Heat Release Studies by pure Rotational Coherent Anti-Stokes Raman Scattering Spectroscopy in Plasma Assisted Combustion Systems excited by Nanosecond Discharges

Dissertation

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By

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Abstract

Heat release studies of plasma assisted combustion have been performed in fuel-air mixtures excited by nanosecond dielectric barrier discharges initially at room temperature and maintained at low pressure (~40 – 50 torr). The following topics have been extensively investigated: (i) the applicability of pure O\textsubscript{2} broadband Rotational Coherent Anti-Stokes Raman Scattering spectroscopy at very low O\textsubscript{2} pressures of ~8 torr or less to obtain rotational temperature, (ii) validation of a proposed low temperature fuel-oxidation kinetics mechanism fully decoupled from NOx chemistry, (iii) characterization of nanosecond pulse discharges in a dielectric barrier discharge cell and a pin-to-pin discharge geometry, and (iv) effect of fuel addition on heat release in a pin-to-pin discharge geometry at low pressure.

For the first topic, the applicability of pure O\textsubscript{2} broadband Rotational Coherent Anti-Stokes Raman Scattering (RCARS) Spectroscopy at very low O\textsubscript{2} partial pressure of ~ 8 torr or less to obtain rotational temperature has been demonstrated. Very good experimental precisions of ~ ± 1 to 2 K has been demonstrated for diffuse and volumetric plasmas excited by a repetitively pulsed nanosecond discharge. It is shown that the electron-multiplication feature of an EMCCD camera increases the signal to noise ratio significantly.
For the second topic, the pure O₂ RCARS system was applied to the dielectric barrier discharge cell to obtain time-resolved temperature measurements in nanosecond pulse discharges in 20% O₂-Ar, H₂-O₂-Ar and C₂-H₂-O₂-Ar mixtures, initially at room temperature, operated at a high pulse repetition rate of 40 kHz, in plane-to-plane double dielectric barrier geometry at a pressure of 40 Torr. Nitrogen was deliberately excluded from the system so as to decouple NOₓ chemistry from the plasma fuel-oxidation processes. It was found that a 0-D model predictions for temperature are in very good agreement in the baseline mixture without fuel and the hydrogen containing mixtures. However, the model predicts that the heat release in hydrogen containing mixtures is only weakly dependent on equivalence ratio, which is inconsistent with experimental results. Furthermore, in C₂H₂ containing mixtures, the model consistently under-predicts the temperature, further delineating the need for more accurate low-temperature plasma/combustion chemistry decoupled from NOₓ processes for both hydrogen and ethylene fuels.

For the third topic, plasma characterization has been carried out for the mixtures in the aforementioned dielectric barrier discharge cell in addition to air-fuel mixtures in a pin-to-pin discharge geometry. The pin-to-pin discharge was excited by a nanosecond discharge at 60 Hz. Broadband plasma emission images were obtained for both types of discharges using an (ICCD) camera. In the dielectric barrier discharge, the 20% O₂-Ar and O₂-Ar-H₂ mixtures were both shown to be diffuse and volumetric. The O₂-Ar-C₂H₄ mixtures, on the other hand, showed significant striation and plasma constriction. In the pin-to-pin discharge, the plasma filament in both air and air-hydrogen was fairly homogeneous along the discharge gap, but radially decreases outward from the filament centerline. The energy coupling to the plasma for both types of discharges was determined using current-voltage waveforms. The dielectric barrier
discharge couples a very small amount of the energy, \(\sim 0.1\) mJ/pulse, that is stored in the capacitive load formed during breakdown to the plasma. Good agreement between these energy coupling results and a prediction from a 0-D analytical model was found. On the other hand, the pin-to-pin discharge has a higher energy loading of \(\sim 3\) mJ/pulse and a model is currently in development.

On the fourth topic, in the pin-to-pin discharge geometry it is demonstrated that a fast heating and a slow heating regime exist in air and air-fuel mixtures and are clearly distinct from each other after the onset of the discharge pulse. It is indicated that air-ethylene mixtures do not exhibit a clear distinction between slow and fast heating. In all cases, with increasing fuel addition, the rate of the heat release increases. Radial temperature profiles were taken for air at three different time points relative to the onset of the pulse. The radius was found to be the same in all three cases, strongly indicating that there is no contraction or expansion of the plasma filament. Preliminary results with a 1-D model still in development show very good agreement, which is promising. It is expected that the model will attribute fast heating primarily to collisional quenching of \(\text{N}_2\) excited states in air and air-hydrogen containing mixtures. In ethylene mixtures, ethylene oxidation processes are expected to have a larger contribution as experimental results indicate a strong dependence on equivalence ratio. Slow heating is expected to be dominated by V-T transfer from vibrationally excited \(\text{N}_2\) by collisional quenching of \(\text{O}\)-atoms, with additional release by fuel-oxidation.
Dedicated to my husband, David Patrick Sheehe,
For his support and for bringing tranquility into my life,
To my parents, Glen Lanier and Dr. Mary Sánchez Lanier,
For inspiring and nurturing a deep love of science,
And to my grandparents, Rozier and Victoria Sánchez,
My life long role models
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5.10 Comparison of predicted and experimental temperature by RCARS during the discharge burst as a function of burst size. The mixtures include 20% O$_2$-Ar, and C$_2$H$_4$-O$_2$-Ar at 40 torr. The C$_2$H$_4$-O$_2$ plasma chemistry mechanism utilized was developed by Wang [6]. The modeling approach here is that of continuous excitation with (E/n)$_{eff}$$\sim$88 Td. If not shown, experimental precision in the 95% confidence interval does not exceed the symbol size.

5.11 Comparison of predicted and experimental O-atom number density, [O], by TALIF during the discharge burst as a function of burst size. The mixtures include 20% O$_2$-Ar, and H$_2$-O$_2$-Ar at 40 torr. The C$_2$H$_4$-O$_2$ plasma chemistry mechanism utilized was developed by Wang [6]. The modeling approach here is that of continuous excitation with (E/n)$_{eff}$$\sim$88 Td. If not shown, experimental precision in the 95% confidence interval does not exceed the symbol size.

5.12 Schematic mechanism for low temperature hydrocarbon oxidation and autoignition from reference [7].

6.1 Waveforms from the “February 2nd” data-set obtained in air-ethylene mixture for $\phi$=1.47. The blue waveform is voltage, kV, the red is current, A, and the green is the instantaneous power as given by equation 4.3.1, in units of kW.

6.2 Waveforms from the “February 2nd” data-set obtained in air-hydrogen mixture for $\phi$=0.87. The blue waveform is voltage, kV, the red is current, A, and the green is the instantaneous power as given by equation 4.3.1, in units of kW. The waveforms are “zoomed” in to show only the prepulse. The main pulse and third pulse are not shown.

6.3 ICCD images of the pre-pulse discharge in Air, at 52 torr. The camera gate is 100ns and there is no gain. The image on the left was taken when the polarity at the top electrode was positive and the one on the right when the polarity was negative.
6.4 ICCD images of the main pulse discharge in Air, at 52 torr. The camera gate is 100ns and there is no gain. The image on the left was taken when the polarity at the top electrode was positive and the one on the right when the polarity was negative. 

6.5 The radial intensity from the middle of the discharges shown in figures 6.3.1 and 6.3.2 are plotted against the radial distance to yield four curves (one from each image). The radial distance was determined using the electrode dimensions. 

6.6 ICCD images of the discharge in air with added hydrogen at $\phi=0.83$, at 52 torr. The camera gate is 10ns and there is no gain. The image on the left was taken during the pre-pulse discharge, and the image on the right during the main pulse. The polarity in both cases was positive. 

6.7 The radial intensity from the middle of the discharge shown in figures 6.3.4 are plotted against the radial distance to yield two curves (one from each image in the figure). The radial distance was determined using the electrode dimensions. 

6.8 ICCD images of the main pulse discharge in air with added hydrogen at $\phi=0.83$, at 52 torr. The camera gate is 10ns and there is no gain. The four images were taken in succession and the polarity in all cases was positive. 

6.9 The radial intensity from the middle of the main pulse discharge shown in figures 6.2.5 are plotted against the radial distance to yield four curves (one from each image in the figure). The radial distance was determined using the electrode dimensions. 

6.10 The blue and black curves from figure 6.2.7 are shown only in this figure with the anticipated FWHM of the broadened plasma diameter due to instability formation. 

6.11 Pure rotational RCARS spectra obtained in air at 52 torr. The camera gain is set to 200 and an exposure time of 40 seconds. The top spectrum (black) has no additional pre-amplification and S/N of $\sim 11.12$. The bottom spectrum (blue) has an additional 4x pre-amplification applied to the read-out node and S/N of $\sim 17.56$. Both were taken 174.04 $\mu$s after the rise of the pre-pulse current.
6.12 Pure rotational RCARS spectra obtained in air at 52 torr. The camera gain is set to 200 and an exposure time of 60 seconds. The inferred temperature is 297.43K with \( \chi^2 \) of 0.3, and S/N is \( \sim 15 \).

6.13 Spectra obtained in air with added \( \text{C}_2\text{H}_4 \) at \( \phi = 1.47 \), camera gain of 200, pre-amplification at 4x, and exposure of 100 seconds, at 174.04 \( \mu \)s after the pre-pulse (timing discussed later in section), and 52 torr. The blue is the RCARS spectrum with inferred temperature was 931.10 K with a \( \chi^2 \) value of 0.4. The green curve is the background spectrum, taken with the Stokes beam blocked.

6.14 Spectra obtained in air at 52 torr, camera gain of 200, pre-amplification at 4x, and exposure of 60 seconds, with no discharge present. The blue is the RCARS spectrum with inferred temperature was 297.83 K with a \( \chi^2 \) value of 0.3. The green curve is the background spectrum, taken with the Stokes beam blocked.

6.15 RCARS spectrum (red) obtained in red with its corresponding theoretical spectrum from CARSFT (black), obtained in air with added \( \text{C}_2\text{H}_4 \) at \( \phi = 1.47 \), 1.57 ms after the pre-pulse current, at 52 torr, camera exposure time of 100s, EM gain set to 200, and a pre-amplification gain of 4x. The inferred temperature is 307.5 K with a \( \chi^2 \) of 0.2.

6.16 RCARS spectrum (red) obtained in red with its corresponding theoretical spectrum from CARSFT (black), obtained in air with no discharge present at 52 torr, camera exposure time of 100s, EM gain set to 200, and no pre-amplification. The inferred temperature is 297.43 K with a \( \chi^2 \) of 0.3.

6.17 Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is air only. The blue dots were taken when the focal length was 150mm, with a camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The red dots were taken when the focal length was 500mm, with a camera exposure of 40s, EM gain of 200, and with no pre-amplification. The pressure is 52 torr. The uncertainty in the time axis is \( \pm 50 \) ns and the uncertainty in the temperature is \( \pm 25 \) K.

6.18 Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is air only. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is \( \pm 50 \) ns and the uncertainty in the temperature is \( \pm 25 \) K.
Inferred RCARS temperature results with respect to time. Time zero is with respect to the main-pulse current. The mixture examined is H\textsubscript{2} at \(\varphi=0.83\). The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is \(\pm 50\) ns and the uncertainty in the temperature is \(\pm 25\) K.

Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is H\textsubscript{2} at \(\varphi=0.42\). The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is \(\pm 50\) ns and the uncertainty in the temperature is \(\pm 25\) K.

Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is H\textsubscript{2} at \(\varphi=0.14\). The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is \(\pm 50\) ns and the uncertainty in the temperature is \(\pm 25\) K.

Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is C\textsubscript{2}H\textsubscript{4} at \(\varphi=1.47\). The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is \(\pm 50\) ns and the uncertainty in the temperature is \(\pm 25\) K.

Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is C\textsubscript{2}H\textsubscript{4} at \(\varphi=0.87\). The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is \(\pm 50\) ns and the uncertainty in the temperature is \(\pm 25\) K.

Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is C\textsubscript{2}H\textsubscript{4} at \(\varphi=0.48\). The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is \(\pm 50\) ns and the uncertainty in the temperature is \(\pm 25\) K.
6.26 Inferred RCARS temperature results at 1.74µs before the main pulse with respect to the radial axis. The mixture is pure air at 52 torr. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the temperature is ±25.4 K. The magenta curve is a four term Gaussian fit to the raw data with a goodness of fit value of 0.9944. The FWHM max of this fit is ~2mm.

6.27 Inferred RCARS temperature results at 1.75µs after the main pulse with respect to the radial axis. The mixture is pure air at 52 torr. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the temperature is ±25 K. The magenta curve is a four term Gaussian fit to the raw data with a goodness of fit value of 0.9944. The FWHM max of this fit is ~2mm.

6.28 Inferred RCARS temperature results at 174.04 µs after the main pulse with respect to the radial axis. The mixture is pure air at 52 torr. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the temperature is ±25 K. The magenta curve is a two term Gaussian fit to the raw data with a goodness of fit value of 0.9944. The FWHM max of this fit is ~2mm.

6.29 Comparison of time-resolved temperature model predictions with experimental temperature results by RCARS for air at 52 torr. The model predictions are shown in the solid line. The experimental results are shown as black symbols. Time zero is with respect to the pre-pulse.

6.30 Comparison of time-resolved temperature model predictions with experimental temperature results by RCARS for air-H₂ at φ=0.14 at 52 torr. The model predictions are shown in the solid line. The experimental results are shown as black symbols. Time zero is with respect to the pre-pulse.

6.31 Preliminary 1D modeling results in air with added H₂ at φ=0.14. The Solid lines are the model predictions and the symbols are the inferred translational temperatures by RCARS. The blue curve is the number density of electronically excited nitrogen.

6.32 Preliminary 1D modeling results in air with added H₂ at φ=0.14. The Solid lines are the model predictions and the symbols are the inferred translational temperatures by RCARS. The red curve is the vibrational temperature of N₂ for the first vibrational level, v01.
Chapter 1: Introduction

1.1 Background

Plasma-assisted combustion, where the combustion processes are coupled with highly non-equilibrium plasma-discharges, has recently attracted intense interest due to the potential to enhance and further control fundamental combustion processes. For example, using nanosecond discharges Starikovskii [8] demonstrated a significant decrease in ignition temperature by ~600K where there was also an observed increase in the flame’s blow-off velocity by a factor of two. Both results were striking as the discharge energy input was very low, on the order of tens of milli-joules per cm3. Similarly, both Adamovich et. al [9] and S.M. Starikovskaya et. al [10] determined that the ignition delay time was reduced by at least an order of magnitude for similar nanosecond discharge energy inputs. In the same way, Marcum et al [11] demonstrated an increase in the flame speed by a factor of two or greater in comparable discharges and Laux et al [12] found that nanosecond repetitively pulsed plasma reduced lean extinction limits up to 70% with a power consumption less than 1% of the power released by the flame.

These combustion enhancements could shape the future of hypersonic flight. Previously, the United States has demonstrated the ability to achieve flight Mach numbers of 6 to 7 in the 1960’s with the very successful, and world’s only hypersonic airplane, X-15 [13]. However, the X-15 was powered by rocket propulsion, where fuel consumption is high; a Saturn 5 rocket consumes about 560,000 gallons of propellant in the first 2 ¾ minutes of flight [14]. This
has motivated research into an alternative air-breathing engine called the scramjet (supersonic combustion ramjet) where the intake flows through the combustion chamber at supersonic speeds (~Mach 1.5). At such high speed airflows, the residence time of the fuel in the combustion chamber is very low, on the order of a millisecond, which is comparable or shorter than the ignition delay time [15]. Furthermore, the combustion process may occur under lean conditions due to the short mixing times and reduced fuel payloads, which can be outside of normal flammability limits. The prospect of using short-duration plasma discharges to significantly reduce ignition delay times and extend the flammability limits of combustion in hypersonic flight is quite promising.

An understanding of the kinetic mechanisms responsible for the observed control and enhancement of combustion processes is two-fold. First, it must begin with identification of how the discharge energy is distributed amongst different degrees of freedom in molecules, as well as the fraction of discharge energy generating species by dissociation and ionization in addition to thermalization by electron impact or by collisional quenching of excited states. According to Starikovskiy [1], the deposition of the energy in the plasma, and thus, the plasma composition, is controlled primarily by the reduced electric field, E/n. Generally, E/n is a function of gas density, applied voltage and the geometry of the discharge. The electric field can be expressed in units of V/cm and the number density in cm$^3$. Thus, it is convenient to express the E/n in units of Townsends, where 1 Td$= 10^{-17}$ V cm$^2$. Figure 1.1 illustrates the fractional power dissipated by electrons into different molecular degrees of freedom for a stoichiometric mixture of air-hydrogen as a function of E/n. At E/n$\sim 200$ Td, which is comparable to the experimental E/n for the work presented in this thesis, $\sim$20% of the energy goes into dissociation of O$_2$, $\sim$50% into N$_2$ dissociation, and $\sim$20% into N$_2$ vibrational excitation. Hence,
even at low temperature, such a composition is highly non-equilibrium, and there now exists a
super-population of radical or excited species that can participate in new combustion pathways
or in reactions proceeding on new potential energy surfaces. As such, the combustion process
could potentially be controlled by a deliberate selection of E/n such that the plasma
composition achieves the desired results. Such precise control of the direction of the energy
deposition of the plasma is possible over relatively short time scales when there is not enough
time for electron multiplication above the breakdown threshold or for recombination below the
threshold to significantly change the electron number density and plasma conductivity. Short
high voltage pulses on the nanosecond timescale with a limit near a constant bias allows for
selective and extremely non-equilibrium excitation. This is one of the motivations behind using
the high-voltage, nanosecond discharges utilized in this work.

![Image of Figure 1.1: Fractional power dissipated by electrons into different molecular degrees of freedom as a function of E/n for a stoichiometric mixture of air-H₂ [1]](image-url)

*Figure 1.1: Fractional power dissipated by electrons into different molecular degrees of freedom as a function of E/n for a stoichiometric mixture of air-H₂ [1]*
The impact of the super-equilibrium population of radicals and excited species resulting from the energy partitioning on the conventional combustion chemistry must be determined. For instance, previous work by our group at Ohio State showed that 50% of the discharge energy in a dielectric barrier discharge excited by a repetitive nanosecond discharge goes into $O_2$ dissociation by electron impact. The resulting product, $O$-atoms, is largely responsible for initiating oxidation reactions [16]. This is in contrast to conventional combustion chemistry, where the initiation usually starts with abstraction of an $H$-atom by an $O_2$ molecule to produce $OH$ which then participates in chain propagating or chain branching reactions leading to ignition [7, 17-21].

Conventional chemistry also incorporates the Zel’’dovich mechanism for the production of NO. It is dominated by two chain propagating and chain branching reactions [22, 23].

$$N_2 + O \rightleftharpoons NO + N \quad \text{(R1)}$$

$$N + O_2 \rightleftharpoons NO + O \quad \text{(R2)}$$

It should be emphasized that the Zel’dovich reaction mechanism dominates NO formation in conventional combustion. Samaniego et al [22] demonstrated that the mechanism is responsible for ~75% of NO formation in oxygen-natural gas turbulent diffusion gas flames. However, reactions (R1) and (R2) are strongly dependent on temperature due to the high activation in the initiation reaction, (R1), which is ~ 76.5 kcal/mole ~ 3.3 eV ~ 373 nm [22, 23]; thus, this reaction typically occurs at high temperatures.

Previous work by our group has also shown, for the same discharge, that models incorporating the conventional Zel’dovich reactions fail to predict NO formation after a single discharge pulse, as illustrated in figure 1.2. The predicted NO number density after the discharge
pulse, [NO], is shown as a smooth black curve and the experimental [NO] by LIF as black symbols. As can be seen, the peak predicted [NO] is not only less than the experimental value by almost an order of magnitude, but the qualitative trends disagree as well [2]. No conclusive mechanism was determined, but two possible reactions for NO formation, (R3) and (R4), were suggested for the low temperature non-equilibrium nanosecond discharge.

\[
N_2(X, v \geq 12) + O(3P) \rightleftharpoons NO + N(4S) \quad \text{(R3)}
\]

\[
N(4S) + O_2(b^1\Sigma) \rightleftharpoons NO + O(3P) \quad \text{(R4)}
\]

The proposed reactions (R3) and (R4) constitute reactants that are predominately generated in the discharge by electron impact and/or indirectly by collisional quenching of electronic excited states. Thus, in plasma assisted combustion, it is important to consider how the plasma chemistry impacts combustion chemistry.

![Graph showing mole fractions of various species over time](image)

*Figure 1.2 Experimental O-atom and NO concentration, both in symbols, and species concentration predicted by a kinetic model incorporating the Zel'dovich mechanism for NO formation after a single pulse discharge in air. P=60 torr, pulse energy =1.0 mJ. [2]*

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The need for elucidating chemical mechanisms becomes clear when examining the role of \( O_2(a^1\Delta) \), which is generated exclusively by the discharge in plasma assisted combustion. For example, the reaction of \( O_2(a^1\Delta) \) with \( \text{H} \) atoms to produce \( \text{HO} \) and \( \text{O-} \) atoms, reaction (R5), will proceed on an entirely different reaction potential energy surface than the reaction between ground state \( O_2 \) and \( \text{H} \), reaction (R6).

\[
\text{O}_2(a^1\Delta) + \text{H} \rightleftharpoons \text{OH} + \text{O} \quad \text{(R5)}
\]

\[
\text{O}_2(X^3\Sigma) + \text{H} \rightleftharpoons \text{OH} + \text{O} \quad \text{(R6)}
\]

Normally, reaction (R6) is not available at low temperatures because it has low reaction probability when molecular oxygen is in its ground state, \( O_2(X^3\Sigma) \), due to an endothermic barrier arising mostly from the zero-point energy difference between \( O_2(X^3\Sigma) \), and \( \text{OH}(X^2\Pi) \), (-0.714 eV) [24]. This leads to a threshold energy of \( \sim 0.56 \text{ eV} \) from pure classical calculations, \( \sim 0.72 \text{ eV} \) in quantum mechanics, and \( \sim 0.75 \text{eV} \) experimentally [25, 26]. It has been hypothesized that the excitation of \( O_2 \) to \( O_2(a^1\Delta) \) would increase the rate of the reaction, (R5) relative to reaction (R6) provided that the potential energy surface of reaction (R5) does not have any endothermic barriers. This would increase the rate of chain propagation and chain branching [27]. Starik et al [28] very explicitly ascribes any combustion enhancement by \( O_2(a^1\Delta) \) to the direct participation in reaction (R5) in their proposed mechanism. Ombrello et al [29, 30] isolated the kinetic effects resulting from \( \text{O-} \), \( O_2(a^1\Delta) \), and \( O_3 \) from other species. They found that even low concentrations, on the order of a few parts per million, each of these species can significantly enhance flame speed. As there has been no experimental rate reaction yet determined for reaction (R5), they adjusted the rate until the results of the kinetic modeling matched their experimental results.
Skrebkov et al. [31] has recently proposed a new mechanism for conventional combustion that credits reactions involving vibrationally excited HO$_2$ as largely responsible for self-heating and ignition in hydrogen combustion. In other words, HO$_2$ in this mechanism is crucial to the combustion process where in most proposed or accepted mechanisms, HO$_2$ cannot sustain combustion alone. It leads one to wonder if the discharge could also increase the vibrationally excited HO$_2$ population and proceed down pathways involving this species that result in a reduced ignition time or even if the current accepted mechanism is inaccurate. Obviously, the underlying mechanisms in plasma assisted combustion are still not fully understood.
understood. One of the goals of this work is to assess the applicability of coupling both plasma chemistry and conventional combustion chemistry mechanisms available in the literature as a starting point for elucidating kinetic mechanisms and the development of a more comprehensive plasma assisted combustion model.

The processes in both plasma chemistry and conventional chemistry are typically highly temperature dependent [7, 23, 25, 32]. Recently, Wu et al [3] has shown that that the evolution of the hydroxyl radical, [OH] in a pin-to-pin discharge with respect to time changes significantly with temperature. Figure 1.3 shows their experimental results for four different temperatures (room temperature and three cases where the gas was preheated). At 300 K, [OH] reaches its maximum at \(~1\mu\text{s}\); at 400 K at \(~10\mu\text{s}\), and at 600 K at \(~50-70\mu\text{s}\). Finally, at 800K, [OH] has three distinct peaks in the profile. The first peak reflects the initial formation of [OH] in the discharge, the second peak corresponds to chain reactions below the self-ignition threshold and is limited by accumulation of intermediate species, and the third final peak out at \(t \geq 1\text{ms}\) is the [OH] footprint associated with ignition. The kinetic mechanism for these processes are still not understood [3] and Wu et al [3] did not postulate any possible mechanisms responsible for the trends observed in their [OH] profiles. However, more recently, a kinetic model has postulated that the vibrational excitation of \(N_2\) plays an important role [1]. In conventional mechanisms, the \(HO_2\) radical and \(H_2O_2\) are considered chain-terminating. Under the conditions of the discharge in figure 1.3, it is thought the majority of the energy after breakdown goes into vibrational excitation of \(N_2\). These vibrationally excited molecules could then potentially participate in fast, near resonant, V-V transfer with \(HO_2\), which would eventually lead to \(HO_2\) dissociation, generating \(H\)-atoms and \(O_2\) molecules, as illustrated in reactions (R8) and (R9)

\[
N_2(X, v + 1) + HO_2(v_1, v_2) \rightleftharpoons N_2(X, v - 1) + HO_2(v'_1, v'_2)
\]  

(R8)
\[ HO_2(v_1', v_2') \rightleftharpoons H + O_2 \]  \hspace{1cm} (R9)

The reaction (R9) proceeds on a global reaction potential energy surface that is shared by the O+OH reaction channel as shown in reaction (R10) [17-19, 21, 26, 33, 34].

\[ HO_2(v_1', v_2') \rightleftharpoons O + OH \]  \hspace{1cm} (R10)

To be more precise, H+O\_2 and O+OH are connected via the intermediate HO\_2, and the overall reaction can be written as in reaction (R11).

\[ H + O_2 \rightleftharpoons O + OH \]  \hspace{1cm} (R11)

Quantum mechanical calculations show that the potential energy surface for reaction (R11) is dominated by a HO\_2 (X^2A') potential energy well with a large density of states. The well is \( \sim 2.4 \) eV below the H+O\_2 asymptote [35] and \( \sim 2.72 \) eV below the O+OH asymptote [18]. In spite of a higher activation barrier, the back reaction into the O+OH channel from the HO\_2 is favored because the long range interactions in this channel are stronger. Thus, this theoretical potential energy surface is significant for three reasons. First, if the postulated vibrational excitation of HO\_2 is correct, then the vibrational excitation in the nanosecond discharge will help overcome the potential energy barrier for dissociation into one of the two possible reactions channels, (R9) or (R10). Second, this means that there could be in fact two potential decomposition channels for the vibrationally excited HO\_2, instead of the single pathway (R9) mentioned in the review of the kinetic model [1]. Third, if the dissociation of HO\_2 preferentially favors the O+OH reaction channel, the products of which are both chain propagating and chain branching radical species, then the vibrational excitation of N\_2 could lead to extensive chain propagation and branching. As of yet, there has not yet been any direct evidence of vibrationally excited HO\_2,
which underscores the need for further insights into these fundamental kinetic processes in plasma assisted combustion using kinetic models.

Because these processes in plasma assisted combustion are highly temperature sensitive, an experimental determination of temperature constitutes a critical measurement for elucidating fundamental phenomena and for validation of plasma chemical kinetic mechanisms. This thesis reports temperature measurements by picosecond pure Rotational Coherent Anti-Stokes Raman Scattering Spectroscopy (RCARS) for two different nanosecond discharge systems, a dielectric barrier discharge and a pin-to-pin discharge.

Coherent Anti-Stokes Raman Scattering Spectroscopy (CARS) is a well-established diagnostic method that has been used extensively in combustion environments [36]. Its application as a plasma diagnostic has also been reported by several groups. As one example, Devyatov et al. [37], reported CARS measurements of vibrational levels v=0-4 in a 200 nsec duration pulsed discharge in nitrogen at 60 torr. The results suggested that collisional processes involving excited electronic states of N$_2$ result in increased vibrational level populations in the ground electronic state for time scales of several hundreds of microseconds after decay of the plasma itself. Recent picosecond vibrational CARS measurements of Montello et al. [38] have confirmed this result. Montello et al. has also reported measurements of rotational/translational temperature and vibrational distribution function in a Mach 5 non-equilibrium wind tunnel [39]. As a final example, Messina et al. [40] used CARS to demonstrate significant vibrational loading in an atmospheric pressure, nanosecond pulse, point-to-point discharge. Similar to the work of Devyatov and Montello, Messina reported an increase in N$_2$ vibrational temperature in air plasmas at time delays exceeding approximately 1 μsec after discharge initiation, reaching a maximum at ~50 μsec delay.
The selection of pure rotational CARS was based on two primary characteristics of the plasmas under study. First, our anticipated temperatures were quite low, of order $300 – 600$ K. Pure rotational CARS has the advantage of readily providing well resolved rotational structure, resulting, at least potentially, in high accuracy and precision at low temperatures [41]. Second, the studies are performed at relatively low pressure, 40 Torr for the work to be presented here, with the partial pressure of $O_2$ even lower (~8 Torr or less). It was anticipated, therefore, that it would be crucial to compensate for the low number densities by utilizing sufficiently high laser beam intensities where Stark broadening and Stimulated Raman pumping effects could lead to significant systematic error if the more common vibrational Q-branch CARS were to be used [42]. However, Pélat et al [43] found if stark broadening effects are present, the distortions are experienced symmetrically across the rotational manifold and rotational temperature is nearly independent of power, provided that saturation effects are not present. Woodmansee et al [44] also demonstrated that the relative intensities of the rotational lines is not affected by Stark broadening as well as stimulated Raman pumping effects. Magnotti et al [42] recently showed that stark broadening will not affect measurements and can be neglected if the stark shift is comparable to the Raman transition line-width. The maximum power utilized in this experiment does not exceed 12.7 GW/cm$^2$. According to Magnotti et al., the Stark shift is $<$ 0.03 cm$^{-1}$ for both $O_2$ and $N_2$ at these powers. Since the Raman linewidths are on the order of 0.1 cm$^{-1}$, starkshift $<$ raman linewidths and stark broadening can be neglected. Magnotti et al. further showed that stimulated Raman pumping effects does not alter the ground state rotational temperature because the effects are similar for all transitions. Therefore, it was anticipated that the effect of Stark broadening and stimulated Raman pumping effects at the maximum power
capabilities of the RCARS system in this work will have negligibly small effects on temperature inference.

Finally, it should be noted that a modeless broad-band laser is used as the source for the pump and Stokes in the experiments reported in this thesis because improvement in precision has been demonstrated using a broadband source. Vestin et al [45] reported high precision with standard deviations for ambient air on the order of ± 1K for 1000 shots (~0.1%) and ± 4 K for 350 spectra (~1%), versus the ~4-5% reported in the literature for N₂ RCARS. The improved precision is largely due to the averaging of the RCARS signal over all possible combinations of ω₁ and ω₂ within the spectral profile of the broadband laser source and the modeless structure of the source.

1.2 Objectives

As stated previously, a primary goal of this work is to assess the applicability of coupling both plasma chemistry and conventional combustion chemistry mechanisms available in the literature as a starting point for elucidating kinetic mechanisms and the development of a more comprehensive plasma assisted combustion model. Because these processes are highly temperature sensitive, an experimental determination of temperature constitutes a critical measurement for elucidating fundamental phenomena and for validation of plasma chemical kinetic mechanisms. This thesis reports temperature measurements by picosecond pure Rotational Coherent Anti-Stokes Raman Scattering Spectroscopy (RCARS) for two different nanosecond discharge systems, a dielectric barrier discharge and a pin-to-pin discharge.

The work presented here for the dielectric barrier discharge is specifically motivated by a desire to perform fundamental plasma chemical fuel oxidation measurements in which argon
is used in place of the more standard nitrogen as a diluent gas. The choice of argon is deliberate, primarily for three reasons. First, and most fundamentally, both ground and excited state N₂ can participate in a variety of reactions producing nitrogen containing species such as NO or NO₂, thus removing N₂ from the system simplifies the kinetics and allows the focus to be on the primary chemical oxidation processes. Second, argon has a thermal diffusivity which is similar to that of nitrogen, and as such the heat transfer properties of the mixtures being studied more accurately mimic those of air. Finally, due to the rather high energy of argon’s first excited electronic state, ~11.2-eV, a larger fraction of discharge energy will be deposited into oxygen, producing the desired dissociation and excited electronic states in argon plasmas relative to nitrogen.

In contrast, the work presented here for the pin-to-pin discharge is specifically motivated by a desire to perform fundamental plasma chemical fuel oxidation measurements where there is significant vibrational loading of N₂ molecules and to investigate how this impacts fuel oxidation processes. It has only been recently that vibrational loading in pin-to-pin discharges have been characterized for the two cases of dry air and pure N₂ [46-49]. There is very little data on how these processes are affected by fuel addition [1, 3]. To date, the work done by Wu et al [3] is one of the first to report experiments in a pin-to-pin discharge with fuel added. Their [OH] temporal profiles for different fuels at different temperatures are shown in figure 1.3. However, they were unable to qualitatively explain all of the experimental data due to the lack of validated kinetic models in these temperature ranges. It is the main objective of this work to present temporal temperature measurements where the initial temperature is at ambient room temperature for validation of a 1-D kinetic model.
1.3 Structure of this Thesis

The remaining chapters of this thesis are organized as follows: Chapter 2 is theory chapter focusing on two separate topics. First, the Townsend Mechanism is explained because concepts introduced here are used throughout the thesis. Second, the CARS process is described in detail, starting with a general approach from nonlinear optics. Chapter 3 details the experimental arrangements for the two discharge systems in addition to the data processing of CARS. Chapter 4 considers the dielectric barrier discharge system. It introduces some concepts concerning plasma instabilities and presents experimental results for plasma characterization, including ICCD images and current-waveforms. At the end of chapter 4, the RCARS results are discussed in detail. Chapter 5 compares the experimental results with those of a 0-D kinetic model after detailing the 0-D model. Chapter 6 focuses on the pin-to-pin experimental results, including plasma characterization and RCARS temporal results. It concludes with a brief introduction to a 1-D kinetic model that is still in the stages of development. Preliminary results from this model are compared with the experimental pin-to-pin RCARS results. Finally, chapter 7 provides a summary of key results from the two experiments and comparison with modeling in addition to suggestions for future work.
Chapter 2: The Townsend Breakdown Mechanism and Coherent Anti-Stokes Raman Scattering Spectroscopy

Gas discharge plasmas are generated and maintained by the input of electrical power. The characteristics of the discharge are found in connection with the gas pressure, gas composition, and boundary conditions at the discharge electrodes and walls. In particular, the evolution and relaxation of the electron energy distribution function are defined by the production and loss of charged particles, as well as charge carrier transport (i.e. field drift and diffusion). However, all discharges experience an electric breakdown where the non-conducting gas becomes conducting. The process of breakdown that leads to a conducting channel can be complex with many stages, but the majority of breakdown phenomena begin with an electron avalanche, and this is true for both the dielectric barrier discharge and the pin-to-pin discharge that are investigated in this work. To illustrate the role of the electron avalanche, the classical Townsend mechanism will be described in section 2.1, with the description taken primarily from J. Meichsner, Alexander Fridman, and Alexandre V. Chirokov [50-52]. In particular, the drift-diffusion approximation that will be described in chapter 5 with regards to the 0-D kinetic model for the dielectric barrier discharge cell, not only looks remarkably similar to the Townsend mechanism, but builds on the concepts introduced here in this chapter.

Studying the subsequent heat release after these systems are excited by the nanosecond discharges is crucial in elucidating the fundamental processes and towards validation for any model attempting to reproduce the macroscopic phenomena occurring in
these systems using proposed kinetic mechanisms. However, plasma assisted combustion systems are inherently difficult to probe and the system’s response to electromagnetic radiation readily provides a noninvasive technique to study the structure and dynamic processes occurring in real time. In particular, Coherent anti-Stokes Raman Scattering spectroscopy (CARS) has been developed extensively over the past thirty years to probe temperature and major species concentrations in combustion environments[41, 53]. CARS is one of many third-order processes. These processes are the strongest non-linear processes in centrosymmetric media (e.g. gas phase) and include saturation spectroscopy, Doppler-free polarization spectroscopy, doppler-free two-photon absorption, Raman induced Kerr Effect (RIKE), stimulated Raman Gain Spectroscopy, (SRGS), Coherent Raman Ellipsometry, (CREM), and CARS. The theoretical understanding of third-order non-linear processes, and in particular, CARS, is presented in this section. There are many different theoretical treatments of CARS ranging from the time and frequency domains to a diagrammatic approach; approaches can be purely classical, semi-classical, or quantum mechanics. However, all of them begin with equation (2.2.1). The approach taken here closely follows Druet et al [54] chosen specifically because the development of the CARSFT code utilized in this work was based in part on the theoretical considerations given by [54]. Finally, the concepts developed by Druet et al. will be applied to the pure-rotational CARS computational model developed by Martinsson et al [41, 55] as an example for the application of CARS to thermometry and species concentration, and the characteristics of both O₂ and N₂. RCARS spectra are described.

2.1 The Townsend Breakdown Mechanism

The Townsend mechanism describes the electrical breakdown in gases between a discharge gap consisting of two parallel metal plate electrodes with distance d and uniform
electric field strength, $E$ that is given by $E=V/d$. The starting point is the generation of free electrons at the cathode due to an external source, which are considered primary electrons in this mechanism. (For this work it will be the high voltage generator described in section 3.3). These primary electrons provides a very low initial current, $i_0$. The primary electrons drift collectively to the anode in the uniform electric field and ionize the gas in the process. This ionization generates an avalanche because the newly generated electrons proceed along with the primaries on their drift from the cathode to the anode. In a gas at pressure $p$, the first Townsend coefficient, $\alpha$, describes the number of electron-ion pairs per unit that are produced in this collective drift towards the anode. It is given by equation 2.1.1, where $n_e$ is the electron density, $v_i$ is the ionization frequency with respect to one electron, $v_d$ is the electron drift velocity, and the ionization rate coefficient is given by $k_i \left( \frac{E}{n_0} \right)$. It should be noted that the parameter $\left( \frac{E}{n_0} \right)$ is referred to as the reduced electric field, which can be related to pressure at constant temperature, and thus, to electron mobility, $\mu_e$ which is inversely proportional to pressure.

$$\alpha = \frac{v_i}{v_d} = \frac{1}{v_d} k_i \left( \frac{E}{n_0} \right) = \frac{1}{\mu_e} \frac{k_i(E/n_0)}{E/n_0} \quad (2.1.1)$$

Thus, the change in electron density, $n_e$, per unit length, $z$, along the discharge gap, is directly proportional to the first Townsend coefficient.

$$\frac{dn_e}{dz} = \alpha n_e \quad (2.1.2)$$

Rearranging and integration of equation 2.1.2 yields equation 2.1.3, where the coefficient of $n_{e0}$ is the initial electron density (primary electrons).

$$n_e(z) = n_{e0} \exp(\alpha z) \quad (2.1.3)$$
From equation 2.1.3, it is clear that the number of electrons rises exponentially with increasing path length \( z \) of the electron. The new electrons in turn are accelerated in the uniform electric field. It should be emphasized that electron losses due to recombination and attachment to electronegative molecules have been neglected because ionization is very low during breakdown.

Often, the first Townsend coefficient is used as a similarity parameter, \( \alpha/p \), to express the effect of pressure on the number of ionizing collisions per unit length, which is related to the mean free path of the electron.

\[
\frac{\alpha}{p} = f \left( \frac{E}{p} \right) \tag{2.1.4}
\]

Within the mean free path of the electron, the electron accelerates due the applied electric field. The mean kinetic energy gained can be related to the reduced electric field.

\[
\varepsilon_{kin} = eE \lambda_e \sim \left( \frac{E}{n_e} \right) \sim \left( \frac{E}{p} \right) \tag{2.1.5}
\]

If the kinetic energy gained exceeds the ionization threshold, new electrons are generated upon impact with the neutral gas. This process also produces corresponding positive ions. These ions are accelerated in the opposite direction of the electrons, toward the cathode. It should be noted that the second Townsend coefficient, \( \beta \) takes into account the ionization of neutral gas atoms by ion-neutral collisions. According to J. Meichsner [50], the cross section for such ionizations is very low in comparison with the electron-neutral collisions and usually can be neglected. As such, the second Townsend coefficient is not discussed here.

Eventually, the ions hit the cathode surface, which generates secondary electrons. The third Townsend coefficient, \( \gamma \), describes both the probability of electron generation and the
number of electrons generated per impinging ion. The coefficient depends on the cathode material, the state of the cathode surface, type of gas and the reduced electric field. In some discharges, the coefficient also incorporates any impact of photons and metastable atoms and molecules on the secondary electron generation. In such cases, the coefficient \( \gamma \) is considered an effective coefficient. Nonetheless, the number of ions produced for each electron that arrives at the anode can be calculated using equation (2.1.3) and given by equation (2.1.6).

Because we are considering one electron, \( n_{e0} = 1 \), and because first ion is already at the cathode, we must subtract 1.

\[
\exp(az) - 1 \tag{2.1.6}
\]

Therefore, the number of secondary electrons is simply the number of ions multiplied by the probability, \( \gamma \), for some number of electrons generated upon bombardment.

\[
\gamma [\exp(az) - 1] \tag{2.1.7}
\]

It should be noted that typical values for \( \gamma \) range from 0.01 to 0.1 and that the secondary electrons drift to the anode as well and participate in the same kind of processes that the primary electrons did.

Finally, according to J. Meichsner [50], if steady state conditions are assumed, the electron density at the anode is the total discharge current density, \( i_{eA} \), and can be expressed by equation (2.1.8), where \( i_0 \) is the initial current density described previously.

\[
i_{eA} = i_0 \frac{\exp(az)}{1 - \gamma [\exp(az) - 1]} \tag{2.1.8}
\]

The denominator will approach zero, if the current density tends to infinity. This occurs as soon as the electric field becomes sufficiently high. At this point, the current within the discharge...
becomes self-sustained. Thus, the breakdown condition in the gap is primarily controlled by the secondary electron emission from the cathode and can be expressed through the following two equations

\[ \gamma [\exp(\alpha z) - 1] = 1 \]  (2.2.9)

\[ \alpha z = \ln \left( \frac{1}{\gamma} + 1 \right) \]  (2.2.10)

The breakdown voltage and electric field can be derived by using equations (2.1.9-2.1.11). It should be noted that equation (2.1.11) is the similarity parameter, \( \alpha/p \), given by equation 2.1.4, where the functional form is expressed as an exponential dependence on the reduced electric field, which is the most common functional form found in the literature, and applied in the development of the 0-d model for the dielectric barrier discharge cell in chapter 5 (see equation (5.1.12)).

\[ \frac{\alpha}{p} = A \exp \left( \frac{B}{E/p} \right) \]  (2.1.11)

where \( A \) and \( B \) are empirical constant. Combining equations (2.1.9-2.1.11) gives the following for the voltage and electric field:

\[ V = \frac{B(pz)}{C+\ln(pz)} \]  (2.1.12)

\[ \frac{E}{p} = \frac{B}{C+\ln(pz)} \]  (2.1.13)

where \( C = \ln \left[ \frac{\ln A}{\ln(1+\frac{1}{\gamma^2})} \right] \).
2.2 Introduction to pure Rotational Coherent Anti-Stokes Raman Scattering Spectroscopy

CARS occurs in media with Raman active modes. As shown in figure 2.1, incident photons at frequencies $\omega_P$ and $\omega_S$, termed pump and Stokes, respectively, induce a coherent oscillating polarization in the material of interest, which is at maximum when the energy difference between the photons is equal to a molecular resonant frequency. A third photon, termed the probe, at frequency $\omega_{\text{probe}}$, anti-stokes Raman scatters from this polarization coherently, in what is known as the “phase-matching direction.” Due to symmetry, a similar wave at $\omega_{\text{probe}} + (\omega_P - \omega_S)$, termed Stokes, is also observed with the CARS signal.

There are two major categories of CARS, vibrational CARS (VCARS) and rotational CARS (RCARS). In vibrational CARS, the difference frequency excites the vibrational modes, whereas in rotational CARS, the rotational modes are excited, such that $\omega_R = \omega_P - \omega_S$. It should be noted that in this work, a broadband modeless dye laser is the source for both the pump and Stokes photons. This is particularly beneficial because the photon pairs exciting the rotational transitions come from numerous combinations of frequencies from within the broad bandwidth of a single pulse. This minimizes fluctuations that originate from the dye laser and yields both higher precision and accuracy [53, 56, 57]. Furthermore, because the probe is narrowband in this work, (≤ 0.1 cm$^{-1}$) and the system is dominated by Doppler broadening (≤ 0.09 cm$^{-1}$), the resolution is limited purely by the spectrometer which ranges from 0.02 to 0.04nm (1.4 to 2.8 cm$^{-1}$) depending on slit width (25 to 50µm).
Rotational CARS is observed in a volume of gas with a rotational frequency, $\omega_R$, when two beams with frequencies $\omega_1$ (pump) and $\omega_2$ (Stokes) are passed through the sample, such that $\omega_R = \omega_p - \omega_S$. A new wave is generated at the anti-Stokes frequency, $\omega_{\text{CARS}} = \omega_{\text{probe}} - (\omega_p - \omega_S)$, in the phase matching direction when a third wave at $\omega_1$ (probe) inelastically scatters off the coherent rotations driven by the pump and Stokes beams. The probe beam can occur either instantaneously with or at some time after the pump and Stokes beams. Due to symmetry, a similar wave at $\omega_{\text{probe}} + (\omega_p - \omega_S)$ is also observed with the CARS signal.

A mathematical description for this non-linear process begins with a very general description for all non-linear interactions of materials with electromagnetic fields. First, let us build a qualitative picture of how these nonlinear process occur. Typically, upon application of an electric field, positive and negative charges will move in opposite directions, resulting in a charge separation (and hence, dipole). We can think of an atom or molecule as consisting of a hard positive ionic core surrounded by a soft jello-like electron cloud with elasticity dependent on the species. Hence, a small displacement of the electrons can occur upon application of an electric field. This small movement with negative charges in one direction and positive charges in the other, results in a collection of induced electric-dipole moments. In other words, the effect of the electric field is to induce a polarization in the medium. The more elastic, or polarizable, the electron cloud is, the stronger the effect of the electric field. However, the
induced polarization upon application of an electromagnetic wave is not static. Because an electromagnetic wave is oscillating, the induced dipoles and polarization also oscillates. The ion cores are much heavier than the electrons, and at high frequencies (the UV and visible region for instance), it is only the electron motion that we need concern ourselves with. The response of an electron to the optical field is that of a particle in an anharmonic well. Provided that the anharmonicity is small, we can describe the polarization as a power series as a function of time and the electric field. (In the treatment here, we neglect any coupling of the electron to the magnetic field of the EM wave because these effects are typically very small.)

\[
\vec{P}(\vec{r}, t) = \vec{P}^{(1)}(\vec{r}, t) + \vec{P}^{(2)}(\vec{r}, t) + \vec{P}^{(3)}(\vec{r}, t) + \ldots + \vec{P}^{(n)}(\vec{r}, t)
\]  

(2.2.1)

Where \(\vec{P}^{(1)}(\vec{r}, t)\) is linear in the electric field, \(\vec{P}^{(2)}(\vec{r}, t)\) is quadratic, \(\vec{P}^{(3)}(\vec{r}, t)\) is cubic, and so on. \(\vec{P}^{(1)}\) is associated with linear effects such as dispersion and absorption. \(\vec{P}^{(2)}\) vanishes in media with inversion symmetry such as centrosymmetric crystals, gases, and liquids. In materials with no inversion symmetry, the term typically is responsible for frequency doubling or parametric conversion such as is utilized in optical parametric oscillators. Nonetheless, there are two assumptions implicit in equation (2.3.1). First, it is assumed that the polarization response to the applied field is instantaneous. Second, because the response is assumed to be instantaneous, the medium must be lossless and dispersionless (this is more readily apparent through the Kramers-Kronig relations).

All of the terms in equation (2.2.1) can be given explicit expansion if the electromagnetic waves are assumed to be monochromatic plane waves. The total field vector, \(\vec{E}\), can be expanded as a function of it’s components, \(\vec{E}_i\), with frequency \(\omega_i\) and wave vector \(\vec{k}_i\):
Using equations (2.2.2) and (2.2.3), it is now possible to write more explicit expressions for the higher order polarization terms in equation (2.2.1). If steady state conditions are assumed, then for a given frequency component, \( \omega_s \), a higher order polarization term with order \( n \) in the field is written as:

\[
\vec{p}^{(n)}(\vec{r}, \omega_s) = \frac{1}{2} \vec{p}^{(n)}(\vec{r}, \omega_s) \exp\left[-i(\omega_s t - \vec{k}_s \cdot \vec{r})\right] + c. c. \tag{2.2.4}
\]

With \( \vec{p}^{(n)}(\vec{r}, \omega_s) \) given by:

\[
\vec{p}^{(n)}(\vec{r}, \omega_s) = \left(\frac{1}{2}\right)^{n-1} \chi^n(-\omega_s, l_1 \omega_j, l_2 \omega_{j_2}, \ldots, l_n \omega_{j_n}) \times \vec{E}_{l_1}(\vec{r}, j_1) \vec{E}_{l_2}(\vec{r}, j_2) \ldots \vec{E}_{l_n}(\vec{r}, j_n) \tag{2.2.5}
\]

Where \( \chi^n \) is the non-linear susceptibility tensor of order \( n \) with tensor rank \( n+1 \), and the following conditions hold:

\[
l_i = \pm 1
\]

\[
\omega_s = \sum_{i=1}^{n} l_i \omega_j \tag{2.2.6a}
\]

\[
\vec{k}_s = \sum_{i=1}^{n} l_i \vec{k}_{j_i} \tag{2.2.6b}
\]

\[
\vec{E}_{l_i}(\vec{r}, j_1) = \begin{cases} \vec{E}(\vec{r}, j_1) & \text{if } l_i = +1 \\ \vec{E}^*(\vec{r}, j_1) & \text{if } l_i = -1 \end{cases} \tag{2.2.6c}
\]

We shall now consider a classical approach to the above system of equations using Maxwell’s equations. The oscillating coherent polarization at frequency \( \omega_s \) generates an electromagnetic

\[
\bar{E} = \sum_l \vec{E}_l(\vec{r}, t) \tag{2.2.2}
\]

\[
\vec{E}_l(\vec{r}, t) = \frac{1}{2} \vec{E}(\vec{r}, \omega_l) \exp\left[-i(\omega_l t - \vec{k}_l \cdot \vec{r})\right] + c. c. \tag{2.2.3}
\]
wave with corresponding frequency \( \omega_s \). The wave equation for a non-magnetic homogeneous and isotropic medium can be written as:

\[
\left( \nabla^2 + \frac{n^2(\omega_s)}{c^2} \frac{\partial^2}{\partial t^2} \right) \vec{E}(\vec{r}, t) = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} \tilde{p}^{(n)}(\vec{r}, t, \omega_s)
\]

(2.2.7)

Where \( \tilde{p}^{(n)}(\vec{r}, t, \omega_s) \) is given by equations (2.2.4) and (2.2.5) and is assumed to be the only source for the electromagnetic wave at frequency \( \omega_s \). It should be emphasized that this source polarization is a function of the frequencies, phases, and states of polarization of the incident EM waves. These parameters in addition to the nonlinear susceptibility tensor directly impact the growth and polarization properties of the signal wave.

It should be emphasized that the source polarization term in equation (2.2.7) is not unique. It is a linear combination of all the possible, distinct, mechanisms that can generate the signal wave. For example, if three photons are incident on a centrosymmetric medium with frequencies \( \omega_1 \) and \( \omega_2 \) such that \( \omega_3 > \omega_1 > \omega_2 \), then there are two third-order polarization terms at the frequency \( \omega_4 = \omega_3 - (\omega_1 - \omega_2) \)

\[
\tilde{p}^{(3)}(\vec{r}, t, \omega_4) = \tilde{p}^{(3)\text{CARS}}(\vec{r}, t, \omega_5) + \tilde{p}^{(3)\text{SRS}}(\vec{r}, t, \omega_5)
\]

(2.2.8)

The first term in equation (2.2.8) is the CARS component, such that:

\[
\tilde{p}^{(3)\text{CARS}}(\vec{r}, t, \omega_4) = \frac{1}{2} \tilde{p}^{(3)\text{CARS}}(\vec{r}, \omega_4) \exp[-i(\omega_4 t - \vec{k}_4 \cdot \vec{r})] + c.c
\]

(2.2.9)

where

\[
\tilde{p}^{(3)\text{CARS}}(\vec{r}, \omega_4) = \left( \frac{1}{4} \right) \chi^{(3)\text{CARS}}(-\omega_4, \omega_3, \omega_1, -\omega_2) \times \vec{E}_3(\vec{r}, \omega_3)\vec{E}_1(\vec{r}, \omega_1)\vec{E}_2^*(\vec{r}, \omega_2)
\]

(2.2.10)
The second term in equation (2.2.8) is stimulated Raman scattering (inverse Raman scattering), abbreviated SRS. It is an interaction between waves $\omega_4$ and $\omega_1$; it is given by equation (2.2.12) where $\vec{k}_4$ is the anti-Stokes wave-vector.

\[
\vec{p}^{(3)\text{SRS}} (\vec{r}, t, \omega_4) = \frac{1}{8} \chi^{(3)\text{SRS}} (-\omega_4, \omega_3, -\omega_1, \omega_2) \vec{E}_4 (\vec{r}, \omega_4) \vec{E}_1^* (\vec{r}, \omega_1) \vec{E}_2 (\vec{r}, \omega_2) \exp[-i(\omega_4 t - \vec{k}_4 \cdot \vec{r})] + c. c
\]

(2.2.12)

This SRS polarization component is typically the smaller of the two in a CARS experiment, because while the susceptibility components are of comparable magnitude, polarization is proportional to the CARS EM-wave, which is considerably less than the initial applied EM waves.

Therefore, there are two separate problems to solve in nonlinear optical spectroscopy, (1) derivation of all the relevant nonlinear susceptibility terms, and (2) calculation of the electric field solution of the wave equation, (see equation (2.2.7)). The approach taken here for the nonlinear susceptibility is a quantum mechanical approach because it can be applied generally to both the time domain (ultra-fast spectroscopy) and frequency domain (nanosecond). Furthermore, use of the density operator in particular lends itself well to a macroscopic approach on a quantum mechanical level. In addition, it is applicable to third order nonlinear Raman processes when Raman –resonant terms dominate and classical treatments are inadequate under such conditions. It should be noted that the classical Placzek model of
molecular polarizabilities does lead to rapid calculation of meaningful results and according to Druet et al [54], gives good insight into the physical mechanisms. However, we shall first follow the quantum mechanical treatment with the density operator and diagrammatic approach of Druet et al [54] to find a general solution for the third order CARS nonlinear susceptibility. Following this quantum mechanical treatment, a solution of the wave equation will be quoted in section 2.6 because it reveals the important properties of the signal generation including phase-matching and the spatial resolution for CARS measurements using focused beams.

2.3 Third-order Non-linear Polarization by Quantum Mechanics

As previously stated, the approach for the nonlinear third order susceptibility is using quantum mechanics, where the equation of motion is solved by using the density operator $\rho$ by means of a perturbative treatment of the field interactions. The density operator in general represents the quantum state of the molecules at point $\vec{r}$. However, in gases, the translational wavefunction using the density operator can quickly become a little complicated. Instead, it is assumed that the translational motion of the molecules is unchanged after application of the optical field. It should be emphasized that velocity changing collisions are neglected. In this way, a classical approach can be used for the translational motion. The density operator for a class of molecules with velocity $\vec{v}$ is simply the integral over the velocity distribution function $F(\vec{v})$:

$$\rho(\vec{r}, t) = \int \rho(\vec{r}, t, \vec{v}) F(\vec{v}) d^3\vec{v}$$ (2.3.1)

Where $\rho(\vec{r}, t, \vec{v})$ is the solution of the density operator evolution equation for the class of molecules with velocity $\vec{v}$, which is, in the laboratory frame:
\[
\frac{\partial}{\partial t} \rho(\vec{r}, t, \tilde{\nu}) + \tilde{\nu} \cdot \nabla \rho(\vec{r}, t, \tilde{\nu}) + \frac{\partial \rho}{\partial t}\bigg|_{\text{damping}} = \frac{-i}{\hbar} [H_0 + V(t), \rho(\vec{r}, t, \tilde{\nu})]
\]  

(2.3.2)

\(H_0\) is the Hamiltonian for an unperturbed isolated molecule with a discrete spectrum of eigenstates \(|\alpha\rangle, |\beta\rangle, |\gamma\rangle, \) and so on, that corresponds to eigenenergies \(\hbar \omega_\alpha, \hbar \omega_\beta, \hbar \omega_\gamma, \) etc. The interacting Hamiltonian, \(V(t)\), describes the coupling of the molecules with the electromagnetic fields in the electric dipole approximation, which assumes that the wavelength of the applied EM wave is much larger than the molecules responsible for the nonlinear optical response. Thus, from the molecule’s perspective at a given point in time, the E-field is essentially uniform spatially. In addition, before interaction with the EM field, the molecule is assumed to be in some initial state described by a wavefunction belonging to the same basis set as the ground state wavefunction. The perturbed wavefunction is written using this same basis set and it is a superposition of unperturbed wavefunctions where the ground state is assumed to dominate [58].

The interacting Hamiltonian is given by:
\[V(t) = \vec{\mu} \cdot \vec{E}(\vec{r}, t)\]  

(2.3.3)

The damping term \(\frac{\partial \rho}{\partial t}\bigg|_{\text{damping}}\) depends on the system of the interest. It usually includes stochastic processes such as molecular collisions and spontaneous emission. There are a variety of collisional theories to choose from and each have their own approximations that lead to a rather “simple” expression for the damping term [59]. Druet et al [54] lists three of these possibilities, (1) the assumption of stationary stochastic processes, (2) the impact approximation, and (3) the isolated line approximation. The CARSFT model mentioned in section 3.2 utilizes all three of these possibilities. Typically, with these approximations the damping term is expressed as a relaxation matrix. These assumptions are only valid when
pressures are under 1 atm. As the pressures in the work are \( \sim 0.05 \) atm, these assumptions are justified.

To illustrate these three approximations, consider a line frequency at \( \omega_{\alpha\beta} \) with width \( \gamma_{\alpha\beta} \), and an excitation with detuning \( \Delta\omega \) from the line. The impact approximation assumes that the collisional duration time, \( \tau_c \), is much shorter than (1) the time interval, \( \gamma_{\alpha\beta}^{-1} \), between collisions, and (2) the interaction time, \( \Delta\omega^{-1} \), between the molecules and EM-wave. The isolated line approximation assumes that there are no overlapping or lines so close together such that a collisional energy transfer from one line to another has appreciable probability. Thus, the terms that represent this coupling (off diagonal matrix elements, \( \rho_{\alpha\beta} \), can be neglected. At higher pressures, these coupling terms cannot ignored and are responsible for the collisional narrowing of Raman lineshapes observed in both spontaneous Raman and CARS.

These three approximation gives the following for the damping term:

\[
\begin{align}
\frac{\partial \rho_{aa}}{\partial t} \bigg|_{\text{damping}} &= \gamma_{aa} \rho_{aa} + \sum_{\beta \neq \alpha} W_{\alpha\beta} \rho_{aa} \\
\frac{\partial \rho_{\alpha\beta}}{\partial t} \bigg|_{\text{damping}} &= \gamma_{\alpha\beta} \rho_{\alpha\beta} = \left( \frac{(\gamma_{aa} + \gamma_{\beta\beta})}{2} + \gamma_{\alpha\beta}^e \right) \rho_{\alpha\beta} 
\end{align}
\]

where \( \gamma_{aa} \) is inversely proportional to the finite lifetime of state \( |\alpha\rangle \), \( \tau_a = \frac{\pi}{\gamma_{aa}} \). The finite lifetime results largely from spontaneous emission and inelastic collisions. The line broadening of the absorption line between states \( |\alpha\rangle \) and \( |\beta\rangle \) resulting from phase-interrupting elastic collisions is given by \( \gamma_{\alpha\beta}^e \). Finally the transition probability for a transition between states \( |\alpha\rangle \) and \( |\beta\rangle \) occurring due to an inelastic collision is given by \( W_{\alpha\beta} \). From equations (2.4.4a) and (2.4.4b) it is apparent that the damping term results in a Lorentzian line broadening.
It is assumed that all the EM waves are propagating parallel to each other along the z-axis. In the planar BOXCAR phase matching geometry that is employed in this work, the phase matching angles are on the order of \( \sim 0.6^\circ \). Given the very small angle, the assumption of \( \vec{k} \)-vector collinearity is valid for the work in this thesis and the system of equations reduces to a 1-dimensional approximation where \( \rho(\vec{r}, t, \vec{v}) \) is a function of the spatial coordinate \( z \) and the velocity component \( \vec{v}_z \). This reduces the second term in equation (2.3.2) to:

\[
\vec{v} \cdot \nabla \rho(\vec{r}, t, \vec{v}) = v_z \frac{\partial \rho}{\partial z} \tag{2.3.5}
\]

The solution to the equation of motion given by equation (2.3.2) is expanded in successive powers of \( V(t) \) due to the application of perturbation theory.

\[
\rho(z, t, v_z) = \rho^{(0)}(z, t, v_z) + \rho^{(1)}(z, t, v_z) + \rho^{(2)}(z, t, v_z) + \cdots + \rho^{(n)}(z, t, v_z) \tag{2.3.6}
\]

This solution is then substituted back into equation (2.4.1) to yield the net third-order polarization generated by the ensemble of molecules at frequency \( \omega_s \).

\[
\bar{P}^{(3)}(z, t, \omega_s) = N \text{Tr}\left[\rho^{(3)}(z, t, \omega_s)\vec{\mu}\right] + c. c. \tag{2.3.7}
\]

\[
= N \sum_{\alpha, \beta} \mu_{\alpha\beta} \int_{-\infty}^{+\infty} \rho^{(3)}_{\alpha\beta}(z, t, v_z, \omega_s) F(\vec{v}) dv_z + c. c.
\]

Note that the two terms \( \rho^{(3)}(z, t, \omega_s) \) and \( \rho^{(3)}(z, t, v_z, \omega_s) \) are the Fourier components of \( \rho^{(3)}(z, t, \omega_s) \) and \( \rho^{(3)}(z, t, v_z) \), respectively. Clearly, \( N \) is the number density. Finally, two last assumptions have been made here. First, all the eigenstates, \( |\alpha\rangle, |\beta\rangle, |\gamma\rangle \) and so on, were assumed to be non-degenerate so that the dipole operator, \( \vec{\mu} \), only has one matrix element connecting a pair of states. Second, it is assumed that in the discharge cell, rotational levels thermalize quickly and a Maxwell-Boltzmann velocity distribution is valid, such that the velocity
distribution is given equation 2.4.8, where $M$ is the molecular mass and $k_b$ is the Boltzmann constant:

$$F(v_z) = \left(\frac{M}{2\pi k_b T}\right) \exp \left[-\frac{(M v_z^2)}{2\pi k_b T}\right]^2$$

(2.4.8)

2.4 Diagrammatic derivation of $\chi^{(3)CARS}(\omega_3, \omega_1, \omega_2, -\omega_1)$

Comparison between equations (2.2.5) and (2.3.7) can lead to an expression for the third order nonlinear susceptibility tensor. However, this term is fairly large because it not only contains the intrinsic permutation symmetry which arises from the principles of causality and reality, but also the combinations of the different time-orderings in which the three optical frequencies occur. In other words, there are many time-orderings for which the frequency components in $V(t)$ can occur for each of the three applied EM waves. The density matrix itself is a statistical average of the many products of the wave-function and its complex conjugate; each of these products represent a possible evolution of the molecular state. However, we are only interested in those terms in the density matrix that are associated with CARS. According to Druet et al [54] and Gustafson et al [60], a time ordered diagrammatic representation can both precisely define and simplify the calculations for any time-ordered contribution to the density operator matrix. Here, the diagrammatic representation is a double-sided Feynman-like diagram where the time sequence of the density matrix elements with their successive perturbations is represented from bottom to top. Each perturbation is represented by a vertex on the left-hand or right-hand side depending on which subscript of the density matrix is changed by the interaction. For example, in the pure state case where the density operator is given by $\rho = |\psi\rangle\langle\psi|$, the evolution of $|\psi\rangle$ is depicted on the left hand side and it’s complex conjugate evolution, $\langle\psi|$, on the right hand side. Thus, the doubled sided diagrams allow
depiction of the time ordering of the perturbations of the wavefunction with respect to that of its complex conjugate which is important when the two cannot be decoupled (e.g. when broadening is negligible). It should be noted that the diagrams are sufficient even when the stats are not pure.

The rules for the double sided diagrams are as follows:

(1) Time evolution
   a. Time increases upward on the two parallel vertical bars

(2) Vertex
   a. Represents perturbation (or interaction) by an EM wave

(3) Eigenstates indicated below and above each vertex
   a. The Eigenstates between which the interaction Hamiltonian is operating

(4) Segment pointing from vertex
   a. Left placement
      i. Interaction is with a forward propagating wave
   b. Right placement
      i. Interaction is with a backward propagating wave

(5) Right or left vertical bar
   a. Placement of vertex on left bar corresponds to wavefunction
   b. Placement of vertex on right bar corresponds to the complex conjugate

The most general form for the perturbation is an integral expression which describes the evolution of the density matrix via its propagation through the intermediate states and interaction with the perturbations [61]. The integrations are performed with respect to the
variable $\tau$. Druet et al. [54] states that the matrix element $\rho_{\alpha\beta}^{(n+1)}(z, t, \omega_z)$ can be derived from the lower order density matrix element $\rho_{\alpha'\beta'}^{(n)}(z - v_z, t - \tau, \omega_z \pm \omega_j, v_z)$ by the use of equation (2.4.1) and the diagram illustrated in figure 2.2.

$$\rho_{\alpha\beta}^{(n+1)}(z, t, \omega_z) = \frac{i}{\hbar} \mu_{\alpha'\alpha} \bar{E}_j e^{\pm \phi j} \int_0^\infty d\tau \exp[-i\tau(\omega_{\alpha\beta} - i\gamma_{\alpha\beta})] \times \exp[-i(\pm \omega_j)(t - \tau) + i\pm kjz - v_z \omega_{\alpha'\beta'} \hbar n(z - v_z \tau, t - \tau, \omega_z \pm \omega_j)] \quad (2.4.1)$$

Here, $\omega_{\alpha\beta} = \omega_\alpha - \omega_\beta$ is the transition frequency for the transition $\alpha \to \beta$, and $\gamma_{\alpha\beta}$ is the linewidth of that transition (this incorporates the damping effects as described in section 2.3). The upper sign of $\pm /$ is taken when the segment in pointing down from the vertex, and the lower sign when it is pointing up from the vertex. If the transition from $\beta' \to \beta$ is considered instead of $\alpha' \to \alpha$, the dipole operator matrix $\tilde{\mu}_{\alpha'\alpha}$ must be replaced by $-\tilde{\mu}_{\beta'\beta}$.

**Figure 2.2:** Space-time domain diagrams connecting $\rho_{\alpha'\beta'}^{(n)}(z - v_z, t - \tau, \omega_z \pm \omega_j, v_z)$ and $\rho_{\alpha\beta}^{(n+1)}(z, t, \omega_z)$ in the case of an interaction with field components (a) $\exp[-i(\omega_j \tau + i(\pm kjz)]$ and (b) $\exp[i(\omega_j \tau - i(\pm kjz)]$

In rotational CARS, one must combine three vertices, at $\omega_3$, $\omega_2$, and $\omega_1$, in order to get the Polarization component, $\rho_{\alpha\beta}^{(3)\text{CARS}}(z, t, \omega_4 = \omega_3 - \omega_1 - \omega_2)$. The number of possible combinations for these vertices is quite large, which is even more so if numerous molecular states are used. However, for RCARS, there are four general energy levels that we are primarily interested in, as illustrated in figure 2.3. If the starting point is the initial density operator, $|a\rangle(a)$, and $|n\rangle$ is taken for the first transition, there are 24 susceptibility terms proportional to
Another 24 terms are obtained if \( |n'\rangle \) is taken for the first transition. If \( |n\rangle \) or \( |n'\rangle \) is used twice, an additional 48 terms are generated. Another 96 combinations are generated if \( |b\rangle \) is used as the initial state instead of \( |a\rangle \). Thus, there are at least 192 contributions in the susceptibility term proportional to \( \rho^{(0)}_{bb} \) and another 192 contributions proportional to \( \rho^{(0)}_{aa} \).

Assuming \( |n\rangle \) and \( |n'\rangle \) are not initially populated, these 384 terms constitute the entire susceptibility for the four-level system corresponding to the energy diagram for RCARS in figure 2.3.

![Energy diagram for RCARS with energy levels labeled for reference](image)

The majority of these 384 terms are negligible in RCARS if resonance conditions are considered. For example in RCARS, the scattering intensity is at a maximum when \( \omega_1 - \omega_2 \) is equal to a rotational quanta. In other words, we are only interested in those terms containing the Raman resonance \( \omega_{ba} - \omega_1 + \omega_2 \). Out of these 384 terms, there are 16 proportional to \( \rho^{(0)}_{aa} \) and another 16 proportional to \( \rho^{(0)}_{bb} \). When \( |n\rangle \) is the first transition, eight are distinct; these are illustrated in figure 2.4. The other 24 terms can be found through permutations on \( n \) and \( n' \). All 24 of these terms form the Raman part, \( \chi^{ab} \), of the third order nonlinear susceptibility (see equation 2.4.3)
Figure 2.4: Diagrammatic representation in the space-time domain of the Raman resonant contribution to $\chi^{(3)}$CARS where $|n\rangle$ is the first transition. The top four diagrams are contributions proportional to $\rho_{aa}^{(0)}$ and the bottom four are proportional to $\rho_{bb}^{(0)}$. The corresponding energy denominators are under the diagrams.

The spatial component of $\chi^{ab}$, with associated EM-wave polarizations, $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$, ($\hat{e}_i$ is the unit polarization vector of field $E(r, \omega_j)$, is as follows:

$$\hat{e}_4 \chi^{ab} \hat{e}_3 \hat{e}_1 \hat{e}_2 =$$

$$\frac{N}{\hbar} \sum_n \left( \frac{\mu_{4an} \mu_{1bn}}{\omega_{nt} - \omega_4 - i\gamma_{nt}} + \frac{\mu_{1an} \mu_{4bn}}{\omega_{nt} + \omega_4 + i\gamma_{nt}} \right) \times$$

$$\left[ \sum_n \left( \frac{\mu_{1bn} \mu_{2na}}{\omega_{nt} + \omega_2 - i\gamma_{na}} + \frac{\mu_{2bn} \mu_{1na}}{\omega_{nt} - \omega_2 - i\gamma_{na}} \right) \rho_{aa}^{(0)} - \left( \frac{\mu_{2bn} \mu_{1na}}{\omega_{nt} - \omega_2 - i\gamma_{nb}} + \frac{\mu_{1bn} \mu_{2na}}{\omega_{nt} + \omega_1 - i\gamma_{nb}} \right) \rho_{bb}^{(0)} \right]$$

(2.4.2)

where $\mu_{i\beta} \cdot \hat{e}_i = \mu_{i\alpha \beta}, N \rho_{aa}^{(0)}$ and $N \rho_{bb}^{(0)}$ are the initial number densities of the molecule in states $|a\rangle$ and $|b\rangle$. Again, it was assumed that states $|n\rangle$ and $|n'\rangle$ were not initially populated.
The rest of the 384 terms previously mentioned include terms for non-resonant processes such as two photon sum or difference frequency. Because they are non-resonant, these terms are very small and are all grouped together in a single non-resonant nonlinear susceptibility, $\chi^{NR}$.

Finally, if the molecules have a manifold of levels (e.g. many rotational levels), then the third order nonlinear susceptibility for CARS is:

$$\chi^{(3)CARS}(-\omega_4, \omega_3, \omega_1, -\omega_2) = \sum_{a,b} \chi^{ab} + \chi^{NR}$$  \hspace{1cm} (2.4.3)$$

Equation (2.4.3) can be related to the well-known spontaneous Raman scattering cross section $\frac{d\sigma}{d\Omega}$, which is given by:

$$\frac{d\sigma}{d\Omega} = \frac{1}{c} \omega_1 \omega_2^3 \left| \sum_n \frac{\mu_{1bn} \mu_{2an}}{\hbar (\omega_{na} - \omega_1 + i\gamma_{ba})} \right|^2$$  \hspace{1cm} (2.4.4)$$

Comparison of equations (2.5.2-2.5.4) gives the resonant part of the nonlinear-susceptibility in terms of the spontaneous Raman scattering cross section and is as follows:

$$\sum_{a,b} \chi^{ab} = \frac{N}{\hbar} \frac{1}{\omega_{ba} - \omega_1 + i\gamma_{ba}} \times \sum_{a,b} \left( \rho_a^{(0)} - \rho_b^{(0)} \right) \frac{d\sigma}{d\Omega} \frac{c^4}{\omega_1 \omega_2^2} \frac{1}{(\omega_{ba} - \omega_1 + \omega_2 - i\gamma_{ba})}$$  \hspace{1cm} (2.4.5)$$

2.5 Pure Rotational Coherent Anti-Stokes Raman Scattering Spectroscopy Computer Code

Example

The population of both the rotational and vibrational modes are temperature dependent, and thus, temperature information, as well as concentration can be extracted from CARS spectra. Martinsson and Aldén [41, 62], developed a computer code for rotational CARS to extract this information. From sections 2.2-2.4, it is clear that this information is encoded in the third-order non-linear susceptibility of the system, $\chi^{(3)CARS}$, as it is dependent on both the number density and the population difference density. The susceptibility describes how the
system couples to the applied EM fields on a molecular level. Because only rotational energy levels are excited, molecular rotational energy levels themselves are coupled to the EM field and \( \chi^{(3)} \), given by equations (2.4.3) and (2.4.5), is summed over all the rotational levels and over all the species \( n \) in the mixture, as shown in equation (2.5.1). Presumably, this summation is truncated at higher \( J \) where the population is not appreciable. The transition matrix elements were expressed in terms of the Raman cross section and were averaged over all molecular orientations in the ensemble. It should be noted that the laser frequencies were assumed to be far away from any electronic excitation (as it was implied the preceding sections).

\[
\chi^{(3)} = \chi_{nr} + \frac{1}{2} \sum_n \sum_{J_n} \frac{a_{J_nJ_n'}}{\omega_{J_nJ_n'} - \omega_1 + \omega_2 - \left( \frac{1}{2} \right) p J_n J_n'}
\]

(2.5.1)

In equation (2.5.1), \( \chi_{nr} \) is the non-resonant susceptibility of the gas mixture—which is a mole-fraction average over all the different species \( n \) in the mixture—and \( \omega_1 \) and \( \omega_2 \) are frequency components of the broadband pump and Stokes beams. The summation is over all the species \( n \) in the mixture and over all the different rotational quantum levels for species \( J_n \). Again, it is assumed that all the species are in their ground electronic state. The rotational Raman transitions are species specific and are denoted by \( \omega_{J_nJ_n'} \), where \( J_{nr} \) is equal to \( J_n + 2 \) for rotational CARS due to the Raman selection rule. In addition, \( p \) is the pressure and \( \Gamma_{J_nJ_n'} \) is the rotational Raman line broadening coefficient for species \( n \) for the transition between \( J_n \) and \( J_n' \).

The term \( \left( \frac{1}{2} \right) p \Gamma_{J_nJ_n'} \) in (equation 2.5.1) is qualitatively equivalent to the damping term \( i \gamma_{ba} \) in equation (2.4.5) and explicit information for this term can be found in [55]. Finally, the amplitude \( a_{J_nJ_n'} \) is equal to:

\[
a_{J_nJ_n'} = \frac{N}{\hbar} \frac{4}{45} b_{J_n} F_n(J_n) \zeta_{n,n'}^2 \Delta \rho_{J_nJ_n'}
\]

(2.5.2)
where $b^{J'J}_{n'}$ is the Placzek-Teller coefficient, which is a $J$-dependent coefficient that determines the rotational contribution to scattering amplitudes for diatomic molecules, $F_n(J_n)$ the correction to the rotational line-strength due to centrifugal distortion, and $\zeta_{n,v}^2$ is the polarizability anisotropy change due to vibrational anharmonicity. Finally, the normalized population difference, $\Delta \rho_{J_nJ_{n'}}$, is given by

$$
\Delta \rho_{J_nJ_{n'}} = \frac{g_{J_n}(2J_n+1)}{Q_{J_n}} \left[ \exp\left(-\frac{E(v_nJ_n)}{kT}\right) - \exp\left(-\frac{E(v_nJ_n+2)}{kT}\right) \right] \tag{2.5.3}
$$

where $g_{J_n}$ is a statistical weighting factor that depends on the nuclear spin, $Q_{J_n}$ is the parity-separated partition function, and $E(v_nJ_n)$ is the energy level of the molecule in vibrational state $v_n$ and rotational state $J_n$. It should be emphasized that equation (2.5.3) is the nuclear-rotational partition function for the normalized population difference.

The statistical weighting factor that is dependent on the nuclear spin is different for $O_2$ and $N_2$. Depending on the nuclear quantum state, homonuclear diatomic molecules will occupy rotational levels with even $J$, or odd $J$, or both. This is because the Pauli exclusion principle necessitates that the total wavefunction, including nuclear spin, be symmetric or antisymmetric with respect to the interchange of two identical nuclei [63, 64]. Thus, the wavefunctions of homonuclear diatomics are required to be eigenfunctions of the exchange operator $\hat{P}_{12}$ and the symmetry constraint on the total wavefunction is:

$$
\hat{P}_{12}\Psi = \pm \Psi \tag{2.5.4}
$$

where the plus sign holds for bosons and the minus sign for fermions. If the nuclear spin quantum number $I$ is integral, then the plus sign of equation (2.5.4) applies. If it is half-integral, the wavefunction must be antisymmetric and the negative sign applies in equation (2.5.4). It
should be emphasized that the wavefunction in equation 2.5.4 is the total wavefunction, such that

\[ \Psi = \psi_{el} \psi_{vib} \psi_{trans} \psi_{rot} \psi_{nuc} \]

where \( \psi_{el} \) is the electronic wavefunction, \( \psi_{vib} \) the vibrational wavefunction, \( \psi_{trans} \) the translational wavefunction, \( \psi_{rot} \) and \( \psi_{nuc} \) the rotational and nuclear wavefunctions, respectively. The vibrational wavefunction is always symmetric because it is a function of the displacement of the nuclei from equilibrium, and hence, not on the coordinates of the two nuclear. In addition, the translational wavefunction is also symmetric because the random motion of the molecules is isotropic. Therefore, we must only concern ourselves with the rotational, nuclear spin, and electronic wavefunctions.

The parity of the rotational wavefunction is dependent on \( J \) in homonuclear diatomics. To perform the interchange of the nuclei on the rotational wavefunction, a \( \hat{C}_2 \) operation is sufficient.

\[ \hat{C}_2 \psi_{rot} = (-1)^J \psi_{rot} \]  \hspace{1cm} (2.5.5)

Equation 2.5.5 clearly illustrates that the rotational wavefunction for a homonuclear diatomic is symmetric for even \( J \) and antisymmetric for odd \( J \). On the other hand, the nuclear spin wavefunction can have symmetric, antisymmetric, or both parts. For a given \( I \), there are \( 2I + 1 \) values of the projection of the spin onto the Z-direction. For spin-1/2 particles, this gives two orientations, \( \alpha \) (spin up) and \( \beta \) (spin down). There are a total of \((2I + 1)^2\) ways to combine these two spins on the two nuclei, which generates different nuclear spin wavefunctions. It turns out the parity and the corresponding weights for the \((2I + 1)^2\) nuclear spin wavefunctions are given by
\[(2I + 1)^2 = (2I + 1)(I + 1) + (2I + 1)I\]  \hspace{1cm} (2.5.6)

\[\text{total} = \text{symmetric} + \text{antisymmetric}\]

The total spin of \(^{16}\text{O}_2\) is zero and for \(^{14}\text{N}_2\) the total spin is 1. Both target species in this work are bosons. However, there is only one possible nuclear spin combination for \(^{16}\text{O}_2\), and it is symmetric with a statistical weight of 1. Conversely, \(^{14}\text{N}_2\) has a total of 9 different states, with 6 symmetric combinations and 3 antisymmetric combinations.

Finally, the electronic configurations for \(\text{O}_2\) and \(\text{N}_2\) must be considered. The \(\hat{P}_{12}\) operator can be broken down into three steps, \(\hat{C}_2\) where the nuclei are exchanged, \(\hat{i}_{el}\) to invert the electronic coordinates through the center of symmetry, and finally \(\hat{a}_{el}\) reflects the electronic coordinates through a plane perpendicular to the twofold rotation axis. The effects of these last two operations can be deduced from the electronic term symbols. The subscript \(g/u\) indicates if the wavefunction is symmetric or antisymmetric upon inversion, respectively. The superscript \(+/-\) reveals symmetry upon reflection, with the positive corresponding to symmetric and the negative to antisymmetric. The ground state electronic state of \(\text{O}_2\) is \(X^1\Sigma_g^{-}\); it is therefore symmetric (the operation of \(\hat{C}_2\) gives negative parity). \(\text{N}_2\) has a symmetric ground state, \(X^1\Sigma_g^{+}\). There are several excited states of nitrogen that are considered in the pin-to-pin work. However, the mole fraction of these excited states is very small and because they are quenched very rapidly after the discharge by atomic oxygen, any contributions by these excited states are very small. Thus, they are not considered.

The results of the \(\hat{P}_{12}\) operator on the total wavefunction for \(\text{O}_2\) and \(\text{N}_2\) are tabulated in table 2.1. As can be seen, the only allowed \(J\) levels of \(\text{O}_2\) are even. \(\text{N}_2\) has both even and odd \(J\)
levels, but the intensities for the even J are expected to be at least two times higher than the odd J because of the nuclear weights of 6 and 3 for even and odd, respectively.

Table 2.1 Symmetry of O\textsubscript{2} and N\textsubscript{2} wavefunctions under nuclear exchange

<table>
<thead>
<tr>
<th>SYMMETRY UNDER P\textsubscript{12}</th>
<th>(X^1\Sigma^\text{g}_\text{O}_2) (WEIGHT 1)</th>
<th>(X_1\Sigma^\text{g}_\text{N}_2) (WEIGHT 3)</th>
<th>(X_1\Sigma^+_\text{N}_2) (WEIGHT 6)</th>
<th>(\Psi\text{total})</th>
<th>(\Psi_\text{el})</th>
<th>(\Psi_\text{vib})</th>
<th>(\Psi_\text{trans})</th>
<th>(\Psi_\text{rot})</th>
<th>(\Psi_\text{nuc})</th>
<th>ALLOWED J</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X^1\Sigma^\text{g}_\text{O}_2) (WEIGHT 1)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Even (0,1,2,4,6,...)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X_1\Sigma^\text{g}_\text{N}_2) (WEIGHT 3)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>_</td>
<td>_</td>
<td>Odd (1,3,5,7,...)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X_1\Sigma^+_\text{N}_2) (WEIGHT 6)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Even (0,1,2,4,6,...)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figures 2.5 plots theoretical RCARS spectra for O\textsubscript{2} (top spectrum) and N\textsubscript{2} (bottom spectrum) at 300K (room temperature), \(~0.05\) atm (approximate pressure of experiments), and with a probe line width of \(~1.4\) cm\(^{-1}\), which is the experimental instrumental resolution, using the CARSFT code (discussed in section 3.2). The theoretical spectra are produced by first calculating the nonlinear susceptibility and then convolving with laser instrument functions to obtain a theoretical intensity. As can be seen, the N\textsubscript{2} spectrum has more rotational lines because both even and odd rotational lines are allowed; the statistical weighting difference between the odd and even lines are also evident in the N\textsubscript{2} spectrum. In addition, The N\textsubscript{2} spectrum is more intense than the O\textsubscript{2} spectrum. This is not because the rotational Raman cross section of N\textsubscript{2} is larger than that of O\textsubscript{2}, but because in the experimental conditions, N\textsubscript{2} comprises \(~70\%) of the volume, while O\textsubscript{2} is \(~20\%). The Raman cross-section of O\textsubscript{2} is in fact \(~2\) times that of N\textsubscript{2}[65] and the larger number density compensates for the smaller cross section.
Figure 2.5: Theoretical spectra using the CARSFT code for O\textsubscript{2} (top spectrum) and N\textsubscript{2} (bottom spectrum). The input parameters are 300K, p=0.05atm, and probe line width 1.4 cm\textsuperscript{-1}.

It should be emphasized that the difference in the line strengths among the J-rotational lines in figure 2.5 is not directly proportional to a Boltzmann distribution among the rotational levels. Instead, the difference in line strengths arises because the intensity of the CARS transition is proportional to the normalized population difference, $\Delta\rho_{J_n,J_n'}$, which is given by equation (2.5.3). In particular, Martinsson and Alén et al [62] calculate the intensity of a
theoretical RCARS spectrum, \( I_{4}^{(CARS)} \), by using equation (2.5.7) for each of the rotational lines where it is integrated over the two broadband laser profiles and one narrowband profile.

\[
I_{4}^{(CARS)}(\omega_4) = \int \int \int |\chi^{(3)CARS}|^2 l_1(\omega_1) l_2(\omega_2) l_3(\omega_3) \delta(\omega_1 - \omega_2 + \omega_g - \omega_4) d\omega_1 d\omega_2 d\omega_3
\]  

(2.5.7)

In equation (2.5.7), \( l_x(\omega_x) \) is the laser intensity of beam \( x \) at frequency \( \omega_x \), \( \chi^{(3)CARS} \) is given by equations (2.5.1-2.5.3), and the Dirac delta function, \( \delta \), couples the frequency components of the incident beams to the frequency components of the anti-Stokes beam. Equation (2.5.7) can be derived from the classical-wave equation given by equation (2.2.7). In particular, if the one-dimensional approximation is taken (described in previous sections) and \( E_i \) is an envelope of frequencies, using the classical wave equation given in equation (2.2.7) it can also be shown that the intensity of the RCARS signal is also equal to the following [54]:

\[
I_{4}^{(CARS)}(\omega_4) = \frac{16\pi^4\omega_4^2}{c^4\eta^2 n_2 n_3} |\chi^{(3)CARS}|^2 l_1(\omega_1) l_2(\omega_2) l_3(\omega_3) \left[ \sin \left( \frac{\delta k z}{2} \right) \right]^2
\]  

(2.6.8)

Where \( \delta k = k_1 - k_2 + k_3 \), \( \eta = \frac{t}{\sqrt{2}} \), and \( n_i \) is the frequency dependent first-order refractive index given by \( n_i = n(\omega_i) = \sqrt{1 + 4\pi \hat{e}_i \chi^{(1)}(\omega_i) \hat{e}_i} \).

From equation (2.6.8), it is clear that CARS depends on phase matching (\( \delta k = k_1 - k_2 + k_3 \)) in addition to the probe volume length, \( z \). If there is a mismatch in the phase matching, a corresponding decrease in the RCARS signal occurs. For example, if \( \delta k z - \Delta k z = 3 \), then the CARS signal drops by an order of magnitude [36]. In systems where the beams are not diffraction-limited or the refractive index is not very large, the phase-matching is easily achieved by a collinear arrangement of the incident beams. However, this leads to an unambiguous
resolution. It also introduces difficulty in distinguishing the RCARS signal from the probe beam as they are very close in signal frequency, within a few nm. Instead of a collinear arrangement, the phase matching scheme employed here is one of BOXCARS. Both the collinear and BOXCARS phase-matching geometrical arrangements are illustrated in figure 2.6.

![Collinear and BOXCARS phase-matching geometries](image)

*Figure 2.6: Cars phase matching approaches. Top: collinear, bottom: crossed beam or BOXCARS.*

In BOXCARS, the incident beams are arranged geometrically on a lens, such that there is an angular separation of the input frequencies until they reach the focal point, and again after the focal point. Hence, no RCARS can be generated until the incident beams meet at the focal point. The focal point is not an infinitely small point. Rather, spot size is determined by the beam waist which is dependent on the coherence of the beam and the focal length. This beam waist can be visualized as a cylinder, with a radial dimension, and length, z. The probe volume length can be shortened or lengthened for a given focal length by changing the angular separation of the beams. A larger angle corresponds to a shorter probe volume length and vice versa. In this way, the RCARS diagnostic can achieve high spatial resolutions. The angular separation also allows the probe beam to be spatially separated from the RCARS signal. By choosing the pump and Stokes beam frequencies so they are very different from the probe beam frequencies, the RCARS signal can be separated from the pump beam using long pass or
short pass filters. However, the trade-off for a higher angular beam separations (and higher spatial resolution) is a lower signal because a smaller volume corresponds to fewer molecules coupling to the applied EM fields. It should be noted that the appropriate phase matching angle can be determined by simple geometric considerations such that the angles are given by:

\[ n_2 \omega_2 \sin \theta = n_4 \omega_4 \sin \phi \]  \hspace{1cm} (2.5.9)

\[ n_1 \omega_1 \sin \alpha = n_3 \omega_3 \sin \beta \]  \hspace{1cm} (2.5.10)

\[ n_1 \omega_1 \cos \alpha = n_2 \omega_2 \cos \theta \]  \hspace{1cm} (2.5.11)

\[ n_2 \omega_2 \cos \theta + n_4 \omega_4 \cos \phi = n_1 \omega_1 \cos \alpha + n_3 \omega_3 \cos \beta \]  \hspace{1cm} (2.5.11)
Chapter 3: Experimental Apparatus

This work presents investigations of combustion processes that are coupled with two different highly non-equilibrium plasma systems. The commonality between the two systems is not only the low-pressure conditions (40 to 52 torr), but the high-voltage generator utilized to produce the nanosecond voltages, a discharge gap of 1-cm, and the diagnostic techniques utilized to probe the systems. They differ significantly in the electrode geometries and contain some minor differences in the gas composition. The first system constitutes a dielectric barrier discharge where a dielectric barrier is placed in the discharge gap between rectangular electrodes in a plane-to-plane geometry. The second system has no such dielectric barrier in the discharge gap; the electrodes are bare to the discharge and the electrodes are spherical, rather than rectangular. The gas composition for the former consists of Ar/O₂/fuel, and the latter has Air/fuel, where fuel is H₂ or C₂H₄ (both were examined). It should be noted that the first system throughout the thesis is referred to as the dielectric barrier discharge and the second system as the pin-to-pin discharge.

3.1 Pure Rotational Coherent Anti-Stokes Raman Scattering

Broadband pure Rotational Coherent Anti stokes Raman scattering (RCARS) is the primary diagnostic for this work and was similarly patterned for investigation in the dielectric barrier and the pin-to-pin discharges. The advantage of broadband CARS over narrowband or scanning CARS, is that it not only allows single shot acquisition of transient phenomena, but
reduces the overall spectra acquisition time when it is possible to average several spectra [56]. The general diagnostics set-up is illustrated in Figure 3.1. This was assembled by the author in its entirety for this work.

The second harmonic output of a picosecond Nd:YAG, ~150ps pulse duration, (Ekspla SL333) is divided into two beams using a half wave-plate and a thin-film polarizer. The ratio of power between the two beams can be adjusted by rotating the half-wave plate. The high power beam that is vertically polarized, is reserved to pump a homebuilt broadband modeless dye laser (described below). The horizontally polarized low-power beam is used to produce the probe pulse and passes through a second half wave plate to rotate the polarization so that it is orthogonal to the polarization of the pump pulse. For this work, the probe beam has horizontal polarization and energies ranging from ~1 to 5 mJ/pulse. The broadband modeless dye laser
was homebuilt by Aaron Montello [66] and is patterned after the work done by Sukesh Roy [56].

The schematic for the dye laser is shown in Figure 3.2.

![Figure 3.2: Schematic of the broadband modeless dye laser.](image)

In contrast to most lasers, there is no optical cavity in this dye laser, which allows generation of a broadband output free of any modal structures. There are three 10cm wide cuvettes. The first cell (oscillator) is side pumped with ~20% of the total energy pumping the modeless dye laser, and followed consecutively by side and end pumped amplifier cells, each pumped with 40% of the total energy input. A broadband high reflector is placed within 3mm of the first cuvette, allowing ~80% temporal overlap between the reflected photons of the spontaneous emission from the oscillator cuvette and the 532nm side-pump within the oscillator cuvette; this results in amplified spontaneous emission (ASE) from the first cell, which is intensified further in the two subsequent cells. It should be emphasized that the ASE from
this oscillator cuvette is highly non-uniform. It is critical to use an iris as a spatial filter to select the most uniform and intense portions of this output to further amplify. The outputs from the second and third stages are also spatially filtered by insertion of an iris. The second cuvette (pre-amp), is set approximately at Brewster’s angle into the propagating ASE pulse from the oscillator to suppress any horizontal polarization components in that pulse. The third cuvette (amp) is end pumped to improve the spatial profile of the beam. Both of these amplifier cuvettes are stationed such that there is maximum temporal overall between the outputs from the previous stage and the pulse pumping the cell; this occurs when gain is maximized. The last optic of this dye laser consists of a 600 mm lens to pseudo-collimate the dye beam.

A solution of Rhodamine 597 in methanol was used to generate the broadband output of the broadband modeless dye laser with a conversion efficiency of 16.8%, indicative that the medium is not saturated at these levels. The output is centered at ~573 nm with a FWHM of 210.33 cm⁻¹, or 6.8 nm, as shown in figure 3.3. For RCARS, the dye laser output is divided into two beams, a pump and Stokes, using a 50-50 beam splitter coated for vertically polarized light. A half wave plate and a polarizing beam splitter cube was inserted into the pathway of each beam so that the pump is vertically polarized and the Stokes is horizontally polarized. For this work, the energy outputs of each range from ~1 to 3.65 mJ/pulse.

As illustrated in figure 3.1, the pump, Stokes, and probe beams are focused into the test cell using a planar-BOXCARS phase matching configuration [36] (see section 2.5) producing a cylindrical probe volume with less than a 100-µm diameter and variable length depending on focal length of the focusing lens. The diameter of the probe volume was estimated based on the observations that the beams passed cleanly through a 100 µm pin hole, but not a 50-µm pinhole, regardless of whether the focal length was 500 mm or 150 mm. The interaction length
is measured by passing a thin microscope glass slide, with thickness of 100 µm, along the length of the probe volume and recording the FWHM of the integrated resulting non-resonant signal (figures 3.5 and 3.6).

![Dye Profile](image)

Figure 3.3: Profile of the dye laser output captured using a 0.75-m spectrometer equipped with a 1200 line/mm grating and an electron multiplied charge coupled device (EMCCD). The camera gate was set to 1 second and accumulated in the software 200 times. The gain is set to 100.

The RCARS signal is spatially filtered with two irises (not shown on the schematic) and focused using a 100mm spherical lens into a 0.75-m spectrometer equipped with a 1200 line/mm grating (Shamrock 750). The spectra are detected using a back-illuminated electron-multiplying charge coupled device (EMCCD, Andor). As will be discussed in chapter 4, it was found that the electron multiplying feature significantly improved the sensitivity for the RCARS system. For the work presented here, the EM-gain of the camera was set to 200 unless otherwise noted and the exposure time ranged from 20 to 250 seconds (200 to 2500 laser shots). In particular, the exposure time ranged from 20 to 40 seconds for the dielectric barrier discharge cell investigations and from 100 to 250 seconds for the pin to pin discharge work.

To further aid in signal discrimination and noise reduction due to scatter from the probe beam, a polarization approach was employed, which was developed by Vestin et al [57] and
utilized by Zuzeek et al [67] in her pure-rotational CARS work in low-pressure plasmas. Here, the signal and probe have orthogonal polarizations, as illustrated in figure 3.1.4, allowing for than a factor of 1000 reduction in the polarized stray light by insertion of a high extinction XEP-thin-film-polarizer from CVI into the CARS signal path. However, the CARS resonant and non-resonant signals are reduced to 9/16 and 1/9 of their values for parallel polarizations, respectively. This in fact helps to reduce the influence of the non-resonant background on the CARS spectrum.

![Figure 3.4: Planar BOXCAR phase matching configuration and corresponding polarizations utilized in this work. The pump, probe and stokes enter the first lens and focus at the middle of the test cell with vertical and horizontal polarizations respectively. The Stokes, Probe, CARS, and Pump beams exit the cell and through the second lens with horizontal and vertical polarizations respectively.](image)

mounted on a translation stage into the probe and Stokes beam paths. Using this variable delay, the temporal overlap of all three beams was maximized by maximizing the non-resonant signal obtained from a microscope glass slide. This was held constant for the entirety of this work.
The two different systems presented their own technical challenges, which could be partially overcome by changing the focal length. The dielectric barrier discharge had a long focal length of 500 mm whereas the pin-to-pin used a shorter 150 mm focal lens. For the dielectric barrier discharge, the main reason for using a longer focal length was to compensate for low signal resulting from low number density. Here, the target species is O\textsubscript{2}, with experimental partial pressures of \~6 to 8 torr. As shown in figure 3.5, this resulted in a probe volume length of \~3.9 mm which is the FWHM of a one term Gaussian fit to the experimental data with an R\textsuperscript{2} value of 0.9862.

![Figure 3.5: The integrated non-resonant signal obtained from a microscope glass slide for a focal length of f=500mm. The fit shown is a one term Gaussian with R\textsuperscript{2}=0.9862.](image)

On the other hand, the plasma in the pin-to-pin discharge had dimensions on the order of a few mm. As will be discussed in chapter 6, using a focal length of 500 mm artificially lowered the overall temperatures obtained by CARS because the probe volume encompassed both the hot discharge and the cooler surroundings. Switching to a shorter focal length of 150 mm, shortened the probe volume to \~0.5 mm, which is \~13\% of the previous volume length, as demonstrated in figure 3.6.
Figure 3.7: RCARS obtained in static room air, at room pressure and temperature. The energy input for both spectra are approximately the same, but not identical as laser power fluctuates by ~1% on a weekly basis. However, the camera conditions are identical: a 1-second exposure, 100-EM-gain, 3mHz read-out rate, and no preamplification is set.

Switching the focal length from 500 mm to 150 mm reduced the signal by ~55% as shown in Figure 3.7. The spectra shown here were obtained in similar conditions, in static room air at room pressure and temperature under similar RCARS energy inputs. The spectra
displayed in figure 3.7 are background subtracted out, but no other modifications to the spectra have been made (such as dividing by the non-resonant signal).

3.2. RCARS Data Analysis

The RCARS data presented in this work was analyzed using both in-house written software and the widely used Sandia CARSFT code[68, 69]. The CARSFT code calculates the theoretical spectra for CARS and allows least squares fitting to the experimental data. Because the intensity is proportional to the square root of the third-order nonlinear CARS susceptibility, the theoretical spectra generated is this susceptibility itself. Thus, before comparison with the code, the square-root of the spectrum must be taken. Nevertheless, the theoretical spectrum can have a convolution with a line shape that can either be single or double. The single convolution is a convolution with a spectrum that combines both the pump and probe. In the double convolution, each laser is considered separately for convolution with the theoretical spectrum. It is this second approach that is used in this work. It should be noted that there is an option to read the laser shape in from a file, which is particularly useful if the probe is broadband (which is not the case in this work) because the code assumes a default Gaussian line shape for the lasers. Any line-shape read in from file is also advantageous because it will include information regarding the spectrograph resolution and associated optical system. However, for this work, the default Gaussian line-shape was utilized and the code was allowed to iterate the line widths during the minimization routine to save on computational time for reasons related to grid size, which is discussed next.

The grid size in the code is determined by the minimum of the smallest Raman line width in addition to the pump and probe laser widths. If the probe laser line shape is read in from a file, the line width is assumed to be an approximate value and still used in determine the
grid size, although it is not used in the calculation itself as it should not be allowed to vary during
a fit. This typically results in a reasonable grid that allows calculations within a few minutes.
However, at low pressures and high pressures (not moderate pressures), the code assumes an
isolated line model where each transition is considered to produce a Lorentzian lineshape
centered at the transition wavenumber. In the least-squares fit, each of the Lorentzian
equations is evaluated at that wavenumber and the results are summed. (This approach is valid
at high pressure, only if the temperature is sufficiently high that there is no mixing of adjacent
lines (collisional narrowing). This isolated line model slows down the calculations considerably,
increasing the time to ~5 minutes per spectrum. To reduce the computational time, the
pressure was increased, and the line widths for the pump and probe decreased substantially and
allowed to iterate during the calculations. It should be emphasized that this treatment of the
lineshapes in the code does not reflect the physical reality of the experiments where the
spectral resolution is limited by the instrumental function. In the experiments, the expected
Doppler broadening at 40 torr and 300 K is on the order of 1.2 GHz ~ 0.001 nm ~ 0.04 cm⁻¹. In
addition, the probe laser linewidth is ≤ 0.1 cm⁻¹. Furthermore, pressure and natural broadening
is much less than 0.5 cm⁻¹. The instrumental function limits the spectral resolution to ~0.02 nm,
which is ~1.4 cm⁻¹. Therefore, increasing the pressure in the CARSFT code and increasing the
probe linewidth to ~ 1 cm⁻¹ to emulate the instrumental function is justified.

While not important for this work, the code does use a different profile for high
temperatures, which is a Voigt profile. This accounts for Doppler broadening. However, Dicke
narrowing and hard collisions profiles are not included in this code. It should be emphasized
that the Doppler contribution is often under-estimated for BOXCARS since pump and probe are
assumed parallel.
Before the spectra were compared to theory in CARSFT, they were processed using in-house codes written in MatLab. The first step was to subtract background light from the spectrum. The background light was collected by blocking the Stokes beam. The prevented the generation of RCARS and allowed recording of the scattering of the probe and pump beams. Recall from figures 3.1 and 3.4 that the RCARS signal travels alongside the pump beam. If the pump is blocked, rather than the Stokes Beam, the background subtraction results in a heavily slanted baseline due to residual Stokes beam, as shown in Figure 3.8.

Figure 3.8:
Top: Typical RCARS spectrum in Ar-O$_2$ at 40 torr at a burst size of 451 pulses with background subtracted, where the background is taken with the Pump beam blocked. Bottom: Typical RCARS spectrum in Ar-O$_2$ at 40 torr with no discharge present with background subtracted, where background is taken with the Stokes beam blocked.
Next, the shape of the broadband dye laser was removed from the spectra by dividing by a “non-resonant” reference spectrum. This reference spectrum was obtained daily before data collection by insertion of a 1mm thick microscope glass slide in the middle of the RCARS probe volume. This microscope slide has no resonances in the spectral range of interest, and, thus, the CARS signal generated mirrors that of the broadband dye laser. This reference spectrum also accounts for the convolution of the probe with this broadband dye laser. A typical non-resonant reference spectrum is shown in figure 3.9.

![Background Subtracted Non-Resonant](image)

*Figure 3.9: Typical non-resonant reference spectrum obtained using a 1mm thick microscope glass slide. A background spectrum has been subtracted from the spectrum shown here. The red curve is a two term Gaussian fit with $R^2$ value of 0.9902.*

It was found that an auto-correlation of the dye laser profile was not sufficient to account for the dye laser profile, as it had been in Zuzeek’s work [70]. It was also found that it was not possible to obtain a useable non-resonant signal using argon as in Montello’s or Cutler’s investigations [42, 66, 69], which was preferable because such a signal would have accounted for the test cell optics. However, the very polarization approach utilized to reduce the non-
resonant signal in effort to maximize the CARS signal, rendered the non-resonant signal too weak to capture a true full profile.

Figure 3.10: Typical RCARS spectrum after division by a non-resonant reference spectrum in Ar-O\textsubscript{2}, P=40 torr, no discharge present. The spectrum has already been background subtracted and normalized before division.

Division by the non-resonant reference spectrum introduces an exponential curvature in the baseline, as shown in figure 3.10. This baseline is fit to an exponential curve and subtracted from the spectrum. The spectrum is then normalized and the square root of the intensities were taken to convert from intensity to susceptibility for comparison with the CARSFT theoretical spectra. Figure 3.11 shows a typical spectrum that is input into the CARSFT code.

Finally, CARSFT compares theoretical spectra to the experimental spectra by iterating parameters temperature, pressure, composition, and line widths, to minimize the function, \( \chi^2 \), where ‘k’ is the pixel number of wavelength of the spectrum.

\[
\chi^2 = \sum_k \frac{(\text{theory}(k) - \text{data}(k))^2}{\text{data}(k)}
\]  

(3.2.1)
As can be concluded from equation 3.2.1, it is assumed that the optimum description for the set of data and the fit, is one which minimizes the weight sum of squares of deviations between the data and the fitting function. It can generally be considered a “goodness of fit” parameter. When values of $\chi^2$ are less than one, the fits between the data and theory is fairly reasonable, as judged by eye. When $\chi^2$, is greater than one, there are significant discrepancies by visual inspection. For this work $\chi^2$ values range from 0.02 to 0.4, depending on the noise level in the baseline.

![Figure 3.11: Typical RCARS spectrum that goes into the CARSFT code. This was taken in Ar-O2, P=40 torr, no discharge present.](image)

### 3.3 High Voltage Generator

The high voltage generator used in this work was custom designed and built at the Ohio State University [71, 72]. It is capable of generating alternating polarity pulses with peak voltage of 10-30 kV with pulse duration from 30 to 60 ns at a pulse repetition rate up to 50 kHz. This high voltage is produced by using magnetic pulse compression. The output voltage is regulated by varying the voltage of a DC power supply (Heizinger HN 1200-01, 0-1200 V, 0-100 mA) which
provides input to the pulse generator. It should be noted that increasing DC input voltage reduces the output pulse duration. Nonetheless, it was found that these output high-voltage pulses can be approximated by a Gaussian shaped pulse:

\[ U = U_{peak} \exp \left[ -\left( \frac{t - t_0}{\tau} \right)^2 \right] \]  \hspace{1cm} (3.3.1)

Figure 3.12, taken directly from [71], shows typical positive and negative polarity pulse waveforms for DC input voltages 560 V, 640 V, 720 V, and 800 V, in 10 torr of N\(_2\) at a frequency of 10 Hz. For these input voltages, it was found that \( \tau \) in equation (3.3.1) is 45 ns, 38 ns, 30 ns, and 26 ns, respectively, and for pulse duration at FWHM of 75, 63, 50, and 44 ns, respectively.

\[ \text{Figure 3.12: Typical positive and negative pulse waveforms generated by the high voltage generator for different input DC voltage, in N}_2 \text{ at P=10 torr and frequency 10 Hz.} \]

It should also be noted the high voltage generator produces its own trigger output pulse 400 ns before the main high voltage pulse for synchronization with optical diagnostics. This output trigger pulse has very little jitter relative to the main high-voltage pulse generated for the discharge; there only ~1 ns jitter for positive polarity pulses and less than ~2ns jitter for the negative polarity pulses. However, this trigger pulse was not utilized for synchronization in this
work for two reasons. First, the arrival of the beams at the RCARS prove volume is about 1.5 ms to 2 ms after the laser fires. This means that if the laser were triggered by the rise of the main pulse output of the high voltage generator, the plasma would already have been generated and dissipated before the arrival of the beams at RCARS probe volume. By delaying the laser trigger, it could be possible to sync the arrival of the beams with the next high voltage generator output. However, it was noticed that for the pin-to-pin work there was significant jitter in the main pulse, ~50 ns relative to a trigger in from the Stanford delay generator. It was therefore decided to use an 8-channel digital delay generator as the master clock. Similar synchronization schemes were used for investigations in dielectric barrier discharge cell and the pin-to-pin (described further in sections 3.4 and 3.5).

3.4 Dielectric Barrier Test Cell

The dielectric barrier discharge cell employed in this work is similar to those previously used in our lab for plasma assisted combustion studies [2, 73-75]. Here, the copper electrodes with dimensions 14 mm x 65 mm are encased in an acrylic plastic (as opposed to being situated in a silicon-adhesive-filed macor) and there is no direct contact between the ambient air and the electrodes. The edges of the electrodes are curved to enhance electric field uniformity, and thus, plasma uniformity.

![Figure 3.13: Schematic of dielectric barrier discharge test cell.](Image)
The design of the test cell is illustrated in figure 3.13. It comprises chiefly of a rectangular quartz channel that is 220 mm long, and 22 mm by 10 mm inner cross section, with wall thickness of 1.75 mm. This rectangular quartz channel is attached via Torrseal adhesive to two MDC ‘t-nipples’ to enable connections to both the gas delivery system and to another MDC flange modified for optical access. These modified flanges typically consist of a “kwik” flange that has a bore with a lip for an optical window to rest on. Optical windows are easily attached by epoxying the window onto this lip of the bore in the MDC flange. Thus, it is possible to easily switch among different optics to match current experimental needs.

H₂, C₂H₄, and O₂-Ar mixtures (premixed) at various equivalence ratios were used for investigations at a constant standard volumetric flow rate of 700 sccm. Fuel and flow rates through the test cell were metered by MKS mass flow controllers. A calibration curve for these controllers was obtained using a DryCal rotameter (Defender 520). It was observed during this calibration that the flow rates fluctuated on average less than 0.5%. A tee was inserted into the flow out gas line, to connect to a pressure sensor about a foot away from the cell and to a variable valve at the other end of the tee that connected to the vacuum pump. The total pressure was set to 40 torr by use of the variable valve and held constant for the duration of the experiment. It should be noted that the C₂H₄- mixtures leave a deposit on the windows that simultaneously reduces the CARS signal and increase probe beam scatter. Thus, the experiment was paused several times daily for window cleaning once the signal fell below a certain threshold for cleaning.

The electrodes are attached to the high voltage generator described in section 3.3, which is operated in a repetitive burst mode as illustrated in figure 3.14. In this mode, a rapid burst of a predetermined number of pulses is generated. The burst is also repeated, but at a
slower rate. In this work, a varying burst size from 15 to 401 pulses, or 0.37 ms to 10 ms long bursts, was examined. These individual pulses were repeated at a rate of 40 kHz. The peak applied voltage of a single pulse is 20-kV. The whole burst is repeated at 10 Hz, which matches the laser diagnostic repetition rate. The current and voltage waveforms are discussed in more detail in chapter 4. All the RCARS data presented in this work for the dielectric barrier discharge is taken at Δt=35 µs after the end of the burst. The standard flow is set to a total of 700 sccm for all mixtures, which means the peak velocity in the cell is ~1.0 m/s, for a residence time of ~0.065 s in the discharge region, which is 35 ms before the next burst occurs. Thus, the flow rate is sufficiently fast to ensure the flowing gas experiences only a single burst, but sufficiently slow that the probed gas experiences the full set of pulses within the burst.

![Repetitive Burst Mode](image)

*Figure 3.14: Schematic of Timing Scheme for Dielectric Barrier Discharge Cell.*

The test cell is mounted onto a vertical translation stage to allow alignment of the dielectric barrier discharge plasma to the RCARS probe volume. Synchronization of the RCARS probe volume and the plasma was made possible by utilizing two separate Stanford Research delay generators, one 8-channel capable of triggering in “burst” mode and the other a standard 4-channel, incapable of triggering in “burst” mode. The 8-channel delay generator served as the master clock and triggered the high voltage generator in “burst” mode and generated a single pulse at 10 Hz to trigger the second 4-channel delay generator. This second 4-channel generator
produced two 50-Ω pulses, one to trigger the laser flash-lamps, and the second, 1.5 ms later, to trigger the electro-optic (Qswitch). Because of the long delay from laser trigger to the RCARS probe volume, additional delays as a function of burst size, was included in the synchronization. For short bursts, up to 51, an extra delay was set on the 8-channel. For longer bursts, from 101 pulses and up, an additional delay was set on the 4-channel triggering the laser. It should be noted that the laser triggered the camera.

### 3.5 Pin to Pin Discharge Test Cell

The pin-to-pin discharge cell is similar to those used in previous work at the Ohio State University [66, 76, 77] to study stable, reproducible point-to-point discharges where the filament dimensions are sufficiently small to achieve significant specific energy loading, yet large enough to both readily enable diagnostic studies and reduce mass diffusion effects. However, the cell design was modified to fit the needs for an RCARS diagnostic and the new test cell was fabricated by Tim Henthorne, the OSU chemistry department glass blower. As shown in figure 3.15, chief among the modifications was an increase of the cell diameter from 1.5” to 3” to achieve a spatial resolution with a steeper phase matching angle than used in the dielectric barrier discharge work. Two side arms extending from the cell center with a 2” diameter and 3” arm length were added to the cell design in addition to two small side arms extended above and below for insertion of electrical feed throughs (MDC high power, 20,000-V, 15-A, 1-pin-del-seal-CF). All of the cell ends are torr-sealed into MDC flanges. These changes to the cell design makes it possible to easily repurpose the cell for other experimental needs. For instance, the electrical feed-throughs can be exchanged for higher or lower voltage and current requirements. OH-LIF, O-atom TALIF, and NO LIF laser diagnostics can easily be performed using the smaller side arms, or to conserve gas, additional gas inlet and outlets can be added so that
the flow can be directed down the 2” side arms rather than the main body of the cell with the 3” diameter. Changing the optical windows for different laser diagnostics is fairly straightforward because just like in the dielectric barrier discharge cell, windows are epoxied into the bore of MDC flanges; the flanges can easily be attached and removed. For this reason, the large windows are epoxied into large ISO flanges that use band clamps (rather than claw clamps) for ease of exchange. Also note that the cell in this pin-to-pin investigation is entirely composed of glass rather than a plastic acrylic as in the previous experiments to increase the longevity of the cell. The acrylic cell requires threaded bores drilled into the cell itself and plastic screws. Both the plastic screws and the threading in the cell strips easily over time.

Figure 3.15: Schematic of the pin-to-pin test cell. Note that the optical access in the center corresponds to side arms with diameter of 2” and length 3”.

The copper electrodes themselves are 2.6” long and are bare to the discharge gas; there is no dielectric inserted between the electrodes. As shown in figure 3.16, the top 0.5” is hollow to allow the electrodes to slide over the electrical feed-throughs. There are two threaded thru holes in this top hollow 0.5” of the electrode, so that the electrode can be anchored to the feed
through via screws. This allows the electrode gap to vary to meet the desired experimental conditions. The bottom ~7.5 mm of the electrodes consist of solid ~7.5 mm spheres. Using calipers, the top electrode was measured to be 7.47 mm and the bottom electrode to be 7.36 mm. For the work here, the electrode gap was set to 9.0 cm.

The electrodes are attached to the high voltage generator described in section 3.3, which is operated in single pulse mode. In this mode, a single trigger was sent to the high voltage generator at 60 Hz. This generated a current-voltage waveform of three separate pulses, a pre-pulse, a main-pulse, and a third small pulse in the voltage waveform only with peak applied voltages of ~ 4.4 kV, 4.6 kV, and 1.0 kV, respectively. The waveform is discussed further in section 6.1.

![Schematic of spherical electrodes for pin-to-pin discharge cell.](image)

The test cell is mounted onto a vertical translation stage mounted onto two horizontal translation stages that are transverse to each other to allow alignment of the pin-to-pin plasma.
to the RCARS probe volume. Alignment was done in real-time at the beginning of each day by subtraction of the background from the RCARS spectrum and recognizing that an intensity ratio of two peaks provided a rough comparison for temperature between two spectra. For example, the intensity ratio of a peak at 528.2 nm to a peak at 530.1 nm should increase with temperature as peak at 528.2 nm becomes more populated and the peak at 530.1 nm becomes less. Again, synchronization of the RCARS probe volume and the plasma was made possible by utilizing two separate Stanford Research delay generators, one 8-channel as the master clock and the other a standard 4-channel, triggering the laser, which then triggers the camera. Because the laser is triggered at 10 Hz and the high voltage generator is triggered at 60 Hz, every 6\textsuperscript{th} waveform generated is probed by RCARS. A variable delay for the laser trigger is set on the 8-channel Stanford box such that the RCARS can temporally scan relative to the pre-pulse from 1ms beforehand to 2.5ms afterwards. The standard volumetric flow was set to match previous O-atom TALIF and NO LIF experiments under similar conditions. Air was set to 310 sccm for all mixtures. H\textsubscript{2} was set to 18 sccm for $\phi=0.14$, 54 sccm for $\phi=0.42$, and 107 sccm for $\phi=0.83$. Ethylene had the following standard flow rates 4, 10, 18, and 36sccm for $\phi=0.19$, $\phi=0.48$, $\phi=0.87$, and $\phi=1.47$, respectively. This corresponds to a flow velocity of ~20 mm/s at room temperature for each of the mixtures, at 52 torr, and a circular cross section with a 3” diameter. This is sufficiently fast that to ensure that the RCARS probe volume length of 0.5mm experiences one pulse and that most heat diffuses out of the discharge region before the next pulse.

Just like in the dielectric barrier discharge cell, H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, and O\textsubscript{2}-Air mixtures (premixed) at various equivalence ratios were used for investigations. It should be noted that the pin-to-pin discharge contains nitrogen, while the dielectric barrier discharge did not. Fuel and flow rates through the test cell were metered by MKS mass flow controllers. A tee was inserted into the
flow out gas line, to connect to a pressure sensor about two feet away from the cell and to a variable valve at the other end of the tee that connected to the vacuum pump. The long distance between the discharge cell and the pressure sensor was necessary for two reasons. The RCARS test cell was translated entirely out of its area every day for RCARS alignment. This spanned a distance just over a foot. Furthermore, the gas line itself was at the top of the cell, which was over a foot off the table. The pressure was choked to a read-out pressure of 40 torr. Due to the large distance between the cell and the pressure sensor, this corresponded in actuality to a pressure of 52 torr. It should be noted that just like in the dielectric barrier discharge cell, the C$_2$H$_4$ mixtures leave a deposit on the windows that simultaneously reduces the CARS signal and increase probe beam scatter. Thus, the experiment was paused several times daily for window cleaning once the signal fell below a certain threshold for cleaning.
Chapter 4: Dielectric Barrier Discharge Cell Studies

The main objective of this work is to produce reliable, spatially and temporally resolved experimental temperature data for various combustion mixtures excited by nanosecond duration, high voltage electric discharges. In general, both plasma and combustion chemistry consists of many chemical reactions that are typically highly temperature dependent. It is crucial to produce accurate temperature data as a complement to species concentration data for validation of plasma chemical oxidation models in plasma assisted combustion systems.

The plasma chemical oxidation model used in the plane-to-plane dielectric barrier discharge configuration incorporates an energy equation for the temperature on the centerline with one-dimensional flow equations. By inclusion of heat transfer to the walls, which is assumed to be the dominant energy loss mechanism, this one-dimensional approximation becomes “quasi”-one dimensional. Application of this approximation in the kinetic and heat transfer analysis can only be justified if the plasma is diffuse and uniform throughout the experiment. If the plasma is non-uniform, it becomes difficult to decouple the non-equilibrium chemistry effects from thermal heating occurring in filaments and hotspots. Not to mention that such filaments and hotspots would require a complex and computationally intensive three dimensional model. This chapter will first briefly overview mechanisms that can lead to such filamentations, or plasma instabilities. It will then examine UV images for any evidence of such instabilities in the plane-to-plane dielectric barrier discharge plasmas. Finally, measurements of
energy coupled by the nanosecond high voltage electric pulses will be presented and compared with theoretical models.

4.1. Origin of Plasma Instabilities

Plasma instabilities can arise from a variety of phenomena. For low pressure, low temperature, non-equilibrium plasmas such as those examined in this work, instabilities typically arise from the system’s tendency to restore thermodynamic quasi-equilibrium between different degrees of freedom (i.e. electron, vibrational, and translational for instance). A very good conceptual and mathematical description of the underlying mechanisms of this tendency is provided by Alexander Fridman and Lawrence A Kennedy [51], Hass [78], and Nighan and Wiegand [79]. The discussion that follows is taken from their description concerning thermal and ionization instabilities leading to contraction in the plasma—where the plasma “self compresses” into one or several bright current filaments. Such contraction significantly changes plasma parameters and the plasma filament formed is close to quasi-equilibrium and no longer the desired strongly non-equilibrium. This is another reason why a volumetric and diffuse plasma is so desirable.

The most basic mechanism for a thermal instability is an ionization instability, which is a closed chain of casual links that is described in equation (4.1.1). This chain is initiated when a localized increase in electron density, \( \delta n_e \), does not dissipate rapidly.

\[
\delta n_e \uparrow \rightarrow \delta T_0 \uparrow \rightarrow \delta n_0 \downarrow \rightarrow \delta \left( \frac{P}{n_0} \right) \uparrow \rightarrow \delta n_e
\]  

(4.1.1)

Under these conditions, the electron impact intensifies locally, resulting in a gas Joule heating and an increase of temperature \( \delta T_0 \). If pressure is constant, \( p=n_0 T_0 \), then the localized
heating decreases the gas density, $\delta n_0$, and therefore, a corresponding increase in the reduced electric field, $\delta (E/n_0)$ (assuming the electric field, E, is constant). Finally, the increase of the reduced electric field, $\delta (E/n_0)$, further intensifies the electron concentration, $\delta n_e$, thereby creating a positive feedback loop. It should be emphasized here that the ionization rate increases with increasing reduced electric field, $E/n_0$. As such, a very small, initialized localized overheating, $\delta T_{00}$ (the initial perturbation of temperature), grows exponentially:

$$\delta T_0(t) = \delta T_{00} \exp(\Omega t)$$ \hfill (4.1.2)

Here, the parameter, $\Omega$, of the exponential growth is referred to as the instability increment. This can be related to the ionization rate directly by linearization of the differential equations for heat and ionization balance, which are dependent on the discharge conditions. Nonetheless, such an exponential increase in the temperature is what leads to the formation of the hot filaments (or contraction). Typically, these instabilities occurs on a millisecond timescale. If the characteristic time of energy coupling by the discharge pulse is reduced, it could potentially prevent such instabilities from forming [80]. This is one of the motivations behind using a nanosecond discharge in this work. These instabilities could also be inhibited by the addition of a diluent that can enhance diffusion and thermal conductivity, not only delaying onset of ionization heating, but preventing these from forming by carrying away the increased heat.

The ionization heating instability just described is initiated primarily by electron impact resulting in gas heating. This would most definitely be the dominant thermal mechanism for plasmas composed of monoatomic gases. However, molecules have additional degrees of freedom—both rotational and vibrational. For these gas mixtures, a localized increased in
electron density, $\delta n_e$, can lead to intermediate vibrational excitation rather than directly to $\delta T_0$.

It should be noted that for the systems of interest, there exists fast vibrational excitation and a relatively slow vibrational VT-relaxation, $\tau_{VT} \nu_{T_p} \gg 1$, where $\tau_{VT}$ is the VT relaxation time and $\nu_{T_p}$ is defined below. (Andrey Starikovskiy [81, 82] states timescales as long as tens of microseconds for atmospheric pressures). Thus, for this work, thermal instability could be sensitive to VT-relaxation. In cases where thermal instability is sensitive to VT-relaxation, the instability increment, $\Omega$, can be expressed as:

$$\Omega_T = \frac{b}{2} \pm \sqrt{\frac{b^2}{4} + c}$$  \hspace{1cm} (4.1.3)

Where the parameters ‘b’ and ‘c’ are:

$$b = \frac{1}{\tau_{VT}} \left(1 - \frac{\partial \ln \nu_{T_p}}{\partial \ln \nu_{T}}\right) + \nu_{T_p} (2 + \hat{\nu}_{VT})$$  \hspace{1cm} (4.1.4)

$$c = \frac{\nu_{T_p}}{\tau_{VT}} \left(-\frac{\partial \ln n_e}{\ln n_0}\right) \left(1 - \frac{\partial \ln \tau_{VT}}{\partial \ln \nu_{T}}\right)$$  \hspace{1cm} (4.1.5)

Here $\nu_{T_p}$ and $\hat{\nu}_{VT}$ are:

$$\nu_{T_p} = \frac{(\gamma - 1)}{\gamma \left(\frac{\varepsilon_v}{p}\right)}$$  \hspace{1cm} (4.1.6)

$$\hat{\nu}_{VT} = \frac{\partial \ln \nu_{VT}}{\partial \ln T_0}$$  \hspace{1cm} (4.1.7)

where $\varepsilon_v$ is the vibrational energy of the molecule, $\gamma$ is the specific heat ratio, $p$ is the pressure, and $\sigma$ is the plasma conductivity. Thus, $\nu_{T_p}$ is the frequency of gas heating by electric current under constant pressure. On the other hand, $\hat{\nu}_{VT}$, is a dimensionless factor. It accounts for the sensitivity of vibrational relaxation time to changes in temperature. This factor is usually $\sim 3$ to $5$. 

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Analysis of equation 4.1.2 shows that there exist two possible “modes” for instability, a thermal mode and a vibrational mode. This is because in order for thermal growth to occur, \( \Omega_T \) in equation 4.1.3 must be positive. There are two roots in equation 4.1.3, and, hence, the origin of the two modes. If the negative root is considered, ‘c’ must be less than \( b^2 \), and the mode is considered thermal. If the positive root is taken, the ‘c’ parameter must be greater than zero, \( c > 0 \) for a vibrational mode.

The *thermal mode* arises exclusively when the negative root of equation 4.1.3 is considered. Since the rate of vibrational excitation is high, \( \tau_{VT} V_{T_p} \gg 1 \), not only is ‘c’ less than \( b^2 \), but it is significantly less so, \( c \ll b^2 \). Under this condition, equation 4.1.3 becomes:

\[
\Omega_T = |b| \approx -v_{T_p}(2 + \hat{\tau}_{VT}) = k_{VT} n_0 \frac{h \omega}{c_p T_0} (\hat{k}_{VT} - 2) \tag{4.1.8}
\]

\[
\hat{k}_{VT} = \frac{\partial \ln k_{VT}}{\partial \ln T_0} \tag{4.1.9}
\]

Like \( \hat{\tau}_{VT} \) in equation 4.1.4, \( \hat{k}_{VT} \) is also a dimensionless factor. Instead of accounting for the sensitivity of the vibrational relaxation time to changes in temperature, it shows the sensitivity of the rate coefficient for V-T relaxation to changes in temperature. This factor is usually \( \sim 3 \) to 5. Note that in this case, there contain no terms for ionization in the increment instability parameter, \( \Omega_T \). Note also the multiplication of the frequency of heating by \( (\hat{k}_{VT} - 2) \). This factor arises from Laundau-Teller formula, which assumes a harmonic oscillator and results in a strong exponential dependence of the relaxation rate coefficient on the gas temperature. Thus, in the thermal mode instabilities are driven by local thermal heating due to VT relaxation. Even small increases of the translational temperature significantly decreases VT relaxation time, \( \tau_{VT} \), further intensifying the energy release within the gas due to vibrational relaxation. If thermal
conduction is insufficient to dissipate heat and back pumping of vibration is inefficient in reabsorbing this energy, the gas temperature will continue rise, producing a runaway condition. 

Since the pressure remains, to the first order, constant during the linear stage of the instability, the gas density drops and local electrical conductivity rises sharply, producing local concentrations in the current flow. In other words, a bright filament is formed.

The **vibrational mode**, on the other hand, arises when only the positive root of equation 4.1.3 is considered. Unlike the thermal mode, terms containing the electron density and ionization rates are retained. Here, $c > 0$ (note that ‘b’ can be negative, so the negative root is still a real possibility) and equation 4.1.3 becomes:

$$\Omega_T = \frac{c}{|b|} \approx k_{VT} n_0 \frac{\tilde{k}_i}{k_{VT}^{-2} (\nu_{Tp} \tau_p)^{-1}}$$

(4.1.10)

And:

$$\tilde{k}_i = \frac{\partial \ln k_i}{\partial \ln T_e}$$

(4.1.11)

$\tilde{k}_i$ is another dimensionless factor which essentially is the sensitivity of the ionization rate to electron temperature. Clearly, from equation X.10, the vibrational mode of instability is mostly characterized by the frequency of vibrational relaxation, not the rate of VT relaxation. The frequency of vibrational relaxation is driven by electron vibrational excitation; there is enhanced pumping of vibration by electrons during the instability that increases the energy stored in vibration. As the vibrational temperature increases during the instability, vibrational relaxation intensifies, leading to an increase of the translational temperature and corresponding decrease in the gas density. This results in decreasing gas density, increasing temperature at near constant pressure, as well as an increase in the reduced electric field, $\delta(E/n_0)$. Finally, the
increased reduced electric field, $\delta (E/n_0)$, further intensifies the electron concentration, $\delta n_e$, thereby creating a positive feedback loop.

Plasma chemistry can greatly impact the formation of thermal instabilities arising from any of the phenomena discussed above. This is particularly true if the reactions occur on a time scale comparable to vibrational excitation and before instabilities develop. The plasma chemistry can stabilize if there are endothermic reactions present that will consume any vibrational energy available and decrease the vibrational temperature. This means that if enhanced vibrational pumping should occur, these reactions will prevent net energy storage in vibration that could potentially lead to thermal runaway. On the other hand, if there are any exothermic reactions in the plasma chemistry or non-resonant V-V exchange, the heat release could exacerbate any instabilities that may be forming.

In addition to thermal instabilities, there are two more mechanisms that should be mentioned here. First, the ionization instability controlled by the dissociation of molecules, and the stepwise ionization instability. Both are very similar to the process described in equation (4.1.1) and are also a closed chain link with positive feedback. The casual link in ionization instability controlled by the dissociation of molecules is outlined in equation (4.1.12).

$$\delta n_e \mapsto \delta (\text{dissociation}) \mapsto \delta T_e \mapsto \delta n_e$$

(4.1.12)

It is clear that instead of heating by electron impact, the heating results from an intensification of molecular dissociation. Any initial increased electron density results in an intensification of molecular dissociation. The molecular dissociation by electron impact occurs through dissociative states and 20-30% of the total energy is immediately transferred to the translational motion of the fragments [1], for instance as is illustrated in (R1).
\[ e^- + O_2 \rightleftharpoons e^- + 2O + \Delta E \]  \hspace{1cm} (R1)

Because some of the energy in the dissociation is transferred to the translational motion of the fragments, the electron velocities increase (and therefore the electron temperature, $\delta T_e$). The increased velocities in the electrons result in further ionization and intensifying the electron concentration. An increase in the electron temperature leads to further intensification of the molecular dissociation, closing the chain with a positive feedback loop. It should be noted that in this case, the increment instability is highly dependent on the dissociation time. A gas mixture composed of molecules that do not readily dissociate, would be unlikely to lead to ionization instabilities.

The *stepwise ionization instability* is virtually identical to that outlined in equation (4.1.12). Instead of leading to molecular dissociation, a localized increase in electron concentration leads to further population of electronically excited species which ionize at a faster rate than those populating ground electronic states. This ionization results in intensification of the electron concentration, closing the chain and providing potential feedback.

\[ \delta n_e \mapsto \delta(\text{electronic excited states}) \mapsto \text{acceleration of ionization} \mapsto \delta T_e \mapsto \delta n_e \]  \hspace{1cm} (4.1.13)

Both the *ionization instability controlled by the dissociation of molecules*, and the *stepwise ionization instability* are tied directly to an overall intensification of electron concentration, which leads to another motivation for using dielectric barrier discharge. The current is restricted in these discharges by charging of a dielectric surface, which “self-limits” the energy loading into the plasma. This rapidly reduces the voltage across the discharge gap and helps stabilize the plasma.
It should be noted, however, that both the ionization instability controlled by the dissociation of molecules, and the stepwise ionization instability can also result in a thermal effect, rather than to a direct increase in the electron temperature. Andrey Starikovski [81, 82] rightly observes that for the former, electronic excitation to a repulsive state dissociates to products with high translational energy leading to a chain of events similar to those discussed above for the vibrational and thermal modes. For both the former and latter, the increment of stability must be directly proportional to the rate of electronic excitation. Therefore, the heat release associated with electronic excitation can proceed from three routes: 1) increased translational energy from molecular dissociation in a repulsive excited state, 2) the quenching of electronic states, or, 3) the recombination of neutrals and ions (if ionization should occur in either the ground state or an excited state). All of these phenomena occur on a nanoscale timescale (or less) which is in direct contrast to the thermal mechanisms reported previously that occur on a micro-to-milli-second time scale. Thus, these phenomena must play a direct role in the formation of plasma instabilities for nanosecond discharges.

4.2 Experimental Plasma ICCD images

A volumetric and diffuse plasma fairly free of constrictions was reported in previous studies [70] that utilized the same test cell, and high voltage generator operating under the same parameters as in this work (discussed in sections 3.2 and 3.3). However, these mixtures consisted primarily of air instead of the 20% O₂ in an argon buffer. Yet, as shown in table 4.1, the similarity parameters for electron motion in non-thermal discharges for argon and nitrogen are strikingly similar [51]. Furthermore, the thermal diffusivity and thermal conductivity for argon and nitrogen are both \( \sim 1.5 \times 10^{-4} \) W/(cm·K) at 300 K [51]. The Ar-O₂-fuel mixtures in this work were expected to also exhibit similar volumetric and diffuse behaviors. As will be
discussed below, this desired volumetric and diffuse behavior was indeed observed in initial ICCD images taken from the side of the cell. However, further investigation revealed significant constriction when viewed along the other dimension (ICCD images taken from the cell’s end).

Table 4.1: Estimated Similarity Parameters Describing the Neutral Collision Frequency, Mean Free Path, Mobility, and Conductivity of Electron at $E/p = 1/30 \text{ V cm}^{-1} \text{ Torr}^{-1}$

<table>
<thead>
<tr>
<th>Gas</th>
<th>Neutral Collision Frequency $\lambda_p$ (10$^{-2}$ cm Torr)</th>
<th>Mean Free Path $\nu_{en}/p$ (10$^9$ s$^{-1}$ Torr$^{-1}$)</th>
<th>Electron Mobility $\mu_p$ (10$^6$ cm$^2$ Torr V$^{-1}$ s$^{-1}$)</th>
<th>Electron Conductivity $\sigma_p/n_e$ (10$^{-13}$ Torr cm$^2$ ohm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>3</td>
<td>4</td>
<td>0.45</td>
<td>0.7</td>
</tr>
<tr>
<td>Ar</td>
<td>3</td>
<td>5</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>$N_2$</td>
<td>3</td>
<td>4</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>He</td>
<td>6</td>
<td>2</td>
<td>0.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Dr. David Burnette, a post-doctorate researcher in our group, characterized the plasma structure for the nanosecond dielectric barrier discharge used in this work throughout the duration of the burst using broadband plasma emission images taken with a Princeton Instruments PIMAX ICCD camera with a UV-lens (UV-Nikon 105mmf/4.5 Nikon). Images were taken for three different mixtures, (1) a baseline mixture with no fuel, 20% O$_2$-Ar (2) 20% O$_2$-Ar with added hydrogen fuel, such that $\phi=0.5$, and (3) 20% O$_2$-Ar with added ethylene fuel, such that $\phi=0.5$. The gate is set to 5 $\mu$s to incorporate a single discharge pulse (pulse duration of ~100 ns) within the burst. For every set of conditions, two sets of images were taken. One set is taken through the long side wall of the quartz channel, with a cross section of 220 mm long and 10 mm high. The other set is taken from the end of the cell, with a smaller cross section of 22 mm wide x 10 mm high. When the images are taken from this perspective, there is significant reflection from the channel walls which obscures the plasma emission boundary. To determine the cell boundaries, images were taken without the discharge when the cell was illuminated with an argon pen lamp. A rectangular region corresponding to the channel cross section was
extracted from these images, which is shown in the dashed lines in figures 4.1 – 4.3. The electrodes are located above and below the plasma in all images. The single-shot images correspond to a specific pulse within a burst, and were taken during different burst events.

Figure 4.1 shows a series of broadband, single-shot ICCD camera images of repetitively pulsed nanosecond discharge plasma emission for the baseline case with no fuel at P=40 torr, and discharge pulse repetition rate of 40 kHz. The images are taken both through the side wall and through the end window of the discharge cell, using a 5 µs gate. The first pulse clearly exhibits some filamentary structure, but this dissipates by the second pulse. However, in both sets of images, the plasma appears diffuse and uniform throughout the burst duration.

Figure 4.1: ICCD images of the plasma, taken both from the side and from the end of the discharge cell during the discharge burst in a 20%-80% O₂-Ar mixture. P=40 Torr, camera gate 5 µs. Pulse number in the burst is identified in the images. In an image taken from the end of the cell, approximate cross section of the quartz channel and the extent of the electrodes are indicated.
Images taken when hydrogen fuel is added at $\phi = 0.5$ are shown in figure 4.2. These images are remarkably similar to the baseline mixture where the first pulse shows some striation in the plasma that dissipates by the second pulse and after this the plasma remains volumetric and diffuse for the duration of the burst. The addition of hydrogen fuel does not appear to result in any plasma instabilities. However, end window images show that the total plasma volume contracts by the 20th pulse, relative to those end window images in the baseline case shown in figure 4.1.

Figure 4.2: ICCD images of the plasma, taken both from the side and from the end of the discharge cell during the discharge burst in a $\phi = 0.5$ H$_2$-O$_2$-Ar mixture. P=40 Torr, camera gate 5 μs. Equivalence ratio and pulse number in the burst is identified in the images. In an image taken from the end of the cell, approximate cross section of the quartz channel and the extent of the electrodes are indicated.
Images taken when ethylene fuel is added instead of hydrogen at $\phi=0.5$ are shown in figure 4.3. Side wall images demonstrate noticeable discharge striation, particularly later in the burst, by the 400th pulse. As was seen in figure 4.2 in images taken through the end wall, the addition of fuel results in an overall contraction of the plasma volume. However, this contracted volume is not constant throughout the burst. Instead, as the burst size increases, so does the contraction of the plasma volume. This is a result that is surprising and requires further investigation. As will be seen later, the striation and volume constriction of the plasma does impact the temperature after the burst.

The increased instability upon ethylene addition relative to addition of H$_2$ and the baseline case without fuel, can arise from a variety of factors. First, ethylene has a lower ionization potential of $\sim$10.5 eV (or 125,822 cm$^{-1}$) compared to that of O$_2$ at 12.2 eV (or 98,399 cm$^{-1}$) and H$_2$ at 15.43 eV (or 124,451 cm$^{-1}$) [83]. Lowering the ionization potential could increase the ionization rate. As discussed previously, an increased ionization rate could lead to increased
ion-ion recombination, which is accompanied by heat release. The increased ionization rate could also lead to an overall increase in the electron concentration, resulting in the formation of a bright filament, as illustrated previously in equation (4.1.12). However, if one considers the vibrational mode, it is clear that ethylene offers multiple avenues for vibrational excitation due to more degrees of freedom in comparison to that of H₂. This increases the potential for a higher population of vibrational excited states which could participate in a closed, feedback loop that contribute to plasma instabilities. It is possible that such a higher vibrationally excited population could lead to accelerated ionization, and thus instabilities, as described in equation (4.1.13). However, Zhiyao Yin [80] has recently demonstrated that the most likely mechanism for this instability is thermal. He preheated various air-fuel mixtures for nanosecond dielectric barrier discharges with significant stratification at room temperature prior to the onset of high voltage. It should be emphasized that the pressure was varied with temperature so that the density, and thus, E/n, remained constant. It was found that preheating the gas to 373 K or higher enabled a uniform, diffuse, and volumetric plasma for air and air-H₂ mixtures, while ethylene required a higher temperature of 473 K before becoming diffuse. It is hypothesized that the stabilizing effect of preheating is largely attributed to an enhanced thermal diffusivity which increases with temperature (thermal diffusivity is proportional to the average collision velocity in the bulk).

4.3 Experimental determination of energy coupled in to plasma

As was discussed in chapter 1, there are many avenues into which energy can be deposited in a plasma such as thermal, vibrational, ionization, electronic excitation, and dissociation. To create the discharge, a high voltage is applied across the discharge gap. Therefore, the question must be posed, just how much of this electrical energy is deposited into
these multiple avenues? In other words, it is desirable to know just how much electrical energy is converted. From circuit theory, we know that the instantaneous power is the rate at which energy is converted from electrical energy of the moving charges to some other form and is given by [84, 85]:

\[ P(t) = V(t)I(t) \]  

(4.3.1)

Therefore, the total amount of energy converted for a given amount of time would be the integral of equation (4.3.1) with the boundary conditions given by the time frame of interest. This is often referred to as the energy coupled into the plasma, \( Q \), where \( t_1 \) and \( t_2 \) are the boundary conditions.

\[ Q = \int_{t_1}^{t_2} V(t)I(t)dt \]  

(4.3.2)

From looking at equation 4.3.2, it appears that experimentally determining the coupled energy into the plasma is fairly straight-forward. All one has to do is measure the voltage and current waveforms using standard high voltage and current probes, and then apply the trapezoidal rule to approximate the integral in equation (4.3.2).

*Figure 4.4: Current, Voltage, and Instantaneous Power waveforms obtained for 20% O\(_2\) in argon at 40 torr, the 100\(^{th}\) pulse in a burst of 451 pulses. The red curve is the voltage, in kV. The blue curve is the current, in amps. The black curve is the instantaneous power as defined in equation 4.3.1.*
The current and voltage of the dielectric barrier discharge cell was probed using two different kinds of probes—the standard high voltage probe and current probe, and a custom-designed probe. The standard high voltage probe and current probes were utilized first to obtain the current and voltage waveforms in the dielectric barrier discharge cell. Figure 4.4 shows a typical current, voltage, and instantaneous power waveform for 20% \( \text{O}_2 \) in argon at 40 torr obtained using these standard probes. Recall from section 3.3, that the high voltage generator is operated in burst mode with pulses repeated at 40 kHz and the burst repeated at 10-Hz. The waveforms shown in figure 4.4 are all of the 100\(^{th}\) pulse in a burst of 451 pulses. The red curve is the applied voltage, and it is \( \sim 20 \text{ kV} \) and \( \sim 70 \text{ ns} \) in duration at FWHM. The current is shown in black with a peak of \( \sim 7.5 \text{ Amps} \). The blue curve is the instantaneous power which is given by equation (4.3.1). Integration of this blue curve with respect to time gives the coupled energy into the plasma (equation 4.3.2). For this particular waveform, the coupled energy is approximately 0.7 \( \text{mJ/pulse} \). Current and voltage waveforms taken in other gas mixtures show very little deviation from the traces shown in Figure 4.4 (if at all) and their approximate coupled energies were taken to be 0.7 \( \text{mJ/pulse} \) as well [86].

As stated previously, the second method of probing the current and voltage involved a custom-designed probe. This was designed specifically for measuring nanosecond pulse discharge waveforms where common mode noise can introduce substantial systematic error and have been utilized in previous work for measurements in dielectric barrier discharge cells [80, 87]. Figure 4.5 shows a schematic diagram of the custom designed current and voltage probes. Briefly, the probes consist of two identical low inductance (\( \sim 0.1 \text{ nH} \)) feed through capacitive voltage divider probes with an attenuation factor. One of these is connected to the electrode leads on the test cell and the other probe to the high voltage generator. Subtraction
of the two obtained waveforms simultaneously gives the voltage between the electrodes and cancels the common mode voltage (noise). Two identical shunt current probes (R=0.5 Ω, with six 3 Ω resistors arranged radially to reduce inductance) are isolated from the high voltage probes by 1:1 transformers. Here, the common mode current (noise), $I_{\text{comm}}$, is canceled using the asymmetric connection of the probes instead of a simple subtraction between two waveforms. The actual pulse current, $I_{\text{pulse}}$, is half the difference between the two current waveforms:

$$I_{\text{pulse}} = \frac{1}{2}(I_+ - I_-) = \frac{1}{2}[(I_{\text{pulse}} + I_{\text{common}}) - (-I_{\text{pulse}} + I_{\text{common}})] \quad (4.3.3)$$

It is unknown if the custom designed probes were calibrated shortly before application in this work [86]. However, the probes were calibrated before use in Yin et al [87], which was shortly before application of the probes to this work. Briefly, this calibration procedure used square-wave voltage pulses with known amplitudes and rise/fall times. This enabled the stray phase-shift between the voltage and current probes to be determined under an “open load” condition which is when no break-down occurs in the discharge and, therefore, no energy is coupled into the load (or, very close to zero).
The coupled pulse energy obtained from the custom designed probes was \(~0.08\) mJ/pulse, which is about a factor of 10 less than what was obtained using the standard high voltage and current probes, \(~0.7\) mJ/pulse. These experimental coupled pulse energies will be compared with predictions from the plasma assisted combustion model in chapter five, which includes a description for the analytic model for energy coupling in a nanosecond discharge [88].

4.4 RCARS Results in the Dielectric Barrier Discharge Cell

The main focus of this work was to obtain temperature by picosecond pure rotational CARS, for which the experimental set-up was shown in figures 3.1 and 3.13. For this dielectric barrier discharge investigation, the target species is only O\(_2\), rather than N\(_2\) or both N\(_2\) and O\(_2\)—which is much more common in the literature. Recall from chapter 1, that the goal is to decouple the NO\(_x\) chemistry from the fuel-oxidation process, which is a main motivator for the removal of N\(_2\) from the system. Under the conditions of the experiment, the partial pressure of the target species ranges from 6 to 8 torr. Due to the low number density, at higher temperatures (400 – 600 K) more laser energy was coupled into the system to overcome the resulting lower signal from the increased number of populated rotational levels. There was
some concern that the increased laser intensity could lead to Stark broadening, a significant factor in choosing rotational RCARS over vibrational CARS. However, recall from section 3.1 that the maximum total energy input was 12.3 mJ/pulse and the minimum energy input was ~3 mJ/pulse for this work. This is less than half of the total energy inputs used in previous pure rotational CARS work by Zuzeek, where input energies totaled more than ~60 mJ/pulse [73] and her target species of nitrogen had a higher partial pressure of ~30 torr. Because the laser power is greatly reduced in this work relative to that of Zuzeek, ~20% of her laser powers, Stark broadening effects were not anticipated at the higher laser powers utilized in despite the much lower number density of the target species in this work. However it should be emphasized that if Stark broadening effects are present, it will be much less than the instrumental resolution of ~1.4 cm\(^{-1}\), and as previously discussed in chapter 1, much less than the Raman linewidth and can thus be ignored.

A comparison of two spectra illustrated in Figure 4.6 is strongly indicative that additional broadening to the intrinsic instrument function of ~ 1.4 cm\(^{-1}\) did not occur in this work when operating at full power of ~12.3 mJ/pulse ~10 GW/cm\(^2\). Both spectra shown have been processed for the Sandia CARSFT code. Briefly, this processing includes background subtraction, normalization, division by the reference non-resonant spectrum, and, finally, taking the square root of the intensity. Both spectra were taken at 40 torr with a gas composition of 20% O\(_2\) in argon and the camera gain was set to 200. However, the exposure times were adjusted to account for the different input energies. The blue spectrum shown has a total input energy of ~12.3 mJ/pulse and a corresponding exposure time of 20 seconds; this is the maximum amount of energy that can be coupled into the system. On the other hand, the red spectrum was taken
when the total input energy was set to a minimum, which was 3 mJ/pulse, ~254 kW, and the exposure time of 450 seconds was 22.5 times longer than the previous case of 20 seconds.

![Comparison of Laser Energy](image)

**Figure 4.6:** Spectra obtained in 20% O\(_2\) in argon at 40 torr. The camera gain is set to 200. The blue spectrum has energy input of 12.3 mJ/pulse and camera exposure time of 20 seconds. The red spectrum has energy input of 3 mJ/pulse and camera exposure time of 450 seconds.

Figure 4.6 clearly demonstrates that the signal to noise when the energy is at minimum is poor, with a signal to noise ratio of ~3, whereas when the energy is at a maximum, the S/N is increased by more than four times to ~17. The lower signal to noise ratio when the energy is at a minimum is a direct result from the resulting lower signal from the lower energy inputs; the RCARS signal is proportional to the square of the applied electric field (see chapter 2 for more details). However, more importantly, both the high energy and low energy case show no significant difference in the in line width; there is no evidence of additional broadening that occurs when operating at maximum power that could affect the inferred temperatures providing justification for the assumption that Stark broadening at these powers is negligible. The inferred temperature for the maximum energy case is ~295 K, which matches the temperature usually maintained in the building. The temperature extracted from the minimum temperature spectrum is much lower, at ~283 K, which is clearly incorrect. This arises chiefly
from the lower resolution in the spectrum; the higher ‘J’ lines are obscured by both the higher S/N and decreased signal. These missing peaks cause the CARSFT code to shift to lower temperatures where the peaks do not exist. It is absolutely critical that the full spectrum is resolved in order to obtain an accurate temperature.

As stated in section 3.1, it was also found during the course of the dielectric barrier discharge work that the electron multiplying feature of the EMCCD camera significantly improved the signal to noise (S/N) of the raw spectra. To illustrate this, figure 4.7 shows a collage of four spectra obtained in 20\% O\textsubscript{2}/Ar at 44 torr (8.8 torr partial pressure of O\textsubscript{2}) under ambient room conditions (no discharge and gas flow is still ~1m/s). In each case, the spectra were averaged for 10 laser shots (1 second exposure). The EM-gain settings from top to bottom are 0 (disabled), 50, 100, and 200, where the maximum setting is 255. The improvement in signal to noise ratio is clear, increasing from essentially zero, with gain disabled, to ~15 with gain set to 200.

Seven different gas compositions were investigated in the dielectric barrier discharge cell: (1) 25\% O\textsubscript{2} in argon, (2) 26\% O\textsubscript{2} in argon with H\textsubscript{2} at \(\varphi=0.1\), (3) 26\% O\textsubscript{2} in argon with H\textsubscript{2} at \(\varphi=0.8\), (4) 20\% O\textsubscript{2} in argon with H\textsubscript{2} at \(\varphi=1.0\), (5) 20\% O\textsubscript{2} in argon with C\textsubscript{2}H\textsubscript{4} at \(\varphi=0.1\), (6) 20\% O\textsubscript{2} in argon with C\textsubscript{2}H\textsubscript{4} at \(\varphi=0.5\), and (7) 20\% O\textsubscript{2} in argon with C\textsubscript{2}H\textsubscript{4} at \(\varphi=1.0\). The difference in the O\textsubscript{2} percentages among the different mixtures is because it was not realized that the MKS flow meters needed to be recalibrated until later in the experiment, until after the data had been taken and analyzed for mixtures (1) – (3). After calibration of the flow meters, the gas compositions were recalculated for mixtures (1) – (3) and what was thought to have been 20\% O\textsubscript{2} in argon, was in actuality a higher O\textsubscript{2} percentage. After calibration, steps were taken to ensure that the actual O\textsubscript{2} percentage in argon was indeed 20\%.
All RCARS measurements were taken 35 µs after the end of the burst. For this work, ten to eleven different burst sizes were examined for the mixtures: 15, 21, 31, 51, 101, 151, 201, 251, 301, 351, and 401 pulses. The largest burst size of 401 pulses was not examined for any of the mixtures with added C₂H₄ because the high voltage generator was unable to generate pulses.

Figure 4.7: O₂ RCARS spectrum at O₂ partial pressure of 8.8 torr O₂. 10 laser shot average EM gain at 0 (disabled). 50, 100, and 200, from top to bottom.
with the peak applied voltage of 25 kV at this burst size for this gas composition; the maximum power limits had been reached. Three to five data points were collected for each of the burst sizes in each of the gas compositions to obtain an uncertainty in the measurements. It should be noted that a data iteration of 5 was applied to the majority of the work. However, due to time constraints, only 3 data iterations for each burst size were analyzed for the gas composition consisting of (7) 20% O\textsubscript{2} in argon with C\textsubscript{2}H\textsubscript{4} at \(\phi=1.0\). Regardless, two parameters, the standard deviation and 95% confidence interval, were used to quantify the uncertainty and were calculated from the sample set obtained for each burst size. The standard deviation, \(\sigma\), which measures how closely the data iterations are clustered about the mean is given by equation (4.4.1) where \(n\) is the sample size, \(x_i\) is a data iteration, and \(\bar{x}\) is the mean [89].

\[
\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}
\]  

(4.4.1)

However, it is not possible to determine the “true” mean or “true” standard deviation from a limited sample size because by their very definition, the sample size is infinite, which is not possible to achieve in reality. It is possible to determine a probability for a given range where the true mean is likely to exist. This confidence interval of the true mean, \(\mu\), is given by equation (4.4.2), where \(t\) is the student’s \(t\) whose value is determined by the sample size and the desired probability of confidence (i.e. 95% probability, 99.95%, etc) [89].

\[
\mu = \bar{x} \pm \frac{t\sigma}{\sqrt{n}}
\]  

(4.4.2)

Tables 4.2 – 4.8 summarizes the inferred average temperature results, their corresponding standard deviation, and 95% confidence intervals, and sample size for each burst size for each of the seven gas mixtures examined.
Table 4.2: Average temperature data for each burst size in 25% O<sub>2</sub> in argon. The sample size, standard deviations, 95% confidence interval for each burst size is also given. Finally, the average standard deviation and 95% confidence interval is given at the bottom of the table.

<table>
<thead>
<tr>
<th>Pulses</th>
<th>Average Temperature, K</th>
<th>Standard Deviation, K</th>
<th>95% Confidence Interval, K</th>
<th># of Data Iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>298</td>
<td>0.7</td>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>0.5</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>21</td>
<td>301</td>
<td>0.4</td>
<td>0.4</td>
<td>5</td>
</tr>
<tr>
<td>31</td>
<td>302</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
</tr>
<tr>
<td>51</td>
<td>302</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
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<tr>
<td>101</td>
<td>309</td>
<td>0.08</td>
<td>0.07</td>
<td>5</td>
</tr>
<tr>
<td>151</td>
<td>317</td>
<td>0.02</td>
<td>0.02</td>
<td>5</td>
</tr>
<tr>
<td>201</td>
<td>321</td>
<td>3.0</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td>251</td>
<td>331</td>
<td>0.2</td>
<td>0.2</td>
<td>5</td>
</tr>
<tr>
<td>301</td>
<td>336</td>
<td>0.6</td>
<td>0.6</td>
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<td>5</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.3: Average temperature data for each burst size in 26% O<sub>2</sub> in argon with added H<sub>2</sub> at ø=0.1. The sample size, standard deviations, 95% confidence interval for each burst size is also given. Finally, the average standard deviation and 95% confidence interval is given at the bottom of the table.

<table>
<thead>
<tr>
<th>Pulses</th>
<th>Average Temperature, K</th>
<th>Standard Deviation, K</th>
<th>95% Confidence Interval, K</th>
<th># of Data Iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>300</td>
<td>2.0</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
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<td>5</td>
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<tr>
<td>21</td>
<td>300</td>
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<td>0.02</td>
<td>5</td>
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<td>315</td>
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<td>0.1</td>
<td>5</td>
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<td>251</td>
<td>350</td>
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<td>0.8</td>
<td>5</td>
</tr>
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<td>351</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>401</td>
<td>358</td>
<td>2.0</td>
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<td>5</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>
Table 4.4: Average temperature data for each burst size in 26% $O_2$ in argon with added $H_2$ at $\phi=0.8$. The sample size, standard deviations, 95% confidence interval for each burst size is also given. Finally, the average standard deviation and 95% confidence interval is given at the bottom of the table.

<table>
<thead>
<tr>
<th>Pulses</th>
<th>Average Temperature, K</th>
<th>Standard Deviation, K</th>
<th>95% Confidence Interval, K</th>
<th># of Data iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>300</td>
<td>2.0</td>
<td>3.0</td>
<td>3</td>
</tr>
<tr>
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<td>25</td>
<td>305</td>
<td>1.0</td>
<td>1.0</td>
<td>4</td>
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<tr>
<td>31</td>
<td>313</td>
<td>2.0</td>
<td>2.0</td>
<td>4</td>
</tr>
<tr>
<td>51</td>
<td>315</td>
<td>1.0</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>101</td>
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</tr>
<tr>
<td>151</td>
<td>333</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td>201</td>
<td>346</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td>251</td>
<td>356</td>
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<td>301</td>
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</tr>
<tr>
<td>351</td>
<td>375</td>
<td>1.0</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>401</td>
<td>388</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5: Average temperature data for each burst size in 26% $O_2$ in argon with added $H_2$ at $\phi=1.0$. The sample size, standard deviations, 95% confidence interval for each burst size is also given. Finally, the average standard deviation and 95% confidence interval is given at the bottom of the table.

<table>
<thead>
<tr>
<th>Pulses</th>
<th>Average Temperature, K</th>
<th>Standard Deviation, K</th>
<th>95% Confidence Interval, K</th>
<th># of Data iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0.6</td>
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</tr>
<tr>
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<tr>
<td>31</td>
<td>310</td>
<td>0.1</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
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<td>314</td>
<td>2.0</td>
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<td>5</td>
</tr>
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<td>5</td>
</tr>
<tr>
<td>151</td>
<td>335</td>
<td>0.0</td>
<td>0.0</td>
<td>5</td>
</tr>
<tr>
<td>201</td>
<td>345</td>
<td>0.004</td>
<td>0.004</td>
<td>5</td>
</tr>
<tr>
<td>251</td>
<td>360</td>
<td>7.0</td>
<td>7.0</td>
<td>5</td>
</tr>
<tr>
<td>301</td>
<td>375</td>
<td>0.2</td>
<td>0.2</td>
<td>5</td>
</tr>
<tr>
<td>351</td>
<td>385</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
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<td>5</td>
</tr>
<tr>
<td><strong>Average</strong></td>
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<td>1</td>
<td></td>
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</tbody>
</table>
Table 4.6: Average temperature data for each burst size in 20% O$_2$ in argon with added C$_2$H$_4$ at $\phi=0.1$. The sample size, standard deviations, 95% confidence interval for each burst size is also given. Finally, the average standard deviation and 95% confidence interval is given at the bottom of the table.

<table>
<thead>
<tr>
<th>Pulses</th>
<th>Average Temperature, K</th>
<th>Standard Deviation, K</th>
<th>95% Confidence Interval, K</th>
<th># of Data iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>298</td>
<td>2</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
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<td>5</td>
</tr>
<tr>
<td>21</td>
<td>305</td>
<td>2</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>31</td>
<td>311</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>51</td>
<td>315</td>
<td>5</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>101</td>
<td>334</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>151</td>
<td>355</td>
<td>3</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>201</td>
<td>375</td>
<td>6</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>251</td>
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<td>5</td>
</tr>
<tr>
<td>301</td>
<td>408</td>
<td>9</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>351</td>
<td>440</td>
<td>17</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>

401 N/A because pulser is above power threshold limit at the given conditions

Average Temperature | 5 | 5

Table 4.7: Average temperature data for each burst size in 20% O$_2$ in argon with added C$_2$H$_4$ at $\phi=0.5$. The sample size, standard deviations, 95% confidence interval for each burst size is also given. Finally, the average standard deviation and 95% confidence interval is given at the bottom of the table.

<table>
<thead>
<tr>
<th>Pulses</th>
<th>Average Temperature, K</th>
<th>Standard Deviation</th>
<th>95% Confidence Interval</th>
<th># of Data iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>300</td>
<td>0.5</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>302</td>
<td>1.0</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>21</td>
<td>303</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td>31</td>
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<td>2.0</td>
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</tr>
<tr>
<td>51</td>
<td>317</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td>101</td>
<td>345</td>
<td>0.1</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>151</td>
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<tr>
<td>201</td>
<td>399</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td>251</td>
<td>423</td>
<td>11.0</td>
<td>11.0</td>
<td>5</td>
</tr>
<tr>
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<td>466</td>
<td>17.0</td>
<td>16.0</td>
<td>5</td>
</tr>
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<td>351</td>
<td>512</td>
<td>25.0</td>
<td>30.0</td>
<td>4</td>
</tr>
</tbody>
</table>

401 N/A because pulser would load above power threshold limit at the given voltage conditions

Average Temperature | 5 | 6
Table 4.8: Average temperature data for each burst size in 20% O\textsubscript{2} in argon with added C\textsubscript{2}H\textsubscript{4} at $\phi$=1.0. The sample size, standard deviations, 95% confidence interval for each burst size is also given. Finally, the average standard deviation and 95% confidence interval is given at the bottom of the table.

<table>
<thead>
<tr>
<th>C\textsubscript{2}H\textsubscript{4} $\phi$=1.0</th>
<th>20% O\textsubscript{2} in argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulses</td>
<td>Average Temperature, K</td>
</tr>
<tr>
<td>0</td>
<td>293</td>
</tr>
<tr>
<td>15</td>
<td>297</td>
</tr>
<tr>
<td>21</td>
<td>302</td>
</tr>
<tr>
<td>31</td>
<td>310</td>
</tr>
<tr>
<td>51</td>
<td>313</td>
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<tr>
<td>101</td>
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<td>151</td>
<td>360</td>
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<tr>
<td>201</td>
<td>387</td>
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<td>431</td>
</tr>
<tr>
<td>351</td>
<td>476</td>
</tr>
<tr>
<td>401</td>
<td>N/A because pulser is above the power threshold limit at the given conditions</td>
</tr>
<tr>
<td>Average</td>
<td>4</td>
</tr>
</tbody>
</table>

It can be seen from Tables 4.2 through 4.8, that the average precision (defined as the 95% confidence interval) for all the burst sizes in the baseline 20% O\textsubscript{2}-Ar mixture without fuel and for hydrogen containing mixtures is $\sim \pm 1 – 2$ K. Clearly, ethylene-containing mixtures all have lower average precision, $\pm 5-8$ K, associated with them relative to the baseline and hydrogen-containing mixtures. Furthermore, the imprecision in the ethylene containing mixtures increases with increasing burst size, up to $\pm 30$ K for a burst size of 351 K. The lower precisions in these mixtures chiefly arises from the plasma instabilities demonstrated in the broadband plasma emission ICCD images (see section 4.2). The observed striation increases with burst size, which directly reflects the increasing imprecision with increasing burst size. The baseline and hydrogen-containing mixtures were shown to be diffuse and volumetric, hence the higher precision.

It should be noted that a minor portion of this greater uncertainty associated with all of the ethylene mixtures could be partially attributed to the higher temperatures experienced...
relative to the hydrogen mixtures because such an increase in temperature would increase the number of rotational levels populated and decrease the intensities of the peaks, thus, reducing the S/N ratio. However, this is not the case. Further analysis of tables 4.2 through 4.8, reveals that the uncertainty for the mixtures without ethylene, that the precision is largely independent of the burst size, and thus, temperature.

The independence of the baseline and hydrogen containing-mixtures show that the precision is not affected by EMI noise. Previous work by Zuzeek [70] in the discharge cell with air-ethylene mixtures demonstrated that precision decreased with increasing burst size due to EMI noise that increased with increasing burst size. Figures 4.8 – 4.11 illustrate the effect of EMI noise on S/N. Figure 4.8 shows a spectrum with its CARSFT, taken when there is no plasma and no added fuel, and the signal to noise ratio is ~29. Upon addition of a discharge consisting of the smallest burst size examined (15 pulses, this results in a modest increase in temperature of 25 K in the ethylene mixture of phi=0.5, yet the S/N drops from ~29 to ~22, as shown in Figure 4.9. When looking at a larger burst size of 351, the effect of EMI noise is more pronounced. Both Figures 4.10 and 4.11 display spectra with their corresponding CARSFT for a burst size of 351 pulses, but the former is for a mixture of C₂H₄ φ=0.5 and the latter for H₂ φ=1.0. Both have comparable S/N with ~15. However, there is a temperature difference of over 150 K between the two spectra. Therefore, the chief contributor to the uncertainty in this case is not an increase in temperature, but rather, an increase in the EMI noise and it can be concluded that temperature has minimal impact on the overall uncertainty in the dielectric barrier discharge work. It can also be concluded from Figures 4.10 and 4.11 that any significant difference in uncertainties in the data-sets between ethylene and hydrogen cannot be attributed to EMI, because the S/N is comparable for both types of gas mixtures.
Figure 4.8: Spectrum taken in 25% O₂ in argon with no discharge present at 40 torr, with camera gain 200, and exposure time of 20 seconds. The black spectrum is the data after processing for CARSFT code. The red spectrum is the best-fit theoretical spectrum from CARSFT code with temperature 302 K. The χ² value is 0.14. The average S/N is ~29.

Figure 4.9: Spectrum taken in 20% O₂ in Ar with added C₂H₄ φ=0.5, with discharge present at a burst size of 15 pulses, at 40 torr, with camera gain 200, and exposure time of 20 seconds. The black spectrum is the data after processing for CARSFT code. The red spectrum is the best-fit theoretical spectrum from CARSFT code with temperature 325 K. The χ² value is 0.06. The average S/N is ~22.
Figure 4.10: Spectrum taken in 20% O₂ in argon with added C₂H₄ φ=0.5, with discharge present at a burst size of 351 pulses, at 40 torr, with camera gain 200, and exposure time of 40 seconds. The black spectrum is the data after processing for CARSFT code. The red spectrum is the best-fit theoretical spectrum from CARSFT code with temperature 543 K. The $\chi^2$ value is 0.14. The average S/N is ~15.

Figure 4.11: Spectrum taken in 20% O₂ in argon with added H₂ φ=1.0, with discharge present at a burst size of 351 pulses, at 40 torr, with camera gain 200, and exposure time of 40 seconds. The black spectrum is the data after processing for CARSFT code. The red spectrum is the best-fit theoretical spectrum from CARSFT code with temperature 385 K. The $\chi^2$ value is 0.14. The average S/N is ~15.
Analysis of Tables 4.2 through 4.8 also reveals that the C₂H₄ ϕ=1.0 mixture has a somewhat larger average confidence interval ± 8 K relative to the other ethylene mixtures (± 5-6 K). This cannot be attributed to an increase in temperature and it could hypothesized that this mixture is very much more unstable than all of the other mixtures examined. However, this particular mixture had the fewest number of data iterations analyzed due to time constraints (3 instead of 5). A smaller sample size increase the range in the confidence interval. Therefore, it cannot be concluded definitely that the stoichiometric ethylene mixture of C₂H₄ ϕ=1.0 is indeed the most unstable of the mixtures, only that it experiences the largest uncertainty which is most likely due to a combination of fewer data iterations and instability comparable to the other ethylene mixtures.

Finally, there is one last observation from analyzing the tables: some data sets have a sample size of four rather than five. There was an occasional inferred temperature that deviated significantly from the set and statistically was considered a “bad” point. For example, there was one spectrum for the C₂H₄ ϕ=0.5 mixture that had an inferred temperature of 705 K—this was almost 200 K hotter than the rest of the data set (average of 512 K). It was hypothesized that these randomly hot spectra resulted from the formation of a filament at or near the location of the RCARS probe volume; the ICCD images discussed in the previous section show evidence of such filamentary formation in the discharge in the ethylene containing mixtures.

However, in summary, the average standard deviation for the dielectric barrier discharge work ranged from ± 1 to 5 K and the average confidence interval from ± 1 to 8 K. Hydrogen mixtures uncertainties averaged ~ ± 1 K and the two fuel-lean ethylene mixtures averaged ± 5-6 K with the stoichiometric at ±8 K. The larger uncertainty of the ethylene
containing mixture reflects the instabilities observed in the ICCD images because the difference in the uncertainties between the hydrogen and ethylene mixtures cannot be attributed to higher temperatures and EMI noise.

The average temperature results for the burst sizes examined in the various mixtures are presented in figures 4.12 and 4.13 with their respective error bars. The error bar is the 95% confidence interval of the precision obtained for that particular burst size for the given mixture. If not shown, the experimental precision does not exceed the size of the symbols shown. As can be seen from the figures, for all gas mixtures, the temperatures are fairly comparable when there is no plasma present, and up to a burst size of 15 pulses. At a burst size of 21 pulses, the temperatures for the different mixtures begin to deviate from each other. The larger the burst size, the more significant the deviation. Furthermore, the overall temperature increase with burst sizes also increases as more fuel is added, with ethylene addition consistently resulting in a higher temperature rise than hydrogen. The one exception to this trend appears to be ethylene, where $\phi=0.5$ is hotter than $\phi=1.0$. The order of temperature increase is as follows: $H_2 \phi=0.1 < H_2 \phi=0.8 < H_2 \phi=1.0 < C_2H_4 \phi=0.1 < C_2H_4 \phi=1.0 < C_2H_4 \phi=0.5$. This ordering is clearly illustrated in figure 4.14, where the overall temperature rise is plotted vs. equivalence ratio for the two different types of fuel. The temperature for hydrogen containing mixtures increases approximately linearly with equivalence ratio. However, the ethylene containing mixtures exhibit highly nonlinear behavior with respect to the equivalence ratio. It is hypothesized that the non-linear behavior of the ethylene mixtures is due to the filamentation that occurs in these mixtures. On the other hand, such non-linearities could arise from V-V transfer or V-T relaxation. As discussed previously in sections 4.1 and 4.2, ethylene has many vibrational degrees of freedom and could potentially heat the mixture rapidly via such pathways.
Figure 4.12: Average inferred temperature for hydrogen mixtures with 95% confidence interval error bars. If not shown, experimental uncertainty does not exceed the size of the symbols shown. Note that the lines are just connecting the symbols.

Figure 4.13 Average inferred temperature for ethylene mixtures with 95% confidence interval error bars. If not shown, experimental uncertainty does not exceed the size of the symbols shown. Note that the lines are just connecting the symbols.
In spite of the non-linear dependence of the overall temperature increase on equivalence ratio for ethylene mixtures, the temperature increases approximately linearly with burst size in all mixtures investigated. There is one exception, the $\varphi=0.1$ case (red line in figure 4.12), where there is a “kink” in the linearity at a burst size of 251 pulses. The data in figures 4.12 and 4.13 were fit to a linear function and relatively good fits were found with an average $R^2$ value of 0.9942, with the exception of the $H_2$ $\varphi=0.1$ case which had an $R^2$ value of 0.9577, as shown in figures 4.15 and 4.16. A linear behavior with respect to burst size because it was hypothesized that each pulse would couple the same amount of energy into the plasma and partition comparably given the short time-scales. The comparison of these inferred temperature results shown in Figures 4.12 through 4.16 to modeling predictions are given in the next chapter after an introduction to the model itself.
Figure 4.15: Average temperature rise for hydrogen fuel as a function of burst size. The experimental data is shown in the markers and the corresponding linear fits as a solid line.

Figure 4.16: Average temperature rise for ethylene fuel as a function of burst size. The experimental data is shown in the markers and the corresponding linear fits as a solid line.
Chapter 5: Dielectric Barrier Discharge Model and Comparisons with Experimental Data

As discussed in chapter 4, uniform and diffuse plasmas are desirable for three main reasons. First, because it minimizes thermal heating effects such as those arising from filament formation. Second, because it enables point or line measurements that can be representative of the entire discharge volume. Finally, because it justifies the application of a “simple” 0-D model to the dielectric barrier discharge system studied in this work. The model has been validated in previous work in nanosecond discharges in air and air-H2, -CH4, -C2H6, and –C3H8 mixtures, using measurements of O-atom concentration by TALIF [2, 16], and temperature by both RCARS and LIF [38, 67, 73]. This is the first time the model has been applied to Ar-O2, Ar-O2-H2, and Ar-O2-C2H4 mixtures.

The 0-D model consists of two separate units because the kinetics of the energy coupling during a nanosecond discharge pulse and the subsequent plasma chemical processes occur on two vastly different time scales. The first part, a nanosecond discharge model, consists of approximate closed-form analytic solutions for time-dependent electric field and electron density in plasma are used to predict the energy coupling of the applied pulse to the plasma as a function of T, P, and pulse waveform; these processes occur on the time scale of nanoseconds. It should be noted that the pulse waveform is approximated as a Gaussian pulse which is then inserted into the nanosecond discharge model to obtain the charged densities and electric fields
within the plasma as a function of time. These results from the nanosecond discharge model are then used for the kinetic modeling of plasma chemistry and temperature, where processes occur on a time scale from microseconds to milliseconds. An overview for the two separates parts of the model is provided in this chapter, which will be concluded by comparison of the model predictions for the dielectric barrier discharge system of interest in this thesis for which a schematic is shown in figure 5.1.

5.1. Nanosecond Discharge Model

The nanosecond discharge model analyzes the nanosecond pulse breakdown kinetics, sheath development, and energy coupling of the pulse to a plasma with a dielectric barrier and plane-to-plane electrode geometry. It takes into account the charged species and electric field variation across a discharge gap to yield the time dependent electric field and time dependent electron density. This information is used to determine the energy coupling as a function of temperature, pressure, and pulse waveform. The first description of this model by Dr. Adamovich appeared in [88] and the description that follows here is adopted from this reference.

![Figure 5.1: Schematic of the dielectric barrier discharge cell, reproduced from [88] with permission](image-url)
The development of the model begins with four initial equations that are derived using the drift-diffusion approximation for a non-electronegative gas (where electron attachment and ion recombination processes are not considered largely important). Only one dimension is considered, $x$, which is along the discharge gap. Ignoring the other one (or two) dimensions is only valid if the plasma properties along those directions are uniform in comparison with the ‘$x$’ direction. Three of out the four one-dimensional equations are as follows:

\[
\frac{\partial n_+}{\partial t} + \frac{\partial \Gamma_+}{\partial x} = \alpha(E, p)|\Gamma_+| - \beta n_+ n_e = \nu_i n_e - \beta n_+ n_e \tag{5.1.1}
\]

\[
\Gamma_+ = -D_+ \frac{\partial n_+}{\partial x} + \mu_+ n_+ E \tag{5.1.1a}
\]

\[
\frac{\partial n_e}{\partial t} + \frac{\partial \Gamma_e}{\partial x} = \alpha(E, p)|\Gamma_e| - \beta n_+ n_e - \nu_i n_e - \beta n_+ n_e \tag{5.1.2}
\]

\[
\Gamma_e = -D_e \frac{\partial n_e}{\partial x} + \mu_e n_e E \tag{5.1.2a}
\]

\[
\frac{\partial \varphi}{\partial x} = -\frac{e}{\varepsilon_0} (n_+ - n_e) \tag{5.1.3}
\]

In this formulation, $n_+$ is the positive ion number densities, $n_e$ the electron number densities, the plasma potential is given by $\varphi$, the electric field $E$ is given by $E = -\frac{\partial \varphi}{\partial x}$, the ionization frequency $\nu_i$ is given by $\nu_i = \alpha \mu_e |E|$, where $\alpha$ is the first Townsend coefficient which describes the number of electron-ion pairs per unit that are produced in a collective drift of the electrons towards the anode, $\beta$ is the second Townsend coefficient which accounts for electron losses, $\Gamma_+$ and $\Gamma_e$ are the drift diffusion fluxes of the positive ion and electrons respectively, $\mu_+$ and $\mu_e$ are the positive ion and electron mobilities respectively, $\mu_+$ and $\mu_e$ are the positive ion and electron mobilities respectively, and the positive ion diffusion coefficient, $D_+$, is given by $D_+ = \mu_+ k_b T_i / e$, where $T_i$ is the positive ionic temperature. Finally, the electron diffusion coefficient, $D_e$, is given by $D_e = \mu_e k_b T_e / e$. 

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The fourth initial starting equation calculates the voltage across the gap, \( V_{\text{gap}}(t) \), as a function of time, where the parameters, including gap distance, \( L \), are the dielectric plate thickness, \( l \), and dielectric constant, \( \varepsilon \), are constant. It should be emphasized that \( V_{\text{app}}(t) \) is the applied voltage that has been approximated as a Gaussian pulse.

\[
\frac{dV_{\text{app}}(t)}{dt} = \left( 1 + \frac{2l}{\varepsilon L} \right) \frac{dV_{\text{gap}}(t)}{dt} + \frac{2l}{\varepsilon \varepsilon_0 L} \times \int_0^L \left[ \Gamma_e(x, t) - \Gamma_p(x, t) \right] dx \tag{5.1.4}
\]

Equation (5.1.4) essentially describes the gap voltage reduction during the pulse due to charge accumulation on the surfaces of the dielectric plates. Thus, it is analogous to the charging of two capacitors with a combined capacitance of, \( C_d = \frac{\varepsilon_0 \varepsilon A}{2l} \), where \( A \) is the dielectric plate surface area.

The applied electric field, \( E_{\text{app}}(t) \) is given as a function of the applied voltage with the same fixed parameters, with the addition of \( \tau \), which is the duration of the applied voltage pulse.

\[
E_{\text{app}}(t) = \frac{V_{\text{app}}(t)}{L + \frac{2l}{\varepsilon}} = \frac{V_{\text{peak}}}{L + \frac{2l}{\varepsilon}} \exp \left[ -\left( \frac{t-t_{\text{peak}}}{\tau} \right)^2 \right] = E_{\text{peak}} \exp \left[ -\left( \frac{t-t_{\text{peak}}}{\tau} \right)^2 \right] \tag{5.1.5}
\]

There are five boundary conditions. First, the potential must be zero at \( t=0 \) when there is no applied field. Second, at \( x=0 \), the potential must be equal to \( V_{\text{gap}}(t) \).

\[
\phi(x, t = 0) = \frac{V_{\text{app}}(t=0)}{L + \frac{2l}{\varepsilon}} x \tag{5.1.6}
\]

Second, when \( x=L \), the potential must be equal to the applied voltage across the gap.

\[
\phi(t, L) = V_{\text{gap}}(t) \tag{5.1.7}
\]

Third, when \( x=0 \) and in the vicinity of the cathode, the electron density must be very small in comparison to the positive ion density, such that \( n_e < < n_+ \). Under such conditions, \( n_e \)
approaches zero and first term on the right in equation (5.1.1a) and all the terms to the right in equation (5.1.1) go towards zero. Furthermore, in the Townsend mechanism as described in chapter 2, the secondary electrons in the avalanche are the result of ionic bombardment on the cathode. Recall that the probability of electron ejection is given by the third Townsend coefficient. Thus, the flux of electrons can be given by the flux of the ion times the probability for an electron ejection, such that [90]:

$$\Gamma_e|_{x=0} = -\gamma \Gamma_+|_{x=0}$$

(5.1.8)

Substitution of 5.1.8 into 5.1.1, and recalling that $E = -\frac{\partial \varphi}{\partial x}$, then at $x=0$, the change in the positive ion density is given by:

$$\frac{\partial n_+}{\partial t} = -\mu_e \frac{\partial}{\partial x} \left( n_+ \frac{\partial \varphi}{\partial x} \right)$$

(5.1.9)

It should be emphasized that although $n_e$ tends towards zero at $x=0$, there is some electron density on the dielectric surface, $n_{ew}$, so that the boundary condition requires $n_e = n_{ew}$.

Similarly, the fourth boundary condition occurs when $x=L$; this is in the vicinity of the anode, such that $n_+ \to 0$ and the second right term in equation (5.1.2a) also goes to zero, such that [90]:

$$\frac{\partial n_+}{\partial t} = -\mu_e \frac{\partial}{\partial x} \left( n_+ \frac{\partial \varphi}{\partial x} \right)$$

(5.1.10)

Finally, at $t=0$, there must be no charge such that $n_e = n_+ = n_0$.

The first Townsend coefficient, which describes electron impact ionization, is given by the Townsend formula in chapter 2, (equation 2.1.4 and 2.1.11), with the functional form taken from Surzhikov et al. [90] and Adamovich et al [88]. Here, $p^* = p$ (torr) *300/T.
The electron-ion recombination rate (second Townsend coefficient) and both the electron and positive ion mobilities are taken from reference [90]. It should be noted that the electron temperature, $T_e$, is assumed to be equal to 1 and ion temperature $T_i$ is equal to 300K.

$$\beta = 2 \times 10^{-7} \left( \frac{300}{T_e} \right)^{1/2} \text{ cm}^3/\text{s}$$

$$\mu_e = 400 \left( \frac{760}{p^*} \right) \frac{\text{cm}^2}{V_s}$$

$$\mu_i = 2.75 \left( \frac{760}{p^*} \right) \frac{\text{cm}^2}{V_s}$$

For nanosecond discharges, electron losses and ionic drift have no discernible effect on the electron and ionic density distributions because the pulse is so short. As a result, there are only two dominant processes in the discharge, (1) electron impact ionization, which is given by equation (5.1.12), and (2) charging of the dielectric surface. Hence, the quasi-neutral plasma and the sheath region (where $n_e$=0, $E$=$E_s$) can be considered separately. Because in a quasi-neutral plasma, the electron density must be approximately equal to the positive ion density, it follows that, $n_e$=$n_+$. There is no longer any need to consider two separate equations for the change of the electron and positive ion number densities with respect to time; only one equation is needed. Furthermore, the effects of diffusion on the timescale of the pulse duration is minimal, and, thus, can be also neglected. Under these conditions, if it is assumed that a constant voltage is applied with an infinitely sharp rise time, then then the system of equations (5.1.1) – (5.1.4) reduces to three zero-dimensional equations, as follows:
where $l_s$ is the sheath width, and $v_c + v_s$ is the characteristic frequency for charging the capacitors formed by the two dielectric layers and by the sheath.

\[
v_c = \frac{2le\mu e n_0}{\varepsilon_0 L (1 + \frac{2l}{\varepsilon L})}
\]  

\[
v_s = \frac{2l_x \mu e n_0}{\varepsilon_0 L}
\]  

The ionization frequency, $v_i$, which is approximated as:

\[
v_i = A_p p^* \exp \left[ \frac{B_p^*}{E_p} \right], \quad A_p = 3.7 \times 10^8, \quad B_p = 318, \quad \frac{E_p}{p^* < 200 \frac{V}{cm \; torr}}
\]  

For this simplified system, the initial conditions at $t=0$, require that $n(t=0) = n_0$, such that:

\[
E_p(t = 0) = E_s(t = 0) = \frac{V_{app}(t=0)}{L + \frac{2l}{\varepsilon}}
\]  

It is immediately obvious that the system of equations (5.1.13) – (5.1.15) is open—there is no equation yet given for $l_s(t)$. After voltage is applied, the electrons begin to drift towards the anode and generate an electron avalanche which in turns yields an ion for each electron. The ions move away from the anode toward the cathode due to the applied field. In these systems this movement typically manifests as fast ionization waves. In this sense, the sheath boundary is the front of the ionization wave. If it is assumed that this wave travels very rapidly from the
anode to its quasi-stationary position at $x = l_s$ near the cathode, then $l_s(t)$ can be treated in quasi-steady state limit where $\frac{dl_s}{dt} \approx 0$.

$$l_s^\infty = \frac{1}{\alpha_s} \ln \left( \frac{n_\infty}{n_0} \right) = \frac{\mu E_s^0}{v_{is} E_s^\infty} \ln \left( \frac{n_\infty}{n_0} \right)$$  \hspace{1cm} (5.1.21)

Where $n_\infty$ is the steady state electron density in the plasma, $E_s^\infty$ is the quasi-steady-state E-field in the sheath, and the ionization frequency in the sheath, $v_{is}$, which is given by:

$$v_{is}(E_s) = \alpha \mu_e |E_s| = A_s E_s \exp \left(-\frac{B_s p^*}{E_s}\right), \quad A_s = 3.6 \times 10^6, \quad B_s = 342, \quad 100 < \frac{E}{p^*} < 800 \frac{V}{cm}$$  \hspace{1cm} (5.1.22)

The location of $l_s$ can be explicitly found under the quasi-steady state limit from (5.1.21) if the electrode thickness is much smaller than the gap, that is, if $\frac{2l}{\varepsilon} \ll L$. Under this condition, for a field varying with time, $v_i^0 = v_i(E_0)$, $a = \exp \left(\frac{3B_p p^*}{2E_0}\right)$, and the electric field, $E_s^\infty$, and the number density, $n_\infty$, for the sheath are as follows:

$$E_s^\infty = \frac{\varepsilon L}{2l} E_{app}(t)$$  \hspace{1cm} (5.1.23)

$$n_\infty = \frac{v_i^0 (a-1)}{v_i \ln a}$$  \hspace{1cm} (5.1.24)

It should be noted that $E_0$ is the breakdown field, that is, when the field in the plasma falls to $\frac{1}{2}$ its value at $t_0$. If ionization frequency is much faster than the variation in the applied field, such that, $\frac{1}{\tau} \ll v_i^0$, then $E_0 = E_{app}(t_0)$. In addition, under this assumption, the solution for the electric fields in the quasi-neutral plasma and sheath, as well as the corresponding number densities as a function of time are given in reference [88] (the number density in the sheath is relatively constant as it is considered to be in a quasi-steady state). These solutions are critical
to in obtaining an analytic form for the coupled energy. Plugging these solutions into the power density equation, \( w(t) = \varepsilon_\mu_0 n(t)E_0^2(t) \), which is then integrated with respect to time, and finally, multiplication by the plasma volume, \( \approx \text{AL} \), gives the pulse energy coupled to the plasma.

It is helpful to separate the energy coupled by the breakdown field and any additional energy afterwards because after breakdown, the coupled energy is typically much reduced due to the plasma shielding.

\[
Q_{\text{breakdown}} \approx \left( \frac{1}{1 + \frac{2\pi}{\varepsilon_0}} \right) Q_{\text{cap, breakdown}} = \left( \frac{1}{1 + \frac{2\pi}{\varepsilon_0}} \right)^* \frac{1}{2} C_{\text{tot}} V_0^2 = \left( \frac{1}{1 + \frac{2\pi}{\varepsilon_0}} \right)^* \frac{\varepsilon_0 A}{2} \left( L + \frac{2\pi}{\varepsilon_0} \right)^2 E_0^2
\]

(5.1.25)

The two dielectric layers in the dielectric barrier discharge cell together with the sheath form a capacitor at the moment of breakdown. This stored energy is contained entirely in equation (5.1.25) in the term, \( Q_{\text{cap, breakdown}} \). As can be seen by equation (5.1.25), the energy coupled into the plasma is controlled entirely by the applied waveform which has been approximated as a Gaussian pulse and the number density in the discharge region. It can also been seen that the coupled energy is close to the energy that is stored into the capacitor formed upon breakdown.

After breakdown, the load no longer behaves as a capacitor, but rather as a constant resistance in an RC circuit with a time constant, \( \tau_{\text{RC}} \), where \( \alpha = \exp \left[ \frac{3B_{\text{pp}}}{E_0} \right] \).

\[
\tau_{\text{RC}} = \frac{1}{\varepsilon_{\text{tot}}} = v_i^0 \left( \frac{a-1}{\alpha \ln \alpha} \right) \gg \frac{1}{\tau}
\]

(5.1.26)

In this way, the field in the quasi-steady state plasma can simply be found by equating the displacement current in the external circuit and the conduction current in the plasma. This
approach yields an electric field that is proportional to the time derivative of the applied electric field and the following for the coupled energy after the breakdown:

\[
Q_{after} \approx Q_{cap,peak} \frac{\sqrt{2\pi}}{1 + \frac{21}{vRC} t} \cdot \frac{E_{tot} v_{peak}^2 / 2}{vRC} \cdot \sqrt{2\pi} \tag{5.1.27}
\]

\(Q_{cap,peak}\) is the peak energy stored by the capacitor formed by the two dielectric layers and the sheath. Equation (5.1.27) was obtained by Adamovich [88] by use of an error function. The error function is an approximation that is valid when there exists a high over-voltage such that the breakdown voltage, \(V_0\), is significantly lower than the peak voltage of the pulse. At low over-voltage where \(V_0 \approx V_{peak}\), than the coupled energy decreases by a factor of \(\sim 2\).

Finally, assuming high over-voltage, the total coupled energy, is the sum of equations (5.1.25) and (5.1.27).

\[
Q_{coupled} = \left( \frac{1}{1 + \frac{21}{vRC} t} \right) \cdot \frac{1}{2} C_{tot} \cdot \left[ V_0^2 + V_{peak}^2 \cdot \frac{\sqrt{2\pi}}{vRC} \right] \tag{5.1.28}
\]

When operating in burst mode, when pulses are repeated at a high repetition rate, recent work [87] has shown that the coupled pulse energy is nearly independent of pulse repetition rate and remains constant throughout a burst as long as temperature remains constant. When temperature is no longer constant, the coupled pulse energy scales nearly proportionally to the number density. This is in good agreement with the nanosecond discharge pulse prediction.

It should be stressed that the nanosecond discharge model that has been presented is only accurate if the electron density remaining from the previous discharge pulse is much less than the peak electron density in the plasma generated during the pulse.
Recently a high fidelity numerical model developed by Nagaraja [91] provides added confidence in the 0D kinetic model used here in this work. The model is essentially a one-dimensional plasma drift-diffusion fluid model that couples the plasma processes to plasma chemistry. It includes solving the Poisson equation for the electric field, coupled with equations for the electron number density and ion number densities. It also incorporates detailed charged species kinetics, including electron impact, and Penning ionization. Nonetheless, five predictions were compared between the present model and the more comprehensive model (and thus more computationally intensive) model by Nagaraja in [91]. The predicted parameters include the time dependent electric field, \(E_p(t)\), and electron density, \(n(t)\), for a quasi-neutral plasma, the time dependent electric field, \(E_s(t)\), at the sheath boundary, the sheath location, \(l_s\), and the coupled energy to the plasma. For all these parameters, the agreement between the two models was very good with some deviations that were attributed largely to differences in the electron impact ionization rates utilized.

5.2 Plasma Chemistry Kinetic Model

The plasma chemistry model predicts the initial energy partitioning into the many channels available to it including dissociation, ionization, as well as the many different internal energy levels of molecules and atoms. It then predicts the evolution of energy, such as heat release from exothermic reactions or heat absorption by endothermic V-V transfer processes. It also predicts the time-resolved temperature and species concentrations during a burst of multiple pulses and well into the after-glow.

The plasma chemistry model is essentially a set of ordinary differential equations for the creation and loss of number densities for neutral, charged, and excited species (i.e. electronic
and vibrational excitation). The species concentration equations are then coupled with the two-term Boltzmann equation for the energy distribution function for plasma electrons; the Boltzmann equation solver uses electron impact cross sections and calculates the electron energy distribution function, as well as rate coefficients for electron impact ionization, dissociation, electronic and vibrational excitation used by the rest of the model, if such experimental rates are not readily available from the literature. The rate coefficients of remaining kinetic processes such as ion-molecule reactions, reactions of excited electronic species, and electron recombination, attachment, and detachment are taken from experimental data. In addition, the plasma chemistry model couples conventional combustion reaction mechanisms with conventional plasma chemistry.

Non-equilibrium O₂-Ar plasma chemistry is incorporated into this set of equations, which has been expanded to include hydrogen and ethylene dissociation processes in the plasma [2, 4]. The dominant radical species generation processes in H₂-O₂-Ar and C₂H₄-O₂-Ar plasmas are listed in Table 5.1. From Table 5.1, it is clear that kinetic processes involving low-energy metastable electronic states of oxygen, O₂(a¹Δ) and O₂(b¹Σ) are missing. They have been deliberately neglected because the predicted discharge energy fraction going into electron impact excitation to generate these states is quite low. This is then coupled with one of two conventional H₂-O₂ chemistry mechanisms developed by, (1) Popov [4], with the low-temperature rate coefficient of reaction \( O + OH \rightarrow H + O₂ \) corrected as discussed in [38], \( k=2.4 \times 10^{-11} \exp(109/T) \text{ cm}^3/\text{s} \), and (2) Konnov [5]. For the ethylene containing mixtures, one of two hydrocarbon combustion mechanism was utilized, one developed by Wang [6] and the GRI Mech 3.0 [92]. These conventional combustion mechanisms have been developed and validated for relatively high temperatures, significantly higher than in the present work; they may well be
inaccurate for the present system of interest. Assessing applicability of these mechanisms is one of the objectives of the present work.

Table 5.1: Dominant primary radical species generation processes in the plasma

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate, cm³/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + e⁻ = O(3P) + O(3P,3D) + e⁻</td>
<td>σ¹ [93]</td>
</tr>
<tr>
<td>Ar + e⁻ = Arₘ + e⁻</td>
<td>σ² [94]</td>
</tr>
<tr>
<td>H₂ + e⁻ = H + H + e⁻</td>
<td>σ³ [93]</td>
</tr>
<tr>
<td>C₂H₄ + e⁻ = products + e⁻</td>
<td>σ⁴ [93]</td>
</tr>
<tr>
<td>O(1D) + Ar = O + Ar</td>
<td>5·10⁻¹² [96]</td>
</tr>
<tr>
<td>O⁺(3D) + O₂ = O + O₂</td>
<td>5·10⁻¹¹ [96]</td>
</tr>
<tr>
<td>O⁺(3D) + H₂ = H + OH</td>
<td>1.1·10⁻¹⁰ [4]</td>
</tr>
<tr>
<td>O⁺(3D) + C₂H₄ = O + O + C₂H₃</td>
<td>1.1·10⁻¹⁰ [97]</td>
</tr>
<tr>
<td>Arₘ + O₂ = Ar + O + O</td>
<td>2.1·10⁻¹⁰ [98]</td>
</tr>
<tr>
<td>Arₘ + H₂ = Ar + H + H</td>
<td>6.6·10⁻¹¹ [98]</td>
</tr>
<tr>
<td>Arₘ + C₂H₄ = Ar + C₂H₃ + H</td>
<td>5.4·10⁻¹⁰ [98]</td>
</tr>
</tbody>
</table>

¹ Calculated by the Boltzmann solver from experimental cross sections
² Total cross section for excitation of argon metastable states 3P₀,2
³ Sum of electronic excitation cross sections (b¹Σ, b¹Σ, c¹Π, a³Σ, c¹Π, and d¹Π)
⁴ Three dissociation channels into C₂H₃ + H, C₂H₂ + H₂, and C₂H₂ + H + H

The plasma chemistry model also couples a 0-D energy equation for temperature. It incorporates the dominant energy loss mechanism for a slow plasma flow heated by a repetitively pulsed nanosecond discharge, which is conduction to the quartz test section walls. It is given by equation (5.2.1) where νₚₑᵣ is the repetition rate of the burst, hᵢ are the enthalpies for a species i (includes excited states), \( \frac{dn_i}{dt} \) is the rate at which a given species, nᵢ, changes with respect to time, λ(T) is the thermal conductivity, L is the test section height, L/π is the spatial scale for heat transfer conduction with uniform generation in the rectangular geometry, ρ is the
mass density, and \( C_p \) is the specific heat at constant pressure. Note that the temperature of the wall, \( T_w \), is set to 300 K. Finally, \( \frac{Q_{coupled}^{*}AL}{\rho C_p} \) is the coupled energy per unit mass.

\[
\frac{dT}{dt} = \dot{q} - \left( \frac{\lambda(T)}{\rho C_p} \right) \left( T - T_w \right) - \frac{1}{\rho C_p} \sum_i \dot{h}_i \frac{dn_i}{dt} - \frac{\lambda(T)}{\rho C_p} \left( \frac{T - T_w}{\pi^2} \right) \tag{5.2.1}
\]

The parameters to predict time-resolved temperature and species concentrations during a burst and in the afterglow was input into the plasma chemistry model. Keep in mind that the plasma chemistry model is fairly large with the numerous coupled species concentration equations, two-term expansion Boltzman equation for plasma electrons, and the energy equation (equation (5.2.1)). For long discharge bursts of \(~100-500\) pulses, the modeling calculations become very time consuming since the code needs to manage repetitive increase and reduction of time step by \(~6\) orders of magnitude to resolve every discharge pulse while minimizing the run time in the afterglow between pulses. For this work, Adamovich replaced the pulse-periodic discharge excitation during the burst by a continuous excitation at a constant “effective” reduced electric field, \((E/N)_{eff}\), and the same time-averaged discharge power. As will be discussed in section 5.3, this effective \(E/N\) was determined by matching the results of model predictions from pulsed-periodic and from continuous excitation for a burst of 21 pulses in \(O_2\)-\(Ar\).

5.3. 0-D Model Predictions and Comparison with Experiment

For the following discussion regarding the model predictions and comparison with experiment, it should be noted that the experimental results for the absolute O-atom number density with respect to the burst, were obtained by Sherrie Bowman using Two Photon
Absorption Laser Induced Fluorescence (TALIF). The experimental procedure and results are described in more detail in her thesis [86].

Figure 5.2 plots the experimental and predicted waveforms for a single pulse with positive polarity in a 20% O₂-Ar mixture. The experimental waveforms were obtained using the custom designed high bandwidth probes as discussed in section 4.3. The experimental applied electric field, \( E_p \), shown in figure 5.2 was calculated from the experimental applied voltage using equation (5.3.1), where \( U_p \) is the experimental pulse voltage, \( L = 10 \, mm \) which is the discharge gap, \( l = 1.75 \, mm \) which is the thickness of the quartz walls, and \( \varepsilon = 3.8 \) which is the dielectric constant of quartz.

\[
E_p = \frac{U_p}{L + \frac{2l}{\varepsilon}}
\]  

(5.3.1)

![Figure 5.2](image)

*Figure 5.2* Experimental (dashed lines) and predicted (solid lines) applied electric field, electric field in the plasma, and time-resolved stored / coupled energy during the discharge pulse. 20%-80% O₂-Ar, \( P=40 \, \text{torr}, T=300 \, K \).

It can be seen from Figure 5.2 that the calculated experimental peak applied electric field is 18 kV/cm and that peak energy stored in the capacitor exceeds 1mJ. However, very little energy stored in the capacitive load couples into the plasma because the breakdown voltage
occurs early during the pulse duration, well before the peak applied voltage. As a result, plasma shielding prevents much additional energy from being coupled into the plasma and the majority of the stored energy is reflected back to the high voltage generator. It should be noted that the low breakdown voltage largely results from a combination of the very long duration of the pulse, (~75ns), and the slow rise-time.

Figure 5.2 also plots the predictions from the nanosecond pulse discharge model for the applied electric field and the field inside the plasma. The predicted applied electric field (solid red line) results were generated from a fit to the experimental applied voltage which consisted of a linear combination of Gaussians. The predicted time-dependent stored / coupled energy is shown, as well as the asymptotic value of the coupled energy to the plasma. As can be seen in figure 5.3, the predicted energy coupling of 0.12 mJ/pulse using the predicted curves in Figure 5.2 is in good agreement with the experimental value, providing support for the nanosecond discharge model. Finally, the predicted electric field in the plasma is shown in blue and illustrates that the breakdown occurs at a low field, $\sim 3$ kV/cm. After breakdown, the field in plasma remains low due to shielding in spite of high applied electric field (up to 18 kV/cm).

Figure 5.3 plots the predicted time dependent reduced electric field, electron density, and O-atom number densities for a single pulse at the conditions of figure 5.2 using the nanosecond discharge model. As can be seen, within a few ns after breakdown at $E/N \sim 240$ Td, the field drops to $E/N \sim 40$ Td. During this time, the electron density increases and charges separate. Due to this charge separation, the electric field is reduced and electron impact ionization is essentially terminated. This levels the electron density to $n_e \approx 10^{12}$ cm$^3$. (Recall from section 5.2 that the electric field after breakdown is proportional to the time derivative of the applied electric field.) Nearly 80% of the energy coupled to the plasma occurs when the
reduced field is well above $E/N \sim 30$ Td. This considerably reduced the energy fraction going into excitation of low lying forbidden singlet $O_2$ states ($a^3\Delta$) and ($b^1\Sigma$). According to Vasil’eva et al [99], in Ar-$O_2$ mixtures efficient energy conversion of the plasma coupled energy into these forbidden singlet $O_2$ states occurs below $E/n \sim 25$ Td and is most efficient at $E/n \sim 10$ Td. Therefore, it is valid to neglect processes including these singlet $O_2$ states in the plasma chemistry model.

![Figure 5.3](image)

*Figure 5.3  Reduced electric field in the plasma, electron density, time-resolved energy coupled to the plasma discharge pulse, and $O$-atom number density predicted by the $O-D$ kinetic model at the conditions of figure 5.2.*

The predicted temporal $O$-atom concentration for a single pulse is illustrated in figure 5.3. As can be seen, the majority of $O$-atoms are generated at high $E/N$ values, reaching a predicted value of $[O] \sim 2.0 \times 10^{13}$ cm$^{-3}$ at the end of the pulse. This means that almost 50% of the net discharge pulse energy goes into oxygen dissociation, both by electron impact and by energy transfer by argon metastables, with the latter being the dominant channel. The remaining energy, $\sim 30\%$, is rapidly thermalized, with any temperature increase on the nanosecond scale due to heat release from argon metastables and $O$ ($^1D$) quenching reactions:

$$Ar_m + O_2 \rightarrow Ar + O + O$$

(Ra)
\[ O( ^1D) + O_2 \Rightarrow O + O_2 \]  

(Rb)

It should be emphasized that the results shown in Figures 5.2 and 5.3 are for a single pulse. By contrast, the results illustrate in Figure 5.4 result from the entirety of a burst, that is, for multiple pulses. Figure 5.4 plots two separate temporal profiles, solid and dashed lines, for O-atom number density, \([O]\) and temperature predicted by the kinetic model for a discharge burst consisting of 21 pulses in 20%-80% O\(_2\)-Ar at 40 torr. Note that the symbols at the end of the burst are \textit{experimental} O-atom concentrations obtained by TALIF. The solid and dashed curves represent two different approaches to the modeling of an entire burst. First, for solid lines, each of the 21 pulses in the burst was entirely resolved, using the time dependent \(E/n\) and \(n(t)\) parameters shown in figure 5.3. Here, excitation is discrete and repetitively pulsed. This results in the step-wise \([O]\) dependence on time (solid blue line in figure 5.4), which results from rapid O-atom generation on the \(\sim 100\) ns time scale during individual discharge pulses. On the other hand, for the second approach (the dashed lines), single pulses were not resolved in the burst, and instead, were replaced by a continuous excitation at a constant effective \(E/n\), \((E/n)_{\text{eff}} \sim 88\) Td. In this second approach, the burst is not viewed as a train of separate pulses. Regardless, both approaches yield O-atom number densities at the end of the burst that are consistent with the experimental results (black symbols in Fig. 5.3.3). However, it should be noted that the effective \(E/n\), \((E/n)_{\text{eff}}\), that was used in the second approach was chosen such that the O-atom number density at the end of the burst matched the more accurate predictions from the first approach, where the burst is a train of pulses. This yielded the \((E/n)_{\text{eff}}\) of \(\sim 88\) Td.

The use of continuous excitation over a train of pulses, results in an over prediction for the rate of temperature rise on the time scale of the 20-pulse burst, \(\sim 0.5\) ms, as shown in figure

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5.4. But, use of the continuous excitation on a longer time scale of 10ms, which would correspond to a 400-pulse burst, the difference in predictions from the two approaches is much less, ~ 10%, as illustrated in figure 5.5. Therefore, the replacement of the pulse train by the simplified continuous excitation for modeling of long discharge bursts is justified.

Figure 5.4: Two separate model predictions for temporal profiles of O-atom number density, [O], and temperature in 20%-80% O₂-Ar for a discharge burst consisting of 21 pulses, at P=40 torr. Two different approaches were used, (1) for solid lines, each pulse in the burst was resolved entirely for discrete, repetitively pulsed excitation, and (2) for dashed lines, single pulses were not resolved and were replaced with a continuous excitation at a constant effective E/N, (E/N)_{eff} ~ 88 Td. It should be noted that for approach (1), the time-resolved E/N and n(t) from figure 5.3 were utilized for each of the 21 pulses.

Figure 5.5 compares the predicted and experimental temporal profiles of the O-atom density, [O], in the after-glow of a 21-pulse discharge burst in the baseline mixture with no fuel addition. Again, the solid curves are where the burst is treated as a train of pulses, and the dashed curves where it is a continuous excitation. As can be seen, regardless of the modeling approach, the experimental O-atom number density is approximately a factor of 2 higher than modeling predictions. Recall from earlier in this section that the coupled discharge energy is very close to the experimental value (figures 5.2 and 5.3). This means that in order to match the experimental points to the model, it would require all of the coupled discharge energy going
into O ($^3\text{P}$) formation, rather than the predicted 50% (figures 5.4 and 5.5); in this case, there would be no O-atom formation by metastable argon and O ($^1\text{D}$) as these species would not be produced by the discharge pulse. This would suggest that the experimental specific energy loading during the burst of 21-pulses is higher than predicted by the model. However, as discussed in section 4.2, ICCD images show no instances of plasma instabilities in the baseline mixture with no fuel. It is currently unknown why the model under-predicts the O-atom number density, $[O]$, in the after-glow of a 21-pulse burst.

![Figure 5.5: Comparison of predicted and experimental temporal profiles of O-atom number density, $[O]$ in the afterglow of a 21-pulse discharge burst. Again, the mixture is 20-80% O$_2$-Ar at P=40 torr. The solid line is the modeling approach where the burst is a train of pulses. The dashed line is where the burst is continuous.](image)

Figure 5.6 compares the temporal temperature profiles as a function of burst size for the predicted kinetic modeling results and those obtained experimentally by RCARS for 20% O$_2$-Ar mixtures with and without hydrogen. Note that the modeling approach here is that of continuous excitation and the H$_2$-O$_2$ chemistry is described using the model developed by Popov [4] with one of the reaction rates corrected (see section 5.2 for details). As discussed in chapter 4, the experimental temperatures increases approximately linearly with burst size for all four mixtures shown in Figure 5.6, and addition of fuel increases the heating rate. While addition of
ethylene fuel showed a linear dependence of the heating rate on equivalence ratio, hydrogen-containing mixtures did not. In particular, for the baseline 20% O₂-Ar mixture (no fuel), the temperature increases approximately linearly from room temperature to T~350K after 400 pulses. This is consistent with the discharge energy being approximately the same throughout the burst, as hypothesized in chapter 4. This linear trend in the baseline 20% O₂-Ar mixture is well produced by the model, even though the heating rate is somewhat over-predicted. The model also predicts more rapid heating upon addition of fuel, even though the coupled energy is virtually the same among the 20%-O₂-Ar and hydrogen containing mixtures, as is discussed thoroughly in [86]. It also predicts a weak dependence of the heating rate on the equivalence ratio, which is not observed in the experimental data. The weak dependence in the model predictions is a direct result from the low temperatures because there is no chain branching. Hence, the energy release in plasma chemical reactions is therefore limited by plasma radical generation rather than by the amount of fuel, which is why the predicted overall temperature rise for the three hydrogen-containing mixtures are comparable.

Figure 5.6. Comparison of predicted and experimental temperature by RCARS during the discharge burst as a function of burst size. The mixtures include 20% O₂-Ar, and H₂-O₂-Ar at 40 torr. The H₂-O₂ plasma chemistry mechanism utilized was developed by Popov [4]. The modeling approach here is that of continuous excitation with \((E/n)_{eff}^{\sim}88\) Td. If not shown, experimental precision in the 95% confidence interval does not exceed the symbol size.
Figure 5.7 shows the temporal O-atom number density, \([O]\), profiles as a function of burst size for predicted kinetic modeling results and those obtained experimentally by TALIF for 20% \(O_2\)-Ar mixtures with and without hydrogen. Again, the modeling approach here is that of continuous excitation with the \(H_2-O_2\) chemistry described by Popov’s mechanism [4].

![Graph showing O-atom number density vs. number of pulses.](image)

*Figure 5.7 Comparison of predicted and experimental O-atom number density, \([O]\), by TALIF during the discharge burst as a function of burst size. The mixtures include 20% \(O_2\)-Ar, and \(H_2-O_2\)-Ar at 40 torr. The \(H_2-O_2\) plasma chemistry mechanism utilized was developed by Popov [4]. The modeling approach here is that of continuous excitation with \((E/n)_{eff}\sim88\) Td. If not shown, experimental precision in the 95% confidence interval does not exceed the symbol size.*

As illustrated in Figure 5.7, the experimental and predicted O-atom number density in 20% \(O_2\)-Ar rapidly increases over the first \(\sim50\) pulses, after which it then continues to increase, but gradually, up to \([O]\sim 3 \times 10^{15}\) cm\(^{-3}\). At this point, the O-atom production both by direct electron impact and by energy transfer from metastable Ar\(_m\) atoms becomes very nearly balanced by ozone production, which consumes O-atoms, as illustrated in reactions (R1) and (R2).

\[
O + O_2 + M \rightleftharpoons O_3 + M \quad (R1)
\]
\[
O_3 + O \rightleftharpoons O_2 + O_2 \quad (R2)
\]
While the model under-predicts the O-atom generation rate, particularly during the first ~50 pulses, by a factor of 2, the predictions do converge with experimental results for significantly longer burst durations. Furthermore, model predictions agree that the addition of hydrogen both slightly decreases the amount of O-atoms generated and increases the rate of O-atom loss. For instance, adding 3.8% of hydrogen to the baseline 20% O$_2$-Ar mixture ($\varphi=0.1$) results in an O-atom density reduction by almost an order of magnitude from $[O] \sim 3 \times 10^{15}$ cm$^{-3}$ to $[O] \sim (3-4) \times 10^{14}$ cm$^{-3}$. It should be noted that the O-atom generation by Ar$_m$ metastable atoms in reactions (Ra) and (Rb) (see page 118) does decrease upon addition of hydrogen because hydrogen dissociation consumes Ar$_m$ metastable atoms (see table 5.1). However, the increased rate of O-atom loss due to hydrogen oxidation remains the dominant effect. Analysis of the dominant O-atom generation and removal channels show that this occurs via the reduced mechanism [73, 100]:

\[
O(^1D) + H_2 \rightleftharpoons H + OH \quad (R3)
\]

\[
H + O_2 + M \rightleftharpoons HO_2 + M \quad (R4)
\]

\[
O + HO_2 \rightleftharpoons OH + O_2 \quad (R5)
\]

\[
OH + HO_2 \rightleftharpoons H_2O + O_2 \quad (R6)
\]

\[
H + OH \rightleftharpoons O + H_2 \quad (R5)
\]

\[
H + HO_2 \rightleftharpoons H_2O + O \quad (R7)
\]

\[
H + HO_2 \rightleftharpoons OH + OH \quad (R8)
\]

\[
H + HO_2 \rightleftharpoons H_2 + O_2 \quad (R9)
\]
Under the conditions of this work where temperature is low, near room temperature, and O-atom densities are high, reactions (R3-R8) are dominant. As a result, the entire oxidation process proceeds without chain branching. Chain branching doesn’t occur until the temperature increases to $T \approx 500-600$ K, and at these intermediate temperatures, the reverse reactions (R7) and (R9) are dominant.

The sensitivity of the present model to the H$_2$-O$_2$ oxidation mechanism is probed by replacing Popov’s mechanism with Konnov’s mechanism [5]. These results are compared with the experimental data in figures 5.8 and 5.9.

Figure 5.8 Comparison of predicted and experimental temperature by RCARS during the discharge burst as a function of burst size. The mixtures include 20% O$_2$-Ar, and H$_2$-O$_2$-Ar at 40 torr. The H$_2$-O$_2$ plasma chemistry mechanism utilized was developed by Konnov [5] instead of Popov [4]. The modeling approach here is that of continuous excitation with $(E/n)_{eq} \sim 88$ Td. If not shown, experimental precision in the 95% confidence interval does not exceed the symbol size.
As can be seen from figure 5.8, the predicted temperature rise using Konnov’s mechanism agrees somewhat better with the experimental temperature rise. This is largely because the rate for the three body recombination of the O-atom in this mechanism is slower than in Popov’s.

\[ O + O + M \rightleftharpoons O_2 + M, \quad \text{with} \quad M = Ar \]  

(R10)

However, the reduction in rate for (R10) causes the predicted quasi-steady-state of the O-atom density shown in figure 5.9 to be somewhat higher in the baseline O$_2$-Ar with no fuel. Conversely, this quasi-steady state O-atom density upon hydrogen addition is under-predicted by a factor of two. This is largely because the net-rate of O-atom removal is over-predicted, almost entirely due to the higher rate coefficient for the reaction, (R11), where \( k_{T=300K} = \)}
\[ k_{T=300K} = 3.45 \times 10^{-11}\text{cm}^3/\text{s}, \text{in the Popov mechanism.} \]

\[ O + OH \rightleftharpoons H + O_2 \]  \hspace{1cm} (R11)

Nonetheless, both the Popov and Konnov reaction mechanisms for H\textsubscript{2}-O\textsubscript{2} oxidation predict a water number density, [H\textsubscript{2}O], at the end of the burst that is close to the O-atom number density, [O], generated in the baseline O\textsubscript{2}-Ar mixture without fuel at the end of the burst. The Popov mechanism and the Konnov mechanisms both predict [H\textsubscript{2}O] \approx 4 \times 10^{15} \text{ cm}^{-3}. Therefore, because the O-atom and H\textsubscript{2}O number densities are comparable, the H\textsubscript{2}-O\textsubscript{2} oxidation is limited entirely by the O-atom generation in the plasma without fuel where the O-atom mole fraction is \sim 0.2\%, and [O]/[O\textsubscript{2}] \sim 1\%. This also demonstrates that there is virtually no chain branching occurring at these low temperatures because there is no further H\textsubscript{2}O production beyond that which resulted from the generation of [O] in the plasma. It is therefore reasonable to estimate any additional temperature rise caused by H\textsubscript{2}-O\textsubscript{2} oxidation as the difference between the net oxidation enthalpy for the production of water in (R12) and the net O-atom formation enthalpy in (R13) times the O-atom mole fraction, \chi_0 (equation 5.3.2), generated in the O\textsubscript{2}-Ar mixture without fuel as illustrated in equation (5.3.3). This yields a temperature rise of \sim 25 \text{ K}, an estimate that is lower than the experimental result, but is close to the kinetic model predictions.

\[ O + H_2 \rightleftharpoons H_2O \quad \Delta h_{R12} \approx 5.1 \text{ eV} \sim 511 \text{ kJ/mol} \]  \hspace{1cm} (R12)

\[ O_2 \rightleftharpoons O + O \quad \Delta h_0 \approx 2.8 \text{ eV} \sim 249 \text{ kJ/mol} \]  \hspace{1cm} (R13)

\[ \chi_0 = \frac{n_O}{n} \frac{3 \times 10^{15} \text{ cm}^{-3}}{1.3 \times 10^{18} \text{ cm}^{-3}} \approx 2.3 \times 10^{-3} \]  \hspace{1cm} (5.3.2)
Figure 5.10 Comparison of predicted and experimental temperature by RCARS during the discharge burst as a function of burst size. The mixtures include 20% O₂-Ar, and C₂H₄-O₂-Ar at 40 torr. The C₂H₄-O₂ plasma chemistry mechanism utilized was developed by Wang [6]. The modeling approach here is that of continuous excitation with (E/n)_{eff} ~ 88 Td. If not shown, experimental precision in the 95% confidence interval does not exceed the symbol size.

Figure 5.11: Comparison of predicted and experimental O-atom number density, [O], by TALIF during the discharge burst as a function of burst size. The mixtures include 20% O₂-Ar, and H₂-O₂-Ar at 40 torr. The C₂H₄-O₂ plasma chemistry mechanism utilized was developed by Wang [6]. The modeling approach here is that of continuous excitation with (E/n)_{eff} ~ 88 Td. If not shown, experimental precision in the 95% confidence interval does not exceed the symbol size.

Figures 5.10 and 5.11 compare the experimental measurements and modeling predictions for temperature, T, and O-atom number density, [O], as a function of burst size for
ethylene containing mixtures. The conventional fuel oxidation mechanism and excitation approach used here is a hydrocarbon chemistry model developed by Wang [6] and the continuous excitation approach with \((E/n)_{\text{eff}} \sim 88 \text{Td}\). Again, the experimental temperature and O-atom number density, \(\left[O\right]\), for the baseline 20% \(O_2\)-Ar mixture without fuel are in good qualitative agreement with model predictions. However, upon addition of ethylene, the model considerably under-estimates temperature, at most by a factor of 2 at \(\varphi=0.5\). The model temperature predictions begins deviating from the experimental temperature data when the burst size reaches \(\sim 100\) pulses, and the deviations increase with increasing burst size. This corresponds to when the ICCD images begin showing volume contraction and increasing striation in the plasma, both of which continue to increase with burst size. It is likely that the differences between the model and the experimental data can be partially attributed to these plasma instabilities, particularly since the deviations reflect the growth of these instabilities with burst size.

The O-atom number density in figure 5.11 is also considerably under-estimated, particularly for lean mixtures where it is off at most by a factor of 6 at \(\varphi=0.08\) where the \(C_2H_4\) mole fraction is 0.5%. Similar results are predicted if a different combustion mechanism, the GRI mech 3.0, is used [92]. The main difference between the two is that the Wang mechanism includes a third possible initiation mechanism, (in addition to H-abstraction from a fuel molecule and unimolecular dissociation,) where the production of vinylidene then engenders free radicals that eventually participate in reactions participating in or leading to chain propagation and chain branching, as illustrated in reactions (R14) and (R15).

\[
C_2H_4 + M \rightarrow H_2CC + H_2 \quad (R14)
\]
While the present model under-predicts both O-atom number density and temperature in the ethylene containing mixtures excited by a repetitively pulsed burst, in the previous work it has accurately predicted O-atom generation and decay in ethylene containing mixtures by a single nanosecond pulse discharge [16] where the pathways and rates of dominant O-atom removal are well known (reactions R16 and R17) [6].

\[
\begin{align*}
C_2H_4 + O & \rightleftharpoons CH_3 + HCO \\
C_2H_4 + O & \rightleftharpoons CH_2 + CH_2O
\end{align*}
\] (R16) (R17)

However, these ethylene containing mixtures, which are excited by a single nanosecond pulse discharge, contained air where both nitrogen plasma and nitrogen combustion chemistry processes play a role [16]. It is possible that other processes become dominant upon removal of nitrogen from the system, because as discussed in chapter 4, the experimental data for all the mixtures with fuel addition show increasing heating rate with increasing addition of fuel, be it hydrogen or ethylene. This is in contrast to the model, which predicts that the heating rate is largely limited by radical prediction in the plasma, particularly in hydrogen containing mixtures. It may very well be that at these low temperatures that some fuel radicals, like alkyl hydroperoxyl radicals play a larger role in the oxidation mechanism when it is decoupled from NOx chemistry. In particular, alkyl peroxy radicals and their derivatives are not included in both the Wang and GRI Mech 3.0 combustion mechanisms [6, 92]. Alkyl peroxy radicals for the past two decades have played a central role in many proposed low temperature hydrocarbon combustion chemistry mechanisms that have been validated for a variety of hydrocarbon fuels and conditions [7, 32, 101-104]. It is true that as temperature increases, alkyl peroxy radicals
become unstable, but at the conditions for this work, the temperature never increases much past \(~500\) K in ethylene containing mixtures. Thus, it is entirely possible that alkyl peroxy radical can participate in reactions producing OH radicals and alkyl hydroperoxy radicals, both of which participate in chain propagating and/or chain branching reactions, as illustrated in figure 5.12.

![Schematic mechanism for low temperature hydrocarbon oxidation and autoignition from reference [7]](image)

Figure 5.12 Schematic mechanism for low temperature hydrocarbon oxidation and autoignition from reference [7]

There may also exist a simpler, alternate explanation for why the model under-predicts both O-atom number density, [O], and temperature in ethylene containing mixtures. Perhaps the energy loading per molecule is higher in the discharge than predicted by the model. If this is the case, the plasma volume must be smaller than originally thought to cause a higher energy loading because the nanosecond discharge model predicts a coupled pulse energy that is comparable to experimental results. Such a constriction of the time averaged volume occupied by the plasma is observed in the ICCD images discussed in chapter four. It was shown as the burst size increases, so too does the volume constriction and striation observed in the plasma. This is consistent with previous results on ignition of mildly preheated (T=100 -200 °C) H₂-air
and C₂H₄ mixtures excited by repetitive nanosecond discharge [75], which demonstrated nearly uniform large volume ignition of the hydrogen containing mixtures and distinctly non-uniform ignition of ethylene. However, the hydrogen-containing mixtures also deviate from model predictions (experimental result show different heating rates for the different equivalence ratios, while the model predicts heat rates nearly independent of the equivalence ratio), which is why it is suggested that perhaps the low temperature hydro-carbon oxidation mechanism itself needs to be re-visited. Nonetheless, while precluding low-temperature oxidation investigations, preheating the discharge cell is expected to reduce plasma filamentation considerably such that more accurate measurement results can be obtained in hydrocarbon-O₂-Ar mixtures.

5.4 Summary

A zero-dimensional kinetic model has been exercised to model Ar-O₂-H₂ and Ar-O₂-C₂H₄ mixtures excited by a repetitively pulsed nanosecond discharge in a plane-to-plane dielectric barrier discharge geometry, operated with a high pulse repetition rate of 40-kHz at a pressure of 40 torr. Temperature and O-atom number density, [O], predictions as a function of burst size have been compared with experimental temperature results by pure rotational Coherent Anti-Stokes Scattering, and experimental O-atom number density, [O], by Two photon Absorption Laser Induced Fluorescence. The experimental temperature results demonstrate high accuracy of pure rotational psec CARS measurements at low partial pressures of O₂ (6-8 torr) in non-equilibrium plasmas. The average standard deviation for the dielectric barrier discharge work ranged from ± 1 to 5 K and the average confidence interval from ± 1 to 8 K. Hydrogen mixtures uncertainties centered on ± 2 K and the two fuel-lean ethylene mixtures centered on ±5 K with the stoichiometric at ±8 K. The larger uncertainty of the ethylene containing mixture reflects
the instabilities observed in the ICCD images because the difference in the uncertainties
between the hydrogen and ethylene mixtures cannot be attributed to higher temperatures and
EMI noise.

The 0-D model assumes a diffuse and volumetric plasma which allows the zero-
dimensional treatment and decouples the energy coupling during the nanosecond discharge
(nanosecond discharge model) and the subsequent plasma chemistry because they occur on
two disparate time-scales. The non-equilibrium O₂-Ar plasma chemistry was expanded to
include hydrogen and ethylene dissociation processes. This was coupled to two different H₂-O₂
and hydrocarbon conventional oxidation mechanisms. Continuous excitation replaced
repetition pulsed excitation where \((E/n)_{\text{eff}} \sim 88\) Td was chosen such that the predicted O-atom
number density at the end of a 21-pulse burst matched that predicted where excitation is
discrete and repetitively pulsed. This plasma chemistry model requires the solutions from the
nanosecond discharge model in order to work. The nanosecond discharge model assumes
residual electron density from a previous pulse is much less than the peak electron density
generated in the plasma during a pulse. It also assumes that only two dominant processes
occur, electron impact ionization, and the charging of the dielectric surface. This assumption
allows the quasi-neutral plasma and sheath regions to be considered separately. The sheath is
assumed to move rapidly to its quasi-steady-state and is, therefore, treated in the quasi-steady-
state limit. It is also assumed that the ionization frequency is much faster than the variation of
the applied electric field. These assumptions yield a closed analytic solution for the energy
coupled to the plasma at breakdown (see equation 5.1.25). The two dielectric layers in the
discharge together with the sheath form a capacitor at the moment of breakdown. Thus, the
energy coupled into the plasma is entirely controlled by the applied waveform which is
approximated as a Gaussian pulse. After breakdown, the load behaves as a constant resistance in an RC circuit and the electric field is proportional to the time-derivative of the applied electric field. Finally, when operating in burst mode, the coupled pulse energy is nearly independent of the pulse repetition and remains constant throughout the pulse as long as temperature is constant. When temperature is no longer constant, coupled pulse energy scales nearly proportionally to the number density.

In H$_2$-O$_2$-Ar mixtures, the kinetic modeling predictions, using the chemistry mechanism suggested by Popov with the corrected rate-constant, are in fairly good agreement with the data, predicting temperature rise and O atom accumulation in long discharge bursts, up to 450 pulses. However, the Konnov mechanisms agrees somewhat better with the temperature data, but deviates more significantly from the [O] atom data. The weak dependence on equivalence ratio by the hydrogen containing mixtures is predicted by the model using both hydrogen oxidation mechanisms which shows no chain branching at low temperature, meaning that energy release is limited entirely by O-atom generation in the plasma. Both the Popov and Konnov mechanisms also predict that the production of water is also limited by the O-atom generation. Therefore, additional heating upon addition of hydrogen fuel, due to its partial oxidation by radicals generated in the plasma, can be estimated by the difference in the net oxidation enthalpy for water production and the O-atom formation enthalpy times the O-atom fraction in the mixture. This gives $\Delta T \sim 25$ K, which is lower than experimental results, but close to model predictions. However, the experimental data shows that the hydrogen-containing mixtures do have a strong non-linear dependence on equivalence ratio, indicating that heat release is not limited by the radical production in the plasma.
In \( \text{C}_2\text{H}_4\text{-O}_2\text{-Ar} \) mixtures, the model consistently under-predicts both temperature and \( \text{O} \) atom number density. The most likely reason for difference between the experimental data and the model predictions is discharge non-uniformity developing when ethylene is added to the mixture, at fairly low temperatures involved. However, given that the experimental heating rates for hydrogen containing mixtures do not appear to be limited by the radical production in the plasma, as the model predicts, it may very well be that the low-temperature hydrocarbon mechanism needs to be revisited, perhaps one that would include alkyl peroxy radicals. Nonetheless, to reduce the effect of plasma filamentation, future measurements will be conducted in mildly preheated hydrocarbon-oxygen-argon mixtures, such as has been done in our recent work [29]. This will also allow studying kinetics of \( \text{O} \) atom decay and energy release in plasmachemical reactions at the conditions when chain branching plays a significant role, but it will preclude close investigations of low-temperature oxidation mechanisms.
In chapter 1, the topic of plasma assisted combustion was introduced. Under this umbrella exists a subset known as transient plasma ignition, where short (10-50 ns), high voltage (kV), pulses are utilized to ignite combustion over conventional spark plug ignition. This typically results in shorter ignition delay times, higher peak pressures, increased net heat release and extension of the lean flammability limits [1, 105, 106]. The transient discharges generally consist of multiple streamer channels that have high E/N values (~500 Td) at the front of a fast ionization wave resulting from the short voltage rise times, but low E/n values exist within the streamer channels themselves on the order of ~20 to 30 Td. It should be noted that there is an over-voltage requirement of 1.1 to 2 times for the formation of these streamers, that is, the E-field must exceed the breakdown voltage threshold requirements by 1.1 to 2 times. This results in a significant amount of energy going towards ionization resulting in an anode-directed avalanche that rapidly creates a conductive channel (streamer) [107, 108]. (An anode-directed streamer propagates in two directions, towards the anode and cathode).

In transient plasma ignition, there are two general stages leading to ignition[1]. The first is a non-equilibrium plasma stage, where the discharge generates electrons that transfer energy into electronic excited states, meta-stables, radicals, and vibrationally excited states. As a result, new reaction pathways are generated that proceed on new potential energy surfaces. The second stage is a spatially distributed thermal phase that takes place in the after-glow of the
discharge. It largely consists of exothermic fuel oxidation reactions that lead to ignition. However, ignition does not take place over the entirety of the streamer channel. Rather, ignition kernels are typically formed at the ends of streamer channels where the energy deposition was at its highest during the discharge (usually at the anode). In fact, Pendleton et al [105] showed that the temperature in the streamer channels remain close to room temperature up to 100ns after the discharge. Nonetheless, it is clear that both gas heating and the production of active species (electronic excited states, radicals, etc) control the kinetics of ignition and combustion in transient plasma ignition. In particular, gas heating during and after the discharge is critical in understanding plasma initiated combustion because it both controls the rates of exothermic reactions and the rates of recombination. After all, flame propagation only occurs when the rate of exothermic reactions is higher than the recombination rate of dissociated species [107, 108].

Gas heating is still not largely understood in these systems [1, 3, 105, 107, 108]. It is the goal of this work to probe the heat release temporally during and after a streamer-like discharge by examination of the translational energy via RCARS. Here, a pin-to-pin geometry is used where a non-uniform streamer-like discharge is generated. While it is not identical to the streamers used in transition ignition combustion, it is highly reproducible and, therefore, allows reconstruction of the effects of gas heating on the kinetics.

Eight different gas compositions were investigated in the pin-to-pin discharge cell at a low pressure of 52 torr and with a virtually static flow rate of ~ 0.02m/s: (1) Air (2) Air with H₂ at φ=0.14, (3) Air with H₂ at φ=0.42, (4) Air with H₂ at φ=0.82, (5) Air C₂H₄ at φ=0.19, (6) Air with C₂H₄ at φ=0.48, (7) Air with C₂H₄ at φ=0.87, and (8) Air with C₂H₄ at φ=1.47. It should be emphasized that while Markus et al [107] discovered that different gas mixtures required
different input voltages to ignite the mixtures, it was found in this work that the coupled energy into the systems is virtually identical across the different compositions for the given out-put pulses from the high voltage generator, as will be discussed in section 6.1.

This chapter is divided into eight parts, starting with the experimental coupled pulse energies in these plasmas for the different mixtures and following with ICCD images in air and the air-H$_2$ mixture at $\varphi=0.83$. The next three sections cover the RCARS experimental uncertainty in the pin-to-pin discharge system, the temporal RCARS results, and a summary of those results. This is then followed by spatial RCARS results in air only at three different delays relative to the main pulse. The chapter concludes with examination of previous work and possible processes contributing to the observed temporal trends in the pin-to-pin-discharge.

6.1 Experimental determination of energy coupled in to plasma

Just as in the dielectric barrier discharge experiments, it is desirable to know how much of the applied electrical energy is converted into other forms in the plasma. Recall from section 4.3 that the coupled energy can be empirically determined by application of equations (4.3.1) and (4.3.2) to experimentally obtained current and voltage waveforms. However, for the pin-to-pin discharge there is no need to obtain these waveforms using two different kinds of probes as common mode noise as a source of systematic error was not a concern. All of the waveforms collected in the pin-to-pin discharge were obtained using the standard high-voltage and current probes and each waveform was “single shot”—there was no averaging.

Three sets of waveforms were obtained. The first set is titled “February 2nd” and were collected on an oscilloscope with a resolution of 4-ns and the oscilloscope was triggered using the $T_0$ from the master clock (8-channel Stanford delay generator discussed in section 3.5). All
eight gas mixtures were probed to collect the data for this set. It should be noted that a “jitter analysis” was performed on this first data-set. The second two data sets, “February 10” and “February 17th” were both obtained on an oscilloscope with a higher resolution of 0.2ns and triggered using the rise of the voltage pulses (usually main pulse). Only one gas mixture, air, was probed to obtain these two data sets.

As previously mentioned in section 3.5, the high voltage generator for this work operated in “single pulse” mode at 60-Hz and was triggered by a Stanford delay generator which acted as master clock for experimental synchronization. However, in spite of receiving only a single pulse trigger from the master clock, the high voltage generator generated a waveform consisting of three pulses, a pre-pulse, main pulse, and third pulse, as illustrated in figure 6.1. The peak applied voltages, amperages, and coupled pulse energies for each pulse was analyzed for the three data sets collected using the same statistical tools outlined in section 4.4, where the standard deviation is given by equation (4.4.1) and the 95% confidence interval (CI) by equation (4.4.2).

It should be emphasized that the waveforms obtained from the different gas mixtures in the first set, February 2nd, were remarkably similar; this is important because it means the amount of energy coupled in each of the gas mixtures is the same. However, as will be discussed later in the chapter, it is possible that the partitioning of the energy differs between the hydrogen and ethylene containing fuel mixtures. Nonetheless, given the remarkable similarity of the waveforms among the mixtures, they were considered the same for statistical analysis.
A total of ten waveforms were collected over the three different data sets. Analysis was performed on only five of these waveforms. Three of these came from the February 2\textsuperscript{nd} data set, (1) air, (2) air-H\textsubscript{2} at $\phi=0.87$, and (3) from air-C\textsubscript{2}H\textsubscript{4} at $\phi=1.47$. The last two waveforms were those taken in air from the February 10 and February 17\textsuperscript{th} data sets. The results of the analysis are tabulated in tables 6.1 and 6.2. However, it should be noted that n/a is supplied when there is no significant difference from the baseline. For instance, it was not possible to determine the FWHM for the third pulse in the majority of the current waveforms because the baseline is very noisy.

![Waveforms in C\textsubscript{2}H\textsubscript{4} fuel, phi=1.47 at 52 torr](image)

Figure 6.1: Waveforms from the “February 2\textsuperscript{nd}” data-set obtained in air-ethylene mixture for $\phi=1.47$. The blue waveform is voltage, kV, the red is current, A, and the green is the instantaneous power as given by equation 4.3.1, in units of kW.

Table 6.1 lists the peak applied voltage and current for each of the three pulses in the five waveforms. The average peak applied voltage for the pre-pulse is $\sim 4.4 \pm 0.4$ kV (95% CI). This error is $\sim 9\%$ of the value. The corresponding average peak current is $4.0 \pm 1.1$ A; the error here accounts for 27.5% of the value. For the main pulse, the average peak applied voltage is $\sim 4.6 \pm 0.0$ kV and the average peak current is $26.7 \pm 1.1$ A. Finally, the third pulse has almost
negligible values, with a peak voltage at \( \sim 1.0 \pm 0.2 \text{ kV} \) and a peak current at \( 0.6 \pm 0.2 \text{ A} \). The third pulse clearly has the highest uncertainties for the peak values of the three pulses as they account for over 30% of the peak values. This is not surprising given the smaller sample size because the values lie much closer to the baseline. Nonetheless, it is expected that the majority of the energy is coupled into the main pulse rather than the pre-pulse or the almost negligible third pulse because the main pulse has the peak values that are consistently higher.

Table 6.1 Experimentally determined peak applied voltages and current for each of the three pulses from five different mixtures. These results were used to calculate the average, standard deviation, and 95% CI.

<table>
<thead>
<tr>
<th></th>
<th>Feb 2nd, Air</th>
<th>Feb 2nd, ( \sigma=0.83 ) C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</th>
<th>Feb 2nd, ( \sigma=1.47 ) C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</th>
<th>Feb 10 Air</th>
<th>Feb 17 Air</th>
<th>sample size</th>
<th>Average</th>
<th>standard deviation</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PREPULSE</strong></td>
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<td></td>
</tr>
<tr>
<td>Peak Applied Voltage, KV</td>
<td>4.2</td>
<td>4.4</td>
<td>4.0</td>
<td>4.7</td>
<td>4.6</td>
<td>5</td>
<td>4.4</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Peak Applied Current, A</td>
<td>4.0</td>
<td>6.0</td>
<td>5.8</td>
<td>5.1</td>
<td>4.1</td>
<td>5</td>
<td>5.0</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>MAINPULSE</strong></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak Applied Voltage, KV</td>
<td>4.6</td>
<td>4.6</td>
<td>4.6</td>
<td>4.6</td>
<td>4.6</td>
<td>5</td>
<td>4.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Peak Applied Current, A</td>
<td>26.2</td>
<td>28.0</td>
<td>27.0</td>
<td>27.0</td>
<td>25.7</td>
<td>5</td>
<td>26.8</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>THIRD PULSE</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Peak Applied Voltage, KV</td>
<td>1</td>
<td>n/a</td>
<td>0.8</td>
<td>1.0</td>
<td>1.0</td>
<td>4</td>
<td>1.0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Peak Applied Current, A</td>
<td>0.6</td>
<td>n/a</td>
<td>0.4</td>
<td>0.8</td>
<td>n/a</td>
<td>3</td>
<td>0.6</td>
<td>0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

To calculate the coupled energy for each of the pulses, it was necessary to determine the integration boundary limits for equation (4.3.2). Two different boundary constraints were chosen for each pulse, a tight boundary limit and a long boundary limit. The tight boundary limit wraps tightly around each pulse and the resulting coupled energy are taken as the values for each pulse. However, close examination of each pulse reveals that there is some structure occurring immediately after each sharp pulse that looks remarkably like electrical “ringing” as shown in figure 6.1. This ringing is the reason for the second longer boundary constraint. While it appears that the ringing will cancel itself out upon integration, application of the second boundary limit investigates whether or not this is the case. The results from both integration limits are listed in Table 6.2, where integration time 1 refers to the tight boundary limit and
integration time 2 to the long boundary limit. The FWHM of the peak applied voltage and currents are included in the table for comparison with the integration limits.

![Waveforms for Hydrogen Fuel at phi=0.83](image)

*Figure 6.2: Waveforms from the “February 2nd” data-set obtained in air-H$_2$ mixture for $\phi=0.87$. The blue waveform is voltage, kV, the red is current, A, and the green is the instantaneous power as given by equation 4.3.1, in units of kW. The waveforms are “zoomed” in to show only the pre-pulse. The main pulse and third pulse are not shown.*

| Table 6.2: Experimentally determined current and voltage FWHM for each of the three pulses for five different waveforms for five different mixtures. The integration times 1 and 2 refer to integration limits for equation 4.3.2. Integration time 1 is referred to as tight boundary limit in the text and integration time 2 as the long boundary limit. These results were used to calculate the average, standard deviation, and 95% CI. |

<table>
<thead>
<tr>
<th></th>
<th>Feb 2nd, Air</th>
<th>Feb 2nd, H$_2$, $\phi=0.83$</th>
<th>Feb 2nd, C$_3$H$_8$, $\phi=1.47$</th>
<th>Feb 10, Air</th>
<th>Feb 17, Air</th>
<th>sample size</th>
<th>Average</th>
<th>Standard deviation</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PREPULSE</strong></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Integration time 1, ns</td>
<td>360</td>
<td>320</td>
<td>296</td>
<td>337</td>
<td>372</td>
<td>5</td>
<td>337</td>
<td>30</td>
<td>38</td>
</tr>
<tr>
<td>Voltage FWHM, ns</td>
<td>92</td>
<td>60</td>
<td>68</td>
<td>108</td>
<td>71</td>
<td>5</td>
<td>80</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>Current FWHM, ns</td>
<td>102</td>
<td>96</td>
<td>92</td>
<td>85</td>
<td>101</td>
<td>5</td>
<td>95</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td><strong>MAINPULSE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Integration time 1, ns</td>
<td>288</td>
<td>228</td>
<td>232</td>
<td>318</td>
<td>2185</td>
<td>5</td>
<td>650</td>
<td>859</td>
<td>1066</td>
</tr>
<tr>
<td>Integration time 2, ns</td>
<td>976</td>
<td>596</td>
<td>944</td>
<td>887</td>
<td>2543</td>
<td>5</td>
<td>1189</td>
<td>772</td>
<td>958</td>
</tr>
<tr>
<td>Voltage FWHM, ns</td>
<td>48</td>
<td>41</td>
<td>48</td>
<td>42</td>
<td>41</td>
<td>5</td>
<td>44</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Current FWHM, ns</td>
<td>44</td>
<td>44</td>
<td>48</td>
<td>47</td>
<td>44</td>
<td>5</td>
<td>45</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td><strong>THIRD PULSE</strong></td>
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</tr>
<tr>
<td>Integration time 1, ns</td>
<td>354</td>
<td>n/a</td>
<td>8900</td>
<td>592</td>
<td>796</td>
<td>4</td>
<td>2660</td>
<td>60</td>
<td>95</td>
</tr>
<tr>
<td>Voltage FWHM, ns</td>
<td>100</td>
<td>n/a</td>
<td>120</td>
<td>110</td>
<td>90</td>
<td>4</td>
<td>105</td>
<td>12</td>
<td>19</td>
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<tr>
<td>Current FWHM, ns</td>
<td>100</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.2 shows that the tight boundary limit for the pre-pulse is \( \sim 337 \text{ns} \) long and the main pulse \( \sim 266 \text{ns} \). These fully encompass their corresponding pulses and are about three to six times longer than the duration of the pulse. The pre-pulse applied voltage has an average duration of \( \sim 80 \pm 25 \text{ ns} \). This is comparable to the pulse duration in the dielectric barrier discharge work. On the other hand, the main pulse is much shorter, with a duration of \( \sim 44 \pm 5 \text{ ns} \). Finally, the third pulse applied voltage is roughly 105ns. On the other hand, the long boundary limit is about five to ten times the length of the tight boundary limit so that it can fully encompass the ringing. The ringing stretches over \( \sim 2841 \text{ns} \) after the pre pulse and 923ns after the main pulse.

The calculated coupled pulse energies using these two integration times are listed in table 6.3 for each of the five waveforms examined. It can be seen that the average coupled pulse energy for the pre-pulse is \( 0.8 \pm 0.2 \text{ mJ} \). If ringing is included, this increases to \( 1.0 \text{ mJ} \), which is a 25\% increase. The coupled energy for the main pulse is on average \( 2.8 \pm 0.2 \text{ mJ} \). If ringing is included, there is no change in the overall coupled pulse energy. It is clear that the ringing after the pre-pulse has a more significant impact on the overall coupled pulse energies than the ringing after the main pulse. Finally, the total coupled energy over the entire waveform is on average \( 3.8 \pm 0.4 \text{ mJ} \). Because the third pulse couples only \( \sim 0.02 \text{ mJ} \), which is only 0.5\% of that total, it can be considered negligible. On the other hand, \( \sim 74\% \) of the energy is deposited during the main pulse and \( \sim 21\% \) during the pre-pulse.
Table 6.3: Empirically determined coupled pulse energies using equation 4.3.2 for each of the three pulses from five different waveforms. Coupled energy 1 and 2 are calculated using different limits, which are integration time 1 (tight boundary limit) and integration time 2 (long boundary limit) respectively. These results were used to calculate the average, standard deviation, and 95% CI.

<table>
<thead>
<tr>
<th>Pulse Type</th>
<th>Feb 2nd, Air</th>
<th>Feb 2nd, H₂</th>
<th>Feb 2nd, C₂H₆</th>
<th>Feb 10, Air</th>
<th>Feb 17, Air</th>
<th>Sample Size</th>
<th>Average</th>
<th>Standard Deviation</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREPULSE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coupled Energy 1, J</td>
<td>0.0008</td>
<td>0.0010</td>
<td>0.0009</td>
<td>0.0008</td>
<td>0.0006</td>
<td>5</td>
<td>0.0008</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>Coupled Energy 2, J</td>
<td>0.0010</td>
<td>0.0013</td>
<td>0.0010</td>
<td>0.0008</td>
<td>0.0007</td>
<td>5</td>
<td>0.0010</td>
<td>0.0002</td>
<td>0.0003</td>
</tr>
<tr>
<td>MAINPULSE</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Coupled Energy 1, J</td>
<td>0.0029</td>
<td>0.0030</td>
<td>0.0030</td>
<td>0.0026</td>
<td>0.0026</td>
<td>5</td>
<td>0.0028</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>Coupled Energy 2, J</td>
<td>0.0029</td>
<td>0.0030</td>
<td>0.0030</td>
<td>0.0026</td>
<td>0.0026</td>
<td>5</td>
<td>0.0028</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>THIRD PULSE</td>
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<td></td>
</tr>
<tr>
<td>Coupled Energy, J</td>
<td>0.00003</td>
<td>na</td>
<td>0.00003</td>
<td>0.00002</td>
<td>0.00003</td>
<td>4</td>
<td>0.00002</td>
<td>0.00002</td>
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<tr>
<td>TOTAL ENERGY</td>
<td>0.0039</td>
<td>0.0043</td>
<td>0.0040</td>
<td>0.0037</td>
<td>0.0034</td>
<td>5</td>
<td>0.0038</td>
<td>0.0004</td>
<td>0.0004</td>
</tr>
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</table>

Finally, a jitter analysis was performed on the first data set, Feb 2nd, to determine the uncertainty in the time axis for the temporal RCARS results. This was achieved by capturing 8 to 9 waveforms that were triggered by the master clock (single shot, no averaging) and recording the peak voltage and amperage for each pulse in all eight gas mixtures investigated in this work. Because all of the gas mixtures were treated as the same, this yielded 67 points each for pre-pulse current and voltage, and 65 points for main pulse current and voltage. Table 6.4 presents the statistical analysis of these points.

Table 6.4: The average time after the trigger for the peak value, both voltage and current, is given in nanoseconds. The corresponding standard deviation is given as well, as is the 95% CI. The data-set for the pre-pulse includes 67 data points and 65 for the main pulse, where each of the eight gas mixtures contribute 8 to 9 data points to the total.

<table>
<thead>
<tr>
<th>Pulse Type</th>
<th>Time after trigger, ns</th>
<th>Standard deviation, ns</th>
<th>95% CI, ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRE-PULSE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
<td>2583.0</td>
<td>13.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Current</td>
<td>2609.1</td>
<td>14.1</td>
<td>3.5</td>
</tr>
<tr>
<td>MAIN PULSE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
<td>8588.0</td>
<td>51.6</td>
<td>12.8</td>
</tr>
<tr>
<td>Current</td>
<td>8602.1</td>
<td>49.5</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Table 6.4 shows that if considering the standard deviation, the pre-pulse has a jitter of ~14 ns and the main pulse has a jitter of ~52 ns; the main pulse experiences about four times the jitter that the pre-pulse experiences. Table 6.4 also shows that the confidence intervals are
about four times smaller than the standard deviations. This is because the sample size was so large with 67 and 65 data points for the pre-pulse and main pulse, respectively. Comparison of the jitter with the voltage FWHM (table 6.2) shows that the jitter of the main pulse is on par with the FWHM (~45ns). On the other hand, the jitter of the pre-pulse is only 0.2% of the FWHM. Clearly, the pre-pulse output is far more stable than the main pulse with respect to the master clock. The exposure time for RCARS was increased from 20-40 s (dielectric barrier discharge) to 100-350s to average out the existing larger jitter. Nonetheless, both jitters are less than 100 ns and as will be shown in section 6.4, this is an order of magnitude less than the time scale of the processes responsible for heat-release in this system.

6.2 Plasma Characterization by ICCD images

Plasma uniformity and thermal instabilities were discussed in detail in chapter four with respect to the dielectric barrier discharge cell. However, it is difficult to quantify and to ascertain with certainty what might be possible sources for the formation of any instabilities. Yet it was shown that the ICCD images offered a qualitative assessment and thermal ionization instabilities were posited as a possible source for instability in the dielectric barrier discharge system. Here in the pin-to-pin discharge, there is no longer a dielectric barrier that yields a breakdown consisting of a fast ionization wave with a spherical wave propagation [71], but both discharges are of the pulsed avalanche breakdown type [109]. In particular, the pin-to-pin discharge can be likened to a streamer discharge consisting of a single inhomogeneous filament that is highly reproducible, and more importantly, large enough to enable optical diagnostic studies as well as reduce mass diffusion effects. It is critical that the filament is stable so that measurements are reproducible and can be compared with any model that is developed for the pin-to-pin discharge. The stability of this filament is qualitatively characterized by ICCD images.
taken in two different mixtures, air and air-hydrogen at $\varphi=0.83$. The UV images were obtained with a Princeton Instruments, PIMAX ICCD camera with a UV lens (UV-Nikon 105mmf/4.5 Nikon). The gate is set to 100ns and wrapped around a single pre-pulse or main-pulse discharge. The gain is set to zero and all images are “single-shot”; there is no averaging.

Figure 6.3 has typical two images side by side that were taken in the pure air mixture, during the pre-pulse discharge. Recall from section 3.4, that the high voltage generator outputs pulses of alternating polarity. The image on the left has positive polarity at the top electrode and the image on the right has negative polarity. In both cases, the filament is quite reproducible; ten images were taken and there were no visible changes, as judged by eye. As can be seen, the filament is quite diffuse. There is some higher intensity of emission located near the cathode, which is the top electrode when polarity is positive and the bottom electrode when the polarity is negative; this localized stronger emission near the cathode is more apparent when the pulse has positive polarity, as seen in the image on the left in Figure 6.3. This is not the case when examining images taken during the main pulse, as shown in figure 6.4 where the intensity is mostly uniform across the gap. For both the pre-pulse and main pulse discharges, it is evident that the plasma intensity decreases with increasing distance radially from the centerline of the plasma (and therefore, it is not homogeneous). It is apparent that the pre-pulse spans a larger radius than the main-pulse. This is further illustrated in figure 6.5, where radial intensities from the middle of the discharge in all four images in figures 6.3 and 6.4 are plotted versus the radial distance, $r$. 

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Figure 6.3: ICCD images of the pre-pulse discharge in Air, at 52 torr. The camera gate is 100ns and there is no gain. The image on the left was taken when the polarity at the top electrode was positive and the one on the right when the polarity was negative.

Figure 6.4: ICCD images of the main pulse discharge in Air, at 52 torr. The camera gate is 100ns and there is no gain. The image on the left was taken when the polarity at the top electrode was positive and the one on the right when the polarity was negative.

To determine the radial distance in figure 6.5, it was necessary to estimate the number of millimeters per pixel. This was done by dividing the electrode diameter by the number of pixels spanning the diameter of the electrode. The number of pixels spanning the diameter of the electrode was determined using each of the four images in figures 6.3 and 6.4. This procedure was repeated twice for each image because the electrode boundaries are not clearly defined and resulted in a 95% confidence interval of ±0.27 mm for the gap distance, which is ~
9.0mm. Finally, the middle of the discharge is roughly at \( r = 193 \) pixels, which was set to \( r = 0 \)mm to generate the x-axis in figure 6.5. As can be seen from figure 6.5, the maximum plasma intensity is centered on \( r = 0 \) for both the pre-pulse and main pulse. The FWHM of these curves was used to determine the plasma diameters of the pre-pulse and main pulse. The FWHM of the pre-pulse is \( \sim 2 \) mm and the main pulse is \( \sim 1 \) mm. These two diameters will be incorporated into model development for two discharges. However, as will be discussed in section 6.7, this differs from the radial profiles obtained using spatial radial profiles.

![Radial Plasma Intensities from Middle of Discharge, Air](image)

*Figure 6.5* The radial intensity from the middle of the discharges shown in figures 6.3 and 6.4 are plotted against the radial distance to yield four curves (one from each image). The radial distance was determined using the electrode dimensions.

Finally, to determine the stability of the discharge upon addition of fuel, images were also obtained in air-hydrogen mixtures at \( \phi = 0.83 \) with a shorter gate of 10ns. Figure 6.6 presents initial images taken during the pre-pulse and main pulse discharge, left to right, respectively. The high voltage output had positive polarity in both cases. As can be seen, the images look remarkably similar to those obtained in air; the filaments are quite uniform along the discharge gap for a given ‘r’, and the radial intensity decreases with increasing distance; although, the pre-pulse does exhibit some localized intensity near the electrodes—this was also
observed in the pre-pulse discharge obtained in air. Again, the radial intensity from the middle of the discharge from these two images were plotted against the radial distance as well to determine the plasma diameters. As shown in figure 6.7, the diameter of the pre-pulse is ~ 2mm and ~ 1mm for the main pulse, which are identical to the diameters obtained in air.

![Figure 6.6 ICCD images of the discharge in air with added hydrogen at φ=0.83, at 52 torr. The camera gate is 10ns and there is no gain. The image on the left was taken during the pre-pulse discharge, and the image on the right during the main pulse. The polarity in both cases was positive.](image)

![Figure 6.7: The radial intensity from the middle of the discharge shown in figures 6.6 are plotted against the radial distance to yield two curves (one from each image in the figure). The radial distance was determined using the electrode dimensions.](image)
After obtaining the images in figure 6.6, four successive images at the shorter gate of 10ns for both the pre-pulse and main-pulse were taken to further probe the stability. The pre-pulse was very stable and successive images were virtually identical. However, the main-pulse showed some curvature along the discharge gap direction, $x$, as shown in figure 6.8.

The curvature along the discharge gap resulted in the maximum intensity at the middle of the discharge shifting along the radial axis; it was no longer consistently at $r=0$. To quantify this effect, the intensity distributions from each of the successive images are plotted along the
radial axis, which is illustrated in figure 6.9. As can be seen, the peak shifts range from \( r = -0.3 \text{mm} \) to 0.5mm. Because the instability is random, it is expected that a longer gate time would result in an apparent broadening of the plasma diameter, going from 1mm to \(~2\text{mm}\). This anticipated broadening was determined by using the blue and black curves as demonstrated in figure 6.9. It was assumed that because these two curves exhibited the largest radial shifts, that this would be a good approximation for the broadening. The half maximum on the left side of the blue curve and the right side of the black curve were used to determine the anticipated FWHM of the anticipated broadened plasma diameter at larger exposure times.

![Radial Plasma Intensities from Middle of Discharge, Air with H₂ at phi=0.83](image)

*Figure 6.9: The radial intensity from the middle of the main pulse discharge shown in figure 6.7 are plotted against the radial distance to yield four curves (one from each image in the figure). The radial distance was determined using the electrode dimensions.*

It is not possible to quantify any impacts on the RCARS measurements (if any) resulting from the instabilities upon addition of fuel. However, at least half of the FWHM of each curve shown in figure 6.10 fall within the 0.5mm RCARS probe volume. It is therefore anticipated that the average temperatures in the RCARS probe volume may decrease slightly because the RCARS probe volume will not always center on the hottest temperature. On the other hand, it is
possible, that the instabilities may sometimes result in higher temperatures. Longer RCARS exposure times will help to average these effects. Furthermore, it is anticipated these effects will fall within the range of the RCARS uncertainty because the uncertainty of RCARS in this work is determined using the same mixture of air-hydrogen at $\phi=0.83$. Thus, the instabilities should be accounted for.

![Radial Plasma Intensities from Middle of Discharge, Air with H\textsubscript{2} at phi=0.83](image)

**Figure 6.10:** The blue and black curves from figure 6.9 are shown only in this figure with the anticipated FWHM of the broadened plasma diameter due to instability formation.

### 6.3 RCARS Uncertainty in the Pin-to-Pin Discharge

The main focus of the work in the pin-to-pin discharge is to obtain time resolved temperature measurements by pure rotational CARS to probe the evolution of heat release in the streamer-like discharge. All RCARS measurements were taken at different times with respect to the pre-pulse or main pulse by varying the delay for the 10 Hz laser trigger from the master-clock, while the 60 Hz trigger sent to the high voltage generator was fixed in time. For the presented temperature results, two different *time zero* are chosen and both are taken with
respect to the $T_0$ trigger from the master clock. The first is taken at that point just as the pre-pulse current begins to rise; it is not the point at which the peak amplitude occurs. The second time zero is that moment when the main pulse current begins to rise. As illustrated in table 6.5, these times were determined by taking the average of eight different waveforms (one for each of the different gas compositions). The pre-pulse was determined to be at 2.562 µs with a 40ns uncertainty (95% CI) and the main pulse at 8.577 µs with 63ns uncertainty (95% CI). Both of these uncertainties are larger than those obtained using the jitter analysis. It is thought that this might be due to instabilities arising from fuel addition. In any case, the main pulse and pre-pulse are 6.015-µs apart.

Table 6.5: Using all of the waveforms from the “Feb 2nd” data set discussed in section 6.1, the time zero was determined to be the point at which the current begins; This time is relative to the $T_0$ trigger from the master-clock (8-channel Stanford delay generator).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Pre-pulse, µs</th>
<th>Main pulse, µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>2.592</td>
<td>8.664</td>
</tr>
<tr>
<td>$H_2$, $\phi$=0.83</td>
<td>2.456</td>
<td>8.428</td>
</tr>
<tr>
<td>$H_2$, $\phi$=0.42</td>
<td>2.548</td>
<td>8.536</td>
</tr>
<tr>
<td>$H_2$, $\phi$=0.14</td>
<td>2.596</td>
<td>8.624</td>
</tr>
<tr>
<td>$C_2H_4$, $\phi$=1.47</td>
<td>2.552</td>
<td>8.602</td>
</tr>
<tr>
<td>$C_2H_6$, $\phi$=0.87</td>
<td>2.552</td>
<td>8.600</td>
</tr>
<tr>
<td>$C_2H_4$, $\phi$=0.48</td>
<td>2.592</td>
<td>8.584</td>
</tr>
<tr>
<td>$C_2H_6$, $\phi$=0.19</td>
<td>2.604</td>
<td>8.576</td>
</tr>
<tr>
<td>Average, µs</td>
<td>2.562</td>
<td>8.577</td>
</tr>
<tr>
<td>Standard deviation, µs</td>
<td>0.048</td>
<td>0.071</td>
</tr>
<tr>
<td>95% Confidence Interval, µs</td>
<td>0.040</td>
<td>0.0631</td>
</tr>
</tbody>
</table>

The target species in this work includes both N₂ and O₂. Unlike the dielectric barrier discharge cell discussed previously, the gas mixtures contain air rather than argon, of which ~78% is N₂ and ~18% O₂. Both species have similar rotational constants, 1.6375 and 1.4264 cm⁻¹, respectively, which means their pure rotational spectra overlap and it is not possible to
completely isolate the CARS signal from \( \text{N}_2 \) or \( \text{O}_2 \) alone. Thus, the target species in this work is both \( \text{O}_2 \) and \( \text{N}_2 \). This reduces complications that could arise from a low target number density, as was experienced in the dielectric barrier. However, the signal strength is anticipated to be much higher because \( \text{N}_2 \) has a much higher partial pressure in this work (~40.56 torr partial pressure in a pure air mixture at 52 torr). It is true that the Raman cross section of \( \text{N}_2 \) is about half that of \( \text{O}_2 \), but the higher number densities more than compensate because instead of five times the signal observed in the dielectric barrier discharge cell, it would be about 2.5 times that observed signal [65, 110]. In addition, preliminary modeling results based on the work of Montello et al [76] predicted temperatures on the order of 400 – 500 K for anticipated coupled pulse energies \( \sim 8 \text{ mJ/pulse} \). Given the low temperatures and desire to probe the translational energies during the discharge (rather than vibrational), pure rotational CARS was desirable over vibrational CARS.

It was found that peak temperatures were about 100 to 400 K hotter than predicted (as discussed later in this section) and that it was necessary to utilize the “pre-amplification” option of the EMCCD camera to further enhance the signal; this is in addition to utilizing the EM gain of 200. The pre-amplification gain is the same that is encountered in most standard CCD chips and is added in the read-out node. Figure 6.11 illustrates this pre-amplification enhancement by comparing two different spectra that were both taken in air at 52 torr with a camera gain of 200 and an exposure time of 40 seconds. Both spectra were taken during the alignment process of the plasma to the RCARS probe volume, and as such, were not processed in CARSFT. But, they do have their respective background subtracted out and are normalized to themselves for ease of comparison. The top spectrum, shown in black, did not have any pre-amplification applied to the read-out node. The \( S/N \) is ~11, using the peak with the highest intensity at a Raman shift of
76.1 cm⁻¹. The bottom spectrum, shown in blue, has a pre-amplification of 4x applied to the readout node. The S/N is ~ 18, again using the peak with the highest intensity, but at a Raman shift of 138.9 cm⁻¹. While the improvement in signal to noise ratio using the pre-amplification is not even a factor of two, it does reduce the necessary time of exposure from 80 to 40 seconds for a spectrum obtained in air with a temperature of ~600K. When taking hundreds of spectra per day, a reduction time of 20 seconds can save an hour or two of time per day. This in turn results in a savings time of five to ten hours a week.

The S/N of ~18 obtained from the bottom spectra shown in figure 6.11, with temperature ~600 K (judged by eye) and pre-amplification 4x, is comparable to spectra obtained in the dielectric barrier discharge cell with similar temperatures (figure 4.10). Recall that figure 4.10 has a S/N of ~ 15 and was acquired in the dielectric barrier discharge cell for a mixture of 20% O₂ with added C₂H₄ at φ=0.05; the inferred temperature was 543 K—which is only ~ 50 K less than the estimated temperature of 600 K for the bottom spectrum in figure 6.11 in the pin-to-pin discharge. However, similar S/N, ~15, was also obtained for spectra obtained when there is no discharge present in the pin-to-pin cell, and, hence, at ambient room temperature, as shown in figure 6.12. The increase noise, therefore, is not a result of decreased signal resulting from higher temperatures or from electromagnetic interference from the high voltage generator. This implies that the larger noise in the spectra for the pin-to-pin discharge is a direct result of increased scatter off the non-AR coated windows used in the pin-to-pin work.
Figure 6.11: Pure rotational RCARS spectra obtained in air at 52 torr. The camera gain is set to 200 and an exposure time of 40 seconds. The top spectrum (black) has no additional pre-amplification and S/N of ~11.12. The bottom spectrum (blue) has an additional 4x pre-amplification applied to the read-out node and S/N of ~ 17.56. Both were taken 174.04 µs after the rise of the pre-pulse current.
Figure 6.12: Pure rotational RCARS spectra obtained in air at 52 torr. The camera gain is set to 200 and an exposure time of 60 seconds. The inferred temperature is 297 K with $\chi^2$ of 0.31, and S/N is ~15.

The comparable signal to noise ratio for spectra obtained with and without the discharge present also means that the stronger emission from the nitrogen plasma (relative to that of an argon plasma) does not have an overall impact on the noise, and is only a concern at high temperatures (~1000 K or higher) where the RCARS signal is lower than the plasma emission and it is no longer possible to increase signal strength by using longer camera exposure times. It should be emphasized that there was no apparent plasma emission in the RCARS spectra for the dielectric barrier discharge work. However, nitrogen plasmas appear to have emission in the wavelength region of interest, as demonstrated in Figures 6.13 and 6.14, which both show an RCARS spectrum before processing in blue and its corresponding background in green. The former is taken 174.04 µs after the rise of the pre-pulse current in air with added ethylene at $\varphi=1.47$ with an exposure time of 100 seconds. As can be seen, the baseline has intensity at $\sim 1 \times 10^4$ counts and peak emission around 531 nm with peak intensity $\sim 2.5 \times 10^4$. The background has quite bit of structure to it that almost look like peaks on top of the broad emission.
Figure 6.13: Spectra obtained in air with added C_H_4 at ø1.47, camera gain of 200, pre-amplification at 4x, and exposure of 100 seconds, at 174.04 μs after the pre-pulse (timing discussed later in section), and 52 torr. The blue is the RCARS spectrum with inferred temperature was 931.10 K with a χ^2 value of 0.403114. The green curve is the background spectrum, taken with the Stokes beam blocked.

Conversely, figure 6.14 was obtained in air with no discharge present, and a shorter camera exposure of 60 seconds. The baseline is a sloping linear line with maximum at ~ 1x10^4 counts and minimum ~0.5x10^4 counts. The baseline arises purely from probe beam scatter, as discussed in section 3.2 and illustrated in Figure 3.8. Once the background is subtracted out, the
signal to noise ratio is \(~15.2\) using the most intense peak at 530.4nm; this is comparable to the S/N obtained with plasma emission. Again, the plasma emission does not add to the overall noise seen in the RCARS spectra for the pin-to-pin discharge.

The plasma emission shown in figure 6.13 appears intense enough to introduce some distortion into the first couple of weak peaks in the RCARS spectrum upon background subtraction. Figure 6.15 displays an RCARS spectrum obtained 1.57 ms after the pre-pulse current in air with ethylene at \(\phi=1.47\) with an exposure time of 100 seconds at 52 torr. The inferred temperature is 307.5 K and the \(\chi^2\) value is very good, at 0.23. Comparison of this figure with an RCARS spectrum obtained in air with no discharge, (figure 6.16) shows that there is no significant distortion in the first couple of weak peaks upon subtraction of a background containing plasma emission.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_15.png}
\caption{RCARS spectrum (red) obtained in red with its corresponding theoretical spectrum from CARSFT (black), obtained in air with added \(\text{C}_2\text{H}_4\) at \(\phi=1.47\), 1.57 ms after the pre-pulse current, at 52 torr, camera exposure time of 100s, EM gain set to 200, and a pre-amplification gain of 4x. The inferred temperature is 307 K with a \(\chi^2\) of 0.23.}
\end{figure}
It should be noted that it was not possible to spatially filter this plasma emission using a telescope and a pinhole, because in spite of an AR coating for 532nm, there was significant probe beam scatter that overwhelmed the RCARS signal. Instead, the plasma emission was reduced by a factor of two by using well-placed irises and a collimating lens with a longer focal length than the focusing lens instead of matching the two focal lengths. For this work, the collimating lens was 200mm (the focusing lens was 150mm). This meant the collimating lens had to be moved further away from the cell, which created room in between the cell and the lens for a small beam dump for the pump and probe beams immediately after the cell, and a sheet of non-reflecting black material with a slit large enough only for the RCARS signal to pass. The small beam dump and the sheet of black material blocked the majority of the plasma emission from reaching the collimating lens. Two more irises were placed in the RCARS signal path after the collimating lens to further reduce probe beam scatter and plasma emission. Finally, it should also be emphasized that it is not possible to wrap a very short camera “gate”
around the temporal point of interest to decrease the amount of emission captured by the camera. The EMCCD camera does not have a physical shutter. Therefore, an exposure time of 100 seconds is capturing all the plasma emission from 1000 pre-pulses and 1000 main pulses.

The increased noise in the spectra in comparison to those procured in the dielectric barrier discharge cell is not the source of higher uncertainty (relative to the dielectric barrier discharge cell). Table 6.5 lists three sets of data iterations for two different mixtures in the pin-to-pin discharge cell. The last set of data iterations was obtained in $\phi=0.83$ H$_2$ where there was no discharge present, and thus, at ambient room temperature. The standard deviation and 95% confidence interval are ±0.7 K and ±1 K, respectively. Both are comparable to what was obtained for the conditions where there was no discharge present in and when there was discharge present for both the no-fuel case and the hydrogen mixtures in the dielectric barrier discharge (see section 4.4). On the other hand, once fuel is added, the standard deviations and the 95% confidence intervals skyrocket to a average value of ~±24 K and ±26 K, respectively. It should be noted that the data iterations for the two different fuel cases were not taken on the plasma discharge center-line. They were instead taken at $r=0.75mm$, which is well within the plasma diameter. However, the temperatures were lower relative to figures 6.18 through 6.21 at the similar time intervals presented later in this chapter. This was deliberate to reduce the camera exposure time. Regardless, the first set of data iterations presented in table 6.6, were taken 174.08 $\mu$s after the rise of the pre-pulse current in air-hydrogen mixture at $\phi=0.83$. This corresponds to the hottest temperature data points in figures 6.18 through 6.21 which are presented in the next chapter. The second set of data iterations were taken earlier, at 5.94 $\mu$s after the pre-pulse current, which corresponds to the rise of the main pulse current and in an air-hydrogen mixture at $\phi=0.42$. Given the consistency of the uncertainties for the two very
different time points, temperatures, and equivalence ratios, the two data iteration sets were deemed sufficient to determine the uncertainty in the pin-to-pin discharge. Therefore, the average standard deviation and 95% confidence interval, \( \sim \pm 22 \) K and \( \pm 25 \) K, respectively, are applied to all the data points collected in the pin-to-pin discharge when there is a discharge present. The uncertainty is likely high because ICCD images show that the plasma becomes increasingly more unstable as fuel is added and, given the large uncertainty, an exposure time of 100 to 200 seconds was not sufficient to average the random movements of the plasma. For clarity, the uncertainty when there is a discharge present refers to the 95% confidence interval only, \( \pm 25 \) K.

Table 6.6: Data iterations for two different mixtures, \( \phi=0.83 \) H\(_2\) and \( \phi=0.42 \) H\(_2\). For the mixture \( \phi=0.83 \) H\(_2\), obtained 174.04µs after the pre-pulse, camera exposure time was 200 seconds, for \( \phi=0.42 \) H\(_2\) it was 100 seconds, and the room temperature results where there is no discharge, had a camera exposure time of 60 seconds.

<table>
<thead>
<tr>
<th>Iteration</th>
<th>Temp K</th>
<th>standard deviation</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi=0.83 ) H(_2): 174.08 µs after the pre-pulse</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>568</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>511</td>
<td></td>
<td></td>
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<tr>
<td>3</td>
<td>514</td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>517</td>
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<td>549</td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td>558</td>
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<td></td>
</tr>
<tr>
<td>Average</td>
<td>536</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \phi=0.42 ) H(_2): 5.94 µs after the pre-pulse</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>312</td>
<td>20</td>
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<td>312</td>
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<td>313</td>
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</tr>
<tr>
<td>4</td>
<td>308</td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>306</td>
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<td></td>
</tr>
<tr>
<td>Average</td>
<td>310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \phi=0.83 ) H(_2): Room Temperature, no discharge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>293</td>
<td>0.7</td>
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<td>293</td>
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<tr>
<td>Average</td>
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</tbody>
</table>
Previously, in section 3.3, it was noted that inferred temperature results obtained from a probe volume length of $\sim 3.9$ mm and those from $\sim 0.5$ mm exhibited very different temperature profiles. The large uncertainty of $\pm 25$ K cannot account for the differences, as shown in figure 6.17, which presents the inferred RCARS temperature results for a mixture of air only with respect to time. Time zero is taken with respect to the pre-pulse current. The mixture examined is air only. The results from the longer probe volume of $\sim 4$ mm (500 mm focal length) are shown in red and the exposure time is 40 seconds with an EM camera gain of 200, and no pre-amplification. The results from the shorter probe volume of $\sim 0.5$ mm (150 mm focal length) are shown in blue, and the exposure time is 100 to 200 seconds with an EM camera gain of 200 and a pre-amplification set to 4x. The data given as red dots is consistently lower in temperature than that of the blue dots, with differences ranging from more than 25K to 300 K. This is indicative that the probe volume generated from the 500 mm lens spans an area larger than the plasma diameter. This is further supported by ICCD images discussed in the previous section 6.3, which gives plasma diameters on the order of 1 to 2 mm. Because the probe volume is spanning an area larger than the plasma, the inferred temperature results are averaged over both the hot plasma gas and cooler gas outside the discharge region. The inclusion of the cooler outside region lowers the overall temperature. It should be noted that given a thermal diffusivity of $1.9 \times 10^{-5}$ m/s, it would take $\sim 9.5$ milliseconds for any thermal gradient to smooth out entirely over a distance of 2 mm in a one-dimensional approximation, which is approximately on the order of the plasma diameter. Therefore, diffusion of the hot gas into the cooler surrounding region is not expected to raise the overall average temperature in a larger RCARS probe volume.
Figure 6.17: Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is air only. The blue dots were taken when the focal length was 150mm, with a camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The red dots were taken when the focal length was 500mm, with a camera exposure of 40s, EM gain of 200, and with no pre-amplification. The pressure is 52 torr. The uncertainty in the time axis is ± 50 ns and the uncertainty in the temperature is ±25 K.

6.4. Temporal RCARS Results in the pin-to-pin discharge

The temporal results for the pin-to-pin discharge are presented in this section and shown in figures 6.18 – 6.25. As previously discussed in this chapter, eight different gas mixtures were probed by an RCARS probe volume of ~0.5mm: (1) Air (2) Air with H₂ at Ø=0.14, (3) Air with H₂ at Ø=0.42, (4) Air with H₂ at Ø=0.82, (5) Air C₂H₄ at Ø=0.19, (6) Air with C₂H₄ at Ø=0.48, (7) Air with C₂H₄ at Ø=0.87, and (8) Air with C₂H₄ at Ø=1.47.

The evolution of the temperature observed in the different gas mixtures with respect to time has an overall shape that is remarkably similar to what Montello et al [77] observed for dry air in a pin-to-pin discharge cell with similar electrode dimensions and geometry even though their work was done at higher pressures (100 torr), at higher energy loading (~14 mJ instead of ~3.8 mJ), and a larger electrode gap (10 mm instead of 9 mm). In their work, there were two
distinct heating regimes that took place after the onset of the discharge. The first consisted of a rapid heat release on the order of a few microseconds. This was followed by a slow heat release that took place over hundreds of microseconds. Finally, the temperature decays due to diffusion before the onset of the next pulse. These two heating regimes are not only distinct after the main pulse in the air mixture investigated in this work, but in all of the three hydrogen mixtures examined, as illustrated in figures 6.18 through 6.21. It should be noted that because there is only ~ 6 µs time lapse between the pre-pulse and main pulse, the fast heating regime and slow heating regime terminology is not applied after the onset of the pre-pulse. Finally, figures 6.22 through 6.25 show that the distinction between the slow and rapid heating regimes in ethylene is not as clear, for two reasons. First, because it was not possible to obtain a full profile of the slow heating regime in these mixtures due to low signal resulting from high temperatures. Second, because there is indication that the rapid heat rise observed in the ethylene mixtures continues well into the slow heating regime. Therefore, it was decided to ignore the “slow heating” regime in these ethylene containing mixtures and collect data after the onset of the main pulse for ~ 2.07µs. This duration is deliberate and was chosen because as will be discussed in more detail below, the non-ethylene containing mixtures all consisted of a rapid heating period on the order of ~2.07 µs.

These trends for each mixture are discussed in more detail for each of the gas mixtures in the rest of this section, starting with the pure gas mixture and following with the hydrogen containing mixtures in descending order with respect to the equivalence ratio (0.82, 0.42, and 0.14), and finishing with the ethylene containing mixtures (again, in descending order with respect to the equivalence ratio). After this thorough discussion, the general trends are summarized in the next section and tabulated in tables 6.7 and 6.8. Section 6.6 will present
radial temporal results in air at three different time points, ~5µs after the pre-pulse (~1µs before the main pulse), about halfway through the rapid heating region, and at the end of the slow heating region. Finally, the temporal results discussed in this section are compared with predictions from a preliminary 1-D kinetic model.

![Graph showing air, pin-to-pin temporal evolution](image)

*Figure 6.18: Inferred RCARS temperature results with respect to time. Time zero is with respect to the pre-pulse current. The mixture examined is air only. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is ±50 ns and the uncertainty in the temperature is ±25 K.*

(1) *Pure Air*

Figure 6.18 shows the temporal evolution in the pin-to-pin discharge cell for air only with respect to the pre-pulse current. There are four distinct regions that are labeled in the figure. In order of time with respect to the main pulse, they are: (1) Heat release from the Pre-pulse, (2) fast heating, (3) slow heating, and (4) diffusion. After the onset of the pre-pulse there is a net positive heat release of ΔT ~ 28 K. During the first half of the main pulse discharge (~48 ns) there is heat release of ΔT ~33 K in pure air. The fast heating region of ~2.07µs includes this main pulse discharge, and the net heat release over this entire region is ΔT ~ 142 K. The slow
heating immediately follows after a time lapse of ~6 µs and has a duration of ~160 µs, yielding in an additional heat release of ΔT ~ 209 K and a maximum temperature of ~ 680 K. Over the next 17ms before the onset of the pre-pulse, all of the heat diffuses out of the discharge region and the temperature drops to ~335 K.

Figure 6.19: Inferred RCARS temperature results with respect to time. Time zero is with respect to the pre-pulse current. The mixture examined is H₂ at ø=0.83. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is ± 50 ns and the uncertainty in the temperature is ±25 K.

(2) Air with added H₂ at ø=0.83

Figure 6.19 shows the temporal evolution in the pin-to-pin discharge cell for air with added hydrogen at ø=0.83 with respect to the pre-pulse current. Again, there are four distinct regions that are labeled in the figure. In order of time with respect to the pre-pulse, they are:

(1) Heat release from the Pre-pulse, (2) fast heating, (3) slow heating, and (4) diffusion. After the onset of the pre-pulse, there is a net positive heat release of ΔT ~ 50 K. During the first half of the main pulse discharge (~48 ns) there is additional heat release of ΔT ~100 K. The fast heating region of ~0.6 µs includes this main pulse discharge, and the net heat release over this
entire region is $\Delta T \sim 160$ K. This is immediately followed slow heating of $\Delta T \sim 332$ K that takes place over $\sim 160 \mu$s after a time lapse of 7.50 $\mu$s. The maximum temperature reached at the end of slow heating is $\sim 802$ K. Over the next 17ms before the onset of the pre-pulse, all of the heat diffuses out of the discharge region and the temperature drops to $\sim 317$ K.

![Figure 6.20: Inferred RCARS temperature results with respect to time. Time zero is with respect to the pre-pulse current. The mixture examined is $H_2$ at $\phi=0.42$. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is $\pm 50$ ns and the uncertainty in the temperature is $\pm 25$ K.](image)

**Figure 6.20**

(3) Air with added $H_2\ \phi=0.42$

Figure 6.20 shows the temporal evolution in the pin-to-pin discharge cell for air with added hydrogen at $\phi=0.42$ with respect to the pre-pulse current. Again, there are four distinct regions that are labeled in the figure. In order of time with respect to the pre-pulse, they are: (1) Heat release from the Pre-pulse, (2) fast heating, (3) slow heating, and (4) diffusion. After the onset of the pre-pulse, there is a net positive heat release of $\Delta T \sim 28$ K. During the first half of the main pulse discharge ($\sim 48$ ns) there is no net heat release. The fast heating region of $\sim 1.37 \mu$s includes this main pulse discharge, and the net heat release over this entire region is $\Delta T \sim 28$ K.
This is immediately followed by slow heating of $\Delta T \sim 247$ K that takes place over ~166 $\mu$s after a time lapse of 0.7 $\mu$s. The maximum temperature reached at the end of slow heating is ~748 K. Over the next 17 ms before the onset of the pre-pulse, all of the heat diffuses out of the discharge region and the temperature drops to ~327 K before the onset of the pre-pulse.

Figure 6.21 shows the temporal evolution in the pin-to-pin discharge cell for air with added hydrogen at $\phi=0.14$ with respect to the pre-pulse current. Again, there are four distinct regions that are labeled in the figure. In order of time with respect to the pre-pulse, they are:

1. Heat release from the pre-pulse,
2. fast heating,
3. slow heating, and
4. diffusion.

After the onset of the pre-pulse, there is a net positive heat release of $\Delta T \sim 29$ K. During the first half of the main pulse discharge (~48 ns) there is no net heat release. The fast heating region of ~2.07 $\mu$s includes this main pulse discharge, and the net heat release over this entire region is $\Delta T$.

(4) Air with added $H_2$, $\phi=0.14$
This is immediately followed by slow heating with additional heat release of $\Delta T \sim 140$ K that takes place over $\sim 160$ µs after a time lapse of $\sim 6$ µs. The maximum temperature at the end of slow heating is $\sim 688$ K. Over the next 17 ms before the onset of the pre-pulse, all of the heat diffuses out of the discharge region and the temperature drops to $\sim 337$ K.

Figure 6.22 Inferred RCARS temperature results with respect to time. Time zero is with respect to the main pulse current. The mixture examined is $C_2H_4$ at $\phi=1.47$. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is $\pm 50$ ns and the uncertainty in the temperature is $\pm 25$ K.

(5) Air with added $C_2H_4 \, \phi=1.47$

Figure 6.22 shows the temporal evolution in the pin-to-pin discharge cell for air with added ethylene at $\phi=1.47$ with respect to the pre-pulse current. There are now six regions labeled in the figure. In order of time with respect to the pre-pulse, they are: (1) Pre-pulse heat release, (2) main pulse discharge, (3) fast heating, (4) boundary, (5) slow heating, and (6) diffusion. After the onset of the pre-pulse there is a net positive heat release of $\Delta T \sim 53$ K. During the first half of the main pulse discharge ($\sim 48$ ns) there is no net heat release. The fast heating region includes this main pulse discharge, and at least $\sim 2.07$ µs of net heat release of $\Delta T$
~ 168 K. This is immediately followed by a boundary region spanning ~68 µs. In the previous mixtures, there are at least two temperature points, ~ 8.07 µs and 18.07 µs, within this boundary region. For the ethylene containing mixtures, it was not possible to obtain these two points because the RCARS signal was less intense than the plasma emission. This meant that longer exposure times did not render a viable spectrum. Because the RCARS signal was so weak at these two points, it is more than likely that the temperatures inside this region are greater than 900K. Furthermore, it follows that within this boundary region there must be a temperature drop because the slow heating region starts with a temperature of ~836 K. It is unknown if the boundary region contains a rapid heat release such that the two regions of fast and slow heating blend together and should be considered one region. On the other hand, are the fast and slow heating regions two distinct regions with their boundaries somewhere within the boundary region? Because it is unclear whether or not the fast and slow heating regions are indeed distinct, the time intervals for the two shown on figure 6.2 are given in intervals to account for the unknown boundary region. Nonetheless, for the next ~100µs after the boundary region, there is a net heat release of ΔT ~ 95 K (from 836 to 931 K) and an observed net heat release of ΔT ~ 404 K if the slow heating region stretches over 160µs and any unknown heat release during the boundary region is neglected. Over the next 17ms before the onset of the pre-pulse, all of the heat diffuses out of the discharge region and the temperature drops to ~307 K.

It should be noted that because of the difficulty in obtaining points in the boundary region, it was decided to only focus on the region of ~2.70 µs before the boundary region and ignore the “slow heating” region for the rest of the ethylene mixtures. Furthermore, it should also be emphasized that while the figures for these mixtures have been marked with a “fast”
and “slow” heating region to aid in comparison with previous figures, the distinction between the two regions remains unclear.

Figure 6.23  Inferred RCARS temperature results with respect to time. Time zero is with respect to the pre-pulse current. The mixture examined is C₂H₄ at φ=0.87. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is ± 50 ns and the uncertainty in the temperature is ±25 K.

(6) Air with added C₂H₄ φ= 0.87

Figure 6.23 shows the temporal evolution in the pin-to-pin discharge cell for air with added ethylene at φ=0.87 with respect to the pre-pulse current. Again, there are six regions labeled in the figure. In order of time with respect to the pre-pulse, they are: (1) Pre-pulse heat release, (2) main pulse discharge, (3) fast heating, (4) boundary, (5) slow heating, and (6) diffusion. After the onset of the pre-pulse there is a net positive heat release of ΔT ~ 16 K. During the first half of the main pulse discharge (~48ns) there is no net heat release. The fast heating region of ~2.07 µs includes this main pulse discharge, and the net heat release over this entire region is ΔT ~ 173 K. There is no data given for the boundary and slow heating regions,
after which all of the heat diffuses out of the discharge region over the next 17ms before the onset of the pre-pulse and the temperature drops to ~340 K.

![Figure 6.24 Inferred RCARS temperature results with respect to time. Time zero is with respect to the pre-pulse current. The mixture examined is C$_2$H$_4$ at $\phi=0.48$. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is ± 12.3 ns and the uncertainty in the temperature is ±25.4 K.](image)

(7) **Air with added C2H4 $\phi=0.48$**

Figure 6.24 shows the temporal evolution in the pin-to-pin discharge cell for air with added ethylene at $\phi=0.48$ with respect to the pre-pulse current. Again, there are six regions labeled in the figure. In order of time with respect to the pre-pulse, they are: (1) Pre-pulse heat release, (2) main pulse discharge, (3) fast heating, (4) boundary, (5) slow heating, and (6) diffusion. After the onset of the pre-pulse there is a net positive heat release of $\Delta T \sim 25$ K. During the first half of the main pulse discharge (~48ns) there is no net heat release. The fast heating region of ~2.07 $\mu$s includes this main pulse discharge, and the net heat release over this entire region is $\Delta T \sim 122$ K. There is no data given for the boundary and slow heating regions,
after which all of the heat diffuses out of the discharge region over the next 17ms before the onset of the pre-pulse and the temperature drops to ~335 K.

Figure 6.25: Inferred RCARS temperature results with respect to time. Time zero is with respect to the pre-pulse current. The mixture examined is C$_2$H$_4$ at φ=0.48. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the time axis is ±50ns and the uncertainty in the temperature is ±25 K.

Figure 6.25 shows the temporal evolution in the pin-to-pin discharge cell for air with added ethylene at φ=0.19 with respect to the pre-pulse current. Again, there are six regions labeled in the figure. In order of time with respect to the pre-pulse, they are: (1) Pre-pulse heat release, (2) main pulse discharge, (3) fast heating, (4) boundary, (5) slow heating, and (6) diffusion. After the onset of the pre-pulse there is a net positive heat release of ΔT ~ 34 K. During the first half of the main pulse discharge (~48 ns) there is no heat release. The fast heating region of ~2.07 µs includes this main pulse discharge, and the net heat release over this entire region is ΔT ~ 92 K. There is no data given for the boundary and slow heating regions, after
which all of the heat diffuses out of the discharge region over the next 17ms before the onset of the pre-pulse and the temperature drops to \(~336\) K.

### 6.5 Summary of RCARS temporal results in the pin-to-pin-discharge

As discussed in section 6.4, there were two distinct heating regimes that took place following the onset of the main pulse discharge for the non-ethylene containing mixtures. These results are summarized in tables 6.7 and 6.8. The first heating regime consisted of a rapid heat release on the order of a few microseconds, ranging in duration between 0.6 to 2.07 \(\mu\)s. In general, as fuel addition increased, the shorter the time span for this rapid heat release. This was followed by a slowing heating that took place over 160 \(\mu\)s after a time lapse of \(~6\) to 7.5 \(\mu\)s. The notable exception being the air-hydrogen mixture at \(\phi=0.48\) where the slow heating took place over approximately 166 \(\mu\)s after a time lapse of \(~0.7\) \(\mu\)s. Finally, the temperature decayed due to diffusion over the next \(~17\) ms before the onset of the next pulse and the temperature dropped to temperatures ranging from 317 to 337 K. In general, as the amount of fuel is increased, the lower the temperature after diffusion (and before the onset of the next pre-pulse).

However, the rapid and slow heating regions are not distinct in the ethylene containing mixtures for two reasons. First, because the investigation was limited to \(~2.07\) \(\mu\)s. Second, because there was indication this rapid heating may exist over a longer duration because the temperatures in the boundary region are greater than 900 K.
Table 6.7: Duration of the different regions after the onset of the main pulse and the low/high temperatures for the eight different gas mixtures examined.

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>Rapid heating Duration, µs</th>
<th>slow heating duration</th>
<th>Low Temperature, K</th>
<th>High Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>2.07</td>
<td>160</td>
<td>335</td>
<td>680</td>
</tr>
<tr>
<td>Air-H₂ φ=0.83</td>
<td>0.60</td>
<td>160</td>
<td>317</td>
<td>802</td>
</tr>
<tr>
<td>Air-H₂ φ=0.42</td>
<td>1.37</td>
<td>166</td>
<td>327</td>
<td>748</td>
</tr>
<tr>
<td>Air-H₂ φ=0.14</td>
<td>2.07</td>
<td>160</td>
<td>337</td>
<td>688</td>
</tr>
<tr>
<td>Air-C₃H₈ φ=1.47</td>
<td>n/a</td>
<td>n/a</td>
<td>307</td>
<td>528</td>
</tr>
<tr>
<td>Air-C₃H₈ φ=0.87</td>
<td>n/a</td>
<td>n/a</td>
<td>340</td>
<td>525</td>
</tr>
<tr>
<td>Air-C₃H₈ φ=0.48</td>
<td>n/a</td>
<td>n/a</td>
<td>335</td>
<td>487</td>
</tr>
<tr>
<td>Air-C₃H₈ φ=0.19</td>
<td>n/a</td>
<td>n/a</td>
<td>334</td>
<td>471</td>
</tr>
</tbody>
</table>

Nonetheless, from Table 6.8, it is clear that the net heat released after 2.07µs from the onset of the main pulse increases as the amount of ethylene increases. The notable exception to this trend is the air-ethylene mixture at φ=1.47 where the net heat released is comparable to that of the air-ethylene mixture at φ=0.83. However, this exception is a fuel-rich mixture, not a fuel-lean mixture. It is possible that conditions near the stoichiometric conditions would have comparable net heat released, but once too little or too much fuel is added, the net heat released would begin to decrease.

Conversely, the net heat released during the rapid heating region upon addition of hydrogen does not appear to change—the different mixtures have comparable heat releases. Again, there is one notable exception, the air-hydrogen mixture at φ=0.48, which is higher by ~50 K. However, if all three regions after the discharge are accounted for after the main pulse (rapid heating, heat loss, and slow heating), then the overall net heat released increases with increasing amounts of hydrogen fuel.
All eight of the mixtures examined exhibited overall net heat release after the onset of the pre-pulse. Table 6.8 shows that for ethylene lean mixtures, increasing the amounts of ethylene results in a decreasing amount of energy released as heat. Because the energy coupled for the different ethylene mixtures is the same, this may be indicative that as the ethylene content increases, less energy is deposited into the translational mode and more energy is deposited into other channels. The notable exception to this, again, is the single ethylene rich mixture at $\phi=1.47$, which releases more energy after the pre-pulse than the ethylene-lean mixtures. Conversely, increasing the amount of hydrogen does not appear to effect a corresponding increase in the net heat released after the pre-pulse. The notable exception to this is the hydrogen mixture closest to the stoichiometric condition at $\phi=0.83$.

Table 6.8: Summary of the net heat released for the eight different gas mixtures investigated after the pre-pulse, and the three regions after the main pulse

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>After pre-pulse</th>
<th>rapid heating after main pulse</th>
<th>slow heating after heat loss</th>
<th>Net heat release after main pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>28</td>
<td>143</td>
<td>209</td>
<td>319</td>
</tr>
<tr>
<td>Air-H$_2$ $\phi=0.83$</td>
<td>50</td>
<td>132</td>
<td>333</td>
<td>441</td>
</tr>
<tr>
<td>Air-H$_2$ $\phi=0.42$</td>
<td>28</td>
<td>194</td>
<td>247</td>
<td>394</td>
</tr>
<tr>
<td>Air-H$_2$ $\phi=0.14$</td>
<td>29</td>
<td>140</td>
<td>211</td>
<td>331</td>
</tr>
<tr>
<td>Air-C$_2$H$_4$ $\phi=1.47$</td>
<td>53</td>
<td>168</td>
<td>404</td>
<td>571</td>
</tr>
<tr>
<td>Air-C$_2$H$_4$ $\phi=0.87$</td>
<td>16</td>
<td>173</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Air-C$_2$H$_4$ $\phi=0.48$</td>
<td>25</td>
<td>138</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Air-C$_2$H$_4$ $\phi=0.19$</td>
<td>34</td>
<td>92</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

6.6 Radial RCARS results in Air

The RCARS results that have been presented and discussed thus far have been for measurements taken at the center line of the plasma with respect to time. However, as mentioned previously in section 6.3, the discharge in the plasma can be likened to a streamer.
Streamer propagation is highly dependent on the evolution of the avalanche radius which is critically dependent on the ionization rate (first Townsend coefficient) [51]. It is therefore necessary to model the pin-to-pin discharge in at least two dimensions, along the radial and discharge gap axes. In section 4.1, it was mentioned during the ionization instability discussion that the ionization rate itself is temperature dependent. It therefore follows that in order to model the streamer in 2d, effectively it would be helpful to know the radial temperature distribution following heat release from the pre-pulse before the on-set of the main pulse. Towards this end, temperature measurements along the radial axis in the middle of the gap were taken at three different time points in air with one before the onset of the main pulse and two after the main pulse commences. The results are fitted to a Gaussian profile which is used to estimate the FWHM of the radial profile, as shown in figures 6.26 through 6.28.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure626.png}
\caption{Inferred RCARS temperature results at 1.74µs before the main pulse with respect to the radial axis. The mixture is pure air at 52 torr. The camera exposure time of 100-200seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the temperature is ±25.4 K. The magenta curve is a four term Gaussian fit to the raw data with a goodness of fit value of 0.9944. The FWHM max of this fit is ~2mm.}
\end{figure}
Figure 6.2 shows the results for the radial profile taken at 1.74 µs before the main pulse with its four term Gaussian fit. The fit is fairly good, with a “goodness of fit”, $R^2$ value of 0.99. The FWHM of this fit is ~2mm. It should be noted that the temperature was ~335 K before the onset of the main pulse, which means $\Delta T \sim 68$ K at this point of time, relative to the peak temperature of 353.8 K. Because the diameter is still approximately on the order of the pre-pulse discharge ~4.25 µs after the pre-pulse, it confirms that mass diffusion effects aren’t significant on the micro-second time scale.

In section 6.1, it was determined that the main pulse plasma diameter was on the order of 1 mm. As shown in figures 6.27 and 6.28, both of the radial profiles taken after the main pulse have FWHM of ~2 mm, which is twice the main pulse discharge diameter. The radial profile taken 1.75 µs after the main pulse onset appears to have a little bit of a flat top and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.27.png}
\caption{Inferred RCARS temperature results at 1.75µs after the main pulse with respect to the radial axis. The mixture is pure air at 52 torr. The camera exposure time of 100-200seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the temperature is ±25 K. The magenta curve is a four term Gaussian fit to the raw data with a goodness of fit value of 0.9944. The FWHM max of this fit is ~2mm.}
\end{figure}
occurs half-way into the fast heating regime, as illustrated in figure 6.27. Conversely, the last radial profile shown in figure 6.28 was taken 174.04 µs after the main pulse, at the peak/end of the slow heating region. Clearly, there is no spatial expansion in the temporal profiles during the second half of the rapid heating region and the throughout the entirety of the slow heating period.

\[ \text{Figure 6.28 Inferred RCARS temperature results at 174.04 µs after the main pulse with respect to the radial axis. The mixture is pure air at 52 torr. The camera exposure time of 100-200 seconds, EM gain of 200 and a pre-amplification set at 4x. The uncertainty in the temperature is ±25 K. The magenta curve is a two term Gaussian fit to the raw data with a goodness of fit value of 0.9944. The FWHM max of this fit is ~2mm.} \]

The radial temperature profiles in air show a radial diameter of 2 mm after the pre-pulse, 2 mm halfway through the rapid heating region after the main pulse, and 2 mm again at the end of the slow heating regime. This indicates that there is no contraction or expansion of the filament during the experiment.

6.7 Preliminary Modeling Results

Dr. Ivan Shkurenkov, a post-doctoral researcher in our group, has been developing a 1-D model to predict processes in the pin-to-pin discharge. The first description of his model
appeared in 2014 [111]. As shown in the ICCD images of section 6.2, the discharge filament is located in the center between the spherical electrodes, along the electrode symmetry axis with filament diameters on the order of ~1-2mm. Given that the diameter of the electrodes (~7.5mm) is much larger than the filament diameter, it is clear that the electrode curvature has no significant effect on discharge parameters. Therefore, the model does not explicitly account for the electrode dimensions, but rather, for the filament diameter, which is determined experimentally by the ICCD images. It should be emphasized that the model does not account for the radial distribution of the plasma because it is assumed the radial flux of charged species during the discharge pulse (pre-pulse ~95 ns, main pulse ~45 ns) are much lower than axial fluxes. Therefore, the discharge parameters are controlled by transport of species in the axial direction which justifies the use of a one-dimensional model where the spatial coordinate, x, is along the discharge gap, and normal to the electrode surfaces.

Unlike the 0-D model described in chapter 5, this one-dimensional model retains diffusion terms and couples the time-dependent conservation equations for the number densities of electrons, charged species (cations and anions), excited species (electronic and vibrational), and neutral species with the equation for the electron temperature, the Poisson-equation for the electric field, and heavy species energy equation. Processes such as V-V and V-T are included as well. Rate-coefficients, electron impact cross-sections, and quenching coefficients are all empirical and taken from the literature. It should be noted that the Boltzmann equation was used to solve the electron energy distribution function in the two term approximation described in [112]. However, if electron-electron collisions are not neglected, the equation is essentially two dimensional (axial coordinate and electron energy) which dramatically increases the computational time. Instead of explicitly coupling the Boltzmann
equation with the system of equations previously stated, a library of electron energy
distribution functions (EDDF) over a wide range of E/n as functions of the mean electron energy
(electron temperature) is used. In this way, the EEDF is recalculated during the code time when
the composition of the plasma, including the number densities of excited species, has changed
significantly. This also accounts for non-local effects such as electron thermal conductivity.
Nonetheless, this system of equations is solved self-consistently using the same time scale for all
equations. Boundary conditions for the system are similar to those described in chapter 5. The
positive species number density at electrodes is zero and the neutral particles fluxes to
electrodes are zero as well. The temperature at the electrode surface is assumed to be
constant. Finally, the boundary condition as described by equation (5.1.8) is applied to this
model as well, where the secondary electron emission coefficient (third Townsend coefficient),
is given by γ=0.1 [113].

Preliminary modeling predictions compared with experimental RCARS results are shown
in figures 6.29 and 6.30, for air and air-H$_2$ at ø=0.14, respectively. Both figures show the
preliminary modeling predictions are in very good agreement with the experimental data,
although the rate of diffusion predicted by the model is a bit slower than the experimental
results. Nonetheless, what is very interesting about the two figures is that the modeling
predictions are almost identical, even though the slow heating temporal profile in H$_2$/air is
slightly broader than in air, a result that is also observed experimentally. Also, there appears to
be no discernible increase in peak temperature upon addition of hydrogen, which is a somewhat
surprising result. Future work will model higher equivalence ratios for hydrogen (ø=0.42 and
0.83), as well as ethylene containing mixtures and sensitivity analysis of the model for the three
different mixtures of air, air-hydrogen, and air-ethylene.
Figure 6.29 Comparison of time-resolved temperature model predictions with experimental temperature results by RCARS for air at 52 torr. The model predictions are shown in the solid line. The experimental results are shown as black symbols. Time zero is with respect to the pre-pulse.

Figure 6.30 Comparison of time-resolved temperature model predictions with experimental temperature results by RCARS for air-H$_2$ at $\varphi=0.14$ at 52 torr. The model predictions are shown in the solid line. The experimental results are shown as black symbols. Time zero is with respect to the pre-pulse.
Previous work has been done in pin-to-pin discharge geometries in a variety of pressures and temperatures (mostly atmospheric pressure and room temperature) for air-fuel mixtures excited by nanosecond discharges \([46-49, 76, 107]\). This collective work has exhibited the same trend of a rapid and slow heating regime that was observed in the experimental data in sections 6.4 and 6.5. Based on the large agreement of the dominant processes at play, it is expected that the analysis of the model developed by Dr. Ivan Shrukenov will have similar conclusions. Therefore, the predicted general conclusions described in the next couple of paragraphs are taken from references \([46-49, 76, 107]\), not from Dr. Shrukenov’s 1-D model.

In general the processes are complex and develop over a large range of timescales. On the nano-scale timescale, dominant processes include electron impact, rotation-translational energy transfer, and quenching of electronic excited state. On the microsecond time scale, V-V, V-T, and V-R processes are important, but only will occur if there is sufficient vibrational excitation. It should be noted there is usually high vibrational excitation of \(N_2(X,v)\) in its ground electronic state during the discharge in a pin-to-pin geometry. Vibrational loading has been reported for levels as high as \(v=16\) \((20\, \text{mJ/pulse energy coupling})\) at \(P=1\,\text{atm}\) \([47]\). Finally, on the millisecond timescale, a complete energy relaxation is observed.

The fast gas heating during and immediately after the discharge, which results in modest heating, is expected to be largely due to collisional quenching of electronically excited states, including \(O(\text{^3}D)\) formed by electron impact dissociation of \(O_2\) or by collisional quenching with electronically excited nitrogen. Note that typically \(N_2(A)\) plays a smaller role in this process because it has a lower number density and slower reaction rate. In mixtures with fuel addition, it is expected that the H-atom abstraction of a fuel molecule is expected to be a contributor as well because as seen in section 6.4, there is additional energy release during rapid heating upon
addition of fuel. Thus, reactions (R1-R3) are expected to dominate heat release during this time interval.

\[ N_2(a, A, B, C) + O_2 \rightarrow N_2(X, v) + O + O + \text{heat} \hspace{5cm} (R1) \]

\[ N_2(a, A, B, C) + H_2 \rightarrow N_2(X, v) + H + H + \text{heat} \hspace{5cm} (R2) \]

\[ N_2(a, A, B, C) + C_xH_y \rightarrow N_2(X, v) + C_xH_{y-1} + H + \text{heat} \hspace{5cm} (R3) \]

The vibrationally excited nitrogen molecules produced in reactions (R1) – (R3) can then undergo V-V transfer, reactions (R5-R6), which takes places over tens of microseconds, sometimes hundreds, depending on pressure. However, because vibrational transfer occurs most readily under near resonant conditions, very little heat is released during the transfer of the quanta.

\[ N_2(v + 1) + N_2(w - 1) \rightleftharpoons N_2(v) + N_2(w) \hspace{5cm} (R5) \]

\[ N_2(v) + N_2(w) \rightleftharpoons N_2(v - 1) + N_2(w + 1) \hspace{5cm} (R6) \]

However, based on reaction (R1) and given the large expected energy deposition into these excited N\textsubscript{2} states at these discharge conditions, a significant fraction of O-atoms should be produced in addition to those generated by electron impact in the plasma. These O-atoms can participate in V-T transfer with vibrationally excited nitrogen molecules, which could be the dominant contributor in slow heating observed in this work.

\[ N_2(X, v) + O \rightleftharpoons N_2(X, v - 1) + O \hspace{5cm} (R7) \]

Montello et al [77] notes the V-T rate for (R7), is \( \tau_{VT} \sim 2-4 \text{ atm} \cdot \mu\text{s} \) at \( T=500-1000 \text{ K} \). Under their conditions of 100 torr, this yielded a characteristic relaxation time for vibrationally excited
molecular nitrogen of $\tau \sim 200$-400 $\mu$s, which is fairly close to the experimentally observed time of $\sim 160$ $\mu$s for the slow heating in the gas mixtures investigated in this work.

Figures 6.31 and 6.32 support the hypothesis that the majority of rapid heating is due to collisional quenching of electronically excited N$_2$ and that slow heating is due to the V-T transfer between vibrationally excited N$_2$ to atomic oxygen. Both figures are recent preliminary modeling predictions from the 1D kinetic model for the lean hydrogen mixture at $\varphi$=0.14 and time-zero is with respect to the rise of the main pulse current. Figure 6.31 compares the time evolution for the number density of electronically excited N$_2$ with the predicted translational temperature and experimental inferred temperature by RCARS. As can be seen in the figure, the peak density of electronically excited N$_2$ occurs during the main pulse. The rapid heating corresponds with the decrease in the number density, further suggesting the depletion of electronically excited N$_2$ plays a dominant role in rapid heating, perhaps via reactions (R1)-(R2).

Figure 6.31 Preliminary 1D modeling results in air with added H$_2$ at $\varphi$=0.14. The Solid lines are the model predictions and the symbols are the inferred translational temperatures by RCARS. The blue curve is the number density of electronically excited nitrogen. Time zero is with respect to the main pulse.
Figure 6.3 shows the temporal evolution of the vibrational temperature for N$_2$ for the first vibrational level. As can be seen in the figure, the increase in vibrational temperature corresponds with decrease in the population density of electronically excited N$_2$, further providing support that reactions (R1)-(R2) are taking place. These two reactions would deplete the electronically excited N$_2$ population while vibrationally loading the population of N$_2$ (in its ground electronic state). This vibrational temperature then begins to decrease when slow heating begins to occur. It would appear that the decrease in the vibrationally excited population of N$_2$ should correspond to a process involved in the slow heating process, probably through the reaction previously suggested, (R7), where the heat is released by a V-T energy transfer to atomic oxygen.

In summary, very rapid gas heating is expected to be dominated by deactivation processes of electronically excited N$_2$, particularly by reactions (R1-R3). Thus, high vibrational loading of N$_2$ by both electron impact and processes (R1-R3) is expected. This high vibrational
loading will slowly relax due to both V-V processes and by (R7). The slow gas heating, therefore, is expected to be largely due to V-T transfer among vibrationally excited N$_2$ molecules and O-atoms as illustrated in reaction (R7) as a result of the high vibrational loading.
Chapter 7: Conclusions

This thesis has presented heat release studies of fuel oxidation by non-equilibrium nanosecond pulse discharges in two different discharge systems, a dielectric barrier discharge and a pin-to-pin discharge. The construction and implementation of a diagnostic system incorporating pure Rotational Coherent Anti-Stokes Raman Scattering (RCARS) spectroscopy for low temperature and low pressure systems has been described. Predictions from a 0-D kinetic model have been compared with experimentally measured \( \text{O}_2 \) rotational temperature in the dielectric barrier discharge. Preliminary predictions from a 1-D model currently in development have been compared with experimentally measured \( \text{O}_2-\text{N}_2 \) rotational temperatures in the pin-to-pin discharge. Detailed discussion and overview of these results have been made following chapter 5 and 6. A summary of the key findings in the dielectric barrier discharge cell and the pin-to-pin will be made here, along with suggestions for future work.

7.1 Dielectric Barrier Discharge Cell Conclusions

This thesis has presented results of time-resolved rotational temperature, by pure rotational Coherent Anti-Stokes Raman Scattering Spectroscopy (CARS) in the dielectric barrier discharge cell. These experiments were conducted in nanosecond pulse discharges in \( \text{H}_2-\text{O}_2-\text{Ar} \) and \( \text{C}_2\text{H}_4-\text{O}_2-\text{Ar} \) mixtures, initially at room temperature, operated at a high pulse repetition rate of 40 kHz, in plane-to-plane double dielectric barrier geometry at a pressure of 40 Torr. ICCD images show that \( \text{O}_2-\text{Ar} \) and \( \text{H}_2-\text{O}_2-\text{Ar} \) plasmas, while showing some filamentary structure during the first pulse that dissipates by the second pulse, remain diffuse and volume-filling during the
entire burst. The hydrogen containing mixture does show some plasma volume contraction that is present from the second pulse and throughout the duration of the burst. On the other hand, images taken in the C$_2$H$_4$-O$_2$-Ar plasma demonstrate significant discharge striation and a total plasma contraction that increases with burst size.

It is demonstrated that experimental precision of approximately \( \sim \pm 1 \) to 2 K can be readily achieved in the volumetric and diffuse 20% O$_2$-Ar and O$_2$-Ar-H$_2$ mixtures with partial pressure of O$_2$ as low as \( \sim 6 \) torr. Ethylene containing mixtures have exhibit less precision, with an average 95% confidence interval averaging about \( \pm 6 - 7 \). The larger uncertainty of the ethylene containing mixture reflects the plasma instabilities observed in the ICCD images because the difference in the uncertainties between the hydrogen and ethylene mixtures cannot be attributed to higher temperatures and EMI noise.

The experimental temperatures for all mixtures increase approximately linearly with time. The rate of heat release increases with increasing addition of fuel, with one exception where in ethylene mixtures the mixture at \( \varphi=0.5 \) has the fastest heating rate, an unexpected result that needs further study. The hydrogen containing mixtures exhibited a strong linear dependence on the equivalence ratio while the ethylene mixtures showed a non-linear dependence. These results are compared with kinetic modeling calculations, using two different H$_2$-O$_2$ and C$_2$H$_4$-O$_2$ chemistry mechanisms. In H$_2$-O$_2$-Ar mixtures, the kinetic modeling predictions, using the chemistry mechanism suggested by Popov, are in fairly good agreement with the data, predicting temperature rise and O atom accumulation in long discharge bursts, up to 450 pulses. The modeling results show that adding hydrogen to the mixture results in additional temperature rise, due to its partial oxidation by radicals generated in the plasma, essentially without chain branching. In particular, the model shows that fuel-oxidation is limited
by the amount of radicals generated in the plasma rather than by the amount of fuel. However, this is inconsistent with experimental results that demonstrated the heat release is dependent on equivalence ratio.

In C$_2$H$_4$-O$_2$-Ar mixtures, the model consistently under-predicts both temperature and O atom number density. One possible reason for difference between the experimental data and the model predictions is discharge non-uniformity developing when ethylene is added to the mixture, at fairly low temperatures involved. To reduce the effect of plasma nonuniformity, future measurements will be conducted in mildly preheated hydrocarbon-oxygen-argon mixtures, such as has been done in our recent work [29]. This will preclude investigations in low-temperature oxidation, but will allow studying kinetics of O atom decay and energy release in plasmachemical reactions at the conditions when chain branching plays a significant role. The mixture at $\phi=0.1$, is lower compared to the results obtained at $\phi=0.5$ and $\phi=1.0$. The mixture at $\phi=0.5$ has the fastest heating rate, an unexpected result that needs further study.

It has been suggested that the poor agreement between the 0-D model predictions and experimental data for the ethylene mixtures is largely due to the striations and plasma contractions at larger burst size, particularly at larger burst sizes where the plasma volume contracts significantly and the agreement between the model and experimental data further deviates. While these plasma instabilities may play a role, the strong dependence of the experimental heat release on equivalence ratio is indicative that the kinetics are not limited by the radical production in the plasma and that the low-temperature plasma oxidation mechanism itself is invalid. The different heating rates in the different equivalence ratios for the hydrogen-containing mixtures when the model predicts comparable rates further indicates that the low-temperature oxidation mechanism is still not fully understood. Future work could incorporate
alternative low temperature mechanisms into the model, such as those conventional mechanisms incorporating alkyl peroxy radicals. Alternatively, future work could also use CARS, stimulated Raman, or resonance Raman scattering to probe the mixtures for transient species in the plasma and propose an entirely new mechanism based on the findings.

7.2 Conclusions for pin-to-pin discharge

This thesis has presented results of time-resolved rotational temperature, by pure rotational Coherent Anti-Stokes Raman Scattering Spectroscopy (CARS) in the pin-to-pin discharge cell. These experiments were conducted in nanosecond pulse discharges in Air, Air-H₂, and Air-C₂H₄ mixtures, initially at room temperature, operated at a single pulse repetition rate of 60 Hz, in the pin-to-pin geometry at a pressure of 52 torr. ICCD images show that Air and Air-H₂ plasmas, have fairly uniform intensity along the discharge gap and an inhomogeneous intensity that gradually decreases radially outward from the plasma filament center. The hydrogen containing mixture does show some plasma instabilities during the main pulse. However, it is suggested that because the instabilities are stochastic, it will result in a broader plasma filament on average.

It is demonstrated that experimental precision of approximately ~ ± 25 K can be readily achieved in the plasma filament. The larger scatter in the experimental data is due to the discharge itself, not to the experimental set up because precision of ~ ± 1 K is achieved in the baseline mixtures with no discharge present.

The experimental temporal temperatures profiles for the baseline air and hydrogen-containing mixtures exhibits a fast and slow heating regime after the main pulse. The fast heating takes place over ~2 µs and the slow heating over a period of ~160 µs. The ethylene
containing mixtures do not exhibit a clear distinction between slow and fast heating as there is indication of further rapid heating past ~2 µs after the main pulse. However, these temperatures could not be resolved as they were above 900K. Future work will be necessary to fully delineate the temporal temperature profile of the ethylene containing mixtures past ~2 µs after the main pulse. Nonetheless, all mixtures exhibit more rapid heating upon addition of fuel, be it hydrogen or ethylene after a discharge pulse. It should be noted that there is one exception. The ethylene containing mixtures show an inverse relationship to the equivalence ratio after the pre-pulse. In other words, the rate of heat release after the pre-pulse slows with increasing ethylene addition. This result is unexpected, especially because the coupled pulse energy is the same across all the mixtures examined. It is hopeful that the 1-D model currently in development will reproduce this trend.

Radial temperature profiles were taken for air at three different time points, about two microseconds before the main pulse, halfway through the rapid heating region, and at the end of the slow heating regime. The radius was found to be ~2 mm in all three cases. This is strongly indicative that there is no contraction or expansion of the filament.

Due to previous work in the lab, it is expected the model will attribute fast heating primarily to collisional quenching of N₂ excited states in air and air-hydrogen mixtures. In ethylene containing mixtures, ethylene oxidation processes will play a large role here as experimental results indicate a strong dependence on equivalence ratio. On the other hand, slow heating will be dominated by V-T transfer with additional heat release by fuel-oxidation.

Preliminary results with the 1-D model still in development show very good agreement, which is promising. However, the lean hydrogen mixture at ø=0.14 is very similar to the base-
line case without fuel. It is not apparent in this case that the model predicts additional heat release from hydrogen oxidation. As experimental results show that heat release increases with increasing hydrogen addition, it is a surprising result. Future work on the model to include the higher hydrogen equivalence ratios as well as a sensitivity analysis is needed, in addition to incorporating ethylene plasmachemical processes to model the ethylene-containing mixtures.

7.3 Final Conclusions

It is obvious that studying the heat release in plasma assisted combustion systems can greatly benefit the understanding of the plasma assisted oxidation processes by both validating a model and isolating areas where there are deviations. The dielectric barrier discharge investigations clearly show that the understanding of low-temperature plasma kinetics is still not where we would like it to be. However, the good agreement between the baseline and hydrogen containing mixtures with the model provide a promising starting point for the development of a more comprehensive model. Additional species concentration measurements could provide additional information that would aid in formulating a new low-temperature oxidation mechanism. While the pin-to-pin discharge model is still in development, it too would greatly benefit from additional species concentration measurements, which would significantly expand the results for fuel-oxidation in this discharge system and provide additional validation data for plasma assisted combustion models.


83. *Ion Energetics Data*. NIST Standard Reference Database Number 69. Gaithersburg, MD 20899: National Institute of Standards and Technology.


