Nitric Oxide and Other Characterizations of an Atmospheric Pressure Plasma Jet

THESIS

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Abstract

This thesis presents the characteristics of an atmospheric pressure plasma jet (APPJ) that was used for surface chemistry at the University of Maryland. Recently, APPJs have gained popularity in the medical field to decontaminate surfaces, heal wounds, and cancer treatment. The motivation for this study is that many APPJs lack NO measurements. Characteristics done on this jet include charge-voltage (QV) measurements, time resolved spectroscopy, optical emission spectroscopy (OES) and NO-PLIF. QV measurements were done in order to find the energy of the plasma throughout the jet which was on the order of magnitude of $10^{-4}-10^{-5}$ Joules/period. The time resolved spectroscopy showed that the plume of the plasma changes with time. The use of optical emission spectroscopy revealed that oxygen, nitrogen and NO were present in the plasma even if there was none being pumped through the jet. NO number density was calculated from taking PLIF measurements. It was found that helium mixtures create more NO than the argon mixtures.
Dedication

Jan Pulcini
For always encouraging me to do my best and being my biggest fan.

Donald Pulcini
For always teaching me new things and being proud no matter what.
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Chapter 1: Introduction

Throughout the years, plasma chemistry/physics has been the topic of many studies. Plasma is a partially-ionized, quasi-neutral gas that can be produced by applying a voltage across two electrodes thereby ionizing and exciting a gas. The electrical energy is transferred to the plasma by accelerating charged gaseous medium species which is contained in the electric field. The number density of charged particles present and the conductivity of the gas are proportional. This allows the medium to develop electrical conductivity and electromagnetic forces to induce reactions. Fundamentally, plasma is considered as the fourth state of matter beside solids, liquids and gases [1]. This chapter provides an overview of plasma jets and their applications, and describes the motivations for the research presented.

1.1 Overview of Atmospheric Pressure Plasma Jets

In recent years, atmospheric pressure plasma jets (APPJs) have gained popularity in industrial technologies and medical applications. APPJs are currently used as a way to apply thin films in industry and are used throughout the medical field to decontaminate surfaces, heal wounds, and for cancer treatment [2]. There are many advantages and disadvantages to using plasma jets compared to other plasma sources.
Compared to other plasma sources, APPJs are able to be applied directly to the source. They have a small length, millimeters to centimeter range, at which they can be used which can be considered an advantage or disadvantage depending on what it is being used for. The small APPJ can be used to penetrate small areas, porous structures and complex geometry of objects. APPJs are usually low in temperature therefore the surface is not damaged when the jet is being used. Other plasma sources need a vacuum chamber to run where the plasma jet overcomes this disadvantage. Without the vacuum chamber, difficulties arise when running the APPJs such as: arcing between electrodes and a higher voltage is necessary in order for the gas to breakdown at 760 torr. Arcing can be prevented by the presence of an insulating material between the electrodes or by making the electrodes pointed in corona discharges [3]. There have been many modifications to the plasma jet to suit each research project.

Plasmas have become popular in industry especially with material surfaces. APPJs have been used to coat films onto surfaces due to the plasma gas staying close to room temperature. This makes APPJs attractive for surface modifications to temperature-sensitive materials. One study showed that the APPJ changed the chemistry of the surface to improve the adhesive bond strength of polyethylene. They found that the modification takes place while the surface is being hit with the plasma jet and outside of the plasma jet after the treatment. [4] Similarly to the polyethylene study, another study was completed with polypropylene film, which is used for protective overcoats and food packaging. Due to its hydrophobic surface characteristics, polypropylene film has its disadvantages, such
as wettability, printability and adhesion. The study showed that the APPJ was advantageous over low-pressure plasma. The advantages included no vacuum equipment and less expensive equipment, which can be efficient and integrated into an in-line process. The APPJ changed the hydrophobic material into a hydrophilic material making it easier for wettability, printability and adhesion [5]. Woven textiles have also been of interest in APPJs research. APPJs have been used as an environmentally friendly process in the textile industry because it does not use chemicals or water. Comparable to the polypropylene study, the non-woven textiles use the APPJ to modify the hydrophobic textile to a hydrophilic. This leads to modifying the inner surface of the porous surface. [6]. Industry has been finding ways to make use of the APPJ especially with temperature-sensitive material and hydrophobic surfaces.

APPJs have also been used in medical applications such as decontamination of surfaces, wound healing and even cancer treatment. Because a lot of medical equipment is temperature-sensitive it is hard to sterilize it and thus gets thrown away. To make the medical field a more environmentally friendly place, APPJs have been used to sterilize temperature-sensitive materials. The APPJ gets rid of contaminates by using a variety of different antimicrobial agents to interact and decontaminate the equipment. This makes it economical and environmentally friendly [7]. Another way the APPJ is utilized in the medical field is in wound healing. When the APPJ was applied to open wounds in rats, they found that the wound healed faster than the control group. The plasma was found to affect the biological function in cells and tissues, which caused the wound to heal more
rapidly. [7]. It is believed that the production of NO is a key ingredient to induce wound healing [8] Another study found that the APPJ was used in the field of dermatology, where it lead to diverse reactions in tissue without damaging the healthy tissue. They are still investigating whether the APPJ can be used for atopic dermatitis and other skin diseases treatment, and cosmetic applications by rejuvenating the skin and decreasing wrinkles [9]. APPJs have also been used in cancer treatment. When the APPJ was applied to cancer cells, it was found to be toxic to the cells which caused the cells to die and decreases cells reproductively and colonize. The APPJ only targeted the cancerous cells and not the healthy ones. However, this is not true for all cancers, only a few such as brain cancer cells T98G [10].

1.2 Motivations for Study

At the University of Maryland, UMD, Dr. Oehrlein’s research group has used the APPJ to modify and deactivate biomolecules. In surface chemistry and biological activity, x-ray photoelectron spectroscopy and an enzyme-linked immunosorbent assay have measured alterations. UMD was able to successfully characterize the surface; however, characterizing the plasma jet was restricted [11]. Collaboration ensued between Dr. Oehrlein’s research group at UMD and Dr. Lempert’s research group at The Ohio State University, OSU, to perform plasma diagnostics. The diagnostics that were performed were charge-voltage, QV, measurements, optical emission spectroscopy, (OES); time resolved spectroscopy, and NO planar laser induced fluorescence, PLIF.
The design of the jet was based on the jet used by Barts et al. [2]. They used this jet with 1% O$_2$ in a controlled environment composed of N2/Ar mixtures to measure lippopolysaccharide using x-ray photoelectron spectroscopy. They found that when N2 concentration was varied from 20% to 100% that the surface became modified when the jet was applied. The reactive oxygen species are quenched when the plasma excites the N2 therefore preventing the oxygen from modifying the film surface. In order to show that the reactive oxygen species were quenched they measured the biological activity, optical emission and ozone production of the jet using O2, N2 and O2/N2 admixtures. Their results showed that for APPJ treatments of surfaces, plasma-environment interactions are essential to consider [2]. Because N2 and O2 were being used in this study, it is important to consider the production of nitric oxide. They lacked the equipment to measure NO, which is why this study was completed.

QV measurements were performed to calculate the energy in the APPJ. Due to collisions with other particles, the electrons lose their energies, which lowers the power coupling efficiency to less than that of a vacuum plasma. Manley derived the dissipated power in a parallel-cell-type atmospheric pressure dielectric barrier discharge, AP-DBD, from the QV Lissajous diagram [12]. In Figure 1, an example of the Lissajous diagram can be seen [12]. The diagram has a parallelogram shape with charge on the y-axis and voltage on the x-axis. The slopes of the lines represent the capacitances of air and the dielectric electrode of the reactor where AB and CD represents the slope of the capacitance of the dielectric electrode, and the slopes of BC and AD represent the slopes
of the capacitance reactor. $V_m$ represents the maximum applied voltage and $V_0$ is the breakdown voltage [12].

![Figure 1: Schematic of the QV Lissajous Diagram](image)

For these diagrams, voltage traces across the high voltage are taken and across a capacitor. The voltage across the capacitor is then used to calculate the charge with the use of Equation 1 below.

$$V = \frac{q}{c}$$  \hspace{1cm} (1)
Once the charge is calculated, it can be used to evaluate the energy. The high voltage and the $\Delta q$ are used to approximate the energy. The energy is calculated by using Equation 2 below where $q$ is the charge that was calculated and $V_1$ is the high voltage.

$$E = \int V_1(t) \, dq \approx \sum_{i=1}^{\infty} V_1(t) \frac{q_{i+1} - q_{i-1}}{2}$$  \hspace{1cm} (2)

Time-resolved spectroscopy and OES has uses in the diagnostics of plasmas. Time-resolved spectroscopy can show how the plasma changes with respect to time. In an APPJ, the plasma is not constant in shape or intensity, which can affect how the plasma reacts in different experiments. OES can help determine what is present in the plasma. In some cases, different species are present right outside of the opening to the jet than at the end of the plasma plume, which could affect also plasma induced reactions on the surface.

Nitric Oxide, NO, is present in many living organisms to assist in many physiological processes, although too much can be harmful [13]. Therefore, when an APPJ is used in biomedical processes, it is important to measure the NO being produced. There have been many ways to measure NO such as OES, absorption spectroscopy and even using an NO detector, however, none of these techniques give way to spatially resolved NO measurements [13]. Laser Induced Fluorescence (LIF) is a technique used in combustion and low pressure plasmas to investigate NO density [14]. In APPJ research, there are very few measurements of NO taken using LIF.

Eckbreth describes fluorescence as “the spontaneous emission of radiation from an upper energy level which has been excited in any of a variety of ways e.g., collisions
with photons, electrons or molecules” [15]. Lasers are a way to stimulate fluorescence in gases. A way for LIF to be used in combustion is to make the laser a sheet to make sure it reaches the entirety of the reactants, which is known as Planar LIF, PLIF. The sheet is produced with lenses arranged in various ways [16]. PLIF has been used for combustion diagnostics and to characterize gas and liquid phase fluid flow situations in order to determine species concentration, partial pressure, temperature, flow velocity, or flow distribution/visualization [14]. The fluorescence created from the laser can then be collected by a camera such as an intensified charge coupled device (ICCD) camera.

1.3 NO Chemistry

The Zeldovich mechanism describes the production of NO in air at thermal equilibrium. This mechanism can be seen below in Equations 3 and 4. Equation 5 is often included in the extended Zeldovich mechanism. All three reactions are reversible and have strong temperature dependences. Due to the fact that the concentration of atomic species in air is exceptionally small at low temperatures equilibrium, NO production is very slow [13].

\[ N + O_2 \leftrightarrow NO + O \]  
\[ N_2 + O \leftrightarrow NO + N \]  
\[ N + OH \leftrightarrow NO + H \]
However, in plasmas, NO can be efficiently produced by the “enhanced” Zeldovich process, seen below in Equation 6. $N_2^*$ is a manifold of excited N$_2$ electronic states as described by Shkurenkov et al. [17].

$$N_2^* + O \leftrightarrow NO + N$$  \hspace{1cm} (6)

NO became a popular research topic among the combustion world due to the fact it is produced in many combustion reactions. NO is an air pollutant formed from car emissions and stationary combustion sources such as electric power generating systems and gas-fired stoves. At high temperature combustion reactions, more NO is produced because the reactions seen in Equations 3 and 4 are endothermic and the equilibrium constant is high at higher temperatures. NO can become a problem in the atmosphere because it can produce smog and acid rain [14].

Although NO is an important molecule in combustion chemistry, it has also become an important molecule in biological chemistry and medicine. NO is vital in maintaining the body. It can act as an intercellular messenger or help wounds and tissues heal because it is easily diffused through tissues. Heinlin et al found NO generated from outside of the body by the plasma healed wounds approximately 24.6% more rapidly than in the control group. They also found that vasodilation and normalized microcirculation, direct bactericidal effects, improvement of nerve conduction velocity, stimulation of fibroblasts and vessel growth are all improved when NO is produced with the plasma [9].
NO is important throughout the body; it has been known to be an antibacterial agent and provides signals to regulate biological functions. NO kills invading pathogens, works as a primary vasoregulator and antihypertensive agent and also regulates inflammation, collagen production, angiogenesis and apoptosis. It works so well throughout the body because it is a free radical that can react with many biological molecules [7].

NO has become more and more accepted for sterilization. It is known as a universal anti-microbial factor for more than 45 different bacteria, various fungi and parasites. Since NO can decontaminate mostly all pathogens, identification of the microbe is not necessary making the process more useful [7]. Therefore NO-therapy is a great technique for treatment and prevention of many infections throughout the human body.

The goal of this study was to characterize the plasma jet that was used at the University of Maryland for surface chemistry. This thesis provides the details of this study including QV measurements, time resolved spectroscopy, OES and NO-PLIF. In Chapter 2, the materials and methods can be found. This includes how each part was constructed and details of how the experiments were completed. Chapter 3 goes into details about the results and discusses what was found. Chapter 4 discusses conclusions and future work that could be done.
Chapter 2: Experimental Methods

Figure 2 is a picture of the plasma jet set up. The plasma jet was made using a 12 inch alumina tube with a quarter inch outer diameter. The electrodes were constructed by copper tubing cut to approximately a half inch in length and wires soldered on to each one. To prevent the plasma from arcing between electrodes, a piece of Teflon was cut and placed between the electrodes and then placed behind the high voltage electrode. At the other end of the jet, polyurethane tubing was used to connect to the gas lines. The jet was placed on a 3-axis translation stage for easy movement.
Figure 2: Plasma Jet Setup

The power supply for the plasma jet was the PVM500/DIDRIVE10 Hydrogen and Chemical Production Corona Cell Plasma and Dielectric Driver, which can be seen in Figure 3. Only two controls were used to run the plasma, VA1 and S1/RFreq. The VA1 is the independent voltage level control, which was set at 25V. The S1/RFreq is the main power switch and frequency control. This control was adjusted to get the most output before the plasma began to arc. This was generally between 0.1 and 0.2 amps. The power supply frequency was approximately 25kHz and the voltage was approximately 7V.
Figure 3: Plasma Jet Power Supply

An injection seeded, Q-switched Nd:YAG laser (Continuum Surelite III or Precision 8010) used the second harmonic output to pump a tunable dye laser (Continuum ND6000) to produce light at 624nm. The dye laser used R640 dye. To generate the 226nm UV beam that is needed for NO PLIF, the dye laser output was mixed with the third harmonic out of the Nd: YAG laser. This was done using a Type I BBO crystal, which was controlled by an autotracker device.

The most important measurement to be taken was NO Planar Laser Induced Fluorescence (PLIF). In order to form the sheet from the laser to take the measurements, two UV lenses were used: a plano-convex, 100mm focal length cylindrical lens and a
plano-concave, -25mm focal length lens. The -25mm lens was placed in front of the 100mm approximately 25mm apart. Each lens was posted to a translation stage to ensure that the beam was as sharp as it could be for the PLIF measurements to be made. Below is Figure 4, that depicts the laser setup for the PLIF experiment.

![Laser diagram for NO PLIF](image)

*Figure 4: Laser diagram for NO PLIF*

The PLIF images were taken with a PIMAX ICCD camera with a Cerco UV lens (100 F/2.8-2178 175). The camera was placed in gated mode with 200 accumulations and variable gain depending on the intensity of the image.
To do the time-resolved images, a voltage probe was used to trigger the oscilloscope and camera. In WinSpec, the delay time was changed every 4 microseconds from 1 to 40 microsecond, matching the 25kHz A/C sine wave driving the jet. The camera averaged 200 accumulations during each image, and the gate width was set to 2 microseconds.

The OES measurements were taken using a SpectraPro 300i spectrometer (Model: PK244M-01AA-C1) with a near IR camera. The wavelength on the spectrometer was changed in 10 nm increments from 695 nm-1000 nm through the program WinSpec on the computer. The jet was moved to ensure that the area right in front of the opening was lined up with the slit on the spectrometer. To see if different products were made in different areas of the plasma, the jet was moved 1 mm, 2mm, and 4 mm from the original starting spot. The spectra were spliced together using Matlab.

The QV measurements were taken using three different capacitors: 10 nF, 22 nF and 47 nF. The set up can be seen below in Figure 5. A high voltage probe was used to measure the voltage across the HV electrode on the jet and power supply. The ground electrode of the jet and ground of the power supply was connected to the capacitor with a voltage probe measuring the voltage across the capacitor. Both voltage probes were connected to an oscilloscope where the voltage traces were shown.
Figure 5: QV measurements setup
Chapter 3: Results and Discussion

3.1: Voltage Traces

With the QV measurements, the voltage traces were taken over the high voltage electrode and across the capacitor. Once these were taken, the charge was calculated from the voltage across the capacitor. The charge was then used in calculating the energy by taking the integral of \( Udq \). Below is a figure of each of the voltage traces for the high voltage electrode and the capacitor. These can be seen in Figure 6. The green line represents the high voltage traces, while the blue represents the capacitor voltage traces. This data is from pure argon with the 10 nF capacitor. This is representative of how all of the voltage traces look. The high voltage traces exhibit sine waves, whereas the capacitor voltage traces exhibit less sinusoidal behavior.
With these voltage traces, charge was calculated by taking the capacitor voltage and multiplying it by the capacitor value (10, 22, or 47 nF). The charge was then used to calculate the change in charge ($\Delta q$) and the difference in voltages were also calculated to get the actual voltage across the series, $V_1(t) - V_2(t)$.

$$V = \frac{q}{C}$$

Both of these were used to calculate the energy. The total energy was calculated by summing up all of the energies.

$$E = \int V_1(t) dq \approx \sum_{i=1}^{\infty} V_1(t) \frac{q_{i+1} - q_{i-1}}{2}$$
This was for period of 2.5 cycles, therefore, the total energy was divided by 2.5 to get the energy for one period, which is 40 μsec. The energies for each gas admixture and capacitor can be seen below in Table 1. The energies are on the magnitude of approximately 0.1 mJ/period, with the lowest energy coming from the oxygen mixtures.

<table>
<thead>
<tr>
<th></th>
<th>10 nF</th>
<th>22 nF</th>
<th>47 nF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Argon</strong></td>
<td>-0.166</td>
<td>-0.109</td>
<td>-0.132</td>
</tr>
<tr>
<td><strong>Argon/Air</strong></td>
<td>-0.169</td>
<td>-0.119</td>
<td>-0.159</td>
</tr>
<tr>
<td><strong>Argon/Nitrogen</strong></td>
<td>-0.147</td>
<td>-0.156</td>
<td>-0.213</td>
</tr>
<tr>
<td><strong>Argon/Oxygen</strong></td>
<td>-0.785</td>
<td>-0.116</td>
<td>-0.121</td>
</tr>
<tr>
<td><strong>Helium</strong></td>
<td>-0.142</td>
<td>-0.089</td>
<td>-0.129</td>
</tr>
<tr>
<td><strong>Helium/Air</strong></td>
<td>-0.139</td>
<td>-0.152</td>
<td>-0.169</td>
</tr>
<tr>
<td><strong>Helium/Nitrogen</strong></td>
<td>-0.149</td>
<td>-0.128</td>
<td>-0.180</td>
</tr>
<tr>
<td><strong>Helium/Oxygen</strong></td>
<td>-0.047</td>
<td>-0.094</td>
<td>-0.178</td>
</tr>
</tbody>
</table>
With this data, a QV Lissajous diagram was plotted by using the charge, $q$, column and the voltage, $V(t) - V_2(t)$, of the jet. This was done for all of the different conditions. In Figure 7, the Argon 10 nF is plotted. This plot has a parallelogram shape pointed towards the negative side due to the randomness of the voltage. Compared to the other QV measurements for argon, the 10 nF has the most parallelogram-like shape.

![Figure 7: QV Lissajous Diagram of Argon with a 10 nF capacitor](image)

In Figure 8 and Figure 9 below, are the QV Lissajous Diagram of Argon with a 22 nF capacitor and with a 47 nF capacitor, respectively. The argon 22 nF Lissajous diagram has a thin middle compared with the other two, while the argon 47 nF Lissajous diagram has a thicker middle compared with the other two. The argon 47 nF Lissajous diagram
also has a lot of small bumps throughout the parallelogram. These results seem to happen with the rest of the QV Lissajous diagrams. Some have more of a parallelogram shape; some have a football-like shape and others have a curvy figure similar to the argon 47 nF Lissajous diagram.

Figure 8: QV Lissajous Diagram of Argon with a 22 nF capacitor
3.2 Plasma Images

Prior to obtaining the PLIF images, emission images of the plasma were taken in order to see how the different gas combinations affects plasma structure. Below, in Figure 10, are images of the plasma for argon, argon/2% nitrogen, argon/2% air, argon/2% oxygen, helium, helium/2% nitrogen, helium/2% air and helium/2% oxygen, with a 0.001 second exposure time and zero gain. The mass flow rate used was 2 L/minute and the max temperature change is 161.65 K.
Figure 10: Images of Plasma A-100% Argon B-Argon/2% Nitrogen C-Argon/2% Oxygen D-Argon/2% Air E-100% Helium F- Helium/2% Nitrogen G- Helium/2% Air H-Helium/2% Oxygen

It can be seen in Figure 10 that the argon plasma images are filamentary while the helium plasma images are more diffuse and “cone” shaped. The argon/2% oxygen is not as vivid as the rest of the images, but still is filamentary. The helium images are more intense than the argon images. The helium images look similar to a candle flame with no filaments present. The black spot present in the images is a burn mark from the camera and has nothing to do with the plasma.

Between the gases the plasma images are different also. The pure argon is long and only filamentary at the end of the plasma while the pure helium is medium in length and seems to get brighter as the plasma extends further from the jet opening. The argon/2% nitrogen plasma is short and has small filaments along the plasma with longer
filaments present. The helium/2% nitrogen is also short with the brighter portion of the plasma at the bottom. The argon/2% air plasma has many filaments present throughout the plasma both small and large. It is longer than the nitrogen plasma and also more vivid. The helium/2% air is also long like the argon/2% air, but like the rest of the helium plasma images it is bright and coned shaped. It has the brighter portion at the top unlike the helium/nitrogen. The argon/2% oxygen plasma is very dim but like the rest of the argon plasmas, it is also filamentary. It is shorter than the air and nitrogen plasma with small and a few large filaments along the plasma. The helium/2% oxygen plasma is medium in length and not as vivid as the rest of the helium plasmas. Its brightness is based more in the middle, but get dimmer as the plasma gets further from the jet opening.

On all of the images, there are small filaments present on the jet where the edge of the ground electrode is located. The cause of these filaments is unclear. Further examination is needed.

3.3 Time Resolved Emission Images:

Time resolved spectroscopy was performed to study the plasma dynamics at different times of the voltage trace waveform. The time resolved spectroscopy was done with pure argon and pure helium. The argon time resolved images can be seen below in Figure 11. Similar to the argon plasma images, the time resolved argon images were long and thin with a plume shape. The plume changes in each image, which are 4 microseconds apart. It begins with the plume being short, skinny and barely visible and continues to become more vivid and longer. At 8 microseconds, it can be seen that there
is a dual wave. The brightness starts, dies out and begins to start up again at the end of the image. For the images taken between 1-16 microseconds, the plasmas are long and rather narrow; however, for the images taken between 20-36 microseconds, the plasma begins to form a plume shape and continues to elongate with time. At 32 microseconds, the plume looks exactly like the plasma image above with the long, bright plume.

Figure 11: Time Resolved Argon Images

In Figure 12 below, time resolved helium images can be seen. Similar to time resolved argon images, time resolved helium also display characteristics with respect to time in the voltage waveform. Unlike argon however, the helium plasma never forms a
filament, but always exhibits a plume shape. These plumes are similar to the ones that were observed previously in the plasma images shown in Figure 10. A distinct plume does not become visible until 8 microseconds and at 12 microseconds, the plasma exhibits its brightest plume. This plume is thinner than the other plasma images, but still is consistent as a plume shape instead of a filament as in the argon images. At approximately the 20 microsecond mark the plasma becomes less visible again until the 28 microsecond mark where the plasma reappears.

Figure 12: Time Resolved Helium Images
3.4 Spectrally Resolved Emission Spectroscopy

Once the time resolved imaging was done, optical emission spectroscopy was performed to identify emitting species present within the plasma. Below in Figure 13 are the argon and argon mixture OES spectra, which were obtained near the exit of the tube. In Table 2, the lines are assigned for both Argon and Argon/2% Air. Obviously, argon lines are present in all four spectra, but are not as relatively intense in the argon mixture cases. In the vicinity of 950 nm the emission is intense in the air and nitrogen mixtures. These three spectra are difficult to distinguish between because the lines that are shown are overlapping. A prominent line in the argon OES is the 777 nm line which corresponds to oxygen, which can be seen in all cases. The 777 nm line is most likely present because the air in the room is mixing in with the plasma to produce excited O$_2$.

<table>
<thead>
<tr>
<th>Line (nm)</th>
<th>Molecule</th>
<th>Line (nm)</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>696.543</td>
<td>Ar I</td>
<td>840.821</td>
<td>Ar I</td>
</tr>
<tr>
<td>738.398</td>
<td>Ar I</td>
<td>842.461</td>
<td>Ar I</td>
</tr>
<tr>
<td>750.387</td>
<td>Ar I</td>
<td>870.325</td>
<td>N I</td>
</tr>
<tr>
<td>751.465</td>
<td>Ar I</td>
<td>870.705</td>
<td>O$_2$</td>
</tr>
<tr>
<td>763.511</td>
<td>Ar I</td>
<td>953.049</td>
<td>N I</td>
</tr>
<tr>
<td>777.194</td>
<td>O I</td>
<td>953.882</td>
<td>O$_2$</td>
</tr>
<tr>
<td>794.818</td>
<td>Ar I</td>
<td>954.487</td>
<td>O$_2$</td>
</tr>
<tr>
<td>800.616</td>
<td>Ar I</td>
<td>955</td>
<td>O$_2$</td>
</tr>
<tr>
<td>801.478</td>
<td>Ar I</td>
<td>971.646</td>
<td>N I</td>
</tr>
<tr>
<td>811.531</td>
<td>Ar I</td>
<td>974.038</td>
<td>N I</td>
</tr>
<tr>
<td>826.452</td>
<td>Ar I</td>
<td>995-999</td>
<td>N$_2$</td>
</tr>
</tbody>
</table>
The OES helium cases, which can be seen in Figure 14, were not as consistent as the argon cases. Table 3 shows helium and helium/2% air lines. The helium cases were very noisy with fewer transition peaks than in the argon. The pure helium has a few peaks with very low intensity. There were no transitions observed past 850 nm in pure helium.
cases, but there are transitions in the mixtures. In the helium mixture cases, it’s hard to
definitely observe the helium peaks because the intensity was so low comparable to the
noise. There are overlapping nitrogen and oxygen lines again in the mixture cases, but
lack of intensity and noise make it difficult to clearly label each. Each mixture case has a
peak around 860 nm, however, the intensity varies with each case. It’s unclear if the
nitrogen mixture case has a peak at around 975 nm, but the helium/air and helium/oxygen
both have peaks at around there with more intensity than the rest of the peaks present in
the spectra. The pure helium has a prominent peak around 777 nm, which corresponds to
oxygen. With the spectrometer not having the resolution needed for other wavelengths, it
was difficult to get better resolution and more lines for each case.

Table 3: Identified Spectral Lines for Helium and Helium/2% Air

<table>
<thead>
<tr>
<th>Line (nm)</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>706.5</td>
<td>He I</td>
</tr>
<tr>
<td>749.9</td>
<td>He I</td>
</tr>
<tr>
<td>777.194</td>
<td>O I</td>
</tr>
<tr>
<td>809.411</td>
<td>He I</td>
</tr>
<tr>
<td>836.174</td>
<td>He I</td>
</tr>
<tr>
<td>870.325</td>
<td>N I</td>
</tr>
<tr>
<td>870.705</td>
<td>O₂</td>
</tr>
<tr>
<td>953.049</td>
<td>N I</td>
</tr>
<tr>
<td>953.882</td>
<td>O₂</td>
</tr>
<tr>
<td>954.487</td>
<td>O₂</td>
</tr>
<tr>
<td>955</td>
<td>O₂</td>
</tr>
<tr>
<td>971.646</td>
<td>N I</td>
</tr>
<tr>
<td>974.038</td>
<td>N I</td>
</tr>
</tbody>
</table>
When NO-PLIF images were taken, similar plasma image results were observed. The PLIF images show that the helium images are more intense than the argon ones, but that the argon images are longer, with both results similar to the plasma images. These
images show that the helium PLIF images have a short cone shape while the argon PLIF images are long and slender. In Figure 17 below, these results are shown. Also shown in this figure is an image of 100ppm NO, which was taken in order to have a concentration calibration image.

![100% Argon](image)

![100% Helium](image)

![100 ppm NO](image)

**Figure 15 NO-PLIF images**

Once the PLIF images of the pure gases were complete, PLIF images for the gaseous mixtures were done. However, instead of using only 2% mixtures, the gas mixtures were varied using 0.5%, 1%, 2% and 5%, to see how adding more of the mixed gas would change the amount of NO produced.

Figure 18, below, shows a set of PLIF images of argon/air. This mixture has a thicker plume shape similar to the 100ppm NO image. As more air was introduced into
the mixture, the more intense the PLIF images were and the longer the plume became. Also as more air was added, a small plume-like-hole became present in the middle of the plasma.

![Image of PLIF images for different mixture percentages](image)

**Figure 16: Argon/Air mixture NO PLIF**

PLIF images for the argon/nitrogen mixtures were much less intense than the air mixtures for NO PLIF. The images can be seen below in Figure 19. There is no plume present, but at the top and bottom of the tube two weak spots can be seen, possibly due to diffusion of air into the jet which dissociates \( \text{O}_2 \) upon reaction with electronically excited \( \text{Ar}^* \) or \( \text{N}_2^* \), leading to weak NO formation via \( \text{N}_2^* + O \leftrightarrow NO + N \). It gets brighter as more nitrogen
is added. However, the lack of a distinct NO PLIF plume is due to lack of oxygen present in the plasma.

![Image of Argon/Nitrogen NO PLIF](image)

**Figure 17: Argon/Nitrogen NO PLIF**

In Figure 20, helium/air PLIF images can be seen. The helium/air images were similar to the argon/air where each image had a plume shape. The 0.5% mixture was intense with a short plume and as the mixture was increased, the plume became less intense, but the plume became longer and the hollowed plume appeared. The helium/air images are the most similar to the 100 ppm NO images.
The helium/nitrogen PLIF images were quite similar to the helium/air, but drastically less intense. There is a slight plume shape in each image and as more nitrogen was added, the longer the plume became for each image. As more nitrogen is added, the plume becomes more distinct. Similar to the argon/nitrogen, however, there are bright spots present at the top and bottom of the jet opening where the brighter spot is located at the bottom. It cannot be distinguished whether or not the helium/nitrogen have a hollowed plume within the plume. Figure 21 shows these results.

*Figure 18: NO PLIF Helium/Air*
Once the PLIF images were taken, the 100 ppm NO images were used alongside the PLIF images to quantify how much NO was present in each set by calculating the number density of each gas mixture. The equations used to calculate the number density can be seen below, along with a sample calculation for Argon/2% Air in Appendix A.

\[
n_{NO, discharge} = n_{NO, calibration} \frac{S_{F, discharge}}{S_{F, calibration}} \frac{Q_{y, calibration}}{Q_{y, discharge}}
\]

where \( Q_y \) is,
where \( Q \) is,

\[
Q = \sum n_i \sigma_i v_i
\]

Below in Tables 2 and 3 are the quenching cross sections used and the constants that were used also. The quenching cross section for helium was assumed to be similar to argon there were no experimental constants found in literature. The cross section for argon was calculated from the rate coefficients for quenching NO in Paul’s paper. The paper stated that the rate coefficient was less than \( 0.02 \times 10^{-11} \text{cm}^3/\text{s} \). It was assumed to be taken as \( 0.02 \times 10^{-11} \text{cm}^3/\text{s} \). The cross section was calculated by the equation below and a sample calculation can be seen in Appendix A.

**Table 4: Quenching Cross Sections**

<table>
<thead>
<tr>
<th>Species</th>
<th>Argon</th>
<th>Helium</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
</table>
Table 5: Constants Used for the Number Density Calculation

<table>
<thead>
<tr>
<th>$n_{NO, \text{calibration}}$</th>
<th>2.45E+15 cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sum_{p'p} A'_{p'p}$</td>
<td>4.95E+06 s$^{-1}$[14]</td>
</tr>
</tbody>
</table>

Figure 22 shows where the number density was calculated and Table 4 shows the quantitative number density for each gas mixture. It can be seen that helium has more NO present, which corresponds to what was seen in the NO PLIF images. The helium is one to two orders of magnitude larger than the argon in all cases. The number density was calculated and averaged in a 10X10 square right outside of the opening of the tube.

![Figure 20: 10X10 square where the number density was calculated](Image)

Table 6: Number Density for the NO PLIF Gas Mixtures

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>Number Density (cm$^{-3}$)</th>
<th>Gas Mixture</th>
<th>Number Density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Argon</td>
<td>2.23E+13</td>
<td>100% Helium</td>
<td>7.44E+13</td>
</tr>
<tr>
<td>Ar/0.5% Air</td>
<td>1.12E+14</td>
<td>He/0.5% Air</td>
<td>3.85E+14</td>
</tr>
<tr>
<td>Ar/1% Air</td>
<td>7.12E+13</td>
<td>He/1% Air</td>
<td>3.71E+14</td>
</tr>
<tr>
<td>Ar/2% Air</td>
<td>8.42E+13</td>
<td>He/2% Air</td>
<td>3.10E+14</td>
</tr>
<tr>
<td>Ar/5% Air</td>
<td>1.74E+14</td>
<td>He/5% Air</td>
<td>3.74E+14</td>
</tr>
<tr>
<td>Ar/0.5% N$\text{}_2$</td>
<td>1.19E+13</td>
<td>He/0.5% N$\text{}_2$</td>
<td>1.95E+13</td>
</tr>
<tr>
<td>Ar/1% N$\text{}_2$</td>
<td>1.21E+13</td>
<td>He/1% N$\text{}_2$</td>
<td>1.86E+13</td>
</tr>
<tr>
<td>Ar/2% N$\text{}_2$</td>
<td>1.23E+13</td>
<td>He/2% N$\text{}_2$</td>
<td>2.11E+13</td>
</tr>
<tr>
<td>Ar/5% N$\text{}_2$</td>
<td>1.14E+13</td>
<td>He/5% N$\text{}_2$</td>
<td>1.78E+13</td>
</tr>
</tbody>
</table>
Chapter 4: Conclusions

4.1 Important Findings

The most important part of this study is the NO PLIF. The most important finding was that the helium discharge produced substantially more NO than argon discharge. Specifically, the helium mixture produced approximately one order of magnitude more NO than the argon mixtures. The helium mixtures images showed a plume like shape while the argon mixtures showed more of a line than a plume. It is also important to note that the air mixtures contained more NO in both argon and helium over plasma the nitrogen mixtures.

The time resolved spectroscopy showed that the APPJ acts differently at different moments in time. The argon showed that the most plume shape was from 28-32 μsec. The plume at these two times was brightest and the most plume shaped. At 8 μsec, the plasma can be seen exhibiting a dual wave. The helium also showed the best plume shape was from 28-32 μsec. The 12 μsec image for helium shows the longest and brightest line, however, it is not a plume shape. Having the plasma act differently at various times could affect the way the APPJ reacts to surfaces depending on where the plasma is on the voltage trace.
The QV measurements showed that energy calculated from the voltage traces are all along the same magnitude except for the oxygen mixtures which is a bit lower than the others. These energies are approximately 0.1 mJ/period.

4.2 Recommended Future Work

An important thing to measure would be the helium and argon quenching rates. Helium or argon could be gradually added into 100 ppm NO/N\textsubscript{2} and the signals could be compared. This could be used to calculate the quenching rates.

It was noticed that where the electrodes were placed and their positioning affects the way the plasma looks to the naked eye. An experiment could be completed to see where the best place to put the electrodes and where the electrode positioning makes the plasma the best.
References


Appendix A: Number Density Sample Calculation

Sample Calculation of the Argon Cross Section

\[ \sigma = \frac{k_x}{\langle v \rangle} \]

\[ \sigma = \frac{0.02 \times 10^{-11} m^3/s}{\left[ \frac{8 \left( 1.38 \times 10^{-23} \frac{kg \ m^2}{s^2} \right) (300K)}{\pi(40 \ amu)(1.67 \times 10^{-27} kg)} \right]^2} = 4.797 \times 10^{-14} m^2 \]

Sample Calculation at for Argon/2% Air at pixel: 217, 54:

\[ n_{NO,Calibration} = 100 ppm \ \frac{101325 \ Pa}{1.38 \times 10^{-38} \ \frac{kg \ m^2}{s^2} \times 300K} \times 1 \times 10^{-6} \ \frac{m^3}{cm^3} \]

\[ = 2.4475 \times 10^{15} \ cm^{-3} \]

\[ Q_{Argon} = \frac{101325 \ Pa}{1.38 \times 10^{-38} \ \frac{kg \ m^2}{s^2} \times 300K} (0.98) (0.02 \times 10^{-11} \ cm^2) \left( 1 \times 10^{-6} \ \frac{m^3}{cm^3} \right) \]

\[ = 4.798 \times 10^6 \ \frac{1}{s} \]
\[ Q_{oxygen} = \frac{101325 \text{ Pa}}{1.38 \times 10^{-38} \frac{\text{kg m}^2}{s^2} \times 300K} \frac{(0.004)(30 \times 10^{-20}m^2)}{X} \left[ \frac{8 \left( 1.38 \times 10^{-23} \frac{\text{kg m}^2}{s^2} \right) (300K)}{\pi (32 \text{ amu})(1.67 \times 10^{-27} \text{ kg})} \right]^{\frac{1}{2}} = 1.304 \times 10^7 \frac{1}{s} \]

\[ Q_{Nitrogen} = \frac{101325 \text{ Pa}}{1.38 \times 10^{-38} \frac{\text{kg m}^2}{s^2} \times 300} \frac{(0.016)(0.014 \times 10^{-20}m^2)}{X} \left[ \frac{8 \left( 1.38 \times 10^{-23} \frac{\text{kg m}^2}{s^2} \right) (300K)}{\pi (28 \text{ amu})(1.67 \times 10^{-27} \text{ kg})} \right]^{\frac{1}{2}} = 2.603 \times 10^4 \frac{1}{s} \]

\[ n_{NO, discharge} = \]

\[ = \frac{2.447 \times 10^{15} \text{ cm}^{-3}}{13546(2.75)} \frac{600}{4.95 \times 10^6 \frac{1}{s} + \left( 4.798 \times 10^6 \frac{1}{s} + 1.304 \times 10^7 \frac{1}{s} + 2.603 \times 10^4 \frac{1}{s} \right)} \]

\[ = 1.817 \times 10^{14} \frac{1}{\text{cm}^3} \]