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CHARACTERIZATION AND ANALYSIS OF BALL PLASMOID DISCHARGES

BY

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DISSERTATION

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Abstract

Ball plasmoid discharges are uniquely long-lived plasmas that are generated by a pulse of several kiloJoules of stored energy over the surface of a grounded volume of water. The plasmoid has a visible lifetime on the order of a few hundred milliseconds, part of which appears to persist without power input. Predictions of the recombination time of ball plasmoids using air plasma models dictate that the system should dissipate within a millisecond—this discrepancy indicates that there is likely some unexplained mechanism (physical, chemical, or otherwise) by which ball plasmoids are stabilized. The search for this potential mechanism has motivated the work described in this thesis for the past several years.

Ball plasmoid discharges are considered to be laboratory analogues of ball lightning, a naturally-occurring and still unexplained phenomenon. To date, ball lightning has not been reproduced in the laboratory, therefore studies aimed at explaining the formation and lifetime of ball lightning must rely on laboratory analogues. Like ball plasmoids, the reported lifetime of ball lightning (seconds) is several orders of magnitude longer than what would be expected at atmospheric pressure. An understanding of the mechanism(s) responsible for the long lifetime of ball plasmoids could perhaps provide insight into the stability of ball lightning.

To gain a comprehensive understanding of the chemistry that occurs during a ball plasmoid discharge, several techniques were implemented to analyze various physico-chemical properties of the plasmoid. Experiments using mass spectrometry, emission spectroscopy, microwave interferometry, and electrical analyses in ambient air and other gases are described throughout this thesis. The combination of these results furthers our understanding of the composition of these plasmoids. We have identified the major ions present in the plasmoid and have shown through statistical analysis of water clusters that the electrolyte contributes to the formation more than the ambient environment. Emission spectroscopy reveals emission from a wide variety of molecular and atomic species, including OH and NH radicals, H_α , H_β , O I, N I, W I, Cu I, Fe I, Cu II, and Fe II, and facilitates a deeper discussion of molecular excitation and dissociation processes than has been presented to date in the literature. Finally, preliminary measurements of plasmoid discharges in argon indicate that the resistance of the plasmoid is significantly different in a rare-gas atmosphere compared to

ambient air.

While this work does not answer all of the questions surrounding the stability of ball plasmoids, unexplored avenues of experimentation and analysis were investigated at higher energies than previously reported. Results inferred from these experiments provide a foundation from which further studies of this system can be undertaken.

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Chapter 1

Introduction

The primary motivation for the work presented in this dissertation is the search for a physico-chemical mechanism by which ball plasmoid discharges are stabilized. The chapters that follow describe experiments which were designed to probe different components of the discharge, all with the end goal of gaining a more thorough chemical understanding of the system. The diagnostics used for these analyses were performed independently from one another and are described as such. Each individual chapter contains its own introductory material, experimental description, and interpretation of results. This introductory chapter serves to provide additional context for the results described in Chapters 2-4, a more general description of the current state of understanding of ball plasmoid discharges, and brief overviews of the experimental methodologies used in this work.

With this structure, it was also appropriate to include a Chapter which discusses the combined results of the previous Chapters to provide context and to facilitate a broader discussion of the chemistry and physics of the discharge. Furthermore, a set of experiments are described and a small set of preliminary data are included to provide a foundation from which the next iteration of this experiment can begin.

1.1 Plasmas

Plasmas comprise 99.9% of the observable universe, and plasma is often referred to as the fourth state of matter. This medium results from the breakdown and partial ionization of air or other gas, which makes the gaseous environment partially conductive. First described by Lamgmuir in the early 20th century [1], plasmas have been used as tools across several industries, particularly the semiconductor processing industry, and they remain a highly active area of both fundamental and applied research. Plasmas occur naturally on Earth in forms such as aurorae, lightning, and flames, but the majority of plasma in the universe is found in space. The stars and the space between them are both comprised of plasma, albeit with entirely different properties. In the laboratory, plasmas are generated in many different configurations using various techniques. Plasmas are generally characterized by their temperature, degree of ionization, density, power deposition, or operating

pressure (Figure 1.1). Furthermore, plasmas can be generated using direct-current (DC) sources (which include glow, corona, and nanosecond square-wave discharges), AC sources with frequencies ranging from several tens of Hz (fluorescent lighting) to tens of MHz (plasma etching), microwaves, pulsed lasers, and shock tubes, to name only a few.

There are two general regimes concerning plasma discharges and plasma science, namely non-equilibrium (non-thermal) and equilibrium (thermal) plasmas. Thermal plasmas are those which result from high energy input and therefore have a fairly large (10^{-2} -unity) degree of ionization. In thermal plasmas such as lightning or arc discharges, the energy (temperature) of the electrons, ions, and neutrals (background gas) are equal. Conversely, non-equilibrium plasmas have a considerably smaller degree of ionization (10^{-6} - 10^{-2}) and the electrons carry the majority of the energy. Since “heavy particles” are several orders of magnitude heavier than electrons, the velocity distribution of the electrons in the plasma drives the chemistry and physics of the discharge. Additionally, since energy transfer between electrons and heavy particles is inefficient for inelastic collisions, the temperature of the background gas stays relatively low. Thus, these plasmas are referred to as low-temperature plasmas (LTPs) or cold plasmas.

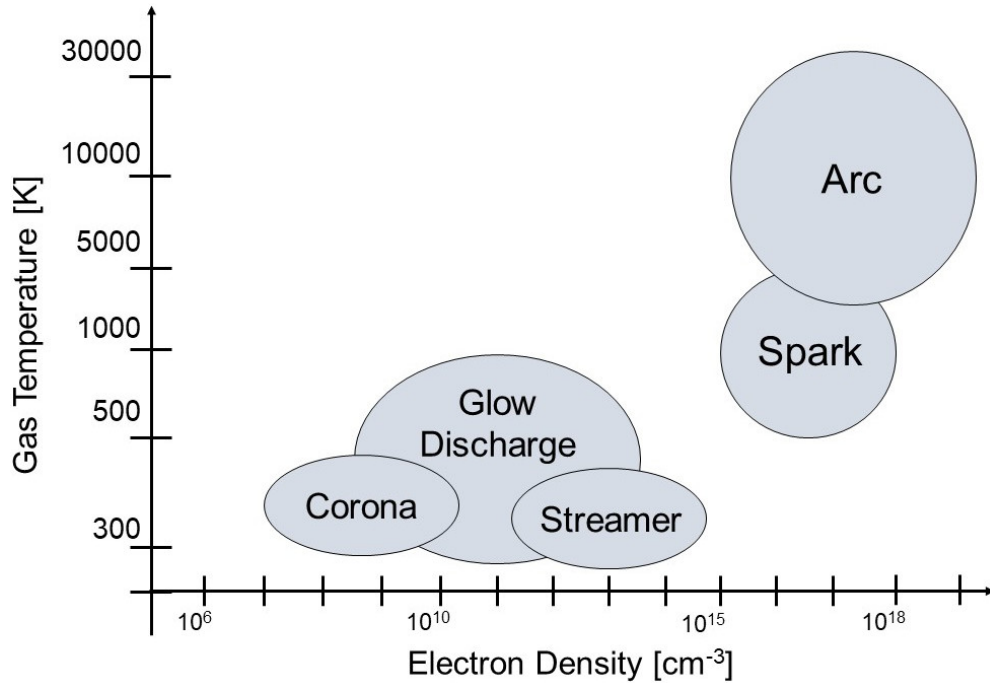


Figure 1.1: Figure illustrating several types of plasma categorized by gas temperature and electron density. Data for figure collected from [2–4].

Plasmas contain ions, free electrons, and excited neutral atoms and molecules. Each of the components of the plasma participate in several processes, each of which influences the bulk properties and behavior of

the plasma. Energetic free electrons in the plasma drive ion production via ionization by electron impact, and low-energy electrons participate in excitation and scattering processes. Ions and electrons participate in charge-exchange collisions and recombination processes, and also carry the majority of the current through the plasma. Excited atoms and molecules participate in a myriad of chemical reactions during the lifetime of the discharge, which span several orders of magnitude in time. Furthermore, there are several timescales on which important plasma processes occur, for example, elastic collisions of electrons with atoms and molecules take place in nanoseconds, while chemical reactions can occur on millisecond or second timescales [4]. The behavior of a plasma is highly dependent on the velocity distribution of its free electrons, namely the plasma’s electron energy distribution function (EEDF), the electric and magnetic field fields present, and the pressure and temperature of the background gas.

1.1.1 Plasmas vs. Plasmoids

Plasmoids are an interesting subset of plasma; after they are generated, plasmoids eventually detach from the electrodes which provide power. Plasmoids are defined as “plasma-magnetic entities”– plasmas which have structure/shape, but are not confined to any electrodes. Plasmoids were first reported in the 1950’s [5] and are generally spherical or toroidal in shape. Plasmoids present additional challenges in the realm of plasma diagnostics in that it is difficult to fully describe the temporal behavior of the EEDF and the (numerous) physico-chemical processes occurring in the plasmoid. Additionally, though fluid mechanics and diffusion are important to understand for traditional plasma diagnostics, the flow of plasma species between the ionized medium and surrounding environment must be understood to fully describe a plasmoid as it relaxes to equilibrium. In other words, it is much easier to study systems which are tethered to electrodes at reduced pressure and which produce a well-defined electric field, compared to a highly-dynamic partially-ionized cloud which is floating through ambient air.

1.2 Ball Plasmoid Discharges

Ball plasmoids are uniquely long-lived plasma discharges at atmospheric pressure which are generated by discharging energy stored in a capacitor bank over a liquid surface. Ball plasmoids were first generated in the laboratory in 2002 by a pair of Russian physicists [6], and after this first publication, several other groups replicated these experiments [7–15]. Much of the initial interest in this type of plasma discharge was due to claims that this plasmoid was an example of ball lightning created in a laboratory setting. Ball lightning, which will be described briefly below, is a natural phenomenon that has eluded scientific understanding

and explanation for many years. This section describes the current state of understanding of ball plasmoid discharges and expands on what information must be collected to gain a comprehensive understanding of the system.

Several groups have described the production and analysis of ball plasmoid discharges in their respective laboratories [6–17]. Each of these groups uses the same general technique to generate the discharge, however, there are some subtleties in electrode construction, for example, that result in slightly different results for each version of the experiment. Differences that become important for physical interpretation of experimental results are discussed in Chapter 4. While none of the results described herein contradict the results reported by other groups, our interpretations of these results do suggest additional chemistry not yet reported in the literature and the importance of electrode geometry on the electrical properties of the discharge.

Prior to the inception of the current version of this experiment, the most detailed analysis of ball plasmoid discharges was described by Versteegh et al. [9] (and in the Master’s Thesis from which this article was produced). To summarize this work, a series of general physical measurements were performed to determine the background gas temperature in the plasmoid, and they also used probes to measure the space-charge density across the lifetime of the plasmoid. Emission spectroscopy was also performed to identify emitting species and to estimate the number density of electrons in the discharge. A collisional radiative model (CRM) for calcium (a major impurity present in their electrolyte) was also constructed and compared with emission data.

While this work was extremely beneficial in guiding our experiments, there are some points mentioned in [9] with which this author does not necessarily agree or thinks must be explained in greater detail. The first is the description of the electron temperature. In [9], the authors claim that the electron temperature can “hardly exceed 1 eV”, and that “the electron temperature decreases from around 5000 K at the beginning [of the discharge] to approximately 3000 K at 75 ms.” While this description can provide an estimate for a “single-point” electron temperature, it does not provide a description of the EEDF, which is a more complete physical description of the free electrons in the plasma. In low-temperature plasma physics it is well known that electron distribution functions can deviate from a Maxwellian population, and the high-energy “tail” of this non-equilibrium EEDF becomes extremely important for production of ions and excited neutral species in LTPs. As of this writing, no detailed description of the EEDF for ball plasmoid discharges has been reported.

The second point of contention is the reported electron number density. In [9] the electron number density is determined using the well-known Stark broadening technique applied to several atomic emission lines. The values that are reported for the electron density are quite high (10^{14} - 10^{16} cm $^{-3}$) during the early times of

the discharge, and this author is skeptical of densities that large, for two reasons. First, at atmospheric conditions, the average lifetime of a free electron in a plasma is on the order of 10 ns [18] (determined by the rate of three-body attachment). Second, the power density required to sustain a density of electrons that large is likely several orders of magnitude larger than the power density of the plasmoids described in this work. Furthermore, it is likely that there is a gradient in electron density as a function of distance from the electrodes— without high spatial resolution, there is no discrimination between regions of high and low density, which would in turn effect the calculated electron density.

While perfectly acceptable to make assumptions to make data analysis more straightforward, one key assumption that may have been made in error is that self-absorption of emitted photons from the center of the plasmoid was neglected. This becomes particularly important for Stark broadening analysis, for example; without all broadening mechanisms accounted for, the effect of the electric field induced by free electrons may be over-estimated. Data are presented in Chapter 4 which suggest that self-absorption occurs when photons are emitted from excited atomic species in the plasmoid. In [9], the authors also rely primarily on broadening of the H_β line, which is the weaker of the two transitions of hydrogen reported in their work by a factor of approx. 16 (determined by a ratio of f-values [19]). The emission signals recorded around 486 nm are quite broad and do not have a large S/N, which would (in this author’s opinion) lead to questionable fits. Finally, the figure which reports the electron density results shows error bars which span several orders of magnitude and are obscured by a legend in some cases, which brings the validity of these results into question.

The combination of the several factors presented above motivated repeating some of the measurements reported in [9] to test their validity and to extend the analyses performed in that work. The experiments described in the following chapters were performed at higher energies than previously reported, which facilitates more power deposition to the plasmoid. Furthermore, these measurements were performed without any additional electrolyte added to the cathode; this was previously thought to be integral to ball plasmoid formation [6]. At ambient conditions, water vapor can collisionally quench atomic and molecular excited states produced during the discharge, therefore, minimizing the amount of water vapor present in the plasmoid allowed for additional excited states to be identified. In the following section, the experiments and instruments used to perform these measurements will be summarized.

1.2.1 Plasma Diagnostics and Their Application to Ball Plasmoids

There are many techniques and instruments that one can use to measure different components of a plasma, and for the sake of brevity, not all of them will be described here. Ball plasmoid discharges are also unique

in that many traditional plasma diagnostic techniques would not be effective or would take a tremendous amount of effort to gain only a small amount of information. For example, the current gold standard for measuring electron density and behavior in a plasma is the Langmuir probe. A probe of this type is essentially a wire (or pair of wires) to which a known potential is applied, and that probe is inserted into the plasma volume. This in turn forms a sheath at the surface of the wire, and can be used to measure the potential, electron density, and electron temperature of the plasma. However, there are several issues with a technique of this type, the foremost being that it is an intrusive technique. We did not want to introduce any additional components into the plasmoid that could promote the formation of additional plasma sheaths during the discharge. Furthermore, the current-voltage characteristics of each Langmuir probe must be known in detail to extract meaningful information from the technique. Thus, minimally- or non-intrusive techniques were implemented to study ball plasmoid discharges.

Physical and Electrical Properties

In addition to the use of various instrumentation, measurements of the electrical profiles are performed to understand the behavior of the discharge circuit and the factors that effect plasmoid formation. Current and voltage profiles are collected for every plasmoid discharge, and these data are then used to calculate the resistance and power change across the lifetime of a plasmoid discharge. Time constants (i.e., RC constants) are determined for each of these data sets by fitting the profiles to exponential functions; this analysis has revealed that our electrode construction facilitates two dynamic processes, namely spark channel formation and cathode jet formation. We have also empirically determined the potential at which cathode jet production (and therefore plasmoid formation) occurs. Furthermore, the change in resistance during a discharge is attributed to conductivity changes in the plasmoid, either as a result of decreasing electron density or by the rapidly-changing size of the plasmoid

The gaseous environment in which the plasmoid is formed was also adjusted in a set of experiments to examine the changes of the electrical profile as a result of the background gas. The background gas determines much of the chemistry that occurs during a plasma discharge, for example, discharges in oxygen readily form anions at atmospheric pressure to due (three-body) electron attachment processes and readily form ozone. Oxygen is also a good quencher of excited states; minimizing the oxygen concentration in the plasmoid's environment is likely to change the chemistry associated with the discharge. Ball plasmoid discharges in pure nitrogen and pure argon environments are described in Appendix A.

Charged Species

To probe the ionic composition of the plasmoid, an ambient mass spectrometry technique was used. Mass spectrometry (MS) relies on measuring the mass-to-charge (m/z) ratios of ions present in a sample. In short, ions are generated from a sample of interest using one of many ionization techniques, and these ions are then accelerated toward a detector using a series of high-voltage lenses. Along their trajectory, ions are separated by their m/z values either by passing through a mass filter (e.g., a quadrupole) which applies an RF field to the packet of ions, or by their transit time across a certain length. Figure 1.2 shows a simplified diagram of a mass spectrometer similar to this description. Over the past few decades ambient ionization and sampling techniques have become much more prevalent and have allowed much more complicated systems to be analyzed. This was advantageous to the atmospheric plasma community—spatially-resolved number densities of ions in air plasmas and at plasma-surface interfaces have been needed to both understand fundamental processes and to improve current models of these systems. Other techniques can be challenging to implement in these plasma systems, for example, cavity-enhanced methods may be necessary to overcome the low density of ions relative to neutrals in the plasma if using absorption spectroscopy, for example.

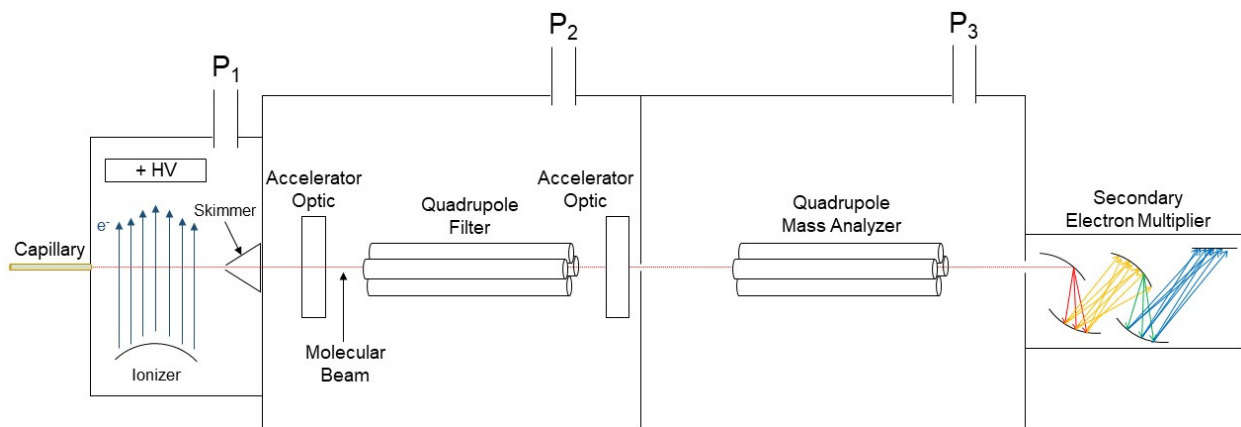


Figure 1.2: An example of a typical configuration of a mass spectrometer operating at atmospheric pressure. This particular schematic represents a “molecular beam” instrument. P_1 - P_3 represent differential pumping stages of the instrument to reach $\sim 10^{-7}$ - 10^{-8} Torr at the detector. A secondary electron multiplier is used as the detector for this instrument.

For this experiment, a commercial high-performance instrument with a custom sampling interface was utilized. No additional ionization was performed in this analysis; ions that were produced by the discharge were sampled directly from the interior of the plasmoid. These experiments produced results which identify the types of ions produced during the discharge and allowed us to show (via statistical analysis of deuterated water clusters) that the electrolyte composition directly effects the chemistry of the plasmoid. There were a

few drawbacks using this technique, however— the balance between measurement speed and mass resolution was tipped toward mass resolution, so only a few mass spectra were collected across the lifetime of the discharge. Additional MS experiments (perhaps with better time and spatial resolution) could be performed on ball plasmoid discharges to describe the formation and energy distribution of ions in the system.

Excited Neutrals

Emission spectroscopy is the standard technique used for analysis of excited neutral atoms and molecules in plasma diagnostics, mainly due to the relative ease of performing emission experiments. Emission spectroscopy relies on the collection of light emitted from atoms and molecules, and dispersing this light to observe signals at discrete wavelengths resulting from the radiative decay of these excited species. A radiative transition from an excited state to a lower energy state occurs at a unique wavelength which depends on the quantum mechanical properties of the emitting species. This allows for each signal in an emission spectrum to be assigned to an atom or molecule, which also can provide information about the chemistry occurring in the system. Three regions of the electromagnetic spectrum were probed in this dissertation, ranging from the optical through the mid-infrared, and each of these studies adds to the understanding of the chemical composition and degree of excitation of the plasmoid.

1.2.2 Ball Lightning and Ball Plasmoids

The phenomenological motivation for this work is to determine an explanation for the peculiar behavior of ball lightning. Ball lightning is a mysterious natural phenomenon which has been known since the Middle Ages, with thousands of eyewitness reports available on the web and in some non-scientific publications. This author has personally received several correspondences from eyewitnesses describing ball-lightning like phenomena in nature, some much more believable (i.e., with video evidence) than others. Several articles and books [20–22, 22–30] provide summaries of eyewitness reports of ball lightning; since this dissertation focuses on ball plasmoids, the reader is referred to those works.

Eyewitness reports should never be regarded as data from which knowledge can be gleaned; all of these accounts should be viewed through a skeptical lens. However, in 2014, a group in China recorded ball lightning in nature with scientific instruments (a slitless spectrograph in this case) for the first time, and ultimately published this observation in *Physical Review Letters* [31]. What is truly remarkable about this measurement is that ball lightning was observed completely by accident; the group initially intended to measure the emission from cloud-to-ground lightning, and while their instruments were recording, emission from ball lightning was captured. This measurement confirmed the speculation that ball lightning, though

extremely rare, is in fact a real and naturally-occurring phenomenon. This has reinforced scientific curiosity regarding the phenomenon, and there are (to our knowledge) several groups studying the formation mechanism and stability of ball lightning. Attempts have been made in the literature to describe ball lightning using various physical, chemical, and fluid models, but none of the proposed models has been verified to the point where one can conclusively state that ball lightning has been generated in a laboratory setting. Thus, there remains a search for a suitable laboratory analogue of natural ball lightning.

Ball plasmoid discharges are considered by some to be ball lightning. This author, however, does not agree with this assessment of the properties of ball plasmoids. It is this author's opinion that there could potentially be physico-chemical processes occurring in both ball lightning and in ball plasmoids, but there are many observables related to ball lightning that do not seem to be shared with ball plasmoid discharges. There are order-of-magnitude differences in the reported lifetimes of ball plasmoids versus ball lightning, and the emission spectra we present in Chapter 4 are dissimilar to what has been reported by Cen et al. [31]. Furthermore, the voltage to which the capacitors are charged, the current which is generated during the discharge, and the length of the pulse used to generate a ball plasmoid are significantly different from a natural lightning strike.

It is therefore not accurate to view the results contained in this thesis as answers to particular questions about ball lightning. However, data collected throughout the experiments described herein suggest potential avenues for future research projects, which could hopefully facilitate an understanding of ball lightning. A brief statement regarding ball lightning is included in the introductory chapter of [18]:

“Still it is reasonable to deduce that there is some type of plasma-related atmospheric phenomenon that underlies the ‘ball lightning’ sightings. One may hope that someday the proper scientific tools are brought to bear so that a true understanding may follow.”

This short passage echoes the overarching motivations of the experiments described in the following chapters.

Chapter 2

Mass Spectrometry of Atmospheric-Pressure Ball Plasmoids

Ball lightning is a naturally occurring atmospheric event that has perplexed researchers for centuries, and there is to date no complete explanation (chemical, physical, or otherwise) as to why ball lightning behaves the way that it does. There has been considerable effort to try to both produce and measure the properties of ball lightning type discharges over recent years, and this collected work has begun to reveal some interesting physical and chemical phenomena. We are able to produce water-based plasma ball discharges using high-voltage equipment, and these self-contained plasmoids are considered to be similar to natural ball lightning. In this article we present the first mass spectrometric analysis of water-based ambient ball plasmoids. Using an extremely simple sampling technique, we were able to detect several chemical species within the interior of the plasmoid. Several molecules that are common to plasmas generated in air were observed in the mass spectra, such as $[\text{NO}_2]^+$ and $[\text{NO}_3]^+$. More interestingly, we observed the protonated water clusters $[(\text{H}_2\text{O})_2\text{H}]^+$ and $[(\text{H}_2\text{O})_3\text{H}]^+$, ammonia (NH_3) as a component of a copper cluster, and several anions. Furthermore, many species observed in the mass spectra are in the form of hydrated clusters.

2.1 Introduction

Ball lightning is a one-in-a-million [32] atmospheric phenomenon that is poorly understood due to its rarity and unpredictability. Eyewitness accounts across several centuries describe large balls of light moving across the sky for several seconds during thunderstorms, with some reports detailing powerful explosions occurring when the ball of light dissipates. Images and video recordings of ball lightning phenomena have been captured by amateurs and are readily available via an internet search, however it was only last year that the first scientific measurements and analysis of naturally-occurring ball lightning were reported [31]. Cen *et al.* set out to observe cloud-to-ground lightning strikes during a thunderstorm in China's Qinghai Plateau, and by a brilliant stroke of luck ball lightning was observed immediately after a cloud-to-ground lightning strike. Their observation site was 0.9 kilometers from the site of the ball lightning, which had a reported lifetime

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of 1.64 seconds and a diameter of approximately 1.1 meters. The ball lightning event was characterized using emission spectroscopy, and emission lines from components of soil (iron, silicon, calcium, nitrogen) were observed in the spectra [31].

There is some debate in the literature regarding plausible theories that explain the properties of ball lightning [23, 24, 33–36], and to date there is no concrete physical or chemical explanation as to how ball lightning is formed and how these spheres of plasma can last for an extended period of time without energy input from an external power source. Perhaps the most fascinating aspect of ball lightning is this extended lifetime. It is remarkable that at atmospheric pressure and temperature, self-sustaining plasmas can last for more than a second. Simulations which model upwards of 600 chemical processes that could occur in ambient plasma discharges show that most reactions within this type of plasma should be complete in a millisecond or less [37, 38], however ball lightning seems to defy the current understanding of atmospheric-pressure plasmas. Given the complexity of the system in question, a true phenomenological explanation of the formation mechanism and lifetime of ball lightning will most likely be a combination of several different physical and chemical processes.

In order to truly answer the fundamental questions surrounding the long lifetime of ball lightning, it is essential to generate plasmas that are at the very least semi-analogous to natural ball lightning. Tesla was the first to observe a “fireball” type discharge [39], and efforts to reproduce his experiments have led to direct current (DC) electrical discharges that can produce plasmas similar to ball lightning. Traditionally, DC plasma generating apparatus produce arc, corona, glow, or dielectric barrier discharges between two electrodes at atmospheric pressure [40]. These discharges are usually well behaved and are easily characterized with a variety of diagnostic techniques [2, 3].

Additionally, ambient DC plasmas have been thoroughly characterized by mass spectrometry (MS) due to their use as ionization sources [41, 42]. If the electrode configuration is such that it allows for the plasma to form and grow in one place, a free-floating and self-sustaining plasma can be produced. Since these self-contained plasmas last for an extended period of time with no external source of energy they are referred to as “plasmoids.”

Using a water-based technique, Egorov and Stepanov were the first to produce a plasmoid discharge of this type in a laboratory [6], and several other groups have produced discharges similar to what they described [7–9]. To summarize this work, a bank of large capacitors was charged to several kV, and using high-voltage switches a short pulse of current was applied across two electrodes, one of which was fully submerged in a container full of water. The other electrode (the cathode in this case) was positioned such that just the tip slightly protruded from the surface of the water in the bucket. A plasmoid began to form,

and buoyant forces generated from local heating of the ambient air around the tip of the cathode caused the plasmoid to rise upward and away from the tip of the cathode.

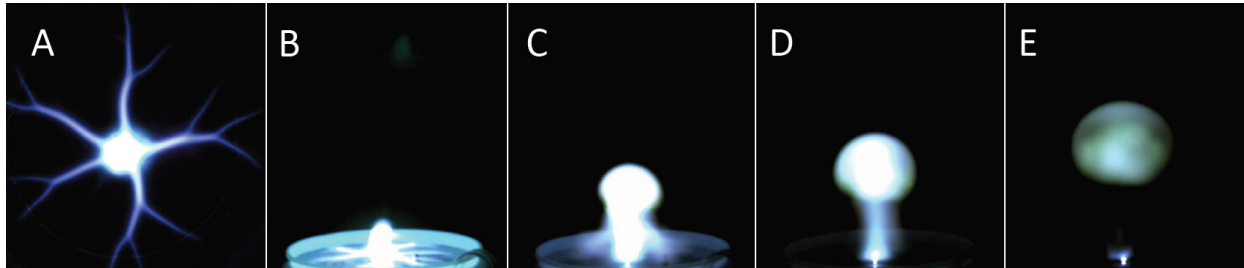


Figure 2.1: Images of a plasmoid discharge from start to finish. (A,B): pre-initiation phase, (C,D): buildup phase, (E): detachment phase. (B-E) were obtained from a single discharge via high-speed videography (Pixelink ®PL-B&42U). (A) was obtained from a separate discharge under identical conditions, top-down camera setup.

There are three distinct phases to this type of plasmoid formation (Figure 1): the pre-initiation, buildup, and detachment phases [12]. First, current begins to flow from one electrode to the other, and “streamers” or “spider legs” begin to form and extend over the surface of the water rather than through the bulk electrolyte solution. In the center, above the cathode, a small ball of plasma begins to form. Next, the ball of plasma begins to grow in size and rise due to buoyant forces while still receiving continuous current from the cathode. Finally, when the capacitor has discharged a sufficient amount of energy, no additional plasma is formed, and a self-sustaining plasmoid remains for an extended period of time. In other words, the energy stored in the capacitor at the end of a discharge event is not sufficient to allow for additional plasmoid formation. Using our experimental setup, the detachment phase can last up to 200 ms, with an entire discharge event (pre-initiation, buildup, and detachment phases) lasting up to 400 ms.

Versteegh et al. have provided the most detailed insight into the underlying chemistry and physics of water-based plasmoid discharges using emission spectroscopy and probe measurements [9]. In this work, emission lines from H, Na(I), Ca(I), Ca(II), Cu(I), OH radical, and CaOH were observed in the ultraviolet/visible. Along with qualitative identification of chemical species present within the plasmoid, these specific emission lines reveal that the electron temperature of the discharge cannot be very high (< 1 eV), otherwise emission lines from more highly energetic atoms and molecules would have been observed. Furthermore, intensity ratios of a pair of Ca(I) lines were used to estimate the electron temperature to be 5000 K (0.43 eV) at the time of the initial pulse and 2500 K (0.22 eV) after 225 ms. Further investigation into the rotational temperature of the hydroxyl radical showed a non-thermal distribution of temperatures, leading to the hypothesis that the products of water dissociation contain the necessary energy to sustain visible emission for an extended period of time. Additionally, Stark broadening of Cu(I) lines in the pre-initiation

phase of the discharge was used to estimate electron densities in the plasma to be on the order of 10^{16} cm^{-3} at 10 ms and 10^{14} cm^{-3} at 75 ms.

2.2 Experimental

2.2.1 Plasmoid Generator

The equipment that we use in our laboratory has been described previously [11], but some of the key components will be highlighted here for the sake of clarity and understanding. Our power supply can produce up to $\pm 10 \text{ kV DC}$ and wiring our capacitors in parallel can generate greater than mF capacitances, thereby generating several kJ of energy. A schematic of the hardware and circuitry is shown in Figure 2. The following description of the experimental setup was the same for every trial unless specifically noted otherwise. Voltage and capacitance parameters were chosen in part because of safety concerns, but discharges under these conditions are typically well behaved. It is also important to mention that, much like natural lightning strikes, no two plasmoid discharges are exactly alike. In other words, under identical conditions the lifetime, shape, rise velocity, and electrical behavior of plasmoid discharges can vary.

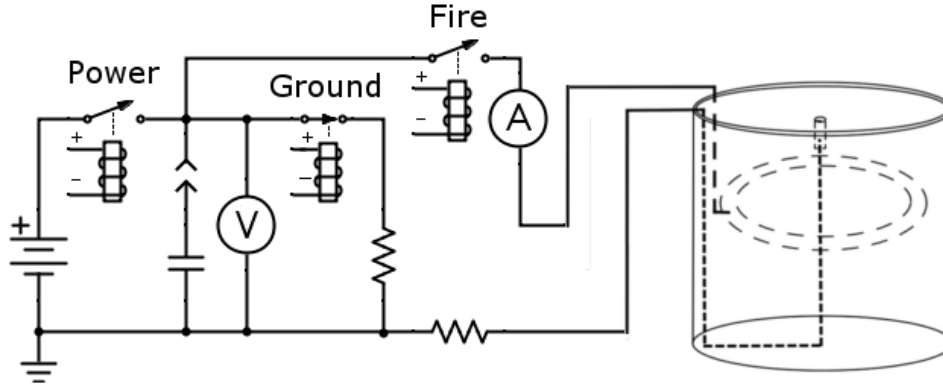


Figure 2.2: Circuit diagram of plasmoid generating apparatus. V is a voltage divider across which voltage measurements are taken, A is a Hall effect current sensor.

An $873 \mu\text{F}$ parallel-plate, oil-filled capacitor (Maxwell) was charged to $+4000 \text{ V DC}$ using a Glassman EK Series high-voltage power supply. The current being transferred from the capacitor to the plasmoid generator and eventually to ground was regulated by a series of three Ross Engineering high-voltage E Series relays. An Arduino® Uno microcontroller controlled the timing of these relays and recorded current and voltage measurements. Current pulses were applied across two electrodes, one of which was fully submerged

in a very dilute solution of hydrochloric acid in water, a more detailed description of which is given in the next section. One full plasmoid discharge will also be referred to as a “shot” at other points in this article.

2.2.2 Electrode Materials and Discharge Containers

Some of the properties of the physical apparatus were changed for different sets of experiments, namely the electrode material and size of the container in which the electrodes were submerged. The fill solution for the discharge containers was prepared with either deionized water or D_2O and concentrated HCl . The vessel would be filled with deionized water or D_2O , and HCl would be added dropwise until the desired conductivity of the solution was reached. Conductivity measurements were taken with a handheld meter (Oakton PCSTest™35). For this set of experiments, the conductivity was set to 200 μ Siemen.

The cathodes for these experiments consisted of either a solid copper rod or a solid tungsten rod, each with a six mm diameter. The electrode was insulated from the surrounding aqueous environment with a piece of alumina tubing having an inner diameter of six mm and an outer diameter of eight mm. This was done in order to electrically isolate the cathode from the water, in other words to ensure that current would travel above the surface of the water. Copper was chosen for two reasons: the distribution of the naturally occurring isotopes (^{63}Cu and ^{65}Cu) is well known and easily observed via MS, and copper ionizes easily, allowing for the formation of small cluster ions around a metallic center. Tungsten was chosen because it is extremely robust and can stand up to repeated trials with minimal degradation, therefore no tungsten ions were observed in any MS experiments, making it an ideal cathode for deuterium substitution experiments where we wanted to minimize the interaction of metal ions with water clusters and other ions.

Two different containers were used in this work, the first being a store-bought polyethylene five-gallon bucket, the second being a custom acrylonitrile butadiene styrene (ABS) plastic bowl (Figure 3) with a fill volume of approximately 200 mL. The plastic bowl was printed using an AirWolf 3D XL printer. The exact dimensions of the electrodes within the five gallon bucket have been described previously [11], and we made no deviations in setting up this container. The dimensions of the bowl however are different in the following ways: the surface of the electrolyte is formed by the top portion of the bowl which has a diameter of twelve cm and a lip depth of one cm. Additionally, the anode is positioned six cm below the tip of the cathode and the diameter of this lower portion of the bowl is 4.5 cm. The lip at the top of the bowl provides a significant surface area of electrolyte over which plasmoid formation can occur. The anode used in the bowl was considerably smaller than the anode used in the bucket, and was constructed using thick copper wire rather than a solid ring. The wire was bent into a circle with an outer diameter of 4.5 cm, and was positioned at the bottom of the bowl. The other major advantage to using this bowl was the reduced volume required

to perform discharges; this allowed for discharges over solutions in D₂O.

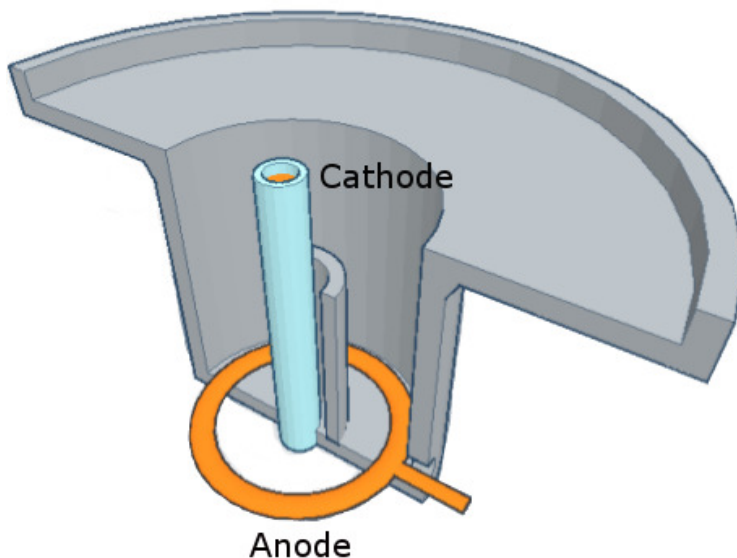


Figure 2.3: Schematic depicting a cross-section of the “bowl” plasmoid generator.

2.2.3 Mass Spectrometer and Sampling

This work was performed with a Thermo Scientific LTQ-Orbitrap XL mass spectrometer, using both an ion trap and an Orbitrap for analysis of plasmoid composition. The ion trap was operated in low mass mode with a range of m/z 15-200 and at a pressure of 10^{-5} Torr, and the Orbitrap had a mass detection range of m/z 50-2000 (< 5 ppm mass accuracy) with a mass resolution of 100 000, and was operated at approximately 8×10^{-10} Torr. The ion trap and Orbitrap have temporal resolutions of 60 and 600 ms per scan, respectively [43].

The sampling technique was extremely simplistic in order to avoid adding or removing ions or chemical species to or from the plasmoid discharge. A stainless steel capillary (Figure 4) with a length of 30 cm and an inner diameter of 0.8 mm was held at a potential of ± 35 V and was positioned eight cm above the tip of the cathode. It is important to note that the images shown in Figure 4 were obtained from one shot, and the only thing that is changing position in those images is the plasmoid itself. Figure 4A shows the position of the capillary relative to the plasmoid generator, and Figure 4B shows that as the plasmoid rises the geometry of the setup allows the capillary to sample from within the plasmoid.

The pressure differential between the ambient environment and the inlet to the mass spectrometer was sufficient to draw the contents of the plasmoid into the instrument for analysis with appreciable signal. No additional ionization of the plasmoid contents was performed. As a result of the temporal resolution of the

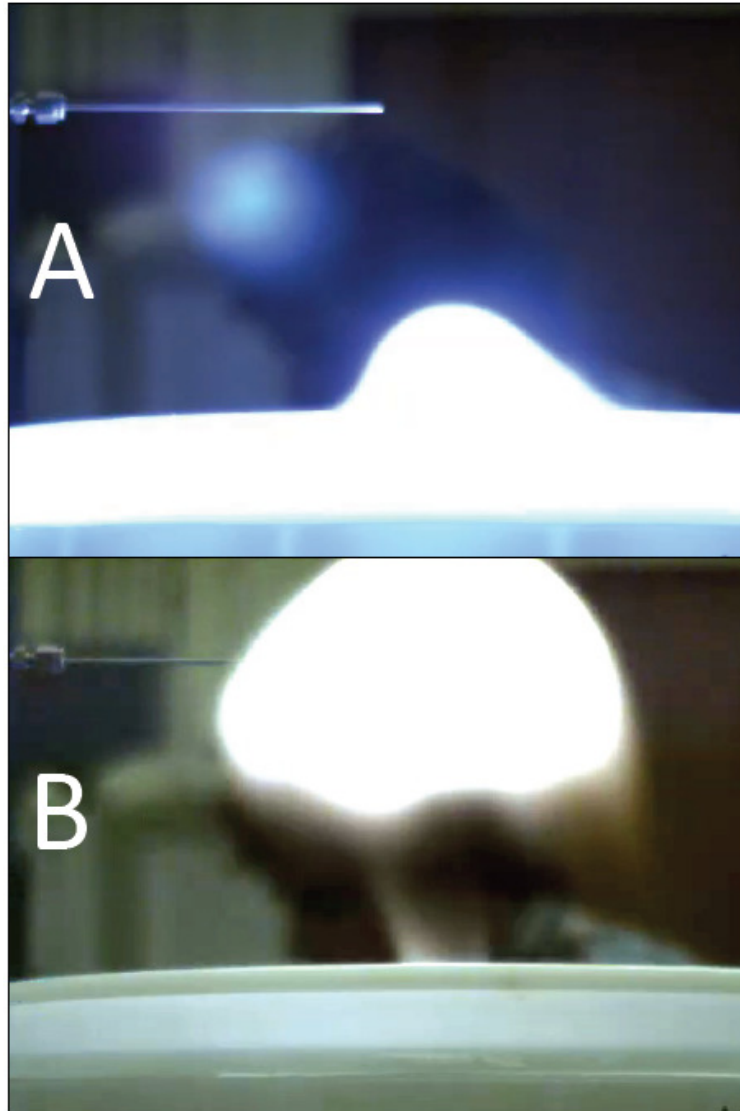


Figure 2.4: Images of the stainless steel capillary relative to the position of the plasmoid discharge. (A): the pre-initiation phase, (B): the detachment phase.

Table 2.1: Singly-charged copper based ions observed in plasmoid discharges.

Ion	Average Ion Fraction	Average Deviation	Mass Accuracy
$[\text{Cu}]^+$	0.02	± 0.01	1 ppm
$[\text{Cu NH}_3]^+$	0.03	± 0.01	2 ppm
$[\text{Cu H}_2\text{O}]^+$	0.14	± 0.06	3 ppm
$[\text{Cu (NH}_3)_2]^+$	0.006	± 0.004	4 ppm
$[\text{Cu NH}_3 \text{ H}_2\text{O}]^+$	0.04	± 0.02	1 ppm
$[\text{Cu (H}_2\text{O)}_2]^+$	0.14	± 0.07	4 ppm
$[\text{Cu(CH}_3\text{CN)}]^+$	0.09	± 0.06	4 ppm

different traps, several mass spectra were obtained for one plasmoid discharge event, and averaging these spectra provided a comprehensive survey of the internal composition of the plasmoid over a complete shot.

2.3 Results and Discussion

2.3.1 Orbitrap MS

The mass spectra obtained when using a copper cathode and the Orbitrap mass analyzer showed consistent signals from several singly-charged ions, a summary of which is given in Table 1. Figure 5 shows a representative mass spectrum obtained when using the Orbitrap, and shows more than a dozen resolved signals. Average ion fractions were obtained by dividing the raw intensity of the signal by the total raw intensity. The deviations in ion fraction were taken across seven trials for all ions except $[\text{Cu(CH}_3\text{CN)}]^+$, the deviation of which was taken across three trials. Mass accuracies are reported in parts per million. All of the spectra described in this article were externally calibrated using the signal from $^{63}\text{Cu}^+$.

The first trend that can be observed in these spectra is the presence of copper clusters. This presence of copper ions was a result of using a copper cathode for this set of experiments. Figure 5 also shows signals from both isotopes of copper (only ^{63}Cu cluster ions are labeled on the spectrum). On closer inspection, ^{65}Cu clusters containing the same ligands can be assigned using the expected mass differences, and the ratio of intensities between the ^{63}Cu and ^{65}Cu clusters corresponds to the natural abundances of the copper isotopes. Additionally, water was also a component of many ions in the collected spectra. There are two plausible ways in which water could be associated with the plasmoid. First, water can be pulled up into the plasmoid from the electrolyte solution contained within the bucket due to the intense localized heating at the tip of the electrode. Second, water could associate with the plasmoid through humidity in the surrounding air. How water associates with the plasmoid is not entirely obvious, however this will be discussed later in the article.

The presence of ammonia in the interior of the plasmoid is also significant: to our knowledge, this is

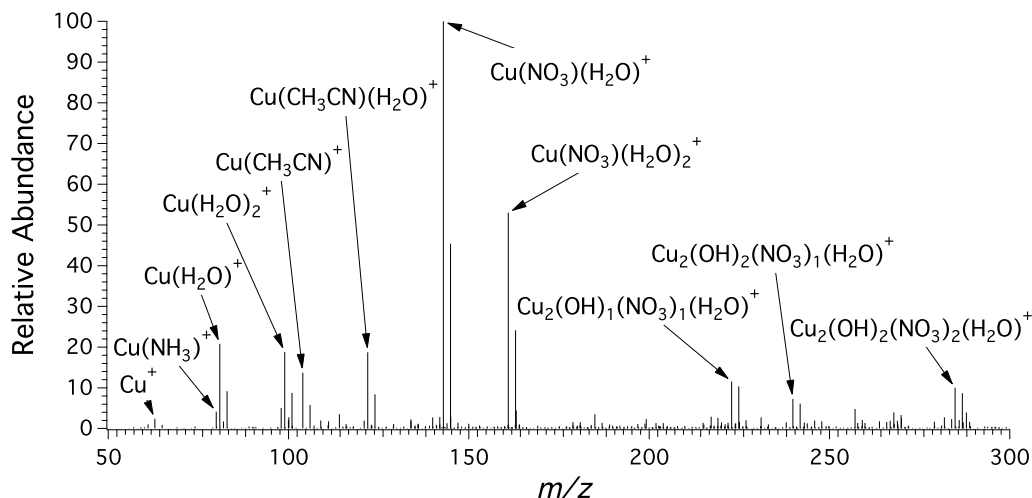


Figure 2.5: An example Orbitrap mass spectrum of a plasmoid generated with a copper electrode over a solution of water. The labels indicate only ^{63}Cu -containing ions.

the first observation of ammonia in an ambient, water-based plasmoid discharge. To determine whether the presence of ammonia as a ligand was a result of ammonia molecules from the ambient air interacting with copper ions or if in fact ammonia is formed in the process of plasmoid formation, discharges were performed over a heavy water solution. Figure 6 shows the expected mass shifts for each isotopologue of the $[\text{Cu}(\text{NH}_3)]^+$ ion. This indicates that ammonia is formed as a product during a plasmoid discharge.

2.3.2 Ion Trap MS

Although the Orbitrap has a much higher mass resolution than the ion trap, many low mass ($m/z < 50$) ions that were suspected to be in the interior of plasmoid were not detected in the Orbitrap. This was especially important in the search for protonated water clusters, the protonated dimer and trimer having molecular weights of m/z 37 and m/z 55, respectively. Therefore we performed IT-MS scans of individual plasmoid discharges, all of which reveal a consistent pattern of signals generated by small singly-charged ions, a list of which is provided in Table 2. Ion fractions were calculated by dividing the raw intensity of the signal by the total raw intensity. The deviations in ion fraction were taken across six trials for all ions. The mass accuracy is reported in parts per thousand.

Figure 7 shows two examples of ion trap spectra. The resolution is notably lower, however the signal-to-noise ratios of the signals were significant enough to allow assignment of low molecular weight ions. It is important to note that in Figure 7B the deionized water-based electrolyte was changed to a heavy water based electrolyte with the same concentration of HCl. Each signal from water-containing ions within the

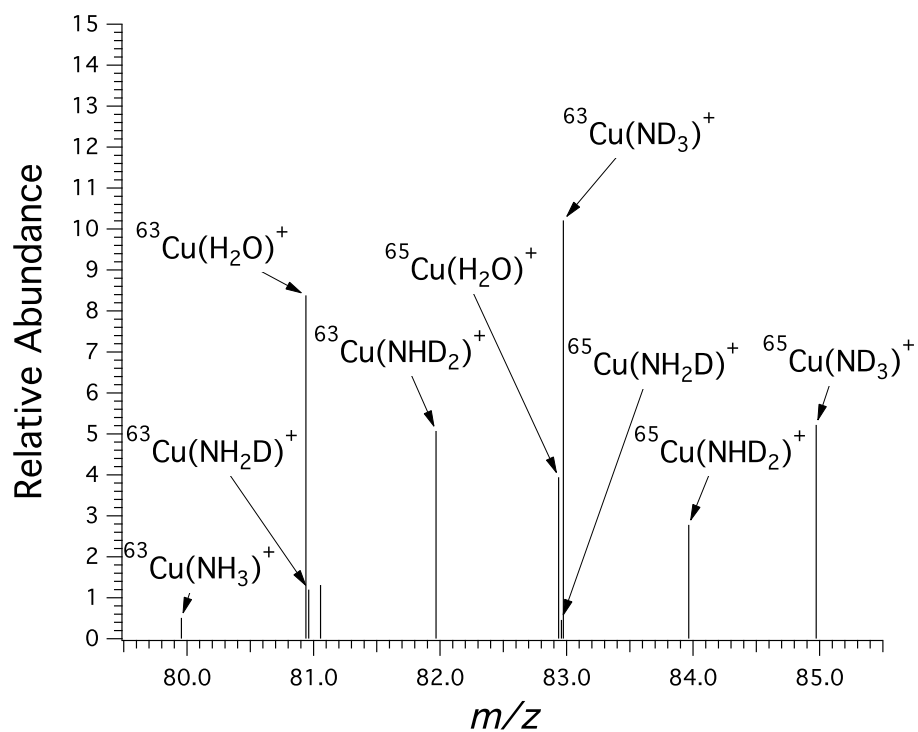


Figure 2.6: Portion of an Orbitrap mass spectrum of a plasmoid discharge using a copper cathode above a solution of D₂O showing deuteration of ammonia. Ions containing both copper isotopes are labeled accordingly.

Table 2.2: Singly-charged, low mass ions observed in the ion trap.

Ion	Average Ion Fraction	Average Deviation	Mass Accuracy
$[\text{NO}]^+$	0.05	± 0.03	4 ppt
$[\text{H}(\text{H}_2\text{O})_2]^+$	0.13	± 0.05	5 ppt
$[\text{NO}(\text{H}_2\text{O})]^+$	0.12	± 0.06	3 ppt
$[\text{H}(\text{H}_2\text{O})_3]^+$	0.1	± 0.04	3 ppt

plasmoid had the appropriate mass shifts resulting from deuterium substitutions. An attempt was made to perform MS/MS analysis on the protonated water clusters to further confirm their identities, however no significant signals were observed during this set of experiments. This is most likely a result of the difficulties encountered when trying to fragment low molecular weight ions for MS/MS analysis. However, the position of the signals and the distribution patterns of the clusters in the ion trap spectra are sufficient to prove the identities of the protonated water clusters.

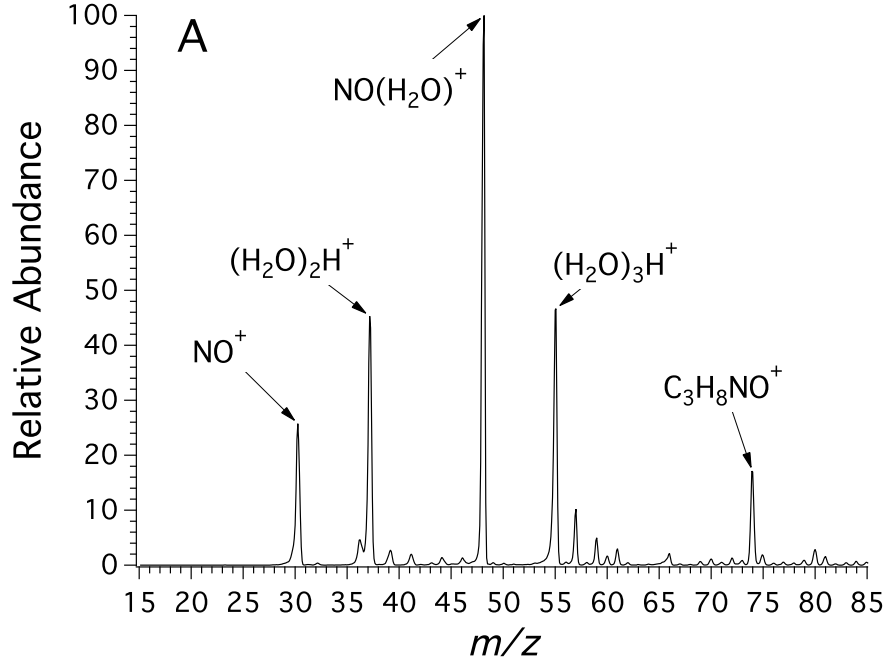


Figure 2.7: Ion trap mass spectrum collected from electrolyte comprised of deionized water.

2.3.3 Negative Mode MS

In addition to positive mode scans we also performed negative mode scans in an effort to identify negative ions in the plasmoid. In low pressure plasma discharges, negative ions are relatively rare due to the inefficiency of

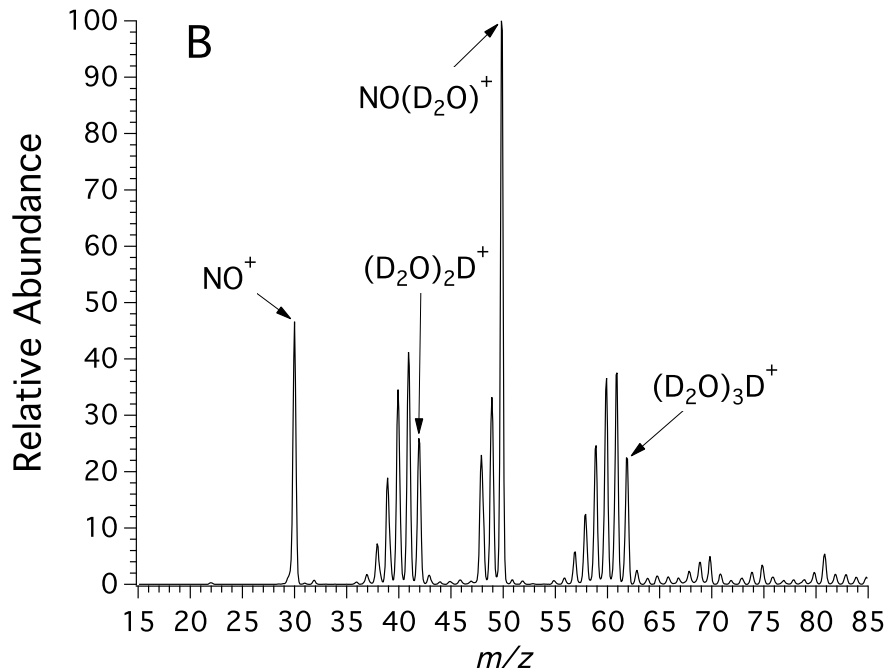


Figure 2.8: Ion trap mass spectrum collected from electrolyte comprised of D_2O .

radiative attachment. However the higher pressure at ambient conditions leads to more efficient production of negative ions through three-body attachment. We observed that the number density of anions is much less than that of positively charged species in the plasmoid interior: when comparing plasmoid discharges under identical conditions, we observed that the raw intensity of the positive mode signals was approximately thirty times larger than that of the negative mode signals. Several discharges were analyzed using negative mode in both the Orbitrap and the ion trap, and four negatively charged ions were observed: $[NO_2]^-$, $[NO_3]^-$, $[HN_2O_5]^-$, and $[HN_2O_6]^-$. Other than those of the nitrate anion, our observations of these ions were not entirely consistent from shot to shot. This is most likely the result of the already small number densities of anions fluctuating between discharges.

2.3.4 Statistical Analysis of Deuterated Isotopes

. In order to get a better sense of the chemical processes occurring during a plasmoid discharge, the distribution of deuterium within the isotopologues of the protonated water clusters was analyzed. What is readily apparent without performing any calculations is that many of the ions observed in the plasmoid are generated from the electrolyte solution in the discharge container. This can be seen in Figure 7B, where a D_2O solution was used in place of a solution of deionized water. The signals in the ion trap spectra show

that any low mass ions that contain hydrogen underwent deuterium substitution to all allowed isotopologues, however the distribution of these deuterium atoms is not readily apparent on first inspection.

We first attempted to develop a model that explained the distribution of these protonated water cluster isotopologues in the plasmoid to be a result of protons and deuterons randomly combining assuming a binomial distribution. A binomial distribution is defined as:

$$\text{Population}(k) = \binom{n}{k} P_D^k (1 - P_D)^{n-k} \quad (2.1)$$

where population refers to the fractional population of each isotopologue, n is the number of total number of possible substitutions that can occur for the particular cluster, k is the number of deuterium substitutions that have occurred for the particular isotopologue, and P_D is the fraction of hydrogen atoms in the form of deuterium: $P_D = n_D / (n_D + n_H)$. We found that it was not possible to fit the observations with this model for any value of P_D . This model assumes that the clusters were formed from individual hydrogen and deuterium atoms, which is not physically accurate for this system, so the failure of this simple model may not be too surprising.

A two-parameter model of a binomial distribution of water clusters was then created using the following relationship:

$$\text{Population}(k_1, k_2) = \binom{n_1}{k_1} P_{D_2O}^{k_1} (1 - P_{D_2O})^{n_1 - k_1} \binom{n_2}{k_2} P_D^{k_2} (1 - P_D)^{n_2 - k_2} \quad (2.2)$$

where n_1 and n_2 are the total number of H_2O/D_2O molecules and H^+/D^+ ions in each cluster ($n_1 = 2$ or 3 , $n_2 = 1$ in all cases), k_1 and k_2 are the number of deuterated species of each form (D_2O and D^+), and P_{D_2O} and P_D are the fractions of water molecules and protons in deuterated forms from which the clusters are presumed to be formed.

This new model assumes that clusters are formed from water molecules (H_2O or D_2O) from the electrolyte and/or ambient air, along with protons (H^+ or D^+) produced from a potentially different isotopic distribution of water. Models of this two-parameter distribution for both the protonated water dimer and trimer are shown in Figure 8. The two clusters were analyzed independent of other ions present in the plasmoid, and the average fractional populations of each signal across four mass spectra are shown in Figure 8. The error bars on the experimental data represent three standard deviations across the four shots, and are quite large due to the shot to shot variability described above.

Using equation (2) as a model, the available fractional amounts of D_2O and deuterium were varied and fit to the experimental data using a simultaneous fitting procedure. The optimized values of P_{D_2O} and P_D

were calculated to be 0.66 ± 0.04 and 0.47 ± 0.07 over a 95 % confidence interval, respectively. This model offers a fairly satisfactory fit to the experimental data, given the shot-to-shot variability represented in the error bars.

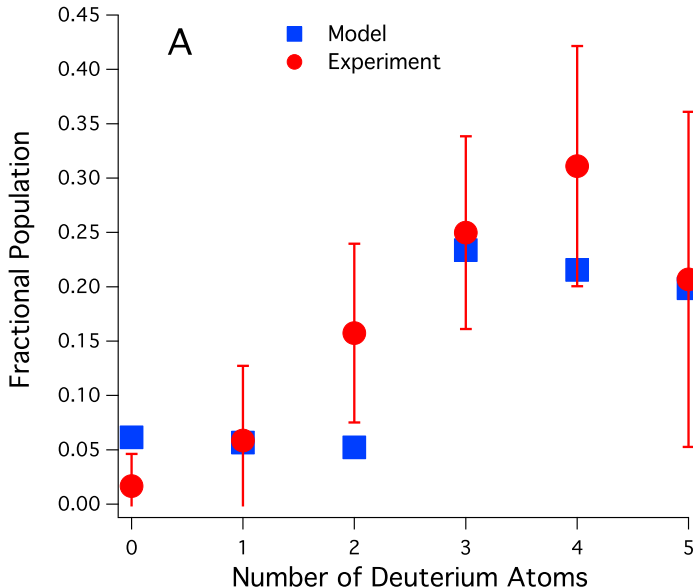


Figure 2.9: Comparison of statistical model described by Equation 2 to the experimental distributions of deuterated water clusters for the protonated water dimer. $P_{D_2O} = 0.66 \pm 0.04$ and $P_D = 0.47 \pm 0.07$. The error bars represent three standard deviations.

Within the context of this model, it is apparent that the mixing of atoms in the plasmoid is not entirely random. The water molecules within the clusters, which could conceivably originate exclusively from the electrolyte or from the ambient air, appear to come from both sources, with a slightly higher preponderance of D_2O from the electrolyte. The slightly lower value of P_D compared with P_{D_2O} is intriguing, and suggests that protonation of water clusters might occur at later stages of the plasmoid, after more H_2O from the ambient air has been incorporated. If the reproducibility of the plasmoids can be improved, it may be possible to better constrain the chemical formation of these water cluster ions. However, at this point the observations conclusively demonstrate that plasmoid composition is not determined exclusively by the electrolyte composition.

2.4 Conclusions

In this article we have presented the first chemical analysis of plasmoid discharges using mass spectrometry. The simplicity of the sampling technique allowed for a qualitative survey of some of the ions that are

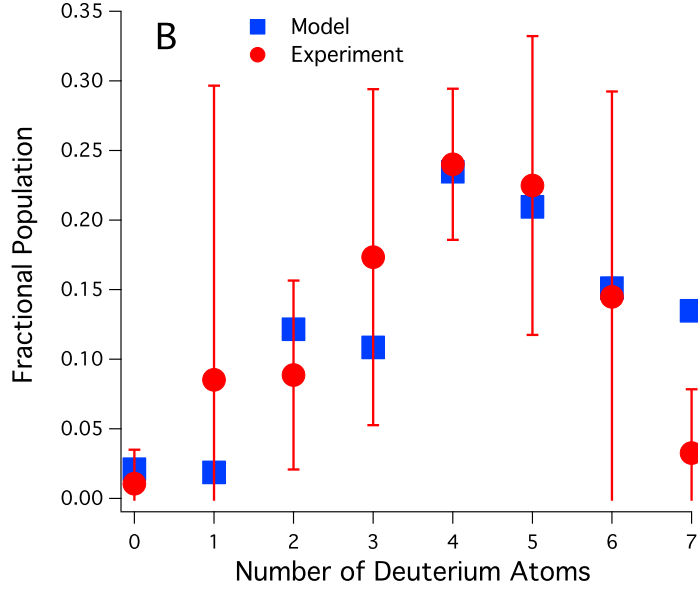


Figure 2.10: Comparison of statistical model described by Equation 2 to the experimental distributions of deuterated water clusters for the protonated water trimer. $P_{D_2O} = 0.66 \pm 0.04$ and $P_D = 0.47 \pm 0.07$. The error bars represent three standard deviations.

formed in or contained by this particular type of plasmoid discharge. The statistical model that we present shows that a two-parameter binomial distribution can be used to describe the distribution of hydrogen and deuterium atoms in small protonated water clusters. Additionally, this model shows that ambient plasmoids are composed of molecules from both the electrolyte and the surrounding environment. Finally, the types of ions observed in the mass spectra, namely water clusters and NO_x species, are in agreement with what has been observed in other DC plasma discharges by MS [41, 42].

The reproducibility of plasmoid discharges presents the greatest obstacle toward a true physical understanding of plasmoid stability. Efforts are underway to improve the hardware and control electronics that are used to generate laboratory plasmoids. Further characterization of plasmoids, both by MS and by spectroscopic and imaging methods, can be expected to provide additional information about the composition and dynamics in these fascinating objects that may ultimately lead to an understanding of their chemical and physical properties.

Chapter 3

Infrared Emission Spectroscopy of Atmospheric-Pressure Ball Plasmoids

We report the first (to our knowledge) infrared emission spectra collected from water-based laboratory ball plasmoid discharges. A “ball plasmoid” results from a unique type of pulsed DC plasma discharge in which a sphere of plasma is seen to grow and eventually separate from a central electrode and last for a few hundred milliseconds without an external power source before dissipating. Typical recombination rates for plasmas at ambient conditions are on the order of a millisecond or less, however ball plasmoids have been observed to last a few hundred milliseconds, and there is no explanation in the literature that fully accounts for this large discrepancy in lifetime. The spectra are dominated by emission from water and from hydroxyl radical; PGOPHER was used to fit the experimental spectra to extract rotational temperatures for these molecules. The temperatures of the bending and stretching modes of H₂O were determined to be 1900±300 K and 2400±400 K, respectively and the rotational temperature of OH was found to be 9200±1500 K.

3.1 Introduction

Low-temperature and atmospheric-pressure plasmas have developed as essential tools across several industries over the past few decades. The tunability of plasma discharge parameters allows for the selection of chemically and physically reactive components of the ionized medium, and operating a discharge at ambient pressures fosters numerous applications of plasmas in different settings. For example, the electron density and temperature, identities and number densities of reactive ions and radicals, UV photon flux, and flow rate of gases can all be tuned and optimized for interactions with different surfaces ranging from plastics to human teeth to the top layers of the skin. There has been much development of plasmas as tools for semiconductor processing [44, 45], medicine [46–48], dentistry [49], air purification [50], wastewater [51] and biomedical [52–56] sterilization, as agents for controlled mutagenesis [57], and in the food processing and sterilization industry [58, 59]. Additionally, ambient plasmas are attractive as soft ionization sources for

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mass spectrometry [41, 60, 61], especially due to the much less complicated sample preparation required for ambient ionization using plasmas.

Plasmas that are self-sustaining and have a definitive shape but are not confined between two electrodes or any external fields are referred to as plasmoids. A several-kilovolt capacitive discharge above the surface of a weak electrolyte can be used to generate water-based plasmoids [6] which take the form of a sphere, thus this particular type of discharge is referred to as a “ball” plasmoid discharge. In contrast to other direct-current (DC) plasma discharges (arc, corona, glow, dielectric barrier) [40], ball plasmoid discharges are generated by intentionally designing the electrodes such that a tremendous pulse of current causes a plasma to form at the tip of the cathode, above the surface of the electrolyte [6–9]. While still forming, the plasma grows, rises, and eventually separates from the cathode and can be seen as a distinct sphere of plasma for an extended period of time. The discharge occurs in three phases (Figure 1): the pre-initiation, buildup, and detachment phases [12, 13]; it is perhaps the detachment portion of the discharge, when an autonomous plasmoid can be observed, that is the most interesting. Plasma discharges at ambient pressures are not expected to last for more than a millisecond without an external power source [37, 38], however ball plasmoids emit light for approximately 200 milliseconds even when no current flows between the electrodes.

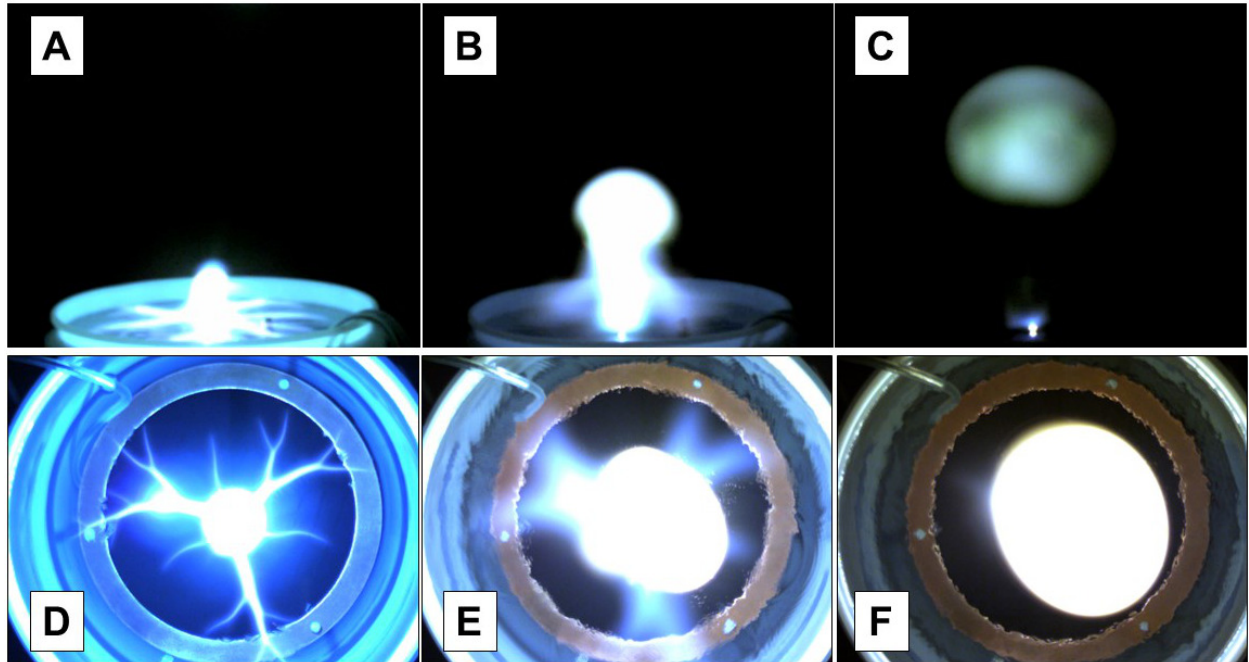


Figure 3.1: Images obtained from high-speed videography of plasmoid discharges. A-C: initiation, propagation, and detachment phases of the discharge. D-F: top-down view of the same phases shown in A-C, taken from an identical discharge on the same day.

Recently, several groups have begun to characterize ball plasmoid discharges in attempts both to explain

the long lifetime of the plasmoid and to study the mechanism of ball plasmoid formation [7, 9, 11–13], and this collection of papers has provided a foundation for more detailed studies of the system. Our goal for the experiments described in this article is two-fold: to expand the emission spectroscopy performed by Versteegh et al. [9] into the infrared, and to confirm the molecular assignments obtained from infrared absorption spectroscopy presented by Friday et al. [11]. In addition to identifying the molecules which are emitting in the infrared, we aim to determine rotational temperatures for each of the emitting molecules, which will provide a more complete picture of the energy distribution of products generated during plasmoid formation and will also allow for an approximation of the gas-kinetic temperature of the plasmoid to be made.

Ball plasmoids are considered to be laboratory analogues of ball lightning, a puzzling and currently unexplained natural phenomenon which was only recently observed in the field with scientific instrumentation [31]. Although rare, there are numerous reports available in the literature describing a luminous sphere of light dancing through the sky, sometimes lasting tens of seconds before dissipating. Some reports describe a quiet fizzling out of the light, but others indicate that the ball leaves destruction in its wake as it disappears with tremendous energy. There is also debate in the literature over the theories describing the formation and other properties of ball lightning [24, 33–36], often with little or no experimental evidence, therefore there is currently no explanation (or set of explanations) as to why ball lightning behaves in these mysterious ways.

3.2 Experimental

3.2.1 Plasmoid Discharge Source

The equipment and electronics that we use to generate plasmoid discharges have been described previously [11, 13], however some changes have been made to the circuitry to better control and monitor the discharge. To provide as accurate a description of the apparatus as possible, the key components of the system will be described. The next paragraph describes the general process by which ball plasmoids are generated, and the following paragraphs describe additional components of the system. As is always the issue with performing these measurements, there is a high shot-to-shot variability in successive plasmoid discharges. Much in the same way that no two lightning strikes are alike, identical conditions can produce plasmoid discharges with different underlying characteristics (size, lifetime, amperage, rise velocity, etc.).

The electrode setup is contained within a store-bought five-gallon polypropylene bucket which is filled with deionized water. The conductivity of the water is adjusted using concentrated HCl. Conductivity measurements are taken with a hand-held, waterproof meter (Oakton PCSTest™35). The cathode is positioned

such that just the tip of the electrode protrudes above the surface of the water approximately 1-2 mm. The cathode which is used in all of the following experiments is a solid tungsten rod with a diameter of 6 mm. The cathode is insulated from the electrolyte using a tube of alumina with an inner diameter of 6 mm and an outer diameter of 8 mm. No metal ions from the cathode were desired to be present in the discharge during these experiments, so tungsten was chosen for its high durability and resistance to sputtering and spalling. This cathode was chosen in order to minimize ion-neutral and ion-electron interactions caused solely by electrode materials, thus producing a plasmoid from only molecules in the air and molecules just above the surface of the electrolyte [13]. A copper ring is used as the anode and is positioned perpendicular to the orientation of the cathode, in other words the plane of the anode is parallel to the surface of the electrolyte. This entire electrode is submerged in the weakly conductive aqueous solution with a final depth of approximately 12 cm below the surface of the electrolyte.

Figure 2 provides an illustration of the circuitry used in our laboratory. A Glassman EK Series high-voltage DC power supply is used to charge large parallel-plate, oil-filled capacitors (Maxwell) to 1-10 kV. The capacitors can be used individually or can be wired in parallel to generate capacitances up to two milliFarads. Three Ross Engineering E Series high-voltage relays are used to make connections that will charge the system, send current pulses to the discharge container, or ground the system. An Arduino® Uno microcontroller board controls the timing of these switches, and the same microcontroller is used to record voltage and current measurements via a voltage divider and Hall effect sensor, respectively. High-speed videography is performed with a Pixelink® PL-B&42U camera with a frame rate of 98 fps. Discharge parameters are chosen based both on the geometry of the setup and an optimization of safety to personnel and equipment, therefore no discharges above 7 kV are ever performed due to physical limitations of the equipment (temperature rating of power resistors, arcing concerns, etc.). Future additions and improvement to the circuitry will allow for larger voltages and capacitances to be used safely and successfully.

The parameters of the discharges described in this article are the following: the capacitor (873 μF) was charged to 6 kV, the conductivity of the electrolyte was set to 320 μSiemen , and the tip of the cathode was set flush to the tip of the alumina insulator which was positioned to protrude approx. 1-2 mm above the surface of the electrolyte. The conductivity of the electrolyte did not change significantly between experiments due to resistive heating. All spectra were recorded on the same day, under identical conditions.

3.2.2 Spectroscopic Measurements

Infrared emission spectroscopy was performed using a Bruker VERTEX 70 Fourier-transform infrared spectrometer in a double-pass configuration at 4 cm^{-1} resolution and a (mirror) scan rate of 40 kHz. Spectra

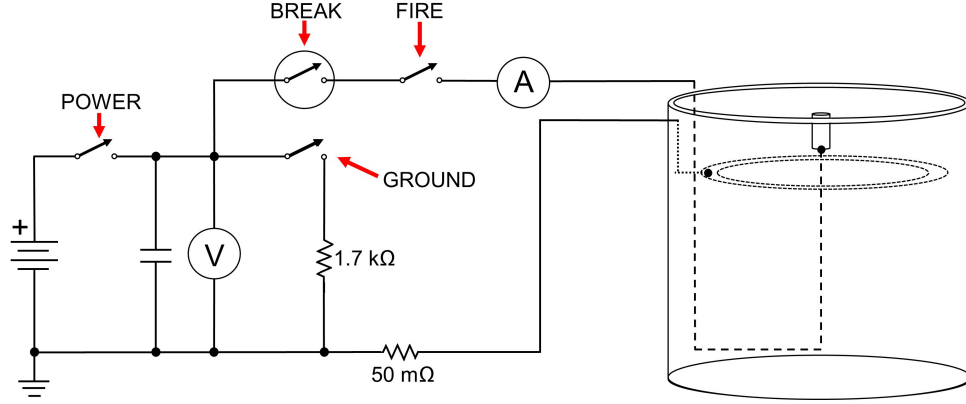


Figure 3.2: A simplified circuit diagram of the plasmoid discharge circuit. The “POWER” relay delivers current to the capacitor bank, the “FIRE” relay delivers the pulse to the electrodes, “BREAK” is the vacuum relay which breaks current to the electrodes, and finally the “GROUND” relay grounds the system. V and A are a voltage divider and a Hall effect current sensor, respectively.

were collected between $1000\text{-}5000\text{ cm}^{-1}$. The time-domain interferogram data from the spectrometer were high-pass filtered using a second-order Butterworth filter, Hanning apodized, and Hilbert transformed (phase correction) to generate emission spectra. The lineshapes in these spectra are ultimately dictated by the response function of the instrument (a Hanning function Fourier transformed to a *sinc* function in this case), thus the experimental lineshapes are best described by a Lorentzian profile with a FWHM of 4 cm^{-1} . Only one scan was used for each measurement, and it is important to note that the spectrometer and discharge electronics (each with their own small internal triggering delays) were triggered by hand. The spectrometer and discharge were triggered independently by two individuals after a countdown; no time-resolved measurements could be performed using this setup.

Figure 3 provides a birds-eye view of the experimental setup. The HeNe laser within the instrument was used in conjunction with additional optics placed outside of the instrument to align the light emitted from the plasmoid into the spectrometer. To confirm the placement of the optics, a flame from a butane lighter was held where the plasmoid would be discharged and at points along which the emitted light was presumed to be traveling. The intensity counts on the detector were monitored in real time as the flame was brought in and out of the optical path. The intensity counts at the detector would increase by a few orders of magnitude when emitted light from the flame was detected. An opaque sheet was also placed between the plasmoid and the optics to isolate the emitted light. A hole was cut into the sheet such that the tip of the electrode was masked but the plasmoid itself was not. This eliminated the possibility of light from the hot cathode interfering with our measurements. This also minimized reflections off of other surfaces in the laboratory.

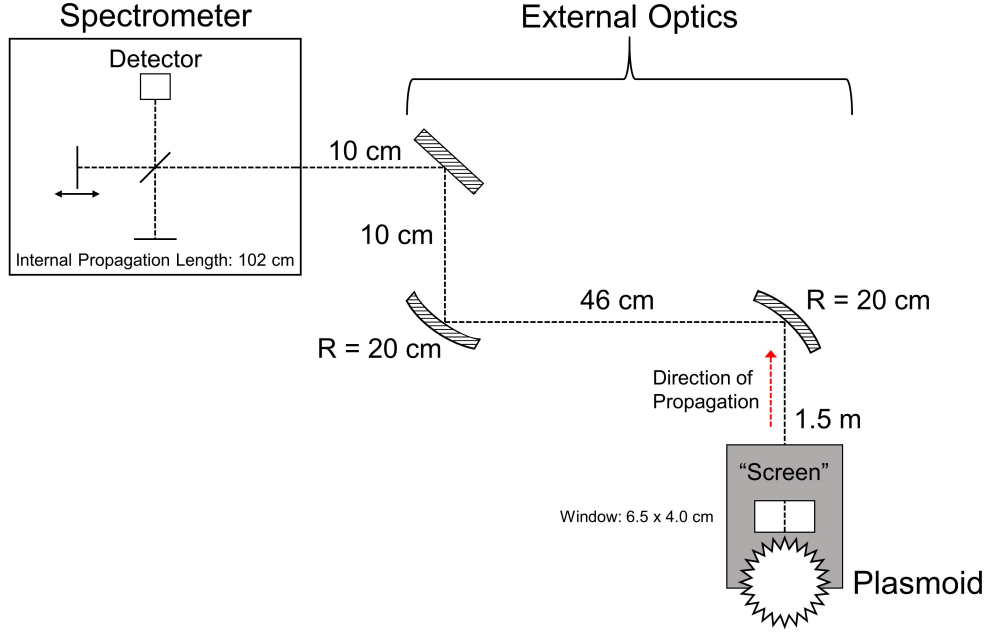


Figure 3.3: Bird's eye view of optical setup for experiment. Relevant distances and focal lengths are provided (not to scale).

3.3 Results and Discussion

3.3.1 Emission Spectra

Figure 4 shows several spectra that were obtained over the course of the experiment. A cursory examination of these data shows that water dominates the spectra, but a closer inspection shows that emission from hydroxyl radical is also present. Using the HITRAN [62] database in conjunction with the PGOPHER [63] program, a simulated mixture of these molecules was generated and compared to the experimental spectra. The simulated spectrum displayed in Figure 4 (the uppermost spectrum) shows good agreement with the experiment in terms of the molecules that are emitting from the plasmoid.

Given that there was a significant pathlength between the plasmoid and the spectrometer in these experiments, it was necessary to account for absorption by water and CO_2 along this optical path. In order to address this issue, the observed spectra were divided by an absorbance spectrum of CO_2 and water (298 K, 2.06m pathlength, Lorentzian lineshape; 4 cm^{-1} linewidth, 1 atm) generated using HITRAN online (<http://hitran.iao.ru/>). In each spectrum this resulted in a significant increase in emission signal in the regions where atmospheric CO_2 and water readily self-absorb, however there is little effect on the intensity between $2400\text{-}3200 \text{ cm}^{-1}$ (where emission from OH is present). The corrected spectra used in fitting can be found in the supplementary material.

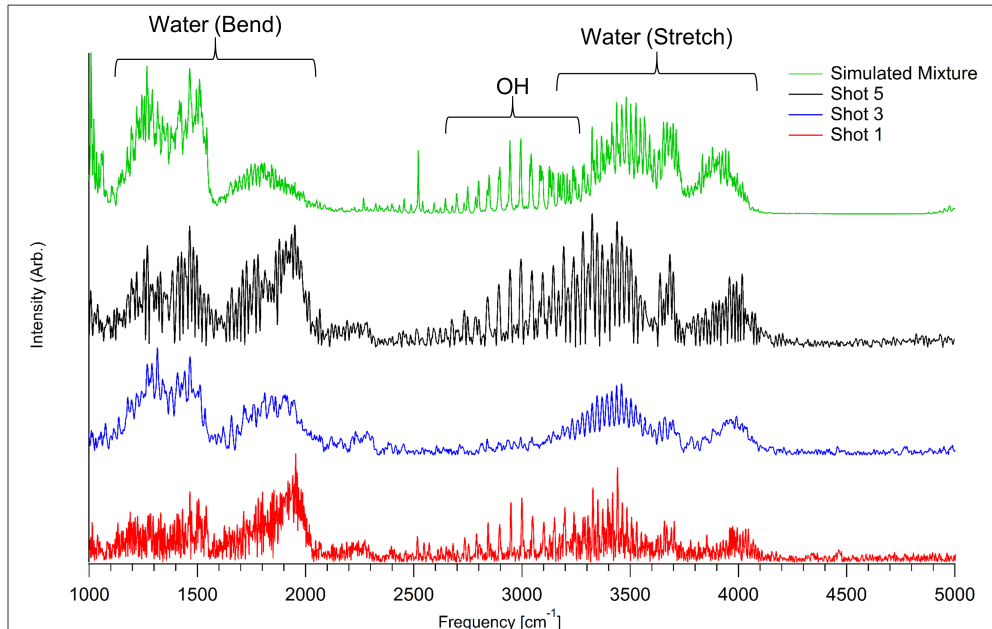


Figure 3.4: Upper curve: simulated spectrum of a mixture of H_2O and OH . Lower curves: three examples of emission spectra collected from ball plasmoid discharges, offset for clarity. Spectra were obtained under identical conditions.

As would be expected, the difficulties associated with obtaining a spectrum after triggering the discharge resulted in missing the emission from the plasmoid in some cases. Some of the spectra exhibited only a broad and featureless continuum spanning approximately 2000 cm^{-1} ; these spectra were rejected as unusable. Furthermore, there were trials in which we thought that emission from the plasmoid was collected by the instrument, however only instrumental noise was observed in the spectra, which speaks to the importance of triggering the discharge and spectrometer simultaneously.

3.3.2 Fitting

The PGOPHER [63] program was used to fit the corrected spectra to simulated spectra of water and hydroxyl radical. At the outset of our rotational analysis we attempted to fit a mixture of both of these molecules to the experimental data, however PGOPHER’s functionality allows for only a single rotational temperature to be floated during fitting. We expected the temperatures of different plasmoid constituent molecules to be rather different from one another, therefore, each molecule was fit separately. Furthermore, vibrational excitation (and relaxation) occurs differently for each degree of freedom in nonequilibrium air discharges, thus the three vibrational modes of water are also expected to have slightly different values of rotational temperature. The generic fitting procedure involved generating a spectrum of the molecule of interest using

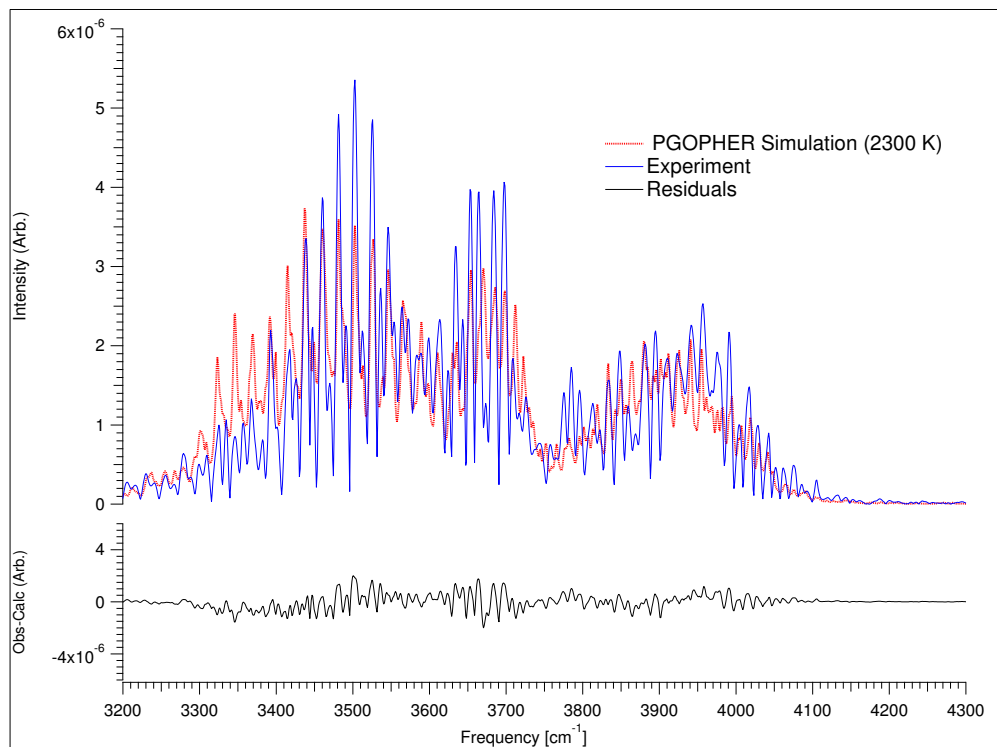


Figure 3.5: Example of a fit to the stretching modes of water. This fit is to the spectrum obtained from Shot 4 (see Table 1).

the HITRAN line list (imported directly into PGOPHER), modifying the simulation to reflect emission data as per Western’s [63] suggestions, overlaying an experimental spectrum in the software, adjusting the scale of the experimental spectra, and finally floating the value for rotational temperature until the fit converged.

When first fitting the data to a spectrum of water we noticed that the fits would converge on a rotational temperature, however some of the residuals appeared to be the result of an unphysical fit. Indeed, when good results were returned from fits to the stretching modes, fits to the bending mode were poor. To resolve this issue, the stretching modes and bending mode of water were analyzed independently; the symmetric and asymmetric stretching modes were fit together, but the bending mode was fit separately. As a result of significant hot band emission, the emission profile of the bending mode was not fully reproduced by the PGOPHER simulations (although hot bands were included in the simulations), resulting in fits taking longer to converge. Fits were performed between $3200\text{--}4300\text{ cm}^{-1}$ and $1000\text{--}2500\text{ cm}^{-1}$ for the stretching modes and bending mode, respectively (see supplemental material). Numerical results from each of the fits to H_2O are shown in Table 1, and an example of a complete fit is provided in Figure 5. The rotational temperatures we report show the extent of molecular excitation in the discharge and are comparable to those obtained from the emission of water in oxy-acetylene flames [64].

Table 3.1: Calculated rotational temperatures for the vibrational bands of water.

Shot	$T_{rot}^{stretch}$ [K]	T_{rot}^{bend} [K]
1	2300	2000
2	3300	1800
3	1700	2400
4	2200	1400
5	2300	1700
Average:	2400 ± 400	1900 ± 300

A similar procedure was used to determine the rotational temperature of hydroxyl radical. The spectra were fit from $2800\text{--}3200\text{ cm}^{-1}$, again holding the Lorentzian linewidth constant at 4 cm^{-1} . An example of a fit to OH is shown in Figure 6, and numerical results of the fits are presented in Table 2. In one particular instance (Shot 3, shown in Figure 4), the intensity of the signals in the OH emission region were comparable to the noise floor, which resulted in the fits not converging on a rotational temperature. Therefore the values we report for hydroxyl radical are obtained from four separate spectra rather than five. The average rotational temperature of OH was found to be 9200 K, which is high for ambient plasmas. This value is however lower than what has previously been reported for this system [9]; the measurements reported herein were most likely made later in the discharge when compared to those of Versteegh et al. Since the rotational temperature of each constituent molecule must rapidly decrease to room temperature over the course of the discharge, it follows that the rotational temperature would be lower when probing later in the discharge. Time-dependent measurements would be extremely beneficial for the confirmation of rotational temperatures at different stages of the discharge.

There is also an unknown source of emission in the experimental spectra between approximately $2250\text{--}2400\text{ cm}^{-1}$. There are several potential molecular sources for this emission, including CO_2 and CO; the $4.3\text{ }\mu\text{m}$ band of CO_2 [65] and the vibrational band of CO [66] overlap in this region, however this signal is most likely not a result of emission from CO, as the vibrational band of CO is centered approximately 100 wavenumbers to the red of the anomalous feature. We attempted to fit the corrected spectra to a simulation of CO_2 in the same fashion described above, but fits to this molecule did not fully reproduce the shape or intensity of the observed feature, even at high temperatures (see Figure 7). This region is further complicated by the fact that self-absorption by CO_2 readily occurs in this frequency range. Thus the identity of the cause of the signal in this region remains a mystery; however, the emission profiles shown in Figure 7 do seem to correspond to that of CO_2 in *some* way. Friday et al. [11] present evidence which suggests that CO_2 may be present in the plasmoid as a result of electrode oxidation, but this does not refute the possibility of gaseous CO_2 emitting from plasmoids produced with a tungsten electrode. Additional measurements of discharges with less shot-to-shot variability would allow for a much more concrete understanding of emission in this

region, and improved spectral resolution would allow for a more traditional Boltzmann analysis of a set of known transitions.

The average rotational temperature for OH reported here is limited by the spectral resolution and lack of a thorough Boltzmann analysis, however the procedure used to fit the data provide a reasonable estimate of the rotational temperature. The high temperatures of water and hydroxyl radical indicate that upper vibrational and rotational states of plasmoid constituent molecules are highly populated, which is expected for a nonequilibrium air plasma. These upper states could be populated directly during the discharge via vibrational/rotational excitation processes, or by chemical reactions in the plasmoid. For example, highly-excited OH radicals are thought to be generated by electron impact ionization of water molecules, while other less excited radicals could be generated by excitation of previously-formed OH via other mechanisms. A more thorough analysis of better-resolved transitions could facilitate a two or three temperature model of OH rotational distribution, which has been studied extensively in the literature [67,68].

When comparing the spectra collected in this set of experiments to the spectrum presented by Friday et. al [11] (referred to as “the absorption spectrum” here for clarity), several differences can be noted. First, our emission spectra show signals indicative of OH from 2800-3200 cm^{-1} , while no evidence of OH absorption is present in the absorption spectrum. Our spectra also show high S/N for all of the vibrational modes of water, while the absorption signals corresponding to the bending mode shown in the absorption spectrum have a much smaller S/N. It is not surprising that the S/N of the bending mode is much greater in the emission spectra— it is likely that the plasmoid is highly vibrationally and rotationally excited and emission from these excited state molecules is occurring frequently. The high temperature of the plasmoid also increases the contribution from vibrational hot band transitions, which are especially prevalent in the bending mode. The two unassigned features presented in the absorption spectrum are not directly observable in our emission spectra, however this does not immediately dismiss the presence of these signals in our spectra as the observed emission profiles are incredibly complex. This complexity is further increased by the possible presence of water clusters in the plasmoid, as many of the rovibrational bands of protonated water clusters are centered within the rovibrational bands of free water molecules [69]. It is unclear at this level of spectral resolution whether emission from protonated water clusters is being detected, but this notion should not be dismissed since the protonated water dimer and trimer have been shown to be present in ball plasmoid discharges [13].

It is difficult to make a direct comparison between emission and absorption spectra collected from ball plasmoid discharges because very little is known about the optical thickness of these plasmoids. Emission spectroscopy of optically thick spheres results in collection of signals from the outermost edge of the sphere,

Table 3.2: Calculated rotational temperatures for hydroxyl radical.

Shot	T_{rot}^{OH} [K]
1	7600
2	8200
3 ^a	N/A
4	12200
5	8600
Average:	9200 ± 1500

a: S/N results in fits that do not converge.

which is not the ideal case for ball plasmoids, as plasmoids have been shown to be surrounded by an “envelope” which is cooler than the interior of the plasmoid [9]. The temperature differences between the interior and exterior of the plasmoid most likely facilitate different chemistry in the center of the plasmoid and at the air-plasmoid interface, and further study of this system with improved spatial resolution is needed in order to study the different temperature regimes with ball plasmoid discharges.

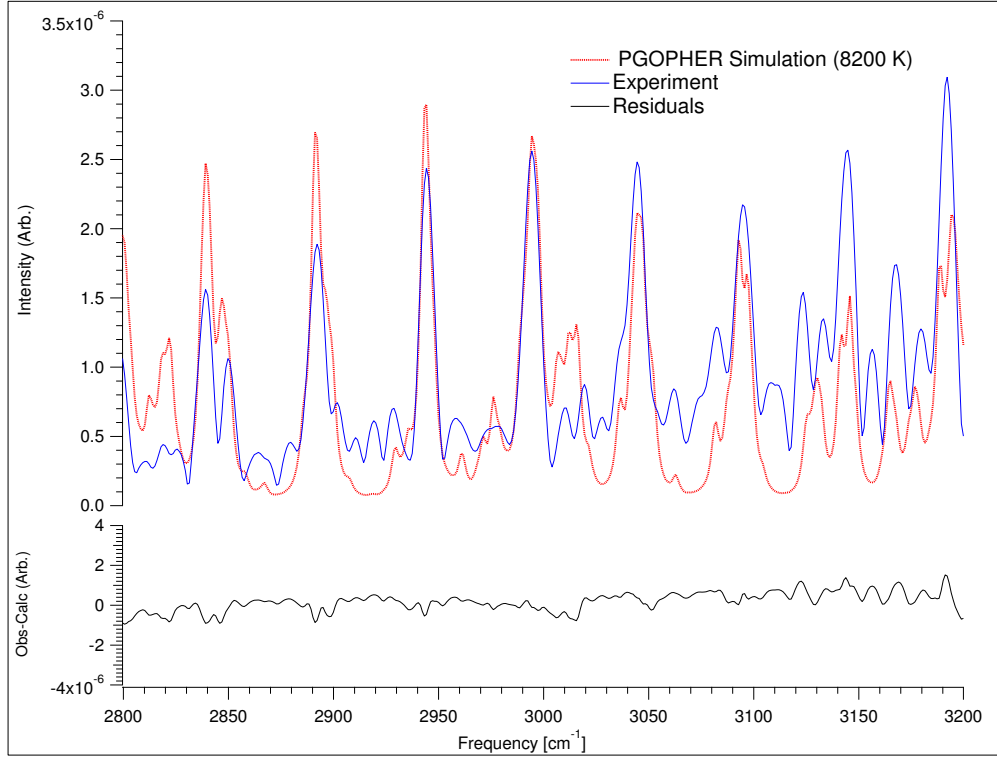


Figure 3.6: Example of a fit to hydroxyl radical. This fit is to the spectrum obtained from Shot 2 (see Table 2).

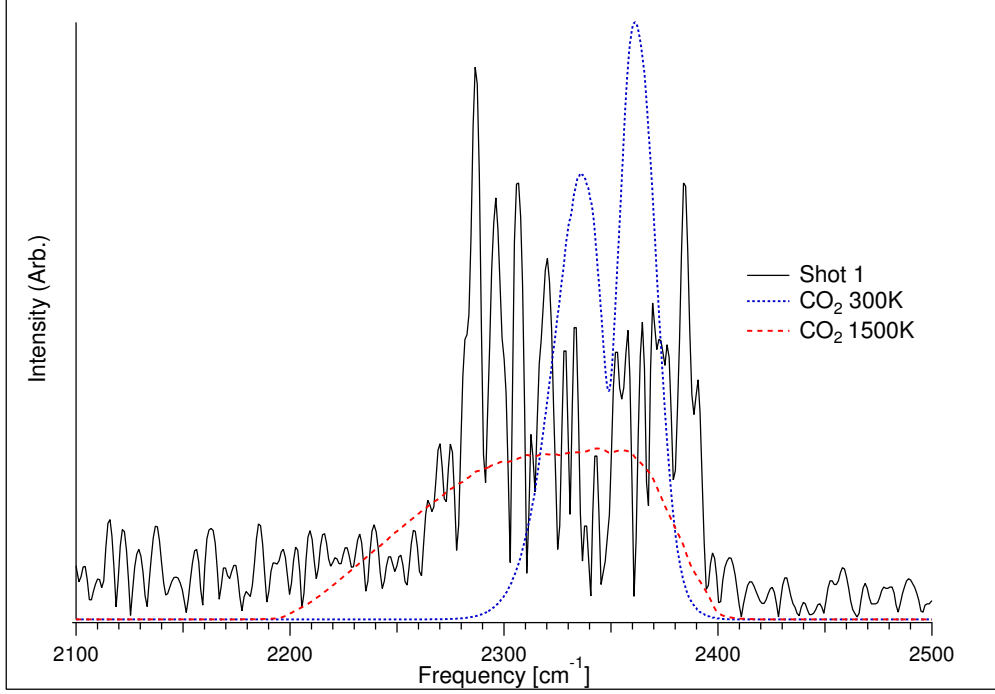


Figure 3.7: Comparison of the emission profiles of CO_2 at room and high temperatures to the unexplained signal observed between $2100\text{-}2400\text{ cm}^{-1}$ in an experimental spectrum (Shot 1 in this case).

3.4 Conclusions

In this work we have presented the first analysis of ball plasmoid emission in the infrared. Using a relatively simple spectroscopic setup, we were able to collect spectra that show emission from water and hydroxyl radical. These molecules are unsurprising to observe in ambient plasma discharges and have been observed in this type of discharge using absorption spectroscopy [11]. We are able to report quantitative information about the plasmoid after reducing the spectral collection time (compared to the three-second acquisition time of Friday et al.), but more importantly this analysis centered on fitting spectra which show rotational structure of constituent molecules. The rotational temperatures that were extracted from the fits of the observed spectra begin to show the energy distribution among molecules in the plasmoid and confirm the measurements of Versteegh et al., reinforcing the fact that ball plasmoid discharges are highly nonthermal and result in rapid heating and rapid cooling of constituent molecules.

In order to move this work forward experimentally and answer the ultimate question of why ball plasmoid recombination occurs much more slowly than is expected, a two-fold approach is being undertaken. First, we are expanding the spectral regions in which we are probing; we are working to examine the plasmoid in the near-IR and in the UV/visible to monitor molecules such as N_2^+ and N_2^* . As the principal component

of ambient air, it is highly likely that the molecular processes in which nitrogen participates are key to understanding the relaxation processes of the plasmoid. We also plan to re-examine hydroxyl radical with improved spectral and temporal resolution compared to the previous work [9]. This will facilitate a greater understanding of the energy distribution as a function of time and will also provide insight into the reactions which are (or are not) occurring during the three phases of the discharge.

Chapter 4

Electrical Properties and Physical Chemistry of Ball Plasmoid Discharges

Ball plasmoid discharges are a unique type of atmospheric-pressure plasma discharge with a lifetime on the order of a few hundred milliseconds without attachment to a power source. These discharges are generated by a moderate current pulse over the surface of a grounded aqueous electrolyte, and the spheroidal plasmoid that results from this geometry bears some resemblance to ball lightning. This article presents several experiments designed to probe characteristics of ball plasmoid discharges in a systematic fashion and at higher discharge energies than previously reported. We provide a detailed analysis of the current and voltage profiles generated using two different electrode materials and over a range of discharge energies. Optical and near-infrared emission spectra collected over this energy range show the production of excited species previously unobserved in this system, such as atomic tungsten and imidogen radical (NH). These spectra also facilitate a deeper discussion of the chemistry of ball plasmoids in terms of the associated kinetics, likely reaction pathways, and the contribution of vibrational energy to molecular excitation. Finally, measurements of the attenuation of a low-power laser demonstrate that absorption spectroscopy of ball plasmoid discharges would be both feasible and informative.

4.1 Introduction

Recently, several publications have described the generation and subsequent analysis of ball plasmoid discharges [6–17]. Ball plasmoids are uniquely long-lived and are generated via a pulse of stored energy from a capacitor bank over the surface of an electrolyte at atmospheric pressure. Tens of kiloJoules of stored energy facilitate moderate current flow (on the order of tens of Amps, depending on the magnitude of the stored energy) between a central cathode and a surrounding liquid anode. The plasma formed at the cathode has been shown to be comprised of metal vapors, water vapor, excited atoms and molecules, and various ions. This geometry facilitates the formation of a spheroidal plasma which eventually detaches from the electrodes and exists as a self-sustaining plasmoid for approximately 100 ms before dissipating.

In addition to this long lifetime, there are several components of the discharge which are also interesting.

For example, it has been shown [15] that the early stages of ball plasmoid formation are governed by the development of arcs between the central electrode and grounded electrolyte, and that these arc channels are highly dynamic. The thermal nature of these arcs and their interaction with the liquid electrolyte coupled to the nonthermal properties of the plasmoid as it becomes detached and begins to dissipate present an interesting challenge to describe the system fully. There are also processes occurring on several time scales that must be considered for these discharges; e.g., electron impact excitation and ionization, chemical reaction processes, and fluid dynamic effects. Since the first description of the production of ball plasmoids in 2002 [6], incremental progress has been made in understanding the physics and chemistry of these discharges, however, more experiments and models are needed to fully describe all of the properties of these discharges.

This system is considered to be somewhat analogous to ball lightning— a natural phenomenon that has defied understanding since its first documentation. Ball lightning is a rare atmospheric event which is described as a luminous sphere of lightning moving through the sky in random patterns for an extended period of time before dissipating, either with a quiet hiss or a cacophonous explosion [?, 22, 29, 70]. Until recently, many were skeptical of the existence of ball lightning; however, Cen et al. [31] were able to capture naturally occurring ball lightning emission with a spectrograph in the field. There is still healthy discussion and debate in the literature regarding the formation mechanisms and apparent stability of ball lightning [20–28], and the quality of the various experiments undertaken to reproduce the phenomenon [22, 29, 30]. Of the theories and experiments that have been presented to date, none have been verified to the point where one can unequivocally state that ball lightning has been reproduced in the laboratory— this also includes the ball plasmoid model.

In this article, we present a set of experiments designed to study ball plasmoids in a well-defined parameter space. We expand on the work presented in [10] by performing measurements of current and voltage as a function of discharge energy and analyzing the resulting waveforms to describe the electrical properties of the discharge. We present optical and near-infrared emission spectra of the discharge under various conditions to extend and complement the work presented in [9] and [12]. We report emission from several atomic and molecular species, some of which have not yet been observed in ball plasmoid discharges. Using these emission data, we discuss the physical chemistry that could potentially be occurring in the discharge, specifically the processes by which plasmoid constituents are produced and excited. Finally, we demonstrate a simple experiment designed to assess the feasibility of performing optical absorption spectroscopy of this system using low-power lasers.

4.2 Experimental

4.2.1 Plasmoid Generator

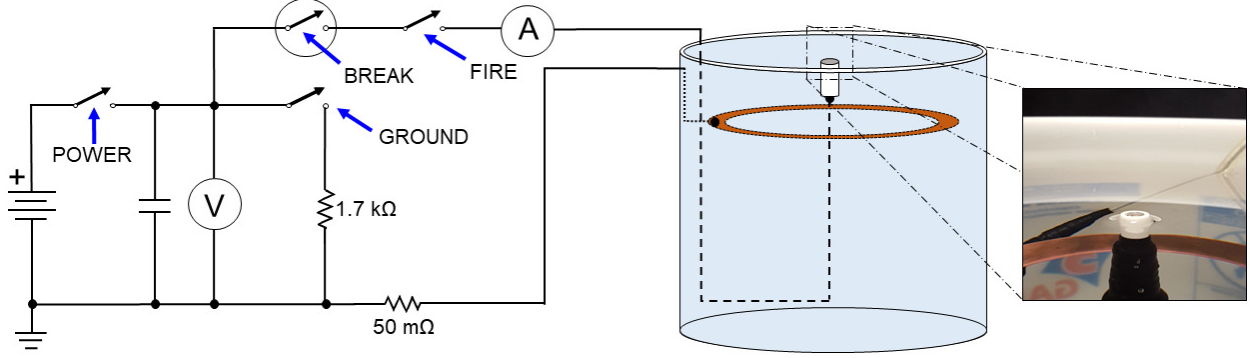


Figure 4.1: Simplified circuit diagram of plasmoid generator circuit. (A): Hall-effect current sensor (V): voltage divider. Inset: photo of a pristine tungsten electrode and alumina insulator.

Ball plasmoids are generated by means of a pulsed discharge over the surface of a grounded electrolyte (Figure 1) [13, 14]. A Glassman EK Series high-voltage DC power supply is used to charge a parallel-plate capacitor bank (Maxwell) up to 10,000 V (DC); typical discharge potentials fall between 5000-8000 V. An Arduino Uno microcontroller board controls three Ross Engineering E-series high voltage switches and a GigaVac G50WF vacuum relay, all of which govern current flow through the system. The same microcontroller is used to record outputs from various diagnostics including voltage, current, photodiode signal, and others (as needed) at approximately 1 kHz. The microcontroller is also used in some cases to trigger external events (e.g. camera acquisition) when able. For the experiments described in this article, time = 0 is defined as the point at which the microcontroller code is initiated and the discharge sequence begins; this event is physically triggered by activating an SPST spring-return switch.

The stored energy from the capacitor bank is delivered to an electrode setup which is partially submerged in deionized water contained within a 20 L polypropylene bucket. The cathode is a solid metal rod with a 6 mm outer diameter, and this cathode is insulated from the surrounding aqueous environment with a tube of dielectric material. The insulator is placed flush with the tip of the cathode, and the electrode is positioned such that the tip of the electrode protrudes approximately 1-2 mm above the surface of the electrolyte. Two different cathodes (and insulators) were used for these experiments: tungsten/alumina (Al_2O_3) and copper/quartz (SiO_2). The anode is a commercially-available copper ring gasket (Kurt J. Lesker, DN200CF) with a 222 mm outer diameter, 203 mm inner diameter, and a 2 mm thickness. This ring is fully submerged at a depth of approx. 6.5 cm below the cathode and establishes the electrolyte as

an electrical ground. The conductivity of the electrolyte is set by adding concentrated HCl dropwise to the deionized water. All discharges described in this article were performed at a conductivity of 300 μS unless stated otherwise; conductivity measurements were obtained with a calibrated Oakton PCSTest35 hand-held conductivity meter.

This iteration of ball plasmoid discharge circuitry facilitates the highest stored energy reported to date, to our knowledge. Table 1 provides a comparison of discharge energies previously reported in the literature. Values are calculated according to $U = \frac{1}{2}CV^2$, where U is stored potential energy, C is capacitance of the bank, and V is the potential applied to the capacitor.

Table 4.1: Summary of maximum potential energies (and associated references) used to generate ball plasmoids to date.

Potential Energy [kJ]	Reference
54.5	This Work
42.1	[11]
29.4	[8]
28.5	[10]
15.7	[14]
12.8	[15]
12.2	[12]
11.5	[9]
9.08	[6, 16, 17]
6.98	[13]
6.38	[7]

4.2.2 High-Speed Videography

Two high-speed cameras were used to monitor and characterize ball plasmoid discharges. For day-to-day operation of the experiment, a PixelLink PL-B742U camera with a Computar LP390-30.5 lens was used to record 640×480 pixel color images with a 1 ms exposure time at 85.3 frames per second. This translates to approximately 12 ms between successive frames. Additionally, a Phantom v5.2 camera with a 135 mm focal length Canon telephoto lens was used to record 1920×1200 pixel monochrome images of the discharge with 1 ms exposure time at 1000 frames per second. The Phantom camera provides additional diagnostics in the sense that the camera has absolute time resolution synchronized with the discharge electronics, and the resulting images are obtained at better image resolution, which facilitates more accurate size, brightness, and velocity measurements.

4.2.3 Emission Spectroscopy

Two spectrometers were used to record emission spectra of ball plasmoid discharges. For emission measurements, a screen was placed between the discharge and the spectrometer such that the emission from the hot cathode was blocked from the spectrometer’s field of view.

An Ocean Optics Jaz spectrometer (250-860 nm, 1 nm resolution FWHM) was used with Ocean Optics optical fiber to obtain low-resolution spectra. The spectrometer was controlled via SpectraSuite software with no additional modifications. The instrument is wavelength and intensity calibrated and the spectra are corrected for attenuation from the optical fiber. The spectrometer was operated with a 5 ms integration time and no spectral averaging was performed. Data were acquired by establishing an internal trigger; the instrument would collect data continuously when the recorded intensity across the entire bandwidth of the detector increased above the background intensity by 2%. This resulted in the collection of multiple spectra (up to thirteen in some cases) from a single discharge. To avoid saturating the instrument, the distance between the fiber and the plasmoid was adjusted and neutral density filters were also used in some cases.

A TRIAX 190 spectrometer was used to collect moderate-resolution spectra in the NIR (~ 750 -950 nm full bandwidth) in a Czerny-Turner configuration. The instrument had a 0.19 m focal length (f/3.9) with a 50 mm square grating (Thorlabs GR50-0610; 1000 nm blaze, 600 grooves mm^{-1}). Signal was collected with an air-cooled Hamamatsu C7041 CCD with a Hamamatsu array sensor (S7031-0906; 532×64 pixels). Integration times varied between 5 ms and 150 ms. The wavelength range of the spectrometer was set by manually rotating the grating. The spectrometer was wavelength calibrated using an argon arc lamp. A TTL pulse from the microcontroller was used to trigger the spectrometer after a 120 ms delay (from time = 0).

4.2.4 Laser Attenuation Measurements

To gain a sense of the optical depth of the discharge and to assess the feasibility of absorption spectroscopy experiments, three different wavelengths of laser light were passed through the plasmoid, and the attenuation of the beams (or lack thereof) was recorded at a photodiode. The signal from the lasers was measured using a ThorLabs DET36A Si detector (350-1100 nm), sampled at ~ 1 kHz, with additional focusing optics. Three low-power lasers were used in this set of experiments: a 250 mW blue-violet diode laser at 405 nm, a 5 mW green laser pointer at 532 nm, and a 0.5 mW HeNe laser at 633 nm (Thorlabs). Approximately 10% of the 405 nm beam power was picked off using an N-BK7 window rotated to Brewster’s angle (Figure 2); this 20 mW beam was used to perform attenuation measurements. Spectra of the 405 and 532 nm lasers were obtained with a high-resolution grating spectrometer to determine the mode structure and bandwidth of the

lasers. Each of these lasers appeared to have two modes near their central wavelengths; the bandwidth of the 405 and 532 nm lasers were approximately 2.3 nm and 2.9 nm, respectively.

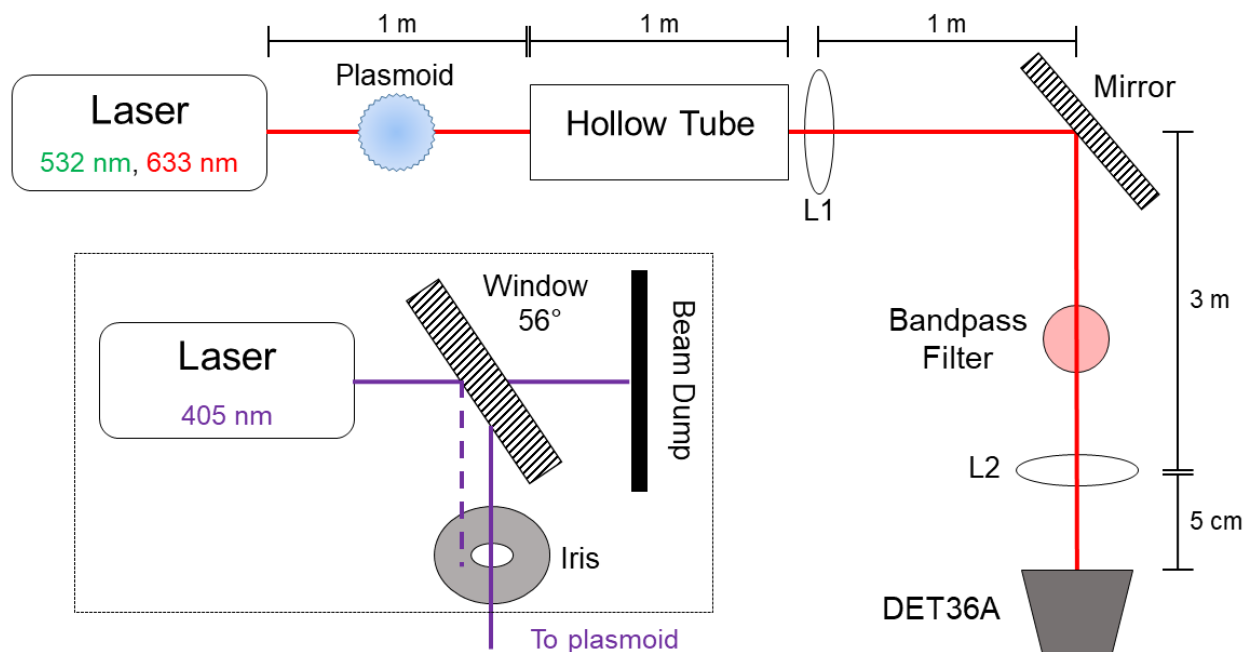


Figure 4.2: Diagram of the optical configuration used for laser attenuation measurements. Lengths are not to scale. L1: 100 cm lens, L2: 5 cm lens. Inset: optics used to pick $\sim 10\%$ of the 405 nm beam's power for attenuation measurements.

The optical setup is shown in Figure 2. The laser passed directly through the vertical axis of the discharge, passed through a one-meter long tube to reduce the solid angle over which light was collected, and was focused onto a flat Ag-coated mirror using a 100 cm N-BK7 plano-convex spherical lens. After the mirror, a set of bandpass filters was used (at the corresponding wavelengths) to isolate the signal from the laser. The beam was then re-focused onto the detector chip using a 5 cm CaF_2 plano-convex spherical lens. Neutral density filters were also used to reduce the power incident on the detector chip to avoid saturation effects.

If there were to be a significant density of absorbing species with transitions at these laser wavelengths, a decrease in signal would be observed at the detector. Great care was taken to collect the entirety of the laser spot at each optic— if the spot was at all occluded, steering of the laser resulting from the plasmoid's index of refraction (i.e., the plasmoid itself acting like a lens) would have been observed as attenuation. Furthermore, since these optics were not AR coated, backreflections returning to the laser were minimized wherever possible. Scattering of the beam by particulates could also result in a decrease in signal at the detector, however, these signals would likely be transient as the particles would pass through the beam at high

velocities [71]. Furthermore, the beam diameter through the plasmoid is rather large, so only large-diameter particles would contribute to complete attenuation of the beam.

4.3 Results and Discussion

4.3.1 Videography



Figure 4.3: A series of images obtained using the Phantom v5.2 high-speed camera from a single plasmoid discharge. A scale bar is included.

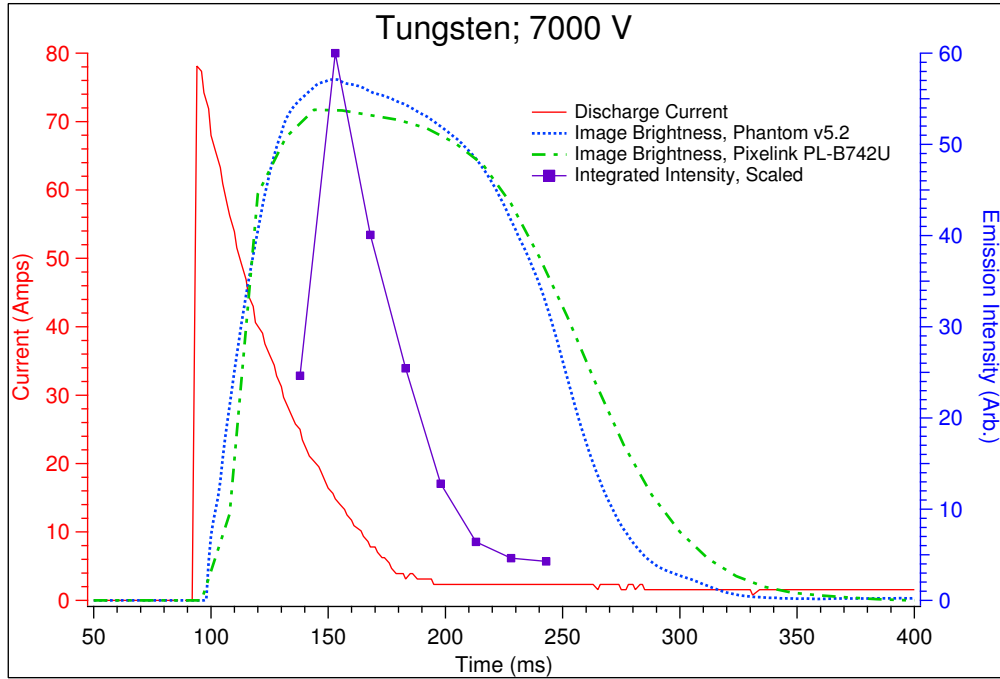


Figure 4.4: Luminosity curves for each camera overlayed with the current waveform collected from a 7000 V discharge with a tungsten electrode. Scaled integrated emission intensity is labeled with square markers.

Figure 3 shows a series of images collected with the Phantom v5.2 camera with the parameters described in the previous section. A scale bar is included, and the times provided in the images indicate the time after

the discharge is initiated. It is easily visualized that towards the end of the discharge an autonomous plasmoid exists with no evident power input from the electrode. As stated above, these images are taken 1 millisecond apart, as are the current data recorded from the microcontroller. Therefore, analysis of these images with image processing software (ImageJ, for example) can produce a luminosity profile of the discharge, and this profile can then be overlayed onto the voltage and current traces. An example luminosity profile is included in Figure 4.

Figure 4 also displays points corresponding to the integrated intensity of each emission spectrum in a time series recorded with the Jaz spectrometer (purple squares). Emission spectra are recorded 17 ms apart; this is determined by the integration time and data transfer rate of the instrument. Given that there was no synchronization of the spectrometer and the discharge circuitry, the point at which the first spectrum was recorded must be estimated. This was done in the most consistent and unambiguous way possible: the time at which the visible emission from the discharge was greatest (determined from the maximum of the luminosity profile) was matched with the spectrum with the largest integrated emission intensity. Preceding and subsequent spectra are positioned in 17 ms increments in time before or after this spectrum. This imparts an estimated uncertainty of ± 10 ms. Note that times labeled on the emission spectra shown in section 3.3 were determined using this method, and that these times are relative to time = 0 as defined in Section 2.1.

4.3.2 Electrical Diagnostics

Figures 5 and 6 are current traces collected at different discharge potentials for tungsten and copper electrodes. The profiles shown here are similar to those reported by other groups with similar discharge circuitry [10–12,15]. This is the first presentation of multiple current profiles as a function of discharge potential and electrode composition. The “FIRE” switch (see Figure 1) closes at 50 ms, and the first visible emission at the cathode occurs at approximately 100 ms, after which plasma begins to form. Streamers (arcs) emerge from the cathode and extend over the surface of the electrolyte, and significant current begins to flow, reaching a maximum after a few ms. Once current flow increases, a jet of plasma begins to form at the cathode. At this point, the discharge current and potential begin to decrease exponentially as the plasma grows in size and eventually detaches from the cathode.

The current and voltage waveforms do not vary significantly with discharge potential or electrode material, and the maximum current increases linearly with potential (Figures 5 and 6). The maximum currents recorded for different electrode materials are not significantly different.

It is apparent that current still flows late in the discharge in some cases. This current is the result of

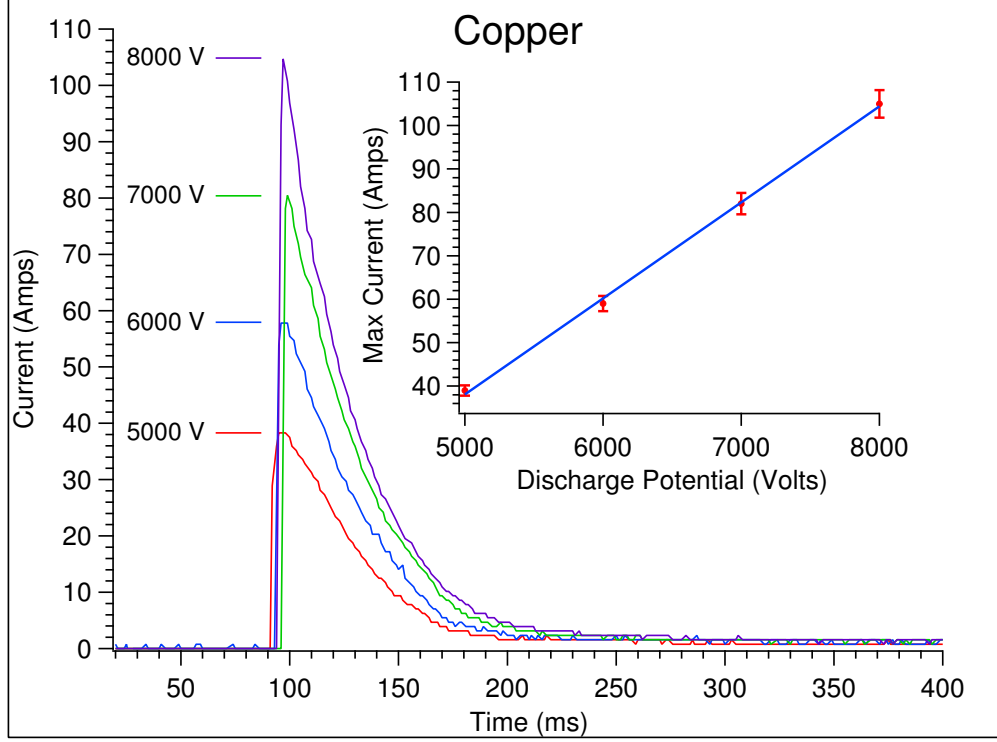


Figure 4.5: Discharge current profiles as a function of discharge potential recorded using a copper electrode. Inset: maximum discharge current as a function of discharge potential for a copper electrode.

an electrical connection between the cathode and the electrolyte resulting from spark channel formation (see Section 3.2.1). The 10-bit resolution of the A/D converter used in the microcontroller (4.9 mV per bit) combined with the properties of the Hall effect sensors gives uncertainties of ± 0.8 A for high-current discharges (75 A max and above) and ± 0.3 A for moderate-current discharges (< 75 A max). Electrode materials appear to have only a slight influence on the electrical properties of ball plasmoid discharges. However, as will be shown below, the electrode material greatly influences the emission spectrum of the plasmoid.

Current and Voltage

Figure 7 provides an example analysis of the electrical characteristics of a plasmoid discharge (8000 V in this case). Resistance and power were calculated from experimental data according to Ohm's Law and the definition of electrical power ($P = IV$). Current profiles were fit to an exponential with a time constant of 32.7 ± 0.8 ms. Voltage profiles were fit to a biexponential: this indicates that a fast time constant $\tau_1 = 24 \pm 2$ ms governs the voltage at early times, while a larger constant $\tau_2 = 270 \pm 40$ ms is dominant at longer times. The presence of the two time constants is a result of the electrode geometry (see below).

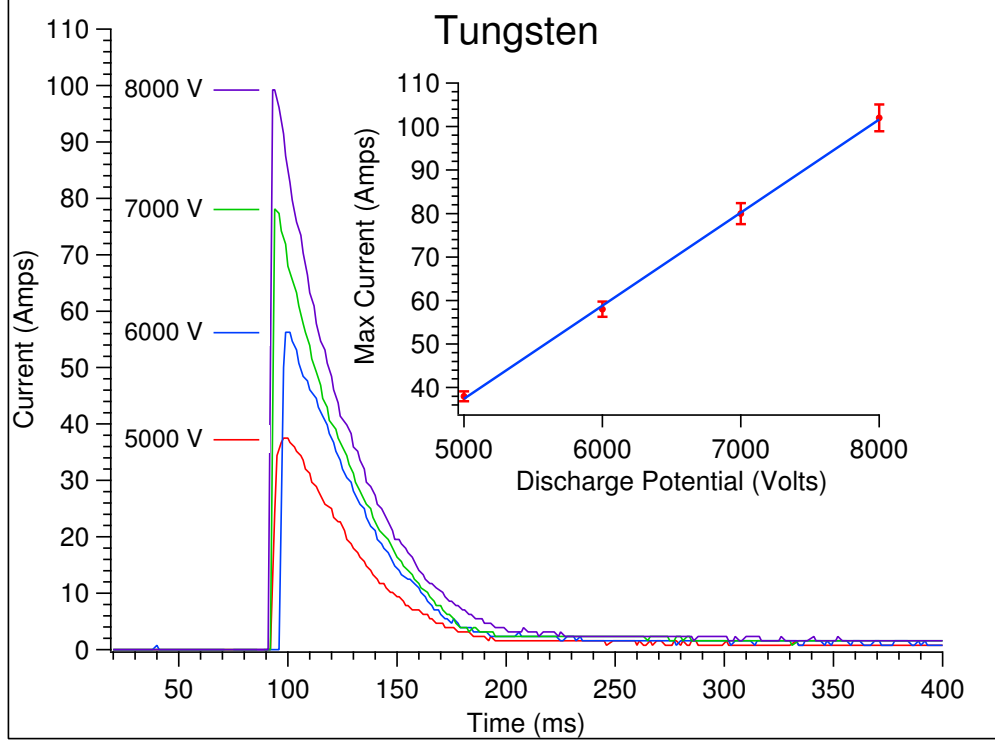


Figure 4.6: Discharge current profiles as a function of discharge potential recorded using a tungsten electrode. Inset: maximum discharge current as a function of discharge potential for a tungsten electrode.

τ_1 governs the first portion of the discharge during which there is significant current flow and a jet is produced from the tip of the cathode. The effect from τ_2 is always present, but becomes much more significant after the current and voltage have significantly decreased. At this point there is no longer a jet produced at the cathode, but there is still an electrical connection between the cathode and the electrolyte and current continues to flow on the order of less than 300 mA (this is the detection limit of the Hall effect sensor). This connection is established at the start of the discharge via spark channels and is a result of the close proximity of the cathode to the electrolyte. Indeed, positioning the cathode below the surface of the insulator tube increases the air gap between the cathode and the electrolyte and does not facilitate spark channel formation. This observation indicates that, although our electrode geometry allows for the analysis of plasma components without potential interference from water, it is not feasible to use the electrical profiles reported here to determine the point in time at which the plasmoid detaches from the electrodes. However, this limitation only applies to the electrode geometry and circuit described here.

The plasma jet formed at the tip of the cathode cannot be sustained at or below a certain potential. We have determined that (for these experimental conditions) a plasmoid will not form at potentials less than ~ 2800 V. Intentionally charging the capacitor bank to a voltage that will not produce a plasmoid but

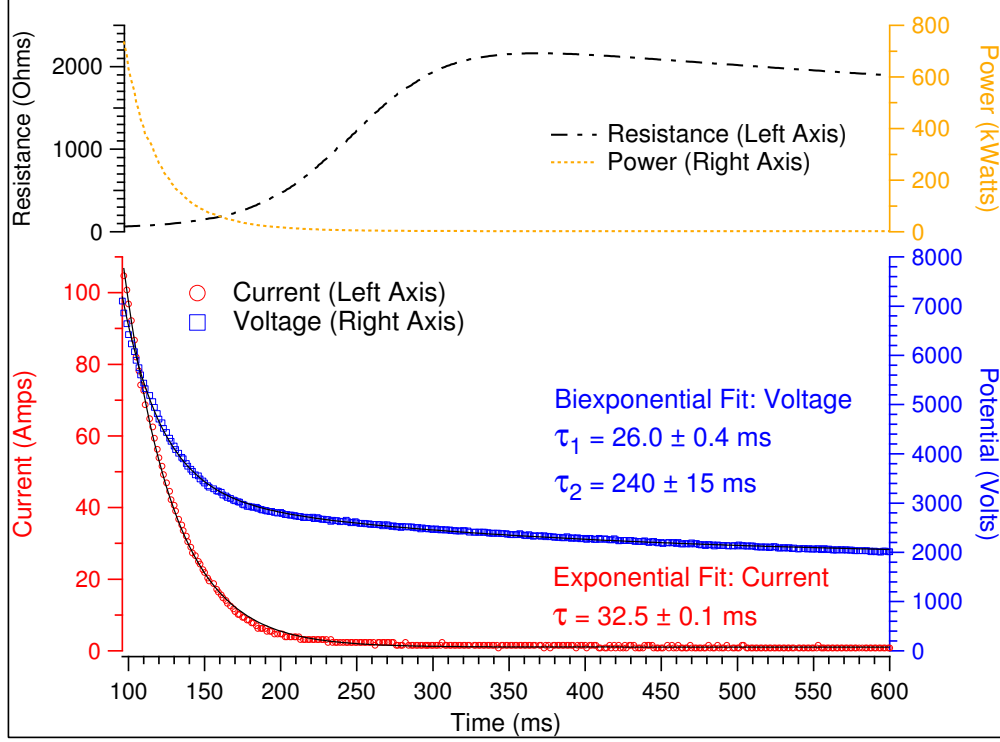


Figure 4.7: Fits to the current (red circles) and voltage (blue squares) profiles recorded during an 8000 V discharge, and the associated resistance (black dashes) and power (gold circles).

does establish spark channel connections generates a voltage waveform that can be described by a single exponential. Current diagnostics and videography of the cathode recorded from discharges at 2500 V (see Appendix E) show that no plasmoid is formed, yet a small amount of current flows via spark channels similar to the initiation phase described in [15].

Resistance

The resistance across the lifetime of the discharge is not constant (Figure 7). Rather, the resistance profile rapidly increases to a maximum value before slowly decreasing towards the end of the discharge. A similar observation was presented in [10]. This trend is present no matter the parameters used to produce the plasmoid, although the magnitude of the resistance change can vary. The most likely explanation for this increase in resistance is a decrease in the conductance of the plasma resulting from two possible mechanisms:

1. As the plasma conductivity is proportional to the square of the electron density, a decrease in electron density would manifest as a decrease in overall conductivity and increase in resistivity. This assumes that as current decreases, the electron density of the plasmoid also decreases.
2. The dynamic nature of the arcs observed via high-speed videography in [15] could also explain this

increase in resistance: as the lengths of the streamer channels increase (and the conductivity of the channels remain essentially constant) the conductance will subsequently decrease.

The temperature of the electrolyte also increases in the vicinity of the electrode, but the bulk temperature of the electrolyte does not significantly increase during a discharge, so there is likely some negligible contribution to the increase in resistance from heating of the electrolyte.

Detachment

The autonomous nature of the plasmoid is important to discuss in more depth, as this is critical for claims that this system is somewhat analogous to ball lightning. Most publications describing ball plasmoids include a statement regarding the physical detachment of the plasmoid from the electrode based on visual appearance and/or position [6–14, 16, 17]. While the cathode may still be glowing from residual current flow, the plasmoid rises (due to buoyant forces) tens of cm above the electrode and does not appear to be connected by any luminous channels. Skeptics could argue, however, that lack of visible emission does not necessarily guarantee a lack of electrical connection.

To this end, Egorov and Stepanov [17] show that the voltage across the electrodes in their setup has decreased to zero by 100 ms into their discharge (which would be equivalent to approximately 200 ms for our circuit), while the luminosity of the plasmoid does not fully decay for another several hundred ms. They argue that because there is no potential drop, no current can flow to the plasmoid. Additionally, the current waveforms reported by Stelmashuk and Hoffer [15] show a distinct point at which current flow through the circuit stops, which they have indicated as the beginning of the autonomous phase. It is possible that this point is more easily determined due to the 4 mH inductor added to their circuit, however, this is a more accurate and systematic way to determine the point at which the plasmoid becomes a self-sustaining entity than has been discussed previously. As discussed above, our electrode geometry does not facilitate a quantitative method for determining the point at which the plasmoid detaches from the electrodes.

4.3.3 Emission Spectroscopy

Figures 8 and 9 show examples of time series of emission spectra collected across a single discharge using a copper electrode and a tungsten electrode (respectively). The signals observed in these spectra have been assigned to atomic or molecular transitions where possible. Atomic transitions were assigned using the NIST Atomic Spectral Database (ASD) [72] based on wavelength proximity and magnitudes of Einstein A coefficients. A comprehensive list of identified atomic transitions can be found in the Supplementary Material. Individual rovibronic transitions within molecular emission bands (e.g., OH $A^2\Sigma^+ \rightarrow X^2\Pi$) are not

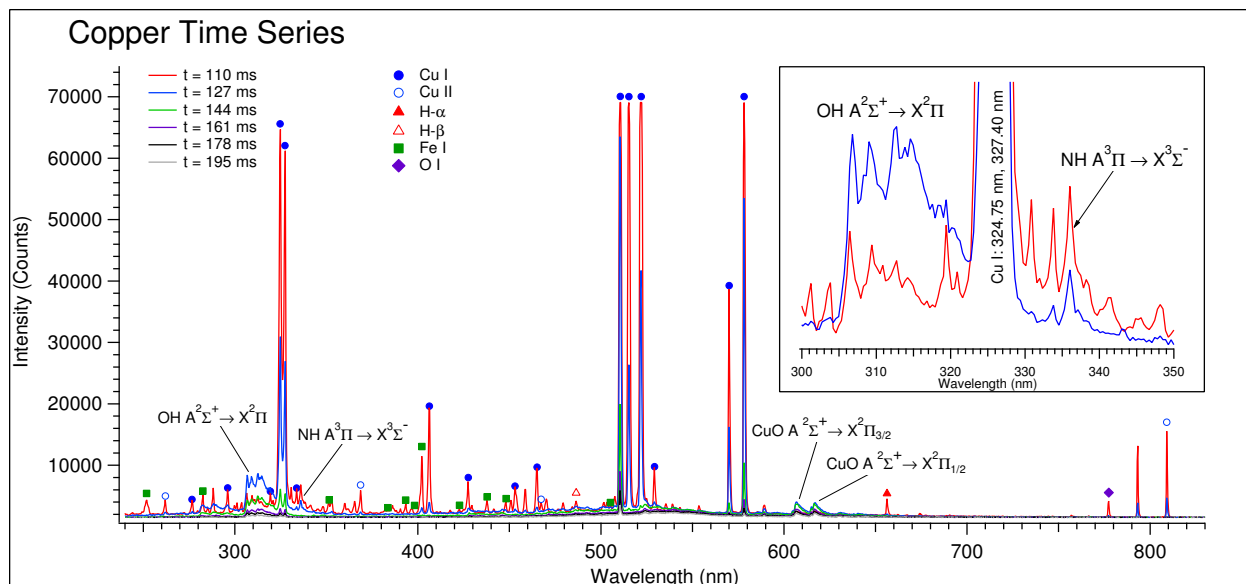


Figure 4.8: Example of a series of spectra collected during a single 7000 V discharge with a copper electrode with assigned electronic transitions. Inset: magnified spectra between 300-350 nm showing emission from molecular species. Note that not all transitions are labeled; a full list of assignments can be found in Appendix E.

identified due to insufficient resolution. Atomic signals are the most prevalent at early times; emission from excited molecules is (generally) observed several milliseconds later than that of excited atoms.

Emission spectra collected from these discharges provide a wealth of information. Spectra of discharges with a copper electrode show emission from many atomic transitions of copper and the $A^2\Sigma^+ \rightarrow X^2\Pi$ band of OH radical similar to what has been reported previously [9]. Additionally, emission lines of atomic iron, hydrogen (Balmer-series H- α and H- β), oxygen, and nitrogen have also been assigned. Lines of hydrogen likely arise from dissociation of water from the electrolyte and subsequent radiative decay. It is possible that N I and O I are formed from dissociation of ambient nitrogen and oxygen. Other molecular bands are also present in copper electrode spectra, including the NH $A^3\Pi \rightarrow X^3\Sigma^-$ band (this is the first observation of this emission band in ball plasmoid discharges) and the CuO $A^2\Sigma^+ \rightarrow X^2\Pi_{1/2,3/2}$ bands. CuO is formed as metallic copper vapor is oxidized during the discharge. Possible formation pathways of NH are discussed below.

Tungsten electrode spectra are rich in atomic emission signals superimposed onto continuum emission. Many neutral tungsten transitions are present in the visible, and a larger number of atomic iron lines are observed in tungsten electrode spectra compared to copper electrode emission spectra. The presence of iron in these spectra can be explained by the iron impurities in the electrodes and the insulators used to generate the discharges. It is also possible that the cutting and polishing of the electrodes imparts a small amount of

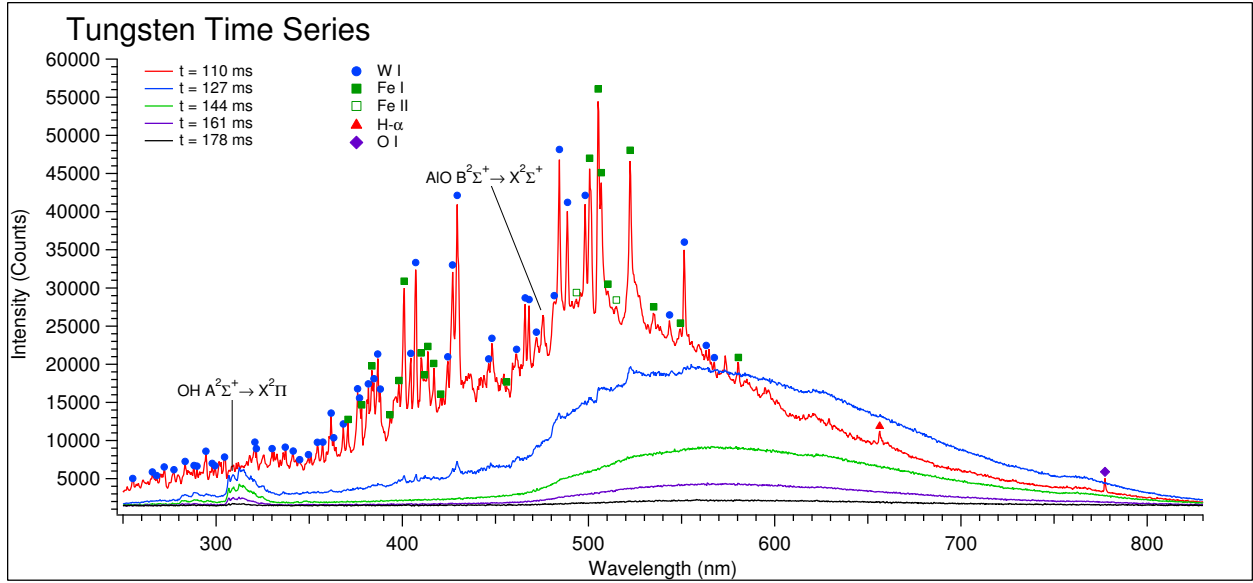


Figure 4.9: Example of a series of spectra collected during a single 7000 V discharge with a tungsten electrode with assigned electronic transitions. Note that not all transitions are labeled; a full list of assignments can be found in Appendix E.

iron to the exposed surface from which the discharge emanates.

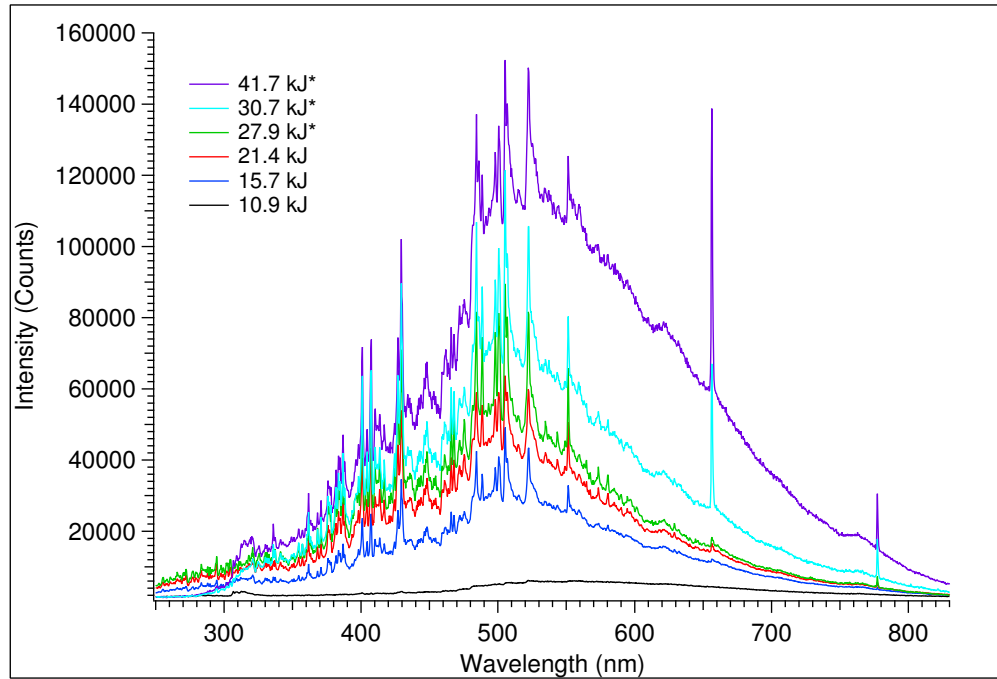


Figure 4.10: Emission spectra from tungsten electrode collected at varying discharge energy. Asterisks indicate that spectra were corrected for distance and/or neutral density attenuation.

Higher discharge energies are achieved by increasing the voltage or by increasing the capacitance (Figure

10). At these higher discharge energies, the underlying continuum (and therefore the total visible emission) from plasmoids produced with a tungsten electrode is more intense, and the S/N of atomic and molecular signals generally increases as a function of increasing discharge energy for both copper and tungsten.

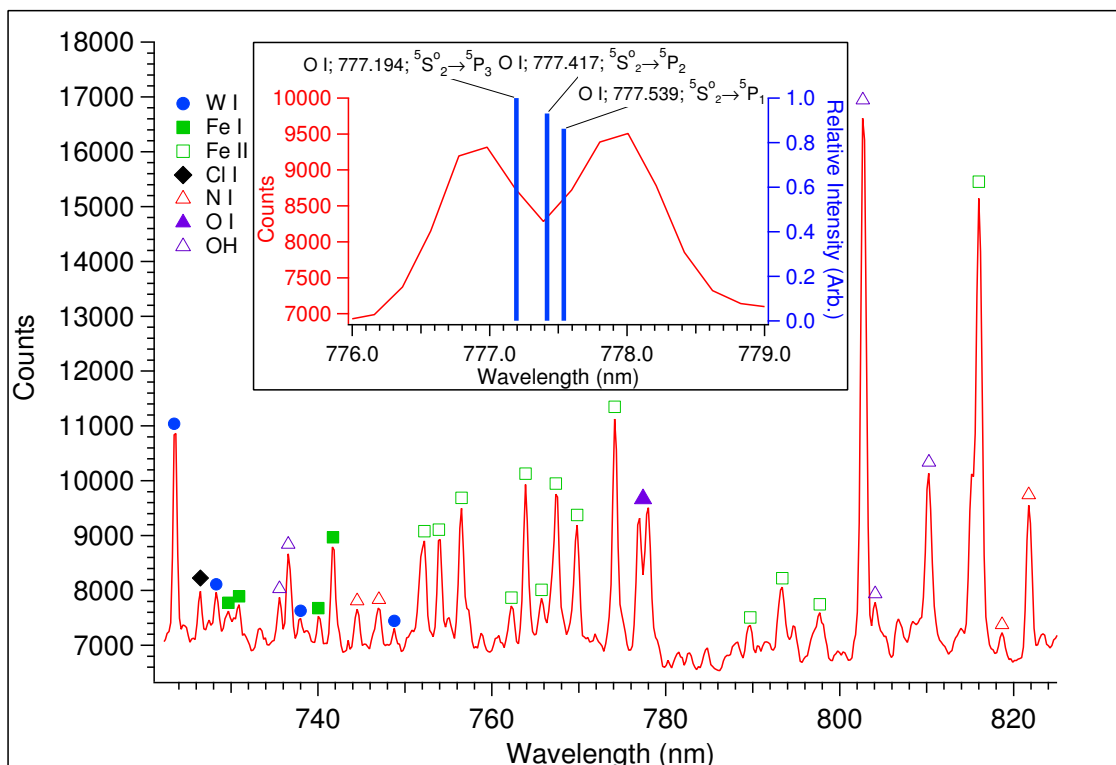


Figure 4.11: Example emission spectrum collected from a 6000 V discharge with the TRIAX spectrometer. Inset: self-reversed emission line from atomic oxygen overlaid with a stick spectrum of the O I 777 triplet; relative intensities obtained from the NIST ASD [72].

Emission spectra recorded in the NIR (Figure 11) show signals from several transitions of singly ionized iron and several transitions of atomic tungsten and nitrogen. Additionally, self-absorption of the O I 777 nm ($^5S^{\circ} \leftarrow ^5P$) triplet emission signal is observed in many cases. The self-reversal and broadening of this line, shown in the inset of Figure 11, indicate that photons emitted from excited states of O I experience a temperature and/or electron density gradient when traveling from the center of the plasmoid. One possible explanation of these results could be that the emitted photons travel from a hot and dense “core” outward and through a cooler and less dense environment before being collected by the spectrometer. This interpretation is consistent with the cool “shell” model for ball plasmoids proposed by Versteegh et al. [9].

Simulations of OH and NH emission spectra were generated in PGOPHER [63] using molecular constants from the literature [73,74] and were fit to the experimental spectra to determine their rotational temperatures. The resolution of the collected spectra is not sufficient to perform a Boltzmannian-type fit of individual

transitions, rather the overall shapes of the emission profiles of these molecules were fit to a rotational contour. Numerical results from these fits are included in Tables 2 and 3, and example contour profiles are included in Appendix E. Similar to what we reported previously [14], these temperatures are slightly lower than those presented in [9]. Rotational temperatures are large at early times in the discharge and decrease as a function of time as the plasmoid relaxes to equilibrium. Finally, it appears as though the maximum rotational temperature increases with discharge energy; this could be caused by higher currents resulting in more electrons with sufficient energy to populate upper rotational levels of these molecules.

Table 4.2: Series of calculated rotational temperatures of OH and NH from a single 8000 V discharge.

Time ^a [ms]	T _{rot} ^{OH} [K]	T _{rot} ^{NH} [K]
0	— ^b	—
17	—	4900±1200
34	—	4700±1100
51	7100±900	3200±800
68	6200±800	3300±1000
85	5900±800	—
102	5400±700	—
119	4800±700	—
136	4400±600	—
153	3700±500	—
170	3100±400	—

a: Times are relative to time = 0.

b: A dashed line indicates no emission or insufficient S/N across the fitting region.

Table 4.3: Variations in maximum rotational temperature as a function of stored energy for a tungsten electrode.^a

Energy [kJ]	T _{rot} ^{OH} [K]	T _{rot} ^{NH} [K]
10.9	5000±400	— ^b
15.7	5200±500	—
21.4	6500±300	5400±1600
27.9	6800±900	5700±1700
30.7 ^c	6000±700	4800±400

a: Determined by averaging the maximum rotational temperature across multiple discharges.

b: A dashed line indicates no emission or insufficient S/N across the fitting region.

c: Fits are poorer quality; an ND filter effected the emission profile in the UV and blue regions of the spectrum.

The emission spectra collected from these experiments can provide additional information regarding the physical chemistry occurring during the discharge. However, given the information that has been collected, we cannot describe the shape or maximum (or maxima) of the electron energy distribution function (EEDF) or all of the reactions that occur during the plasmoid’s lifetime. We can, however, present arguments regarding the EEDF and the chemistry based on the nature of low-temperature plasmas in air in conjunction with the data presented above.

Atoms and Electrons

Emission signals from singly ionized copper and iron indicate that electrons with energy sufficient to ionize these species (7.63 and 7.90 eV, respectively [75, 76]) could be present in the discharge. It is likely that the EEDF has a high-energy tail which facilitates ionization of these species, but the relative populations of these electrons compared to lower energy electrons is unknown. Furthermore, radiative transitions from excited states of singly ionized copper possibly indicate the presence of electrons with energies greater than 7.90 eV. For example, the upper state energy of the $2[5/2]_3 \rightarrow 3F^\circ_2$ transition of Cu II (262.07 nm) is 13.39 eV [72], which is almost twice the ionization energy of neutral copper.

These excited states could be populated by direct electron impact, but stepwise ionization (which does not necessarily require highly energetic electrons) is more likely in a low-temperature plasma [3]. The pulse width of the discharge is also such that additional electrons are available for collisions as the discharge progresses, which could facilitate ionization after an initial electronic excitation. Excited states can also be populated “from above,” i.e., from radiative or dielectric recombination of the atomic ion in the early stages of the discharge [77, 78]. With a limited knowledge of the mechanisms that populate these states, it is difficult to extract quantitative information from these spectra regarding the electron temperature, for example.

Imidogen

Emission from hydroxyl radical has been reported in ball plasmoid discharges previously [9, 14], however, this (to our knowledge) is the first observation of emission from imidogen ($\text{NH } A^3\Pi \rightarrow X^3\Sigma^-$) in a ball plasmoid discharge. The presence of both NH and atomic nitrogen indicate that, in addition to the dissociation of water leading to formation of OH, ambient nitrogen is likely also being dissociated by some pathway to form N I and NH. The dissociation energy of nitrogen is 9.79 eV, and while it is possible that electrons of this energy are generated during the discharge, the mechanism by which molecular nitrogen is dissociated is unclear. Under these conditions, two pathways could produce NH, both of which are initiated by dissociation of molecular nitrogen. Dissociation of N_2 could proceed via direct electron impact with a 9.79 eV electron, or by stepwise vibrational excitation of a nitrogen molecule to the dissociation limit. The contribution of vibrational energy to this process is discussed in the next subsection. The liberated nitrogen atoms could then react with a water molecule to form OH and NH, or combine with atomic hydrogen produced from the dissociation of water. Given that NH is a radical, it will likely be consumed rapidly after it is formed; the production of ammonia is perhaps the primary consumption pathway for NH.

Vibrational Excitation

At these discharge conditions (i.e., at atmospheric pressure and low electron temperature) the contribution from vibrational energy to molecular excitation and dissociation is likely significant [79–82]. We have previously shown that ball plasmoid discharges are vibrationally excited [14], and the data reported above warrant a deeper discussion of vibrational excitation of ball plasmoid constituents in general.

In low-temperature plasma discharges, the cross sections σ_{vib} and rate constants k_{vib} for vibrational excitation of molecules by electron impact are, generally, rather large at low electron temperatures (Table 4). The electron temperatures at which these constants are maximized are between 1.7–3.5 eV for N_2 and 0.1–1.5 eV for O_2 , while for water these values are maximized at slightly larger temperatures ($k_{vib} = 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ between 5–10 eV) [3]. At similar values of electron temperature, the cross sections (and therefore the rate constants) for other excitation processes (e.g., electronic excitation, ionization, and dissociation) can be much smaller [83].

Table 4.4: Relevant collisional constants of N_2 and O_2 . Data obtained from reference [3] can be found on pages 97–98.

	N_2 , 2 eV	O_2 , 1 eV
$\sigma_{vib} [\text{cm}^2]$ [3]	3×10^{-16}	10^{-17}
$k_{vib} [\text{cm}^3 \text{ s}^{-1}]$ [3]	3×10^{-8}	10^{-10}
$k_{elec} [\text{cm}^3 \text{ s}^{-1}]$ [83]	1.47×10^{-10}	1.24×10^{-10}
$k_{ion} [\text{cm}^3 \text{ s}^{-1}]$ [83]	4.5×10^{-12}	1.60×10^{-14}
$k_{diss} [\text{cm}^3 \text{ s}^{-1}]$ [83]	5.01×10^{-11}	2.25×10^{-12}

4.3.4 Laser Attenuation

The HeNe laser (633 nm) and blue-violet diode laser (405 nm) described in Section 2.4 were not attenuated by the plasmoid (see Appendix E). However, the green laser (532 nm) was significantly attenuated by plasmoids generated from tungsten and slightly attenuated by copper plasmoids. Figure 12 shows the voltage outputs of the photodiode collected from these experiments overlayed with the current traces from the discharges. “Background” signal resulting from emission of the plasmoid (collected with the laser off) at 532 nm is also included. This figure clearly shows that as the plasmoid is formed, the signal at the diode decreases as a result of the laser being absorbed.

The question of what species is absorbing the laser is complex due to the numerous species present in the plasmoid. Based on the emission spectra, it is clear that there is a significant amount of electronically excited metal vapor present in the plasmoid— this indicates that neutral metal vapor could also be present. There are several transitions of neutral tungsten and iron present between 530–534 nm in addition to a series of

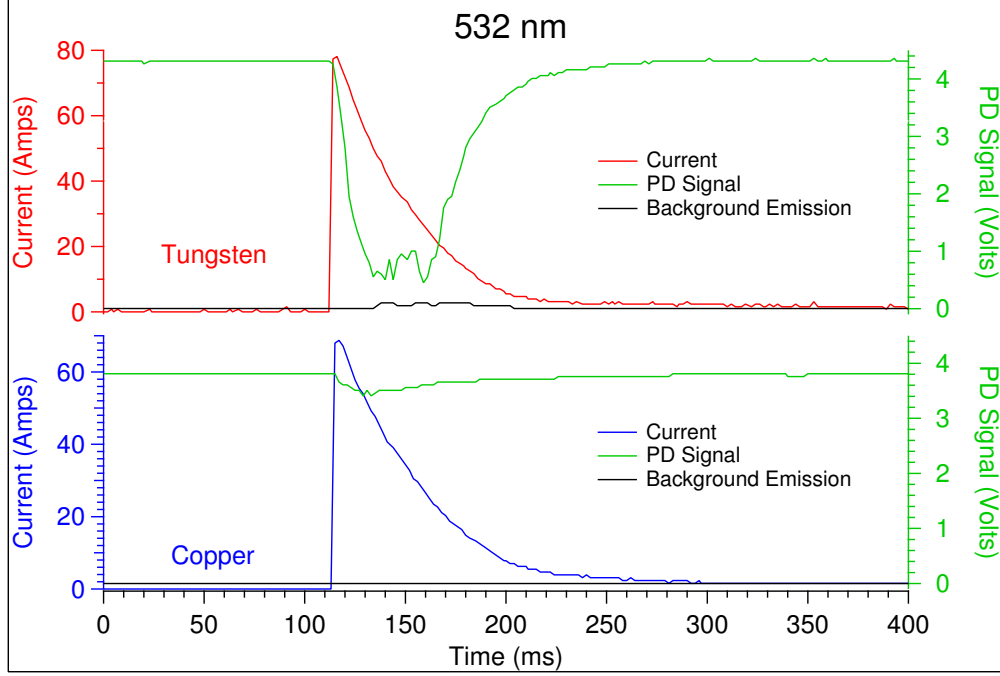


Figure 4.12: Voltage outputs from photodiode ($\lambda=532$ nm) overlayed with current profiles of ball plasmoid discharges at 7000 V. Attenuation of the laser is observed between ~ 100 -250 ms.

overlapping atomic oxygen transitions located at 532 nm ($^5D^{\circ} \leftarrow ^5P$) [72]. Cross sections and f-values of these transitions were determined using the description provided in [19] in conjunction with Einstein coefficients provided in the NIST ASD [72]. It is useful in this case to define an absorption coefficient α_i :

$$\alpha_i [\text{cm}^{-1}] = \sigma_{abs} n_i \quad (4.1)$$

σ_{abs} is the cross section for photon absorption (cm^2) at the wavelength of the transition, and n_i is the number density of species i present in the gas phase (cm^{-3}). To determine α for the species mentioned above using Equation 1, estimates of the number densities of these species were made.

For neutral metal vapor, the mass of the electrode before and after a series of ten discharges at identical conditions was recorded. It was found that at 7000 V, approximately 0.5 mg of electrode material is lost to the plasmoid per discharge. This value was used to establish a reasonable upper bound of 10^8 cm^{-3} for the number density of metal vapor present in the plasmoid. These values combined with the photon absorption cross section yields an absorption coefficient α of approximately 10^{-3} cm^{-1} for neutral tungsten and iron near 532 nm. These values suggest that these species could absorbing the laser.

It is unlikely that O I (5P) is absorbing at this wavelength; the lower state of this transition is approx. 10.8 eV above the ground state, and at 5000 K, equilibrium dictates that the density of O I (5P) would

be on the order of 10^5 cm^{-3} . This value was calculated assuming a density of 10^{16} cm^{-3} for O I, which was estimated assuming a 0.1% conversion of ambient oxygen to O I via dissociation of ambient O_2 . It is, therefore, rather unlikely that this atomic level of oxygen is significantly populated in this system.

It may also be possible that a molecular species is absorbing the laser, however, the f values of transitions of molecular species thought to be present in the discharges are several orders of magnitude smaller than that of the atomic transitions in this region, which results in an even smaller absorption coefficient (by several orders of magnitude).

4.4 Conclusions

In this article, we have presented several experiments which further examine the physics and chemistry of ball plasmoid discharges. We have presented an analysis of the electrical profiles generated with our circuit and electrode construction and have discussed the nature of the observed resistance change across the lifetime of the plasmoid. Optical and NIR emission spectroscopy data were used to calculate rotational temperatures of excited molecules generated during the discharge and to gain additional insight into the physical chemistry occurring throughout the lifetime of the plasmoid. These data have facilitated a more in-depth discussion of the kinetics which govern the reactions occurring in the plasmoid and several possible pathways for production of N I, O I, and NH. We have discussed vibrational excitation of species in the plasmoid and the contribution of vibrational energy to molecular dissociation. Finally, we have shown that absorption spectroscopy of ball plasmoid discharges is feasible and warrants further experimental effort.

Vibrational excitation of plasmoid constituents should be examined in more detail. It is well known that vibrational excitation and dissociation of ambient nitrogen can contribute to chemical reactions in plasmas, but more interestingly, vibrationally excited nitrogen can serve as a reservoir of sorts for chemical energy. It has been shown that the rate constants for vibration-translation (VT) relaxation of nitrogen are several orders of magnitude smaller than that of vibrational excitation [3,83]. We have shown above that vibrational excitation of nitrogen is likely occurring in ball plasmoid discharges, and it stands to reason that excited molecular nitrogen could be contributing to chemical reactions occurring in the plasmoid throughout its visible lifetime. In other words, vibrationally excited nitrogen could be one of the key components that contributes to the prolonged lifetime of these discharges.

The experiments and results presented in this article highlight the importance of parameterizing ball plasmoid experiments to whatever extent possible. By performing measurements at higher energies than previously reported, we have shown that additional interesting chemistry and physics are occurring during the

discharge. We have also shown that, while the electrical properties of the discharge (i.e., current and voltage) do not change significantly between electrode materials, the emission spectra (and therefore the chemistry of the discharge) do in fact change. This suggests the possibility of studying ball plasmoid discharges using other durable electrode materials, such as platinum, or perhaps changing the composition of the electrolyte.

There are still several physical parameters relating to ball plasmoids that must be quantified experimentally. These currently unknown variables mainly include the number densities of plasmoid constituent species, especially ground state densities of atoms and molecules produced in the plasmoid and the number density of electrons across the lifetime of the discharge. The laser attenuation measurements described above indicate that absorption spectroscopy could be implemented to measure densities of species in the plasmoid, which would remove ambiguity from relying on emission spectra, which rely solely on excited state populations and do not give accurate ground state densities without a thorough collisional-radiative model. The most informative absorption experiments would utilize a broadband excitation source, thus allowing signals from all absorbing species within the bandwidth of the source to be recorded.

One promising method that could be used to quantify the electron number density as a function of time is microwave interferometry [84, 85]. By measuring the phase shift and attenuation of an X-band beam after passing through the plasmoid, the electron number density can be quantified for this system. These data could then be compared to values previously obtained by Stark broadening [9]. The determination of the number densities of atomic and molecular species and the electron number density (in conjunction with results presented in this article) will also allow detailed kinetic and collisional radiative models of ball plasmoid discharges to be constructed and tested.

Chapter 5

Conclusions and Future Directions

As discussed in the beginning of this thesis, each of the previous chapters was presented an isolated experiment or set of experiments in and of themselves, and each had a standalone interpretation of results. Multiple techniques and methods were used to probe the composition and properties of the discharge. The results from these experiments should be discussed together, now that each of the individual studies has been described in sufficient detail. The following chapter provides additional interpretation of our results and attempts to crystallize our current chemical and physical understanding of ball plasmoid discharges. From these collective data, a possible mechanism for energy “storage” via molecular excited states in these discharges is described.

The results presented in this thesis also lead to additional questions about the plasmoid. This chapter also provides a discussion of experiments which could be performed to gain additional information about the chemical and physical behavior of the discharge. Some of these experiments are much more developed in thought and in preliminary data collection than others; these studies would therefore be excellent starting points for the next iteration of this project. From a different perspective, this chapter could be considered to be an early draft of a program funding proposal, which could be submitted to an agency for review at a later date.

5.1 Summary of Results

Although each previous chapter has provided a great amount of detail regarding our experimental results and our interpretation of those results, for the sake of cohesion, each of the chapters will be summarized briefly here.

5.1.1 Chapter 2- Mass Spectrometry and Ion Composition

The first set of data that were published were those from the mass spectrometry experiments. These experiments, although simple in design, addressed a very fundamental question regarding the composition of

the plasmoid: the identities of the ions produced during the discharge. Previously, emission from atomic ions was observed from ball plasmoid discharges using OES [9], but no additional study regarding ions has been performed since that initial report. We have shown that there are indeed ions present in the plasmoid, and that they are produced from a combination of electrode materials, the electrolyte, and some ambient species. These ions were mainly observed as clusters, mainly around a metallic center. Given the experimental setup (namely the sampling method and ion transit time), it is likely that ions produced toward the end of the discharge (or that form as a result of charge-exchange collisions) were primarily analyzed. The distance between the plasmoid interior and the mass analyzers was extremely long; it is therefore likely that these ions underwent multiple collisions along their route to the detector. Finally, substituting the deionized water electrolyte for a heavy water electrolyte indicates that the water cluster distribution in the gas phase is significantly influenced by the composition of the electrolyte.

5.1.2 Chapter 3- Infrared Emission Spectroscopy: H_2O , and OH

Infrared emission spectroscopy studies extended the spectral window across which we have observed emission from ball plasmoids. For the first time, emission from excited molecules (namely water and hydroxyl radical) was collected from ball plasmoid discharges in the infrared, and the emission spectra were processed to extract quantitative information. These emission spectra were fit to synthetic spectra generated using PGOPHER with line parameters contained within the HITRAN database, and rotational temperatures were extracted from these contour fits. It is important to note that these fits allowed a single rotational temperature, however, these temperatures are good estimates which facilitate future studies of the system. The temperatures of the bending and stretching modes of H_2O were determined to be 1900 ± 300 K and 2400 ± 400 K, respectively. These temperatures are comparable to what one would observe from water in an oxy-acetylene flame. The rotational temperature of OH was found to be 9200 ± 1500 K, which is considerably lower than the previous value presented in [9], however, it is quite likely that our emission spectra were recorded much later in the discharge. This is further explained by the fact that OH radical is most excited at early times in the discharge, and as the discharge recombines, the OH temperature decreases as a function of time. In other words, OH is rapidly excited to a high rotational temperature, and the rotational temperature decreases as the plasmoid equilibrates.

5.1.3 Chapter 4- Electrical Diagnostics and Emission Spectroscopy

Several experiments and their various analyses are presented in Chapter 4. In this work, analysis of the electrical profiles collected from ball plasmoid discharges was performed in a more systematic fashion than

previously reported. We have demonstrated that the current profiles of the discharge (at various conditions) can be fit to a single exponential with a time constant $\tau = 32.7 \pm 0.8$ ms, while the voltage traces must be fit to a biexponential. This analysis, and the determination of the magnitudes of the two time constants which govern the voltage profile, reveal that there are two simultaneous processes occurring at the cathode. The first process (and the process represented by the faster time constant $\tau_1 = 24 \pm 2$ ms) is the formation of a jet at the surface of the cathode. The second ($\tau_2 = 270 \pm 40$ ms) is established via spark channels from the cathode—this occurs within the first several microseconds of the discharge. Since these two processes occur simultaneously, it is difficult to mathematically determine when one process transitions to the other, i.e., when the voltage stops decreasing as a result of jet formation. Therefore, we cannot accurately or reproducibly determine the point in time at which the plasmoid becomes detached from the electrodes.

Spectra collected in the optical show emission from numerous excited atomic and molecular states, which indicates a rich chemistry occurring during the discharge. Initially atomic signals dominate the spectra; signals from H_α , H_β , O I, N I, W I, Cu I, Fe I, Cu II, and Fe II are assigned in spectra collected from different electrodes under various conditions. These species are likely produced by dissociation, including that of ambient nitrogen and oxygen and water vapor produced from both the electrolyte and background humidity. Furthermore, emission from excited states with large upper-state energies are observed—this possibly indicates the presence of 13.39 eV electrons, for example; or perhaps demonstrates that stepwise excitation of ball plasmoid constituent species occurs during the discharge. As time progresses (i.e., after 20-40 ms), molecular emission from OH and NH radicals is observed. These species are intermediates in what is likely a very complex reaction set, and the observation of emission from imidogen (a measurement which we report for the first time) begins to raise additional questions about the chemistry of the discharge. The rotational temperatures of these species tend to increase with stored energy and indicate the extent to which these molecules are excited, and furthermore provide targets for future spectroscopic studies, either in emission or in absorption.

Finally, a simple set of experiments was performed with the goal of demonstrating the feasibility of applying absorption spectroscopy to ball plasmoid discharges. Three wavelengths of low-power laser light were passed through the plasmoid, and the attenuation of the beam (or lack thereof) was measured at a visible photodiode. No attenuation occurred at 405 nm or 633 nm, however, attenuation of the beam occurred at 532 nm for both tungsten and copper electrodes, indicating that absorption of the beam is occurring. This absorption signal likely results from the presence of iron and tungsten vapors generated during the discharge.

5.1.4 Conspectus

The collective results from the experiments described in the chapters of this thesis provide a wealth of information regarding the chemistry and physics of the discharge. This collected set of experiments also begins a larger discussion which relates back to the initial question posed in this thesis regarding the stability (and, by extension, the long lifetime) of ball plasmoid discharges. Specifically, we have probed both macroscopic (i.e., electrical) and microscopic (i.e., ion and excited state composition) properties of the plasmoid, and the question now becomes whether the mechanism responsible for the stability of the plasmoid is a macroscopic or microscopic phenomenon.

Under these conditions, and as has been demonstrated in Chapter 4, the bulk behavior of the plasmoid is likely dominated by molecules late in the lifetime of the discharge. Indeed, emission spectroscopy reveals that molecules such as OH dominate the spectra at long lifetimes. Furthermore, the mass spectrometry results described in Chapter 2 indicate that cluster ions readily form as a result of the discharge. This process occurs on long time scales compared to inelastic collision processes, for example, and is therefore likely to occur late in the lifetime of the plasmoid. In fact, since these experiments probed the composition of the plasmoid at such late times (and far from the electrode), it is difficult to determine what ions are produced early in the discharge with MS– emission spectroscopy measurements must be used to identify short-lived species produced near the electrode. These two combined data sets indicate that atomic ions are produced early in the discharge, while larger and larger clusters are likely produced as a result of chemistry or collisions. It is also noteworthy that the exact location and conditions under which primary ions are generated in a ball plasmoid discharge are not understood; there are multiple dynamic processes occurring at the electrode surfaces and in the bulk of the plasmoid, and a better understanding of the formation of the discharge must be sought.

Our preliminary results with various background gases also seem to indicate that the formation of a spherical body is more favorable in a diatomic gas such as air or nitrogen, as opposed to a rare gas. The data presented at the end of this chapter and in Appendix A indicate that nitrogen is in fact important for the formation of a ball plasmoid, and additional study must be undertaken to study nitrogen in these discharge. The physical chemistry of plasma discharges in nitrogen is particularly interesting due to the vibrational kinetics of the plasma and the production of several excited electronic states. These excited states of nitrogen, particularly the metastable states, are prime candidates for energy reservoirs.

5.1.5 A Possible Mechanism for Energy Storage in Ball Plasmoids

This discussion focuses on *molecular* mechanisms of energy storage which could be significant in ball plasmoid discharges. However, given the complexity of the discharge, it is likely that this explanation is not solely responsible for the long lifetime of the plasmoid. It is more likely that the physical chemistry of the discharge works in concert with fluid dynamic effects, especially at long lifetimes, to form a sphere or torus of cool plasma that lasts several tens of milliseconds before dissipating. For the sake of brevity, two particular types of molecules will be discussed, namely water clusters and metastable nitrogen species.

First, the formation of water clusters indicates that chemistry involving water either from the electrolyte or the ambient air contributes to the composition of the plasmoid. In the MS work presented in Chapter 2, we observed many cluster ions, which are presumably formed when ionized and other excited species combine with one another during the course of the discharge. These species can either be from the electrode (i.e., Cu^+) or produced during the discharge (i.e., NH_3 , NO_x), and our emission spectroscopy experiments have demonstrated that these species can be produced in various excited states. Dissociative recombination of water cluster ions with free electrons can produce water molecules in various states of excitation [86], which could in turn dissociate further to form OH. In this way, chemical energy can be stored within the water cluster ions which have been shown to be present in the plasmoid.

Another possible reservoir for chemical energy (which has been extensively studied in other contexts) are the metastable electronic states of molecular nitrogen. The first metastable state of nitrogen is the A $^3\Sigma_u^+$ state at 6.2 eV [87]. Although the population of electrons with energies sufficient to electronically excite ambient nitrogen to this state is not known, our results in Chapter 4 indicate that electrons having energies well above this threshold could be present in the discharge. Indeed, in many air plasmas generated under similar conditions, these metastable excited states of nitrogen are readily formed.

This electronic state is particularly interesting due to its rather long (~ 2 second) radiative lifetime, in addition to the chemistry that can be facilitated by this state. This state (and other excited states) of nitrogen is known to participate in energy pooling reactions [87], which transfer the energy stored in this metastable electronic excited state to a collision partner. For example, an excited nitrogen molecule in the A state can collide with itself to populate the B $^3\Pi_g$ and C $^3\Pi_u$ electronic states. These metastable states can also undergo associative ionization to produce a ground-state nitrogen molecule and a secondary electron, which can in turn drive additional plasma chemical processes. Or, N_2 A $^3\Sigma_u^+$ molecules can collide with ambient oxygen molecules to promote dissociation to form O I or form an excited oxygen molecule (a $^1\Delta_g$, for example). Given the long lifetime of the A $^3\Sigma_u^+$ state, these processes could occur throughout the lifetime of the plasmoid, which could in turn drive the chemistry of the plasmoid even into the autonomous phase.

5.2 Future Work

In addition to those results which have been analyzed and interpreted to the point of publication, there has also been a considerable amount of effort devoted to exploring different experimental avenues related to ball plasmoid discharges. At the time of the compilation of this thesis, there are two main experiments which are in the preliminary stages, namely the background gas composition project and the interferometry project. Some data have been collected from these experiments, and these data indicate that more study using both of these techniques would be highly beneficial.

The data from these experiments are housed in Appendices A and B; references to the data contained in these appendices will be made throughout this section. The experiments contained within Appendix A (the gas composition project) are much more developed, and a sufficient amount of preliminary data to allow for a cursory discussion has been collected. This discussion will, therefore, focus on experiments discussing gas composition experiments– the reader is referred to Appendix B for an introduction to microwave interferometry experiments.

5.2.1 Background Gas Composition

As mentioned above, the entire set of preliminary data from a series of ball plasmoid discharges in nitrogen and argon is included in Appendix A. However, for the sake of clarity for this discussion, example images of ball plasmoid discharges are also included below.

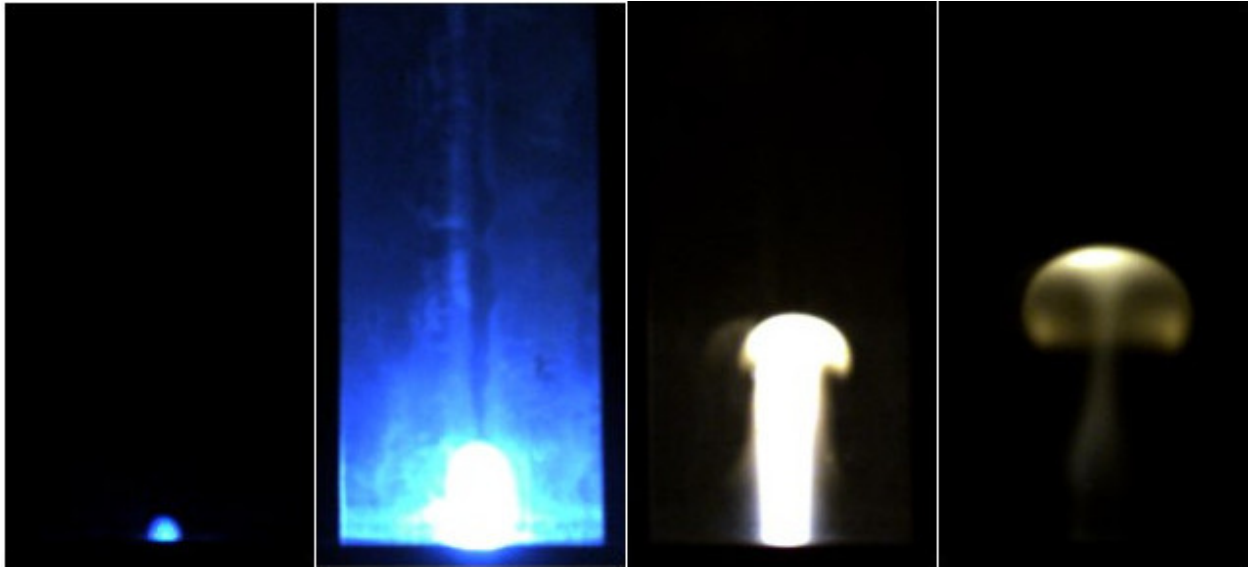


Figure 5.1: Series of images collected from a ball plasmoid discharge in N_2 .

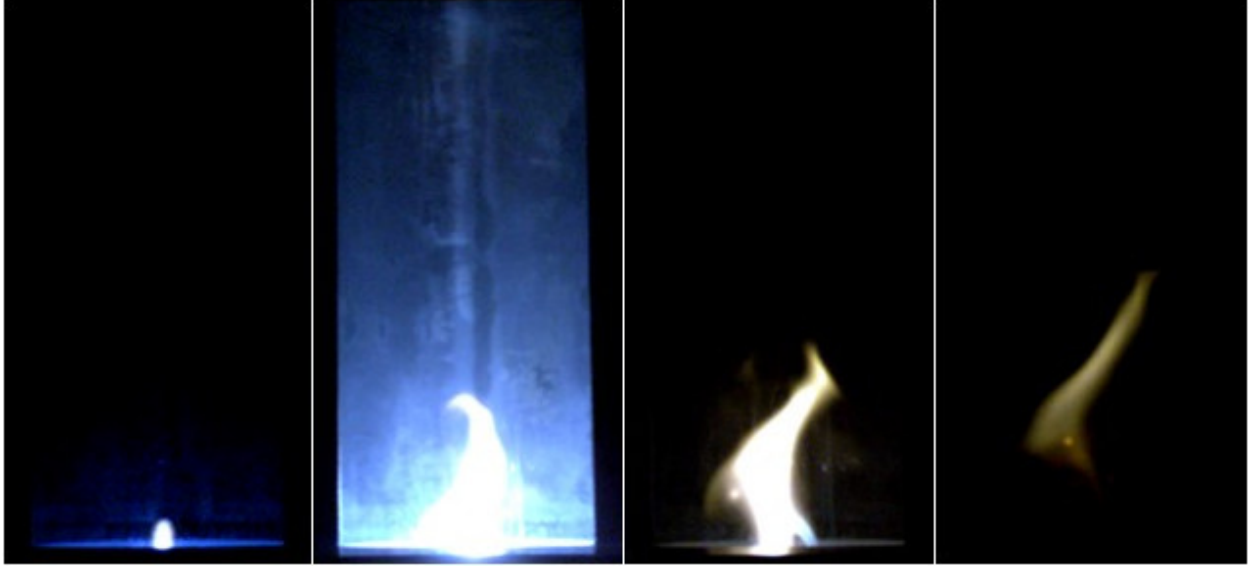


Figure 5.2: Series of images collected from a ball plasmoid discharge in Ar.

Figures 5.1 and 5.2 are series of images collected via high-speed videography of the discharge obtained in N_2 and Ar, respectively. Although the electrical profiles of these identical discharges (tungsten electrode, 7000 V, approx. $300 \mu S$ conductivity) were very similar, the shape of the discharges are quite different. In nitrogen, the “typical” spheroidal shape of the plasmoid is observed, and the discharge is fairly symmetric. However, in an argon environment, the structure of the plasmoid is drastically different. In these discharges, it appears as though the initial spark channel formation and beginning stages of the cathode jet are similar, but these images indicate that the later stages of ball plasmoid discharges in argon are much more flame-like. Only in some instances were spherical plasmoids generated in Ar discharges. In other words, it does not appear as though the “ball” component of ball plasmoid discharges are readily formed in an argon atmosphere.

This observation seems to indicate that the presence of nitrogen is important for the formation of ball plasmoids— in the absence of nitrogen, the discharge has a completely different shape. It is also possible that the presence of oxygen is important for the chemistry of the plasmoid, as oxygen readily facilitates the formation of ozone and NO_x species in air plasmas, however, the contribution from molecular oxygen alone is currently unexplored. Additional gases (i.e., He, O_2 , H_2) should also be considered for these experiments, as each gas will facilitate a slightly different chemistry, from which conclusions regarding ball plasmoid stability can be drawn. However, the use of these gases should be chosen based on the desired molecular excited state of interest. For example, the first electronic excited state of hydrogen has an energy of 11.4 eV, and given the energy of the plasmoid discharge, it is unlikely that this state will be produced in significant abundance.

Furthermore, the vibrational kinetics of the discharge tend to drive the bulk behavior of nitrogen plasmas, so this gas would be of particular interest for studying the chemical kinetics of the discharge. In particular, this experiment could isolate the effect of vibrational excitation on the plasmoid and could allow for the evolution of the vibrational distribution of molecular excited states to be quantified. It may also be possible that the vibrational quanta of the nitrogen molecule is able to store energy as a result of the slow rate of vibration-translation relaxation compared to the rate of vibrational excitation by electron impact [80–82].

It is important to note several intricacies of these experiments that must be considered and addressed individually in future work:

1. **Spatial and Temporal Resolution.** Generally, the fact that many of these experiments were performed with minimally-acceptable spatial resolution and bearable temporal resolution, additional effort should be made to improve these diagnostics. For example, the shape and intricacies of the current profiles are likely not resolved with the currents sensors used in these experiments and the 1 kHz sampling rate of the Arduino.
2. **Videography.** For diagnostics in various gaseous environments, a good quality camera should be used (i.e., a Phantom camera). A high (≥ 1000 fps) frame rate and good resolution can be achieved with a camera of this type, which would facilitate accurate size, velocity, and lifetime determinations. At the present state of the experiments, these parameters are not satisfactory.
3. **Energy.** Discharges were only generated between 5000-8000 V for this set of data; more voltages outside of this range should be explored. This is particular important for Ar, as the breakdown voltage of Ar (0.6 kV cm^{-1}) is considerably less than that of air (4 kV cm^{-1}). The thermal conductivities of these gases are also quite different, which will also contribute to differences in ball plasmoid discharges in air versus argon. Furthermore, only a single capacitor discharge was tested in this round of experiments; multiple capacitors should be used in future trials to increase the power deposition to the plasmoid.
4. **Humidity.** When working in the sealed chamber, it does not take sufficiently long for the humidity and background temperature to increase inside of the chamber. Indeed, after an afternoon of performing approx. 20 discharges (within normal conditions), a large amount of water can be seen clinging to the inside walls of the tube, and the environment within the chamber is warm. In addition to potentially installing a humidity sensor on the piston, perhaps the chamber should be cleaned and allowed to fill with room-temperature air after a series of discharges. The presence of an excess of humidity could bring about unwanted effects during the discharge, or could mask signals of interest.
5. **Cathode.** The integrity of the cathode must also be monitored closely. It is difficult to remove the

electrode from the bucket once the chamber has been secured in place. It is therefore recommended that future experiments polish the tip of the cathode and replace the insulator every time a set of experiments in the chamber are to be run. Furthermore, the vertical positioning of the cathode must also be precisely controlled– we have observed that the cathode spot(s) form differently depending on the position of the cathode surface relative to the top of the insulator.

5.2.2 Current Breaking and Lifetime

Much of the discussion surrounding the electrical profiles of the discharge presented in Chapter 4 includes information regarding two separate processes occurring at the cathode during a typical plasmoid discharge. These processes include initial spark channel formation to allow the flow of current between electrodes, and the second is a jet produced at the tip of the cathode. In the present configuration, i.e., with the current discharge code (see Appendix C), the spark channels are present throughout the lifetime of the discharge. The current pulse width of the circuit is approx. 500 ms– one would imagine that quenching the current to the discharge at an earlier time would remove the current flow (and therefore power deposition) to the plasmoid. This is also a mechanical way to determine the point in time at which the plasmoid becomes detached from the electrodes. Since this circuit contains a vacuum relay to break the current, additional sets of experiments should also focus on the effects of changing the length of the pulse and how this relates to ball plasmoid lifetime.

5.2.3 Modeling

Given the effort that has been devoted to the understanding of ball plasmoids, by both our laboratory and by several other groups, we now have a more detailed understanding of the chemical composition of the plasmoid, and we have a better idea of what ions are formed during the discharge. This (admittedly) cursory understanding should be used to direct the next research projects into the physico-chemical components of the discharge. Furthermore, the project (in this author’s opinion) has reached the “maturity” level such that detailed modeling of the system should be undertaken. The need to combine well-controlled experiments with detailed models is great for ball plasmoid discharges, but can also be said as a general statement about many of the cutting-edge experiments in plasma science.

Chemical kinetic modeling of the plasmoid would, therefore, be a worthwhile endeavor. Given that we have proposed that the energy contained within ball plasmoids could be stored in molecular excited states, it would be interesting and valuable to understand how these states form and in what concentrations. The spatial distribution of these excited states could also be determined via these models, which would

indicate different chemistries occurring in different regions of the plasmoid. Finally, the time evolution of the concentration of these species would elucidate the species which persist on the same timescale as the plasmoid lifetime.

Appendix A

Varying Atmospheric Conditions for Ball Plasmoid Generation

At the outset of this Appendix, it is important to include the disclaimer that there will be little discussion of the meaning of the results in this Appendix. This Appendix serves the main purposes of describing the construction of the chamber and “housing” the preliminary data; interpretation of results collected from these experiments is included in Chapter 5.

A.1 Ball Plasmoids in Non-Air Environments

Air is a complex mixture in which to generate a plasma, even under controlled laboratory conditions. The high rate of collisions at atmospheric pressure makes measuring reaction rates difficult, especially when intermediates are quenched or react rapidly in air. This complexity is usually mitigated by reducing the pressure and controlling the gas composition of the plasma. For our purposes, it is imperative that the plasmoid be generated at atmospheric pressure, as this is key to the claim that ball plasmoids are analogous to ball lightning. Perhaps a future iteration of this experiment would involve the study of ball plasmoids at a slightly reduced pressure (thereby simulating the upper terrestrial atmosphere, for example). The chamber described below could potentially be used for this purpose with some modification.

Plasma discharges obey the Paschen curve for the gases in which they are generated. For a gas at a given pressure and electrode distance, there is a voltage at which the gas will break down and become conductive, thereby forming a plasma. For air, this value is approx. 4 kV per cm, but this value is generally different for other gases. For example, the breakdown potential for argon at atmospheric pressure is approx. 0.8 kV per cm, thus a ball plasmoid discharge would likely have different properties in an argon environment. This behavior can ultimately have an effect on the overall resistance of a plasma, which could in turn effect the physical processes occurring in the plasma.

In order to examine the effects of background gas composition on ball plasmoid discharges, a chamber designed to displace ambient air with other gases in a controlled fashion was constructed. In previous iterations of this experiment, efforts have been made to change the background gases, however, this was not

done in a controlled way. This chamber was designed with this fact in mind, and is also designed to be large enough to encompass the volume of the plasmoid. Of particular interest is the structure and dynamics of the streamers that are produced in the discharge. Streamer formation and propagation processes are highly dependent on both the pressure and the background gas composition [88].

A.2 Chamber Construction

A description of the design and construction of a chamber to be used for ball plasmoid experiments in various background gases follows. There are diagrams and measurements for specific parameters pertaining to the chamber, and several photos of the chamber are also included for the reader's reference. Following this section, preliminary data collected from these experiments are discussed.

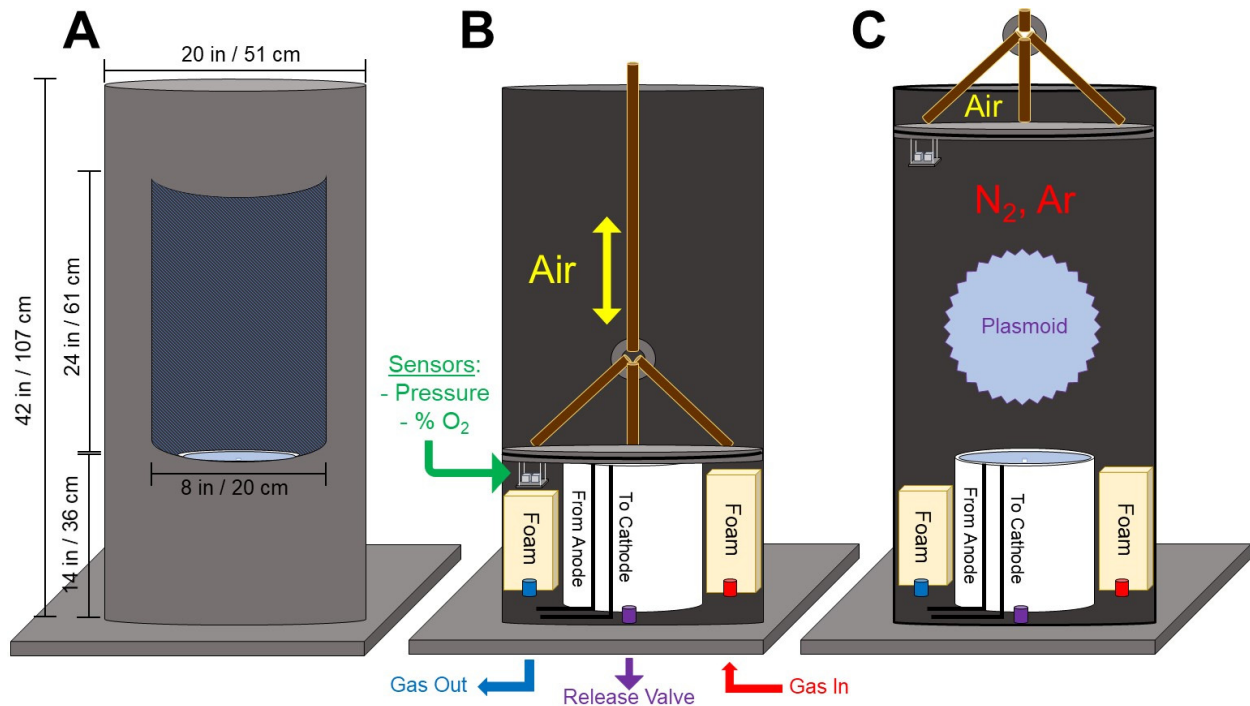


Figure A.1: Diagram of chamber and piston used to vary background gas composition. A: outer view and dimensions of chamber, B: cross section of chamber with piston lowered, C: cross section of chamber with piston raised and under a nitrogen/argon atmosphere.

An 8-inch (21 cm) $\times$ 24-inch (61 cm) window was cut into a 42-inch (107cm) tall piece of PVC tubing with a 20-inch (51 cm) outer diameter. A 1/16 inch (2 mm) thick piece of polycarbonate sheeting was then fit to the inner diameter of the tube and secured with an adhesive to the inner wall of the PVC tube. This thin sheet forms the sealed inner wall of the tube while allowing sufficient access for videography and other

measurements to be taken. The tube is mounted to a PVC base into which a 1/4 inch (6 mm) wide, 1/2 inch (12 mm) deep groove matching the circumference of the tube was cut. A strip of silicone was placed into this groove to serve as a gasket. The tube is placed vertically into the groove, and the tube is then secured to the PVC base with four feet on opposite sides of the tube body.

A series of holes were cut into the PVC base; two are for the high-voltage wires connecting the cathode and anode to the rest of the circuit, and three were for plumbing for gas lines. 1/4 inch NPT connections were used with quick-connect valves for a gas inlet and outlet, and a 1/4 inch NPT 15 psi pressure relief valve was used as a safety measure for pressurizing the chamber. Compressed air was used to pressurize the chamber prior to performing any discharges. In order to support the pulley properly and secure the chamber to the ground, a Unistrut frame was constructed around the chamber. It is also important to mention that, **for safety reasons**, adequate ventilation of the laboratory and the gas outlet were established. A large volume of nitrogen is used in a single discharge, and without significant air exchange there is a suffocation risk.

A piston with a diameter matching the inner diameter of the PVC tube plus the polycarbonate sheet was constructed using a piece of 2 mm thick rubber sheeting pressed between two PVC discs. “Feet” were added to the bottom of the piston to prevent the piston from coming unseated while moving upward in the chamber. A bar spanning the top of the piston was fitted with a hook so a pulley system could be used to lift the (heavy) piston lid vertically along the axis of the tube. Two holes were cut through the piston to allow for electrical connections to a pressure (Freescale Semiconductor MPX5100AP) and oxygen (Grove) sensor to be made; the holes were sealed with silicone after wire bundles were secured in place. The sensors were connected to the Arduino by a length of wire connected with banana plugs. Data relevant to the concentration of oxygen in the chamber were collected with a code separate from the code which operates the discharge (See Appendix C).

Prior to generating a discharge, the electrolyte is prepared and the electrode is placed into the bucket. The high-high voltage wires are then secured to the outside of the bucket with tape and/or zip ties. This is all done without the tube in place; it would be prohibitively difficult to work with the electrode if the tube were in place. Once the electrode is secured, the tube is lowered into the groove and secured to the base. Foam is placed between the outside edge of the bucket and the polycarbonate sheet to reduce the volume that air can occupy in the chamber, thereby reducing the time required to displace air from the chamber. The piston is lowered into the chamber and comes to rest on the top of the bucket, at which point a baseline oxygen concentration measurement is obtained. See Appendix C for sample acquisition code for this process.

The gas inlet and outlet are then opened, allowing for air below the piston to be displaced from around



Figure A.2: Photo of the chamber used for gas composition experiments.

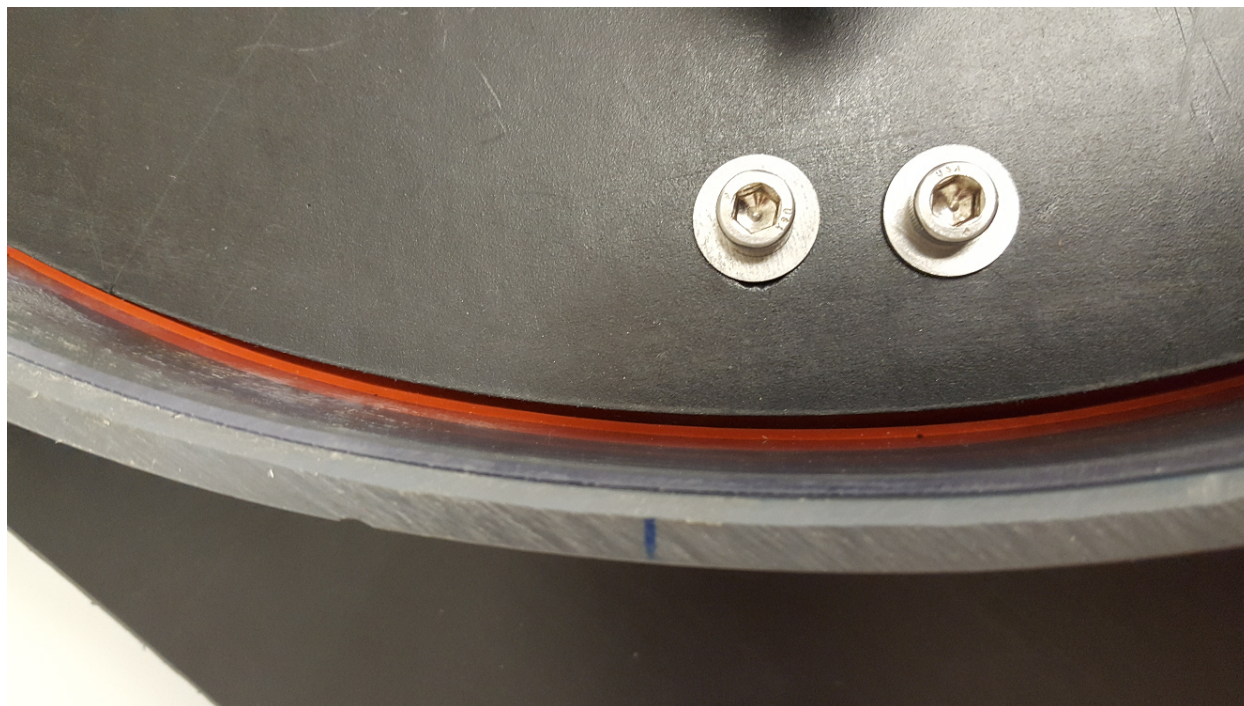


Figure A.3: Top-down photo of the piston resting in the gas composition chamber. The orange rubber sheet is used to seal the piston against the inner wall of the chamber. Small air gaps are used to let a small backing pressure of gas escape the chamber.

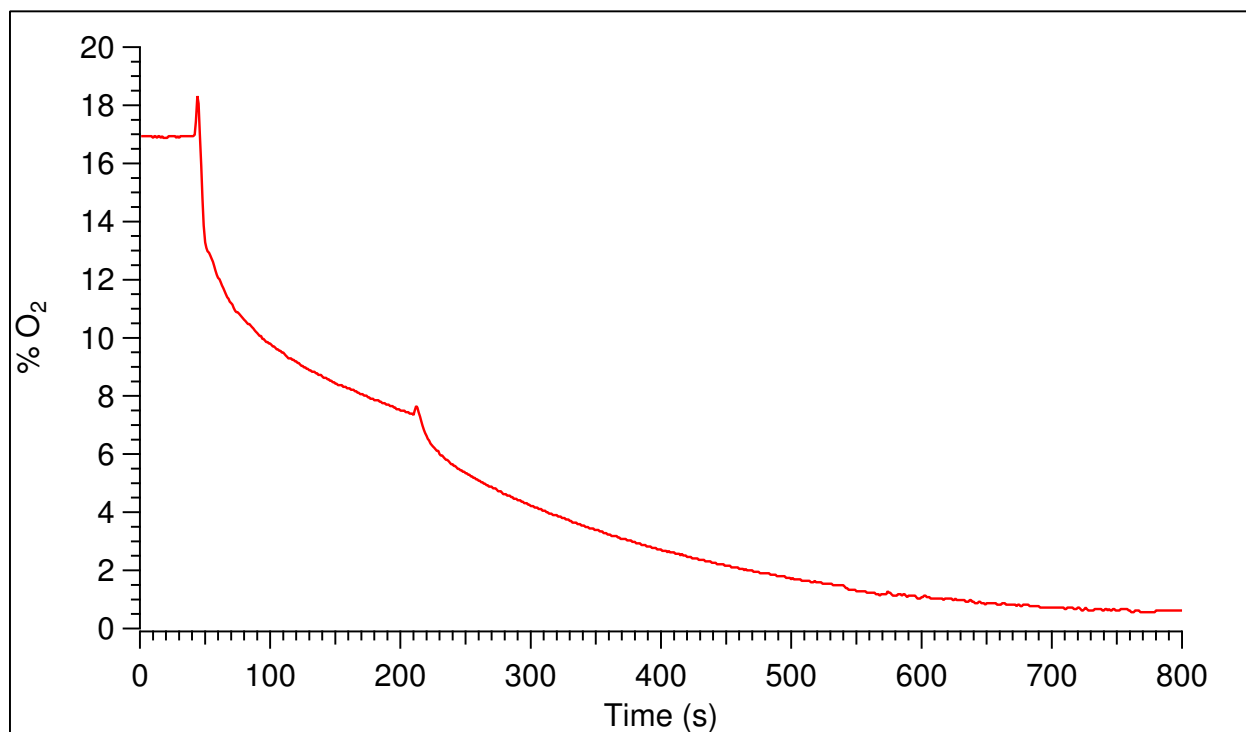


Figure A.4: Oxygen concentration in the chamber over time with addition of N₂.

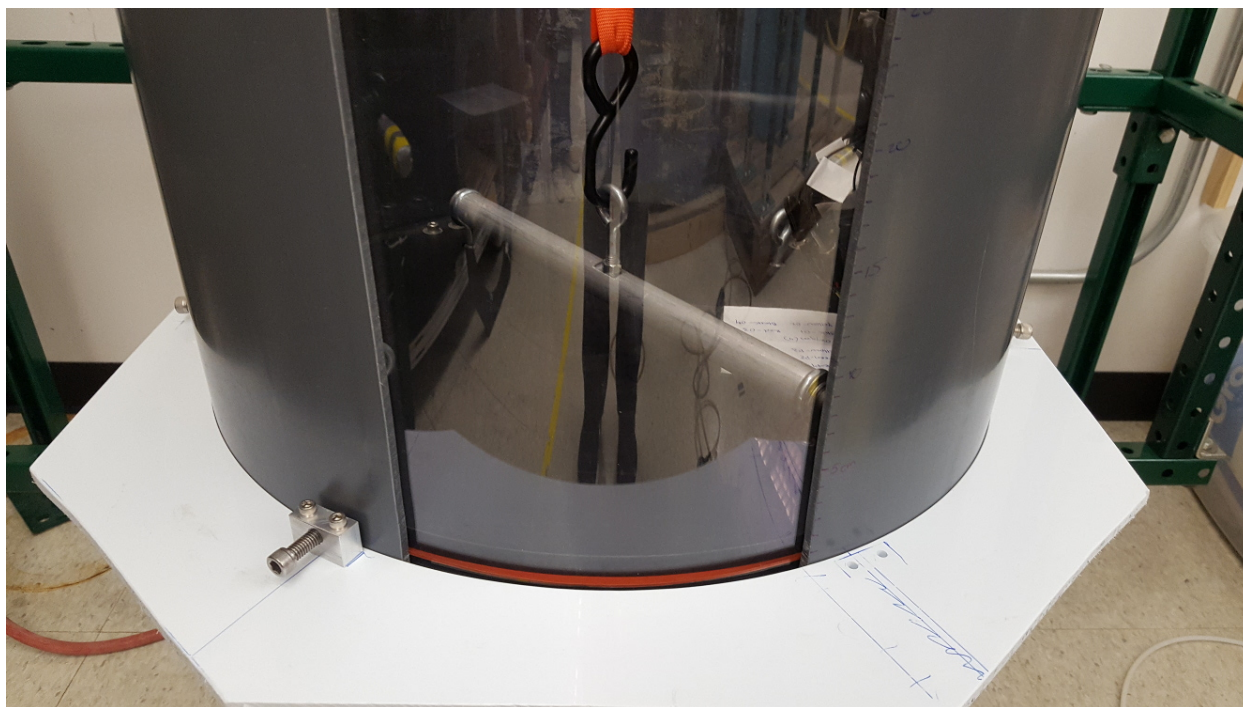


Figure A.5: Photo of the piston lowered in the gas composition chamber.

the bucket. When the concentration of oxygen reaches 2%, the gas outlet is closed. A positive pressure of gas is then generated in the chamber, and this pressure pushes against the rubber sheet of the piston, effectively sealing the piston against the inner wall of the chamber. The positive pressure helps lift the piston upward, and the chamber fills with the gas being added in a controlled fashion. As long as a positive pressure of gas is maintained (in other words, as long as leaks flow outward and not inward), we can be sure that air is being displaced with either nitrogen or argon. When the piston reaches its full height, it is secured in place using the pulley. The gas flow is then reduced, while ensuring that a small amount of gas is leaking from the chamber. This small leak ensures that no ambient air will enter the chamber once it has been filled, and that there is no additional turbulence in the chamber as a result of gas flow. Indeed, the chamber can reach concentrations of 0.2% oxygen and hold this concentration effectively even when no gas is introduced to the system (Figure A.4).

A.3 Preliminary Data

The following section includes preliminary data collected using the chamber setup described above. The data presented in this section are very new (and exciting), however, much more time should be invested in this experiment before conclusions are drawn from the data. This process will be discussed below, and is

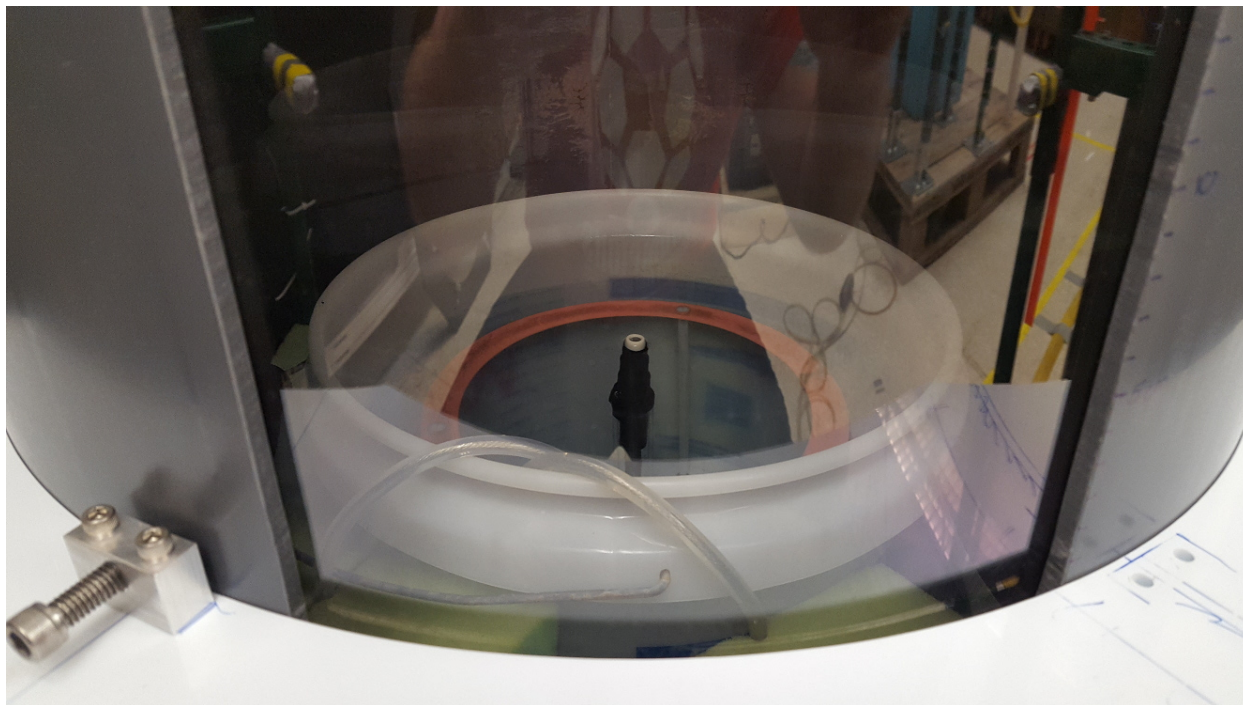


Figure A.6: Photo of the electrode in the bucket when the piston is raised.

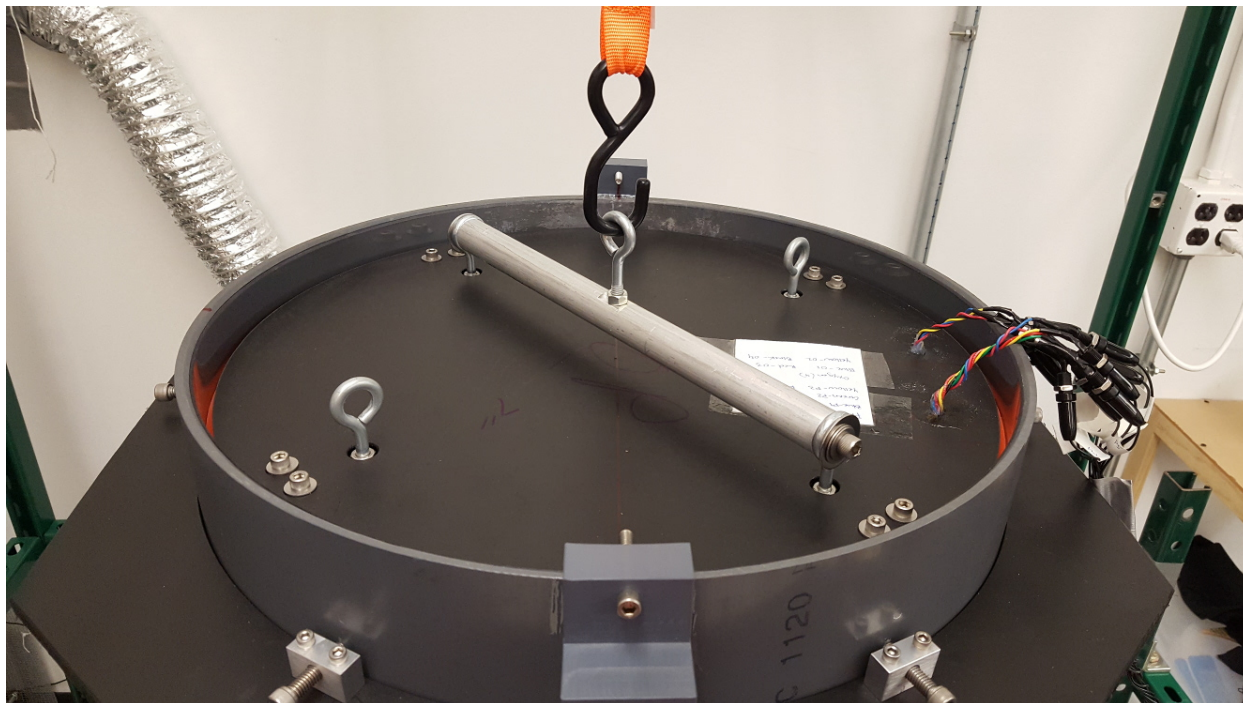


Figure A.7: Photo of the top of the chamber when the piston is raised. Electrical connections to sensors are visible on the top side of the piston.

referenced in Chapter 5. The results from these experiments will also be discussed in the context of what is currently known about ball plasmoid discharges, and how the results can guide future experiments.

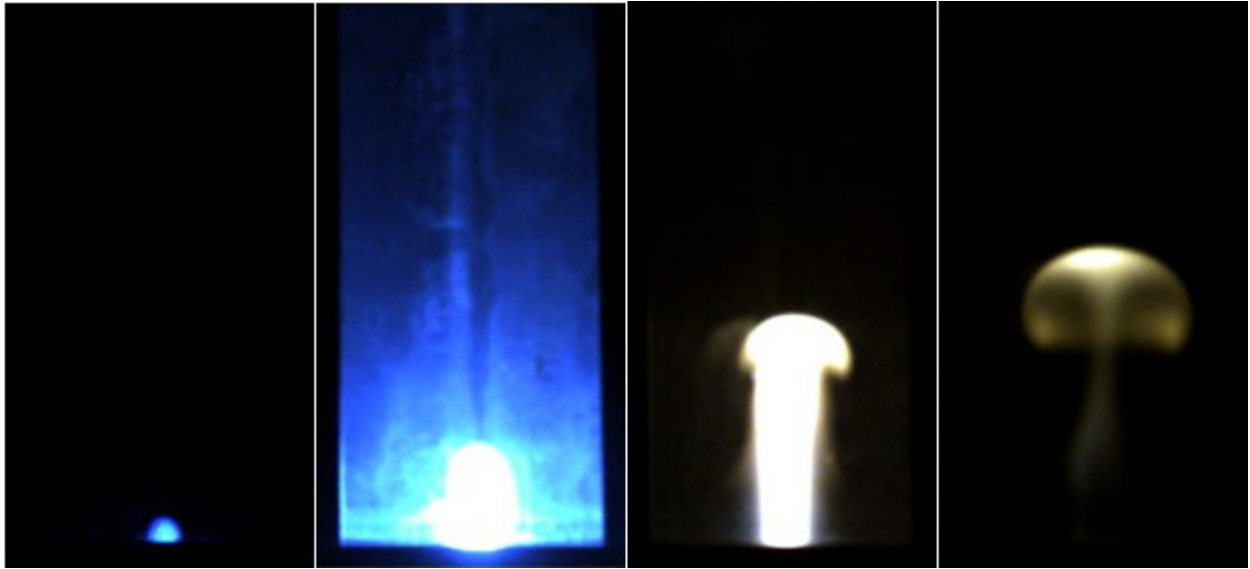


Figure A.8: Series of images collected from a ball plasmoid discharge in N_2 .

The images included in Figures A.8 and A.9 show the progression of a ball plasmoid discharge in a nitrogen atmosphere and in an argon atmosphere, respectively. On first inspection, it is apparent that there are drastic differences between the appearance of a discharge generated in nitrogen and a discharge generated in argon.

Figures A.10 and A.11 provide a full analysis of the electrical profile (as described in Chapter 4) for a 7000 V ball plasmoid discharge in a nitrogen and argon atmosphere, respectively. Between these two figures, the only notable difference is the qualitative shape of the resistance curve— it appears as though the resistance of the discharge increases more rapidly in nitrogen than in argon; this could be a result of the different properties of the gas. It is important to note that these data were collected over a small range of parameters in fast succession— therefore none of the data presented in this Appendix are publication-worthy in their present state. However, despite the lack of reliable statistics on this data set, insight can still be gained from a cursory inspection of the data.

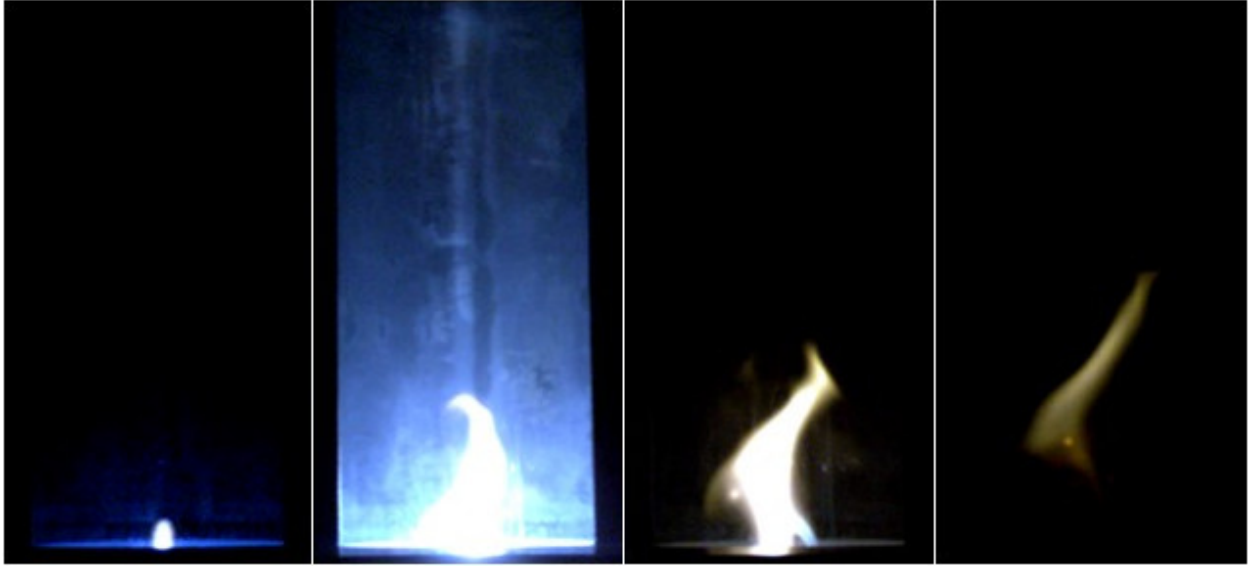


Figure A.9: Series of images collected from a ball plasmoid discharge in Ar.

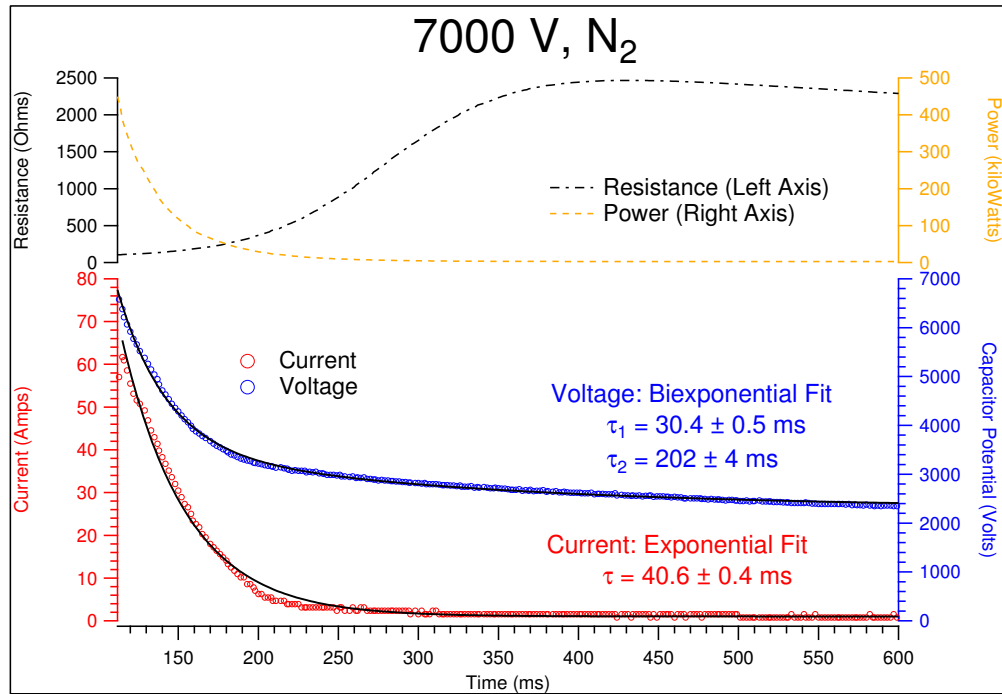


Figure A.10: Electrical analysis of an 7000 V plasmoid from a tungsten electrode in a nitrogen atmosphere.

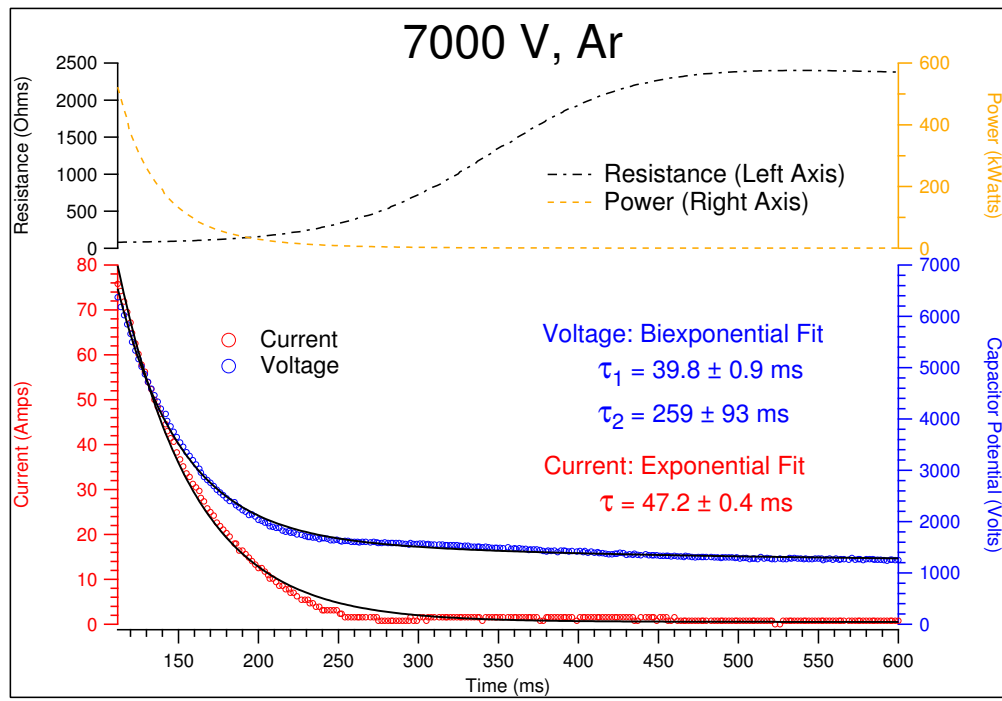


Figure A.11: Electrical analysis of an 7000 V plasmoid from a tungsten electrode in an argon atmosphere.

Appendix B

Construction of an X-band Microwave Interferometer for Electron Density Measurements

Of the components which comprise a plasma, electrons are the most influential to the behavior of the plasma in the bulk. Electrons (and ions) carry the majority of the current through the plasmoid, and based on the EEDF, will also determine the identities of excited states produced during the discharge. It is therefore of great importance to quantify the density (and temperature) of electrons present in a plasma to fully understand the physics and chemistry occurring during the discharge.

Historically, immersive Langmuir probes are used to measure the electrical properties of a plasma, however, this method is not applicable for the diagnostics of ball plasmoids for several reasons. First, a detailed understanding of the current/voltage response of the probe is necessary to extract quantitative information, and this requires a tremendous amount of calibration. The probes are also made of conductive materials, which (if positioned improperly) could pose a potential risk for arcing, but also generate additional sheath effects at the surface of the wires.

It was therefore desired to implement a non-intrusive technique that could be placed far enough from the plasmoid and the electrodes to probe the electron density in the plasmoid. Stark broadening measurements using emission spectroscopy would be suitable in this case, however, these measurements had already been reported, and it would have been more valuable for the understanding of the system as a whole to either confirm or refute the electron densities reported in [9] with an independent technique.

Thus, microwave interferometry was chosen to probe the electron density of the plasmoid. At microwave frequencies, plasmas behave as dielectric materials, and these materials will attenuate and induce a phase shift in an X-band (8-12 GHz) beam as a result of these dielectric properties. A Mach-Zender type interferometer can be designed to probe the plasmoid, provided that the probe and reference waves can be made equivalent in amplitude and phase. Based on the descriptions of an instrument of this type provided in [85], we have constructed a relatively portable microwave interferometer. Rather than using a klystron as a source of the microwave needed for this type of instrument, we are relying on a series of RF multipliers and amplifiers to provide the probe and reference signals. This approach, while more economical, has proven to be problematic, and more effort must be put into this instrument to optimize its function (see below).

B.1 Instrument Design

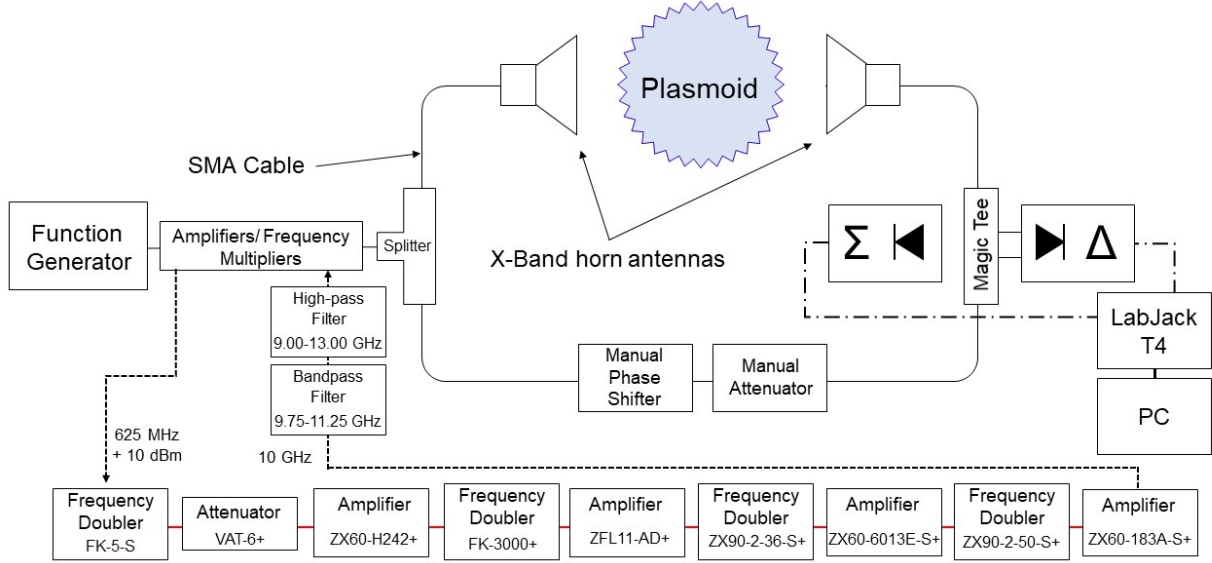


Figure B.1: Diagram of the microwave interferometer circuit.

Figure B.1 shows the diagram of the components used to generate the X-band beam. A function generator (HP 8657 A) supplies the 625 MHz +10 dBm input signal to the RF components. After passing through all of the components in the multiplication stage, the frequency is multiplied by a factor of 16 to a final frequency of 10 GHz. In addition to the frequency multipliers, there are also several amplifiers and a +6 dBm attenuator; these components balance insertion losses and maintain input power requirements for each amplifier. This turned out to be detrimental to the output beam frequency; this will be described below.

After the desired frequency and power are established, this signal beam is then split into two beams of equal power using a coaxial tee. At this point in the circuit, the two beams will be referred to as the “reference” beam and the “probe” beam. The probe beam is propagated through free space (and ultimately the plasmoid) using a pair of X-band microwave horns which are secured to a stage which surrounds the polypropylene bucket. Figure B.2 shows the position of these horns relative to the position of the electrode, and Figure B.3 shows a side-on view of the horns relative to the bucket and how the stage is positioned relative to the discharge. The horns are spaced 30 cm apart. The reference beam does not propagate through free space; rather this beam is subjected to a manual phase shifter and attenuator which are used to null the signal before probing the plasmoid.

The two beams are then recombined at a magic tee, which is a custom piece of brass WR90 waveguide with a very specific geometry. The magic tee generates signals at two points, one of which represents the sum of the amplitude of the two beams, and the other, the difference. These signals are rectified by a pair of microwave diodes, and the voltage across the diode is converted to power using standard voltage/power curves for RF components.

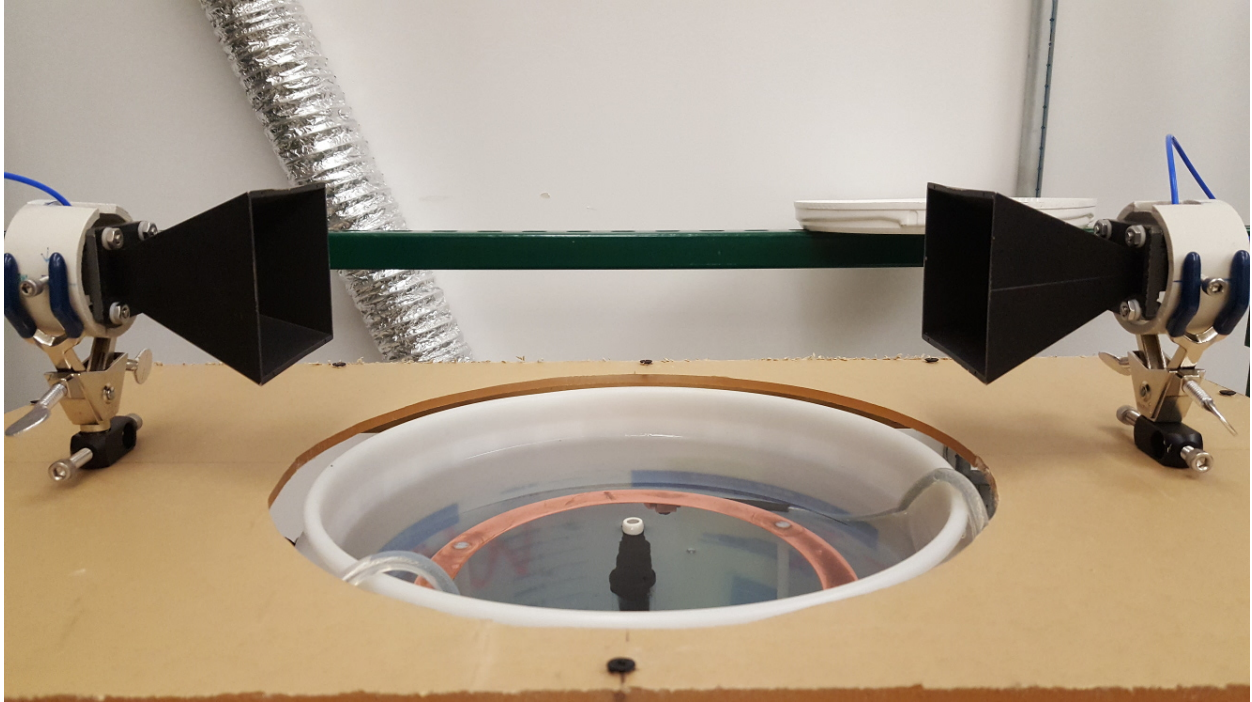


Figure B.2: View of the vertical position of X-band horns relative to the cathode.

The voltage at the two outputs is read using a LabJack T4 data acquisition system via an Ethernet connection. A laptop with an internal solid-state hard drive and fast processor was used to ensure rapid data collection at a rate of 10 kHz. Data are collected using the LJStreamM application available from LabJack. Data are collected across 2 channels with 12-bit A/D (bit) resolution from 0-2.5 V at a rate of 10 kHz. Data are automatically written to a text file. Data may be broken into separate files, however, there are no losses of data from one written file to the next. In order to sync the acquisition electronics of the interferometer to the discharge electronics, a TTL pulse was sent from the Arduino to the LabJack as soon as the code is initiated. The +5 V pulse to the LabJack is observed as a delta function at 10 kHz, thus the rising edge of the pulse is used as the “global” start to the discharge. This point reflects time = 0.

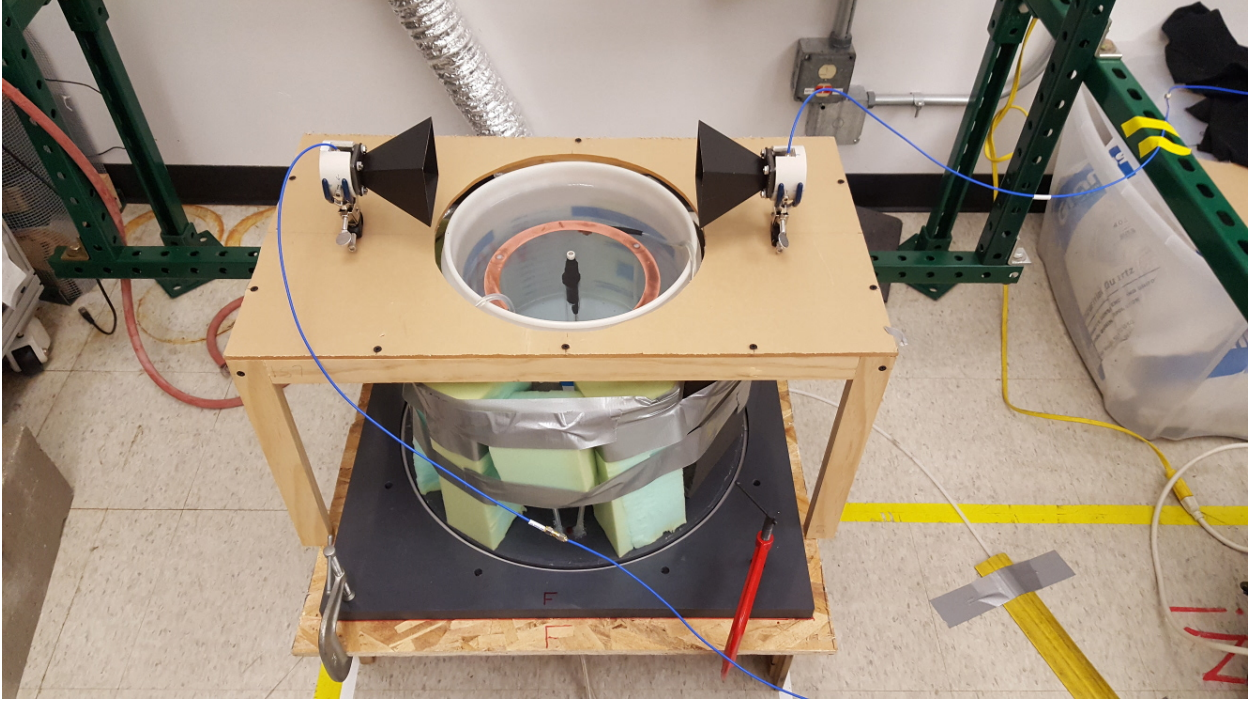


Figure B.3: Side-angle view of the position of X-band horns relative to the bucket.

B.2 Preliminary Data

It is easily observed in Figures B.3 and B.4 that there is not one single frequency output from the instrument, rather, there is interference in the single output trace which results from multiple frequencies being present. Indeed, a Fourier transform of the data shown in B.3 produces the trace shown in B.4, which show peaks in frequency space at 9.5 GHz and below. This is undoubtedly why a Klystron is a better source for this instrument; klystrons produce single-frequency signals, while the use of multiple frequency multipliers likely resulted in unwanted harmonics bleeding through the system. Attempts were made to filter the output so as to isolate a single frequency, however, after two iterations, the instrument is not likely to be able to measure phase shift or attenuation data reliably due to overlap of multiple harmonics.

Despite the frequency issues within the circuitry of the instrument, attempts were made to see if the instrument was able to measure signals of materials with dielectric properties. A piece of acrylic was moved in and out of the beam path to behave as a dielectric material, and responses were observed when this was done. Once we were confident that we could measure some type of signal, experiments with plasmoid discharges were undertaken. The figure below provides preliminary data from measurements of 6000 V plasmoid discharges from a tungsten electrode.

It is clear that there is a response from the instrument when a plasmoid discharge passes between the

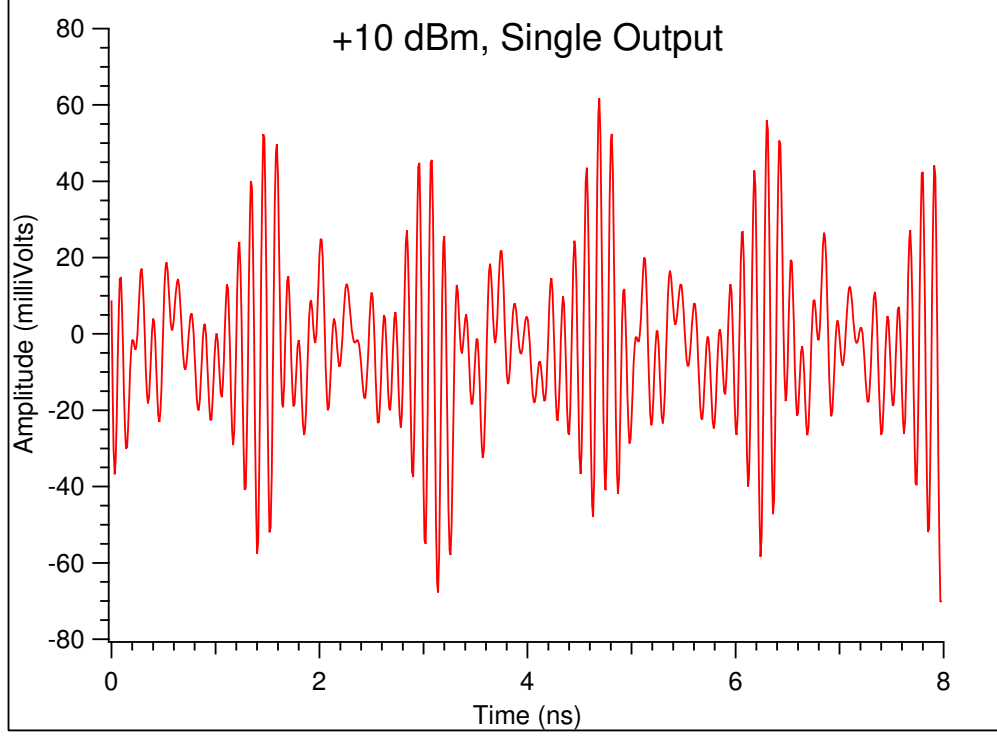


Figure B.4: Oscilloscope trace of single output from microwave interferometer, recorded at +10 dBm power output from the function generator.

horns, however, this is not a quantitative measurement. One concerning observation is worth noting: in the third channel (green trace), there is an unexplained negative potential that is formed where the voltage should not change, which seems to “decay” exponentially back to ground. This channel is used to monitor the output of a TTL signal from the Arduino which indicates that the discharge has begun; the signal in this channel should be either 0 or 5 volts. This decreasing voltage also happens to correspond to the point in time at which the signal changes in both arms in the interferometer. This similarity calls into question the nature of the signal being measured, and more investigation into this questionable signal is imperative to improve the functionality of the instrument.

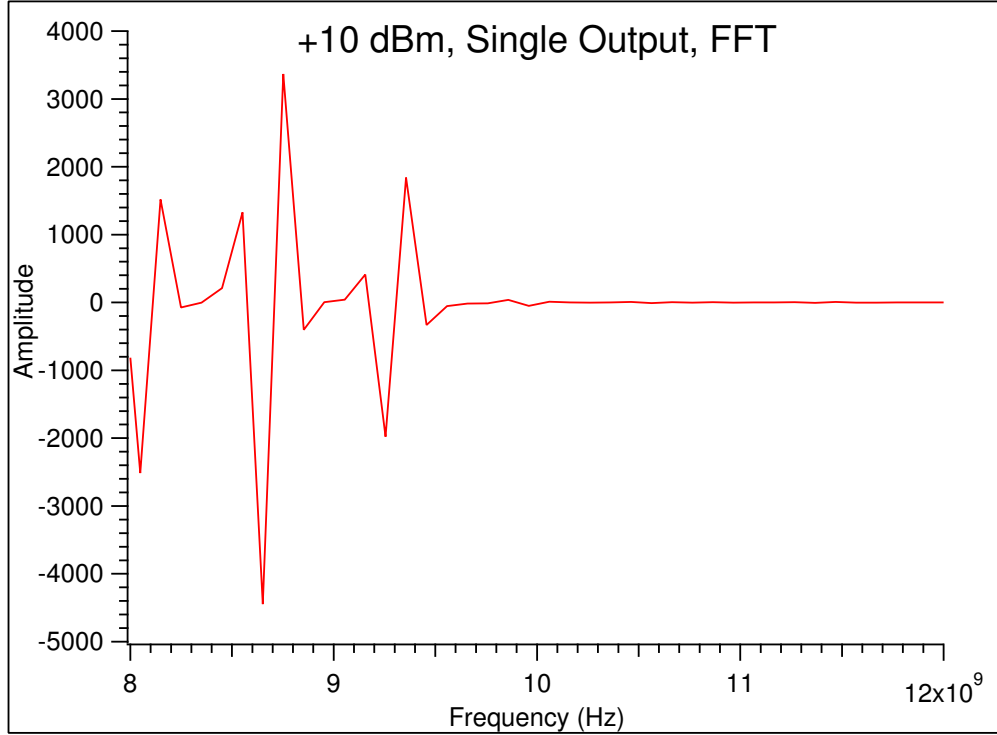


Figure B.5: Fast Fourier-transform of oscilloscope trace shown in Figure B.4.

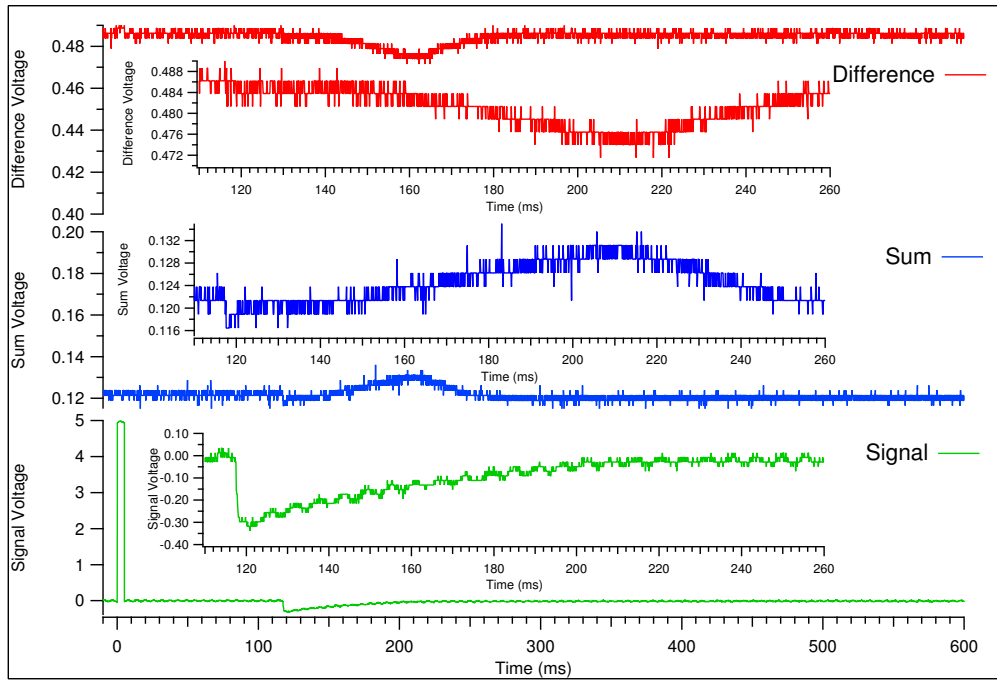


Figure B.6: Preliminary data collected from the interferometer. Insets are regions in which signal is observed. Time = 0 is defined as the rising edge of the TTL pulse sent from the Arduino to the LabJack.

Appendix C

Example Arduino Code

The following sets of code were used to generate and analyze ball plasmoid discharges. The codes were written in the Arduino IDE language, which is similar to C/C++. The codes have been commented where deemed important.

Day-To-Day Discharges:

```
// Humidity Sensor Stuff
#include "DHT.h"

#define DHTPIN 13

#define DHTTYPE DHT22

DHT dht(DHTPIN, DHTTYPE);


// Control Switch

const int control = 2; // The input that starts the trial.

// Output Switches

const int FireSwitch = 4; // The output that controls the fire switch relay.
const int GroundSwitch = 6; // The output that controls the ground switch's relay.
const int VR = 8; // The output that controls the Gigavac vacuum relay.
const int TTL = 10; // port from which 5V pulse will leave

// Measurement Inputs

const int Humidity = 13; // the input that reads the humidity sensor
const int Voltage = A5; // The voltage across the capacitor bank
const int CurrentIn = A2; // The Hall sensor's analog input.
const int Intensity = A3; // The visible photodiode analog output.

// Settings

const int Fire = 500; // pulse width **assume a 10ms delay**
```

```

const int FireBreak = 300; // how long the VR goes HIGH
const int FireGround = 300; // when the GND switch closes
const int record = 2000; //number of milliseconds to collect data total
int count = 0; // count for the loop used to get the voltage baseline
unsigned long time0 = 0; //the time when the fire switch is flipped
unsigned long now = 0; //the current time

void setup()

    pinMode(FireSwitch, OUTPUT);
    pinMode(GroundSwitch, OUTPUT);
    pinMode(VR, OUTPUT);
    pinMode(TTL, OUTPUT);
    pinMode(control, OUTPUT);
    pinMode(Humidity, INPUT);
    pinMode(CurrentIn, INPUT);
    pinMode(Voltage, INPUT);
    pinMode(Intensity, INPUT);
    Serial.begin(115200); // Communication with computer
    dht.begin(); // Humidity Sensor Start
    atmosphere();

void atmosphere()

    int initialvoltage = analogRead(Voltage);
    float h = dht.readHumidity();
    float t = dht.readTemperature();
    if (isnan(t) || isnan(h))
        Serial.println(" Failed to read from DHT");

    else
        Serial.print("Humidity: ");
        Serial.print(h);
        Serial.print(" %");
        Serial.print("Temperature: ");

```

```

Serial.print(t);
Serial.print(" *C ");
Serial.print(initialvoltage);
Serial.println("");

void loop()

digitalWrite(GroundSwitch, HIGH);
if (Serial.available() > 0) //if a character has been sent, enter this "if"
while (Serial.available())
    char text = (char)Serial.read(); //empty serial port, available = 0 again
    delay(5);

while (digitalRead(control) == HIGH)
    delay(50); // make sure there wasn't a fluke HIGH in the control
    if(digitalRead(control) == HIGH)
        delay(150); // wait .15 sec before firing - make sure the camera will be ready
        // Currently doesn't go through loop or wait .5 seconds
        count = 0;
        digitalWrite(TTL, HIGH);
        delay (5);
        digitalWrite(TTL, LOW);
        while(count < 50) //take 50 data points to confirm the voltage
            now = millis();
            reads();
            count = count + 1;

run(); //run the commands

```



```

void reads()

    int currentin = analogRead(CurrentIn); // Raw
    float currentinvoltage = (currentin-511)/1.28;
    // Scaled and converted to Amps (for 300 A sensor)
    int voltage = analogRead(Voltage); // Raw
    float voltageout = (voltage+2.2732)/.0955;

    Serial.print(now); // time
    Serial.print("\n");
    Serial.print(currentinvoltage); // current to the bucket
    Serial.print("\n");
    Serial.print(voltageout); // voltage across the capacitors
    Serial.println("\n");

void run()

    reads();

    time0 = millis(); //set time0
    now = millis(); //set now

    // When the fire switch closes and the pulse begins.
    digitalWrite(FireSwitch, HIGH);
    while(time0 + Fire > now) //when the pulse should be fired
        reads();
        now = millis(); //update now to the current time

    // When the vacuum relay breaks the current
    digitalWrite(VR, HIGH);
    while(time0 + Fire + FireBreak > now)
        reads();
        now = millis();

    // When the ground switch closes.

```

```

digitalWrite(GroundSwitch, LOW);

while(time0 + Fire + FireBreak + FireGround > now)
    reads();

    now = millis();

//Reset for fire switch.
digitalWrite(FireSwitch, LOW);
while(time0 + record > now)
    reads();

    now = millis();

// Reset for Vacuum Relay
digitalWrite(VR, LOW);
while(time0 + record + 300 > now)
    reads();

    now = millis();

// Reset for Ground Switch
digitalWrite(GroundSwitch, HIGH);
while(time0 + record > now)
    reads();

    now = millis();

```

Testing Interferometer Signals:

```
const int Sum = A3; // The voltage across the capacitor bank (analog input)
const int Difference = A4; // The output that controls the ground switch's relay.

void setup()
{
    //
    pinMode(Sum, INPUT);
    pinMode(Difference, INPUT);
    Serial.begin(115600);
}

void loop()
{
    // put your main code here, to run repeatedly:
    float sum = analogRead(Sum); // Bits
    float sumvoltage = sum*.0049000; // Voltage of Sum Arm
    float difference = analogRead(Difference); // Bits
    float differencevoltage = difference*.0049000; // Voltage of Difference Arm
    Serial.print(sumvoltage,5); // Print voltages to 5 decimal places
    Serial.print("\n");
    Serial.println(differencevoltage,5);
    delay(300);
}
```

Testing Oxygen Sensor:

```
// Grove - Gas Sensor(O2) test code
// Note:
// 1. It need about about 5-10 minutes to preheat the sensor
// 2. modify VRefer if needed

const float VRefer = 5;          // voltage of adc reference

const int pinAdc    = A4;

void setup()

    // put your setup code here, to run once:
    Serial.begin(112500);
    Serial.println("Grove - Gas Sensor Test Code...");

void loop()

    // put your main code here, to run repeatedly:
    float Vout =0;
    Serial.print("Vout =");
    Vout = readO2Vout();
    Serial.print(Vout);
    Serial.print(" V, Concentration of O2 is ");
    Serial.println(readConcentration());
    delay(60000);

float readO2Vout()

    long sum = 0;
    for(int i=0; i<32; i++)
```

```

        sum += analogRead(pinAdc);

sum >>= 5;
float MeasuredVout = sum * (VRefer / 1023.0);
return MeasuredVout;

float readConcentration()

// Vout samples are with reference to 3.3V
float MeasuredVout = readO2Vout();
//float Concentration = FmultiMap(MeasuredVout, VoutArray,O2ConArray, 6);
//when its output voltage is 2.0V,
float Concentration = MeasuredVout * 0.21 / 2.0;
float Concentration_Percentage=Concentration*100;
return Concentration_Percentage;

```

Appendix D

Supplemental Data for Chapter 3

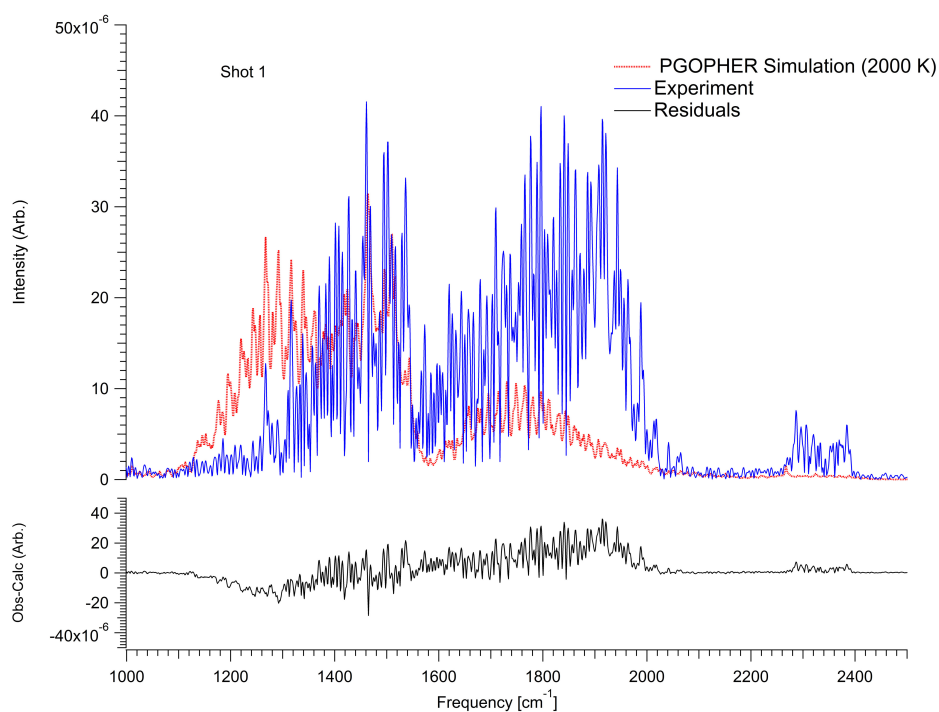


Figure D.1: Results of fit to bending mode of water for Shot 1.

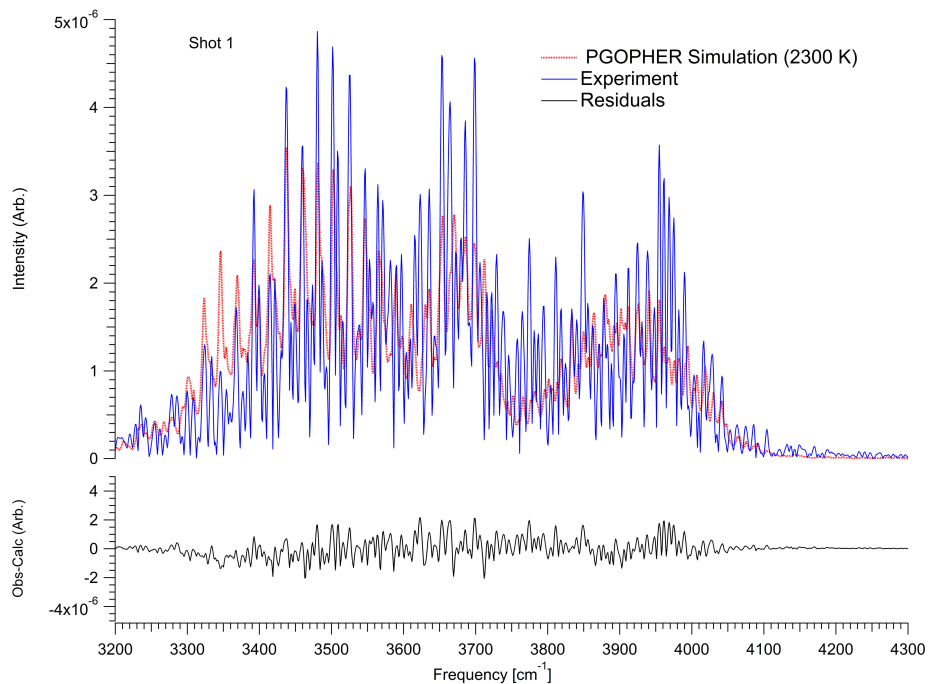


Figure D.2: Results of fit to stretching modes of water for Shot 1.

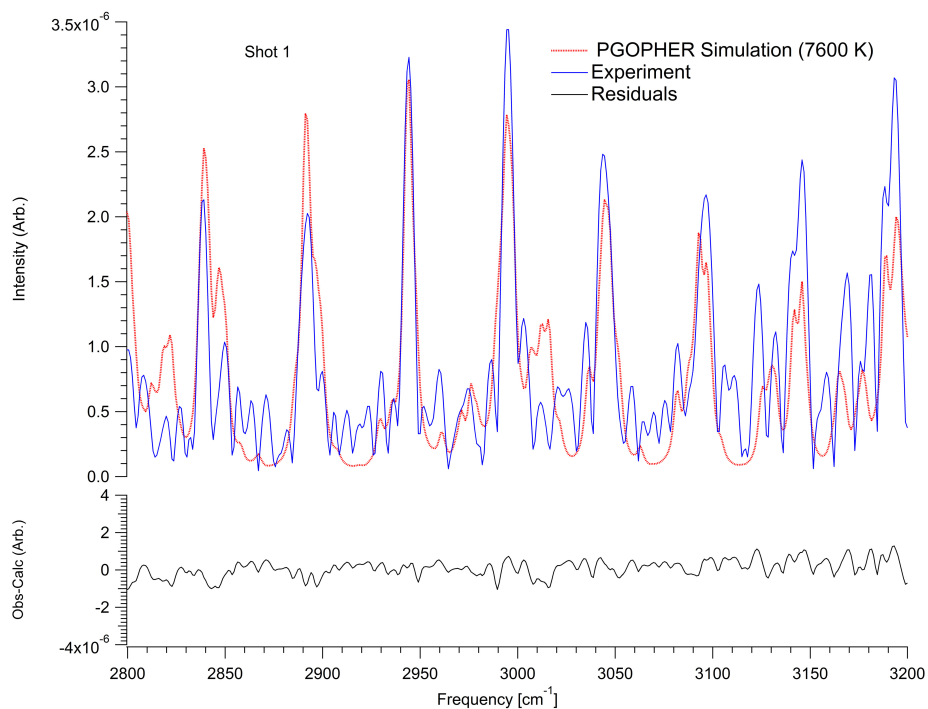


Figure D.3: Results of fit to OH for Shot 1.

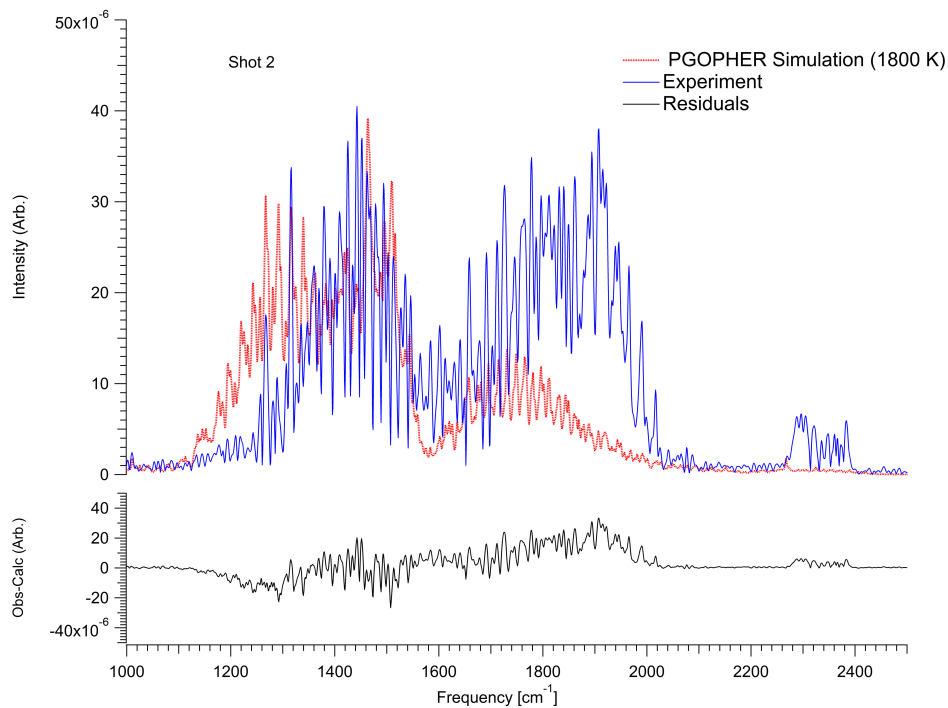


Figure D.4: Results of fit to bending mode of water for Shot 2.

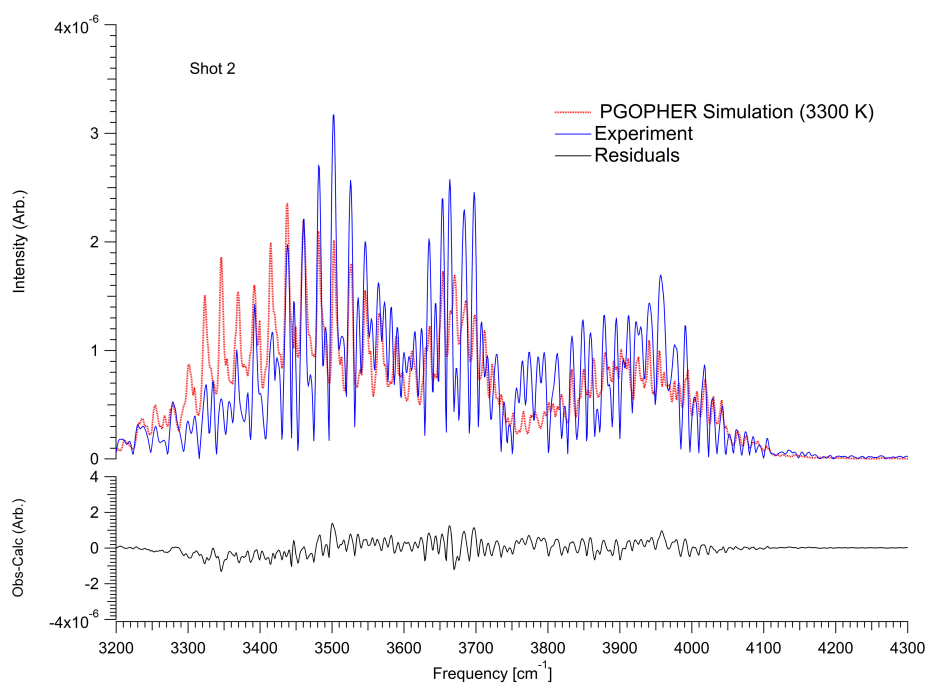


Figure D.5: Results of fit to stretching modes of water for Shot 2.

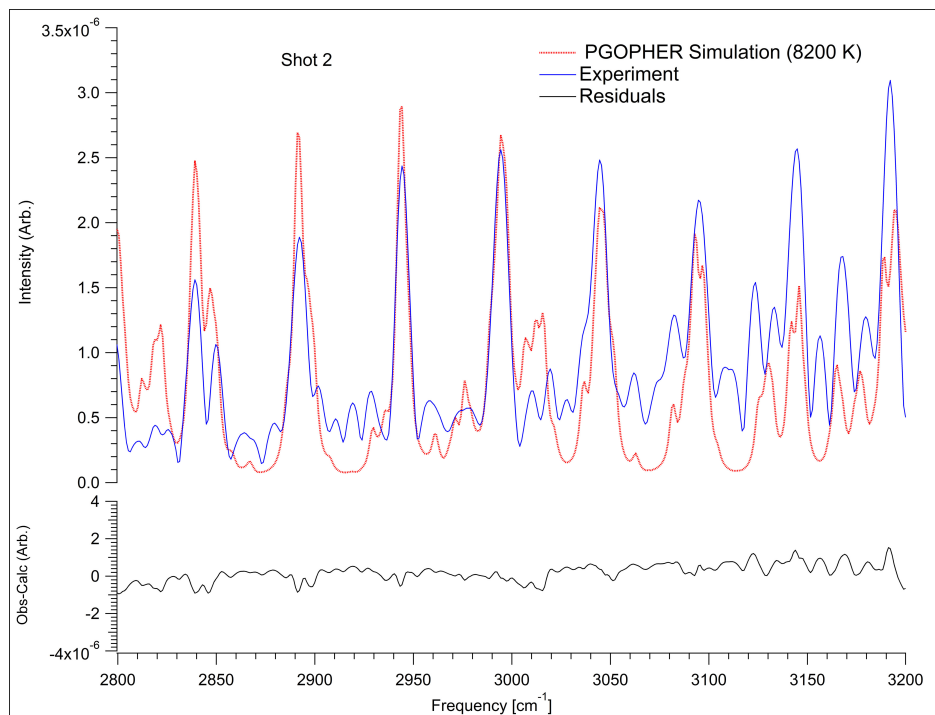


Figure D.6: Results of fit to OH for Shot 2.

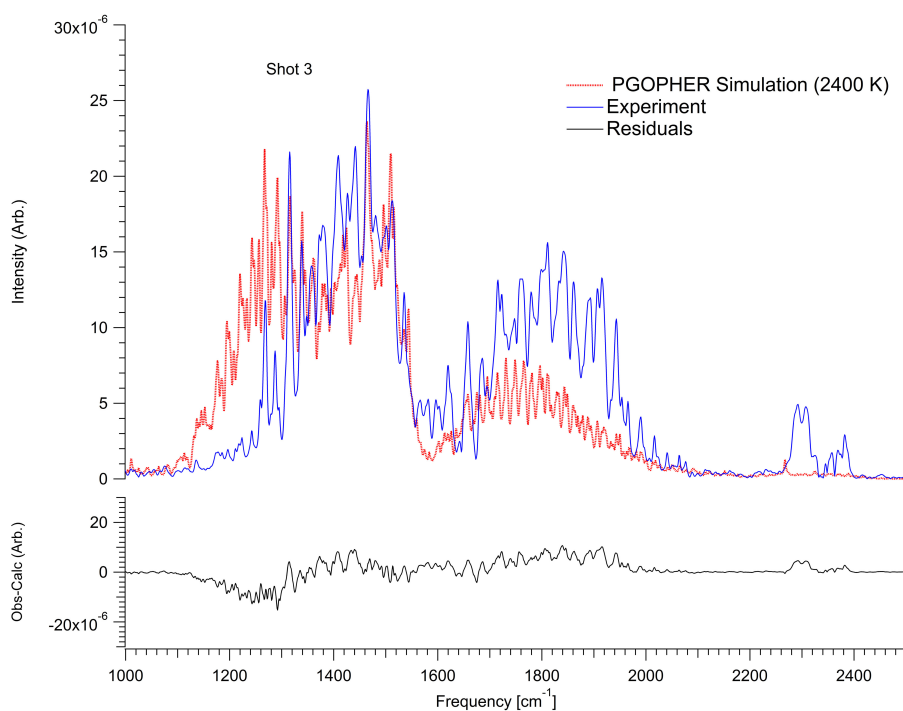


Figure D.7: Results of fit to bending mode of water for Shot 3.

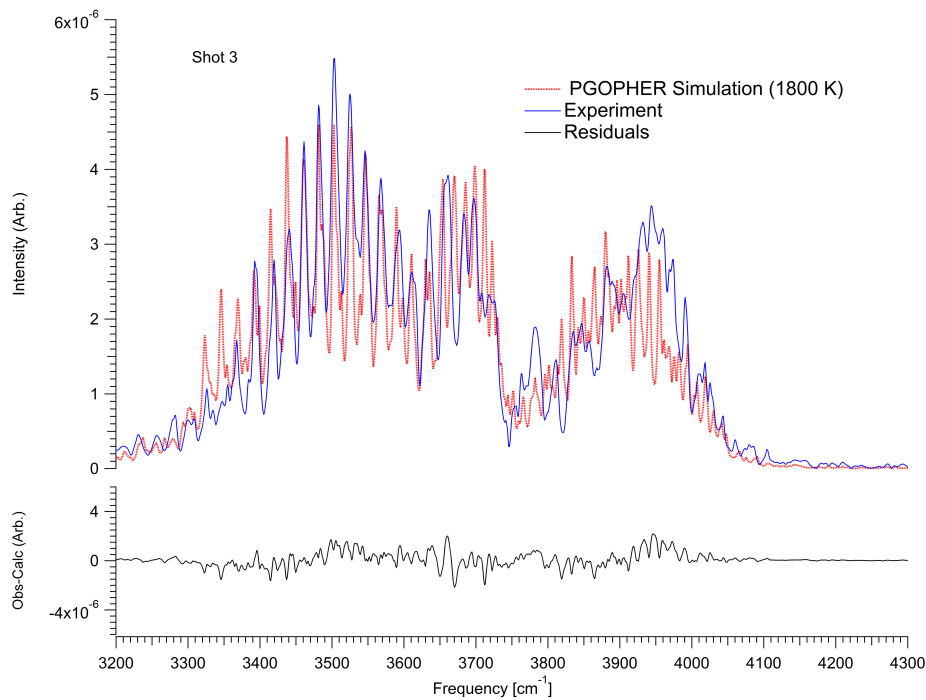


Figure D.8: Results of fit to stretching modes of water for Shot 3.

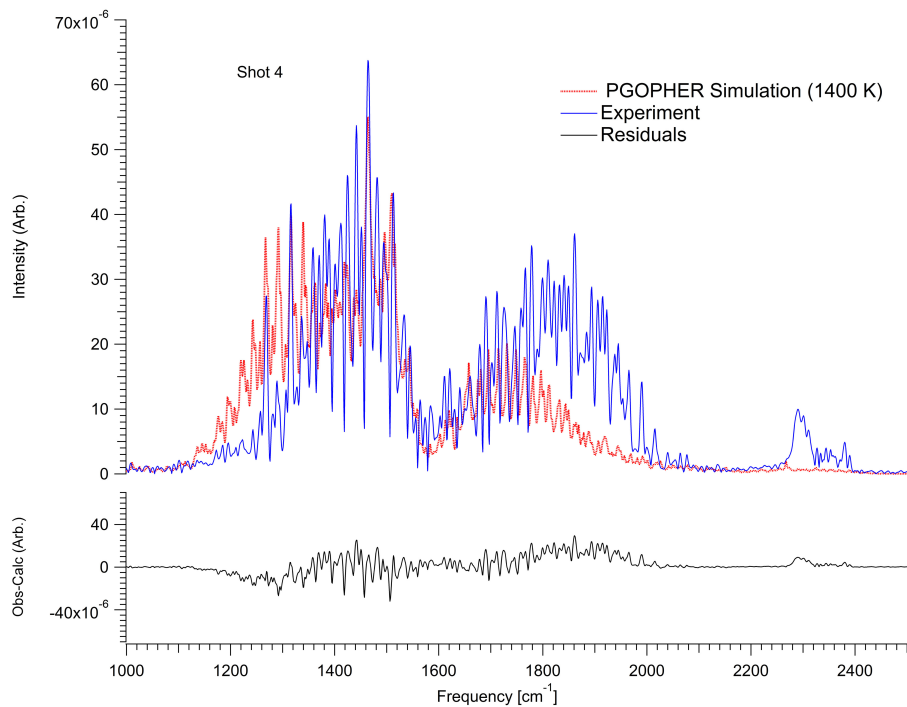


Figure D.9: Results of fit to bending mode of water for Shot 4.

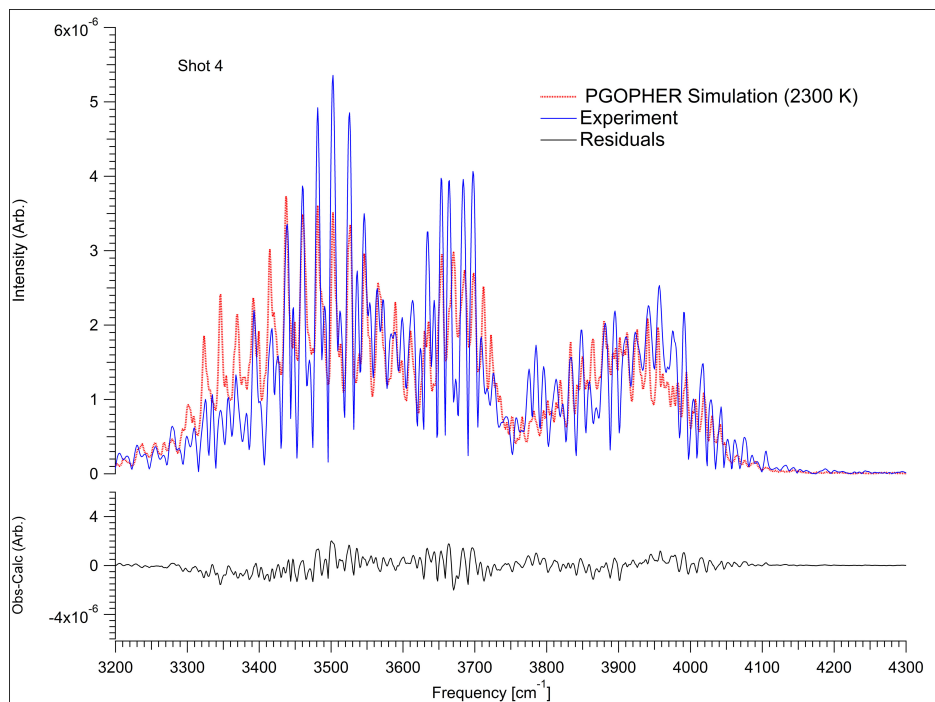


Figure D.10: Results of fit to stretching modes of water for Shot 4.

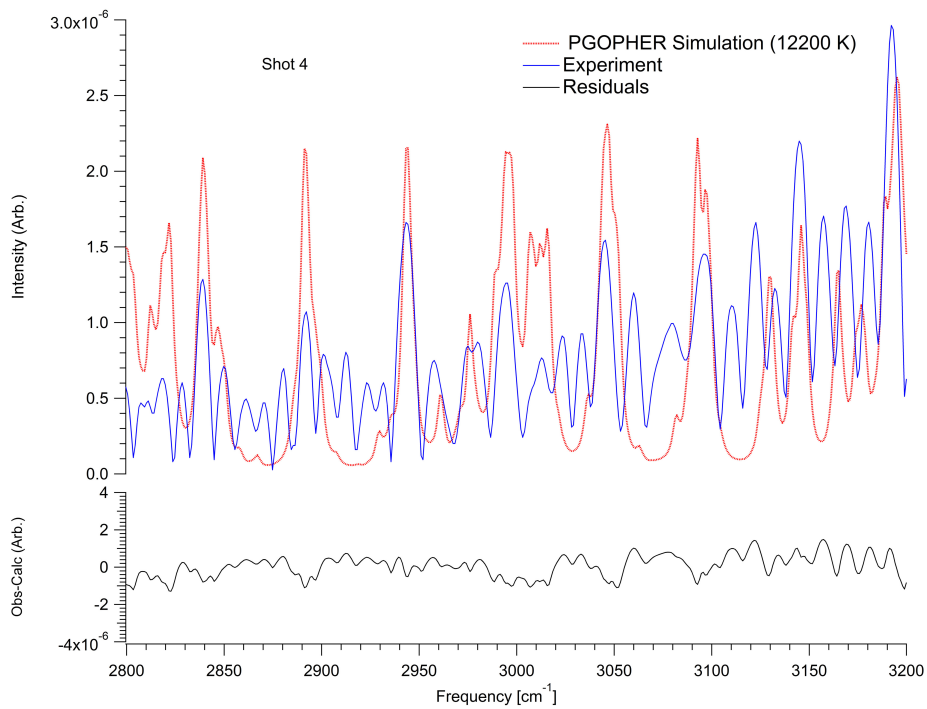


Figure D.11: Results of fit to OH for Shot 4.

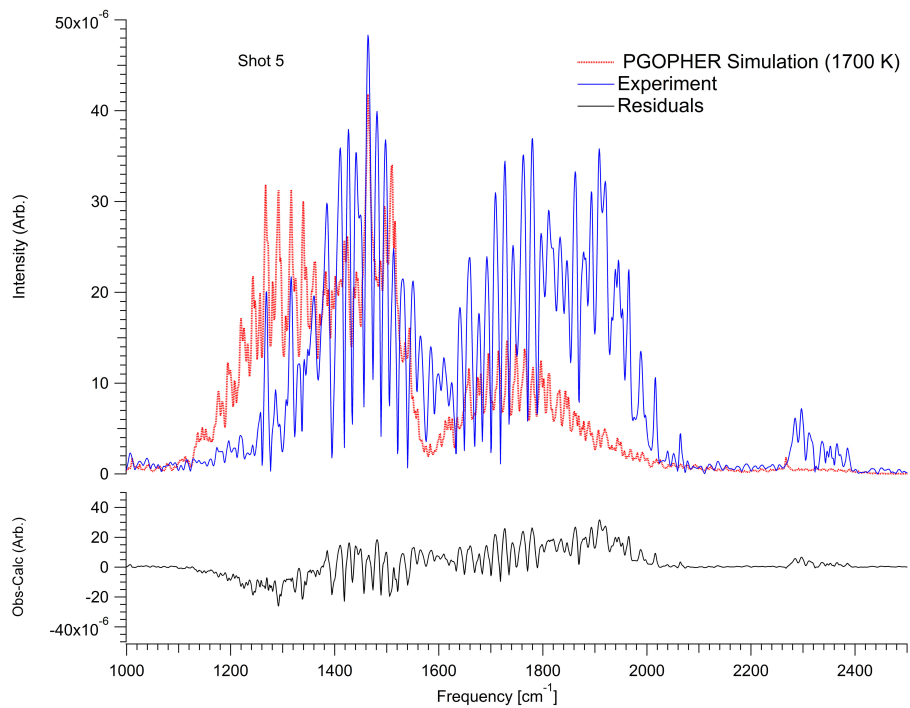


Figure D.12: Results of fit to bending mode of water for Shot 4.

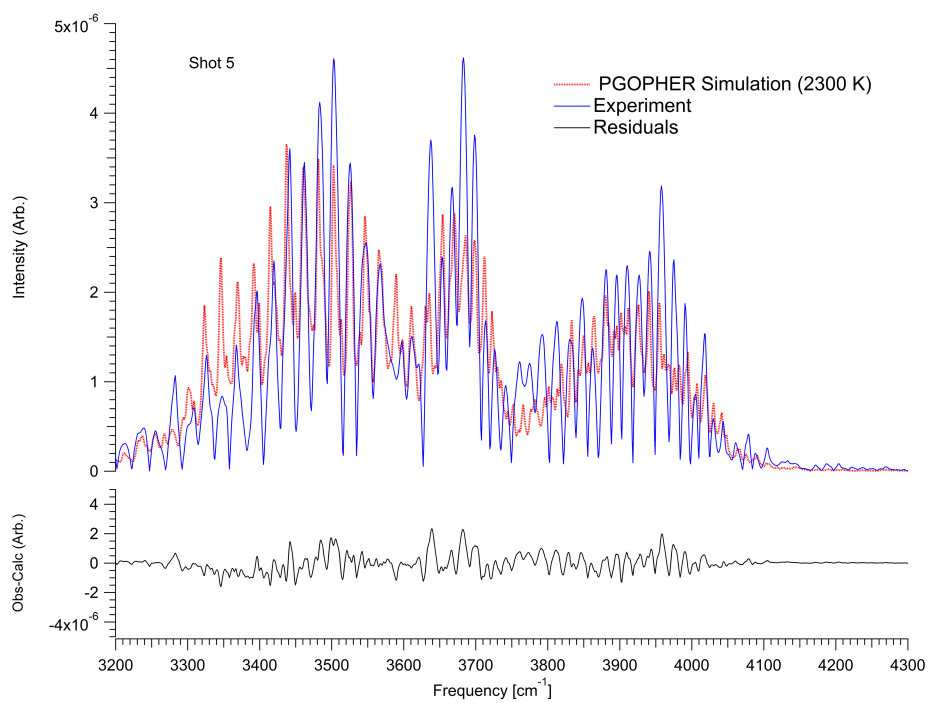


Figure D.13: Results of fit to stretching modes of water for Shot 5.

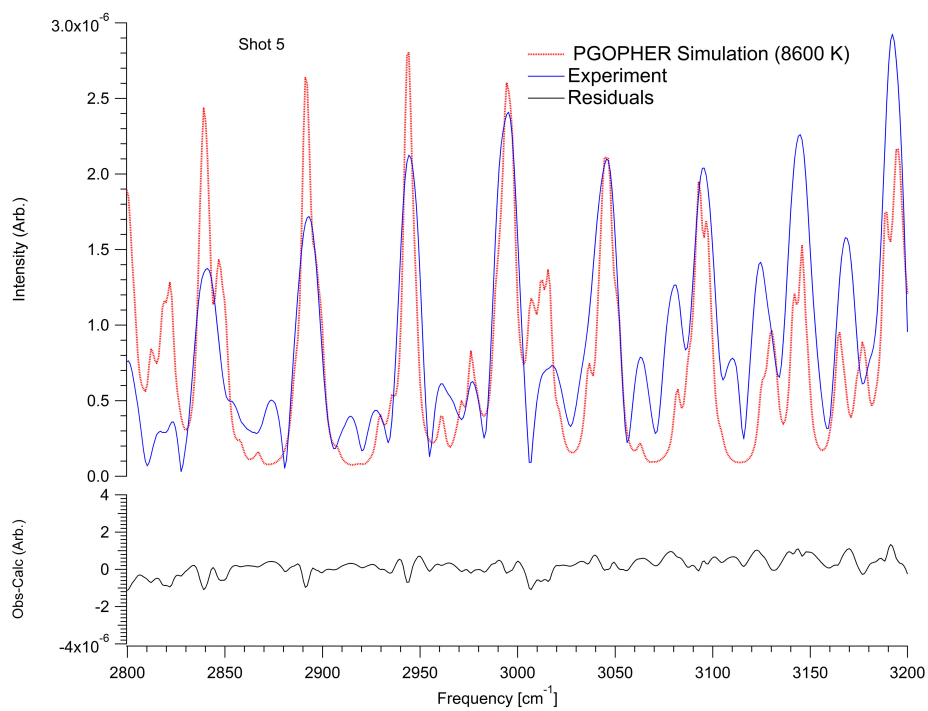


Figure D.14: Results of fit to OH for Shot 5.

Appendix E

Supplemental Data for Chapter 4

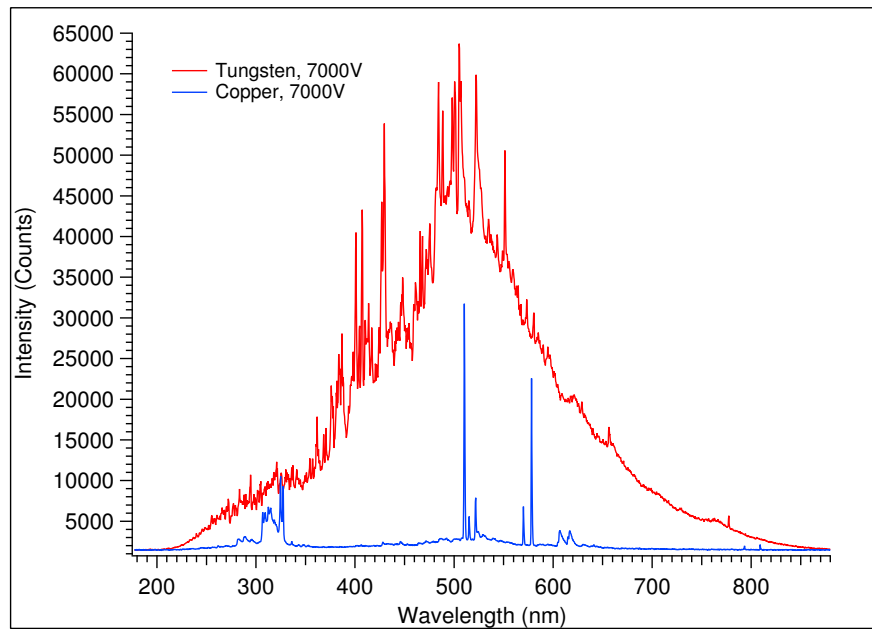


Figure E.1: Emission spectra collected from the two electrode materials described in these experiments.

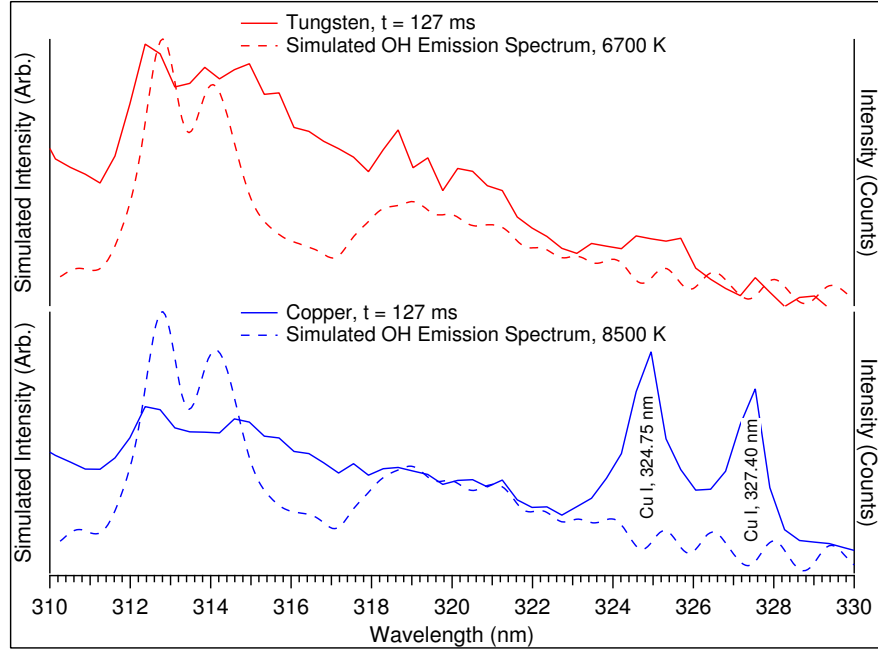


Figure E.2: Overlays of two best-fit spectra (generated with PGOPHER [63]) with experimental spectra.

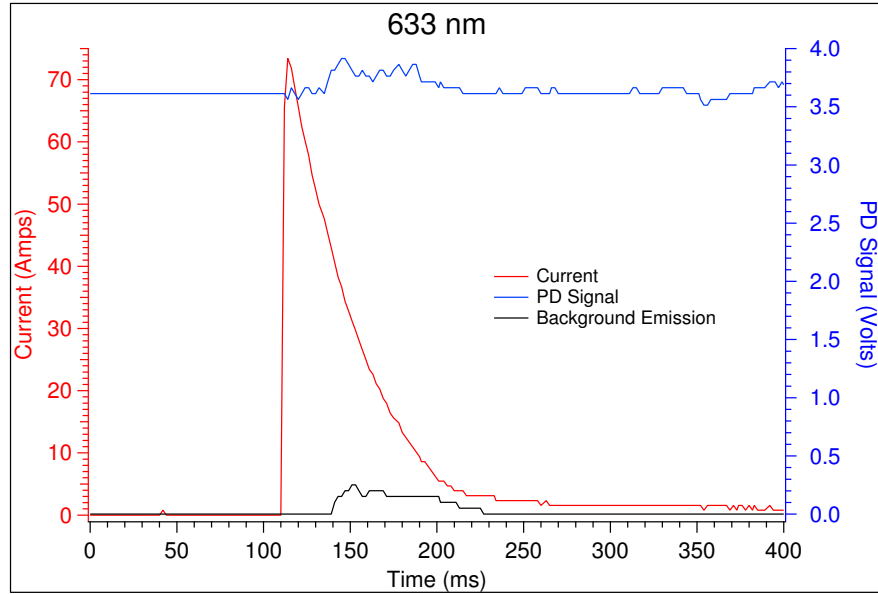


Figure E.3: Voltage output from photodiode ($\lambda=633$ nm) overlaid with a current profile of a ball plasmoid discharge from a tungsten electrode at 7000 V.

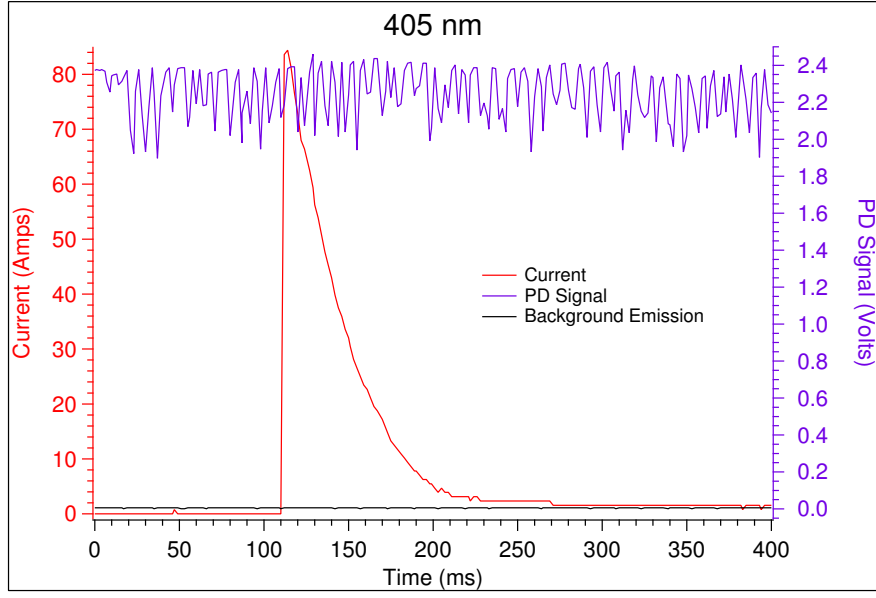


Figure E.4: Voltage output from photodiode ($\lambda=405$ nm) overlaid with a current profile of a ball plasmoid discharge from a tungsten electrode at 7000 V.

Table E.1: Assigned electronic transitions of neutral copper (observed when using a copper electrode). Transitions were assigned using the NIST Atomic Spectral Database [72].

Wavelength [nm]	Transition
276.64	$2P^{\circ}_{3/2} \rightarrow 2D_{3/2}$
296.12	$2F^{\circ}_{7/2} \rightarrow 2D_{5/2}$
319.41	$4D^{\circ}_{3/2} \rightarrow 2D_{3/2}$
324.75	$2P^{\circ}_{3/2} \rightarrow 2S_{1/2}$
327.40	$2P^{\circ}_{1/2} \rightarrow 2S_{1/2}$
333.78	$4F^{\circ}_{7/2} \rightarrow 2D_{5/2}$
406.26	$2D_{5/2} \rightarrow 2P^{\circ}_{3/2}$
427.51	$4D_{7/2} \rightarrow 4P^{\circ}_{5/2}$
453.08	$2S_{1/2} \rightarrow 2P^{\circ}_{3/2}$
465.11	$4D_{7/2} \rightarrow 4F^{\circ}_{9/2}$
510.55	$2P^{\circ}_{3/2} \rightarrow 2D_{5/2}$
515.32	$2D_{3/2} \rightarrow 2P^{\circ}_{1/2}$
522.01	$2D_{3/2} \rightarrow 2P^{\circ}_{3/2}$
529.25	$4D_{7/2} \rightarrow 4D^{\circ}_{7/2}$
570.02	$2P^{\circ}_{3/2} \rightarrow 2D_{3/2}$
578.21	$2P^{\circ}_{1/2} \rightarrow 2D_{3/2}$

Table E.2: Assigned electronic transitions of singly ionized copper.

Wavelength [nm]	Transition
262.07	$2[5/2]_3 \rightarrow 3F^{\circ}_2$
368.66	$1G_4 \rightarrow 3F^{\circ}_3$
467.36	$2[1/2]^{\circ}_0 \rightarrow 2[1/2]_1$

Table E.3: Assigned electronic transitions of neutral tungsten (observed when using a tungsten electrode).

Wavelength [nm]	Transition
277.40	$^{\circ}_2 \rightarrow ^5D_3$
283.36	$^{\circ}_3 \rightarrow ^5D_4$
320.83	$^{\circ}_2 \rightarrow ^5D_2$
330.08	$^{\circ}_4 \rightarrow ^5D_3$
337.14	$^{\circ}_1 \rightarrow ^5D_1$
341.43	$^{\circ}_3 \rightarrow ^5D_4$
344.88	$^{\circ}_3 \rightarrow ^3D_3$
361.75	$^5P^{\circ}_3 \rightarrow ^7S_3$
363.19	$^5D^{\circ}_2 \rightarrow ^5D_1$
376.01	$^5D^{\circ}_3 \rightarrow ^5D_2$
381.75	$^5F^{\circ}_3 \rightarrow ^7S_3$
384.75	$^5F^{\circ}_1 \rightarrow ^5D_0$
386.80	$^7D^{\circ}_4 \rightarrow ^7S_3$
388.14	$^5P^{\circ}_3 \rightarrow ^5D_3$
404.56	$^5F^{\circ}_2 \rightarrow ^7S_3$
407.19	$^{\circ}_2 \rightarrow ^3D_3$
424.44	$^7D^{\circ}_5 \rightarrow ^5D_4$
426.98	$^{\circ}_3 \rightarrow ^5S_2$
429.46	$^7P^{\circ}_2 \rightarrow ^7S_3$
461.33	$^7P^{\circ}_4 \rightarrow ^5D_4$
465.99	$^7D^{\circ}_1 \rightarrow ^5D_0$
468.05	$^7D^{\circ}_3 \rightarrow ^5D_3$
472.04	$^{\circ}_2 \rightarrow ^3P^{\circ}_2$
481.61	$^{\circ}_2 \rightarrow ^3P^{\circ}_2$
484.38	$^7D^{\circ}_2 \rightarrow ^5D_2$
488.69	$^7F^{\circ}_5 \rightarrow ^5D_4$
498.25	$^7F^{\circ}_1 \rightarrow ^5D_0$
543.50	$^7F^{\circ}_1 \rightarrow ^5D_1$
551.47	$^7D^{\circ}_1 \rightarrow ^5D_2$
563.19	$^5D^{\circ}_3 \rightarrow ^3H_4$
567.54	$^{\circ}_2 \rightarrow ^5G_2$
722.61	$^5F^{\circ}_5 \rightarrow ^5G_5$
728.58	$^5F^{\circ}_5 \rightarrow ^5G_6$
738.13	$^5F^{\circ}_5 \rightarrow ^3G_5$
748.34	$^{\circ}_1 \rightarrow ^5P_2$

Table E.4: Assigned electronic transitions of neutral iron.

Wavelength [nm]	Transition
251.81	$x^5D^{\circ}_1 \rightarrow a^5D_2$
282.57	$z^3G^{\circ}_5 \rightarrow a^5D_4$
370.86	$w^5G^{\circ}_2 \rightarrow b^3F^{\circ}_3$
378.19	$s^3G^{\circ}_3 \rightarrow b^3D_2$
383.63	$t^3D^{\circ}_2 \rightarrow a^3D_2$
386.96	$x^3G^{\circ}_5 \rightarrow a^3G_4$
393.36	$w^3P^{\circ}_2 \rightarrow c^3P_1$
398.18	$z^3H^{\circ}_4 \rightarrow a^3G_4$
401.02	$^5D^{\circ}_4 \rightarrow b^3D_3$
402.19	$z^3H^{\circ}_4 \rightarrow a^3G_3$
410.07	$z^3F^{\circ}_4 \rightarrow a^5F_5$
411.85	$^1I^{\circ}_6 \rightarrow a^1H_5$
413.70	$y^1D^{\circ}_2 \rightarrow a^1P_1$
416.89	$e^7G_2 \rightarrow z^5F^{\circ}_2$
420.55	$e^7F_2 \rightarrow z^5F^{\circ}_2$
422.74	$e^5G_6 \rightarrow z^5F^{\circ}_5$
437.78	$v^3D^{\circ}_2 \rightarrow a^3D_1$
448.16	$e^3D_1 \rightarrow z^5P^{\circ}_1$
456.01	$e^5G_4 \rightarrow z^5P^{\circ}_3$
500.61	$e^7D_5 \rightarrow z^7F^{\circ}_5$
505.16	$z^5F^{\circ}_4 \rightarrow a^5F_4$
506.88	$e^7D_3 \rightarrow z^7P^{\circ}_4$
510.40	$w^5D^{\circ}_3 \rightarrow c^3P_2$
522.32	$x^3P^{\circ}_0 \rightarrow b^3D_1$
532.00	$v^5P^{\circ}_2 \rightarrow b^3D_3$
534.97	$e^3G_4 \rightarrow z^3G^{\circ}_5$
549.35	$e^3D_3 \rightarrow y^5D^{\circ}_4$
729.28	$e^7P_4 \rightarrow y^5P^{\circ}_3$
730.79	$x^3F^{\circ}_3 \rightarrow c^3F_3$
740.17	$w^3D^{\circ}_1 \rightarrow c^3F_2$
741.87	$u^5D^{\circ}_2 \rightarrow c^3F_3$

Table E.5: Assigned electronic transitions of singly ionized iron.

Wavelength [nm]	Transition
493.54	$^2[3]^{\circ}_{7/2} \rightarrow ^6D_{7/2}$
514.95	$^2[5]^{\circ}_{9/2} \rightarrow ^6P_{7/2}$
752.51	$^4F_{9/2} \rightarrow ^4D^{\circ}_{7/2}$
754.02	$^6F_{5/2} \rightarrow w^6P^{\circ}_{7/2}$
756.62	$^6F_{7/2} \rightarrow w^6P^{\circ}_{7/2}$
762.12	$w^6P^{\circ}_{3/2} \rightarrow e^6D_{3/2}$
763.62	$^2P_{3/2} \rightarrow ^4P^{\circ}_{3/2}$
765.76	$^6F_{3/2} \rightarrow w^6P^{\circ}_{5/2}$
769.76	$^2P_{3/2} \rightarrow v^4F^{\circ}_{5/2}$
774.16	$^6D_{1/2} \rightarrow w^6P^{\circ}_{3/2}$
789.45	$^4F_{5/2} \rightarrow w^6P^{\circ}_{3/2}$
793.49	$^4D_{7/2} \rightarrow ^4P^{\circ}_{5/2}$
797.66	$^6D_{3/2} \rightarrow v^4F^{\circ}_{5/2}$
816.10	$^6F^{\circ}_{5/2} \rightarrow e^6D_{7/2}$

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