ELECTRON LOSS KINETICS IN NON-SELF-SUSTAINED PLASMAS AND THE EFFECT OF VIBRATIONAL NONEQUILIBRIUM

DISSERTATION

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By

Kraig Frederickson, B.S., B.A.

*****

The Ohio State University
2006

Dissertation Committee:

Professor Walter R. Lempert, Advisor
Professor Terry A. Miller
Professor Heather C. Allen

Approved by

_________________________________
Advisor
Graduate Program in Chemistry
ABSTRACT

Kinetic rates pertinent to electron loss mechanisms within a non-self-sustained plasma are investigated. In an oxygen containing plasma the examined mechanism is three-body electron attachment to O₂. When oxygen is absent from the gas, the dominant electron loss mechanism is electron-ion recombination.

The equilibrium rate coefficients for three-body electron attachment to O₂ are determined for the species-specific third body collision partner in an N₂/O₂ gas mixture at 300 K. These rate coefficients are compared to literature values and are found to be on the same order of magnitude but a factor of 2-4 larger.

A state of vibrational nonequilibrium is then imposed upon the system wherein the vibrational level populations, which are highly non-Boltzmann, are characterized by a vibrational temperature (>2000 K) which is nearly an order of magnitude greater than the translational/rotational temperature (∼350 K). It is demonstrated that the vibrational excitation activates the O₂⁻ electron detachment pathway, completely mitigating three-body electron attachment to O₂.

Lastly, a kinetic model is used to compare energy transfer rates in an RF coupled, laser sustained N₂/CO molecular plasma. The plasma is generated and maintained by a cw CO gas laser that causes associative ionization of CO. An RF field coupled to the
plasma increases the average electron energy of the system, reducing the electron-ion recombination rate. It is shown that while the rates used predict the vibrational level populations with reasonable accuracy, the agreement is not as good between the predicted and observed translational temperatures of the system.
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VITA

February 22, 1977. . . . . . . . . . . . . . . . . . . . . . . Born – Morgantown, West Virginia

June 1999. . . . . . . . . . . . . . . . . . . . . . . Bachelor’s of Science-Chemistry
Bachelor’s of Arts-Physics
Pacific Lutheran University.

1999 – 2000. . . . . . . . . . . . . . . . . . . . . . . Teaching Assistant.
The Ohio State University.

2000 – 2006. . . . . . . . . . . . . . . . . . . . . . . Research Assistant.
The Ohio State University.

PUBLICATIONS

Research Publications


FIELDS OF STUDY

Major Field: Chemistry
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CHAPTER 1

INTRODUCTION

A plasma, in its simplest approximation, is an ionized gas that is quasi-neutral on a macroscopic scale. Once ionized the physical properties of the gas are altered, with the most prominent change being a significant increase in the electrical conductivity. In addition the characteristics of the free electrons influence the nature of the plasma. For example, plasmas have been shown to absorb microwave and radio frequency electromagnetic waves. This absorption is due to the free electrons within the plasma transferring the energy of the wave to the neutral and ionic species through collisions. Plasmas, in general, can be divided into two categories; thermal and non-thermal.

A thermal plasma is one in which the heavy species and the electrons are at approximately the same temperature. These types of plasmas typically exist at high temperatures (on the order of $10^3$-$10^4$ K). Examples of thermal plasmas include fusion plasmas, plasma torches (for welding and cutting metal) and atmospheric plasmas created by objects (shuttles or meteorites) entering the atmosphere at high speeds.

A non-thermal plasma is characterized by the heavy species and the electrons possessing dramatically different temperatures. In this type of plasma the heavy species exhibit a much lower temperature than the free electrons. A common example of a non-
thermal plasma is the discharge within a fluorescent light bulb. The heavy species is approximately room temperature, while the electrons can exhibit a temperature on the order of 1000-3000 K. Depending upon the conditions of the non-thermal plasma (total pressure, electron temperature, heavy-species temperature, etc.), chemical reactions, which typically occur at high temperature, may occur at much lower temperatures. An example of this type of reaction is the formation of ozone.

Non-thermal plasmas can then be further classified, based upon the method of ionization that is used to generate them, as either self-sustained or non-self-sustained. A self-sustained discharge is one in which the primary electric field, defined as the field which couples the majority of the power to the gas, is of sufficient strength to ionize the gas by direct electron impact or by field ionization. For example, a simple DC glow discharge is classified as self-sustained because the DC field is sufficient to increase the kinetic energy of free electrons to the point that electron impact ionization occurs. While electron impact ionization facilitates the increase of the electron number density, it also leaves the discharge susceptible to the development of run-away ionization caused by the Joule heating instability, which manifests itself as the glow-to-arc transition. The instability usually develops at high field strength or high temperature but is dependent upon other factors such as the gas pressure and volume.

A non-self-sustained discharge is one in which the primary applied field is of insufficient strength to cause electron impact ionization. For these types of plasmas there must be an external source of electrons supplied to create conductivity. Examples of sources include UV radiation, photocathodes and, more recently, high-voltage, short pulse duration field ionizing “pulses” as described below.
Figure 1.1. Diagram showing cycle which leads to instability development within a non-thermal self-sustained discharge [1].

As mentioned above self-sustained discharges are susceptible to the Joule heating instability. As seen in Fig. 1.1 Joule heating increases the temperature of the system. This temperature increase results in an increase in the ionization rate, creating more free electrons. Joule heating within the system is then enhanced due to the greater electron number density. The cycle continues until the non-thermal plasma converts to a thermal plasma which is indicated by the glow-to-arc transition. A non-self-sustained discharge is not vulnerable to this type of instability because there is no link between Joule heating and free electron production. In fact, as will be discussed later, in some nonequilibrium cases there is an inverse relationship between Joule heating and free electron production wherein an increase in temperature causes a decrease in the ionization rate.

There are many applications of nonequilibrium air plasmas. Due to the nonequilibrium nature the plasmas remain translationally cold compared to equilibrium/thermal plasmas, while the energy available (primarily in vibration) makes
many chemical pathways accessible that would not be under equilibrium conditions. In this way heat-sensitive materials, such as biological samples, may be involved in the plasma processes without being destroyed. Additionally, nonequilibrium plasmas may be created at high-pressure leading to a wide range of experimental conditions which can be explored.

Currently, high-pressure, low-temperature, nonequilibrium plasmas are widely used in material processing applications. Such applications include etching and deposition. More recently, these types of plasmas have led to development of new excimer ultraviolet sources, surface treatment devices, environmental technologies (such as air pollution control) and applications in the biological and medical fields.

Instead of giving a cursory description of the multiple applications of nonequilibrium plasmas a single application will be examined in depth. Some of the work within the Nonequilibrium Thermodynamics Laboratory at The Ohio State University concerns the development of a Discharge Oxygen Iodine Laser (DOIL), which is similar to a Chemical Oxygen Iodine Laser (COIL). The lasing transition of this laser is the \(^{2}P_{1/2} \rightarrow ^{2}P_{3/2}\) of atomic iodine, which emits at 1315 nm and has been shown capable of producing power in the multi-kilowatt to megawatt range [2]. Excitation of the iodine to the upper level is achieved through energy transfer from the long-lived (radiative lifetime \(\approx 1\) hour) metastable state \(O_2(a^1\Delta)\) as shown in (1.1) [3].

\[
O_2(a^1\Delta) + I(^{2}P_{3/2}) \rightleftharpoons O_2(X^3\Sigma) + I(^{2}P_{1/2})^* \quad (1.1)
\]
The difference between the COIL and DOIL is the method by which the population inversion is created. In the COIL the O$_2$(a$^1\Delta$) is created through a chemical reaction, an example of which is shown in (1.2) [2].

$$\text{Cl}_2 + \text{HO}_2 \rightarrow \text{O}_2\left(a^1\Delta_g\right) + 2\text{Cl}^- + \text{H}^- \quad (1.2)$$

However, there are many technical difficulties involved in operating a COIL such as excessive weight, hazardous liquid storage and operation of a two-phase pumping system. These obstacles have spurred interest in an alternative method of creating O$_2$(a$^1\Delta$).

The DOIL relies upon an electric discharge to form O$_2$(a$^1\Delta$). Formation of O$_2$(a$^1\Delta$) within a discharge occurs through direct electron impact excitation as shown in (1.3).

$$\text{O}_2\left(X^3\Sigma\right) + e^- \rightarrow \text{O}_2\left(a^1\Delta\right) + e^- \quad (1.3)$$

A stable method of electrically pumping an oxygen-iodine laser would reduce the complexity and weight associated with establishing the population inversion in the gain medium.

Formation of O$_2$(a$^1\Delta$) is no trivial task, however, and its production must be maximized to achieve high-power output. It is known [4] that the reduced electric field (E/N), defined as the field strength divided by the heavy species number density, which optimizes the production of O$_2$(a$^1\Delta$) is $\approx 5\times 10^{-17}$ Vcm$^2$. Self-sustained discharges are typically established at E/N$\approx 1-5\times 10^{-15}$ Vcm$^2$ and therefore non-self-sustained conditions are optimum for O$_2$(a$^1\Delta$) production. Additionally, it is known that the gain threshold for lasing is highly temperature dependent as seen in (1.4) [5].
\[
\frac{[O_2(a^1\Delta)]}{[O_2(X^3\Sigma)]} = \frac{1}{1 + 1.5 \exp \left( \frac{403}{T} \right)}
\]  

(1.4)

The lower the temperature of the system, the smaller \(O_2(a^1\Delta)/O_2(X^3\Sigma)\) can be. If the end result is to produce a technique capable of establishing high yield gain for an oxygen-iodine laser, it must be a nonequilibrium environment where the translational temperature is low (\(\approx\)100-200 K) and the discharge is tuned so that the average electron energy \(\approx 0.98\text{eV} \ (\approx 11,000 \text{ K})\) [6]. Additionally, a large volume plasma would be advantageous \((10^2-10^6 \text{ cm}^3)\) as it would result in a larger volume gain medium and therefore a greater power output.

Recent work reported by Hicks, et al [6] has shown that \(O_2(a^1\Delta)\) can be produced in a non-self-sustained crossed discharge. A high voltage, short pulse duration, high repetition rate ionizing field, initiates the discharge, but is only responsible for a small (\(\approx 5\%)\) fraction of the total power delivered to the gas. Perpendicular to the ionizing field is a low voltage, high-current (order amps), DC sustainer field at \(E/N\) values which optimize production of \(O_2(a^1\Delta)\). Ideally, the sustainer voltage will maintain the discharge for a prolonged time interval, maximizing production of \(O_2(a^1\Delta)\).

However, it is well known that in high-pressure, low temperature \(O_2\) containing plasmas the dominant electron removal mechanism, three-body electron attachment to \(O_2\) shown in (1.5), is very rapid.

\[
O_2 + e^- + M \rightarrow O_2^- + M^* \tag{1.5}
\]

In fact this mechanism is so fast that maintaining an electron number density of \(10^{13} \text{ cm}^{-3}\), even assuming the most energy efficient form of ionization (an electron beam), at 1 bar...
and room temperature, would require ≈10GW/m³. This power requirement is prohibitively large for a plasma on the macroscopic scale. With respect to the DOIL, the plasma lifetime would be expected to be dominated by three-body electron attachment to O₂. At typical conditions of 10% O₂ in He at 120 torr and an average electron energy of 1eV the plasma lifetime would be expected to be approximately 6.7 μs. However, as can be seen in Fig. 1.2 the plasma lifetime is on the order of 40-60 μs (the current trace is truncated by the subsequent discharge pulse). In a nonequilibrium environment energy may be made available to activate additional chemical pathways while still maintaining the low temperature nature of the plasma. It is the effect of the nonequilibrium
conditions on the electron production and loss mechanisms that will be the focus of the study presented.

The first study to be presented in this dissertation involves the determination of the rate coefficients associated with the three-body attachment mechanism in air. It has been shown that the rate of attachment depends on the identity of the third body collision partner as depicted in (1.6) and (1.7).

\[
\begin{align*}
O_2 + e^- + O_2 &\rightarrow O_2^- + O_2^+ \\
O_2 + e^- + N_2 &\rightarrow O_2^- + N_2^+
\end{align*}
\] (1.6) (1.7)

In this case it was determined that there is a difference of approximately one order of magnitude between the rate coefficient of (1.6) and (1.7). It will be shown that while other electron loss mechanisms may occur, such as electron-ion dissociative recombination, (1.8),

\[
N_2^+ + e^- \rightarrow 2N_2
\] (1.8)

the dominant pathway is three-body electron attachment to O₂ and the rate coefficients associated with the separate third body collision partners will be determined.

The second study to be presented demonstrates the mitigation of the three-body electron attachment mechanism (1.5). Creating and sustaining a high-pressure, low temperature, large volume air plasma requires a large amount of energy ($\approx 10\text{GW/m}^3$) to replenish electrons ($\approx 14\text{ eV/electron-ion pair}$) lost to attachment because three-body electron attachment is so rapid. If the rate of attachment could be reduced, or alternatively if it could be offset by enhancing detachment (1.9),

\[
O_2^- + M \rightleftharpoons O_2 + M + e^-
\] (1.9)
the total power budget of air plasmas could be drastically reduced. It will be shown that while electron detachment from O$_2^-$ does not occur below $\approx$370 K at equilibrium conditions, nonequilibrium vibrational excitation of the third body collision partner, M, results in an electron detachment rate which is increased by many orders of magnitude ($\approx$ 5 at 300 K). In other words, we shall show rapid O$_2$ attachment is completely mitigated by vibrational excitation of the heavy species.

The last study to be presented regards increasing the physical dimensions of a N$_2$/CO plasma, formed, initially, by a CO laser. As will be discussed in more detail in the subsequent chapters, a plasma is initiated by vibrational excitation of the gas species. The lower vibrational levels are populated by resonant absorption of laser radiation at the fundamental vibrational frequencies (1.10). Then, Vibration-to-Vibration collisional transfer populates vibrational levels that are inaccessible to the laser (1.11). This is followed by associative ionization (1.12)

$$AB(q) + h\nu \rightarrow AB(q+1) \quad q=1 \rightarrow 10 \quad (1.10)$$

$$AB(n) + AB(m) \rightarrow AB(n-1) + AB(m+1) \quad n \leq m \quad (1.11)$$

$$AB(v) + AB(w) \rightarrow (AB)_{2}^{+} + e^- \quad E_v + E_w > E_{\text{ion}} \quad (1.12)$$

which occurs in collisions between two highly vibrationally excited molecules, provided that the sum of the vibrational energy, $E_v + E_w$, exceeds the ionization potential [7].

The disadvantage to this technique is that outside the rather small laser volume ionization does not occur. Therefore, the volume of the plasma is restricted to that defined by the incident laser beam. It will be shown that coupling an external, sub-breakdown RF field to the associatively ionized plasma increases the plasma volume.
Additionally, the data will be compared to a numerical model in an attempt to gain insight regarding the processes that occur in this complex system.
CHAPTER 2

EXPERIMENTAL

The body of this work involves determination of mechanistic rates within a plasma environment. To determine mechanistic rates temporally and spatially resolved number densities must be determined. For this work number densities must be determined for free electrons and for individual rotational and vibrational levels of molecules. Because of the nonequilibrium nature of some of this study, temperatures must be extracted for both the vibrational and translational/rotational mode of the molecules.

A variety of scientific techniques may be used in the study of these types of systems. Non-intrusive diagnostic techniques were desired for these studies. In the case of electron diagnostics the choices are limited to Langmuir probes, Thomson scattering and microwave attenuation. Langmuir probes are intrusive and alter the system that is being investigated and are therefore ill-suited. Thomson scattering is limited to relatively high electron number densities (>$10^{13}$ cm$^{-3}$) and high electron temperatures (>several eV) due to both the low absolute signal levels and interference from molecular Rayleigh scattering. Therefore, to determine the free electron number density microwave attenuation was chosen.
Multiple techniques may also be employed to determine the rotational and vibrational level populations of the molecules within the plasma environment. While absorption, emission and scattering are all, in principle, valid techniques to probe the population distributions of the component species, there are advantages to Raman scattering which make it a better choice for determining the vibrational and rotational populations. Traditional infrared spectroscopy cannot be used because the molecules examined are infrared inactive. Any type of fluorescence technique would require a tunable laser to resolve the populations of the ground electronic state by scanning the pump wavelength. Additionally, each of the molecular components would need to be investigated separately. There is also the possibility that quenching of the excited state levels may be different for each level, which complicates the data analysis and increases uncertainty. Raman scattering exhibits qualities that make it the superior choice. The probe laser used must be fairly high power (100mJ/10ns pulse) but may be a fixed frequency so that no tuning is required. Multiple energy levels can be probed in concert and extraction of the population information is simple and straightforward. In addition molecules, which are infrared inactive, can be investigated using Raman scattering. Furthermore, Raman scattering is a point measurement, not a line of sight measurement, and therefore it offers spatial resolution that absorption and spontaneous emission techniques cannot offer.

2.2 Experimental for Rate Coefficient Measurements

A schematic of the apparatus used to determine attachment rates is shown in Fig. 2.1. The plasma was created by a pulsed electron beam (Kimball Physics EGH-8101) which was operated at 80keV primary beam voltage and at 10 Hz repetition rate for all
Figure 2.1. Experimental Schematic for Measurement of Rate Coefficients.

sets of conditions. The rise and fall times of the primary electron beam pulse are approximately 150ns, while the width of the pulse was varied in the range 5-40µs. A beam current of approximately 1mA was used for all data sets. An aluminum foil window of approximately 0.018mm thickness and cross sectional area of about 20 mm² separated the main body of the electron gun from the experimental cell. A 5-arm stainless steel cell with a volume of approximately 15 liters was mounted to the end of the electron gun. Approximately 40keV of energy is absorbed from the primary electron beam as it passes through the foil window into the sample cell. An unbiased Faraday Cup was used to measure the beam current once it had passed through the foil window. The total pressure of the sample gas is varied between 25-600 torr. Various compositions of the sample gas were explored holding the partial pressure of one component constant
and varying the partial pressure of the other. The flow rate of the gases within the cell was approximately 10 cm/s and the residence time of the gases within the cell was on the order of a few seconds.

Time-dependent electron density is determined by attenuation of 40 GHz microwave radiation. A set of waveguides directs the microwaves from the output transmitter to the receiver within the experimental cell. These waveguides define a small volume (~1cm$^3$) within which the plasma should be homogeneous approximately 1 cm from the foil window. In addition the waveguides were oriented so that the greater dimension of the waveguide cross-section was parallel to the aluminum foil window. The waveguides were constructed of thin brass foil and formed a rectangular pipe approximately 15 cm long and with a cross section of 1 cm by 0.3 cm. A waveguide was pressed into the transmitter and receiver of the microwave system and the spacing between the waveguides was approximately 1 cm. The transmitter and receiver were mounted to flanges and formed part of the steel cell. Due to the divergence of the primary electron beam upon passing through the foil window, the waveguides were positioned as close to the foil window as possible and were separated as much as possible, while still maximizing microwave throughput. By keeping the waveguides as close to the foil window as possible the density of primary electrons within the probed region would be maximized and therefore the density of secondary electrons should be maximized as well. The separation was chosen to minimize the impact of the primary beam with the waveguides and maintain a high microwave throughput. The transmitted microwaves are sent from the receiver to the detector, which is a Herotek tunnel diode detector. A Stanford Research Systems 300 MHz amplifier was used to amplify the
output from the detector by a factor of ≈25 (2 stages, factor of 5 each) and set to a 50 ohm impedance. A 400MHz oscilloscope was used to record the signal from the amplifier and all electron density measurements were averaged 256 times. The time-dependent microwave measurements were output to a computer for curve fitting using the program Sigmaplot. The time resolution of the system is limited by the rise time of the primary electron beam pulse and corresponds to a maximum frequency of approximately 7MHz.

Various mixtures and pressures of oxygen and nitrogen were used in the apparatus. The total pressure varied from approximately 25-600 torr and the percent composition of oxygen varied in the range 0.5-25% with nitrogen being the balance in each case. It was important to choose gas conditions at which the three-body attachment rate did not exceed the resolution of the instrument but at which the rate of electron removal was still dominated by the three-body attachment mechanism.

2.3 Experimental for Mitigation Experiment

A series of microwave attenuation measurements were also acquired from an electron beam generated plasma in which all heavy species were excited using a CO laser. The previously described electron beam and microwave attenuation apparatus were again used but, with the addition of a CW CO laser and an injection-seeded, cavity locked Ti:Sapphire laser.

As can be seen in Fig. 2.2, the beams from both lasers are input orthogonally to both the axes of the primary electron beam and the microwave waveguides. The CO laser beam is focused (focal length =500mm) to a diameter of approximately 0.5mm at a distance of 1cm from the foil window along the electron beam axis. Focusing creates a
Figure 2.2. Experimental Schematic for Mitigation Experiment. Waveguide axis is orthogonal to both laser beam axes and electron beam axis.

cylindrical region, 1cm long and about 1mm in diameter, of vibrationally excited molecules. The cryogenically cooled CO laser was designed in collaboration with the University of Bonn and constructed at The Ohio State University. It is tuned to emit a substantial percentage of its power on the v=1→0 and v=2→1 fundamental transitions with the majority of the remaining power output in the next 10 vibrational transitions. The CO laser is operated in continuous mode and is used to vibrationally excite the
diatomic species N₂, O₂ and CO by a process that will be described in detail in Chapter 4. Input along the same axis as the CO laser beam is the output from the injection-seeded, cavity locked Single Longitudinal Mode (SLM) Ti:Sapphire laser (Δν≈0.002 cm⁻¹), which was used to acquire spectrally filtered pure rotational Raman spectra, as illustrated in Fig. 2.3. The optical purity of the Ti:Sapphire laser output was increased using a Stimulated Brillouin Scattering Phase Conjugate Mirror before it was focused into the CO laser pumped volume via a dichroic mirror and lens of 400mm focal length. Scattered photons were collected at 90° by replacing one of the waveguides with an optical window and detected using an Optical Multichannel Analyzer (OMA) consisting of a 0.25 m spectrometer and intensified CCD camera. A rubidium vapor filter is placed into the collection path between the plasma cell and the ICCD detector. The filter strongly attenuates (5-6 orders of magnitude) elastically scattered light from the laser, which is tuned to the strong rubidium absorption resonance at ≈780.1 nm. However, frequency shifted light is transmitted through the filter with nearly 100% efficiency. The volume element imaged by the rotational Raman system was approximately 1cm in length and 0.01cm in diameter. A translational stage was used to displace the dichroic mirror horizontally with respect to the CO laser beam to allow for spatial resolution of the optically pumped region. The linear flow rate was approximately 10cm/s and the residence time of the gases within the cell was on the order of a few seconds. Flowing the gases was required to remove products and cool the vibrationally excited region. A schematic of the experimental set-up is shown in Figures 2.2 and 2.3. Figure 2.2 shows the relevant components for measuring the free electron number density while Figure 2.3
Figure 2.3. Experimental Schematic for rotational Raman temperature measurement.

shows the rotational Raman scattering instrument, which was used to extract the heavy-species temperature.

The composition of the sample gas had to be changed to include 5% CO to allow for the vibrational loading of the diatomics within the mixture. Data could be acquired at pressures from 50-600 torr, but were typically collected around 300 torr and 1%-20% O₂.

2.4 Experimental for rf Plasma Expansion

A schematic of the final experimental apparatus is shown in Figure 2.4. Again, a broadband continuous wave CO laser described in the previous section is used to irradiate a gas mixture. The mixture consists of nitrogen containing approximately 1.5% CO and trace amounts (approximately 300 ppm) of NO. The total pressure of the gas mixture is approximately 300 torr. The residence time of the gases in the cell is approximately 1 second.
Figure 2.4. Experimental diagram of vibrationally resolved Raman scattering instrument. The optical cell translates vertically (in and out of the plane of the page).

The output of the CO laser is focused (500mm) into a six arm cross pyrex absorption cell containing the gas mixture. Focusing the beam increases the power loading per CO molecule along the laser beam path. This produces a vibrationally excited gas mixture approximately 2 mm in diameter and 10 cm long. Two circular copper electrodes (3 cm diameter) placed above and below the path of the CO laser beam are used to apply an RF field to the optically pumped plasma. The absorption cell is supported by a vertical translation stage fitted with a micrometer that produced precision movement on the order of ±0.005 mm. In addition the CaF$_2$ lens used to focus the CO laser beam was on a vertical translating mount to allow displacement of the pump beam from a Nd:YAG probe beam which is used to determine the vibrational distribution function of the component gases by means of vibrational (Q-branch) Raman scattering. This setup permitted the movement of the Raman laser probe beam vertically with
In this experiment, two copper electrodes are placed above and below the optically pumped plasma with a separation of approximately 13 mm. Connected to these electrodes is a 13.56 MHz, 600W ENI ACG-6B RF power supply via a modified MFJ-949E tuner, which is used for plasma impedance matching. Tuning the impedance so that the reflected RF power does not exceed 5-10% of the forward power was typical for these experiments. Setting the output wattage of the RF power supply to 100 W produced a peak-to-peak voltage of 4 kV measured by a high voltage probe. At these conditions, the peak reduced electric field did not exceed $E/N \approx 1 \times 10^{-16} \text{ V} \cdot \text{cm}^2$. This low value of the reduced electric field precludes electron impact ionization and ionization instability.
development as described in Fig. 1.1. Therefore, electrons in the optically pumped plasma enhanced by the RF field are produced only by the associative ionization mechanism, (1.12).

To acquire spontaneous Raman spectra of the optically pumped plasma, a pulsed Nd:YAG laser tuned to the second harmonic (532 nm) and operated at 10 Hz was used to probe the gas mixture. Each laser pulse had an output energy of 200 mJ and a duration of approximately 10 ns. The Nd:YAG laser probe beam was combined with the CO laser pump beam using a 90° CaF₂ dichroic mirror which was coated to allow transmission of the CO laser beam while reflecting the Nd:YAG beam. Spatial resolution of the Raman spectra was enhanced by focusing of the probe beam using a 400 mm focal length lens. A notch filter was used to attenuate the 532 nm line resulting from elastic scattering. The Stokes shifted signal was in the range of 600 to 612 nm, which is well outside the attenuation profile of the notch filter. To maximize the signal to noise the image of the plasma was rotated using two 2 inch diameter mirrors so that it was oriented parallel to the vertical input slit of the OMA spectrometer. In addition the signal was focused with f/4 lenses to match the 0.25 meter f/4 spectrometer. This resulted in a solid angle of approximately 0.049 sr, corresponding to an area defined by the monochromator slits and probe beam of approximately 2-5mm in length by 50-100 µm in thickness. The detector used to acquire the Stokes shifted signal was a microchannel plate intensified charge-coupled device (ICCD) camera. By using a pulser to gate the intensifier the signal to noise increased by eliminating much of the spontaneous emission from the optically pumped cell. The quantum efficiency of the detector was on the order of 6% at the Stokes wavelength and the signal was integrated for a duration of 30s (300 laser “shots”).
Within the monochromator, a 1800 line/nm grating was used which resulted in a spectral resolution of approximately 1.5 Angstroms and a spectral range of approximately 10 nm. The resolution was adequate to resolve the individual Q-branch vibrational bands, but insufficient to obtain any rotational fine structure.

Uncertainty in the relative band intensities of the Raman spectra of the laser-excited plasma from which the experimental vibrational level populations are derived is estimated to be 10%-20%. For Raman spectra of the optically pumped plasma enhanced by the RF field, the uncertainty is somewhat greater (20-25 %) due to a lower signal-to-noise ratio. Uncertainty in the ratio of vibrational populations of levels $v=0$ and $v=1$ is estimated to be 6%.
CHAPTER 3

THREE-BODY ATTACHMENT RATE COEFFICIENTS

Interest in the rate of three-body electron attachment to oxygen stems from upper ionospheric chemistry and the field of plasma chemistry and its applications. In the upper atmosphere molecules are ionized by the high energy solar or cosmic radiation. Oxygen, being a more reactive and abundant component of the atmosphere, is involved in many of the chemical processes that occur in the upper atmosphere. One of the most important processes being the formation of ozone. In addition with the recent emphasis on atmospheric environmental responsibility (Kyoto Treaty), understanding the chemical mechanisms that oxygen participates in within the upper atmosphere is tremendously important. Additionally, with emerging plasma applications such as MHD power generation, nonthermal plasma ignition and the Discharge Oxygen Iodine Laser (DOIL), understanding and predicting the rate of reaction of the three-body electron attachment process becomes increasingly important.

3.2 Review of Previous Rate Coefficient Data

The earliest works on electron attachment in air were performed by Loeb [8], Wahlin [9] and Bailey [10]. These works explored a theory proposed by J. J. Thomson [11] stating that a free electron must undergo, on the average, a number of impacts, n,
with an attaching molecule before it attaches to form an ion in a simple two body process, Eq. (3.1).

\[ M + e^- \rightarrow M^- \]  \hspace{1cm} (3.1)

An alternate theory proposed by Wellisch [12] stated that the free electrons must possess a minimum amount of energy to attach to a molecule otherwise the electron would remain permanently free. Using the Rutherford alternating current method, Loeb [8] showed Thomson’s theory to be correct and hypothesized that \( n \) is a characteristic property of the attaching gas and determined values for \( \text{N}_2, \text{H}_2, \text{O}_2 \) and air. Most importantly, Loeb determined that electrons will not attach to \( \text{N}_2 \) and, therefore, \( \text{O}_2 \) was the molecule responsible for electron attachment in air. In that work there was slight variance in the value of \( n \). However, \( n \) was assumed to be constant because it remained at the same order of magnitude over a wide range of pressures and gas compositions. Loeb reasoned that because \( n \) is computed using the electron mobility, which is a function of gas pressure and field strength, any variation in \( n \) with pressure, gas composition or field strength was attributed to the uncertainty of the electron mobility at those conditions.

In response to the work of Loeb another study was performed by Bailey in which the current was measured at multiple points along a uniform field within a sample of dry air. Bailey concluded that \( h \), the attachment coefficient, which is the reciprocal of \( n \), was not constant and that it varied with \( u \), the velocity of “agitation” (or velocity of collision). This correction to the definition of \( h \) is of utmost importance and it makes intuitive sense. The electron affinity of an attaching gas is finite. If the energy of the free electron exceeds the electron affinity, the electron should remain free. The attachment coefficient
should therefore be a function of the average electron energy and was determined to be so by Bailey.

However, work performed by Cravath [13] indicated that the attachment coefficient, $h$, did show dependence upon the pressure of the gas. This work was an attempt to develop a new apparatus to measure the attachment coefficients of gases as a function of $E/P$, a schematic of which is shown in Fig. 3.1. This was the first case in which the electrons are removed from the drift tube by means of a control grid. An alternating voltage applied to a grid, which was positioned between the electron source (filament) and the detector caused the electrons to collide with the grid wires, removing them from the drift tube, while the ions remained relatively unaffected due to their greater mass. The attachment coefficient, $h$, was then calculated using the ratio of the attenuated electron current to the total electron current, Eq. (3.2) and (3.3).
\[
\ln \left( \frac{I}{I_0} \right) = -\frac{h vx}{L W} 
\]  

(3.2)

\[
h = \frac{4 \times 300 m k^2 E}{3 e x} \ln (1 - R_i)
\]  

(3.3)

For these equations I is the electron current at some distance x from the electron emitting filament, I\(_0\) is the current with the collecting grid off, h is the attachment coefficient, W is the drift velocity of electrons, v is the average random speed of the electron, L is the mean free path of the electron, x is the distance from the electron source, m is the mass of the electron, e is the charge of the electron, k is the electron mobility, E is the field strength and R\(_i\) is the ratio of the current received by the detector with the grid on to the current received by the detector when the grid is off.

Cravath, however, did not believe his results at the time because they were contrary to the results of Bailey [10], which showed that the attachment coefficient was independent of pressure. The pressure independent results were considered more reliable due to greater consistency within the data set and the simpler conditions at which experiments were conducted. It is unfortunate that Cravath doubted his results. The analysis of the data comparing h for air to that of pure O\(_2\) showed a discrepancy. In the analysis Cravath scaled the value of the attachment coefficient to account for the collisions with N\(_2\) that could not result in attachment. It was determined that the corrected attachment coefficient for air was less than half of the corresponding value in pure O\(_2\), when they should be identical. This was the first indication that the attachment mechanism was not a simple two-body process where an electron collides with a molecule and is captured.
Bradbury [14] attempted to explain the increase in attachment coefficient, \( h \), as \( E/P \) increased, which was seen by Cravath and other investigators. The probability of electron capture was determined for oxygen and oxygen mixtures within an apparatus similar to that of Cravath and the dependence on the average electron energy is shown in Fig. 3.2. The difference being that the electron source was a photocathode being irradiated with a UV lamp (mercury arc lamp) and that multiple grids were used at various displacements from the electron source. This work was performed at various \( E/P \) and the electron current was measured at two different displacements and used to calculate the probability of capture, \( h \). While the attachment data showed dependence upon the average electron energy, it did not show any pressure dependence. However, as \( E/P \) increased Bradbury did find that the attachment coefficient passed through a
minimum and then began to increase. The increase in attachment coefficient with increasing \( E/P \) was attributed to an electron impact induced electronic transition in \( \text{O}_2 \). Bradbury theorized that at higher \( E/P \) (≈ 4-8 V/(cm torr)) the electron collides inelastically with an \( \text{O}_2 \) molecule, promoting the \( \text{O}_2 \) to an excited electronic state. Since the electron has lost all of its energy in the inelastic collision, it now possesses the energy of an electron at a much lower \( E/P \) (≈ 1 V/(cm torr)) and exhibits a greater attachment coefficient similar to that found at low values of \( E/P \). In addition Bradbury attempted to explain the discrepancy between the attachment probability of pure \( \text{O}_2 \) and that of air that Cravath demonstrated, but failed. Bradbury attributed the discrepancy to the electron undergoing inelastic collisions with \( \text{O}_2 \) as stated above. This explanation fails to explain the discrepancy in \( h \) when the average electron energy is below the threshold for the electronic transition to occur. Below that energy, there should be no inelastic collisions according to Bradbury’s theory, but the discrepancy still exists.

Bloch and Bradbury [15] attempted to provide a mechanism by which an oxygen molecule captures a free electron. They claim that the formation of the negative ion results in the excitation of the molecule, which later is stabilized through relaxation. Using energetic arguments Bloch and Bradbury deduce that the vibrational mode of the attaching diatomic must be excited. Excitation of the rotational mode was discounted because it would require the electron affinity to be on the order of the spacing of two rotational levels, which would be much less than \( kT \) and result in a thermally unstable ion. Further, using arguments based on the order of magnitude of the probability of capture, \( h \), and its definition, (3.4), Bloch and Bradbury determined that \( \text{O}_2 \) would
be excited to the first vibrational level and that correspondingly the electron affinity of O$_2$ must be 0.19eV. The quantities given in Eq. (3.4) are $m$, the mass of the electron, $M$ the mass of the molecule, $a$ is the orbital dimension of the electron and is related to the electron affinity, $A$, by $A = \frac{\hbar}{2ma^2}$, $n'$ is the vibrational quantum number and $\delta$ is the mean of the elongation in the ground state of the nuclear oscillation. Since $h_n'$ is experimentally determined to be on the order of $10^{-4}$ and $(m/M) = 0.33 \times 10^{-4}$ and $(\delta/a) \approx 1/10$, $n'$ must be 1. The result of this argument is that the electron affinity of O$_2$ must be approximately 0.19eV as determined by $A \leq n'\hbar\omega$ where $\omega$ is the angular frequency of the vibration. The value for the electron affinity is determined from the vibrational level spacing of O$_2$ and is the difference between the ground vibrational level and first excited level.

The first work found corroborating the hypothesis of Cravath, that the attachment mechanism at low E/P was not a simple two-body process, was performed by Bortner and Hurst [16 & 17]. Rates for electron attachment in oxygen were measured in a drift tube in various buffer gases at higher pressures (1-8mmHg O$_2$ in 600-1600mmHg N$_2$) and at lower values of E/P (0.2-2.0). Drift velocities within the gas mixtures used were measured simultaneously. Free electrons were generated from a collimated beam of alpha particles directed into the center of a drift tube. A uniform electric field is established within the tube perpendicular to the alpha particle beam. There are two detectors, one above and one below the collimated beam. The drift velocity is measured from the center of the tube to one of the detectors and the free electron current is
measured at the other. The free electrons pass through a gate (starts clock) and the time between the gate pulse and the first detector pulse determines the drift velocity, while the current determined at the second detector in effect counts all of the electrons which remain unattached after traversing the drift tube. A convolution integral was performed of the instrument response and the time-dependent current function. The maximum of the resulting function was determined and plotted for different values of the attachment probability, $\alpha$ (cm$^{-1}$ mmHg$^{-1}$), and the drift velocity. These standardized curves indicated the current pulse peak height and once the drift velocity and pulse height had been measured the attachment probability was determined by comparison to these standardized curves. Bortner and Hurst have defined the attachment probability, $\alpha$, as being dependent on both the distance traveled and the pressure of the attaching gas instead of on the number of collisions.

Bortner and Hurst found that as the partial pressure of the attaching gas (O$_2$) was varied at constant E/P, the attachment probability, $\alpha$, changed. In addition increasing the partial pressure of the N$_2$ buffer gas while keeping the partial pressure of O$_2$ constant also caused the attachment probability to increase. This was the first case in which the attachment rate was conclusively shown to depend on the pressure of both the attaching gas (O$_2$) and the buffer gas (N$_2$). This dependence led Bortner and Hurst to propose possible mechanisms for the formation of O$_2^-$ using the earlier ideas of Bloch and Bradbury. The mechanisms proposed were a two step process involving the formation of a short-lived transition state, Eq. (3.5), and a three-body process, Eq. (3.6). For Eq. (3.5), a number of subsequent stabilizing processes were postulated, which include radiative
stabilization and various forms of collisional relaxation. The forms of collisional relaxation include energy transfer from $O_2^*$ to another molecule ($O_2$ or $N_2$) or a three-body collision in which the two neutral molecules each acquire some of the energy from the short-lived transition state.

It is important to note the change in definition of the attachment probability from the early work of Loeb, Wahlin, Bailey, Cravath and Bradbury. The early work defined the probability of attachment on a per collision basis, while Bortner and Hurst changed the definition to be dependent upon distance traveled and the pressure of the attaching gas. This change of definition of the attachment probability allowed Bortner and Hurst to determine the attachment probability as a function of the partial pressures of gases. From this formulation the dependence of the attachment probability on the non-attaching buffer gas ($N_2$) became apparent. Work performed by the early investigators did not vary the relative amounts of the gases in a comprehensive way and therefore missed the pressure dependence exhibited by a three-body attachment mechanism.

Working independently of Bortner and Hurst, Chanin, Phelps and Biondi [18 & 19] also determined the attachment mechanism to occur by a three-body process. It was found that at low $E/P$ (<1Vcm$^{-1}$mmHg$^{-1}$) the attachment coefficient, $\alpha/P$, varied with the pressure of the gas, while at larger $E/P$ (>11Vcm$^{-1}$mmHg$^{-1}$) the attachment coefficient was independent of pressure as shown in Fig. 3.3. Thus, resolving the issue of the bimodal nature of the attachment probability as a function of average electron energy that
Bradbury first encountered (Fig. 3.2). The measurements were performed in a drift tube similar to that of Cravath and Bradbury. Electrons were generated from UV photons incident on a photocathode. A control grid was placed between the photocathode and the detector to act as a gate. The grid does not allow electrons or anions to pass until a voltage is applied. In this way it was possible to acquire a time-resolved current waveform, an example of which is given in Fig. 3.4. In their work they collected all of the free electrons (the initial smaller peak) and ions (the larger subsequent peak) formed by attachment. In previous work either the number of electrons were measured or the

Figure 3.3. Pressure and E/P dependence of electron attachment rate of O₂ [18].
Figure 3.4. Waveform used by Chanin, Phelps and Biondi. Once integrated gives electron and ion densities.

number of ions were measured, but not both. By integrating the current waveform obtained from their drift tube they were able to calculate \( \alpha \), the attachment probability, explicitly using Eq (3.7).

\[
\alpha = \left( \frac{1}{L} \right) \cdot \ln \left[ \frac{N_i + N_e(L)}{N_e(L)} \right] \tag{3.7}
\]

In this case \( \alpha \) was determined as a function of pressure, average electron energy, gas composition and distance traveled. In Eq (3.7) \( N_i \) is the number of anions collected, \( N_e(L) \) is the number of free electrons collected and \( L \) is the distance between the
photocathode and the detector. The attachment rate, $\nu_A$, is related to the attachment probability, $\alpha$, by the electron drift velocity, $\mu$, and is given in Eq (3.8). Therefore, the attachment rate may be determined for various sets

$$\alpha = \frac{\nu_A}{\mu} \quad (3.8)$$

$$\nu_A = \sum_i k_A^{(i)} n_i n_{O_2} \quad (3.9)$$

of conditions. If the attachment rate is defined by Eq. (3.9), then the attachment rate coefficients for specific third body collision partners can be determined. In Eq.(3.9) $k_A^{(i)}$ is the species-specific rate coefficient for three-body attachment, $i$ is the index representing the different species present in the mixture and $n_i$ is the number density of the individual species.

In addition Chanin, Phelps and Biondi resolved the discrepancy between the attachment in air and the attachment in pure $O_2$ found by Cravath. This discrepancy occurs because of the three-body nature of the attachment mechanism. The overall rate of attachment depends upon the ability of the third body to remove energy from the anion. Chanin, Phelps and Biondi determined the attachment coefficients for $O_2$, $N_2$ and $He$ as a function of average electron energy and are shown in Fig. 3.5.

A hypothesis was offered in an attempt to explain the species-dependence of the rate coefficient. When $O_2$ first captures a free electron, the molecule is believed to be left in an excited vibrational level. This excited intermediate must be stabilized by a collision with a third body. Examination of the degrees of freedom indicates that $He$ can remove energy only in the form of translation, while $N_2$ and $O_2$ may transfer energy to
Figure 3.5. Attachment rate coefficient vs. average electron energy for various gases [19].
translational, rotational or vibrational modes. It is known, however, that the V-V transfer rate between \( \text{N}_2 \) and \( \text{O}_2 \) is very small, five orders of magnitude smaller than intraspecies \( \text{O}_2 \) V-V [20] and therefore can be assumed to be negligible. This analysis would indicate that \( \text{O}_2 \) would be more effective as a third body collision partner than either \( \text{N}_2 \) or \( \text{He} \), with \( \text{N}_2 \) being more effective than \( \text{He} \). Additionally, Chanin, Phelps and Biondi proposed a possible “accidental resonance” between \( \text{O}_2 \) and \( \text{O}_2^- \). While no such resonance exists, the difference in the vibrational energy spacings for \( \text{O}_2 \) and \( \text{O}_2^- \) is smaller than for \( \text{N}_2 \) and \( \text{O}_2^- \) (1090.9 \( \text{cm}^{-1} \) for \( \text{O}_2^- \), 1580.2 \( \text{cm}^{-1} \) for \( \text{O}_2 \), 2358.6 \( \text{cm}^{-1} \) for \( \text{N}_2 \)) [21]. Therefore, the V-V exchange rate for \( \text{O}_2 \) and \( \text{O}_2^- \) would be expected to be larger than for \( \text{N}_2 \) and \( \text{O}_2^- \) since the rate, in general, decreases with increasing difference in vibrational energy.

In addition to the above mode analysis there is the possibility of stabilization by charge transfer. Instead of the excited intermediate transferring energy to the third body, the electron may be transferred. Charge transfer cannot occur with \( \text{He} \) or \( \text{N}_2 \) as the third body (since the negative ions are not stable, but may occur with \( \text{O}_2 \)). So, charge transfer may be responsible at least in part for the larger rate coefficient associated with \( \text{O}_2 \).

The work of Pack and Phelps [22 & 23] regards collisional detachment of an electron from the oxygen anion. Using an apparatus identical to that of Chanin, Phelps and Biondi, the detachment frequency was determined for pure \( \text{O}_2 \) as a function of temperature at low \( E/P \). It was found that electron detachment does not occur below approximately 370 K and that the detachment frequency is highly temperature dependent, while the attachment frequency is nearly constant at higher temperatures. A plot showing the heavy-species temperature dependence of the attachment and detachment frequencies is shown in Fig. 3.6. Additionally, Pack and Phelps revised the value of the \( \text{O}_2 \) electron
Figure 3.6. Attachment and detachment frequencies for O₂ vs heavy species temperature [22].

affinity to be 0.43eV. Claims were also made as to the validity of the Bloch and Bradbury mechanism of attachment. In the electron detachment measurements Pack and Phelps [23] claimed that they were unable to make the anion more stable by increasing the pressure of the system. They argued that if electron attachment resulted in a vibrationally excited anion, increasing the pressure would increase the vibrational relaxation rate and make the anion more stable. They concluded that since the stability of the anion does not increase with pressure, the anion which results from attachment is
most likely in v=0. This implies that the attachment mechanism is three-body and not a
two-step process which progresses through a short-lived intermediate.

3.3 Review of Three-Body Attachment to Oxygen

It is now known that the attachment of a free electron to molecular oxygen occurs
by a three-body mechanism at low average electron energies. In an air-like plasma a free
electron is captured by an oxygen molecule in a three-body collision. Collision with a
third body, such as another oxygen or nitrogen molecule, is required to carry away the
bond energy as seen in Eq. (3.10).

\[ \text{O}_2 + e^- + M \rightarrow \text{O}_2^- + M^* \quad \quad \quad M = \text{O}_2 \text{ or N}_2 \quad (3.10) \]

Previous experiments have shown that the nature of the third body is important (Chanin,
Phelps and Biondi). That is, it has been shown that molecular oxygen is a more effective
third body collision partner than nitrogen in an air-like plasma. It is believed that the
anion is formed in the ground vibrational level and the excess energy is carried away by
the third body partner in the translational, rotational and possibly the vibrational mode.
Chanin, Phelps and Biondi have theorized that oxygen is a more effective third body
stabilizer than nitrogen due to a near resonance between the electron affinity of O\(_2\)
(0.43eV) and the v=0→2 transition in O\(_2\). A general rate equation for reaction (3.10) is
given in Eq. (3.11)

\[ \frac{dn_e}{dt} = S - k_{A}^{(1)} n_{O_2}^2 n_e - k_{A}^{(2)} n_{O_2} n_{N_2} n_e \quad (3.11) \]

where \( n_x \) represent the number densities of the respective species, \( k_{A}^{(x)} \) are the
corresponding rate coefficients for the different third body species, and \( S \) is the electron
formation rate, which depends upon the process used for free electron creation. Electron
energy and gas temperature have a large effect on the rate coefficients for the three-body process and must be taken into consideration when evaluating the coefficients. The dependence of the three-body attachment rate coefficient on the average electron energy can be seen in Fig. 3.5 for several gases. Additionally, the dependence on temperature is shown for O₂ and He at temperatures of 77 and 300 K.

As described earlier, previous work examining the three-body attachment rate used a drift tube. In these types of experiments ionization occurs at a cathode within the drift tube. A constant voltage pulls the electrons toward a collector, which measures current. As the electrons drift toward the collector they collide with the sample gas. In an air-like gas mixture some of the free electrons will attach to oxygen by the three-body mechanism. Any unattached electrons reach the collector much more quickly than the oxygen anions formed by attachment. A schematic of a typical drift tube is found in Fig. 3.1 and a sample current waveform is found in Fig. 3.4. Analysis performed using information provided by the current waveform, coupled with the drift velocity yields the attachment rate.

As described in Chapter 2, experiments performed for this thesis utilized a pulsed electron beam for ionization. In this case it is best to use the solution to Eq. (3.11) with S=0 and fit the decay of the electron density after the falling edge of the beam pulse. This technique was used by Hirsch, Eisner and Slevin [24] to determine the rate of three-body attachment to oxygen in pure O₂ and in an air-like mixture of 4N₂:O₂. The advantage of this approach is that there is no need to assume an electron drift velocity to extract the attachment rate. However, Hirsch, Eisner and Slevin obtained the electron
number density by observing the microwave frequency shift instead of microwave attenuation.

3.4 Review of Microwave Attenuation Process

The experimental apparatus used for determining O₂ attachment was described in detail in Chapter 2. To determine the rate coefficients for the three-body attachment mechanism in O₂/N₂, the number density of free electrons is determined as a function of time. Instead of employing a drift tube, which requires knowledge of the electron drift velocity in the sample gas, microwave attenuation can be used. Beginning with Maxwell’s Equations and using the linearized Langevin Equation it is possible to model the absorption of microwaves by free electrons within a plasma. Much of the following derivation is outlined by Tanenbaum [25]. Given below are Maxwell’s Equations, Eq.’s (3.12)-(3.15). If it is assumed that the plasma is vacuum-like (i.e. ε=ε₀ and μ=μ₀), the

\[ \nabla \cdot D = \rho_e \quad (3.12) \]
\[ \nabla \cdot B = 0 \quad (3.13) \]
\[ \nabla \times E = -\frac{\partial B}{\partial t} \quad (3.14) \]
\[ \nabla \times H = J + \frac{\partial D}{\partial t} \quad (3.15) \]

displacement current, D, and the magnetic field intensity, H, are defined in Eq.’s (3.16) and (3.17). In addition the definition of current density, J, is given in Eq. (3.18), where e is the electron charge, nₑ is the number density of free electrons and u is the average electron velocity. Substitution of D, B and J into Maxwell’s equation (3.15) results in

\[ D = \varepsilon_0 E \quad (3.16) \]
\[ B = \mu_0 H \quad (3.17) \]

\[ J = -n_e e u \quad (3.18) \]

Eq. (3.20). The linearized Langevin equation for a sinusoidal perturbation is given in Eq. (3.21). In this case the nonlinear nature of B is considered negligible and the magnetic field is approximated as a constant. Applying the curl operator to (3.19), substituting for \( \nabla \times B \) using (3.20) and using the identity shown in Eq. (3.22) decouples these coupled equations. It is assumed that for a weakly ionized plasma that the current density, \( \rho_C \), is zero. If \( B_0 = 0 \), substitution of the average electron speed, \( u \), into Eq. (3.20) and decoupling results in Eq. (3.23) which describes the electric field (a similar equation results for the magnetic field).

\[ \nabla \times \nabla \times E = \nabla \left( \nabla \cdot E \right) - \nabla^2 E \quad (3.22) \]

\[ \nabla \times E = -\frac{\partial B}{\partial t} \quad (3.19) \]

\[ \nabla \times B = \mu_0 e_0 \frac{\partial E}{\partial t} - \mu_0 n_e e u \quad (3.20) \]

\[ u = -\frac{e}{m_e (\nu - i\omega)} (E + u \times B_0) \quad (3.21) \]

\[ \nabla \times (\nabla \times E) = \nabla \left( \nabla \cdot E \right) - \nabla^2 E \]

This equation has the general form of the wave equation, which has the well known solution found in Eq. (3.24) for a one-dimensional wave propagating in time. If Eq. (3.24) is substituted back into Eq. (3.23), the result is Eq. (3.25). If \( k \) has both a real and

\[ E(x, t) = E_0 e^{i(kx - \omega t)} \quad (3.24) \]
an imaginary part, it becomes clear that the imaginary part describes attenuation of the electric field within a medium. For example, if it is assumed that \( k \) is given by Eq. (3.26), then substitution of \( k \) into Eq. (3.24) yields Eq. (3.27). Upon examination of Eq. (3.27),

\[
k = \beta + i\alpha
\]  \hspace{1cm} (3.26)

\[
E(x, t) = E_0 e^{i(\beta x - \omega t)} e^{-\alpha x}
\]  \hspace{1cm} (3.27)

it is clear that the imaginary part, \( \alpha \), leads to attenuation of the electric field within the medium. If the absolute electron number density is to be obtained the value of \( \alpha \) must be determined. It can be shown, provided two simplifying assumptions are made (Eq. (3.28) and (3.29)), that the imaginary part of \( k \) is given by Eq. (3.30). In Eq. (3.30) \( \nu_c \) is the electron-neutral collision frequency (collisions/sec), \( \omega \) is the microwave frequency in angular units (rad/sec) and \( \omega_p \) is the plasma frequency defined in Eq. (3.31).

\[
\frac{\omega_p^2}{\omega \nu_c} \ll 1
\]  \hspace{1cm} (3.28)

\[
\omega \approx \nu_c
\]  \hspace{1cm} (3.29)

\[
k_{\text{imaginary}}(\omega) = \frac{\omega_p^2 \nu_c}{2c(\omega^2 + \nu_c^2)}
\]  \hspace{1cm} (3.30)

\[
\omega_p^2 = \frac{n_e e^2}{\epsilon_0 m_e}
\]  \hspace{1cm} (3.31)

Lastly, it is important to note that the electric field power, \( P \), is proportional to \( E^2 \). The result is that the microwave absorption coefficient, \( \varphi \), is twice the imaginary part of the
wave number, k, and is given in Eq. (3.32). The function, which describes the power within the medium, is given in Eq. (3.33), where

$$\phi(\omega) = 2k_{\text{imaginary}} = \frac{n_e e^2}{cm_e e_0} \frac{\nu_c}{(\omega^2 + \nu_c^2)}$$  \hspace{1cm} (3.32)

$$P(x, t) \propto E_0 e^{i2(k_R x - \omega t)} e^{-2x}$$  \hspace{1cm} (3.33)

$k_R$ is the real part of the wave number. It is important to note that in Eq. (3.32) $\omega$ is the angular frequency (rad/sec) of the microwave radiation and $\nu_c$ is the electron-neutral collision frequency (collisions/sec). It is quite apparent from Eq. (3.33) that the attenuation of the wave is governed completely by the second exponential term. Using a typical Beer’s law formulation of the attenuation process, it follows that the electron number density, $n_e$, can be determined using Eq. (3.34). In this case $V_T$ is the voltage due to the attenuated transmitted microwaves, $V_0$ is the voltage due to the unattenuated transmitted microwaves and D is the path length through the electron beam generated plasma.

$$n_e = \frac{m_e c e_0}{e^2} \frac{\omega^2 + \nu_{\text{coll}}^2}{\nu_{\text{coll}}} \frac{1}{D} [-\ln \frac{V_T}{V_0}]$$  \hspace{1cm} (3.34)

Unfortunately, work performed by Utkin [26] and Ionikh [27] has indicated that Eq. (3.34) overestimates the electron number density. Utkin shows that in a nonhomogeneous plasma environment careful selection of the path length, D, is required for Eq. (3.34) to provide a reasonable number density. Ionikh demonstrated that even in a homogeneous glow discharge Eq. (3.34) results in artificially high electron number densities. The work of Ionikh showed when the number densities derived from the microwave attenuation measurements are compared to the number densities derived from
a field extracted current, it is found that the microwave attenuation measurement is much larger (1-2 orders of magnitude) than the field extracted current measurement. It is important to note that the attenuation of microwaves by free electrons is proportional to the absolute electron number density. However, the proportionality constant determined from Eq.(3.34) is too large. Therefore, if microwave attenuation is to be used to measure electron number density a calibration must be performed. Fortunately, in this case the absolute electron number density is not required to extract the attachment rate, which will be obtained from a nonlinear least squares fit to the microwave voltage trace.

4.4 Results and Discussion

The attachment rate was determined for a variety of mixtures of oxygen and nitrogen at a temperature of 298 K. Fitting of the decay traces was performed using the analytical solution for the rate equation, Eq. (3.11), shown in Eq. (3.35), where $\nu_A$ is defined in Eq. (3.36) and $S=0$.

$$n_e(t) = n_\infty e^{-\nu_A t}$$  \hspace{1cm} (3.35)

$$\nu_A = k_A^{(1)} n_{O_2}^2 + k_A^{(2)} n_{O_2} n_{N_2}$$  \hspace{1cm} (3.36)

It is assumed, for now, that electron loss due to electron-ion recombination processes are negligible, the justification for which will be addressed later in more detail. A typical fit of the three-body attachment model to the data is shown in Fig. 3.7, for the case of 1.5 torr O$_2$ and 400 torr N$_2$ at 1mA and 80keV. To extract rate coefficients attachment rates obtained from fits such as that shown in Fig. 3.7 were plotted against the partial pressure of one of the gas components, while the other component was held constant. In the case
of constant partial pressure of nitrogen a quadratic polynomial was fit to the rate vs. \( \text{nO}_2 \), as shown in Eq. (3.37).

\[
\nu_A(n_{\text{O}_2}) = A n_{\text{O}_2}^2 + B n_{\text{O}_2} + M
\]  \hspace{1cm} (3.37)

The quadratic term is \( A = k_{A}^{(1)} \) and the linear term is \( B = k_{A}^{(2)} n_{\text{N}_2} \). Two fits of this type are shown in Fig. 3.8 and 3.9 corresponding to fixed partial pressures of \( \text{N}_2 \) equal to 50 and 100 torr, respectively. For constant partial pressure of oxygen the rate vs. \( n_{\text{N}_2} \) data was fit with a linear regression, shown in Eq. (3.38).

\[
\nu_A(n_{\text{N}_2}) = C n_{\text{N}_2} + D
\]  \hspace{1cm} (3.38)

Figure 3.7. Electron density decay and fit for 1.5 torr \( \text{O}_2 \), 400 torr \( \text{N}_2 \) 1mA, 80keV.
Parameters from that fitting routine give $C = k_A^{(2)} nO_2$ from the slope and $D = k_A^{(1)} nO_2^2$ from the y-intercept. Two fits of this type are shown in Fig. 3.10 and 3.11 for fixed partial pressures of $O_2$ equal to 1.5 and 3 torr, respectively. Due to the nature of the data (large values of $n$) it is believed that the quadratic fit provides the best value for $k_A^{(1)}$ (the curvature of the quadratic) and that the linear fit provides the best value for $k_A^{(2)}$ (the slope of the line). As will be discussed below, and in more detail in Chapter 4, due to parallel electron-ion recombination processes the rate of electron removal does not go to zero as $nX \rightarrow 0$. Pure attachment, therefore, does not correctly describe the $nX \rightarrow 0$ limiting behavior and therefore examining the curvature of the quadratic and the slope of

![Figure 3.8. Plot of Attachment rate vs. nO2 at 50 torr N2. Curvature gives k_A^{(1)}.](image-url)
the linear regression will provide a better representation of the actual rate coefficients. The value for $k_A^{(2)}$ was determined from plots of $nN_2$ vs. $v_A$ at two constant pressures of O$_2$, 1.5 and 3 torr. From plots of $nO_2$ vs. $v_A$ the value of $k_A^{(1)}$ was extracted at 50 and 100 torr of N$_2$. The average value for $k_A^{(1)}$ was $5.8 \times 10^{-30}$ cm$^6$/s and the value of $k_A^{(2)}$ was $5.8 \times 10^{-31}$ cm$^6$/s. Shown in Table 3.1 are the rate coefficients for O$_2$ ($k_A^{(1)}$) and for N$_2$ ($k_A^{(2)}$) as the third body determined from this experimental data and compared to the values reported by Chanin, Phelps and Biondi.

As stated previously, the attachment rate coefficients given in Table 3.1 were obtained by ignoring electron-ion recombination. It is important, therefore, to verify that the measured decay is indeed dominated by the three-body attachment mechanism. To explore this, the coupled differential equations which describe both three-body attachment and electron ion recombination, were solved numerically to find if there would be a large disparity between the two models at the conditions that were used. Seen below, Eqs. (3.39) and (3.40), are the coupled differential equations which incorporate

<table>
<thead>
<tr>
<th>Rate coefficient</th>
<th>Experimental Data</th>
<th>Chanin, Phelps and Biondi</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_A^{(1)}$</td>
<td>$5.8 \pm 0.8 \times 10^{-30}$ cm$^6$/s</td>
<td>$2.8 \times 10^{-30}$ cm$^6$/s</td>
</tr>
<tr>
<td>$k_A^{(2)}$</td>
<td>$5.8 \pm 0.9 \times 10^{-31}$ cm$^6$/s</td>
<td>$1.6 \times 10^{-31}$ cm$^6$/s</td>
</tr>
</tbody>
</table>

Table 3.1. Rate coefficients determined from experimental data and compared to those reported by Chanin, Phelps and Biondi [19].
three-body electron attachment and electron-ion recombination (3.41) in the electron removal process.

\[
\frac{dn_e}{dt} = S - k_A^{(1)} n_{O_2}^2 n_e - k_A^{(2)} n_{O_2} n_N n_e - \beta_{c} n_e n_e
\]  \hspace{1cm} (3.39)

\[
\frac{dn_+}{dt} = S - \beta_{c} n_ e n_e
\]  \hspace{1cm} (3.40)

\[
N_4^+ + e^- \rightarrow 2N_2
\]  \hspace{1cm} (3.41)

In Eqs (3.39) and (3.40) the new terms are \( \beta_{c}=2x10^{-6} \) cm\(^3\)/s, the electron-ion recombination rate, S, the electron impact ionization rate and \( n_+ \), the number density of
Figure 3.10. Plot of attachment rate vs. $nN_2$ at 1.5 torr $O_2$. Slope gives $k_A^{(2)}$.

cations. These equations were solved numerically for three different cases; (1) three-body attachment is the dominant mechanism and recombination is neglected, (2) electron-ion recombination is the dominant mechanism and three-body attachment is neglected, and (3) neither three-body attachment or electron-ion recombination dominate and both mechanisms compete. Because the model considers the effect of electron-ion recombination, which exhibits second order kinetics (to be discussed more thoroughly in the subsequent chapter on attachment mitigation), the number density of electrons must be determined. Therefore, the microwave attenuation data must be calibrated. Using the
method to be described in Chapter 4, the ionization rate, \( S \), was determined from a sample of pure \( N_2 \) (in which attachment is negligible and recombination dominates) and scaled linearly with the gas pressure. Note that the underlying assumption is that the electron beam ionization rate, \( S \), is independent of gas composition, but scales linearly with gas density. As will be shown in Chapter 4, knowing \( S \) as a function of total pressure, and assuming that \( O_2 \) mixtures are dominated by attachment, the steady-state electron number density is given by Eq. (3.42),
\[ n_e = \frac{S}{v_A} \]  

(3.42)

where \( v_A \) is the attachment rate determined from the fit of the decay curves such as that shown in Fig. 3.7. Numerical solutions were acquired for each of the data points in Figs. 3.8-3.11 and the greatest difference between the attachment dominated and the attachment/recombination calculation was found for the 1 torr O\(_2\) with 50 torr N\(_2\) case. The calculation of the decays is dependent upon the initial number densities of electrons and cations. If the number densities of the two species are similar, the model calculations for the attachment dominated and the attachment/recombination case are nearly identical.

Figure 3.12. Numerical modeling of the rise in number density for the electrons and cations, which is used to establish the initial conditions for the calculated decay.
However, if the number density of cations exceeds that of electrons by one order of magnitude, the calculated decays are significantly different and therefore careful selection of the initial conditions is required. To that end the rise in number density of electrons and cations was calculated and is shown in Fig. 3.12. It was found that the relative number densities of the two species depended upon the length of the electron beam pulse. At short pulse lengths (10-20 µs) the ratio of cations to electrons was approximately 1:1 to 2:1. At longer pulse durations (≥100 µs) the number density of cations can exceed that of electrons by a factor of about five. The data used to determine

![Graph](image-url)

Figure 3.13. Numerical modeling of decay of 1 torr O₂ in 50 torr N₂ showing the effect of electron-ion recombination on the attachment rate.
the rate coefficients for three-body attachment was acquired at a pulse duration of 10 μs and therefore the appropriate initial conditions for the decay is approximately a 2:1 ratio of cations to electrons. A decay was calculated from the initial conditions determined from the rise and is shown in Fig. 3.13. It is clear from Fig. 3.13 that at these experimental conditions the effect of electron-ion recombination is minimal and the electron loss mechanism is attachment dominated. We conclude that the rate coefficients are greater than that quoted in the literature by a factor of about 2 for O₂ and a factor of approximately 3-4 for N₂ while the difference of one order of magnitude between $k_{A}^{(1)}$ and $k_{A}^{(2)}$ remains. Additionally, it is found that electron loss is dominated by attachment at all pressure conditions examined in this project.
CHAPTER 4

MITIGATION OF THREE-BODY ATTACHMENT

The previous chapter explored the rate coefficients for the dominant electron loss mechanism within an air-like plasma. It was shown that when oxygen is present within the plasma, at low average electron energy, electrons quickly attach to form the molecular anion $O_2^-$ by a three-body process. However, recent work by Hicks, et al [6] has shown that in non-self-sustained discharges the plasma lifetime is much longer than expected. While it is well known that the attachment coefficients depend strongly on the average electron energy, it seems unlikely that at the low field strength employed by Hicks that the increased plasma lifetime is due solely to an increase in electron temperature. In addition it is clear that within a discharge it is possible to tune the field strength so that the average electron energy is resonant with the fundamental vibrational energies of the gases, thus causing vibrational excitation of the plasma gases. It has been reported by a number of authors [28, 29 & 30] that vibrational excitation can result in activation or deactivation of a reactive pathway. Therefore, it is reasonable to postulate that the increase in the plasma lifetime shown by Hicks may be due to the combined effects of an increase in the electron temperature and the vibrational deactivation of the three-body attachment mechanism that dominates oxygen-containing plasmas.
4.2 Background: Vibrational Activation of Electron Detachment

Overcoming the activation energy of a chemical reaction by preferentially exciting the vibrational mode of a molecule has been shown to occur for a variety of types of reactions including those shown in (4.1) and (4.2) [31].

\[ A + BC(v) \rightarrow AB(v') + C \]  \hspace{1cm} (4.1)

\[ A + BC(v') \Leftrightarrow (ABC)^* \rightarrow \text{Products} \]  \hspace{1cm} (4.2)

Specific examples, of which, include isotopic replacement of one of the atoms in the molecule, such as H₂ becoming HD, or substitution of the halide in a hydrogen halide (HCl becoming HI). An energy diagram of the above process is shown in Fig. 4.1. For

![Energy Diagram](image)

Figure 4.1. Diagram showing activation of reactive pathway by vibrational excitation of the reactants [31].
the isotopic substitution example shown in (4.3), the reaction is more than a factor of $10^3$

faster than the thermal reaction, (4.4), at 298 K.

\[ ^{37}\text{Cl} + ^{35}\text{Cl}(v = 1) \rightarrow ^{37}\text{Cl}(v = 1, 0) + ^{35}\text{Cl} \]  
(4.3)

\[ ^{37}\text{Cl} + ^{35}\text{Cl}(v = 0) \rightarrow ^{37}\text{Cl}(v = 0) + ^{35}\text{Cl} \]  
(4.4)

Previous work by Pack and Phelps has alluded to the possibility that vibrational activation of electron detachment may occur in oxygen containing environments [22]. It will be shown that in an air-like electron beam generated plasma vibrational excitation increases the plasma lifetime.

In an air-like electron beam generated plasma ionization is initiated and maintained by electron impact of the primary electron beam with the sample gas, resulting in secondary ionization as shown in Eq (4.5). The primary electrons possess enough energy to ionize several molecules and still escape the region of interest (30keV primary, \(\approx 10\)eV ionization potential). Once liberated, the secondary electrons equilibrate quickly with the heavy species and are therefore at approximately room temperature. In an air-like plasma the dominant cation is \(\text{N}_4^+\). Initially, \(\text{N}_2\) is ionized, but quickly becomes \(\text{N}_4^+\) by process (4.6). There are several mechanisms by which the free secondary electrons are captured. These include electron-ion recombination (4.7) and three-body attachment to \(\text{O}_2\) (4.8).

\[ \text{N}_2 + e^-(\text{primary}) \rightarrow \text{N}_2^+ + e^-(\text{secondary}) + e^-(\text{primary}) \]  
(4.5)

\[ \text{N}_2^+ + \text{N}_2 \Leftrightarrow \text{N}_4^+ \]  
(4.6)

\[ \text{N}_4^+ + e^-(\text{secondary}) \rightarrow 2\text{N}_2 \]  
(4.7)

\[ \text{O}_2 + e^- + M \Leftrightarrow \text{O}_2^- + M \]  
(4.8)
As discussed in the previous chapter the third body collision partner, M, may be either O\textsubscript{2} or N\textsubscript{2} but the relative effectiveness as a third body is greater for O\textsubscript{2}. In a cold, air-like plasma the dominant mechanism for electron removal is three-body attachment to O\textsubscript{2}, which at high pressures can exceed the electron-ion recombination rate by several orders of magnitude. It will be shown in this chapter that an increase in plasma lifetime occurs when vibrational excitation activates the electron detachment pathway, thereby shifting the equilibrium of process (4.8). Further it will be shown that the effect is sufficiently strong that the three-body electron attachment process is completely mitigated.

4.3 Vibrational Nonequilibrium Treanor Distribution

The Treanor Distribution [32] describes a system of anharmonic oscillators in which relaxation is dominated by collisional exchange of vibrational quanta. In this model the most probable distribution is found with the constraints that the total number density is constant, the total energy of the system is constant and, most significantly, that the total number of vibrational quanta is constant. Problems within statistical mechanics are typically approached starting with the statistical weight, W [33].

$$W = \frac{N!}{\prod n_v !}$$  \hspace{1cm} (4.9)

The system being considered is subject to the following three constraints.

$$\sum_v n_v = N$$  \hspace{1cm} (4.10)

$$\sum_v E_v n_v = E$$  \hspace{1cm} (4.11)

$$\sum_v v n_v = V$$  \hspace{1cm} (4.12)
The above constraints represent a fixed number density, \( N \) (4.10), a constant total energy, \( E \) (4.11), and a constant total number of vibrational quanta, \( V \) (4.12). In each of the constraining equations \( n_v \) is the number density of vibrational level \( v \), \( E_v \) is the total energy of the molecule in vibrational level \( v \) (not the vibrational energy) and \( v \) is the quantum number which represents the number of vibrational quanta for that level. To maximize the statistical weight subject to the above constraints the method of Lagrange’s undetermined multipliers is used. It is convenient to start by taking the natural log of (4.9).

\[
\ln W = \ln N! - \sum_v \ln n_v!
\]

(4.13)

The method of Lagrange’s undetermined multipliers follows the form of Eq. (4.14)

\[
\sum_j \left( \frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} \right) \delta x_j = 0
\]

(4.14)

where \( f \) is the function to be maximized and \( g \) represents a constraint on the function \( f \). In the event there are multiple constraints on the system a separate Lagrange multiplier is used for each constraint. Applying (4.14) to (4.9)-(4.12) results in (4.15), wherein \( \alpha \), \( \beta \)

\[
\sum_v \left( \frac{d \ln W}{dn_v} - \alpha - \beta E_v - v \gamma \right) dn_v = 0
\]

(4.15)

and \( \gamma \) are the Lagrange multipliers associated with the system constraints. If each of the \( dn_v \) are treated independently Eq.(4.15) simplifies to

\[
\frac{d \ln W}{dn_v} - \alpha - \beta E_v - v \gamma = 0
\]

(4.16)

when \( n_v \) are at the most probable values. Applying Stirling’s Approximation (4.17)

\[
\ln N! \cong N \times \ln N - N
\]

(4.17)
to (4.13), eliminates the factorial and ln $W$ simplifies to Eq.(4.19).

$$\ln W = N \times \ln N - N - \sum_v (n_v \ln n_v - n_v)$$

(4.18)

$$\ln W \cong N \times \ln N - \sum_v n_v \ln n_v$$

(4.19)

Substitution of (4.19) into (4.16) yields (4.20).

$$\ln n_v = -\alpha - \beta E_v - v\gamma$$

(4.20)

so that

$$n_v = e^{-\alpha} e^{-\beta E_v} e^{-v\gamma}$$

(4.21)

$\alpha$ and $\beta$ are immediately evaluated by recognizing that $\exp(-\alpha) = n_0$ and $\beta = 1/kT$, where $n_0$ is the total number density of molecules, $k$ is Boltzmann’s constant and $T$ is the translational temperature. Defining a population factor for the $v$th vibrational level results in Eq.(4.22),

$$n_v = n_0 \exp \left( -\frac{E_v}{k\theta_i} \right)$$

(4.22)

which describes the population of that level in terms of $\theta_i$, the vibrational temperature of level $v=i$. The last Lagrange multiplier, $\gamma$, can then be expressed in terms of the vibrational temperature of the first excited vibrational level. This is done by equating (4.22) and (4.21), for $v=1$ with the result

$$\gamma = \frac{E_1}{k\theta_1} - \frac{E_1}{kT}$$

(4.23)

Finally, substituting the results for $\alpha$, $\beta$ and $\gamma$ into (4.21) yields the Treanor distribution as a function of $v$ and $T$, shown in (4.24).
n_v = n_0 \exp \left( -\frac{vE_{1}}{k\theta_{1}} + \frac{vE_{1} - E_{1}}{kT} \right) \quad (4.24)

It is important to note that (4.24) describes a highly non-Boltzmann distribution when the first level vibrational temperature, $\theta_1$, is larger than the translational temperature $T$. Additionally, the larger $\theta_1/T$ becomes the greater the departure from a Boltzmann distribution, as shown in Fig. 4.2. If $\theta_1=T$, then the Treanor distribution reduces to the Boltzmann distribution.

A state of vibrational non-equilibrium described by the Treanor distribution has

![Graph showing the Treanor Distribution for CO for various translational temperatures at $T_{Vib}=3000K$. The Boltzmann line is when $T_{Trans}=3000K$.](image)

Figure 4.2. Treanor Distribution for CO for various translational temperatures at $T_{Vib}=3000K$. The Boltzmann line is when $T_{Trans}=3000K$.  

60
been created by a process often referred to as anharmonic collisional up-pumping [33 & 34]. The most common example uses a CO laser to excite carbon monoxide to a state of extreme vibrational nonequilibrium, initially demonstrated by Subramaniam [34] and developed further by Flament [35], Adamovich [7] and Lee [36].

CO laser anharmonic up-pumping, as depicted below in (4.25) and (4.26), is a two step process. The first step is resonant absorption of CO laser output by relatively low lying (v<≈10) CO vibrational levels (4.25). The second step is collisional V-V exchange (4.26) where due to anharmonicity the principle of detailed-balance (4.27) indicates the rate coefficient for the forward process of (4.26) exceeds that of the reverse. A diagram of the anharmonic defect is shown in Fig. 4.3.

\[
\text{CO}(v) + h\nu \rightarrow \text{CO}(v+1) \quad v=0\rightarrow10 \quad (4.25)
\]

\[
\text{CO}(v) + \text{CO}(w) \Leftrightarrow \text{CO}(v-1) + \text{CO}(w+1) \quad v\leq w \quad (4.26)
\]

\[
k_r = k_f \exp\left(-\frac{\Delta E}{kT}\right) \quad (4.27)
\]

Figure 4.3. Diagram of the anharmonic defect as it relates to the detailed-balance equation.
A spectrum of the CO laser output is shown in Fig. 4.4 and an experimentally determined vibrational distribution function (VDF) for CO laser pumped CO is shown in Figure 4.5. Notice the plateau at intermediate $v$, which deviates from equilibrium Boltzmann behavior, and the decaying tail at high $v$. The decaying tail is due to the increase in V-T rate as well as additional reactions that become energetically accessible at higher vibrational levels.

As high lying vibrational levels become populated new chemical pathways become accessible, such as carbon production (4.28), superelastic electron heating (4.29), associative ionization (4.30) and Vibration-to-Electronic energy transfer (4.31).

\[
\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}_2 + \text{C} \quad (4.28)
\]

\[
\text{CO}(v) + e^{-}(\epsilon) \rightarrow \text{CO}(v-\Delta v) + e^{-}(\epsilon+\Delta\epsilon) \quad (4.29)
\]

\[
\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO} + \text{CO}^{+} + e^{-} \rightarrow (\text{CO})_{2}^{+} + e^{-} \quad (4.30)
\]
Additionally, as shown by Lee [36], the vibrational quanta in CO can be transferred by a mechanism analogous to (4.26) to the vibrational mode of a different diatomic molecule, an example of which is shown in (4.32). Once the first vibrational level is populated by interspecies V-V, then intraspecies V-V transfer occurs, populating the higher vibrational levels, as seen in (4.33).

\[
\text{CO}(X^1\Sigma, v \sim 40) + \text{CO}(w) \rightarrow \text{CO}(A^1\Pi, v = 0) + \text{CO}(w-\Delta w) \tag{4.31}
\]

\[
\text{CO}(v) + \text{N}_2(w) \rightleftharpoons \text{CO}(v-1) + \text{N}_2(w+1) \tag{4.32}
\]

\[
\text{N}_2(v) + \text{N}_2(w) \rightleftharpoons \text{N}_2(v-1) + \text{N}_2(w+1) \tag{4.33}
\]
While N\textsubscript{2} is shown in (4.32) and (4.33), Lee [36] has demonstrated that in air-like gas mixtures the analogous process also occurs in O\textsubscript{2}. By this mechanism it is possible to preferentially excite the vibrational mode of all the diatomics within the gas mixture, while the translational and rotational modes remain comparatively cold. An example of a VDF for an air-like mixture is shown in Figure 4.6, where the corresponding translational/rotational temperature has been determined to be approximately 420-640 K whereas the first-level vibrational temperatures, determined from (4.34) are 2080 K, 2220

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{vdf.png}
\caption{Vibrational Distribution Function for an air-like gas mixture at 740 torr of 5\% CO, 16\% O\textsubscript{2} and the balance in N\textsubscript{2} [36].}
\end{figure}
K and 3050 K for N₂, O₂ and CO, respectively [36]. In Eq. (4.34) \( T_v \) is the first-level vibrational temperature, \( \theta_v \) is the characteristic vibrational temperature for the molecule of interest and \( f_0 \) and \( f_1 \) are the relative populations of vibrational levels 0 and 1.

\[
T_v = \frac{\theta_v}{\ln \left( \frac{f_0}{f_1} \right)}
\]

Lastly, it is important to reiterate if free electrons are present, produced either by external ionization (electron beam) or through associative ionization (4.30), than the electron temperature can increase due to superelastic collisions, (4.29). This process has been demonstrated experimentally by Adamovich and Rich [37].

To summarize, the overall effect of the anharmonic up-pumping process is that the diatomic molecules will exhibit a vibrational temperature, \( T_v \), of a few thousand Kelvin while the translational and rotational modes exhibit a temperature of only a few hundred Kelvin. In addition the electrons resulting from associative ionization may exhibit a temperature greater than that of the rotational/translational temperature of the heavy species, in some cases as high as \( T_v \).

We will show in this chapter that when the anharmonic up-pumping process is used to vibrationally excite an electron beam generated CO/O₂/N₂ plasma, the free electron lifetime increases by two orders of magnitude. Further, we will conclusively demonstrate, using pure rotational Raman scattering, that the effect is due to vibrational nonequilibrium and not due to ordinary equilibrium heating.
4.4 Rotational Raman Scattering

As discussed in the previous chapter, rate coefficients can be highly temperature dependent. Therefore, before any observed kinetic enhancement can be attributed to internal mode disequilibrium it is essential to obtain an accurate heavy species temperature. To that end spectrally filtered pure rotational Raman scattering measurements were performed to acquire the translational temperature of the gaseous species.

Rotational Raman scattering is a technique well suited to acquiring temperatures within a high-pressure plasma environment. Of primary importance is the non-intrusive nature of this technique. The temperature within the experimental cell varies from 300 K at the wall of the cell to some elevated temperature within the optically pumped region of interest. Complications arise due to the incident CO laser. An accurate measurement of the temperature requires the probe be placed within the optically pumped region. Even if the probe could withstand the incident infrared radiation, absorption of those photons would cause misleading results. Additionally, a probe would have dimensions much larger than the volume sampled by Rotational Raman scattering.

Additionally, there are advantages to using Rotational Raman scattering instead of fluorescence measurements. Temperature measurements obtained from the IR emission of CO are fairly common for air-like plasma environments. However, the emission signal from the optically pumped region, while possessing the same non-intrusive nature of Rotational Raman scattering, risks attenuation along the detection pathway [38]. A cold CO molecule along the detection pathway may absorb the signal from the lower $j$ values of emitting CO. This results in a rotational distribution that is described by a
temperature that is artificially high. More importantly, however, is that emission is a line-of-sight measurement and therefore would not provide spatial resolution, which as we will see is extremely important. Rotational Raman scattering, which probes the ground electronic rotational distribution, cannot have optical thickness issues similar to those exhibited by the emission technique because the signal is not resonant with any molecular transition. This results in a more reliable method of temperature extraction.

The quantum mechanical model of spontaneous Raman scattering involves the transition of a molecule to a “virtual state” which is a superposition of states for that molecule. An incident photon excites a molecule to the higher lying “virtual state”. Relaxation occurs from the “virtual state” back to a lower lying state by emission of a photon. The emitting photon, typically called the scattered photon, may be elastically or inelastically scattered. Elastically scattered photons are classified as Rayleigh scattering and the scattered photon is the same frequency as the incident photon. Inelastically scattered photons are categorized as Raman scattering and the scattered photon has either gained or lost energy and is therefore at a different frequency than the incident photon. The two different cases of Raman scattering are classified as Stokes shifted ($\nu_S < \nu_I$) and anti-Stokes shifted ($\nu_S > \nu_I$). A diagram of the Raman scattering process is given in Fig. 4.7(a) and (b). The basic theory of Raman scattering is outlined in Appendix A. It is shown that for pure rotational Raman scattering the scattering intensity is proportional to the polarizability anisotropy and that $\Delta J = \pm 2$.

It becomes clear that the rotational temperature can be determined from the rotational Raman scattering spectrum. The rotational Raman lines within a spectrum couple levels where $\Delta J = \pm 2$. Additionally, the population of the individual rotational
levels can be determined from the intensity of the spectral line using the cross-section. However, the cross sections must be known for all of the lines present within the spectrum. Not only do the cross-sections vary with molecular species, but with rotational level as well. The cross-sections for N$_2$ are determined from the 6$\rightarrow$8 transition, which is 5.4x10$^{30}$ cm$^2$/sr at 488nm. The cross-sections for O$_2$ are determined from the 7$\rightarrow$9 transition, which is 14x10$^{30}$ cm$^2$/sr at 488nm. The cross-sections for CO are determined
from the $6 \rightarrow 8$ transition, which is $0.61 \times 10^{30}$ cm$^2$/sr at 488nm [39]. Typically, the rotational transition with the largest cross section of a molecule is tabulated and cross-sections for the other transitions are obtained by scaling with the Placzek-Teller b factors [40]. The species in this work are linear and therefore the b factors given in (4.35)-(4.37) are used.

$$b_{J+2,J} = \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)}$$ (4.35)

$$b_{J-2,J} = \frac{3J(J-1)}{2(2J+1)(2J-1)}$$ (4.36)

$$b_{J,J} = \frac{J(J+1)}{(2J-1)(2J+3)}$$ (4.37)

A temperature for the system can be extracted by fitting the populations of the individual rotational levels to the rotational distribution function. This technique becomes complicated by the presence of multiple species within the gas mixture. A synthetic spectrum, which is a sum of the individual spectra of the separate chemical species, can be constructed for a given temperature and compared to the experimental spectrum.

4.5 Results and Discussion I. Data

The data presented here were acquired using the electron beam/microwave attenuation apparatus used to determine the three-body rate coefficients in Chapter 3. The only major change to the system was the addition of a CO laser used to create vibrational excitation. A complete description of the experimental apparatus may be found in the Rate Coefficients Measurement and Mitigation sections of Chapter 2. As a baseline case, shown as the open circles in Fig. 4.8, the time-dependent electron number
density in pure N$_2$ was acquired at 300 torr. As stated previously, the initially formed N$_2^+$ is rapidly converted to N$_4^+$ by process (4.6) with rate coefficient $k_{\text{conv}}= 5 \times 10^{-41} (300/T)^{2.14}$ m$^6$/s $[41]$. At 300 torr the conversion time for process (4.6) is on the order of the gas kinetic collision time, $\approx 10^{-10}$ s. The resulting rate equation describing the evolution of the electron-ion recombination controlled plasma is given by

$$\frac{dn_e}{dt} = S - \beta_{ei} n_i n_e = S - \beta_{ei} n_e^2$$

(4.38)
where it is assumed that the positive ion number density is equal to the electron number density. In (4.38) $S$ is the ionization rate due to electron impact and $\beta_{ei}$ is the rate coefficient for electron-ion recombination (4.7), with reported value $2 \times 10^{-12} \text{ m}^3/\text{sec}$ ($N_2^+$ $\beta_{ei} = 2.9 \times 10^{-13} \text{ m}^3/\text{s}$) [42]. Equation (4.38) represents simple second order kinetics with analytical solutions

$$\frac{n_e(t)}{n_\infty} = \tanh[n_\infty \beta_{ei} t] = \tanh[t\sqrt{S\beta_{ei}}] \quad \text{(generation)} \quad (4.39)$$

$$\frac{n_e(t)}{n_\infty} = \frac{1}{1 + n_\infty \beta_{ei} t} \quad \text{(decay)} \quad (4.40)$$

$$n_\infty = \sqrt[3]{\frac{S}{\beta_{ei}}} \quad (4.41)$$

where $n_\infty$ is the steady state electron number density. Note that the solution for the decay results from setting $S=0$ for times exceeding the electron beam pulse duration. Assuming that the secondary electrons thermalize quickly with the heavy species, the electron temperature, $T_e$, is approximately 300 K.

As can be seen from (4.39)-(4.41), the shape of the electron density rise and fall is determined completely by the product

$$n_e \beta_{ei} \equiv \frac{1}{\tau} \quad (4.42)$$

The solid curve in Fig. 4.8 is a least squares fit of the experimental data to (4.39) and (4.40), where $\tau$ is treated as an adjustable parameter. A summary of the results is given in Table 4.1. The rise and fall portions of the curve were fit separately with corresponding best fit values, $1/\tau$, equal to $1.1 \pm 0.03 \times 10^5 \text{ s}^{-1}$ for the rise and $6.1 \pm 0.1 \times 10^4 \text{ s}^{-1}$ for the fall. Assuming $\beta_{ei} = 2 \times 10^{-12} \text{ m}^3/\text{s}$, the inferred ionization rate, $S$, from the
Table 4.1. Inferred ionization rate, $S$, and decay rate, $\tau$, for 300 torr pure N$_2$.

<table>
<thead>
<tr>
<th></th>
<th>Rise</th>
<th>Fall</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/\tau$ (s$^{-1}$)</td>
<td>$1.1 \pm 0.026 \times 10^5$</td>
<td>$6.1 \pm 0.12 \times 10^4$</td>
</tr>
<tr>
<td>$S$ (m$^3$s$^{-1}$)</td>
<td>$6.1 \pm 0.57 \times 10^{21}$</td>
<td>$1.9 \pm 0.15 \times 10^{21}$</td>
</tr>
</tbody>
</table>

Rise data is $6.05 \times 10^{21}$ m$^{-3}$s$^{-1}$ whereas that for the fall is $1.9 \times 10^{21}$ m$^{-3}$s$^{-1}$. The corresponding values of $n_\infty$ are $5.5 \times 10^{16}$ and $3.1 \times 10^{16}$ m$^{-3}$, respectively. While the origin of the difference is not completely understood, it is likely indicative of a systematic uncertainty caused by the primary electron beam. Possible sources include build-up of space charge during the primary electron beam pulse, incomplete N$_2^+$ conversion, statistical error associated with least squares fitting and/or waveguide heating due to the primary electron beam striking the waveguides. It is believed, therefore, that the decay portion of the data is subject to less systematic interference than the rise.

While the above analysis is all based on the shape of the experimental microwave attenuation curve, we note that in principle it is straightforward to relate absolute electron density, $n_e$, to the observed attenuation by means of the simple 1-dimensional expression [26]

$$n_e = \frac{m_e c \epsilon_0}{\epsilon^2} \cdot \omega^2 + \frac{v^2_{\text{coll}}}{v_{\text{coll}}} \cdot \frac{1}{D} \cdot \frac{[- \ln \frac{V_e}{V_0}]}{V_0}$$

(4.43)

where $m_e$ is the electron mass, $c$ is the speed of light, $\epsilon_0$ is the vacuum permittivity, $\epsilon$ is the elementary charge, $\omega$ is the frequency of microwave radiation, $v_{\text{coll}} = 4.5 \times 10^{10}$ s$^{-1}$ is the electron neutral collision frequency, and $D$ is the path length of the microwaves through the plasma region. While not shown, the absolute peak attenuation observed for
the data in Fig. 4.8 is ~ 0.10, corresponding to \( n_\infty \) of ~ \( 1.2 \times 10^{18} \) m\(^{-3}\). We note that this value is a factor of ~ 40 greater than that inferred from the shape of the decay curve. This admittedly substantial difference, while not completely understood, is likely due to some combination of uncertainty in the assumed value of \( \beta_{ei} \) and/or \( \nu_{\text{coll}} \), which is calculated. Other work performed by Utkin [26] and Ionikh [27] has shown that the microwave absorption coefficient used to determine absolute electron number densities results in artificially large values. It is clear that the attenuation of the microwave signal is proportional to the electron number density, but there is uncertainty in the value of the proportionality constant. Therefore, we stress that inference of \( n_\infty \) from (4.43) is given for completeness only and that none of the conclusions which follow are dependent upon its absolute value. In addition, because of the uncertainty involving (4.43) determination of the absolute number density will be performed utilizing the decay time constant, \( 1/\tau \), from (4.42) that is obtained from the fitting routine. While this method requires a well-characterized value of \( \beta_{ei} \) and a constant ionization rate, \( S \), the overall uncertainty in \( n_\infty \) will be less when compared to using (4.43).

A second set of measurements was performed in a pair of CO/O\(_2\)/N\(_2\) mixtures, again at 300 torr total pressure. These mixtures contained 5% CO, 10 or 20% O\(_2\), with the balance being N\(_2\). The electron beam was operated with identical current and voltage as used for the pure N\(_2\) case. CO was added to enable vibrational loading using the CO laser, as described in the previous section. As can be seen in the lower trace of Fig. 4.9, which is a raw microwave voltage versus time trace for a 20% O\(_2\) mixture, the electron density of the cold (non-excited) gas mixture reflects the 10 \( \mu \)s duration square pulse
from the electron gun. In this case, the steady state electron density is reached rapidly because free electrons are lost almost instantaneously through three-body attachment to O₂. When the gas mixture is vibrationally excited, as illustrated in the upper trace of Fig. 4.9, not only does the steady state electron density increase, but the rising and falling edges show noticeable curvature indicating substantial reduction in the rate of attachment. Note that the discontinuities in the upper trace is a result of the microwave probing both excited and cold regions of the plasma simultaneously, as discussed in the experimental section.

Figure 4.9. Comparison of electron number density between a cold and optically pumped gas mixture seeded with 5% CO.
Figure 4.10. Diagram of difference in volume of optically pumped region and electron beam sustained plasma.

Ignoring, for now, the large volume disparity (Fig 4.10) between the cold and laser excited regions, it is clear from the long tail in the decay that rapid O$_2$ attachment has been substantially mitigated. However, the net rate of electron removal by O$_2$ attachment is highly temperature dependent. More specifically, while the forward rate for (4.8) is relatively temperature independent, the backward O$_2^-$ detachment rate is highly sensitive to the heavy species temperature, increasing by three orders of magnitude between 300 and 550 K (see Fig. 3.6) [23]. Therefore it is imperative that accurate temperature measurements be performed in order to determine whether the observed tail in Fig. 4.9 is due to vibrational loading of the diatomic gas, or simply because of an increase in the rotational/translational temperature of the heavy species. To
that end a series of spatially resolved rubidium vapor filtered pure rotational Raman measurements were performed, using the instrument described in detail in Chapter 2. Figure 4.11(a) shows the experimental (dotted) S-branch spectrum obtained on the centerline of the CO laser pumped region, but with the CO laser blocked. The inferred rotational temperature, from a least squares fit to a standard spectral model (the solid curve), is 303 ± 10 K (2σ). Figure 4.11(b) shows the corresponding centerline spectrum obtained with CO laser excitation. The inferred temperature is found to increase, but only slightly, to 350 ± 10 K (2σ). Note that in Fig. 4.11(b), the increasing Raman signal starting at wavelengths below ~ 782 nm is due to incomplete rejection of Rayleigh and stray scattering by the vapor filter.

As will be shown in subsequent sections, if the observed long tail in the plasma

Figure 4.11(a). Rotational Raman S-Branch and fit for cold O₂/N₂ mixture. T= 303 ± 10 K (2σ)
decay is a thermal effect, a temperature increase of the order 300 – 350 K would be required, rather than the observed 50 K. We conclude, therefore, that the observed attachment mitigation cannot be a thermal effect and must be due to vibrational energy loading.

In addition radially resolved temperature measurements were performed, by translating the Raman probe laser with respect to the fixed CO excitation laser, in order to more quantitatively determine the volume of the vibrationally excited region. As can be seen in Fig. 4.12, the diameter of the excited region is approximately 0.10 cm, which is a factor of ten less than the total path length between the waveguides, an issue which will be discussed below.
Figure 4.12. Spatially resolved heavy species temperature of optically pumped O$_2$/N$_2$ mixture.

Least squares fitting analysis was performed on the O$_2$/N$_2$ mixtures using two different limiting kinetic models, reduction in the forward three body attachment process (4.8), and acceleration in the backwards, detachment, process. In either case, the first step is to subtract the contribution to the microwave absorption due to the non-pumped (cold) region of the plasma. Note that this simple subtraction is justified because the pumped region is quite small and the per unit length attenuation from the cold gas is more than an order of magnitude less than that from the vibrationally excited region. To
reduce noise associated with this subtraction the cold trace was approximated by a square pulse, with amplitude determined from a fit to the cold data.

The reduced attachment limiting case, which assumes that detachment is sufficiently slow that it can be ignored, results in the simple first order kinetic rate expression

$$\frac{dn_e}{dt} = S - k_A^{(1)} n_{O_2}^2 n_e - k_A^{(2)} n_{O_2} n_{N_2} n_e = S - \nu_A n_e$$

(4.44)

with analytical solutions

$$\frac{n_e(t)}{n_\infty} = 1 - e^{-\nu_A t}$$

(4.45)

$$\frac{n_e(t)}{n_\infty} = e^{-\nu_A t}$$

(4.46)

$$n_\infty = \frac{S}{\nu_A}$$

(4.47)

where $n_\infty$ and $S$, again, are the steady–state electron density and electron impact ionization rate, respectively. Note in particular that the attachment rate is strongly dependent upon the third-body collision partner, with $k_A^{(1)}$, corresponding to $O_2$ as the third body equal to $2.5 \times 10^{-42}$ m$^6$/s and $k_A^{(2)}$, corresponding to $N_2$ as the third body collision partner, equal to $0.14 \times 10^{-42}$ m$^6$/s, an order of magnitude slower [19]. As was shown in Chapter 3 the attachment rate coefficients may be larger than the values quoted by [19]. Therefore, throughout this chapter both the coefficients quoted by [19] and those determined in Chapter 3 will be used to determine an equilibrium attachment rate for comparison. These coefficients are $5.8 \times 10^{-30}$ and $5.8 \times 10^{-31}$ cm$^6$/s for $O_2$ and $N_2$, respectively.
respectively. For cold 20% O$_2$/N$_2$ mixtures at 300 torr these rate coefficients correspond to first order rate constants, $\nu_A$, equal to 1.1x10$^7$ s$^{-1}$ and to 3.03x10$^7$ s$^{-1}$ for the quoted coefficients and the recently determined coefficients, respectively. For cold 10% O$_2$/N$_2$ mixtures at 300 torr these rate coefficients correspond to first order rate constants, $\nu_A$, of 3.5x10$^6$ s$^{-1}$ and 1.03x10$^7$ s$^{-1}$ for the quoted coefficients and the recently determined coefficients, respectively. Figures 4.13 and 4.14 show the experimental data (open circles) and corresponding least squares best fits to Eq. (4.45) and (4.46) for the 10% and 20% O$_2$/N$_2$ mixtures, respectively. Note that the fits to an assumed exponential rise and fall, while not unreasonable overall, do exhibit some systematic error, particularly in the rate of drop of the early portion of the decay. The best fit values of $\nu_A$, inferred from the least squares fit, are tabulated in Table 4.2, along with the reported equilibrium values. As in the pure N$_2$ case the fitting routine infers different rates for the rise and fall of the electron number density.

<table>
<thead>
<tr>
<th></th>
<th>$\nu_A$ (s$^{-1}$) Rise</th>
<th>$\nu_A$ (s$^{-1}$) Decay</th>
<th>$\nu_A$ (s$^{-1}$) Equilibrium Old</th>
<th>$\nu_A$ (s$^{-1}$) Equilibrium New</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% O$_2$/N$_2$</td>
<td>2.8 ± 0.1 x10$^5$</td>
<td>8.6 ± 0.12 x10$^4$</td>
<td>1.1 x 10$^7$</td>
<td>3.0 x 10$^7$</td>
</tr>
<tr>
<td>10% O$_2$/N$_2$</td>
<td>3.6 ± 0.2 x10$^5$</td>
<td>8.4 ± 0.12 x10$^4$</td>
<td>3.5 x 10$^6$</td>
<td>1.0 x 10$^7$</td>
</tr>
</tbody>
</table>

Table 4.2. Attachment frequencies obtained from least squares fitting of the rise and fall portions of the experimental CO laser pumped data in Figs. 13 and 14 to (4.45) and (4.46), compared to equilibrium literature values from [17] and the newly determined coefficients from Chapter 3.
Figure 4.13. Data and fit to attachment only model for a 10% O₂/N₂ mixture at 300 torr.

As stated previously the attachment rate, unlike the detachment rate, is relatively flat as a function of temperature [18], so that the observed decrease cannot be attributed...
to the ~50 K increase in the heavy species temperature observed in the Raman spectra. However, it is possible that the vibrational nonequilibrium may result in a diminishing effect on the forward rate of process (4.8). If attachment will not occur when either O₂ or the third body is vibrationally excited, then the attachment rate will be reduced due to the depletion of the number of molecules available for the three-body attachment process. However, in this nonequilibrium vibrational environment approximately 30% of the O₂ and 25% of the N₂ is in a vibrationally excited state [36]. If the vibrational excitation limits the number of molecules available for the three-body attachment process, the net rate would be reduced by about a factor of two. Therefore, it is clear that the vibrational

Figure 4.14. Data and fit to attachment only model for a 20% O₂/N₂ mixture at 300 torr.
excitation does not affect the forward rate for process (4.8) to the extent exhibited by the data.

Electron heating, by means of process (4.29) exhibits the correct trend in that the three-body attachment coefficient is known to decrease with increasing electron temperature [19]. However, based on a linear extrapolation of the data found in reference [19], an electron temperature of approximately 10-20 eV is necessary in order to explain the observed two order of magnitude increase in the plasma lifetime. This is an unrealistic electron temperature, greatly exceeding the vibrational temperatures of order tenths of eV for each of the diatomic species, and therefore electron heating is also ruled out as an explanation for the observed increase in plasma lifetime.

From the above arguments it is clear that reduced attachment does not provide a credible mechanism to explain the observed increase in plasma lifetime. As an alternative to reduced attachment, the second limiting case model considered is one in which three-body electron attachment is balanced by rapid detachment. In this case it is assumed that vibrational excitation creates a pool of “rapid” detachers, with number density \( n_d \). The corresponding time-dependent electron and negative ion densities are described by the coupled rate equations

\[
\frac{dn_e}{dt} = S - \beta_e n_e n_e - \nua n_e + k_d n_d n_d
\]

(4.48)

\[
\frac{dn}{dt} = \nua n_e - k_d n_d n_d - \beta_d n_d n_d
\]

(4.49)

where \( n_e \) and \( n \) are the number densities of cations and anions, respectively. Note that it is necessary to include ion–ion recombination as well as electron–ion recombination. If detachment is assumed to be rapid, then the steady-state approximation becomes valid for
the time-dependent anion number density and it is easy to show that the steady-state anion number density is given by

\[
[n_\text{-}]_{ss} = \left( \frac{\nu_A}{\nu_d + \beta_i n_+} \right) n_e
\]  

(4.50)

Upon substitution of (4.50) into (4.48), and assuming that \( \nu_d \gg \beta_i n_+ \) and \( n_+ = n_e \), then (4.48) simplifies to

\[
\frac{dn_e}{dt} = S - \beta_{\text{eff}} n_e^2
\]  

(4.51)

where the following definitions have been made.

\[
\beta_{\text{eff}} = \beta_{ei} + \beta_a \frac{\nu_A}{\nu_d}
\]  

(4.52)

\[
\nu_d = k_d n_d
\]  

(4.53)

The form of (4.51) is identical to that of (4.38), with identical solutions

\[
\frac{n_e(t)}{n_e} = \tanh[n_e \beta_{\text{eff}} t] \quad \text{(generation)}
\]  

(4.54)

\[
\frac{n_e(t)}{n_e} = \frac{1}{1 + n_e \beta_{\text{eff}} t} \quad \text{(decay)}
\]  

(4.55)

\[
n_e = \sqrt{\frac{S}{\beta_{\text{eff}}}}
\]  

(4.56)

except that \( \beta_{ei} \), the rate coefficient for electron–ion recombination, is replaced by \( \beta_{\text{eff}} \), defined by (4.52).

The balanced attachment/detachment model is motivated by the fact that the electron affinity of O\(_2\) is relatively low, \(~0.43\) eV [23]. From a purely energetic perspective, third body collision partners, either O\(_2\), N\(_2\), or CO, with two or more
vibrational quanta have internal energies very near (0.38 eV for O\textsubscript{2}) or exceeding (0.57/0.52 eV for N\textsubscript{2}/CO, respectively) this amount. It is reasonable therefore that collisions between O\textsubscript{2}\textsuperscript{-} and a vibrationally excited third body with two or more quanta (4.57) could result in a high probability of detachment.

\[ \text{O}_2^- + \text{M}_2 (v \geq 2) \rightarrow e + \text{O}_2 + \text{M}_2 \]  \hspace{1cm} (4.57)

Figures 4.15 and 4.16 are similar to Figs. 4.13 and 4.14, except that the voltage temporal traces for the 300 torr, 10\% and 20\% O\textsubscript{2} mixtures are fit to (4.54) and (4.55), the balanced attachment/detachment model, with the product \( n_e \beta_{\text{eff}} \) treated as an adjustable parameter. In both cases it can be seen that the fit to both the rise and fall is excellent. Unlike the pure N\textsubscript{2} case, however, inferring a value for \( \beta_{\text{eff}} \) is more problematic. In particular it must be recalled that the environment is now highly non-uniform due to the relatively small volume of the optically pumped region. In addition, inference of absolute number density from (4.43) requires an assessment of the effective microwave path length, D. Utilizing a value of 0.10 cm, based on Fig. 4.12, resulted in a value (~10\textsuperscript{19} m\textsuperscript{-3}) that is considered too high to be credible. Basically, it was observed that the absolute attenuation was similar to the pure N\textsubscript{2} case. If it is assumed that this attenuation occurs across a path one order of magnitude smaller, then the corresponding electron density is a factor of ten higher. Of course this ignores spatial non-uniformity issues, in particular diffusion of electrons, perhaps heated by process (4.29), out of the directly CO laser excited region.
An alternative approach is to assume that the electron ionization rate, $S$, is unchanged from that determined from the pure $N_2$ case. Specifically combining (4.42) and (4.56) results immediately in the alternative expression for $\beta_{\text{eff}}$

$$\beta_{\text{eff}} = \frac{1}{\tau^2}$$

(4.58)

where $\tau$ is defined analogously to eqn. (4.42), as $1/n_{e}\beta_{\text{eff}}$. Best fit values of $\beta_{\text{eff}}$ inferred in this manner, along with reported equilibrium values for $\beta_{ci}$ and $\beta_{ii}$, [41] are given in Table 4.3. Focusing again on the decay data it can be seen that $\beta_{\text{eff}}$ is slightly faster, by a

Figure 4.15. Data and fit to balanced attachment/detachment model for a 10% $O_2/N_2$ mixture at 300 torr.
Figure 4.16. Data and fit to balanced attachment/detachment model for a 20% O\textsubscript{2}/N\textsubscript{2} mixture at 300 torr.

<table>
<thead>
<tr>
<th></th>
<th>(\beta_{\text{eff}}) (m\textsuperscript{3}/s) Rise</th>
<th>(\beta_{\text{eff}}) (m\textsuperscript{3}/s) Decay</th>
<th>(\beta_{\text{ei}}) (m\textsuperscript{3}/s) Equilibrium</th>
<th>(\beta_{\text{ii}}) (m\textsuperscript{3}/s) Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% O\textsubscript{2}/N\textsubscript{2}</td>
<td>1.4 ± 0.24 x10\textsuperscript{-11}</td>
<td>8.8 ± 1.22 x10\textsuperscript{-12}</td>
<td>2x10\textsuperscript{-12}</td>
<td>2x10\textsuperscript{-12}</td>
</tr>
<tr>
<td>10% O\textsubscript{2}/N\textsubscript{2}</td>
<td>1.9 ± 0.38 x10\textsuperscript{-11}</td>
<td>1.1 ± 0.128 x10\textsuperscript{-11}</td>
<td>2x10\textsuperscript{-12}</td>
<td>2x10\textsuperscript{-12}</td>
</tr>
</tbody>
</table>

Table 4.3. Effective electron loss rates from least squares fitting of experimental data in Figs. 4.15 and 4.16 to (4.54) and (4.55) compared to equilibrium values of \(\beta_{\text{ei}}\) and \(\beta_{\text{ii}}\) from [17].
factor of approximately four to five, but still of the same order of magnitude as the literature values for both electron-ion recombination, $\beta_{ei}$, and ion-ion recombination, $\beta_{ii}$. We stress that this analysis is meant to be qualitative only since inferred values of $\beta_{\text{eff}}$ are clearly directly coupled to any uncertainty in the absolute value of $n_{\infty}$.

We can make an estimate of the minimum vibrational excitation required to sufficiently increase the detachment rate in a manner consistent with the above result. If it is assumed that the detachment rate is of gas kinetic order, so that every collision between a suitably excited “rapid” detacher with $O_2^-$ results in electron detachment, then from simple hard sphere kinetics, $k_d \sim 2.5 \times 10^{-16} \text{ m}^3/\text{s}$ at 300 torr. If, in addition, it is assumed that $\nu_d = \nu_A = 1.1 \times 10^7 \text{ s}^{-1}$, for the 20% $O_2$ mixture, then the fraction of required rapid detachers, $n_d/N$ is $\sim 0.005$. By examination of the vibrational distribution function (VDF) in Fig. 4.17, taken from the data of [36], it can be seen that the fraction of molecules with $\nu \geq 2$ is approximately 0.08, more than a factor of ten greater than the minimum required. A similar analysis can be made for the 10% $O_2$ mixture. In this case, again assuming $\nu_d = \nu_A$ where $\nu_A$ is now equal to $3.5 \times 10^6 \text{ s}^{-1}$, the required rapid detacher fraction is even lower, $n_d/N \sim 0.001$.

4.6 Results and Discussion II. Numerical Modeling

The two simplified models presented above were explored because they provide physical insight and the resulting analytical solutions are readily amenable to least squares curve fitting. They have the inherent disadvantage however of representing rather ideal limiting cases. As a compliment to the previous analyses we have also directly obtained numerical solutions to (4.48) and (4.49). A parametric study was
Figure 4.17. Vibrational Distribution Function for a 20% O₂/CO/N₂ mixture. Data taken from [36].

<table>
<thead>
<tr>
<th></th>
<th>ν₁ (s⁻¹)</th>
<th>ν₄ (s⁻¹)</th>
<th>β₅₂ (cm³/s)</th>
<th>β₄₂ (cm³/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% O₂/N₂ 300 torr</td>
<td>1.1 x 10⁷</td>
<td>1.1 x 10⁷</td>
<td>11 x 10⁻⁶</td>
<td>2 x 10⁻⁶</td>
</tr>
<tr>
<td>10% O₂/N₂ 300 torr</td>
<td>3.5 x 10⁶</td>
<td>3.5 x 10⁶</td>
<td>11 x 10⁻⁶</td>
<td>2 x 10⁻⁶</td>
</tr>
</tbody>
</table>

Table 4.4. Rates determined from comparison of experimental data to numerical modeling using (4.48) and (4.49).
performed, a few results of which are given in Figs 4.18-4.20. The parameters used to create the “best-fit” modeled curves for the decay portion of the data are found in Table 4.4 (the rise is qualitatively similar). Because \( \nu_d/\nu_A \) is the important parameter and not the absolute values of the rate constants themselves, only the rate constants determined from the quoted equilibrium rate coefficients will be used for comparison within the numerical model. Additionally, it is necessary to estimate the conversion between the time-dependent microwave voltage and absolute electron number density since the relative contribution of attachment/detachment and recombination is, in general, dependent upon this.

The conversion was estimated by combining (4.42) and (4.58), to yield

\[
n_\infty = \tau S \tag{4.59}
\]

Again using the value of \( S \) from the pure \( \text{N}_2 \) data, along with the value of \( \tau \) from the balanced attachment/detachment limiting case, we arrive at an estimate of \( n_\infty = 1.4 \times 10^{16} \) m\(^{-3}\), for the 10% \( \text{O}_2/\text{N}_2 \) mixture which is approximately fifty percent of that inferred for the pure \( \text{N}_2 \) case. Since the absolute absorption is relatively low, a few percent, the time-dependent electron density is assumed to be proportional to the observed transmission.

It is also necessary to provide an initial condition for the anion number density. To estimate this, it is assumed that a rapid equilibrium is established for process (4.8) within the vibrationally excited region. It immediately follows that if \( t = 0 \) is defined as the time when the electron beam is turned off, the initial anion density is given by (4.60).

\[
\left[ n_{\text{O}_2^-} \right]_o = n_\infty \left( \frac{\nu_A}{\nu_d} \right) \tag{4.60}
\]
Figure 4.18. Computer Model comparison to electron density data for 10% O₂/N₂ mixture where ν_d/ν_a=1.0 for various values of β_ei.

Figure 4.18 shows a comparison of the 10% O₂/N₂ data with modeling results in which the ratio ν_d/ν_a is assumed equal to 1.0 and β_ei is varied between 1.1 x 10⁻¹⁰ m³/sec and 1.1 x 10⁻¹² m³/sec. As described above, for this case \[
\left[ \frac{n_{o_2}}{n_{o_2}} \right]_o
\]
is assumed equal to \( n_\infty = 1.4 \times 10^{16} \) m⁻³. \( \beta_{ii} \) is assumed equal to the equilibrium N₂ value, \( 2.0 \times 10^{-12} \) m³/sec. It can be seen that the middle curve, with \( \beta_{ei} = 1.1 \times 10^{-11} \) m³/sec produces excellent agreement with the data. Moreover, as can be seen in Fig. 4.19, which is identical to Fig. 4.18 except that the ν_d/ν_a ratio has been increased to 10, and \[ \left[ \frac{n_{o_2}}{n_{o_2}} \right]_o \] reduced correspondingly
Figure 4.19. Computer Model comparison to electron density data for 10% O\textsubscript{2}/N\textsubscript{2} mixture where v\textsubscript{d}/v\textsubscript{a}=10 for various values of \(\beta\).  

according to (4.60), it is clear that further increase in the detachment rate has very little effect. However, as shown in Fig. 4.20, which models \(v_d/v_a = 0.10\), reducing the rate of detachment is very significant. In fact, while not shown in Fig. 4.20, further decrease of \(\beta\) to values less than \(\sim 10^{-12}\) m\textsuperscript{3}/sec has negligible effect. More specifically, for \(v_d/v_a = 0.10\), it is not possible to accurately simulate the plasma decay for any assumed value of \(\beta\). This technique, therefore, establishes a lower limit for the detachment frequency, \(v_d\).

We conclude that under the nonequilibrium conditions produced by CO laser pumping, attachment is mitigated and the plasma decay is controlled by recombination. Specifically the results above indicate that the detachment rate, \(v_{d}\), must be equal to the
attachment rate, $\nu_A$, or exceed it in order to replicate the experimental data. We particularly note that at room temperature and 300 torr total pressure the equilibrium value of the detachment rate, $\nu_d$, is $\sim 45 \text{ s}^{-1}$ [22]. This implies, assuming $\nu_d/\nu_a = 1$, an increase in the detachment rate of approximately five orders of magnitude over the equilibrium value.

We conclude with a brief discussion of the discrepancy between recombination rates resulting from this work and previously reported equilibrium values. While it was not our intent to quantitatively determine these rates, it is nonetheless expected that the inferred values would approximately equal those previously reported. A possible
explanation is that the discrepancy arises from the non-homogeneity of the microwave probed region. Within the CO laser defined volume, where the vibrational loading is maximized, it is clear that three-body attachment is completely mitigated so that the effective electron loss rate is determined by recombination. It is also clear that at some distance from the CO laser centerline the vibrational loading becomes negligible and rapid attachment again dominates. It is this region which the subtraction procedure is intended to correct for. However, in the intermediate region, where vibrational loading is not maximized but still significant, the effective electron loss rate will be intermediate between that dominated by attachment and recombination. Such non-uniformity will result in a path averaged electron loss rate that is faster than that predicted using equilibrium recombination rates, resulting in an inferred value of \( \beta_{ei} \) which is artificially greater than equilibrium. We stress again, however, that this systematic discrepancy does not impact the primary conclusion, confirmed in Fig. 4.9, that vibrational excitation results in complete attachment mitigation.
As discussed in the first chapter there are many applications of high-pressure, low temperature, large volume air plasmas. However, the power budget for these types of plasmas is prohibitively large. While the previous chapter demonstrated a method by which the power requirements are decreased resulting in an increase of the ionization fraction, it relied on vibrational excitation from a CO laser. This technique is inherently small volume because attachment mitigation will only occur in a volume slightly larger than that of the CO laser beam volume at its focal point. To increase the volume of an air plasma to the extent that it becomes practical for real-world applications ($\approx 10^2$-$10^6$ cm$^3$) requires a different technique.

Expansion of a plasma by an RF discharge is a highly efficient technique by which a large volume plasma may be created. However, it is important that the RF field be sub-breakdown such that the plasma is operated at non-self-sustained conditions. A self-sustained discharge is prone to instability development, which leads to the glow-to-arc transition. As discussed in Chapter 1 Joule heating leads to run-away ionization and causes the plasma to collapse to an arc. In a non-self-sustained discharge this type of instability does not develop. Additionally, as will be shown there is an inverse
relationship between the sub-breakdown RF field and the associative ionization mechanism. As the RF field is increased the plasma is heated. However, as was discussed in Chapter 4 (Mitigation) as the temperature of the plasma increases the V-T rate increases causing a truncation of the plateau in the VDF, so that the rate of associative ionization decreases. Therefore, provided the RF field is sub-breakdown the inverse relationship between the field strength and the associative ionization rate actively imposes stability.

5.2 Review of Formation of Optically Pumped Plasma

The previous chapter discusses the process of Anharmonic Up-pumping and therefore it will only be reviewed here. As described by the Treanor Distribution a state of vibrational nonequilibrium may be achieved through collisional V-V quanta exchange for a number of diatomic molecules. Processes (5.1) and (5.2) depict how the

\[
\begin{align*}
CO(v) + h\nu & \rightarrow CO(v+1) & v=0 \rightarrow 10 \\
CO(v) + CO(w) & \rightleftharpoons CO(v-1) + CO(w+1) & v \leq w
\end{align*}
\] (5.1)

\[
\frac{k_R}{k_F} = e^{-\frac{\Delta E}{kT}}
\] (5.3)

Anharmonic Up-pumping process occurs for CO. The lowest excited vibrational levels are populated by resonant absorption of approximately the first 10 fundamental vibrational frequencies from a CO gas laser (5.1). Higher levels become populated through collisional V-V exchange exhibited in (5.2). The V-V exchange process occurs due to the anharmonic defect between vibrational levels, which becomes larger as the difference between v and w increases. The detail-balance equation given in (5.3)
indicates the forward rate of (5.2), which is exothermic, will exceed that of the reverse rate.

At the higher lying vibrational states ($v \approx 20$) chemical pathways that were energetically inaccessible become possible. Of the multiple processes the most important to the formation of a plasma is the associative ionization mechanism, Eq. (5.4).

$$\text{CO}(v) + \text{CO}(w) \rightarrow (\text{CO})_2^+ + e^- \quad (5.4)$$

$$E_v + E_w > E_{\text{ion}} \quad (5.5)$$

This process occurs when the available vibrational energy exceeds the ionization energy of the molecule of interest (5.5). In this case the ionization potential of CO is on the order of 14eV. Unfortunately, the vibrational nonequilibrium quickly dissipates outside of the CO laser beam. Associative ionization ceases once the vibrational temperature has decreased to an extent that there is insufficient vibrational energy to satisfy condition (5.5). For typical CO laser pumped, non-O$_2$ containing plasmas the vibrational temperature is sufficient to cause associative ionization in a cylindrical volume of approximately 0.5cm diameter by 10cm length [43].

Multiple chemical pathways occur in a CO laser-initiated plasma that is created in a CO/N$_2$ environment. As previously stated vibrationally excited CO undergoes associative ionization to form a free electron and a dimer cation (5.4). Additionally, free carbon is also created by the disproportionation reaction (5.6).

$$\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}_2 + \text{C} \quad (5.6)$$

Mass spectrometric measurements of CO/Ar glow discharges have shown that the dominant cations are $(\text{CO})_2^+$ and cluster ions of the general form $C_n(\text{CO})_2^+$ where $n=1-15$.
If a small percentage (few millitorr) of O$_2$ is added, the dominant cation becomes O$_2^+$ and the dimer and cluster ions disappear nearly completely [44]. Previous measurements of anharmonically up-pumped CO/Ar and CO/N$_2$ plasmas show that the addition of small amounts of O$_2$ or NO can increase the electron number density significantly [45]. Presumably, an equivalent process occurs wherein the dominant dimer and cluster ions are replaced by O$_2^+$ or NO$^+$, which are then the dominant cation within the system. The increase in electron number density occurs because the electron-ion recombination rate is slower for O$_2^+$ or NO$^+$ ($\beta_{ei}=3-5\times10^{-8}$ cm$^3$/s) than for the dimer or cluster ions ($\beta_{ei}=2\times10^{-6}$ cm$^3$/s) [46]. Regardless of which cation is dominant, electron-ion recombination is the principal electron loss mechanism.

5.3 Thomson/rf Discharge

If a free electron is heated within a static external electric field, there will be a force acting on the electron. This electrostatic force is simply the product between the electric field and the charge of the electron. The electrostatic force will accelerate the electron along the electric field lines. If the electric field is not static, but oscillating, the free electron will oscillate with the external field. The force acting upon the free electron increases the average energy of the electron until the electron either exits the external field or is captured or lost.

The above discussion can be extended to the case of a laser-initiated plasma (such as the plasma initiated by anharmonic up-pumping) being placed within an external radio-frequency electric field. In this situation the radio-frequency electric field will exert a force upon the free electrons created by the associative ionization mechanism.
(5.4). If the dipole of the external field is perpendicular to the axis of laser propagation, the electrons will be accelerated out of the laser beam volume and the average electron energy will increase. Within a CO/N$_2$ plasma the free electrons are lost by electron-ion recombination. It is well known that electron-ion recombination rates are dependent upon the average electron energy. Therefore, the applied rf field will decrease the electron-ion recombination rate causing an increase in the volume of the laser-initiated plasma. The decrease in the electron-ion recombination rate will occur for multiple reasons. First, the ability of the cation to capture the free electron is diminished by the increase in the average electron energy. According to Biondi [47] in the case that dissociative recombination dominates autoionization (electron ejection) when a cation dimer captures a free electron, the recombination rate coefficient, $\beta_{ei}$, varies as $T_e^{-1/2}$. Second, it is known that inelastic collisions between electrons and molecules can occur wherein the electron imparts some of its kinetic energy to an internal mode of the molecule. Which molecular mode becomes excited is dependent upon the average electron energy and this dependence is shown in Fig. 5.1 [48]. As stated in Chapter 2 in the work presented here $E/N \sim 1 \times 10^{-16}$ Vcm$^2$. The previous chapter has shown that vibrational excitation of O$_2$ impairs the ability of O$_2$ to remove electrons from the system by increasing electron detachment from O$_2^-$. If the rf field results in vibrational excitation of molecules outside of the CO laser beam volume, it is reasonable to hypothesize that the associative ionization process will be maintained by the rf field and/or that the electron affinity of the ion is overcome by vibrational excitation causing electron detachment. Finally, a result of increasing the average electron energy within the plasma is that the vibrational nonequilibrium is enhanced as well. In the absence of the external
Figure 5.1. Relative distribution of field energy between molecular modes as a function of the reduced electric field [48]. 1). Vibrational mode of O₂. 2). Rotational mode of O₂ and N₂. 3). Elastic losses. 4). Vibrational mode of N₂. 5). Electronic excitation of N₂. 6). Electronic excitation of O₂. 7). Ionization of O₂ and N₂.

rf field the vibrational nonequilibrium which is created and sustained by the CO laser is limited to a region of comparable size to the volume of the laser beam.

An important aspect of a Thomson discharge is that it is an example of what is known as “non-self-sustained”. This refers to the nature of the applied rf field. In the case of a Thomson discharge the applied field is kept at sub-breakdown levels. That is, the field is not strong enough to increase the average electron energy to the point that electron impact ionization occurs. If electron impact ionization occurs the discharge is no longer non-self-sustaining but becomes self-sustaining. A self-sustaining discharge is characterized by the ability of the external field to increase the electron number density...
within the gas by causing direct electron impact ionization. However, these types of discharges are subject to development of instability and possible runaway ionization, which results in the glow-to-arc transition. The development of the instability depends upon the applied field and pressure of the system. This dependence is shown in the Paschen curves [49] for various gases in Fig 5.2. In some cases the experimental conditions required (pressure, electron number density, etc) preclude the use of a self-sustained discharge. Additionally, examination of Fig. 5.1 indicates that if preferential excitation of the molecular modes is desired (i.e. excitation of vibrational mode) a self-sustained discharge would be ill-suited to the task. For example, the Discharge Oxygen-
Iodine Laser demands the production of singlet O₂ (a¹Δ). The reduced electric field which optimizes the production of O₂ (a¹Δ) (≈5×10⁻¹⁷ Vcm²) is at a significantly lower value of E/N than would be found for a self-sustained discharge (≈1-5×10⁻¹⁵ Vcm²) [2 & 6].

5.4 Vibrationally Resolved Raman Scattering Theory

Vibrationally resolved Raman scattering was the technique used to determine the populations of the vibrational levels for each molecular species within the gas mixture. This technique was chosen because of the experimental simplicity and the straightforward analysis of the data. While infrared spectroscopy could be used to determine the vibrational level populations of CO, this technique is less useful in this case because the major component of the gaseous mixture (N₂) lacks a permanent dipole and is therefore infrared inactive. Additionally, infrared emission or absorption is a line-of-sight measurement, which lacks the spatial resolution of Raman scattering. Other techniques, such as LIF, could be used in principle, but are not practical since the transitions to be probed lie in the vacuum ultraviolet region of the spectrum (<190nm).

The general theory of Raman scattering has been presented in the previous chapter on the activation of electron detachment by vibrational excitation. This section elaborates upon the earlier more general case of Raman scattering and focuses specifically on the pertinent details of vibrationally resolved Raman scattering. From Chapter 4 it is clear that the intensity of the radiation scattered into the solid angle is dependent upon the polarizability tensor, which describes the likelihood of a transition between two levels. The scattered intensity is given by (5.7)-(5.10) [40].
In the above equations $I$ is the scattering intensity, $\Phi$ is the incident laser irradiance, $N$ is the number of scatters, $\Omega$ is the solid angle collected, $\theta$ is the scattering angle, $\omega_s$ is the angular frequency of the scattered photons, $k_{\omega}$ is a constant and $\sigma'$ is the scattering cross-section. The polarizability tensor operator can be approximated by a Taylor series expansion as a function of the normal coordinates of the molecule as seen in (5.11).

$$\hat{\alpha}_{\rho\sigma}(Q) = (\alpha_{\rho\sigma})_0 + \sum_k \left( \frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_k \sum_l \left( \frac{\partial^2 \alpha_{\rho\sigma}}{\partial Q_k \partial Q_l} \right)_0 Q_k Q_l + \cdots \quad (5.11)$$

In this case $\rho$ and $\sigma$ refer to the different components of the molecular polarizability. Recall that the polarizability tensor elements are determined from (5.12).

$$\left( \alpha_{\rho\sigma} \right)_{v_y v_y} = \left< v_F \left| \hat{\alpha}_{\rho\sigma}(Q) \right| v_I \right> \quad (5.12)$$

Substitution of the Taylor series approximation to the operator (5.11) into (5.12) results in (5.13).

$$\left( \alpha_{\rho\sigma} \right)_{v_y v_y} = (\alpha_{\rho\sigma})_0 \left< v_F \left| v_I \right> \right> + \sum_k \left( \frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 \left< v_F \left| Q_k \left| v_I \right> \right> + \frac{1}{2} \sum_k \sum_l \left( \frac{\partial^2 \alpha_{\rho\sigma}}{\partial Q_k \partial Q_l} \right)_0 \left< v_F \left| Q_k Q_l \left| v_I \right> \right> + \cdots \quad (5.13)$$

In this approximation the $v_x$ are the harmonic oscillator vibrational wavefunctions for the specific vibrational levels and $Q_x$ are the normal coordinates for the vibrational modes.
The total vibrational wavefunction, \( \varphi \), in the harmonic oscillator approximation is the product of the harmonic oscillator wavefunctions for the normal mode vibrations as seen in (5.14)

\[
\varphi_{\nu_i} = \prod_k \varphi^k_{\nu_i}(Q_k)
\]  

(5.14)

where the \( \varphi^k_{\nu_i}(Q_k) \) are the harmonic oscillator wavefunctions for normal mode \( k \) in vibrational level \( \nu_i \). If the \( \varphi_{\nu_i} \) are substituted into the Taylor series expansion (5.13) and derivatives of order greater than one are neglected, the result is (5.15).

\[
\left( \alpha_{\rho\sigma} \right)_{\nu_i \nu_i} = \left( \alpha_{\rho\sigma} \right)_{\nu_i \nu_i} \left( \prod_k \varphi^k_{\nu_i}(Q_k) \prod_k \varphi^k_{\nu_i}(Q_k) \right) + 
\sum_k \left( \frac{\partial^2 \alpha_{\rho\sigma}}{\partial \varphi^k_{\nu_i}(Q_k)} \right) \left( \prod_k \varphi^k_{\nu_i}(Q_k) \mid Q_k \mid \prod_k \varphi^k_{\nu_i}(Q_k) \right)
\]  

(5.15)

Orthogonality arguments are then used to simplify the above. For harmonic oscillator functions the following properties apply

\[
\langle \varphi^k_{\nu_i}(Q_k) \mid \varphi^k_{\nu_i}(Q_k) \rangle = \begin{cases} 
0 & \text{for } v^k_F \neq v^k_i \\
1 & \text{for } v^k_F = v^k_i
\end{cases}
\]  

(5.16)

\[
\langle \varphi^k_{\nu_i}(Q_k) \mid Q_k \mid \varphi^k_{\nu_i}(Q_k) \rangle = \begin{cases} 
0 & \text{for } v^k_F = v^k_i \\
\left(v^k_i + 1\right)^{1/2} b_{v_i} & \text{for } v^k_F = v^k_i + 1 \\
\left(v^k_i\right)^{1/2} b_{v_i} & \text{for } v^k_F = v^k_i - 1
\end{cases}
\]  

(5.17)

where

\[
b_{v_i} = \left( \frac{\hbar}{8\pi^2 c v^k_i} \right)^{1/2}
\]  

(5.18)
It is clear that the first term in (5.15) corresponds to Rayleigh scattering since the only non-zero terms are those terms where the initial and final state are the same (from (5.16)). The second term in (5.15) corresponds to the Stokes and anti-Stokes vibrational Raman transitions (from (5.17)). Therefore, the harmonic oscillator polarizability tensor matrix element \( (\alpha_{\rho\sigma})_{F,I} \) for a Stokes transition is

\[
(\alpha_{\rho\sigma})_{v_{F}v_{I}} = \left( v_{I}^{k} + 1 \right)^{1/2} b_{v_{I}} \left( \frac{\partial \alpha_{\rho\sigma}}{\partial Q_{k}} \right)_{0}
\]

(5.19)

and for an anti-Stokes is

\[
(\alpha_{\rho\sigma})_{v_{F}v_{I}} = \left( v_{I}^{k} \right)^{1/2} b_{v_{I}} \left( \frac{\partial \alpha_{\rho\sigma}}{\partial Q_{k}} \right)_{0}
\]

(5.20)

These equations represent a \( \Delta v = \pm 1 \) for a normal mode vibration of a molecule. It is important to note that for the anti-Stokes transitions \( v_{I}^{k} \neq 0 \). The significance of (5.19) and (5.20) is that they indicate that the harmonic oscillator cross-section for a vibrational Raman transition is a function of the vibrational quantum number, \( v_{I} \). In the case of the Stokes branch the cross-section scales as \( v_{I} + 1 \). This scaling of cross-section is important when determining the vibrational level relative populations, which will be used to determine the vibrational temperature of the gas.

It is important to note that the above analysis is based upon the molecule being described by the harmonic oscillator approximation. However, the anharmonic up-pumping process is inherently non-harmonic. If the above analysis is repeated using a more appropriate wavefunction for the system, such as the Morse potential, the cross sections are then described by (5.21) and (5.22) [39]
\[ I_v \propto (v+1) \frac{(k-2v-1)(k-2v-3)}{(k-2v-2)^2 (k-v-1)} \quad (5.21) \]
\[ I_v \propto v \frac{(k-2v-1)(k-2v+1)}{(k-2v)^2 (k-v)} \quad (5.22) \]

for the Stokes and anti-Stokes transitions, respectively. In the above equations \( k=\omega_\lambda/\omega_{\lambda c} \) and describes the anharmonicity of the molecule. While the deviation in cross-sections determined by (5.19)-(5.22) may reach as much as 33\% at high vibrational levels (\( v=40 \)), at the lower vibrational levels probed in this work the deviation is only a few percent [36]. Therefore, the anharmonic effect on the scaling of the cross-section was ignored when determining relative vibrational level populations.

5.5 Description of Kinetic Model

The data acquired is compared to a kinetic model consisting of four coupled differential equations. This model was developed and performed by Dr. Igor Adamovich [50] and a more thorough description of it is provided in Appendix B. Each of the differential equations predicts a different property of the system. The first equation states that the total time rate of change of the number densities at a fixed location in space, \( \frac{\partial n_k(x,y,t)}{\partial t} \), is equal to the sum of contributions from mass diffusion, \( \nabla \Gamma \), and sources of gain and loss, \( Q_k \) (5.23). The second equation describes the RF field within the experimental region, dictated by the free charge distribution (5.24). It is better known as the Poisson equation. The third equation, similar to the first, describes the distribution of vibrational energy and considers excitation due to the laser and the RF field, \( V-V \) intraspecies transfer as well as many forms of vibrational relaxation which include \( V-T \)
transfer and interspecies V-V (5.25). The final equation, energy balance, describes the translational/rotational temperature within the experimental region (5.26).

\[
\frac{\partial n_k(x,y,t)}{\partial t} + \nabla \Gamma_k = Q_k
\]  

(5.23)

\[
\nabla^2 \phi(x,y,t) = \frac{1}{\varepsilon_0} \sum_k q_k n_k(x,y,t)
\]  

(5.24)

\[
\frac{\partial E_{\text{vib},j}(x,y,t)}{\partial t} + \nabla \left[ D_j \nabla E_{\text{vib},j}(x,y,t) \right] = R_j^{\text{laser}} + R_j^{\text{field}} - R_j^{\text{relax}}
\]  

(5.25)

\[
\frac{5}{2} k_B N \frac{\partial T(x,y,t)}{\partial t} + \nabla \left[ \lambda \nabla T(x,y,t) \right] = k_B N \left( y_{\text{CO}} R_{\text{CO}}^{\text{relax}} + y_{N_2} R_{N_2}^{\text{relax}} \right)
\]  

(5.26)

For this system of equations the greatest uncertainty is in the vibrational relaxation rates. Therefore, the components of this rate (V-T, V-E, etc) are treated as adjustable parameters within the model. Additionally, instead of determining the VDFs of the gases from the numerical solution of the master kinetic equation developed by Flament [35], the VDFs are approximated by the analytical theory of V-V pumped anharmonic oscillators demonstrated by Gordiets and Zhdanok [51].

Solution of the system of coupled differential equations ((5.23), (5.24), (5.25) and (5.26)) requires solving for properties of the system which vary over different time scales. Specifically, the characteristic time scales for reaching a quasi-steady state distribution in the electric field is on the order of 10^{-6} s. The characteristic time scales for the vibrational populations and electron density are on the order of 10^{-4}-10^{-3} s. Lastly, the gas temperature characteristic time scale is on the order of seconds. Therefore, a numerical solution for this system of differential equations was obtained by first solving for the coupled equations which include the electric field ((5.23) & (5.24)) over the
electric field characteristic time (10⁻⁶ s). The equations which describe the vibrational populations and electron density (electron density is in the “fast” equation, but it is determined by the vibrational populations so that is the rate-limiting step for electron density) ((5.25) and (5.26)) are then solved for the appropriate characteristic time scale (10⁻⁴-10⁻³ s). This process is continued iteratively until a steady-state spatial distribution for each of the properties is achieved over the slowest characteristic time scale, that of the translational temperature (1 second).

Certain approximations were made to facilitate the solution of the coupled differential equations. For example, the circular electrodes used in the experiment were modeled as square electrodes possessing the same surface area (width of 2.66cm). The CO laser beam was assumed to have a Gaussian beam profile wherein the 1/e² radius was 1mm. Additionally, the gas mixture was approximated as well. The experimental gas mixture was a NO seeded 1.4% CO in N₂ mixture at 300 torr total pressure. To simulate the additional V-T relaxation associated with the NO seeding, the model approximated the mixture as 1% He, 1.4% CO in N₂ at 300 torr total pressure. The RF voltage amplitude and frequency are U₀=1500V and νRF=10MHz, respectively. Lastly, the system of equations was solved using standard stiff PDE solver PDECOL [52].

5.6 Results and Discussion I. Experimental Measurements

Previously, it was shown that RF coupling to free electrons produced in an optically pumped CO plasma enhances the vibrational nonequilibrium induced along the path of the incident laser beam [1]. The current results show that this effect is not limited to the volume occupied by the CO laser beam, which is approximately 2 mm in diameter.
and 10 cm long. Indeed, as can be seen in Figs. 5.3 and 5.4, the N₂ Raman spectra band intensities (i.e. the fractional vibrational level populations) increase when the RF field is applied, both at the CO laser beam axis (see Fig. 5.3), and at a vertical displacement from the CO laser beam (see Fig. 5.4). Note that the Raman spectra with the RF applied have been scaled and baseline corrected to match the intensity of the v=0 peak when the RF is off. This effect is also illustrated in Fig. 5.5, which shows absolute fractional vibrational level populations. From Fig. 5.5, one can see that the vibrational level populations for v=1-4 become greater when the RF field is applied. As discussed earlier, the RF power is coupled to the vibrational mode of the diatomic molecules via collisions with the free electrons produced by associative ionization in the laser-sustained plasma.

Figure 5.3. Raman spectra of vibrationally excited N₂ for the coaxial orientation of the pump and the probe laser beams, with the RF field on and off.
Analysis of the spontaneous Raman spectra of N\textsubscript{2} provides insights into the vibrational population distribution. Since, as discussed earlier, anharmonicity effects are small, the vibrational level fractional populations are essentially proportional to the intensity of the corresponding peaks after scaling by \(1/(v + 1)\). When the spectra of the RF and laser sustained plasmas for a coaxial alignment of the pump and probe beams are compared, the increase in fractional population of states with larger \(v\) becomes apparent. By comparing the relative peak heights a greater fractional population is found in states with larger \(v\) for the RF sustained plasma. This is illustrated in the Boltzmann plot for that case in Fig. 5.5.

![Figure 5.4. Raman spectra of vibrationally excited N\textsubscript{2} with a 2.25mm vertical separation between the pump and probe laser beams, with the RF on and off.](image)

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A similar analysis of the case in which the probe and pump beam are not coaxial show a similar result. At a vertical separation of 2.25 mm, when an RF field is not applied, the vibrational nonequilibrium is diminished. However, when a vertically aligned RF field is applied the vibrational loading of the molecule intensifies. This is demonstrated in the Raman spectra and fractional population analysis shown in Figs. 5.4 and 5.5. It is important to note that at each probe position the fractional population of states with higher $v$ becomes greater when the RF field is applied. By subjecting the plasma to the RF field a wider distribution of vibrational states is obtained. The error

![Figure 5.5. N$_2$ vibrational level populations for two different locations of the probe laser beam.](image)
bars in Fig. 5.5 correspond to an uncertainty of ± 10%, which results from the uncertainty in the vibrational level line intensity minus the baseline.

The broadening of the vibrational state distribution may be characterized semi-quantitatively by defining an equivalent “first-level” Boltzmann temperature (the distribution, in general, is non-Boltzmann). The equivalent first-level Boltzmann temperature is the slope of the vibrational distribution function at \( v = 0 \), defined as follows:

\[
T_v = \frac{\theta_v}{\ln\left(\frac{f_0}{f_1}\right)}
\]

In (5.27), \( \theta_v = 3353^\circ \text{ K} \) is the characteristic vibrational temperature for \( \text{N}_2 \) and \( f_0/f_1 \) is the ratio of the fractional populations for vibrational levels \( v = 0 \) and \( v = 1 \).

The translational/rotational temperatures were inferred from the Raman spectra by comparing the peak intensities of a vibrationally pumped sample to that of a vibrationally cold sample. These temperatures were calculated as follows,

\[
T_H = T_C \cdot \left(\frac{I_C}{I_H}\right)
\]

where \( T_C \) is the cold gas temperature (300° K), \( I_C \) is the intensity of the cold peak and \( I_H \) is the sum of the intensities of the transitions, scaled by \( 1/(v+1) \), in the vibrationally hot spectra. Note that this method provides only a rather crude estimate of the temperature since the rotational band structure is ignored. In addition, at large displacements between the pump and probe beam the probe beam path begins to become blocked, causing the probe beam to scatter. This might well introduce an additional error in the inference of temperature. The experimental data will be compared to the model predictions in the following section.
5.7 Results and Discussion II. Kinetic Model

The model results provided by Adamovich give the first level vibrational temperatures for CO and N\textsubscript{2} as well as the translational temperature and the electron density for the He/CO/N\textsubscript{2} model plasma. Solutions for each of these properties are shown in Figs. 5.6-5.9. The left side of the contour plots is with the RF field off and the right side is with the RF field applied. In the case when the RF field is applied the values shown in the figures are averaged over a complete oscillation of the RF field (values will be higher when instantaneous voltage is highest, lower when instantaneous voltage is zero). Notice in Figs. 5.6 and 5.7 that the vibrational nonequilibrium is enhanced when the RF field is applied. The first level vibrational temperature for both species increases along the laser beam centerline (CO \(T_v=3700\text{K}\rightarrow 4300\text{K}\), N\textsubscript{2} \(T_v=2500\text{K}\rightarrow 2900\text{K}\)). In addition the RF field increases the dimensions of the nonequilibrium vibrational region by approximately a factor of 2 in the x direction.

Examination of Fig. 5.8 shows that the electron number density is predicted to decrease when the RF field is applied, from \(n_e=8\times10^{10}\ \text{cm}^{-3}\) to \(6\times10^9\ \text{cm}^{-3}\). This density decrease is attributed to the increase in the V-T rates due to the larger translational temperature. The larger V-T rates deplete the high CO vibrational levels (\(v\approx30-35\)) as shown in Fig. 5.10, which reduces the rate of associative ionization. The inverse relationship between temperature and ionization rate prevents the development of the heating instability and stabilizes the plasma. However, this stabilizing effect limits the amount of RF power that can be coupled into the plasma (fewer electrons available to be heated by external field). The maximum RF power coupled to the plasma can be increased, which would increase the electron density, by lowering the translational
Figure 5.6. Predicted first level vibrational temperature of CO in the optically pumped CO/N₂ plasma without (left) and with (right) RF field applied.

Figure 5.7. Predicted first level vibrational temperature of N₂ in the optically pumped CO/N₂ plasma without (left) and with (right) RF field applied.
Figure 5.8. Predicted electron density distribution in the optically pumped CO/N\textsubscript{2} plasma without (left) and with (right) RF field applied.

Figure 5.9. Predicted translational/rotational temperature distribution in the optically pumped CO/N\textsubscript{2} plasma without (left) and with (right) RF field applied.
temperature of the system. Increasing the gas flow would increase the convective cooling, resulting in a lower translational temperature. The lower translational temperature would decrease the V-T relaxation rate causing an increase in the rate of ionization.

Comparisons of the data to the model of the vibrational temperature for N\textsubscript{2} and the translational/rotational temperature at various vertical displacements are shown in Fig. 5.11 and 5.12. For both figures the error bars represent an uncertainty of ± 5%, which results from the uncertainty in the vibrational level line intensity discussed earlier. Illustrated in Fig. 5.11 are the first level equivalent Boltzmann temperatures for varying
Figure 5.11. Comparison of the measured and calculated $N_2$ vibrational temperature in the optically pumped CO/$N_2$ plasma with and without RF field applied (at $x=0$).

degrees of separation between the probe and pump beam in the vertical plane. Note that the equivalent Boltzmann temperatures never drop below 2000 K when the RF field is applied, even at a displacement of more than 5 mm. It is important to note that the increase in vibrational temperature is not due to simple heating of the species present. The translational/rotational temperature does not approach the vibrational temperature in any of the cases presented, as shown in Fig. 5.12. It should also be noted that the translational/rotational temperatures given in Fig. 5.12 differ from those presented in Chapter 4. The temperature difference of approximately 150-200 K is a result of multiple factors. First, the gas mixtures in each case are different. The addition of large amounts
of O₂ in Chapter 4 limit the VDF of CO to lower values of v. At lower values of v the V-T rates are much lower and more of the energy remains in the vibrational mode of the molecular species instead of being transferred into the translational/rotational modes which would result in heating. Second, the flow rates are not the same. The flow rate was carefully measured for the cases shown in the previous chapter, while they were not measured for the purposes of the data presented here. Convective cooling would be less for a slower flow rate, which may be the case for the RF coupled associatively ionized plasma. This could account, at least in part, for the greater translational/rotational temperature obtained. Finally, some of the difference may simply be attributed to error resulting from using (5.28) as discussed above. In Fig. 5.11 the model represents the data.
well when the plasma is sustained solely by the laser. However, when the RF field is applied the difference between the calculation and the data increases. This difference is within approximately 20% except at the maximum displacement (y/d=0.94). It should be noted that at this large of a displacement the probe beam is less than 1mm away from the electrode so that scatter from the electrode may add uncertainty to the determination of the vibrational temperature.

The calculated translational/rotational temperature is compared to the experimentally determined translational/rotational temperature in Fig. 5.12. At small probe beam displacements and with the RF field off the agreement between the model and the data is quite good. However, the disparity between the model and data increases at large y-displacements. When the RF field is applied, the difference between the model and the data increases significantly. In addition this disparity increases with increasing y-displacement. The difference between the model and data can be attributed to two factors. Primarily, the method of extracting translational/rotational temperatures from the vibrationally resolved Raman data is relatively crude. The rotational lines are not resolved and therefore the translational/rotational temperature measured can only be considered a rough estimate (±10%) which results from S/N. Secondly, there is uncertainty in the temperature dependence of the V-T rates of CO at high vibrational level. If the temperature dependence of the V-T rates is weak, the gases would be heated to a greater extent before the associative ionization mechanism begins to be inhibited. Conversely, if the temperature dependence is large, a lower temperature would result in the inhibition of the associative ionization mechanism. Lastly, electrode heating may cause the increase in temperature observed at large displacement.
Not only are the CO V-T relaxation rates temperature and v dependent, but most likely there is dependence upon the collision partner as well. There are numerous trace species associated with this laser initiated plasma, such as those resulting from the CO disproportionation reaction (carbon clusters) or NO molecules. The V-T rates corresponding to collisions with these trace elements are currently unavailable. These rates were approximated by adding 1% He to the CO/N₂ gas mixture in the calculation. While the addition of He was a “best guess” attempt at replicating the trace species V-T rates, the uncertainty associated with this method remains significant. Most importantly, however, more accurate rotationally resolved temperature measurements would reduce the uncertainty associated with comparison of the calculation and data.

The data presented here has shown that the volume of the associatively ionized plasma can be increased with suitable application of a sub-breakdown RF field. Additionally, the model indicates qualitative agreement with the experimental data. However, a quantitative comparison of the model and data shows that there are issues that need to be resolved, specifically the translational/rotational temperature difference exhibited by the model/data comparison. Of primary importance is the need to acquire rotationally resolved temperature measurements of the system.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

This work involves the examination of rates of chemical processes within air-like high-pressure nonequilibrium plasmas. These processes include the three-body electron attachment mechanism in an \( \text{O}_2/\text{N}_2 \) gas mixture, the activation of electron detachment from the \( \text{O}_2 \) anion by vibrational excitation and the examination of the vibrational quanta transfer rates within an anharmonically, laser-pumped RF coupled plasma.

The three-body electron attachment rate coefficients were determined by microwave attenuation of an electron beam generated \( \text{O}_2/\text{N}_2 \) plasma. The overall electron loss rate within the plasma afterglow was determined by nonlinear least squares fitting of the microwave voltage at numerous experimental conditions. From these rates the contribution of the specific gas species was determined. It was found that in a three-body collision between \( \text{O}_2 \), an electron and a third body, the rate was dependent upon the identity of the third body. In an air-like mixture it was determined that \( \text{O}_2 \) was approximately one order of magnitude more efficient than \( \text{N}_2 \) at stabilizing the three-body attachment process. The rate coefficient for \( \text{O}_2 \) as the third body was found to be \( 5.8 \times 10^{-42} \text{ m}^6/\text{s} \) and \( 5.8 \times 10^{-43} \text{ m}^6/\text{s} \) when \( \text{N}_2 \) was the third body. These rate coefficients are on the
same order of magnitude as those determined by previous investigators (CPB, Hurst & Bortner), but approximately a factor of two larger for O₂ and 4-5 larger for N₂.

Activation of the electron detachment pathway from the O₂ anion by vibrational excitation is investigated. It is shown that in an electron beam generated anharmonically pumped nonequilibrium air-like plasma, the plasma lifetime is increased by approximately two orders of magnitude. While the detachment rate is highly heavy-species temperature dependent, the temperature increase associated with the anharmonic pumping is insufficient to account for the change in the detachment rate. Additionally, the three-body attachment rate is dependent upon the average electron energy. However, the electron temperature required to cause a change in the plasma lifetime of two orders of magnitude is approximately 10-20eV, which is much hotter than what can be reasonably obtained in this type of plasma. Depletion of the pool of attaching molecules was considered as well. It was determined from the VDFs that if vibrational excitation diminished the number densities of molecules which can undergo attachment, the attachment rate will only decrease by a factor of ≈2. However, a plausible explanation for the increase in plasma lifetime was reached by examining the electron detachment mechanism. If it is presumed that a suitably vibrationally excited molecule (v ≥ 2) causes electron detachment at nearly a gas kinetic rate, it is clear from the VDFs that the population of these “fast detacher” molecules is sufficient to result in the demonstrated change in plasma lifetime.

The V-T relaxation rates were investigated when the associatively ionized plasma was coupled with a sub-breakdown RF field. A master kinetic model was created to predict the behavior of this RF coupled plasma. The results indicate that the model
simulates the plasma quite well in the absence of the RF field. However, application of the RF field to the anharmonically pumped plasma leads to an increasing discrepancy between the data and the model. While the model exhibits the general trend of increasing vibrational and translation temperature when the RF field is applied, the calculation underestimates the magnitude of the effect. The greatest difference between the calculation and the data is found for the translational temperature of the system. Reasons for this behavior are possibly twofold. First, the method of temperature extraction is admittedly crude, ignoring the rotational structure of the species. A large uncertainty in this measurement increases the difficulty in determining the cause of the discrepancy between the calculation and the data. Conversely, if it is assumed that the temperature measurement provides adequate results, the discrepancy indicates that the V-T rates used in the calculation are not appropriate. More importantly, though, is the demonstration of the substantial increase in plasma volume associated with the application of a sub-breakdown field. This aspect of the work has ramifications in the on-going development of a Discharge Oxygen Iodine Laser.

Future Work

While the work regarding the rate coefficients for the three-body electron attachment mechanism has not shown a substantial change in the values of the coefficients, further work can be performed investigating other third body collision partners and the process by which three-body attachment occurs. For example, the hypothesis that O$_2$ is a more efficient third body collision partner because the vibrational energies are closer to those of the O$_2$ anion can be explored. It would be expected that the plasma lifetime would decrease with the addition of another non-attaching gas, such
as CH$_4$ ($\nu_4 \approx 1306$ cm$^{-1}$), with fundamental vibrational energies closer to those of the O$_2$ anion ($\nu \approx 1090$ cm$^{-1}$).

Additionally, investigation of the three-body attachment mechanism itself would be of interest. It is known that a three-body collision between O$_2$, an electron and a third body results in attachment. However, which mode of the third body removes the excess energy is not known. It has been postulated that attachment produces vibrational excitation of the third body. While some investigators have cast doubt upon that possibility [23], that question has not been definitively answered. A fluorescence experiment probing the excited vibrational levels of O$_2$ using the Schumann-Runge bands would indicate whether the third body extracted energy from the anion via the vibrational mode. Probing the vibrational levels of the molecules using Raman scattering would not be feasible due to the small number density of vibrationally excited species resulting from electron attachment.

Work involving the effect of vibrational excitation on the electron loss rates within a plasma can be pursued as well. Of foremost importance is acquiring an accurate electron temperature of the anharmonically pumped electron beam generated plasma. The effect of electron temperature upon the attachment and detachment rates has been discussed. However, the electron temperature has not been determined experimentally. To quantify the effect of vibrational excitation on the detachment mechanism more accurately the electron temperature must be known with some certainty. This could be done using Thomson scattering. Thomson scattering could also resolve the issue of non-homogeneity within the anharmonically pumped electron beam generated plasma. Because Thomson scattering is a point measurement instead of a line-of-sight
measurement the non-uniform nature of the vibrational loading could be ignored. In addition the uncertainty in the electron density measurement might be resolved. The microwave absorption coefficient tends to give artificially large number densities, while the number densities derived from the plasma lifetime are averaged over a non-uniform region, thus giving more reasonable but lower electron number densities.

Data involving the electron-ion recombination rate of N$_4^+$ is scarce and there is little to no information on the heavy-species or electron temperature dependence of this rate. An external field could be coupled to the electron beam generated plasma and the electron temperature dependence of the electron ion recombination rate of N$_4^+$ could be determined. Additionally, it was assumed in the work regarding electron detachment that the vibrational loading of the gaseous sample had no effect on the electron-ion recombination rate. Conclusively showing this through experiment would reduce the uncertainty in determining the effect of vibrational excitation on the detachment mechanism.

Lastly, the results of the RF field coupling to the associatively ionized plasma indicate that a more accurate temperature measurement is required. The uncertainty in the translational temperature is too large to state conclusively whether or not the V-T rates used in the model are an accurate representation of the experiment. Rotationally resolved Raman scattering measurements would provide highly accurate translational temperatures for this system and retain the spatial resolution required for comparison to the calculation.


27. Ionikh [private communication].


APPENDIX A

The intensity of Raman scattered light depends upon the square of the polarizability of the molecule with respect to an incident electromagnetic wave [40]. The scattering intensity, $I$, is given by (A.1) where $\mu_{fi}$ is the total transition dipole moment

$$I = k'_{\omega} \omega_s^4 \mu_{fi}^2 N \Omega \sin^2 \theta$$  \hspace{1cm} (A.1)

$$k'_{\omega} = \frac{1}{32\pi^2 \varepsilon_0 c^3}$$  \hspace{1cm} (A.2)

matrix element representing a transition between levels $f$ and $i$, $\omega_s$ is the frequency of the scattered radiation, and $\theta$ is the angle between the molecular dipole and the electric dipole of the incident electromagnetic wave. The more the polarizability changes with nuclear displacement the greater the Raman scattering intensity. Quantum theory indicates the probability of a transition occurring depends upon the transition electric dipole moment. For the specific case of Raman scattering the molecular polarizability is determined from the transition electric dipole moment. In true quantum mechanical fashion the transition dipole moment for a Raman scattering event is expressed in (A.3) where $(\mu)_{fi}$ is the total transition electric dipole moment and $P$ is the

$$(\mu)_{fi} = \langle \Psi_f | P | \Psi_i' \rangle$$  \hspace{1cm} (A.3)

transition electric dipole moment operator. The functions, $\Psi_f'$ and $\Psi_i'$, represent the time-dependent perturbed wavefunctions of the final and initial states of the molecule,
respectively. These perturbed wavefunctions for the initial and final states are expanded
as a series, (A.4), of unperturbed basis wavefunctions represented by ($\Psi_i^{(0)}$)
\[
\Psi_i' = \Psi_i^{(0)} + \Psi_i^{(1)} + \Psi_i^{(2)} + \ldots
\] (A.4)
and the subsequent higher order corrections to the unperturbed wavefunction ($\Psi_i^{(1)}$, $\Psi_i^{(2)}$)
which result from perturbation theory. The first order correction for the perturbed
wavefunctions for both the initial and final states can be expanded as linear combinations
of the unperturbed wavefunction, (A.5).
\[
\Psi_i^{(1)} = \sum_m a_{p_m}^{(1)} \Psi_m^{(0)}
\] (A.5)
\[
\Psi_i^{(2)} = \sum_m a_{p_m}^{(2)} \Psi_m^{(0)}
\] (A.6)
The expansion of the wavefunctions $\Psi_f'$ and $\Psi_i'$ (A.4) are substituted into the definition of
the total transition electric dipole moment, (A.3), and the result is (A.7).
\[
(\mu)_f = \left\langle \Psi_f^{(0)} + \Psi_f^{(1)} + \Psi_f^{(2)} + \ldots | P | \Psi_f^{(0)} + \Psi_f^{(1)} + \Psi_f^{(2)} + \ldots \right\rangle
\] (A.7)
The operator, P, is then distributed among the terms in the ket resulting in the subsequent
sum.
\[
(\mu)_f = \left\langle \Psi_f^{(0)} + \Psi_f^{(1)} + \Psi_f^{(2)} + \ldots | P | \Psi_f^{(0)} \right\rangle + \\
\left\langle \Psi_f^{(0)} + \Psi_f^{(1)} + \Psi_f^{(2)} + \ldots | P | \Psi_f^{(1)} \right\rangle + \\
\left\langle \Psi_f^{(0)} + \Psi_f^{(1)} + \Psi_f^{(2)} + \ldots | P | \Psi_f^{(2)} \right\rangle + \ldots
\] (A.8)
Then the linear combinations of unperturbed wavefunctions, (A.5) and (A.6) are
substituted for the higher order correction terms in (A.8).
\[(\mu)_n = \langle \psi^{(0)}_f + \sum_r a^{(1)}_{fr} \psi^{(0)}_r + \sum_r a^{(2)}_{fr} \psi^{(0)}_r + \cdots | p | \psi^{(0)}_i \rangle +
 \langle \psi^{(0)}_f + \sum_r a^{(1)}_{fr} \psi^{(0)}_r + \sum_r a^{(2)}_{fr} \psi^{(0)}_r + \cdots | p | \sum_r a^{(1)}_{fr} \psi^{(0)}_r \rangle +
 \langle \psi^{(0)}_f + \sum_r a^{(1)}_{fr} \psi^{(0)}_r + \sum_r a^{(2)}_{fr} \psi^{(0)}_r + \cdots | p | \sum_r a^{(2)}_{fr} \psi^{(0)}_r \rangle + \cdots \tag{A.9} \]

In (A.9) the constants \(a_{nm}^{(n)}\) are determined from the electric dipole interaction Hamiltonian, \(H_p\), and are therefore proportional to powers of E. The constant \(a_{nm}^{(1)}\) is proportional to E, \(a_{nm}^{(2)}\) is proportional to \(E^2\), \(a_{nm}^{(3)}\) is proportional to \(E^3\) and so on.

Examining the first term in (A.9) it is clear that distributing the operator and ket among the bras gives (A.10).

\[\langle \psi^{(0)}_f + \sum_r a^{(1)}_{fr} \psi^{(0)}_r + \sum_r a^{(2)}_{fr} \psi^{(0)}_r + \cdots | p | \psi^{(0)}_i \rangle = \langle \psi^{(0)}_f | p | \psi^{(0)}_i \rangle +
 \langle \sum_r a^{(1)}_{fr} \psi^{(0)}_r | p | \psi^{(0)}_i \rangle + \tag{A.10}
 \langle \sum_r a^{(2)}_{fr} \psi^{(0)}_r | p | \psi^{(0)}_i \rangle + \cdots \]

Applying the same procedure to the second and third terms in (A.9) yields (A.11) and (A.12).

\[\langle \psi^{(0)}_f + \sum_r a^{(1)}_{fr} \psi^{(0)}_r + \sum_r a^{(2)}_{fr} \psi^{(0)}_r + \cdots | p | \sum_r a^{(1)}_{fr} \psi^{(0)}_r \rangle =
 \langle \psi^{(0)}_f | p | \sum_r a^{(1)}_{fr} \psi^{(0)}_r \rangle +
 \langle \sum_r a^{(1)}_{fr} \psi^{(0)}_r | p | \sum_r a^{(1)}_{fr} \psi^{(0)}_r \rangle + \tag{A.11}
 \langle \sum_r a^{(2)}_{fr} \psi^{(0)}_r | p | \sum_r a^{(1)}_{fr} \psi^{(0)}_r \rangle + \cdots \]
\[
\left\langle \Psi_f^{(0)} + \sum_r a_r^{(1)} \Psi_r^{(0)} + \sum_r a_r^{(2)} \Psi_r^{(0)} + \ldots | p | \sum_r a_r^{(2)} \Psi_r^{(0)} \right\rangle = \\
\left\langle \Psi_f^{(0)} | p | \sum_r a_r^{(2)} \Psi_r^{(0)} \right\rangle + \\
\left\langle \sum_r a_r^{(1)} \Psi_r^{(0)} | p | \sum_r a_r^{(2)} \Psi_r^{(0)} \right\rangle + \\
\left\langle \sum_r a_r^{(2)} \Psi_r^{(0)} | p | \sum_r a_r^{(2)} \Psi_r^{(0)} \right\rangle + \ldots \\
\text{(A.12)}
\]

The terms are then grouped according to their dependence upon \(E\), which is determined by the coefficient of each term in (A.10)-(A.11). The total transition electric dipole moment can be treated as an expansion, shown in (A.13),

\[
(\mu)_n = (\mu^{(1)})_n + (\mu^{(2)})_n + (\mu^{(3)})_n + \ldots \\
\text{(A.13)}
\]

where the first term is dependent upon \(E\), the second term is dependent upon \(E^2\), the third term is dependent upon \(E^3\) and so on. Collecting the terms based on their \(E\) dependence and substituting the perturbed wavefunction back for the linear combination of unperturbed wavefunctions results in (A.14)-(A.16).

\[
(\mu^{(1)})_n = \left\langle \Psi_f^{(0)} | p | \Psi_i^{(0)} \right\rangle + \left\langle \Psi_f^{(0)} | p | \Psi_i^{(0)} \right\rangle \\
\text{(A.14)}
\]

\[
(\mu^{(2)})_n = \left\langle \Psi_f^{(0)} | p | \Psi_i^{(0)} \right\rangle + \left\langle \Psi_f^{(2)} | p | \Psi_i^{(0)} \right\rangle + \left\langle \Psi_f^{(1)} | p | \Psi_i^{(0)} \right\rangle \\
\text{(A.15)}
\]

\[
(\mu^{(3)})_n = \left\langle \Psi_f^{(0)} | p | \Psi_i^{(0)} \right\rangle + \left\langle \Psi_f^{(3)} | p | \Psi_i^{(0)} \right\rangle + \left\langle \Psi_f^{(2)} | p | \Psi_i^{(0)} \right\rangle + \\
\left\langle \Psi_f^{(2)} | p | \Psi_i^{(0)} \right\rangle \\
\text{(A.16)}
\]

For Raman scattering the terms that are dependent upon \(E\) are the most important. The higher order terms (those dependent upon \(E^2\) and \(E^3\)) refer to higher order nonlinear Raman processes. So, examination of (A.14) indicates that a number of different transitions are possible. However, if the initial and final state are the same (i=f) then the
transition is associated with Rayleigh scattering. Raman scattering is described by the case that \( i \neq f \) and the transition electric dipole moment for this process is given by (A.17)

\[
\left( \mu_{(i)}^{(f)} \right)_0 = \left( \alpha \right)_i E_0
\]

where \( (\alpha)_i \) is the transition polarizability tensor element for a Raman transition from state \( i \) to state \( f \). It is convenient when analyzing experimental data to use a scattering cross section to determine the intensity of the scattered radiation. The scattering from a gas sample is given by (A.18)

\[
I = \sigma' \Phi N \Omega
\]

where \( I \) is the intensity of the scattering radiation, \( N \) is the number of scattering species, \( \sigma' \) is the scattering cross-section with units \( \text{m}^2 \text{sr}^{-1} \text{molecule}^{-1} \), \( \Omega \) is the solid angle of the collected signal and \( \Phi \) is the magnitude of the incident irradiance. Comparison of (A.1), (A.17) and (A.18) indicates that the scattering cross-section is a function of the square of the transition polarizability tensor matrix element.

It is important to determine the selection rules for the transitions which occur in Rotational Raman Scattering. If a linear rotor, like \( \text{O}_2 \) or \( \text{N}_2 \), is placed in an oscillating electric field, \( E \), the components of the polarizability vary with the angle between the internuclear axis of the molecule and the electric field dipole of the incident oscillating radiation. The total induced dipole moment, \( \mu_T \), is the sum of the x, y, and z components of the molecule as shown in (A.19) where \( \theta \) and \( \varphi \) represent the difference in angle between the electric dipole reference frame and that of the molecule.

\[
\mu_T = \mu_x \sin \theta \cos \varphi + \mu_y \sin \theta \sin \varphi + \mu_z \cos \theta
\]
The applied electric field must also be resolved into components within the molecular frame of reference and the results are shown in (A.20)-(A.22).

\[ E_x = E \sin \theta \cos \phi \]  \hfill (A.20)

\[ E_y = E \sin \theta \sin \phi \]  \hfill (A.21)

\[ E_z = E \cos \theta \]  \hfill (A.22)

If the individual components of the total induced transition dipole are defined by (A.23), substitution into (A.19) yields (A.24).

\[ \mu_q = \alpha_q E_q \]  \hfill (A.23)

\[ \mu_T = \alpha_x E_x \sin \theta \cos \phi + \alpha_y E_y \sin \theta \sin \phi + \alpha_z E_z \cos \theta \]  \hfill (A.24)

Using the definitions (A.25)-(A.28) and some mathematical manipulation of (A.24) results in the total induced transition dipole moment in terms of the mean polarizability, \( \alpha \), the spherical harmonic, \( Y_{2,0}(\theta, \phi) \), the electric field, \( E \), and the variation of the polarizability, \( \Delta \alpha \).

\[ \alpha_\perp = \alpha_x = \alpha_y \]  \hfill (A.25)

\[ \alpha_\parallel = \alpha_z \]  \hfill (A.26)

\[ \alpha = \frac{1}{3} \left( \alpha_\parallel + 2 \alpha_\perp \right) \]  \hfill (A.27)

\[ \Delta \alpha = \alpha_\parallel - \alpha_\perp \]  \hfill (A.28)

\[ Y_{2,0}(\theta, \phi) = \left( \frac{5}{16\pi} \right)^{\frac{1}{2}} \left( 3 \cos^2 \theta - 1 \right) \]  \hfill (A.29)

\[ \mu_T = \left( \alpha + \frac{4}{3} \left( \frac{\pi}{5} \right)^{\frac{1}{2}} \Delta \alpha Y_{2,0}(\theta, \phi) \right) E \]  \hfill (A.30)
The first term in (A.30) does not couple different rotational levels and so it is ignored. The second term does couple different rotational levels and therefore it will be used to determine the matrix elements for rotational transitions shown in (A.31).

$$\langle J', M'_J | \mu_J | J, M_J \rangle = \frac{4}{3} \binom{\pi}{5} \sqrt{\frac{1}{2}} \ E \Delta \alpha \langle J', M'_J | Y_{2,0} | J, M_J \rangle$$  \hspace{1cm} (A.31)

Group theory can be used to show that transitions described by the above matrix elements are non-zero only if $J'=J\pm 2$.

To determine whether matrix elements can be non-zero it is necessary to determine whether the integrand is a basis of the totally symmetric irreducible representation of the group to which the molecule belongs. If the integrand is not a basis, the integral will necessarily be zero. The requirement for the rotational Raman scattering selection rule for a linear rotor (O$_2$, N$_2$) is found in (A.32).

$$\Gamma^{(J')} \times \Gamma^{(2)} \times \Gamma^{(J)} = \Gamma^{(0)}$$  \hspace{1cm} (A.32)

The direct product of the irreducible representations of the system can be decomposed using (A.33).

$$\Gamma^{(J_1)} \times \Gamma^{(J_2)} = \Gamma^{(J_1+J_2)} + \Gamma^{(J_1+J_2-1)} + \cdots + \Gamma^{(|J_1-J_2|)}$$  \hspace{1cm} (A.33)

It is found that for the condition of (A.32) to be satisfied $J'=J, J\pm 1, J\pm 2$. The case of $J'=J$ describes Rayleigh scattering and can therefore be excluded from consideration. Examination of the symmetry properties of the Clebsch-Gordon coefficients or the Wigner 3-j symbols, which describe the magnitude of the coupling of angular momenta within a system, indicate that $J'=J\pm 1$ results in a change of phase of the spherical harmonic wavefunction under rotation. The change of phase results in a change in the symmetry of the integrand in (A.31). This symmetry rule is summarized by (A.34),
which shows that \( \Delta J \) must be even if the integrand is to possess totally symmetric character. Therefore the selection rule for a rotational Raman transition of a linear rotor is \( J' = J \pm 2 \).
A set of two-dimensional time-dependent differential equations was used to model the rf enhanced laser-initiated plasma [50]. The first equation represents the rate of change of the number density and transport of the ions (B.1).

\[
\frac{\partial n_k(x, y, t)}{\partial t} + \nabla \Gamma_k = Q_k
\]  

(B.1)

with definitions

\[
\Gamma_k = D_k \nabla n_k(x, y, t) - \frac{q_k}{|e|} \mu_k \nabla \phi(x, y, t)n_k(x, y, t)
\]

\[
Q_e = S - \beta_e n_e n_e = Q_+
\]

\[
S = k_{ion} N^2 y_{CO}^2 \sum_{E_v + E_w > E_{ion}} f_v f_w f_{CO}
\]

and conditions

\[
n_k(x, 0, t) = n_k(x, d, t) = 0
\]

\[
\frac{\partial n_k(0, y, t)}{\partial x} = \frac{\partial n_k(\pm W, y, t)}{\partial x} = 0
\]

\[
n_k(x, y, 0) = 0
\]

In the above equations the flux of species \( k \), \( \Gamma_k \), is given in terms of the mass diffusion coefficient, \( D_k \), the mobility, \( \mu_k \), the electric potential, \( \phi(x, y, t) \) and the number density of
species \( k \), \( n_k(x, y, t) \). The rate of change in the number density for the species is given by \( Q_k \), where \( S \) is the associative ionization rate, \( \beta_{ei} \) is the electron-ion recombination rate and \( n_e \) and \( n_r \) are the number densities of the electrons and cations, respectively. The associative ionization rate is a function of the associative ionization rate coefficient, \( k_{\text{ion}} \), the total number density, \( N \), the mole fraction of CO, \( y_{\text{CO}} \), and the sum of all possible collisions between vibrationally excited CO molecules that have the requisite energy to cause ionization. The terms \( f_{v,\text{CO}} \) and \( f_{w,\text{CO}} \) are the relative populations of vibrational level \( v \) and \( w \) of the CO molecule subject to the constraint that the sum of the vibrational energies is greater than the energy of ionization. The constants \( q_k, e, d \) and \( W \) are the charge of species \( k \) (\( \pm e \)), the electron charge, the distance between electrodes and the radius of the electrodes, respectively.

The effect of the RF field is described by the Poisson equation given in (B.2).

\[
\nabla^2 \phi(x, y, t) = \frac{1}{\varepsilon_0} \sum_k q_k n_k(x, y, t) \tag{B.2}
\]

The following conditions are applied to (B.2).

\[
\phi(x, 0, t) = 0
\]

\[
\phi(x, d, t) = U_0 \cos(2\pi vt)
\]

\[
\frac{\partial \phi(0, y, t)}{\partial x} = \frac{\partial \phi(\pm W, y, t)}{\partial x} = 0
\]

\[
\phi(x, y, 0) = \frac{U_0 y}{d}
\]

Additional constants in (B.2) are \( U_0 \) and \( v \) which are the amplitude and frequency of the applied RF voltage.
Transfer of vibrational quanta is modeled by (B.3), which includes the diffusion of vibrational quanta throughout the volume as well as the rate of excitation by the laser, the RF field and the rate of relaxation of vibrational quanta to other molecular modes.

\[
\frac{\partial E_{\text{vib},j}(x,y,t)}{\partial t} + \nabla \left[ D_j \nabla E_{\text{vib},j}(x,y,t) \right] = R_j^{\text{laser}} + R_j^{\text{field}} - R_j^{\text{relax}}
\]

(B.3)

The initial and boundary conditions are included below.

\[
E_{\text{vib},j}(x,0,t) = E_{\text{vib},j}(x,d,t) = E_{\text{vib},j}(\pm W,y,t) = E_{\text{vib},j}(T_0)
\]

\[
E_{\text{vib},j}(0,y,t) = 0
\]

\[
E_{\text{vib},j}(x,y,0) = E_{\text{vib},j}(T_0)
\]

For (B.3), \(j\) is an index which indicates the molecular species, \(E_{\text{vib},j}(x,y,t)\) is the average vibrational energy, \(R_j^x\) are the rates of vibrational quanta change for laser excitation, electron impact excitation and vibrational relaxation. Lastly, \(T_0\) is the translational temperature of the gas without laser excitation or the applied RF field.

Finally, (B.4) describes the translational temperature of the species within the plasma.

\[
\frac{5}{2} k_B N \frac{\partial T(x,y,t)}{\partial t} + \nabla \left[ \lambda \nabla T(x,y,t) \right] = k_B N \left( \gamma_{CO} R_{CO}^{\text{relax}} + \gamma_{N_2} R_{N_2}^{\text{relax}} \right)
\]

(B.4)

The following initial and boundary conditions apply.

\[
T(x,0,t) = T(x,d,t) = T(\pm W,y,t) = T_0
\]

\[
\frac{\partial T(0,y,t)}{\partial x} = 0
\]

\[
T(x,y,0) = T_0
\]
In (B.4), $k_B$ is Boltzmann’s constant, $N$ is the total number density of molecules, $y_x$ is the mole fractions of species $x$, $T(x,y,t)$ is the translation temperature and $\lambda$ is the thermal diffusivity. Additionally, the following definitions for the average vibrational energy and the vibrational quanta excitation and relaxation rates are required.

$$E_{vib,j} = \sum_v E_{v,j} f_v$$  \hspace{1cm} (B.5)

$$E_{v,j} = \omega_{e,j} v \left[ 1 - x_{e,j} (v + 1) \right]$$

$$R_{laser}^{CO} = \sum_{v,j} \frac{A_{v,j} B_v \left( \frac{c}{v} \right)^3 I_v \theta S_j \exp \left( -\frac{B_j (J + 1)}{T} \right) E_v f_v}{8\pi c k_B T}$$  \hspace{1cm} (B.6)

$$R_{j}^{field} = \frac{\tilde{j} \cdot \tilde{E}}{Nk_B}$$  \hspace{1cm} (B.7)

$$R_{relax}^{j} = E_i \frac{6\tilde{Q}_{i0} \Delta E}{T \delta_{VV}^2} (v_0 + 1)^2 \exp \left( -\frac{2\Delta E}{T} \right) y_j N +$$

$$E_i Q^{(01)} f_i f_{i'} - f_i f_{i'}' y_j N$$  \hspace{1cm} (B.8)

For the above equations $E_{v,j}$ is the energy in vibrational level $v$ for species $j$, $\omega_e$ is the harmonic oscillator vibrational energy, $x_e$ is the anharmonic correction to the vibrational energy, $A_v$ is the Einstein spontaneous emission coefficient, $B_v$ is the rotational constant, $v$ is the laser line frequency, $I_v$ is the laser line power density, $\theta$ is the absorption line shape function, $S_j$ is the Honl London factor, $J$ is the rotational quantum number, $v_0$ is the quantum number at which the Treanor distribution is minimized (plateau forms), $\delta_{VV}$ is an adjustable parameter representing short range interspecies V-V transfer, $y_j$ is the mole fraction of species $j$, $f_v$ is the relative population of vibrational level $v$ and $\tilde{j}$ is the
electric current. In (B.8), the first term on the right-hand side represents intraspecies relaxation of the vibrational energy, while the second term represents relaxation of the vibrational energy by interspecies V-V transfer an example, of which, is shown in (B.9).

\[
\text{CO}(v) + \text{N}_2(w) \rightarrow \text{CO}(v-1) + \text{N}_2(w+1)
\]  

(B.9)

The quantities \( \tilde{Q}_{i,0} \) and \( Q_{1,0}^{(0,1)} \) are the rates for intraspecies and interspecies V-V transfer, respectively. The solution to this system of differential equations with the given definitions for the vibrational quanta rates and the average vibrational energy require knowledge of the vibrational level populations for each of the molecular species (CO or \( \text{N}_2 \) in this case). Solution of the master kinetic equation given by Flament, et al [35] provides the population information for this nonequilibrium, nonuniform plasma, however, this would require solving approximately 100 coupled two-dimensional differential equations of the form given by (B.10).

\[
\frac{\partial f_{v,j}(x, y, t)}{\partial t} + \nabla \left[ D_{v,j} \nabla f_{v,j} \right] = \text{R}_{v,j}^{\text{pump}} + \text{R}_{v,j}^{\text{field}} + (V-T)_{v,j} + (V-V)_{v,j} + (V-E)_{v,j}
\]  

(B.10)

Fortunately, the vibrational distribution functions which result from the numerical solution of the master kinetic equation [35], ignoring the space diffusion terms, are readily approximated at steady-state by the analytical theory of vibration-to-vibration pumped anharmonic oscillators demonstrated by Gordiets and Zhdanok [51].

\[
f_v = f_0 \exp \left( -\frac{E_v + \Delta E v (v-1)}{T_v} \right); \quad v \leq v_0 = \frac{1}{2} + \frac{T}{2x_v T_v}
\]  

(B.11)
For (B.11) and (B.12), \( E_1 = \omega x (1 - 2xe) \), \( \Delta E = \omega x e \), \( T_v = E_1 / \ln(f_1 / f_0) \), which is the first level vibrational temperature and \( \nu_A = E_1 / E_1 \) is the vibrational level at which the vibration-to-electronic transfer process (B.13) becomes accessible.

\[
\text{CO}(X^1\Sigma, \nu \approx 40) + \text{CO} \rightarrow \text{CO}(A^1\Pi, \nu \approx 0) + \text{CO}
\]

(B.13)

The parameters \( P_{10}^M \), \( \tilde{Q}_{10}^M \), \( \delta_{VT}^M \) and \( \delta_{VV}^M \) are used to determine the vibrational level and species specific rate coefficients for vibration-to-translation (\( P_{10}^M \) and \( \delta_{VT}^M \)) and vibration-to-vibration (\( \tilde{Q}_{10}^M \), \( Q_{w+1, w}^w \) and \( \delta_{VV} \)) transfer. These rate coefficients are given by (B.14)-(B.16).

\[
P_{v+1, v}^M = P_{10}^M (v + 1) \exp(\delta_{VT}^M v)
\]

(B.14)

\[
Q_{v+1, v}^{w+1} = (v + 1)(w + 1) \left[ Q_{1,0}^S \exp(-\delta_{VV} |v - w|) \right] + \left[ \frac{3}{2} - \frac{1}{2} \exp(-\delta_{VV} |v - w|) \right] + Q_{1,0}^L \exp(-\Delta_{VV} (v - w)^2)
\]

(B.15)

\[
\tilde{Q}_{1,0} = Q_{1,0}^S + \frac{\delta_{VV}^3}{12\Delta_{VV}} \left( \frac{\pi}{\Delta_{VV}} \right)^{1/2} Q_{1,0}^L
\]

(B.16)

For (B.14)-(B.16), \( \tilde{Q}_{1,0} \) represents the intermolecular potential and is determined from the quantities \( Q_{1,0}^S \) and \( Q_{1,0}^L \) wherein the superscripts S and L denote a short and long range interaction. The quantities \( \Delta_{VV}, \delta_{VV} \) and \( \delta_{VT} \) are adjustable parameters, which correspond to long range V-V, short range V-V and short range V-T effects.
Solution of the system of coupled differential equations (B.1)-(B.4) requires solving for properties of the system which vary over different time scales. Specifically, the characteristic time scales for reaching a quasi-steady state distribution in the electric field is on the order of $10^{-6}$ s. The characteristic time scales for the vibrational populations and electron density are on the order of $10^{-4}$-$10^{-3}$ s. Lastly, the gas temperature characteristic time scale is on the order of seconds. Therefore, a numerical solution for this system of differential equations was obtained by first solving for the coupled equations which include the electric field ((B.1) & (B.2)) over the electric field characteristic time ($10^{-6}$ s). The equations which describe the vibrational populations and electron density (electron density is in the “fast” equation, but it is determined by the vibrational populations so that is the rate-limiting step for electron density) ((B.3) & (B.4)) are then solved for the appropriate characteristic time scale ($10^{-4}$-$10^{-3}$ s). This process is continued iteratively until a steady-state spatial distribution for each of the properties is achieved over the slowest characteristic time scale, that of the translational temperature (1 second).