

Spectroscopic Imaging of Aluminum Containing Plasma

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*I would like to dedicate this work to my parents, without whose love and support I
would not be able to be here today.*

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Imagination will often carry us to worlds that never were. But without it we go nowhere.

Carl Sagan

Abstract

This dissertation aims to characterize laser-induced plasma from a physics point of view as warm, dense matter. Use of nominal nanosecond pulsed laser radiation initiates a plasma with electron temperatures of the order of 10 electron volts and electron densities of the order of air species densities at standard ambient temperature and pressure. For laser ablation and/or optical breakdown at or near a solid surface, the electron density can amount to be 1000 times greater. Spectroscopic investigations of the plasma emissions provide a method by which the electron density, temperature, and shockwave expansion may be determined. Of particular interest are the earliest of times following ablation of an aluminum target sample. At these times, observed spectral line profiles become distorted due to self-absorption effects. Here, experimental corrections to self-absorbed Al 394.4 and 396.15 nm, ground state transitions and the hydrogen Balmer series alpha, beta, and gamma lines are calculated by retro-reflecting the plasma emission back through the plasma volume. The plasma are initiated by laser ablating an Al alloy 6061 target sample in a 90 percent hydrogen and 10 percent nitrogen gas atmosphere at 840 Torr with 1064 nm Nd:YAG 14 ns laser pulses. Electron densities are calculated by fitting the corrected profiles to Voigt profiles. The widths of the lines are used with empirically developed formulas to infer the electron density. The temperature of the plasma is found by using the Boltzmann plot method constructed from the Balmer series lines. Spatially resolved, diatomic molecular aluminum monoxide spectra are fit to theory spectra to infer the plasma temperature along the axis of the laser incidence at time delays greater than 2.5 microseconds following target ablation. Computer tomography methods, including Abel inversion, are used to find the radial profile of the inferred temperatures. Finally, a series of measurements of the plasma shockwave are presented to determine the geometry of the shock front expansion using the shadowgraph imaging technique.

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Chapter 1

Introduction

The device based on light amplification by stimulated emission of radiation, known as the laser, certainly is one of the most practical inventions of the 20th Century. Its importance to the field of experimental physics is unparalleled. Since the inception of the laser, some of the very first experiments to be performed were those involving laser-induced breakdown phenomena. Under such an experiment, the light output of the laser is tightly focussed to greatly increase the irradiance of the beam, defined as the power of the field incident on a unit area. The laser radiation is efficiently absorbed by the target material, causing atoms and molecules to dissociate or breakdown into ions and free electrons forming a so-called laser-induced plasma.

Laser-induced breakdown spectroscopy (LIBS) is an analytical and experimental method that takes advantage of the characteristic spectroscopic emissions of laser-induced optical breakdown and the subsequent plasma emissions. The methods of LIBS, frequently associated with laser ablation, are relatively easy in terms of the difficulty of performing experiments. The ability to obtain first order, quantitative and qualitative data about a plasma has made LIBS, and other spectroscopic studies of laser-induced plasma events, a popular technique in a wide variety of fields ranging from forensics (1) to geophysics (2) and to planetary science (3; 4). However, in depth studies of laser-induced plasma are still required as many analytical methods rely on assumptions of plasma equilibrium and opacity. This dissertation focusses on key aspects of the physics necessary to study and develop diagnostic methods for laser-induced plasma and laser ablation plasma through direct spectral observations of plasma emissions. The primary focus is on the earliest times of the plasma evolution when the plasma is at its hottest and most dense state and the plasma is least likely to

be in equilibrium and optically thin. Also of interest is the ability to spectroscopically probe the rapidly propagating shockwave that is accompanied with the formation of laser plasma.

1.1 Plasma Initiation

At the heart of this study, and those that aim to study the physics of the early time evolution of laser-induced plasma, is the formation of the plasma by tightly focussing laser radiation and the subsequent effects this has on the emanating radiation. The plasma is formed by tightly focussing pulsed laser radiation. This deposits a large amount of energy onto a small area in a short amount of time. The material in the focal volume of the laser efficiently absorbs the deposited energy causing the material to be vaporized and thus creates the plasma. The excited material then undergoes photoionization and electron impact ionization processes. A nominal 10 ns pulsed laser is capable of delivering 1 to 10,000 GW/cm² depending on the laser energy per pulse, the quality of the laser beam shape, and the focusing characteristics of the laser beam. The desired irradiance of the beam at breakdown is largely dependent upon the application.

Plasma is only initiated when the irradiance delivered to the sample surface is greater than the breakdown threshold. The breakdown threshold is the characteristic irradiance required to initiate the optical breakdown event for a particular material. This threshold for gasses is greater than that for solid targets due to the decreased density of gasses relative to solids. Characteristic breakdown thresholds are on the order hundreds of GW/cm² for gaseous samples near atmospheric pressure while the thresholds for liquids and solids are two to three orders of magnitudes lower (5). The exact breakdown threshold is material dependent and also depends on the pressure and temperature of the ambient conditions (6). For example the breakdown threshold of nominal laboratory air is approximately 100 GW/cm², while the breakdown threshold

for copper in air is approximately 1 GW/cm^2 . Tables of breakdown thresholds for various parameters and ambient conditions are contained in Reference (6).

Ionization to the plasma state is achieved through multi-photon ionization, initially, or by avalanche ionization processes after a critical level ionization is achieved. For excitation with ultra violet laser pulses the ionization is primarily due to multi-photon ionization, while for breakdown initiation with infrared laser pulses, cascade ionization dominates the ionization process. The formation of the plasma is considered to be a two step process. The first process requires the presence of a small amount of free electrons. The source for these free electrons can either be due cosmic ray interactions or from the laser directly ionizing some material in the focal volume. The next stage is based on the rapid ionization of the rest of the material in the focal volume through collisional processes.

Direct ionization is an unlikely consequence of the laser-material interaction given the ionization energy of common materials ($>10 \text{ eV}$) when compared to that of a nominal Nd:YAG nanosecond pulsed laser operating at its fundamental wavelength of 1064 nm (1.2 eV). Rather, the ionization process needs to be a staged process, as described, that can either be collisional or multi-photon ionization. Avalanche (collisional) type ionization occurs as an electron is involved in the scattering process with an atomic target. Energy from the incident electron transfers enough energy to the atom such that one of the bound electrons receives enough energy to exceed the ionization potential of the atom. The product of the electron/atom collision can be two electrons, one liberated and one incident, and an ion. The electron impact ionization can also occur over many collisions in which each collision brings an electron to a higher energy state until ionization is reached. In the multi-photon process a photon of some amount of energy is absorbed by the atom and causes an electron to move to an excited state. This happens over and over again until ionization is reached. The distinction between the two processes falls upon a characteristic irradiance that is given by about 10^{14} W/cm^2 (7).

The above distinctions apply, generally, to nanosecond pulsed laser ablation for plasma initiation. For so-called ultrashort pulse lasers, with pulse durations of the order of 10's to 100's of femtoseconds, tunnel ionization is a distinct possibility. Tunnel ionization is a purely quantum mechanical effect in which a bound electron has the possibility to escape the atomic potential barrier by means of tunneling through the Coulombic potential wall of the atom. A parameter of the rate equation of multi-photon ionization, known as the Keldysh parameter, gives the relative importance of the tunneling ionization component (8; 9; 10). This parameter is given relative to the ratio of the peak power of the incident laser field to the ionization potential of the atom. For a value greater than one, tunnel ionization becomes important. For similar ionization potentials this requires a much higher incident laser power to be obtained, such those encountered in femtosecond laser-induced plasma initiation.

After the plasma is formed, plasma dynamics interactions of the constituent material become important. Energy that was absorbed by the laser is diffused throughout the plasma via collisional and radiative processes. The thermal and dense plasma also expands into the less dense, surrounding atmosphere. The plasma density of electrons and states, velocity, momentum, and temperature are described by the so-called two fluid model (7), a set of five partial differential equations which account for the atomic state distributions of the atom, the rate of change of the electron density, and the electrodynamics of the plasma. A full description of this model proceeds by separating the fast motion of the electrons from the slower hydrodynamic solutions.

In addition to the fluid dynamics of the radiating and expanding plasma, a shockwave is formed as a direct result of the plasma initiation process. The shockwave, sometimes referred also as a blast wave, is formed due to the nearly instantaneous supply of energy to a very small region of space. The formation and expansion of this shockwave can be modeled using the Sedov-Taylor blast wave model (11; 12). This blast wave propagates through the plasma and eventually into the surrounding atmosphere. The solutions in this model show that the shockwave propagates along spherical symmetry. Deviations exist between the model and the actual expansion of

the plasma and the shockwave. For nanosecond pulsed breakdown, the laser interacts with regions of relatively higher density caused by the compression of the plasma shockwave. Anisotropic absorption of the laser energy occurs and asymmetries are observed (13; 14). The asymmetry leads to the formation of plasma vortices (15; 16)

1.2 Laser-Induced Breakdown Spectroscopy

Lasers are one of the most practical inventions of the 20th century and likely one of the most important in the field of experimental Atomic, Molecular, and Optical physics. The laser was first invented by Theodore Maiman in 1960 (17). Following soon after this seminal moment in experimental physics, reports of laser-induced breakdown experiments soon followed. The first reported measurement of plasma produced following tight focussing of a laser beam were reported by Brech and Cross in 1962 (18), followed soon after by the reports of plasma produced following laser ablation of a target sample by Linlor in 1963 (19) and Runge in 1964 (20). The reports of optically induced breakdown in gaseous samples were first reported by Maker *et al.*, also in 1964. The first breakdown experiment initiated in a liquid (water) sample was achieved in 1969 by Buzukov *et al.* (21). This period of time is often quoted as the birth of a rich and varied field of study known as laser-induced breakdown spectroscopy (6). Another of the early physical recognitions of laser-induced breakdown experiments was that of matrix effects (22; 23). Matrix effects are characteristic disruptions in the observed signal from a laser-induced plasma due to the sample and the ambient observation conditions.

Due to the characteristics of a laser-induced plasma, time resolved measurements are a natural desire for quantitative analysis. Naturally, the availability of the charge-couple device (CCD) and intensified charge couple device (ICCD), which incorporates a photosensitive, photon multiplier that is time gated, were major advances for LIBS. In the earlier years of LIBS, studies utilized streak cameras and fast photo-detectors (24). Other pre-CCD instruments included linear diode arrays coupled to so-called optical

multichannel analyzers, which are computers designed to operate photo-detectors, single element photomultiplier tubes, and boxcar integrators.

In 1981, the term LIBS was used for the first time (25). Investigations of the 1980's began to demonstrate the applicability of the methods of laser-induced breakdown. This work focussed mainly on the detection of specific types of dust and containments in aerosols (26). Much of this work also focussed on the determination of limits of detection, the smallest amount of a material present in a sample that could be detected and correlated to a spectroscopic emission. Applications of these methods are highlighted by the use of laser-sparks for aiding in process monitoring of aluminum alloys (27; 28), as well as with the development of a so-called LIBS backpack (29). The purpose of such an instrument is to make a fully field ready and capable laser-spectrometer-detector system which would bring the field of laser spectroscopy to touch in applications that range from archeology to forensics to defense applications. (30; 31; 32; 33).

All of the above requires a calibration standard so that emission intensities can be correlated to analyze sample compositions (6). Such determinations are typically made by applying partial least squares analysis with the so-called principal component analysis, as well. The calibration curves that are used to determine the sample constituent concentrations are highly affected by a non-ideal plasma state, *i.e.*, non-optically thin, non-equilibrium, and nonhomogeneous plasma conditions that often characterize laser-induced plasma. This often leads to researchers avoiding lines that may be self-absorbed due to the non-linearities they cause in the calibration curve (34). At the forefront of the LIBS field is the development of the so-called calibration-free LIBS methods in which equilibrium considerations are relaxed greatly (35). Alternate methods also seek to incorporate neural network analysis to the plasma analysis (36). Also, in addition to applications of gaseous, liquid, and solid target sample interrogation, has been the development of double pulsed optical breakdown methods in which a second laser pulse is used to initiate breakdown in the initial plasma (37; 38; 39). Such a method allows for characterizations of the plasma state through improved quality of the spectral signals.

Laser-induced breakdown spectroscopy is now a powerful, analytical, and diagnostic tool that is used throughout the scientific community with applications in analytical chemistry, geophysics, applied physics, and materials science, and, as well, reaches out to other disciplines with applications in forensics, geology, and archeology. LIBS is a relatively easy experiment to perform which requires little sample preparation and is easily applied to solid, liquid, and gas samples. When coupled with principle component type analysis, LIBS can be quantitatively used with complex systems to determine elemental compositions (40). The current LIBS experiments and analysis on the Mars Curiosity rover best exemplify the versatility and diversity of extensions of LIBS, where LIBS is being used for geochemical analysis of Martian soil and rocks (3). Further, application of LIBS is sought for process monitoring in industrial settings, such as real time monitoring of metal alloys and thin film depositions (27; 41; 42). Laser ablation of specific target materials, such as aluminum, is also considered as analog system for studying combustion events from high explosive materials to mitigate cost and safety concerns (43). Laboratory scale experiments are also advantageous in astrophysical applications (44) and combustion studies using femtosecond lasers (45). Also of note, are the recent resurgence and applications of molecular spectroscopy, particularly through the advent of LAMIS (Laser Ablation Molecular Isotopic Spectrometry), which makes use of the large shifts of molecular isotopes to perform sample interrogations (46).

The basics of a LIBS experiment are tightly focussing light from a pulsed laser source on to a target sample of interest. Light emissions from the resulting plasma are then imaged onto the entrance slit of a spectrometer which disperses the light and a characteristic spectrum is recorded. State of the art recording devices are intensified charged couple devices (ICCD). Many types of dispersive elements are used in LIBS experiments. ICCD's coupled to Czerny-Turner style spectrometers, which feature a grating blazed for a specific wavelength that rotates on a turret to disperse a particular spectral region, are capable achieving rather small spectral resolutions ($\sim 0.1\text{\AA}$) and nanosecond level temporal resolutions; however, such instruments are large (~ 1 meter)

due to the large focal lengths needed by the spectrometers to resolve small features. One may also consider use of an Echelle type spectrometer. This type of instrument uses multiple grating orders that are focussed to different spatial regions on a rectangular detector to achieve resolutions of the order of 0.1 nm over several hundreds of nm in spectral coverage. However, Czerny-Turner spectrometers coupled with an ICCD are useful for more detailed studies of the physics associated with laser-induced plasma for measured line profiles.

Spectroscopic observations of the plasma are largely determined by the ambient experimental conditions of the plasma formation and the temporal resolution of the experiment. For laboratory based studies, one typically uses nanosecond pulsed laser radiation for plasma initiation. One chooses the time following plasma initiation at which the spectra are observed based on the type of spectra that are desired to be observed. At the earliest times following plasma initiation, the plasma is still in a stage of ionization. The electrons are being liberated from their associated nuclei as the target material is vaporized. This results in an emission that is dominated by continuum emissions that correspond to free-free and bound-free electronic transitions.

The exact timing of the continuum emission domination depends on the laser pulse characteristics. For so-called ultrashort pulse laser ablation (10's to 100's of femtoseconds), the amount of time that the laser is incident on the sample is less than the time required for the bulk sample to absorb the energy from the laser, have the electron enter the excited states, and become unbound from the atom. As such very little, if any, extra energy is absorbed from the laser by free electrons and the continuum emissions that are observed in femtosecond laser ablation are quite diminished as electronic collisions at standard temperature and pressure are of the order of 10 to 100 femtoseconds. For nanosecond ablation, the laser pulse duration is much greater than the time required to reach ionization and, as such, laser radiation is still incident on the plasma volume after ionization has occurred. The free electrons absorb the energy from the laser, which leads to a much stronger and prolonged continuum emission. Figure 1.1 displays the characteristic timing of the signal intensity that may be observed from

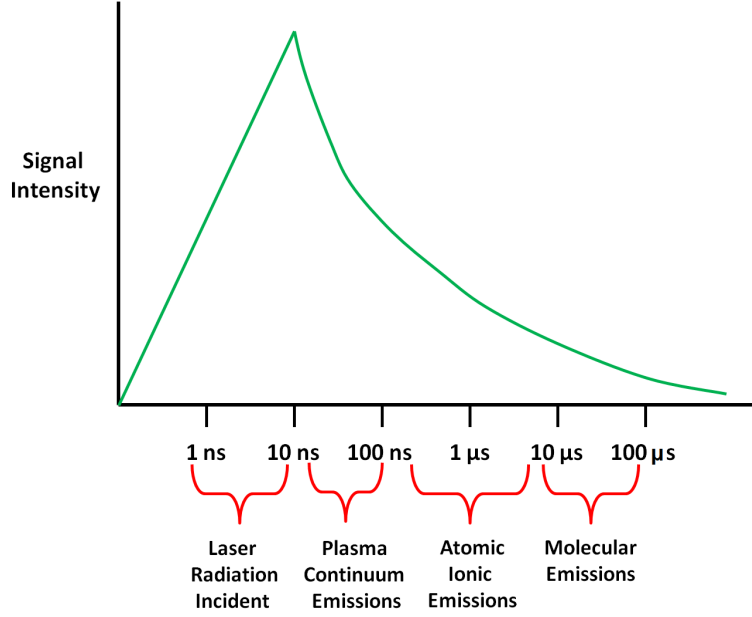


Figure 1.1: Typical temporal evolution of laser-induced breakdown plasma initiated on the surface of a metal target sample. The corresponding initial conditions are for nominal 10 ns, 100 mJ laser pulses and for ablation in ambient laboratory air.

a laser ablation experiment using 10 ns laser pulses to initiate the plasma with an energy per pulse of 100 mJ. Also indicated in the figure are the types of spectra that one would expect to observe at the given time scales.

The general trend of the curve presented in Figure 1.1 is a rapid rise in the signal intensity. Rapid rise in the intensity along the leading edge of the laser pulse also results in a rising electron density that approaches a critical value of 10^{21} cm^{-3} for Nd:YAG laser pulsed, depending upon the inverse square of the laser wavelength (7). For electron densities greater than this value, the plasma becomes reflective. After reaching a peak intensity, the plasma is no longer absorbing laser energy and begins to solely radiate energy and the signal intensity will rapidly diminish as the time following plasma initiation increases. This signal intensity decrease is accompanied by the reduction of plasma free electrons through recombination and inverse bremsstrahlung processes. Throughout this process the plasma is expanding and, as well, is interacting with a rapidly propagating shockwave. For nanosecond ablation, one can expect the continuum emissions to last for 100 to 500 ns. As the continuum subsides, energy is

radiated by the free electrons, the free electrons begin to recombine with available nuclei, and emissions from atomic ions begin to become distinguishable from the continuum.

Shortly after ionic emissions emerge from the spectral continuum, atomic emissions become distinguishable. These emissions tend to dominate until about $1\ \mu\text{s}$ following the plasma formation process. The plasma decay process is observed by a decay on the plasma temperature and electron density, N_e . The higher these two quantities are the more opaque the plasma is and the less stable ions and atoms are likely to be and more likely electrons are going to be liberated from the atom. Aside from the index of refraction, the electron density and temperature are two of the more fundamental quantities in describing the plasma state. Information about these two quantities can be found from the spectroscopic line profiles.

As the plasma decays, the atomic and ionic emissions, which are predominantly broadened due to collisional broadening of charged and neutral particles, begin to narrow. After the atomic emissions have become sufficiently narrow and the plasma temperature and N_e are difficult to gain information about from the narrowed lines, molecular emissions become observable. In order for molecules to form, the plasma temperature needs to decay to sufficient levels such that bonds holding the molecules together are stable. Molecular emissions can be expected to appear anywhere between 1 and $5\ \mu\text{s}$ following plasma initiation and can last upwards of 100 to $200\ \mu\text{s}$ following plasma initiation, depending on the molecule, the target sample, and the plasma initiation conditions. For breakdown in gaseous environments, molecular emissions tend to occur much earlier in the plasma emission decay. The exact timing is also subject to considerations of the laser power.

The plasma state is also affected by the ambient conditions. In addition to the amount of energy the laser deposits onto a sample, the pressure can greatly affect the plasma emissions. At lower pressures there are less particles to be ablated and thus ablation at lower pressures produces a less dense plasma that more rapidly decays, which is associated with weaker spectral signal intensities, reduced continuum

emissions, and relatively earlier times at which atomic and molecular emissions appear. Likewise, ablation of a solid target sample produces a higher density plasma, relative to gaseous breakdown, due to the higher availability of free electrons due to the higher electron density of solids *vs.* gases (10^{22} *vs.* 10^{19} cm^{-3}). The temperature of the plasma is largely controlled by the laser energy that is deposited on the sample surface. The more laser energy that is available to initiate breakdown, the more energy that will be absorbed by the electrons and the higher the temperature that can be achieved. In some cases this temperature can exceed 100,000 Kelvin at the earliest times following ablation and subsides to typically 5,000 to 10,000 Kelvin by about 10 μs (5).

1.3 Plasma Spectroscopy

From a spectroscopic point of view, the characteristic shapes of spectroscopic emissions have been of interest since the late 1940's, prior to the invention of the laser. At this time the focus was not on laser-spectroscopy methods, but rather spectroscopy of plasma, primarily from electric discharges. Due to the relatively high density of free electrons in plasma, the shapes of spectral lines from these sources are strongly dependent on the interaction of charged particles with charged and neutral particles in the plasma. Often, the impacting particle is termed the perturber and the target is referred to as the radiator. This interaction is defined by the Stark broadening of atoms and molecules. Calculations of the Stark broadening are split into two approximations: the Impact approximation and the Quasistatic approximation, details of which are expanded upon in Chapter 2.

Though the first description of the line shape of Stark-broadened spectral lines is attributed to J.P. Holtsmark (47), much of the early theoretical descriptions of Stark broadening in plasma emissions was completed by M. Baranger and focussed on hydrogen plasma emissions (48; 49; 50; 51; 52). These works were soon followed on by the works of S. Sahal-Brechot (53; 54) and H.R. Griem (55; 56; 57; 58; 59). Specifically, the work of Griem, which is culminated in the volumes of several books

on the subject of plasma spectroscopy (55; 56; 57), is considered to be the first seminoe set of works in the field of Stark broadening of plasma spectroscopy. His theoretical simulations of line widths are by far the most widely used within the field of Laser-Induced Breakdown Spectroscopy for electron density determination from Stark broadened spectral line widths. Most significant among these accomplishments are his calculations of hydrogen Balmer series Stark profiles with the application of Holtsmark distributions for calculations in both the Quasistatic and Impact approximations.

These initial works on the subject were developed using semi-classical approaches to describe the collisional interaction of the charged particles. A simpler semi-empirical method, requiring less atomic data, was developed shortly after. Fully quantized approaches to the problem of charged particle collisions soon followed, as well. The first fully quantal approach to Stark broadened was initiated by Jablonski in which the microfield produced by the locally strong electric field of charged particles is used to describe deflections in the trajectories of the perturbing particles (60). Simulation methods of Stark broadening have also been developed which consider a simple model for the correlation function of the microfield, in order to capture the dynamics of the field (61). This method is termed the MMM approach (Modified Microfield Method) (62). Also, an extension of the simulation theory is the FFM method (Frequency Fluctuation Model), which calculates many profiles in order to account for opacity (63). More advanced methods of Stark broadening simulations exist as well (64). Some of these models seek to incorporate the dynamical effects of ions and accelerations of the electrons due to the strength of the local microfield into the calculations (61; 65). Other, similar works have done so by also publishing profiles for the hydrogen Balmer series α , β , γ lines which depend on the temperature, electron density, and reduced mass of the radiator-perturbed collision particle pair (66; 67).

The current state of Stark broadening theory is defined largely by the compilation of tables containing broadening parameters of lines (68; 69; 70; 71; 72). This is particularly advantageous for the savvy experimentalist whose interest is obtaining a rapid result. The tables are based off of the experimental validations of Stark broadening and are

subject to intense scrutiny and require independent measurements of the electron density and temperature, as well as validations of several other criteria including rigorous evaluation of error bars and self-absorption effects (73). Reference (73) also provides a succinct description of the modified semi-empirical method for calculating Stark widths of line profiles. At the fore-front of the plasma spectroscopy field are tabulations of empirically based formula for the determination of Stark broadening (74; 75; 76; 77). Such methods serve a similar purpose to the so-called Stark tables but also seek to include more physics into the empiricism. They also include more data points in their formulation than those found in Stark tables, where an individual is often left with only one or two data points from which to extrapolate experimental results.

An interesting sequence of Stark broadening calculations has been made by M. Dimitrijevic and S. Sahal-Brechot and their collaborators (78; 79; 80). Their work has been aimed at the creation of a database of useful lines for astrophysical plasma sources. These typically include lines that are subject only to the Impact approximation. This work continues the initial works of Griem through the use of a modified semi-empirical approach. The culmination of this work is a data base called Stark-b, which is a collection of Stark broadening parameters for many lines of astrophysical interest (81). The range of application of this database is between 10^{12} to 10^{18} cm^{-3} perturber densities and all calculations are carried out using the so-called Impact approximation. This reference is of particular interest for the purposes of this dissertation due to the significant attention that has been paid to aluminum emissions from this sequence of evolving Stark broadening calculations.

Due to the astrophysical importance aluminum, it has a long history of being studied in plasma spectroscopy applications in both a theoretical and experimental sense. As a result, many laboratory scale experiments involving aluminum containing plasma have been performed. Also owing to the continued prevalence of aluminum in both the laser-induced breakdown spectroscopy and plasma spectroscopy fields is the wide spread use of aluminum metal alloys throughout most industries, its use in laser processing of

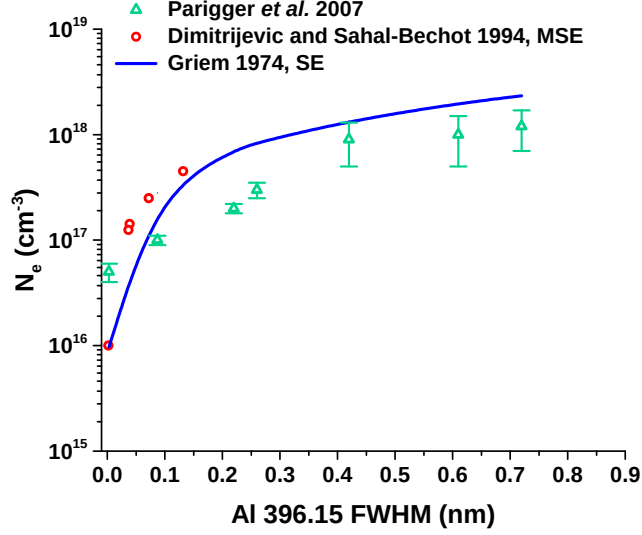


Figure 1.2: Comparison of Al 396.15 nm line widths *vs.* N_e using various Stark broadening theories.

metal layers, and its applications in explosive and combustion technologies (82). Some of the first works in regards to the experimental measurement of aluminum Stark broadened profiles were completed by Flueier *et al.* (83), in which the Al lines were measured from an AlCl_3 flow stream through an arc discharge plasma. The line widths of Al ground state 394.4 and 396.15 nm emissions, as well as Al^+ 358.7 nm emissions, were associated with an N_e as calculated from observed hydrogen Balmer series lines whose line widths were treated using the semi-empirical Stark broadening theory. The densities determined in this effort were $1.5 \times 10^{17} \text{ cm}^{-3}$ with temperatures near 15,000 Kelvin. Others sought to use plasma shock tubes to initiate completely homogeneous and locally equilibrated plasma to verify the results of Stark profiles for Al ground state transitions (84). The densities were determined from laser interferometry techniques. Stark widths of the Al 394.4 and 396.15 nm line were found to be 0.35 and 0.45 nm, respectively, at a density of 10^{17} cm^{-3} . Similar efforts have been performed for ions of interest (Al^+ 281.61 and 466.3 nm lines) in Al laser ablation (85). Figure 1.2 shows a comparison of line width *vs.* N_e results from popular Al line width references for Stark broadened Al 396.15 nm lines.

Further works and applications of Al spectral emissions are littered throughout the LIBS literature. Of particular interest are those that seek to address line shape effects due to self-absorption, the absorption of energy from higher temperature and density states from lower temperature and density states of the same transition. Self-reversed line profiles have been studied as a means of determining the electron density (86; 87; 88). An expression of the total line profile that includes a self-reversed, Stark broadened line was sought. Others have attempted experimental validations of the extent of self-absorption of Al lines through comparisons to coincident H_α spectral emissions (89; 90). Such efforts assumed that the H_α line electron density determination was not affected by self-absorption. Self-reversal and self-absorption line shape affects are a general concern for Al emissions in LIBS due to the frequency with which Al containing alloys are used and the strength of the $3s^23p \rightarrow 3s^24s$ ground state transitions, which are highly susceptible to self-absorption line distortions. Another recent work, sought to improve upon the line width *vs.* N_e relationships that had been laid out by calculations in the MSE (91). Like many other previous works, this attempt relied on correlations of measured Al line widths with N_e measured from the hydrogen Balmer series α and β lines. Others have taken on similar tasks for Al ions using the purely semi-empirical Impact approximation calculations (92; 93).

Aluminum lines have also been applied in many studies of Al ablation as a temperature and electron density diagnostic. Popular lines that are used for the density diagnostic include the Al 394.4 and 396.15 nm ground state transitions. Densities are inferred by extracting the line width. Temperatures are inferred typically from so-called Boltzmann plots, graphical solutions of atomic state distributions that have been applied to a Boltzmann distribution, and can include many Al neutral transitions at 308.21, 309.27, 394.4, and 396.15 nm, as well as, singly ionized species such as the Al^+ 281.61, 358.7, 704.4, and 747.29 nm transitions. A study of the spatial variations of the density in nominal air breakdown showed densities ranging from $4-8 \times 10^{17} \text{ cm}^{-3}$ and temperatures of 10,200 Kelvin over distances of 5 mm from the the Al sample surface (94). The density was found from the Al^+ 281.61 nm line and breakdown was initiated

using 532 nm Nd:YAG laser radiation. This study was not time resolved. In a similar spatial study in which a plasma was initiated using 0.4 ns pulsed 170 joule energy per pulse laser (95), densities were found to be in excess of 10^{22} cm^{-3} . The densities were inferred from hydrogenic Lyman series Al spectra. It is worth noting that such laser energies are exceedingly difficult to achieve with a nominal LIBS apparatus.

Other have sought to use both atomic and molecular emissions to find the temperature. Piehler *et al.* used diatomic aluminum monoxide (AlO) and Al neutral emissions to find temperatures of approximately 4000 Kelvin (96). Densities were also inferred from the Al^+ 747.29 nm and were found to be $2 \times 10^{17} \text{ cm}^{-3}$ at a 1 μs time delay following ablation. Lightstone *et al.* showed that in a spatially and temporally resolved study of Al laser ablation that AlO emissions predict higher temperatures than those inferred from Boltzmann plots at similar time delays (97). The AlO temperatures indicated were nearly 4500 Kelvin while the atomically inferred temperatures were less than 2000 Kelvin at a delay of 40 μs . Lam *et al.* recently reported on synthesis of alumina particles following ablation on an alumina target that was submerged in water (98). Densities were reported to be as high as 10^{19} cm^{-3} 200 ns following ablation and Al temperatures were inferred to be between 3400 and 6000 Kelvin when considering rotational *vs.* vibrational AlO emissions at 2.2 μs following ablation. It is important to note that, while the authors do not attempt to correct for self-absorption, they recognized its significance by indicating that the density that is reported is likely affected by self-absorption, although the extent to which was not made clear. It is interesting that almost all of the above mentioned electron densities were all inferred to be below 10^{18} cm^{-3} , which avoid densities at which the line shape requires some consideration of self-absorption.

1.4 Motivations

This work is motivated towards filling in the gaps in the fundamental physics that under lie the experimental and analytical methods of LIBS. Confluences of the rapidly

propagating shockwave associated with the plasma formation with measured spectra still leave much to be known, particularly at the earliest times in the plasma evolution. Information that can be learned of this shockwave from spectral emissions will be invariably important towards the progress of LIBS and spectroscopic diagnostics of laser-induced plasma research. This is due, in part, to the relative ease in which passive optical spectra can be experimentally obtained from a plasma emissions source compared to so-called probing methods.

Such information is also important towards continued advances in the diagnostic applications of the LIBS methods. Many applications of LIBS rely the methods of calibration free LIBS. Two of the main assumptions in this method are partial local thermodynamic equilibrium (PLTE) and the optically thin nature of the plasma. However, these two principles often go improperly or completely unestablished by many researchers. In time averaged studies on the scale of millisecond integration times, the early time evolution of the plasma affects the spectra which are desired to be measured at later times. Self-absorption represents the prime deviation from the case of an optically thin plasma.

While the existence of self-absorption is never really or has ever been under question, when and how important these impacts are remain unanswered, particularly in cases of moderate self-absorption where there may be no obvious changes in spectroscopic line profile. This dissertation seeks to further understand these elements through detailed experimental measurements of aluminum and hydrogen Balmer series line shapes collected from aluminum laser ablation experiments in controlled gas atmospheres. The detailed line shape studies will seek to further understand the affects that self-absorption plays in the determination of the N_e and temperature.

Previous studies guide when and what is measured in this dissertation. Work done to determine the electron density of Al lines has primarily considered the density region below 10^{18} cm^{-3} (79; 83; 92; 93) for Al neutrals and single ionized species. As a starting point for this research, recent investigations of the electron density found following laser-ablation of an aluminum target in nominal laboratory air are considered.

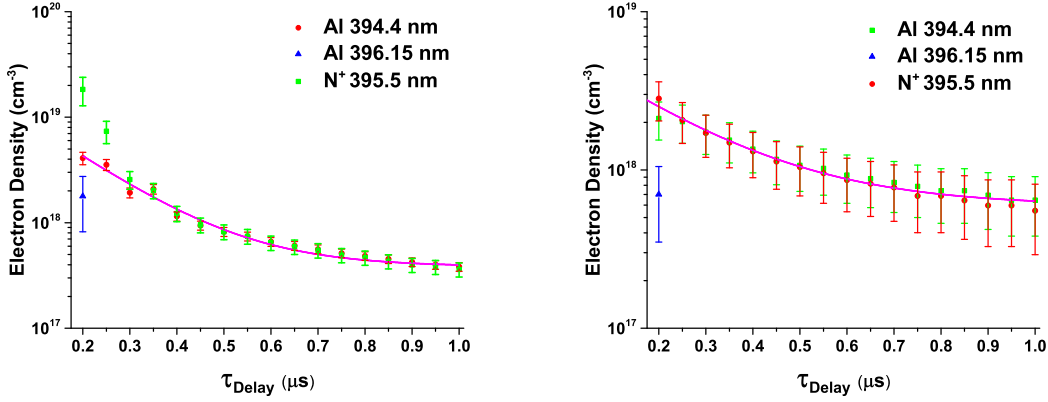


Figure 1.3: Electron density results from Al and N⁺ transitions determined from Stark width (left) and shift (right) diagnostics. The figures are copies from Reference 99.

For PLTE to exist, it is required that energy dispersion between specific elements be efficient and complete over some scale of distance. Such a principle is controlled by the time and length duration of collisions within the laser-induced plasma (99). The electron density results of this work are re-produced in Figure 1.3 and show the N_e found from Al ground state $3s^23p \rightarrow 3s^24s$ transitions at 394.4 and 396.15 nm as well as the singly ionized nitrogen line at 395.5 nm. Deviations in the electron density between the different lines, especially under consideration of the present error bars, indicate the presence of self-absorption. This is primarily observed in the line width diagnostic, due to sensitivity issues of the line shift diagnostic.

The results of this effort show that the self-absorption affects appear to manifest for densities greater than 10^{18} cm^{-3} and delays earlier than 300 ns at the experimental conditions in the previous effort (12 ns pulse, 190 mJ 1064 nm Nd:YAG laser ablation in ambient laboratory air). One should note that the timing of such events is difficult to compare across differing experiments and should take greater heed of the density at which self-absorption was inferred to take place.

Also of interest are the plasma dynamics at early times in the plasma evolution and the information that may be gleaned about dynamics of the plasma shockwave from direct and spectroscopic imaging methods. Of particular interest will be the variations

of the plasma N_e and temperature diagnostics as function of plasma plume position in reference to the plasma shockwave. Such works are of interest not only for the fundamentals of the formation of laser-produced plasma, but also for the applications to studies of high explosive events, where the interest is to use the cheaper and safer laboratory scale events as a scaled study of the larger and more dangerous field size explosive tests that are currently performed. The current state of such efforts are determining what these scalings laws may be (100; 101).

In this aspect of the dissertation, the interest will be at time delays both early in the plasma evolution, shortly after the plasma has been initiated, and also at longer time delays, greater than $1\ \mu\text{s}$, where atomic recombination is mostly over and molecular recombination occurs. The interest at these later times is of course the influence of the shockwave on the gradient of the plasma quantities but also the possibility of chemical and other kinetic dynamics that may occur.

Previous studies have shown that at later time delays such affects may occur. One such study showed a temporal minimum in the temperature inferred from titanium monoxide emissions following ablation of a titanium target sample (102). The minimum occurred at a delay of approximately $40\ \mu\text{s}$. Other recent works have shown that temperature determined in a laser-induced plasma could depend on plasma interactions with the laser-induced shockwave (103; 104). The breakdown in these works was initiated in nominal laboratory air. Temperatures were inferred from fitting to diatomic molecular aluminum monoxide emissions. The temperature results from this work are displayed in Figure 1.4. While these results do not show a characteristic minimum temperature, there was sufficient evidence to posit that a spatially resolved study could show interesting temporal and spatial gradients.

Figure 1.4 also shows an example fit to aluminum monoxide spectra at a time of $20\ \mu\text{s}$ following plasma initiation. This fit shows strong interferences from hydrogen Balmer series beta line emissions. This line was used to infer the electron density and was found to be $4.55 \times 10^{16}\ \text{cm}^{-3}$. The presence of the interfering line was due to residual moisture in the air. It was posited, as a result of these measurements,

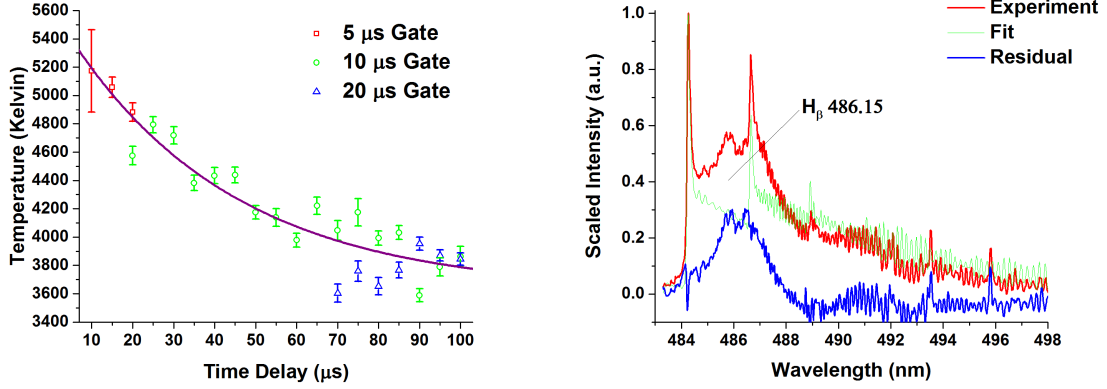


Figure 1.4: Temperature results from Reference 103 (left) and Example fit to AlO spectra with strong H_β interferences, also from Ref. 103.

that spatial variations in the temperature and molecular and atomic signal intensity should be observed due to an influx of oxygen from the ambient atmosphere as the plasma shockwave expands and eventually dissipates. Figure 1.5 shows spatially and temporally resolved aluminum monoxide spectra collected in laboratory air at time delays ranging from 30 μs to 130 μs . These images show that the AlO spectra expand, much like the shockwave does. After some time, the signal intensity diminishes and contracts. Such images show more than enough evidence that a detailed study of the shockwave effects associated with measured spectral emissions and the electron densities and temperatures inferred from them merit further consideration.

In this dissertation, the self-absorption effects of spectral emissions and the subsequent effects that result on inferred electron densities and temperatures are considered as the primary interest. These results will have a direct impact on temperature and electron density determinations from atomic spectra at early investigated time delays. Such efforts are highlighted extensively in this dissertation. This is done through a detailed experimental characterizations of laser-induced plasma initiated on the surface of an Al alloy target sample that is laser ablated in controlled gas atmosphere. These results are presented in Chapters 4 and 5, where Chapter 4 focusses on the determination of an experimental correction factor to account for self-absorption line

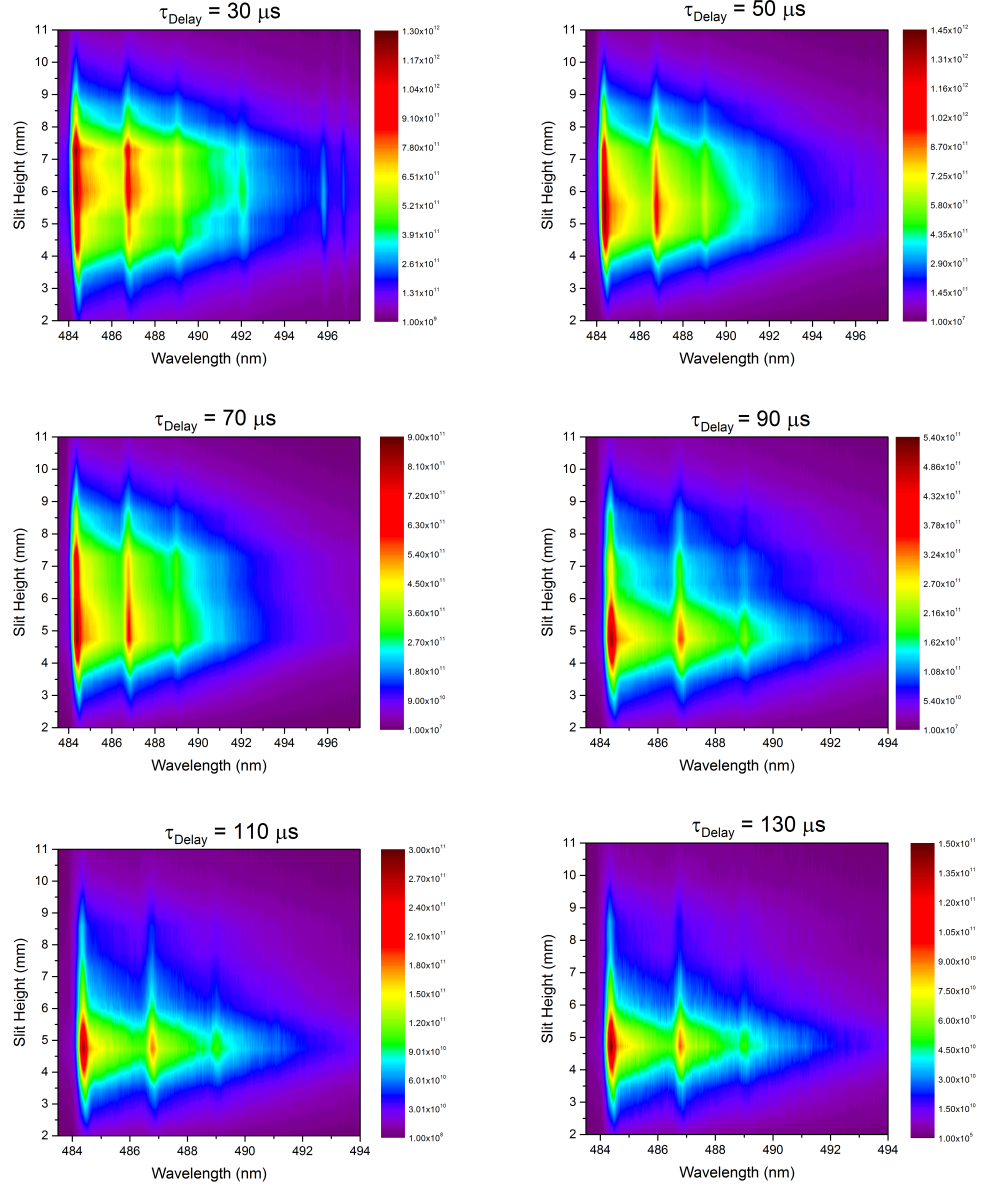


Figure 1.5: Temporally and spatially resolved AIO spectra from air laser-induced breakdown following ablation of an Al target sample.

distortions and the consequences that application of this factor has the electron density determination. Chapter 5 focusses on consequences for the temperature determination. In Chapter 6, molecular AlO emissions are considered at later time delays in the plasma formation (greater than $1\ \mu\text{s}$), in an effort to understand the spatial dependence of spectral emissions at times when the plasma shockwave has slowed considerably and is on the verge of equilibrating with the surrounding atmosphere. This chapter also presents a method of determining radially resolved spectra from spatial resolved spectral measurements along the height of the plasma plume using plasma symmetry arguments. Chapter 7 presents measurements of the shockwave expansion through the use of shadowgraph imaging techniques. Chapter 2 contains supporting theoretical descriptions of the methods used throughout this work. Details of the experiments that were performed are contained in Chapter 3.

Chapter 2

Theoretical Basis

The scope of this dissertation largely deals with experimental measurements of laser-induced plasma through measured emission spectra. This chapter serves to describe the theoretical basis from which the experimental determinations are made. The experimental methods rely on optical emission signals of the transient laser-induced plasma event. In such passive measurements, one typically relates the entire shape of a spectroscopic line to the electron density, N_e , and temperature, T_e . In this chapter, the theoretical shapes of these line profiles, as well as sources of line distortions, specifically self-absorption, and the characteristic emissions of diatomic molecules will be discussed.

2.1 Plasma Emissions

Plasma are rich physical systems due to the many collisional processes that occur between the free electrons and other charged and neutral particles. Laser-induced plasma adds further complexity due to the temporal dependence of the emissions and the time and space dependent shockwave that forms and propagates through the rapid expansion of vaporized material and ionized species from the energy deposition of the laser. This makes plasma spectroscopy and spectral studies of laser-induced plasma a rich and interesting combination of many types of physics.

In later sections, information is presented in regards to the specifics about spectroscopic line emissions and the characteristic shapes they take on due to the underlying physics giving rise to the spectral lines. In this section, the basic processes that lead to and affect plasma emissions are presented.

First, radiometric quantities, as they pertain to laser plasma, are considered. Plasma emits radiation that is characterized by a quantity known as the local emission coefficient, given as

$$\epsilon(\vec{r}) = \frac{d^2\Phi(\vec{r})}{dVd\Omega} \quad (2.1)$$

where $d\Phi(\vec{r})$ is the radiant flux, a directional quantity, dV is a plasma volume element, and $d\Omega$ is the differential solid angle through which the plasma emits. The units of the emission coefficient are $[\text{W}/\text{m}^3/\text{sr}]$. Plasma emissions, however, are readily observed using spectral quantities such the spectral irradiance $[\text{W}/\text{m}^2/\text{nm}]$ or the spectral radiance $[\text{W}/\text{m}^2/\text{nm}/\text{sr}]$. Such quantities are somewhat confusingly used interchangeably and are often misinterpreted as the intensity. The intensity is a directional quantity that pertains to the radiant flux of an emission through a solid angle of emission.

The spectral irradiance or radiance may be related to the emission coefficient through the so-called Abel and Radon integral transformations (105; 106; 107). The Radon transform assumes no emission symmetry and is given by

$$L(\rho, \phi) = \int \int \epsilon(x, y) \delta(x \cos \phi + y \sin \phi - \rho) dx dy \quad (2.2)$$

where x and y are the cartesian coordinates of an emission that correspond to the radial coordinates ρ and ϕ and δ is the Dirac delta distribution (108). The emission coefficient is found by taking the inverse transformation of the above integral function. The Abel transform is a specific type of Radon transform in which one assumes a certain type of symmetry. For laser-induced plasma one may assume cylindrical symmetry along the plasma axis in which breakdown is initiated. The Abel transform for a cylindrically symmetric plasma is

$$L(y) = 2 \int_r^R \frac{\epsilon(r) dr}{\sqrt{r^2 - y^2}} \quad (2.3)$$

where r is the radial coordinate of the plasma, R is the radius of the plasma, and y is the coordinate along the height of the plasma (cylinder). Figure 2.1 depicts the

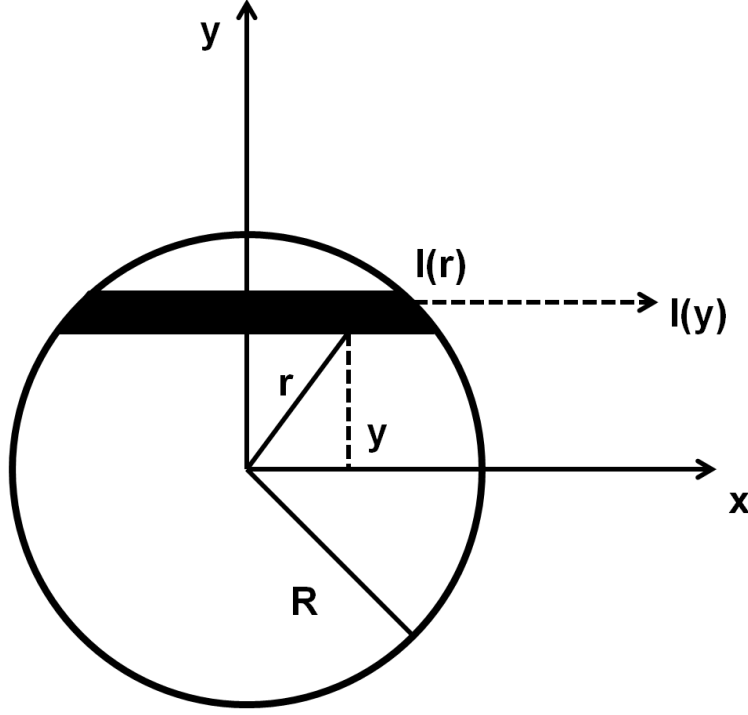


Figure 2.1: Cylindrically symmetric intensity emission related to its radial distribution through Abel inversion. The z-axis is in and out of the page.

cylindrical Abel transformation. Such relations allow one to numerically reconstruct the radial profile of a plasma from a measurement or series of measurements of the plasma spectral emissions along an axis of symmetry (109).

In an ideal world, the spectral irradiance and radiance pertain to optically thin emissions. However, the emission of the plasma is not necessarily limited to cases of being optically thin. Though this is often assumed to make comparisons between theory and experiments easier, particularly in LIBS, it is often the case that some emissions experience some type of absorption. Re-absorption in a plasma is determined by the equation of radiation transport, expressed in differential form as

$$\frac{dL(\lambda, x)}{dx} = \epsilon(\lambda, x) - \kappa(\lambda, x)L(\lambda, x) \quad (2.4)$$

where λ indicates a wavelength dependence, x is a spatial coordinate, and $\kappa(\lambda, x)$ is the absorption coefficient, with units of $[\text{m}^{-1}]$.

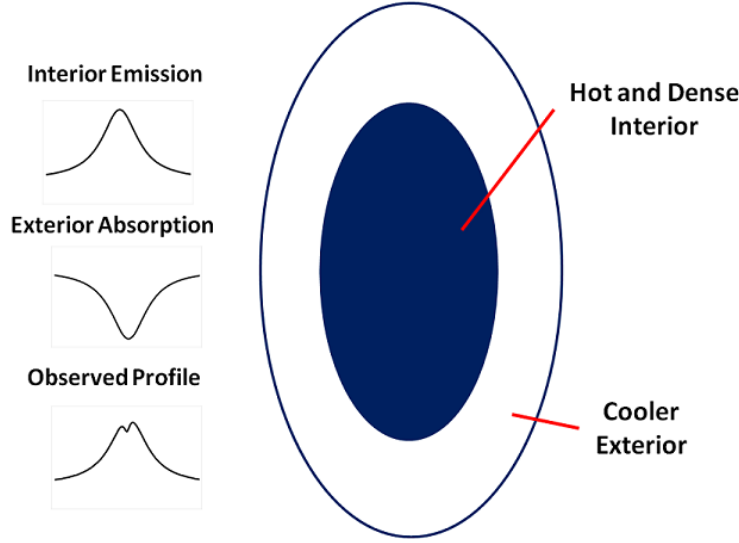


Figure 2.2: Plasma kernel model showing the favorable situation for self-absorption to occur in laser-induced plasma

A special case of plasma absorption is self-absorption, where in spectral emissions become absorbed due a similar spectral transition occurring in a different region of the plasma. Typically this region is cooler and less dense. For laser-induced plasma, a plasma kernel is quickly formed as energy from the laser is efficiently absorbed by the sample. This hot and dense central region quickly begins to expand and forms a cooler and less dense outer region of the plasma. The plasma kernel emits through this outer region. Energy from the higher density and temperature emission is absorbed by the cooler emission, and thus a natural situation for self-absorption to occur exists in laser-induced plasma. In this model, ground state transitions are more likely to experience self-absorption since these lines are far more likely to exist in both the kernel and outer regions of the plasma. The result of this absorption is a distorted (broadened, shifted, and flattened peaks) spectral line profile. An extreme case of self-absorption is line self-reversal, in which a prominent absorption near the line center is observed. Figure 2.2 depicts the described model of self-absorption, showing a self reversed line profile.

2.1.1 Discrete Emission

Dispersion of energy through the plasma is governed by collisional and radiative processes. As already noted, radiative processes in plasma have an effect on spectral emissions. Radiation occurs when a bound electron is excited due to the absorption of a free photon. Another photon is emitted after the electron relaxes to its lower state. This is known as a spontaneous emission and its rate is governed by the so-called Einstein A coefficient, or transition rate, given as

$$\frac{dn_u}{dt} = A_{ul}n_u \quad (2.5)$$

where u and l refer to the upper and lower states of the transition, respectively, n_u is the population of the upper state, and A_{ul} is the transition rate, which is characteristic to a particular transition. The life time of a transition is inversely proportional to this value. In laser-induced plasma, probing methods are often used, such as laser-induced fluorescence (110). This corresponds to a case of stimulated emission. The rates of these transitions are governed by the Einstein B-coefficients, B_{ul} or B_{lu} , or the stimulated emission and absorption coefficients.

There are two fundamental quantities of theoretical importance in describing discrete emissions from atoms. The first is the oscillator strength, f_{ul} , and the second is the line strength, S_{ul} . Both give the relative strength of a particular transition frequency. While both quantities are important, for theoretical calculations of spectral emissions, the line strength is highlighted here. This is due to the symmetric nature of the quantity and also due to the extremely fundamental nature as both the oscillator strength and the transition rate can be expressed in terms of the line strength. Specifically the transition rate can be expressed as

$$A_{ul} = \frac{64\pi^4\nu_{ul}^3}{3hc^3g_u}S_{ul} \quad (2.6)$$

where ν_{ul} is frequency position of the transition from upper state u to lower state l and g_u is the statistical weight of the upper state. The line strength is also convenient for displaying the source of atomic spectra and the selection rules that govern their emission. The line strength in general is given by

$$S_{ul} = \left| \langle u | \hat{T}_k^{(q)} | l \rangle \right|^2 \quad (2.7)$$

where $\hat{T}_k^{(q)}$ is the operator that gives rise to the emission (111). For atomic emissions this operator can either be the electric dipole or magnetic multipole operators. Here, it is noted that for neutral atoms this operator is most often given by the electric dipole operator. Atomic transitions with a strong line strength are said to be allowed transitions while weak atomic transitions are forbidden. The exact allowed or forbidden quality of the atomic emission is determined by the rules from total angular momentum considerations.

2.1.2 Continuum Emission

Continuum emission in laser-induced plasma comes from many sources. There are the emissions due to recombination of free electrons with ions and molecules. Free electrons are captured into some excited state of the atom and, thus, this is sometimes referred to as free-bound emissions. Photon emission occurs during the absorption process. The inverse process of recombination is photo-ionization, which is one of the sources of free electrons during the formation of laser-induced plasma. The emission of bound-free electrons is complex and ultimately depends on many factors, including the population of the level by which the electron is captured, the atom the electron is being bound to, and a quantity known as the effective gaunt factor. It is far more succinct to indicate that this radiation is proportional to $1/\lambda^2$. It is also important to note that tabulations of the emission coefficients for such emissions can only be performed using exact expressions for hydrogen and hydrogenic ions. Numerical simulations are required for calculation of the free-bound/bound-free emissions of all other atoms.

Radiation also occurs due to deflections of free electrons from their given trajectories due to the strong ion microfield present in plasma. This is termed free-free emission and is more commonly known as bremsstrahlung radiation. In the quantum mechanical treatment, bremsstrahlung radiation corresponds to transitions between continuum states (105). In the limit of long wavelengths, the radiation due to free electrons takes on the form of a black body radiator.

2.2 Line Profiles

From a broad perspective, in a quantitative LIBS approach, the characteristic line shape of a spectroscopic emission contains a pathway to study and understand the underlying physical principles of a laser-induced plasma. For the passive methods of LIBS, broadened spectroscopic lines are used to determine the parameters of a plasma. Doppler, Stark, Van der Waals, and other forms of pressure broadening all exhibit a characteristic line profile that are typically a function of N_e and/or T_e . In so-called probing methods, such as Thompson Scattering, Rayleigh Scattering, or Raman Spectroscopy, a characteristic line profile is observed, as well (112). It is easy to see then, how important the shape of a line profile can be when studying the physics of a laser-induced plasma.

No matter the emission source, all spectral lines have a width associated with them. This width is called the natural width of a line and its occurrence is due to the lifetime associated with an excited state and the uncertainty in energy levels involved in the transition (105; 113). The shape of this profile is Lorentzian in nature and can be modeled by describing the electron as a classical oscillator between energy states. In this model, radiative energy losses by the electron corresponds to a damping coefficient and the oscillating electron is governed by the damped harmonic oscillator equation with standard initial conditions

$$\ddot{x} + \gamma\dot{x} + \omega_0^2x = 0. \quad (2.8)$$

One typically describes the resulting Lorentzian solution to Equation 2.8 as a normalized line profile as

$$\mathcal{L}_{Nat}(\omega) = \frac{I_0}{2\pi} \frac{\gamma}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2} \quad (2.9)$$

where γ is the full width at half maximum (FWHM) of the profile and ω_0 is the frequency at line center. The width of this line corresponds directly to the lifetime of the transition between two levels

$$\delta\omega = \frac{\Delta E_k}{\hbar} = \frac{1}{\tau_k} \quad (2.10)$$

where the subscript k indicates the k^{th} energy level of the atom and τ_k is the life time of this level. In the more realistic and useful case, where the transition is between two different excited states, $|i\rangle$ and $|k\rangle$, of the same atom, the line width corresponds to

$$\delta\omega = \frac{1}{\tau_i} + \frac{1}{\tau_k}. \quad (2.11)$$

The width of the line due to its lifetime is often extremely small in comparison to the other line broadening mechanisms, such as that due to the instrumental profile. For example, a typical instrumental width may be on the order of 0.5 Å while the natural width of the famous sodium D2 line, at 589.0 nm, is 10^{-4} Å.

In LIBS experiments, the total observed profile is the convolution of all the simultaneous physical phenomena giving rise to single spectral line. The dominating effects contributing to the overall line profile of a spectroscopic emission in a nominal laser-induced plasma are instrument broadening, Doppler broadening, and collisional broadening. Doppler broadening occurs due to the thermal motion of particles in the plasma. The velocity distribution of these particles is given by a Maxwellian distribution,

$$n(v_i)dv_i = \frac{N_j}{v_p\sqrt{\pi}} e^{-(v_i/v_p)^2} dv_i, \quad (2.12)$$

where N_j is the density of molecules in the j^{th} level, $n(v_i)dv_i$ is the number of molecules in the j^{th} energy level with the velocity component dv , and v_p is the most probable velocity, found from

$$v_p = \sqrt{\frac{2k_B T}{m}} \quad (2.13)$$

with k_B the Boltzmann constant, T the temperature, and m the mass of the molecule. The resulting intensity profile in angular frequency space is given by

$$I(\omega) = I_0 e^{-\left(\frac{(\omega - \omega_0)^2}{0.36\delta\omega_D^2}\right)} \quad (2.14)$$

with the width of the line given by

$$\frac{\delta\lambda_D}{\lambda} = \sqrt{\frac{8 \ln 2 k_B T}{mc^2}} \quad (2.15)$$

where c is the speed of light and I_0 is the normalized line amplitude. The Doppler width of a line, can then be seen to depend on the temperature and the type of atom that is undergoing the thermal motion. This width can also be quite small. Again, consider the Na D2 line. For a temperature of 5000 Kelvin, the Doppler width amounts to 0.1 Å, which for most LIBS experiments, is well below the instrumental width of the apparatus used.

The instrumental width also has a distinct profile that depends on the type of equipment being used in a given experiment. For most Czerny-Turner style spectrometers and nominally available ICCD detectors with sensitivity in the ultra violet and visual parts of the electromagnetic spectrum, this profile is typically approximated as a Gaussian distribution of detector pixels. The total width of this profile is the result of a convolution of effects due to the extent of the spectrometer slit, the size of the detector pixels, and the dispersion of the spectrometer being used. It is worth noting that the convolution of two Gaussians is a Gaussian distribution with a width equivalent to the sum in quadrature of the two convolved Gaussian widths, a direct result of the Fourier-convolution theorem (114). Thus, in principle, one could

determine the level of Doppler broadening and temperature despite its small size for a purely Doppler broadened line.

In actuality, all lines measured from an experimental plasma are the convolution of all the concurrent plasma physics that affect measured spectra. The most useful result of convolved line profiles, especially for laser-induced plasma, is the Voigt profile which is the convolution of Gaussian and Lorentzian line profiles (115). This profile is described by the integral equation

$$V(x, y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2} dt}{y^2 + (x - t)^2} \quad (2.16)$$

where x and y are constants that account for the Gaussian and Lorentzian components of the line profile as

$$x = \frac{\lambda - \lambda_0}{\Delta\lambda_G} 2\sqrt{\ln 2} \quad (2.17)$$

and

$$y = \frac{\Delta\lambda_L}{\Delta\lambda_G} \sqrt{\ln 2} \quad (2.18)$$

where λ_0 is the wavelength of the line center, $\Delta\lambda_G$ is the width of the Gaussian line component and $\Delta\lambda_L$ is the width of the Lorentzian line component.

The resulting profile carries both Gaussian and Lorentzian line components. Near line center, or the line kernel, defined as the region interior to the line FWHM ($\Delta\lambda$), Gaussian characteristics dominate. In the line wings, defined as the region exterior to the FWHM, the rapid rate of the decay from the exponential nature of the Gaussian profile is dwarfed by the Lorentzian line profile characteristics. Figure 2.3 shows a comparison of normalized Gaussian, Lorentzian, and Voigt line profiles with the same width.

The Voigt profile is particularly useful in LIBS plasma since line broadening is dominated by Stark broadening. The width of many non-hydrogenic lines under Stark broadening are either approximated or are given exactly as Lorentzian line profiles. Using a Voigt profile for simulations of the measured lines allows one to determine

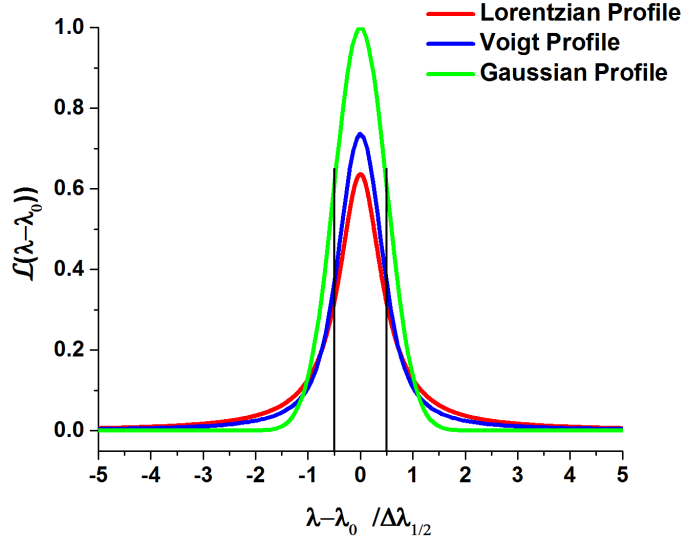


Figure 2.3: Comparison of normalized Gaussian, Lorentzian, and Voigt profiles. The vertical lines demarcate the line kernel from the line wings.

more precisely the line parameters (width and shift), which depend on the electron density of the plasma while including the effects of the instrument function.

The dominate broadening effect for laser-induced plasma for nominal time delays of the order of 100 ns to 10 μ s is due to Stark effects. The line profile of the Stark effect for a given transition depends largely on the strength of two competing approximation methods for calculating the profile, both of which are described in the next section.

2.3 Stark Broadening

Stark broadening is a type of pressure broadening that pertains strictly to collisions of charged particles with charged and/or neutral particles. It is a dominant form of line broadening in plasmas of all types due to the presence of strong, localized microfield distributions due to the ionized nature of plasma. Given this interaction, one may describe the perturbation of the Hamiltonian for the Stark effect as

$$\Delta \hat{H} = -e\vec{r}\vec{E}(t) \quad (2.19)$$

where $\vec{E}(t)$ is the time varying electric field strength, which is described by

$$\vec{E}(t) = \frac{1}{4\pi\epsilon_0} \sum_i z_i e \frac{\vec{r}_i(t)}{(r_i(t))^3} + \frac{1}{4\pi\epsilon_0} \sum_j e \frac{\vec{r}_j(t)}{(r_j(t))^3} \quad (2.20)$$

where $\vec{r}_i(t)$ and $\vec{r}_j(t)$ are the positions of the ion, of charge z_i , and the electron. It is clear from the above expressions that, in order to come to a solution of the line profile under the collisions of charged particles, one must consider the time-dependent Schrödinger equation. This approach is quite difficult and no single, general methodology exists for this solution.

The line profile under Stark broadening, which is strictly different than the more commonly known Stark effect which describes the shifting of energy states due to the presence of an external electric field, is determined by the way in which the collisional process between the charged particle, typically referred to as the perturbed or perturbing particle, is described. Typical perturbing particles in theory calculations of Stark broadening include protons, and electrons. The two methods are known as the Quasistatic and Impact approximations. Due to the collisional nature of electrons in the Stark broadening theory, in both approximations the line width and total profile become dependent on the electron density.

2.3.1 Impact Approximation

In the Impact approximation, one assumes the electric field generated by the plasma free electrons varies rapidly through time. This amounts to the collisional time being much shorter than the time between two collisional events. The trajectories of the electrons, which are a straight line for neutral particle interactions and hyperbolic for charged particle interactions, are assumed to be fixed and back scattering is to be considered negligible. The result is a classical analogous picture in which the phase of the electromagnetic wave train of pulses is abruptly changed. The line profile of a transition due to high frequency occurring events, such as those with the an

electromagnetic wave train pulse, in general, is found using Fourier transform methods,

$$L(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{i\omega s} C(s) ds \quad (2.21)$$

where $C(s)$ is simply the Fourier transform of the line shape function. This method of line shape inversion is generally applied to all forms of pressure broadening (116) and is common place in calculations of Stark broadened lines (61).

The direct line profile of the spectroscopic line under the Impact approximation is given by a Lorentzian line profile. This line shape assumes that the line is completely isolated from neighboring energy states, and, for most heavy elements in which the perturbing particle is an electron, this approximation holds true. A major result of the Impact approximation is that the width of the Stark broadened line depends on the electron density. Griem's numerical formulation shows

$$\Delta\lambda = w \frac{N_e}{10^{16}} + 1.75\alpha \left(\frac{N_e}{10^{16}} \right)^{1/4} (1 - 1.2)\rho w \quad (2.22)$$

where w is the electron width Stark broadening parameter, α is the ion broadening Stark parameter, and ρ is the Debye shielding parameter (93). The two broadening parameters are numerically simulated values that depend on the temperature.

Initial calculations of the line profiles in the Impact approximation were completed using a semi-classical method. These methods are aimed at calculating two collisional parameters which indicate the relative importance of electron and ion collisions with atoms, typically denoted as w and α (or A), respectively. Both of these quantities are temperature dependent and are characteristic to a Stark broadened transition. In this model, second order perturbation theory is used to include collisional influences from dipole, polarization, and quadrupole interactions (53; 54). This method was developed to describe the interactions of single electrons outside of closed shells and is only

applicable to hydrogenic species. The semi-classical model was replaced by the semi-empirical method and its subsequent updates which are termed as the modified semi-empirical method. In general, the semi-empirical method is simpler than its predecessor and requires much less data on the atomic energy levels of the Stark broadened atom. This is done so by making the assumption that there are no major violations to the isolated line assumption.

All of these calculations assumed that the lines were isolated energetically from their nearest neighbors. This ensures that the width of the line is greater than these energy separations. Non-isolation causes a degeneracy in the energy levels and the Impact approximation breaks down. This tends to occur at instances when the electron density is quite large ($> 10^{19}\text{cm}^{-3}$) or when the transition of interest arises from high principle quantum number energy states.

2.3.2 Quasistatic Approximation

In the Quasistatic approximation, one assumes that the microfield is a constant in time at the position of the radiating atom or molecule during the lifetime of the emission process. The result is many different types of perturbers (dipoles, quadruples, ions *et c.*) that interact with the radiating atom. As such, one speaks of a distribution of effects giving rise to the total line profile with each type of perturbed having its own shape. The first calculation of microfield distributions was performed by J. Holtsmark in 1919 (47). In general, a Holtsmark distribution may be described by the following characteristic function

$$\phi(t; \mu, c) = e^{it\mu - |ct|^\alpha} \quad (2.23)$$

where c is scaling parameter, μ is a location parameter, and the parameter α determines the shape of the profile and takes on a value of $3/2$. This Holtsmark profile is similar to Gaussian and Lorentzian profiles in that they all share the same general form of the characteristic function, each having a different shape parameter. The shape parameter for a Gaussian is 2 and is 1 for a Lorentzian.

In order to make calculations in the Quasistatic approximation, the Holtsmark distribution is typically expressed as

$$H(\beta) = \frac{2\beta}{\pi} \int_0^\infty dx \sin(\beta x) e^{-x^{3/2}} \quad (2.24)$$

where the parameter β is the normalized field strength and is typically given in terms of the strength of the microfield

$$\beta = \frac{F}{F_0}. \quad (2.25)$$

Here, F_0 is termed the Holtsmark field strength and is given by

$$F_0 = 2.603 \frac{ze}{4\pi\epsilon_0} n_z^{3/2} \quad (2.26)$$

where n_z is the perturbed density. The integral expressions of the Holtsmark distribution for a given type of perturber cannot be evaluated analytically and require numerical simulations for calculation of the Holtsmarkian distribution. The total line profile is the summation over all microfield distributions.

An approximate formula for a generic Holtsmark line profile may be given as

$$\mathcal{L}(\omega) \propto \frac{1}{(\omega - \omega_0)^{5/2}} \quad (2.27)$$

where the profile is given in frequency space. Figure 2.4 shows the differences between a Lorentzian and Holtsmarkian line profile functions in the line wings, where the differences are greatest. Differences between the Holtsmarkian and the Lorentzian become most prominent far into the line wings. Popular calculations of Stark broadened spectra in the Quasistatic approximation were performed by Griem (55; 56). These volumes contain tabulated profiles for the hydrogen Balmer series.

As has already been alluded to, the Impact approximation most often and most exactly pertains to atoms in which there are more than two perturbers. This situation is most likely to apply to heavy atoms such as aluminum or carbon. Small exceptions

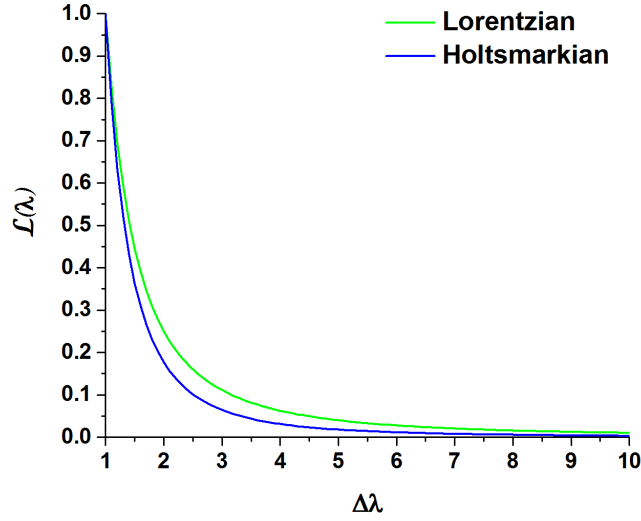


Figure 2.4: Differences in the decay in the wings of Lorentzian and generalized Holtsmarkian line profiles

to the line profile in the Impact approximation occur near the line center where ion dynamics change the line shape due to the microfield (Holtsmark) distribution. There are also strong Holtsmarkian influences far into the wings of a spectral line. As the Impact approximation becomes more difficult to satisfy due to non-isolated lines, particularly at electron densities greater than 10^{19} cm^{-3} , the Stark broadened emissions begin to take on quasistatic characteristics due to the increasing prevalence of the local microfield. The quasistatic effects are most prominent for electronic perturbers when there are no other effects present. This primarily pertains to hydrogen emissions and pure hydrogen plasma.

2.4 Molecular Spectroscopy

A significant portion of this dissertation relies on extracting information on the plasma state from molecular emissions. Thus, it is worthwhile to briefly discuss the calculation of diatomic spectra since extraction of the plasma information relies on fitting to theoretical calculations of diatomic emission spectra.

The general structure of the molecular emission is determined by the molecular Hamiltonian. Due to the additional degrees of freedom associated with molecules, *i.e.*, from vibrations and rotations, the Hamiltonian takes on electronic, vibrational, and rotational components. As well, contributions due to the motion of the molecular nuclei and nucleonic spins are present in the total molecular Hamiltonian. Rotations and vibrations are quantized in this Hamiltonian and transitions between vibrational and rotational quantum numbers correspond to the vibrational and rotational spectral lines. The general structure of a molecular emission is that each electronic state is characterized by its own potential energy curve. The upper and lower potential are further split into the quantized vibrations. Further still, the vibrational states are split rotationally. This is depicted in Figure 2.5. The potentials, V , are plotted against the internuclear separation coordinate, $\vec{R}$. The potentials shown in the picture are not quite harmonic in nature and rather are called Morse potentials, named after the empirical formulations of P.M. Morse (117). The resulting organization of the spectral emission is electronic transitions with corresponding vibrational components, with corresponding rotational components. This leads to band like structure, as all the vibrational components of a particular transition, v to v' , arise from nearly the same electronic position.

The following discussion on the calculation of molecular spectra pertains only to diatomic molecules since they are the simplest of all molecules and, as such, these spectra are the easiest molecular spectra to calculate. The discussion of molecular structure is greatly simplified when one recognizes that the molecular nuclei are significantly more massive than the electrons and that the nuclei move much slower than the electrons. Under this assumption the nuclei are held in fixed positions relative to the electronic structure. This is known as the Franck-Condon principle and allows for the positions of rotational and vibrational transitions to remain constant during the lifetime of a transition.

The spectra of diatomic molecules are most often calculated from the line strength, as given in Equation 2.6. In the case of molecular emission spectra, as calculated by

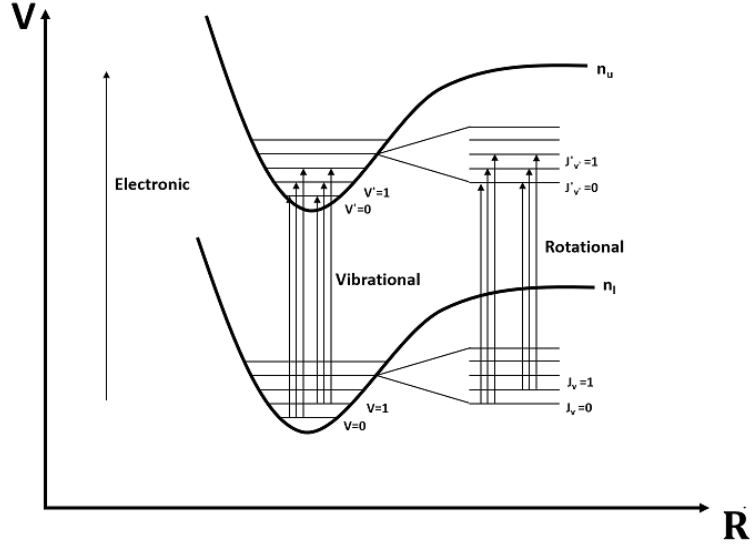


Figure 2.5: Molecular potentials between two electronic levels showing the source of electronic, vibrational, and rotational spectra.

Eq. 2.7, the tensor operator becomes the electric dipole operator. The wave functions of the upper and lower states are described by the quantum numbers n , v , J , and M , where J and M represent the total angular momentum and spin orbit angular momentum quantum states. The states v and n are used to describe the vibrational state and an index that represents all other states, respectively.

In order to calculate the diatomic line strength, it is factored into a useful expression that separates the electronic, vibrational, and rotational components of the emissions into a simple expression

$$S_{ul} = S_{elec}(n'v', nv)q(v', v)S(J', J) \quad (2.28)$$

where the primed coordinates reference the upper state and the factored components are the electronic transition strength, the Franck-Condon factors, and the Hönl-London factors, in order of their appearance in the above expression. The Hönl London factors

are calculated from

$$S(J', J) = \frac{1}{2J+1} \left| \sum_{a'} \sum_a \langle nvJM|a\rangle \langle J\Omega qk|J'\Omega'\rangle \langle a'|n'v'J'M'\rangle \right|^2 \delta_{S'S} \delta_{\Sigma'\Sigma} \quad (2.29)$$

where Ω is the z' component of the total angular momentum, S represents the spin, Σ is the spin of the z' component, and a is used to indicate that the calculations are to be carried out in Hund's case (a) basis. The primed coordinates represent upper states. In Hund's case (a) basis, the electronic and nuclear spin orbit and total angular momenta add vectorially.

The Hönl-London factor accounts for the rotational aspects of the spectrum due to the spin components that comprise its calculation. One makes calculations of the electronic and vibrational structure by considering the Franck-Condon factors and electronic line strength together as one electronic-vibrational line strength, which is given as

$$S(n'v', nv) = \sum_{k=-q}^q \left| \langle nv|\hat{T}_k^q|n'v'\rangle \right|^2. \quad (2.30)$$

This expression is evaluated by making the Born-Oppenheimer approximation (series expansion of the operator) to give

$$\langle nv|\hat{T}_k^q|n'v'\rangle \approx \langle n|\hat{T}_k^q|n'\rangle = R_{nn'}(r) \langle v'|v\rangle \quad (2.31)$$

where $R_{nn'}(r)$ is the electronic transition moment and $\langle v'|v\rangle$ is termed the overlap integral (118; 119). To make the calculation of the spectrum, the electronic transition moment is Taylor expanded and subsequently combined with the Franck-Condon factors, given by

$$q(v', v) = \langle v'|v\rangle^2 = \left| \int_0^\infty \psi_{v'}(\vec{r}) \psi_v(\vec{r}) d\vec{r} \right|^2 \quad (2.32)$$

to form the electronic-vibrational line strength as

$$S(n'v', nv) = (a_0 + a_1 \vec{r}^{(1)}(v'v) + a_2 \vec{r}^{(2)}(v', v))^2 q(v', v) \quad (2.33)$$

The quantities $\bar{r}^{(k)}$ are called the r-centroids and account for the positional effects of the spectrum along the inter-nuclear axis, which is the axis laying in the plane that intersects both atomic nuclei in the diatomic molecule.

When one models molecular spectra using the above description, the population of states that is applied to the calculation of the emission rate coefficient from Equation 2.6, is a Boltzmann distribution. The result is a temperature dependent diatomic emission. Figure 2.6 shows sample calculations of aluminum monoxide $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ emission spectra using the described method (120). The figure also indicates which components of the spectrum are due to rotational and vibrational transitions. The entire spectrum corresponds to a single electronic transition and the subsequent vibrational transitions with a net change of 0, ($\Delta v = 0$). The temperature of the calculated spectrum is 4000 Kelvin.

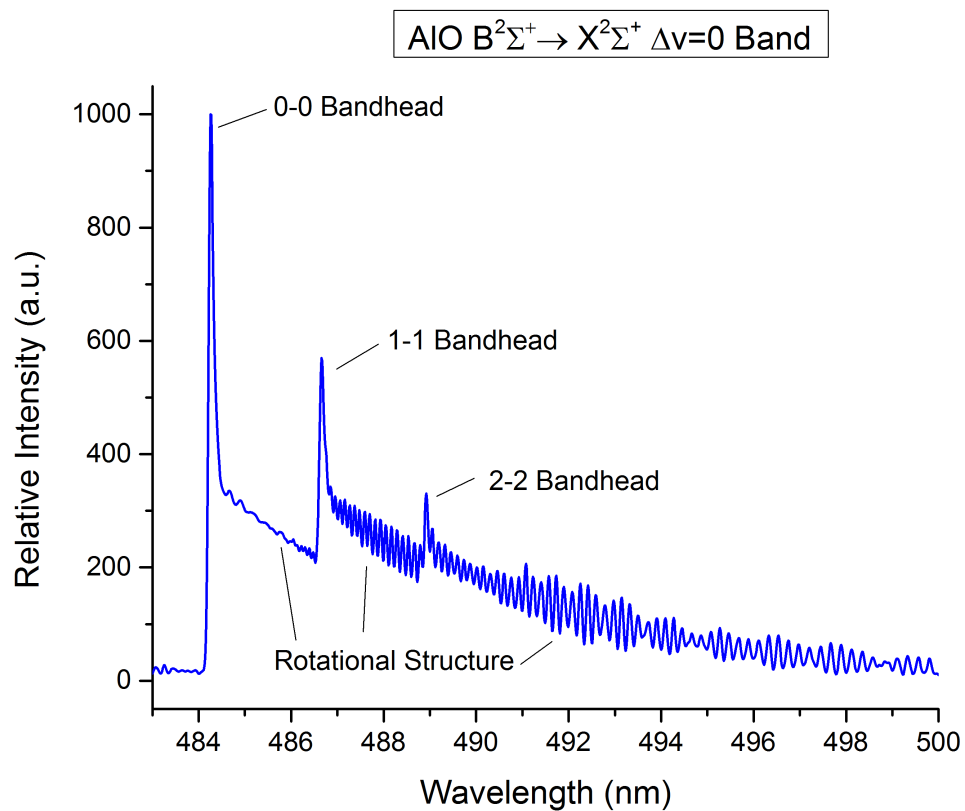


Figure 2.6: Theoretical diatomic molecular aluminum monoxide emission spectra showing an emission temperature of 4000 Kelvin

Chapter 3

Experimental Methodology

In this chapter, the various experimental methodologies used to measure the laser-induced plasma are described. At various times throughout this work several different aspects of plasma imaging were of interest. A prime component of this work is spectroscopic imaging of the plasma with time, space, and spectral resolution. This work was motivated to evaluate potential self-absorption effects in spectroscopic line profiles, study relationships of hydrogen Balmer series and aluminum line widths *vs.* N_e , and to determine the plasma temperature. The spatial distribution of molecular species was also investigated spectroscopically for temperature determinations along the plasma plume height. Atomic and molecular spectroscopy experiments were performed at the University of Tennessee Space Institute (UTSI). Simultaneous spectroscopic images were collected with shadowgraph imaging techniques to measure the plasma shockwave directly for a direct comparison of spectroscopic and shockwave physics. This work was performed at Sandia National Laboratories (SNL).

3.1 Plasma Initiation and Breakdown

The basic LIBS apparatus used at the UTSI facility consists of a proto-typical, pulsed laser ablation apparatus. Laser light from an Nd:YAG, Q-switched laser (Qunata-Ray DCR-2A) is steered such that is vertically incident onto the target sample. The target sample for the work performed at UTSI was a square 2×2 cm Al alloy 6061 target for atomic spectroscopy studies and was a sheet of alumina (Al_2O_3) sheet for molecular studies. The laser used the fundamental wavelength output (1064 nm) of the laser and had an average pulse width of 14 ns, as measured by a silicon photodiode and an

Table 3.1: Chemical composition of Al alloy 6061 by weight percentage

Element	Percent
Aluminum	95.8-98.5
Magnesium	0.8-1.2
Silicon	0.4-0.8
Iron	0-0.7
Copper	0.15-0.4
Chromium	0.04-0.35
Zinc	0-0.25
Manganese	0-0.15
Titanium	0-0.15

oscilloscope. The energy per pulse of the system was measured to be 120 mJ/pulse using a ThorLabs PM100USB power and energy meter. The resulting irradiance at breakdown was approximately 2 GW/cm².

Light from the plasma was imaged onto the slit of a Jobin Yvon HR640, 0.64 meter Czerny Turner style spectrometer outfitted for use with either 1200, 1800, or 3600 grooves/mm gratings. The plasma emissions were imaged onto the spectrometer slit using a ThorLabs LA4545 uncoated, plano-convex, ultra violet-fused silica (uv-fs) 2 inch lens, with focal length of 100 mm. The slit width was held at 50 μm for the UTSI experiments. The plasma was initiated by focusing the laser light with a 2 inch uv-fs, with focal length of 125 mm. The sample was situated such that the laser was incident on the square surface of the sample and the breakdown was initiated vertically with respect to the extent (width) of the slit. The height of the slit was parallel to the incident laser beam. The slit width was 50 μm and the slit height is approximately 5 cm. The laser focus was arranged such that breakdown was initiated both on the surface of the target sample and in the surrounding gas atmosphere. Table 3.1 shows the weight percentage composition of the Al alloy 6061 target. This is important to note since the trace elements will contribute to the measured LIBS signal and, in some cases, may be used for quantitative analysis (121; 122). The alumina sample was 96% pure. The impurities of this sample are not known.

Measured spectra also have contributions from the gas atmosphere present during ablation. The UTSI ablation experiments were all performed in a controlled gas environment that consisted of a mixture of ultra high purity (UHP) hydrogen and nitrogen gas at a ratio of 9 to 1, *i.e.*, the chamber was filled with 90% hydrogen and 10% nitrogen gases. The atmosphere was controlled by loading the sample mounted to a chamber, which had six ports of optical windows. One the ports was used to mount the Al sample by placing the sample on an optical post onto a chamber window blind. The five other windows were 0.5 inch diameter and 1 cm thick uncoated uv-fs glass.

The chamber was outfitted with two gas inlets and one gas outlet. The gas inlets were used to mix the UHP hydrogen and nitrogen gases via partial pressure addition. The gas outlet was used to evacuated the chamber before and after experimentation. The gas outlet was connected to a mechanical/diffusion pump apparatus so that the chamber could be evacuated as needed. Figure 3.1 shows pictures of the vacuum chamber, pump apparatus, and the samples that were used.

Prior to performing the experiments, the chamber was evacuated using a mechanical/diffusion pump system. The mechanical pump was used to bring the system pressure down to 10 mTorr and the diffusion pump was used to bring the system pressure down to 1×10^{-5} Torr (1.33×10^{-3} Pa). This was necessary to ensure that there were as few as possible containments in the chamber during the experiments, such as those from residual atmospheric moisture and other atmospheric particulates. The entire chamber, including the sample and post, were cleaned in an acetone methanol bath. The optical windows were also cleaned using methanol and standard optical component cleaning techniques. The chamber pressure was monitored using a differential pressure gauge. The gauge casing volume was evacuated using the vacuum pump system so that the gauge operated as an absolute pressure gauge, which made reading the pressure easier during the experiments. The chamber pressure was kept at 840 Torr throughout the measurement process.

The spectral images were collected using an Andor iStar ICCD (334 T Series) capable of a spatial resolution of $13.3 \mu\text{m}$ and a temporal resolution of 2 ns. The

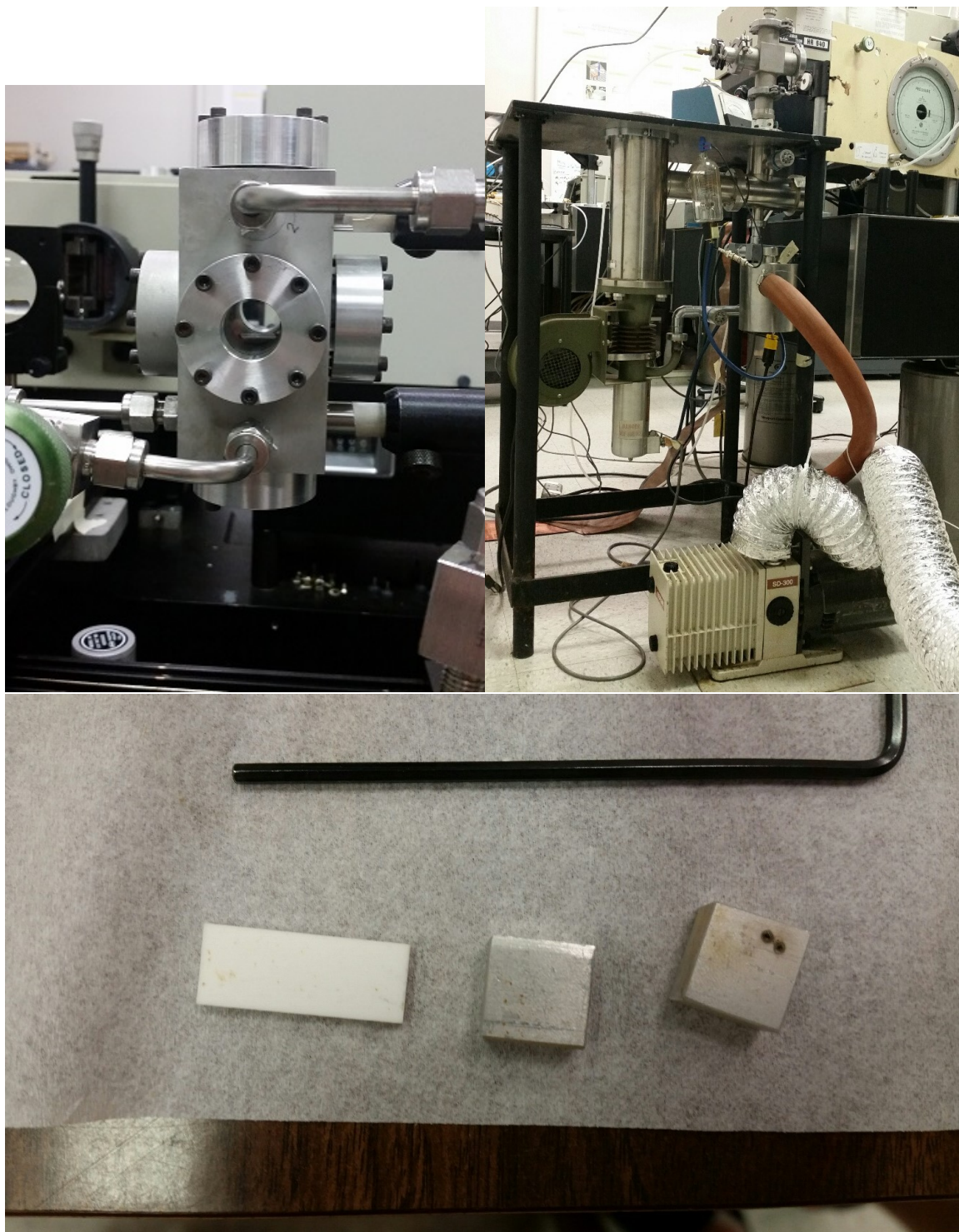


Figure 3.1: Pictures of the gas chamber (top left) the diffusion and mechanical vacuum pumps connected to the pressure system (top right), and the aluminum and alumina samples with an Allen wrench for size comparison (bottom).

intensifier is used to gain the level of temporal resolution; however, it causes the spatial resolution to be reduced from the size of the detector pixels to the 19 μm resolution. The detector is an array of 1024×1024 pixels that could be "binned" together to form larger effective pixels, which is desirable to increase the signal to noise ratio (SNR) in many cases. The UTSI experiments were performed using an arrangement of 128×1024 , vertical $\times$ horizontal detector pixels. Groups of 8 vertical pixels were binned together to make this arrangement. The full resolution capability of the horizontal extent was used to achieve the best possible spectral resolution. The overall spatial resolution in this arrangement is 0.1 mm, in the image plane, at the detector. Timing between the ICCD measurements and the firing of the laser pulse was achieved by synchronizing the laser Q-Switch output with an external synchronization input on the ICCD.

Prior to spectroscopic analysis, all data were calibrated for the system sensitivity and wavelength response. Calibrations of this nature are required since detectors, spectrometers, and other optical equipment age and are naturally more sensitive in differing spectral regions. The wavelength calibration is carried out for all investigated wavelength regions of interest. The method for the calibration is to compare the pixel position of a measured line at several pixel positions. The known wavelengths from the measured lines are then used to generate the calibrated wavelengths. In this procedure, gas discharge lamps containing specific elements were used. These details are presented in Appendix B. Table 3.2 shows the wavelength regions for the spectra of interest, the time delays of interest, and the gratings that were used during the spectral measurements. The atomic spectra of interest were the ground state Al $3s^23p \rightarrow 3s^24s$, 394.4 nm and 396.15 nm transitions, the hydrogen Balmer series α , β , and γ (H_α , H_β , and H_γ) lines, and the ionic Al $3s3p \rightarrow 3s4f$, 281.61 nm transition. These data were collected with a 1200 grooves/mm grating in the first 2.15 μs following ablation of the Al target sample. The molecular spectra that were to be investigated were the aluminum monoxide (AlO) $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ $\Delta v=0$ ro-vibrational band, with a band head at 484 nm. These data were collected in delays ranging from 2.5 to 20 μs following ablation of the alumina target sample using an 1800 grooves/mm grating. The gate

Table 3.2: Details on the wavelength ranges and time delays for which spectra collected at UTSI were investigated.

Spectra	λ range	τ_{Delay}
H $_{\alpha}$	645-665	0-2.25 μ s
H $_{\beta}$	475-495	0-2.25 μ s
H $_{\gamma}$	425-445	0-2.25 μ s
Al 394 and 396	385-405	0-2.25 μ s
Al $^{+}$ 281	270-290	0-2.25 μ s
AlO	480-500	1-20 μ s

width used in the first 100 ns was 10 ns and from 100 ns to 2.15 μ s the gate width was 50 ns. The AlO spectra were collected using a 1.25 μ s gate width.

All of the measured spectra represent the observation and accumulation of 100 individual laser shots. This was done to increase the spectroscopic signal quality. Measuring spectra in such a configuration is suspect to matrix effects, characteristic changes in the measured spectra due to the sample surface. The prime matrix effect that could be expected are changes in the shape of the plasma due to the shape of the crater formation or laser drilling during repeated ablation at a single position. The difference in such effects for 1 *vs.* 100 laser shots is expected to minimal. Matrix effects are most pronounced for low ambient pressures, on the order of 100 Torr or less (123; 124). At the near atmospheric pressures used in this work, matrix effects are expected to be minimal due to the smaller amount of material that is vaporized at atmospheric pressures and plasma shielding effects. Plasma shielding occurs as top portions of the plasma form before lower sections, along the axis of laser incidence, and block laser energy from reaching the lower portion. Further, the sample was translated between each set of measurements.

The intensity calibration was performed using an Ocean Optics Deuterium/Halogen-Tungsten lamp (DH-2000-Bal). The intensity calibration is carried out by comparing the measured detector response against manufacturer response curves for the lamp in use and requires that the wavelength calibration be performed first, since the sensitivity response of the detector is wavelength dependent. Further details in regards

to the intensity calibration procedures are contained in Appendix B. The spectral resolutions are found as a result of the wavelength calibration procedure. The average resolution with the 1200 grooves/mm grating was 0.15 nm and the resolution of the 1800 grooves/mm grating in the vicinity of the AlO measurements was 0.1 nm.

3.2 Self-Absorption Apparatus

The goal of the self-absorption apparatus is to calculate an experimental correction factor. This correction factor is then applied to the measured spectra to find spectroscopic line profiles in the absence of self-absorption effects. The basis of this method is to reflect the plasma emissions back through the plasma before spectroscopic imaging and make comparisons between spectra measured with and without the plasma reflection. Such a method is not new, and has been previously applied to plasma (125; 126) and flame spectroscopy studies, where a flame was produced behind the flame of interest (127).

The plasma imaging onto the spectrometer slit is as previously described in previous descriptions of laser-induced plasma spectroscopic investigations (128). The plasma was retro-reflected using a 3 inch plane mirror with a reflectance of 90%. Light from the plasma needed to be imaged onto the reflecting mirror. This was accomplished by using a copy of the lens used to image the plasma light onto the spectrometer slit, hereafter referred to as the self-absorption lens. Imaging the plasma reflection back onto the plasma is the most important and difficult aspect of this experiment, due in part to the size of the plasma and also, in part, due to the significant opportunities for losses of the optical signal along the reflection path length. As such, the alignment procedure of the lenses and mirror with the plasma and spectrometer slit was delicate and great care was taken during this part of the experiment.

As a general rule, the lens used to image the breakdown onto the spectrometer slit was fixed in its position (excluding necessary fine adjustments) to reduce the number of parameters during the alignment procedure. The self-absorption lens and the reflecting

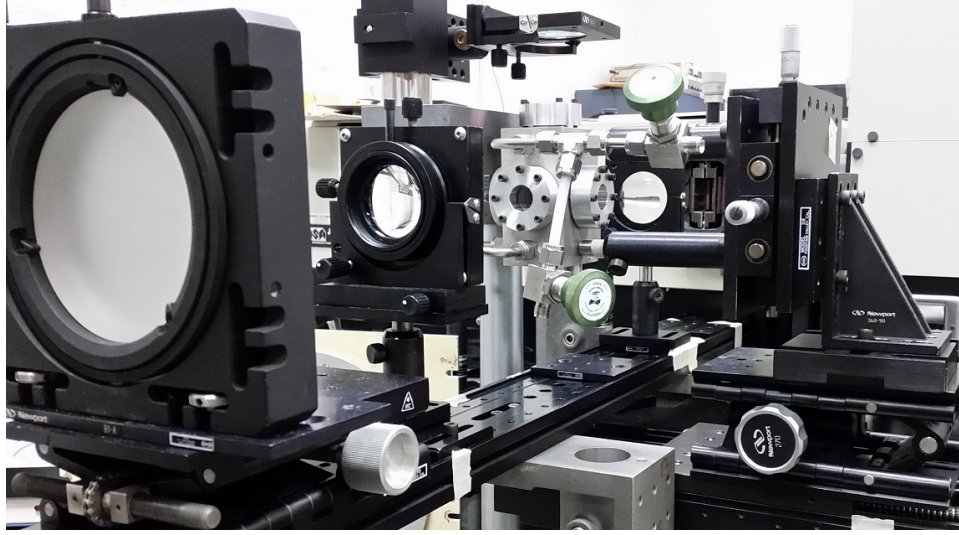


Figure 3.2: Picture of the slit assembly showing the self absorption mirror and lens as well as the gas chamber in its position during the spectral measurements.

mirror were such that each had 5 axis of fine adjustments (3 Cartesian coordinates and 2 angular axes). The rough positions of the optical elements were determined by the focal length of the optics, *i.e.*, both lenses were placed at $2\times$ the focal length, or back focal length from the plane side as given by the thick lens approximation (129), which gave better alignment results. This alignment yielded a 1 to 1.05 imaging ratio at the detector. Figure 3.2 shows images of the optical rail that housed the self-absorption optical elements and Fig. 3.3 shows a block diagram showing the general experiment layout and also indicates the axes of fine adjustment for each optical element of the apparatus.

While the alignment procedure was quite tedious, two metrics were used to determine when a proper alignment was achieved. The first was zero order imaging, which showed the relative position of the plasma and its image. The ratio of the signal intensity of these images can also be used to indicate the quality of the alignment. Such images are shown in Figure 3.4. The second metric was the ratio of measured spectra with and without the plasma reflection. Balmer series H_β spectra measured at a $5\ \mu\text{s}$ time delay were used for this, since it is unlikely that H_β spectra are self absorbed at this time in the plasma evolution in nominal laboratory air induced breakdown, such that

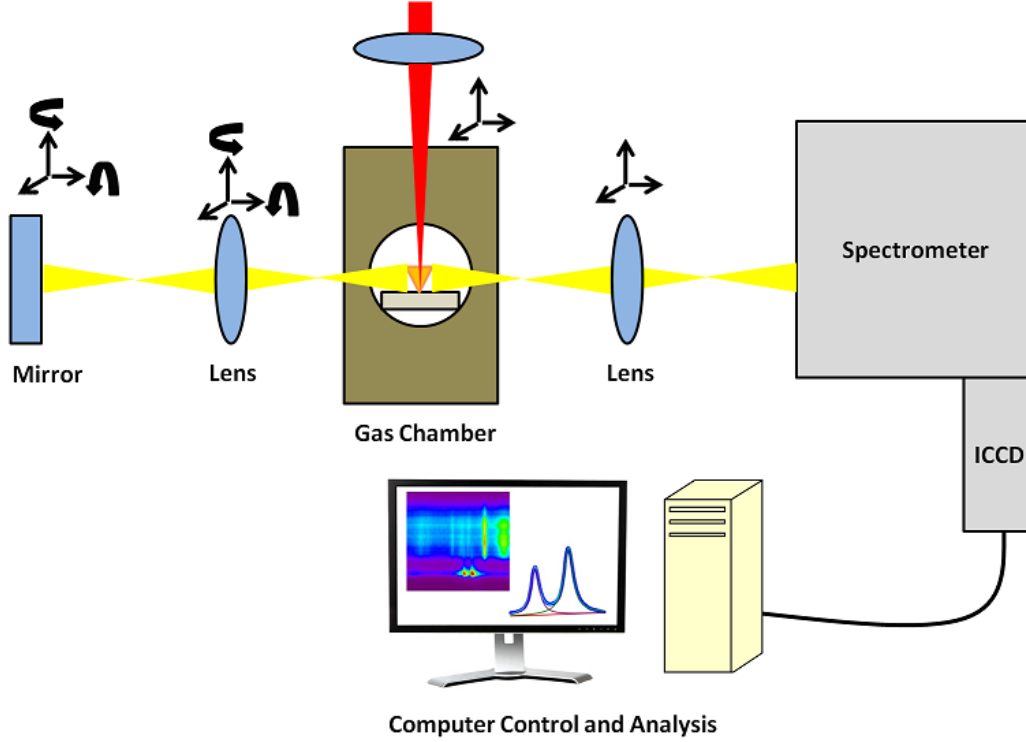


Figure 3.3: Block diagram of the apparatus used for the self-absorption experiments.

line profile distortions were not expected (77; 130). Figure 3.5 shows a measured ratio and the corresponding H_β spectra. These two quantities were maximized by adjusting the fine adjustments on the mirror and self-absorption lens. The best possible ratio is determined by the optical losses of the optical elements of the system and is found to be 1.8. When the windows from the chamber were added to the system this value is further reduced, such that a measured ratio between 1.2 and 1.4 is adequate for the self-absorption analysis.

3.3 Sandia National Laboratory Experiments

Simultaneous shadowgraphs and plasma emission spectra were measured to assess characteristics of the plasma shockwave in reference to the measured spectra. These experiments were performed at Sandia National Laboratories (SNL). The experiments at SNL were performed using a custom built Applied Spectra, J200 LIBS instrument.

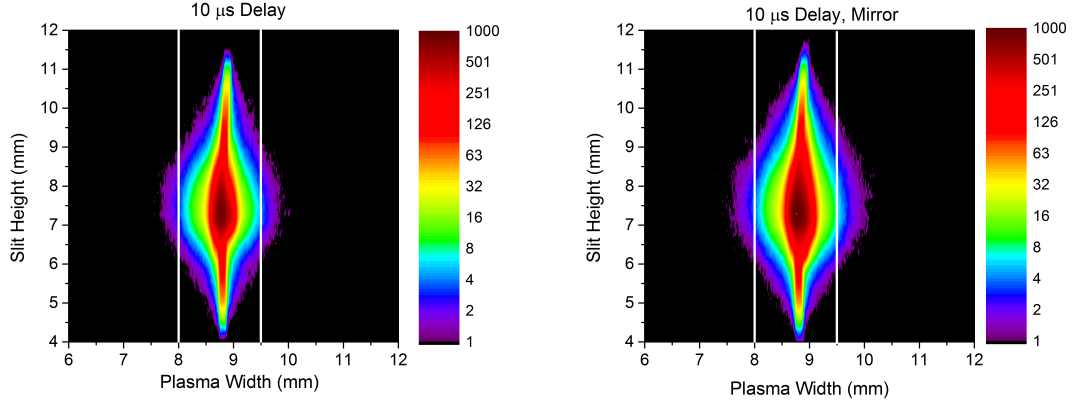


Figure 3.4: Zero order plasma images used to align the self-absorption apparatus. The white analysis markers are used to indicate similar positions in both images.

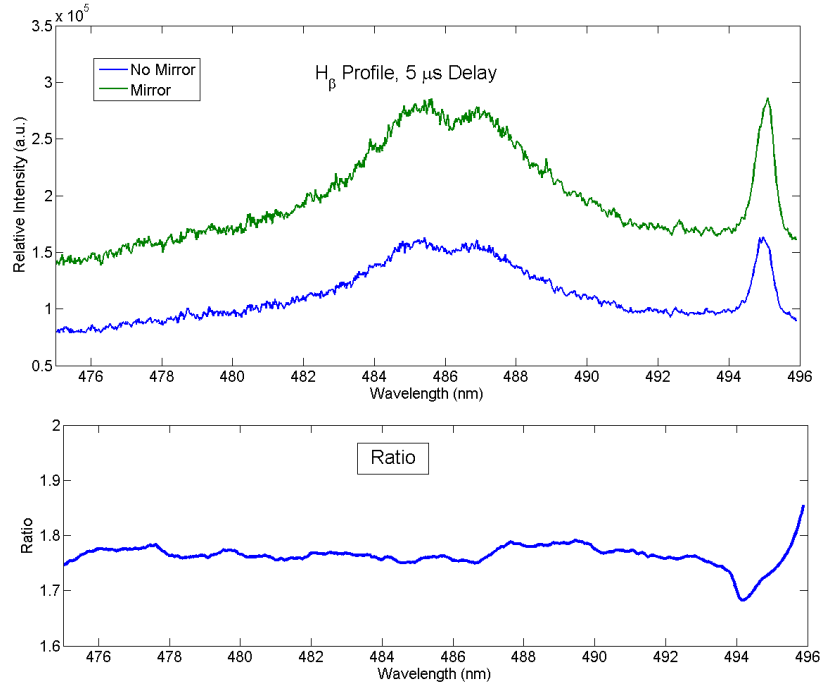


Figure 3.5: Measured H_β spectra used for mirror self-absorption alignment (top) and the corresponding ratio of cases measured with and without the mirror (bottom)

The advantage of using this piece of equipment rather than assembling the necessary parts for a LIBS apparatus individually, as was done at UTSI, was that the timing of the various components were controlled through a single field-programmable gate array (FPGA) board and a pre-built LabView control program that came with the equipment.

The plasma was produced using an Nd:YAG, Quantel Ultra Light laser using the fundamental wavelength of 1064 nm with an 8.6 ns pulse width, as measured by a photodiode and oscilloscope. The energy per pulse at breakdown was 38 mJ/pulse. The corresponding peak irradiance at breakdown was approximately 2 GW/cm². The SNL experiments were performed in nominal laboratory air. It is important to note that the laboratory air in this case corresponds to air in Albuquerque, NM, where the air is much dryer than in many places and the elevation (approximately 5280 feet or 1 mile) results in a significantly reduced density of air, by about 1/3, compared to sea level. Breakdown was initiated such that a single plasma was produced on the surface of the Al target.

Light from the plasma was imaged onto the slit of a Princeton Instruments Isoplan SCT320 spectrometer installed with an 1800 grooves/mm grating with a focal length of 0.33 meters. Spectra were recorded using a Princeton Instruments PiMax 2 ICCD with a detector configuration of 1024×256 detector pixels each with a size of 25 × 25 μm . During data collection, groups of 2 vertical pixels were binned together to give a total vertical spatial resolution of 50 μm .

The sample was an Al alloy 6061 sheet that was 5 cm square with a thickness of 1 mm. Ablation occurred on the narrow edge of the sheet and was translated between each data collection of 100 laser shots/ICCD accumulations. Breakdown was initiated such that the laser was vertically incident on the Al target. Spectra were collected at systematically varied time delays ranging from 0-1 μs in the wavelength region 200-800 nm. In the first 100 ns following ablation, the spectra were measured in 5 ns delay steps with a 5 ns gate width, between 100 and 400 ns delays the spectra were collected in 20 ns delays steps using a 10 ns gate width, and from 400 to 100 ns delays the spectra were

collected in 50 ns delay increments using a 20 ns gate width. The spectral region covered by the spectrometer was approximately 35 nm for a single spectrometer wavelength position. In order to obtain a single image over the entire desired wavelength range, the spectra needed to be "glued" together using the manufacturer supplied ICCD control software (Princeton Instruments WinSpec). This required a 5 nm overlap between spectroscopic images to escape the ICCD edge effects from the circular shape of the intensifier. This process required 21 total spectroscopic images. The overlap regions between images were stitched together by taking a weighted average of the signal intensity. The pixel corresponding to the center of the overlap between the two images had an equal weight. The weight then reduced/increased proportionally based on the distance from this pixel position. For example, with a 3 pixel overlap center at pixel c and intensity I_c . The weighted average is then given by

$$I_c = \frac{1}{2}I_1 + \frac{1}{2}I_2 \quad (3.1)$$

$$I_{c-1} = \frac{2}{3}I_1 + \frac{1}{3}I_2 \quad (3.2)$$

$$I_{c+1} = \frac{1}{3}I_1 + \frac{2}{3}I_2 \quad (3.3)$$

where I_1 and I_2 are image pixel image intensities being glued together at the pixel position I_i .

The resulting spatial resolution was 0.05 mm at the image plane of the detector and the overall spectral resolution varied, as expected, over the wavelength range of interest. Table 3.3 shows the spectral resolution and resolving power of the apparatus at several wavelengths across the wavelength range. The resolution was determined during the wavelength calibration which was carried out using an Hg/Ne-Ar lamp (Princeton Inst. Dual Switchable Light Source). The resolving power is a quantity used to determine the quality of a spectrometer-detector arrangement.

Both relative and absolute intensity calibrations were performed. Relative calibrations were performed using a Tungsten lamp in the 400-800 nm range. A

Table 3.3: Resolutions and resolving power of the Sandia apparatus at selected wavelengths

Wavelength (nm)	Resolution (nm)	Resolving Power
253	0.10	2608
365	0.07	5000
435	0.07	5959
546	0.07	7479
640	0.05	12800
760	0.01	7835

Deuterium lamp (Gooch and Housego OL UV-40 UV Standard of Spectral Irradiance) was used to perform the absolute intensity calibration. The lamp is calibrated in the wavelength range 200-400 to have an exact spectral irradiance with a determined uncertainty (3% at 250 nm) at a distance of 30 cm from the lamp. Using spectral irradiance makes it such that the solid angle of the plasma emission did not need to be known. Further details on the calibration procedure are contained in Appendix B.

The shadowgraphs were imaged using an iDS composite metal oxide semiconductor (CMOS) (N1-120ML-M-GL) camera coupled with a planar-apochromatic (PL-APO) 5 $\times$ objective (f=200mm), such that the laser light used to investigate the desired shadows is collimated upon entry into the camera imaging system. The laser used for the shadowgraph images was a picosecond pulsed Continuum Helios 532-2-50 laser with an output wavelength of 532 nm and a pulse width of 700 ps. The laser light was beam expanded and passed through an attenuator to reduce the laser light intensity to make imaging easier and protect the imaging optics from over exposure. The shadowgraphs were viewed 90⁰ relative the observation of the spectra. Figure 3.6 shows a block diagram of the apparatus in edge on and top views. Timing between the shadowgraph laser, ablation laser, and ICCD measurement were controlled by an output pulse from the master Applied Spectra timing board.

Due to the geometry and relatively small size of the Applied Spectra box, the plasma light needed to be steered such that the light was incident onto the spectrometer slit as shown in the block diagram of Figure 3.6. The plasma light was collected using a

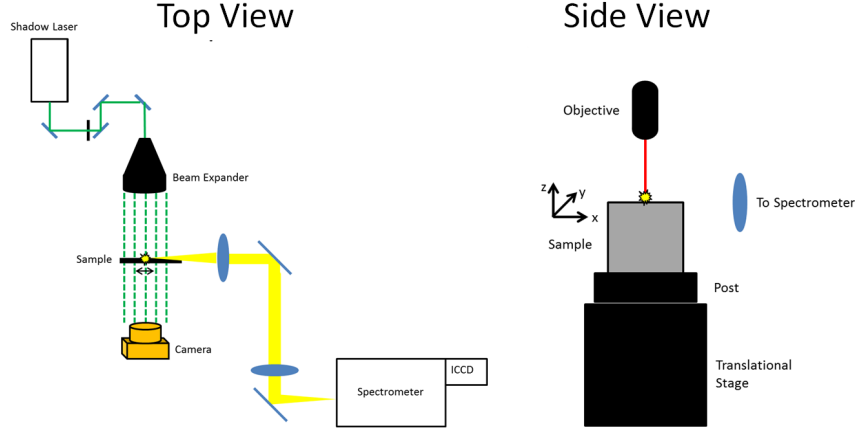


Figure 3.6: Block diagrams of the simultaneous LIBS and shadowgraph apparatus used at SNL showing side and top views.

Thorlabs LA4545 uncoated uv-fs lens. The light was imaged onto the spectrometer using a Thorlabs LA4984 uncoated uv-fs 2 inch plano-convex lens with focal length 200 mm. The mirrors used to steer the plasma light were 2 inch Thorlabs, PF-20-03-F01, uv enhanced aluminum mirrors. The imaging of the system of 1 to 1.8.

The side view of the apparatus shows the orientation of the Al sample sheet relative to the breakdown. The objective used to initiate breakdown has a focusing of 300 mm. The sample was attached to an xyz translational stage with the ability to move in 0.01 mm steps. The z -axis was used to bring the sample into focus. The x -axis positioned the sample in the laser beam path and the y -axis translated the sample relative to the spectrometer slit. Due to variations in the way in which the sample was loaded into the apparatus, the potential for slightly non-perpendicular alignment between the spectrometer slit width and the sample surface existed. This caused the sample surface to move relative to the shadowgraph camera and ICCD during the measurement. The angular deviation from a perfectly perpendicular position was inferred to be no more than one degree from spatially and spectrally resolved contour plots. The sequence of 21 images was collected over a total of 0.4 mm, so height variations for an entire delay in the wavelength range of 200-800 nm were minimal, however, large and noticeable

changes due exist between differing delays. The largest changes occurred when the sample needed to be changed.

Chapter 4

Plasma Self-Absorption

In this chapter, the line profile distortions of self-absorbed atomic and ionic emissions from the conducted laser-induced plasma experiments are investigated. Atomic and ionic aluminum and hydrogen emissions are used to study the electron density gradient along the height of the plasma emission from the spatially resolved spectral recordings. Here, weight is given to the N_e diagnostic in reference to self-absorption phenomena. Subsequently, this chapter focusses mostly on the fundamentals of finding the electron density from measured spectral emissions in the passive state of LIBS experiments.

For this, N_e diagnostics from atomic hydrogen and aluminum emissions are considered. The use of hydrogen in this vein is due to the ease with which the Balmer series is observed and also due to its prominence in the the plasma spectroscopy field. This is the reason the experiments were conducted in the 90% hydrogen and 10% nitrogen gas atmospheres. This provides a gauge for the densities determined from the Al line widths. Specifically the Al $3s^23p \rightarrow 3s^24s$ ground state transitions with unperturbed line centers at 394.4 and 396.15 nm in addition to the hydrogen Balmer α , β , and γ lines with unperturbed line centers at 656.28, 486.14, and 434.1 nm, respectively, are considered.

The density of laser-induced plasma shortly after formation of the plasma approaches electron density values of 10^{19} cm^{-3} and possibly greater. The physics of the spectral emissions at these densities is different than at 10^{17} cm^{-3} , just as the physics for a plasma at 10^{14} cm^{-3} is different than a plasma at 10^{17} cm^{-3} , and so on (73). In order to study the interesting plasma dynamics of a rapidly expanding plasma at early times in the plasma development, one needs to consider these differences.

This was accomplished by measuring the aluminum and hydrogen spectra at systemically varied time delays over two sequences: 1) using delays ranging from 10 to 100 ns following plasma initiation and 2) using delays ranging from 150 ns to 2.15 μ s. This was done in an effort to completely cover the realm of the lines emergence from the continuum and their narrowing until the line width approaches the instrument width. Figures 4.1-4.4 show spectroscopic intensity contour plots of the Al, H $_{\alpha}$, H $_{\beta}$, and H $_{\gamma}$ lines, respectively. Due to the general nature of the plasma evolution and the deeply broad nature of the H $_{\beta}$ and H $_{\gamma}$ lines, the Al and H $_{\alpha}$ lines begin to emerge long before the other two lines become distinguishable from the spectral continuum. As such, the Al and H $_{\alpha}$ line evolutions are shown for the first 100 ns following ablation. After this time the Al lines become considerably narrower and approach an N $_e$ and line width region that is well characterized. The same is true for the H $_{\alpha}$ line, except it remains much broader for a longer temporal duration and is useful as an N $_e$ diagnostic for densities between 10^{15} to 10^{16} cm $^{-3}$.

Figures 4.1 and 4.2 show that the early time, shortly after the plasma is formed, is dominated by continuum emissions from free-free and bound-free electronic transitions. This begins to subside by about 50 ns and the atomic spectra begin to become distinguishable from the background. The H $_{\alpha}$ emissions dominate the images shortly thereafter. In these images, one can notice a slight stand-off from the sample surface as shown in the Al contour plot. This is due to the focusing conditions of the laser onto the sample surface, namely, the focus was such that a gas breakdown plasma was also produced prior to the surface breakdown. This is evidenced by the presence of less intense H $_{\alpha}$ emissions closer to the surface, in the vicinity of slit heights of 5-6 mm.

The H $_{\beta}$ and H $_{\gamma}$ become distinguishable at later delays. The H $_{\beta}$ double peak structure is present at 150 ns, however, the width of the line is much greater than the wavelength range shown in Fig. 4.3. The line continually narrows thenceforth. The H $_{\gamma}$ line is barely distinguishable from the spectral continuum at a delay of 150 ns. Subsequent analysis of these measured lines is to determine the level of self-absorption and the line distortion affects it has on the spectral emission. This is done in an effort

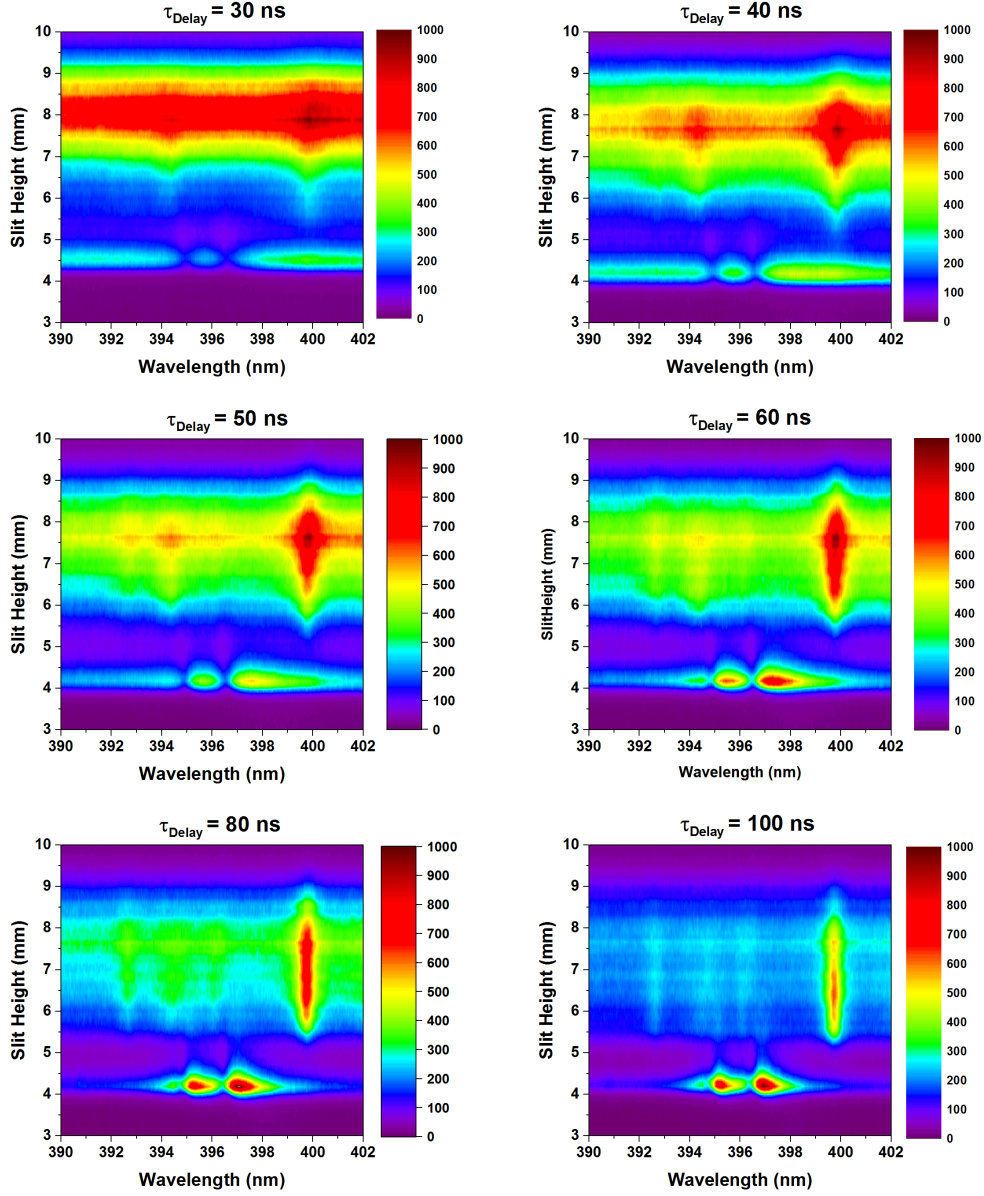


Figure 4.1: Temporal evolution of Al 394.4 and 396.15 nm spectra in the first 100 ns following ablation. The gate width is 10 ns.

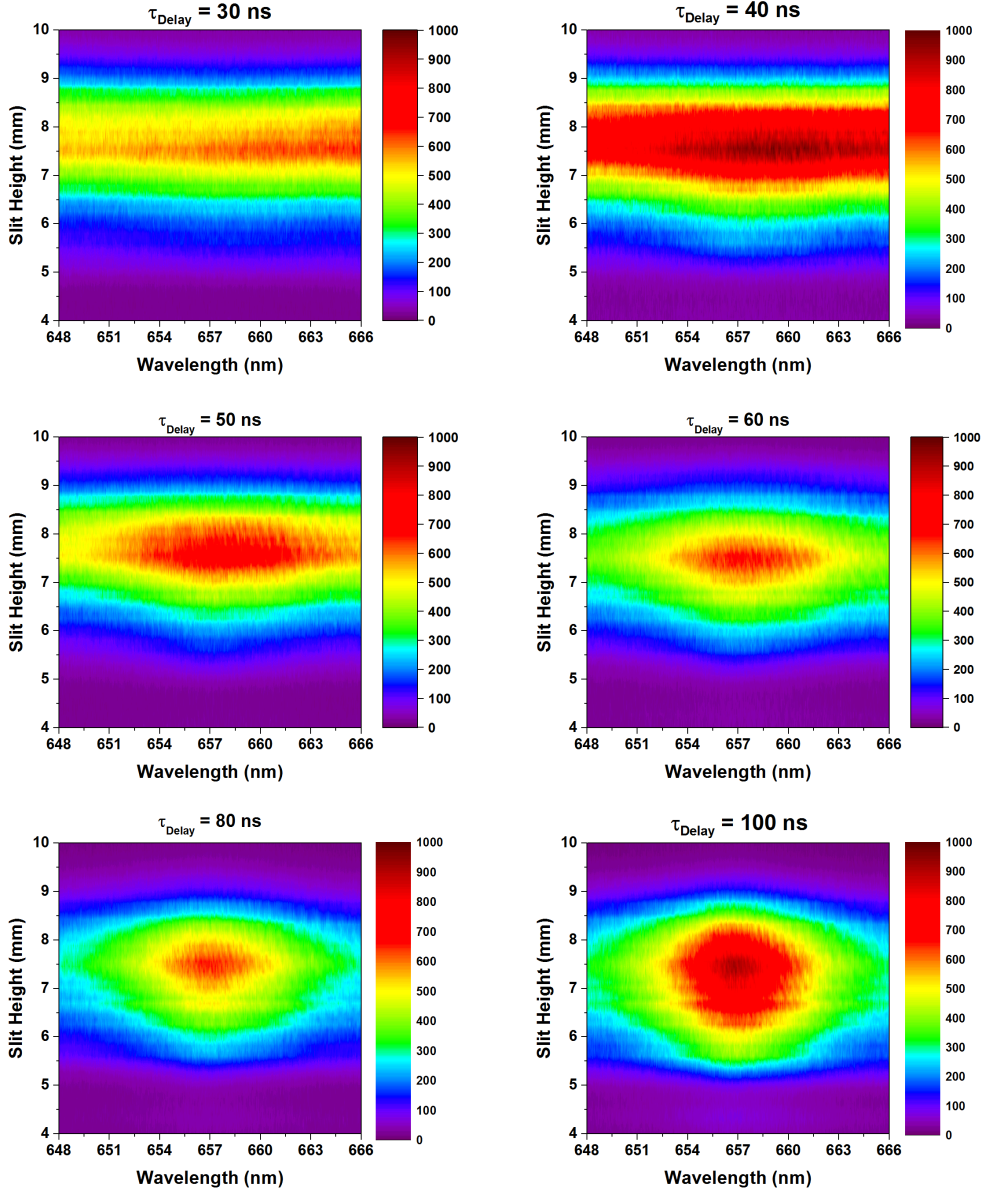


Figure 4.2: Temporal evolution of H_α spectra in the first 100 ns following ablation. The gate width is 10 ns.

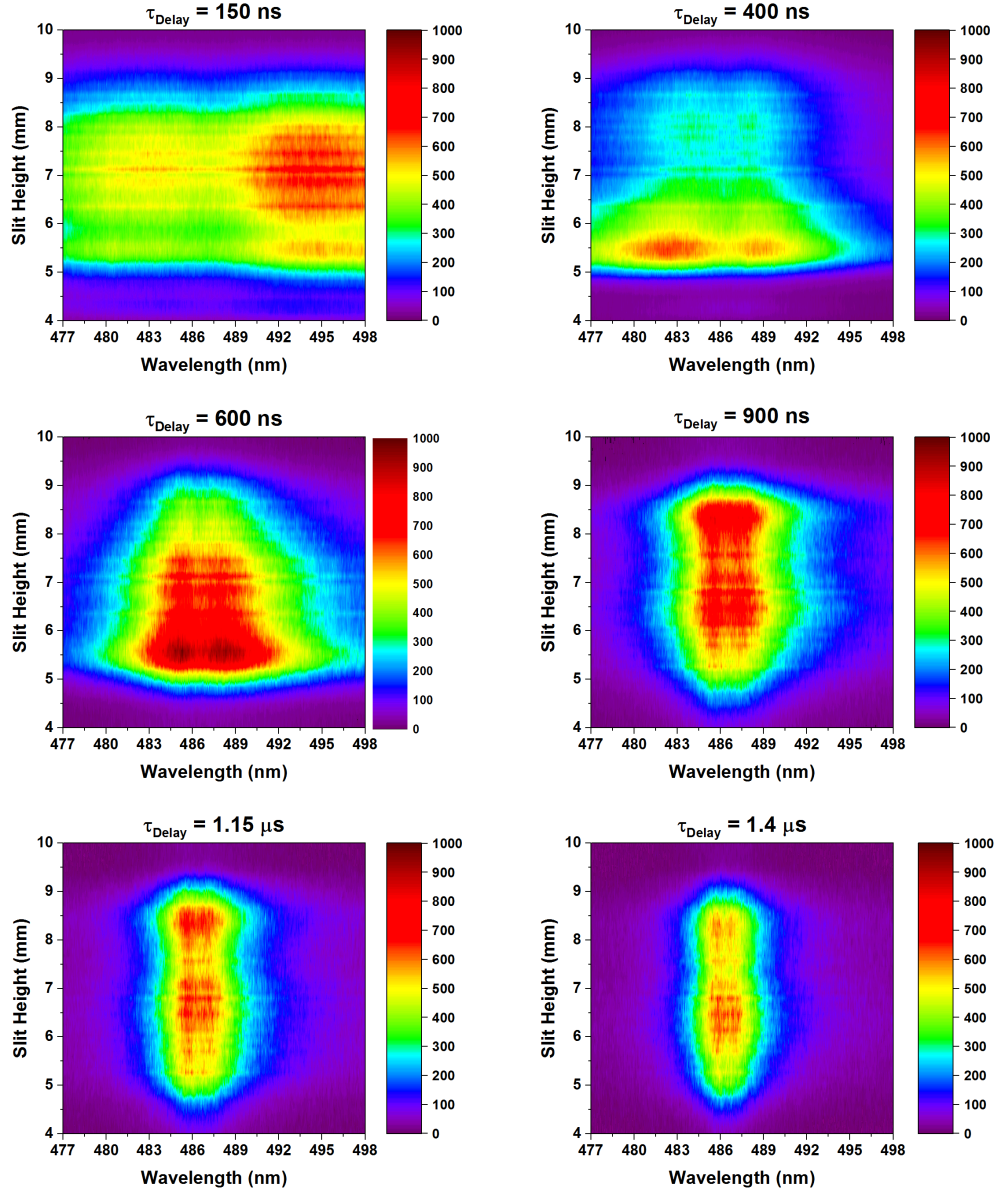


Figure 4.3: Temporal evolution of H_β spectra for delays ranging from 150 ns to 1.4 μ s. The gate width is 50 ns.

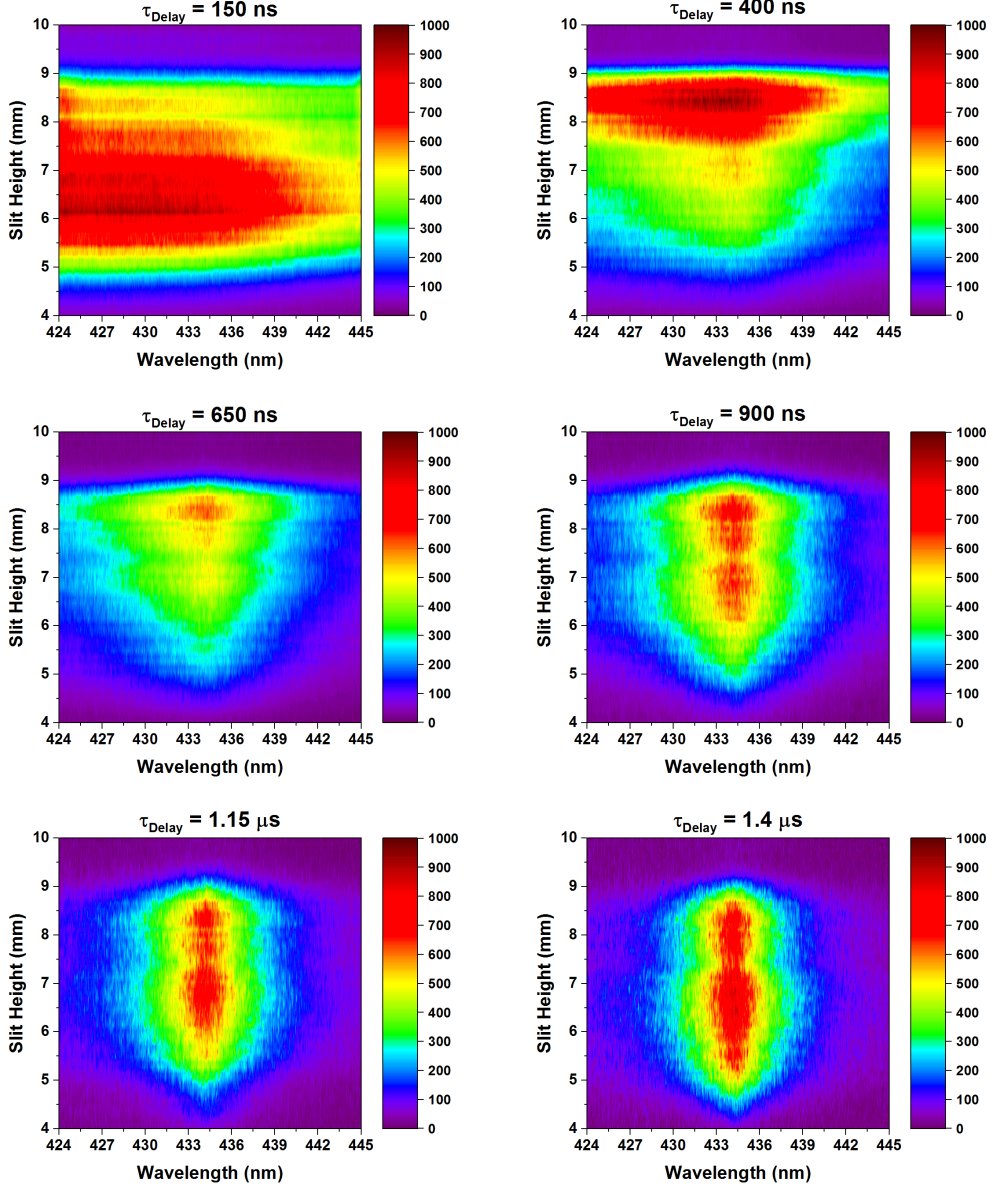


Figure 4.4: Temporal evolution of H_γ spectra for delays ranging from 150 ns to 1.4 μs . The gate width is 50 ns.

to further increase the accuracy of the N_e diagnostic so that a greater understanding of the early time development of the laser-induced plasma may be achieved.

4.1 Self-Absorption Corrections

Two of the key physics that need to be incorporated into the N_e determination at the elevated electron densities encountered in laser-induced plasma are self-absorption and changes in the Stark broadened line shape that occur from the increased prominence of ion dynamics and accelerations of the free electrons due a stronger plasma micro-field. First, the impact that self-absorption line distortions have on the electron density diagnostic are considered.

The theoretical description of self-absorption has already been given in Chapter 2. Here, experimental corrections for self-absorption are considered. Recall that the distortions of the line profile begin with extra broadening of the line accompanied by flattening of the line profile peak, in the presence of moderate self-absorption. In these instances, it may be very difficult to tell measured spectra are distorted due to self-absorption, compared to the rather extreme case where line self-reversal is evident. As such, an experimental diagnostic that can correct for the line distortions in both cases is employed.

The method that is chosen is the so-called "Duplication Method", in which the emitting source is duplicated in such a manner that the duplication must emit through the original plasma. This method is not new and has been used in flame spectroscopy studies (127). For the duplication in plasma spectroscopy, one may also chose to reproduce a copy of the plasma directly behind the initial plasma plasma of interest. This has obvious challenges in simultaneously creating two plasmas that are exactly the same. As such, many researchers prefer to use the so-called mirror method of reproducing the plasma emission (125; 126). In this method, one retro-reflects the plasma emissions back through the emitting volume. Subsequently, the plasma and its image are simultaneously imaged in the spectroscopic recording process. Precise

details on how this duplication is achieved in the present effort are given in Chapter 3.2.

The goal of the method is to tabulate an experimental correction factor which is applied to recorded spectra to account for self-absorption line distortions. The basis of the method requires spectra to be recorded with and without the plasma duplication. This factor is given by

$$K(\lambda) = \frac{\ln y(\lambda)}{y(\lambda) - 1} \quad (4.1)$$

where the quantity $y(\lambda)$ is given by

$$y(\lambda) = \frac{R(\lambda) - 1}{R_c(\lambda) - 1} \quad (4.2)$$

where $R(\lambda)$ is the ratio of recorded spectra with and without the plasma duplication and $R_c(\lambda)$ is the ratio of the continuum emissions recorded with and without the plasma duplication. It is important to note that both quantities are wavelength dependent. The source of this equation is a direct result of considering the above ratios within the equation of radiation transport (125; 126). A derivation of the above correction factor, from first principles, is provided in Appendix A. Due to this relationship, it is noted that $K(\lambda)$ is also related to the optical thickness of the emission source.

A rudimentary analysis of the above equations shows that self-absorption distortions are expected to be most prominent near line center, where the ratio of the line in reference to the continuum is greatest. Far from line center, the line profile asymptotically approaches the spectral continuum and the correction factor tends toward one. In this way, the correction factor can only take on values that are greater than or equal to one. In the practical world of calculations, wavelength averaged values that are very nearly but slightly less than one are also acceptable. The behavior of $K(\lambda)$ in the line wings also becomes more unpredictable due to the asymptotic nature with which the line profile approaches the continuum and measured noise can have a significant impact on calculation of $K(\lambda)$.

4.2 Fitting

A key aspect in this analysis is the determination of $R(\lambda)$ and $R_c(\lambda)$. This is accomplished by fitting of the spectroscopic line profiles for each of the measured line profiles. To simulate the Stark broadening of the Al emissions, a Lorentzian line profile is used. This is an exact description of the line profile of Stark broadened emissions for most non-hydrogenic spectra that are energetically isolated from near by atomic energy states (78; 79). For the measured hydrogen Balmer series lines, a Lorentzian line profile is chosen to approximate the Stark broadened line profile. It is noted that the exact profile for Stark broadened hydrogen shows Holtsmarkian and Lorentzian profile components; however, the difference between the Lorentzian profile and Holtsmarkian profile near line center is nearly indistinguishable. The strength of the Holtsmarkian profile does not begin to manifest until a distance of several (3-5) line widths from the line center. This distance, in wavelength units from line center, is much greater than the spectral coverage of the spectroscopic images that were recorded.

In both cases, the Lorentzian line profile that is used to describe the Stark broadened emissions is convolved with a Gaussian profile, in order account for the broadening of spectral lines due to the experimental apparatus. This is done using a Voigt profile with a fixed Gaussian width equivalent to the instrument width that was determined during the wavelength calibration process. In the case of the spectra presented in this chapter, this value amounts to 0.15 nm. Early attempts at spectral deconvolution were based on approximations of adding Lorentzian line widths and Gaussian in quadrature. One such formula in this attempt is given by

$$\Delta\lambda_V = 0.5346\Delta\lambda_L + \sqrt{0.2116(\Delta\lambda_L)^2 + (\Delta\lambda_G)^2} \quad (4.3)$$

where $\Delta\lambda_V$, $\Delta\lambda_L$, and $\Delta\lambda_G$ are the Voigt, Lorentzian, and Gaussian line widths, respectively (105; 131). The purported accuracy of the above formula is 0.02% (131). Assuming that two of $\Delta\lambda_V$, $\Delta\lambda_L$, or $\Delta\lambda_G$ are known, one could then infer the third

line width. This method is troubling, however, for purposes in which only the Gaussian and Voigt widths are to be measured. This is due to the quadratic dependence of the Lorentizan line width on the Voigt line width, upon inversion of the above expression. This poses an ill-conditioned solution since both roots are positive and, as such, direct simulation of the Voigt profile for fitting and line width extraction is preferred.

Due to the integral nature of the Voigt profile, there is no analytical expression for the Voigt profile and, instead, it must be numerically calculated during fitting. Many algorithms exist for the calculation of the Voigt profile, which has become a vibrant sub-field in the world of quantitative and computational spectroscopy (132; 133; 134; 135; 136; 115; 137; 138). Most of these methods center on numerically calculating the Faddeeva function, which is given by

$$W(z) = e^{-z^2} \operatorname{erfc}(-iz) \quad (4.4)$$

where $z = x + iy$ and $\operatorname{erfc}(-iz)$ is the complex complementary error function (139). The Faddeeva function also is known as the plasma dispersion function. The Voigt function is exactly equal to the real component of the Faddeeva function. Details on this derivation are provided in Appendix D.

Many simulations of the Faddeeva function exist, beginning with tables of numerically evaluated values and moving towards more complex computer simulations (139; 134). Most simulations of the Faddeeva function center around series expansions that approximate the integral expression of the error function. In this work, the Algorithm 916 method (140) is used because of the rapid convergence of the method in the upper half plane. This is useful since information from only the real part of the plasma dispersion function is desired. This algorithm was also chosen because, in no small part, it was published with an attached MatLab routine which made for easy implementation into the fitting routines used. The Algorithm 916 method tabulates the Faddeeva function by splitting the solution into line segments. The error function is then evaluated on these segments using nominal series expansions methods. An

advantage of this routine is the presence of an error tolerance term which allows the user to set the accuracy (and also the computation time) of the calculated Voigt profile.

Fitting is accomplished using established routines within the so-called Matrix Laboratory (MatLab) scripting language. The fitting algorithm that is chosen is the default MatLab non-linear least squares fitting routine, which is the Trust-Region algorithm. The Trust region algorithm that is used is a variant on the Levenburg-Maurquardt method, which solves nonlinear fitting problems using iterative methods to minimize a parameter vector (141; 142). The Trust-Region method implements bounds on the step size between the parameter vector from one iteration to the next (143; 144). This allows for a greater tolerance of seed inputs, keeps the minimized parameter vector solution from blowing up to a non-physical solution, and also helps the algorithm settle on a local minimum more rapidly.

For fitting of a single spectral emission, three parameters were identified for fitting: the line width, the line shift from its unperturbed line center, and an amplitude parameter. In the case where multiple lines are present in a collected spectrum, a summation of each of the three above parameters is fit for each line. In addition to the parameters describing the spectral lines, the baseline offset is described by approximating to a line function of the form $y(\lambda) = m\lambda + b$. This allows for determination of a wavelength dependent offset. One may note that the continuum on which the measured spectra are superimposed does have an exact wavelength dependence. Due to the small spectral regions that are investigated with each line of interest (no more than 25 nm) and the dominance of the desired spectral emissions in each spectral region, it is sufficient to approximate the continuum emission with a linear function. In so-doing, the total sum of the three line shape parameters for each line present in the fit plus the two parameters used to describe the linear baseline offset are fit to the spectra. For example, when fitting measured 394.4 and 396.15 nm Al spectra, a total of eight parameters, 6 to describe the spectral lines and 2 to describe the continuum emission, are fit.

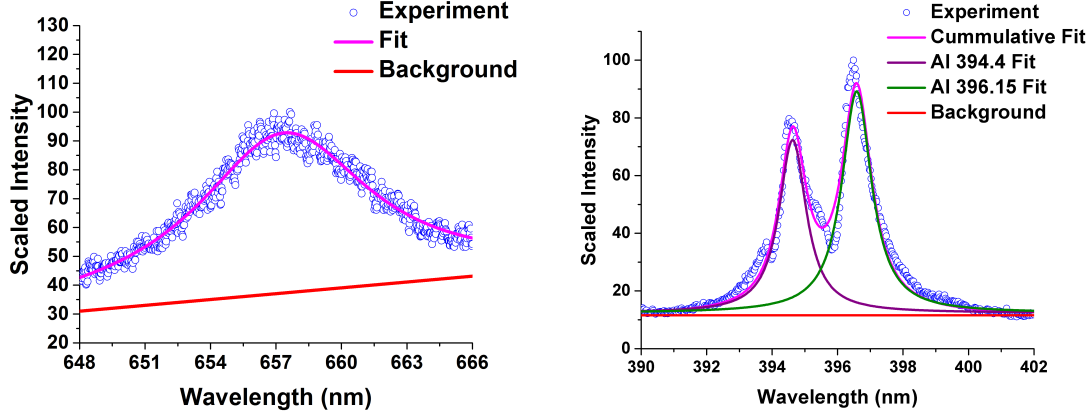


Figure 4.5: Fitted H_α (left) and Al 394.4 and 396.15 nm (right) spectra at a time delay of 70 ns. The slit heights are 5.98 and 4.35 mm, respectively.

Figure 4.5 shows example fits to Al and H_α spectra at a time delay of 70 ns. These fits were performed as part of the self-absorption analysis and represent fits to the case where the data was collected without the mirror. The height of the fitted H_α line is 5.98 mm and the height of the Al spectra are fit at a height 4.35 mm. The Al surface is approximately at a slit height of 4 mm. The width of the fitted H_α line is 9.7 ± 0.2 nm and the width of the two Al lines are 1.3 ± 0.2 and $1.45 \pm$ nm, for the 394.4 and 396.15 nm transitions, respectively.

As a final remark on the fitting to the measured spectra, the nuances of fitting H_β emissions are elaborated upon. An example fit is depicted in Figure 4.6. The inherent double peak structure of the H_β line presents a major difficulty when fitting to extract a line width. The double peak structure occurs as a result of the Stark broadening. Attempts have been made to characterize empirical procedures for accurately fitting the double peak structure (145; 146). These methods rely on fitting multiple profiles to approximate the double peak. While an overall improvement in the goodness of fit may be achieved by following such a procedure, the method is incorrect and leads to a filling in of the central dip that corresponds with the double peak. The double peaked, Stark broadened H_β is a single line profile. A preferred method, and the one applied in this work, is to fit a single Voigt profile, as recommended by the efforts of

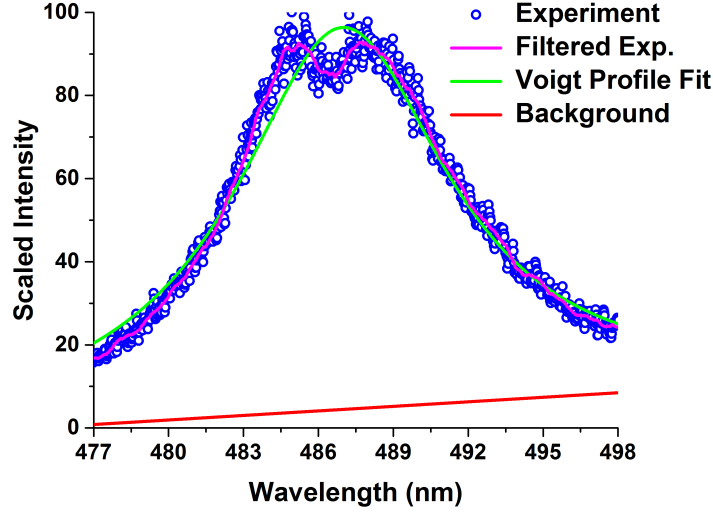


Figure 4.6: Fitted H_β spectra to a single Voigt profile. Also shown are filtered spectra used to extract the density dependent peak separation.

Konjević *et al.* (76). If one wishes to fit this double peak structure accurately, one should consider freely available H_β Stark profiles given by Gigosos *et al.* (66). These profiles are preferred due to the inclusion of ion dynamics in the profile simulations and the asymmetry of the double peak structure that they capture for elevated electron density. For extraction of the peak separation, one may prefer to filter the spectra. This was done in Fig. 4.6 and is indicated by the purple curve.

4.3 Electron Density Determinations

After the self-absorption corrected profiles have been obtained, one needs a reliable method for determining the electron density. This is done by examining the line widths of the fitted spectra, but also requires a proper method of determining the N_e from the line width. While the hydrogen Balmer series was extensively studied under the Quasistatic treatment of Griem (56), these methods do not adequately address ion dynamics and accelerations of the electron due the local microfield. These effects cause

the line width to narrow. Applications of such methods become particularly important as the N_e becomes greater than 10^{18} cm^{-3} .

4.3.1 Balmer Series Hydrogen

While simulations of Stark broadened emissions are useful, calculations of the line profiles can be quite complex and cumbersome to calculate. Even though the line shape contains the underlying physics of a spectral emission, it is customary for use in experimental studies to only extract the line width (FWHM) in an attempt to determine the N_e , typically by fitting a Lorentzian line profile to an observed emission. The line width dependence of the N_e is known to follow a power law, where the power is less than one (56).

In the case of hydrogen, the H_α and H_β lines are considered and empirical formulae are presented for the line widths and shift of the H_α line and line width and peak separation of the H_β line. These formulae are constructed from precise measurements of the two Balmer series lines by Parigger *et al.* (65) that were subsequently analyzed using the formalism of the convergent theory of Oks (61; 147; 148). The prime advancements of this theory are the indirect coupling of electron and ion broadening principles and accelerations of the electron from the plasma microfield, as well as an improved treatment of the plasma ion dynamics.

In line with the standard Stark table approach, tables of Stark widths and associated N_e from References (61) and (65) are utilized. It is noted that Tables 9.7-9.9 in Reference (61) are exactly the same as Tables 2-4 in Ref. (65). The data presented in Tables 3 and 4 of (65) were used to develop the N_e *vs.* FWHM ($\Delta\lambda$) and N_e *vs.* red shift ($\Delta\delta$) formulae for the H_α line widths and red shifts, respectively. The linear least squares fits were performed in a linearized, Log-Log space. The results of the fitting are shown below in Figure 4.6 (a) and (b) for the widths and shifts, respectively.

The error bars on the data points are representative of the indicated errors in the line widths and shifts, in addition to the accuracy of the given line parameter diagnostic.

For example, for the H_α line, this accuracy amounts to approximately 20 percent. The goodness of fit in each case is indicated by considered the adjusted R^2 . For the H_α line width and red shift these values amounted to 0.9551 and 0.9879, respectively. The resulting formulae are displayed below in Equations 4.5 and 4.6. These equations have been algebraically manipulated from the original Log-Log form to represent a power law formulation.

$$\Delta\lambda_{H_\alpha}[\text{nm}] = 1.31 \left(\frac{N_e[\text{cm}^{-3}]}{10^{17}} \right)^{0.64 \pm 0.03} \quad (4.5)$$

$$\Delta\delta_{H_\alpha}[\text{nm}] = 0.055 \left(\frac{N_e[\text{cm}^{-3}]}{10^{17}} \right)^{0.97 \pm 0.03} \quad (4.6)$$

The H_β line width and peak separation empirical formulae were constructed using the data presented in Tables 2 and 1 of Reference (65), respectively. The double peak structure of the H_β line is directly related to the strength of the microfield, and thus the N_e , and is a characteristic of the Stark broadening of hydrogen emissions (77; 149). Because of this double peak, it is quite difficult to determine the Stark red shifts of the H_β line, however, the peak separation is an adequate alternative method for N_e determination. The N_e in the referenced tables were calculated by associating the magnitude of the peak separation with an H_β FWHM. Figure 4.6 (c) and (d) show the Log-Log linear fits to the H_β line widths and peak separations, respectively. Again, the Log-Log fits have been manipulated to represent power law formulations.

$$\Delta\lambda_{H_\beta}[\text{nm}] = 4.50 \left(\frac{N_e[\text{cm}^{-3}]}{10^{17}} \right)^{0.71 \pm 0.03} \quad (4.7)$$

$$\Delta\lambda_{ps}[\text{nm}] = 1.32 \left(\frac{N_e[\text{cm}^{-3}]}{10^{17}} \right)^{0.61 \pm 0.03} \quad (4.8)$$

The error bars for the H_β line widths are found in similar fashion to the H_α line widths and red shifts, using the known accuracy of the H_β line width diagnostic of 5 percent. The error bars for the peak separation were found by carrying out standard

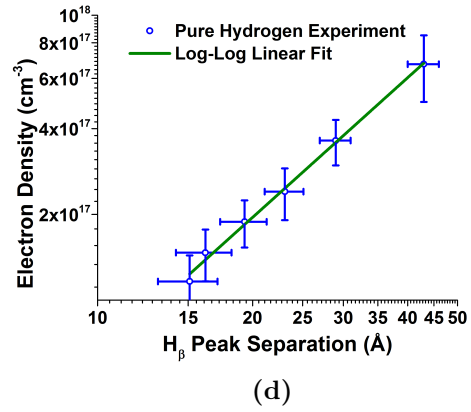
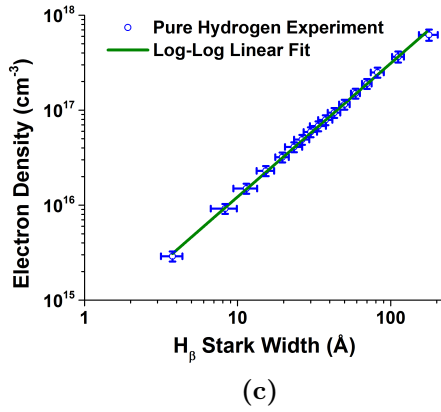
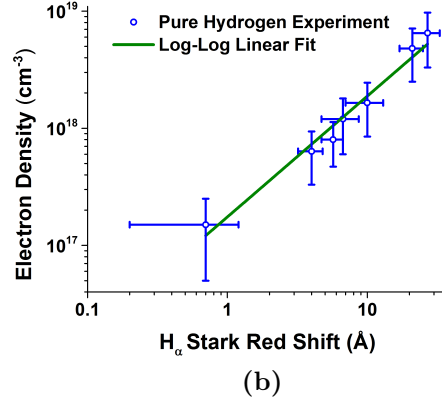
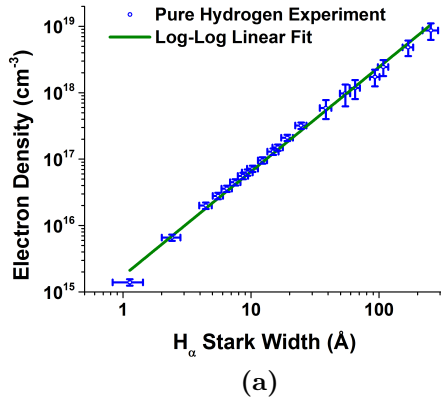


Figure 4.7: Log-Log linear least squares fitting to (a) $H_\alpha \Delta\lambda$ vs. N_e (b) $H_\alpha \Delta\delta$ vs. N_e (c) $H_\beta \Delta\lambda$ vs. N_e (d) $H_\beta \Delta\lambda_{ps}$ vs. N_e

error propagation analysis using the reported errors from Table 1 of Reference (65). The adjusted R^2 values for the line width and peak separation formulae are 0.9996 and 0.9978, respectively.

Finally, the useful ranges of the presented formulae above are noted. For large N_e , the H_β line is quite broad and is difficult distinguish from free-free and free-bound spectral continua, particularly in laser-induced plasma experiments, especially at early plasma decay times. The H_α line becomes increasingly narrower for decreasing N_e and it is difficult to evaluate the line width within experimental error margins for densities less than 10^{16} cm^{-3} . Figures 4.6 (a) and (b) show a scope of several orders of magnitude (10^{15} to 10^{19} cm^{-3}) in the range of N_e from both the H_α and H_β line widths. For practical purposes, it is most useful and less error prone for the H_β line widths to be considered in the density range starting at 10^{15} cm^{-3} and approaching an upper limit of 10^{18} cm^{-3} . For applications where the density may approach 10^{19} cm^{-3} it is recommended that H_α line profiles be considered.

The H_β peak separation is quite limited in its range of applicability. For N_e less than 10^{15} cm^{-3} , the double peak is barely present, while for densities greater than 10^{18} cm^{-3} the double peak structure becomes inherently asymmetric and its magnitude becomes difficult to extract from a measured line profile. It is also noted that the peak separation is also temperature dependent. For these reasons, the above peak separation formula is best applied when the N_e is expected to be approximately 10^{17} and up to an upper limit of 10^{18} cm^{-3} . For the H_α line shift it is difficult to measure experimentally with the correct level of precision given the limitations of most LIBS experimental set ups. Of the four formulae, the H_α red shift is expected to be the most error prone and is best applied when the N_e is expected to be large.

4.3.2 Temperature Dependence

The theories developed in both the Impact and Quasistatic approximations show a temperature dependence in the line width *vs.* N_e relationship. In the methods employed

by Griem (56), this temperature dependence is approximately given as decaying by $T^{1/4}$ (58). This is also true for tabulated Balmer series profiles tabulated by Gigosos *et al.* (66). While the formulae in the above section were described as being inherently temperature dependent based on their applications to laser-induced plasma studies, here a formula generated for the H_α line width that has an explicit temperature dependence is presented.

Following a similar method and using the same tables from the above two references, the temperature dependence of the empirical formulae was investigated. Only entries from the H_α line width tables were used that had an associated temperature. The temperatures in the referenced tables were inferred using Boltzmann plot methods. The determined formula, which is presented below in Equation 4.9, was determined by performing a three parameter linear least squares minimization and is given by

$$\log(\Delta\lambda) = -9.1624 + 0.5085 \times \log(N_e) + 0.2344 \times \log(T). \quad (4.9)$$

The algebraic minimization was performed on Log-Log linearized calculations of the H_α line width, inferred N_e , and inferred temperature. Minimization parameters were assigned to each of the logarithm of the temperature and the electron density, as well as an offset term.

The temperature dependent formula also did not consider the errors, due to the way in which errors are considered in the least squares minimization, namely, as a weighting matrix. The diagonal elements of the weighting matrix are applied to ordered pairs of data, *i.e.*, groupings of the offset, linearized N_e , and linearized temperature. The errors presented in Reference (65) do not organize well into ordered pairs in which a similar error, by percentage, applies to each member of the ordered pair. As such, application of this formula should be done so under caution.

The formula is also only applicable to temperatures less than 99,000 Kelvin and N_e in the range of 10^{15} to $3 \times 10^{17} \text{ cm}^{-3}$. When the temperature is known and the N_e is in the above, specified range, Equation 4.9 may be applicable as a density determination

method, however the simpler, density only dependent line width empirical formula is the preferred and more versatile method for applications in electron density diagnostics of H_α spectra in laser-induced plasma.

4.3.3 Aluminum

In similar fashion to the hydrogen Balmer series formulae, it is advantageous to have a simplistic method for determining the N_e from the line width of the two Al lines considered here. Al line widths that were collected in a hydrogen gas atmosphere at a pressure of 100 mTorr and were collected with H_α and H_β spectral emissions following ablation of an Al target were used as the so-called benchmark (91). The densities in that work were calculated from the H_α and H_β line widths. The N_e calculation was treated using the convergent theory of Oks. This is an important distinction for N_e diagnostics that are expected to have determined values greater than 10^{18} cm^{-3} .

The N_e and corresponding line widths were taken from Tables 1 and 2 in Reference (91). A power-law description of the density was fit to these results. The power-law was chosen to keep with the simple power-law description of the density as a function of the line width intact for the Al lines, in similar fashion to the hydrogen empirical formulae. The results of such fitting are shown in Figure 4.7. Here, the concern is only with the line width *vs.* electron density diagnostic, even though the shift of non-hydrogenic spectral lines also has an explicit N_e dependence under Stark broadening theory. The error bars in Figure 4.7 are taken directly from the Tables 1 and 2 in the Reference (91).

Rather than present empirical formulae, as with the H_α and H_β descriptions, the power law description given in the above figure is sufficient as an N_e diagnostic from the Al lines. In order to generate empirical formulae for the Al lines, one would need to complete an exacting study in which the density and temperature of the emitting source, ideally a laser-induced plasma, were known and the instrument width, effects due to self-absorption, spatial inhomogeneities, and temporal simultaneity are

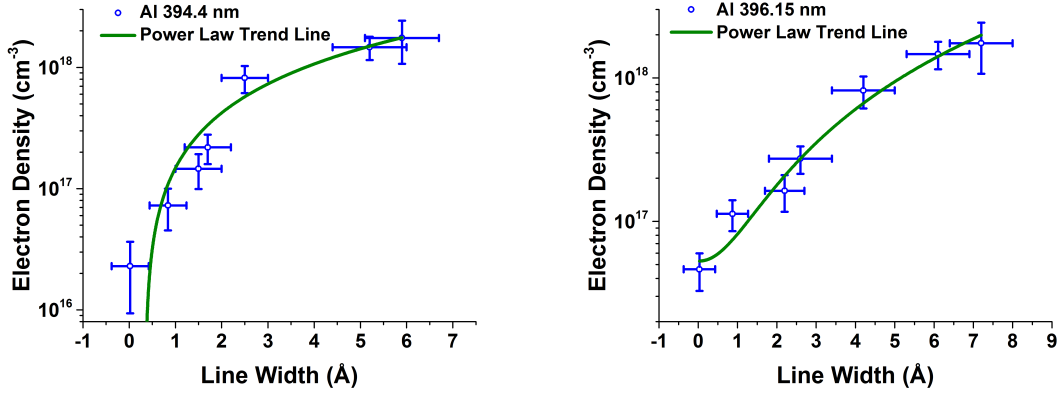


Figure 4.8: Power law fits to benchmark N_e vs. line width for the ground state Al 394.4 (left) and 396.15 (right) nm transitions

all considered. Also, an exacting description of the the Stark profile would need be considered across several orders of magnitudes of the electron density ($\sim 10^{16}$ to 10^{19} cm^{-3}) and would likely require Quasistatic line profile considerations. Such a study would be no small feat and is not in line with the current work where information of the plasma state obtained from line profile considerations is far more desirable. Such an effort should be the subject of an extension of this work.

4.4 Results

4.4.1 Corrected Spectra

The process of obtaining the self-absorption corrected profiles used the following steps: i) fit the spectra recorded with the mirror, ii) fit the spectra recorded without the mirror, iii) calculate $R(\lambda)$ and $R_e(\lambda)$, iv) calculate $K(\lambda)$ and apply to the data collected without the mirror, and v) fit the corrected profiles to infer N_e from the line widths. Figure 4.9 shows calculated correction factors that correspond to the fitted H_α spectra shown in Fig. 4.5. Also indicated in the figure is the average correction factor, which is shown as the red line. This is used as a metric to indicate temporal and spatial variations in the self-absorption correction factor.

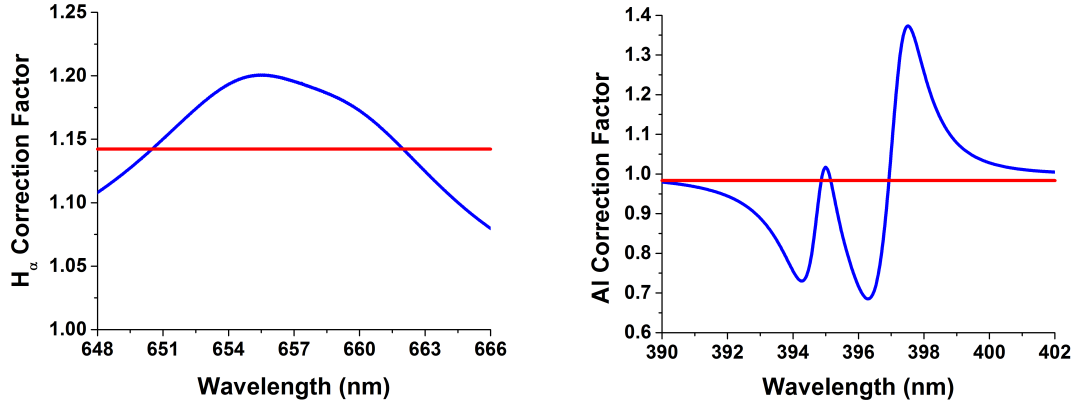


Figure 4.9: Tabulated correction factors for H_α (left) and Al (right) spectra at 70 ns time delays and slit heights of 4.35 and 6.6 mm slit heights, respectively. The red line indicates the average correction factor

The H_α correction factor does not show a symmetric profile. This is not unexpected due to the nature of Stark broadening. The H_α causing the absorption to take place is likely to be at a lower temperature and N_e and will exhibit a smaller Stark width and shift resulting in an asymmetric absorption. Also of prominence, is that the correction factor has a maximum that corresponds with the H_α line center at 656.28 nm. The average correction factor of 1.14 indicates that some amount of self-absorption effects have been taken into account.

The correction factor corresponding to the two measured Al lines is drastically different than the H_α correction factor. This is mostly due to the measurement being for two spectra rather than a single spectrum. Absorption peaks, or minima, are visible near the unperturbed Al line centers which dip well below the theoretical minimum correction factor of 1. The maximum of the correction factor corresponds to the Stark shifted line peaks. The wings of the lines tend towards one. This is also true for the H_α correction factor and is to be expected, as the effects of self-absorption are expected to be most prominent near the line center. The reason for the correction factor to be significantly less than 1 is related to the determination of the spectral background. The background is best estimated far from the line center, as much as $5 \times$ the FWHM. Such an estimation is not practical in the present effort given the relatively small spectral

windows being considered. Also inhibiting the background determination is the fact that the spectra are dominated by the Stark broadened emissions, showing strong interferences upon each other. The strongest of these interferences occur between 393 and 397 nm. This makes determining the ratio of the continuum rather difficult. The average correction factor for the Al spectra is 0.98 and would apparently indicate no self-absorption effects have taken place, on the average; however, this does not account for the given wavelength dependent effects and as such the average correction factor does not seem to be an appropriate metric for the Al lines, with interfering neighboring lines.

The resulting corrected spectra and their corresponding fits are shown in Figure 4.10. At a cursory look, the H_α line appears to have minimal changes. This is not the case. The line takes on a much greater amplitude, as the scales in Figs. 4.5 and 4.10 have the same scaling factor applied to the measured intensity. As the correction factor is very nearly equal to 1 in the line wings, the overall resulting increase of the line amplitude at the line center is a reduction in the fitted line width and, therefore, a reduction in the N_e is determined. The width of uncorrected line shown in Fig. 4.5 is 9.87 ± 0.2 nm and the width of the corrected line is 10.0 ± 0.2 nm. Under consideration of the error bar, there is a limited change in the line width and the inferred N_e . In the presented case, the limited change is due to a slight increase in the spectral wings due to a non-unity correction factor at 648 and 666 nm (see Fig. 4.9). The N_e corresponding to the line width of the corrected image is $2.4 \pm 0.3 \times 10^{18} \text{ cm}^{-3}$.

The shifts of the H_α spectra shown in Figures 4.5 and 4.10 are 1.1 ± 0.2 and 1.0 ± 0.2 nm, respectively. Though a small change in the line shift does occur, it is well within the error margins, which includes contributions from the fitting process and the accuracy of the experiment. The N_e corresponding to the line shift is $2.2 \pm 0.4 \times 10^{18} \text{ cm}^{-3}$. The larger error margin in the inferred N_e as compared to that inferred from the line width is due to the relative difficulty in accurately measuring the line shift, which is considerably smaller than the line width and is much more similar to the spectral

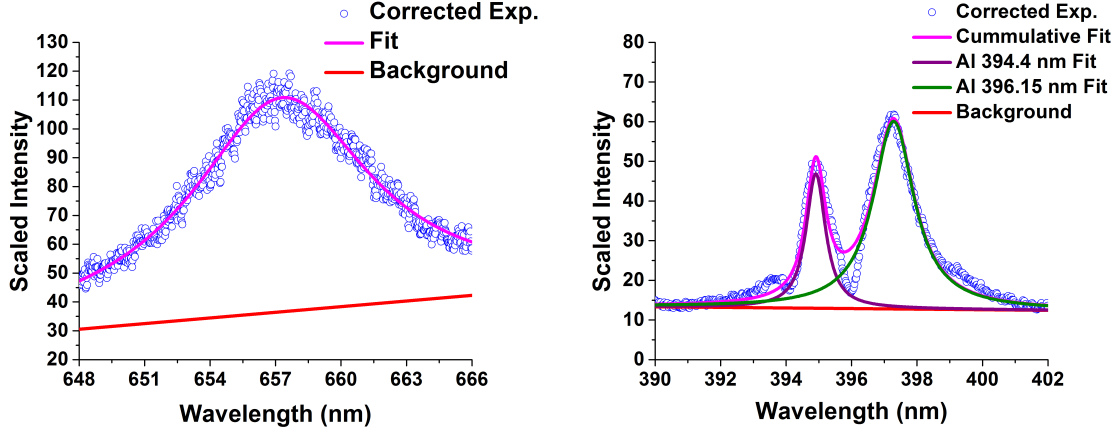


Figure 4.10: Self-absorption corrected H_α (left) and Al (right) spectra at 70 ns time delays and slit heights of 4.35 and 5.98 mm slit heights, respectively.

resolution. Given an appropriate consideration of the error margins, the line width and line shift N_e diagnostics for the H_α line indicate the same electron density.

Table 4.1 shows the spatial variation of the tabulated experimental correction factor for the H_α spectra collected at time delay of 70 ns. The table shows the slit height at which the spectra were collected, the change in the line width after application of the correction factor, the average correction factor, and the inferred N_e . Values of the average self-absorption correction factor that are significantly less than one are not physically meaningful in the model of self-absorption. As such, only values that are nearly one are included. The limited scope of Table 4.1 in view of the rest of the presented figures (1.5 *vs.* 6 mm) is due to the difficulty in aligning the self-absorption apparatus. The methods used to align the self-absorption apparatus are accurate to 0.5 mm due to the limitations of the fine adjustments of the optical components employed. It is also important to note that the alignment procedure was performed to optimize the alignment for a slit height that was near the surface, which is approximately at a slit height of 4.0 mm.

Table 4.1 also shows moderate changes in the line widths. It is important to note that the entire spectral profile changes when the correction factor is applied. Thus even if no line width changes were to be reported, self-absorption effects have still

Table 4.1: Spatial variation of the average experimental correction factor for H_α spectra. The middle two columns show the original and corrected line widths and the final column indicates the corrected electron density.

Height (mm)	K_{corr} Avg	$H_\alpha \Delta\lambda$ (nm)	$H_\alpha \Delta\lambda$ Corr (nm)	$N_e \times 10^{17} \text{ cm}^{-3}$
5.44	0.94	7.4 ± 0.2	5.3 ± 0.2	8.8 ± 3.0
5.66	1.12	8.4 ± 0.2	8.8 ± 0.2	19.7 ± 3.0
5.88	1.06	9.2 ± 0.2	8.3 ± 0.2	17.9 ± 3.0
6.09	1.05	9.8 ± 0.2	9.8 ± 0.2	23.3 ± 3.0
6.31	1.01	10.5 ± 0.2	10.4 ± 0.2	25.5 ± 3.0
6.53	0.91	11.1 ± 0.2	10.0 ± 0.2	23.9 ± 3.0
6.75	0.86	11.6 ± 0.2	9.4 ± 0.2	21.7 ± 3.0

been taken into account. The conclusion in such a case is that self-absorption does not have a great impact on the N_e diagnostic. The results in Tab. 4.1 show that there is a moderate self-absorption effect for H_α occurring for a density of $2 \times 10^{18} \text{ cm}^{-3}$. Self-absorption effects have been shown to be apparent in measured H_α spectra in laser-induced plasma systems. In air breakdown, self-absorption effects were shown to be present due to differences in the N_e determined from N^+ emissions at 648.2 and 661.1 nm from the H_α N_e (150). The N_e were found to be 1.4 and $2 \times 10^{18} \text{ cm}^{-3}$ for the N^+ and H_α spectra, respectively. Self-absorption distortions of H_α emissions measured following the laser ablation of an ice surface have also been reported (151). Prominent self-reversal effects were noted to occur for an N_e of $6 \times 10^{18} \text{ cm}^{-3}$.

The line widths of the uncorrected Al 394.4 and 396.15 nm spectra shown in Figure 4.5 are 1.3 ± 0.2 and 1.45 ± 0.2 nm, respectively. The corrected line widths are 0.9 ± 0.2 and 1.4 ± 0.2 nm, respectively. The Al 394.4 nm line width is significantly reduced while the fitted line width of the Al 396.15 shows only a slight reduction. Inspection of the corrected spectra shown in Figure 4.10, show a significant increase in the resolution between the two Al lines. As well, there is an apparent reduction in the widths of both lines. The fitting process is subject to errors due to additional spectral interferences which seem to occur near 399 and 393.5 nm, which correspond to singly ionized nitrogen and aluminum lines, respectively. Such effects are observed by the fact the fitting procedure failed to fit the increased resolution between the two Al lines of interest.

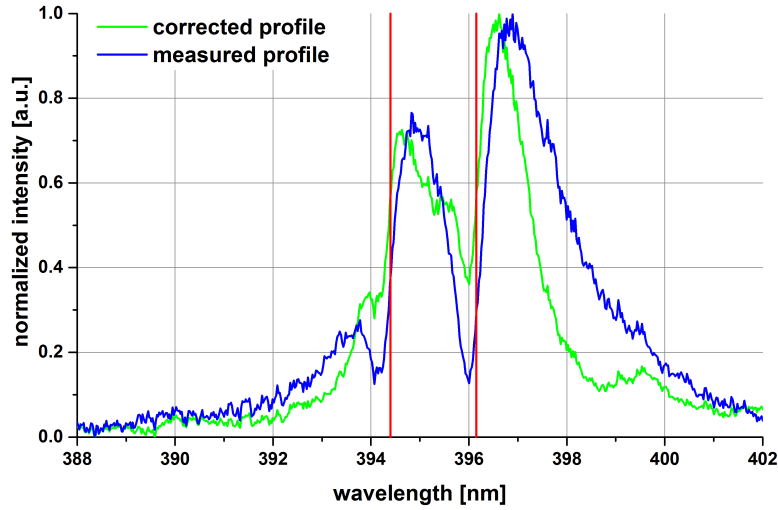


Figure 4.11: Self-absorption corrected Al spectra plotted against the original measurement indicating self-reversal of the Al lines.

The Al 396.15 nm line appears to be narrower than the fit results seem to indicate by as much as 10%. The inferred N_e of the Al lines are 3.0 ± 1.0 and $8.2 \pm 3.0 \times 10^{18} \text{ cm}^{-3}$ for the Al 394.4 and 396.15 nm lines, respectively. Given the presented error margins and the possible 10% reduction the Al 396.15 nm line width, the two Al lines provide an N_e diagnostic that is in agreement between the two lines.

4.4.2 Line Reversal

An interesting case of self-absorption is the extreme case characterized by self-reversal, whereby an absorption occurs near the unperturbed line center. The ability to correct for moderate self-absorbed lines is useful; however, the real strength of the self-absorption correction factor is the ability to correct self-reversed emissions of lines with interfering neighbor spectra, such as is the case with the Al 394.4 and 396.15 nm lines. Figure 4.11 shows measured *vs.* self-absorption corrected Al spectra at a time delay of 60 ns that was collected at a slit height of 4.5 mm, which is 0.5 mm above the ablation surface. The blue lines indicate the positions of the unperturbed line centers.

The spectra shown in Figure 4.11 are characterized by self-reversed line profiles prior to application of the self-absorption correction factor. There are deep absorptions present in the measured spectra at the line centers of the two Al lines. Such absorptions, given the early time following laser ablation and the relatively close nature to the sample surface, are hallmarks of line self-reversal. After application of the correction factor the absorptions disappear and the Al lines take on much narrower line profiles. Spectral interferences from singly ionized nitrogen lines at 395.5 and 399 nm also become apparent after the correction factor is applied to the uncorrected, Al spectra.

The widths of the fitted, corrected spectra show line widths of 1.1 ± 0.2 and 1.7 ± 0.2 nm for the Al 394.4 and 396.15 nm lines, respectively. The N_e from the two lines are found to be 3.8 ± 1.0 and $10 \pm 2.0 \times 10^{18} \text{ cm}^{-3}$. The large disparity between the two inferred electrons densities is due to the presence of the interfering N^+ 395.5 nm line, which causes the fitted width of the Al 394.4 nm line to be underestimated relative to the Al 396.15 nm line. The result is an under estimation of the N_e found from the Al 394.4 nm line.

The ability to correct self-absorption line distortions that manifest as self-reversal of two interfering neighboring spectra represents an opportunity to further understand the plasma production process following laser ablation of target samples using spectroscopic diagnostics. Also, measured lines in many target samples, particularly metal alloys, are accompanied by neighboring, interfering spectral lines. Previous applications of the doubling mirror method for self-absorption corrections in laser-induced plasma (125) indicated that the correction factor could only be applied to isolated spectral lines in which an accurate tabulation of the continuum was measured far from line center. Such effects have proven to be challenges and also result in additional sources of error outside of the nominal systematic errors associated with a laser-induced breakdown spectroscopy experiment. In spite of these challenges, self-reversed spectra have shown the ability to be corrected through application of the wavelength dependent correction factor. A key aspect in the achievement presented here is the use of a wavelength dependent continuum in the tabulation of the experimental correction factor. Further

considerations and continued improvements in the method in which the continuum emissions are extracted from the fitting process will only aid the development of plasma self-absorption diagnostics.

4.4.3 Ion Self-Absorption

It is a general assumption that ions do not experience self-absorption in laser-induced plasma. This is false. In the model of the self absorption, it is possible for any type of transition to experience self-absorption; however, due to the typically high energy states of ions corresponding to optical transitions (10-20 eV), it is rather unlikely that ions experience self-absorption. In this vein, an Al^+ transition was chosen to study self-absorption effects. The line of interest is the $\text{Al}^+ 3s3p \rightarrow 3s4s$ 281.61 nm line. Figure 4.12 shows the temporal and spatial evolution of the measured line in the first 400 ns following ablation of the Al target. Of note in Fig. 4.12 are the presence of magnesium ion lines at 279.55 and 280.27 nm and a neutral magnesium emission near 285 nm. These lines occur due to the impurities of Al alloy target that was used as the ablation target.

Early in the plasma evolution, the images shown in Figure 4.12 show a very strong spectral continuum, particularly in the slit height region between 6 and 9 mm. The continuum persists until 100 ns and begins to subside thereafter. The relative strength of the continuum in this sequence of images as compared to the hydrogen and Al images perviously displayed is due to the strength of the free electron background in the ultra violet. The Al^+ and Mg^+ emissions become distinctly noticeable by a 70 ns time delay, with the Mg^+ emissions showing a stronger signal intensity than the Al^+ emission. The Mg^+ lines persist for a longer duration than the Al^+ line, which begins to sharply fade in signal intensity by 150 ns. This progression is displayed in Figure 4.13 for a slit height of 4.35 mm. The black vertical lines in the figure show the line positions of the Mg^+ and Al^+ lines.

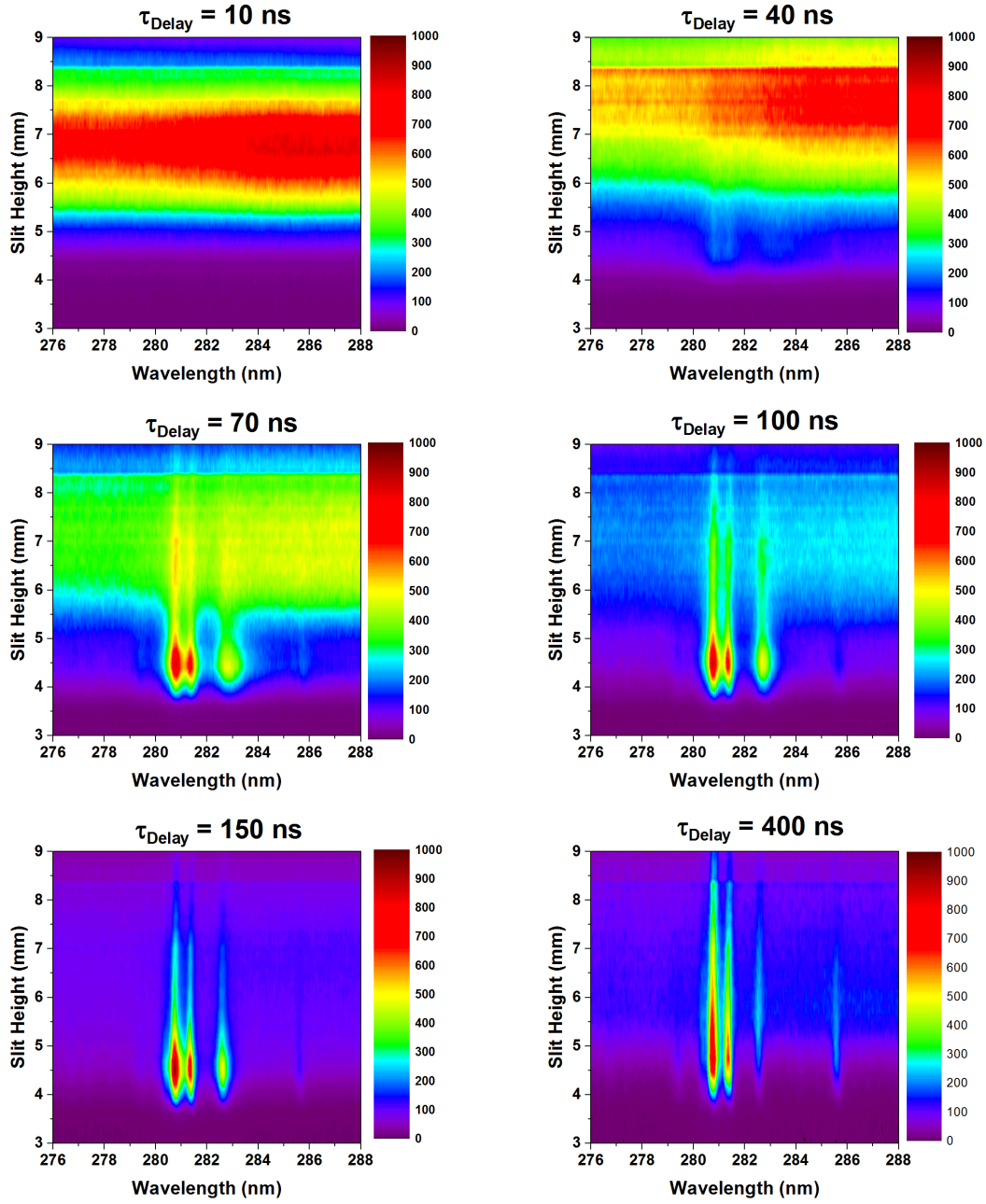


Figure 4.12: Temporal and spatial evolution of Al^+ and Mg^+ spectral emissions in the first 400 ns following ablation.

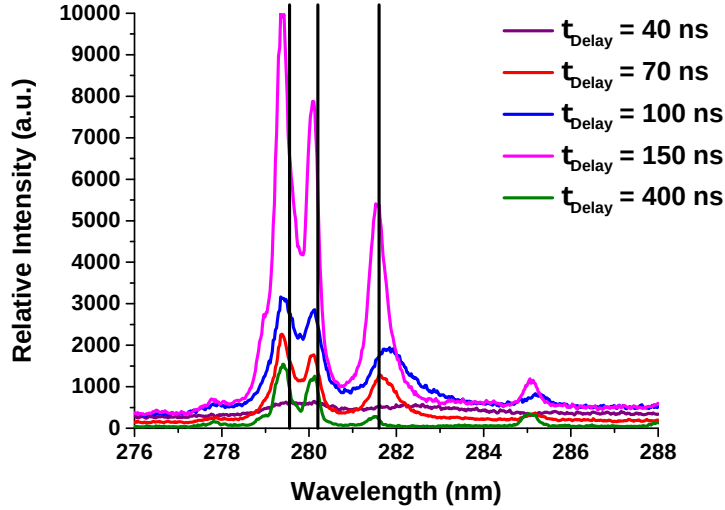


Figure 4.13: Temporal evolution of the Al^+ spectra for a slit height of 4.35 mm.

The Al^+ spectra were corrected following the same procedures as for the atomic spectra. Changes in the profiles of the corrected lines are readily apparent. The measured *vs.* corrected profiles are shown in Figure 4.14. The most notable of the line profile changes that occurs is in the inflation of the signal intensity of the corrected image relative to the fitted background, which remains largely unaffected by application of the correction factor. Increased resolution of both the Mg^+ and Al^+ lines are also present, by virtue of an increase of each of the line amplitudes. Such a change is indicative of self-absorption.

The width of the fitted Al^+ 281.6 nm line before application of the correction factor is 1.2 ± 0.2 nm. After application of the correction factor, the line width was determined to be 1.3 ± 0.2 nm. The width is actually shown to slightly increase, thus showing a slightly higher N_e . The N_e are calculated using the Stark width calculations and experimental comparisons of Allen *et al.* and Colon *et al.* (92; 93). The N_e are determined to be 2.9 ± 0.8 and $3.2 \pm 0.8 \times 10^{18} \text{ cm}^{-3}$ for the measured and corrected spectra, respectively. These densities also confirm that Al 394.4 nm line under predicted the N_e , as was posited previously since that measurement was made for delay of 70 ns and the Al^+ lines show the density for a 100 ns delay.

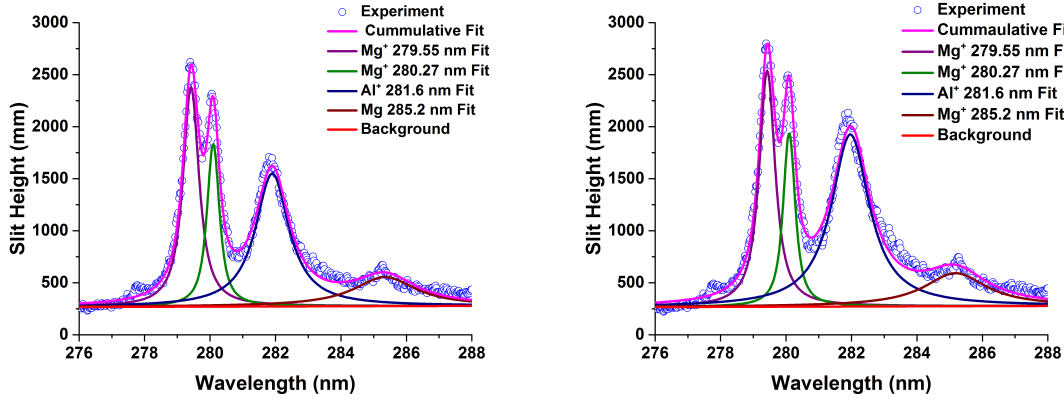


Figure 4.14: Fitted Al^+ and Mg^+ spectra as measured (left) and after application the correction factor (right). The slit height is 4.35 mm and the time delay is 100 ns.

Under consideration of the error bars, the line widths and densities are not changed following application of the self-absorption correction factor. While the numerical results are unaffected by self-absorption, it is important to note that the line shapes have changed while correcting for self-absorption. This shows that for moderate self-absorption, the Al^+ 281.6 nm line width N_e diagnostic is unaffected. For more extreme cases of self-absorption, *i.e.*, self-reversal, one would absolutely need to correct for self-absorption. Knowledge that a line width diagnostic is rigid against self-absorption is a great tool for the plasma spectroscopist and will be of great benefit for the determination of the electron density early in the plasma evolution, especially since ions become distinct from the continuum much earlier in the plasma evolution.

Self-absorption effects were previously seen to be weak for Al transitions measured for Al laser-induced plasma in an argon gas atmosphere backfilled to a pressure of 750 Torr (93). Self-absorption was assumed to be weak by assuming that the Al ion density was equivalent to the electron density and attempting to couple this value with the ionic transition rates to determine an absorption coefficient. Such a method represents an interesting possible future calculation; however, an exacting measurement of the plasma size, using spatially resolved detectors, would be required. The electron densities in Reference (93) were measured to be a maximum of $8 \times 10^{17} \text{ cm}^{-3}$.

Chapter 5

Plasma Parameter Determination

In this chapter, the results of inferring the electron density and temperature are presented. Of particular interest is the temporal trend of the N_e . Due to the physical restrictions of the self-absorption apparatus, plasma plume height inferences are difficult to ascertain. Also of interest are simultaneous evolutions of the N_e and the temperature. The N_e are inferred using the methods described in Chapter 4. The method of determining the temperatures relies on the assumption of a Boltzmann distribution to the atomic population of states, which allows for the use of the Boltzmann plot method. For this consideration, the temperature is found by using the measured H_α , H_β , and H_γ line profiles.

5.1 Atomic State Distributions

Much of the information that can be gained about the state of the plasma revolves around the state distributions between differing energy levels of spectral emissions in the atom. This is particularly true for the plasma temperature. These distributions are based off of Maxwell-Boltzmann statistics. The population of states distribution is given by

$$\frac{N_i}{N} = \frac{g_i}{Q(T)} e^{-E_i/k_B T} \quad (5.1)$$

where N_i is the population of the i^{th} state with energy E_i , $Q(T)$ is the partition function, N is the total population of all states, T is the temperature, k_B is the Boltzmann constant, and g_i is the statistical weight of the i^{th} state. The intensity of a transition

from upper state u to lower state l is given by

$$I_{ul} = N_u h \nu_{ul} A_{ul} \mathcal{L}(\nu) \quad (5.2)$$

where N_u is the population of the upper state, A_{ul} is the transition rate, and $\mathcal{L}(\nu)$ is the line profile. Application of the state distribution given in Equation 5.1 gives the resulting intensity distribution as

$$I_{ul} = h \nu N_u \frac{g_u A_{ul}}{Q(T)} e^{-E_u/k_B T}. \quad (5.3)$$

Application of Equation 5.3 to measured spectral lines allows for the determination of the temperature of an emitting source and allows for an experimental determination of the temperature of the plasma from a series observed spectral lines using the so-called Boltzmann plot method. In this method, one linearizes the the above Boltzmann intensity distribution, resulting in

$$\ln\left(\frac{I_{ul} \lambda_{ul}}{g_u A_{ul}}\right) = \left(\frac{-E_u}{k_B T}\right) + \ln\left(\frac{h c N_u}{Q(T)}\right) \quad (5.4)$$

where λ_{ul} is the wavelength of a particular transition. One then fits the measured line intensities (I_{ul}) against the upper energy states of the measured spectral lines. The slope of the corresponding fit is directly related to the quantity $-1/k_B T$. The accuracy of the method relies on selecting a number of lines with a large spacing of the upper level.

If one wishes to consider the use of ions in the temperature determination, appropriate considerations of the state distributions must be accounted for. This is done so in the Saha equation (152; 153), which is given by

$$\frac{N_e N_z}{N_j} = \frac{2 g_z}{g_j a_0^3} \left(\frac{k_B T}{4 \pi E_H}\right)^{3/2} e^{-(E_z - \Delta E_j)/k_B T} \quad (5.5)$$

where the subscript z is used to indicate ionic quantities, E_H is ionization energy of hydrogen, ΔE_j is the ionization energy of the j^{th} state, and N and N_z are the total density states and density of ionic states, respectively. This equation is derived by assuming a general transition occurs between any two states. The resulting population distribution is given by

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-(E_i - E_j)/k_B T}. \quad (5.6)$$

Due to the ionic nature of interactions with the continuum, generalization to continuum states are also necessary. In this case, the number modes on a normalized volume element, V , gives the population of the continuum state k between N_k and dN_k as

$$\frac{dN_k}{N_j} = \frac{V g_z}{g_j \pi^2} e^{-(E_k - E_j)/k_B T} k^2 dk \quad (5.7)$$

for the number of electron-ion pairs and free electrons on the interval k to dk . Integration over all continuum states gives

$$\frac{N_e}{N_j} = V \frac{2g_z}{g_j a_0^3} \left(\frac{k_B T}{4\pi E_H} \right)^{3/2} e^{E_j/k_B T}. \quad (5.8)$$

The Saha equation is then found by letting the volume be given by $V = 1/N_z$. Fitting to the Saha equation is sometimes referred to as a Saha-Boltzmann plot method.

The advantage of using ions and the Saha equation in experimental temperature determinations is that the energy spacing between transitions of many ions is quite large ($\sim 5\text{eV}$) and can increase the accuracy of the fits used to infer the temperature. Also, especially for many transitions with metallic target samples, a large number of ionic transitions are readily observed in the nominal ultra violet and visual parts of the electromagnetic spectrum. Both the Boltzmann and the Saha-Boltzmann plot methods are subject to arguments of the plasma opacity, homogeneity, and local thermodynamic equilibrium (LTE). LTE is thermal equilibrium that is confined to a local scale. For a steady state, optically thin plasma the so-called McWhirter criterion describes the

necessary conditions for LTE to exist and is given as

$$N_e \geq 1.6 \times 10^{12} \Delta E^3 \sqrt{T} \quad (5.9)$$

where ΔE is the largest energy spacing for a given spectral series. This describes the spread of energy through collisions in the plasma. One can see that a critical N_e is needed to meet the necessary collisions to spread the energy to meet equilibrium conditions (154; 155; 156). In laser-induced plasma, the McWhirter criterion must be supplemented with the calculation of diffusion lengths and times for electronic collisions to account for the transient nature of the laser-induced plasma system (157).

5.2 Electron Density Results

Electron density results have been presented in reference to the corrected self-absorption line distortions of Chapter 4. Here, the temporal trends in the densities that were determined are presented. Results that have been self-absorption corrected are evaluated. This was completed only for selected slit heights, again, due to the physical restrictions of the self-absorption experiments. For this reason the evaluation of the temporal evolution of the N_e found from the Al 394.4 and 396.15 nm lines and the H_α and the H_β lines were completed for slit heights of 5.22 and 5.44 mm, respectively. The results of the N_e inferences, using the methods outlined Ch. 4.3, are shown in Figures 5.1 and 5.2, for the Al and hydrogen Balmer lines, respectively. The red line in each of the figures displays a linear fit to the N_e *vs.* time delay data, as represented in the Log-Log scales. The large gap in the inferred N_e in both figures between delays of 150 and 400 ns is due to the representation of the data on the Log-Log scale and the 250 ns delay step that was used.

The N_e analysis was carried out for spectra that could be reliably fit. For the H_β line, reliable fits were difficult to complete prior to 400 ns time delays for all investigated slit heights due to the extremely wide nature of this line at the densities that were expected

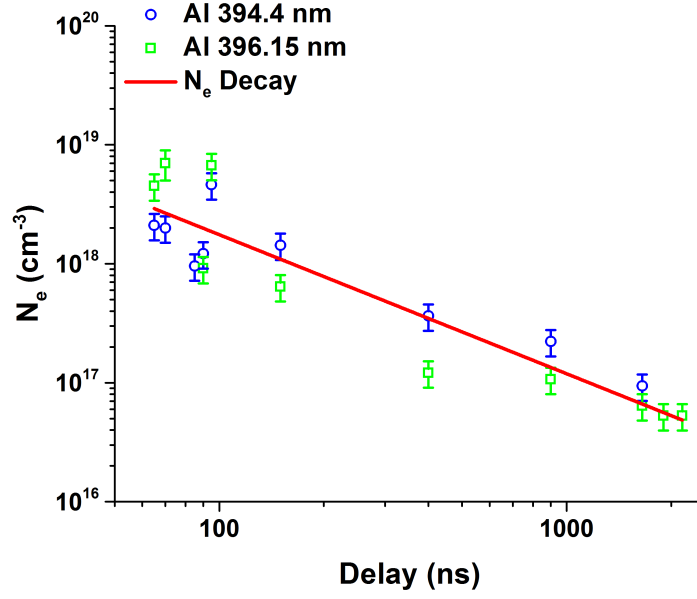


Figure 5.1: Temporal evolution of N_e inferred from Al 394.4 and 396.15 nm spectra for a slit height of 5.22 nm. The red line indicates the decaying trend of the N_e .

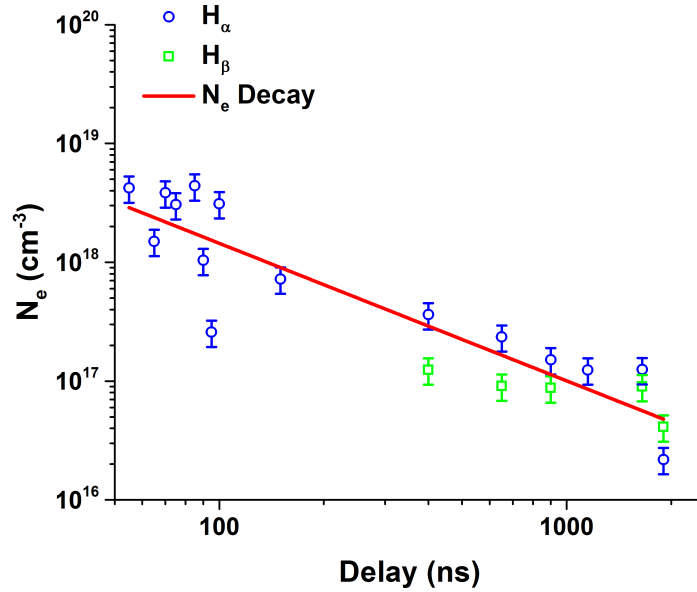


Figure 5.2: Temporal evolution of N_e inferred from H_α and H_β spectra for a slit height of 5.44 nm. The red line indicates the decaying trend of the N_e .

to be encountered. Such a wide line also makes it rather difficult to fit the spectral continuum, especially when the spectral coverage of the measured data is significantly less than the full line width.

In other instances, for the Al lines and the H_α line, the fitting routine sometimes returned run away fitted parameters, where the fitted spectral lines were arbitrarily wide, approximating the spectral continuum as the fitted line profile, or were arbitrarily small, approximating the fitted line profile as the instrument function with a negligibly small Lorentzian component. Results corresponding to such instances were omitted from the fits shown in Figures 5.1 and 5.2. The N_e found from the Al lines were considered together and, likewise, the N_e indicated by both Balmer series lines were considered together in each fit. This was done since similar species should show a similar N_e . Any congruence between the N_e from different species is then subject to spatial resolution and plasma equilibrium arguments thenceforth.

Early in the decay of the Al surface plasma, where the Al 394.4 and 396.15 nm lines were used to infer N_e , large differences between the N_e between the two Al lines are noted. Prior to 100 ns, this difference is seen be as much as an order of magnitude. Such large differences can occur to due to fitting errors and the presence of the mentioned, interfering nitrogen and aluminum ions in Chapter 4. Later in the plasma decay, a general congruence between the two line width diagnostics exists. It is not unexpected for the Al 396.15 to predict a larger N_e than the 394.4 nm, as has been previously observed (99). The general decay of the N_e is from approximately 7×10^{18} to 9×10^{16} cm^{-3} over the first 2 microseconds of the plasma evolution.

The N_e calculated from the H_α and H_β lines shows a similar decrease. These lines indicate a decay from approximately 4.5×10^{18} to 3×10^{16} cm^{-3} over the same time range. It should be noted that the Balmer series lines are used to indicate the N_e for a different region of the breakdown, where influences due to the Al surface are expected to be diminished and lower N_e may expected to be calculated. The slopes of each of the lines representing the decay of the N_e are -1.17 and -1.16 for the Al and hydrogen Balmer series line plots, respectively. This indicates that the two plasma regions are

Table 5.1: Fitted line widths of the H_α , H_β , and H_γ lines and the inferred N_e

Delay (μs)	H_α $\Delta\lambda$ (nm)	H_β $\Delta\lambda$ (nm)	H_γ $\Delta\lambda$ (nm)	N_e (10^{17} cm^{-3})
0.15	7.0 ± 0.2	—	—	13.6 ± 3.4
0.4	4.3 ± 0.2	—	—	6.4 ± 1.6
0.65	2.7 ± 0.2	12.1 ± 0.2	—	3.6 ± 0.9
0.9	1.9 ± 0.2	7.3 ± 0.2	7.9 ± 0.2	2.0 ± 0.5
1.15	1.5 ± 0.2	5.3 ± 0.2	6.7 ± 0.2	1.3 ± 0.3
1.4	1.2 ± 0.2	—	5.0 ± 0.2	1.0 ± 0.3
1.65	—	3.6 ± 0.2	4.5 ± 0.2	0.7 ± 0.2
1.9	1.0 ± 0.2	3.1 ± 0.2	3.7 ± 0.2	0.6 ± 0.2
2.15	0.9 ± 0.2	2.7 ± 0.2	3.3 ± 0.2	0.5 ± 0.1

decaying at roughly the same rate. This also indicates consistency within the methods used to correct for self-absorption for the Al and Balmer series lines and the methods used to calculate the N_e .

5.2.1 H_γ line width *vs.* N_e

As a part of the electron density analysis, the line widths of the H_α , H_β , and H_γ lines were compared to the determined N_e . This was done since the H_γ line was not included in the N_e determination methods of Chapter 4.3. This analysis was omitted due to the lack of availability of line width *vs.* N_e data in which the total line profile of the H_γ line was considered using tabulated Stark profiles with advanced considerations of ion dynamics in the line width determination.

The H_γ line width analysis was performed for a slit height of 5.9 mm and only for time delays greater than 150 ns, when the H_γ line begins to show some emergence from the spectral continuum. These results are shown in Table 5.1 for the delay range of 0.15 to 2.15 μs . Entries that have been omitted, which are represented by the dash (—), were done so because the line width could not be determined during Voigt profile fitting. Early, in the first 0.4 μs for the H_β line and in the first 0.65 μs for the H_γ line, the line widths are too wide to be determined and are omitted from the analysis.

The N_e results in Table 5.1 were calculated using the H_α and H_β line width formulae presented in Chapter 4.3. When both line widths were available for use, the N_e

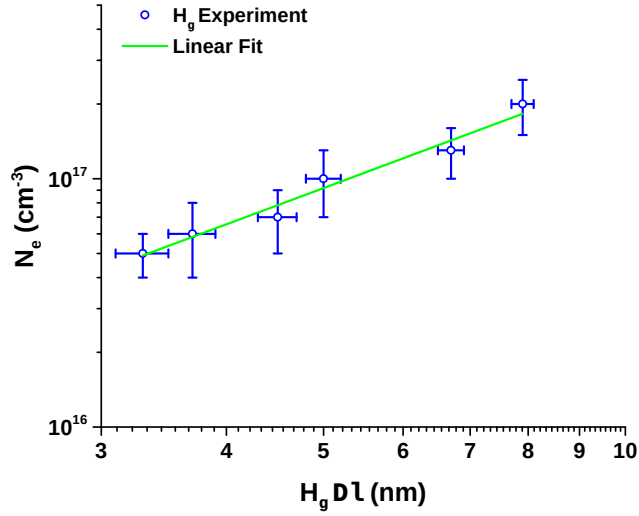


Figure 5.3: Increase of the H_γ line width with increasing N_e

represented an equal consideration of both line width diagnostics. In most cases, the congruence between the two line width diagnostics was nearly exact, and, within consideration of the error bars, was the same for each entry in the table. The only instance where the inferred N_e differed greatly with respect to the presented error margins occurred for the $0.65 \mu s$ time delay, where the H_α line width showed an N_e of $3.3 \times 10^{17} cm^{-3}$ and the H_β line width indicates a value of $3.9 \times 10^{17} cm^{-3}$. The average of the two values was taken. The N_e when only the H_α line width was available for use only considers this line width diagnostic. Figure 5.3 shows the variation of the H_γ line width relative to the determined N_e . The green trend line in the Log-Log plot represents the increase of the H_γ line width with increasing electron density.

Figure 5.3 is analogous to the plots used in Chapter 4.3 to generate the empirical N_e *vs.* line width diagnostic formulae. There are, however, several important differences. The empirical formulae from Ch. 4.3 were developed from spectra that were treated with exacting calculations of the Stark profile of the lines, where as, in the current effort a Lorentzian approximation was considered. The overall change in the line width is likely to be small, however, an exacting line shape consideration procedure would be

Table 5.2: Atomic data for the hydrogen Balmer series needed for the temperature calculation.

Line	λ (nm)	g_u	A_{ul} (10^8s^{-1})	E_u (eV)
H_α	656.28	18	0.441	12.09
H_β	486.15	32	0.0842	12.75
H_γ	434.04	50	0.0253	13.05

preferred for the development of an empirical formula for the H_γ line width *vs.* N_e . There is also a limited scope in the range of N_e (1-2 orders of magnitude) for which there is a determined line width. Several orders of magnitude ($\sim 10^{15} - 10^{18}$) would be ideal for the development of an empirical formula for an N_e diagnostic from the H_γ line width. This work is best served for future considerations with an experimental apparatus with spatial and temporal resolution and instrumentation with a much wider spectral coverage to account for the extremely broad nature of the H_β and H_γ lines for N_e greater than 10^{18} cm^{-3} .

5.3 Temperature Results

Temperatures were inferred using the Boltzmann plot method as applied to the measured H_α , H_β , and H_γ line profiles. This analysis was performed along the same slit height of 5.9 mm as the H_γ line width *vs.* N_e investigation. For use in the Boltzmann plot method, one needs to determine the atomic constants A_{ul} , g_u , and E_u for each transition that is to be used in the Boltzmann plot method, as given by Equation 5.3. This information for the Balmer series lines is collected in Table 5.2. The source of this information is the NIST (National Institute of Standards and Technology) atomic spectra database (158).

The intensity that was used in the Boltzman plots was the integrated line intensity of the calculated fit of the spectra. The use of the fitted intensity profile rather than the measured profile was used to reduce the affects that the measured signal noise had on the determined temperatures. The integrated peak intensities were calculated

Table 5.3: Inferred temperatures and N_e using the hydrogen Balmer series line shape diagnostics

Delay (μ s)	Temperature (Kelvin)	N_e (10^{17} cm^{-3})
0.9	52000 ± 7300	2.0 ± 0.5
1.4	25000 ± 3500	1.0 ± 0.3
1.9	15000 ± 2100	0.6 ± 0.2

numerically using the Gauss-Chebyshev quadrature rule for numerical integration (159). This method of numerical integration was used to decrease the errors of inferred result as compared to nominal trapezoidal or Simpson's rules for numerical integration. The Gauss-Chebyshev quadrature rule applies Chebyshev polynomials of the first kind over an abscissa of the target data set. The extent of the abscissa can then be reduced in size to increase the accuracy of the integrated data set. The fitted profiles that were numerically integrated were background subtracted prior to numerical integration. The background used for this subtraction was the fitted background.

Since the temperature relied on using all three Balmer series lines, the temperatures could only be inferred for times when all three lines were able to be fit. This was further restricted to instances in which the data could have the self-absorption correction factor applied and then be integrated. The result was only three time delays for which a temperature could be determined. These results, along with the corresponding N_e are presented in Table 5.3. The temperatures that are found are rather high when compared to other values determined from the H_α , H_β , and H_γ lines following gaseous breakdown in a hydrogen atmosphere. Temperatures from a previous study completed by Parigger *et al.* (160) were approximately 20000, 16000, and 11000 Kelvin. The breakdown was initiated in pure hydrogen gas environment at a pressure of 810 Torr using 150 mJ/pulse 7.5 ns Nd:YAG laser pulses. The N_e found between the two works are roughly similar within consideration of the presented error bars.

A better indication on the comparison of N_e and temperatures inferred from differing experiments is the relation between the determined temperature and N_e . This is displayed Figure 5.4. The data are represented on a Log-Log scale and a linear fit

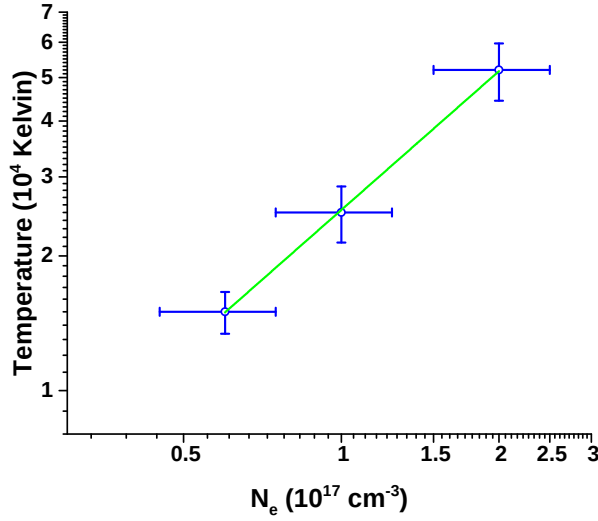


Figure 5.4: Linear fit to the N_e *vs.* inferred temperatures.

was performed to infer a slope of 1.0 ± 0.1 . The previous effort showed a temperature *vs.* N_e slope in Log-Log space of 0.61 ± 0.06 (160). This was used to confirm that plasma expansion was frozen and isentropic. Under such expansion the decay of the electron density is related to $\gamma - 1$, where $\gamma = 5/3$ for diatomic gases and is the ratio of specific heats at constant pressure and volumes. In the current effort, the result indicates a value of $\gamma = 2$. An important difference to note between the two efforts is that the present study represents laser ablation and not gaseous breakdown, where the plasma expansion dynamics may be different. Farther from the surface, there is less impact to the ablation surface, a more consistent result may be found at such heights. The current study is also subject to the considerable affect that the plasma shockwave may have on the inferred plasma parameters.

A general comment that must be considered, as well, when interpreting the presented temperature results is that the Al laser-ablation experiments were performed for the explicit purpose of investigating self-absorption distortions and subsequent corrections to the measured line profiles. This was shown to be plausible as the investigated Al, Al^+ , and H_α lines all showed changes, to varying degrees, under

these self-absorption corrections, which had the described consequences on the N_e calculations. The purpose of these experiments was not to calculate the temperature of the plasma and, as such, the temperature results that are presented should be accepted with a fair amount of skepticism.

The temperature trend that is presented is limited to just three time delays and were calculated using only three lines from the same spectral line series. The spacing of the upper energy levels is just under 1 eV. Boltzmann plots as temperature diagnostics are most accurate when many lines with large upper energy level spacings (≥ 10 eV) are used (34). This study was also spatially and temporally resolved and is subject to the inherent inhomogeneities of the transient laser-induced plasma. Temperature considerations are better served for future works in which the laser-induced plasma thermal equilibrium is considered and temperatures inferred from Boltzmann plots and other probing methods, such as Thompson scattering, are also applied. Thompson scattering is the scattering of photons with electrons and produces a method for determining the plasma N_e and temperature without the assumption of atomic state distributions from the characteristic scattering spectrum (161; 162; 163). This also produces a method for accounting for plasma inhomogeneities through spatial and temporal resolved measurements, which affords for the ability to calculate diffusion lengths and times in a spatially resolved study.

Chapter 6

Molecular Spectroscopy

In this chapter, the spatial dependence of the diatomic molecular aluminum monoxide spectra and the temperatures inferred from the emission spectra are investigated. The spatial dependence of the molecular spectra provides a method for studying the plasma at times past when atomic spectra have narrowed sufficiently, such that their line widths are approximately equal or less than the instrument function line width. Furthermore, ionic contributions begin to diminish and temperature characterizations at later times in the plasma evolution would require a large spectral coverage to measure enough lines to be used with the Boltzmann plot method. Such time scales typically begin to occur at about $1\ \mu\text{s}$ following plasma initiation.

The times when the molecular spectra become apparent depends on the plasma formation conditions (pressure and energy per pulse). The timing also depends on the plasma processes that give rise to the molecular emissions. Gaseous breakdown with carbon constituents has been known to produce diatomic carbon emissions at delays on the order of $1\ \mu\text{s}$ while AlO emissions do not become prevalent until $10\ \mu\text{s}$ in air laser ablation experiments (164; 165). Recall that molecular recombination occurs for much lower temperatures and densities than for atomic recombination. Another significant contribution to the spatial and temporal dependence of molecular emissions are the plasma dynamics that are occurring at a given point in space and time. One immediately thinks of the plasma shockwave interaction with the plasma. In this way, studies of molecular emission may provide insight into the plasma dynamics at time scales long after the energy deposition on the target surface has occurred.

This dependence is considered by measuring spatially resolved AlO spectra in the controlled hydrogen/nitrogen gas mixed atmosphere and is investigated following

ablation of an alumina target. This is done in an effort to distinguish the source of oxygen that is used in the formation of AlO. In plasma emission, AlO is observed as aluminum recombines with ambient oxygen atoms from the the plasma formation conditions in nominal air ablation scenarios. AlO emissions are also often studied in conjunction with aluminized flames, where the desire is to better understand the combustion chemistry of aluminized flames (43; 166; 167). In these instances, the AlO molecule is an intermediate step in the oxidation of aluminum particles, which forms alumina. As such, distinguishing between the source of AlO, provides the opportunity to study the chemistry that may be occurring at later times in the plasma evolution. Of particular interest is correlation of such chemistry with the plasma shockwave dynamics.

Figures 6.1 shows measured $B^2\Sigma^+ \rightarrow X^2\Sigma^+$, $\Delta v=0$ AlO emission spectra at selected time delays following ablation of alumina target samples in the 90% and 10% gas mixed atmosphere between 2.5 and 20 μs time delays following ablation of the alumina target. The measurement made at the 2.5 μs time delay shows strong emissions from the H_β line, the source of which is from the controlled gas atmosphere. Also present in this image are nitrogen lines near 493 and 496 nm. These lines persist until 7.5 μs . The H_β spectra quickly diminishes in signal intensity and by the 5 μs time delay has a minimal impact on the measured AlO spectra. In the time delays ranging from 5 to 10 μs , there is a decline in the AlO signal intensity near the target surface, which has an approximate slit height of 5.4 mm. These times are also characterized by a clear upward expansion in the AlO signal intensity. The alumina sample was used to highlight the dynamics of surface particles during the ablation plasma decay.

Between 10 and 15 μs time delays, an obvious change occurs in the intensity profile along the spectrometer slit height. A clear minimum in the signal intensity develops between two regions of greater signal intensity near the sample surface and near the upper plasma boundary, which persists past the 20 μs time delay. This indicates that a region of decreased AlO is present, as the emitting AlO particles travel outward from

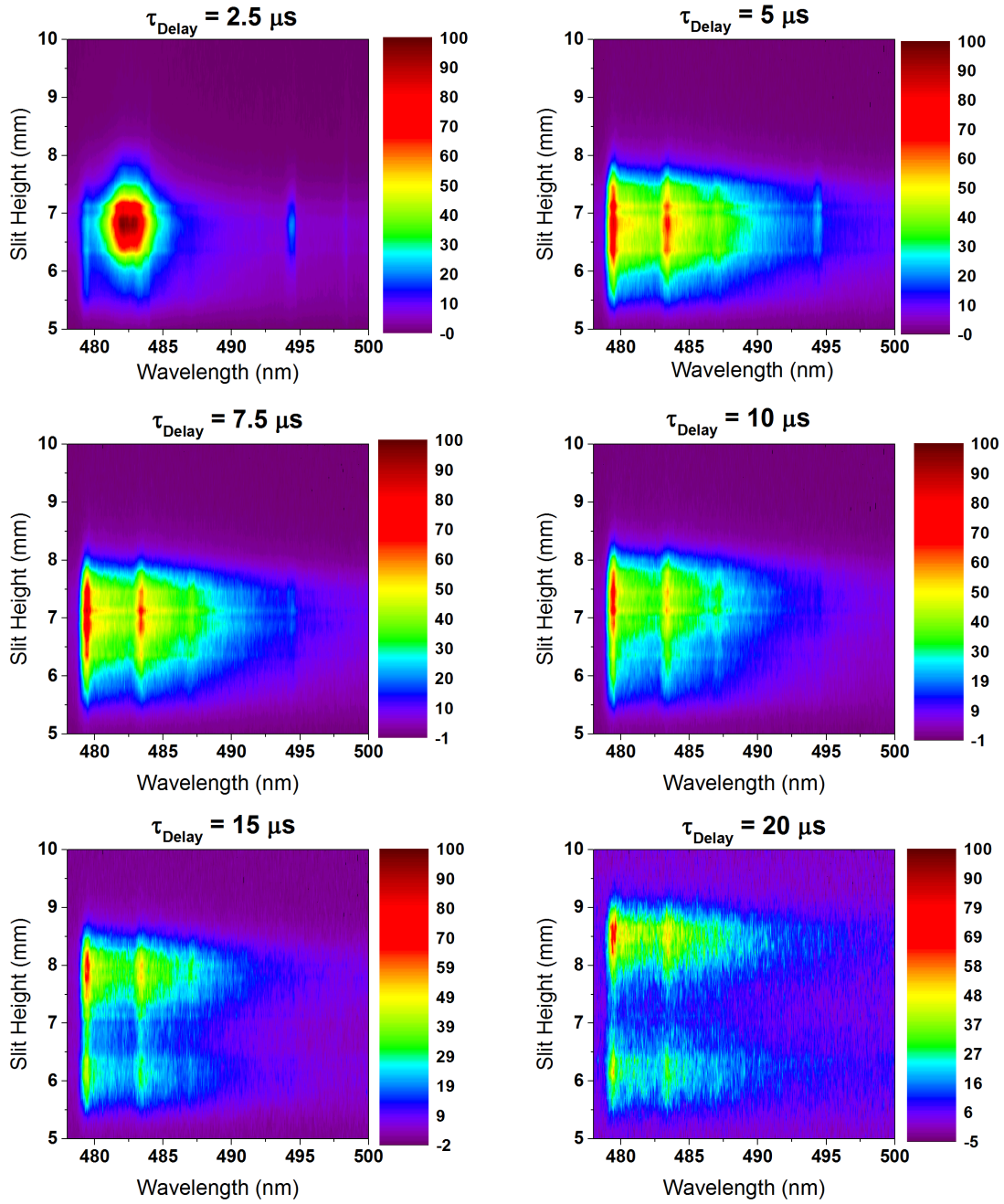


Figure 6.1: Spatially and temporally resolved $B^2\Sigma^+ \rightarrow X^2\Sigma^+ \Delta v=0$ AIO emission spectra for time delays ranging from 2.5 to 20 μs following target ablation.

the target surface with the expanding plasma, while a region of the particles remains closer to the surface.

Correlations of the spatial and temporal evolution of the AlO emission spectra with the plasma temperature are of great interest. The measured AlO spectra are fit to theoretical calculations of the molecular spectra in an effort to better interrupt the spatial variation of the measured spectra in reference to the plasma dynamics. Radial distributions of the AlO signal intensity are also presented using the so-called Abel inversion procedures at a time delay of $5\ \mu\text{s}$ and also to the observed H_β emissions.

6.1 Fitting

The prime indicator of the plasma state from molecular spectra is the temperature. This is due to the temperature dependence of vibrational and rotational components of the molecular spectrum, the population of which follows a Boltzmann distribution. In order to infer the temperature, a reliable method for simulating the diatomic spectrum and a method for fitting the spectra to the theoretical calculations are needed. Theory spectra are readily calculated from a quantity known as the diatomic line strength. It is analogous to its atomic counterpart, as described in Chapter 2.

Calculation of the diatomic line strength is a difficult and challenging task. A complete description of which could be the subject of a whole dissertation due the high accuracy requirement of the molecular rotational constants and the subsequent vetting of the spectral line positions that are required of the calculated line strength. Rather than to seek to make improvements to existing methods, recently calculated AlO line strengths are used in the description of the presented laser-induced plasma decay process. However, a few brief comments on how the line strengths that are used and how they differ from other commercially available softwares for the calculation of the diatomic spectra, such PGOPHER, NEQAIR and SPECAIR (168; 169; 170), are presented.

The general procedure for the calculation of diatomic spectra is that accurately collected spectra are used to calculate the diatomic constants, including the energy term values. The Hönl-London factors are calculated for the known line positions. Upper and lower level potential energy curves are then calculated using the Rydberg-Klien-Rees Algorithm. These potentials are used to numerically solve the Schrödinger equation and the result is used to calculate the Frank-Condon factors and the r-centroids. The Hönl-London factor, r-centroid, and Frank-Condon factors are then combined to form the diatomic line strength. The Hönl-London factor is used as the selection rule for allowed *vs.* forbidden molecular transitions. Allowed transitions are those with a non-vanishing line strength and the Hönl-London factor is the only term in the factored line strength expression, from Equation 2.28, that is permitted to be analytical zero. Further details on these steps can be found in References (119; 171; 172). Exact details pertaining to the AIO line strengths can be found in Reference (173). An important aspect of the AIO line strength calculation is the inclusion of the r-centroids into the calculation of the electronic-vibrational line strength.

For the purposes of fitting, a MatLab program was created that calculates diatomic spectra from a condensed version of the line strength tables that have recently been published by Parigger *et al.* (120). The reason for the use of a condensed line strength file is two fold. First, there is a vast improvement in the speed of the numerical calculation due to reduced file i/o communications. The second is that there is an abundance of information present in a typical line strength file that is of interest to the curious spectroscopist but is not used in the calculation of the diatomic spectra. Examples of extraneous information include the parity and branch to which particular ro-vibrational lines belong to.

The diatomic spectra are calculated in the model of free spontaneous emissions. Stated simply, this is given by

$$I_{ul} = h\nu A_{ul} N_u \quad (6.1)$$

where ν is the vacuum wavenumber corresponding to the frequency of the transition from upper state u to lower state l , A_{ul} is the transition rate coefficient, and N_u is the population of the upper state. In this model, the distribution of populated levels (N_u) is given by a Boltzmann distribution. The resulting intensity expression in the case of free spontaneous emission then becomes

$$I_{ul} = \frac{16\pi^3 c (a_0 e)^2 N_0 C_{abs}}{3\epsilon_0 Q} C_\nu \nu_{ul}^4 S_{ul} e^{-hF_u/kT} \quad (6.2)$$

where Equation 2.6 expresses the spontaneous rate emission coefficient in terms of the line strength. In the above expression, a_0 is the first Bohr radius, e is the electronic charge, c is the speed of light, N_0 is the total species population, h is Planck's constant, Q is the partition function, F_u is the upper energy state term value, k is the Boltzmann constant, and C_{abs} and C_ν are absolute and relative calibration constants, respectively. From the above expression, it is obvious that the only quantities that need to be known from the line strength file are the line strength, the vacuum wavenumber position for a particular transition, and the upper energy term value for a particular transition. The above expression is what is implemented in the MatLab program used to perform the diatomic spectra data fitting. Further details on the programming of this implementation and the numerical methods associated with the program are further elaborated upon in Appendix E.

The experimentally collected spectra are fit to the theoretically calculated spectra using a Nelder-Mead algorithm. The Nelder-Mead method is a geometrical method of optimization in which a simplex is created based off of the number fit parameters to be minimized (174; 175). The dimensionality of the simplex is one less than the number of fit parameters, with each fit parameter representing one of the vertices in the simplex. For example, in a three parameter fit, the simplex is a triangle and in a four parameter fit the simplex is a triangular tetrahedron. The size of the simplex is then systematically and iteratively reduced in size by changing the vertex positions until a user input tolerance is met. The final positions of the simplex vertices determine the

optimized fit parameters. This minimum corresponds to the first local minimum that is encountered during the minimization process. The Nelder-Mead algorithm requires the use of initial parameter guesses to seed the algorithm and create the initial simplex.

The parameters that were to be considered during the fitting process were a linear baseline offset, the temperature of the molecular spectra, and the line width, or spectral resolution, of the molecular spectral lines. The baseline offset and temperature parameters are always varied during fitting, even throughout the following discussion on the error analysis. The molecular line width is determined to be the spectral resolution. For the resolutions encountered throughout the experiments in this work, the result is a single line shape that is the convolution of many molecular transitions. Small changes, within the width of the instrument function line width, have been shown to display an affect on the temperature that is determined during fitting with the Nelder-Mead algorithm (103; 104). This is accounted for during the error analysis process. The error of the fitting process is investigated through the use of Monte-Carlo like simulations of the fitting process.

An example fit to AIO spectra collected at time delay of $5\ \mu\text{s}$ and slit height of 6.5 mm is shown in Figure 6.2. This fit was performed using a spectral resolution of 0.1 nm and the inferred temperature is 4190 Kelvin. Of particular note in the image is the difference between the resolution of the collected spectra and the fitted spectra. This is due to the diminished signal to noise ratio of the measured spectra due to the spatial resolution. If one were to add all the vertically resolved data or perform some type of windowed, weighted average to the data, the measured spectra would more closely match the line resolution of the fitted spectra. The fit shows that the AIO spectra have what appears strong noise contributions where one would expect to see rotational lines. It is likely, while there is some noise in the measured spectra, that what appears to be noise is actually unresolved rotational lines that have diminished in signal intensity due to the spatial resolution of the experiment.

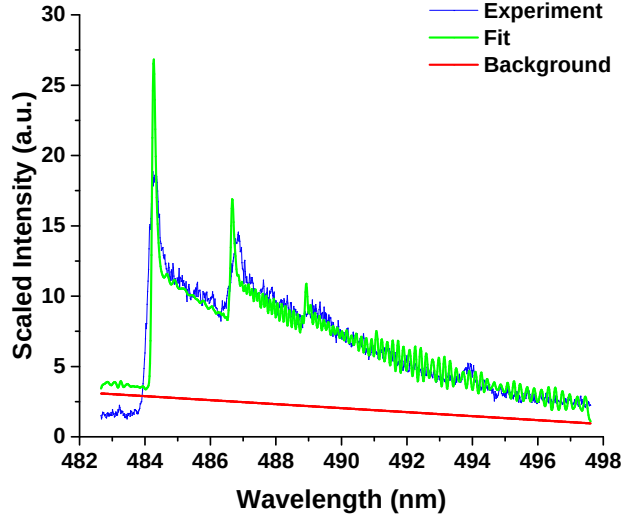


Figure 6.2: Fit to measured AIO spectra at a slit height of 6.5 mm at a time delay of $5 \mu\text{s}$

6.1.1 Error Analysis

Due to the nature of the Nelder-Mead fitting algorithm, one needs to consider a robust error analysis of the fitted parameters the minimization algorithm returns. It is in general accepted that any minimization algorithm will have a difficult time in returning a global minimum of its parameters in any sort of time that is computationally meaningful. The Nelder-Mead algorithm is no exception to this rule. Furthermore, any method that requires an initial seed of parameters to be minimized will be subject to effects associated with differing results from two differing parameter vector seeds. This is particularly true for the Nelder-Mead algorithm, where the fitted results are known to depend upon the parameter initializations (176).

In this dissertation, a statistical ensemble of fitted parameters using Monte-Carlo like analysis methods is chosen to perform the error analysis. A Monte-Carlo method is a type of data simulation routine in which some model is known based off of a set of input parameters that can be determined through some optimization methods and

the errors are determined by successively iterating the model to create a distribution of potential results (177).

The input parameters are taken to be the measured parameters of an experiment. The error analysis is performed by successively altering these parameters randomly within established regions. Error analysis takes place after first fitting the molecular spectra to infer an initial temperature and baseline offset. The baseline offsets were randomly varied within 25% of the initially fit baseline through addition of signal noise to the baseline, the use of which is based off of previous investigations of molecular temperature inferences from titanium monoxide emissions (118; 178). Additionally, the spectral resolutions were allowed to vary within 50% of the determined instrument function width, the maximum amount that the width can systematical change due to this width and still be within the instrument function. Both sources of error were varied simultaneously while the spectra were then fit 1000 times through successive application of the Nelder-Mead fitting algorithm, which has been termed NMT (Nelder-Mead Temperature).

An additional fit is performed in which the the baseline offset, temperature, and line width all are allowed to vary as fit parameters. The result is 1002 fits and inferred temperatures. The error in the inferred temperature is found by considering the so-called 68.3, 95.5, 99.7% percent rule which assigns a normal distribution to the results of the error analysis and is referred to as the "three sigma rule of thumb". A so-called 3 sigma rule exists for non-normal distributions in which approximately 98% of all values are within three standard deviations of the mean (179). The 1, 2, and 3- σ errors of the inferred temperatures correspond to 68.3, 95.5, 99.7% of inferred values, respectively, that lie within the fitted initial temperature. Figure 6.3 shows a histogram of the error analysis results for the sample fit that is displayed in Figure 6.2. Overlaid on the image is a Gaussian distribution with a width corresponding to the inferred temperature and 1- σ error of 4190 ± 290 Kelvin. This distribution is seen to have been widened by the tight grouping of many results near 4600 Kelvin.

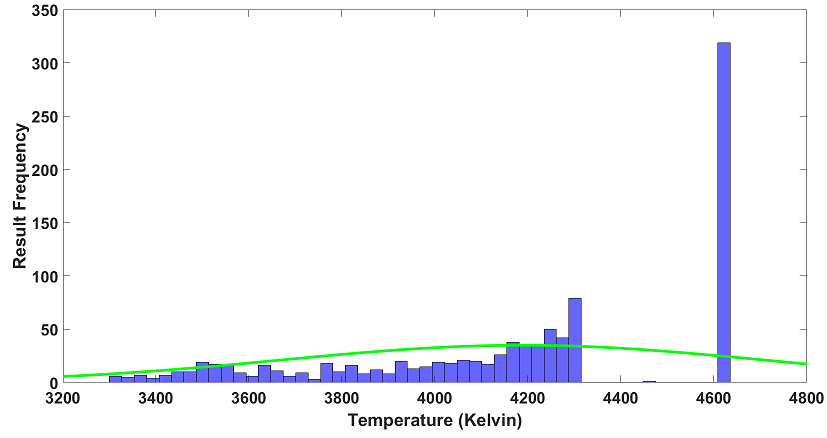


Figure 6.3: Histogram of the 1002 temperatures used to infer the temperature error for a time delay of $5 \mu\text{s}$ and a slit height of 6.5 mm.

6.2 Results

6.2.1 Atomic and Molecular Interferences

At the $2.5 \mu\text{s}$ time delay, there are significant interferences between the H_β line and the measured AIO spectra. In theory, one could use these results to simultaneously determine the temperature and electron density at a given plasma plume height and time delay. Figure 6.4 shows example fits to H_β spectra for 5.0, 6.0, 7.0 and 8.0 mm slit heights. The H_β spectra were fit to Voigt profiles without any pre-treating of the data, *i.e.*, without any attempts to subtract the AIO emission components, as had been previously done with measured confluences of AIO and H_β spectra (103; 104). This would have proved to be a rather difficult task due to decreased sensitivity in the spectral signal due to the spatial resolution and would have resulted in rotational components from the the AIO entering the H_β fit. Also, due to the double peak structure of H_β and the position of the line relative to the AIO vibrational peaks, any vast improvement in the fitting method would certainly have to consider simulated H_β Stark broadened profiles, rather than a single peaked Voigt profile. Simultaneous fitting of the simulated H_β and AIO spectra would then be desirable.

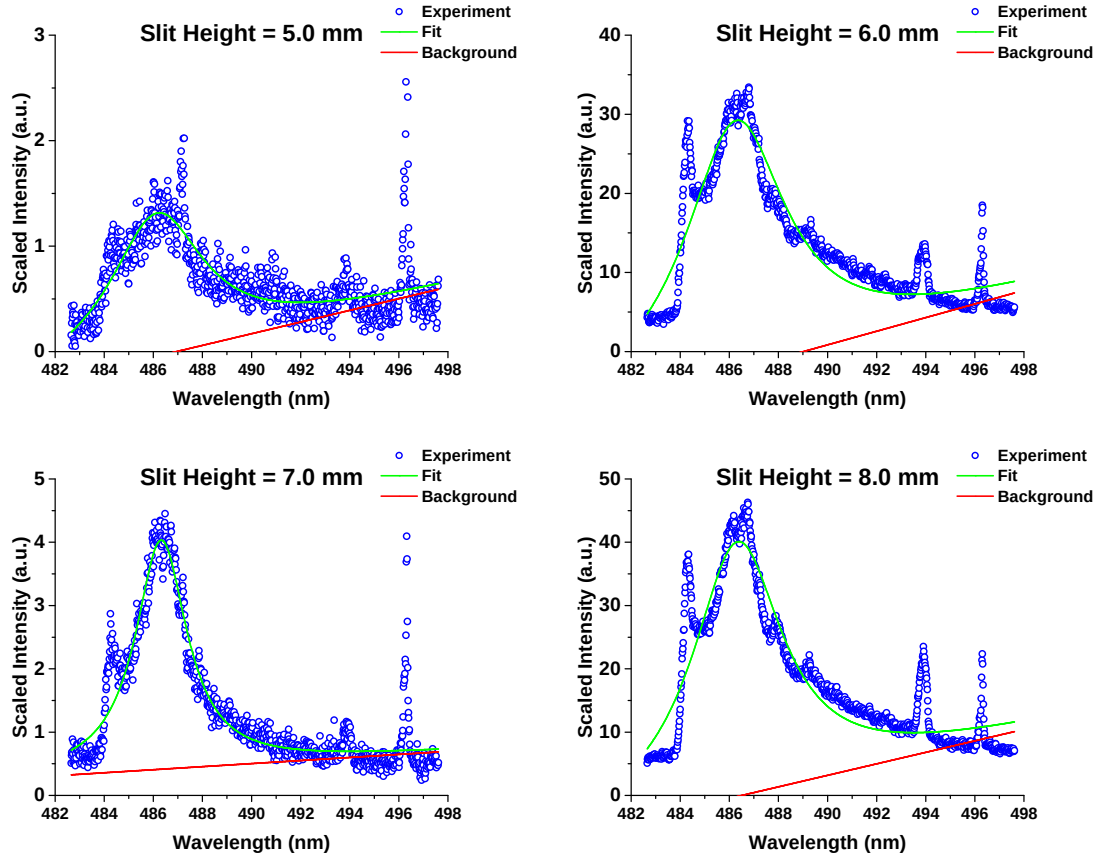


Figure 6.4: Fitted H_β spectra measured with AIO spectra at selected slit heights for the $2.5 \mu\text{s}$ time delay.

Of particular interest from the fits displayed Figure 6.4 is the potential artificial broadening of the fitted spectra for the 5.0 mm slit height. This obviously gives rise to a larger N_e . The quality of the fits improves towards the center region of the plasma and then diminishes once again as both the AlO and H_β signal quality diminishes with increasing distance from the ablation surface, where temperatures and N_e are expected to rapidly fall off. The results of the inferred N_e along the plasma plume height are shown in Figure 6.5 and shows an inflated N_e near the sample surface. This could be due to the extra broadening present due to the diminished quality of the fit, but it could also represent an area of increased N_e that is localized to the ablation surface, which one would expect during a laser ablation experiment. There is a characteristic minimum in the N_e near a slit height of 6.5 mm, which is close to the center of AlO and H_β signal intensity, as seen from Fig. 6.1. This is followed by a rise in the N_e before it once again falls off to an asymptotic value in regions where there are little plasma emissions.

The N_e at the minimum is $3.4 \pm 0.6 \times 10^{16} \text{ cm}^{-3}$. This occurs for a slit height of 6.5 mm. The density at the two maxima on either side of the minimum are 1.9 ± 0.5 and $1.2 \pm 0.3 \times 10^{17} \text{ cm}^{-3}$, which correspond to slit heights of 5.6 and 7.2 mm, respectively. Such a gradient is showing that the density is greatest at some small distance, approximately 0.5 mm, from the sample surface. The minimum roughly corresponds to the center of the maximum of the H_β emissions. This N_e gradient shows that a shell of higher density exists at 2.5 μs delay in the plasma evolution about an assumed plasma center. Such an effect could also be due to the plasma shockwave dynamics, which causes an increase in the number of collisions and an increase in the N_e along the leading edge of the plasma shockwave.

The temperatures at this time were inferred by fitting the AlO spectra. These results are displayed in Figure 6.6. The inferred temperatures show quite large errors, however, the trend along the slit height is rather similar to the N_e . The surface temperature is rather constant and reaches a relatively small peak, compared to the surrounding values, of 4436 ± 375 Kelvin at a slit height 5.44 mm. The temperature

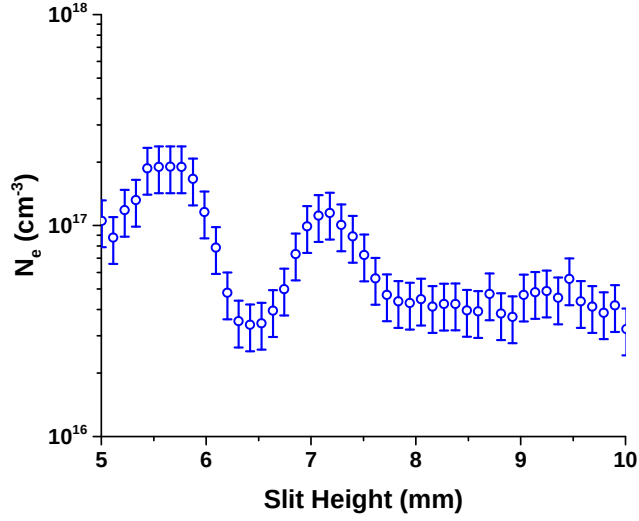


Figure 6.5: Inferred N_e from H_β line widths along the plasma plume height at the $2.5 \mu\text{s}$ time delay.

then reaches a minimum of 3451 ± 225 Kelvin at a slit height of 6.4 mm before increasing again to a value of 3963 ± 390 Kelvin at a slit height 7.0 mm. The positions of the maxima and minimum temperatures are roughly at the same slit heights as the maxima and minimum N_e .

Similarities in the N_e and temperature gradients corroborate each other. The N_e that is determined from the H_β line may be inflated by the presence of the AlO spectra but the trend that is observed is true. Likewise, the AlO spectra may be affected by the diminishment of the signal intensity from the spatial resolution and the presence of the H_β lines, resulting in larger inferred errors, but the trend that is observed is true. This indicates that a plasma shell model applies to laser ablation, about some central position. In this model, a region of higher density exists in an expanding region outside the plasma center. These gradients result from the propagation of shockwave, which result from the plasma formation process. Such results are important to be known for radial reconstruction of the spectral intensity.

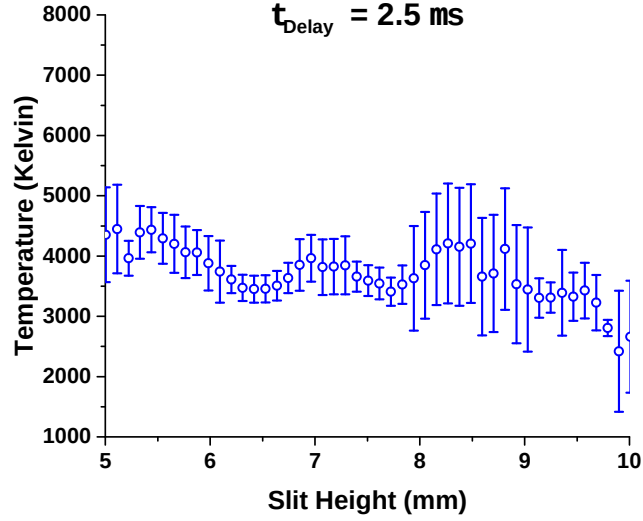


Figure 6.6: Temperatures inferred along the slit height from AlO emission spectra at the $2.5 \mu\text{s}$ time delay.

6.2.2 AlO Temperature Results

The results of analyzing the temperature along the slit height are presented in Figure 6.7. These results show the temperature evolution in the first $20 \mu\text{s}$ following ablation of the alumina target sample. The most notable feature of Fig. 6.7 are the large error bars on most of the inferred temperatures. Contributions to such large errors, which are on the order of 300-500 Kelvin, come from the incompletely resolved rotational AlO lines as a result of the spatially resolved measurements. The fitted spectra also shows slight errors in the wavelength calibration procedure due to non-agreement in line positions between the measured and theory AlO spectra, which adds a significant source of error due to the included variations in the spectral resolution. These reasons illustrate the need for a statistical analysis of the temperatures produced from a measurement of molecular spectra.

The errors could be improved by applying a weighted average filter to the measured spectra. This would increase the signal intensity of the rotational spectral components and would produce a better fit. This would also produce a blending of the spatially

resolved spectra, which would defeat the purpose, to some extent, of performing a spatially resolved spectral study. The result of applying such a filter on the inferred temperatures would be a flattening of the results. Temperatures would be more likely to be similar to neighboring, spatially resolved spectra and any inference about the spatial dependence on the inferred temperatures would be diminished.

The temporal trend of the inferred temperatures is seen to be minimal, particularly when considered with the relatively large calculated temperature error margins. The spatial temperature trends are slightly more revealing. Early, at $5\ \mu\text{s}$ the temperature near the sample surface is 4500 ± 100 Kelvin. The temperature quickly drops to 3000 ± 350 Kelvin by $12.5\ \mu\text{s}$ and begins to cool over an extended region, as seen by the gradual rise of the temperature at the $15\ \mu\text{s}$ time delay between slit heights of 5 and 6 mm. After 6 mm, the inferred temperatures have abnormally tight error bars. This is due to the decreased AlO signal intensity between heights of 6.5 and 7 mm. This is also seen in the slit heights of 6.5 and 7.5 mm in the temperatures inferred at the $20\ \mu\text{s}$. The temperatures that are inferred in the gap region are also seen to have exceedingly large temperatures and errors. In the regions in the $15\ \mu\text{s}$ temperature results, where the AlO signal intensity becomes strong once again the temperature are seen to rise to 4100 ± 200 Kelvin. In this region, in the $20\ \mu\text{s}$ temperature results, the temperatures are rather difficult to make any inference from due to the large error bars in the inferred temperatures. This is due to the rapidly decaying AlO signal intensity.

Recall that the source for the AlO in the measured molecular spectra is due to the ablation of an alumina target sample (Al_2O_3). As such, there is no new oxygen from the ambient conditions, as would be encountered in laboratory air ablation experiments, to create more AlO particles through chemical kinetics. The interface between surface and atmospheric AlO emissions in an alumina ablation experiment in laboratory air would likely cause the region between the surface plasma and higher region of the plasma to become filled in. Interesting future works should consider such a scenario. Of particular interest will be the temperature gradient in the gap between the two plasma regions. A recent investigation involving molecular titanium monoxide emissions from

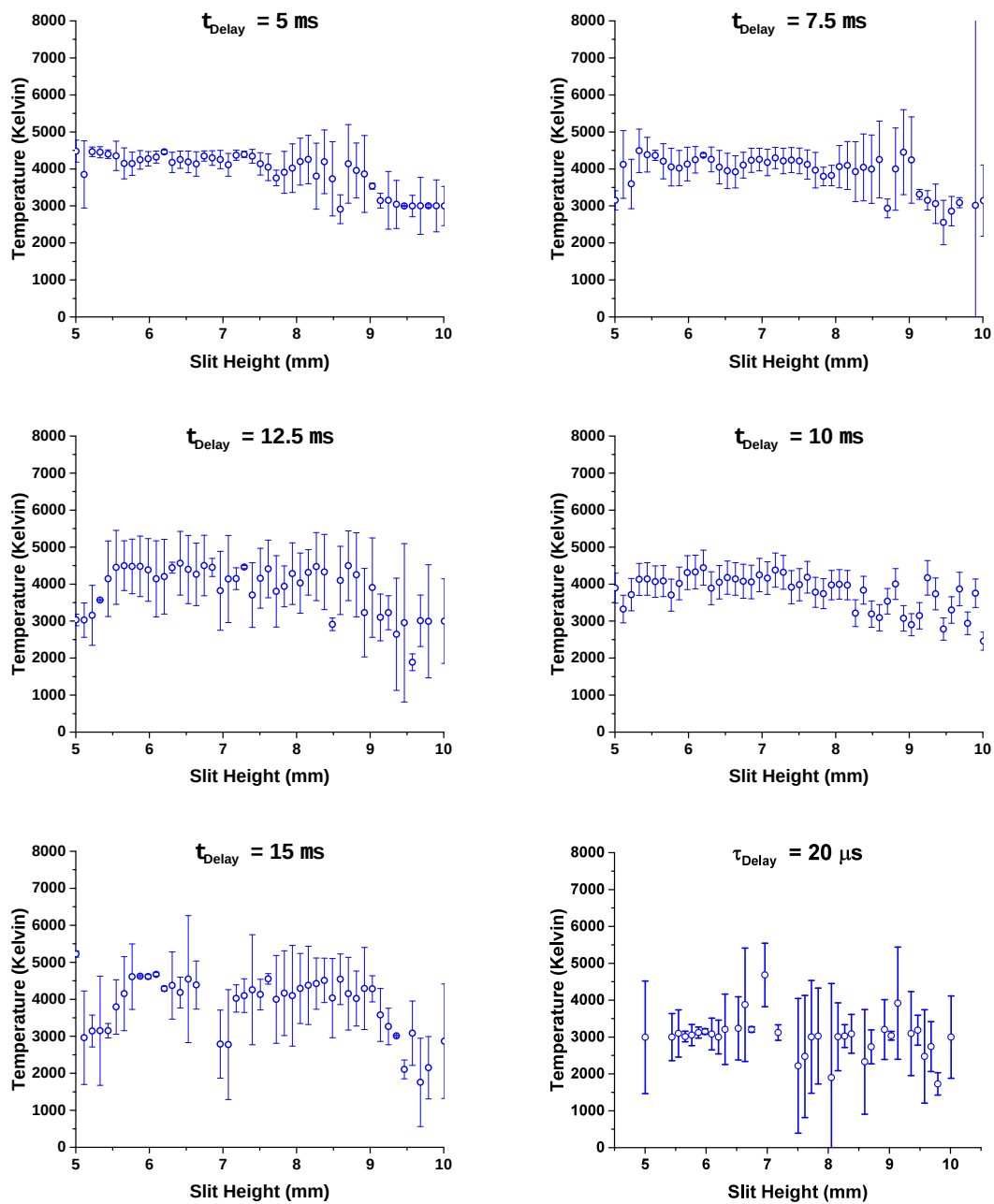


Figure 6.7: Inferred AIO temperatures along the slit height for selected time delays

laser in ablation of titanium samples in laboratory air showed that this region has lower temperatures (102). The correlation of such a temperature trend would be interesting to associate to the chemical kinetics of the plasma molecular formation of AlO at microsecond time delays.

As well, correlations of the plasma temperature to the shockwave observed at microsecond time delays would be of interest. In addition to associations between the temperature inferred from molecular emissions, the plasma shockwave would be of interest for future studies. The measurement made at $7.5\ \mu\text{s}$ shows characteristic rises and falls in the temperature between slit heights of 5 and 7 mm. Such rises and falls could correspond to the compression of the plasma due to the presence of a shockwave. Unfortunately, due to the large error bars presented in this chapter, such correlations are ill advised currently. However, future studies in which the plasma shockwave is imaged directly and coincidentally with molecular spectra would provide the tools necessary to make such correlations.

6.3 Spatial Deconvolution

As a final consideration for this chapter, radial distributions of the AlO spectral intensity are briefly considered. The spatial dependence along the height of the plasma corresponds to a measurement of the vertically resolved, signal intensity, $I(z, \lambda)$. Through the Abel inversion relations that were presented in Chapter 2, measurements of $I(z, \lambda)$ may be used to reconstruct the radial spectral intensity profile, $I(r, \lambda)$, of a measured series of spectra. The AlO spectra measured at a time delay of $5\ \mu\text{s}$ were used to complete such a task. It is usually a requirement of the Abel inversion method, that cylindrical symmetry be present, however slight asymmetries generally exist with laser-induced plasma experiments due to non-ideal beam shapes and plasma shielding affects. Furthermore, in laser ablation, inherent spatial asymmetries exist due to the presence of the sample surface.

The Abel reconstruction was completed using a symmetrization method in which top and bottom components of the spectral emission along the plasma vertical axis (z -axis) are allowed to show differing symmetries. This procedure was developed for use in inductively coupled plasma emissions and considers a weighted average between the top and bottom plasma symmetry regions to reconstruct the total radial intensity profile (180). This method requires that the top and bottom components each be roughly symmetric and is useful to extract slight differences between the plasma top and bottom regions. Details on this method and the calculation of the Abel reconstructed spectra are presented in Appendix C.

The reconstructed spectra corresponds to a radial position at the plasma center ($r = 0$). The radial coordinate is given relative to the plasma center. The AIO emissions at a time delay of $5 \mu\text{s}$ were assumed to have a plasma symmetry at distance of 2 mm from the sample surface. The symmetrization process was carried out using this position as $z = 0$. The radial intensity distribution that is calculated is applicable only to this slit height. An example fit to a reconstructed AIO spectra is shown in Figure 6.8. The fit shows a dramatic increase in the noise. This is due to the fact that the Abel inversion process requires that the vertically resolved spectra be differentiated. Differentiation of molecular spectra is a rather difficult task and often results in a significant increase in noise due to the many lines that are present. The Abel inversion procedure that is employed alleviates this concern, to a certain extent, since the derivative of $I(z, \lambda)$ is calculated using a series expansion of an orthogonal set of polynomials. This reduces the noise addition to just a few percent, however, a noticeable effect is still present.

The temperature of the fit shown in Figure 6.8 is 4672 ± 60 Kelvin. The rest of the reconstructed temperatures along the plasma radius for the $5 \mu\text{s}$ time delay are presented in Figure 6.9. The error bar of the temperature for the $r = 0$ position is relatively tight in consideration of the rest of the inferred error bars. The radial distribution of temperatures is clearly effected by the inherent plasma asymmetry due to the plasma surface. In the negative radial direction, the inferred plasma

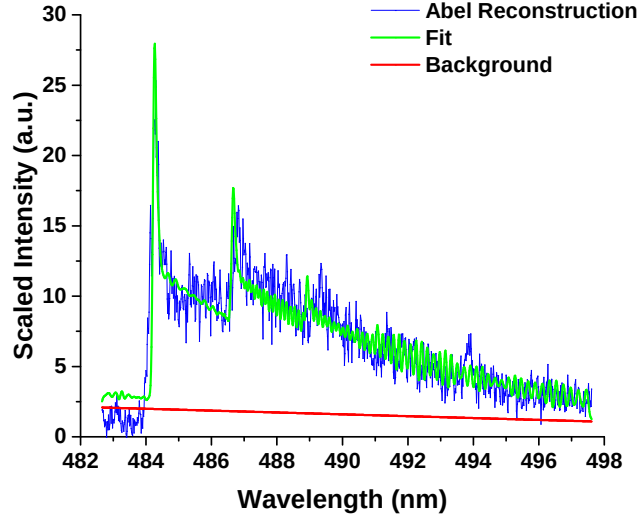


Figure 6.8: Fit to Abel reconstructed AIO spectra at a time delay of $5 \mu\text{s}$ for a radial position of $r=0$ mm.

temperatures settle towards a value of 3000 Kelvin. In the forward radial direction, the inferred plasma temperatures show a relatively constant value near 4000 Kelvin. After 1 mm in both radial directions, the temperatures become highly error prone. This is likely due to a low AIO signal quality that had noise added to it through Abel inversion.

The measurement at the $2.5 \mu\text{s}$ time delay was also Abel reconstructed to see if the interesting N_e gradients along the plasma height could be correlated with a density gradient along the plasma radius. The image was split into two symmetry regions using a slit height of 6.75 mm. The N_e results are found after fitting the reconstructed AIO and H_β spectra. These results are depicted in Figure 6.10. The lack of true plasma symmetry to be split into two regions, the interferences of the AIO and H_β spectral signals, and the additional noise present in the reconstructed signal due to the Abel inversion procedure all make the radial reconstruction procedure quite difficult. There is, however, some cause for hope as the reconstructed profile indicates a minimum N_e at the assumed center. At the minimum, the density is approximately $2.3 \pm 0.6 \times 10^{16} \text{ cm}^{-3}$. In the backward radial direction the plasma N_e approaches a maximum value

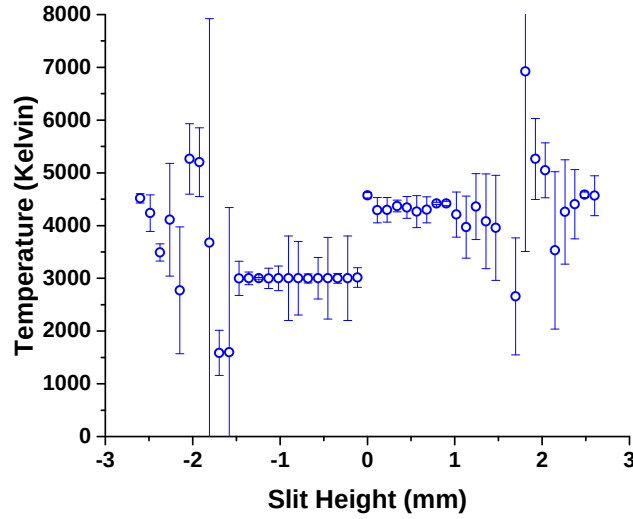


Figure 6.9: Temperature inferred along the plasma radius after fitting Abel reconstructed AlO spectra at a time delay of $5 \mu\text{s}$

of $2.4 \pm 0.6 \times 10^{17} \text{ cm}^{-3}$ and in the forward radial direction the maximum density approaches $1.2 \pm 0.3 \times 10^{17} \text{ cm}^{-3}$, with radial positions of -1.3 and 1.4 mm, respectively. These results are consistent with what was seen in the plasma height N_e results. Due to the asymmetry from the alumina surface, the wings of the N_e decay could not be determined in the radial direction. The symmetrization procedure (180; 181) was only applied to slit heights between 5 and 8.5 mm.

The inversion of plasma spectra observed in laser ablation experiments is best served using Radon transform considerations. The plasma symmetrization process may prove to be useful under certain scenarios, but these will likely need to be limited to localized regions in the ablation plasma, such as near the target surface, where one can make a convincing argument that the plasma exhibits the described top and bottom type symmetries. Previous applications of the symmetrization process have proved to be quite useful for laser-induced plasma experiments in which breakdown was initiated in a hydrogen gas atmosphere (181). The symmetrization process was applied to H_β spectra and was used to show gradient effects in the radial distribution of the electron density. These results showed differences of a factor of 2 in the inferred N_e along the plasma

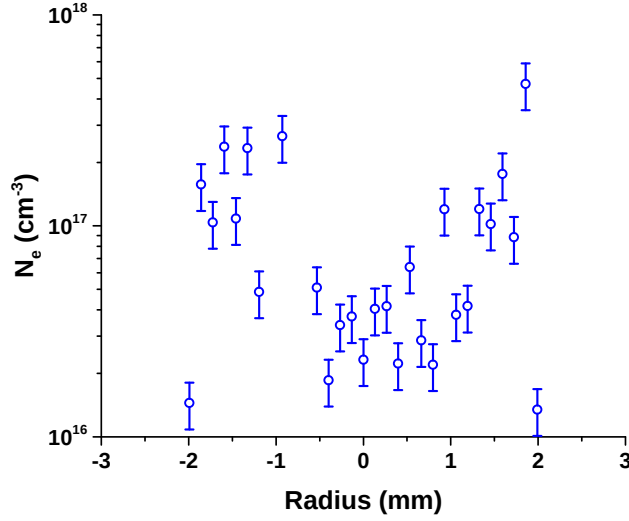


Figure 6.10: Inferred N_e along the plasma radius from Abel reconstructed H_β spectra at a $2.5 \mu\text{s}$ time delay, indicating maxima near ± 2.0 mm and a minimum near the center.

radius. Most interestingly the largest N_e were shown to be in outer regions of the plasma radial distribution, as was shown for the H_β inference made at $2.5 \mu\text{s}$. Without the presence of the interfering AIO spectra and under a carefully designed experiment, atomic spectra in a laser ablation plasma could have the symmetrization procedure applied for the Abel reconstruction of radial spectroscopic profiles and determined quantities, which would be useful for studies of the early time development of laser ablation plasma.

Future works along this line of research should consider situations where the plasma symmetrization process may be applied and look for temperature diagnostics that show radial distributions along the lines of those shown in the $7.5 \mu\text{s}$ time delay temperatures from Figure 6.7. One might also consider the use of optical, color filters to locate regions of the AIO emission and attempt to corroborate these distributions with vertically resolved and radially reconstructed inferred temperatures. Other future works might consider the differences between quantities determined from Abel reconstructed spectra and reconstructions of the quantities determined along the plasma z-axis. Noise was

shown to cause many problems in both the atomic and molecular profile reconstruction results and a method which circumvents some of these effects is desirable.

Chapter 7

Plasma Shockwave Dynamics

In this chapter, the application of measured emission spectra to diagnostics of the plasma shockwave dynamics are considered. Recall that the plasma initiation process results in the formation of a shockwave that rapidly propagates through the plasma and interacts with the ambient atmosphere at an expanding boundary layer created by the plasma expansion. As the shockwave propagates through the plasma, gradient effects in the spatially determined temperature and N_e are expected. This represents a method for understanding the plasma-shockwave interaction in a physically significant manner.

To study the plasma emission and shockwave effects, simultaneous spectroscopic and shadowgraph experimental imagery techniques are employed. Shadowgraph imagery of the time evolution of the plasma is used to study the dynamical process of the formation and propagation of the shockwave associated with the production of a laser-induced plasma. A shadowgraph is the image of a density gradient. The target of interest is illuminated by a light source and is imaged. In this case, the light source is a pulsed laser, owing to spatial and temporal resolution of the imaged shadow. While the target is illuminated, regions of higher density will appear as dark regions in the image. Shadowgraphy is similar to other flow visualizations and imaging methods, such as Schlieren photography; however, the shadowgraph is simpler in both practice and theory, due to the use of screens and blocks used to measure positive and negative fluid gradients in Schlieren methods (182; 183). The intensity of the imaged intensity field is related through the Laplacian of the index of refraction.

There are two forms of shadowgraphy: 1) focused shadowgraphy and 2) direct shadowgraphy (14). In the former, the target and its shadowgraph are imaged onto

a screen. Recording of the shadowgraph is then completed by imaging the composite target and shadow image that is projected onto the screen. In the later, the shadow and the target, including the illumination source, are imaged directly onto the collection optics of the recording device used to record the shadowgraph. The two techniques are roughly equal in their merits. The focused shadowgraphy method does preserve the integrity of experimental equipment when using a laser as the shadowgraph illumination source.

In this chapter, direct shadowgraphs are collected. The shadowgraphs were collected at the Sandia National Laboratories (SNL) facilities and were also simultaneously imaged with optical spectroscopy methods in the nominal 200-800 nm wavelength ranges. The applications of such works, in addition to a greater understanding of the plasma-shockwave interaction, are also aimed at understanding the emissions of high explosive events. Active research is aimed at determining the scaling of the temperature, electron density, and shockwave expansion symmetry between the laboratory scale plasma shockwave and emissions of large scale high explosive events (100; 101).

7.1 Plasma Shockwave

The plasma formation process creates a laser produced shockwave that subsequently expands into the ambient surroundings. In the case of vacuum ablation, this expansion is considered to be mostly free, with expansion speeds nearing 100 km/s, while, in cases of plasma initiation in ambient conditions, near atmospheric pressure, the shockwave expansion is slowed by the interaction with atmospheric particles (14). In some cases, for atmospheric pressure breakdown events, this slowing can be almost immediate. Reports have shown the pressure of the shockwave may exceed 100 MPa, or approximately 1000 atmospheres. This pressure dramatically decreases over time and was reported to drop by two orders of magnitude after just 1-2 μ s following plasma initiation (14). The leading edge of such a pressure gradient gives rise to the observed

shockwave, which subsequently propagates through the plasma plume and into the ambient atmosphere.

This shockwave can be modeled by the Taylor-Sedov point blast model (184). The Taylor-Sedov point blast model describes the expansion using a similarity solution in which the time and space evolution of the blast wave are contained within a single parameter. The result is that the solutions to the Euler equations for fluid flow become ordinary differential equations, rather than partial differential equations. The original formulation of the point blast wave model, showed the propagation of a spherical wave. Further works have shown the position of the shock front, $R(t)$, expands as a function of time as

$$R(t) = \xi \left(\frac{E}{\rho} \right)^{1/n+2} t^{2/n+2} \quad (7.1)$$

where E is the energy released by the blast, ξ is a constant that accounts for the specific heat capacity of the expanding material, ρ is the density of the ambient atmosphere in which the shock front expands into, and n is an integer constant (185). Such a model is used to describe the expansion of a shockwave following laser ablation of a target sample. For planar, cylindrical, and spherical geometry, the constant n is given by values of 3, 2, and 1, respectively. Figure 7.1 shows a comparison of these three expansion geometries as a function of time. In the Log-Log plot, one should note that the slopes of the lines for the different models correspond to the temporal exponent.

A major difference between the expansion of the shock front from an explosion and the propagation of the shock front in a laser produced plasma is due to interactions of the laser with leading edge of the shock front along the axis of laser incidence. During the plasma initiation process, energy is absorbed by the target sample and becomes ionized. Free electrons absorb any extra laser energy, particularly for nanosecond ablation. The absorption of this laser energy leads to heating of the plasma material. This alters the geometry of the shock front expansion in the direction of laser incidence. Such an effect is termed a laser-supported detonation wave (13; 186). The

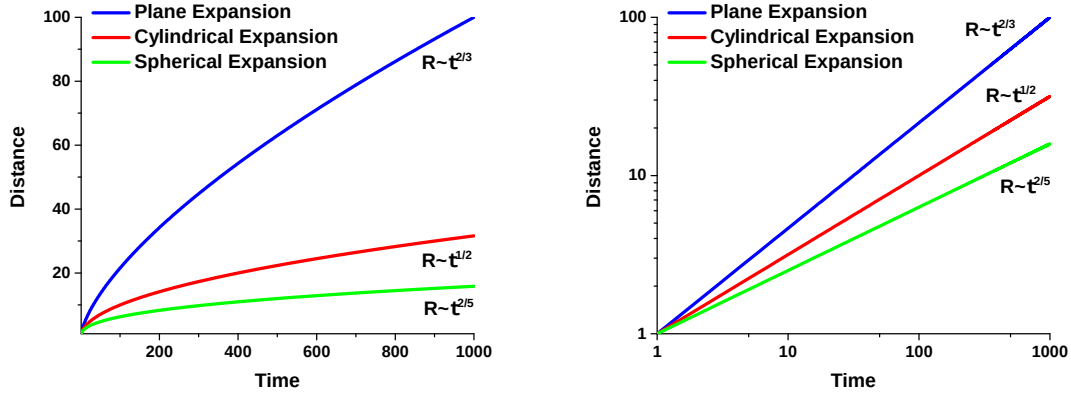


Figure 7.1: Comparison of planar, cylindrical, and spherical blast wave shock front expansion models shown in real space (left) and linearized Log-Log space (right)

characteristics of such a wave are dependent upon the ambient conditions and the duration of the laser pulse used to initiate breakdown.

7.2 Simultaneous Shadowgraphs and LIBS

The collection of simultaneous shadowgraph and plasma emission spectra collected at SNL was accomplished as described in Chapter 3.3. Post processing of the emission spectra began with the relative and absolute calibration of the data. Absolute calibrations were performed in the wavelength range of 200-400 nm resulting in a usable wavelength region of 250-400 nm. The reduction in the usable wavelength region is due to the decreased sensitivity of the detector for ultra violet wavelengths. The spectra were collected at systemically varied time delays ranging from 0 to 1 μ s following ablation of the target sample. Relative calibrations were performed on the wavelength region between 400 and 800 nm. The first step in analyzing the data, similarly to the spectra collected at UTSI, was to visualize the results. Figure 7.2 shows absolutely calibrated spectral images of the plasma decay in the time range of 0 to 800 ns following ablation in the wavelength range of 250 to 400 nm. Figure 7.3 shows the corresponding relatively calibrated spectral images in the same time domain for the spectral range of

400 to 800 nm. Due to the movement of the sample surface throughout the spectral image collection, the height of the sample surface in each of the images in Figs. 7.2 and 7.3 changed relative to the ICCD.

After the first 200-300 ns, the contour plots become difficult to glean any information about the spectral details of specific emissions due to the continually narrowing nature of the spectral lines and the relatively large spectral viewing area. However, these images do show the bulk behavior of the plasma spectral emissions over the course of the first 800 ns of the plasma evolution. The absolutely calibrated images show that in the first 50 ns following ablation there are strong UV continuum emissions that subside and reach a minimum by 50 ns. Following this minimum, the plasma spectral emission appears prominently from the spectral continuum, beginning with strong ionic emissions from Al^+ and Mg^+ lines near 280 nm and Al^+ and Al^{2+} near 360 nm. Near the 200 ns time delay, atomic emissions become evident and by 260 ns neutral Al emissions at 308.21, 308.27, 394.4, and 396.15 nm become obvious as narrow emissions. Also visible are a grouping of neutral Al emissions between 305 and 307 nm.

The relatively calibrated spectra show a similar temporal trend. Strong continuum emissions are followed by the emergence of atomic and ionic emissions. The continuum emission appears to subside earlier in this sequence of emissions. The spectral continuum is expected to be strongest in the ultra violet. By 50 ns, atomic and ionic emissions become readily obvious. Many of the lines that appear in this sequence of images are second order emissions of spectra that were observed in the absolutely calibrated images. Also visible are Cu lines that arise from the Al alloy sample impurities. These lines appear in the vicinity of 515 nm and 705 nm. The infamous oxygen 777 nm triplet lines are also observed, as well as nitrogen and hydrogen emissions that are present due to the breakdown occurring in air. The source of the hydrogen is the moisture in the air. Of particular note are the N^+ 500.14 nm line and the H_α line at 656.28 nm. The N^+ line is prominent very early in the plasma evolution

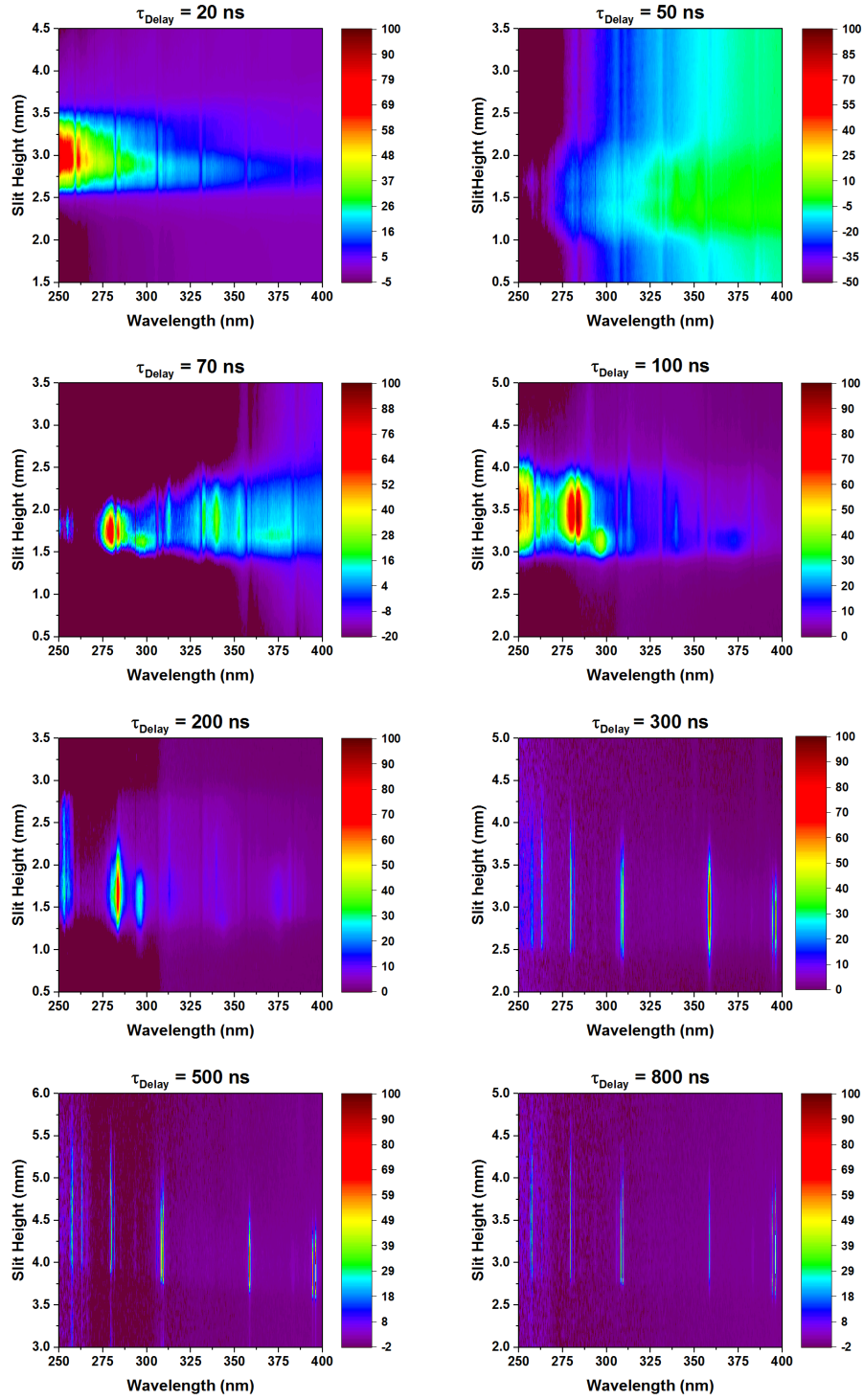


Figure 7.2: Absolutely calibrated spectral data in the wavelength range 250-400 nm, for time delays ranging from 0 to 800 ns

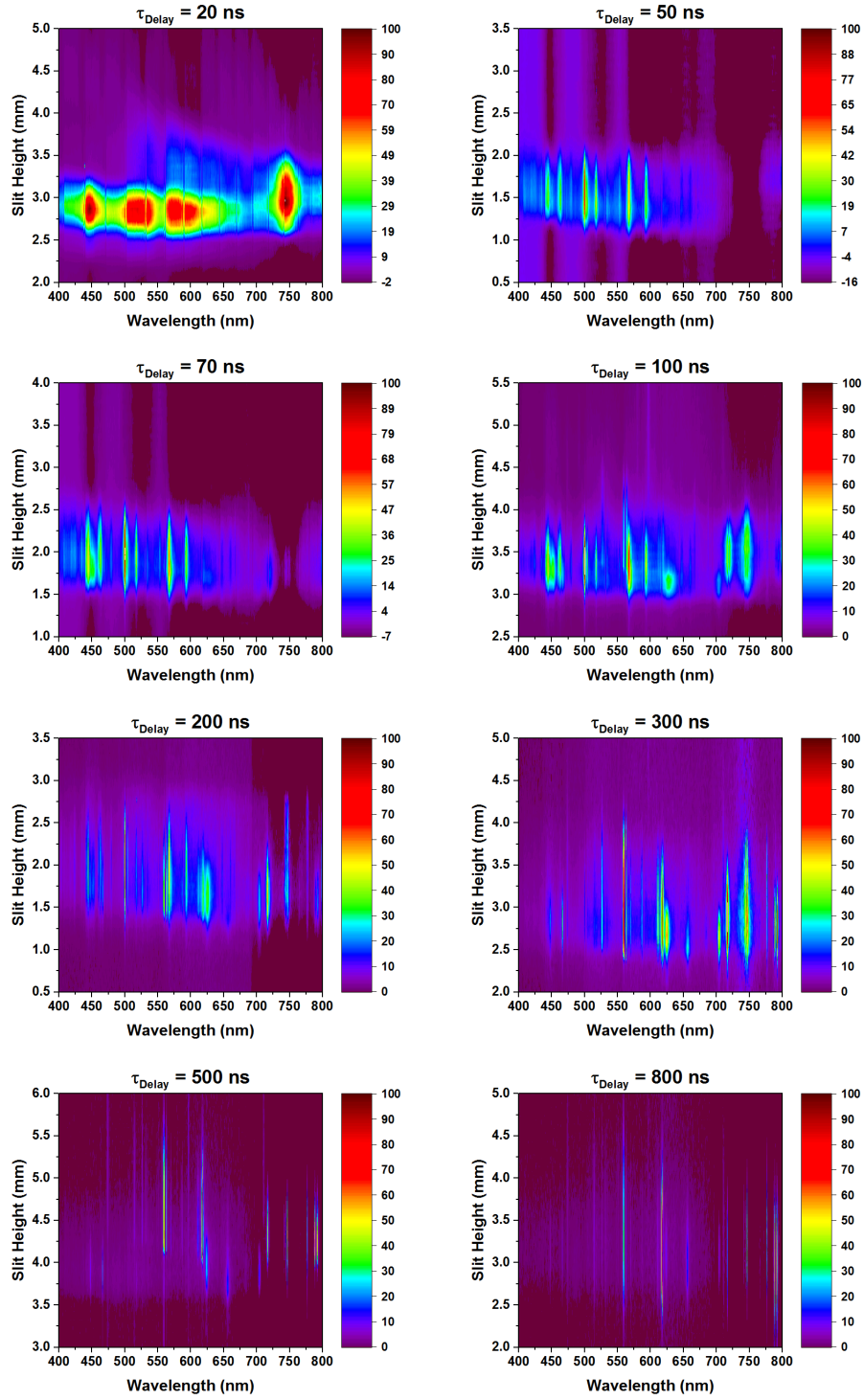


Figure 7.3: Relatively calibrated spectral data in the wavelength range 400-800 nm for time delays ranging from 0 to 800 ns

and becomes extremely narrow by 260 ns. The H_α line is difficult to distinguish from the spectral continuum until 200 ns following target ablation.

7.3 Shadowgraphs

The shadowgraphs were collected using a CMOS camera using the direct shadowgraph method. That is, the laser light was directly incident on the focusing optics/objective of the camera. The shadowgraphs were collected simultaneously to the emission spectra, however, each shadowgraph represents a single laser ablation event at a specified time delay, while the spectra represent an accumulation from 100 laser ablation events. In order to reduce the amount of data produced by these images, only one shadowgraph was saved from each sequence of 100 laser shots used to produce each image in the step and glue procedure described in Chapter 3.3. Accordingly, each time delay produced 21 shadowgraphs of single ablation events to be analyzed, since each spectrum on the 200 to 800 nm wavelength range was the result of 21 ablation sites to be imaged.

The shadowgraphs were analyzed for the spectra collected in the first 1.5 μ s following ablation. The target spectra that were to be recorded in this region were atomic and ionic Al emissions, as well as contributions from the ambient conditions which primarily resulted from nitrogen ionic emissions. Figure 7.4 shows a sample of the collected shadowgraphs. The shadowgraphs were collected using the direct shadowgraph method, which achieved the high degree spatial resolution using a 700 picosecond back light laser source. This sequence of images shows the expansion of the shock front in both directions that are parallel (shockwave height) and perpendicular (shockwave width) to the direction of laser incidence. The black, block like feature in the images is the Al target surface.

Early in the shockwave expansion, there is an obvious difference in the rate of expansion of the height than with the shock front width. This is evidenced by the extra lobe feature that can be seen most prominently in the 50 and 70 ns delay images. The background pattern is a diffraction pattern from the laser and lens used to view

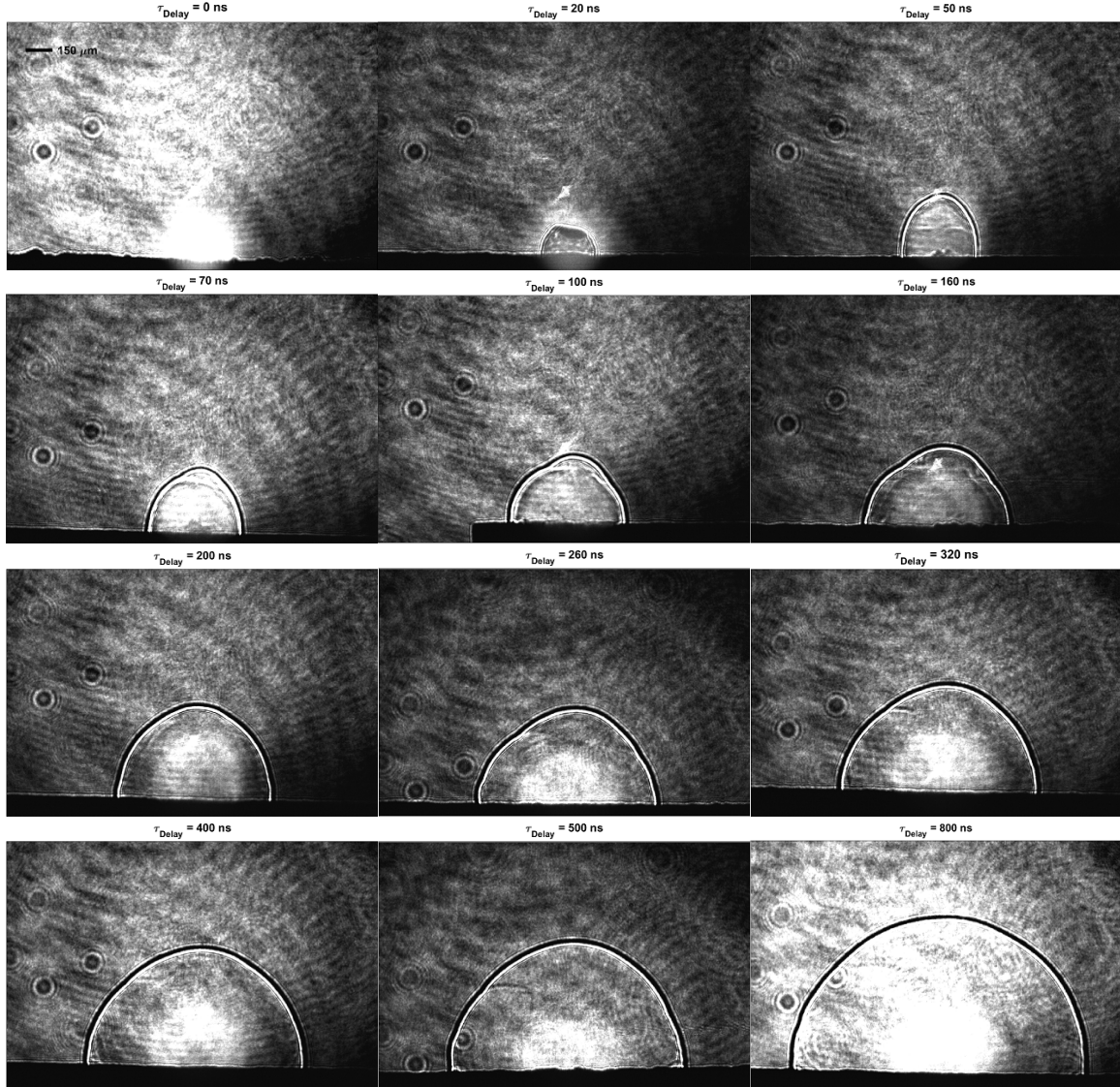


Figure 7.4: Shadowgraphs collected shown for selected time delays

and focus the shadowgraphs. This characteristic pattern is the same in every image, although the sample surface changed position relative to the camera between every time delay. Larger changes in the position relative to the camera occurred when the sample needed to be changed. Also visible in the images collected prior to 200 ns are significant amounts of internal structure that corresponds to the dynamics of the plasma kernel (15; 16).

7.3.1 Image Analysis

The first step in analyzing the SNL shadowgraphs was to convert the recorded PNG images, which were recorded in 8-bit RGB color space coordinates, to 8-bit gray-scale PNG images. This was done to reduce the number of channels of analysis and remove any ambiguities that may arise from differing analysis results that may have arisen from the three differing color channels, *i.e.*, if the blue and green channels indicated the shockwave to be in a different position than the red channel. The images are also cropped to a size of 1500 by 1200 pixels to increase the overall speed of the image analysis and reduce the amount of data that is analyzed.

The shadowgraphs were analyzed using edge detection methods to locate the sample surface and the shock front position in reference to the sample surface. Edge detection image analysis finds areas of sharp contrast in a recorded image. For edge detection in the recorded shadowgraphs, the Fast Canny edge detection algorithm is employed (187). The method analyzes the image by first applying a Gaussian smoothing filter to the image to remove noise from the image pixel intensities. The gradient of the smoothed image is taken in both the vertical and horizontal pixel directions. Pixels that do not represent a local maximum in the image are then suppressed in a process that is termed "non-maximum suppression". The final step in the edge detection algorithm is for the Hysteresis operator to be applied (187), which selects the remaining image pixels to be not an edge, an edge, or in between. If an in between point is linked with an edge,

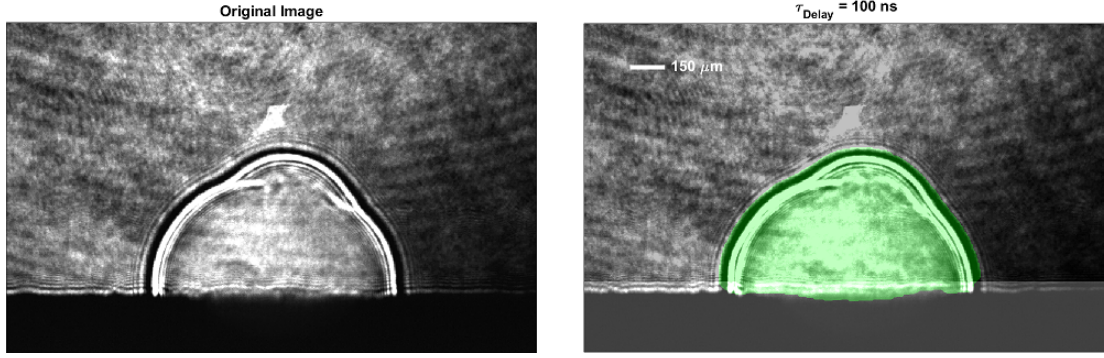


Figure 7.5: Comparison of original shadowgraph (left) and the result of the image analysis (right) for a time delay of 100 ns.

the in between point is determined to be part of the edge. The selection of the edge *vs.* not edge *vs.* in between nature is done through the use of a threshold value.

The edges that needed to be detected were the Al surface and the shock front. The height and width of the shock front are determined by finding the area between the surface and the edge that is determined to be the shock front. Finding the surface consistently in every analyzed image requires the use of a background image in which the only edge present is the surface. The background image is subtracted from the original image and the position of the edge that represents the surface is marked. The edge corresponding to the shock front is found and then the area between the surface and the detected shock front is found. Figure 7.5 shows an example of a measured *vs.* analyzed image for a shadowgraph collected at a time delay of 100 ns. The green overlay in the analyzed image represents the area interpreted to be the shock front.

Since the position of the surface changed between each shadowgraph, reliably determining the surface position was a difficult task. A background image for each delay sequence investigated (all shadowgraphs collected at the time delay corresponding to the same spectral images) was chosen to be to one from the set of images that produced the least amount of variation from the surface of each image in a delay sequence. The image was then made to have a gray-scale, monochrome background for all pixels that did not represent the Al alloy sample. This was done to reduced the creation of extraneous edges in the surface edge detection, as the diffraction pattern

was different in every image due to the vertical motion of the sample relative to the camera. This had a minimal impact on the detection of the shock front edge in the background subtracted shadowgraphs, but does give rise to the pale looking target sample and region just above the sample in the analyzed image. This may have caused some heights to become artificially larger or smaller than the actual shock front would indicate, but any impact was mitigated by taking the average of the determined heights and widths for an entire delay sequence. The determined widths are expected to have little impact due to the background subtraction and sample surface edge detection.

The heights and widths are taken to be the maximum height and width of the green image overlay shown in Figure 7.5 along its horizontal and vertical axes. This gave the maximum width and height of the shock front. In some instances, the edge detection was either incomplete, selecting an area that was significantly smaller than the actual shock front, or over complete, selecting an area that was much greater than the shock front. These images and results were removed from the determined heights and widths so as to not skew the averages and standard deviations that were to be calculated. Over complete image detection occurred when the edge detection algorithm selected parts of the diffraction pattern background as an edge. Incomplete edge detection occurred for no apparent reason when inspecting the incompletely analyzed images. Incomplete and over complete edge detection likely occurs due to the automated selection of the threshold value used in the application of the Hysteresis operator. Instances of incomplete and over complete edge detection were infrequent enough that removal of these images from the analysis did not have a major impact on the calculation of average heights and widths for each delay sequence.

7.4 Shadowgraph Results

The image analysis and spectral analysis were combined to provide a description of the plasma emission processes in reference to the expansion of the shockwave. This was done by determining the geometry with which the plasma shockwave expands

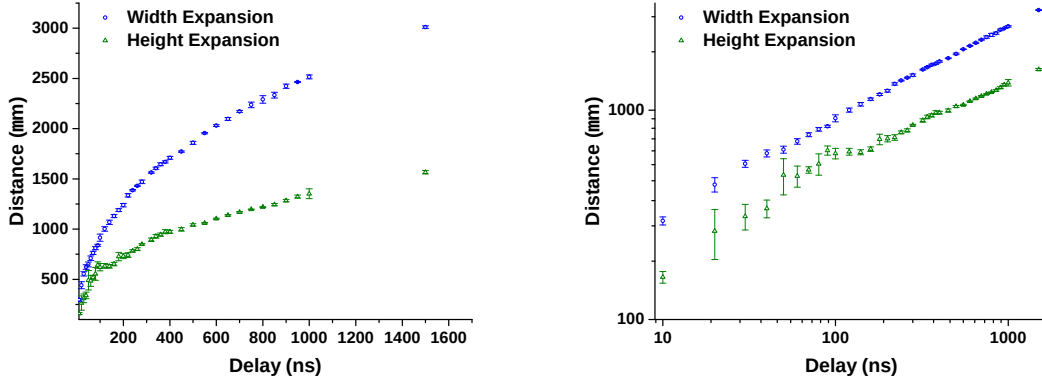


Figure 7.6: Expansion of the shock front heights and widths in linear (left) and Log-Log (right) scales

along its height and width. Each of the 21 shadowgraphs that were collected at the corresponding time delays were subjected to the described image analysis to extract the height and width of the shock front. The results of this analysis are presented in Figure 7.6 and in Table 7.1 for selected time delays. Each data point in the figure is the average of all available shadowgraphs that were collected in a given delay sequence. The error bars represent the standard deviation of all the heights and widths that were determined at each time delay. The shockwave width and heights are presented in normal and Log-Log scales in order to make changes in the rate of expansion most obvious.

Early in the plasma evolution, a strong halo due to the plasma light emissions are present in the shadowgraphs displayed in Figure 7.4. This resulted in an inflation of the heights that were determined by the image analysis program, as the halo caused a depression feature to form in the detected edge. The overall slope of these results is unchanged in the Log-Log representation of the determined heights, but does, however, cause the heights to have a larger value. This does not greatly affect the subsequent analysis, but it is important to note.

The inferred widths and heights were represented in the Log-Log scale so that any changes in the rate of expansion would become readily obvious. No such change is

Table 7.1: The shockwave height and width expansion results at selected time delays

Delay (ns)	Height (μm)	Width (μm)
10	159 ± 10	296 ± 13
20	265 ± 71	441 ± 35
30	311 ± 44	555 ± 21
40	339 ± 33	622 ± 24
50	491 ± 96	649 ± 22
60	485 ± 56	710 ± 16
70	519 ± 18	764 ± 16
80	554 ± 64	811 ± 16
90	642 ± 32	839 ± 10
100	621 ± 36	915 ± 35
120	634 ± 34	1002 ± 22
140	630 ± 17	1068 ± 21
160	652 ± 17	1130 ± 15
180	726 ± 42	1189 ± 15
200	731 ± 26	1239 ± 17
240	848 ± 7	1387 ± 7
280	894 ± 17	1471 ± 18
340	829 ± 17	1606 ± 11
400	973 ± 15	1709 ± 14
500	1042 ± 12	1859 ± 15
600	1104 ± 6	2030 ± 8
700	1168 ± 7	2172 ± 10
800	1219 ± 4	2291 ± 38
900	1283 ± 12	2422 ± 21
1000	1352 ± 48	2516 ± 19
1500	1566 ± 17	3012 ± 12

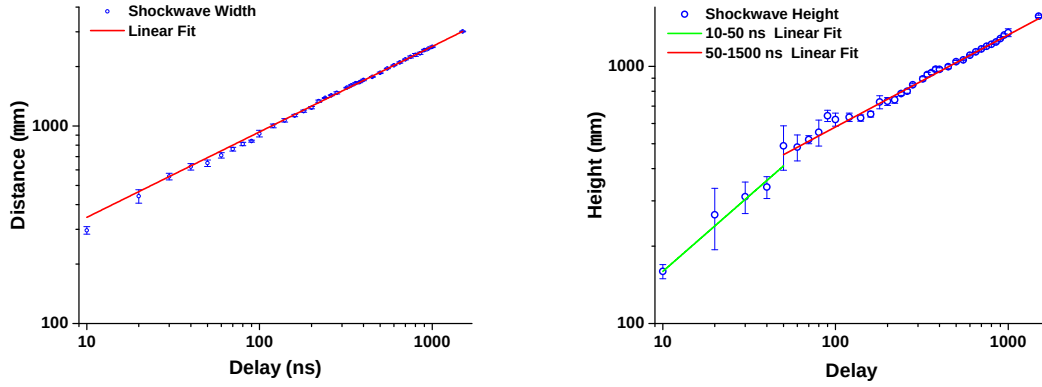


Figure 7.7: Linearized fits to extract the expansion geometries of the shock front width (left) and height (right)

easily detected in the rate of expansion of the shockwave width. Such a change in the rate of expansion is noticed in the inferred heights. This transition occurs between 50 and 70 ns. Figure 7.7 shows fits to the linearized width and shift data in an attempt to determine the geometry of the shock front expansion according to Equation 7.1. The slope of the line fit to the width data is 0.432 and the adjusted R^2 of the fit is 0.998. This slope is very nearly equal to $2/5$ and, as such, is indicative of a spherical expansion in the width of the shock front, or the direction that is perpendicular to the laser incidence.

The height expansion clearly shows two regions with differing rates of expansion. The transition between the rates of expansion is unclear due to the mentioned difficulties in accurately determining the height of the shock front. Determining the time of this transition is further made ambiguous by the presence of an outlier at the 90 ns time delay. Fitting was performed assuming that the change of the expansion rate occurred at the 50 ns time delay. The slope of the fitted line over the first 50 ns is 0.586 and the adjusted R^2 of this fit, corresponding to the green trend line in the right image of Figure 7.7, is 0.975. The determined slope of the line of the rest of the inferred heights is 0.358 and the adjusted R^2 of this fit, the red trend line in the right image of Fig. 7.7, is 0.994. The decreased goodness of fit metric as compared to the

other fits for the first 50 ns of the height data is due, in part, to the small number of data points (5 *vs.* 37) and, in part, due to the larger error bars relative to the rest of the inferred heights and widths.

These results indicate that the expansion of the shock front in the direction that is parallel to the laser incidence is planar in nature. After about 50 ns the transition occurs and the shock front geometry is approximately spherical in nature. This is consistent with the results of the expansion rate of the shockwave widths and is consistent with the Taylor-Sedov blast wave model. The change in the shockwave expansion rate along the axis of the laser incidence is due to interactions between the laser and the plasma, through which, the shock front is undoubtedly expanding through at a time delay of 50 ns. Since a nanosecond pulsed laser is used to initiate the breakdown, the plasma formation time is much less than the laser pulse duration. As such the plasma interacts with the laser pulse via an absorption of the laser energy by available free electrons. This added energy causes a more rapid expansion of the shock front.

One would expect that once the laser energy is no longer incident, the expansion rate would no longer be affected by the absorption of laser energy. Such an observation was made by Boueri *et al.*, in which the expansion of the shock front was observed following ablation of a nylon polymer target (13). Multiple laser power, wavelengths, and pulse durations were considered in that effort. Pulse energies ranged from 1 to 5 mJ. For 4 ns, 1064 nm laser radiation ablation, the so-called laser-supported detonation wave was observed, which altered the expansion geometry of the shock front in the direction of the laser incidence. The duration of this wave was seen to be dependent on the laser power and was also seen to have an effect that lasted between 10 and 30 ns. Similar results were shown following the ablation of an Al target in 1 atmosphere of ambient argon (14). The laser power that was used was 100 mJ and the duration of the elevated rate of expansion of the shock front expansion was 80 ns. The reason for the extra duration of the laser-supported detonation wave is due to non-uniformities that result from an area of increased electron density and temperature from the propagation of the

laser-supported detonation wave. The non-uniformity leads to non-isotropic spreading of the absorbed laser energy. Finally, a remark is made that no inferences on the internal plasma shockwave were made in the first 200 ns. This should be the subject of continued research.

7.5 Spectroscopic Results

Here, the plasma electron density is related to the plasma shockwave dynamics. The plasma N_e are inferred from ionic emissions in the first microsecond following plasma initiation on the Al target sample. The N_e was determined along the height of the plasma image that was focused on the spectrometer slit. The electron densities in the first microsecond following ablation were determined using two sources, the $\text{Al}^+ 3s3d \rightarrow 3s4f$ 358.7 nm line and the $\text{N}^+ 3s^22p3s \rightarrow 2s^22p3d$ 500.14 nm line. Since the plasma is dominated by the spectral continuum in the first 100 to 200 ns. The N_e from the N^+ line was inferred using the Stark width table entries found in Reference (68) while the density from the Al^+ line was inferred using the Stark widths and N_e inferred from the works completed by Fluerier *et al.* (83).

These methods refer to the use of the measured line width to extract the N_e . The line widths were determined by fitting the measured spectra to a Voigt profile, using the same procedure as outlined in Chapter 4. The Gaussian component of the line widths were taken to be the instrument width, which was determined to be 0.07 nm by way of the wavelength calibration. The extracted widths that are used in the N_e analysis are the Lorentzian component of the Voigt profile. Figures 7.8 and 7.9 show the variation of the determined N_e from both line width diagnostics at selected time delays. The green lines in Figs 7.8 and 7.9 indicate the spatially averaged electron density for that particular time delay. Spatially averaged spectra were found by summing each of the vertical tracks from the spatially resolved spectra. The values of the averages represented by the green line are presented in Table 7.2.

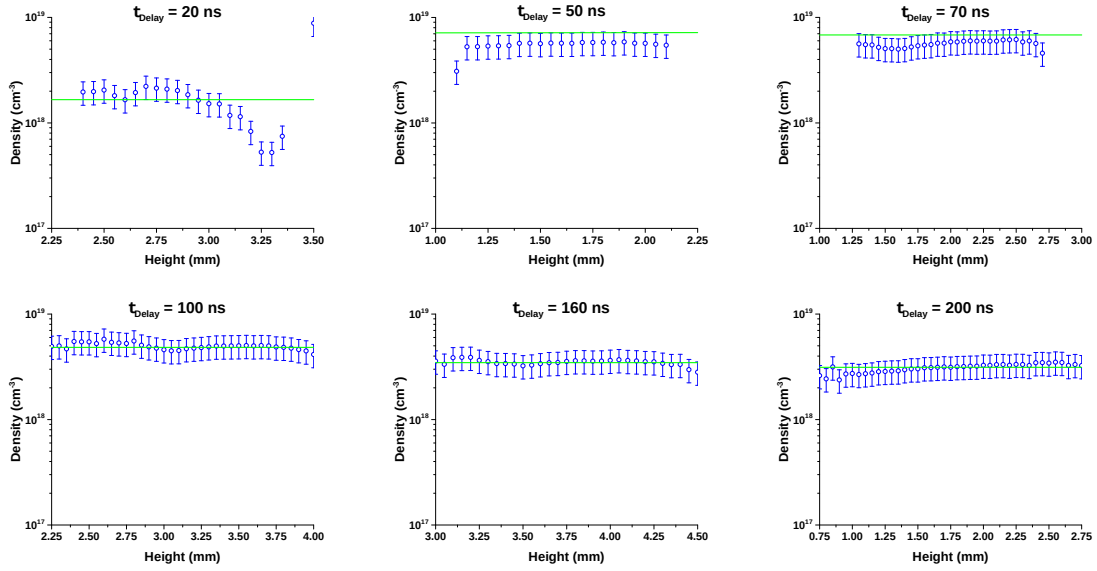


Figure 7.8: N_e inferred from the spatially resolved N^+ 500.14 nm line at selected time delays

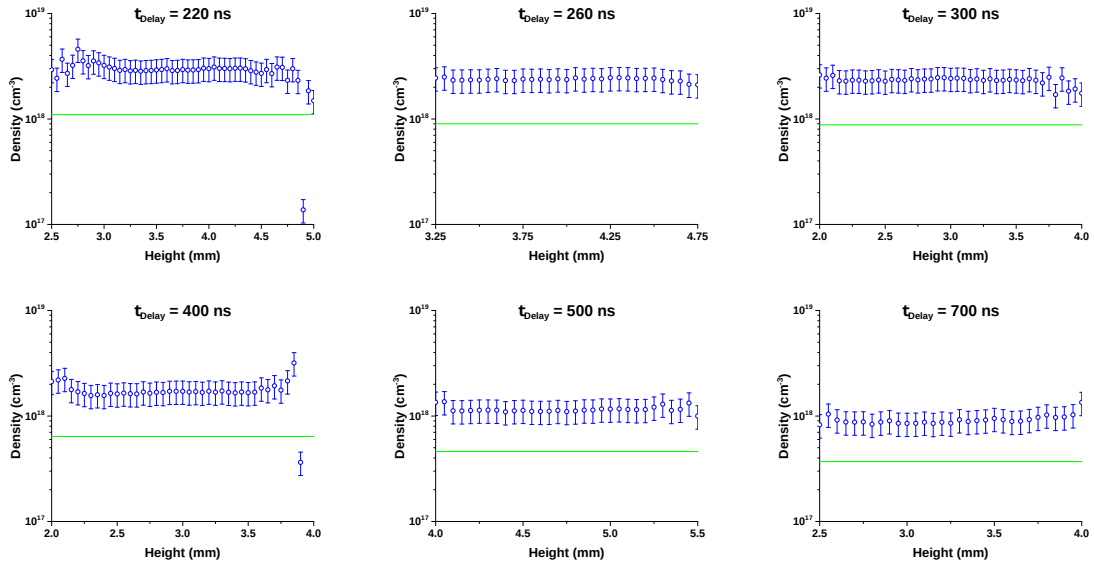


Figure 7.9: N_e inferred from the spatially resolved Al^+ 358.7 nm line at selected time delays

Table 7.2: Spatially averaged N_e calculated from N^+ and Al^+ line widths at time delays corresponding to the spatially resolved N_e results shown in Figs. 7.8 and 7.9.

Line	Delay (ns)	$N_e \times 10^{17} \text{ cm}^{-3}$	Line	Delay (ns)	$N_e \times 10^{17} \text{ cm}^{-3}$
N^+ 500.1	20	17.0 ± 4.0	Al^+ 358.7	220	11.0 ± 3.0
	50	72.0 ± 18		260	9.0 ± 2.0
	70	56.0 ± 14		300	8.8 ± 2.0
	100	48.0 ± 12		400	6.4 ± 2.0
	160	35.0 ± 9.0		500	4.6 ± 1.0
	200	31.0 ± 8.0		700	3.7 ± 1.0

The spatially resolved and spatially averaged N^+ N_e , in general, show a good agreement in the determined values. The value calculated for a time delay of 20 ns is less than the value found at 50 ns. This is due to the relative strength of the continuum at 20 ns and the fact that the spectral line is still gaining in signal intensity as more nitrogen ions are created during the plasma evolution process. Subsequent to this time, there is a characteristic decay in the N_e , which is expected to occur as the plasma expands and cools into the ambient atmosphere. The N_e found from the spatially resolved Al^+ line widths consistently underpredicts the spatially resolved values. This is likely to occur due to the fact that a narrower emission may dominate the sum of the spatially resolved data in terms of line amplitude. It is also probable that effects in the line width determination occur due to a diminished signal intensity in the spatially resolved data as compared to the spatially averaged data. The fitting program employed is also likely to infer a larger line width for a line with a relatively small peak amplitude relative to the fitted spectral background.

The spatially averaged N_e results as a function of time delay are shown in Log-Log format in Figure 7.10. The fitted lines indicate the temporal decay of the electron density. The N^+ decay shows a slope of -0.61, while the decay of the N_e inferred from the Al^+ line widths is -0.98. Differences in the decay rate may come as a result of the different species being considered. It is also possible that a change in the rate of the plasma decay occurs. This may occur after the free electron background has greatly subsided. Physically this represents a reduction in the number of electron collisions

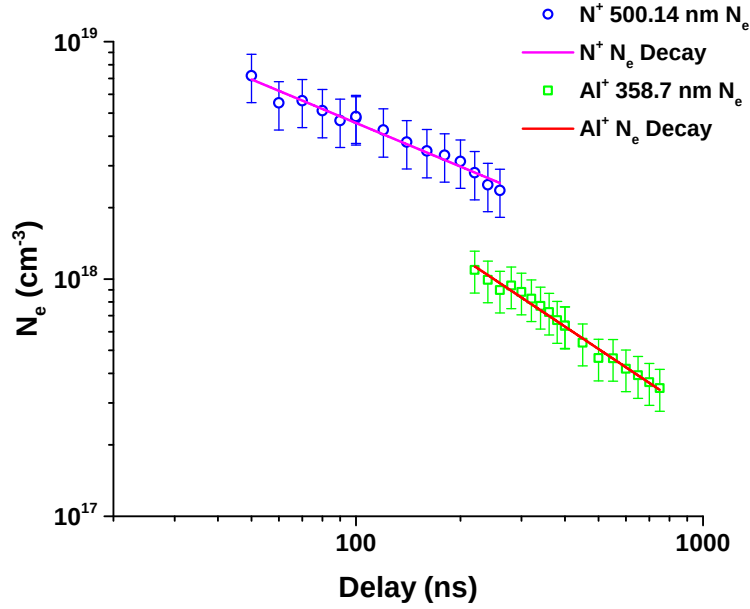


Figure 7.10: Spatially averaged N_e from the Al^+ 358.7 nm and N^+ 500.14 nm line width N_e diagnostic as a function of time delay

with atoms and ions. There is evidence for such a change in the rate to occur between 180 and 260 ns, as the tail of the $N^+ N_e$ shows a more rapid decline and the $Al^+ N_e$ shows a more gradual decline between these times.

Recall that the sample surface moved between each data set, thus the absolute scale of the heights presented in Figures 7.8 and 7.9 becomes somewhat irrelevant without any knowledge of the height that corresponds to the sample surface. Blurring due to the intensifier, binning of vertical detector pixels, and the overall magnification of the system makes determining the position of the sample surface relative to the spectrometer slit and detector rather difficult; however, an estimate of the surface position is obtainable from Figs. 7.2 and 7.3. With this knowledge and recalling that the system magnification was 1.8, inference of the N_e relative to the shock front position is possible. For this consideration the shock front heights can only be considered due to the geometry of the measurements, *i.e.*, along the slit height.

At a 20 ns delay the sample surface shows a slit height near 2.3 mm. In the spectral image plane, the shock front will be at a height of approximately 2.8 ± 0.2 mm. This height roughly corresponds to a significant decrease in the electron density that is greater than the presented error bars. As the high pressure shock front propagates through the plasma, the large pressure gradient will result in an increase in electronic collisions thus creating a higher N_e . The leading edge of the shock front is then expected to show a smaller N_e in advance of the shock front.

At a delay of 50 ns the sample surface is at a position of approximately 1.2 mm which places the shock front height approximately at 2.0 ± 0.2 mm. This is beyond the distance where the line width N_e diagnostic was usable due to signal intensity considerations relative to the continuum, although the plasma boundary is also beyond this position. This is also the case for the rest of the spatially resolved N_e results presented in Figures 7.8 and 7.9. Minor variations in the N_e are present at these times but, within consideration of the presented error bars, these variations are difficult to correspond to physical phenomena occurring within the plasma. In order for such a determination to occur, one would need to generate a much bigger plasma, which would require a greater laser energy per pulse. However, the correlation of the N_e measurements made at 20 ns shows the great importance and need to understand the plasma quantities in reference to the shock front and that these spatial variations need to be incorporated into codes that predict the radiation of plasma and high explosive events, for which laser-induced plasma may serve as a laboratory scale analog.

Chapter 8

Future Recommendations

The work on spatially and temporally resolving plasma phenomena reveals insight into the complex dynamics of the laser-induced plasma generation. This dissertation focussed on both aluminum line characteristics and the formation of aluminum monoxide molecules along with measurements of the emitted radiation. There is much yet to understand and characterize in regards to the shapes of spectroscopic lines as they emit from plasma and the time related evolution of the plasma itself. Here, continued avenues of research interest that will have an impact on the overall state of knowledge in the fields of spectral line shapes, laser-produced plasma spectroscopy, and laser-induced breakdown spectroscopy are presented.

8.1 Plasma Equilibrium Studies

Increased abilities to measure spatially resolved spectra represent an opportunity to overcome the inherent challenges presented by the inhomogeneous nature of laser-produced plasma. Plasma equilibrium has been widely studied. Relaxations in these theories have resulted in the partial local thermodynamic equilibrium studies that are currently used in calibration-free LIBS studies. The relative importance of establishing the plasma equilibrium state is wildly important as laser-produced plasma phenomena are considered for use as surrogates for high-explosive events and other large scale applications, such as stellar modeling of white dwarf stars (44). Many works on the astrophysical importance of spectroscopic investigations, including line shape studies of hydrogen and hydrogenic atomic species and, of late, molecular line shapes in absorption in reference to exoplanet research have been presented at recent meetings

of the International Conference on Spectral Line Shapes, the biannual meeting of the spectroscopic line shape community.

One such pathway to studying the equilibrium state of laser-produced plasma is through the use of so-called probing methods, such as Thompson scattering. In a Thompson scattering experiment, typically a green laser beam is incident on a target and its characteristic scattering spectrum is measured. Satellite peaks of the laser beam in the measured spectrum, due to scattering of photons and electrons, are dependent on the temperature and the density of electrons. An important advantage of the Thompson scattering method is that the temperature and N_e calculations are independent of assumptions of state population distributions used in the Boltzmann plot method and there is no requirement of an optically thin plasma.

An interesting and relatively new avenue of research along this vein is the application of simultaneous LIBS and Thompson Scattering measurements (188; 189). Comparison of the independent temperatures and N_e found by way of the Thompson scattering measurement could provide insights into the applicability of spatially resolved, optical spectroscopy measurements for the use of validations of local thermodynamic equilibrium. Such a study would not only be important for understanding the fundamentals of laser-produced plasma, but would also be important for correlations between scalings of laser-produced plasma and high explosive events and would, as well, champion the applicability of optical spectroscopy measurements of laser-produced plasma.

8.2 Spatial Deconvolutions

Continued application of spatial de-convolutions of emission spectra are of interest, particularly for laser-ablation studies. Plasma symmetry arguments are a general concern and limitation in the application of the Abel and Radon transforms for spatial plasma deconvolutions. Particularly for laser-ablation events, the inherent plasma asymmetry, due to the presence of a sample surface, requires the use of Radon

transform techniques. In the future, such methods may be considered, particularly for molecular emissions, where the spectroscopic signal intensity, $I(z, \lambda)$, might exhibit a different symmetry than the plasma itself. In such a situation, spectral measurements are made along many lines of sight at varying angles. The goal of such a study would also be to designate where the source of the emissions truly are emanating from. One could devise an experiment in which optical spectra and direct images, coupled with appropriate color filters, are measured and deconvoluted simultaneously to make correlations between the two radial distributions. The symmetrization process that was presented in Chapter 6 should also not be abandoned. Comparisons of radial reconstructed spectra, and subsequent N_e and temperature inferences, should be compared to radial reconstructed N_e and temperatures that are found along the plasma plume height. The symmetrization process showed promise for atomic emissions in laser ablation scenarios and should be considered for use of atomic emissions that are known to emanate from the ablation surface.

8.3 Integration with Plasma Emission Models

Modeling of laser-produced plasma spectral emissions and plasma qualities (temperature and electron density) requires experimental validations to appropriately model the breakdown event and model the spectral emissions. Continued measurements of laser-induced plasma following breakdown on an aluminum surface are of interest for this application. Initial interest will be in the establishment of a plasma emission model which will incorporate the plasma ionization processes resulting in the state populations of selected transitions. As well, the model should predict the electron density and the plasma temperature. Initial characterizations of the modeling results in reference to experimental results should first consider the ability of the model to predict the spectral emissions through comparisons of spectral signal changes as a function of time in the plasma evolution, for selected transitions of interest.

8.4 Advanced Line Shape Considerations

Much was made of the importance of the spectral line shape in this effort. Continued study of spectral line shapes in laser ablation plasma will allow for further insight into the plasma formation and emission processes. For example, future considerations of the line profile of non-hydrogenic emissions at N_e greater than the 10^{19} cm^{-3} should consider the quasistatic effects that will give rise to a Holtsmarkian line shape near the line center and far into the line wings. For such a study one could consider femtosecond ablation in order to achieve better coupling to the sample surface and to avoid the plasma pumping that is encountered in nanosecond ablation. The critical density of fs laser ablation is approximately $2 \times 10^{22} \text{ cm}^{-3}$ for 250 nm excitation and would allow one to investigate N_e near solid electron densities. While the H_β line is an ideal N_e diagnostic near 10^{17} cm^{-3} and H_α is preferred for N_e of the order of 10^{18} cm^{-3} , the hydrogen Lyman series could be considered for N_e near solid state electron densities.

Another ideal aluminum line choice for such a measurement in laser-induced plasma would be an isolated (few neighboring spectral lines) ion, such as the Al^+ 281.62 nm line. This line is also advantageous since it is a spin singlet for both the upper and lower transition levels, while other well studied Al ions, such as the Al^+ 358.7 nm line, have spin triplet states in either the upper or lower or both transition levels resulting in interfering spectral neighbors. The reason to use such a line is that a great amount of isolation is needed to be able to consider the line shape differences, especially far into the line wings, at distances of 3-5 times the line width from the line center. This would require the use of a pure Al target sample rather than an Al alloy target. Such a study would also present the opportunity to consider the convolutions of Lorentzian, Holtsmarkian, and Gaussian line shapes, an interesting future aspect of numerical investigations.

Also of interest, are the continued studies of self-absorbed spectral line profiles. The self-absorption profile of a spectroscopic line and its spectral line shape can be

modeled simultaneously using the escape factor method, which models the amount of radiation that is emitted by a source (190). The ability to model both profiles of the spectroscopic emission simultaneously represents an interesting opportunity to develop advanced line width determination methods for the consideration of self-absorbed line profiles.

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Appendix

Appendix A

Self-Absorption Correction Factor

In this Appendix, a summary of the derivation of the experimental correction factor used to account for self-absorption of spectroscopic emissions is presented. This derivation is not new; however, such information is vital in understanding the application of the correction factor. Further, it provides insight into the physical connection between the experimental correction factor and the optical depth, $\tau(\lambda)$, which in turn provides a sound physical interpretation of self-absorption effects.

The source of self-absorption can easily be seen through analysis of the equation of radiation transfer in its differential form, given as

$$\frac{dL(\lambda, x)}{dx} = \epsilon(\lambda, x) - \kappa(x, \lambda)L(\lambda, x) \quad (\text{A.1})$$

where $L(\lambda, x)$ is the spectral radiance (in radiometric units), $\epsilon(\lambda, x)$ is the local emission coefficient, and $\kappa(\lambda, x)$ is the absorption coefficient (given in units of $[\text{m}^{-1}]$). Here λ refers to spectral dependence and x refers to spatial dependence. If one defines the optical depth, which determines the significance of the amount of radiation transport for a given wavelength and position, as

$$d\tau = -\kappa(\lambda, x) dx \quad (\text{A.2})$$

equation [A.1](#) reduces to

$$\frac{dL(\lambda, x)}{d\tau} = L(\lambda, x) - S(\lambda, x) \quad (\text{A.3})$$

where $S(\lambda) = \epsilon(\lambda, x)/\kappa(\lambda, x)$. The x functional dependence is carried through equations [A.1](#) to [A.3](#) to indicate that initially there is no requirement that the plasma

is homogenous. In the case of a homogenous plasma, and in the optically thin ($\tau \ll 1$) condition, a solution to equation A.3 is

$$L(\lambda) = S(\lambda)(1 - e^{-\tau(-l,\lambda)}). \quad (\text{A.4})$$

In the case of a spectroscopic emission, it is noted that the absorption coefficient may be expressed as

$$\kappa(\lambda, x) = \kappa^*(\lambda, x)\mathcal{L}(\lambda, x) \quad (\text{A.5})$$

where $\kappa^*(\lambda, x)$ is the integrated absorption coefficient and $\mathcal{L}(\lambda, x)$ is the wavelength dependent line shape function corresponding to the spectroscopic emission. With this information in hand, the intensity profile of a spectroscopic emission for optically thin and homogenous emission is given as

$$L(\lambda) = \frac{A_{ul}n_uhc}{4\pi\lambda_0}\mathcal{L}(\lambda)\frac{(1 - e^{-\tau(-l,\lambda)})}{\kappa^*(\lambda)} \quad (\text{A.6})$$

where A_{ul} is the transition rate from upper state u to lower state l , n_u is the population of the upper level, h is Planck's constant, c is the speed of light, and λ_0 is the unperturbed wavelength of the resulting spectroscopic line.

Recall that the self-absorption correction factor is defined as

$$K(\lambda) = \frac{\kappa^*(\lambda)l}{1 - e^{-\tau(-l,\lambda)}} \quad (\text{A.7})$$

such that the equation for spectroscopic emission reads as

$$L(\lambda) = \frac{A_{ul}n_uhc}{4\pi\lambda_0}\mathcal{L}(\lambda)\frac{l}{K(\lambda)}. \quad (\text{A.8})$$

The experimental method for finding the correction factor is based off of comparisons between measurements made with and without a mirror used to reflect the plasma

image through itself. This ratio may be expressed as

$$R(\lambda) = \frac{L_m(\lambda)}{L(\lambda)} \quad (\text{A.9})$$

where the term with subscript m in the numerator indicates a measurement of the spectral line profile made with the reflecting mirror and the denominator indicates a measurement of the spectral line profile made without the reflecting mirror. Since $L_m(\lambda)$ is comprised of the measured profile in addition to the reflection of the measured profile, it can be written as

$$L_m(\lambda) = L(\lambda) (1 + G(\lambda)e^{-k(\lambda)l}) \quad (\text{A.10})$$

where the factor $G(\lambda)$ is used to account for the losses in the optical system from the additional lenses and the reflecting mirror. One also has to consider the ratio of the measure continuum

$$R_c(\lambda) = \frac{L_{m,c}(\lambda)}{L_c(\lambda)} = \frac{L_c(\lambda) \times (1 + G(\lambda))}{L_c(\lambda)} = 1 + G(\lambda) \quad (\text{A.11})$$

where a special point is made to indicate the wavelength dependence of the ratio of the continua due to the wavelength dependence of $G(\lambda)$. This ratio has no dependence on the absorption factor since a continuum emission, by definition, does not have atomic states to populate and, as such, is non-existent.

Expressing the factor that accounts for losses in terms of the ratio of the continua, an expression for the ratio of the emission profiles is obtained as

$$R(\lambda) = 1 + (R_c(\lambda) - 1) e^{-k(\lambda)l}, \quad (\text{A.12})$$

which, when solved for the exponential term, gives

$$e^{-k(\lambda)l} = \frac{R(\lambda) - 1}{R_c(\lambda) - 1} \quad (\text{A.13})$$

Recalling that the optical depth is defined in terms of absorption coefficients and exponentiating the above expression, the optical depth can be written as

$$\tau(\lambda) = \ln \left| \frac{R_c(\lambda) - 1}{R(\lambda) - 1} \right|. \quad (\text{A.14})$$

Substitution of this expression into the definition of $K(\lambda)$ gives the experimental correction factor used through out this work

$$K(\lambda) = \frac{\ln |y|}{y - 1} \quad (\text{A.15})$$

where y is defined as

$$y = \frac{R(\lambda) - 1}{R_c(\lambda) - 1}. \quad (\text{A.16})$$

As a final remark, consider briefly the experimental correction factor for some values of the optical depth. As has already been stated in Chapter 4, the lower limit for the experimental correction factor is 1. This corresponds to a correction factor of 1, an optical depth of 0, or $R(\lambda) = R_c(\lambda) = 1$, which has no effect or change on the line profile and there is no self-absorption, as expected for an optically thin plasma. The method fails for large values of the optical depth, or for a plasma with a high optical thickness. In this scenario, $R_c(\lambda)$ would become exceedingly large in comparison to $R(\lambda)$ making it difficult to determine and measure experimentally.

Appendix B

Experimental Calibrations

This Appendix describes the details and procedures involved with the spectral calibrations of the different experiments of this dissertation. Spectroscopic calibrations, both wavelength and intensity, are of the utmost importance in terms of obtaining numerically significant results from observed spectra and, as such, details on the procedures that were used are presented here.

B.1 Wavelength Calibration

The wavelength calibration of a spectrometer-detector arrangement is vitally important in determining the electron density from Stark widths and shifts of lines. As such, an accurate calibration of the wavelength response of the system is tantamount. There are two types of spectral wavelength calibrations. The first describes the wavelength response of the dispersive element of the spectrometer in use for a particular experimental arrangement. For a Czerny-Turner spectrometer the angular dispersion, β , between two wavelengths, λ , is given by

$$\frac{d\beta}{d\lambda} = \frac{m}{d \cos \beta} \quad (\text{B.1})$$

where $m = 1, 2, 3, \dots$, is the spectral order in which the lines are observed. The resulting linear distance, or linear dispersion, x , on a detector between wavelengths is given by

$$\frac{dx}{d\lambda} = \frac{-mf}{d \cos^3 \beta} \quad (\text{B.2})$$

where f is the focal length of the spectrometer. The previous two equations are used in computer software that communicates with the spectrometer and determines what wavelengths are viewed. However, these equations are insufficient in describing the wavelength response of the system. Equipment ages and detectors are naturally more responsive and sensitive at different wavelengths. As such, experimental corrections are needed.

The procedure that is used is based off measuring the pixel positions of spectral lines with a known wavelength response. These are typically low temperature gas discharge lamps. The general procedure is to record the pixel position of the known line and then either fit or interpolate the wavelength response from many of these measurements. In some cases, one type of lamp with one source (Ne-Ar, H, Hg *et c.*) will have many lines over the observation wavelength range, and one can use a single measurement of these lines.

In other cases, there will be too few or only one line with an available lamp in the measured spectral range. One may shift the spectrometer to different wavelength positions by a small amount to create a synthetic set of known lines from a single wavelength position. In so doing, one typically assumes that the shift in the wavelength position of the known line is linear due to the movement of the spectrometer grating. This is a safe assumption so long as the shifts in the spectrometer grating position are small (on the order of 1-3 nm) and are considered only for small spectral viewing regions (~ 25 nm). Take, for example, the H_β line at 486.15 nm. The surrounding wavelength regions are particularly barren in terms of lines from other typical gas-discharge lamps one would use in a wavelength calibration procedure. By shifting the spectrometer up and down by 2 nm from the original spectrometer position, one can obtain a set of three lines with wavelengths of 484.15, 486.15, and 488.15 nm.

In the wavelength calibration procedure used in this dissertation, spectroscopic images are recorded using the same number of bins and vertical tracks as were used to collect the original data, in order to perform a spatially dependent wavelength calibration. Horizontal grouping of pixels are calibrated independently so that a

1024×128, horizontal×vertical pixel image is calibrated such that each set of pixels, 1...1024, is mapped to its appropriate wavelength position for each of the 128 vertical bins. In order to extract the pixel positions of the peaks of the measured lamp spectra, the implicit MatLab peak finding algorithm was used to extract the peak values and their pixel locations. The wavelengths are then matched to the pixel positions and are then mapped to the correct wavelength positions by performing a cubic spline interpolation.

For the spectra collected at SNL, two gas discharge lamps were used: 1) Hg and 2) Ne-Ar. Two spectral images were recorded, one for each lamp, using the exact same procedure as with the UTSI data calibration. The two images were then normalized separately and then added to together to form a single image for the calibration procedure to be used on the wavelength range of 200-800 nm. The UTSI spectra were calibrated in a similar fashion, adding several normalized images together to form a single image; however, many smaller spectral windows were viewed. In order to calibrate these wavelengths, many different lamps were employed. These lamps, the wavelength range upon which they were applied, and the lines that were used are summarized in the Table B.1. It is important to note that, while the wavelengths and types of lamps used on the specified regions summarized in this table may apply to the use of several different spectrometer gratings, each time a different grating is used, its own calibration is performed. Specifically, on the wavelength region between 480-500 nm, AlO spectra collected using an 1800 grooves/mm grating used the same lamp and line for the wavelength calibration, but a separate calibration for this grating was performed.

B.2 Intensity Calibration

The intensity calibration corrects the intensity response of the spectrometer-detector arrangement. Several components of this system have expected responses and are made for observations in a specific range. Gratings are blazed to operate at specific angles

Table B.1: Summary of wavelength calibration lamps used on specific wavelength regions for calibration of spectra measured at UTSI

Wavelength	Lamp	Lines
650-670	Hydrogen	H $_{\alpha}$ Shift
480-500	Hydrogen	H $_{\beta}$ Shift
425-445	Hydrogen	H $_{\gamma}$ Shift
385-405	Ne-Ar	Ar 394.9 and 404.44 Shift
270-290	Hg	Hg 275.97 Shift

and are optimized for operation within a specific set of wavelengths. The photosensitive materials used in detectors and intensifiers are also targeted toward specific parts of the electromagnetic spectrum, *i.e.*, the uv, visual, near IR, mid IR *et c.*, both by design and by the physical characteristics of the materials.

The basic principle of an intensity calibration is to compare the measured intensity response of the spectrometer-detector arrangement against a calibrated light source with a known intensity response as a function of wavelength. These sources are produced by most optics related companies. There are two types of intensity calibrations: absolute and relative. In an absolute calibration, great care is taken by the manufacture to precisely measure the spectral radiance, [W/m²/sr], or spectral irradiance, [W/m²/nm], as a function of wavelength. In either case, the goal of the calibration is to tabulate a factor that is applied to the collected data. The obtained result is a calibrated data set. The general procedures of each are fairly similar, however there are some important differences that need to be distinguished. This is done by briefly explaining the procedures of both in the following subsections.

B.2.1 Relative Intensity Calibration

In a relative intensity calibration, one only requires a calibrated light source with a known intensity response as a function of the wavelength. This light source is placed such that its output is incident on the spectrometer slit and a spectrum is collected. The image will look like a spectral continuum. The recorded spectrum is then fit against the manufacturer supplied intensity response curve. This curve must be interpolated

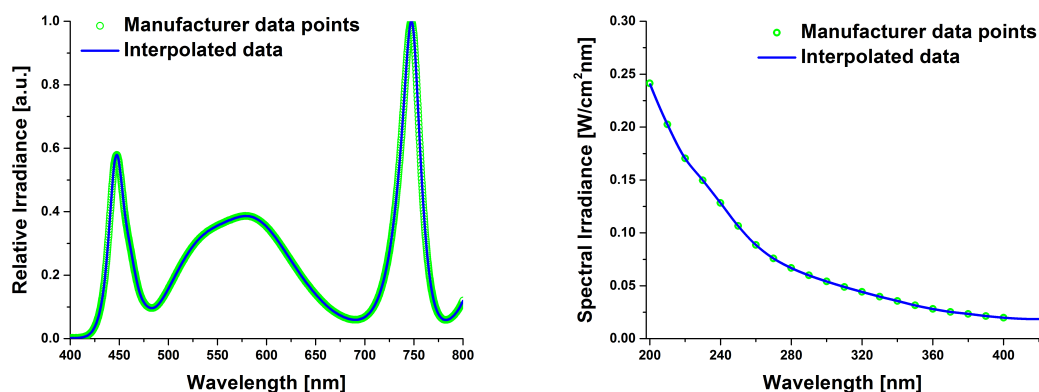


Figure B.1: Interpolated manufacturer intensity calibration lamp response curves for relative (left) and absolute (right) calibration lamps .

so that the response is known at the measured wavelengths. Figure B.1 shows sample interpolations for both a relative and absolute lamp response curves. This is required for the fitting process. The result of fitting the measured response to its known response is used to tabulate a calibration factor which describes how much the measured response differs from the expected response. This is calculated as a simple division of the measured response by the fit. This factor is then applied to the measured spectra. As with the wavelength calibration, the intensity calibration is performed for an individual spectrum along the height of a spectroscopic image and each tabulated correction factor is applied to the corresponding vertical track of the measured spectra.

An important aspect of the intensity calibration is to obtain a correction factor that is unperturbed by the measurement noise that typically accompanies a measured spectral continuum. This noise can be relatively small and may be within tolerable levels for nominal quantitative analysis of an emission spectrum; however, it needs to be corrected in the calibration procedure to reduce the propagation and increase of noise by applying a noisy correction factor to slightly noisy data. This is accomplished by aggressively smoothing the measured lamp response. In many instances, this requires multiple applications of a Savitsky-Golay filter (177) with a window size that may range from 101 to 501 points in length.

B.2.2 Absolute Intensity Calibration

The general procedure of an absolute calibration is similar in nature to the relative calibration. The lamp response is measured, is appropriately smoothed, and fit to determine a calibration factor. The units of the lamp determine the relative difficulty of the absolute calibration. For a lamp that has a standard calibration for its spectral radiance, $[\text{W}/\text{cm}^2/\text{nm}/\text{sr}]$, the calibration is quite difficult to perform since one needs to consider the unit area through which the lamp is emitting. This response is required to be known exactly on the optical path that is being calibrated, which is the path from the laser ablation site to the spectrometer slit. This can be measured through the use of an integrating sphere. In the case of a lamp that is calibrated for its spectral irradiance output, $[\text{W}/\text{cm}^2/\text{nm}]$, the calibration is easier since there is no inherent directionality to the spectral irradiance. All that is required is that the lamp have its output placed at the laser ablation site. For a proper calibration, the output must be as perpendicular as possible to the line-of-sight along the optical path to the spectrometer slit. One must also account for the distance at which the lamp's known response is calibrated and the actual distance of the optical path. The decrease in signal intensity is subject to the so-called inverse square law, where by the intensity of light emissions decreases by one over the square root of the distance from the radiating object.

In this work, the absolute calibration that is performed made use of a spectral irradiance calibrated lamp with a response that is calibrated for 30 cm of distance from the emission source. The optical path length where the absolute calibration was applied (selected SNL measurements) was 91 cm. The inverse square law was applied to the manufacturer response curve and this result was used to calculate the correction factor; however, rather than using a fitting procedure a direct calculation of the factor was completed using the measured response and the supplied known lamp response, while still interpolating the known response at the measured wavelengths. In order for the absolute calibration to be completed correctly, a fitting procedure should not be

used since this will alter the units of the known response through inclusion of fitting parameters, *i.e.*, amplitudes and offsets.

The final result is a measured spectrum with units of spectral irradiance, $[\text{W}/\text{cm}^2/\text{nm}]$, rather than the so-called arbitrary units, [a.u.], of the relative calibration. The method employed in both intensity calibration processes determines a factor which describes the ratio of calibrated units to measured photons by the intensified detectors. One could also determine a correction factor that is given simply by taking the difference between the known response and measured response to find an additive calibration factor (191). Both the additive and multiplicative calibration factors are equal in the ability to calibrate the intensity response, however, the multiplicative factor is the preferred usage in this dissertation due to its more intuitive nature, in that it relates the number of measured photons to an associated unit through a ratio consideration. The accuracy of the absolute intensity calibration is approximately 14%. This was found by considering the accuracy of the calibration lamp, which was approximately 3%, as given by the manufacturer, and the accuracy in the ability to measure a signal intensity, which was estimated to be 10%. These values were used with standard error propagation calculations.

Finally, a remark is made on the timing resolution of the calibration procedures. The emitting sources for the wavelength, relative, and absolute intensity calibrations are constant over long periods of time, so long as each lamp is given about a half hour of warm up time before making a measurement so that the lamp can reach a steady state of operation. The steady state applies to the voltage that is being supplied from the wall outlet through the internal circuitry of the lamp. Since all the lamps that were used in the calibration procedures (wavelength and intensity) were held constant, the time resolution of the measurement is somewhat irrelevant, especially in terms of the delay at which the measurement takes place since the lamp is always on for the purposes of calibration. Rather, timing is utilized to produce a high quality signal. This is done by using long gate exposures, typically on the order of milliseconds.

Appendix C

Spatial Deconvolution Methods

This Appendix is devoted to presenting the details of the symmetrization process that is applied to the spatially resolved signal intensity along the plasma z -axis, or plasma plume height, that is in turn used to calculate the radial signal intensity. This method is applied to the Abel transform, which, recall is given by

$$I(z, \lambda) = 2 \int_r^R \frac{I(r, \lambda) dr}{\sqrt{r^2 + z^2}} \quad (\text{C.1})$$

where the quantity $I(z, \lambda)$ is taken to be the measured signal intensity along the axis of the laser incidence and $I(r, \lambda)$ is the determined radial intensity distribution. The vertically resolved data is to be measured at discrete positions separated by some distance δ . The upper limit of the integral, R , should be taken to be much greater than the vertical separation, δ .

Inversion of the Abel transform to find the radial intensity distribution relies on the differentiation of the vertical signal intensity. This process typically introduces quite a bit of noise and error into the deconvolved, radial intensity. In general, spectra are also rather difficult to differentiate. This may be overcome by the use of a complete orthogonal set of polynomials, which are minimized to find expansion coefficients of a series expanded, radial intensity (192). The expansion is given as

$$I(r, \lambda) = \sum_{n=0}^N A_n I_n(r, \lambda) \quad (\text{C.2})$$

where the function $I_n(r, \lambda)$ is given by

$$I_n(r, \lambda) = 1 - (-1)^n \cos\left(n\pi \frac{r}{R}\right) \quad (\text{C.3})$$

and the first series term is given by

$$I_0(r, \lambda) = 1. \quad (\text{C.4})$$

Such a procedure allows one to perform Abel inversion over measured spectra without the need to apply a smoothing filter, which can alter any line profile considerations. This also reduces errors of the inversion results to just a few percent for selected, well behaved spectral line profiles (181).

The Abel inversions are calculated using a formalized MatLab script (193). This code implements the series expansions given above, which are Chebychev polynomials of the first kind. Using a least squares fitting, the expansion coefficients are determined and the radial intensity distribution is reconstructed. The number of terms to be included in the expansion, N , is determined by the user. Including more in the expansion will lead to a higher level of introduced noise in the radial reconstruction. Using too few terms will result in a poorly reconstructed spectrum. For a balance of reconstruction quality to signal noise addition, a series length of $N = 10$ is recommended and applied in this work.

A major challenge in the application of the Abel inversion to vertically resolved intensity profiles in laser-induced plasma is the argument of signal intensity symmetry. For air breakdown plasma and for selected regions localized to the target surface in laser ablation plasma, these symmetry arguments can be relaxed. The ablation plasma is inherently asymmetric due to the presence of a target surface. Other asymmetries may arise due to a poor quality of the laser beam shape being used for breakdown initiation and plasma shielding effects during the optical breakdown process.

These asymmetries may be relaxed such that top and bottom sections of such a plasma may show symmetry; but, the top and bottom sections are allowed to show slightly different symmetries from each other. A procedure for dealing with such cases with inductively coupled plasma has been previously presented and developed (180). Under such a procedure a symmetrizing profile is created through a weighted average procedure in which the average of the two symmetry regions is considered as

$$I_0(z, \lambda) = \frac{I(z, \lambda) - I(-z, \lambda)}{2} \quad (\text{C.5})$$

where $z = 0$ represents the meeting of top and bottom plasma symmetry regions. The plasma asymmetry intensity profile coefficients are then given by

$$G(\pm z, \lambda) = \frac{I(\pm z, \lambda)}{I_0(z, \lambda)}. \quad (\text{C.6})$$

Asymmetric Abel inverted radial profiles are then tabulated from

$$I(r, \pm z, \lambda) = G(\pm z, \lambda) I_0(r, \lambda) \quad (\text{C.7})$$

where $I_0(r, \lambda)$ is the Abel inversion of $I_0(z, \lambda)$. This method can be used to extract subtle differences that may arise due slight asymmetries in the determined plasma quantities, such as the N_e and the temperature.

Appendix D

Faddeeva Function

In this Appendix, the proof that the well known Voigt integral is equivalent to the real part of the Faddeeva function is provided. For complex arguments, $z = x + iy$, the Faddeeva function is defined in terms of the complex complementary error function as

$$w(z) = z^2 \text{erfc}(-iz) \quad (\text{D.1})$$

and may be expressed as

$$w(x, y) = w(x + iy) = \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{e^{t^2} dt}{x + iy - t} \quad (\text{D.2})$$

where the expression for the complex complementary error function has been substituted into the Faddeeva function. This expression can be algebraically manipulated to be expressed as

$$w(x, y) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2} dt}{y - i(x - t)}. \quad (\text{D.3})$$

Removing the complex component of the denominator by complex conjugation yields

$$w(x, y) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2} (y + i(x - t)) dt}{y^2 - (x - t)^2} \quad (\text{D.4})$$

which can be expressed in Real and Imaginary components as

$$w(x, y) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{ye^{-t^2} dt}{y^2 - (x - t)^2} + \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{(x - t)e^{-t^2} dt}{y^2 - (x - t)^2}. \quad (\text{D.5})$$

The Faddeeva function is now of the form

$$w(x, y) = V(x, y) + iU(x, y) \quad (\text{D.6})$$

where $V(x, y)$ is the real expression of Equation D.5 and $iU(x, y)$ is the imaginary expression from D.5. Analysis of the real part of Eq. D.5 gives the expression for the Voigt function integral in general form as

$$V(x, y) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{ye^{-t^2} dt}{y^2 - (x - t)^2}, \quad (\text{D.7})$$

where the appropriate substations for x and y , as given in Chapter 2, must be applied to convolve Gaussian and Lorentzian line profiles into a Voigt profile.

Appendix E

Programming

Programming in this dissertation is based off efficient use of the so-called Matrix Laboratory, or MatLab, workspace. This is because of its wide use throughout the scientific industry and thus makes for ease in computing results and communicating the methods by which they were arrived at. For the sake of efficiency, many small functions that have a single purpose are written, rather than create one long analysis program that would do every thing all at once. These small functions are then called as needed, similar to the way library functions are used in C and Fortran, except there is the significant memory load associated with using the MatLab interface. Efficient programming in MatLab is necessary in order to receive a timely result when programming with this scripting language, although, there are many advantages of using MatLab. Two are the ease with which it handles matrices and vectors and the large number of available, pre-built analysis functions. The disadvantages are as already alluded to. MatLab has a large memory usage compared to C and Fortran and other scripting languages, such as Python. In order to make the best use of MatLab's advantages, vectorizing programs whenever possible is recommended. MatLab can do array, component by component multiplication without ever having to use a loop structure. Another method of increasing performance with MatLab is to use functions and assign as few internal and output variables as possible to these functions during execution. Functions are preferred over programs since the functions only store their outputs to memory and only temporarily store intermediate values to memory, making them more fluid and quicker to execute.

Work is completed from the MatLab command line when it comes time to process data. This is done by always loading data to the MatLab workspace with the file name

and data attached to the same index. The following listing is used to load data into the MatLab work space, all from the same directory, with the same file extension.

```
1 % fileload.m
2 %
3 % Loads files from an entire directory of the same file extension ...
   into a
4 % cell array that is stored in matlab workspace. Also Stores file ...
   names for
5 % later use.
6 % inputs:  x - string containing file extension, e.g. '*.txt'
7 % outputs: dat    - cell array containing data
8 %          fname - cell array of file names
9 %
10 % David M. Surmick, 04-14-2016
11
12 function [dat, fname]=fileload(x)
13 dummy=dir(x);
14 fname={dummy.name};
15 dat=cell(length(fname),1);
16 for i=1:length(fname)
17     dat{i}=load(fname{i});
18 end
```

The input for this function is a string containing the file extension. Once the data is loaded into the MatLab it is easy to loop functions over entire spectroscopic images and store the results in the function outputs. The function outputs can then either be stored as *.mat* files, which are binary files in which the MatLab variable work space is stored, or the outputs can be written to Ascii files as necessary using the *dlmwrite* command, a MatLab internal function which writes data to a file with a fixed file delimiter type. The rest of this Appendix is devoted to three instances of MatLab programming that illustrate the above methods: 1) the intensity calibration program,

2) the Voigt fitting program, and 3) an implementation of a Nelder-Mead fitting routine for diatomic spectral analysis.

E.1 Intensity Calibration Program

While the methods of performing the wavelength calibration are rather intuitive and simple to implement, the methods and reasoning behind an intensity calibration represents a difficulty for most new comers in the world of spectroscopy. For this reason, the programmatic implementation of the intensity calibration is elaborated upon. Details about the calibration process are already contained in Appendix B. The intensity calibration is accomplished by fitting a measured source to its expected response. The intensity calibration implementation is rather simple. Wavelength and intensity data is read as a functional input and is simply fit to the expected response. In the case shown below, the response is a manufacturer supplied data response curve. This curve needs to be interpolated so that the response is known at the wavelength points in the experimental spectrum, which also coincide with the measured calibration curve data. This is fed to the function as an input.

The function calls a fitting sub-function to achieve the fitting, which is a MatLab requirement to perform non-linear curve fitting using internal MatLab fitting functions. The function then calculates the fit to the expected response. This fit is used to generate the factor by which the experimental data needs to be multiplied in order to match the expected response. These two calculations are the outputs of the function. The output factor is then easily applied to the experimental data through MatLab's implicit array multiplication through the command line input. Below is the intensity calibration code that was used.

```
1 % OcOptLampFit.m
2 %
3 % Caluclates intensity calibration factors by fitting to manufacturer
```

```

4 % supplied calibration lamp response curves.
5 % inputs - wl      - n x 1 array for calibrated wavelengths
6 %           dat     - n x 1 array for calibration data set
7 %           intcal  - n x 1 array for manufacturer response curve
8 % outputs - factor - n x 1 array of calibration factors
9 %           fit     - n x 1 array of fit used to calculate cal factors
10 % Sub-functions: OcOptFit
11 %
12 % David M. Surmick, 3-15-2016
13
14 function [factor,f]=OcOptLampFit(wl,dat,intcal)
15
16 global y
17 y=intcal;
18
19 % Normalize Data Inputs
20 dat=dat/max(dat);
21 intcal=intcal/max(intcal);
22
23 % Make data set greater than 0
24 if min(dat) < 0
25     dat=dat+abs(min(dat));
26 else
27     dat=dat;
28 end
29
30 % Fitting
31 theta=[1 1];
32 lb=[-Inf 0];
33 ub=[Inf Inf];
34
35 [vals, ~, residual, ~, ~, ~, jacobian]= ...
    lsqcurvefit(@OcOptFit,theta,...
36                                     wl,dat,lb,ub);

```

```

37
38 f=vals(1)+vals(2)*intcal;
39 factor=f./dat;
40
41 % R^2
42 SSRes=sum((dat-f).^2);
43 SSTot=(length(f)-1)*var(f);
44 Rsq=1-(SSRes/SSTot);
45 RsqAd=1-(1-Rsq)*((length(f)-1)/(length(f)-length(vals)-1))
46
47 STDEV=std(residual);
48 J=inv(transpose(jacobian)*jacobian);
49 sigma=((STDEV)^2)*J;
50 SE=sqrt(diag(sigma));
51 errs=full(SE);
52
53 [vals' errs]
54
55 figure
56 plot(wl,f,wl,dat,wl,factor)
57 end
58
59 function F=OcOptFit(p,x)
60 global y
61
62 F=p(1)+p(2)*y+0*x;
63
64 end

```

E.2 Voigt Fitting Program

The program used to perform Voigt fitting is included in this Appendix due to the highly fundamental nature the fitting process plays in many aspects of the analysis

methods presented throughout this dissertation. Both the determination of the electron density and the temperature inferred from the atomic and ionic emissions relies on the results of the fitting process. As described in Chapter 4, the Faddeeva function is used to calculate the Voigt profiles in this work. The implementation of this calculation uses the Algorithm 916 method (140). The attached reference for this algorithm also comes with a published MatLab implementation for calculation of the Faddeeva function. For this reason, a description of its exact implementation is omitted in the Appendix.

The Voigt fitting function is mostly designed with a purpose of fitting, rather than a profile calculation and fitting purpose. Again, this function works off of data that has been pre-loaded into the MatLab workspace. Specifically, the inputs are two arrays. One contains the experimental wavelengths and the other is the measured spectrum. These data are then normalized to a maximum peak intensity of 100 arbitrary units prior to fitting. This is done in an effort to speed up the fitting process by making the parameter initializations uniform for each instance of fitting in an entire image and minimize the amount of distance these parameters need to traverse before reaching their optimized values.

Fitting is achieved by using MatLab's *lsqcurvefit* command, which is a nonlinear fitting routine that defaults to the previously described Trust-Region algorithm from Chapter 4. In similar fashion to all of MatLab's pre-built fitting routines, one must create a fitting function to pass inputs into the fitting routine. This is done using the sub-function *doubleVFit*. This function calculates the Voigt profile. The inputs of this function are an array p and an array x . The array x is the experimental wavelengths at which the spectra were measured and p contains the parameters that are iteratively optimized by the MatLab fitting routine. This function is iteratively called by the fitting routine until the optimized parameters are found. The fitting parameters are a linear offset, in addition to the amplitude, width, and shift of each line that is being fit. Each of these parameters are initialized with a value of one.

The fitting function calls the routines that calculate the Voigt profile from the Faddeeva function. These are *voigt1*, *Faddeyeva*, and *FaddeyevaDriver*. The latter two

programs are the published routines that calculate the Faddeeva function. The *voigt1* function calculates the real component of the Faddeeva function and alters the input of the function, which are the experimental wavelength and the regular Voigt profile parameters: Lorentzian and Gaussian line width parameters, the line shift, the line center, and line amplitude. The line centers and Gaussian line widths are known prior to fitting. These are fed to the rest of the sub-functions in the program through the use of global parameters.

After the fit has been performed, the program fashions the fitted output. The input wavelength and spectrum as well as the total and individual fitted profiles for each line and fitted offset are stored in the *profile* matrix and are the first output of the function. The other outputs are the fitted parameters and the associated errors. An optional output is a constructed table showing these results in tabular form. This table is also output to the command line, whether or not it is called as a function output. The errors and the adjusted R^2 value, which is used as the goodness of fit metric, are calculated using standard least squares approaches. These methods make use of the Jacobian matrix used in the Trust-Region optimization method.

The linear baseline offset is included as a fit parameter because it is far more difficult to estimate the baseline of a data set and then subtract the background than it is to incorporate this into the fit. It also produces fitted line shape parameters that have an implicit method for quantifying the error in the fitted results via the goodness of fit metric. If one were to subtract a background and then fit, there would be no way to know the effect this had on a determined line width without subtracting many different, slightly varied backgrounds and then doing a statistical analysis on the fitted results. In the fitting method, many backgrounds are optimized until a correct one is found, in which all the parameters are minimized. Computationally and organizationally, this is much more easily accomplished than a statistical analysis of many background subtractions. Shown below is an example of one of the Voigt fitting routines. This particular code was used to fit Al 394.4 and 396.15 nm spectra simultaneously. In this

case, a sum of two Voigt profiles, one for each Al line, and linear baseline offset are calculated in the *doubleVFit* function.

```

1 % doublevoigtfit.m
2 %
3 % Fits summation of two voigt profiles to spectra. Voigt profiles are
4 % calculated using fadeeva function.
5 % inputs: x      - matrix of wavelengths for fitting
6 %          dat    - matrix of spectra to be fit
7 % outputs: profile - matrix of fitted profiles
8 %          results - fit parameter results
9 %          err     - fit parameter errors
10 %          tab     - table of fit parameters and errors
11 % Sub-functions: doubleVFit, voigt1, Faddeyeva, Faddeyeva_driver
12 %
13 % David M. Surmick, 04-06-2016
14
15 function [profile, results, errs1, OUT] = doublevoigtfit(x,dat)
16
17 % Global Variables
18 global shift x01 x02 wg;
19 shift=min(x);
20 x01=394.4;
21 x02=396.15;
22 wg=0.061;
23
24 % Normalize Data
25 dat=(dat/max(dat))*100;
26
27 % Fitting
28 theta=ones(1,8);
29 lb=zeros(1,length(theta)); % lower bound is zero
30 ub=zeros(1,length(theta));

```

```

31 for i=1:length(theta) % upper bound is Infinity
32     lb(1,i)=0;
33     ub(1,i)=Inf;
34 end
35 lb(1,1)=-Inf;
36
37 ub(1,4)=5; % shift bounds
38 ub(1,7)=5;
39
40 xs=x-shift; % Shift Origin
41
42 [vals, ~, residual, ~, ~, ~, jacobian]= ...
    lsqcurvefit(@doubleVFit,theta,xs,dat,lb,ub);
43 y = doubleVFit(vals,xs);
44 bkg = vals(1)+vals(2)*xs;
45
46 p1=bkg+voigt1(xs,xol-shift,wg,vals(3),vals(4),vals(5));
47 p2=bkg+voigt1(xs,xol-shift,wg,vals(6),vals(7),vals(8));
48
49 profile=[x dat y bkg p1 p2];
50
51 % R^2 Calculation
52 SSRes=sum((dat-y).^2);
53 SSTot=(length(y)-1)*var(y);
54 Rsq=1-(SSRes/SSTot)
55 RsqAd=1-(1-Rsq)*((length(y)-1)/(length(y)-length(vals)-1))
56
57 figure
58 plot(x,dat,'.',x,y,x,bkg)
59
60 % Parameter Error Calculation
61 STDEV=std(residual);
62 jac=jacobian;
63 J=inv(transpose(jacobian)*jacobian);

```

```

64 sigma=((STDEV)^2)*J;
65 SE=sqrt(diag(sigma));
66 errs=full(SE);
67 errs1=[0;errs];
68
69 results=[RsqaAd;vals']; % print table of results to screen
70 params = {'RsqaAd';'Offset:','Slope:','Amplitude 1:','Shift 1:',' ...
           Lor Width 1:','...
           'Amplitude 2:','Shift 2:',' Lor Width 2:'};
71
72 OUT=table(results,errs1,'RowNames',params)
73
74 end
75
76 % 5 Parameter Lorentzian Fit Function with Origin Shift
77 function F = doubleVFit(p,x)
78 global shift xo1 xo2 wg;
79 xo11=xo1-shift;
80 xo22=xo2-shift;
81 F = p(1)+(p(2)*x)+voigt1(x,xo11,wg,p(3),p(4),p(5))+...
82     voigt1(x,xo11,wg,p(6),p(7),p(8));
83 end
84
85 function [z] = voigt1(a,xo,wg,amp,d,wl)
86
87 % converting to dimensionless coordinates
88 x=2*sqrt(log(2)).*(a-(xo+d))./(wg);
89 y=sqrt(log(2)).*(wl/wg);
90
91 w=Faddeyeva(x+1i*y);
92 z=amp*sqrt(log(2)/pi)/wg.*real(w);
93
94 end

```

E.3 MatLab NMT Fitting

In this section, the specifics associated with implementation the NMT fitting routines in the MatLab scripting language and details associated with the statistical error analysis are discussed. The basics of the NMT program is that converts tables of diatomic line strengths into theoretical diatomic, molecular spectra for a specific temperature and spectral resolution. The theoretical spectrum is then fit to experimentally measured spectra by leaving the temperature, linear baseline offset, the spectral resolution as fit parameters. Fitting is accomplished using the described Nelder-Mead algorithm from Chapter 6.

The MatLab implementation of this code is based heavily upon the codes developed by Jim Hornkohl at the University of Tennessee Space Institute. While his Fortran implementations lack a user friendly graphical interface, the programming of the codes is designed for speed and transparency. Some speed may given up in the MatLab implementation, but the ability to repeatability call the program from the MatLab command line makes for a greater ability in varied program inputs in terms of quickness of repetition. Furthermore, programming speed and memory consumption costs due to the MatLab environment can be made up by using intrinsic MatLab vectorization and its built-in Nelder-Mead fitting routine, *fminsearch*, to avoid run away fitting scenarios in which the Nelder-Mead chooses extreme fit parameters. The remaining sections of this Appendix describe various sections of the NMT codes that are implemented in MatLab. The code listing is supplied at the very end of this Appendix. For the sake of transparency, any MatLab code that has been described in text and not in the listings supplied with this Appendix is type set using *italics* to differentiate from the surrounding text.

E.3.1 MatLab NMT

The implementation of the MatLab NMT is heavily based on codes that have already been implemented in Fortran 90 and Visual Basic programming languages. The

advantage of designing a MatLab implantation is due to increased use of MatLab throughout the scientific community. The basics of the program are to fit input spectra to theoretically calculated spectra using the line strength files published in (120). To speed up the program, the published line strength files need to be reduced to contain only the essential parts required for calculation of diatomic spectra. These values are the line strength, the energy term value of the upper state, and the vacuum wavenumber of the transition.

The entire AIO analysis is carried in the program *NMTbatchprocess.m*. The code contains several subfunctions that perform specific tasks in the program to speed up calculations and to aid in the transparency of the programming. The program works by finding all the lines in the reduced line strength file that are within the spectral regions defined by the minimum and maximum wavelengths of the experimental spectrum and then assigns these lines a Gaussian profile. The total theoretical spectrum is taken to be the sum over all these profiles. The subfunction *SynthSpec* is used to complete these tasks and adds the background to the spectrum.

The subfunction *NMT* is tasked with completing the Nelder-Mead fitting. It passes arguments to the *SynthSpec* function to tabulate the theory spectra for fitting, including the baseline offset parameter. *NMT* calls one two subfunctions to define the theory spectrum that is to be fit: *FitSpec*, used to fit only the temperature and linear baseline offset, or *FitSpec1*, used to fit the temperature, linear baseline offset, and line FWHM. This is due to the way in which the intrinsic MatLab fitting functions are designed. Due to restrictions on the inputs to these fitting functions, global parameters needed to be invoked so that variables could be fed to different sub-functions of the total program.

The sub-function *NMTErr* is used to perform the error analysis of the fitted results by iteratively fitting the spectra for different parameters 1000 times. These methods are described in further detail in the next section. The function *NMTbatchprocess* is used to loop the entire Nelder-Mead temperature determination and error analysis over an entire ICCD image and stores the outputs in MatLab cell arrays that contain the fitted diatomic profiles, the error analysis temperatures, the resulting temperature

with error bars, the varied baselines, and the varied FWHM. The main section of the program submits the subfunction *NMTWrapper* to be computed in parallel. It submits the code, tells the program to wait until the the entire batch command has completed, collects the results, and saves the results in summary files.

The inputs of the program are a matrix containing all the wavelengths, a separate matrix containing all the experimental spectra, the number of iterations to be used in the error analysis, the lowest and highest tracks in an images to fit, and the file name of the image being analyzed. This file name is used to generate the file names for the summary files so that every analysis or results file carries a similar file name to its original experimental file. The outputs of the *NMTbatchprocess* function are the same as *NMTWrapper*. The *NMTbatprocess* function was designed to be called from the MatLab command line and as such requires that the data already be loaded into the MatLab workspace.

E.3.2 Error Analysis

The error analysis is based off the Monte Carlo type simulations that were described in Chapter 6. Here a few details on its implementation are provided. The error analysis provides a statistical distribution of 1002 temperature results. The first step to perfrom the initial fit. Then a fit is performed in which the temperature and FWHM are varied. Then 1000 fits are performed over 1000 random baseline offsets and 1000 random spectral resolutions. The baseline is allowed to vary between 25% of the initial inferred value and the spectral resolution is allowed to vary by 50% from the experimentally known value. The FWHM parameter is fixed during these 1000 fitting iterations. The initial temperature fit and the temperature that was fit by varying the FWHM parameter are also included in the error analysis to get to the total of 1002 temperatures.

The error is inferred by assigning a normal distribution results and using the 68.3-95.5-99 rule for normal distributions to find the 1, 2, and 3- σ errors in the temperature

results (177). This is completed by counting the number of temperatures that are within the given percentages of the initial temperature fit. The error is then taken to be the average of the difference between the highest and lowest values on the 1, 2, and 3- σ intervals.

E.3.3 Parallel Computing in MatLab

In order to more efficiently compute the error analysis of the AIO temperature results, it was necessary to use parallel computing to simultaneously run multiple fitting iterations of the NMT error analysis. Converting code to be able run in parallel is usually a non-trivial task which requires a large amount of time to specifically program which iterations will run on which computer nodes of a given cluster. This also requires knowledge of the cluster that is to be used for a specific calculation. In MatLab, this challenge is automatically alleviated by the scripting language nature of the MatLab software. It comes with pre-packaged parallel commands that automatically farm out segments of code to cluster nodes. The most common of these commands is *parfor*, which executes MatLab *for* loops (equivalent to Fortran *DO* loops) in parallel. Since different iterations of the loop will run on a different node, the order of the iterations is not necessarily going to be that which is specified by the iteration number, *i.e.*, loop iteration 4 can be executed before loop iteration 2. The *parfor* command requires that the loop iterations do not depend on any other iteration of the loop. While this is not ideal for solving partial differential equations numerically by use of any kind of finite difference method, it is useful for repeating calculations with different inputs for each repetition.

MatLab parallelization is also easily run on a local computer with multiple physical processors or nodes, as well as on remote cluster. All that needs to be known is the name of the cluster the code will be run. Running MatLab parallel on the local machine is conveniently given the name as the *local* cluster. All calculations were run using the *local* cluster. There are two ways to use MatLab parallel computing abilities:

1) through use of the *parpool* command or 2) through the use of the *batch* command. The *parpool* command is the simpler of the two and can be used more interactively to see command line and function outputs. It simply initiates a parallel session on the specified cluster. One then executes MatLab programming nominally, except for the use of other MatLab parallel commands. After the desired calculations it is proper procedure to close the MatLab parallel session so as to not waste computer resources.

The *batch* command is slightly more elegant in the potential number of implementations and is also slightly more difficult to learn and make proper use of for efficient programming. In MatLab *batch*, one creates a job file which is submitted to the cluster. The job then sits in a queue and waits to be executed in turn. The user typically generates a program to be executed on the cluster which manages the job submission, retrieves the results of the batch job, post processes the results, and then saves any necessary outputs. The advantage of using *batch* is that the code runs continuously in the background of the local machine and only uses as much of the local computer resources as are needed and are currently available. When run on a non-local cluster, the user maintains access to the local MatLab console and can even shut down the local machine. Reliable connections are only needed when submitting the job and retrieving the results.

Other more advanced commands are also available for use in MatLab parallelization. These allow the user control over which processes are sent to certain cluster nodes and provide other methods of executing code in parallel that may not necessarily be executed in a *parfor* loop. An example is the *spmd*, which stands for *Single Program Multiple Data*, and allows for code to execute in parallel. MatLab also allows for segmented arrays, such that data arrays can be split and submitted to a different processor node, analysis can be performed on each node in parallel, and a result array is reconstructed from the separated data array. In the *NMTbatchprocess* function, only *parfor* executions are utilized. This was done in an effort to keep the code as simple as possible when building the programs. Value was placed on transparency rather than efficiency. The *NMTbatchprocess* function, should work continue along a similar vein

of research, should be optimized and should also consider optimization for use on a non-local computing environment. The following is the complete Nelder-Mead fitting analysis program.

```

1  % NMTbatchprocess.m
2  %
3  % Batchprocess NMTErr fitting using MatLab parallel using the batch()
4  % implementation. Program works on a whole ICCD image. Can be ...
    looped over
5  % a sequence of images.
6  % inputs:  x      - Experimental wavelengths (matrix)
7  %          y      - Experimental spectra (matrix)
8  %          iter   - # of iterations in error analysis
9  %          Nmin   - highest track position to fit
10 %          Nmax   - lowest image track position to fit
11 %          fname  - file name of image
12 % outputs: same as NMTErr.m
13 %
14 % David M. Surmick, 5-9-2016
15
16 function [I,T,res,blo,fwhm] = ...
    NMTbatchprocess(x,y,iter,Nmin,Nmax,fname)
17 tic % start batch program timer
18
19 % batch process in parallel
20 clust=parcluster('local');
21 N=5;
22 job=batch(clust,@NMTWrapper,5,{x,y,iter,Nmin,Nmax},'Pool',N);
23
24 % get batch results
25 wait(job, 'finished')
26 diary(job) % print commandline outputs
27 results=fetchOutputs(job); % get results

```

```

28 I=results{1};
29 T=results{2};
30 res=results{3};
31 blo=results{4};
32 fwhm=results{5};
33
34 % write results to summary files
35 fnames=regexprep(fname, '-pre.txt', '');
36 a=num2str(Nmin);
37 b=num2str(Nmax);
38 fnames1=strcat(fnames, '-', a, '-', b);
39 save(strcat('results\', fnames1, 'results.mat')...
40 , 'I', 'res', 'blo', 'fwhm', '-v7.3')
41 save(strcat('results\', fnames1, '-Temps.mat'), ...
42      'T', '-v7.3')
43 q=Nmax-Nmin+1;
44 r=Nmin-1;
45 for i=1:q
46     h(i)=(i+r)*2*25)/1000;
47     A(i,1)=h(i);
48     A(i,2)=res{i}(1);
49     A(i,3)=res{i}(2);
50     A(i,4)=res{i}(6);
51 end
52 dlmwrite(strcat('results\', fnames, 'Temps.txt'), ...
53         A, 'delimiter', '\t', 'precision', 16, 'newline', 'pc')
54
55 delete(job) % remove job from MatLab queue
56
57 toc % end batch process timer
58
59 end
60
61 % NMTWrapper.m

```

```

62 function [I,T,res,blo,fwhm]=NMTWrapper(x,y,z,n,m)
63
64 % adjust itteration loop indices based off of n (lowest fit track)
65 % and m (highest fit track)
66 q=m-n+1;
67 r=n-1;
68
69 %pre-allocate result outputs
70 I=cell((m-n+1),1);
71 T=cell((m-n+1),1);
72 res=cell((m-n+1),1);
73 blo=cell((m-n+1),1);
74 fwhm=cell((m-n+1),1);
75 for i=1:q
76     I{i}=zeros(z+2,4);
77     T{i}=zeros(z+2,1);
78     res{i}=zeros(1,8);
79     blo{i}=zeros(length(x),z);
80     fwhm{i}=zeros(z,1);
81 end
82
83 % cal NMTErr for fitting and error analysis
84 parfor i=n:m
85     [I{i-r},T{i-r},res{i-r},blo{i-r},fwhm{i-r}]=NMTErr(x(:,i),y(:,i),z);
86 end
87
88 end
89
90 % NMTErr.m
91 function [I,Temps,res,blo,fwhm] = NMTErr (x,y,iter)
92
93 tic % start function timer
94
95 % initialize temperature and profile output arrays

```

```

96 Temps=zeros(iter+2,1);
97 I=cell(iter+2,1);
98 for i=1:iter+2
99     I{i}=zeros(length(x),4);
100 end
101
102 % initial fit
103 fwhm=0.1;
104 Ti=3000;
105 [I{1}(:, :), v]=NMT(x, y, fwhm, Ti, 1e-6, 'ALO-LSF.txt', 1);
106 Temps(1,1)=v(3);
107 bloi=v(1)+x*v(2); % fitted offset
108 T=v(3);
109
110 % varried fwhm fit
111 [I{end}(:, :), v]=NMT(x, y, fwhm, Ti, 1e-6, 'ALO-LSF.txt', 2);
112 Temps(end,1)=v(4);
113
114 % make random fhwm and base line offsets
115 blo=zeros(length(x),iter);
116 a=fwhm-fwhm/2;
117 b=fwhm+fwhm/2;
118 fwhm1=(a)+(b-a).*rand(iter,1);
119 for j=1:iter
120     for i=1:length(bloi)
121         blo(i,j)=(bloi(i)-0.25*bloi(i))+((bloi(i)...
122             +0.25*bloi(i))-(bloi(i)-0.25*bloi(i))).*rand(1,1);
123     end
124 end
125
126 % fit for temp iter times using random fhwm and base line offset
127 parfor i=1:iter
128     yi=y+blo(:,i);
129     [I{i+1}(:, :), v]=NMT(x, yi, fwhm1(i), Ti, 1e8, 'ALO-LSF.txt', 1);

```

```

130     Temps(i+1,1)=v(3);
131 end
132
133 % calculate temperature error bar
134 % 1-sigma errors
135 Td=Temps;
136 s1=round(0.6827*iter,0);
137 s2=round(0.9545*iter,0);
138 s3=round(0.9973*iter,0);
139 dummy=zeros(s1,1);
140 for i=1:s1
141     [~,b]=min(abs(Td-T));
142     dummy(i)=Td(b);
143     Td(b)=2*max(Td);
144 end
145 T1=sum(dummy)/length(dummy);
146 sig1=(abs((max(dummy)-T1))+abs((T1-min(dummy))))/2;
147
148 % 2-sigma errors
149 Td=Temps;
150 dummy=zeros(s2,1);
151 for i=1:s2
152     [~,b]=min(abs(Td-T));
153     dummy(i)=Td(b);
154     Td(b)=2*max(Td);
155 end
156 T2=sum(dummy)/length(dummy);
157 sig2=(abs((max(dummy)-T2))+abs((T2-min(dummy))))/2;
158
159 % 3-sigma errors
160 Td=Temps;
161 dummy=zeros(s3,1);
162 for i=1:s3
163     [~,b]=min(abs(Td-T));

```

```

164     dummy(i)=Td(b);
165     Td(b)=2*max(Td);
166 end
167 T3=sum(dummy)/length(dummy);
168 sig3=(abs((max(dummy)-T3))+abs((T3-min(dummy))))/2;
169
170 Tavg=sum(Temps)/(iter+2);
171 res=[T Tavg T1 T2 T3 sig1 sig2 sig3];
172
173 toc % end function timer
174
175 end
176
177 % NMT.m
178 function [profile,vals] = NMT (WL_exp,Dat,FWHM,T,tol,x,FIT)
179
180 % global variables
181 global bFac gFac WLk Tuk TuMin Sk n0 nSpec fwhm delWL temp wl_max;
182
183 % constants in mks units
184 h=6.62606957e-34;
185 c=2.99792458e8;
186 kb=1.3806488e-23;
187 bFac=(100*h*c)/kb; % Boltzmann factor in cgs units
188 gFac=2*sqrt(log(2));
189 nSpec=length(Dat);
190 temp=T;
191 fwhm=FWHM;
192
193 % get fitting range
194 wl_min=min(WL_exp);
195 wl_max=max(WL_exp);
196 delWL=(wl_max-wl_min)/(nSpec);
197

```

```

198 % read MatLab LSF file
199 [p]=load(x);
200 WN=p(:,1);
201 Tu=p(:,2);
202 S=p(:,3);
203
204 % convert vacuum wavenumber to air wavelength
205 a0=2.72643e-4;
206 a1=1.2288;
207 a2=3.555e4;
208 r=1+a0+(a1./(WN.*WN))+(a2./(WN.*WN.*WN.*WN));
209 WL=1e7./(r.*WN);
210
211 % get LSF table wavelengths in experimental range
212 A=find(WL>wl_min & WL<wl_max);
213 WLk=WL(A);
214
215 % get Term Values and LineStrengths at WLk
216 Sk=S(A);
217 Tuk=Tu(A);
218 TuMin=min(Tuk);
219
220 % get experimenal wavelength position that most closely matches Line
221 % Strength Table wavelength
222 n0=zeros(length(WLk),1);
223 for i=1:length(WLk)
224     [~,n0(i)]=min(abs(WL_exp-WLk(i)));
225 end
226
227 % Fitting
228 options=optimset('TolX',tol,'MaxIter',1e8,'MaxFunEvals',1e8); % ...
    Nelder Mead Paramters
229 switch FIT
230     case 1 % fit offset, temperature

```

```

231     theta=ones(3,1);
232     theta(3)=T; % temperature seed
233     vals=fminsearch(@(x) FitSpec(x,WL_exp,Dat),theta,options);
234     bkg=vals(1)+vals(2)*WL_exp; % calculate fitted offset
235     [I,bkg1]=SynthSpec(WL_exp,vals(3),FWHM,Dat,bkg); % ...
        calculate fit
236     case 2 % fit offset, fwhm, temperature
237         theta=ones(4,1);
238         theta(3)=FWHM; % fwhm seed
239         theta(4)=T; % temperature seed
240         vals=fminsearch(@(x) FitSpec1(x,WL_exp,Dat),theta,options);
241         bkg=vals(1)+vals(2)*WL_exp; % calculate fitted offset
242         [I,bkg1]=SynthSpec(WL_exp,vals(4),vals(3),Dat,bkg); % ...
            calculate fit
243     end
244     profile=[WL_exp Dat I bkg1];
245
246     end % main function
247
248     % temperature, offset fit function
249     function [err] = FitSpec (p,WL_exp,Dat)
250
251     global fwhm
252
253     bkg=p(1)+p(2)*WL_exp;
254     [F,-]=SynthSpec(WL_exp,p(3),fwhm,Dat,bkg);
255     c=F\Dat;
256     z=F*c;
257     err=norm(z-Dat);
258
259     end % fit spec
260
261     % temperature, fwhm, offset fit function
262     function [err] = FitSpec1 (p,WL_exp,Dat)

```

```

263
264 bkg=p(1)+p(2)*WL_exp;
265 [F,-]=SynthSpec(WL_exp,p(4),p(3),Dat,bkg);
266 c=F\Dat;
267 z=F*c;
268 err=norm(z-Dat);
269
270 end % fit spec 1
271
272 % calculate synthetic spectrum for fit
273 function [I1,bkg1] = SynthSpec (WL_exp,T,FWHM,Dat,bkg)
274
275 global bFac gFac WLk Tuk TuMin Sk n0 nSpec delWL wl_max ;
276
277 FWHMk=(FWHM*WLk)/wl_max; % wavelength dependent FWHM
278
279 % Calculate Peak Intensities
280 peak=20-4*log(WLk)+log(Sk)-(bFac/T)*(Tuk-TuMin);
281 peak_k=exp(peaks);
282
283 % calculate syntehtic spectrum
284 I=zeros(nSpec,1); % initialize synthetic spectrum output
285 for i=1:length(WLk)
286     deln=round(2.5*FWHMk(i)/delWL,0);
287     nMin=n0(i)-deln;
288     if nMin < 1
289         nMin=1;
290     end
291     nMax=n0(i)+deln;
292     if nMax > nSpec
293         nMax=nSpec;
294     end
295     for j=nMin:nMax
296         u=abs(gFac*(WLk(i)-WL_exp(j))/FWHMk(i));

```

```

297         I(j)=I(j)+peak_k(i)*exp(-u*u);
298     end
299 end % synthetic spectrum loop
300
301 % normailze data to measured spectrum
302 I=I/max(I);
303 I=I+bkg;
304 sxy=sum(Dat.*I);
305 syy=sum(I.*I);
306 nf= sxy/syy;
307 I1=I*nf;
308 bkg1=bkg*nf;
309
310 end % SynthSpec

```

Vita

David Michael Surmick was born to Cathy and John Surmick on February sixth, 1990 in Reading, PA. David has two sisters, Rachael, his twin, and Janine. He graduated from Exeter Township Senior School in 2008. David went on to study physics at Lycoming College and in 2012 he graduated with a Bachelor of Arts in Astronomy and a Bachelor of Science in Physics with departmental honors while also completing an honors thesis. In September of that year, David accepted a Graduate Research Assistant position working for Dr. Christian Parigger at the Center for Laser Applications at the University of Tennessee Space Institute. In August 2014 David earned his Master's of Science degree while working for Dr. Parigger. He spent two summers in 2013 and 2014 interning at Sandia National Laboratories in the Fire Sciences department working for Walt Gill and Burl Donaldson while working on flame emission spectroscopy experiments. In January of 2016 David began working at Sandia National Laboratories as a year round intern in the Optoelectronics department, working for Daryl Dagel on laser ablation experiments David finished his doctoral dissertation in August 2016.