-to-atom ratio of Mg in the LIBS measurement at around 15-20 µs following laser irradiation. Similar heat diffusion effects have also been observed in ICP plasmas [149].

The main goal of this work is to further investigate the physical phenomena responsible for the observation of a matrix effect in Na-containing aerosol LIBS measurements. An additional goal is to determine the effect of the chemical properties of the bulk matrix element (specifically the IP and volatility) on the LIBS measurement. To accomplish these goals, an \textit{ab initio} modeling and experimental effort was conducted to elucidate the complex plasma and optical emission behavior of Na in the presence of a bulk matrix component.

\subsection{5.6.2 Aerosol Experimental Setup}

The LIBS system used for this work implemented the same major components of the LIBS measurement system shown in Fig. 4.1. However, instead of mounting a solid sample to the translation stage, the translation stage was removed and replaced with a Perkin-Elmer Mira Mist nebulizer. Said nebulizer was connected through capillary tubing to a peristaltic pump, which draws liquid from the sample vial. The nebulizer also required an argon gas source to generate the aerosol spray, and pressure was maintained at a constant 45 psi for all measurements.

The liquid samples, which were nebulized to produce the aerosol spray, were prepared from SPEX CertiPrep ICP-grade elemental standards. Specifically, 10,000 µg/mL solutions of the elemental standards were diluted and mixed to generate 1:0, 1:1, and 1:9 binary mixtures with a constant Na mass density of 1,000 µg/mL. Ultra-purified water was used to dilute the ICP-standard solutions. For this work Na:Cu, Na:Ni, and Na:Si binary mixtures were used. The flow rate of the peristaltic pump was maintained at 0.25 mL/min for all measurements.

The fundamental frequency of the Nd:YAG laser (1064 nm, 80 mJ, 20 ns) was focused into the aerosol spray by a 10 cm focal length to generate the aerosol LIBS plasma. The plasma emission was collected at a 45° angle by a 55 mm focal length 25 mm lens and coupled to the spectrometer through an optical fiber, and 1,000
individual laser shots were accumulated for each aerosol LIBS measurement. The large amount of accumulated laser shots was necessary for two reasons: (i) during laser ablation it was observed through focused shadowgraphy that it was possible for between one and three aerosol droplets to be simultaneously irradiated by the laser pulse that leads to significant variation of the measured plasma emission and (ii) the overall low intensity of the emission signal.

### 5.6.3 Results

The enhancement of the Na D line emission intensity when copper is present in bulk quantities (concomitant mass) within the aerosol spray was first observed in a LIBS measurement by Diwakar et al., and is shown in Fig. 5.7 from Ref [60]. The characteristic emission is measured as the peak to base intensity, and the emission enhancement ratio is defined as the ratio of the peak emission intensity of the Na D line with a concomitant mass to the Na D line emission intensity without a concomitant mass. The sodium emission intensity is greatly increased in the Na:Cu binary mixture compared to the pure Na aerosol spectrum, despite the constant sodium mass density.

The Los Alamos National Laboratory (LANL) ATOMIC suite of atomic structure and plasma emission codes was used to generate synthetic plasma emission
spectra for the pure Na and 1:9 Na:Cu aerosols. The \textit{ab initio} LIBS emission modeling starts with atomic structure calculations performed by solving the Hartree-Fock equations for the neutral (I) and singly ionized (II) ionization states for each element of interest. The accuracy of the modeling performed by the ATOMIC code is sensitive to the accuracy of the underlying atomic data. The calculated electron energy levels are within 1\% of the reported values in the NIST atomic database \cite{121}. However, a 1\% difference in the electron energy level translates to a 5–10 nm error in the predicted center wavelength of the emission wavelength. A 5–10 nm error in the calculated emission line positions results in a predicted LIBS spectrum that would be impossible to compare to experimentally acquired LIBS spectra; therefore, the calculated energy levels are adjusted to their experimentally measured values reported in the NIST atomic database \cite{121}. The atomic transition probabilities and atomic collision quantities are also computed in an \textit{ab initio} manner. The \textit{ab initio} modeling performs LTE calculations that generate level populations and, subsequently, the total emission spectrum for the copper plasma for a range of electron temperatures and densities typical for LIBS.

The input to the ATOMIC required the knowledge of the mass density of
Figure 5.9. Aerosol LIBS measurements of the Na:Cu binary mixture for the mass density ratios given in the figure. An acquisition gate delay of 15 µs and gate width of 1.0 µs was used for the measurement.

the elements within the LIBS plasma, which was estimated to be 0.01 mg/cm$^{-3}$. Further, the plasma temperature was required to be known a priori and was estimated to be 0.8 eV. The result of the ATOMIC modeling is shown in Fig. 5.8. The ATOMIC model predicts a nearly identical enhancement in the Na emission intensity as that reported in the previous work. The ATOMIC model is able to calculate a number of important plasma characteristics including plasma density, ionization, and opacity. The plasma density predicted by the ATOMIC model increased by from $1.19 \times 10^{18}$ to $1.59 \times 10^{18}$ e$^{-}$/cm$^3$) for the 1:9 Na:Cu mixture compared to the 1:1 Na:Cu mixture. Further, the ATOMIC model showed that the free-electron-to-atom ratio decreased from 0.59 to 0.16 for the Na:Cu 1:0 and 1:9 aerosol mixture, respectively. From Eq. 3.13, the atomic emission intensity is related to the electron density through the ionization state of the plasma.

It is not possible to perfectly recreate the experimental conditions under which the previous LIBS work was carried out; however, the experimental setup used in this work implemented a similar nebulizer system and used the same ICP elemental standards to generate the aerosol spray. It was of interest to first attempt to repeat the previously reported LIBS measurements by Diwakar et al. and verify
Figure 5.10. Temporal behavior of the enhancement factor observed in the LIBS measurement for the Na:Cu binary aerosol mixture. A constant acquisition gate width of 1.0 µs was used in the measurement.

the generality of the enhancement result for Na with a concomitant mass [60]. The result of the new aerosol LIBS measurement is shown in Fig. 5.9, and a nearly identical emission enhancement is observed compared to the previous work. The temporal behavior of the emission enhancement for the 1:9 Na:Cu aerosol mixture is shown in Fig. 5.10. The peak enhancement is observed at an acquisition delay of ∼15 µs. The presence of a strong background at early times within the plasma (∼1–3 µs) results in an initial decrease in the emission enhancement, and in general the emission enhancement increases to its peak value of ∼2.5 at ∼15 µs before decreasing. In contradiction to the previous work, the emission enhancement for 1:9 Na:Cu mass ratio is initially below one and gradually increases to its peak value. The temporal behavior in the enhancement factor was repeatable and measurements were performed on multiple days to confirm the generality of the new result.

Based on the new results, which have been supported by ab initio modeling, and the discussion within the literature on the influence of elemental properties of the concomitant mass on the measured atomic emission, additional measurements were carried out using Ni and Si as the concomitant mass.
Similar ATOMIC modeling was carried out for a binary mixture of Na and Ni at a 1:9 mass-density ratio. It was predicted that, due to nickel’s similar elemental properties, a similar temporal Na emission behavior would be observed for binary aerosols with Ni as the concomitant mass. Ni has a similar first IP of 7.63 eV compared to 7.72 eV for Cu, and also has similar values for heat of vaporization ($\sim$300-360 kJ/mol). The result of the ATOMIC modeling is shown in Fig. 5.11, and a clear enhancement similar to that for Cu is seen with Ni. Similar to the result for Cu, the ATOMIC model indicated an increase in plasma density and decrease in the free-electron-to-atom ratio occurred for Na:Ni 1:9 aerosol mixture. The enhancement of the Na emission for the 1:9 aerosol samples is due to the increase in the density of Na I species within the plasma, which occurs due to presence of a concomitant mass. The higher IP of the concomitant mass reduces the plasma ionization state through an increase in the amount of energy required to ionize the aerosol mixture.

The result of LIBS measurements of aerosols containing only Na and of aerosols containing a 1:1 and 1:9 mass density ratio of Na:Ni is shown in Fig. 5.12. A similar enhancement in the Na emission intensity is present in the LIBS measurement for
Figure 5.12. Aerosol LIBS measurements of the Na:Ni binary mixture for the mass density ratios given in the figure. An acquisition gate delay of 15 μs and gate width of 1.0 μs was used for the measurement.

Figure 5.13. Temporal behavior of the enhancement factor observed in the LIBS measurement for the Na:Ni binary aerosol mixture. A constant acquisition gate width of 1.0 μs was used in the measurement.
Na: Ni mixed aerosols, and at low Ni mass densities (1:1 mixture) the enhancement in the Na emission is observed. The temporal behavior of the enhancement factor for the Na: Ni binary aerosol mixtures is shown in Fig. 5.13. The peak Na emission enhancement is observed for both the 1:1 and 1:9 mass density mixtures and occurs at ~15 µs, which matches the results for Cu as the concomitant mass shown in Fig. 5.10. An initial fluctuation in the value of the Na enhancement factor is observed for the Na: Ni binary aerosol mixture similar to the Na: Cu results, and this is due to the decay of the continuum background and the rapid cooling and expansion of the plasma at early times within the plasma evolution. Further, a similar temporal behavior was observed for both the 1:1 and 1:9 Na: Ni aerosol mixtures. These two results suggest that the enhancement in the Na emission is a general result and appears to be related to the mass density of the concomitant mass. However, the overall magnitude of the Na emission enhancement was lower for the Ni mixture compared to the Cu mixture.

Due to the similar elemental properties (first IP and heat of vaporization) of Ni and Cu, it was of interest to investigate the behavior of the measured LIBS emission for Na aerosol with Si as a concomitant mass. Silicon is a metalloid with a higher first IP (8.16 eV) and has approximately half the atomic mass of Ni and Cu. It is expected that the temporal behavior of the Na emission would vary for the Si mixtures compared to the Ni and Cu mixtures. The result of LIBS measurement of the Na: Si mixed aerosol samples is shown in Fig. 5.14. For the 1:0 and 1:1 Na: Si aerosol samples a nearly identical emission was observed; however, for the 1:9 Na: Si mixture a clear enhancement in the Na emission intensity was measured. ATOMIC modeling was not available for this aerosol mixture for comparison to experimental results. The temporal behavior of the Na emission enhancement is shown in Fig. 5.15 for the Na: Si mixed aerosol samples. A similar initial (1–5 µs) behavior is observed for the value of the Na enhancement factor for the Na: Si aerosol samples compared to the Na: Ni and Na: Cu samples. Additionally, similar to the Na: Ni and Na: Cu mixtures, the peak Na emission intensity was observed at ~15 µs for the 1:1 and 1:9 Na: Si aerosol mixtures (not including the first ~5 µs of the plasma emission where the continuum emission influences the measured Na intensity). Further, the Na emission intensity enhancement scales with increasing Si mass density. These results show that a higher first IP and heat of vaporization
Figure 5.14. Aerosol LIBS measurements of the Na:Si binary mixture for the mass density ratios given in the figure. An acquisition gate delay of 15 µs and gate width of 1.0 µs was used for the measurement.

(∼380 kJ/mol) of Si compared to Ni and Cu does not cause a significant change in the temporal behavior or overall variation in the Na emission enhancement. Further, the lower mass of Si compared to Cu and Ni will result in a decreased rate of cooling within the plasma and could further delay the observation of the peak Na emission enhancement, as the Na D line emission results from the atomic emission of Na. The concomitant mass is responsible for variation in a number of plasma parameters, including the plasma density, temperature, and ionization state.

The result of the ATOMIC modeling suggests that the observed increase in the plasma density for Na aerosol particles with a concomitant mass present could be responsible for the measured increase in the Na emission intensity. It was possible to simultaneously observe multiple Cu characteristic emission lines within the Na:Cu aerosol plasma as shown in Fig. 5.16. However, for Ni and Si it was not possible to observe the characteristic emission lines of these elements due to both the low intensity of the characteristic emission lines and the presence of spectral interferences at the location of the most intense emission lines. The spectral interferences consisted of CN and C\(_2\) molecular emission bands, which originated
from elements within the ambient atmosphere. As the concomitant mass was increased the free-electron-to-atom ratio decreased, which resulted in a decrease in the amount of continuum emission (bremsstrahlung) measured (for a given acquisition delay and width), as shown for the 1:1 and 1:9 Na:Cu aerosol mixtures in Fig. 5.16.

Through the use of Eq. 3.18 it was possible to extract the local plasma density of the Na:Cu aerosol plasma. Equation 3.18 was simplified through the assumption that the ion broadening was negligible for the LIBS plasma, and values for the electron impact parameter were found in the literature [150, 151, 152]. The intense characteristic 510.55 nm Cu I emission line was chosen for this analysis and was fit by a Voigt spectral line shape. The Lorentzian component of the Voigt line shape was extracted and the instrumental broadening was subtracted to obtain the broadening of the spectral line due to the Stark effect. The plasma density was calculated to be $1.1 \times 10^{17}$ and $7.5 \times 10^{16}$ e$^-$/cm$^3$ for the Na:Cu 1:9 and 1:1 aerosol mixtures, respectively. The plasma is assumed to be in quasi-LTE conditions (collisionally dominated), satisfying the McWhirter criterion [153], which sets the
lower bound on the electron density for LTE conditions as

\[ n_e \geq 1.6 \times 10^{12} \frac{T_e^{1/2}}{T_e} (\Delta E)^3 \text{ cm}^{-3}, \]  

(5.1)

where the electron temperature \( T_e \) is in K and the energy of the transition \( \Delta E \) is in eV. For a neutral Cu plasma with transition energies in the range of 3–6 eV and plasma temperature of 0.8 eV, a plasma with density \( \gtrsim 2 \times 10^{15} \text{ e}^{-/\text{cm}^3} \) would satisfy this criterion.

The 510.55 and 521.82 nm Cu I emission lines were used to calculate the plasma temperature through the use of Eq. 3.14. The plasma temperature for the 1:1 and 1:9 Na:Cu aerosol mixture was calculated to be 0.59 and 0.57 eV, respectively. The error in the plasma temperature calculation is \( \sim 20\% \) due, primarily, to the error in the spectroscopic information found in the NIST database [152, 121].

It was not possible to calculate the local plasma density or temperature for the pure Na aerosol plasma due to the lack of copper or other observable analyte emission within the aerosol plasma. However, due to the presence of water in bulk quantities within the aerosol plasma it was possible to calculate the bulk plasma density for the pure Na aerosol and the 1:9 Na:Cu aerosol. An example of the Voigt fit applied to the Hydrogen alpha (H\( \alpha \)) emission line at 656.28 nm observed in the Na:Cu 1:9 aerosol LIBS spectrum is shown in Fig. 5.17. From application of Eq. 3.17 it was possible to calculate the bulk plasma density for the 1:0 and 1:9 Na:Cu aerosol mixtures. A plasma density of \( 1.08 \times 10^{17} \text{ e}^{-/\text{cm}^3} \) and \( 4.8 \times 10^{16} \text{ e}^{-/\text{cm}^3} \) was measured for the pure Na aerosol and the Na:Cu 1:9 aerosol mixture, respectively. When the plasma density calculated from the Stark broadening of the Cu emission line was compared to the plasma density calculated from the Stark broadening of the H\( \alpha \) line, a difference between the local and bulk plasma density was observed. The bulk plasma density was observed to be lower for the mixed aerosol sample while the local plasma density is observed to increase as the concomitant density increased. This discrepancy between the local and bulk plasma densities suggests that heat and mass diffusion is occurring between the bulk plasma and the aerosol particle (local) during the plasma evolution, which is similar to recent results reported in the literature [97]. The local increase in the plasma density surrounding the analyte of interest is responsible for the increase in
Figure 5.16. Cu I 510.5, 515.3, and 521.8 nm characteristic LIBS emission lines for the Na:Cu binary aerosol mixture. An acquisition gate delay of 15 µs and gate width of 10 µs was used for the LIBS measurement.

the characteristic emission intensity for the Na D line. Lastly, the copper aerosol LIBS emission was not affected by the presence of Na within the aerosol mixture as shown in Fig. 5.16 for the pure Cu aerosol (Na:Cu 0:1) and Na:Cu 1:1 aerosol mixtures.

5.7 Summary

Recent results [40] have shown that if only the line intensities for a given atomic concentration in the sample are compared, the matrix effect is obscured due to the variations of the plasma parameters that have been observed to compensate for each other’s effects. Previous work suggests that this compensation results from the different coupling of the laser energy to the sample, which leads to the plasma temperature to be dependent on the amount of mass ablated. However, it has also been shown in multiple works [60, 154, 33, 155, 97] that, depending on the matrix or concomitant elemental composition, the matrix effect can substantially affect the analyte signal. Matrix effects, even if they are relatively weak, have to be taken into account in the development of LIBS as a quantitative analytical technique.
applicable to different matrices, both in the approach that uses calibration curves obtained with reference samples, and in calibration-free/Monte-Carlo procedures.

In the larger analytical community, the effect of localized conditions on the individual particles is also relevant to the ICP-MS, ICP-AES, and notably in the laser-ablation ICP-MS (LA-ICP-MS) communities, where such effects are coming under increasing scrutiny with regard to the issues of elemental fractionation and matrix effects [156].

The main conclusion that emerges from this discussion and work is the complexity of the effects caused by the presence of matrix elements at both high concentrations and at extremely low (contaminant) concentrations. The goal of the aerosol LIBS matrix effect study conducted in this work was to experimentally compare the bulk and local plasma properties that leads to the observed Na emission enhancement in aerosols with a concomitant mass present. Additionally, complex ab initio modeling was carried out to elucidate the physical phenomena that occur within the plasma for the different aerosol mixtures. It was found that the Na emission enhancement was found to occur within the aerosol LIBS plasma at the same temporal location regardless of the element comprising the bulk matrix, and
that the Na emission enhancement was related to the mass density of the concomitant element. The increase in the local plasma density (surrounding the aerosol particle) combined with a decrease in the free-electron-to-atom ratio was found to be responsible for the increase in the Na D line emission.
Chapter 6

Improvement of LIBS Sensitivity

6.1 Introduction

Optimization of LIBS has been addressed in a number of previous studies [63, 67, 10, 89]. The efficiency of plasma generation, light collection, and setup geometry have been the primary focus of these works. The sensitivity of LIBS has improved in parallel with the improvement of laser and spectroscopic measurement technology. An example of the advances in laser technology is the use of fs lasers in the LIBS technique, which results in LIBS spectra with improved SBR compared to ns laser ablation [36]. An example of the improvement in spectroscopic measurement technology is the implementation of ICCD detectors for measurement of the LIBS spectra, which allows for temporal gating of the LIBS measurement past the continuum emission. An important characteristic associated with an analytical technique is the SBR of the measurement. One challenge associated with the LIBS technique is the low SBR observed in the LIBS spectra of complex elements and samples. The background consists primarily of bremsstrahlung and recombination emission that occurs at early times during the plasma lifetime. The low SBR ratio has the effect to reduce the absolute sensitivity and reliability of LIBS measurements. It is conjectured that an increase in the SBR of LIBS would improve the ability to characterize the sample composition by increasing the analysis speed and accuracy. Further, an increase in SBR would reduce the amount of material required to perform the analysis, which is necessary if the LIBS technique is to be used in applications such as nuclear forensics or verification measurements. Results
and discussion on the improvement of the selectivity and sensitivity of the LIBS technique through optimization of the laser pulse shape and the use of mid-infrared fs laser pulses are presented in this chapter.

6.2 Laser Pulse Shape

The goal of this work is to control the dynamics of the ionization and recombination processes in the laser-produced plasma to favorably affect the SBR associated with the characteristic line emission from the plasma. Fs laser pulse shaping is performed using an acousto-optic programmable dispersive filter (Fastlite Dazzler™). The effect of the sign and magnitude of the linear chirp applied to the pulse shape as well as more complex pulse shaping on the measured LIBS spectra are presented. The chirp of a laser pulse is the time-dependent change of the pulse frequency. A linear change of this frequency is referred to as group delay dispersion (GDD). An adaptive learning algorithm was developed to automate the complex pulse shape optimization process for maximization of LIBS SBR for nuclear security-relevant materials.

It has been shown recently by Gunaratne et al. [87] that the characteristic line emission intensities of Al and Cu obtained from LIBS measurements are dependent on the laser pulse shape, which can be readily altered by adjusting the nonlinear phase associated with the laser pulse. The authors found that when a transform limited (TL) 30 fs pulse is stretched to 10 ps through the application of a linear chirp (while maintaining a constant spectral bandwidth), little or no effect is observed in the measured characteristic emission intensity. The results presented in the previous work are in contradiction to the reported advantages associated with the use of fs laser pulses in LIBS measurements [157]. The authors primarily focused on the effect of the pulse shape on the intensity of a single characteristic emission line and did not address the effect that the pulse shape has on the SBR of the characteristic emission lines nor did it consider the ratio of atomic to ionic emission lines. The ratio of the atomic to ionic characteristic emission lines is an indicator of the ionization state of the plasma.

Elhassan et al. [157] reported that fs laser ablation increases the analytical capabilities of LIBS measurements due to the reduction of continuum emission and
the rapid achievement of LTE in the plasma. The peak intensities of emission lines resulting from ns laser pulses are considerably higher when compared to fs laser pulses when the pulse energy and fluence are kept constant [158]. Although the pulse duration can be increased to improve the characteristic line emission intensity, such an increase results in a trade-off with the amount of continuum emission due to inverse bremsstrahlung heating of the plasma, and a commensurate decrease in the SBR of the measurement. The goal of this section is to present a preliminary study of the ultrashort laser pulse shape characteristics that deliver the optimum SBR and ionic to atomic line ratio in a material of interest to nuclear forensics- uranium. Further, the result of complex pulse shaping achieved through the implementation of a genetic algorithm is presented.

6.2.1 Laser Pulse Shaping Experimental Setup

The LIBS system used for this work is shown in Fig. 4.1 and employs the fs chirped pulse amplification system and a Fastlite Dazzler T3™ acousto-optic pulse shaper to vary the pulse shape and pulse duration, with the shortest pulses (TL pulse) used in the measurement exhibiting pulse durations of 45 fs and energies of up to 2.0 mJ. The laser beam is focused onto the sample with a 250 mm lens. The calculated focal spot diameter on the sample is ∼26 µm. The signal is collected at an angle of 45° with respect to the incident laser beam with a 4” collection lens and is coupled to the spectrometer though free space. A HORIBA Synapse time-integrated CCD was attached to the iHR 550 spectrometer and was used to measure the LIBS spectrum. For all measured spectra the laser pulse ablated the sample at the same position for 10 shots over the 1.0 s CCD integration window. The entrance slit to the spectrometer was adjusted to maximize the signal without sacrificing the spectral resolution. It has been found that in our setup the resolution of the spectrometer began to be compromised for spectrometer entrance slit widths greater than ∼0.025 mm, which is expected as this is the size of the CCD detector pixels. The uranium sample consisted of a thin strip of the DU available within the laser laboratory at the Pennsylvania State University, and the copper sample consisted of a copper mirror formerly used in a legacy CO₂ laser system.

Laser pulse energy was measured to exhibit a standard deviation of 1.05% over
Figure 6.1. LabVIEW front panel for complex pulse shaping LIBS measurements with a genetic algorithm optimization process implemented.

1 minute (600 shots). The pulse energy was kept constant in the measurement, which results in a constant fluence, but a significant change in the peak power and intensity occurred with variation of pulse duration/shape. The sample was translated to a new sample spot after each 10 shot spectral accumulation. A LabVIEW interface was developed to automate the sample translation, pulse shaping, delay generation, and spectral acquisition, and is shown in Fig. 6.1. Experiments were performed over a range of pulse durations and complex pulse shapes, and the LIBS emission spectra were acquired over a range of spectral regions of interest. For each value GDD associated with the simple pulse shaping, the spectra was measured from 10 different areas on the sample, and were averaged to obtain the reported experimental results. The pulse duration was measured by the use of a single-shot autocorrelator.

The spectral phase can be written as

\[ \Phi(\omega) = \phi(\omega_0) + \phi^{(1)}(\omega - \omega_0) + \frac{1}{2!} \phi^{(2)}(\omega - \omega_0) + \frac{1}{3!} \phi^{(3)}(\omega - \omega_0) + \frac{1}{4!} \phi(\omega - \omega_0) \] (6.1)

and corresponds to the Taylor expansion of the spectral phase about \( \omega_0 \), the central frequency of the laser pulse. The Taylor expansion representation of the phase associated with the laser pulse is used for the simple pulse shaping case where the GDD is controlled by the Dazzler acousto-optic filter. For complex pulse shaping, the phase \( \Phi(\omega) \) is controlled at \( \sim 300 \) discrete wavelength positions across the spectral bandwidth of the laser pulse.
6.2.2 Results

The duration of the laser pulse incident on the sample surface is solely due to the variation of spectral phase (the spectral amplitude is kept constant). The transform limited pulse duration (minimum pulse duration) was measured to be 45 fs. This pulse duration is consistent with the transform limit for the laser pulse at the location of the sample, which was confirmed by calculating the minimum pulse width from the measured spectral bandwidth. Further, Spectral Phase Interferometry for Direct Electric field Reconstruction (SPIDER) measurements were performed to simultaneously measure the amplitude and phase associated with the laser pulse. The SPIDER measurements allow for the verification of the results measured by autocorrelation. For simple pulse shaping the pulse duration was varied solely by the variation of quadratic spectral phase (GDD), ranging from the transform limit up to ∼1.5 ps. Autocorrelation was used to measure the pulse durations < 200 fs, while the longer pulse durations have been calculated from the measured spectrum and the set spectral phase.

It is hypothesized that through favorable control of the ionization process through pulse shaping, it is possible to improve the efficiency of the laser coupling to the material, which results in optimization of the SBR in the LIBS measurement. The specific goal of this work was to systematically study the effect of variation of pulse duration and shape by the use of spectral pulse shaping on the LIBS spectrum. Further, this work addresses some of the discrepancies in the previously reported results [159, 157, 87]. A non-gated CCD camera was used to collect the plasma emission, which integrates the emission signal over the entire temporal plasma evolution (∼100 µs). The measured spectra thus contain superimposed characteristic line and the background continuum emission. The emission lines used to quantify the SBR were selected such that they exhibited high intensity and occurred in a spectral region that had other resolvable spectral lines characteristic for the material of interest. Further, commonly reported emission lines for the elements studied in the LIBS literature were chosen to aid the comparison. Figures 6.2 and 6.3 show the spectra obtained from fs LIBS on copper and uranium, respectively. The emission lines chosen for copper were at 521.82 (Cu I) and 515.32 nm (Cu I), and for uranium the emission lines chosen were at 409.01 nm (U II) and 406.25 nm (U II). The background was calculated through
Figure 6.2. Copper spectrum averaged over 10 measurements for a 45 fs, 2 mJ pulse. Intense 521.82 and 515.32 nm emission lines are present in the spectrum.

Figure 6.3. DU spectrum averaged over 10 measurements for a 45 fs, 2 mJ pulse. 409.01 nm U II and 406.25 nm U I emission lines are notable.

a linear fit to the baseline surrounding both sides of the emission line. The SBR measured with this choice of spectral lines has been found to be lower in uranium than in copper, This is a general result for LIBS of pure uranium and copper, as the energy in the uranium plasma is shared across a much larger number (of order $10^5$) of emission lines compared to copper.

In Fig. 6.4–6.9 the effect of pulse width resulting from application of both positive and negative GDD (positive or negative chirp) is presented. The effect of pulse width on the spectra near the transform limit was studied separately for short (42–250 fs) and longer (250 fs–1.5 ps) pulses. Figure 6.4 shows the measured effect of pulse width on the 521.82 nm copper line. The intensity of this
Figure 6.4. Uranium 409.01 nm peak intensity as a function of pulse width for negative and positive GDD: (a) 45 fs to 250 fs; (b) 250 fs to 1.5 ps.

Figure 6.5. Copper 521.82 nm peak intensity as a function of pulse width for negative and positive GDD: (a) 45 fs to 250 fs; (b) 250 fs to 1.5 ps.

spectral line initially decreases for positive and increases for negative GDD, and continues to increase for pulse durations up to 250 fs. For longer pulse durations, negative and positive GDD of the same magnitude result in different line intensities, suggesting differences in the efficiency of coupling of the pulse energy into the material. The difference is a maximum at 480 fs, where the line intensity for negative GDD is \(\sim 5\) times greater than that measured for positive GDD at the same pulse duration. Further increase of the pulse duration causes the intensity to reach a local maximum and then steadily decrease for both signs of GDD. The increase in intensity and the local maxima observed for longer pulse durations indicate the presence of conditions for which the coupling of laser energy to target is more efficient, which may be due to changes in how the generated heat is transferred to the material [86].

In experimental results for uranium, shown in Fig 6.5, the intensity exhibits a
Figure 6.6. Copper 521.82 nm peak to background ratio (SNR) as a function of pulse width for negative and positive GDD: (a) 45 fs to 250 fs; (b) 250 fs to 1.5 ps.

local maximum at short pulse durations. The line intensity for negative GDD is nearly constant up to 150 fs pulse duration and then begins to increase linearly up to 250 fs. For longer pulse durations the measured LIBS intensity reaches local maxima and minima for both signs of GDD for different values of the magnitude of GDD added to the laser pulse. The line intensities measured from uranium continue to decrease in magnitude for both signs of GDD at longer pulse durations, which is similar to the simple pulse shaping results for copper. The variation in line intensity with pulse duration and GDD in uranium and copper suggest a change in the heat transfer mechanisms occurs during the ablation process. The surface reflectivity of a material exhibits a transient behavior during laser irradiation, and over the first 100 fs the reflectivity increases, after which a rapid decrease of reflectivity is observed in the period 100–500 fs [160]. It is conjectured that the combination of the transient change in surface reflectivity and an increase in the amount of heat diffusion occurring for longer picosecond pulses resulted in the observed behavior.

Figures 6.6 & 6.7 show the experimental results for the SBR for copper and uranium, respectively. It has been previously reported that the utilization of ultrashort transform limited (10’s of fs long) pulses for LIBS produces the greatest SBR [161]. The results presented here, albeit in somewhat different conditions (most notably, the choice of characteristic emission lines and the detector acquisition gate window), are not in agreement with the findings in the literature. In this work it was observed that the shortest possible pulse for a given spectral band-
Figure 6.7. Uranium 409.01 nm peak to background ratio (SNR) as a function of pulse width for both negative and positive GDD: (a) 45 fs to 250 fs; (b) 250 fs to 1.5 ps.

Figure 6.8. Ratio of the intensities of 521.82 nm and 515.25 nm characteristic emission lines in copper as a function of pulse width for negative and positive GDD: (a) 45 fs to 250 fs; (b) 250 fs to 1.5 ps.

Figure 6.9. Ratio of the intensities of 409.01 nm and 406.25 nm characteristic emission lines in uranium as a function of pulse width for both negative and positive GDD: (a) 45 fs to 250 fs; (b) 250 fs to 1.5 ps.
width does not produce the greatest SBR. The peak intensity was observed to be maximized in uranium for pulse durations close to the transform limit; however, a commensurate increase in the continuum background intensity was observed for TL pulses. The aggregate result of these two phenomena is the reduction of the SBR for the transform limited pulse duration.

For both uranium and copper the SBR is reduced as the pulse width decreases from 250 fs to the transform limited pulse duration, as shown in Figs. 6.6(a) and 6.7(a). For longer pulse durations shown in Figs. 6.4(b) and 6.5(b), a local maximum in line intensity, close to the maximum value shown in the short pulse plots Figs. 6.4(a) and 6.4(b), occurred near 250 fs. For application of positive GDD, the SBR decreased sharply with increase in pulse duration for both copper and uranium to the minimum value at the same pulse duration of ~400 fs. This decrease of SBR for copper was more significant than that observed in uranium, as shown in Figs. 6.6 & 6.7. The observation of the maximum SBR at 250 fs for negative GDD and the accompanying decrease of the SBR for shorter and longer pulse durations suggest that the pulse energy was most efficiently coupled into the material near 250 fs pulse duration, which resulted in an increase in the amount of ionization produced during the ablation process. Transitions between physical mechanisms of heat transfer, resulting in less ionization and an increase in background due to material heating, is conjectured to be result in the subsequent decrease of SBR for increased pulse widths resulting from both negative and positive GDD.

The ratio of two characteristic emission line intensities as a function of pulse width for negative and positive GDD is of interest due to the recent investigation of pulse shaping for coherent control of the breakdown process in LIBS [162, 86, 163]. As each characteristic emission line is representative of a discrete electronic transition in the atom, the intensity for each transition is dependent on how effectively the laser pulse energy is coupled to the material and populates the specific upper electron energy levels associated with the transition/emission. Figs. 6.8 and 6.9 show the ratio of the 521.82 to 515.43 nm emission lines for copper and the ratio of the 409.01 to 406.25 nm lines for uranium, respectively. The line-to-line intensity ratio reached a minimum for copper near 1 ps, and for uranium a local minimum was observed near 400 fs. The minimum intensity ratio was observed for both samples for the positive GDD case. The smallest ratio observed for the
negative GDD case in uranium occurred between 45 and 200 fs pulse durations. For long pulse durations generated by either positive or negative GDD, the effect of pulse chirp on individual electronic transitions can be seen. The results in Figs. 6.8(b) and 6.9(b) exhibit distinct minima and maxima in the ratio of the intensity of two characteristic emission lines, which indicate that pulse shape parameters, such as pulse duration and the sign of GDD, have a different effect on the emission line intensities for different emission lines.

Genetic algorithms are a family of evolution inspired computational methods. These algorithms encode a potential solution to a specific problem on a simple binary data structure (which is chromosome-like) and apply mutation and recombination operations. The implementation of a genetic algorithm starts with the choice of an initial population of chromosomes, which is typically initialized from a random generation function. The initial chromosomes are evaluated and the chromosomes that result in the best solution (greatest fitness value) are assigned reproductive opportunities that result in more chances to “reproduce” than chromosomes that are poorer solutions. The favorable chance of reproduction is achieved through discarding a fraction of the chromosomes that result in the poorest solutions, which allows only the “fittest” chromosomes to reproduce. Additional
Figure 6.11. Fitness behavior during the genetic algorithm optimization process.

Figure 6.12. Evolution of lines chosen for optimization with transform limited (TL) pulse and optimized pulse (OP).
mutation operations are applied to the population after each generation to force the solution away from convergence on a local minimum or maximum.

The genetic algorithm implemented in this work for complex pulse shaping is based on the method described by Moore et al. [164]. A schematic of the decision analysis structure for the genetic algorithm developed in this work is shown in Fig. 6.10. The algorithm was implemented into LabVIEW and controlled not just the pulse shape of the laser pulse, but also controlled the LIBS experimental system.

For uranium LIBS measurements it was possible to observe simultaneously both the atomic (U I) and ionic (U II) characteristic emission lines in the LIBS measurement, which was not possible for the copper sample due to the weak emission intensity of Cu I emissions in the near UV spectral region where Cu II emission lines are observed. It is conjectured that manipulation of the pulse shape will alter the ionization state of the uranium plasma, and, thus, can control not only the intensity and SBR of the uranium characteristic emission lines but the ratio of the ionic to atomic emission lines [86]. Figure 6.11 shows the SBR evolution of the 409.01 nm line as a function of iteration number for the genetic algorithm optimization process. The maximum, average, and minimum SBR for the population at each iteration of the algorithm is shown to illustrate the gradual improvement in the solution for the population as a whole. From Fig. 6.11 it is clear that after ~30 iterations the population begins to walk-off from the optimum solution. This walk-off represents an inherent problem with genetic algorithms when there is a lack of a strong feedback mechanism (fitness value is not strongly dependent on small changes in pulse shape) and when the amount of allowed mutation in the population is high.

Through control of the U I and the U II emission line intensities an increase in the sensitivity and selectability of the LIBS measurement for uranium can be realized. The fitness value of the genetic algorithm can be changed from monitoring the SBR of a specific emission line to monitoring the ratio of two characteristic emission lines. The 385.95 nm U II and the 387.10 nm U I emission lines were selected for this work due to the simultaneous presence of both emission lines within the same spectral measurement window and the significant SBR of each line (observed for the TL case). Figure 6.12 shows the uranium LIBS spectra that results
when the optimized pulse shape determined from the genetic algorithm optimization of the U II to U I characteristic emission line ratio is used. The optimized pulse shape resulted in a series of laser pulses separated by a few 10’s of fs over a \( \sim 1 \) ps pulse duration. The pulse shape was calculated from the set residual phase obtained during the optimization process and using the experimentally measured laser spectrum. From Fig. 6.12, laser energy deposition with the optimized pulse shape leads to a reduction of the neutral species emission and enhances the ionic emission, which allows an enhancement of the ionization state of the plasma.

### 6.3 Laser Wavelength

The effect that the laser wavelength has on the LIBS spectrum has been extensively studied in previous reported work [130, 93]. The previous work has shown, similar to the results of fs pulse shaping, that the laser wavelength can be optimized to result in the favorable enhancement of the LIBS characteristic emission intensity and SBR.

Previous single-pulse LIBS experiments have shown that the plasma density and the peak emission intensity of the LIBS signal can be enhanced by 40–50% if 532 nm ns pulses are used in comparison to 1064 nm ns pulses[165]. However, it has been shown that this result is not general, as in other work it has been observed that 266 nm ns laser ablation results in a lower emission intensity compared to 1064 nm ns laser ablation [166].

Due to the increase in inverse bremsstrahlung heating as the laser wavelength is increased, in double-pulse LIBS an enhancement of the peak intensity, plasma temperature, and plasma density have been reported when the second pulse wavelength is increased [167, 93]. The higher intensity and increased stability of the LIBS signal in double-pulse LIBS are desirable and is due to the longer plasma lifetime and re-excitation (inverse-bremsstrahlung heating) associated with the double-pulse LIBS technique [161].

The use of mid-infrared (mid-IR) laser pulses is further desirable due to their eye-safe nature. Mid-IR ultrafast lasers have undergone a significant development in the recent period, producing pulse durations as short as \( \sim 10 \)’s of fs and pulse energies extending to many mJ [168]. Although the latter laser pulse characteristics
make mid-infrared lasers compatible with LIBS measurement requirements, no
LIBS measurement in the fs regime has been reported to date using mid-infrared
laser pulses.

Formation of plasmas induced by typical ns laser pulses involves several pro-
cesses: surface melting, vaporization, vapor ionization, ambient and evaporating
gas breakdown, free electron acceleration within the evaporated cloud, and plasma
heating [9]. With the advent of high-intensity ultrashort laser pulses, the laser
ablation and laser-matter interaction processes noticeably differ from those taking
place with ns lasers [29]. Ultrashort pulses allow for direct coupling of the laser
energy to the sample through inner ionization (1–5 fs), followed by outer ioniza-
tion within the pulse (35 fs), similar to the nanosecond ablation process. Since the
pulse duration is sufficiently short to prevent reheating, plasma formation occurs
by Coulomb explosion in a highly unstable multi-ionized system within ∼200 fs.
The direct ionization of the sample occurs at near solid density, as there is little
or no material removal, which results in reduced threshold fluences and thermal
damage [87].

In this work LIBS experiments driven by mid-infrared (2.05 µm) fs pulses are
studied through time resolved measurements. Ab-initio modeling (ATOMIC suite
of codes) is performed to predict the LIBS emission spectrum resulting from fs mea-
urements at 2.05 µm and traditional 800-nm fs-LIBS. Ablation by mid-infrared fs
pulses results in a plasma with a lower plasma density and temperature compared
to fs-LIBS performed at shorter laser wavelength. LIBS driven by mid-infrared fs
pulses results in a signal-to-background ratio ∼50% greater and a signal-to-noise
ratio ∼40% lower than fs-LIBS at near-infrared laser wavelength.

6.3.1 Fs Mid-IR Experimental Setup

In this work, a two-stage optical parametric amplifier was pumped by the fs
Ti:sapphire chirped-pulse amplification system, and produces 2.05 µm, ∼42-fs
pulses with energies of up to 2.2 mJ [168].

The 800 nm and 2.05 µm laser pulses were both attenuated to 200 µJ and fo-
cused on the sample surface by 30 cm focal length BK7 or CaF₂ lenses, respectively.
The laser pulse energy was measured after the lens for each laser wavelength, but
the energy absorbed by the sample could differ for the two laser wavelengths used. The spot size on the sample surface was approximately 100 \( \mu m \) in both measurements, which is significantly larger than the diffraction limited spot size for both laser wavelengths. The spot size was set to be equal in both measurements by adjusting the distance between the lens and the sample, and was determined by measuring the size of the resulting laser ablation craters using white light surface profilometry.

The copper sample consisted of a copper mirror formerly used for a CO\(_2\) laser system. A fresh sample spot was chosen for each accumulation of 10 laser shots by translating the sample. Optical emission was collected by a 50 mm focal length lens positioned at 45° with respect to the sample surface \((f/# = 2.2)\) and coupled to an optical fiber. The fiber was interfaced to a spectrally calibrated Catalina Scientific SE-200 Echelle spectrometer equipped with an Andor ICCD camera and a Horiba iHR 550 Czerny-Turner spectrometer with a 1800 g/mm grating and an Andor i334T iStar ICCD. The spectrometers were calibrated using an Ocean Optics DH-2000 deuterium-tungsten calibration lamp.

### 6.3.2 Results

Fig. 6.13 shows the LIBS spectrum of copper for both the 800-nm and 2.05 \( \mu m \) fs pulses under a rarefied atmospheric pressure of \( 1.9 \times 10^{-3} \) mbar with three characteristic Cu I emissions clearly present. The spectrum was obtained with a time gating window of 1.0 \( \mu s \) and a delay of 50 ns following the time at which the scattered laser light was first observed in the measured spectrum. In order to provide statistics for the plasma temperature measurement, 10 spectra were taken successively at the same sample location. Emission transitions observed in the full collected spectrum have all been identified to be from neutral copper (Cu I).

Through inspection of Fig. 6.13 the relative changes in the copper characteristic emission lines reveals the difference in the plasma temperature and density when the two laser wavelengths are used. A lower continuum (bremsstrahlung and radiative recombination) emission and peak intensity was observed for the case when 2.05 \( \mu m \) are used when no gate delay was present in the acquisition following irradiation of the sample, as shown in Fig. 6.14. Additionally, emission from low-
Figure 6.13. Czerny-Turner spectrometer measurement of 2.05 µm and 800-nm fs-LIBS of Cu at 1.9×10^{-3} mbar and 50 ns delay yields the characteristic 510.55, 515.32, and 521.82 nm Cu emissions (top). Zoomed region showing 511.2 and 520.1 nm emission lines (bottom).

Intensity Cu I lines at 511.19 nm and 520.08 nm with high (7.99 eV and 7.80 eV, respectively) upper energy levels are more intense due to an increase in the ablation efficiency that leads to a commensurate increase in the plasma temperature and density following ablation by 800-nm pulses, as shown in Fig. 6.13 [165].

In order to determine the plasma temperature, several Cu I emission lines, which are observable in Fig. 6.14, were analyzed and their respective spectroscopic data are shown in Table 6.1. The associated spectroscopic data for each emission line analyzed was obtained from the NIST database [121]. The plasma temperature was calculated using the Boltzman plot method, the two-line method (using the ratio of two closely spaced emission lines associated with different energy levels), and the synthetic spectra method with the criteria and best practices described by
Figure 6.14. Echelle spectrometer measurement of 2.05-µm and 800-nm fs-LIBS of Cu with no delay and at $2.4 \times 10^{-3}$ mbar yields many characteristic Cu I emissions.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>gA ($10^8$ s$^{-1}$)</th>
<th>$E_{\text{low}}$–$E_{\text{up}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>406.26</td>
<td>1.26</td>
<td>3.817–6.868</td>
</tr>
<tr>
<td>427.51</td>
<td>2.76</td>
<td>4.838–7.737</td>
</tr>
<tr>
<td>458.69</td>
<td>1.92</td>
<td>5.102–7.805</td>
</tr>
<tr>
<td>465.11</td>
<td>3.04</td>
<td>5.072–7.737</td>
</tr>
<tr>
<td>510.55</td>
<td>0.08</td>
<td>1.389–3.817</td>
</tr>
<tr>
<td>521.82</td>
<td>4.5</td>
<td>3.817–6.192</td>
</tr>
<tr>
<td>529.25</td>
<td>0.872</td>
<td>5.395–7.737</td>
</tr>
<tr>
<td>570.02</td>
<td>0.0098</td>
<td>1.642–3.817</td>
</tr>
<tr>
<td>578.21</td>
<td>0.033</td>
<td>1.642–3.786</td>
</tr>
</tbody>
</table>

Table 6.1. List of Cu I lines used in the calculation of plasma temperature ($\lambda$: transition wavelength, gA: transition probability, $E_{\text{up}}$: upper level energy, $E_{\text{low}}$: lower level energy

Zhang et al [152]. The plasma is assumed to be in quasi-LTE conditions, satisfying the McWhirter criterion [153], which sets the lower bound on the electron density for LTE conditions at $\gtrsim 2.2 \times 10^{15}$ e$^-$/cm$^3$, as shown in Eq. 5.1.

The halfwidth ($\omega$) of a neutral atom spectral line from Stark effects due to an electron density $n_e$, is given in Eq. 3.18.

The plasma density was determined from Stark broadening of the 510.5 nm Cu I emission line by fitting a Lorentzian line profile (homogenous broadening) to the experimental data following subtraction of the instrumental broadening. The spectra used for this calculation were acquired with a 1.0 µs gate window and a
100 ns gate delay, which are sufficient for LTE to be established and for the intensity of bremsstrahlung emission to be greatly diminished. The Stark broadening was measured to be 0.038 nm and 0.091 nm (FWHM) for the 2.05 µm and 800-nm case, respectively. This corresponds to a plasma density of \( \approx 1.5 \times 10^{17} \text{ e}^{-}/\text{cm}^3 \) for the 2.05 µm case. The 800-nm ablation resulted in a plasma density of \( \approx 5 \times 10^{17} \text{ e}^{-}/\text{cm}^3 \).

The obtained Boltzmann plot for 2.05 µm and 800-nm LIBS of Cu is shown in Fig. 6.15, and has a \( \approx 10\% \) error, which is consistent with the \( \approx 20\% \) error in the spectroscopic data.[169] The Boltzmann plot method resulted in a temperature \( T_{\text{Cu I}} = 0.62 \text{ eV} \) for the 2.05 µm case and \( T_{\text{Cu I}} = 0.8 \text{ eV} \) for the 800-nm case. The plasma temperature obtained for the 800-nm case agrees with previously reported Cu fs-LIBS measurements [170]. The establishment of quasi-LTE (collisionally dominated) for the gate delay and window used in this measurement was confirmed through the good linearity of the calculated Boltzmann plot from the measured LIBS spectra shown in Fig. 6.15.

The ATOMIC calculations presented in this work employ atomic structure
data derived from Cowan’s set of atomic structure codes [112]. The fine-structure resolved calculations include full configuration-interaction (CI) between all the configurations included in the model, and over 60 configurations that spawn around 2000 levels for neutral Cu are used in the emission calculations.

The LIBS plasma is known to exhibit significant temporal and spatial heterogeneity where the temperature, electron density, and the density of each constituent element and ionic species varies significantly within the plasma [78, 171, 172, 173]. However, for simplicity in the complex ab initio modeling presented in this work a homogeneous, steady-state plasma represented by a single electron density and plasma temperature is assumed. This is not an accurate representation of the LIBS plasma and a spatially resolved model of the LIBS plasma would improve the accuracy of this analysis. Additionally, temporal evolution of the plasma as described by Gornushkin et al. could be implemented [173]. Integration of such dynamic and spatially resolved framework with the complex ionization and excitation processes that the ab initio modeling includes has yet to be attempted and would require significant computational resources.

The ATOMIC code was used to produce synthetic spectra for the Cu transitions under LTE conditions at several different plasma temperatures; the 0.62 eV and 0.80 eV case is shown in Fig. 6.16 for comparison with the experimental results. A single correction intensity scaling factor is determined for normalization of the ATOMIC simulated spectrum to the experimental data by performing a least squares fit of the theoretical emission lines to the experimental emission lines.

The ATOMIC plasma emission calculations showed that the population of the upper level for the 510.5 nm Cu I line increased by a factor of four when moving from 0.62 eV and 1×10^{17} \, \text{e}^{-}/\text{cm}^{3} to 0.80 eV and 5×10^{17} \, \text{e}^{-}/\text{cm}^{3}. A factor of 10 increase in the population of the upper electron energy levels for the 515.3 and 521.8 nm lines for the same change in plasma conditions was observed in the ATOMIC modeling. The higher electron energy levels levels of Cu I become more populated when the plasma temperature is increased (relative to the lower energy levels), which results in a commensurate increase in the observed characteristic copper line intensities, as shown in Fig. 6.16.

The lack of observed Cu II emission in the full spectrum can be explained by the calculated average ion charge of 0.115 for the 0.62 eV temperature and
Figure 6.16. Emission spectrum from Cu (red curve) obtained in LIBS driven by mid-infrared (top) and 800-nm (bottom) fs pulses. The measurements are compared to ATOMIC LTE calculations (black curve) performed at the temperature and density matching the measured values.

$1 \times 10^{17}$ e$^-$/cm$^3$ density. For 0.80 eV and $5 \times 10^{17}$ e$^-$/cm$^3$, the average ion charge is predicted to be 0.332. The increased ion charge observed for the 800 nm fs laser ablation measured plasma parameters indicates that a larger fraction of the plasma is ionized, which explains the increased recombination (f-b) and bremsstrahlung (f-f) emission in the measured spectra.

It was found in the ab initio modeling that the lowest (energetically) odd-parity levels arise from strong mixing of the $3d^{10}4p$ and $3d^94s4p$ configurations, and that transitions involving these levels have line strengths that are quite sensitive to the amount of CI included in the calculation. The inclusion of more CI can be achieved by adding more electron configurations to the atomic model; however, this can result in more computationally intensive calculations due to the increase in electron energy levels considered in the model. The calculations presented in this work attempt to strike a balance between ensuring sufficient CI effects are included and a manageable computational cost. The effect of strong mixing and CI sensitivity can be seen in Fig. 6.17, where the 510.5 nm line is predicted to be more intense, and the presence of transitions (522.6 nm line) in the case including
Figure 6.17. ATOMIC calculations depicting the effect of CI on the synthetic spectra for the two measured plasma parameters.

fewer configurations (black line in Fig. 6.17) that were not observed in the measured spectra as shown in Fig. 6.16.

The plasma lifetime was measured by fitting an exponential decay function to the experimental data:

\[ I(t) = A_0 e^{-t/\tau} + C, \]  

where \( I(t) \) is the emission intensity at time \( t \), \( A_0 \) is the absolute emission intensity, \( C \) is a constant offset, and \( \tau \) is the rate of decay for the exponential fit representing the plasma emission lifetime.

The temporal behavior of the copper characteristic emission intensity was studied through the use of a least-squares fitting procedure for the two laser ablation wavelengths over the temporal range of 50–300 ns. The average rate of decay of the plasma emission (\( \tau \)) was determined to be \( \approx 54.0 \) ns and \( \approx 88.0 \) ns for the 2.05 \( \mu \)m and 800 nm fs-LIBS copper measurements, respectively. The plasma persistence was determined through measurement of the integrated intensity (Lorentzian fit) of multiple Cu emission lines. Figure 6.18 shows the temporal evolution for the 515.3 nm copper characteristic emission line for both laser ablation wavelengths.
Figure 6.18. Time evolution of the Cu I 515.3 nm emission line for fs-LIBS with 2.05 µm and 800-nm pulses for delays of 0 to 1000 ns with a gate width of 50 ns following measurement of the scattered laser light off the sample.

The temporal evolution of the plasma emission for mid-IR fs-LIBS exhibits a number of similarities to traditional 800-nm fs LIBS: (i) in the first 50 ns a lower peak intensity is observed that is dominated by the inverse bremsstrahlung, (ii) a peak emission intensity is observed between 50-100 ns, and (iii) a rapid decrease in the emission intensity in the first $\approx 200$ ns following ablation is observed.

The short plasma lifetime in 2.05 µm LIBS measurements can be explained by two mechanisms: (1) the laser-matter coupling is less efficient for the longer wavelengths, leading to less ablation, and (2) lower plasma temperature and density results in a plasma consisting primarily of neutral atoms, as singly ionized atoms would act as a source for neutral emission following electron recombination.

The copper sample was imaged using white light profilometry following ablation by 10 laser pulses for each laser wavelength. A $\approx 300$ µm diameter crater with a central ablation region of $\approx 100$ µm diameter was observed for both laser wavelengths. For 2.05 µm laser pulses an ablation crater with a peak depth of 18 µm was observed following the 10 laser pulses. The 800 nm laser ablation case resulted in an increased peak crater depth of 25 µm following 10 laser pulses. The smaller peak crater depth for the 2.05 µm laser wavelength is an indicator that the laser-matter coupling was less efficient than when 800 nm pulses were used. Further, the decreased amount of ablated matter explains the measured lower plasma density.
for 2.05 µm laser ablation that is directly observed through the lower overall LIBS emission intensity compared to the 800 nm pulses.

The signal-to-noise ratio (SNR) and the signal-to-background ratio (SBR) was calculated for multiple Cu emission lines present in the spectrum for the two laser ablation wavelengths shown in Fig. 6.14. The SNR was calculated for the 521.82, 510.55, and 515.3 nm Cu I atomic emission lines, and was 1082 and 1860 for the mid-IR and 800 nm laser ablation wavelengths, respectively. The SBR was calculated for the same emission lines, and was 8.3 and 4.0 for the mid-IR and 800 nm laser ablation wavelengths, respectively. The reported SNR and SBR values represent the average for the three characteristic Cu I atomic emission lines. The lower plasma temperature and density, which reduced the intensity of bremsstrahlung emission present in the plasma emission results in the increased SBR for the mid-IR laser ablation case. The increased shot-to-shot variation in the background signal for the mid-IR laser ablation combined with the ≈7 times lower copper characteristic emission intensity for the mid-IR laser ablation, which resulted in the lower SNR compared to 800 nm laser ablation.

The lower plasma density and temperature observed in the LIBS measurement of Cu following ablation by 2.05 µm fs-laser pulses can be explained by the reduced multi-photon ionization efficiency at longer wavelengths for the fs-pulses, which reduces the overall plasma density and the energy deposited to the plasma. In the previous ns mid-IR measurements [174], an increase in the plasma temperature and density was observed compared to previous ns-LIBS results at shorter wavelengths [170, 175], which can be explained by the increased inverse-bremsstrahlung heating of the plasma for mid-IR wavelengths with pulse durations long enough to interact with the expanding plasma plume. [176]

6.4 Summary

For the non-gated LIBS system, a maximum increase of ∼30% in the SBR for uranium and ∼20% in the SBR for copper was observed compared to the SBR measured at the shortest (transform-limited) pulse duration for pulses with identical spectral amplitude. It was observed that for pulse durations longer than 1 ps, regardless of the sign of GDD, the SBR and peak characteristic emission
intensity decreased. Through complex pulse shaping, laser energy deposition with a series of femtosecond pulses (optimized pulse shape) was observed to lead to a reduction of the neutral uranium emission while an increase in the ionic emission was observed. Future experimental work will involve a more complete analysis of different spectral lines in uranium, accurate reconstruction of pulse shapes, and the implementation of gated detection in order to remove the contribution of the continuum emission in the measured LIBS spectrum.

It was demonstrated through experimental analysis and theoretical modeling that the copper plasma resulting from ablation by 2.05 µm fs laser pulses exhibits a lower plasma temperature and density as well as a shorter plasma lifetime compared to fs LIBS performed at a shorter laser wavelength (800 nm). The lower plasma temperature and density when mid-IR fs laser pulses are used suggests that the fraction of laser pulse energy absorbed by the sample for the mid-IR pulses is less than that for the 800 nm laser pulses. The lower plasma temperature combined with the short plasma lifetime leads to a reduced continuum emission for mid-IR laser ablation compared to traditional 800 nm laser ablation. An improved SBR ratio for the Cu I emission lines of \(~50\%\) for the mid-IR laser pulses was observed; however, a decrease in the SNR of \(~40\%\) was observed for the mid-IR laser pulses.

Further work is being conducted on integrating the radiation transport into the ATOMIC code and implementing a multi-region model to more accurately simulate the LIBS plasma emission. With dense, inhomogeneous plasmas, such as those observed in previous LIBS measurements [125], an average temperature and density does not accurately represent the plasma that exists with a hot, dense center and cool, rapidly expanding outer layer [125, 177]. Such multi-region models will benefit from further experimental efforts to resolve the spatio-temporal LIBS plasma evolution.

Control of the plasma optical response has been realized through irradiation of the material by temporally shaped femtosecond pulses. The plasma optical response was controlled through a genetic algorithm feedback optimization process, which resulted in an increased SBR and ionic-to-atomic line ratio similar to previous work by Guillermin et al. [86]. Further, the SBR of the LIBS measurement was improved through the implementation of mid-IR femtosecond pulses in the LIBS instrument. Improvement of the SBR will lead to an increase in the sensitivity and
reliability of the LIBS technique for material identification in complex samples.
Chapter 7

Improvement of LIBS
Isotope-Sensitivity

7.1 Introduction

Defined as Special Nuclear Material (SNM) by the Atomic Energy Act of 1954, fissile materials, such as $^{235}$U and $^{239}$Pu, are the principal components used to construct nuclear explosive devices. Detecting the clandestine presence of SNM represents an important capability for U.S. Homeland Security and International Agencies like the United Nations’ IAEA. Remote detection of nuclear materials and their isotopic composition is a critical tool for preventing acts of nuclear terrorism and for verifying a country’s nuclear activities. The National Academy of Engineering identified the prevention of nuclear attacks, specifically detecting nuclear materials at a distance, as one of 14 “Grand Challenges for Engineering in the 21st Century” (www.engineeringchallenges.org). The verification of a country’s nuclear activities and the detection of clandestine programs are the subjects of two of the most visible international debates today – that surrounding the establishment of an international verification structure for Iran’s nuclear program, and North Korea’s continued overt effort to build nuclear weapons and testing program in defiance of international sanctions and condemnation.

Current C-WMD detection methods have both limited distances and analysis times over which they are effective. Moreover, environmental conditions present in the field (e.g., humidity, temperature, and background radiation) can affect
detection range and can limit applicability of these methods even further. An ideal SNM detector must be able to efficiently sense nuclear materials present at trace levels and to perform this detection in near real-time. A detector with such capabilities would provide not only rapid identification of interdicted material or the composition of an environmental sample, but also, ultimately, information on the potential source of said material. Current detection schemes for monitoring clandestine nuclear testing and nuclear fuel reprocessing to provide weapons grade fissile material rely largely on passive air sampling or swipe sampling combined with a subsequent instrumental analysis or some type of wet chemical analysis of the collected material in a laboratory, often located in a different country. Extensive sample preparation and use of laboratory-based analysis limit the ability to perform standoff measurements with the current detection systems. It would thus be useful to develop a remote sensing technique capable of measuring the isotopic composition of a sample, as such a technique could provide forensic information in real-time at a distance, even at trace levels. The importance of isotopic analysis is not limited to nuclear security but is also a critical component of material characterization for geoscience and industry.

7.2 Background

The LIBS technique has been shown in previous work to be capable of performing isotopic analysis under rarefied or inert atmospheric conditions that reduce the magnitude of collisional, Stark, and Doppler broadening of the spectral lines [42, 46]. Novel combinations of interferometric (Fabry-Perot interferometry) and dispersive (Czerny-Turner spectroscopy) methods have been applied to the LIBS technique for the measurement of the isotopic composition of a sample under ambient atmospheric conditions [48]. However, even with the improved capability to perform isotope sensitive LIBS measurements under ambient conditions, thousands of laser shots are required to be integrated onto the detector to obtain a resolvable signal. An important consideration for isotope-sensitive measurements using the LIBS technique is the line width to isotope shift ratio of the spectral line of interest. A typical spectral line at an electron density of $10^{17}$ cm$^{-3}$ has a line width of $\sim 0.01$ nm. $^{235}$U and $^{238}$U have an isotopic shift of 0.025 nm for the
424.43 nm U II spectral line and $^{239}$Pu and $^{238}$Pu have an isotopic shift of 0.005 nm at the 594.522 nm Pu II spectral line.

Another method for isotope sensitive measurements in optical emission techniques is through the analysis of the molecular emission originating from the plasma and expanding vapor plume [178, 49]. The molecular isotope shift can be orders of magnitude larger in molecular than atomic spectra for the same element of interest [49, 50]. For example, the $^{10}$B–$^{11}$B atomic isotope shift is 0.002 nm while the measured isotope shift for BO is 0.73 nm. Atomic isotope shifts are dependent on the spectral line of interest and are not accurately known without experimental measurement [112]. Molecular vibronic emission lines originate from vibrational, rotational, and electronic transitions [179]. The wavelength of the molecular emission is dependent on the vibrational and rotational energy states involved in the transition between two electronic states [49]:

$$\nu = T' - T'' = (T'_e - T''_e) + (G'_v - G''_v) + (F'_J - F''_J)$$

(7.1)

where the upper state is denoted by the single primed symbols and the lower state is denoted by the double primed symbols; $G_v$ is the vibrational energy, $F_J$ is the rotational energy, and $T_e$ is the electronic energy.

Expressions for the rotational and vibrational energy of a molecular system can be found in the literature [179]. The isotope-dependent molecular emission can be readily simulated from the expressions and constants found in the literature combined with the known or predicted isotopic abundance of the element of interest in the sample. The molecular emission intensity is a function of plasma temperature and density of the molecular system within the plasma:

$$I = C_{em} \frac{q_{v'v''} S_{j''j'}}{Q v''} v^4 e^{-E/kT},$$

(7.2)

where $C_{em}$ is the emission coefficient including the density of UO, $q_{v'v''}$ is the Franck-Condon factor, and $S_{j''j'}$ is the Honol-London factor. $Q$ is the partition function and $v$ is the optical emission light frequency. $E$ is the upper energy and $k$ is the Boltzmann constant.

The molecular isotope shift is primarily observed in the vibrational and rotational molecular transitions and is a function of the reduced mass of the diatomic
molecular system. Thus, the molecular isotope shift decreases with increasing atomic number of the element of interest. The electronic molecular transitions are isotope-dependent; however, the magnitude of the electronic isotope shift is significantly smaller compared to the rotational and vibrational transitions. The presence of molecular isotope shifts in both the vibrational and rotational molecular spectra allows for the exploitation of multiple emission lines in a small spectral window for isotopic analysis.

The analysis of molecular spectra within a LIBS plasma for isotope sensitive measurement has been termed Laser Ablation Molecular Isotopic Spectrometry (LAMIS) by the Russo group at Lawrence Berkeley National Laboratory [49].

### 7.3 Laser Ablation Molecular Isotopic Spectrometry of BO

Of interest to in-field measurements is the use of robust and simple detection techniques. LIBS measurements commonly employ complex and expensive ICCD detectors that are capable of gating the measurement past the initial plasma continuum emission [48]. Gating of the measurement is necessary when ns lasers are used in LAMIS measurements, due to the intense continuum emission present from the heating of the plasma through the inverse-bremsstrahlung process. When fs lasers are used in LIBS measurements, a lower continuum background is observed due to the lack of interaction of plasma with the ultra-short laser pulse.

The combination of fs lasers with the LAMIS technique would lend itself to the use of simpler and more robust detectors, such as non-gated CCD detectors. The added complexity of the fs laser in a laboratory environment reduces the usefulness and simplicity of such a measurement in the field; however, with the continuing improvement of fs fiber-based lasers simple and more field-portable fs laser systems are rapidly being realized.

The excited molecular radicals within the plasma originate from plasma-assisted combustion of the elements within the sample with the ambient atmosphere or with other elements present in the sample [50, 49]. Fig. 7.1 shows the BO molecular emission originating from the combustion of B from the sample with oxygen (O)
Figure 7.1. Emission spectrum from three B_4C samples with varying ^{10}\text{B} enrichment. Each sample’s spectrum is averaged over 20 different spots on the sample (200 fs laser shots total).

present in the ambient atmosphere following fs laser ablation. Comparing the measured BO fs-LAMIS spectra with previously reported BO ns-LAMIS spectra from Russo et al., a lower continuum emission and reduced emission line broadening is realized in the fs-LAMIS measurement, due to the lower plasma density and temperature obtained for fs laser ablation [49].

The 579–584 nm spectral region was originally intended to be used in the BO measurement, which is the same spectral region that previous work in the literature exploited [49]. However, due to a relatively high continuum background observed in the LIBS spectrum for this spectral region (when measured with a non-gated detector) the use of a different BO emission region was required for successful non-gated measurement of the spectrum. The 532–540 nm BO emission region was chosen for analysis based on the experimentally determined SBR. The peak near 538.4 nm is likely associated with ^{10}\text{BO}, and the intensity of the emission line is approximately halved in the sample containing 50.37% of ^{10}\text{B} when compared to the sample containing 97.35% of ^{10}\text{B}. For the natural boron sample, the intensity of 538.4 nm emission line was reduced to approximately one fifth of the intensity
found for the 97.35\% $^{10}$B sample.

The measured BO LIBS spectrum exhibited significant intensity variation between the different boron samples, due to a number of experimental parameters that were not related to the sample composition. For example, minor differences between physical properties of the B samples changed the position within the plasma that collection optics were focused upon. Thus, for each sample a slightly different spatial position within the plasma could have been measured with vastly different plasma properties that determine a number of the observed emission features: like intensity, spectral broadening, and continuum emission for example. The spectra shown in Fig. 7.1 were processed through normalization to the sum of the absolute value of the background- and continuum-subtracted spectra for the spectral region of interest. The continuum subtraction consisted of a simple high-pass Fourier filter. The $^{10}$BO and $^{11}$BO emission intensities are not necessarily the same for the two samples in this particular region; however, the resulting regression analysis of the spectra normalized using this method yielded the most accurate reconstruction of the isotopic composition.

The multivariate regression technique utilizes the overall behavior of the emission in the entire measured spectral region to perform the analysis, unlike traditional LIBS isotopic measurements where a single emission line is analyzed to directly compare the ratio of the isotope shifted to non-shifted emission line.

Two multivariate regression techniques are discussed for use in the reconstruction of the isotopic ratio from the measured BO LIBS spectra. The first approach is to analyze discrete data, considering the intensity at each spectral bin as an independent variable. As the spectral data is already in a discrete form, due to the measurement using a CCD detector to resolve the spectra, this method is the simplest. The intensity at each CCD pixel can be treated as an independent predictor variable through the use of a partial least squares regression. Other multivariate regression methods such as principal component analysis and LASSO [180] for example apply a partial least squares regression to the intensity at each CCD pixel.

The $^{10}$B enrichment (the dependent variable) is then a function of a large number of predictor variables, which is equal to the number of CCD pixels across the spectral region used in the analysis. A matrix or vector of regression coefficients is the result of the regression analysis. The regression coefficient vector can be
multiplied by a vector representing the measured spectral intensity to extract the enrichment information.

The discrete method is limited as it does not consider the continuous nature of the wavelength vector, and as a result, is highly sensitive to the spectrometer spectral calibration. For example, consider the scenario of a peak \( I(\lambda) \) shifted by a single bin to \( I(\lambda + \Delta \lambda) \), where a peak is normally not present, due to calibration errors. The change in the two predictor variables’ values propagates through the regression analysis, which results in significant changes in the resulting regression coefficients and reconstructed enrichment. Therefore, the discrete method is highly sensitive to the calibration of the spectrometer or small changes in the grating position that occurs when the grating is rotated. For low-resolution spectrometers the width of single pixel represents a spectral range that is much larger than the uncertainty in the calibration, and the application of the discrete method would result in accurate results.

For higher resolution spectra (such as spectra obtained by large Czerny-Turner spectrometers), a continuous method, discussed in prior work by Nielsen et al., is required for the accurate reconstruction of the enrichment [181]. The continuous method can be thought of as being the the limiting case of the discrete method, as the size of the bin approaches zero (i.e. the number of predictor variables becomes infinite). The regression analysis then results in a constant of regression, \( \beta_0 \), and a regression vector of wavelength, \( \beta(\lambda) \). For example, the percentage of one isotope \( y_i \) could be calculated as

\[
y_i = \beta_0 + \int_{\lambda_l}^{\lambda_u} \beta(\lambda)\alpha_i(\lambda) d\lambda + e_i
\]

(7.3)

where \( \alpha_i(\lambda) \) is the spectral intensity and \( e_i \) is the corresponding residual from the model. The limits of the integral are the upper and lower wavelength boundaries of the spectral region considered.

The continuous method requires first that the regression function in Eq. 7.3 be approximated by a linear combination of a set of basis functions (e.g. cubic splines) [181]. The implementation of an approximate basis function that represents the behavior of the spectra reduces the problem to finding the weights (\( \theta_k \)) associated with the chosen basis function. The regression weights can be found
through traditional discrete multivariate regression methods such as partial least squares. This allows simplification of Eq. 7.3 to

\[ y_i = \beta_0 + \sum \left( \theta_k \int_{\lambda_l}^{\lambda_u} \beta_k(\lambda)\alpha_i(\lambda) d\lambda \right) + e_i \]  

(7.4)

where the integral values depend only on the chosen basis functions and spectra, both of which are known.

The numerical integration is a source of error and represents the major drawback of the continuous method. Due to the use of high-resolution spectra in the multivariate regression, the introduced error due to numerical integration is negligible. The lack of sensitivity of the continuous method on small errors in the calibration of the spectrometer between measurements makes the technique more useful and resilient than discrete methods when high-resolution spectra are available.

The continuous method was chosen for analysis due to the presence of high-resolution spectra and the small errors in the wavelength position of the spectrometer due to calibration and positioning errors associated with the grating. The regression function was approximated through 155 cubic splines and the weights were calculated through a partial least square approach. The number of splines considered in the approximation was chosen based off the minimization of the error in the reconstructed isotopic composition of the boron sample.

The use of the continuous multivariate regression model combined with fs laser ablation for isotope sensitive measurement of boron samples was demonstrated through the measurement of an unknown sample following calibration of the model by two known boron samples (natural 19.9\% 10B and enriched 97.35\% 10B). The unknown sample consisted of a B4C sample obtained from the Penn State Breazeale Nuclear Reactor with a 50.37\% 10B abundance. The result of the analysis of the unknown sample using both ns and fs laser ablation is shown in Fig. 7.2. The application of the multivariate regression model resulted in a measured 52.3\% 10B enrichment for the unknown B4C sample, which had a known enrichment of 50.37\% 10B.
Figure 7.2. Reconstructed (calculated) $^{10}$B abundance (at. %) vs. known $^{10}$B abundance for the three calibration samples using a three-point calibration. For each sample, 20 spectra have been collected, each from a different location on the sample. A $^{10}$B abundance value is reconstructed for each of these spectra, and the average of these values is shown on the plot. Error bars shown are the standard deviation of the reconstructed value over the 20 sampled locations.

7.4 Combustion of Uranium

Of interest to nuclear forensics and verification is the isotope-sensitive measurement of radiological materials, such as uranium, plutonium, neptunium, and strontium. Previous work by Hou et al. has demonstrated application of the LAMIS technique to the measurement of the isotopes of strontium using fs laser filamentation [55]. The combustion of uranium with oxygen in the ambient atmosphere has been reported in the literature [182]. Further, the uranium oxide molecular emission has been reported along with the observed isotope shift due to the presence of $^{16}$O and $^{18}$O during the uranium combustion [178]. However, in the previous work the excited UO radicals were produced through the use of a pulsed laser vaporization source that generated a molecular beam of UO from a uranium metal sample, which was cooled to $\sim$130 K through supersonic expansion. The temperatures and pressures present in the previous work are orders of magnitude different compared
to those found in laser induced plasmas. Therefore, the previous work can be used as a starting point for the initial investigation of the UO molecular emission, but it is expected that the intensity and broadening of the measured UO molecular emission within the LIBS plasma will be significantly different.

Heaven et al. identified a number of UO molecular emission features in the 590–600 nm spectral range [178]; therefore, this spectral window was chosen to elucidate the presence of any UO molecular emission in the measured LIBS spectrum. Fig. 7.3 shows a full-spectrum (maximum wavelength range allowed by achromat collection lenses) LIBS measurement of the DU sample. A number of characteristics of the uranium LIBS measurement are immediately evident: (i) the spectrum consists of thousands of emission lines that are closely spaced, (ii) the presence of a large number of emission lines results in an artificial background being generated by the closely spaced emission lines overlapping, (iii) the U emission line intensities are lower compared to other elements due to the large number of lines present, and (iv) as the wavelength is increased the number of emission lines decreases, and individual isolated uranium emission lines can be observed.

The formation of uranium oxide molecules within the plasma is dependent on the plasma assisted combustion of uranium with oxygen in the ambient atmosphere. It is possible for a thin oxide layer to be present on the sample surface that could contribute to the formation of uranium oxide in the plasma; however, this layer is readily removed with 5–10 “cleaning” laser shots. It is then possible to identify the uranium molecular emission features by the growth of the hypothesized emission features as the ambient atmospheric pressure is increased. In addition, due to the molecular emission being dependent on the formation of molecules within the plasma, the intensity of molecular emission increases at later times in laser plasma due to the plasma temperature decreasing and the ablation plume expanding into the ambient atmosphere, which results in the formation of molecular radicals. Figure 7.5 shows the result of uranium LIBS measurements under ambient atmospheric pressure as a function of the gate delay. Immediately visible in this result is the presence of an emission feature centered at 593.57 nm that exists at plasma lifetimes greater than 8 µs. Review of the LANL Uranium Atlas and the NIST Atomic Line Database [121, 183] reveals that this emission line is not associated with either U I or U II. The 593.38 nm U I emission line is
observed at delay times of 100 ns–2 µs, while the 593.57 nm emission feature is first observed after 500 ns. The delay in the observation of the 593.57 nm emission feature combined with presence of the feature at later plasma lifetimes is indicative of it emanating from uranium oxide.

Additional temporal LIBS measurements were carried out under rarefied atmospheric conditions centered at the 593.57 nm uranium molecular emission, as shown in Fig. 7.4. The rarefied atmosphere reduces the density of uranium oxide formed within the expanding plasma, which results in the commensurate reduction of the overall molecular emission intensity. The uranium molecular emission is clearly reduced in Fig. 7.4 under the rarefied atmospheric conditions compared to the ambient atmospheric results reported in Fig. 7.5. Further, the lifetime of the emission was reduced from ~8 µs to ~2 µs. Due to the high density of uranium within the plasma following ablation of the metal DU sample, very little oxygen is required to allow for the formation of uranium oxide and observation of the
molecular emission [105, 184]. The combination of the long emission lifetime, the emission peaking at later times compared to the atomic emission, and the reduction in the emission intensity under rarefied atmospheric conditions suggests that the 593.57 nm emission feature belongs to an oxide of uranium. It is not possible to further identify the molecular emission feature as UO or another uranium oxide (U_xO_y) from the measured spectra. However, based on the recent work in the literature on UO emission spectra by Dacheng et al. [105] combined with the previous work by Heaven et al. [178], it is hypothesized that the 593.57 nm emission feature is related to UO.

The temporal behavior of the UO molecular emission was further studied for both fs and ns laser ablation through measurement of the persistence of the emission for both laser pulse durations. Fig. 7.6 shows the persistence of the molecular emission following ablation by an average of ten ∼100 mJ 20 ns laser pulses. The molecular emission is observed to initially decay over 3–5 µs before briefly increas-
Figure 7.5. Femtosecond laser ablation of uranium under ambient atmospheric conditions for various gate delays and widths. Ten laser shots were averaged to obtain the measured emission spectrum.

Figure 7.6. Nanosecond laser ablation of uranium under ambient atmospheric conditions for a constant gate width of 1.0 µs. Ten laser shots were averaged to obtain the measured emission spectrum.
Figure 7.7. Femtosecond laser ablation of uranium under ambient atmospheric conditions for a constant gate width of 1.0 µs. Ten laser shots were averaged to obtain the measured emission spectrum.

ing and then continuing to decrease from 5–45 µs. The initial decrease in the emission can be explained by the initial formation of UO within the plasma (initial ablation of U from sample surface and O from the ambient atmosphere near the sample surface) that is contained behind the shockwave that initially prevents interaction with the ambient atmosphere outside the plasma. As the shockwave expands and breaks down at delays greater than 5 µs, the uranium within the plasma is able to interact with the ambient atmosphere, and an increase in the molecular emission is observed, followed by the gradual decay in the emission as the plume expands and cools. This result is in agreement with previous work by Harilal et al. [113], where the authors observed the expanding shockwave confining the molecular emission from AlO from the ambient atmosphere at early delay times. Further, the increase in the molecular emission at ~5 µs is a result of a decrease of the plasma temperature at later delay times that favors the formation of molecules within the expanding vapor plume.

A similar molecular emission persistence study was conducted for fs laser ablation of uranium under ambient atmospheric conditions using 8 mJ 42 fs laser pulses, and is shown in Fig. 7.7. The fs ablation resulted in a factor ~2 reduction
Figure 7.8. Femtosecond laser ablation of uranium under 700 Torr ambient air (black) and under a 440 Torr argon atmosphere (blue). Ten laser shots were averaged with a gate delay of 0.35 µs and gate width of 5.0 µs to obtain the measured emission spectrum.

in the persistence of the molecular emission compared to the ns laser ablation case. For fs laser ablation the molecular emission is observed to first decay at \( \sim 2-5 \) µs before increasing at \( \sim 7 \) µs, similar to the ns laser ablation case. However, the local maximum reached before the continuous decrease in the emission is delayed compared to the ns case and starts at \( \sim 7 \) µs. The delayed increase in the molecular emission for the fs laser ablation case could be due to significant material ejection from the surface being introduced into the expanding plasma/vapor plume, which occurs at \( \sim 4-6 \) µs [92]. However, material ejection has been observed to happen continuously for low energy fs laser ablation [162]. For ns laser ablation the material ablation is observed to occur shortly after irradiation of the sample by the laser pulse (\( \sim 100 \)’s ns) and continues for several microseconds due to the heating and vaporization of the sample, which drives the ejection of material from the sample surface [185].

The spectrum shown in Fig. 7.5 contains a number of closely packed atomic and ionic emission lines that under certain circumstances can interfere with the UO molecular emission. This interference is easily observed in the case of ns laser ablation, where a hot, dense plasma is commonly observed compared to fs
Figure 7.9. Femtosecond laser ablation of uranium under ambient atmospheric conditions for the gate delay/gate width shown in the figure. Ten laser shots were averaged to obtain the measured emission spectrum.

Laser ablation, which results in ionic emission lines being present in the measured LIBS spectrum. Therefore, it is of interest to locate additional molecular emission bands that occur at higher emission wavelengths where the density of uranium atomic and ionic emission lines is lower compared to the 350–600 nm spectral region. Molecular emission modeling for the UO molecular system is currently being carried out by Harilal et al. at Pacific Northwest National Laboratory [184] using constants for the UO system found in previous work by Heaven et al. [186, 178]. The result of this modeling was the prediction of additional UO emission lines in the 700–725 nm spectral region. To confirm the presence of uranium molecular emissions in this region, fs-LIBS measurements were carried out under ambient atmospheric conditions and under 440 Torr argon atmosphere. The results of these measurements are shown in Fig. 7.8. It is evident from the comparison of the two LIBS uranium spectra that none of the emission lines present in the 710–722 nm region are associated with UO; further, the emission lines present in the spectrum are identified from the LANL Uranium Atlas as belonging to either U I or U II [183].

The 710–720 nm spectral region was further studied using ns laser ablation and
Figure 7.10. Femtosecond laser ablation of uranium dioxide, uranium hexachloride, uranium nitrate, and uranium metal centered on the 593.57 nm UO emission. Emissions from U I at 593.3817 nm and UO at 593.57 nm are readily observed. Ten laser shots were averaged with a 0.35 µs gate delay and 5 µs gate width was used to obtain the measured emission spectrum.

was compared to fs laser ablation of the same spectral region, as shown in Fig. 7.9. An additional emission feature centered at 715.75 nm was observed for the ns laser ablation case, but was not present in the fs laser ablation case. The presence of this emission feature in the ns laser ablation is attributed to the molecular emission of a minor element within the sample or ambient atmosphere. It is not known to the author what molecule this emission feature is related to; however, its presence in the ns laser ablation case is due to the increased plasma temperature compared to fs laser ablation that could be populating the transitions involved with this emission. Much like atomic emission, the molecular emission originates from population of upper level energy states associated with the emission, which requires a minimum plasma temperature to obtain significant molecular emission. Further, the formation of the excited molecule/radical within the plasma could require a specific temperature in order to form. For example, the CN emission requires a plasma temperature of ∼7500 K to observe the CN violet emission.

Brown et al. observed the presence of matrix effects in the measured molecular
emission spectra of boron containing samples that had different elemental composition of the bulk matrix [33]. The matrix effects resulted in a variation in the plasma temperature and density. The observed variation in plasma parameters for the different matrix compositions results in significant differences between the measured molecular emission spectra of each boron sample as shown in Fig. 2.4. The observed matrix effect in the molecular emission of B could reduce the ability for the measured spectra to be analyzed for the isotopic composition of the sample without matrix-matched standards of known enrichment. It is not common in nuclear forensics and verification measurements to be able to control the matrix in which the analyte of interest is present, nor is it possible to know this information a priori. Therefore, it was of interest to study the uranium molecular emission from uranium samples that were not of a pure metal form such as uranium oxide, uranium nitrate, and uranium hexachloride for example. The measured UO emission spectra for the latter uranium compounds is shown in Fig. 7.10. The measurements were taken on different days and under different conditions (sample size and orientation varied uncontrollably between the uranium compounds), so the measured emission intensity can not be directly compared. The uranium metal and uranium dioxide sample resulted in the cleanest emission spectra, while the uranium nitrate and uranium hexachloride samples exhibited considerable noise. The SBR for the UO molecular emission was similar for all of the uranium samples. When the ratio of the UO emission to the U I emission at 593.38 nm at 593.57 nm is considered (where the U I emission is treated as an internal standard), the ratio is smallest for the uranium hexachloride sample, suggesting that the overall molecular emission for this sample is reduced.

The temporal behavior of the uranium hexachloride sample was studied following the indication that the uranium molecular emission was reduced for this sample, and is shown in Fig. 7.11. The UO molecular emission is observed for this sample for the first 1.5 µs, while the U I emission is observed for the first 1.0 µs. The 6:1 ratio of chlorine to uranium results in a large plume of excited Cl atoms and ions following laser ablation, which expands with the uranium into the ambient atmosphere. The Cl interacts with the ambient atmosphere and react with both the oxygen and hydrogen in the atmosphere to form HCl and ClO molecules-radicals. This reaction, in a sense, inhibits the combustion of uranium
Figure 7.11. Femtosecond laser ablation of uranium hexachloride under ambient atmospheric conditions. Emissions from U I at 593.3817 nm and UO at 593.57 nm are observed. Ten laser shots were averaged with a constant gate width of 0.5 μs to obtain the measured emission spectrum.

with the oxygen in the ambient atmosphere, thus greatly reducing the measured uranium molecular emission. The molecular emission that is observed is due to the rapid decomposition of the uranium hexachloride sample, forming uranium hydroxides through reaction with water in the ambient atmosphere. Further, the reduced U I emission suggests that the presence of chlorine in the sample greatly reduces the coupling of the laser energy to uranium when compared to the uranium metal.

While the temporal behavior of the UO emission exhibits significant variation between the different uranium samples, the spectral properties (shape and center wavelength) of the UO emission remained constant. This result suggests that – unlike the B molecular emission – the uranium molecular emission does not exhibit strong matrix effects that would affect the isotope sensitivity of the measurement.

The uranium plasma optical emission was imaged onto the slit of the CT spectrometer, which resulted in a spectrally resolved image of the plasma emission at specific points within the plasma evolution. The image was spatially resolved in
the vertical direction perpendicular to the laser beam axis. For this work it was of interest to obtain the radial distribution of the plasma emission, which was obtained from Abel inversion of the imaged plasma emission. The radial distribution of the U I and UO emission for fs laser ablation is shown in Fig. 7.12. The zero position is defined as the centerline of the plasma and the plasma was assumed to be symmetric across the centerline. The U I emission was observed to expand at a greater rate in the radial direction compared to the UO emission for fs laser ablation. The slower radial expansion can be explained by confinement of the UO to the sample surface by the expanding shockwaves, which is similar to previous work for Al I and AlO [113]. Temporal imaging of the expanding uranium plasma was limited to a few gate delays with large gate widths due to the low intensity of the U I and UO emission.

7.5 Uranium Molecular Isotope Shift

There are a number of inherent difficulties involved in performing isotope-sensitive LIBS measurements: (i) the isotope shift of atomic or ionic emission lines is small, \( \sim 1-25 \) pm, (ii) the isotope shift is transition-dependent and can vary greatly for different emission lines of the same element, and (iii) Stark and Doppler broadening within the LIBS plasma can mask the isotope shift. Recent work by Morgan et al. in [48] has shown the combination of an interferometric technique with a dispersive technique is able to improve the resolution of the LIBS measurement.
Figure 7.13. Femtosecond laser ablation of uranium under ambient atmospheric conditions. Emission from U II at 424.43 nm is clearly observed, and the small 25 pm isotope shift is observed but is below the sampling limit of the measurement system. Ten laser shots were averaged to obtain the measured emission spectrum.

by not just dispersing the light in the x-direction, but also in the y-direction on the detector. The combination of an interferometric technique (Fabry-Perot interferometry) with a dispersive technique (Czerny-Turner spectrometer) for high-resolution isotope shift measurements was developed by Jackson et al. in the 1970’s for the accurate measurement of the isotope shift present in the visible arc discharge emission spectrum of krypton [187, 188]. The latter technique is successful for the measurement of the isotope shift of uranium and other elements in emission spectroscopy; however, the technique is limited by the low SBR due to the Fabry-Perot interferometer transmitting only a small portion of the light. The result of this limitation is the requirement to integrate hundreds laser shots onto the detector surface to resolve the emission lines.

According to Nyquist-Shannon sampling theory, if a function \( y(t) \) contains no frequencies higher than \( B \) hertz, the function is completely defined by giving its ordinates in a series of points spaced \( 1/(2B) \) seconds apart. Therefore, a sufficient sample-rate is \( 2B \) samples/second. If we assume that the highest frequency measured in the LIBS spectrum is on the order of the spectral width of a single pixel, then the minimum resolvable shift in the emission spectrum is \( \sim 2–3 \) pixels.
Figure 7.14. Femtosecond laser ablation of uranium under ambient atmospheric conditions. Emission from U I at 593.3817 nm and UO at 593.57 nm is observed. Ten laser shots were averaged with a gate delay of 0.35 µs and 5 µs gate width to obtain the measured emission spectrum.

Figure 7.13 shows fs-LIBS measurement of the DU and HEU samples. The observed shift in the 424.43 nm U II emission line is highlighted in the figure and spans two pixels of the ICCD camera, which is below the minimum sampling rate to accurately resolve the isotope shift. Further, the isotope shift for the 424.16 nm and the 424.62 nm U II emission lines is not resolvable due to the smaller isotope shift (−6 and 5 pm, respectively) of these lines compared to the 424.43 nm U II emission line.

It is evident from the above results that for a field-portable or remote sensing instrument, LIBS measurement techniques that require a limited number of laser shots to be averaged combined with the ability to use simple, robust medium-resolution spectrometers must be developed. The reduction in the number of required laser shots is necessary for real-time analysis of samples as well as for the analysis of trace-level samples where the amount of sample available to be analyzed is limited. The molecular isotope shift of uranium was reported by Russo et al. in [49] to be ~2-3 times the 25 pm isotope shift for the 424.43 nm U II emission.
Figure 7.15. Nanosecond laser ablation of uranium under ambient atmospheric conditions. Emissions from U I at 593.3817 nm, U II at 593.4445 nm, and UO at 593.57 nm are observed. Ten laser shots were averaged with a 3 µs gate delay and 5 µs gate width to obtain the measured emission spectrum.

A series of experiments was carried out using the DU and HEU samples available at The Pennsylvania State University to resolve the molecular isotope shift in the 593.57 nm UO molecular emission. Fig. 7.14 shows the result of fs-LIBS measurement of the DU and HEU sample for a 0.35 µs gate delay and 5 µs gate width. The spatial position within the plasma that the collection optics imaged had to be optimized to increase the UO emission signal. It was found that the best SBR for the UO molecular emission was achieved when the collection optics were focused ∼1 mm off the sample surface at a 45° angle. As the UO emission originates from plasma assisted combustion of the uranium sample with the ambient atmosphere and is further enhanced at later plasma lifetimes when the plasma has expanded and cooled, the offset of the collection optics correlates to where the UO density within the plasma is maximized.

A 0.050 ± 0.007 nm UO molecular isotope shift is observed for fs ablation of the DU and HEU samples, and is a factor of two larger than the 25 pm shift for the 424.43 nm U II emission line. The error in molecular isotope shift is computed
as the spectral range of a single pixel on the ICCD detector when the 1800 g/mm grating in the iHR-550 spectrometer is used. The 593.38 nm U I emission line interferes with the UO emission for the HEU case, as the U I and UO emissions shift and are in closer proximity compared to the DU case. The interference of uranium atomic and ionic lines is more prevalent for ns laser ablation of the DU and HEU samples, as additional U II lines are observed due to the increased plasma temperature compared to fs laser ablation as shown in Fig. 7.15. The 593.44 nm U II emission line is observed for both the DU and HEU samples in the ns-LIBS measurement, and occurs between the U I emission at 593.38 nm and the UO emission at 593.57 nm. The presence of the additional ionic lines further reduces the ability to accurately resolve the UO emission and shift and requires accurate fitting of the three emission lines to deconvolve the spectrum. A $0.050 \pm 0.007$ nm UO molecular isotope shift is observed for the ns ablation, which matches the fs ablation case and confirms the presence of the molecular isotope shift in the measured uranium spectra.

### 7.6 Fs Laser Filamentation

LIBS is an attractive method for remote measurements, but one of the challenges that arises is the ability to produce a small laser focal spot size on the sample surface at large distances [189]. Diffraction as well as optical distortions incurred during propagation through air cause the focal spot size to increase as the propagation distance increases. A commensurate increase in the laser power is required to achieve plasma formation on the sample surface. It is possible to decrease the spot size at longer distances by increasing the aperture of the focusing mirror or lens; however, due to the physical and cost constraints that are usually present, the size of optical components is limited. Further, even high-quality optics suffer from aberrations that, along with the atmospheric distortions, limit the minimum laser focal spot size and intensity that can be produced on the target surface. Currently, remote-LIBS (R-LIBS) measurements employing ns lasers have been demonstrated at distances of up to $\sim 100$ m [18].

In contrast to ns-LIBS, fs-LIBS can take advantage of the complex but favorable nonlinear dynamics of fs laser propagation in air. Self-focusing of an initially
collimated fs laser pulse occurs when its peak power exceeds the critical power, \( P_{cr} = \frac{3.72\lambda^2}{(8\pi n_0 n_2)} \), where \( \lambda \) is the laser wavelength and \( n_0 \) and \( n_2 \) are the linear and nonlinear indices of refraction, respectively. An interplay of plasma defocusing and self-focusing results in a laser filament with a typical intensity on the order of \( 10^{13} \) W/cm\(^2\) [190, 191]. A filament has a central core with diameter in the range of 100–200 µm, which is surrounded by an energy reservoir [190, 192, 193]. Filaments have been shown to be capable of propagating over distances on the order of kilometers [194]. The range of filament propagation is dependent on the initial laser pulse parameters [58] and on the characteristics of the external focusing [193]. Further, the characteristics of filament-induced plasma, including its optical emission, are dependent on the filament spatial evolution [195]. The combination of fs laser filamentation with LIBS is known as Filament Induced Breakdown Spectroscopy (FIBS) [58]. To the best of the authors knowledge the only true remote FIBS measurement was performed by the Rohwetter group on a copper target placed 180 m from the laser and collection optics [58].

7.6.1 Filamentation LIBS of Copper

For remote sensing measurements it is of interest to study the propagation distance dependence on the LIBS emission of samples under fs filamentation ablation. Copper plasma generated at different filament-copper interaction points was characterized by spectroscopic, acoustic, and imaging measurements. The initially collimated laser beam (20 mm diameter at full-width half-maximum) was loosely focused with a 25.4 mm diameter, \( f = 4.0 \) m plano-convex lens to create laboratory-scale filaments. A laser pulse energy of 3.5 mJ pulse duration of 53 fs was used.

Acoustic measurements of sound/ultrasound generated near/in the ablated copper target as well as sound emanating from air as the plasma propagates freely, were conducted to better understand the dependence of plasma characteristics as well as its emission on the location along the filament where it impinges on the target. Yu et al. in Ref. [196] provides a detailed description on the use of acoustic diagnostics for filament length diagnostics. In the setup, a sensitive microphone (PCB Piezotronics 378A13), was placed used to detect the filament-induced acous-
tic signal in the ambient atmosphere. The microphone was placed on a ruled optical rail that allowed for the measurement of filaments as long as 2.5 m. The lock-in rail carrier ensured the distance of the microphone from filament propagation axis was maintained at a constant distance translation of the microphone parallel to the filament. The filament propagation distance dependent acoustic emission was then obtained by sliding the microphone on the rail in steps of 2.0 cm, and is shown in Fig. 7.16.

The measured acoustic emission of the filament can be used to qualitatively determine the filament intensity along the propagation distance, as previously reported by Rohwetter et al.[58]. The filament intensity is related to the free electron density in the filament, and the free electron density can be inferred from the measured acoustic emission of the filament. The filament intensity reaches a maximum 30 cm before the geometric focus of the lens. The length of the resulting filament was determined to be \( \sim 2.5 \) m from acoustic measurements. However, the Cu atomic emission was observed only over a 0.75 m-long portion of the filament. The longer filament length determined by the acoustic measurement suggests that at filament-copper interaction points outside of bounded region shown in Fig. 7.16, the filament intensity is below the breakdown threshold for copper. The intensity profile of the filament was measured using burn paper at multiple positions along the filament propagation, confirming the presence of single filamentation. The filament-copper interaction point where the ionic emission is first observed (approximately \( \sim 50 \) cm) can be considered the point at which the filament intensity has increased above the breakdown threshold of uranium. Similarly, the interaction point at \( \sim 25 \) cm is interpreted as the point at which the filament intensity drops below the copper breakdown threshold.

The dependence of FIBS emission on the filament propagation distance was obtained by varying the length of the filament that is incident on the target. The spectra were measured with a gate width of 1.0 \( \mu \)s and a gate delay of 200 ns following the arrival of the laser pulse on the target.

The filament-copper interaction point was scanned in steps of 10 cm over the length of the filament by sliding the \( f = 4 \) m lens along the optical rail perpendicular to the surface of the copper target. Representative Cu FIBS spectra measured at several filament-copper interaction points are shown in Fig. 7.17. The
Figure 7.16. Peak-to-peak acoustic signal averaged over 100 laser shots as a function of microphone distance from the geometrical focus of the lens \((f = 4 \, \text{m})\) for 53 fs laser pulses at an energy of 3.5 mJ. The region bounded by the vertical dashed lines indicates the locations at which filament-induced line emission from the copper target was observed.

filament interaction points are measured from the geometrical focus of the lens. Fig. 7.18 (a) shows the intensity of Cu I 521.82 nm emission line as a function of filament propagation distance.

The Cu I 521.82 nm emission line was first observed at a distance of \(-50 \, \text{cm}\), and this interaction point can be considered the point at which the filament intensity exceeded the breakdown threshold of the sample. The Cu I 521.82 nm emission line increases slowly at first once the filament intensity increases over the copper breakdown threshold. However, as the filament intensity approaches the maximum intensity measured through the acoustic measurements, the characteristic copper emission rapidly increases. The nonlinear behavior of the copper characteristic emission along the propagation distance of the filament is consistent with recent work that observed nonlinear behavior of the LIBS emission intensity around the breakdown threshold of the sample [197]. Initially only a small portion of the filament core exceeds the breakdown threshold of the sample. As the filament propagates towards the maximum filament intensity the entire core of the filament exceeds the breakdown threshold of the sample and contributes to the ablation and plasma formation on the sample surface. The copper characteristic emission
Figure 7.17. Typical Cu FIBS spectra at several filament-copper interaction points.

Intensity is observed to exhibit a plateau behavior from the point of maximum copper characteristic emission intensity to a point just before the geometric focus of the lens. The filament intensity is directly related to the density of ionized electrons in the air [198], and the high density plasma self-steepens the propagating filament spectrum that results in a blue-shifted asymmetric spectral broadening of the filament spectrum [199, 200, 201].

The continuum optical emission that contributes to the observed background in the LIBS measurement is due to free-bound (recombination) emission, free-free (bremsstrahlung) emission, and the filament emission. These background emissions may last for several $\mu$s after the laser ablation, and overlaps the characteristic emission lines in the measured FIBS spectrum. The presence of this background has a direct effect on the measured emission spectrum and reduces the SBR. The broadband filament emission can be removed through temporally gating the measurement past the short lived filament emission.

As the filament propagates through the ambient atmosphere, complex spatiotemporal evolution is observed that affects the spectral and temporal behavior of the filament. Due to the propagation distance’s dependence on the filament
Figure 7.18. (a) Peak-to-peak intensity (filled circle) and SBR (filled square) of Cu I 521.82 nm emission line. (b) Propagation distance dependent temperature (filled circle) and density (filled square). (c) Acoustic signal detected with a microphone placed 5 cm away from the copper target (filled circle) and acoustic vibration signal detected with a transducer attached to the back face of the copper target (filled square). The lines are to guide the eye.

The evolution (spectrum, intensity, size, etc.), the SBR of the measured characteristic Cu emission lines will vary along the filament propagation distance. It is necessary to study the SBR of the characteristic Cu emission lines along the filament propagation distance to determine if an optimum filament-copper interaction point exists.

Figure 7.18 (a) shows the dependence of the Cu I 521.82 nm emission line SBR on the filament propagation distance. The SBR was calculated as $SBR = (I_{line} - I_B)/I_B$, where $I_{line}$ is spectral amplitude of the Cu I 521.82 nm emission line, and $I_B$ is the constant background intensity obtained by a linear fit near the tail of the characteristic emission line. At low filament intensities the FIBS emission exhibits a high SBR with a relatively low overall emission intensity for the
Figure 7.19. Example of the Lorentzian fit applied to the 510.55 nm Cu I emission line for the −30 cm filament-copper interaction point that was used to calculate the Stark Broadening of the emission line for plasma density calculations.

Cu I 521.82 nm emission line. This result is surprising, as the filament intensity is just above the breakdown threshold of the copper sample and a robust plasma is not formed compared to filament-copper interaction points where the maximum filament intensity is observed.

The plasma temperature was calculated using the Boltzmann plot method, which implicitly assumes the existence of quasi-LTE (collisionally dominated) among the bound states of radiation that resulted in the emission of the Cu I lines included in the analysis [152]. This assumption is valid as long as the minimum plasma density satisfies the McWhirter criterion for plasma density shown in Eq. 5.1. A plasma with density $\geq 2.2 \times 10^{15}$ e$^-$/cm$^{-3}$ would satisfy the minimum set criterion for a Cu plasma. As seen in Fig. 7.18 (b), the McWhirter criterion is met throughout the propagation distance. However, the McWhirter criterion is a necessary but not sufficient criterion for the existence of LTE [152]. Fig. refCuBoltz shows an example of the Boltzmann plot obtained for the copper FIBS measurement at −30 cm, which shows good linearity and confirms (along with the McWhirter criterion being satisfied) the assumption of quasi-LTE being established.

Interpolation of the temperature-dependent electron impact width parameters
reported in [202] as well as the measured Stark broadened spectral line width of the 510.55 nm emission line were used to calculate the electron density. An example of the Lorentzian spectral line fit applied to the 510.55 nm Cu I emission line at filament-copper interaction distance of −30 cm is shown in Fig. 7.19. The FWHM of the Lorentzian fit was extracted along the propagation distance of the filament, and the instrumental broadening was directly removed from the measured FWHM to obtain the electron density at each filament-copper interaction point. Figure 7.18 (b) shows the dependence of the calculated plasma density on the filament propagation distance. The maximum plasma density obtained near the end of the filament propagation is \( n_e = 6.7 \times 10^{17} \text{ cm}^{-3} \). The plasma density increased rapidly at the filament-copper interaction point where the maximum filament intensity was observed, as shown in Fig. 7.18 (b). However, the highest plasma density is observed shortly after the geometric focus of the lens (10 cm). For longer filament propagation distances, the increased plasma density is attributed to the asymmetric spectral broadening of the filament spectrum as the filament propagates through the ambient atmosphere.

A piezo-electric transducer was attached to the back surface of the copper target to detect the acoustic signal being transferred through the copper sample. The
variation of the acoustic signal detected by the microphone placed near the copper target is different from that detected by the transducer, as can be seen from Fig. 7.18 (b). The acoustic signal measured by the transducer shows a general qualitative similarity with the variation in the copper plasma density along the filament propagation distance, as can be seen when comparing Figs. 7.18 (b&c). The acoustic signal generated in the target is composed of ultrasound generated by the recoil of the target following the ejection of mass during the ablation process. Shortly after this initial impulse, a lower magnitude ultrasound emission was detected by the transducer that is related to the pressure exerted on the sample by the expanding plasma. When the microphone is placed near the sample surface, the propagation-distance-dependent acoustic emission correlates with the measured plasma temperature. Both the plasma temperature and density contribute to the magnitude of the acoustic emission measured by the microphone through the generation of supersonic expanding shockwaves.

The ICCD detector was then removed from the spectrometer, and a narrow bandpass filter (515 nm center wavelength with 10 nm FWHM) was acquired to generate orthogonal cross-sectional images of the expanding plasma. The cross-sectional images allowed for direct analysis of the spatial distribution of the copper plasma emission over the propagation distance of the filament, as shown in Fig. 7.21. Along the propagation distance of the filament the plasma, spatial distribution and overall plasma emission intensity varies. The ICCD was gated ~250 ns to remove the coupling of the reflected laser light and filament emission into the detector. The maximum plasma emission was observed at the filament-copper interaction point that exhibited the highest calculated plasma temperature and measured filament intensity. The bandpass filter passes both the characteristic Cu I emissions at 510.5, 515.3, and 521.8 nm as well as the continuum emission. The increase in plasma temperature results in a commensurate increase in the continuum emission through bremsstrahlung emission and correlates well to the imaged plasma emission shown in Fig. 7.21 (i). Although the imaged plasma emission is increased at the peak plasma temperature, the characteristic Cu I 521.82 nm line emission is maximized at the geometric focus of the lens, which is 20 cm from the maximum observed filament intensity as shown in Fig. 7.18 (a).
7.6.2 Filamentation LIBS Uranium

In this section, a technique combining fs filamentation and LAMIS (F2–LAMIS) [55] is demonstrated for the real-time, isotopically sensitive remote detection of uranium at standoff distances (1 m in this work). The result suggests a significant potential for LIBS use in important nuclear security applications. Differences in the variation of the emission intensity along the filament propagation distance were observed for UO (molecular), U II (ionic), and U I (atomic) emissions. However, a nearly constant signal-to-background ratio (SBR) was observed along the filament for UO emission, in contrast to U II and U I emission, where distinct maxima of the SBR are observed near the end of the filament. The constant UO SBR indicates that the filament propagation distance does not have to be extensively optimized for the F2–LAMIS measurement.

A simplified schematic of the experimental setup is shown in Fig. 7.22. The
Figure 7.22. (a) Filament propagation distance resolved acoustic measurement setup. (b) F2–LAMIS spectral measurement setup includes both a remote collection using a fiber-coupled lens placed 1 m from the sample and a high-efficiency short focal length fiber-coupled collection optic placed 55 mm from the sample surface.

Laser pulse energy and pulse duration were set to 8.0 mJ and 42 fs, respectively. The initially collimated laser beam (20 mm diameter at full-width half-maximum) was loosely focused with a 25.4 mm diameter, \( f = 4.0 \) m plano-convex lens to create laboratory-scale filaments. The filament propagation distance was varied by sliding the laser focusing lens mounted on an optical rail. Due to safety requirements established for this experiment which include operation in a sealed environment, the laser pulse was focused through a 5 mm thick optical window placed at the end of the vacuum tube, as shown in Fig. 7.22. The position of the window was varied from 2.5–4.3 m from the sample surface in steps of 30 cm through the addition of sections of flexible vacuum tubing. The vacuum tubing was added in 30 cm increments such that the window was maintained at 0–30 cm from the focusing lens over the propagation distance of the filament. This constraint in the experimental setup results in the variation of laser intensity at the window as the focusing lens is translated, with the commensurate variation of the contribution of the window to self-phase modulation during filament formation. However, the
filament propagation distance effects can still be correlated to the filament axial intensity profile through its direct measurement using acoustic diagnostics.

For the filament propagation distance-dependent measurements, the uranium plasma emission was coupled into an optical fiber using a 55 mm-focal length, 25.4 mm-diameter lens mounted at a 45° angle with respect to the filament axis. For remote detection measurements, a 10-cm lens was placed 1 m from the sample, also at an angle of 45° with respect to the filament axis, and was coupled to an optical fiber. Both fibers were coupled to the iHR-550 spectrometer. Ten laser ablation accumulations were acquired for each spectral acquisition following five cleaning ablations, which ensured the removal of a possible thin oxide layer on the sample surface. The acoustic signal as a function of propagation distance of the filament was then obtained by sliding the focusing lens along an optical rail in steps of 10 cm.

As the filament propagates through air and through the optical window, it undergoes significant temporal modulation and spectral broadening, as previously shown in numerical simulations and experimental measurements [203, 204]. We observed this broadening by inserting an uncoated wedge optic into the filament path at a grazing incidence and coupling the reflected light into a spectrometer. The filament spectrum is shown in Fig. 7.24 for two filament-uranium interaction...
Remote detection of DU and HEU was achieved using a 1.2 m long filament and a 1 m detection standoff, which produced an observable molecular isotope shift of $0.050 \pm 0.007$ nm for the 593.6 nm UO molecular emission band head that is shown in Fig. 7.25, and is approximately a factor of two larger than the largest atomic/ionic isotope shift of 0.025 nm for the U II 424.43 nm emission. A gate delay (1.0 $\mu$s) and width (10.0 $\mu$s) was optimized to maximize the measured molecular emission intensity, which also led to more robust observation of the molecular isotope shift.

In order to characterize the optical emission of plasmas generated at different filament propagation distances, we studied the intensity variation of the UO molecular emission (593.57 nm), the U I atomic emission (591.53 nm), and the U II ionic emission (409.0 nm) using a gate delay and width of 0.35 $\mu$s and 5.0 $\mu$s, respectively. A Gaussian line profile was fit to the measured atomic, ionic, and molecular emission lines. The intensity, area, width, and y-offset of the fitted peak were extracted at different filament-uranium interaction points.

The fitted UO molecular emission intensity and SBR along the propagation distance of the filament are shown in Fig. 7.26. The intensity of the UO emission

\textbf{Figure 7.24.} Measured filament spectrum at $-120$ cm (black) and at $-20$ cm (red).
Figure 7.25. Remote detection F2–LAMIS spectra at 1 m of the DU (black) and HEU (red) samples showing a molecular isotope shift of $0.050 \pm 0.007$ nm for the 593.6 nm UO molecular emission band head.

initially increases with filament propagation distance before reaching a maximum 40 cm before the geometric focus. However, the UO SBR (defined as the ratio of the peak intensity of the emission line and the background intensity) maintained a nearly constant value ($-120-0$ cm). The uranium atomic (591.53 nm) emission initially increases before reaching a maximum ($\sim 500\%$ above the lowest emission intensity) at $-50$ cm and then rapidly decreases, as shown in Fig. 7.27. Similarly, the uranium ionic emission (409.0 nm) initially increases before reaching a maximum ($\sim 600\%$ above the lowest emission intensity) at $-30$ cm and then rapidly decreases, as shown in Fig. 7.28. In contrast to the UO molecular emission, the SBR of the uranium atomic and ionic emissions increases to a maximum ($\sim 50\%$ and $\sim 20\%$ above the minimum value of the SBR, respectively). For the molecular, atomic, and ionic emissions, the peak intensity was observed at different filament-uranium interaction points. The U II, U I, and UO emission peaked at 20, 0, and 10 cm, respectively, after the peak filament intensity shown in Fig. 7.23.

Variation of the emission intensity along the filament propagation distance depends on the origin of the emission (atomic, ionic, or molecular) and on the characteristics of the plasma. The molecular, atomic, and ionic emission intensities are functions of temperature; however, the molecular emission is dependent on the
Figure 7.26. The UO molecular emission exhibits a nearly constant SBR over the propagation distance of the filament. The peak molecular emission intensity increases over the propagation distance of the filament.

density of UO in the plasma, while the atomic and ionic emission is dependent on the density of U I and U II in the plasma, respectively [49].

Treating the plasma as homogeneous and in quasi-LTE, the dependence of emission intensity on plasma temperature at different filament-uranium interaction points can be calculated. The upper energy level associated with the U II 424.43 nm emission is 3.03 eV [183]. In previous studies by Hou et al. [55] and Harilal et al. [205], the plasma temperature along the filament was shown to vary by $\Delta T/T < 10 - 20\%$. If a plasma temperature of $T = 0.8$ eV is assumed, a $\Delta T/T = 10\%$ change in the temperature results in a $\Delta I/I = 30\%$ change in emission intensity. The much greater experimentally measured variation of the U II emission intensity provides evidence that the plasma density also varies along the filament propagation distance.

The maximum in the UO emission intensity suggests that at the optimum filament-uranium interaction point ($\sim 40$ cm) the density of UO within the plasma is maximized. In prior profilometry measurements of the filament ablation craters in similar experimental conditions [55], it has been observed that the greatest mass removal occurs at the peak of the molecular emission. The origin of the molecular emission from a non-oxidized sample has been shown to be due to the formation of
diatomic molecules through reactions with the ambient atmosphere [55, 49, 105]. The much greater increase of both the atomic and ionic emission compared to the UO emission suggests that an increase of the mass of ablated uranium produces a greater increase in the density of neutral and ionized U atoms than the UO molecules.

The differences in the SBR profile of the uranium molecular, atomic, and ionic emission along the filament result from the difference in the variation of the plasma density, the U and UO density in the plasma, and the background. The background consists of bremsstrahlung and recombination emission and increases at a rate commensurate to that of the UO emission. The U I and U II emissions, however, increase at a rate greater than the background emission.

Maximization of the ablated mass and the plasma density at the −20 cm filament-uranium interaction point that leads to an optimization in the SBR for both the atomic and ionic emissions may be a result of the spectral broadening of the filament, which is shown in Fig. 7.24. The broadened filament spectrum increases the efficiency of multiphoton ionization during the filament-uranium interaction and ablation process. This result agrees well with previous work by Gunaratne et al. in [87] that showed a factor of four decrease in the LIBS threshold when the laser bandwidth is doubled from 15 to 30 nm. Further, the broadened filament spectrum may result in a decrease of the pulse duration that could also contribute to the ablation efficiency. [190, 87] At longer filament propagation distances the filament intensity decreases due to energy depletion.

7.7 Summary

The LAMIS technique was extended to fs laser ablation of boron and the isotope sensitive measurement of uranium. The uranium molecular emission was confirmed at 593.57 nm through temporally resolved measurement of the uranium LIBS spectrum under ambient atmospheric and rarefied atmospheric conditions. Further, the UO emission was studied using both ns and fs laser ablation. For the ns laser ablation case, additional uranium ionic emission lines were observed that interfered with the measurement of the UO emission. For both pulse durations a UO molecular isotope shift of 0.050 ± 0.007 nm was observed.
Figure 7.27. The atomic (591.53 nm) emission intensity and SBR increase to their maximum at \( -50 \) cm. The maximum in the atomic emission at \( -50 \) cm indicates that the U density within the plasma is maximum at this filament-uranium interaction point.

Figure 7.28. Dependence of uranium ionic emission (424.43 nm) and SBR on filament propagation distance. The intensity and SBR initially remain nearly constant before rapidly increasing to their maximum at \(-30\) and \(-20\) cm, respectively.
Laboratory-scale femtosecond filaments were produced and used to induce breakdown and plasma generation on copper and uranium samples. Spectroscopic, acoustic, and plasma emission imaging diagnostics were used to study filament-propagation-distance-dependent characteristics of the filament-induced plasmas. It has also been shown that the acoustic signal from the expansion of the filament-induced plasma in air is qualitatively correlated with the temperature of the plasma, while the acoustic wave propagating through the ablated solid target is correlated with the density of the plasma.

The Cu I 521.82 nm emission intensity measured along the filament propagation distance is correlated with the temperature and density of the plasma at the corresponding filament-copper interaction points. As a result of these measurements, it was found that there is an optimum filament-copper interaction point where the emission intensity and SBR of the Cu I 521.28 nm emission line is maximized. Although the results presented here are based on specific experimental conditions (i.e. filaments generated through forced focusing using a 4.0 m focal length lens), the existence of an optimum location along the filament indicates that filament-induced plasma as well as its optical emission characteristics are significantly affected by the propagation-distance-dependent temporal and spectral evolution of the filament.

The utility of F2–LAMIS, the recently demonstrated all-optical remote detection technique, was demonstrated for remote sensing of uranium with isotopic selectivity. This approach could enable real-time remote detection of the isotopic composition of multiple nuclear-security-relevant materials with no sample preparation. In addition, the technique could be used for analysis in geophysics and planetary science, as well as environmental monitoring applications where standoff detection, limited sample preparation, and isotope selectivity are desirable. The peak molecular, atomic, and ionic emission were observed at different filament-uranium interaction points. The difference in the optimization of the atomic, ionic, and molecular emission arises from the origin of the specific emission within the plasma.

The increase in the ablation and ionization efficiency at specific filament-target interaction points could be due to the asymmetric broadening of the filament spectrum due to plasma-induced self-phase modulation and optical Kerr effect, which
occurs as the filament propagates through the ambient atmosphere and the optical window. [206] The molecular emission SBR varied by \( \sim 10\% \) over the filament length due to an increase in the ablated U mass and a commensurate increase in the plasma density. In a recent comprehensive review by Labutin et al. [65] it has been argued that the potential for future use of laser filaments for remote LIBS measurements depends on the continuing advancement of the understanding of the spatial evolution of the laser filament as well as the plasma generation and emission, which this work has partially addressed. In the future it would be beneficial to elucidate the effect of optical window on the filament formation and evolution, compared to the free propagation of the filament.

The measured UO molecular emission exhibited strong broadening, which caused the individual rotational components of the vibrational emission to merge into a wide band head. The gate delay and width were optimized to concurrently observe the isotope shift and to obtain sufficiently high intensity for remote measurements. The combined use of acoustic and spectroscopic measurements allowed a qualitative relationship of the intensity profile of the laboratory-scale femtosecond filaments to the measured acoustic emission to be established. In the future it will be beneficial to optimize the plasma parameters such that the spectral broadening of the UO molecular emission can be reduced. While the observed broad molecular emission band head does not prevent discrimination between nearly pure isotopes of uranium, it makes the measurements of intermediate uranium enrichments much more challenging. It was observed that increasing the acquisition delay to delays greater than \( \sim 10 \) \( \mu \)s resulted in UO molecular emission spectra exhibiting less broadening due to the cooling of the rapidly expanding filament-induced uranium plasma. However, this reduction of broadening was accompanied by reduction of the magnitude of the measured UO emission. The temporal dependence of the UO emission is an indication of the dynamics of population of different vibrational and rotational levels involved in the emission. Combined with the lower plasma density and temperature at longer delay times, the gate delay and width could be varied to optimize the measured molecular emission for more robust discrimination of the isotopes of uranium. Lastly, additional UO molecular band heads could be exploited for uranium isotope analysis; however, there is a lack of published work identifying the location of these band heads.
Conclusions and Perspectives

The timely detection of clandestine nuclear material production and the continuous verification of overt nuclear material production by either a state or non-state actor represent the foundation of both international nuclear nonproliferation and domestic counterproliferation activities. The research in remote sensing is in large part driven by the need to tackle pressing challenges related to the gaps in, or complete lack of, capability to answer critical questions related to a country’s or an organization’s nuclear proliferation activities. Current WMD detection methods have both limited distances and analysis times over which they are effective. Moreover, environmental conditions present in the field (e.g., humidity, temperature, and background radiation) can affect detection range and limit applicability of these methods even further. An ideal detector must be able to efficiently detect nuclear materials present at trace levels, to distinguish between the source of the detected fissile material, such as, $^{235}$U, $^{239}$Pu, or $^{233}$U, to perform this discrimination in near real-time, and to do so in-the-field with no sample preparation. In order to address these requirements and to provide a previously unavailable SNM detection capability, as well as to advance the field of optical emission spectroscopy as a whole, it is essential take advantage of ongoing advances made in the fields of laser physics and chemistry.

The goal of this research was to investigate the development of laser-induced breakdown spectroscopy (LIBS) for the analysis of nuclear-relevant materials with little or no sample preparation, and to understand the physics involved with the observation of a “matrix effect” in the measured signal, which results from the
bulk matrix composition of the sample.

Investigations conducted as a part of this dissertation include experimentation with and analysis of the relevant physics occurring in the LIBS plasma, including the plasma persistence, density, temperature, and spatial distribution. A particular emphasis of the research was to experimentally characterize for the first time the plasma-assisted combustion of uranium within the LIBS plasma following laser irradiation of a uranium sample. In addition to the experimental investigations, *ab initio* modeling was conducted to aid in the understanding of physical mechanisms that result in the observed behavior in the measured emission spectra. Significant findings of this research can be summarized as follows.

The LIBS characteristic line emission is dependent on a number of controllable and uncontrollable measurement parameters including laser wavelength, laser pulse shape, and sample composition for example. The LIBS emission was increased for laser pulses with increased spectral bandwidth generated during fs laser filamentation, which corroborates previous work reported within the literature for traditional fs LIBS. Control of the plasma optical response has been realized through irradiation of the material by temporally shaped femtosecond pulses. For the non-gated LIBS system an increase in signal to background ratio (SBR) for both copper and uranium has been observed for stretched 250 fs laser pulses compared to transform-limited 45 fs laser pulses. The increase in the SBR is due to a decrease in the continuum emission at the optimized pulse duration. The plasma optical response was controlled through a genetic algorithm feedback optimization process, which resulted in an increased SBR and ionic-to-atomic line ratio. Through control of the ion-to-atomic line ratio, direct control on the plasma ionization state has been demonstrated by fs pulse shaping. Further, the SBR of the LIBS measurement was improved through the implementation of mid-IR femtosecond pulses in the LIBS measurement apparatus. Continued improvement of the SBR will lead to an increase in the sensitivity and reliability of the LIBS technique for material identification in complex samples.

A LIBS apparatus has been developed by the author for the study of the “matrix effect” observed in LIBS measurement of binary aerosol samples. A nebulizer was added to the experimental apparatus to allow precise control of the rate and composition of the generated aerosol particles. The characteristic LIBS emission
of the analyte of interest, which results from laser irradiation of aerosol particles, has been found to be affected by the elemental composition of the bulk matrix, as observed for the sodium-containing aerosol particles. The variation in the characteristic Na aerosol LIBS emission was direct evidence of a matrix effect arising from the aerosol measurement, which has been determined to primarily result from perturbations of the plasma properties. Through complex ab initio modeling an increase in the plasma density and decrease in the free-electron-to-atom ratio was predicted for the mixed Na aerosol samples, which was responsible for the enhancement of the Na D line emission. The variation in the Na LIBS emission was found to be temporally dependent. Further, the temporal location of the peak Na LIBS emission was observed to be independent of the elemental composition of the bulk matrix.

The filament propagation-distance-dependent characteristic LIBS emission has been extensively studied for copper and uranium samples. A novel experimental apparatus was developed to allow for filamentation to occur within a sealed experimental chamber per regulations in place for the use of radiological and special nuclear material (SNM) within the laboratory at the Pennsylvania State University. The atomic, ionic, and molecular emission of uranium was observed to be optimized at different filament-uranium interaction locations. The propagation distance dependence of the characteristic emission intensity and SBR is due to the complex spatiotemporal evolution of the filament. The spectral broadening of the laboratory scale filament generated through loose initial focusing of the collimated laser beam was shown to increase over the length of the filament. The spectral broadening results in a decrease in the breakdown threshold, and, thus, an increase in the LIBS emission similar to previous work reported for traditional fs LIBS. However, as the filament propagates further the laser pulse fluence decreases and drops below the breakdown threshold of the sample regardless of the amount of spectral broadening present. Lastly, the extension of fs filamentation laser ablation molecular isotopic spectrometry (F2–LAMIS), the recently demonstrated all-optical isotope-sensitive detection technique, has been demonstrated for the remote isotope-sensitive measurement of uranium.

The major result of this research is the improved understanding of the prospects for the use of LIBS as remote isotope-sensitive detection technique for real-time
analysis of materials relevant to nuclear security. The LIBS characteristic emission has been shown to be dependent on the chemical properties of the elements that compose the sample, which has the effect of reducing the quantitative capability of the LIBS technique. In the larger analytical chemistry community, the dependence of the emission on the elemental properties of the bulk matrix is relevant to the ICP-MS and notably the LA-ICP-MS and ICP-AES fields. This quantitative limitation imposed on the LIBS technique may be overcome by the implementation of complex first-principles modeling, which has been shown to accurately predict the optical response of the LIBS plasma when a matrix effect is known to be present in the experimental measurement. While it has been shown that LIBS is capable of isotope-sensitive measurements, the molecular emission considered in this work exhibited significant broadening that is expected to limit the analysis of uranium samples of intermediate enrichment. Lastly, the presence of multiple characteristic atomic and ionic emission lines has been shown to interfere with the molecular isotope shift measurement.

Several steps of recommended future work are required to overcome the stated challenges. First, it will be beneficial to optimize the plasma parameters such that the spectral broadening of the UO molecular emission can be reduced. The presence of strong line broadening resulted in the individual rotational components of the vibronic emission merging into a wide band head. It was observed that increasing the acquisition delay to \( \gtrsim 10 \) \( \mu s \) resulted in isolated UO molecular emission spectra exhibiting less broadening due to the cooling of the rapidly expanding filament-induced uranium plasma. However, this reduction of broadening was accompanied by reduction of the magnitude of the measured UO emission. The temporal dependence of the UO emission is an indication of the dynamics of population of different vibrational and rotational levels involved in the emission. Combined with lower plasma density and temperature at longer delay times, the gate delay and width could be varied to optimize the measured molecular emission for more robust discrimination of the isotopes of uranium. Finally, additional UO molecular band heads could be exploited for uranium isotope analysis, though there is a lack of published work identifying the location of these band heads. Therefore, an extensive experimental and modeling effort is needed to systematically search through the uranium LIBS spectrum for additional UO emission lines.
Second, a systematic study on the presence and trend of observed matrix effects with the chemical properties of the bulk matrix in LIBS analysis of solid samples must be performed. Careful and tedious sample preparation is required to create the binary mixed solid samples that limited their use in this work. A range of elemental powders of small grain size (<1–5 µm diameter) must be acquired and mixed homogeneously to form pressed pellets capable of being analyzed using LIBS. Measurement of samples where multiple emission lines for each element within the sample are observed must be made to determine if it is possible to predict the presence of a matrix effect from the LIBS spectra without the use of comparative standard samples.

Third, careful measurement of the effect that the laser pulse spectral bandwidth and duration have on the measured atomic, ionic, and molecular uranium LIBS emission should be carried out to elucidate the physical mechanisms behind the difference in the optimization of the characteristic emissions observed in the F2–LAMIS measurements. Fast gated imaging of the expanding laser plasma should be carried out with narrowband filtering to generate a spatial map of the atomic and molecular uranium emissions. Such information would improve the LIBS community’s understanding of the physical mechanisms behind the plasma-assisted combustion of uranium and the temporal behavior of the uranium molecular emission.

With further research into the above areas, a real-time, isotope-sensitive laser-based detection technique capable of remote quantitative measurement may be realized. As a result of the in-depth modeling and experimental efforts undertaken, this dissertation provides the groundwork for future contributions to the field of laser remote sensing with regard to the design and efficacy of an all optical based isotope-sensitive remote measurement technique.
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