INVESTIGATION OF ATMOSPHERIC PRESSURE PLASMA JET PROPERTIES AND OPERATIONS IN AMBIENT AIR

by Tam Nguyen

A thesis submitted to the Department of Chemical and Biomolecular Engineering, Cullen College of Engineering in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemical Engineering

Chair of Committee: Vincent M. Donnelly

Co-Chair of Committee: Demetre J Economou

Committee Member: Megan L Robertson

Committee Member: Jack Wolfe

Committee Member: Paul Ruchhoeft

University of Houston May 2020

Copyright 2020, Tam Nguyen

Acknowledgements

I would like to first thank my advisors: Prof. Donnelly and Prof. Economou for their guidance and patience. I would like also to thank everyone in the lab for their helps, especially Peng Lin for his various simulations featured in this work. Finally, I would like to thank the Department of Energy (Office of Fusion Energy Science) for financial support of this work.

ABSTRACT

Plasma is gas ionized by energizing electrons through electric fields, leading to various collisional reactions that result in a number of reactive species useful in many applications. A main characteristic of plasmas is the creation of luminous excited species that relieve their energy through emissions. The capturing of these emissions: optical emission spectroscopy (OES) is a major method for plasma diagnostic. Atmospheric pressure plasma jet (APPJ) is a type of plasma that is distinctive for the creation of a small plasma jet extending from the plasma reactor (often a quartz tube equipped with electrodes), making the APPJ a prime candidate for plasma medicine applications. This study aims to investigate the fundamental properties of APPJs that are relevant to applications through the use of OES. Firstly, the excitation mechanisms of plasma species in a He APPJ was revealed through spatially and temporally resolved OES, showing the major role of He metastables in excitations of various air species. Secondly, the gas temperature and electron density of Ar/He APPJs were derived by fitting the emission line shapes of N_2 and H. respectively. The gas temperature increases (400 K - 600 K for Ar, 650 K - 750 K for He) with increasing applied power (9 W - 18 W for Ar, 19 W - 24 W for He). Electron density of Ar plasma increases $(2.5 \times 10^{13} \text{ cm}^{-3} \text{ to } 5 \times 10^{13} \text{ cm}^{-3})$ with a grounded copper sheet behind a quartz substrate. Finally, diffusion of air species into a He plasma jet was measured through self-actinometry and controlled by addition of a shielding gas curtain separating the plasma gas from ambient air. Self-actinometry involves adding trace gases (Ar, N_2 , and O_2) into the plasma feed gas and observing changes in Ar, N_2 , O_2 , and He emission intensity in order to correlate emission intensity and mole fractions. Air mole fraction in the plasma center increases along the jet axis from none at 1 mm, to 10^{-3} at 3 mm and 10^{-2} at 5 mm axial distance from the nozzle. Addition of N_2 shielding gas reduces air diffusion by 2 to 3 times.

TABLE OF CONTENTS

ACKNOWLEDGMENTSiii
ABSTRACT iv
LIST OF TABLESvi
LIST OF FIGURESvii
1. INTRODUCTION1
1.1 Atmospheric pressure plasma jets1
1.2 Motivation and objectives
1.3 Dissertation organization
2. LITERATURE REVIEW
2.1 Plasma Ignition
2.2 Atmospheric pressure plasmas16
2.3 Plasma bullets
2.4 Applications of atmospheric pressure plasma jets
3. EXPERIMENTAL METHODS
3.1 Two-ring electrode atmospheric pressure plasma jet
3.2 Time-average emission spectroscopy
3.3 Time-resolved emission spectroscopy
3.4 Ring and needle electrode atmospheric pressure plasma jet
3.5 Ring and needle electrode atmospheric pressure plasma jet with shielding gas apparatus
4. EXCITATION MECHANISMS IN A HELIUM ATMOSPHERIC PRESSURE
PLASMA JET 40
4.1 Spatially-resolved optical emission spectroscopy
4.2 Plasma images
4.3 Time-averaged optical emission spectra
4.4 Time resolved emissions
4.5 Excitation mechanisms
4.6 Aspects of plasma jet evolution
4.7 Summary and Conclusions
5. MEASUREMENT OF GAS TEMPERATURE AND ELECTRON DENSITY IN AN ATMOSPHERIC PRESSURE PLASMA JET
5.1 Measurement of gas temperature

5.2 Measurement of electron density	
5.3 Experimental setup for measurements of gas temperature and	electron density
5.4 Gas temperature and electron density in Ar (0.02% H2) atmosplasma jet	pheric pressure
5.5 Gas temperature and electron density of He (0.02% H2) atmos plasma jet	pheric pressure
5.6 Summary and Conclusions	101
6. RADIAL DISTRIBUTION OF AIR SPECIES DIFFUSING IN HELIUM ATMOSPHERIC PRESSURE PLASMA JET	TO AN RF 80
6.1 Radial distribution of plasma emissions	103
6.2 Theory of self-actinometry	106
6.3 Propagation of error	122
6.4 Self-actinometry calibration	
6.5 Radial mole fraction of air impurity diffusing into the plasma	jet 131
6.6 Comparison with simulation	
6.7 Comparison with published literature	137
6.8 Summary and Conclusions	138
7. SUMMARY AND CONCLUSIONS	140
7.1 Excitation mechanisms in a non-equilibrium He APPJ	
7.2 Measurement of gas temperature and electron density in an atr plasma jet	nospheric pressure
7.3 Radial distribution of air species diffusing into an RF Helium pressure plasma jet	atmospheric
REFERENCES	
APPENDIX A: UV-ABSORPTION MEASUREMENT OF PLAS OF WATER FROM INTERACTION WITH A WATER SUBSTI BOOKMARK NOT DEFINED.55	MA JET UPTAKE RATEERROR!
APPENDIX B: VERIFICATION OF MEASURING RADIAL EN	MISSION IN AN

APPENDIX B: VERIFICATION OF MEASURING RADIAL EMISSION IN AN ATMOSPHERIC PRESSURE PLASMA JETERROR! BOOKMARK NOT DEFINED.61

LIST OF TABLES

Table 1	Parameters A and B for calculation of the Townsend ionization coefficient α
Table 2	Einstein A-coefficients (10^6s^{-1}) and quenching rate constants $(10^{-10} \text{cm}^3 \text{s}^{-1})$ at 900 K. (a):An upper limit, assumed to be the same as quenching by N ₂ . (b): O (777) $(3p^5P)$ quenching rate constants assumed to be the same as O (844) $(3p^3P)$
Table 3	Maximum quenching rate constants $(10^{6}s^{-1})$ for the states indicated in the first column at maximum number densities (cm^{-3}) given along the second row. Bolded numbers are those with estimated quenching rate constants
Table 4	Quenching effect of trace gas (Ar, N ₂ or O ₂) addition on emission yields, He [*] quenching rates, and the resulted quenching factors F_Q

LIST OF FIGURES

Figure 1	Plasma jet in operation	2
Figure 2	Calculation of mean free path	8
Figure 3	Illustration of a discharge gap	10
Figure 4	Schematic structure of a DC discharge	14
Figure 5	Discharge types at various voltage-current ranges	16
Figure 6	Evolution of the plasma temperature (electrons and heavy particles) with the pressure in a mercury plasma arc	17
Figure 7	Corona discharge	18
Figure 8	Dielectric barrier discharge	19
Figure 9	Dielectric-free electrode (DFE) plasma jet	21
Figure 10	Dielectric barrier discharge (DBD) plasma jet	22
Figure 11	DBD-like plasma jet	23
Figure 12	Single electrode plasma jet	24
Figure 13	(a) Propagation mechanism of cathode-directed (positive) streamer.(b) Local electric field lines. A and C stand for cathode for anode and cathode, respectivly	26
Figure 14	High-speed photographs of plasma bullets at 10 kHz, 9 kV sine-wave voltage, 0.4L/min He/O ₂ (20%) feed gas	28
Figure 15	Photographs of donut shaped plasma bullets	28
Figure 16	Radial distribution of number densities of electrons (a), and N_2 (C ³ Π_u) state (b). The dashed-dotted lines show the result at z =1 cm without taking into account Penning ionization	29
Figure 17	High-speed photographs of plasma bullet taken normal to the plasma jet axis. Feed gas is He/N_2 (He: 1 L/min; N_2 : 0.015 L/min) mixture	29
Figure 18	PET surface before (a), and after (b) plasma treatment	30
Figure 19	PEEK etching using APPJ with Ar, or Ar-O ₂ mixtures as the feed gas	30
Figure 20	Surface morphology of APPJ deposited (a) C-ZnO composite coating and (b) TiO ₂ film.	32
Figure 21	Inactivation of <i>Bacillus atrophaeus</i> spores by various aspects of an APPJ	33
Figure 22	APPJ selectivity in killing cancer cells compared to normal cells	33
Figure 23	Schematic of two-ring electrode atmospheric pressure plasma jet	35

Figure 24	(a) Spectrometer configuration. (b) Triggering the ICCD and the plasma sinewave (200 kHz) using a 40 kHz squarewave.
Figure 25	Schematic of ring and needle electrode RF atmospheric pressure plasma jet without shielding gas apparatus
Figure 26	RF atmospheric pressure plasma jet with shielding gas
Figure 27	Schematic of ring and needle electrode RF atmospheric pressure plasma jet with shielding gas apparatus
Figure 28	Experimental system (not drawn to scale) used for OES in the UV/visible/near-IR range
Figure 29	At an observation angle of $\theta_2=40^\circ$, and an average radial extend of the plasma on the substrate $r_p=0.75$ mm, emission is probed from a region d~0.3 mm away from the quartz substrate surface. θ_1 and θ_2 are related by Snell's law $n_1 \sin(\theta_1) = n_2 \sin(\theta_1)$
Figure 30	Geometric details of the optical setup. Collection angles at points A and B are $\sim 1^{\circ}$ and $\sim 3^{\circ}$, respectively
Figure 31	VUV spectrometer probing light from the plasma jet along the axis (a), or at angle (b), to isolate emission only from the surface of the substrate (MgF2 window in this case)
Figure 32	(Color online) (not to scale) False color images of the plasma (10 ns exposure windows) 300 ns after the positive peak (top) and 100 ns after the negative peak (bottom) of the applied voltage
Figure 33	Typical emission spectra from 115 nm to 950 nm, recorded along the axis of the discharge ($\theta_1 = \theta_2 = 0^\circ$). Lines identified by red lettering are second order peaks. The most intense peak was normalized to have an intensity of 1000
Figure 34	Emission intensity ratios as a function of axial position along the plasma jet
Figure 35	Typical emission spectra from 115 to 950 nm, recorded at an angle off of the discharge axis ($\theta_1 = 30^\circ$, $\theta_2 = 20^\circ$. Lines identified by red lettering are second order peaks. The most intense peak was normalized to have an intensity of 1000
Figure 36	Time-resolved He (706.5 nm) emission at three different angles, θ_2 . The applied voltage waveform is also shown. The time-resolved 501.57 nm line at $\theta_2 = 10^\circ$ is also shown
Figure 37	Time-resolved N ₂ (337 nm) emission at $\theta_2 = 0$ and 40°. The applied voltage waveform is also shown

Figure 38	Time-resolved N ₂ (337 nm) emission at $\theta_2 = 0$ and 40° showing expanded intensity scale of Fig. 8. The time-resolved He (706.5 nm) emission at $\theta_2 = 40^{\circ}$ is also shown
Figure 39	Time-resolved N ₂ ⁺ (391 nm) emission at $\theta_2 = 0^\circ$ and 40°. The applied voltage waveform is also shown. The phase shift, $\Delta \phi$, is based on a period of 2500 ns, assuming excitation occurs twice per RF (200 kHz) period
Figure 40	Time resolved H (656 nm) emissions at $\theta_2 = 0^\circ$ and 40° . The applied voltage waveform is also shown
Figure 41	Time resolved OH (309 nm) emissions at $\theta_2 = 0^\circ$ and 40° . The applied voltage waveform is also shown
Figure 42	Time-resolved O (844 nm) emissions at $\theta_2 = 0^\circ$ and 40° . The applied voltage waveform is also shown
Figure 43	Time-resolved VUV emissions of OH, N, O, and at $\theta_2 = 0^{\circ}$ and 40°. The applied voltage waveform is also shown
Figure 44	Decay of N_2^+ and He emission at the substrate surface. Part of the applied voltage waveform is also shown
Figure 45	Fitting of N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$) (0-1) band with two- temperature fit (a), and one- temperature fit (b)
Figure 46	Setup for collection of plasma emission for the purpose of measuring gas temperature and electron density
Figure 47	Emission of Ar $(0.02\% H_2)$ RF plasma jet, over the wavelength range 200-900 nm recorded perpendicular to the axis of symmetry, 4 mm distance from the nozzle
Figure 48	Ar plasma gas temperature as a function of power, measured near the quartz substrate surface with varying distance between substrate and nozzle
Figure 49	Ar plasma gas temperature as a function of nozzle-quartz substrate distance (18 W applied power), probed near the substrate surface
Figure 50	Ar plasma gas temperature as a function of distance from nozzle (18 W applied power), with and without substrate. The substrate was 10 mm away from the nozzle
Figure 51	Ar plasma gas temperature at an axial distance of 4 mm from the nozzle, as a function of Ar feed flow rate. Applied power was 18 W
Figure 52	Ar plasma gas temperature (a), and electron density (b) with no substrate, or quartz substrate of different thickness, or quartz substrate with a grounded copper sheet behind it

Figure 53	Gas temperature as a function of distance from nozzle, at different applied power, with or without a grounded substrate, He feed gas
Figure 54	Gas temperature as a function of Ar (a) or N_2 (b) shielding gas flow rate with 2 slm He feed gas, at 5 mm axial distance from the nozzle
Figure 55	Schematic of elements used for collection of plasma emission
Figure 56	Measured He intensity as a function of N_2 , O_2 , and Ar addition at 1 mm, 3 mm and 5 mm axial distance from the nozzle
Figure 57	Intensity ratio of N_2 , O_2 , and Ar over He as a function of N_2 , O_2 , and Ar mole fractions at 1 mm, 3 mm and 5 mm axial distance from the nozzle
Figure 58	Line-integrated emission (a, calibration site) versus radial center emission (b, mole fraction site)
Figure 59	Line-integrated radial $\frac{I_{He}}{I_{Ar}}$ as a function of added O ₂ mole
	fraction (solid symbols) and $\frac{I_{He}}{I_{Ar}}$ with quenching effect
	removed (open symbols) at 1 mm, 3 mm, and 5 mm axial distance from the nozzle
Figure 60	Line-integrated radial $\frac{I_{He}}{I_O}$ as a function of added Ar mole
	fraction (solid symbols) and $\frac{I_{He}}{I_0}$ with quenching effect
	removed (open symbols) at 1 mm, 3 mm, and 5 mm axial distance from the nozzle
Figure 61	Radial profiles of air species mole fractions at axial distances from the nozzle of 1 mm, 2 mm and 5 mm, with and without shielding gas
Figure 62	Mole fraction radial profiles of O_2 , N_2 and Ar at axial distances from the nozzle of 1, 3, and 5 mm, with (d)(e)(f), and without (a)(b)(c) shielding gas. Solid lines are simulation predictions, broken lines are experimental profiles
Figure 63	Simulated and experiment center mole fractions 137
Figure 64	Experimental setup for UV-absorption of an APPJ impinging on a water substrate
Figure 65	Cycle of a UV-absorption experiment 158
Figure 66	OH absorption (2^{nd} order) with 0.21 slm dry Ar feed gas 159

Figure 67	UV absorbance of OH 309 nm line from plasma jet in contact with a water surface, probed near the surface: a) with 0.2% water in Ar feed as a function of power, b) dry Ar feed as a function of flow rate	160
Figure 68	Side view (a) and Top view (b) of the experimental setup for creating a hollow cylinder shaped light source and acquiring its emission	162
Figure 69	Emission measured from a hollow cylinder-shaped light source	163

1. INTRODUCTION

1.1 Atmospheric pressure plasma jets

Plasma is a partially ionized gas with collective properties, generated by energizing electrons with an electric field. The energized electrons can then react with other species in the gas mixture, producing radicals, excited states and ions. Most excited states have short lifetime and quickly return to a lower energy state by emitting light, which can be measured for determination of plasma properties. Metastables are excited species that cannot return to a lower state by emission, thus they need to collide with another species to transfer their energy.

Traditional low-pressure non-equilibrium plasmas find important applications in materials processing, particularly in the semiconductor industry¹. Recently, non-equilibrium atmospheric pressure plasmas have gained popularity due to many realized or potential applications^{2–4}. Atmospheric pressure plasmas have the advantage of not requiring expensive vacuum systems and can operate in open air.¹ Both low-pressure and atmospheric pressure plasmas have high electron temperatures but low gas temperatures, allowing for applications involving thermally-sensitive materials such as biological specimens. Various discharge configurations have been developed to combat issues such as arcing and high gas temperature,^{2,5} and to tailor the plasma source to particular applications.

The atmospheric pressure plasma jet (APPJ) is a common configuration, especially for applications involving selected area processing (see fig. 1). It consists of a dielectric capillary tube through which a working gas flows, typically helium or argon often with mixed-in impurities. Power is applied to a pair of electrodes to ignite a plasma. The luminous jet typically extends a few cm beyond the nozzle. Upon reaching the substrate, the plasma spreads out radially before extinguishing.⁶ The small size of the impact area allows for precise treatment of the substrate. The working gas exits the nozzle typically in open air, and mixes with the air constituents to form a variety of radicals and metastables^{7,8}, as well as various reactive oxygen-nitrogen species (RONS)^{9,10} that have been shown to play a role in many biological processes. To better control the interactions of the jet with ambient air, the use of a shielding gas was studied to determine how well it separates the plasma from ambient air^{11,12} and how different shielding gas composition affects the species generated in the plasma^{13–15}. Overall, the diffusion of ambient species is strongly determinant of the plasma properties as well as its effectiveness in various applications and thus a subject of great interest.

The chemistry and physics of APPJs have been studied through experiments and modelling^{5,7}. The substrate surface receives an influx of radicals, metastables, ions, photons, and electrons that are all capable of surface reactions, resulting in volatile products feeding back into the plasma. Despite significant progress, the identities, fluxes, and energies of many important species in APPJs remain to be explored.



Figure 1: Plasma jet in operation

1.2 Motivation and objectives

The goal of this study is to investigate the important, fundamental properties of the APPJs that are relevant to applications, mainly though optical emission spectroscopy (OES). These properties are:

(1) Excitation mechanisms of various species

- (2) Gas temperature and electron density
- (3) Radial distribution of ambient species diffusing into an APPJ

An APPJ is comprised of several species, each with its own excitation characteristics, some being vital for the plasma propagation and applications. An understanding of these excitation mechanisms allows better control of the species created in an APPJ. Therefore, we applied spatially and temporally resolved OES to understand the excitation mechanisms of various species in an APPJ.

As the treated substrate of an APPJ is often heat sensitive, control and reduction of gas temperature are paramount. Electron density, on the other hand, determines the rates of chemical reactions in the plasma, and subsequently the strength of the plasma treatment. Both gas temperature and electron density were derived by fitting certain emissions whose shapes are affected by either gas temperature (N_2 emission) or electron density (H emission).

Finally, an APPJ operating in ambient air draws in O_2 and N_2 that create a plethora of reactive species that are desirable for various applications. Determining how much air diffuses into the APPJs, as well as controlling the amount of plasma generated species, is required for many uses, including medical applications. To that end, we installed a shielding gas curtain to separate the APPJ from the ambient air, and employed OES actinometry to measure the absolute number density of air species diffusing into the APPJ, with and without this shielding gas.

1.3 Dissertation organization

Chapter 1 presents the properties of plasmas in general and atmospheric pressure plasma jets (APPJs) in particular, leading into the research objectives of this study: selected fundamental properties of APPJs.

Chapter 2 is a brief literature review of plasma physics, leading into APPJ properties and applications.

Chapter 3 shows the APPJ designs used and diagnostic methods applied.

Chapter 4, 5, and 6 each discusses fundamental properties of the APPJ.

Chapter 4 discusses excitation mechanisms of various APPJ species.

Chapter 5 deals with APPJ gas temperature and electron density.

Chapter 6 deals with radial distributions of ambient species diffusing into an APPJ.

Finally, chapter 7 gives the summary and conclusions of the work.

2. LITERATURE REVIEW

The design of an atmospheric pressure plasma jet takes into account the effect of high pressure on plasma ignition. In this section, we explore the physics and conditions behind plasma creation and how it is impacted by gas pressure, followed by various atmospheric pressure plasma generation schemes adapted for high pressure operations, including the atmospheric pressure plasma jets (APPJs). The physics behind APPJs, particularly "plasma bullets", is then further discussed. Finally, we look at various APPJ applications.

2.1 Plasma Ignition

Plasma is created by ionizing a gas with electric or magnetic fields^{2,16–19}. Initially, the gas is composed of neutrals with a trace density of free electrons. Application of an electromagnetic field accelerates electrons, which then collide with the surrounding gas, resulting in ionization, more electron-ion pairs, and eventually a self-sustained plasma. A self-sustain plasma is one that has achieved a steady state in which the electron loss rate is equal to the electron production rate.

The effect of an electromagnetic field onto charged particles (electrons or ions) is

$$F = q(E + \nu \times B),\tag{1}$$

where F is the force applied, q is electron charge, E is the electric field, v is the electron velocity, and B is the magnetic field. Moved by this force, charged particles collide with

other particles or the chamber wall, both are important in igniting and sustaining the plasma.

Particle-particle collisions are elastic and inelastic^{2,17–19}. In elastic collisions, only the kinetic energy of the particles are impacted. The energy transfer in an elastic collision between an electron and a heavy particle (ion or neutral) is

$$\frac{\Delta E}{E} = \frac{4m_1 m_2 \cos^2 \theta}{(m_1 + m_2)^2},$$
(2)

where ΔE is the amount of energy transferred, E is the initial energy of the electron, θ is the angle of collision, with $\theta = 0$ for head-on collision, m_1 and m_2 are the masses of the two colliding particles. Due to the difference in mass between electrons and heavy particles (neutral and ions), the energy transfer is inefficient, resulting in high energy (hot) electron and low energy (cold) heavy particles. A plasma with hot electrons and cold gas is said to be non-equilibrium, as the electrons and gas are not thermally equilibrated.

Inelastic collisions, on the other hand, also change the potential energy of the particles^{2,17–19}. Possible electron-neutral inelastic collisions include ionization,

$$e + N_2 \to N_2^+ + e, \tag{3}$$

dissociation,

$$e + O_2 \to 2O + e, \tag{4}$$

and excitation,

$$e + He \to He(3^{3}S) + e, \tag{5}$$

where the excited state can then emit a photon and return to a lower energy state,

$$He(3^{3}S) \rightarrow He(2^{3}P^{o}) + hv.$$
 (6)

Among those, the ionization reaction is of utmost importance as it is a pathway through which ion-electron pairs are created to sustain the plasma.

The rate of collisions in a plasma can be expressed in terms of cross sections (roughly the cross section area of the particles) and mean free paths (average distance an electron travels between collisions). We first consider an electron moving through a cuboid xyz^{18} (Fig. 2) with gas density n_g . If each gas particle has a so-called hard sphere cross section,

$$\pi r_{Par}^2 = \sigma,\tag{7}$$

where r_{par} is the radius of the particle, and σ is the resulting cross section, then the total area "blocked" by the particles would be $n_g xyz\sigma$. If the cuboid extends along the z direction one mean free path λ , then the entire cuboid surface would be blocked,

$$n_{g}xy\lambda\sigma = xy,\tag{8}$$

and the mean free path would be

$$\lambda = \frac{1}{n_g \sigma}.$$
(9)

The relationship between collision frequency and mean free path is

$$v = \frac{\bar{v}}{\lambda},\tag{10}$$

where v is the collision frequency and \bar{v} is average thermal electron speed. Then the relationship between collision frequency and cross section is

$$v = \bar{v}n_q\sigma. \tag{11}$$



Figure 2: Calculation of mean free path¹⁸

In addition to collisions between particles, bombardment of the chamber walls can also produce electrons. The minimum amount of energy required for removal of an electron is called the work function $e\phi$.¹⁸ This energy can be provided in the form of photon, internal energy or kinetic energy. An ion recombination at the surface will release both its kinetic energy and internal energy onto the surface, resulting in the release of an electron if the combined total energy is larger than twice the work function (one work function for the recombination electron, one for the free released electron),

$$\frac{1}{2}Mv^2 + eV_i \ge 2e\phi,\tag{12}$$

where $\frac{1}{2}Mv^2$ is the kinetic energy, *M* is the ion mass, *v* is the ion velocity, and *eV_i* is the ionization energy required to produce this ion.

Consider attempting to ignite a plasma inside a gas chamber by applying a potential difference through two opposite chamber walls, resulting in an electric field E which will exert a drift force onto the electrons in the chamber. The drift speed of electron under this electric field is

$$v_{drift} = \left(\frac{e}{mv}\right)E = \mu E,\tag{13}$$

where μ is electron mobility, *e* is electron charge, *m* is electron mass, and *v* is electron velocity¹⁸. If we then take a mean free path for ionization λ_i as the average distance the electron moves between ionization collisions, then the ionization rate is

$$dN = N \frac{dx}{\lambda_i},\tag{14}$$

where N is the local number of electrons. The resulting electron population growth with distance is

$$N(x) = N_0 exp \frac{x}{\lambda_i},\tag{15}$$

where N_0 is the electron population at x = 0.^{16,18,20} This exponential growth earns the electron multiplication the name "avalanche" (Fig. 3).



Fig 3: Illustration of a discharge gap²⁰

Next we estimate the mean free path for ionization λ_i . If we consider the ionization process similar to a reaction with activation energy eV_i , and this energy is supplied by drift energy $E\lambda$ under an electric field E, we arrive at the Townsend's ionization coefficient,

$$\alpha = \frac{1}{\lambda_i} = \frac{constant}{\lambda} exp \frac{-V_i}{E\lambda},$$
(16)

or

$$\alpha = Ap \, exp \frac{-Bp}{E},\tag{17}$$

where A and B are constants depending on the gas, and p is pressure. Table 1 shows typical values for A and B^{16,18,20}.

Gas	A (cm-1 Torr-1)	B(V cm-1 Torr-1)
Air	15	365
CO ₂	20	466
H2	5	130
Ne	4	100
Kr	17	240
N ₂	10	310
H ₂ O	13	290
He	3	34
Ar	12	180
Xe	26	350

Table 1: Parameters A and B for calculation of the Townsend ionization coefficient α^{20} .

For the plasma to be self-sustained, the electron density must be at steady-state: loss equals gain. An initial population of N_0 electrons travelling from the negative electrode to the positive electrode, separated by a distance *d* will result in $N_0 exp \frac{d}{\lambda_i}$ total electrons, with $N_0(exp \frac{d}{\lambda_i} - 1)$ being the net number of electron-ion pairs produced. The ions would drift to the negative electrode and recombine, producing $\gamma N_0(exp \frac{d}{\lambda_i} - 1)$ secondary electrons, where γ is the number of electrons produced per incident ion, called secondary electron emission coefficient. Assuming that the electrons would be lost to the side walls of the containing chamber and the positive electrode, then for the plasma to be selfsustained, the production of electrons by ion-wall recombination must produce the N_0 initial electron population,

$$\gamma N_0 \left(exp \frac{d}{\lambda_i} - 1 \right) = N_0.^{16,18,20} \tag{18}$$

Applying the Townsend's ionization coefficient we have

$$\gamma N_0(\exp(\alpha d) - 1) = N_0, \tag{19}$$

or

$$\alpha d = ln \left(1 + \frac{1}{\gamma} \right), \tag{20}$$

resulting in

$$Apd \exp \frac{-Bp}{E} = ln \left(1 + \frac{1}{\gamma}\right).$$
(21)

The required voltage to achieve self-sustain plasma is called breakdown voltage V_b , which can be related to the breakdown electric field by

$$V_b = Ed. (22)$$

Thus we have

$$V_b = \frac{Bpd}{\ln(Apd) - \ln[\ln(1+\gamma^{-1})]}$$
(22)

as the breakdown DC voltage for a particular gas and electrode material.^{1,16,18}

A typical plasma produced by a DC voltage has the structure shown in Fig. 4. The negative glow is an area with strong excitation and ionization, producing ions that drift to the cathode and create electrons that sustain the plasma, while the positive glow covers the rest of the chamber with weaker ionization and excitation^{18,19}. Instead of supplying a constant DC voltage to the chamber, plasma can also be sustained with a pulsed DC voltage. Advantages of pulsed plasma include possible operation at higher power. The addition of a voltage-off phase also allows for an afterglow period in the plasma, as well as more plasma control by variation of the duty cycle.¹⁹ Discharges sustained by RF and microwave voltage, as well as by magnetic fields are also possible. While they would not exactly follow the breakdown process presented above, the general behavior still applies.



Figure 4: Schematic structure of a DC discharge¹⁸

The breakdown voltage V_b depends on the product of pressure and discharge gap pd. Thus for every gas and electrode material, there exist an optimal pd value that would lead to minimum breakdown voltage,

$$(pd)_{min} = \frac{e}{A} ln \left(1 + \frac{1}{\gamma} \right), \tag{23}$$

where $e \approx 2.72$ is the base of natural logarithms. The breakdown voltage corresponding to $(pd)_{min}$ is

$$V_{min} = \frac{eB}{A} ln \left(1 + \frac{1}{\gamma} \right), \tag{24}$$

with the following reduced electric field,

$$\left(\frac{E}{p}\right)_{min} = B.^{20} \tag{25}$$

The physical meaning of the reduced electric field is the amount of electrical power necessary per electron-ion pair. Unlike V_{min} , which depends on both gas (A and B) and electrode material $(\gamma), \left(\frac{E}{p}\right)_{min}$ only depends on the gas (B).

The Townsend discharge above is the most basic type of discharge, with the lowest current flow through the plasma from one electrode to another¹⁹. The discharge transitions into a corona and then a glow discharge as the current increases and the voltage decreases (Fig. 5). At very high current, the plasma transitions into an arc discharge, often undesirable due to the destructiveness of high current. This glow-to-arc transition can be prevented either by placing a dielectric barrier between the electrodes to block current flow, or by pulsing the applied power such that the plasma never has time to complete the transition to arc.¹⁹



Figure 5: Discharge types at various voltage-current ranges¹⁹

2.2 Atmospheric pressure plasmas

As the required voltage to ignite a plasma V_b scales with the product of pressure and discharge gap pd, increasing the pressure usually requires decreasing the discharge gap. Therefore, a common theme in atmospheric pressure plasmas is the small gap between the electrodes, to minimize the plasma breakdown voltage. Furthermore, as pressure increases and collisions become more frequent, the plasma gas receives more energy from electrons and grows hotter (Fig. 6)^{1,2}. Aside from the plasma configuration, the applied power also plays a role in determining whether the gas temperature reaches the electron temperature. A low amount of power, or pulsed power, shifts the plasma toward lower gas temperature, while high and continuous applied power increases the gas temperature².



Figure 6: Evolution of the plasma temperature (electrons and heavy particles) with the pressure in a mercury plasma arc²

Many atmospheric pressure plasmas, including corona discharges, dielectricbarrier discharges, and plasma jets, operate outside of thermal equilibrium, with hot electrons and cold plasmas gas. These are the plasma sources of interest as hot electrons facilitate reactions for various applications, while cold plasmas gas allow for treatment of heat sensitive materials^{1,2,16–18,20}.

Both corona discharge and dielectric barrier discharge are produced by placing a strong electric field across a pair of electrodes, with gas in between.^{1,2} For a corona discharge, the cathode (powered electrode) takes the form of a needle (Fig. 7) while the anode (grounded electrode) is a plane, resulting in a thin plasma channel connecting the needle to the plane. This thin plasma, the result of a moving front of energetic electrons during the period of negative voltage at the cathode needle, is called a streamer¹⁷. A pulsed DC power supply sustains the plasma such that a transition to an arc discharge is prevented². Since the plasma directly contacts the anode, the substrate to be processed can

simply serve as the anode. However, the small plasma volume presents a challenge for efficient processing of materials. Furthermore, the discharge line starting from the needle tip to the planar electrode is not necessarily normal to the plane, but instead makes contact at unpredictable spots on the planar electrode², causing difficulty in treating the surface evenly. As such, the dielectric barrier discharge became the next candidate for materials processing as it avoids these issues.



Figure 7: Corona discharge²

Compared to the corona discharge, the dielectric barrier discharge utilizes two planar electrodes (Fig. 8), with a dielectric barrier between the two electrodes². In this case, the plasma fills the volume between the two electrodes and is powered by either sinusoidal or pulsed voltage^{2,21}. The inter-electrode gap is kept short, since the breakdown voltage scales with the product of pressure and discharge gap. The dielectric layer serves two purposes: first, direct current flow from one electrode to the other is blocked, thus preventing the plasma from transitioning into an arc discharge; second, as the plasma is separated by a dielectric barrier, it becomes more randomly distributed, allowing for more homogeneous discharge². Despite the advantages over the corona discharge in terms of materials processing, the dielectric barrier discharge has the drawback that the plasma is confined between the two electrodes. Thus, the substrate must either be between the two electrodes, or serve as the grounded electrode. Alternatively, the plasma gas can be fed into a downstream chamber that holds the substrate, at the cost of short-lived species being lost before making contact with the substrate. To prevent these issues, a plasma jet configuration can be employed.



Figure 8: Dielectric barrier discharge.²

Unlike the corona discharge and dielectric barrier discharge, with plasmas confined between two electrodes, the distinctive feature of an atmospheric pressure plasma jet is the creation of a "plasma needle" emanating from the plasma source. This plasma needle, while continuous to the naked eye, in fact consists of discreet "plasma bullets" travelling with speeds of the order of 10^4 m/s, despite a gas flow velocity often at less than 10 m/s ^{5,22}. These plasma bullets are a manifestation of streamers, or ionization waves and will be discussed in depth in the next section (2.3). The key component of a plasma jet apparatus is the capillary tube, usually made of quartz, through which the feed gas flows. Various electrode configurations can be used to power the plasma needle that extends several centimeters beyond the tube nozzle.

An early plasma jet configuration is the dielectric-free electrode (DFE) jet^{5,23} (Fig. 9). As the name implies, the jet features no dielectric barrier between the grounded tube electrode and the powered needle electrode inside the tube. The plasma utilizes a radio frequency (RF) power supply at 13.56 MHz, with He as the feed gas. The lack of a dielectric barrier leads to high power deposition into the plasma, resulting in high gas temperature as well as vulnerability to arcing. Cooling water was included to keep the operating temperature under 300° C, which is still too high for heat sensitive applications. Both the heating and arcing issues can be resolved by addition of a dielectric barrier between the two electrodes, resulting in a dielectric barrier discharge (DBD) plasma jet.



Figure 9: Dielectric-free electrode (DFE) plasma jet.^{5,23}

DBD plasma jets can take various different configurations (Fig. 10). The jet can be produced by two ring electrodes wrapped around a dielectric tube (Fig. 10a), and a RF power supply. For low enough power deposited to the plasma, the resulting gas temperature is cold, barely above room temperature ^{5,22}. The plasma can also be ignited with just one electrode, though at reduced power (Fig. 10b).^{5,24}



(a)



Figure 10: Dielectric barrier discharge (DBD) plasma jet.^{5,22,24}

Slightly differentiated from the DBD discharge is the DBD-like discharge (Fig. 11). The key distinction between DBD discharge and DBD-like discharge appears when treating a grounded conductive surface, in which case the plasma "connects" the substrate to the needle electrode of the DBD-like discharge, effectively creating a non-dielectric barrier discharge. No such interaction happens for the DBD discharge in contact with a grounded conductive substrate. The lack of dielectric barrier between the powered electrode and the substrate can produce arcing. At the same time, when used for treatment of conductive substrates, the plasma resembles non-DBD discharge, and more power can be deposited in the plasma.



Figure 11: DBD-like plasma jet.⁵

Operation with only a single electrode is also possible (Fig. 12a). However, the risk of arcing is also enhanced, making it unsuitable for applications⁵. This drawback can be overcome by the addition of a capacitor (e.g. 50 pF) and a resistor (e.g. 60 k Ω) in the configuration shown in Fig. 12b ^{5,25}. The capacitor and resistor control the discharge current and voltage to the hollow needle electrode, such that arcing is prevented and the gas temperature is kept low.



(a)


(b)

Figure 12: Single electrode plasma jet⁵

The above plasma configurations predominantly use He as the plasma feed gas. Operating a plasma jet with N_2 or air feed gas is also possible, albeit more difficult⁵. Compared to atomic gases like He, molecular gases like N_2 have vibrational and rotational energy levels that can absorb energy during collisions with electrons. Thus electronic energy is wasted without providing any ionization. This problem is exacerbated at high pressure, where collisions become more frequent. Operation with air becomes even more difficult because O_2 is electronegative, contributing to loss of electrons by forming O^- and $O_2^{-.5}$

2.3. Plasma bullets

Despite different gases and configurations, a common attribute among the atmospheric pressure plasma jet (APPJ) is that the plasma plume consists of distinct plasma bullets moving at speeds of the order of 10^4 m/s, thus appearing like a continuous jet to the

naked eye. This speed is higher than any gas flow speed, and is thus not the result of convective gas flow. Instead, the mechanism behind these plasma bullet can be explained using the ionization wave, or streamer, model first proposed by Dawson and Winn ^{5,26,27}. In general, the streamer is a mass of highly ionized gas. The streamer's head harbors a strong local electric field that facilitates ionization, allowing the streamer to propagate into region with weak global electric field. A streamer may be positive or negative, each with a different propagation mechanism.

Positive or cathode-directed streamers travel from anode to cathode, with electrons moving in the opposite direction toward the anode⁷. The propagation mechanism of positive streamer starts with an ionized streamer head. This highly ionized gas is a region where numerous reactions take place, including excitations that result in emission of energetic photons, which can then produce electron-ion pairs in front of the streamer head through a process called photoionization (Fig. 13a). These electrons in front of the streamer head participating in streamer propagation are called seed electrons. The intense local electric field of the streamer head (Fig. 13b) then pulls the seed electrons towards itself, creating an avalanche of electron-ion pairs that prolong the streamer, thus moving the streamer head. Repetition of this process allows for propagation of the positive streamer. Aside from photoionization, the streamer head's powerful local electric field can also tear electrons away from negative ions to produce seed electrons⁷. In the case of repeating streamers following the same path, a large concentration of seed electrons can remain from the previous streamer.



Figure 13: (a) Propagation mechanism of cathode-directed (positive) streamer. (b) Local electric field lines. A and C stand for cathode for anode and cathode, respectivly.⁷

In contrast to positive streamer, negative or anode-directed streamer is one where the streamer head is moving from cathode to anode, in the same direction as the electrons.⁷ In this case, seed electrons are not necessary. Instead, the streamer propagates by following the electron movement and the electron-ion pair avalanche resulting from that movement.

In an atmospheric pressure plasma jet (APPJ), the streamer head initially forms inside the tube, aided by the electric field formed by surrounding electrodes. The streamer head then propagates outside the tube and into the atmosphere through either the positive or negative streamer mechanism, depending on the polarity of the powered electrode. Positive voltage will produce positive streamers, while negative voltage will produce negative streamers⁵. Compared to common streamers (i.e., corona discharge), the APPJ streamers possess two distinctive features⁷. First, the streamers propagate into a highly non-uniform region with strong species concentration and gas gradients, both radially and

axially. The propagation of streamers into such non-uniform regions can lead to behavior unique to APPJs. The second distinctive feature is the repeatable nature of the APPJ streamer. While streamers from corona discharges will often branch out stochastically, the APPJ streamers follow the predictable path along the He flow out of the tube.

The mechanism of formation and propagation of APPJ streamers is of paramount importance for applications, and thus it has been studied via both experiments and simulations. Experimentally, the movement of the plasma bullets has been captured via high-speed cameras (Fig. 14)^{5,28}. Photographs also reveal the donut shape of plasma bullets, being hollow in the middle (Fig. 15)^{5,29}. Also, simulations have revealed that the plasma density (electron density) roughly follows the density of diffused N_2 from air into the plasma (Fig 16)^{5,30}. N₂ is an important species in He plasma jet due to He metastables (He^{*}) capable of ionizing N₂ through a process called Penning ionization. Thus the presence of N_2 allows for He^{*} to contribute to sustaining the plasma, leading to higher plasma density with a He-N₂ mixture. Indeed, Fig. 16 shows simulation for the case without Penning ionization of N₂, leading to lower density of both electrons and the excited N₂ ($C^3\Pi_u$) state. The dependence of the shape of plasma bullets on diffusion of N_2 was further confirmed by adding N_2 into the He feed gas and observing that the plasma bullets exhibit a full round shape with no hollow (Fig. 17)^{5,31}. The mixing of air species into the APPJ is one of the key features that enable various APPJ applications.

Needle 1 cm	(a)
	230 ns
-*	(b)
	240 ns
	(c)
	270 ns
	(d)
	300 ns
	(e)
	330 ns
=	(f)
	360 ns
	(g)
-	390 ns
	(h)
-	420 ns
	(i)
_	450 ns
	(j)
	480 ns
	(k)
	510 ns
	Ð
	540 ns

Figure 14: High-speed photographs of plasma bullets at 10 kHz, 9 kV sine-wave voltage, 0.4L/min He/O₂ (20%) feed gas. ^{5,28}



Figure 15: Photographs of donut shaped plasma bullets.^{5,29}



Figure 16: Radial distribution of number densities of electrons (a), and N₂ ($C^3\Pi_u$) state (b). The dashed-dotted lines show the result at z =1 cm without taking into account Penning ionization. ^{5,30}



Figure 17: High-speed photographs of plasma bullet taken normal to the plasma jet axis. Feed gas is He/N₂ (He: 1 L/min; N₂: 0.015 L/min) mixture.^{5,31}

2.4 Applications of atmospheric pressure plasma jets

Plasma jets can be applied directly on surfaces for various applications, including surface modification, deposition of coatings, and plasma medicine^{2,3}. Surface modification can refer to cleaning and activation of different polymer surfaces^{3,32–37}, which are important for subsequent adhesion or deposition. Application of an Ar APPJ on a polyethylene

terephthalate (PET) surface shows reduced water contact angle, indicating an increased surface energy for improved adhesion (Fig. 18)^{3,32,37}. Etching of polymers by APPJs is also possible, demonstrated by etching of polyether ether ketone (PEEK) using an APPJ with Ar-O₂ mixture as the feed gas (Fig. 19)^{3,38}.



Figure 18: PET surface before (a), and after (b) plasma treatment.^{3,33}



Figure 19: PEEK etching using APPJ with Ar, or Ar-O₂ mixtures as the feed gas.^{3,38}

Compared to surface cleaning, which only requires inert Ar or He feed gas, for deposition the precursor material needs to be supplied to the plasma, either via mixing with downstream plasma or by a separate injection into the plasma-substrate contact site^{3,39}. For example, deposition of C-ZnO films can be carried out by mixing the downstream plasma gas with evaporation of zinc nitrate $Zn(NO_3)_2$ dissolved in aqueous ethanol (Fig. 20a)^{3,40}. The precursor material can also be delivered by spraying directly onto the plasma-substrate contact, resulting in TiO₂ thin films when using titanium isopropoxide TiO₄C₁₂H₂₈ as the precursor (fig. 20b)^{3,41}.





Figure 20: Surface morphology of APPJ deposited (a) C-ZnO composite coating and (b) TiO_2 film^{3,40,41}.

Plasma medicine is an application unique to cold atmospheric pressure plasmas, with atmospheric pressure plasma jets (APPJ) having advantages, due to their unique characteristics. The needle shape of APPJ allows for precise and direct delivery of various plasma species to the treatment site, compared to other configurations that produce plasma in a chamber with only the long-lived species capable of being carried out for treatment. Potential medical applications of APPJs include sterilization, bacterial inactivation, dentistry, wound healing, and cancer cell killing³. The medical effects of APPJs originate from various aspects of the plasma: reactive oxygen (ROS) and nitrogen species (RNS), UV radiation, current flow, and heat to a lesser degree^{9,42} (Fig. 21). Cancer therapy with APPJs in particular is of great interest due to selectivity in killing cancer cells.^{43,44} (Fig. 22).



Figure 21: Inactivation of Bacillus atrophaeus spores by various aspects of an APPJ.



Figure 22: APPJ selectivity in killing cancer cells compared to normal cells.^{43,44}

3. EXPERIMENTAL METHODS

In this study, two APPJ setups were employed, along with various diagnostic techniques. The first setup is used for results discussed in Chapter 4, while the second setup is for discussions in Chapters 5 and 6.

3.1 Two-ring electrode atmospheric pressure plasma jet

This plasma jet is created by flowing helium feed gas (99.999% purity) through a quartz tube (5.5 mm ID and 9.5 mm OD) at 4 standard liters per minute. Two ring electrodes (each 13 mm long) are wrapped around the tube 10 mm and 45 mm away from the tube nozzle (fig. 23). A 200 kHz, 7 kV_{p-p} peak-to-peak sinusoidal voltage waveform is applied to the 10 mm electrode, while the 45 mm electrode is grounded. The high voltage is generated by feeding a sinusoidal voltage waveform from a function generator (BNC model 645) to a RF power amplifier (ENI model 2100L), then to a home-made impedance-matching network to efficiently power the plasma. The matching box consists of an inductor, splitting to a capacitor connected to ground before reaching the electrode (Fig. 23). The resulting high voltage is measured by an oscilloscope (Tektronix TDS 2024B) through a 1000:1 voltage attenuator. The plasma takes the form of a needle emanating from the tube nozzle, reaching up to 2.5 cm in length.



Figure 23: Schematic of two-ring electrode atmospheric pressure plasma jet.

3.2 Time-average emission spectroscopy

Time-averaged OES in the ultraviolet-visible (UV-vis) range was carried out with four spectrometers (Ocean Optics, model HR4000), each with a predefined range of wavelengths. Furthermore, emission was also obtained in the vacuum ultraviolet (VUV) range, which is considered to be below 200 nm. Emission in this region is absorbed by O₂, thus the measurements are usually carried out in a vacuum chamber. In the present study, the plasma jet is impinging on a MgF₂ window on the spectrometer, which is under vacuum. This allows emission along the central axis of the discharge to be obtained for wavelengths extending to the cutoff for MgF₂ at ~115 nm.

3.3 Time-resolved emission spectroscopy

Time-resolved emission was measured by feeding the emission into an optic fiber connected to a spectrometer, consisting of a ISA TRIAX 550 monochromator and an intensified charge-coupled device (ICCD, Princeton Instruments, model PI-Max I) as shown in Fig. 24(a). This ICCD was also used to capture time-resolved images of the plasma jet emission (spectrally unresolved).

The ICCD has a maximum repetition rate of 50 kHz, thus if the plasma is powered by a 200 kHz sinewave voltage, every cycle of the applied plasma voltage cannot be monitored. A function generator (Hewlett Packard model 3325A) was then used to create a 40 kHz frequency square wave pulse that triggered the 200 kHz function generator that drives the plasma, as well as the ICCD (Fig. 24(b)). The 40 kHz pulse rising edge was near the beginning of the 200 kHz sinewave, and after 5 sinewave cycles, the square wave would begin again. After a variable, specified delay with respect to the trigger pulse, the ICCD is triggered at the same point of the sinewave voltage cycle to accumulate emission for a duration long enough to achieve an adequate signal-to-noise ratio.





Figure 24: (a) Spectrometer configuration. (b) Triggering the ICCD and the plasma sinewave (200 kHz) using a 40 kHz squarewave.

3.2 Ring and needle electrode atmospheric pressure plasma jet



Figure 25: Schematic of ring and needle electrode RF atmospheric pressure plasma jet without shielding gas apparatus.

This plasma jet is made by flowing ultra-high purity He or Ar (both at 99.999% purity) through a quartz tube (2 mm ID, 3 mm OD) at various flow rates (1-2 slm). A 5

mm-long ring copper electrode wraps around the tube, acting as the ground electrode, while a tungsten needle is inserted inside the tube, acting as the powered electrode. A sinewave voltage at 13 MHz, 1- 4 kV peak-to-peak is applied to the tungsten needle. This voltage is created by feeding the output voltage from a function generator (BNC model 645) to a RF power amplifier (ENI model 3200 L), then to a home-made matching box (an inductor) to deliver power to the plasma.

3.2 Ring and needle electrode atmospheric pressure plasma jet with shielding gas apparatus

Additionally, a shield gas curtain can be added to the plasma source to separate the plasma from the ambient air (Fig. 26). Inclusion of the shielding gas necessitates a longer ground electrode, such that the shielding gas flow is able to fully develop (Fig. 27). As the ground electrode now covers a longer portion of the tube, the plasma inside the tube is likewise lengthened, leading to higher gas temperature in the plasma plume.



Figure 26: RF atmospheric pressure plasma jet with shielding gas.



Figure 27: Schematic of ring and needle electrode RF atmospheric pressure plasma jet with shielding gas apparatus.

4. EXCITATION MECHANISMS IN A HELIUM ATMOSPHERIC PRESSURE PLASMA JET

The emissions of various species in a plasma gives identifying information of these species as well as their excited states. Since the plasma is powered by a RF 200 kHz sine wave voltage, the emissions are expected to exhibit a time dependence on the order of the voltage cycle. Observation of both time-average and time-resolved emissions reveal the various mechanisms by which the plasma species are excited, along with the temporal evolution of the plasma.

4.1 Spatially-resolved optical emission spectroscopy

The plasma needle impinges on the flat face of a half-cylinder quartz prism with semicircular cross section, placed 20 mm from the nozzle (Fig. 28). Light gathered from the curved side of the prism was focused onto the input of an optical fiber. Emission was detected as a function of angle θ_2 , both in time-averaged and time-resolved modes.



Figure 28: Experimental system (not drawn to scale) used for OES in the UV/visible/near-IR range.

As the plasma jet impinges on the prism, its emission reaches the prism at various angles θ_1 , which will then exit the other side of the prism at various angles θ_2 . The relationship between these two angles is determined by Snell's law (Fig. 59),

$$n_1 \sin(\theta_1) = n_2 \sin(\theta_2), \tag{26}$$

where $n_1 = 1$ and n_2 are the indices of refraction of the plasma gas (essentially empty space) and the prism material (quartz), respectively. As the result, by varying the angle θ_2 at which the light is probed, we can selectively probe light coming only from angle θ_l , assuming a small enough collection angle. If the average radius of the plasma jet cylinder (just before the plasma spreads out on the surface) is $r_p = 0.75$ mm, then each angle θ_l will correspond to emission from plasma at a certain distance away from the substrate, given by

$$d = r_p / \tan(\theta_1). \tag{27}$$

Therefore, by changing the probe angle θ_2 we can effectively spatially resolve the plasma emission. As θ_1 approaches 90°, *d* approaches 0, and θ_2 approaches the critical angle (θ_c), determined by the index of refraction of quartz (n_2). In the range of wavelength of interest, n_2 is a weak function of wavelength^{45,46}. If we take $\theta_2 = 40^{\circ}$, then at 309 nm (OH peak), the corresponding $n_2 = 1.49$, and d = 0.225 mm. On the other hand, at 844 nm (O-atom peak), the corresponding $n_2 = 1.45$, and d = 0.291 mm. Thus the dependence of n_2 on wavelength is not a concern.



Figure 29: At an observation angle of θ_2 =40°, and an average radial extend of the plasma on the substrate r_p =0.75 mm, emission is probed from a region d~0.3 mm away from the quartz substrate surface. θ_1 and θ_2 are related by Snell's law $n_1 \sin(\theta_1) = n_2 \sin(\theta_2)$.

The geometrical details of the optical setup are shown in Fig. 30. The prism radius was 25 mm. The aperture diameter was 6 mm, placed 49 mm away from the curved side of the prism. A 5 mm lens was attached in front of the optical fiber, placed 51 mm away from the aperture. In addition, based on the geometry of the system, the light collection angle for observation along the axis, was $\sim 1^{\circ}$ and $\sim 3^{\circ}$ for light at the nozzle (point A) and at the substrate (point B), respectively.





Emission was also obtained in the vacuum UV (VUV) range, below 200 nm. VUV emissions are measured in two configurations (Fig. 31). In Fig. 31a, emission from the entire plasma jet length is passed onto the spectrometer, while in Fig. 31b, the plasma jet is tilted such that only the emission at the plasma tip is measured.



Figure 31: VUV spectrometer probing light from the plasma jet along the axis (a), or at angle (b), to isolate emission only from the surface of the substrate (MgF2 window in this case).

4.2 Plasma images

The plasma jet is about 1.5 mm in diameter and can extends up to 25 mm from the nozzle into ambient air in the absence of a substrate. If a substrate is present, the plasma then spreads out upon contact. The temporal behavior of the plasma jet is observed by time-resolved imaging of visible light, shown in Fig. 32. The internal boundary of the quartz discharge tube (near the nozzle) is indicated by the yellow box, and the high voltage electrode is located between the dashed red lines.



Figure 32: False color images of the plasma (10 ns exposure windows) 300 ns after the positive peak (top) and 100 ns after the negative peak (bottom) of the applied voltage.

The plasma jet is first seen protruding from the nozzle and touching the quartz substrate at near peak positive voltage. It then reaches its maximum brightness point (upper panel of Fig. 32) and continues to persist long after the maximum voltage has passed. As the voltage proceeds to the negative stage the discharge is observed only inside the tube, downstream from the powered electrode (lower panel of Fig. 32). Other studies^{47–50} have shown clearly defined plasma bullet propagating from the tube to the substrate. Such

behavior is not observed in our setup due to reasons that will be explained later, revealed by observing the temporal behavior of the nitrogen emission.

4.3 Time-averaged optical emission spectra

We measured time-averaged spectra along the jet axis, probing emission from the whole plasma from inside the tube and extending into the atmosphere (Fig. 33). The plasma impinges on either the flat surface of the quartz prism, or the MgF₂ window of the vacuum spectrometer. Since the plasma feed gas is He, strong He emissions (706.5 nm, 728.1 nm, 667.8 nm, etc.) were detected. Other peaks include emissions from H (486.1 nm, 656.3 nm), O (777.2 nm, 844.6 nm), N (174.3 nm, 174.5 nm), OH(A²\Sigma⁺ \rightarrow X²\Pi), N₂(C³\Pi_u \rightarrow B³Π_g), N₂⁺ (B²\Sigma_u⁺ \rightarrow X²Σ_g⁺) and NO(A²\Sigma⁺ \rightarrow X²Π). The NO emission was much weaker than the rest, thus it was accumulated for a longer time with the Ocean Optics UV spectrometer such that good signal-to-noise ratio was achieved. Emissions aside from that of feed gas He originate from either air diffusion or feed impurity.





Figure 33: Typical emission spectra from 115 nm to 950 nm, recorded along the axis of the discharge ($\theta_1 = \theta_2 = 0^\circ$). Lines identified by red lettering are second order peaks. The most intense peak was normalized to have an intensity of 1000.

Air cannot penetrate deep inside the tube by diffusion due to high Peclet number, Pe (~1800),

$$Pe = \frac{uL}{D},\tag{28}$$

where u is the gas convective flow velocity, L is characteristic length scale, and D is diffusivity of air species in He. Due to the highly convective flow N_2 , O_2 and water vapor from the ambient air can back-diffuse only a short distance (<0.5 mm from the nozzle) into the tube. Therefore, species that originate in the feed gas, and those that diffuse in from the ambient air, can be distinguished by whether or not they are present deep inside the tube. To this end, average spectra were taken perpendicular to the jet axis, as a function of the jet axial position, where z=0 is the location of the nozzle and the positive direction is downstream, along the plasma jet flow (Fig. 34). Since the plasma density varies with axial distance, raw intensity alone is not a good metric for observing species mole fraction. Instead, species emission divided by He emission is more representative of the species mole fraction. The theory behind this will be explained in more details in the section about actinometry (Chapter 5). The emission intensity ratios O/He and H/He do not vary with axial distance, indicating that O and H come primarily from feed gas impurities, most likely water. Emission intensity ratios N_2 /He and N_2^+ /He, on the other hand, rise sharply a short distance downstream of the nozzle, implying that N_2 in the plasma is mostly from ambient air diffusion. Unlike all other emissions, OH/He emission intensity ratio shows strongly non-monotonic behavior decreasing along the plasma length before increasing at the nozzle. This is possibly the result of dissociation of OH into O and H inside the jet, thus decreasing OH/He emission intensity ratio inside the tube, before diffusion of water from air adding OH to the plasma, causing an increase in OH/He emission intensity ratio near the nozzle. Overall, air diffusion is the main provider for N_2 in the part of the jet that is outside the tube while species such as O, OH, and H are mainly from feed gas impurities. Therefore, emissions recorded along the axis, except for that of feed gas He, were the result of air diffusion into the plasma plume between the tube nozzle and the substrate, and/or impurities in the He feed gas.



Figure 34: Emission intensity ratios as a function of axial position along the plasma jet.

We now look at time-average emission spectra of plasma near the region where the plasma tip comes into contact with the quartz prism substrate (Fig. 35), accessed by tilting the optic fiber behind the quartz prism such that $\theta_2 = 20^\circ$, resulting in $\theta_1 = 30^\circ$ (as shown in Fig. 30). The VUV region (below 200 nm), as explained, does not involve the quartz

prism and instead has the plasma impinge directly onto the MgF₂ window of the VUV spectrometer. Emission is measured with the jet striking the window at an angle (as shown in Fig. 31). The signal is much lower compared to measurements along the axis, due to the smaller plasma volume being probed (only the plume tip instead of the entire length of the jet). All prominent emissions appear, although the relative intensities change drastically, particularly with much stronger N₂ and N₂⁺ peaks compared to the rest (He, O) due to diffusion of N₂ from air into the plasma plume while the remaining emissions come primarily from feed gas impurities. In the VUV region, H Lyman- α and O-atom emissions were much weaker relative to UV-visible emissions, requiring a wider monochromator slit (~1 mm).







Fig. 35: Typical emission spectra from 115 to 950 nm, recorded at an angle off of the discharge axis ($\theta_1 = 30^\circ$, $\theta_2 = 20^\circ$. Lines identified by red lettering are second order peaks. The most intense peak was normalized to have an intensity of 1000.

4.4 Time resolved emissions

While time-average spectra give us a general look of the species in the plasma and their relative population, time-resolved spectra carry information about the species behavior with respect to the applied voltage sinewave, thus revealing their role in the plasma chemistry. Time-resolved emission was collected with the ICCD-equipped spectrometer (Fig. 24). As explained above, each point was taken by accumulating light into the ICCD at one exact spot in the sinewave cycle until adequate signal-to-noise ratio was obtained. The gate width was set at 50 ns, meaning that for each cycle, the ICCD was open for accumulation for exactly 50 ns, and the increment between each accumulation was 50 ns. As such, there was no overlap between each measurement. Time-resolved emission was taken as a function of angle θ_2 (see Figs. 28 and 29) from 0° to 40°. When $\theta_2 = 0^\circ$, emission from the entire plasma jet length was probed, whereas for $\theta_2 = 40^\circ$ only emission from the plasma jet tip in contact with the quartz substrate was measured. It should be noted that when increasing θ_2 from 0° to 40°, not only do we change the axial segment of the plasma being probed (from entire jet length to only the jet tip), but also the radial position of the plasma (from the jet axis alone, to radially integrated emission from the radial position of the plasma being probed does not make a big difference as the plasma changes more with axial position than it does with radial position.

In Figs. 36-42, the time-resolved emissions are normalized to have the maximum at 1000. The vertical dashed lines are placed at peak positive and negative voltage, as well as zero voltage crossing. Time-resolved He 706.5 nm emission is shown in Fig. 36, at various angles θ_2 from 0° to 40°. At 0°, emission is probed in the radial center of the plasma jet, extending from inside the tube to all the way to the plasma-quartz substrate interface, revealing two broad peaks near the maximum positive and maximum negative voltage, with no emission at the two zero voltage crossings.

At 10°, the majority of the emission originates mostly from the plasma plume region between the nozzle and the quartz substrate, resulting in a large peak near maximum positive voltage due to the plasma jet coming out and touching the quartz substrate at this point in time. At the same time, a small amount of light from inside the tube was still captured. This light is from the plasma inside the tube, near the tube edge (3 mm from the center), coming out to the prism and reaching the optic fiber connected to the spectrometer. Because of this limited capture zone when probing at 10°, inside-tube plasma emission is weak, resulting in a small peak near maximum negative voltage, when plasma is only present inside the tube.

At 40°, only light from plasma near the plasma-quartz interface is collected, and thus only a sharp peak near maximum positive voltage was observed. This peak corresponds to the brief moment where the plasma plume comes into contact with the quartz substrate. Other APPJ studies have reported observing an ionization wave traveling to the substrate during the positive voltage portion of the RF cycle^{5,7,26,30,48–51}. Looking at the rising edge on the left of the emissions near maximum positive voltage collected at all angles from 0° to 40°, one can shed light into the propagation of the plasma jet. It initially forms deep inside the tube and is only strongly detected at 0°, then moves toward the substrate and is seen at 10°, before touching the substrate and can be observed at 40°.

Despite the time- and spectrally-resolved emission showing signs of a plasma bullet moving from nozzle to substrate, such behavior was not observed in the time-resolved imaging of the overall plasma emission (Fig. 32), which shows the entire jet appearing simultaneously when the voltage is high enough. A possible reason is that even though the entire plasma jet lights up simultaneously, measurement of relative plasma emission intensity still shows the position of maximum intensity moving from the nozzle to the substrate during the rising part of the positive voltage portion of the cycle.

About 10 to 150 ns after the positive voltage has peaked, He emission peaks near the substrate (observed at 40°, and also at 20° and 30°, not shown), due to electron impact excitation of He near the substrate surface (Fig. 36). The amount of time between peak positive voltage and peak emission is short because the ionization front can form before the voltage peaks, and subsequently reaches the substrate surface about the same time the peak positive voltage occurs. After the voltage has peaked, the emissions observed at 0° , 10° , and 40° all decrease, albeit at different speeds. Observations at 10° and 40° show the emission dropping sharply to zero almost immediately, implying that the plasma near the substrate dissipates completely, shortly after the peak positive voltage. On the other hand, emission measured at 0° slowly drops to zero. Because measurement at 0° entails the entire plasma length (both inside and outside the tube), we can surmise that this gradual drop in emission at 0° is due to plasma returning inside the tube while slowly dying out. In conclusion, during the positive voltage rises, but the near substrate emission only peaks near peak positive voltage. As the positive voltage decreases, the plasma quickly retreats back inside the tube, where it slowly disappears while the voltage drops to zero.

When the voltage becomes negative, a broad emission peak is observed strongly at 0° and weakly at 10° , representing the plasma that is confined inside the discharge tube. In addition to the He 706.5 line, we also probed the He 501.57 nm line at 0° , the purpose of which will be revealed in Section 4.6.



Fig. 36: Time-resolved He (706.5 nm) emission at three different angles, θ_2 . The applied voltage waveform is also shown. The time-resolved 501.57 nm line at $\theta_2 = 10^\circ$ is also shown.

Fig. 37 and 38 show time-resolved $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ emission. Near peak positive voltage, $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ emission shows sharp peaks at 0° and 40°, similar to He 706.5 nm emission. Again, these peaks are the result of N_2 excitation and subsequent emission near the substrate as the plasma plume protrudes out of the tube and impinges on the substrate during positive voltage. Additionally, close inspection of emission at both 0° and 40° shows two weak emissions, one near peak negative voltage and one near peak negative voltage (Fig. 38). These features reveal the plasma behavior and will be discussed in section 4.6.



Fig. 37: Time-resolved N₂ (337 nm) emission at $\theta_2 = 0$ and 40°. The applied voltage waveform is also shown.



Fig. 38: Time-resolved N₂ (337 nm) emission at $\theta_2 = 0$ and 40° showing expanded intensity scale of Fig. 8. The time-resolved He (706.5 nm) emission at $\theta_2 = 40^\circ$ is also shown.

Fig. 39 shows $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ time-resolved emission. Observation at 40° shows similar behavior as that of N_2 emission: sharp peak at maximum positive voltage attributed to plasma excitation near substrate surface. N_2^+ emission at 0° also shares with N_2 emission the strong emission peak near peak positive voltage, but differs from N_2 emission by having a significant and weakly modulated emission throughout the rest of the voltage cycle, even at the zero-voltage crossing.



Fig. 39: Time-resolved N₂⁺ (391 nm) emission at $\theta_2 = 0^{\circ}$ and 40°. The applied voltage waveform is also shown. The phase shift, $\Delta \phi$, is based on a period of 2500 ns, assuming excitation occurs twice per RF (200 kHz) period.

Figs. 40 and 41 show time-resolved emissions of H (656 nm), OH (309 nm) and O (844 nm) measured at 0° and 40° . H and O emissions at 40° show the same behavior as N₂⁺ emission, peaking sharply near the maximum positive voltage, again due to plasma excitation near substrate surface. OH emission also would have exhibited similar behavior if not for the broadening due to long lifetime of OH, causing it to decay to baseline at 2000 ns, compared to 1600-1700 ns for H and O. On the other hand, at 0° , all H, O, and OH

emissions show a near constant intensity throughout the voltage cycle. O emission still shows a sharp peak near the maximum positive voltage like that of N_2^+ .



Fig. 40: Time resolved H (656 nm) emissions at $\theta_2 = 0^\circ$ and 40° . The applied voltage waveform is also shown.



Fig. 41: Time resolved OH (309 nm) emissions at $\theta_2 = 0^\circ$ and 40° . The applied voltage waveform is also shown.


Fig. 42: Time-resolved O (844 nm) emissions at $\theta_2 = 0^\circ$ and 40° . The applied voltage waveform is also shown.

Fig. 43 shows time-resolved emissions in the VUV region for various species. In this case, the plasma impinges on the MgF₂ window of the VUV spectrometer, as shown in Fig. 31(a). The plasma jet is positioned normal to the window, to probe the entire jet emission. In this VUV region, H and O emissions match their UV-vis counterparts (i.e., almost constant emission throughout the voltage cycle). N-atom VUV emission also exhibit the same behavior.



Fig. 43: Time-resolved VUV emissions of OH, N, O, and at $\theta_2 = 0^\circ$ and 40° . The applied voltage waveform is also shown.

4.5 Excitation mechanisms

Helium emissions are the result of excitation by collisions of energetic electrons with ground state He, as well as by collisions of lower energy electrons with He⁺ or He "metastables" (He^{*}). As the plasma operates at atmospheric pressure, He emissions can get radiation-trapped where the emissions are repeatedly absorbed and re-emitted instead of escaping the region. Therefore, even if a He state has an allowed transition to lower states through emission (such as those in the VUV 50-60 nm range), it can be considered to behave like a metastable due to radiation-trapping. We measured the time-resolved emission of He at 706.5 and 501.57 nm. Their lifetimes (36 and 75 ns, respectively) are much shorter than the RF period (5 µs), thus their time-resolved emission (Fig. 36) is representative of their electron impact excitation time-resolved behavior. He* can be excited either directly by electron impact collision with ground state He, or by optical cascading from higher excited states. In the case of optical cascading, an electron impact collision results in an excited He with much higher energy then He*, which can lose energy by emitting a photon and forming He*. Direct excitation of He* by electron impact can be expected to follow the same time dependence as He time-resolved emission shown in Fig. 36, while excitation of He* by optical cascading is enhanced at high pressure by radiation trapping of VUV light.

The likely dominant VUV emission is $2p^1P^{\circ} \rightarrow {}^1S$ He at 58.433 nm. Because of radiation trapping, this emission will be absorbed and re-emitted in the nozzle region 1000 times (on average) before decaying to the $2s^1S$ metastable state, emitting a 2058.1 nm photon in this cascade process. Radiation transport can take place over a distance of roughly the tube diameter (5.5 mm) until the VUV photon random-walks out of the He flow region, creating He* far away from where the initial electron impact excitation occurs. Since both the $2p^1P^{\circ}$ and the $2s^1S$ metastable can excite a variety of air species (N₂⁺, O, etc.) that would lead to emission, radiation transport results in creation of He* as well as the subsequent emissions of air species far away from the plasma region.

The time dependence of He radiation transport can be measured by the various emissions in the process. However, the He 58.433 nm $(2p^1P^o \rightarrow {}^1S)$, 53.703 nm $(3p^1P^o \rightarrow {}^1S)$, and 52.221 nm $(4p^1P^o \rightarrow {}^1S)$ lines could not be measured as they would be absorbed by the MgF₂ window on the VUV spectrometer. Measurement of the He 2058.1 nm $(2p^1P^o \rightarrow {}^1S)$

→ 2s¹S) emission line also was not possible as the wavelength is beyond the spectrometers available. The solution was to observe the He 501.57 nm emission $(3p^1P^\circ \rightarrow 2s^1S)$, which can be considered to be analogous, thus possessing similar behavior to the He 2058.1 nm $(2p^1P^\circ \rightarrow 2s^1S)$ emission line. As the result, He 501.57 nm time-emission was measured and considered to represent radiation transport of He*.

The He 501.57 nm $(3p^1P^0 \rightarrow 2s^1S)$ time-emission behaves similarly to the He 706.5 nm $(3s^3S \rightarrow 2p^3P)$ emission (Fig. 34). However, the two differ in that He 501.57 nm emission peaks slightly after the He 706.5 nm emission has peaked, likely due to the different energy dependences of the cross-sections for each excitation, combined with a somewhat time-dependent electron energy distribution function (EEDF). Helium ground state is ¹S, thus an electron impact transition directly into a triplet states like 3s³S is optically forbidden, causing the cross section of such reactions to be large just above threshold and to shrink to near zero at higher electron energies. On the other hand, electron impact excitation of ground state He ¹S to singlet states like 3p¹P^o is optically allowed, resulting in a cross section that rises with electron energy above threshold and is nearly constant with increasing energy⁵². The reason why the 706.5 nm line is so strong relative to the 501.57 nm emission is that $3s^3S$ is predominantly created by electron impact excitation with He metastables⁵³ due to the reaction having large cross section with much lower threshold. Therefore, if electron energy rises after the applied voltage has peaked, then the 501.57 nm emission will keep increasing as the 706.5 nm line falls.

He metastables are of great interest in this study as they possess sufficient energy to produce all observed emissions through multiple pathways. However, for this to occur, the excess energy must be released. Therefore, even though He* has more than enough energy to produce $N_2(C^3\Pi_u)$ and return to He ground state, a large amount of translational energy remains (19.8-11.0 = 8.8 eV). Thus for this reaction to occur, it requires an unreasonably large attractive force between He^{*} and ground state N₂ to hold the two reactants in place during the reaction and oppose the huge translational energy that results. Furthermore, third body collisions are very unlikely to occur during the short time when He^{*} and N₂ interact (of the order of half a vibrational period). As the result, N₂(C³Π_u) cannot be excited by He^{*} and instead must be excited by electron impact.

Time-resolved He emission (Fig. 36) during the positive voltage period, also at 0°, consists of a broad feature upon which a weaker sharp peak superimposes near the maximum positive voltage. This sharp peak can be attributed to emission at the surface as it has the same shape as emission observed at $\theta = 40^{\circ}$ near maximum positive voltage. The broad feature, on the other hand, shares the same shape with He $\theta = 0^{\circ}$ emission near maximum negative voltage. As the peak positive and peak negative of the voltage are of the same magnitude, the plasma is expected to have similar density at each voltage peak, and Fig. 30 shows plasma only inside tube near the negative voltage peak. Therefore, we can reasonably assume that the broad He emission seen during negative voltages is due to electron impact inside the tube.

Energetic electrons are confined inside the tube during the negative voltage, and we observed little N_2 emission during negative voltage (Fig. 37). It follows that N_2 does not come into contact with theses in-tube energetic electron during negative voltage, and that there is very little N_2 inside the tube throughout the voltage cycle. We can then surmise that any N_2 emission that was observed must be due to electron impact reactions outside the tube between nozzle and substrate, where N_2 is abundant due to air diffusion. Additionally, we can also confirm this by directly measuring N_2 emissions inside and outside the tube (Fig. 34) and observing that N_2 emission is primarily present outside the tube, with very little inside the tube.

As the voltage rises during the positive voltage period, N_2 emission (Fig. 37) intensity rises similarly to He emission (Fig. 36). But as the voltage falls, N_2 emission plummets more dramatically than does He emission. Because the plasma extends along the axis during this positive voltage period, the slow rise of both He and N_2 emissions can be attributed to excitation of the emerging plasma jet, particularly near the discharge tube-air boundary as that is where the jet first appears. When the voltage drops, the near-substrate plasma quickly extinguishes, leading to a sharp drop in N_2 emission (0° and 40°) and He emission (40° only), which we believe is due to electron impact excitation near the substrate surface.

During the negative voltage period, a small N_2 emission peak is observed near peak negative voltage (Fig. 38). This feature is observed only in N_2 . We ascribe this to a discharge that briefly develops near the substrate surface. This discharge cannot excite or ionize He, owing to its low electron energy. Thus it must be sustained from ionization of N_2 and O_2 , and no electron impact excitation of He emission or He*-induced emissions can occur.

Compared to $N_2(C^3\Pi_u)$ (Fig. 47), $N_2^+(B^2\Sigma_u^+)$ (Fig. 39) has a different time-resolved emission behavior. During positive voltages, N_2^+ emission exhibits a sharp peak, like N_2 , but superimposed on a background emission that persists throughout the voltage cycle, even at the zero voltage crossing. Thus the excitation of this emission must possess a long life time to be independent of the voltage cycle. We ascribe this background emission to Penning ionization,

$$He(2^{3}S) + N_{2} \rightarrow N_{2}^{+}(B^{2}\Sigma_{u}^{+}) + He + e^{-}.$$
 (29)

While $N_2(C^3\Pi_u)$ cannot be excited by He*, the production of $N_2^+(B^2\Sigma_u^+)$ includes the ejection of an electron, which can carry away the excess -1.06 eV as translational energy and allow the reaction to take place. In atmospheric pressure plasmas, He metastables are responsible for excitation of not only N_2^+ , but also various other species^{49,54,55}. According to Xiong et al., Penning ionization by He metastables is the main source of N_2^+ (391 nm) and the O (777 nm) emission⁴⁹. They also showed that N_2 plays an important role in the propagation of the ionization wave by acting as the ion source through Penning ionization by He metastables.

As the radiative lifetime of He* produced $N_2^+(B^2\Sigma_u^+)$ is short (60 ns), the observed time-resolved behavior of $N_2^+(B^2\Sigma_u^+)$ emission is representative of the number density of He*. We have established that the plasma is confined inside the tube during the negative voltage period, and that, even though N_2 originates from air diffusing into the plasma jet, it cannot diffuse into the tube due to high Peclet number. Therefore, during negative voltage, N_2 cannot reach inside the tube where He* resides for ionization to occur.

A possible explanation is that He^{*} is instead transported out of the tube by the gas flow, meeting and ionizing N₂ in air. In order to assess the validity of this explanation we have to look at the time scale of He^{*} creation versus gas flow. He^{*} is produced by electron impacts with He or recombination between He⁺ or He₂⁺ with electrons. The rates of these reactions peak twice per RF period, when the voltage amplitude is at maximum and the plasma is at its densest. On the other hand, the gas residence time is much slower (about 300 times the RF period), and as such, the flow of He* out of the tube will be constant, without any time-dependence behavior from the RF cycle. This constant stream of He* would then be the main source of N₂ ionization into N₂⁺(B² Σ_u^+) during the negative voltage period as it comes into contact with N₂ in air. Yet, N₂⁺(B² Σ_u^+) during the negative voltage shows a clear time dependence in Fig. 39. Therefore, the constant flow of He* from inside the tube out to air due to feed gas flow cannot be the main source of N₂⁺(B² Σ_u^+) production in the negative voltage region.

A possible mechanism for a time-dependent production of He* outside the tube is by radiation transport. In this case, various He excited states would be directly created at the voltage peaks in each RF cycle through radiation transport. The VUV emissions in the 50-60 nm range have very short radiative lifetimes (i.e., 0.5 ns for the 2p¹P^o state⁵⁶). Even with strong radiation-trapping, it would be unreasonable to expect the lifetime to lengthen to values comparable to the RF periods. Thus creation of He* outside the tube by this mechanism would retain a strong time-dependence based on the RF voltage cycle.

As explained above, radiation transport of He* includes numerous cycles of absorption and re-emission of $2p^1P^o$ He-produced photons. Eventually, the $2p^1P^o$ He would then decay into $2s^1S$ metastable state. Furthermore, the 501.57 nm line $(3p^1P^o \rightarrow 2s^1S)$ (Fig. 36) is expected to follow this same decay into a metastable state, and thus is considered to be representative of He* time-dependent production outside the tube. The N₂⁺(B²Σ_u⁺) emission (Fig. 37), resulting from the produced He*does not, however, peak at the same time as when He* production peaks (Fig. 36). Instead, there is a $\Delta \phi = 61^o$ phase shift from when He^{*} production peaks to when $N_2^+(B^2\Sigma_u^+)$ emission peaks (Fig. 39). This can be explained by the lifetime of the He^{*}, which is apparently long enough to cause an observable delay in its reaction products. This lifetime can be estimated from the relationship⁵⁷,

$$tan\Delta\phi = \omega_e \tau_{\phi},\tag{30}$$

where $\Delta \phi$ is the phase shift, τ_{ϕ} is the lifetime, and ω_e is the effective excitation frequency, which is twice the RF frequency ω ,

$$\omega_e = 2\omega = 2 \times 2\pi \times 200 \ kHz, \tag{31}$$

because excitation occurs twice every RF cycle, as the voltage peaks positively and negatively. By this estimation, a lifetime of $\tau_{\phi} = 0.72 \ \mu s$ can be obtained.

Alternatively, one can also estimate the lifetime though the degree of modulation of the $N_2^+(B^2\Sigma_u^+)$ emission time-resolved behavior⁵⁷,

$$\tau_m = \frac{\left[\left(\frac{m}{a}\right)^2 - 1\right]}{\omega_e},\tag{32}$$

where τ_m is the lifetime, and *m* and α are the DC offset and the amplitude of the emission waveform, respectively. In this estimation, we assume the He^{*} production to be sinusoidal, with a DC level equal to its amplitude (i.e., the minima equal zero) at twice the voltage frequency. The negative voltage region N₂⁺(B² Σ_u^+) emission is then assumed to also follow a sinewave, with its own DC offset and amplitude. This estimation results in a He* lifetime of $\tau_m = 2.7 \mu s$.

The disagreement between the phase-shift based estimate $\tau_{\phi} = 0.72 \ \mu s$ and the modulation based estimate $\tau_m = 2.7 \mu s$ can be traced back to possible production of He^{*} outside the tube by gas flow. This He^{*} flow does not have any time-dependence and thus provides a constant background of He^{*} production, resulting in a similarly constant N₂⁺(B²\Sigma_u⁺) emission, which is then superimposed on by the N₂⁺(B²Σ_u⁺) emission from radiation transport. While this constant N₂⁺(B²Σ_u⁺) emission does not impede lifetime estimation by phase-shift ($\tau_{\phi} = 0.72 \ \mu s$), it would lengthen the lifetime estimated by modulation ($\tau_m = 2.7 \mu s$). As the result, the phase-shift based estimation $\tau_{\phi} = 0.72 \ \mu s$ is the more appropriate He^{*} lifetime outside the tube.

The He^{*} lifetime is the result of quenching by various air species diffusing into the plasma gas flow. The He $2s^{1}S$ metastable state is quenched by N₂ and O₂ at rate constants of 1.7×10^{-10} and 5.8×10^{-10} cm³s⁻¹, respectively, near room temperature.⁵⁸ The other He^{*} state ($2s^{3}S$) has similar quenching rate constants by N₂ and O₂ of 0.8 x 10^{-10} and 3 x 10^{-10} cm³s⁻¹, respectively.⁵⁹ If we assume the main He^{*} is He $2s^{1}S$ and use the appropriate quenching rate constants, then the observed 0.7 µs lifetime would be the result of quenching by a partial pressure of 185 mTorr of air near the nozzle. Additional confirmation of this number was made by carrying out two-dimensional laminar flow (Navier-Stokes equations) and mass transfer modelling of ambient air mixing with the helium jet in the open space between the nozzle and the substrate. The model shows that air in the plasma gas increases further away from the nozzle, reaching a partial pressure of

185 mTorr on the jet axis (*r*=0) at an axial distance of ~10 mm from the nozzle. This confirms the conclusions drawn on the excitation mechanism of $N_2^+(B^2\Sigma_u^+)$ emissions, pertaining to how radiation transport produced He* affect its time-resolved behavior.

In addition to Penning ionization by He*, $N_2^+(B^2\Sigma_u^+)$ can also be created by photoionization by the He VUV emission at 58.443 nm, as well as several other nearby lines. The cross section of this reaction is $2x10^{-18}$ cm² at this wavelength.⁶⁰ As the natural lifetime of $N_2^+(B^2\Sigma_u^+)$ is very short compared to $\tau_{\phi} = 0.72 \ \mu s$, if $N_2^+(B^2\Sigma_u^+)$ is indeed created from VUV emissions, then the states that emit this VUV emissions must have lifetime comparable to $\tau_{\phi} = 0.72 \ \mu s$ to produce the observed time dependence. Since such long lifetime of VUV emitting states is unreasonable, photoionization by He VUV emissions is not playing a role in excitation of $N_2^+(B^2\Sigma_u^+)$.

As shown above, $N_2^+(B^2\Sigma_u^+)$ emission at $\theta_2=0^\circ$ can be used to determine time dependent production of He*, as well as its decay by air species quenching between the tube nozzle and the substrate. $N_2^+(B^2\Sigma_u^+)$ emission at $\theta_2=40^\circ$, on the other hand, reveals the He* lifetime and subsequent quenching by air near the substrate surface, during the positive voltage period when the plasma protrudes out of the tube and touches the substrate. Fig. 44 shows the decay of $N_2^+(B^2\Sigma_u^+)$ time-resolved emission $\theta_2=40^\circ$ near maximum positive voltage. This decay represents the quenching of He*, described by

$$-\frac{dn_{He*}}{dt} = \frac{n_{He*}}{\tau_{He*}},\tag{33}$$

where n_{He*} is He* concentration, t is time, and τ_{He*} is the lifetime of the respective He* state. The He* lifetime τ_{He*} is then

$$\tau_{He*} = \frac{t_2 - t_1}{\ln \frac{n_{He*1}}{n_{He*2}}},\tag{34}$$

where n_{He*1} and n_{He*2} are He* concentrations at time t_1 and t_2 , respectively. From Fig. 44, we then obtain a He* lifetime $\tau_{He*} = 100 ns$. Again, this lifetime is mainly the result of quenching with air species diffusing into the plasma gas, and a $\tau_{He*} = 100 ns$ lifetime corresponds to an air partial pressure of 2.5 Torr if He(2s³S) dominates or 1.3 Torr if He(2s¹S) dominates. As explained above, we also verify the experimental result by conducting a two-dimensional fluid flow and mass transfer simulations, which shows a similar air partial pressure of 2.0 Torr near the substrate surface, thus confirming the mechanisms presented here.



Fig. 44: Decay of N_2^+ and He emission at the substrate surface. Part of the applied voltage waveform is also shown.

Time-resolved emission of O at 844 (Fig. 42) along the axis ($\theta_2 = 0^\circ$) behaves similarly to N₂⁺ emission, comprising a peak near maximum positive voltage along with a constant background emission throughout the rest of the cycle. The near substrate emission ($\theta_2 = 40^\circ$) also shows a similar decay rate of ~100 ns, suggesting an analogous excitation mechanism involving collisions with long-lived He*:

$$He(2^{3}S) + O_{2} \rightarrow O(3^{5}P) + O + He$$

$$\Delta E = 5.11 + 10.74 - 19.8 = -3.95 \text{ eV},$$
(35)

$$He(2^{3}S) + O_{2} \rightarrow O(3^{3}P) + O + He$$

$$\Delta E = 5.11 + 10.99 - 19.8 = -3.7 \text{ eV},$$
(36)

$$He(2^{1}S) + O_{2} \rightarrow O(3^{5}P) + O + He$$

$$\Delta E = 5.11 + 10.74 - 20.6 = -4.75 \ eV,$$
(37)

and

$$He(2^{1}S) + O_{2} \rightarrow O(3^{3}P) + O + He$$

$$\Delta E = 5.11 + 10.99 - 20.6 = -4.5 \text{ eV}.$$
(38)

Production of $O(3^5P)$ or $O(3^3P)$ by collisions of O with He^{*} is not feasible because, similar to N₂, reactions with He^{*} must account for the consumption of the excess energy, and transferring that energy as translational energy into the two products alone is not sufficient. On the other hand, in reactions of O₂ with He^{*}, three products are created (two O atoms and one He atom), with the O atoms taking up the excess energy as translational energy. Similarly, reactions of H₂O with He^{*} is also feasible as a third product is created

$$He(2^{3}S) + H_{2}O \rightarrow H_{2} + O(3^{3}P) + He$$

$$\Delta E = 5.09 + 10.99 - 19.8 = -3.72 \ eV$$
(39)

and

$$He(2^{1}S) + H_{2}O \rightarrow H_{2} + O(3^{3}P) + He$$

$$\Delta E = 5.09 + 10.99 - 20.6 = -4.52 \text{ eV}.$$
(40)

Aside from direct production of $O(3^{3}P)$, $H_{2}O$ can also act as a source of $O(3^{3}P)$ by reactions with He* through a two-step process, in which OH is an intermediary.

Unlike all the species emissions studied so far, time-resolved emissions of H (Fig. 40) and OH (Fig. 41) along the plasma axis ($\theta_2 = 0^\circ$) show no sharp peak near maximum positive voltage, instead they exhibit an almost constant emission throughout the cycle. The reason for this difference is due to the origin of H and OH in the plasma. Like N₂⁺ and O, H and OH are excited by He^{*} and show emissions throughout the voltage cycle due to He^{*}'s long lifetime. However, unlike N₂⁺ and O, H and OH are not present in large

quantities in air, and as such diffusion from air into the plasma gas is insignificant. Thus the only appreciable source of H and OH in the plasma gas is through He (99.999%) feed gas impurities, most likely in the form of H_2O .

The excitation of $H(3^2D)$ follows the reactions

$$He(2^{3}S) + H_{2}O \rightarrow H(3^{2}D) + OH + He$$

$$\Delta E = 5.17 + 12.09 - 19.8 = -2.54 \ eV$$
(41)

and

$$He(2^{1}S) + H_{2}O \rightarrow H(3^{2}D) + OH + He$$

$$\Delta E = 5.17 + 12.09 - 20.6 = -3.34 \text{ eV}.$$
(42)

Similar to N_2^+ and O, excitation with He* requires a third product to absorb the excess energy as translational energy. As such, it is only possible for He* to react and excite H₂O but not H directly.

Excitation of OH is as follows,

$$He(2^{3}S) + H_{2}O \rightarrow H + OH(A^{2}\Sigma^{+}) + He$$

$$\Delta E = 5.17 + 4.05 - 19.8 = -10.58 \ eV$$
(43)

and

$$He(2^{1}S) + H_{2}O \to H + OH(A^{2}\Sigma^{+}) + He$$

$$\Delta E = 5.17 + 4.05 - 20.6 = -11.38 \text{ eV}.$$
(44)

 $OH(A^2\Sigma^+)$ time resolved emission has a distinct feature in its long tail following the peak at maximum positive voltage when probing near the substrate ($\theta_2 = 40^\circ$). The same peak observed in N₂⁺, O, and H emissions are sharp, without the long tail, as their emission lifetime demonstrate fast He* quenching near the substrate. In the case of OH, its emission lifetime is the combination of He* lifetime and $OH(A^2\Sigma^+)$ 700 ns lifetime (no apparent quenching by He or air), thus resulting in a longer decay time.

4.6 Aspects of plasma jet evolution:

The evolution of the plasma jet can be gleaned from N₂ time-resolved emission, shown in Fig. 38. Electron impact excitation of N₂ requires lower energy compared to excitation of He, thus N₂ emission can be used to track lower energy electrons, while He emission represents higher energy electrons. N₂ time-resolved emission measurements made either along the axis ($\theta_2=0^\circ$) or at near substrate ($\theta_2=40^\circ$), show a small peak (arrows on the left side of Fig. 38) before the main peak. The lack of this feature in He emission (Fig. 36) shows that this small peak is the result of excitation by lower energy electrons that can excite N₂ but not He. Comparison of observations of the same peak between probing along the axis ($\theta_2=0^\circ$) and probing near the substrate ($\theta_2=40^\circ$) reveals that the peak appears along the axis first (red arrow on the left side of Fig. 38), then near the substrate 390 ns later (green arrow on the left side in Fig. 38). We ascribe this emission to an ionization wave travelling (on average) at 2 cm/(390 x 10⁻⁹ s) = 5 x 10⁶ cm/s, ionizing (and exciting) the gas on its way. The ionization wave produces an ionization channel between the tube and the substrate, with the substrate acting as a counter electrode⁶¹. The plasma plume touches the substrate during the positive voltage period and positively charges the substrate surface.⁶²

When the voltage of the powered electrode moves onto the negative period, electrons are pushed outside of the tube, toward the substrate where they neutralized the positive charge. The electrons collide with various species during this movement, resulting in a weak emission seen near the surface (at θ_2 =40° of N₂ emission in fig. 38), 700 ns before the peak negative voltage. Electrons only start this process once the voltage swings into the negative, and need to reach the substrate before the appearance of the emission peak (Fig. 38), leaving them 500 ns to cross a 2 cm gap from the nozzle to the substrate. The drift velocity of electrons in an electric field can be estimated as

$$v_{drift} = E \times \mu_{He},\tag{45}$$

where v_{drift} is electron drift velocity, *E* is the applied electric field, and μ_{He} is electron mobility in He. Considering that the electron mobility in He at 300 K and 1 atm is 10⁶ cm² /kV-s⁶³, then there needs to be an electric field of at least 4kV/cm on average to move the electrons 2 cm in 500 ns. The 4 kV/cm number is comparable to that measured by Sretenović et al⁶⁴, thus confirming the validity of this hypothesis.

The emission caused by these electrons appears at the same time in both N₂ timeresolved emissions probed at $\theta_2=0^\circ$ or $\theta_2=40^\circ$, as shown in Fig. 38, meaning that this emission is predominantly appearing only at the substrate surface. This is because the electric field needed to move the electrons does not need to be constant along the distance, so long as the 4kV/cm average is achieved. Thus it is entirely possible for the bulk of the electric field strength to concentrate near the substrate⁶⁵, where it energizes the electrons to cause the most excitations and subsequently the most emissions. The increase in N₂ concentration from air diffusion with distance away from nozzle and toward the substrate further enhances this effect.

4.7 Summary and Conclusions

In this section, we studied a helium atmospheric pressure plasma jet emerging from a quartz tube in open air at 1 atm using optical emission spectroscopy. The plasma setup included two copper rings, a 200 kHz radio frequency (RF) electrode and a grounded electrode, wrapped around the tube. Plasma emanating from the tube impinged on a dielectric substrate, either a MgF₂ window sealed to a vacuum UV spectrometer, or the flat face of a half-cylinder quartz prism with semicircular cross section. Time resolved emissions (over the RF cycle) and time-average emissions were probed in two configurations, namely, along the axis where the entire length of the plasma jet was recorded, or at an angle so as to isolate and record only plasma emission near (<0.3 mm) the substrate surface.

Near-substrate time-resolved emission was only briefly observed when the applied RF voltage was near its peak positive value. When the applied voltage turned negative, no emission was present near the surface, except for a weak emission from $N_2(C^3\Pi_u \rightarrow B^3\Pi_g, 337 \text{ nm})$ shortly before the peak negative voltage was reached. By comparing time-resolved emission probed near the substrate to emission probed along the entire jet, we were able to

determine the spatial positions as well as the excitation mechanism of various species. Helium emission (706 mm) was present along the entire plasma, both outside and inside the tube, while emission from H (656 nm), O (777 nm and 844 nm) and OH (309 nm) was mostly from inside the tube, as these originate mainly from feed gas impurities. On the other hand, N₂ comes into contact with the plasma through air diffusion, thus N₂ (337 nm) and N₂⁺(391 nm) emissions were only present in the plasma between nozzle and substrate, when the plasma extends beyond the nozzle, during positive voltage.

Emissions along the discharge, from species either due to air diffusions (N_2^+) or feed gas impurities (H, O, OH) were primarily excited by He metastables (He*). N_2^+ emission was a result of Penning ionization between He* and N_2 diffused from air, yet it was present even during the negative part of the applied voltage cycle, when the plasma was confined inside the tube and did not come in contact with air. It was conjectured that He* from inside the tube were transported outside the tube by a radiation transport process, which requires He VUV emissions in the 50-60 nm range to be radiation-trapped (as is expected at atmospheric pressure), causing them to be absorbed and re-emitted as they moved out of the nozzle, eventually producing $2p^1P^o$ He that decayed into the $2s^1S$ metastable state, responsible for N_2^+ production outside the tube.

As N_2 and He emissions were the result of electron impact excitation, they showed a strong time-dependence with the voltage cycle, especially at the zero voltage crossing where no energetic electrons were present, leading to no emission being observed. Emissions produced by collisions of He^{*} with N₂, O₂ and H₂O, on the other hand, were weakly modulated with respect to the RF period, particularly showing emissions even at the zero voltage crossing. Furthermore, N₂⁺ emission was shifted in phase with respect to the peak negative voltage, which can be used to deduce the effective lifetime of He* responsible for this excitation, as well as the rate of He* quenching by diffused air.

Insight on formation and evolution of the plasma jet can be extracted from timeresolved emissions of He, N₂, and N₂⁺. Helium emission is representative of the number density of higher energy electrons, while N₂ emission reflects the number density of lower energy electrons. N₂ time-resolved emission revealed the presence of a weak ionization wave propagating during the positive voltage part of the cycle, but well before the peak positive voltage. Only N₂ (and not He) was excited by this ionization wave, owing to its low electron energy. Ionization and excitation in the substrate-nozzle gap reached their maximum as the voltage reached its peak positive value, and the plasma in the gap became brightest. This plasma positively charged the insulating substrate, which then attracted electrons towards the substrate, as the applied voltage turned negative, to both neutralize the positive charge and cause a brief N₂ emission near the substrate.

5. MEASUREMENT OF GAS TEMPERATURE AND ELECTRON DENSITY IN AN ATMOSPHERIC PRESSURE PLASMA JET

5.1 Measurement of gas temperature

We measured the gas temperature of the APPJ shown in fig. 25 and 26 by fitting the rotational temperature of the N₂ ($C^3\Pi_{\mu} \rightarrow B^3\Pi_{\mu}$) emission band. This transition spawns numerous emission peaks due to its various vibrational and rotational levels. A transition can be from a certain vibrational level (v' = 0, 1, 2, ...) to another vibrational level (v'' = 0, 1, 2, ...) 0, 1, 2, ...). For each of these distinct vibrational transitions, there are numerous rotational transitions from a certain rotational level (J' = 0, 1, 2, ...) to another rotational level (J'' = 0, 1, 2, ...)(0, 1, 2, ...).^{66,67} As the rotational transitions belonging to a particular vibrational transition are closely spaced together, they form a band as shown in fig. 45. On the other hand, the vibrational transitions are spaced further apart: $(v' = 0 \text{ to } v'' = 0 \text{ peaks at } 337 \text{ nm}, v' = 0 \text{ to } v'' = 0 \text$ v'' = 1 peaks at 357.5 nm, and v' = 0 to v'' = 2 peaks at 380 nm). Due to interference from the NH ($A^3\Pi_i \rightarrow X^3\Sigma^-$) emission at 335.8 nm, the strongest N₂ ($C^3\Pi_u \rightarrow B^3\Pi_g$) transition v' = 0 to v" = 0 that peaks at 337 nm was not used. Instead, the second strongest N₂ ($C^3\Pi_u \rightarrow$ $B^{3}\Pi_{g}$) transition v' = 0 to v'' = 1 that peaks at 357.5 nm was used. The rotational temperature of this transition, which dictates the distribution of the various J transitions that subsequently determines the shape of the band, can be used to measure the gas temperature^{66–70}.

The relationship between the N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$) emission and gas temperature depends on how N_2 is excited to the $C^3\Pi_u$ state. We first assume that the ground state of N_2 is at a rotational temperature that is in equilibrium with the gas temperature due to facile energy transfer and the high collisionality at atmospheric pressure. In an Ar plasma, N_2 ($C^3\Pi_u$) is created by three reactions:

$$e + N_2 (X {}^{1}\Sigma_g) \rightarrow e + N_2 (C {}^{3}\Pi_u, \nu' = 0, 1, 2, ...),$$
(46)

$$Ar^{*} ({}^{3}P_{2}) + N_{2} (X {}^{1}\Sigma_{g}) \rightarrow Ar + N_{2} (C {}^{3}\Pi_{u}, \nu' = 0, 1, 2),$$
(47)

and

$$Ar^{*} ({}^{3}P_{0}) + N_{2} (X {}^{1}\Sigma_{g}) \rightarrow Ar + N_{2} (C {}^{3}\Pi_{u}, v' = 0, 1, 2, 3).^{69}$$
(48)

Electron impact reaction shown by eqn. 46, produces N_2 ($C^3\Pi_u$) with rotational distribution that initially is not in equilibrium with gas temperature. Nevertheless, the high frequency of collisions between N_2 ($C^3\Pi_u$) and the background gas quickly equilibrates N_2 ($C^3\Pi_u$) with the gas temperature⁶⁸ before it can emit and return to the ground state. Emission from this N_2 ($C^3\Pi_u$) can then be fitted to a rotational temperature that is equal to the gas temperature.

Electrons are light enough not to alter the rotational temperature of N₂ molecules during excitation collisions (eqn. 46), leaving the excited N₂ ($C^3\Pi_u$) state with the same rotational temperature as that of the ground state. Unlike N₂ ($C^3\Pi_u$) produced by electron impact excitation, N₂ ($C^3\Pi_u$) produced by Ar* (eqn. 47 and 48) does not carry the same rotational distribution as that of the ground state N₂ due to the energetic Ar* resulting in much higher rotational temperature of the N₂ ($C^3\Pi_u$) state compared to the ground state .^{69,71,72} The N₂ ($C^3\Pi_u$) rotational temperature does not equilibrate to the gas temperature in time before emission occurs.⁶⁹ The result is that the observed emission from N_2 ($C^3\Pi_u$) is the combined emissions of both N_2 ($C^3\Pi_u$) produced by electron impact and N_2 ($C^3\Pi_u$) produced by collisions with Ar*.^{69,71,72}

Because of the presence of two N₂ ($C^3\Pi_u$) populations, each with its own rotational temperature, fitting must be carried out so that it accommodates these two populations. To that end, a two-temperature fit was used instead of a one-temperature fit. The onetemperature fit assumes that all emissions observed are due to N₂ ($C^3\Pi_u$) from electron impacts and thus their rotational temperature is the same as gas temperature. On the other hand, the two-temperature fit assumes that the observed emission is partly due to N₂ ($C^3\Pi_u$) from electron impact and part due to N₂ ($C^3\Pi_u$) from Ar*-N₂ collisions. The ratio between these two populations is unknown and is considered a fitting parameter. The twotemperature fit would then sum up the emissions from the two N₂ ($C^3\Pi_u$) populations and iterate until the best fit is achieved. The higher temperature from the N₂ ($C^3\Pi_u$) that is excited by Ar^{*} is of little value. The lower temperature from N₂ (C³ Π_u) that is excited by electron impact is taken as the gas temperature. In summary, measurement of gas temperature in Ar plasma was done with a two-temperature fit (fig. 45a) while measurement of He plasma gas temperature was instead carried out with a one-temperature fit (fig. 45b).



Figure 45: Fitting of N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$) (0-1) band with two-temperature fit (a), and one-temperature fit (b).

5.2 Measurement of electron density

The electron density was measured by Stark broadening using the H-Balmer β line produced by adding a trace amount of H₂ in the plasma. The shape and width of the H-Balmer β line are the result of many broadening mechanisms, including instrumental broadening, Doppler broadening, Van der Waals or pressure broadening, and Stark broadening⁶⁸. These four broadening mechanisms are divided into Gaussian and Lorentzian components.

The Gaussian component comprises of instrumental and Doppler broadening, the shape of which can be expressed as

$$I_{Gau}(x,\lambda_{Gau}) = \exp\left(\frac{x-\mu}{\frac{\lambda_{Gau}^2}{4\ln^2}}\right),\tag{49}$$

where $I_{Gau}(x, \lambda_{Gau})$ is the intensity, x is wavelength, μ is center wavelength (ideally at 486.1 nm), and λ_{Gau} is the full width half max (FWHM), the width of the distribution at half of its peak intensity. The total Gaussian FWHM λ_G is the result of its two components, instrumental and Doppler broadening, and is calculated by

$$\lambda_{Gau} = \sqrt{\lambda_{instr}^2 + \lambda_{Dop}^2},\tag{50}$$

where λ_{instr} is the FWHM of the instrumental broadening, and λ_{Dop} is the FWHM of the Doppler broadening.

Instrumental broadening, λ_{instr} , is the broadening resulting from the spectrometer. It is usually an approximately Gaussian distribution, and can be obtained from a single atomic emission line, such Ar 750.4 nm, that is only affected by instrumental broadening.

Doppler broadening comes from the thermal velocity of the emitting H atom that either adds or subtract from the wavelength of the photons being observed. On average, the sum of the thermal movement of all the emitting H atoms adds up to a Gaussian distribution, the FWHM of which is a function of gas temperature and can be calculated by

$$\lambda_{Dop} = 7.16 \times 10^{-7} \mu \sqrt{\frac{T_h}{M}},\tag{51}$$

where λ_{Dop} is the Doppler FWHM in Å, μ is the emission wavelength in Å, T_h is the temperature of the emitter (H atoms) in K (assumed to be equal to the gas temperature), and M is the H atomic weight in g/mol. Doppler broadening, together with instrument broadening, make up the Gaussian component of the total H-Balmer β line shape.

The Lorentzian component of the H-Balmer β lineshape, can be expressed as

$$I_{Lor}(x,\lambda_{Lor}) = \frac{1}{\left(1 + \left(\frac{x-\mu}{\frac{\lambda_{Lor}}{2}}\right)^2\right)},$$
(52)

where $I_{Lor}(x, \lambda_{Lor})$ is the intensity, x is wavelength, μ is center wavelength, and λ_{Lor} is the FWMH of the Lorentzian lineshape. The Lorentzian component is a combination of Van der Waals and Stark broadening,

$$\lambda_{Lor} = \lambda_{Stark} + \lambda_{Van \ der \ Waals},\tag{53}$$

where λ_{Stark} is the FWHM of the Stark component and $\lambda_{Van \ der \ Waals}$ is the FWHM of the Van der Waals component.

Van der Waals or pressure broadening is the result of collisions between the emitters (H atoms) and the perturbers (mostly plasma feed gas, which is either Ar or He). As this broadening is directly related to collision rate, it is a function of both species density and gas temperature,

$$\lambda_{Van \, der \, Waals} = 4.09 \times 10^{-13} \mu^2 (\bar{\alpha} \bar{R}^2)^{2/5} \left(\frac{T_g}{\mu}\right)^{3/10} n_{pert} \,, \tag{54}$$

where $\lambda_{Van \ der \ Waals}$ is the FWHM of Van der Waals broadening, μ is the emission wavelength, $\bar{\alpha}$ is the average polarizability of neutral perturbers, \bar{R}^2 is the weighted average of the squared radii of the emitters, T_g is gas temperature, and n_{pert} is the density of the perturbers. In this study, ideal gas is assumed and since pressure is fixed at 1 atm, species density can be calculated from gas temperature. As the result, Van der Waals broadening only depends on gas temperature, and can be simplified as

$$\lambda_{Van\,der\,Waals} = \frac{C}{T_g^{\frac{7}{10}}},\tag{55}$$

where $\lambda_{Van \ der \ Waals}$ is the FWHM of the Van der Waals broadening in Å, *C* is a constant depending on whether Ar or He is used as feed gas, and can be calculated according to Hofmann et al⁷³.

Finally, Stark broadening is the result of electrons perturbing nearby H atoms during their emissions. The emitting H atoms would have their emission energy disrupted by these electrons local electric field, causing the emissions to be either higher or lower in wavelength. On average, the emissions would be broadened into a Lorentzian shape, with width directly tied to the density of the surrounding electrons (Stark broadening). By measuring the width of Stark broadening, one can determine the electron density. The relationship between the Stark broadening FWHM and the electron density is

$$\lambda_{Stark} = 2.5 \times 10^{-9} \alpha_{n'n} n_e^{2/3},\tag{56}$$

where λ_{Stark} is in Å, $\alpha_{n'n}$ is a parameter for each transition n' - n, which can be found in⁷⁴, and n_e is the electron density in cm⁻³. Stark broadening, together with Van der Waals broadening, form the Lorentzian component of the H-Balmer β lineshape.

The overall H-Balmer β lineshape is that of the Voigt function, which is a mathematical convolution of a Gaussian and a Lorentzian shape,

$$I_{Voigt}(x,\lambda_{Gau},\lambda_{Lor}) = \int_{-\infty}^{\infty} I_{Gau}(x',\lambda_{Gau}) I_{Lor}(x-x',\lambda_{Lor}) dx', \qquad (57)$$

where I_{Voigt} is the intensity of the Voigt profile, I_{Gau} and I_{Lor} are the intensities of the Gaussian and the Lorentzian components, respectively, and λ_{Gau} and λ_{Lor} are the FWHM

of the Gaussian and the Lorentzian components, respectively. Since a convolution does not depend on the order of its component, the Voigt profile can also be written as

$$I_{Voigt}(x,\lambda_{Gau},\lambda_{Lor}) = \int_{-\infty}^{\infty} I_{Gau}(x-x',\lambda_{Gau}) I_{Lor}(x',\lambda_{Lor}) dx' .$$
 (58)

In practice, the spectrometer used (TRIAX 550 with a PI-MAX ICCD) did not give a Gaussian line shape. A single line emission was recorded instead, and used as the instrumental line shape in lieu of a Gaussian distribution. Furthermore, the Doppler broadening is small compared to the instrumental broadening (would only increase the FWHM by about 4%) and thus can be ignored.

5.3 Experimental setup for measurements of gas temperature and electron density

The setup used for measurement of gas temperature and electron density is shown in fig. 46. The plasma source is the one ring and needle APPJ, with or without the shielding gas apparatus (Fig. 25, 26). The feed gas is either He (99.999%) or Ar (99.999%) at 1.5 slm flow rate. The applied voltage is sinusoidal at 13 MHz, varying from 1 to 4 kV peakto-peak. Measurements were performed with or without the quartz substrate at varying distance from the nozzle, as well as with or without the grounded copper plate behind the substrate. Additionally, when the grounded copper was present, the thickness of the quartz substrate was also varied. Finally, for experiments with the shielding gas apparatus, the shielding gas flow was varied.

Emissions were taken spatially resolved with respect to the plasma jet axis, with a 2 mm slit to improve spatial resolution. The emission lines of interest were the strongest

vibrational transitions of the N₂ ($C^3\Pi_u \rightarrow B^3\Pi_g$) bands (0-0 at 337 nm, 0-1 at 358 nm, 0-2 at 381 nm) and the H-Balmer β at 486 nm. The H-Balmer β emission was taken with the ICCD-equipped spectrometer, while the N₂ ($C^3\Pi_u \rightarrow B^3\Pi_g$) emission was taken with the Ocean Optics spectrometer.

A small fraction of light at all wavelengths scatters off the grating and other optical components and strikes the ICCD, creating a wavelength-independent background. To minimize this background, an appropriate band pass filter (4-94 or 4784, passing 400-500 nm) was used in front on the optic fiber input slit. Furthermore, a background subtraction was used to produce a clean H-Balmer β line.

The background subtraction procedure included taking two spectra at different center wavelength, both including the H-Balmer β line. One spectrum covered the range 478-500 nm, while the other spectrum covered the range 486-508 nm range. Then, the 486-508 nm intensity array was subtracted from the 478-500 nm intensity array. Each spectrum will have the H-Balmer β line at different parts of the corresponding intensity array, thus subtracting one from the other removes the background from the H-Balmer β emission.



Figure 46: Setup for collection of plasma emission for the purpose of measuring gas temperature and electron density.

5.4 Gas temperature and electron density in Ar (0.02% H₂) atmospheric pressure plasma jet

Time average emission of Ar (0.02% H2) (fig. 47) in an APPJ along the plasma jet axis shows respective Ar peaks, along with N_2 , NO, NH, O, and OH from either air diffusion or feed impurities. When He was instead used as the feed gas, the emission spectra included the same impurity peaks, plus strong He lines (Fig. 47).





Figure 47: Emission of Ar (0.02% H₂) RF plasma jet, over the wavelength range 200-900 nm recorded perpendicular to the axis of symmetry, 4 mm distance from the nozzle.

Gas temperature was measured with the jet impinging onto a quartz substrate, as shown in Fig. 46, but without the grounded copper plate behind the substrate. Emission was collected within 2 mm of the substrate (near-substrate region). The power applied to the plasma and the nozzle-substrate distance were varied (Fig. 48) or only the nozzle-substrate distance was varied with power fixed at 18 W (Fig. 49). Fig. 48 shows that the near-substrate gas temperature increases from 400 K to up to 600 K with increasing power from 9 W to 18 W. Increasing power increases the electron density and in turn the electron-atom collision frequency, resulting in more energy transfer and higher gas temperature.



Figure 48: Ar plasma gas temperature as a function of power, measured near the quartz substrate surface with varying distance between substrate and nozzle.

The near-substrate gas temperature as a function of nozzle-substrate distance was also measured (fig. 49). The gas temperature within 2 mm of the substrate remains fairly constant at 450 K with respect to substrate position. This contradicts the dependence of gas temperature on nozzle-substrate distance shown in fig. 48. This is likely due to day-to-day variations in the ambient conditions (e.g. humidity), directly affecting the plasma. The gas temperature near the substrate surface does not depend on the substrate position because gas heating occurs primarily by the plasma inside the tube and it is largely independent of the conditions outside. The gas temperature outside the tube is expected to depend mainly on gas flow rate (see below).



Figure 49: Ar plasma gas temperature as a function of nozzle-quartz substrate distance (18 W applied power), probed near the substrate surface.

We also looked at the effect of the quartz substrate on gas temperature along the jet axis, this time with a fixed 10 mm nozzle-substrate distance and 18 W applied power. Gas temperature does not depend on axial distance from the nozzle or the presence of the quartz substrate, and instead stays relatively constant at 450 K (Fig. 50). As explained above, gas heating occurs mainly by the plasma inside the tube and is unaffected by the presence of the quartz substrate. Furthermore, for small distances from the nozzle, air diffusion into the plasma jet is not high enough to exert cooling, leading to a flat temperature distribution with respect to axial distance from nozzle.



Figure 50: Ar plasma gas temperature as a function of distance from nozzle (18 W applied power), with and without substrate. The substrate was 10 mm away from the nozzle.

The dependence of gas temperature on feed gas flow rate was also examined. Fig. 51 shows that the gas temperature decreases from 600 K to 400 K as Ar feed flow rate increases from 1.5 slm to 3.0 slm, at constant 18 W applied power, without substrate. This reduction in gas temperature is due to convection cooling due to increasing feed gas flow rate, while maintaining a constant source of gas heating as plasma power was kept constant.


Figure 51: Ar plasma gas temperature at an axial distance of 4 mm from the nozzle, as a function of Ar feed flow rate. Applied power was 18 W.

Unfortunately, for most experimental conditions, the electron density was below the detection limit of the Stark broadening method (10^{13} cm⁻³). To increase the electron density to a measurable value, a grounded copper sheet was attached to the back of the quartz substrate. Gas temperature and electron density were then measured either at the region near the substrate, as a function of substrate thickness, or at the same location with no substrate present (Fig. 52). Gas temperature remains constant at 650 K with and without the grounded copper. The reason is similar to that discussed above, namely, gas heating occurs mainly by the plasma inside the tube, which is unaffected by changes in substrate 10 mm away from the nozzle. Electron density, on the other hand, increases from $3x10^{13}$ cm⁻³ to $5x10^{13}$ cm⁻³ with the addition of the grounded copper. When no nearby ground is present, the plasma seeks ground at "infinity" resulting in weaker plasma, because of the higher resistance to ground. With a ground nearby, the resistance to ground decreases, resulting in stronger plasma (i.e., higher electron density).





Figure 52: Ar plasma gas temperature (a), and electron density (b) with no substrate, or quartz substrate of different thickness, or quartz substrate with a grounded copper sheet behind it.

5.5 Gas temperature and electron density of He (0.02% H₂) atmospheric pressure plasma jet

Gas temperature and electron density were also measured with He feed gas. All the measurements in Fig. 53 were taken on the same day, to minimize drift. Similar to the Ar plasma, the He plasma gas temperature increases from 650 K to 750 K with increasing applied power from 19 W to 24 W, while remaining constant with distance from nozzle (Fig. 53, no substrate). The addition of a grounded substrate 5 mm away from the nozzle also does not affect the gas temperature.



Figure 53: Gas temperature as a function of distance from nozzle, at different applied power, with or without a grounded substrate, He feed gas.

Measurements were also carried out with the plasma source equipped with a shielding gas apparatus (Fig. 36 and 37). As noted before, the increased length of the ground electrode lengthens the plasma, increasing both the power consumption (up to 60 W) and heating inside the tube, resulting in higher gas temperatures in the plasma plume. Both Fig. 54a and 54b show gas temperatures of nearly 1000 K without shielding gas flow. With 9 slm shielding gas flow, the temperature drops to 850 K for Ar shielding gas, and 800 K for N₂ shielding gas. The lower gas temperature with increasing shielding gas flow rate is again due to convective heat removal. The annular cold shielding gas column removes heat from the outer surface of the helium gas column. This is facilitated by the high thermal conductivity of helium, allowing for rapid radial heat transport to the shielding gas and heat removal by the shielding gas flow.



Figure 54: Gas temperature as a function of Ar (a) or N_2 (b) shielding gas flow rate with 2 slm He feed gas, at 5 mm axial distance from the nozzle.

5.6 Summary and Conclusions

In this section, we explored gas temperature and electron density in the one ring and needle electrode APPJ operated with either Ar or He feed gas, with or without Ar or N₂ shielding gas. The feed gas flows through a capillary tube wrapped by a grounded copper electrode. Sinewave voltage at 13.5 MHz, 1- 4 kV (peak-to-peak), 9 W – 24 W power is applied to a needle electrode in the middle of the tube without shielding gas, or 60 W with shielding gas. Gas temperature is measured by fitting the rotational temperature of the N₂ (C³ $\Pi_u \rightarrow B^3\Pi_g$) emission, while electron density is measured by fitting the Stark broadening of the H-Balmer β line.

In a He plasma, electron impact excitation is the only means of exciting N₂ into N₂ (C³ Π_u), thus the N₂ (C³ $\Pi_u \rightarrow B^3\Pi_g$) rotational temperature is representative of the gas temperature. On the other hand, in an Ar plasma, in addition to electrons, Ar* can also excite N₂. The N₂ (C³ $\Pi_u \rightarrow B^3\Pi_g$) therefore emission carries two populations, one with a high temperature from Ar* excitation and another with a low temperature, representative of the gas temperature, from electron impact excitation. In this case, a two-temperature fit was necessary to extract the N₂ (C³ $\Pi_u \rightarrow B^3\Pi_g$) emission rotational temperature that is representative of gas temperature.

As for measurement of electron density, the H-Balmer β line is broadened by many mechanisms, one of which is Stark broadening that is representative of electron density. The H-Balmer β line shape is a convolution of the instrument shape and a Lorentzian shape, which is the sum total of van de Waals broadening and Stark broadening. The van de Waals broadening can be calculated from gas temperature. By fitting the H-Balmer β emission line for the total broadening, we can find the remaining Stark broadening, which can be translated into electron density.

Gas temperature shows similar behavior in both Ar and He plasma. Both demonstrate increasing gas temperature (400 K – 600 K for Ar, 650 K – 750 K for He) with increasing applied power (9 W – 18 W for Ar, 19 W – 24 W for He). The gas is mainly heated by plasma inside the tube before flowing out, without substantial cooling by surrounding air. Therefore, the gas temperature is almost constant along the plasma jet axis. The addition of a grounded copper sheet, either as the substrate or behind a quartz substrate, also does not change the gas temperature, supporting the hypothesis that it is the plasma inside the tube that is mainly responsible for gas heating. Inclusion of a shielding gas apparatus necessitates a longer grounded copper ring electrode, leading to a larger plasma volume inside the tube and subsequently increasing the gas temperature to nearly 1000 K without shielding gas flow. Ar or N₂ shielding gas flow at 9 slm cools the gas down to 850 K at an axial distance of 5 mm from the nozzle.

Unfortunately, electron density was mostly under the 10^{13} cm⁻³ detection limit. Electron density was only measureable in Ar jet with a grounded copper sheet behind a quartz substrate. The result was enhancement of electron density from 2.5×10^{13} cm⁻³ without the copper ground to 5×10^{13} cm⁻³ with the copper ground. Increasing the thickness of the quartz substrate from 3.5 mm to 7.5 mm did not affect either the electron density or the gas temperature.

CHAPTER 6: RADIAL DISTRIBUTION OF AIR SPECIES DIFFUSING INTO AN RF HELIUM ATMOSPHERIC PRESSURE PLASMA JET

As the plasma jet operates in air, diffusion of air species heavily shapes the plasma properties, including the creation of various reactive oxygen and nitrogen species useful for plasma medical applications.^{9,10}. Knowledge and control of this diffusion is therefore imperative for plasma medicine. To that end, we measured the radial distribution of air species diffusing into a plasma jet via actinometry. We also evaluated the effectiveness of blocking air diffusion with a shielding gas curtain, as shown in Fig. 26. The plasma is powered by a 13.7 MHz, 1.7 kV peak-to-peak sinewave voltage, with 2 slm He feed gas and up to 4.5 slm N₂ shielding gas. The method of actinometry requires first acquiring the emissions from species of interest, before converting them to the respective species mole fractions. Therefore, measuring the radial distribution of air species would require obtaining the radial distribution of their emissions.

6.1 Radial distribution of plasma emissions

The plasma is radially symmetric, due to the symmetrical design of the source. Even though the He feed gas is lighter than air, the plasma length is short (~ 1 cm) and we only measure up to 5 mm from the nozzle, thus no obvious gravity effect is present. The plasma radial emission can be used in actinometry to derive the density of various air species diffusing into the plasma gas. Plasma emission is first probed laterally (perpendicular to the axis), then converted into radial emission via Abel inversion. The setup for acquiring the emission is shown in fig. 55. Plasma emission is collected by a lens (15 cm focal length) to produce an inverted image, which is then probed by a spectrometer. Since the plasma

thickness is about 1 mm, the setup needs to have a depth of field (DOF) of at least 1 mm. Therefore, an aperture of 8 mm-diameter was placed in front of the lens resulting in a DOF of 1 mm as calculated by

$$DOF = \frac{\mu}{NA^2},\tag{59}$$

where μ is chosen to be 750 nm as it is close to the emissions in question (He at 706 nm, O at 777 nm, Ar at 811 nm). NA is calculated as

$$NA = \frac{r}{2f},\tag{60}$$

where r is the radius of the aperture, and f is the focal length of the lens. The resulting setup magnifies the image by a factor of 4, thus yielding an inverted image with thickness of 4 mm.



Figure 55: Schematic of elements used for collection of plasma emission.

The lateral distribution of plasma emission is probed with the optic fiber moving laterally, perpendicular to the plane of fig. 55. The fiber core is 0.5 mm in diameter, and axially-resolved images are probed with 0.25 mm increment. The emission lateral distribution is then converted to the corresponding radial distribution using a mathematical process called Abel inversion, based on the following formula

$$f(r) = -\frac{1}{r} \int_{r}^{\infty} \frac{dF}{dy} \frac{dy}{\sqrt{y^{2} - r^{2}}},$$
(61)

where r is radial distance, f(r) is the radial distribution (desired profile), y is the lateral distance, and F(y) is the lateral distribution (measured profile). While the mathematical formula is simple, a direct application of the measured F(y) yields results plagued by artifacts. This is because the formula expects the lateral distribution F to be a smooth curve, or a very large number of points resembling a smooth curve. Since we probe with a 0.25 mm increment over a 4 mm length, the resulting lateral distribution F is discontinuous, resulting in unwanted artifacts. The solution is to employ smoothing.

This smoothing procedure has two steps, interpolation and adjacent-average smoothing. First, the measured lateral distribution F is interpolated by a factor of 100, resulting in 100 points for every 0.25 mm increment. The interpolated F is then adjacent-averaged such that each point of the smoothed F is the average of 300 nearby points of the interpolated F. For example, the 500th point of smoothed F is the average of the 350th point to the 650th point of the interpolated F. Smoothed points near the edge are averaged from fewer points of the interpolated F (i.e., the 100th point of the smoothed F would be the average of the 1st point to the 199th point of the interpolated F). The reason for choosing an

average of 300 points is that the interpolated F has an increment of 0.0025 mm. The fiber diameter, on the other hand, is 0.5 mm. Thus an average of 300 points would result in smoothing over a distance of 0.75 mm, making sure that the signal received is in line with the resolution of the setup.

The smoothed F is then plugged into the Abel inversion formula (43), yielding a smooth radial distribution of the plasma emissions without unwanted artifacts. This method of acquiring the radial emission intensity was verified by applying it to a hollow cylinder-shaped light source and affirming that the resulted cross section emission is ring shaped. Further details are given in Appendix B.

6.2 Theory of self-actinometry

Emissions from He (706.6 nm), Ar (750.4 nm), O (777 nm), and N₂ (337 nm) were collected and converted into mole fractions to study the extend of air diffusion into the plasma jet. The self-actinometry method involves adding a trace amount of gas into the He feed flow to produce a small but measurable change in the emission intensity characteristic of the added gas species. This calibration would then be applied to emission intensities without the added trace gas to determine the amount diffused into the plasma by air diffusion alone. Without any trace gas addition, and ignoring products from plasma reactions, the total number density, n_T , at a particular radial and axial location (r, z) in the plasma jet, is given by the sum of their number densities,

$$n_T = n_{He} + n_{Ar} + n_{02} + n_{N2}. ag{62}$$

While He (706.6 nm), Ar (750.4 nm), and N₂ (337 nm) are excited by electron impact, O (777 nm) is excited by dissociative excitation of O₂ by collisions with He metastables (He^{*})^{49,54,75}. The respective excitation reactions are:

$$He + e \to He (3^{3}S) + e, \tag{63}$$

$$Ar + e \to Ar (4p 2[5/2] 2p_8) + e,$$
 (64)

$$N_2 + e \to N_2(\mathcal{C}^3 \Pi_u) + e, \tag{65}$$

and

$$O_2 + He(2^3S) \to He(3^3S) + O(3^5P) + O,$$
 (66)

where He* is the He ($2^{3}S$) metastable state created by electron impact of ground state He,

$$He + e \to He (2^{3}S) + e. \tag{67}$$

The rate for each reaction can be written as:

$$R_{He}^{0} = k_{He}^{0} n_{e}^{0} n_{He}, ag{68}$$

$$R_{Ar}^0 = k_{Ar}^0 n_e^0 n_{Ar}^0, (69)$$

$$R_{N_2}^0 = k_{N_2}^0 n_e^0 n_{N_2}^0, (70)$$

$$R_{O_2}^0 = k_{O_2}^0 n_{He*}^0 n_{O_2}^0, (71)$$

$$R_{He*}^0 = k_{He*}^0 n_e^0 n_{He*}^0, (72)$$

where n_e^0 , n_{He}^0 , n_{Ar}^0 , $n_{N_2}^0$, $n_{O_2}^0$, and n_{He*}^0 are the concentrations of e⁻, He, Ar, N₂, and O₂, respectively; while k_{He}^0 , k_{Ar}^0 , $k_{N_2}^0$, $k_{O_2}^0$, and k_{He*}^0 are electron energy dependent reaction rate coefficients. The superscript 0 refers to values without addition of trace gas to the He feed flow.

The excited state can either emit, or be quenched to a lower state by surrounding species without any emission. The emission yield can be written as:

$$Y_{He}^{0} = \frac{b_{He}A_{He}}{A_{He} + k_{q,He}^{He}n_{He} + k_{q,He}^{Ar}n_{Ar} + k_{q,He}^{O2}n_{O2} + k_{q,He}^{N2}n_{N2} + k_{q,He}^{e}n_{e}^{0}},$$
(73)

$$Y_{Ar}^{0} = \frac{b_{Ar}A_{Ar}}{A_{Ar} + k_{q,Ar}^{He} n_{He} + k_{q,Ar}^{Ar} n_{Ar} + k_{q,Ar}^{O2} n_{O2} + k_{q,Ar}^{N2} n_{N2} + k_{q,Ar}^{e} n_{e}^{0}},$$
(74)

$$Y_{N_2}^{0} = \frac{b_{N_2} A_{N_2}}{A_{N_2} + k_{q,N_2}^{He} n_{He} + k_{q,N_2}^{Ar} n_{Ar} + k_{q,N_2}^{O2} n_{O2} + k_{q,N_2}^{N_2} n_{N2} + k_{q,N_2}^{e} n_{e}^{0}},$$
(75)

and

$$Y_{O_2}^{0} = \frac{b_{N_2} A_{N_2}}{A_{O_2} + k_{q,O_2}^{He} n_{He} + k_{q,O_2}^{Ar} n_{Ar} + k_{q,O_2}^{O_2} n_{O_2} + k_{q,O_2}^{N_2} n_{N_2} + k_{q,O_2}^{e} n_{e}^{0}},$$
(76)

and

where A_{He} , A_{Ar} , A_{N_2} , and A_{O_2} are the Einstein A coefficients (representative of lifetime) of their respective species; b_{He} , b_{Ar} , b_{N_2} , and b_{N_2} , are the branching ratios; and $k_{q,Y}^X$ are the quenching rate constants of Y by X. The branching ratio in the numerator accounts for the probability of an excited state to emit at a particular wavelength. The branching ratios stay constant and are of no concern. However, quenching involves the density of surrounding species, and therefore must be accounted for when adding trace gases.

Taking into account the emission yields, the emission intensities are given by:

$$I_{He}^{0} = a_{He}^{0} n_{e}^{0} n_{He} Y_{He}^{0}, (77)$$

$$I_{Ar}^{0} = a_{Ar}^{0} n_{e}^{0} n_{Ar} Y_{Ar}^{0}, (78)$$

$$I_{N_2}^0 = a_{N_2}^0 n_e^0 n_{N_2} Y_{N_2}^0, (79)$$

and

$$I_{O_2}^0 = a_{O_2}^0 n_e^0 n_{O_2} Y_{O_2}^0. ag{80}$$

The "0" superscript is for values without trace gas addition. When trace gases are added, the intensities become:

$$I_{He} = a_{He} n_e n_{He} Y_{He}, \tag{81}$$

$$I_{Ar} = a_{Ar}n_e(n_{Ar} + \Delta n_{Ar})Y_{Ar}, \qquad (82)$$

$$I_{N_2} = a_{N_2} n_e (n_{N_2} + \Delta n_{N_2}) Y_{N_2}, \tag{83}$$

and

$$I_{O_2} = a_{O_2} n_{He*} (n_{O_2} + \Delta n_{O_2}) Y_{O_2}.$$
(84)

where Δn_{Ar} , Δn_{N_2} , Δn_{O_2} are the additional gas density due to the added trace gas. The addition of trace gas may perturb the plasma, changing its electron density and electron energy distribution, thereby impacting the reaction rate coefficient. Therefore, in eqn. 84, the electron density n_e , yields (Y_{He} , Y_{Ar} , Y_{N_2} , Y_{O_2}), and the reaction rate coefficient terms (a_{He} , a_{Ar} , etc.) no longer have the 0 superscript to differentiate them from the base values without trace gas addition.

The intensity ratios of Ar and N₂ over He before and after trace gas additions are:

$$\frac{I_{Ar}^{0}}{I_{He}^{0}} = \frac{a_{Ar}^{0} n_{e}^{0} n_{Ar} Y_{Ar}^{0}}{a_{He}^{0} n_{e}^{0} n_{He} Y_{He}^{0}},$$
(85)

$$\frac{I_{N_2}^0}{I_{He}^0} = \frac{a_{N_2}^0 n_e^0 n_{N_2} Y_{N_2}^0}{a_{He}^0 n_e^0 n_{He} Y_{He}^0},\tag{86}$$

$$\frac{I_{Ar}}{I_{He}} = \frac{a_{Ar}n_e(n_{Ar} + \Delta n_{Ar})Y_{Ar}}{a_{He}n_e n_{He}Y_{He}},\tag{87}$$

and

$$\frac{I_{N_2}}{I_{He}} = \frac{a_{N_2} n_e (n_{N_2} + \Delta n_{N_2}) Y_{N_2}}{a_{He} n_e n_{He} Y_{He}}.$$
(88)

By dividing the intensity ratios before gas addition over the intensity ratios after gas addition, and solving for mole fractions of Ar and N₂, we arrive at

$$n_{Ar} = \frac{\Delta n_{Ar}}{\left(\frac{a_{He}a_{Ar}^{0}}{a_{He}^{0}a_{Ar}}\right)\left(\frac{l_{He}^{0}Y_{He}}{l_{He}Y_{He}^{0}}\right)\left(\frac{l_{Ar}Y_{Ar}^{0}}{l_{Ar}^{0}Y_{Ar}}\right) - 1}$$
(89)

and

$$n_{N_2} = \frac{\Delta n_{N_2}}{\left(\frac{a_{He}a_{N_2}^0}{a_{He}^0 a_{N_2}}\right) \left(\frac{l_{He}^0 Y_{He}}{l_{He}Y_{He}^0}\right) \left(\frac{l_{N_2}Y_{N_2}^0}{l_{N_2}^0 Y_{N_2}}\right) - 1}.$$
(90)



Fig. 56. Measured He intensity as a function of N_2 , O_2 , and Ar addition at 1 mm, 3 mm and 5 mm axial distance from the nozzle.

Figure 56 shows that addition of trace gases to the He flow causes small changes in He emission, likely due to changes in the electron density and/or energy distribution. We assume that the reaction rate coefficients (a_{He} , a_{Ar} , a_{N_2}) share similar dependence on electron temperature, thus adding trace gas causes them all to change to the same degree,

$$\frac{a_{He}}{a_{He}^{0}} = \frac{a_{Ar}}{a_{Ar}^{0}} = \frac{a_{N_{2}}}{a_{N_{2}}^{0}},\tag{91}$$

resulting in the following expressions,

$$n_{Ar} = \frac{\Delta n_{Ar}}{\left(\frac{I_{He}^{0}Y_{He}}{I_{He}Y_{He}^{0}}\right)\left(\frac{I_{Ar}Y_{Ar}^{0}}{I_{Ar}^{0}Y_{Ar}}\right) - 1}$$
(92)

and

$$n_{N_2} = \frac{\Delta n_{N_2}}{\left(\frac{I_{He}^0 Y_{He}}{I_{He} Y_{He}^0}\right) \left(\frac{I_{N_2} Y_{N_2}^0}{I_{N_2}^0 Y_{N_2}}\right) - 1}.$$
(93)

While the Δn_{Ar} and Δn_{N_2} terms are the result of added trace gas, their values don't necessarily correspond to the amount of trace gas added, as the added trace gas also potentially affects the inward diffusion of air into the plasma. In this study, the plasma extinguishes before the inward diffusing air becomes substantial, thus Δn_{Ar} and Δn_{N_2} can be approximated to correspond to the amount of trace gas added,

$$\Delta n_{Ar} = \frac{f_{Ar}}{f_{He}} n_T \tag{94}$$

and

$$\Delta n_{N_2} = \frac{f_{N_2}}{f_{He}} n_T. \tag{95}$$

The final expressions of Ar and N_2 mole fractions are then

$$\frac{n_{Ar}}{n_T} = \frac{\frac{f_{Ar}}{f_{He}}}{\left(\frac{l_{He}^0 Y_{He}}{l_{He} Y_{He}^0}\right)\left(\frac{l_{Ar} Y_{Ar}^0}{l_{Ar}^0 Y_{Ar}}\right) - 1}$$
(96)

and

$$\frac{n_{N_2}}{n_T} = \frac{\frac{f_{N_2}}{f_{He}}}{\left(\frac{l_{He}^0 Y_{He}}{l_{He} Y_{He}^0}\right) \left(\frac{l_{AT} Y_{N_2}^0}{l_{AT}^0 Y_{N_2}}\right) - 1}.$$
(97)

Mole fraction of O_2 is more complicated, due to O being excited by He* collisions with O_2 . The absolute number density of He* in the plasma can be realized by analyzing the production and loss of He* at steady state, or

$$\frac{dn_{He^*}}{dt} = 0, \tag{98}$$

leading to

$$k_{He*}^0 n_{He} n_e^0 = n_{He*}^0 (k_{He*}^{He} n_{He} + k_{He*}^{Ar} n_{Ar} + k_{He*}^{O2} n_{O2} + k_{He*}^{N2} n_{N2} + k_{He*}^e n_e^0 + F),$$
(99)

where k_{He*} is reaction rate coefficient for production of He* by electron impact excitation with He; k_{He*}^{He} , k_{He*}^{Ar} , k_{He*}^{O2} , k_{He*}^{N2} , and k_{He*}^{e} are quenching of He* by collisions with He, Ar, O₂, N₂, and e, respectively; and *F* is the volumetric transport loss rate of He* out of the observation region through radial diffusion as well as gas flow. The volumetric transport loss rate F is small compared to the combined quenching rates and thus can be ignored. Quenching of He* by collisions with He* and He₂* can also be ignored. With trace O₂ added, the expression becomes

$$k_{He*}n_{He}n_e = (k_{He*}^{He}n_{He} + k_{He*}^{Ar}n_{Ar} + k_{He*}^{O2}[n_{O2} + \Delta n_{O2}] + k_{He*}^{N2}n_{N2} + k_{He*}^{e}n_{e}).$$
(100)

If we let

$$k_{He*}^{He} n_{He} + k_{He*}^{Ar} n_{Ar} + k_{He*}^{O2} n_{O2} + k_{He*}^{N2} n_{N2} = Q$$
(101)

and ignore the volumetric transport loss rate F, then

$$k_{He*}^0 n_{He} n_e^0 = n_{He*}^0 (Q + k_{He*}^e n_e^0)$$
(102)

and

$$k_{He*}n_{He}n_e = n_{He*}(Q + k_{He*}^{02}\Delta n_{02} + k_{He*}^e n_e),$$
(103)

resulting in

$$n_{He^*}^0 = \frac{k_{He^*}^0 n_{He} n_e^0}{Q + k_{He^*}^e n_e^0} \tag{104}$$

and

$$n_{He*} = \frac{k_{He*} n_{He} n_e}{Q + k_{He*}^{O2} \Delta n_{O2} + k_{He*}^{e} n_e}.$$
(105)

Dividing oxygen emission intensity without added O_2 over the case with added O_2 we arrive at

$$\frac{I_O}{I_{He}} = \frac{a_O^0 k_{He*}^0 n_{He} n_{O_2} Y_O^0}{a_{He}^0 n_{He} Y_{He}^0 Q}$$
(106)

and

$$\frac{I_0^0}{I_{He}^0} = \frac{a_0 k_{He*} n_{He} n_{O_2} Y_0}{a_{He} n_{He} Y_{He} (Q + k_{He*}^{O_2} \Delta n_{O_2})}.$$
(107)

Since the energy dependence of He excitation cross section into the state that emit at 706 nm ($3s^3S$) is similar to that of excitation into He* ($2s^3S$), we can make the assumption that they change in the same way when trace gas is added,

$$\frac{k_{He*}^0 n_e^0}{k_{He*} n_e} = \frac{a_{He}^0 n_e^0}{a_{He} n_e} = \frac{I_{He}^0 Y_{He}}{I_{He} Y_{He}^0},$$
(108)

resulting in

$$n_{O2} = \frac{\Delta n_{O2}}{\left(\frac{I_{He}^{0} Y_{He}}{I_{He} Y_{He}^{0}}\right) \left(\frac{Q + k_{He*}^{O2} \Delta n_{O2} + k_{He*}^{e} n_{e}}{Q + k_{He*}^{e} n_{e}^{0}}\right) \left(\frac{I_{O} Y_{O}^{0}}{I_{O}^{0} Y_{O}}\right) - 1},$$
(109)

and subsequently

$$\frac{n_{O2}}{n_{He}} = \frac{\frac{f_{O2}}{f_{He}}}{\left(\frac{I_{He}^{0}Y_{He}}{I_{He}Y_{He}^{0}}\right)\left(\frac{Q+k_{He*}^{O2}\Delta n_{O2}+k_{He*}^{e}n_{e}}{Q+k_{He*}^{e}n_{e}^{0}}\right)\left(\frac{I_{O}Y_{O}^{0}}{I_{O}^{0}Y_{O}}\right) - 1}.$$
(110)

The expressions for mole fractions of Ar, N_2 , and O_2 have been established to be functions of He and added trace gas flow rates, measured emission intensities, and various quenching rates. Quenching by surrounding species significantly contributes to loss of excited and metastable states and must be taken into account with the quenching rate constants in Table 1 (bolded numbers are estimates). In chapter 6, the measured gas temperature in an APPJ with a shielding gas apparatus was 800-1000 K depending on the flow rate of shielding gas, thus the quenching rate constants were selected at 900 K if available. Otherwise, they were estimated using

$$\frac{k(T_2)}{k(T_1)} = \left(\frac{T_2}{T_1}\right)^{0.5},\tag{111}$$

where $k(T_2)$, and $k(T_1)$ are the quenching rate constants at T_2 and T_1 , respectively.

Table 2. Einstein A-coefficients (10⁶s⁻¹) and quenching rate constants (10⁻¹⁰cm³s⁻¹) at 900 K. (a):An upper limit, assumed to be the same as quenching by N₂. (b): O (777) (3p⁵P) quenching rate constants assumed to be the same as O (844) (3p³P)

		Quenching rate constants				
State	А	He	Ar	O ₂	N ₂	e
Ar (811) (4p 2[5/2] 2p ₈)	36.6 ^[76]	0.24 ^[77]	0.42 ^[77]	11 ^[77]	6.1 ^[77]	
He (706.5) $(3s^3S)$	27.9 ^[56]	0 ^[78]	<12 ^(a)	<12 ^(a)	12 ^[79]	
O (777) (3p ⁵ P)	36.9 ^[80]	0.12 ^[81]	0.36 ^(b)	18 ^[82]	7.4 ^(b)	
O (844) (3p ³ P)	32.2 ^[80]	0.26 ^[83]	0.36 ^[83]	11 ^[83]	7.4 ^[83]	
$N_2(C^3\Pi_u)$	28.6 ^[84]	0.017 ^[85]	0.0097 ^[86]	5.0 ^[87]	0.23 ^[87]	1000 ^[88]
He $(2s^3S)$	-	<10-[89]	3.0 ^[90]	6.0 ^[90]	3.0 ^{[90,91}]	6.5 ^[92]

To study the effect of change in quenching rates, we first assume constant quenching rates (no change in quenching with added trace gas) and use the resulting mole fractions to calculate the contribution of quenching, tabulated in table 2. In general, quenching plays a major role for most excited states. The quenching factor F_Q is the ratio of the mole fraction calculated accounting for quenching, and the mole fraction calculated without accounting for quenching,

$$\frac{n_{Ar, N_2 \text{ or } O_2} (with quenching)}{n_{Ar, N_2 \text{ or } O_2} (without quenching)} = F_Q.$$
(112)

Accurate derivation of air species mole fractions requires accounting for quenching of excited and metastable states. To calculate the quenching rates, however, the species mole fractions are needed. Therefore, an iterative calculation scheme was utilized, first assuming $F_Q = 1$ to produce the initial mole fractions, then iterating until F_Q no longer changes with more iterations.

Table 3. Maximum quenching rate constants (10⁶s⁻¹) for the states indicated in the first column at maximum number densities (cm⁻³) given along the second row. Bolded numbers are those with estimated quenching rate constants.

	Maximum quenching rates (10 ⁶ s ⁻¹)					
State	Α	He	Ar	O ₂	N_2	e
		$2 \ge 10^{19}$	$4 \ge 10^{15}$	$5 \ge 10^{16}$	$2 \ge 10^{17}$	$1 \ge 10^{13}$
Ar (811) (4p 2[5/2] 2p ₈)	36.6	490	0.17	55	120	
He (706.5) $(3s^3S)$	27.9	0	<5	<60	250	
O (777) (3p ⁵ P)	36.9	240	0.15	91	150	
O (844) (3p ³ P)	32.2	520	0.15	55	150	
$N_2(337) (C^3 \Pi_u)$	28.6	35	0.0039	25	4.6	1.0
He $(2s^3S)$	-	< 0.02	1.2	30	60	0.0065

Table 4. Quenching effect of trace gas (Ar, N_2 or O_2) addition on emission yields, He* quenching rates, and the resulted quenching factors F_Q .

	Ar			N2		
Distance from nozzle	$\frac{Y_{He}^{0}}{Y_{He}}$	$\frac{Y_{Ar}^{0}}{Y_{Ar}}$	F_Q	$\frac{Y_{He}^{0}}{Y_{He}}$	$\frac{Y_{N_2}^0}{Y_{N_2}}$	F_Q
1 mm	1.44	1.01	1.41	1.44	1.00	1.44

Table 4 (continued)

3 mm	1.05	1.00	1.06			
5 mm	1.04	1.00	1.05	1.04	1.00	1.83

	O ₂					
Distance from nozzle	$\frac{Y_{He}^{0}}{Y_{He}}$	$\frac{Y_{O_2}^0}{Y_{O_2}}$	$\frac{Q^0}{Q}$	F_Q		
1 mm	1.44	1.07	0.029	0.0257		
3 mm	1.05	1.05	0.907	0.854		
5 mm	1.04	1.04	0.921	0.841		

For all excited states, quenching by electrons can be ignored. In the case of Ar actinometry, the quenching rate constants of Ar $(2p_8)$ and He $(3s^3S)$ by Ar are small enough that O₂ and N₂ dominate the quenching. Therefore, adding trace amount of Ar does not impact the total quenching of Ar $(2p_8)$ and He $(3s^3S)$ at 3 and 5 mm from nozzle, hence

$$\frac{Y_{He}^0}{Y_{He}} \approx \frac{Y_{Ar}^0}{Y_{Ar}} = 1, \tag{113}$$

in eqn. (78). However, due to the small amount of O₂ and N₂ present at 1 mm, the added trace Ar plays a much bigger role in He (3s³S) quenching $\left(\frac{Y_{He}^{0}}{Y_{He}} = 1.44\right)$, and must be accounted for ($F_Q = 1.41$).

For N₂ emission, N₂ (C³ Π_u) is mainly lost by emission and quenching by He and O₂, with negligible N₂ quenching, thus a trace addition of N₂ does not impact N₂ (C³ Π_u) emission yield: $\frac{Y_{N_2}^0}{Y_{N_2}} = 1$. On the other hand, He (3s³S) is mainly lost by N₂ quenching. At 1 mm from nozzle, N₂ from air has yet to diffuse into the plasma, thus the added trace N₂

heavily impacts the emission yield of He $(\frac{Y_{He}^0}{Y_{He}} = 1.44)$ resulting in a significant quenching factor: $F_Q = 1.44$. At 5 mm from the nozzle, however, enough N₂ has diffused into the plasma such that the addition of trace N₂ is no longer impactful: $\frac{Y_{He}^0}{Y_{He}} = 1.04$. However, because the terms $\frac{I_{N_2}^0}{I_{He}^0}$ (no N₂ addition) and $\frac{I_{N_2}}{I_{He}}$ (with N₂ addition) (eqn. 79) are so close, the quenching factor still remains important: $F_Q = 1.83$.

Finally, quenching of O $(3p^5P)$ by O₂ is insignificant, and thus a trace addition of O₂ only results in a negligible increase of O $(3p^5P)$ loss rate: $\frac{Y_{O_2}^0}{Y_{O_2}} \approx 1$. Similar to the case of N₂, at 1 mm little air has diffused into the plasma, hence the addition of trace O₂ becomes a strong source of excited He $(3s^3S)$ and mestastable He $(2s^3S)$ quenching, heavily impacting both the He emission yield $(\frac{Y_{He}^0}{Y_{He}} = 1.44)$ and the He* quenching rate $(\frac{Q^0}{Q} = 0.029)$ leading to very significant quenching factor: $F_Q = 0.0257$. At 3 mm and 5 mm from nozzle, more air has diffused into the plasma to participate in quenching, thus lessening the effect of added trace O₂, resulting in a lesser quenching factor: $F_Q \approx 0.85$.

By carrying out calibration of air species in the center, we could accurately predict their mole fractions in the center via actinometry. The same calibration can be utilized to produce a mole fraction radial distribution following three assumptions: one being that the excitation rate constants of He, Ar, and N_2 behave similarly as electron temperature changes from center plasma to the edge

$$\frac{a_{He}(r)}{a_{He}^{0}} = \frac{a_{Ar}(r)}{a_{Ar}^{0}} = \frac{a_{N_{2}}(r)}{a_{N_{2}}^{0}} = \frac{a_{O_{2}}(r)}{a_{O_{2}}^{0}},$$
(114)

where $a_{He}(r)$, $a_{Ar}(r)$, $a_{N_2}(r)$, and $a_{O_2}(r)$ are excitation rate constants of He, Ar, N₂, and O, respectively, at any one radial distance r away from nozzle. The second assumption involves the various yields changing in the same way as mole fractions shift from plasma center to edge:

$$\frac{Y_{He}(r)}{Y_{He}^{0}} = \frac{Y_{Ar}(r)}{Y_{Ar}^{0}} = \frac{Y_{N_{2}}(r)}{Y_{N_{2}}^{0}} = \frac{Y_{O}(r)}{Y_{O}^{0}},$$
(115)

where $Y_{He}(r)$, $Y_{Ar}(r)$, $Y_{N_2}(r)$, and $Y_0(r)$, are the radial emission yields of He, Ar, N₂, and O, respectively. The final assumption is that the excitation and quenching rates of He* also shares the same trend from center to edge,

$$\frac{Q(r)}{Q} = \frac{k_{He^*}(r)}{k_{He^*}^0},$$
(116)

where Q(r), and $k_{He*}(r)$ are the radial quenching rates and excitation rates of He*, respectively. The radial emission intensity $\frac{I_s^r}{I_{He}^r}$, can be converted into radial mole fractions, $\frac{n_s^r(r)}{n_T}$, as followed,

$$\frac{n_s^r(r)}{n_T} = \frac{\frac{I_s^r}{I_{He}^o}(r)}{\frac{I_s^0}{I_{He}^o}} \frac{n_s}{n_T}.$$
(117)

where s can be Ar, N₂, or O₂. The assumption is only valid for small (r), and becomes invalid with large (r).

The same assumption is applied for derivation of mole fraction radial distributions for the case with shielding gas. The calculation is done in the same way, using $I_s^r/_{I_{He}}$ (with shielding gas) to produce $\frac{n_s^r(r)}{n_T}$ (with shielding gas).

6.3 Propagation of error:

When making complex calculations using numerous factors that carry errors, it is important to take into account the uncertainties of these factors to accurately present the final results. The method for using the errors of individual factors to find the error in the final result is called propagation of error. The linear model of propagation of error states that if

$$X = x_0 + a_u U + a_v V + a_w W \dots, (118)$$

where x_0, a_u, a_v, a_w are constants and U, V, W are independents, then the error is

$$\sigma_x = \sqrt{(a_u \sigma_u)^2 + (a_v \sigma_v)^2 + (a_w \sigma_w)^2 \dots},$$
(119)

where σ_x , σ_u , σ_v , and σ_w are errors of *X*, *U*, *V*, and *W*, respectively.

On the other hand, if the function is nonlinear,

$$X = f(U, V, W, ...),$$
(120)

then it can be written as:

$$X = f(\mu_{u}, \mu_{v}, \mu_{w}, ...) + \frac{\partial f}{\partial U}\Big|_{\mu_{u}, \mu_{v}, \mu_{w}, ...} (U - \mu_{u}) + \frac{\partial f}{\partial V}\Big|_{\mu_{u}, \mu_{v}, \mu_{w}, ...} (U - \mu_{v}) + \frac{\partial f}{\partial W}\Big|_{\mu_{u}, \mu_{v}, \mu_{w}, ...} (U - \mu_{w}),$$
(121)

which has the same form as a linear model, and can be treated as such for the purpose of error calculation. Using the above method, we can derive the propagation of error for the following mathematical operations,

$$\sigma_z = \sqrt{\sigma_x^2 + \sigma_y^2} \text{ for } z = x + y \text{ or } z = x - y$$
(122)

and

$$\sigma_z = z \sqrt{\left(\frac{\sigma_x}{x}\right)^2 + \left(\frac{\sigma_y}{y}\right)^2} \text{ for } z = x \times y \text{ or } z = x \div y, \tag{123}$$

where x and y are independents, and σ_x , σ_y , and σ_z are the errors of x, x, and z, respectively.

6.4 Self-actinometry calibration



Figure 57: Intensity ratio of N₂, O₂, and Ar over He as a function of N₂, O₂, and Ar mole fractions at 1 mm, 3 mm and 5 mm axial distance from the nozzle.

The first step in self-actinometry is calibration by adding trace amount of the species of interest (Ar, N₂, and O₂) and measuring changes in emission intensity of these species as well as of He. In this case, no Abel-inversion was carried out, and the emission was probed line-integrated through the center of the plasma jet (all emissions through the center line) at different axial positions away from the nozzle (Fig. 57). This calibration result is then applied to the radial distribution of species emission (Abel-inverted from spatially-resolved line-integrated emission) to produce mole fractions.



Figure 58: Line-integrated emission (a, calibration site) versus radial center emission (b, mole fraction site).

There is a mismatch between the calibration site (Fig. 58a, line-integrated through the jet center) and the site of the emission where it applies to (Fig. 58b, radially distributed). This mismatch is not an issue for measurements at 3 mm and 5 mm away from the nozzle as significant air has diffused into the plasma jet at those positions such that the radial distribution of air species is relatively flat, resulting in little difference between lineintegrated and radially distributed emission. On the other hand, air has yet to diffuse deep into the plasma at 1 mm, leading to a strongly modulated radial distribution. In this case, line-integrated emission through the center will differ from results that had been Abelinverted to produce emission from only the radial center of the plasma. However, as the plasma is still strongest at the center (highest electron density and electron temperature), emission intensity is heavily weighted towards the center. For the case of He, which is present in equal amount throughout the plasma, the high plasma density at the center will result in strongest He emission intensity at the center, possibly overwhelming emission at the edge, lessening the difference between line-integrated and radial center emission. On the other hand, the mole fraction of air species diffusing into the jet is weighted towards the edge, and the higher plasma density in the center may not be enough to make their emissions strongest in the center, thus the difference between line-integrated and radial center emission remains.

The He 706 nm emission can potentially be an indicator of the relative change in the electron density of highly energetic electrons (> 20 eV) due to the high energy required to excite ground state He to the He ($3s^3S$) state that emits at 706 nm. These highly energetic electrons are also important for the production of He metastables. On the other hand, N₂ 337 nm and Ar 811 nm emissions are more indicative of lower energy electrons, due to the lower energy required to excite the ground state N₂ and Ar to the N₂ (C³Π_u) and Ar (4p 2[5/2] 2p₈) states that emit at 337 nm and 811 nm, respectively. During calibration with trace addition of O₂ to the He feed, the He/Ar intensity ratio remains constant, especially at 3 mm and 5 mm from the nozzle (as shown in Fig. 59) thus,

$$\frac{I_{Ar}}{I_{He}} = \frac{I_{Ar}^{0}}{I_{He}^{0}} = \frac{a_{Ar}n_{Ar}Y_{Ar}}{a_{He}n_{He}Y_{He}} = \frac{a_{Ar}^{0}n_{Ar}Y_{Ar}^{0}}{a_{He}^{0}n_{He}Y_{He}^{0}}.$$
(124)

Addition of only O_2 to the plasma feed gas leaves the He/Ar number density ratio unaffected. Furthermore, Table 4 shows that the yield of He emission at 3 mm and 5 mm is also unaffected,

$$\frac{Y_{He}^0}{Y_{He}} \approx 1,$$
 (125)

with O_2 trace addition. Since Ar has similar quenching characteristics with He, both in the Einstein A-coefficients and the quenching rate constant by O_2 (Table 2), addition of O_2 also does not affect the yield of Ar emission at 3 mm and 5 mm,

$$\frac{Y_{Ar}^0}{Y_{Ar}} \approx 1. \tag{126}$$

As the result, from eqn. 94 we have,

$$\frac{a_{He}}{a_{He}^0} = \frac{a_{Ar}}{a_{Ar}^0}.$$
(127)

Corrections to remove the effect of O_2 trace addition on the He and Ar emission yields (open symbols in Fig. 59) causes the He/Ar intensity ratio to also stays constant at 1 mm with increasing O_2 mole fraction, making Eqn. 127 correct at all distances from nozzle. Since He and Ar emissions are indicative of high energy and low energy electrons, respectively, the fact that He/Ar intensity stays constant with O_2 addition means that the electron energy distribution function (EEDF) is relatively unaffected with O_2 addition. This would prove the validity of assumption Eqn. 108, made during calibration with O_2 trace addition to calculate O_2 mole fraction.



Figure 59: Line-integrated radial $\frac{I_{He}}{I_{Ar}}$ as a function of added O₂ mole fraction (solid symbols) and $\frac{I_{He}}{I_{Ar}}$ with quenching effect removed (open symbols) at 1 mm, 3 mm, and 5 mm axial distance from the nozzle.

Addition of trace Ar, on the other hand, moderately shifts the He/O_2 intensity ratio at 1 mm from the nozzle, but shows little effect at 3 mm and no effect at 5 mm (Fig. 60). Therefore, at 3 mm and 5 mm from nozzle we have,

$$\frac{I_O}{I_{He}} = \frac{I_O^0}{I_{He}^0} = \frac{a_O k_{He*} n_{He} n_{O_2} Y_O}{a_{He} n_{He} Y_{He} (Q + k_{He*}^{O_2} \Delta n_{O_2})} = \frac{a_O^0 k_{He*}^0 n_{He} n_{O_2} Y_O^0}{a_{He}^0 n_{He} Y_{He}^0 Q}.$$
 (128)

Excitation of O by collisions between O_2 and He^* , does not depend on either electron density or electron temperature, but instead has a weak dependence on gas temperature, as the reaction is between two gaseous particles whose velocity is determined by the gas temperature. Assuming that the addition of trace Ar does not significantly influence the gas temperature, we have

$$a_0 = a_0^0.$$
 (129)

Furthermore, the quenching rate constant of O $(3p^5P)$ by Ar is negligible, thus the yield is not affected and

$$\frac{Y_{O_2}^0}{Y_{O_2}} \approx 1.$$
 (130)

Ar quenches He^{*} at half the rate of O_2 , which does not affect He^{*} quenching to a significant extend with O_2 addition at 3 mm and 5 mm. Therefore, the effect of Ar trace addition on He^{*} quenching rate at 3 mm and 5 mm from nozzle can be reasonably ignored,

$$\frac{Q^0}{Q} \approx 1,\tag{131}$$

resulting in,

$$\frac{a_{He}}{a_{He}^{0}} = \frac{k_{He*}}{k_{He*}^{0}}.$$
(132)

Corrections to remove the effect of trace Ar addition on the quenching rates were also applied to Fig. 60 (open symbols). Unlike Fig. 59, this correction does not help keep the He/O intensity ratio constant with Ar addition. Therefore, Eqn. 132 is wrong at 1 mm from nozzle, and relatively correct at 3 mm and 5 mm from nozzle. Even though He excitation to $3s^3S(a_{He})$ and to $2s^3S(k_{He*})$ have similar energy threshold, their rate constants may not behave exactly the same with changing EEDF. We can thus conclude that addition of Ar significantly shifts the EEDF at 1 mm from nozzle, voiding the assumption made for calibration with Ar trace addition and making the Ar mole fraction at 1 mm from nozzle questionable. Ar mole fractions at 3 mm and 5 mm remain correct



Figure 60: Line-integrated radial $\frac{I_{He}}{I_0}$ as a function of added Ar mole fraction (solid symbols) and $\frac{I_{He}}{I_0}$ with quenching effect removed (open symbols) at 1 mm, 3 mm, and 5 mm axial distance from the nozzle.

6.5 Radial mole fraction of air impurity diffusing into the plasma jet

The radial distributions of emission intensity by air species (N_2 , O_2 , and Ar) were measured and converted, using self-actinometry, to mole fractions at various axial distances away from the nozzle (Fig. 61). Quenching of excited and metastable species was accounted for as described above. Error bars were determined using the standard propagation of error analysis explained in section 5.5. The sources of errors are: 1% in gas flow rate, quenching rate constant errors as reported in the literature (varying from 10% to 30% for measured, and as high as 50% for estimated rate constants), and errors in determination of slopes and intercepts of intensity ratios versus added trace gases (Fig. 54).

Fig. 61 shows the experimentally observed radial profiles of air species mole fractions at axial distances from the nozzle of 1 mm, 2 mm and 5 mm, with and without shielding gas. The profiles at 1 mm from the nozzle, show O_2 and Ar, but no N_2 , indicating that O_2 and Ar originate from impurities in the feed gas. In fact, at 1 mm, the N_2 (air) diffusion front is at ~2 mm radial distance from the jet axis. Species mole fractions start out strongly modulated at 1 mm from the nozzle, but become progressively flatter at 3 mm and 5 mm. Without shielding gas, the on-axis (*r*=0) N_2 : O_2 :Ar percentages begin to resemble the composition of air (78:21:1) at 3 mm (80.6±7.4 : 17.7±6.8 : 1.7±0.8) and 5 mm (90.0±3.3 : 7.4±3.0 : 0.6±0.3) as diffusion from air overwhelms the feed impurities.

The addition of shielding gas (4.5 slm N_2) does not affect the O_2 and Ar mole fractions at 1 mm as they originate from He feed impurities. As air becomes the main source of O_2 and Ar at 5 mm from the nozzle, the shielding gas reduces O_2 and Ar density in the plasma by a factor of 2 to 3 times (compared to no shielding gas), while increasing
the on-axis N_2 density by a factor of 1.24, close to the 1.28 expected increase in N_2 density between 100% N_2 in shielding gas and 78% N_2 in ambient air.



Figure 61: Radial profiles of air species mole fractions at axial distances from the nozzle of 1 mm, 2 mm and 5 mm, with and without shielding gas.

6.6 Comparison with simulation

Simulation of air diffusing into the He APPJ was also carried out (Fig. 62), with details shown in another publication.⁹³ Briefly, the simulation first utilizes neutral flow, heat and mass transport models to produce the neutral mole fractions, which is then fed into a plasma dynamics model in a 2-D axisymmetric configuration, resulting in the 2-D profiles of gas temperature, species concentration, electron density, and electron temperature with and without shielding gas. At all axial distances, simulation shows that nitrogen shielding gas reduces oxygen and argon mole fractions while increasing nitrogen mole fractions, as expected. All species radial mole fractions show a minimum at the center, along with monotonic increases toward the edge. This behavior becomes less pronounced as the mole fraction profiles flatten further away from the nozzle, similar to experimental results. Due to O_2 and Ar feed gas impurities in experiment, which was not replicated in simulation, the experimental results match simulation better further away from nozzle, where air diffusion has overwhelmed feed impurities. The small amount of N_2 , O_2 , and Ar near the nozzle may also contributes to inaccuracies in measurements. Looking at the radial position r = 0.45 mm (~ the edge of the plasma column), experimental result reveals nitrogen mole fraction increasing by 100 times from 1 mm to 3 mm, then by 10 times from 3 mm to 5 mm from the nozzle, with and without shielding gas. The shielding gas plays the role of both providing a higher nitrogen content (100% vs 78%) to the plasma ambient and enhancing mass transport from the stronger convective flow in an effort to increase the amount of nitrogen in the plasma.

Comparison between simulated and experiment center mole fractions without shielding gas is shown in Fig. 63. At 1 mm from nozzle, N₂ mole fraction was below

134

detection limit, while O_2 and Ar mole fractions were boosted from feed impurities, thus experiment and simulation are more similar further away from nozzle. Additionally, on log scale, all three species exhibit a larger jump from 1 mm to 3 mm than from 3 mm to 5 mm.

Discrepancy between experiment and simulation results could be traced back to various assumptions made during measurement. As explained above, experiment extends actinometry to collect radial mole fraction distribution by three assumptions: the excitation rate constants of He, Ar, and N₂, the various yields; and the excitation and quenching rates of He*, each behave similarly from plasma center to edge (Eqn. 114, 115 and 116). These assumptions begin to fail with increasing radial distance away from center due to increasingly drastic changes in the plasma. Addition of shielding gas has also been shown to moderately change the mole fractions, introducing errors in the measurements. Furthermore, the fact that the actinometric calibrations were performed using line-integrated emission across the plasma radius and yet were applied to radial emissions may also create its own set of errors. Nevertheless, overall, the main features of experimental results are covered by the simulations.



Figure 62: Mole fraction radial profiles of O₂, N₂ and Ar at axial distances from the nozzle of 1, 3, and 5 mm, with (d)(e)(f), and without (a)(b)(c) shielding gas. Solid lines are simulation predictions, broken lines are experimental profiles.



Figure 63: Simulated and experiment center mole fractions

6.7 Comparison with published literature

The effect of shielding gas on an atmospheric pressure plasma jet has been studied before, especially on the commercially available plasma source kINPen^{94,95}. The shielding gas was found to be extremely effective, reducing air diffusion at 5 mm from nozzle by 5 to 10 times^{12,96}, compared to the 2-3 times air diffusion reduction measured in this study. This discrepancy can be explained by the high amount of power applied to the plasma jet in this study, resulting in higher gas temperature. The plasma jet mentioned here is operated with 40 W power, producing up to 1000 K plasma gas temperature. On the other hand, the kINPen is operated with less than 3.5 W, resulting in less than 320 K plasma gas temperature⁹⁵. Higher temperature could lead to higher diffusivity, thus allowing diffusion to go through the shielding gas, lowering its effectiveness. This explanation can be proven

by lowering the gas temperature during simulation of air diffusion from the simulated gas temperature of 800-1200 K down to 300 K, and observing that the lowered diffusivity at lower temperature increases the shielding gas effect from less than 10 times to about 100 times in reduction of air diffusion. Therefore, we can conclude that the higher gas temperature of the APPJ used here results in the shielding gas not being as effective as previously reported.

6.8 Summary and Conclusions

The radial mole fraction profiles of air species diffusing into a radio frequency, atmospheric pressure plasma jet (APPJ), with 2 standard liters per minute (slm) helium flow were determined by means of optical emission spectroscopy. The probed emissions were transformed into radial emission profiles by Abel inversion, then converted into mole fraction profiles via self-actinometry, using results from a set of calibrations. Selfactinometry involves adding a trace amount of the species of interest (Ar, O_2 , and N_2) and observing the respective change in Ar/He, O₂/He, and N₂/He intensity ratios. Proper corrections due to quenching of the excited states by added trace gas were applied. Experimental results showed that the air mole fraction increased along the axis of the He jet from essentially zero at 1 mm, to 10^{-3} at 3 mm, to 10^{-2} at 5 mm axial distance from the nozzle. Radial species distributions started out center-low at 1 mm, but became progressively flatter at 3 mm and 5 mm from the nozzle. Further, it was found that the Ar, O₂, and N₂ mole fractions matched the ambient air composition at 3 mm and 5 mm from the nozzle, accounting for experimental error. Experimental data were compared to the predictions of a simulation combining a neutral fluid flow, heat and mass transport model,

with a plasma dynamics model. Overall, the simulation captured the main features of the species concentrations and their profiles. It was concluded that actinometry can provide accurate absolute number density of plasma species, even at atmospheric pressure.

The addition of 4.5 slm N₂ shielding gas flowing co-axially and engulfing the He jet, reduced ambient air diffusion by 2 to 3 times. The shielding gas effectiveness in this study was lower than previously reported ^{12,96} (up to more than 10 times reduction in air diffusion). This was attributed to the high operating power (nominal power of 40 W) of the plasma source in this work, leading to higher gas temperature (up to 1200 K), compared to the lower power (3.5 W) and lower gas temperature (320 K) of the kINPen® plasma source used in the other studies⁹⁵. Simulation showed a shielding gas effectiveness in air concentration reduction of only a few times at 1000 K, but up to 100 times at 300 K, confirming that shielding gas becomes less effective at higher gas temperatures.

CHAPTER 7: SUMMARY AND CONCLUSIONS

Atmospheric pressure plasma jet (APPJ) is an emerging plasma configuration for current and future applications, most notably in plasma medicine. The APPJ setup consists of a capillary tube through which flows the working gas, typically He or Ar. Power is applied through one or more electrodes to ignite the plasma. The plasma takes the form of a luminous needle extending a few cm beyond the nozzle. During contact with a substrate, the plasma spreads out radially in a small area before extinguishing.⁶ Under ambient air operating condition, the plasma takes in air species to form reactive oxygen-nitrogen species (RONS)^{9,10} with various medical benefits. The capability for operation in ambient air as well as the small area of impact makes the APPJ ideal for medical treatments. Despite progress in recent years, many important mechanisms in plasma propagation and species productions have not been fully explored. This study aims to investigate the fundamental properties of APPJs that are relevant to applications, mainly through optical emission spectroscopy (OES). These properties include,

- (1) Excitation mechanisms of various species
- (2) Gas temperature and electron density
- (3) Radial distribution of ambient species diffusing into an APPJ.

7.1 Excitation mechanisms in a non-equilibrium He APPJ:

We investigated a He atmospheric pressure plasma jet (APPJ) emerging into open air at 1 atm using temporally- and spatially-resolved optical emission spectroscopy (OES). The reactor consisted of a quartz capillary tube with two copper ring electrodes wrapped around the tube. One electrode was grounded and the other was powered with a 200 kHz radio frequency (RF), 7 kV peak-to-peak sinewave voltage. The plasma plume emanating from the tube end (nozzle) impinged on either a MgF₂ window sealed to a vacuum UV spectrometer, or the flat face of a half-cylinder quartz prism with semicircular cross section. Time-resolved OES was conducted at two spatial positions, namely, along the axis where the entire length of the plasma jet was probed, or at an angle so as to isolate and probe only plasma emission near (<0.3 mm) the surface of a downstream substrate perpendicular to the axis of the jet.

Emissions along the jet axis, due to species originating from either air diffusion (N_2^+) or feed gas impurities (H, O, OH) were mainly excited by He metastables (He*). The plasma extended beyond the nozzle and touched the substrate during the positive voltage part of the RF cycle, while it was confined inside the tube during the negative voltage part of the cycle. Thus, plasma-air contact occurred only during the positive voltage part of the cycle. During this time period, He* metastables were produced by electron impact excitation of ground state He. This reaction could not happen outside the tube during the negative being this time period by a process called "radiation transport". This involves the He 50-60 nm VUV photons being absorbed and re-emitted as they transport out of the nozzle, eventually producing He*. This constant production of He* outside the tube allowed constant N₂⁺ emission throughout the RF cycle. The nitrogen ions were produced in collisions with metastables in a process called Penning ionization.

 N_2 and He emissions showed a strong time-dependence during the RF cycle implying that these species are excited by electron impact. On the other hand, emissions from excitation by He* were weakly modulated due to the long lifetime of He*. The N_2^+ time resolved waveform was phase shifted compared to the peak negative voltage and this

was used to calculate the lifetime of He* responsible for N_2^+ excitation, and subsequently the rate of He* quenching by diffused air.

Time-resolved emissions of He, N₂, and N₂⁺ provided insight into the formation and evolution of the plasma jet. Due to the different threshold energy for excitation, He emission is representative of the number density of higher energy electrons, while N₂ emission reflects the number density of lower energy electrons. The N₂ time-resolved emission suggested the presence of a weak ionization wave moving from the nozzle to the substrate during the positive part of the cycle, but well before the peak positive voltage. Owing to its low electron temperature, this ionization wave can only excite N₂ and not He. Ionization and excitation in the nozzle-substrate gap then intensified and reached a maximum at peak positive voltage. The plasma positively charged the substrate, which then pulled electron towards itself, as the voltage entered the negative period to neutralize the positive charge, resulting in a brief N₂ emission near the substrate.

7.2 Measurement of gas temperature and electron density in an atmospheric pressure plasma jet

We measured gas temperature and electron density in He and Ar APPJ with a needle and ring electrode configuration, with or without Ar or N₂ shielding gas. He or Ar feed gas flowed through a quartz tube. A ring ground electrode was wrapped around the tube while a needle (powered electrode) was placed coaxial with the tube. When shielding gas was used, a longer grounded ring electrode was employed, leading to higher applied power. A 13.5 MHz, $1 - 4 \text{ kV}_{p-p}$ sinewave voltage was applied to the needle electrode. The plasma power was 9 W – 24 W for the setup without shielding gas apparatus, or 60 W

when the shielding gas apparatus was installed. Gas temperature measurement was carried out by fitting the rotational temperature of the N₂ ($C^3\Pi_u \rightarrow B^3\Pi_g$) emission, while electron density was measured by fitting the Stark broadening of the H-Balmer β line.

The mechanism through which N_2 ($C^3\Pi_u$) is excited determines whether the emission is representative of the gas temperature. In the case of He feed gas, N_2 ($C^3\Pi_u$) can only be excited by electron impact excitation, and N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$) has rotational temperature equal to the gas temperature. On the other hand, if Ar is the feed gas, then Ar metastable can also excite N_2 ($C^3\Pi_u$), resulting in emission that has a rotational temperature much higher than the gas temperature. Therefore, fitting the N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$) emission for gas temperature when Ar is present requires a two-temperature fit, to account for a population with much higher rotational temperature, and a population with rotational temperature equal to the gas temperature.

Broadening of the H-Balmer β line is due to various mechanisms, one of which is Stark broadening that can be used to measure electron density. The H-Balmer β emission is a convolution of the (ideally Gaussian) instrumental lineshape and a Lorentzian distribution, which is the combination of van de Waals and Stark broadening. The van de Waals component can be calculated from the gas temperature, thus by fitting the total broadening, the Stark component can be extracted and used to calculate the electron density.

Both He and Ar feed gas resulted in similar gas temperature behavior. For Ar, the temperature increased from 400 K to 600 K as the power increased from 9 W to 18 W, while for He the temperature increased from 650 K to 750 K as the power increased from 19 W to 24 W. The gas temperature was constant with axial distance from the nozzle. This

is because the gas heating was mainly due to the plasma inside the tube. The APPJ with the shielding gas apparatus installed allowed the use of higher power. For a power of 40 W, the gas temperature reached 1000 K without shielding gas flow. In the presence of shielding gas (either Ar or N_2) flow at 9 slm, the gas temperature at an axial distance of 5 mm from the nozzle dropped to below 850 K.

Electron density was found to be mostly below the 10^{13} cm⁻³ detection limit and was only measurable in Ar plasma when a grounded copper plate was placed behind the quart substrate. The electron density increased from an estimated 2.5 x 10^{13} cm⁻³ without the Cu plate to 5.0 x 10^{13} cm⁻³ in the presence of the grounded Cu plate.

7.3 Radial distribution of air species diffusing into an RF Helium atmospheric pressure plasma jet

The radial mole fraction profiles of air species diffusing into a radio frequency, atmospheric pressure plasma jet (APPJ), with 2 standard liters per minute (slm) helium flow were determined by means of optical emission spectroscopy. The probed emissions were transformed into radial emission profiles by Abel inversion, then converted into mole fraction profiles via self-actinometry, using results from a set of calibrations. Self-actinometry involves adding a trace amount of the species of interest (Ar, O₂, and N₂) and observing the respective change in Ar/He, O₂/He, and N₂/He intensity ratios. Proper corrections due to quenching of the excited states by added trace gas were applied. Experimental results showed that the air mole fraction increased along the axis of the He jet from essentially zero at 1 mm, to 10^{-3} at 3 mm, to 10^{-2} at 5 mm axial distance from the nozzle. Radial species distributions started out center-low at 1 mm, but became

progressively flatter at 3 mm and 5 mm from the nozzle. Further, it was found that the Ar, O_2 , and N_2 mole fractions matched the ambient air composition at 3 mm and 5 mm from the nozzle, accounting for experimental error. Experimental data were compared to the predictions of a simulation combining a neutral fluid flow, heat and mass transport model, with a plasma dynamics model. Overall, the simulation captured the main features of the species concentrations and their profiles. It was concluded that actinometry can provide accurate absolute number density of plasma species, even at atmospheric pressure.

The addition of 4.5 slm N₂ shielding gas flowing co-axially and engulfing the He jet, reduced ambient air diffusion by 2 to 3 times. The shielding gas effectiveness in this study was lower than previously reported (up to more than 10 times reduction in air diffusion). This was attributed to the high operating power (nominal power of 40 W) of the plasma source in this work, leading to higher gas temperature (up to 1200 K), compared to the lower power (3.5 W) and lower gas temperature (320 K) of the kINPen® plasma source used in the other studies. Simulation showed a shielding gas effectiveness in air concentration reduction of only a few times at 1000 K, but up to 100 times at 300 K, confirming that shielding gas becomes less effective at higher gas temperatures.

References

¹ A. Schütze, J.Y. Jeong, S.E. Babayan, J. Park, G.S. Selwyn, and R.F. Hicks, *IEEE Trans. Plasma Sci.* **26**, 1685 (1998).

² C. Tendero, C. Tixier, P. Tristant, J. Desmaison, and P. Leprince, *Spectrochim. Acta* - *Part B At. Spectrosc.* **61**, 2 (2006).

³ O. V. Penkov, M. Khadem, W.S. Lim, and D.E. Kim, *J. Coatings Technol. Res.* **12**, 225 (2015).

⁴ D. Mariotti and R.M. Sankaran, J. Phys. D. Appl. Phys. 43, 323001 (2010).

⁵ X. Lu, M. Laroussi, and V. Puech, *Plasma Sources Sci. Technol.* **21**, 034005 (2012).

⁶ W. Yan and D.J. Economou, J. Appl. Phys. **120**, 123304 (2016).

⁷ X. Lu, G. V. Naidis, M. Laroussi, and K. Ostrikov, *Phys. Rep.* 540, 123 (2014).

- ⁸ T. Murakami, K. Niemi, T. Gans, D. O'Connell, and W.G. Graham, *Plasma Sources Sci. Technol.* **22**, 045010 (2013).
- ⁹ J. Ehlbeck, U. Schnabel, M. Polak, J. Winter, T. Von Woedtke, R. Brandenburg, T. Von Dem Hagen, and K.D. Weltmann, *J. Phys. D. Appl. Phys.* **44**, 013002 (2011).

¹⁰ J.S. Sousa, K. Niemi, L.J. Cox, Q.T. Algwari, T. Gans, and D. O'Connell, *J. Appl. Phys.* **109**, 123302 (2011).

¹¹ S. Iseni, S. Zhang, A.F.H. Van Gessel, S. Hofmann, B.T.J. Van Ham, S. Reuter, K.D. Weltmann, and P.J. Bruggeman, *New J. Phys.* **16**, 123011 (2014).

¹² S. Reuter, J. Winter, A. Schmidt-Bleker, H. Tresp, M.U. Hammer, and K.D. Weltmann, *IEEE Trans. Plasma Sci.* 40, 2788 (2012).

¹³ A. Schmidt-Bleker, J. Winter, A. Bösel, S. Reuter, and K.D. Weltmann, *Plasma Sources Sci. Technol.* **25**, 015005 (2015).

¹⁴ A. Schmidt-Bleker, J. Winter, S. Iseni, M. Dünnbier, K.D. Weltmann, and S. Reuter, *J. Phys. D. Appl. Phys.* **47**, 145201 (2014).

¹⁵ S. Reuter, H. Tresp, K. Wende, M.U. Hammer, J. Winter, K. Masur, A. Schmidt-Bleker, and K.D. Weltmann, *IEEE Trans. Plasma Sci.* **40**, 2986 (2012).

¹⁶ L. Bárdos and H. Baránková, *Thin Solid Films* **518**, 6705 (2010).

¹⁷ A. Bogaerts, E. Neyts, R. Gijbels, and J. Van der Mullen, *Spectrochim. Acta - Part B At. Spectrosc.* **57**, 609 (2002).

¹⁸ N.S.J. Braithwaite, *Plasma Sources Sci. Technol.* 9, 517 (2000).

- ¹⁹ H. Conrads and M. Schmidt, *Plasma Sources Sci. Technol.* 9, 441 (2000).
- ²⁰ A. Fridman, A. Chirokov, and A. Gutsol, J. Phys. D. Appl. Phys. 38, R1 (2005).
- ²¹ J. Salge, Surf. Coatings Technol. 80, 1 (1996).
- ²² M. Teschke, J. Kedzierski, E.G. Finantu-Dinu, D. Korzec, and J. Engemann, *IEEE Trans. Plasma Sci.* **33**, 310 (2005).
- ²³ S.E. Babayan, J.Y. Jeong, A. Schütze, J. Tu V, M. Moravej, G.S. Selwyn, and R.F. Hicks, *Plasma Sources Sci. Technol.* **10**, 573 (2001).

²⁴ Q. Li, J.T. Li, W.C. Zhu, X.M. Zhu, and Y.K. Pu, Appl. Phys. Lett. 95, 141502 (2009).

²⁵ X. Lu, Y. Cao, P. Yang, Q. Xiong, Z. Xiong, Y. Xian, and Y. Pan, *IEEE Trans. Plasma Sci.* **37**, 668 (2009).

²⁶ Z. Xiong, X. Lu, Y. Xian, Z. Jiang, and Y. Pan, J. Appl. Phys. 108, 103303 (2010).

²⁷ G.A. Dawson and W.P. Winn, Zeitschrift Für Phys. 183, 159 (1965).

²⁸ X.P. Lu and M. Laroussi, J. Appl. Phys. 100, (2006).

²⁹ Y. Xian, X. Lu, Q. Xiong, Z. Jiang, Y. Pan, Y. Cao, and P. Yang, *IEEE Trans. Plasma Sci.* **37**, 2068 (2009).

³⁰ G. V. Naidis, Appl. Phys. Lett. 98, 141501 (2011).

³¹ S. Wu, Q. Huang, Z. Wang, and X. Lu, *IEEE Trans. Plasma Sci.* **39**, 2286 (2011).

³² D.P. Dowling, F.T. O'Neill, S.J. Langlais, and V.J. Law, *Plasma Process. Polym.* **8**, 718 (2011).

³³ E.R. Ionita, M.D. Ionita, E.C. Stancu, M. Teodorescu, and G. Dinescu, *Appl. Surf. Sci.* **255**, 5448 (2009).

³⁴ N. De Geyter, A. Sarani, T. Jacobs, A.Y. Nikiforov, T. Desmet, and P. Dubruel, *Plasma Chem. Plasma Process.* **33**, 165 (2013).

³⁵ S. Bai, K.K.C. Ho, G. Knox, and A. Bismarck, *Compos. Interfaces* 20, 761 (2013).

³⁶ M. Donegan, V. Milosavljević, and D.P. Dowling, *Plasma Chem. Plasma Process.* 33, 941 (2013).

³⁷ E. Moritzer, C. Budde, and C. Leister, Weld. World 59, 23 (2014).

- ³⁸ K. Fricke, H. Steffen, T. Von Woedtke, K. Schröder, and K.D. Weltmann, *Plasma Process. Polym.* **8**, 51 (2011).
- ³⁹ D. Soysal and A. Ansar, Surf. Coatings Technol. 220, 187 (2013).
- ⁴⁰ O. V. Penkov, D.H. Lee, H. Kim, and D.E. Kim, *Compos. Sci. Technol.* **77**, 60 (2013).
- ⁴¹ H. Fakhouri, D. Ben Salem, O. Carton, J. Pulpytel, and F. Arefi-Khonsari, *J. Phys. D. Appl. Phys.* **47**, 265301 (2014).
- ⁴² M. Keidar, A. Shashurin, O. Volotskova, M. Ann Stepp, P. Srinivasan, A. Sandler, and
 B. Trink, *Phys. Plasmas* 20, 057101 (2013).
- ⁴³ M. Keidar, *Plasma Sources Sci. Technol.* **24**, 033001 (2015).
- ⁴⁴ M. Keidar, R. Walk, A. Shashurin, P. Srinivasan, A. Sandler, S. Dasgupta, R. Ravi, R. Guerrero-Preston, and B. Trink, *Br. J. Cancer* **105**, 1295 (2011).
- ⁴⁵ I.H. Malitson, J. Opt. Soc. Am. 55, 1205 (1965).
- ⁴⁶ C.Z. Tan, J. Non. Cryst. Solids 223, 158 (1998).
- ⁴⁷ B.L. Sands, B.N. Ganguly, and K. Tachibana, *Appl. Phys. Lett.* **92**, 151503 (2008).
- ⁴⁸ J. Shi, F. Zhong, J. Zhang, D.W. Liu, and M.G. Kong, *Phys. Plasmas* **15**, 013504 (2008).
- ⁴⁹ Q. Xiong, X. Lu, J. Liu, Y. Xian, Z. Xiong, F. Zou, C. Zou, W. Gong, J. Hu, K. Chen,
 X. Pei, Z. Jiang, and Y. Pan, *J. Appl. Phys.* **106**, 083302 (2009).

⁵⁰ N. Puač, D. Maletić, S. Lazović, G. Malović, A. Dordević, and Z.L.J. Petrović, *Appl. Phys. Lett.* **101**, 024103 (2012).

⁵¹ C. Jiang, M.T. Chen, and M.A. Gundersen, J. Phys. D. Appl. Phys. 42, 232002 (2009).

⁵² R.M.S. John, F.L. Miller, and C.C. Lin, *Phys. Rev.* **134**, A888 (1964).

⁵³ D.L.A. Rall, F.A. Sharpton, M.B. Schulman, L.W. Anderson, J.E. Lawler, and C.C. Lin, *Phys. Rev. Lett.* **62**, 2253 (1989).

⁵⁴ W.C. Zhu, Q. Li, X.M. Zhu, and Y.K. Pu, J. Phys. D. Appl. Phys. 42, 202002 (2009).

⁵⁵ K. Niemi, J. Waskoenig, N. Sadeghi, T. Gans, and D. O'Connell, *Plasma Sources Sci. Technol.* **20**, 055005 (2011).

⁵⁶ G. Drake, in <u>Springer Handb. At. Mol. Opt. Phys.</u> (2006).

⁵⁷ L.F. Keyser, S.Z. Levine, and F. Kaufman, J. Chem. Phys. 54, 435 (1971).

⁵⁸ A.L. Schmeltekopf and F.C. Fehsenfeld, J. Chem. Phys. **53**, 3173 (1970).

⁵⁹ T.P. Parr, D.M. Parr, and R.M. Martin, J. Chem. Phys. 76, 316 (1982).

⁶⁰ J.A.R. Samson, G.N. Haddad, and J.L. Gardner, *J. Phys. B At. Mol. Phys.* **10**, 1749 (1977).

⁶¹ Q.T. Algwari and D. O'Connell, IEEE Trans. Plasma Sci. 39, 2368 (2011).

⁶² Y. Ito, Y. Fukui, K. Urabe, O. Sakai, and K. Tachibana, *Jpn. J. Appl. Phys.* **49**, 066201 (2010).

⁶³ A. V. Phelps, J.L. Pack, and L.S. Frost, *Phys. Rev.* **117**, 470 (1960).

⁶⁴ G.B. Sretenović, I.B. Krstić, V. V. Kovačević, B.M. Obradović, and M.M. Kuraica, J. *Phys. D. Appl. Phys.* 47, 102001 (2014).

⁶⁵ A. Sobota, O. Guaitella, G.B. Sretenović, I.B. Krstić, V. V. Kovačević, A. Obrusník, Y.N. Nguyen, L. Zajíčková, B.M. Obradović, and M.M. Kuraica, *Plasma Sources Sci. Technol.* 25, 065026 (2016).

⁶⁶ E.J. Tonnis and D.B. Graves, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. **20**, 1787 (2002).

⁶⁷ G.P. Davis and R.A. Gottscho, J. Appl. Phys. 54, 3080 (1983).

⁶⁸ Q. Wang, I. Koleva, V.M. Donnelly, and D.J. Economou, *J. Phys. D. Appl. Phys.* **38**, 1690 (2005).

⁶⁹ Q. Wang, F. Doll, V.M. Donnelly, D.J. Economou, N. Sadeghi, and G.F. Franz, *J. Phys. D. Appl. Phys.* **40**, 4202 (2007).

⁷⁰ V.M. Donnelly and M. V. Malyshev, Appl. Phys. Lett. **77**, 2467 (2000).

⁷¹ T.D. Nguyen and N. Sadeghi, *Chem. Phys.* **79**, 41 (1983).

⁷² D.W. Setser, D.H. Stedman, and J.A. Coxon, J. Chem. Phys. 53, 1131 (1970).

⁷³ S. Hofmann, A.F.H. Van Gessel, T. Verreycken, and P. Bruggeman, *Plasma Sources Sci. Technol.* **20**, 065010 (2011).

⁷⁴ M.A. Gigosos and V. Cardeñoso, J. Phys. B At. Mol. Opt. Phys. 29, 4795 (1996).

⁷⁵ T. Nguyen, E. Hernandez, V.M. Donnelly, and D.J. Economou, J. Vac. Sci. Technol. A

36, 04F406 (2018).

⁷⁶ W.L. Wiese, J.W. Brault, K. Danzmann, V. Helbig, and M. Kock, *Phys. Rev. A* **39**, 2461 (1989).

⁷⁷ N. Sadeghi, D.W. Setser, A. Francis, U. Czarnetzki, and H.F. Döbele, *J. Chem. Phys.***115**, 3144 (2001).

⁷⁸ M.J. Frost, S. Himmelmann, and D.D. Palmer, *J. Phys. B At. Mol. Opt. Phys.* **34**, 1569 (2001).

⁷⁹ A. Hitachi, T.A. King, S. Kubota, and T. Doke, *Phys. Rev. A* 22, 863 (1980).

⁸⁰ A. Hibbertt, E. Biémont, M. Godefroid, and N. Vaeck, J. Phys. B At. Mol. Opt. Phys.
24, 3943 (1991).

⁸¹ X.Y. Liu, J.T. Hu, J.H. Liu, Z.L. Xiong, D.W. Liu, X.P. Lu, and J.J. Shi, *Appl. Phys. Lett.* **101**, 043705 (2012).

⁸² D. Pagnon, J. Amorim, J. Nahorny, M. Touzeau, and M. Vialle, *J. Phys. D. Appl. Phys.*28, 1856 (1995).

⁸³ J. Bittner, K. Kohse-höinghaus, U. Meier, and T. Just, *Chem. Phys. Lett.* **143**, 571 (1988).

⁸⁴ K.P. Huber and G. Herzberg, <u>Molecular Spectra and Molecular Structure</u> (1979).

⁸⁵ E. Gat, N. Gherardi, S. Lemoing, F. Massines, and A. Ricard, *Chem. Phys. Lett.* **306**, 253 (1999).

⁸⁶ V. Puech, F. Collier, and P. Cottin, J. Chem. Phys. 67, 2887 (1977).

- ⁸⁷ F. Valk, M. Aints, P. Paris, T. Plank, J. Maksimov, and A. Tamm, *J. Phys. D. Appl. Phys.* 43, 385202 (2010).
- ⁸⁸ N.D. Lepikhin, A. V. Klochko, N.A. Popov, and S.M. Starikovskaia, *Plasma Sources Sci. Technol.* **25**, 045003 (2016).
- ⁸⁹ A. V. Phelps, *Phys. Rev.* **99**, 1307 (1955).
- ⁹⁰ W. Lindinger, A.L. Schmeltekopf, and F.C. Fehsenfeld, J. Chem. Phys. 61, (1974).
- ⁹¹ G. Myers and A.J. Cunningham, J. Chem. Phys. 67, 3352 (1977).
- ⁹² F. Emmert, H.H. Angermann, R. Dux, and H. Langhoff, *J. Phys. D. Appl. Phys.* 21, 667 (1988).
- ⁹³ P. Lin, J. Zhang, T. Nguyen, V.M. Donnelly, and D.J. Economou, Unpublished (n.d.).
- ⁹⁴ S. Reuter, T. Von Woedtke, and K.D. Weltmann, *J. Phys. D. Appl. Phys.* 51, 233001 (2018).
- ⁹⁵ S. Bekeschus, A. Schmidt, K.D. Weltmann, and T. von Woedtke, *Clin. Plasma Med.* 4, 19 (2016).
- ⁹⁶ H. Jablonowski, M.A.C. Hänsch, M. Dünnbier, K. Wende, M.U. Hammer, K.-D.
 Weltmann, S. Reuter, and T. von Woedtke, *Biointerphases* 10, 029506 (2015).
- ⁹⁷ J. Chauvin, F. Judée, M. Yousfi, P. Vicendo, and N. Merbahi, Sci. Rep. 7, 4562 (2017).
- 98 S. Ma, K. Kim, J. Huh, and Y. Hong, Sep. Purif. Technol. 188, 147 (2017).

⁹⁹ M.H. Yuan, Narengerile, T. Watanabe, and C.Y. Chang, *Environ. Sci. Technol.* 44, 4710 (2010).

¹⁰⁰ K. Hensel, K. Kučerová, B. Tarabová, M. Janda, Z. Machala, K. Sano, C.T. Mihai, M. Ciorpac, L.D. Gorgan, R. Jijie, V. Pohoata, and I. Topala, *Biointerphases* 10, 029515 (2015).

¹⁰¹ H. Jablonowski, R. Bussiahn, M.U. Hammer, K.D. Weltmann, T. Von Woedtke, and S. Reuter, *Phys. Plasmas* **22**, 122008 (2015).

¹⁰² A. Hamdan, J.L. Liu, and M.S. Cha, *Plasma Chem. Plasma Process.* 38, 1003 (2018).

¹⁰³ Y. Yang, Y. Zhang, Z. Liao, X. Pei, and S. Wu, *IEEE Trans. Radiat. Plasma Med. Sci.* **2**, 223 (2017).

¹⁰⁴ J.Q.M. Almarashi, A.A. Alhazime, M.A. Ellabban, and A.A.H. Mohamed, *J. Phys. Conf. Ser.* **869**, 012072 (2017).

Appendix A: UV-absorption measurement of plasma jet uptake of water from interaction with a water substrate

Important applications of APPJs include medicine and water treatment. The skin surface during APPJ treatment is akin to a wet surface, and water treatment involves direct water-plasma contact^{97–104}. As such, the physics taking place during an APPJ interaction with water substrates is of great importance. In this study, we observed the APPJ uptake of water from a water pool acting as the substrate by means of UV absorption.

UV-absorption setup

The method of UV absorption involves passing UV light through the plasma, and measuring the amount of UV light absorbed by plasma species (OH in this case). The absorbance can then be converted to OH number density. The plasma source in use was the one ring and needle configuration without shielding gas apparatus (Fig. 35), using 0.14 slm Ar (0-0.2% added water) feed gas and 19-41 W applied power. The plasma impinged perpendicularly on a water pool acting as the substrate. If the gas flow is too high, the gas will make a hole on the water surface, and the plasma-water interface will be inside the hole, blocked from view. This explains the low flow rate used in the experiment. Light from a UV source was focused on the plasma-water interaction site, then collected into a spectrometer (Fig. 64). A shutter was used to control the UV light. To measure the amount of UV absorbed by OH radicals, the spectrometer must record the OH intensity (309 nm) for four states of the system: plasma on shutter open, plasma off shutter closed, and plasma off shutter closed. The absorbance is then calculated from these four intensities as follows,

$$Absorbance = \frac{Plasma \, off, \, shutter \, open-Plasma \, off, \, shutter \, closed}{Plasma \, on, \, shutter \, open-Plasma \, on, \, shutter \, closed}.$$
 (133)

Due to possible drift of the system (both UV source and plasma emission intensity can shift over time), we have to record all four states within a small time window, yet we need to accumulate enough signal to observe the minute amount of absorption. The solution is to cycle through the four states repeatedly and measure the emission intensities until enough signal-to-noise ratio is achieved (Fig. 65). A cycle is completed in under two seconds to minimize the chance of system drift.

•



Figure 64: Experimental setup for UV-absorption of an APPJ impinging on a water substrate



Figure 65: Cycle of a UV-absorption experiment

UV-absorption results

The 1st order OH band ranges from 306 nm to 312 nm, corresponding to 612-624 nm at 2nd order. Following Eqn. 133, a typical absorbance is shown in Fig. 66. The plasma OH emission matches the absorbance, as it should. The strongest OH peak at 618 nm 2nd order (309 nm 1st order) is used to calculate absorbance.



Figure 66: OH absorption (2nd order) with 0.21 slm dry Ar feed gas

The absorbance by OH increases from 0.001 to up to 0.008 with increasing power from 19 W to 41 W, with 0.14 slm Ar (0.2% water) feed gas, indicating increasing plasma water uptake, possibly due to increasing gas temperature with input power (Fig. 67a). On the other hand, with dry Ar feed, the absorbance stays relatively constant at 0.006 with 0.14 - 0.21 slm Ar flow rate (Fig. 67b).



Figure 67: UV absorbance of OH 309 nm line from plasma jet in contact with a water surface, probed near the surface: a) with 0.2% water in Ar feed as a function of power, b) dry Ar feed as a function of flow rate

Appendix B: Verification of measuring radial emission in an atmospheric pressure plasma jet

The method for acquiring the radial emission of a plasma jet (smoothing followed by Abel inversion of spatially-resolved emission) applied in Chapter 6 was verified by applying it to a hollow cylinder-shaped light source. In this section, we detail the creation of the light source and its measured radial emission.

A metal mesh sheet (86% vacancy) was rolled into a cylinder. Light from a Hg/Ar lamp was reflected onto a sheet of paper surrounding the mesh cylinder such that the light was then directed into half of the mesh cylinder evenly (Fig. 68). The mesh would then reflect the light, creating a hollow cylinder-shaped light source with roughly 1 mm diameter. We then attempt to collect the radial emission of this hollow cylinder-shaped light source (0th order, all wavelengths) using the method established in Chapter 6.

Side view (a)



Figure 68: Side view (a) and Top view (b) of the experimental setup for creating a hollow cylinder shaped light source and acquiring its emission

The resulted radial emission (Fig. 69) is a ring, peaking at 0.5 mm from the center, corresponding to the 1 mm diameter mesh cylinder. The emission in the center going to below zero can be attributed to the mesh cylinder not being perfectly round or the light not covering the mesh cylinder even. However, the error is small enough that we can conclude that the method for acquiring the radial emission works as intended.



Figure 69: Emission measured from a hollow cylinder-shaped light source