Studies of Nitrogen Vibrational Distribution Function and Rotational-Translational Temperature in Nonequilibrium Plasmas by Picosecond Coherent Anti-Stokes Raman Scattering Spectroscopy

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

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2012

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Abstract

Picosecond Coherent Anti-Stokes Raman Scattering (CARS) has been used for measurements of nitrogen Q-branch (ΔJ = 0) spectra in a variety of non-equilibrium plasma environments; the spectra are processed to infer vibrational distribution function (VDF), 1st level vibrational temperature (Tv), and/or rotational-translational temperature (Tr). The implementation of a home built modeless dye laser and portable CARS system is also described.

The first set of measurements reported were performed in the 200–370 torr plenum of a nonequilibrium Mach 5 wind tunnel, where Tv and Tr have been measured simultaneously. Operation of the nominally high reduced electric field (E/n_\text{peak} \sim 500 \text{Td}), nsec pulsed discharge alone results in fairly significant vibrational loading, Tv \sim 720 \text{K} / Tr \sim 380 \text{K}; addition of an orthogonal low E/n (\sim 10 \text{Td}) DC sustainer discharge produces substantial vibrational non-equilibrium, Tv \sim 2000 \text{K} / Tr \sim 450 \text{K}. Effects of injection of CO2, NO, and H2 downstream of the pulser-sustainer discharge are examined, which result in vibrational relaxation accompanied by simultaneous gas heating, Tv \sim 800-1000 \text{K} / Tr \sim 600 \text{K}. The effect of injection of O2 and “cold” N2 are shown to be insignificant for the \sim 2 \text{msec} flow mixing time present.

CARS measurements within very low density flows in the Mach 5 expansion nozzle are also performed, with Tv measured in both the supersonic free-stream and downstream of a bow shock created by a 5 mm diameter cylindrical test object in the
Mach 5 flow. Measurements within 300 μm of the cylinder surface show that for pure \( \text{N}_2 \), or \( \text{N}_2 \) with 0.25 torr \( \text{CO}_2 \) injection, no vibrational relaxation is observed behind the bow shock.

A third set of data is reported from measurements of \( T_v \) and \( T_{rot} \) produced in a plasma assisted combustion reactor. Non-equilibrium vibrational loading is examined for bursts of 40-150 pulses in 100 torr air at \( T_0 = 300 \) K; vibrational energy is seen to increase quasi-linearly with number of pulses, up to \( \sim 100 \) pulses, after which vibrational temperature levels off \( T_v \sim 1300 \) K. These results are found to agree well with nsec discharge modeling predictions. Vibrational energy decay is examined in 100 and 300 torr air, for \( T_0 = 300 \) and 500 K for a variety of discharge burst sizes, and it is noted that the \( T_0 = 500 \) K condition exhibits vibrational energy decay nearly an order of magnitude faster than that observed for \( T_0 = 300 \) K. Additionally, \( T_{rot} \) was measured for bursts of 50 pulses, at \( T_0 = 500 \) K, in air as well as \( \text{C}_2\text{H}_4- \), \( \text{CH}_4- \), and \( \text{H}_2-\text{air} \) mixtures, for \( P_0 = 100, 200, 300 \) torr, \( \phi \sim 0.9-0.36 \). This analysis shows no significant dependence of \( T_{rot} \) on any of the parameters, except for differences between fuel species. Time-resolved thermometry of \( \text{H}_2-\text{air} \) excitation and ignition is reported, with ignition delay time and peak temperature found in good agreement with kinetic modeling calculations.

A final data set involved the measurement of VDF and \( T_{rot} \) in a single-filament-pulse nsec duration discharge in 100 torr \( \text{N}_2 \) and air. Various energy loading conditions are examined, with high vibrational non-equilibrium observed in all cases. Broadening of the dye laser spectral profile allows simultaneous interrogation of \( \text{N}_2(X,v=0-9) \). Immediately after the \( \sim 100 \) nsec pulse moderate vibrational non-equilibrium is observed,
with \( T_v \sim 600-1000 \text{ K} \), and \( T_{rot} \sim 300-400 \text{ K} \) for all conditions. Very notable is the presence of a peak in \( T_v \) typically occurring \( \sim 100 \mu \text{sec} \) after the discharge pulse, with \( T_{v(peak)} \sim 1400-2600 \text{ K} \), depending on the discharge energy loading. Total vibrational quanta was also plotted; this peaks at a similar time as \( T_v \), and also exhibits an increase of 2-4 times the value observed immediately after the pulse.
Unless the Lord builds the house,
the builders labor in vain.

Unless the Lord watches over the city,
the guards stand watch in vain.

In vain you rise early
and stay up late,
toiling for food to eat—
for He grants sleep to those He loves.

Psalm 127:1-2
Acknowledgments

First of all, thanks to Dr. Walter Lempert, my advisor. You have been an invaluable resource in shaping the course of my research, and under your guidance, the past several years have been both very fruitful and rewarding. Your passion for optical diagnostics is truly contagious; I had no idea this would be the outcome of signing up for your class four years ago. Thanks also to Dr. Igor Adamovich, who has been very helpful in acting as co-advisor throughout my time in the group. Your efforts discussing and modeling experimental results are greatly appreciated, as is the significant insight you’ve given in helping further my understanding of non-equilibrium plasmas. Thanks to Dr. Bill Rich, certainly none of this would be possible without the extensive role you’ve had in founding and supporting The Non-Equilibrium Thermodynamics Laboratory. I’ve always enjoyed the benefit of your incredible experience, as well as our discussions and particularly all your stories.

Thanks to Dr. Yvette Zuzeek, you provided a very good introduction to CARS and taught me a lot about good lab practices through your example (not the least of which was learning to hide things I didn’t want to “walk” away…). Many thanks are due to Dr. Munetake Nishihara, you have been exceedingly helpful for all the work we did in the Mach 5 tunnel, as well as the recent help you’ve given performing the Schlieren imaging, and you have been a great resource for me over a wide array of research topics.
Thanks to Dr. Keisuke Takashima, you are an incredible model of hard work and discipline. I’ve always been humbled and amazed by your vast knowledge and incredible abilities in so many fields, accentuated by your incredible humility. Talking with you about research and life has always been enjoyable for me, particularly our trip to the DOE review meeting last May.

Thanks to Mr. Zhiyao Yin, I have significantly enjoyed sharing lab space with you, even if your unceasing desire is to take it all for yourself ;) Seriously though, your constant efforts to improve your experiment have been a great example, and the countless discussions we’ve had about diagnostics and plasmas have been both beneficial for my learning as well as enjoyable. I truly appreciate your friendship. Thanks to Dr. Naibo Jiang, your vast experience implementing complex optical arrangements has been an incredible asset for me, and you have been a blessing to our group. Thanks to Mr. Dave Burnette for your help with the bare-metal electrode work, particularly for the filament ICCD imaging you did for my benefit. To the rest of the NETL group members, you have been fantastic colleagues and I have appreciated working with you all.

Thanks to my family and friends, both here in Columbus as well as back home—your prayers, support, encouragement and friendship have contributed immeasurably to my academic success. With the utmost appreciation, I thank my beautiful wife Melissa, henceforth to be known as Mrs. Dr. Montello ;) You have been an unbelievable support to me throughout my Ph.D., you have encouraged me through the many frustrations that accompany experimental research, you have *sometimes* listened very patiently to my often long-winded descriptions of what exactly I’m working on, and you have endured
many hours of solitude while I’ve been studying, working on data reduction, or writing. Many women have done nobly, but you excel them all; I love you.

Finally, and most significantly, I thank my Lord and Saviour Jesus Christ. Beyond the most important work You have done in Your sacrificial death for my eternal benefit, You have blessed me with a mind that loves to figure things out, and I pray that all the glory is Yours. Lord, let me live everyday as a reflection of the truth of the words You have spoken, “I am the vine, you are the branches; he who abides in Me and I in him, he bears much fruit, for apart from Me you can do nothing.” (John 15:5)
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Chapter 1: Introduction

Non-equilibrium nanosecond duration pulsed plasma discharges have played a central role in many rapidly emerging technological areas over the past several years, including high-speed flow control [1, 2, 3, 4] and plasma assisted combustion [4, 5]. The ability to tailor non-equilibrium flows by control of the loading of internal degrees of freedom (vibrational and electronic states), as well as by control of dissociation and ionization fraction, is central to these efforts. Increasing the practical applications for nsec plasma discharge devices requires improvements in modeling capabilities. In one sense, this is a requirement for increased fidelity models; however, due to the extreme range of spatial and temporal scales involved in these discharge processes, simplification of unnecessary modeling complexities is also highly desirable. To this end, more thorough understanding of the underlying physicochemical processes in these discharges is needed, for which additional experimental investigations are essential. High-speed flows, ignition and combustion processes, and plasma discharges can all be extremely sensitive to disturbances produced by the physical intrusion of mechanical probes, therefore non-intrusive optical diagnostics are crucial for studies in these environments.

1.1 Motivation for CARS Diagnostics

As mentioned, non-intrusive optical diagnostics are fundamental for experimental investigations in the nsec plasma discharge environments of interest. While there are
several optical techniques which can be used for the measurement of major species concentrations and thermometry, Coherent Anti-Stokes Raman Scattering (CARS) spectroscopy offers several key advantages. CARS will be discussed in detail in the next chapter, but a brief introduction highlighting the benefits of the technique will be provided here. CARS is a four wave mixing technique that has been used widely for thermometry and species concentration measurements in combustion and other gas phase reacting and non-reacting flow environments [6, 7]. As will be described, three of the primary benefits of CARS are: the highly directional “laser-like” quality of the generated signal beam, and the capabilities for very high spatial as well as temporal resolution. Another pertinent advantage CARS provides is that since it is a Raman technique, it can access the ground electronic state levels of homo-nuclear diatomics, such as oxygen, nitrogen, and hydrogen, which are inaccessible to many simpler single photon techniques, such as emission and absorption spectroscopy.

Several advancements in the implementation and use of CARS have been demonstrated in recent years. While early experiments using CARS were carried out primarily with nsec pulse duration laser sources, in the past several years CARS has been extended to psec and fsec pulse regimes. In addition to achieving higher temporal resolution by utilizing shorter pulse duration lasers, use of these short pulses lowers the necessary pulse energies, reducing the risk of window damage [8], allowing for the possibility of complete suppression of the non-resonant background [9], and providing opportunities for measurements in harsh environments via fiber coupling arrangements [10].
1.2 Motivation for Mach 5 Studies

Optical diagnostics offer significant possibilities for furthering the understanding of the effects of altering the internal mode energy storage as well as dissociation and ionization fraction in non-equilibrium hypersonic flows. For example, turbulent transition delay in a Mach 5 flow over a $5^\circ$ cone by means of injection of carbon dioxide into nitrogen or air flow has been recently demonstrated [11]. Kinetic modeling calculations [12] suggest that transition delay is caused by absorption of acoustic perturbations in the boundary layer by vibrational energy modes of CO$_2$, possibly also resulting in CO$_2$ dissociation. Another example is relaxation of energy stored in internal degrees of freedom of molecules behind a bow shock, which may significantly increase shock stand-off distance. The presence of vibrationally and electronically excited species in a hypersonic flow may strongly affect the emission signature from the shock layer. Finally, short-pulse electric discharges efficiently loading electronic energy levels of nitrogen and oxygen in air are currently being explored as means of hypersonic flow control, by producing repetitive localized pressure perturbations in the flow [13].

Since the cost of obtaining full-scale hypersonic flight test data or operating large-scale ground test facilities is extremely high, alternative methods of data production are necessary. This provides a significant incentive for the development and use of small scale test facilities which are capable of recreating environments seen in the flow conditions of interest, and which lend themselves to development of optical diagnostics of nonequilibrium hypersonic flows. Our approach to generating a nonequilibrium
hypersonic flow is to use a high-pressure, low-temperature, diffuse electric discharge sustained in the plenum of a small-scale Mach 5 wind tunnel to load internal energy modes of nitrogen and oxygen molecules [14, 15].

Similar to our previous work [14, 15], target parameters for nonequilibrium gas flow include run time for steady-state conditions of 5-10 seconds, with plenum pressures in the range of \( P_0 \sim 200 – 370 \) Torr. Previously published results, which will be reviewed, have shown that the pulser-sustainer electric discharge present in the wind tunnel plenum is capable of producing highly nonequilibrium flow conditions, with rotational-translational temperature inferred by nitrogen UV emission spectroscopy near \( T_{rot} \sim 350 – 400 \) K, and vibrational temperature up to \( T_v \sim 2,000 \) K [16]. Additionally, as these results demonstrated, the flow internal energy mode disequilibrium can be further controlled by injection of “rapid relaxer” species (carbon dioxide, nitric oxide, or hydrogen) into the subsonic nonequilibrium flow, after the discharge section but upstream of the nozzle throat. Qualitatively, the results of the study demonstrated effects similar to what vibrational energy transfer rates predict, however these rates are highly sensitive to the gas (rotational-translational) temperature. To compare experimental vibrational energy relaxation effects with energy exchange rate predictions, simultaneous direct measurement of the gas temperature is necessary.

Additional experimental data characterizing both the vibrational energy loading as well as gas heating of molecular nitrogen in a non-equilibrium flow excited by a non-self-sustained electric discharge in the plenum of a Mach 5 wind tunnel will also be shown. Volume ionization, at plenum pressures in the range of \( P_0 = 200 – 370 \) Torr, is
accomplished using a high peak reduced electric field ($E/n_{\text{peak}} \sim 500 \ Td$), 5 nsec duration pulse discharge, operating at a pulse repetition rate of 100 kHz. An orthogonal DC sustainer discharge ($E/n \sim 10 - 30 \ Td$), which accounts for approximately 80% of the total power loading into the flow, efficiently excites the $N_2$ vibrational energy mode. Theoretical predictions suggest that as much as 80-90% of the DC sustainer input power goes into nitrogen vibrational excitation by electron impact at these reduced electric field values. Temporally and spatially resolved ground and first level vibrational populations of nitrogen, $N_2(X^1\Sigma_g, v = 0-1)$, yielding first level vibrational temperature in the pulser-sustainer discharge, up to $T_v(N_2) = 2000 \ K$, are measured using picosecond Coherent Anti-Stokes Raman Scattering (CARS) spectroscopy [7], which is described in detail.

Measurements using the nsec pulsed discharge alone (i.e. without the DC sustainer) are also presented, the results of which demonstrate that significant vibrational loading occurs, $T_v \sim 720 \ K$ at 300 Torr of pure $N_2$, even at the relatively high nominal reduced electric field, $E/n_{\text{peak}} \sim 500 \ Td$. Our quasi-one-dimensional nanosecond pulse discharge model [17] is used to compare predicted vs. measured energy coupling to the flow, as well as post-breakdown energy loading to nitrogen vibrational states, with good agreement to the values measured by CARS. High resolution Q-branch CARS spectra, with partial resolution of the rotational structure are fit with the Sandia CARSFT least squares fitting code [18], yielding best fit rotational temperatures of $T_{\text{rot}} \sim 380 \ K$ for the pulser operating alone and $T_{\text{rot}} \sim 450 \ K$ for the pulser-sustainer discharge (sustainer voltage $V_{PS} = 4.5 \ kV$).
Additionally, the effect on nitrogen $T_v$ and $T_{rot}$ of injection of CO$_2$, NO, and H$_2$, between the discharge section and the CARS measurement location, which results in partial vibrational relaxation of nitrogen accompanied by gas heating, is also examined. This demonstrates quantitatively the ability to control and tailor the vibrational energy content of the flow prior to its expansion through the Mach 5 nozzle of the wind tunnel. Conversely, addition of oxygen or nitrogen (not excited in the discharge) to the vibrationally excited nitrogen flow did not result in significant vibrational temperature change, due to slow vibration-vibration energy transfer from N$_2$ to O$_2$ for the case of oxygen addition and extremely slow vibration-translation relaxation at these temperatures for either O$_2$ or N$_2$ injection.

Finally, also presented from this group of experimental studies are the results of measurement of nitrogen Q-branch CARS spectra captured in the extremely low density Mach 5 supersonic flow. Measurements are made both in the free-stream as well as at multiple locations behind the bow shock produced by a 5 mm diameter quartz cylinder mounted across the flow. As will be discussed, the utilization of micrometer adjustment translation stages along with pitch/catch optical arms allows for measurement location adjustment in the vertical and stream-wise directions within the flow. CARS spectra are captured as near as 300 μm from the cylinder surface, for the nonequilibrium flow produced by the pulser-sustainer discharge with no relaxer injection, as well as the slightly equilibrated case of 0.25 torr injection of CO$_2$. In both cases, the flow remains highly nonequilibrium, with vibrational temperatures found similar to those measured in the subsonic plenum for the same discharge conditions. The integrated spectra are also
used to estimate local number density, leading to an estimated shock stand-off distance measured to 1.0 mm, very close to the 1.2 mm measured previously by Schlieren imaging and NO PLIF [14, 15].

1.3 Motivation for Elevated Temperature PAC Reactor Studies

As mentioned, applications for nsec pulsed plasma discharges for the area of plasma assisted combustion (PAC) has seen extensive growth over the past several years [4, 5]. Improvements in predictive kinetic PAC fuel-air chemistry modeling efforts have been somewhat hindered by the lack of thermometry and species concentration data that exists in the so-called “intermediate” temperature range which lies above room temperature but below the mixture ignition temperature. Over the past few years, work in our group has gone into the development and use of an elevated initial temperature PAC flow reactor for the measurement of ignition delay time and time-resolved absolute OH number densities for various fuel-air mixtures, by laser induced fluorescence [19, 20].

Recent studies have performed OH concentration measurements, as well as two-line OH thermometry in fuel-air discharges and ignition in hydrogen-air mixtures excited by repetitive nanosecond pulse discharges [21], and compared these results to the kinetic modeling predictions with relatively good agreement. Some uncertainty exists in the OH thermometry, however, motivating the use of CARS as a reference for 5 or 6 line OH thermometry studies yet to be performed, as well as for direct comparison with the kinetic fuel-air chemistry model predictions.
Characterization of the CARS system capability for measuring rotational-translation temperature, $T_{rot}$, has been performed in 100 torr dry air, at both $T = 300$ K, and $T = 500$ K, and reveals typical system accuracy and precision $\sim 3$-$4\%$ of the values measured by thermocouple. For air and three lean fuel-air cases ($C_2H_4$-air, $CH_4$-air, and $H_2$-air), $T_{rot}$ has been measured by CARS at elevated initial temperature, $T_0 = 500$ K, a variety of discharge pressures, $P_0 = 100$-$300$ torr, and a range of equivalence ratios, $\varphi \sim 0.09$-$0.36$, for bursts of 50 pulses, delivered at a pulse repetition frequency of $\nu = 10$ kHz. The results of this show that neither equivalence ratio nor pressure appears to have a significant impact on the temperature produced in these discharges, while changing the fuel does have an effect. For the case of air alone, an increase of $\Delta T_{rot} \sim 30$ K is observed, while for $CH_4$-air and $C_2H_4$-air, $\Delta T_{rot} \sim 50$ and $\sim 70$ K respectively; the case of $H_2$-air falls between the other two fuels.

Measurements of $T_{rot}$ for $H_2$-air excitation and ignition are also reported and compared to the fuel-air chemistry PAC kinetic model. This work is performed at $T_0 = 500$ K, $P_0 = 92$ torr, $\varphi = 0.4$, and for bursts of 50, 99, and 120 pulses, delivered at $\nu = 10$ kHz. The experimental results agree fairly well with the modeling predictions, particularly for the ignition delay time and peak temperature for the case of 120 pulses, while for the other two conditions, the model predicts a slightly higher temperature immediately after the discharge burst than that measured by CARS.
1.4 Motivation for Bare-Metal Electrode Single-Pulse Discharge Studies

While there has been a fair amount of research into low temperature, non-equilibrium plasma discharge processes, relatively few measurements have examined the dynamics of ground electronic state, vibrationally excited nitrogen, \( \text{N}_2(X,v) \). In large part, this is certainly due to the inaccessibility of these levels to simple probing techniques such as single photon absorption or emission, however this is a perfect candidate for measurements by Raman techniques, as previously described, either by spontaneous Raman scattering or CARS. In Ref. [22], Filimonov and Borysow describe the use of CARS for the measurement of ground electronic state, vibrationally excited nitrogen, \( \text{N}_2(X,v = 0-6) \). For this work, a ~1 \( \mu \)sec duration pulsed DC discharge is fired in 5 torr of pure \( \text{N}_2 \), with a maximum current of ~42 A. In this arrangement, the authors observe significant vibrational loading occurring during the discharge pulse, as can be seen in the plot in Figure 1.1. As the figure also shows, vibrational states for \( v > 1 \), open triangles, are characterized by a much higher vibrational temperature, \( T_{v(2-6)} \), than the first level vibrational temperature, \( T_{v(01)} \), represented by the open circles.
Immediately after the end of the discharge pulse, $T_{v(01)} \sim 2200$ K, while $T_{v(2-6)} \sim 6000$ K. In the afterglow, $T_{v(01)}$ continues to grow slightly, as $T_{v(2-6)}$ falls off, and the two vibrational temperatures are equilibrated with each other, as well as with $T_{rot}$ after $\sim 50$-$100$ μsec, where $T_{rot} \approx T_v \sim 3500$ K. A very unexpected result observed in Figure 1.1, is the occurrence of a second disequilibrium phase, from $100$ μsec $< \Delta t < 10$ msec, when $T_{rot}$ again falls significantly below $T_v$. It is expected that if the gas temperature were equilibrated at $T \sim 3500$ K, V-T energy exchange processes should dominate, and barring external influence, the gas should remain in V-T equilibrium while it cools and eventually reaches $T \sim 300$ K. As the plot in Figure 1.2 (also from Ref. [22]) shows, excited vibrational state populations for $v = 1$-$6$ remain nearly constant from the end of

Figure 1.1 Two vibrational temperatures and rotational-translational temperature (open circles – $T_{v(01)}$, open triangles – $T_{v(2-6)}$, solid symbols – $T_{rot}$ from 2 runs) plotted during and after the $\sim 1$ μsec discharge pulse, indicated by the vertical dashed line (Figure 7 in Ref. [22]).
the discharge pulse until \( \Delta t \sim 100 \mu \text{sec} \), when vibrational decay begins to take over, starting with the higher vibrational levels.

![Vibrational level populations vs. time](image)

Figure 1.2 Vibrational level populations vs. time; the vertical dashed line indicates the end of the \( \sim 1 \mu \text{sec} \) discharge pulse (Figure 8 in Ref. [22]).

In Ref. [23], Messina et. al. performed time-resolved CARS measurements for investigation of nitrogen rotational and vibrational temperatures produced in a nsec pulsed pin-to-pin discharge in atmospheric pressure air and methane-air mixtures. In their arrangement, vibrational levels \( v = 0-2 \), with partial rotational resolution, were captured. While the voltage waveforms used in this case had a relatively short full width at half maximum, FWHM \( \sim 70 \) nsec, a relatively long tail \( \sim 200 \) nsec is also present.
Results from two discharge cases in air are shown in Figure 1.3, where the highly non-equilibrium behavior is easily observed.

Figure 1.3 Non-equilibrium rotational and vibrational temperatures ($T_{\text{rot}}$ and $T_{\text{vib}}$ respectively) produced by a single ~200 nsec duration discharge pulse in atmospheric pressure air (Figure 5 in Ref. [23]).

For both discharge loading conditions, the authors note an initial high vibrational temperature during the discharge, $T_v \sim 1400$ K & 2200 K for the lower and higher loading case, respectively, which rapidly relaxes after ~100 nsec-1 μsec down to $T_v \sim 1000$ K. Approximately 20-50 μsec after the pulse, the vibrational temperature reaches a second peak value, $T_v \sim 2000$ K for the lower loading condition, and $T_v \sim 1800$ K for the higher loading condition. In the lower loading case, $T_{\text{rot}} \leq \sim 400$ K for the entire time after the
pulse, while for the higher loading case, immediately after the discharge, $T_{rot} \sim 450-500$ K, and reaches a maximum value of $\sim 900$ K, which occurs during and after the peak in the vibrational temperature for this condition.

In Ref. [24], an attempt was made to recreate the peak in $T_v$ occurring in the afterglow, described in Ref. [23], the results of which can be seen below in Figure 1.4. In this work, it is hypothesized that the occurrence of the peak in vibrational temperature near $\Delta t \sim 20-50$ μsec is the result of V-V exchange from higher vibrational states. This is, perhaps, an obvious guess at where the vibrational energy which moves into the $v = 1$ level comes from, however since the work in Ref. [23] was not able to measure states higher than $v = 2$, it can neither be confirmed nor invalidated. Additionally, as can be seen in Figure 1.4, while the modeling results achieved in Ref. [24] somewhat recreate the shape of the $T_v$ profile, the timing at which the vibrational population rises and falls is off by roughly an order of magnitude (note the log time scale). Observation of additional vibrational levels could add significantly to the understanding of the dynamics of the $N_2(X,v)$ populations, and is an important motivation for the work presented here.
Figure 1.4 Attempt to recreate the vibrational temperature peak occurring in the nsec discharge afterglow in air from Ref. [23] (Figure 4 in Ref. [24]).

Finally, in a very recent work by Lo et. al. [25], spontaneous Raman scattering has been used for the measurement of nitrogen VDF and $T_{\text{rot}}$ in nsec scale plasma discharges produced in 1 atm air. In this work, the discharge is created between a pin and a sphere with radius of curvature of 35.6 mm, where the gap between the electrodes is 6.5 mm. The filament produced is very stable in space and time, and the emission FWHM is 1.1 mm. The voltage pulse has a FWHM ~25 nsec with a peak voltage of $V \sim 25$ kV, peak current of $I \sim 65$ A, and total deposited energy of ~20 mJ/pulse. The experimental arrangement allowed for measurements of nitrogen ground electronic state, vibrational levels $v = 0$-16. In this work, the authors noted that characterization of vibrational populations required defining two vibrational temperatures, $T_{v(0)}$, the “first-
level” vibrational temperature, and $T_{v(1v)}$, the vibrational temperature characterizing levels $v > 1$, in the same fashion as the notation used by the authors in Ref. [22].

Figure 1.5 Non-equilibrium vibrational ($T_{v(01)}$ and $T_{v(1v)}$) and rotational ($T$) temperatures produced by the nsec duration pulsed discharge. $T_{v(01)}$ is the “first-level” vibrational temperature, while $T_{v(1v)}$ is the vibrational temperature characterizing the upper vibrational states (Figure 15 in Ref. [25]).

As can be seen in Figure 1.5, the very high loading in the discharge results in a rotational-translation temperature of $T_{rot} \sim 850$ K, first-level vibrational temperature of $T_{v(01)} \sim 4000$ K, and upper vibrational level temperature of $T_{v(1v)} \sim 6500$ K, immediately after the end of the discharge pulse. After $\sim 10$ μsec, the two vibrational temperatures are nearly equilibrated, due to V-V exchange, with a common $T_v \sim 4000$ K. As time proceeds, the vibrational temperature falls off as the rotational-translation temperature
increases; these two temperatures are then nearly equilibrated by \( \sim 100 \mu\text{sec} \) after the discharge pulse, at \( T \sim 1800 \text{ K} \). While extreme vibrational non-equilibrium is observed for short delay times after the discharge, \( \Delta t \lesssim 10 \mu\text{sec} \), the increase in \( T_v \) from \( 10 \mu\text{sec} < \Delta t < 100 \mu\text{sec} \), observed in Ref. \([23]\) (and shown in Figure 1.3) is not present. The lack of this behavior in the plot in Figure 1.5 may likely be related to the high rotational-translational temperature produced by the discharge. Increasing \( T_{rot} \) causes an increase in the V-T exchange rate, allowing more rapid transfer of vibrational energy into thermal energy.

1.5 Structure of this Thesis

The remaining chapters of this thesis are arranged as follows: Chapter 2 will provide an in-depth discussion of the theoretical background and experimental considerations for the CARS spectroscopic technique. Chapter 3 will discuss the CARS diagnostic system constructed and used for this work, including the modeless dye laser. Chapter 4 will describe the various experimental arrangements used for the experiments performed in the Mach 5 wind tunnel, the elevated temperature PAC reactor, and the bare-metal electrode single-pulse discharge system. Chapter 5 will discuss the extensive results from the measurements performed in both the plenum and supersonic nozzle of the Mach 5 wind tunnel, while the results from the elevated temperature PAC and bare-metal electrode single-pulse discharge studies will be illustrated in Chapter 6. Finally, Chapter 7 will offer a brief review of key results as well as a few suggestions for future work.
Chapter 2: Coherent Anti-Stokes Raman Scattering Spectroscopy

Coherent Anti-Stokes Raman Scattering (CARS) spectroscopy is a four wave mixing technique which has been used extensively for thermometry and species concentration measurements of combustion and other gas phase reacting and non-reacting flows [6, 7]. Three of the primary benefits of CARS are: 1.) the coherence requirements for signal generation, which gives the generated signal beam a highly directional “laser-like” quality, 2.) the extremely localized signal generation volume, which provides high spatial resolution, and 3.) very high temporal resolution, which is of the order of the laser pulse used to generate the CARS signal beam. The collimated signal beam’s characteristics provide the ability to detect and capture the signal several meters from the measurement location, which helps to significantly reduce the contaminative effects of background luminosity. The theoretical underpinnings of the technique will be discussed below; however, as a simple introduction, the CARS process involves the interaction of three input photons and the generation of one new (signal) photon, and can be used to interrogate molecular rotations, vibrations, and less frequently, excited electronic states, with the Q-branch ($\Delta j = 0$) vibrational transitions of interest for this work.

The complete CARS process, which can be thought of as two 2-photon processes, begins with the nearly simultaneous incidence of so-called “pump” and “Stokes” photons on a molecule. While the choice of wavelength for the pump photon is arbitrary, typically the 532 nm second harmonic of a Neodymium doped yttrium aluminum garnet
(Nd:YAG) laser is chosen. With the choice of the pump laser frequency, $\omega_{pump}$, the frequency of the Stokes beam must satisfy $\omega_{Stokes} = \omega_{pump} - \Delta \omega_{Raman}$, where $\Delta \omega_{Raman}$ corresponds to the molecular dependent energy spacing of the Raman active transition of interest. These photons interact with the molecule via the third-order nonlinear susceptibility, $\chi^{(3)}$, creating an oscillating induced polarization in the molecule, and causing a molecular transition to the energy level dictated by the Raman energy. In the second half of the CARS process, a “probe” photon (again the choice is arbitrary, and again the 532 nm YAG is often chosen) interacts with the excited molecule. This interaction occurs as a “scattering” of the incident photon off the oscillating induced polarization, with the result that the probe photon, $\omega_{probe}$, is eliminated, and a new anti-Stokes photon is generated, where the frequency of this new photon satisfies $\omega_{Anti-Stokes} = \omega_{probe} + \Delta \omega_{Raman}$. It is because of the Raman interactions that the CARS process can be applied to homo-nuclear diatomic molecules, such as nitrogen, oxygen and hydrogen, which are of extreme interest in combustion and other reacting and non-reacting air flows, but are inaccessible to single photon techniques such as absorption or emission spectroscopy. The corresponding energy level diagram for the complete CARS process is represented in the schematic of Figure 2.1.
2.1 Internal Molecular Energy

As mentioned above, the molecular dependent energy spacing of the Raman active mode under interrogation bears utmost importance for this diagnostic technique. The vibrational mode transitions of the diatomic molecule nitrogen are of specific concern here; the calculation of the energy level spacing is relatively straightforward. Excluding electronic excitation, the total internal energy of a diatomic molecule, $E_{tot}$, can be well represented as the sum $E_{tot} = E_{vib} + E_{rot}$, where $E_{vib}$ and $E_{rot}$ are terms for the vibrational and rotational energy, respectively. The vibrational energy term, considering the molecule as a simple harmonic oscillator plus the first anharmonicity correction term (a good approximation for low vibrational levels), can be approximated as (in units of cm$^{-1}$):

$$E_{vib}(v) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2$$  \hspace{1cm} \text{Eq. 2.1}
where $\omega_e$ and $\omega_e x_e$ are molecular constants, and $v$ is the vibrational quantum number.

The term for rotational energy can be approximated as (also in cm$^{-1}$):

$$E_{Rot}(v,J) = \left(B_e - \alpha_e \left(v + \frac{1}{2}\right)\right)J(J+1)$$  \hspace{1cm} \text{Eq. 2.2}

where $B_e$ is the equilibrium rotational constant, $\alpha_e$ is the vibration-rotation interaction constant, which accounts for the effects of vibrations changing the molecular moment of inertia, and $J$ is the rotational quantum number.

As previously mentioned, the measurements performed for this work utilize Q-branch transitions, for which the quantum mechanical selection rules are: $\Delta v = \pm 1$, $\Delta J = 0$. Thus the spectral locations for Q-branch CARS transitions, $\omega_{CARS}(v,J)$, for a molecule initially in quantum state $(v,J)$, can then be written as:

$$\omega_{CARS}(v,J) = E_{tot}(v+1,J) - E_{tot}(v,J)$$  \hspace{1cm} \text{Eq. 2.3 (a)}

After inserting the equations for $E_{tot}$ and simplifying, this is reduced to:

$$\omega_{CARS}(v,J) = \omega_e - 2\omega_e x_e (v + 1) - \alpha_e J(J+1)$$  \hspace{1cm} \text{Eq. 2.3 (b)}

This equation deserves some distinction, as it reveals where the CARS spectral features will appear for a given diatomic molecule. To get more of a sense of the appearance of
CARS spectra, the relative spacing between spectral features is also quite helpful. The spectral spacing between vibrational bands, \( \Delta \omega_{CARS}(\tilde{v}, J) \), can be represented as:

\[
\Delta \omega_{CARS}(\tilde{v}, J) \equiv \omega_{CARS}(v + 1, J) - \omega_{CARS}(v, J)
\]

Eq. 2.4 (a)

Inserting Eq. 2.3 (b) and simplifying, this can be re-written as:

\[
\Delta \omega_{CARS}(\tilde{v}, J) = -2 \omega_e x_e
\]

Eq. 2.4 (b)

The spacing between subsequent rotational lines, \( \Delta \omega_{CARS}(v, J) \), can be represented in the same way as:

\[
\Delta \omega_{CARS}(v, J) \equiv \omega_{CARS}(v, J + 1) - \omega_{CARS}(v, J) = -2 \alpha_e (J + 1)
\]

Eq. 2.5

For nitrogen, \( \omega_e = 2358.6 \text{ cm}^{-1} \), \( \omega_e x_e = 14.32 \text{ cm}^{-1} \), and \( \alpha_e = 0.0173 \text{ cm}^{-1} \) [26], which follows the typical relation: \( \omega_e \gg \omega_e x_e \gg \alpha_e \). From this relation, Eqs. 2.4 and 2.5 illustrate the characteristic picture of a Q-branch CARS spectrum. Under low resolution, the individual rotational lines are unresolved, while the vibrational peaks are spread by \( 2 \omega_e x_e \), decreasing in energy as \( v \) increases. To the level of approximation used here, which is quite good for the low lying vibrational levels of nitrogen, the
vibrational band spacing within the spectrum is constant; for nitrogen, $\Delta \omega_{CARS}(\tilde{v},J) \approx 29 \text{ cm}^{-1}$.

As the system resolution increases, individual rotational lines will also become visible within the vibrational bands. The $J$ dependence of these lines indicates that higher rotational lines are spaced farther apart than low lines, making them easier to resolve. For example, the spacing between the $J = 6$ and $J = 7$ lines (near the Boltzmann distribution peak for N$_2$ at $T = 300$ K) is $\Delta \omega_{CARS}(\nu = 0, J = 6) \approx 0.24 \text{ cm}^{-1}$, while the spacing between the $J = 20$ and $J = 21$ lines (at the tail of the same distribution) is $\Delta \omega_{CARS}(\nu = 0, J = 20) \approx 0.76 \text{ cm}^{-1}$. Table 2.1 below lists the Raman shifts for the first several vibrational bands of nitrogen, along with the corresponding Stokes and Anti-Stokes wavelengths, considering 532 nm pump and probe beams.

<table>
<thead>
<tr>
<th>Transition $(\nu''')$</th>
<th>Raman Shift [cm$^{-1}$]</th>
<th>Stokes wavelength [nm]</th>
<th>Anti-Stokes wavelength [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2329.9</td>
<td>607.3</td>
<td>473.3</td>
</tr>
<tr>
<td>1</td>
<td>2301.3</td>
<td>606.2</td>
<td>474.0</td>
</tr>
<tr>
<td>2</td>
<td>2272.6</td>
<td>605.2</td>
<td>474.6</td>
</tr>
<tr>
<td>3</td>
<td>2244.0</td>
<td>604.1</td>
<td>475.3</td>
</tr>
<tr>
<td>4</td>
<td>2215.3</td>
<td>603.1</td>
<td>475.9</td>
</tr>
</tbody>
</table>

Table 2.1 Raman shift and resulting Stokes and Anti-Stokes wavelengths for the first five vibrational transitions in nitrogen.
2.2 Derivation of the CARS Equation

The equation for the CARS signal can be derived following the theoretical course found in Ref. [6]. Starting from the wave equation, derived from Maxwell’s equations, which can be written as:

\[ \nabla^2 \vec{E} - \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \vec{P}}{\partial t^2} \quad \text{Eq. 2.6} \]

where \( c, \mu_0, \vec{E}, \) and \( \vec{P} \) are the speed of light, permeability of free space, applied electric field, and the polarization induced in the medium, respectively. Since the electric field and induced polarization can both be expressed as sums of the functions contributed by each field present (i.e. the three applied laser fields and the generated CARS signal beam), a time dependence of the form \( \exp[-i\omega_j t] \) is assumed, where the \( \omega_j \) term is the frequency of the \( j^{th} \) field. After inserting this functional form into Eq. 2.6, the time differentials are performed, and the wave equation for a single frequency component becomes:

\[ \nabla^2 \vec{E} (\omega_j, \vec{r}) + \frac{\omega_j^2}{c^2} \vec{E} (\omega_j, \vec{r}) = -\mu_0 \omega_j^2 \vec{P} (\omega_j, \vec{r}) \quad \text{Eq. 2.7} \]

Equation 2.7 may be further modified noting that the induced polarization can be expressed as a sum of the linear and nonlinear terms, i.e. the sum of the first through \( n^{th} \) order terms. For the case of an isotropic medium, there are no even power terms in this
sum, and since the terms rapidly decrease in magnitude with increasing order, the induced polarization will be represented as 

$$\vec{P}(\omega_3, \vec{r}) = \varepsilon_0 \chi^{(1)} \vec{E}(\omega_3, \vec{r}) + \vec{P}^{(3)}(\omega_3, \vec{r}),$$

where the first order induced polarization term is expressed as the product of the permittivity of free space, \(\varepsilon_0\), linear susceptibility, \(\chi^{(1)}\), and the electric field. Upon inserting this into Eq. 2.7, and noting that the material permittivity and the speed of light can each be written as \(\varepsilon = \varepsilon_0(1 + \chi^{(1)})\), and \(c^2 = 1/\mu_0\varepsilon_0\), the field component of the CARS signal, at frequency \(\omega_3\), can be expressed as:

$$\nabla^2 \vec{E}(\omega_3, \vec{r}) + \frac{\omega_3^2}{c^2} \frac{\varepsilon}{\varepsilon_0} \vec{E}(\omega_3, \vec{r}) = -\mu_0 \omega_3^2 \vec{P}^{(3)}(\omega_3, \vec{r}) \quad \text{Eq. 2.8}$$

The third order induced polarization term is in general quite complicated, due to the presence of the third order non-linear susceptibility term, \(\chi^{(3)}\), which is a third order tensor. However, based on the macroscopic symmetry, for the case that all incident beams have parallel polarization, and with the pump and probe beams degenerate in energy, the component of the nonlinear induced polarization generating the CARS signal can be expressed as:

$$\vec{P}^{(3)}(\omega_3, \vec{r}) = \varepsilon_0 \chi_{\text{CARS}} E^2(\omega_1, \vec{r}) E^*(\omega_2, \vec{r}) \quad \text{Eq. 2.9}$$

where \(\chi_{\text{CARS}}\) is the nonlinear susceptibility for the CARS process, and \(\omega_1\) and \(\omega_2\) are the frequencies of the pump/probe and Stokes beams, respectively. Assuming an expression
for the electric field as a travelling wave $\vec{E}(\omega_j, \vec{r}) = \vec{E}(\omega_j) \exp[i \vec{k}_j \cdot \vec{r}]$, Eq. 2.9 will produce a term: $\exp[i(2\vec{k}_1 - \vec{k}_2) \cdot \vec{r}]$, where $\vec{k}_j$ is the wave-vector, which has a magnitude of $\omega_j n_j/c$ and points in the direction of propagation, where $n_j$ is the frequency dependent index of refraction. It can be shown that CARS signal generation and growth will only occur significantly when the argument of this exponential is zero, that is, in the $2\vec{k}_1 - \vec{k}_2$ direction, which will be denoted as the $z$ direction. Thus combining Eq. 2.9 with Eq. 2.8 and considering only the $z$ component of the field, the equation becomes:

$$\frac{\partial^2 E_3}{\partial z^2} + \frac{\omega_3^2 \varepsilon}{c^2 \varepsilon_0} E_3 = -\frac{\omega_3^2}{c^2 \chi_{CARS}} E_1^2 E_2^* \exp[i(2\vec{k}_1 - \vec{k}_2)z] \quad \text{Eq. 2.10}$$

where $E_j = E(\omega_j, \vec{r})$. Substituting an assumed solution of the form $E(\omega_3, \vec{r}) = E(\omega_3, z) \exp[i k_3 z]$, Eq. 2.10 will become:

$$\frac{\partial^2 E_3}{\partial z^2} + 2ik_3 \frac{\partial E_3}{\partial z} = -\frac{\omega_3^2}{c^2 \chi_{CARS}} E_1^2 E_2^* \exp[i \Delta k z] \quad \text{Eq. 2.11}$$

with $\Delta k$ defined as $\Delta k = 2\vec{k}_1 - \vec{k}_2 - k_3$. If $\Delta k$ is small, the field variation over small distances will be very small and consequently the second derivative term will be significantly smaller than the first derivative term and can be ignored. This assumption, known as the slowly varying wave approximation, allows the straightforward integration
of the now first-order differential equation, from $z = 0$ to $z = L$, which results in (assuming $E_3(0) = 0$):

$$E_3 = \frac{\omega_3}{2n_3c} \chi_{\text{CARS}} E_1^2 E_2^* \frac{\exp[i\Delta k L] - 1}{\Delta k}$$  \hspace{1cm} \text{Eq. 2.12}

where $L$ is the interaction length. Given that the time averaged beam intensity, $I_j$, can be related to the corresponding electric field as $I_j = n_j c \varepsilon_0 / 2 |E_j|^2$, the CARS equation, representing the time-averaged signal intensity, can be written as:

$$I_3 = \frac{\omega_3^2}{n_1^2 n_2 n_3 c^4 \varepsilon_0^2} I_1^2 I_2 |\chi_{\text{CARS}}|^2 L^2 \left( \frac{\sin \left( \frac{\Delta k L}{2} \right)}{\Delta k L / 2} \right)^2$$  \hspace{1cm} \text{Eq. 2.13}

There are several important features of this equation which can be easily shown to bear significant impact for the employment of this diagnostic. First, $I_3 \propto I_1^2 I_2$, which shows the inherent dependence of the CARS signal intensity on the product of the square of the pump laser intensity and the Stokes laser intensity, demonstrating the need for high peak laser beam intensities in order to generate sufficient signal intensities. Two important scaling relations for diagnostics come out of the material dependence for CARS signal generation $I_3 \propto |\chi_{\text{CARS}}|^2$. Without reproducing the derivation given in Ref. [6], the CARS susceptibility can be written as:
where \( \frac{\partial \sigma}{\partial \Omega} \) is the Raman cross section, \( N \) is the number density, \( \Gamma \) is the molecular damping constant, related to the linewidth for spontaneous Raman scattering, and \( \omega_v \) is the molecular resonant frequency. Two terms in Eq. 2.14 are of particular importance for the present discussion, \( \frac{\partial \sigma}{\partial \Omega} \) and \( N \). The cross section for Raman scattering in nitrogen scales approximately as \( v'' + 1 \) for the Stokes and \( v'' \) for the anti-Stokes processes – while there is a correction to this due to vibrational anharmonicity, this is very small for \( N_2(v < 10) \) and can be ignored here [27]. The quadratic dependence \( I_3 \propto |\chi_{CARS}|^2 \propto \left( \frac{\partial \sigma}{\partial \Omega} \right)^2 \) yields the scaling \( I_3 \propto (v'' + 1)^2 \) for CARS; this is very important for measurements of VDF by CARS, and will be referred to in the section on data processing in the next chapter. The dependence \( \chi_{CARS} \propto N \), results in the nearly quadratic CARS signal intensity dependence on number density at low pressures, \(~1\text{atm} \) and below, also crucially important for diagnostic application.

A fourth significant scaling for the CARS signal is \( I_3 \propto L^2 \), which is a result of the coherent nature of the diagnostic. Clearly this demonstrates a trade-off between signal intensity levels and spatial resolution in the beam propagation direction, with the scale and design of the experiment generally dictating the necessary spatial resolution and the interaction length as a result. Finally, the last major signal scaling to be discussed is \( I_3 \propto \left( \sin \left[ \frac{\Delta k L}{2} \right] / \frac{\Delta k L}{2} \right)^2 \), which has the form of a “Sinc squared” function. This function
equals unity when the argument is zero, and rapidly decays toward zero as the argument varies from zero. With the interaction length fixed, the argument of the sinc squared function is dependent only on the $\Delta k$ term. It is readily apparent from this simple discussion that efficient signal generation and growth will require $\Delta \mathbf{k} = 2\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3 \approx 0$, which is referred to as the phase matching criteria. When this condition is met, signal generated at $z$ will be in phase with that generated at $z + \Delta z$, and constructive interference will result.

2.3 CARS Phase-Matching

There are many experimental arrangements, known as phase-matching geometries, which will satisfy the phase-matching condition. Three of these phase-matching geometries, collinear CARS, BoxCARS, and USED-CARS, have been employed for the present work, and each of them will be introduced and discussed briefly. For each experimental arrangement used in this work, the pump and probe beams were degenerate in energy, therefore the more general non-degenerate case will not be discussed here. Collinear CARS, which is illustrated in the schematic diagram in Figure 2.2 (a), is the simplest of all phase matching geometries. In this arrangement, the one 532 nm beam, which serves as both the pump and probe beams, and the broadband Stokes beam are combined collinearly with a dichroic mirror; the overlapped beams are then sent through a focusing lens. As the beams focus, their intensities increase dramatically, which allows for efficient signal generation. Due to the nearly dispersionless characteristics of most gaseous species in the visible region of the
electromagnetic spectrum, the phase-matching criteria is automatically satisfied by collinear alignment, and the CARS signal beam is generated in the forward direction. After the beam focus, another positive lens is used, now to re-collimate the beams. Beyond this, the CARS beam is separated from the pump/probe and Stokes beams with a dichroic mirror or prism.

In exchange for the simplicity of the optical alignment, the primary drawback of the collinear geometry is poor spatial resolution in the beam propagation direction. Since there is not a minimum intensity threshold for signal generation, CARS signal will be generated throughout the entire beam overlap region. Additionally, in experimental arrangements in which the beams travel through optical windows, a significant amount of non-resonant background (NRB) signal can be generated from the windows. The presence of NRB can greatly complicate or totally preclude measurements of minor species or major species energy levels with moderately low populations. Furthermore, in experimental situations in which the measurement environment is at a significantly lower number density than the laboratory atmosphere, signal generated in the laboratory air, outside of the desired measurement region, can completely overwhelm the signal generated within the test section. Certain experimental scenarios may allow for the use of collinear CARS without significant drawback, but this should be carefully considered.
Figure 2.2 Phase-matching diagrams for (a) collinear CARS, (b) BoxCARS, and (c) USED-CARS.

A schematic arrangement for the BoxCARS phase-matching geometry is depicted in Figure 2.2 (b). In this arrangement, the pump and probe beams are two spatially distinct beams, which are combined with the Stokes beam in such a way that $\mathbf{k}_{1(\text{pump})} + \mathbf{k}_{1(\text{probe})} = \mathbf{k}_{2(\text{Stokes})} + \mathbf{k}_{3(\text{CARS})}$. Solutions of this vector equality can be had in either 2 or 3 dimensions, yielding planar or folded BoxCARS, respectively. The significant advantage of BoxCARS is high spatial resolution; as the CARS signal is only generated where all three input waves are spatially overlapped at the focused beams’ waists, spatial resolution in the transverse direction is typically on the order of 50 μm, while in the longitudinal direction, it is typically of the order of 1 mm or less [28]. A perspective representation of the folded BoxCARS alignment with the focusing and collimating lenses, and the location of the interrogation volume is shown in Figure 2.3. In exchange for the benefits of spatial resolution, the primary drawback for a BoxCARS arrangement
is the increased alignment complexity. Furthermore, because of the very small beam overlap volume, BoxCARS geometries can be sensitive to the effects of beam steering in environments with sharp density gradients, such as turbulent combustion and shock layers.

![Diagram of BoxCARS alignment geometry](image)

Figure 2.3 Perspective view of folded BoxCARS alignment geometry, highlighting the interrogation volume, located at the intersection of the three input beams.

A third phase-matching geometry is the Unstable-resonator Spatially Enhanced Detection (USED) CARS configuration [29, 30], the phase-matching diagram of which is shown in Figure 2.2 (c). As in the collinear case, a single 532 nm beam serves as both pump and probe; in this technique, this beam is enlarged through a telescope, after which the center portion is then removed, creating a green annulus. There are several ways to remove the center of the beam, although the simplest method, used in this work, is simply to suspend a small physical block in the center of the beam with the aid of a fine gauge
wire. The pump/probe beam is then combined coaxially with the Stokes beam using a dichroic mirror, similarly to the collinear case, except that now there is no spatial overlap because the Stokes beam occupies the void created at the center of the pump/probe beam, as seen in the schematic in Figure 2.4 (a).

![Figure 2.4 USED-CARS beam arrangement](image)

Figure 2.4 USED-CARS beam arrangement, showing annular alignment pattern and the location of the generated CARS signal beam.

As the beams pass through the focusing lens, the two regions of the annular pattern remain spatially separated until they arrive near the focal region, when beam overlap and CARS signal generation occurs. Subject to the constraints of the phase-matching criteria, the CARS signal beam appears as a ring outside of the green ring, as illustrated in Figure 2.4 (b). The USED-CARS approach provides ease of alignment similar to the collinear case, as there are only two beams to align instead of the 3 required for BoxCARS. Additionally, the spatial resolution for USED-CARS is moderately high; transverse resolution is on the order of 100 μm and longitudinal resolution, dependent on the choice of lens focal length, is of the order of 2-5 mm.
2.4 CARS Experimental Considerations

There are a few other considerations that should be briefly discussed about utilization of the CARS spectroscopic diagnostic technique. It should be noted that due to the phase-matching requirements, CARS requires two sided optical access; a requirement that may increase complexity or totally prevent use of the diagnostic in certain facilities. Additionally, as with other optical techniques, some care must be taken in choosing lens focal lengths and optic sizes, based on the scale of the test section within which measurements are performed. As was mentioned previously, CARS signal intensity is proportional to the square of the pump laser times the Stokes laser intensity. This does not mean, however, that more is always better; there are several factors effecting limits on the maximum laser pulse energy that can be gainfully employed. Material considerations, such as the damage threshold for windows can limit viable laser intensity, particularly when experimental complexities require windows located close to the beams’ focal region. In various experimental environments, laser induced gas breakdown can also be problematic.

From a spectroscopist’s perspective, there are also more insidious limitations on laser power, including optical Stark effect and stimulated Raman pumping. Stark effect involves the splitting or shifting of atomic and molecular energy levels due to the presence of an external electric field of sufficient magnitude; optical Stark effect is merely when the electric field of a laser causes the phenomenon. Because the resulting shifts are rather small, and the magnitude varies through the interrogation volume as laser
field strength varies, optical Stark effect results in broadening of the features in the CARS spectra, and is thus problematic when trying to capture high-resolution spectra. Stimulated Raman pumping is related to Stimulated Raman Scattering (SRS) which is a highly laser intensity dependent process. In SRS, pump photons inelastically scatter off molecules, leaving the molecules in excited states while generating Stokes shifted light; when laser intensity is sufficiently high, populations of these synthetic, i.e. non-Boltzmann, excited states can be quite significant. In this case, the diagnostic is no longer “non-intrusive” as it is significantly changing the physical condition of the environment it is attempting to measure, and the spectra captured will be indicative of this contaminative effect.
Chapter 3: CARS Diagnostic System

The diagnostic measurements conducted through this course of study were performed with the psec CARS diagnostic system, constructed by the author. The CARS diagnostic system is essentially comprised of 3 components: the Nd:YAG (pump/probe) laser, the broadband dye (Stokes) laser, and the spectrometer, camera and computer used for data collection. A custom designed and built cart was made to house all of these components, allowing the entire system to be easily transported from one lab or experimental area to another. A photograph of an early version of the system can be seen, with several important features noted, in Figure 3.1 below. Overall, system stability was very good. The cart was transported between several labs within the same building multiple times; in general, only very minor alignment tweaks were necessary to run the system in the new location.
3.1 Nd:YAG Laser

An Ekspla SL-333 Nd:YAG laser serves as the CARS pump/probe laser source, as well as the pump for the dye laser. The oscillator of the relatively compact laser, which operates at 10 Hz, outputs pulses of ~2 nsec duration. A stimulated Brillouin scattering cell, filled with CCl₄, then compresses the pulses to approximately 150 psec duration. After two double pass amplification stages and a second harmonic generation
(SHG) crystal, the laser outputs pulses of the same duration, ~150 psec, with variable energy of up to 120 mJ/pulse (532 nm).

The laser can be triggered by a variety of methods; the two regimes used in this work are (1) fully internal triggering and (2) fully external triggering. In the fully internal triggering mode, the laser’s internal clock acts as the system master and, according to the amplification level selected by the user, controls the precise timing of the oscillator and amplifier flashlamps, as well as the Q-switch firing. The system generates a “sync out” TTL pulse simultaneously with the Q-switch firing which controls the exposure timing of the camera. In the fully external triggering mode, the user must supply two input pulses, the first of which fires the oscillator flashlamp, and the second firing the Q-switch. The laser selects the appropriate timing of the amplifier flashlamps, based on the amplification level selected by the user. In either mode, the light pulse output from the laser occurs ~150 nsec after the Q-switch firing, with a timing jitter of ~1-2 nsec.

3.2 Broadband Dye Laser

The broadband dye laser, a schematic of which is seen in Figure 3.2, is patterned after that of Roy, et al. [31]. As can be seen in the schematic, the first half-wave plate and thin film polarizer allow for adjustment of the ratio between pulse energy going to pump the dye laser, versus the energy used for the CARS pump/probe beam(s). The second half-wave plate rotates the polarization of the CARS pump/probe light to match that of the dye laser light when they meet at the test section (typically vertical).
The portion of light used to pump the dye is split into three beams by two non-polarizing beam splitters. The first beam (~20% of total pumping energy), which is reflected off the first beam splitter, is focused through a 100 mm focal length cylindrical lens (oriented to focus the light into a horizontal line) and side-pumps the oscillator cell. As the dye begins to fluoresce, a small portion of it reflects off the carefully aligned broadband coated back mirror; on its return trip through the dye cell, this light causes amplified spontaneous emission (ASE). There is no output coupler mirror, hence no true oscillator cavity, which prevents the development of mode structure in the beam. This is described as “modeless” operation, and is very desirable for the diagnostic utility. The other benefit of not having an output coupler is that it keeps the dye laser pulse duration similar to that of the pump pulse [31].
Unfortunately, preventing the development of mode structure in the beam is, in reality, not as simple as just not using an output coupler; in fact, the walls of the oscillator dye cell can themselves cause etalons to occur in the beam. These etalons have the same effect as longitudinal cavity modes; they effectively put a “ripple” in the gain curve for the laser, causing the broadband spectral output to have mild to extreme oscillations in intensity. An example of these etalons can be seen in the spectrum in Figure 3.3. Clearly, as the plot shows, identifying small intensity peaks would be hopeless with such a baseline. In addition to this, since the CARS signal intensity is proportional to the Stokes laser intensity, these variations in the Stokes beam will also produce extreme variations in the resonant signal. When attempting high-resolution spectroscopy, such effects can obscure resolution of individual rotational lines, or even give rise to fictitious lines within a spectrum. Solving this issue required very delicate alignment of the oscillator cell orientation as well as the angle of the back mirror, while simultaneously monitoring the non-resonant background. If a similar laser were to be built in the future, it would be highly recommended to use an oscillator cell with non-parallel and wedged windows, to reduce the alignment complexity surrounding this issue. With the oscillator cell alignment tuned appropriately, the out-going “beam” is rather misshapen. An iris is used to select a small portion of this light to be amplified in the next stage.
Figure 3.3 Example of CARS spectrum with significant etaloning visible in the NRB.

The light transmitted through the first beam splitter is split by a 50:50 non-polarizing beam splitter; the half (~40% of the total incoming pumping energy) which is reflected off this optic is used to side-pump the pre-amplifier stage. A slight delay in the optical path of this leg is introduced to optimize the gain in the pre-amp cell (this is optimization of the timing of the arrival of the pump light with the pulse coming from the oscillator cell). This beam is focused by a 50 mm focal length cylindrical lens (again set to produce a horizontal line) onto the side of the pre-amplifier cell. This cell is set near Brewster’s angle, in the direction from which the pulse from the oscillator arrives, which suppresses any horizontal polarization component present in that pulse. The output of this stage is also spatially filtered prior to reaching the main amplifier cell.

The final pumping beam, also ~40% of the total pumping energy, is focused by a 400 mm focal length spherical lens and used to end-pump the main amplifier cell. A bending right-angle prism is used to direct this beam such that there is as much overlap as
possible with the incoming dye beam (coming out of the pre-amp). The distance of the focusing lens from the dye cell is set to match the pumping light spot size with the size of the incoming dye beam. The position of the main amplifier cell (controlling the timing of the arrival of the pump and incoming dye beam) is adjusted to generate maximum gain from this stage as well. Care is taken to position compact beam dumps to catch the portions of the pumping beam which are reflected off or transmitted through this cell.

After a final spatial filter, a 600 mm focal length plano-convex lens is used to pseudo-collimate the outgoing beam. In this setup, dye laser beam quality is sufficient for this work, although is not great. One recommendation for future system improvement would be the utilization of a telescope and pinhole spatial filter within the dye laser; due to space requirements, this would likely need to be placed between the pre-amp and main amplifier cells. Dye laser energy efficiency is highly dependent on which dyes are utilized, what dye concentrations are present, and the age of the dye. For the “standard” mix of Rhodamine 640 (R640) and Kiton Red 620 (KR620), for “fresh” dye mixtures, total energy efficiencies up to 10% have been observed, whereas for older dyes of this same mix, efficiency profiles such as that shown in Figure 3.4 are more typical. In Figure 3.4, a plot of broadband dye laser output energy/pulse vs. the total 532 nm energy input into the dye laser can be seen, for the R640-KR620 dye mixture. As the plot shows, dye laser efficiency is slightly dependent on pumping energy, typically ranging between 6.5-8% for this dye mixture.
3.2.1 Laser Dyes and Spectral Output

For this work, two different laser dye mixtures were used; for the experiments in the Mach 5 wind tunnel, the elevated temperature PAC cell, and for a portion of the experiments performed in the bare-metal electrode discharge, the “standard” mix of Rhodamine 640 (R640) and Kiton Red 620 (KR620), mentioned above, was used. A secondary mixture of Pyrromethene 597 (PM597) and Pyrromethene 650 (PM650) dyes was used for the remainder of the bare-metal electrode study. In both cases, one mixture was used in the oscillator/pre-amp cells, with a second, slightly different and more dilute mixture used in the main-amp cell.
The standard R640-KR620 mixture has a solution of 34 mg R640 and 18 mg KR620 dissolved in 750 mL of methanol in the oscillator/pre-amp cells, while the amplifier cell solution is 20 mg R640 and 18 mg KR620 in 750 mL of methanol. As can be seen in Figure 3.5, the broadband output from this mixture has a full width at half maximum (FWHM) of 6-7 nm, and is centered at ~604 nm. The dye laser spectral profile is intentionally centered to the blue side of the location of the N₂(ν = 0) band, which allows it to span the first several vibrational transitions of nitrogen. Additionally, since the ground vibrational state has the highest population, having a lower Stokes laser intensity at this location allows more ability to observe the lower populations of the excited vibrational states without saturating the detector at the ground state band.

![Figure 3.5 Characteristic dye laser output for R640-KR620 mixture.](image)
The alternate mixture of PM597 and PM650 offered a significantly more broad spectral output, as has been previously observed in Ref. [32]. While a specific dye solution was not made from a recipe, PM597 was added to ethanol in both the oscillator/pre-amp mixture and the main amplifier mixture. Small amounts of PM650 dissolved in ethanol were then added, while the spectral output of the dye laser was observed. When the desired spectral output was achieved, addition of the PM650 dye was stopped. In the plot in Figure 3.6, this spectral output can be seen as the dashed blue curve, denoted as the “No optic” case.

![Figure 3.6 Pyrromethene dye mixture spectral output curves attained by varying the dichroic mirror angle.](image-url)
This output is significantly more broad than necessary for the investigation of nitrogen; in an effort to achieve higher spectral intensity at the desired region (~595-608 nm), a long-wavelength passing dichroic mirror with a cutoff wavelength of ~552 nm (Semrock LM-552) was placed between the pre-amp and main amplifier dye cells. At ~45°, the optic design angle, the optic is completely transmissive (apart from surface losses) and as the plot indicates (green line with dots), the dye profile is unchanged, except for the slightly decreased overall intensity. Tuning the mirror to shallower angles produces the series of spectra plotted in the figure, all the way to the final purple dash-dot curve, which is the spectral output at ~0° incidence. As the curves clearly illustrate, decreasing the angle of the mirror red-shifts its reflection band, which introduces loss to the lower wavelength end of the spectrum; the result is increased gain for the wavelength region above the cut-off limit. The output curve plotted in solid red was obtained with the dichroic mirror set close to θ ~ 10°; this is the laser setting used for the experiments employing the PM dye mixtures, and has FWHM of ~10-11 nm, centered near ~600 nm. The plot in Figure 3.7 shows the NRB profile produced, in 700 torr argon, by this spectral output. As this figure shows, the increased bandwidth as well as long ramp in intensity in this dye mixture provides the ability to observe higher excited vibrational states of nitrogen (ν = 4-10+), assuming sufficient populations are present, than those which can be accessed with the R640-KR620 mixture.
3.3 Data Collection System

The final portion of the CARS system is the data collection system, which is comprised of a spectrometer, camera, and computer for data recording. The spectrometer is an Andor Shamrock 750, which has a focal length of 750 mm, and a grating turret with three gratings: 600, 1800, and 3600 lines per mm (lpmm), providing low, medium, and high resolution, respectively. At the exit plane of the spectrometer, there is a mounting flange where a camera is typically mounted. As will be discussed in the next chapter, early results in the Mach 5 wind tunnel were achieved with an Andor Newton CCD attached to the spectrometer exit plane flange. Later data collected in the wind tunnel, and all other experimental data collected, utilized a relay lens magnification system (described below), with an Andor Newton EMCCD.

Figure 3.7 Non-resonant background profile along with the locations of the first 11 vibrational bands in N$_2$. 

![Graph showing the non-resonant background profile along with the locations of the first 11 vibrational bands in N$_2$.]
This back-illuminated camera offers much higher sensitivity in the blue region of the spectrum (where the CARS signal resides), and the electron multiplying (EM) gain feature is capable of providing significant amplification of low intensity signals while introducing very little noise to the spectra. The thermoelectric cooler on the camera chip allowed the sensor to be thermally stabilized at -90°C with the camera connected to ~20°C circulated cooling water, which also helps minimize dark noise. The camera and spectrometer are both connected via USB to a lab computer; Andor Solis software is used to interface with both devices and for data recording.

3.3.1 Relay Lens System

The relay lens magnification system consists of two Nikon F-mount lenses. The first lens, with 35 mm focal length, is attached to the spectrometer exit flange via a custom machined adapter plate as well as an F-mount adapter (Thorlabs NFM1). Care is taken in choosing the adapter plate thickness so that the focal plane of the lens is in the same location as that of the spectrometer; if the alignment is performed perfectly, the spectral “image” will be focused at infinity. The second lens, an 80-200 mm focal length telephoto lens is attached to the camera, again taking care that the focal plane of the camera falls at the proper depth on the chip. The camera with its lens is positioned coaxially with, and pointing toward the lens mounted to the spectrometer. The net effect of the two lenses is a magnification of the spectral “image”, which in this case, results in resolution enhancement. For all the work performed with the relay lens system, the telephoto lens focal length was set to 80 mm, yielding ~2.3x magnification.
Spectral resolution enhancement via this method is not unlimited however, the ultimate limit is set by the spectrometer’s grating. Without the employment of the relay lens system, the resolution limiting factor is the combination of the number (actually size) of the camera’s pixels along with the focal length of the spectrometer; choosing either a longer spectrometer or a camera with smaller pixels could have improved the spectral resolution as the relay lens system did, however this was the simplest and most cost effective method.

A few unwanted side-effects were encountered using the relay lens system. The most significant of these is that since the telephoto lens used was not designed for a camera sensor with the aspect ratio and size of this sensor (1600 pixels wide x 400 pixels tall), the lens clipped the sides of the spectral image, effectively only allowing utilization the central ~50% of the chip. A second side-effect is that as the camera’s software is unaware of the presence of the magnification system, the x-axis ascribed by the software is no longer accurate; this can obviously be corrected for, but it is certainly important to note. A third side-effect, believed to be relatively minor, is the increased optical losses due to the use of multi-element lenses in the beam path. An additional side effect also observed (not unique to this method of resolution enhancement but encountered for any resolution enhancement method) is simply that spreading signal light over a greater number of pixels reduces the per-pixel signal intensity, which can be problematic when attempting to observe weak signals.
Chapter 4: Experimental Setup

The experimental studies described in this work can be separated into three distinct categories, experiments in: a non-equilibrium Mach 5 wind tunnel; an elevated temperature plasma assisted combustion facility; and a low temperature, bare-metal electrode, fat-filament discharge. Each of these experiments had many unique elements and important features, and the experimental arrangement of each will get an individual section within this chapter. Additionally, while the same CARS diagnostic system was used in each study, the specifics of the optical setups and the goals of each experiment were different. Typical operating conditions for each study and any necessary modifications to the CARS system will be discussed in the appropriate section below.

4.1 Mach 5 Wind Tunnel

The experiments conducted for this study were performed in the plenum of a Mach 5 nonequilibrium flow tunnel previously developed and described in detail [14, 15]. Briefly, the laboratory scale wind tunnel, a side-view schematic of which is given in Figure 4.1, operates at plenum pressures from 0.25 to 1 atm with nitrogen or air supplied from high pressure cylinders. The tunnel is constructed from transparent acrylic plastic and is capable of producing steady-state, nonequilibrium, supersonic flow, utilizing a high pressure, diffuse, nanosecond pulser / DC sustainer electric discharge operating in the plenum section. The discharge can be tailored, as will be discussed, to load internal
(vibrational and electronic) modes of nitrogen, while maintaining low translational-rotational temperatures; previous measurements by nitrogen UV emission spectroscopy in a similar discharge arrangement yielded $T_{\text{rot}} \sim 350 – 400$ K.

Figure 4.1 Schematic side-view of the Mach 5 wind tunnel.

Downstream of the discharge section, the gas flows through a choked flow injector with 20 injection ports, 1 mm in diameter, in both the top and bottom channel walls. Gases inducing vibrational relaxation of nitrogen, such as oxygen, hydrogen, nitric oxide, carbon dioxide, etc., can be injected into the flow, which allows further control of the energy distribution amongst the internal molecular modes in the flow. The optical access point in the plenum for CARS measurements is located ~9 cm downstream from the gas injection location. After this, the flow travels an additional ~10 cm before reaching the nozzle throat, which has a height of 1.6 mm, and then passes through the aerodynamically contoured Mach 5 expansion section to the nozzle exit, where the
supersonic optical access point is. Beyond this, there is a diffuser section just upstream of the 8 inch diameter exit pipe leading to a 110 ft^3 vacuum tank and 200 cfm pump.

During the experiment, both the main flow through the discharge and the injection flow are controlled using solenoid valves. The main flow rate is calculated using a 1-D choked flow equation, based on the plenum pressure and the nozzle throat area. The injection flow rate has been both measured directly using a mass flow controller and calculated from the choked flow equation, with both methods giving similar results. At the baseline conditions, nitrogen at $P_0 = 200 – 370$ torr, the mass flow rate through the tunnel is 3.9-7.2 g/sec and the steady-state run time at constant static pressure in the supersonic test section is 5-10 seconds; runs can be repeated every few minutes.

4.1.1 Pulser-Sustainer Discharge

The pulser-sustainer electric discharge is comprised of two fully overlapping discharges, (1) a repetitively pulsed, high voltage nanosecond (nsec) discharge and (2) a transverse DC sustainer discharge. As can be seen in the schematic in Figure 4.2, the nsec pulser electrodes (3 cm x 4 cm copper plates) are flush mounted in the top and bottom walls of the discharge section (nozzle plenum). Both of these electrodes are covered by alumina ceramic dielectric plates 1/16 inch thick, with a 0.5 cm gap in between. The bare-metal sustainer electrodes (4 cm x 0.5 cm copper plates) are placed along the side walls of the discharge section and are removable. In the present experiments, the sustainer electrodes are separated by 3.0 cm. Both the pulser and sustainer electrodes are rounded along the edges to reduce electric field non-uniformity.
The acrylic plastic walls of the channel downstream of the discharge section are also covered with alumina ceramic plates, attached with silicone rubber adhesive, which protects the walls from overheating in the possibility of instability development or arcing in the discharge. The main benefit from using the pulser-sustainer discharge is the ability to generate stable nonequilibrium plasmas at high pressures and high discharge energy loading.

Figure 4.2 Schematic of pulser-sustainer electric discharge geometry.

The repetitive nsec pulsed discharge operates using a high peak voltage (up to 30 kV), short pulse duration (5 nsec), high pulse repetition rate (up to 100 kHz) voltage waveform, produced by a high-voltage nanosecond pulse generator (FID GmbH FPG 60-100MC4). Figure 4.3 shows typical pulse voltage and current traces (top), as well as instantaneous power and coupled pulse energy traces (bottom), measured in a repetitively pulsed discharge in nitrogen at $P_0 = 300$ Torr and $\nu = 100$ kHz, with the DC electrodes present in the test section, but not powered [33]. The waveforms shown are for a pulse
generated 0.1 seconds after the beginning of the pulse burst (i.e. for pulse #10,000). The pulser is operated using an external trigger / function generator. Each high voltage pulse generates volume ionization in the discharge section, and the high voltage is then turned off before ionization / heating instability [34] has time to develop. The high frequency of pulse repetition prevents the plasma from fully decaying before the next ionizing pulse occurs, thus providing pulse-periodic, spatially uniform ionization in the discharge section [1, 2].

![Graph](image)

Figure 4.3 Nsec pulse voltage, current (top), power, and energy (bottom) measurements; P0 = 350 torr N2, ν = 100 kHz, pulse #10,000.
Between the ionizing pulses, energy is coupled to the flow by the DC discharge. The DC electrodes are connected to a Glassman 5 kV, 2 A power supply, operated in a voltage stabilized mode, in series with a 1.5 kΩ ballast resistor. The DC voltage is deliberately kept below breakdown threshold, typically below 4-5 kV, to preclude development of self-sustained (i.e. independent of pulsed ionization) DC discharge in the high pressure flow, which would result in instability development and arcing. The power coupled to the flow by the DC discharge is significantly higher than the repetitively pulsed discharge power. Previously, this approach has been used in our work to sustain high-power discharges in a Mach 3-4 MHD wind tunnel [1, 2], and in an electrically excited gas dynamic oxygen-iodine laser [35].

In the present experiments, the repetitively pulsed discharge is operated for 0.6 seconds, and the DC discharge for 0.55 seconds. A representative DC current profile for the sustainer discharge is visible in Figure 4.4, showing the initial typical “ramp-up” time of 100-200 msec, due to the capacitors charging, as well as the ~400 msec quasi “steady-state” time. In Figure 4.5, digital camera images of the discharge created by the nsec pulser alone and the pulser-sustainer discharge can be seen.
Figure 4.4 Typical DC sustainer discharge current profile, showing DC capacitor “ramp-up” time and “steady-state” region.

Figure 4.5 Images of discharge created by the nsec pulser alone, \( P_0 = 650 \) torr \( \text{N}_2 \), \( \nu = 100 \) kHz (top); and the pulser-sustainer together, \( P_0 = 350 \) torr \( \text{N}_2 \), \( \nu = 100 \) kHz, \( V_{PS} = 2 \) kV (bottom).

The DC power supply is triggered by an externally generated rectangular shaped trigger pulse, the rising edge of which also triggers the function generator that produces a burst of 60,000 trigger pulses for the high voltage nanosecond pulse generator at
ν = 100 kHz pulse repetition rate. The estimated reduced electric fields in the two discharges are significantly different, $E/n_{\text{peak}} \sim 500$ Td in the nsec pulsed discharge and $E/n \sim 10$ Td in the DC discharge (1 Td = $10^{-17}$ V·cm$^2$). At these conditions, a significant fraction of input power in the pulsed discharge is spent on electronic excitation, dissociation, and ionization of nitrogen, while nearly all input power in the DC discharge (up to ~80-90% according to theory [34]) is stored in the vibrational energy mode of nitrogen, with little power going to translational / rotational modes, i.e. to heat. Due to a very long $N_2$ vibrational self-relaxation time at near room temperature, ~1 atm·sec [36], this approach can create essentially vibrationally frozen nitrogen and air flows in the supersonic test section, with vibrational temperature greatly exceeding the rotational-translational mode temperature.

### 4.1.2 Supersonic Measurement Setup

A 5 mm diameter quartz cylinder model is mounted across the supersonic flow, which creates a bow shock, as depicted in the schematic in Figure 4.6 (a). The position of the model relative to the entire tunnel can be seen in Figure 4.1 above. For this work, a 7.5 mm long section of 5 mm diameter quartz tube was secured to the leading edge of a 2 mm diameter stainless steel rod, with the rod mounted to the tunnel walls, as shown in Figure 4.6 (b). The use of the short rod section allows for closer access by the laser beams, which propagate parallel to the rod axis, than a full length 5 mm diameter rod would allow. Previous Schlieren imaging [14, 15] has shown that the bow shock stand-off distance for this arrangement, ~1.1 mm for a plenum pressure of 300 torr, is uniform
in the spanwise direction over a distance nearly double the longitudinal spatial resolution of the USED-CARS geometry used here, which was measured to be \(~3\) mm.

Figure 4.6 Schematic of (a) the bow shock created by a quartz cylinder present in supersonic flow, along with (b) a perspective view highlighting the 2 mm stainless steel support rod.

An experimental arrangement using optical pitch/catch arms, along with two manual translation stages allows for simple adjustment of the CARS measurement location, as depicted by the schematic in Figure 4.7. A 3 inch by 18 inch optical breadboard section, which holds the necessary turning prisms (for the vertical pitch/catch) and CARS focusing and collimating lenses, is attached to the vertical adjustment stage by a right-angle adapter plate. The base of this stage is mounted to a 6 inch by 18 inch breadboard, which also holds a second set of turning prisms, comprising the horizontal pitch/catch. This larger breadboard is mounted onto a horizontally positioned translation stage, providing measurement location adjustment.
down the length of the tunnel. Both stages are fitted with fine adjustment micrometers, providing spatial resolution of 10 μm per division in each dimension.

Figure 4.7 Schematic diagram of wind tunnel with optical pitch/catch arms for 2-D spatial resolution; purple (horizontally mounted) translation stage allows positioning along the flow direction, while the red (vertically mounted) stage provides vertical adjustment

With the laser power set very low, the stages are adjusted to detect the location of the front edge of the cylinder. Monitoring the light coming out of the far side of the tunnel, the position at which the cylinder just begins to eclipse the laser beam is found. Scanning the horizontal stage further reveals the position at which the laser is completely blocked by the cylinder, which is taken to be the cylinder leading edge. The difference between the two locations is measured to be 300 μm. CARS signal levels reduce drastically as the beams become clipped by the cylinder edge, which indicates that this
distance of 300 μm is the closest point to the cylinder surface able to be interrogated using this arrangement.

4.1.3 CARS Optical Setup

In the early measurements conducted in the wind tunnel plenum, the collinear CARS arrangement was used for the sake of experimental simplicity. The plenum windows, initially flush mounted on the tunnel sidewalls and relatively close to the 250 mm lens focus, produced a significant amount of non-resonant background (NRB), greatly limiting the sensitivity of the CARS diagnostic. To counter this, optical extension arms were used, moving the location of the windows further from the lens focal point. Because the flow velocity is relatively slow in the subsonic plenum (Mach ~0.2), the arms do not affect the flow significantly. Later experiments were performed with the USED-CARS alignment geometry, which completely removed the NRB contributed by the windows, and the extension arms were removed.

The only significant difference between the optical layout for the USED and collinear arrangements, apart from the optical extension arms just mentioned, is that the collinear geometry did not use the relay lens magnification system, while the USED geometry did. A diagram of the optical setup for the work performed with the USED-CARS arrangement is pictured in Figure 4.8. As the diagram shows, after the pump/probe and Stokes beams are combined by the dichroic mirror they are focused into the wind tunnel. For the plenum studies, 250 mm focal length lenses was used, while 150 mm focal length lenses were used for the measurements in the supersonic section.
Beyond the tunnel, the beams are re-collimated, and several dichroic mirrors are used to separate the blue CARS signal beam from the green and orange beams, before the signal is sent into the spectrometer.

Figure 4.8 Optical layout for USED-CARS geometry with the Mach 5 wind tunnel.

4.2 Elevated Temperature PAC Reactor

The test section used for this group of experiments is the same that has been used in previous studies in our research group [19, 20, 33], and is shown schematically in
Figure 4.9. The discharge cell / plasma flow reactor consists of a 280 mm long, 22 mm x 10 mm rectangular cross section quartz channel with 1.75 mm wall thickness. Two plane quartz windows are fused to the channel ends, providing the necessary two-sided optical access in the axial direction. The entire flow reactor assembly is placed inside a tube furnace (Thermcraft, Ltd.) with a 6 inch diameter by 12 inch long heated section, to improve plasma stability. A quartz tube coil 1 m long, also located inside the furnace, (see Figure 4.9) serves as a flow-preheating inlet, and is sufficient to preheat the flow to the furnace temperature, as verified by thermocouple measurements.

![Figure 4.9 Schematic of elevated temperature PAC experimental apparatus.](image)

Two ¼ inch diameter quartz-to-stainless-steel adaptors are fused to the inlet and the exit of the cell, connecting it to the gas delivery and exhaust system. Two rectangular copper plate electrodes, 14 mm wide by 60 mm long, are placed outside the top and bottom walls of the quartz channel, halfway between the ends, and are held in place by ceramic clamps, as shown in Figure 4.9. The electrodes are rounded at the edges to reduce field non-uniformity effects, and a 1/16 inch thick high-temperature
perfluoroelastomer sheet (Kalrez, DuPont) is placed between each electrode and the quartz channel wall, reducing air gaps and minimizing corona discharge formation outside the cell. Gas delivery flow rates are controlled by MKS mass flow controllers, and in the case of fuel-air flows, gases are premixed in a 12-inch long in-line flow mixer before entering the cell. One pressure gauge is placed in the gas delivery line upstream of the cell and another is placed downstream in the exhaust tubing. At the present conditions, the pressure drop across the cell is approximately 10 torr; the test section pressure is taken to be the average of the two pressure gauge readings.

The electrodes are connected to the same high voltage nanosecond pulse generator (FID GmbH FPG 60-100MC4) used in the Mach 5 wind tunnel experiments, described in the previous section. In the present work, the pulser is operated in repetitive burst mode, producing bursts of 40-150 pulses at a pulse repetition rate of ν = 10 kHz. Figure 4.10 shows typical nanosecond pulse voltage and current waveforms (top), as well as instantaneous power and coupled pulse energy (bottom) measured in a slightly modified, low-temperature discharge cell of the same geometry as the high temperature cell used for these studies [21]. The plotted waveforms are from pulse #50, in a burst of 125 pulses, measured in room temperature air, \( P_0 = 40 \) torr.
Figure 4.10 Voltage, current, power and energy traces produced by the FID pulse generator; air, $T_0 = 300$ K, $P_0 = 40$ torr, $v = 10$ kHz. Solid lines: voltage and power; dashed lines: current and coupled energy.

The measurements reported in the present work have been performed for both non-igniting and igniting conditions; a burst repetition frequency of 5 Hz was chosen for non-ignition cases, while a burst frequency of 1 Hz was chosen for ignition cases. While the higher repetition frequency was slow enough to ensure the flow through the test cell would only experience one burst of pulses for non-igniting cases, the combined effects of pressure fluctuations from ignition as well as a desire to ensure all combustion products were removed from the cell between bursts required the lower burst repetition rate for igniting cases. Measurements have been made in air and premixed, lean fuel-air flows, at a variety of equivalence ratios ($\phi = 0.1$-0.4), initial temperatures ($T_0 = 300$ & 500 K), and pressures ($P_0 = 90$-300 torr), with the estimated baseline flow velocity through the test
section of \( u = 40 \text{ cm/sec} \). Slow flow velocity allows for efficient flow preheating in the inlet coil (see Figure 4.9), as well as reducing the pressure drop across the discharge cell.

For the current work, the USED-CARS phase matching scheme was utilized, as has been described in the previous section. The only significant difference between the optical layout for the present work (apart from a different test location) is the use of longer focal length lenses, to compensate for the larger size of the test section. In this case, a 500 mm focusing lens was used along with a 300 mm collimating lens.

4.3 Bare-Metal Electrode Single-Pulse Discharge

The experiments conducted for this study were performed in an acrylic test section designed for this work, a schematic of which can be seen in Figure 4.11. The test section is machined from a single acrylic block, with a 1.5” center bore providing the necessary two sided optical access for CARS, as well as single sided optical access in the other dimension, allowing the cell to be used for fluorescence techniques requiring signal collection perpendicular to the laser propagation direction. The diffuse “fat-filament” plasma discharge was created in a 1 cm gap between two copper electrodes. The electrodes have spherical ends, 7.5 mm in diameter; holes matching the electrode leads’ diameter are drilled into the top and bottom walls of the test section and the electrodes are held in place by epoxy, which fixes the discharge gap distance and makes the cell airtight. Gas flows to and from the cell via pipe fittings machined into the backside of the acrylic block. The MKS mass flow controller supplies a flow of 1 slpm (N\(_2\) or air). Window flanges, with o-ring seals, are mounted to the cell with nylon screws to minimize
the presence of metal near the electrodes and eliminate the possibility of alternative current paths. For the current study, all incident laser and generated signal light is in the visible, so BK7 windows are used throughout.

![Diagram of discharge test section](image)

Figure 4.11 Cut-away cross sectional view of discharge test section.

The nsec pulsed discharge used for this work was generated by a pulser unit previously built and extensively used in our group, the same as in Ref. [37]. The pulser delivers high voltage pulses, initiating breakdown in the 100 torr nitrogen or dry air typically between 8-10 kV, as can be seen in the current-voltage waveforms plotted in Figure 4.12. As the plot shows, the current pulse lasts for approximately 100-120 nsec. Varying the voltage of the DC power supply feeding the pulser affects the amount of energy stored within the pulser’s capacitors, and while not significantly impacting the high voltage waveform, the discharge current is strongly affected, as well as the total coupled energy. Table 4.1 below highlights the various parameters of the 5 discharge
cases explored in this work. In addition to the first pulse, which couples most of the energy, there is also a second pulse, typically arriving ~500 nsec after the first pulse, coupling a small additional amount of energy.

![Figure 4.12 Nsec pulser voltage and current waveforms (top) and instantaneous power and energy (bottom); \( P_0 = 100 \text{ torr } \text{N}_2 \), “high current” mode.](image)

<table>
<thead>
<tr>
<th>Discharge Gas</th>
<th>DC Voltage [V]</th>
<th>Peak Current [A]</th>
<th>Peak Power [kW]</th>
<th>Coupled Energy [mJ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>430</td>
<td>8</td>
<td>32</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>20</td>
<td>84</td>
<td>6.4</td>
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<td></td>
<td>486</td>
<td>43</td>
<td>195</td>
<td>13.3</td>
</tr>
<tr>
<td>Air</td>
<td>430</td>
<td>12</td>
<td>50</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>486</td>
<td>48</td>
<td>222</td>
<td>15.7</td>
</tr>
</tbody>
</table>

Table 4.1 Bare-metal electrode single-pulse discharge operating conditions; \( P_0 = 100 \text{ torr} \).
The pulser is operated continuously at 50 Hz, and the diffuse, fat-filament discharge appears quite stable spatially. In addition to spatial stability, the current and voltage waveforms are also both quite stable from one shot to the next. The test section has been mounted on a 3-dimensional manual positioning stage system, allowing for positioning of the laser measurement location in the center of the 1 cm discharge gap, as well as at the center of the plasma filament in the two transverse dimensions. For the present discharge conditions, the plasma fat-filament is ~2 mm in diameter.

4.3.1 CARS Optical Setup

For this work, the folded BoxCARS phase matching geometry has been employed, a schematic of which can be seen in Figure 4.13. As discussed in Chapter 3, a portion of the pulse energy output from the Nd:YAG laser is used to pump the broadband dye laser, while the remaining green light is split with a 50:50 nonpolarized beam splitter, becoming the pump and probe beams. The two green beams and the broadband dye laser Stokes beam are all aligned onto a 2” diameter, 150 mm focal length focusing lens, such that all three beams spatially overlap at their common focal point; precise alignment for phase matching must also be met. Due to the short duration of laser pulses, optical path lengths must be matched closely to ensure temporal overlap of beams in the focal region as well.

While it is not clear in the schematic in Figure 4.13, for the folded BoxCARS arrangement, as previously seen in Figure 2.3, the pump and probe (green) beams are located in the horizontal plane at the lenses’ vertical center, while the Stokes and CARS
(orange and blue) beams are located in the vertical plane at the lenses’ horizontal center. After the focal point, another 2” diameter, 150 mm focal length lens is used to collimate the beams. After this, the pump, probe and Stokes beams are discarded into a beam dump, while the CARS signal beam is sent via a series of mirrors, through a short pass filter and a 100 mm focal length lens onto the spectrometer slit.

![Figure 4.13 Experimental schematic diagram showing folded BoxCARS arrangement.](image)

The folded BoxCARS phase matching scheme is chosen to enhance spatial resolution of the system by minimizing the beam overlap region. The transverse spatial resolution of this arrangement is on the order of 50 μm. Longitudinal spatial resolution was measured by traversing a microscope cover glass (~100 μm thick) through the focal region on a micrometer stage and recording the NRB intensity produced from the glass.
The results of this measurement, which can be seen in Figure 4.14, indicate that 95% of the CARS signal generated comes from a volume ~0.5 mm long.

![Figure 4.14 Folded BoxCARS longitudinal spatial resolution – 95% of signal generated within ~0.5 mm.](image)

4.4 CARS Data Processing

The purpose for CARS diagnostics in the present research is for the measurement of nitrogen vibrational level populations (more commonly referred to as vibrational distribution function, VDF) for the case of vibrationally non-equilibrium environments, and/or nitrogen rotational-translational temperature, $T_{\text{rot}}$, (or simply gas temperature, $T$, in the event of total equilibrium). In principle, inferring $T_{\text{rot}}$ or $T$ is achieved by fitting the measured rotational level populations to a Boltzmann distribution, with temperature as
the fitting parameter. Therefore, whether desiring to obtain VDF or $T_{rot} / T$, the quantum state populations are required. “Data processing” is then the generic term describing the set of procedures performed to extract the needed molecular population distribution information, from experimentally acquired CARS spectra.

Before the actual data processing routine begins, the “zeroth” step is the background subtraction. For most of the research conducted, little to no background luminosity was collected, such that the background spectra captured was a flat-line of camera dark-noise. For the bare-metal electrode studies, however, because the discharge intensity is relatively strong and the filament is located at the CARS collimating lens focal point, some of this light is collected and makes its way into the spectrometer. The camera is a non-intensified CCD, thus it is not capable of fast-gating, and therefore the minimum exposure time possible is ~600 μsec. It was determined experimentally that for time delays of less than ~200 μsec, light from the nsec discharge pulse was visible in the CARS spectra, while for delays longer than this, no background luminosity was measured. After subtracting the background intensity, the rest of the data processing routine can begin.

Understanding the steps involved in the data reduction process requires knowledge of the theoretical underpinnings for CARS signal generation, as presented in the previous chapter, particularly in Eqs. 2.14-15. The three most important items from the aforementioned discussion which need to be dealt with are the dependence of the CARS signal intensity on: the Stokes laser intensity, the number density, and for the case of measuring VDF, the vibrational cross section. As previously discussed, $I_3 \propto I_1^2 I_2$, 
where \( I_i \) represents the intensity of the pump/probe \( (i = 1) \), Stokes \( (i = 2) \), and the CARS \( (i = 3) \) beams, respectively. The narrowband pump/probe beam intensity is the same for all transitions interrogated in the CARS measurement, and therefore cancels out. However, because the broadband Stokes beam intensity profile varies, as can be seen in Figures 3.5, 3.6, and 3.7, accounting for the relative intensity of the Stokes beam at each spectral location is required.

The simplest method to account for the Stokes laser intensity profile is by capturing a non-resonant background (NRB) spectrum, for the same optical arrangement, including the spectrometer and dye laser settings. Significant NRB signal can be generated by filling the CARS interrogation volume with Argon at high pressure (~1 atm or more). Argon is chosen because its non-resonant susceptibility is relatively high and its lack of internal structure ensures a “feature-less” spectrum will be generated, i.e. the NRB spectrum will be dependent only on the Stokes laser intensity profile. The experimental CARS spectrum can then be divided by the NRB spectrum, effectively normalizing to the Stokes laser intensity. After this has been performed, the \( I_3 \propto N^2 \) dependence can be accounted for by taking the square-root of the normalized data.

From this point, the data processing routine for \( \frac{T_{rot}}{T} \) diverges from that for VDF. High-resolution spectra, from which rotational-translational temperature is desired, are fed into the Sandia National Labs equilibrium CARSFT code [18]. In this code, several parameters may be fixed or allowed to float, including \( T \), as the minimization routine finds the least-squares error between the experimental data and a synthetically generated spectrum. When a satisfactory fit is achieved, the code outputs the “best-fit”
temperature, corresponding to $T_{rot}$ or $T$, depending on whether the system is in V-T equilibrium or not. Inferring nitrogen VDF from normalized, square-root spectral data requires a few additional steps; through the course of this research, a few distinct methods were used, each of which will be described briefly in the following sections.

4.4.1 VDF by Collinear CARS

As mentioned, collinear CARS is the simplest phase matching geometry to implement, and was chosen for the initial set of experiments in the Mach 5 plenum. In light of the simple experimental arrangement, a relatively simple data reduction method was used. For this work, low-resolution spectra were captured; after being pre-processed as described above, the maximum value of each vibrational band was measured. Accounting for the varying CARS cross section is now performed to turn the vibrational peak value into a relative number density. As previously described, ignoring anharmonic effects, which are weak for $N_2(v < 10)$ [27], the CARS signal intensity scales quadratically, as $I_3 \propto (v'' + 1)^2$. Because the square-root was taken above to account for the quadratic dependence on $N$, dividing the peak value of each vibrational band by $v'' + 1$ yields $N_v$, the population of each vibrational level, $v$, captured. This simple routine, which was performed manually, was improved for later experimental arrangements, as will be discussed below.
4.4.2 VDF by USED-CARS

As described, the USED-CARS phase matching geometry offers the significant benefits over collinear CARS of eliminating both the NRB signal generated from the cell windows as well as resonant N$_2$ CARS signal generated from the “cold” room air, outside the cell. The medium- and high-resolution spectrometer gratings were used to capture this data, which provided complete spectral separation of the vibrational bands. As an improvement versus simply calculating peak heights, the entire vibrational band is numerically integrated. These values are then divided by $\nu'' + 1$, as described above to account for the varying cross section, again yielding $N_\nu$, in a more robust manner than that performed for the collinear CARS data.

4.4.3 VDF by BoxCARS

The BoxCARS alignment geometry was used to interrogate N$_2$ VDF in the bare-metal electrode single-pulse discharge studies. For this work, the desire was to capture as many vibrational levels as possible, which required the use of the lowest resolution grating. However, this results in some overlap of the individual vibrational peaks, as can be seen in Figure 4.15. To account for this, a curve fitting procedure is used. Each peak in the spectra is assigned a sum of a Gaussian and a Lorentzian function, producing a pseudo-Voigt profile, which can be seen as the blue dashed lines in Figure 4.15. A sum of these curves, the solid red line in Figure 4.15, is then least squares fitted to the pre-processed spectral data, black solid circles, where the linewidth, mean value, and intensity of each individual profile are left as fitting parameters. After a good fit is
achieved, the pseudo-Voigt functions representing each peak are integrated. Finally, the varying vibrational cross section is accounted for, which, as previously described requires dividing the integral of each peak by $v'' + 1$, as the square root of the data has already been taken, yielding $N_v$ for each vibrational level, $v$.

Figure 4.15 Sample spectra illustrating the line fitting technique used for low resolution vibrational spectra captured in the bare-metal electrode discharge studies.
Chapter 5: Results and Discussion Part 1 – Mach 5 Wind Tunnel Studies

As described in the previous chapter, experiments in the Mach 5 wind tunnel have been carried out essentially in three phases: preliminary experiments using collinear CARS in the tunnel plenum, USED-CARS experiments in the tunnel plenum, and USED-CARS experiments in the supersonic section. The results of these three areas of research will be presented in the following sections in that order.

5.1 Collinear CARS Wind Tunnel Plenum Studies

For the sake of initial experimental simplicity, the collinear CARS phase matching scheme was chosen for the first set of experiments. While this geometry can result in various difficulties with data interpretation and hampered sensitivity, in certain environments it can still yield very desirable information. While later studies moved on to more advanced phase matching conditions, the information gained in this portion of the work has merit in its own right.

5.1.1 Low-Resolution Vibrational Spectra

A typical single laser shot CARS spectrum, in a nitrogen flow through with a stagnation pressure of $P_0 = 300$ Torr with the nsec pulser operating alone (i.e. without DC sustainer voltage), can be seen in the plot on the left in Figure 5.1. As the figure clearly displays, the $v'' = 0$ and $v'' = 1$ peaks are both visible, indicating some vibrational
excitation in this regime. The plot on the right in Figure 5.1 shows a typical single shot spectrum for the pulser-sustainer discharge in operation, with the DC sustainer power supply voltage set to $V_{PS} = 4.5$ kV. As can be seen, the vibrational excitation in this condition is much more significant than for the pulser alone, with vibrational levels $v'' = 0, 1, 2, 3$ distinguishable, and higher levels possibly populated. The plots in Figure 5.2 show the same data, plotted with a logarithmic scale on the vertical axis, to allow much more clear visualization of the non-resonant background (NRB), and give a better illustration of the signal-to-noise ratio for this arrangement. Note that these spectra were each captured several hundred msec after the beginning of the nsec pulser operation, in the “steady-state” region (see Figure 4.4).

![Figure 5.1 Typical single shot CARS spectra, 300 Torr N2; (left) nsec pulser alone, (right) pulser-sustainer discharge, $V_{PS} = 4.5$ kV.](image-url)
After spectra such as these are processed and the number densities are inferred and normalized, as previously described, a Boltzmann plot such as that shown in Figure 5.3 is produced. This figure contains the normalized number densities from a sequence of single shot spectra taken from seven consecutive laser shots during one wind tunnel run. As the plot indicates, the first and last data points show weaker vibrational excitation than the others, indicating the beginning and end of DC sustainer voltage application. The \( v'' = 0 \) and \( v'' = 1 \) number density ratio is used to determine the “first level” nitrogen vibrational temperature, \( T_v(N_2) \), as follows:

\[
T_v = \frac{\theta_v}{\ln[n_0/n_1]}
\]  \hspace{1cm} \text{Eq. 5.1}

Figure 5.2 Same data as 5.1, log scale to emphasize NRB contribution.
where $\theta_v = 3353$ K is the energy difference between vibrational levels $v'' = 1$ and $v'' = 0$ in the units of temperature.

Figure 5.3 Normalized Boltzmann plot for one sequence of single shot CARS spectra in the pulser-sustainer discharge, $V_{PS} = 4$ kV, 300 torr N$_2$.

The first level temperature is chosen instead of attempting a fit of all vibrational levels present due to the relatively high uncertainty to which the higher levels are known, owing to the complicating effects of the NRB and the quadratic dependence of the peaks on number density. As Figures 5.1-5.2 indicate, in the case of pulser operating alone, vibrational temperature of $1100 \pm 100$ K is inferred, whereas for the pulser-sustainer discharge with $V_{PS} = 4.5$ kV, the vibrational temperature is $2150 \pm 150$ K.
5.1.2 Vibrational Loading in the Pulser-Sustainer

In order to monitor the temporal characteristics of the vibrational loading of the flow in the discharge relative to the DC sustainer current, the timing of the laser and pulser firing were synchronized. These measurements were conducted at a plenum pressure of 300 Torr, with the DC sustainer power supply voltage set to $V_{PS} = 3.5 \text{ kV}$. By varying the delay between the discharge and laser firing in 10 msec intervals, analysis of the vibrational loading characteristics of the discharge in time was performed. Four single shot spectra were collected for each time delay, and mean and standard deviation statistics were computed for each of these four point data sets. The results of this are plotted in Figure 5.4, with a typical DC sustainer discharge current profile superimposed.

![Graph](image)

Figure 5.4 Temporal evolution of $T_v(N_2)$ during sustainer discharge pulse, $V_{PS} = 3.5 \text{ kV}$, 300 torr $N_2$. 
This analysis demonstrates that the vibrational temperature behavior matches the time-resolved sustainer current profile very closely, as expected. It should be noted that the characteristic time for electron impact vibrational excitation in the discharge is much shorter than the time scale in Figure 5.4 (see discussion below). On the other hand, the estimated characteristic vibrational population decay time at these conditions, due to extremely slow vibration-translation relaxation in nitrogen (of the order of a second), is much longer compared to the flow residence time between the discharge section and CARS measurement location (a few milliseconds). Therefore the results plotted in Figure 5.4 represent a quasi-steady-state, time-resolved, vibrational temperature reached in the pulser-sustainer discharge in nitrogen. Considering the interval from 200 msec through 590 msec as approximately constant sustainer loading, an average \( T_v(N_2) = 1671 \) K is observed, with a 95% confidence interval of +/- 25 K.

The lowest vibrational temperature values seen at the beginning and end of the measurement sequence in Figure 5.4 correspond to the approximate detection threshold for vibrational temperature measurement using the present CARS arrangement, \( T_v(N_2) \sim 800-1000 \) K. There are a few factors that would result in reduction of this threshold. Most significantly, reduction of the NRB would enable more sensitive detection of weak transitions, which was the motivation to move to the USED-CARS alignment geometry. Additionally, increasing laser power would also result in increased detection sensitivity to lower vibrational populations, however care must be taken to prevent saturation effects, both of the CARS process itself and the detection of the \( v'' = 0 \) transition. Note that the time scale for the steep decrease in the vibrational temperature
near the moment when the DC sustainer voltage is turned off is controlled by the flow residence time between the discharge section and the CARS measurement region, several milliseconds. Furthermore, it should also be noted that a few vibrational temperature values at the end of the sequence demonstrate the same level of excitation measured with the pulser operating alone (e.g. see the left plot in Figure 5.1), corresponding to the time after the sustainer discharge turns off but while the pulser is still firing. Spectra taken after the pulser is turned off, beyond the last data point in this plot, show no detectable population of $v'' = 1$.

The set of data displayed in the plot in Figure 5.5 shows the results of varying the discharge pressure as well as the sustainer discharge DC voltage. Each data point results from averaging the vibrational temperature obtained from the 4-5 single shot spectra captured in the “steady-state” region of a single wind tunnel run. The trend line of the mean $T_v(N_2)$, along with the corresponding standard deviations for each pressure condition, are plotted versus the DC power supply voltage setting, $V_{PS}$. As expected, increasing the DC sustainer voltage results in higher vibrational excitation of nitrogen in the flow.
Figure 5.5 Effects of pressure and DC voltage on vibrational temperature of nitrogen.

In Figure 5.6, $T_v(N_2)$ is plotted versus the energy loading per molecule, $\varepsilon_{load}$, (for $V_{PS} = 2-4$ kV), for each pressure condition. To calculate $\varepsilon_{load}$, the voltage between the DC electrodes, $V$, is first calculated from $V_{PS}$, $I$, and $R_{bal} = 1.5\, \Omega$, the DC power supply voltage, discharge current, and the resistance of the ballast resistor, respectively:

$$V = V_{PS} - I \cdot R_{bal}$$  \hspace{1cm} \text{Eq. 5.2}

This voltage is then reduced by the voltage drop across the cathode sheath, $V_0$, estimated from previous measurements of the current-voltage characteristic of the pulser-sustainer discharge [14], $V_0 \approx 290$ V, and DC power loading, $P$, is calculated as:
Finally, the energy loading per molecule, $\varepsilon_{load}$, is:

$$\varepsilon_{load} = \frac{P}{\dot{n}}$$

where $\dot{n}$ is the molecular flow rate, calculated from the mass flow rate through the discharge section / nozzle plenum. As the plot demonstrates, the two higher pressure discharge cases display a consistent, direct relationship between $T_v(N_2)$ and $\varepsilon_{load}$, while the lower pressure 200 Torr case indicates somewhat different behavior (discussed in greater detail below).

Figure 5.6 Effects of sustainer DC discharge energy loading per molecule on $T_v(N_2)$. 83
Figure 5.7 plots vibrational temperature versus the estimated reduced electric field, $E/n$, of the DC sustainer discharge. As is well known [34], the reduced electric field controls the average electron energy and therefore the input energy partitioning among different electron impact excitation channels (vibrational and electronic excitation, dissociation, ionization, etc). In the present work, the reduced electric field was estimated simply as the reduced voltage between the DC electrodes, $V - V_0$, divided by the electrode gap and the number density, assuming 375 K gas temperature in the discharge. This is justified by our previous translational-rotational temperature measurements in the pulser-sustainer discharge at these conditions from N$_2$ emission UV/visible spectroscopy [14, 15], which yield temperature in the range $T = 350$-$400$ K. Figure 5.7 shows essentially identical vibrational temperature behavior for all three pressures for $E/n < ~7$ Td. For the 200 torr case, lower vibrational excitation is observed for $E/n > ~7$ Td than that observed for the other two pressure cases, which remain in good agreement with each other. It was noted that at lower plenum pressures the discharge spatial uniformity decreases, with visible emission being most intense near the side walls of the discharge section, (see Figure 4.5). In this event, a significant fraction of the energy deposition would likely also occur near the side walls, leading to a lower relative vibrational loading at the center of the channel, where the CARS interrogation is performed.
The vibrational temperatures are used to calculate average vibrational energy per molecule, $\epsilon_{avg}$, in the discharge, and the percent of discharge energy loaded into molecular vibrations, $\eta$:

$$\eta = \frac{\epsilon_{avg}}{\epsilon_{load}}$$  \hspace{1cm} \text{Eq. 5.5}

According to theory [34], this fraction should be nearly 90% at 10 Td while dropping off somewhat to ~50% near 3.5 Td. Figure 5.8 shows $\eta$ plotted against E/n for the 370 Torr and 300 Torr cases (for the range of $V_{PS} = 2$-4 kV), along with the theoretically predicted values. While the experimentally measured values are somewhat
lower than those theoretically predicted, the trend observed is similar to the expected result, and there are a few factors which explain the offset. Due to the simple collinear geometry of the CARS measurements, there is a small amount of signal which is collected from outside the test section, i.e. in the vibrationally “cold” room air, which effectively reduces the apparent vibrational temperature. Due to the extreme difference in laser intensity between the focus and the collimated beam, this effect is slight and is estimated to introduce a maximum of approximately three percent uncertainty into the inferred vibrational temperature. This estimate is achieved by comparing the signal generated with the tunnel evacuated (i.e. from nitrogen outside the desired measurement volume) with the v = 0 level peak intensity collected during test runs.

Figure 5.8 Percentage of DC sustainer discharge energy loaded into nitrogen molecular vibrations vs. estimated reduced electric field (1 Td = 10^{-17} V\cdot cm^2).
Additionally, as mentioned, the calculation for reduced electric field was performed with the assumption of spatial uniformity of the local electric field. As previously mentioned, since the pulser-sustainer discharge emission intensity is not spatially uniform (see Figure 4.5), it is likely that the actual E/n at the measurement location is somewhat lower than the simple estimate would suggest. Clearly knowledge of the local electric field is extremely important in understanding discharge processes, and is the motivation of ongoing research in our group [38]. Related to the spatial non-uniformity of the local electric field (affecting the x-axis location of the data), it is quite possible that energy deposition is greater near the edges of the discharge than in the center (affecting the y-axis location of the data) [14, 15]. This effect would lead to an over-estimation of the $\varepsilon_{load}$ near the center of the discharge, thus reducing the apparent $\eta$ value at the measurement location. The results from the lowest pressure 200 Torr case have not been included here, as they were not in agreement with the expected trend, thought to be due to the rather poor discharge spatial uniformity at this condition.

5.1.3 Effects of Relaxant Gas Injection

The final set of experimental data obtained for this portion of the research investigated the injection of gases inducing vibrational relaxation (of nitrogen excited in the discharge) between the discharge section and the CARS measurement location, as shown in Figure 4.1. In the present work, four different injection gases were used: oxygen, hydrogen, nitric oxide, and carbon dioxide. These species have been chosen because the rates of nitrogen vibrational relaxation in these four mixtures vary by several
orders of magnitude. Figure 5.9 plots nitrogen vibrational temperatures measured in these mixtures versus the partial pressure of the injected species, all performed at the same total pressure in the flow of 300 torr. Mole fractions of injection species can be easily calculated from their partial pressures.

As expected, adding oxygen to the vibrationally excited nitrogen flow, up to 17% (nearly “synthetic air”), results in negligible reduction of N\textsubscript{2} vibrational temperature, due to an extremely slow vibration-vibration (V-V) energy transfer rate coefficient:

\[ N\textsubscript{2}(v = 1) + O\textsubscript{2}(v = 0) \rightarrow N\textsubscript{2}(v = 0) + O\textsubscript{2}(v = 1) \] \hspace{1cm} \text{Eq. 5.6}

\[ k_{VV} = 7 \cdot 10^{-17} \text{ cm}^3/\text{sec} \ (T \sim 300 \text{ K}) \] [39]. The characteristic time for nitrogen V-V relaxation at these conditions, \( \tau_{VV} \sim 1/k_{VV}n_{O2} \sim 10 \text{ msec} \) at \( P_{O2} = 50 \text{ torr} \), is longer than the flow residence time between the injection location and the CARS measurement region, estimated to be \( \tau_{res} \sim 2.0 \text{ msec} \). Characteristic time for V-T relaxation for N\textsubscript{2}-O\textsubscript{2} is even longer. Carbon dioxide injection, which results in significant reduction of nitrogen vibrational temperature, even at low CO\textsubscript{2} mole fractions in the flow, illustrates the other extreme. The room temperature rate coefficient for V-V energy transfer:

\[ N\textsubscript{2}(v = 1) + CO\textsubscript{2}(000) \rightarrow N\textsubscript{2}(v = 0) + CO\textsubscript{2}(001) \] \hspace{1cm} \text{Eq. 5.7}

is quite high, \( k_{VV} = 6 \cdot 10^{-13} \text{ cm}^3/\text{sec} \ (T \sim 300 \text{ K}) \) [40] (\( \tau_{VV} \sim 1/k_{VV}n_{CO2} \sim 10 \mu \text{sec} \) for CO\textsubscript{2} partial pressure of only 5 torr). CO\textsubscript{2} vibrationally excited in collisions with nitrogen
relaxes via rapid intramolecular V-V energy transfer to ν₂ (010) and ν₁ (100) modes, with subsequent rapid V-T relaxation. Indeed, the present experimental results demonstrate $T_v(N₂)$ reduction to near threshold of the CARS diagnostic detection sensitivity limit with only a few torr of CO₂ injected into the flow.

![Graph](image)

Figure 5.9 Effects of gas injection on $T_v(N₂)$, $V_{ps} = 5$ kV, 300 torr total mixture pressure.

Nitric oxide and hydrogen represent two intermediate cases. The rate coefficient of V-V energy transfer from nitrogen to nitric oxide:

$$N₂(ν = 1) + NO(ν = 0) \rightarrow N₂(ν = 0) + NO(ν = 1) \quad \text{Eq. 5.8}$$
\( k_{VV} = 1.4 \cdot 10^{-15} \text{ cm}^3/\text{sec} \) at \( T = 300 \text{ K} \), and \( k_{VV} = 2.7 \cdot 10^{-15} \text{ cm}^3/\text{sec} \) at \( T = 400 \text{ K} \) [40] (\( \tau_{VV} \sim 1/k_{VV} n_{NO} \sim 4 \text{ msec} \) and \( \tau_{VV} \sim 3 \text{ msec} \), respectively, for NO partial pressure of 5 torr, which is comparable with the flow residence time). The room temperature V-T relaxation rate coefficient for N\(_2\)-H\(_2\):

\[
N_2(v = 1) + H_2 \rightarrow N_2(v = 0) + H_2
\]  
Eq. 5.9

is \( k_{VT} = 1.4 \cdot 10^{-16} \text{ cm}^3/\text{sec} \) [41] (\( \tau_{VT} \sim 1/k_{VT} n_{H_2} \sim 40 \text{ msec} \) for H\(_2\) partial pressure of 5 torr). Using the temperature dependence suggested in Ref. [42], this rate increases to \( k_{VT} = 3.9 \cdot 10^{-16} \text{ cm}^3/\text{sec} \) at \( T = 400 \text{ K} \) (\( \tau_{VT} \sim 20 \text{ msec} \)) and at \( T = 500 \text{ K} \), it increases further to \( k_{VT} = 9.2 \cdot 10^{-16} \text{ cm}^3/\text{sec} \) (\( \tau_{VT} \sim 10 \text{ msec} \)). Note that, similar to N\(_2\)-O\(_2\), V-V energy transfer for N\(_2\)-H\(_2\) is extremely slow, due to a large difference in vibrational quanta [43].

The vibrational temperatures, \( T_v \), resulting from different relaxant injection partial pressures, \( P_{add} \), can be used to infer the V-V relaxation rate, \( k_{VV} \), (for the NO injection; the V-T rate is calculated in this same manner for the case of H\(_2\) injection) via the following equation:

\[
\frac{dE_v}{dt} \approx \frac{E_v(\tau_{res}) - E_v(0)}{\tau_{res}}
\]

\[
= \frac{P_{add}}{k_B T} k_{VV} \left( 1 - e^{-\theta_v/T} \right) \left( E_{eq}(T) - E_v(0) \right)
\]  
Eq. 5.10
where $dE_v/dt$ is the time derivative of vibrational energy, $P_{add}$ is the injection partial pressure, $T$ is the gas rotational-translation temperature, and $k_B$ is Boltzmann’s constant. The energy in nitrogen vibrations at the CARS measurement location with and without relaxant gas injection, $E_v(\tau_{res})$ and $E_v(0)$, respectively, are defined as functions of $T_v$ by:

$$E_v = \frac{\theta_v}{e^{\theta_v/T_v} - 1}$$  \hspace{1cm} \text{Eq. 5.11}

and the vibrational energy content due to purely thermal effects, $E_{eq}(T)$, is defined as:

$$E_{eq}(T) = \frac{\theta_v}{e^{\theta_v/T} - 1}$$  \hspace{1cm} \text{Eq. 5.12}

where $T \approx 400$ K is the translational / rotational gas temperature at this condition. The transit time between the relaxer injection location and CARS measurement locations was estimated, from the mass flow rate and channel cross section, to be $\tau_{res} = 2.0$ msec.

The results of this analysis are shown in Table 5.1 below, which indicate an apparent value of $k_{VT}(N_2-NO)$ inferred in the present work fairly close to the literature value [40] at $T = 400$ K, within the bounds of the uncertainty in this estimation. The apparent rate $k_{VT}(N_2-H_2)$ inferred here is more than a factor of 2 faster than the literature value at $T = 400$ K [41, 42]. Note, however, that vibrational relaxation of nitrogen from $T_v(N_2) = 1700$ K to $T_v(N_2) = 1200$ K in the presence of NO and H$_2$ (see Figure 5.9) results
in reduction of the average vibrational energy per molecule by \( \Delta E_v = 28 \text{ meV/molecule} \), with the resultant flow temperature rise of \( \Delta T \approx 90 \text{ K} \). At \( T = 500 \text{ K} \), the literature values are \( k_{VV}(N_2-NO) = 3.2 \cdot 10^{-15} \text{ cm}^3/\text{sec} \) \([40]\) and \( k_{VT}(N_2-H_2) = 9.2 \cdot 10^{-16} \text{ cm}^3/\text{sec} \) \([41, 42]\), i.e. close to the rates inferred from the present measurements. While better accuracy for estimating these rates could be achieved with the simultaneous measurement of the flow rotational-translational temperature (which has been performed and will be described in the next section), the issues of flow mixing and residence time are much larger hurdles and are beyond the scope of this study.

<table>
<thead>
<tr>
<th>Energy transfer mechanism</th>
<th>Rate from literature at ( T = 400 \text{ K} )</th>
<th>Rate from this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2(v = 1) + NO(v = 0) \rightarrow N_2(v = 0) + NO(v = 1) )</td>
<td>( k_{VV} = 2.7 \cdot 10^{-15} ) ([40])</td>
<td>( k_{VV} = 3.1 \cdot 10^{-15} )</td>
</tr>
<tr>
<td>( N_2(v = 1) + H_2 \rightarrow N_2(v = 0) + H_2 )</td>
<td>( k_{VT} = 3.9 \cdot 10^{-16} ) ([41, 42])</td>
<td>( k_{VT} = 1.1 \cdot 10^{-15} )</td>
</tr>
</tbody>
</table>

Table 5.1 Estimated nitrogen vibration relaxation rate coefficients compared with literature values.

The measurements summarized in Figure 5.9 demonstrate feasibility of generating low-temperature, high-pressure vibrationally excited flows of nitrogen and synthetic air at steady state, as well as the feasibility of tailoring the vibrational temperature of these nonequilibrium flows using injection of efficient \( V-T \) and \( V-V \) relaxer species downstream of the discharge.
5.2 USED-CARS Wind Tunnel Plenum Studies

Following the work presented in the preceding section, the CARS phase matching scheme was switch from collinear to USED, and the implementation of the relay lens magnification system was performed. These two modifications to the system allow for less uncertainty in the inferred vibrational temperature measurements (due to a signal collection volume entirely within the flow channel), as well as the expanded capability of performing high-resolution CARS spectroscopy, from which simultaneous vibrational non-equilibrium and rotational-translational temperatures can be inferred.

5.2.1 Low Temperature Rotational Thermometry Validation

The first portion of work to be discussed is the demonstration of the capability of the system to measure rotational-translational temperature, $T_{\text{rots}}$, in “cold” nitrogen flows. A sample single-shot spectrum captured in 370 torr pure $N_2$ flowing through the tunnel plenum with no discharge is shown below in Figure 5.10 (a). While under low resolution the spectral output of the Stokes beam from the modeless dye laser appears very similar from one shot to the next, higher resolution reveals significant shot-to-shot spectral profile variation. To partially mitigate this, 20 single-shot spectra are averaged together, an example of which can be seen below in Figure 5.10 (b), taken at $P_0 = 370$ torr and nominal room temperature, $T \sim 300$ K. After the averaging is performed, the spectrum is fitted with the Sandia Carsfit least-squares fitting code. The resulting nitrogen best fit
rotational temperature for the spectrum shown in Figure 5.10 (b) is $T_{rot}(N_2) = 322$ K, with precision equal to +/- 20 K as discussed below.

Figure 5.10 Pure N$_2$ CARS spectra at 370 torr with no discharge, (a) single-shot and (b) 20-shot average, along with Carsfit best synthetic spectra; $T_{fit} = 322$ K.

To quantify measurement precision and accuracy, 60 20-shot average spectra, obtained identically to that of Figure 5.10 (b), have been collected and fit with the Carsfit code. The results of this analysis are shown in the histogram plot in Figure 5.11, along with a Gaussian curve with the same mean temperature, $T_{rot} = 316.6$ K, and standard deviation, $\sigma = 10.0$ K, as the data set. Performing low temperature Q-branch CARS thermometry with a broadband Stokes laser source (i.e. not scanning a very narrow linewidth Stokes beam) is somewhat challenging, considering the relatively few rotational levels populated at low temperatures, compounded by the narrow spacing of these lines. Despite this, the system precision is demonstrated to be quite good, with a
95% confidence interval of +/- 20 K. The system accuracy is comparable, as the true gas temperature for these measurements is ~300 K.

Figure 5.11 Histogram of CARS best fit rotational-translational temperature obtained from Carsfit; nominally room temperature \( N_2, P_0 = 370 \) torr.

5.2.2 Pure Nitrogen Flow, Nsec Pulser Alone

The first discharge condition for consideration is the case of 300 torr pure nitrogen flowing through the tunnel, with the nsec pulsed discharge in operation alone (i.e. no DC sustainer discharge). A typical spectrum is shown in Figure 5.12 (a), from which a value of \( T_{vib} = 761 +/- 74 \) K is inferred, significantly exceeding the gas temperature, \( T_{rot} = 379 +/- 15 \) K. Uncertainties reported are for 95% confidence interval. Figure 5.12 (b) plots the same data, zoomed on the ground vibrational band, along with the Carsfit synthetic spectrum. Ten of these 20-shot averaged spectra have been collected.
and processed for this condition, as well as for the conditions of 200 and 370 torr nitrogen flowing through the nsec pulser discharge. The results of these runs have been plotted and are shown below in Figure 5.13, along with error bars showing the 95% confidence bounds, as well as the corresponding percent of energy going into molecular vibrations, compared with the total energy input.

![Figure 5.13](image)

Figure 5.13 Sample 20-shot average spectra, pulser alone, 300 torr N₂ showing (a) Non-equilibrium v = 0 and v = 1 peaks, and (b) v = 0 peak with Carsfit synthetic spectra.

Since the nanosecond pulse peak voltage exceeds 20 kV (see Figure 4.3), the estimated peak reduced electric field in the 5 mm gap between the pulser electrodes is very high, E/n\text{peak} \sim 300 – 400 Td at P_0 = 200 – 400 Torr. At these high reduced electric fields, the discharge energy fraction going to vibrational excitation of nitrogen by electron impact is predicted to be very low, less than 3% [34]. However, kinetics of
energy coupling to the plasma in a nanosecond pulse discharge is more complex. Although the electric field before breakdown is very high, field in the plasma after breakdown is reduced considerably due to charge separation in the sheath, resulting in plasma shielding. Since the applied voltage continues to vary after breakdown, this generates displacement current in the external circuit, equal to the conduction current in the plasma between the electrodes [17]. This causes additional energy coupling to the plasma at relatively low reduced electric fields, i.e. at the conditions when a significant fraction of input energy may be loaded directly into the vibrational energy mode of nitrogen by electron impact.

Figure 5.13 Rotational and first-level vibrational temperature, as well as corresponding energy fraction into molecular vibrations, for nsec pulsed N₂ discharge alone, vs. discharge (plenum) pressure.
To evaluate the discharge pulse energy fraction stored in nitrogen vibrations, we used an analytic model of the nanosecond pulse discharge in a quasi-one-dimensional plane geometry, with both electrodes covered by dielectric layers [17]. Briefly, the model incorporates key effects of pulsed breakdown, plasma shielding, and sheath development on a nanosecond time scale. The model predicts pulse energy coupled to the plasma during and after breakdown vs. discharge geometry, pressure, temperature, and pulse voltage waveform parameters. In the model, the experimental pulse voltage waveform, shown in Figure 4.3 [33], was approximated by a superposition of Gaussian shape pulses, as shown in Figure 5.14. Multiple voltage peaks in the experimental waveform are due to pulse reflections off the load (the discharge) and the pulse generator. The reflected pulses couple additional energy to the plasma generated during the incident pulse. It can be shown [17] that after breakdown and sheath formation, the field in the quasi-neutral plasma, $E_p(t)$, which controls the energy loading kinetics, is given as:

$$E_p(t) = \frac{1}{1 + \frac{\varepsilon l_s}{2l} \frac{dV_{app}(t)}{dt}} \approx \frac{\varepsilon_0}{2l e_n \mu_e} \frac{dV_{app}(t)}{dt}$$

Eq. 5.13

where $V_{app}(t)$ is the applied voltage, $\mu_e$ and $n_e$ are electron mobility and quasi-steady-state electron density reached after breakdown, $l$ and $\varepsilon$ are the thickness of the dielectric layers and the dielectric constant, and $l_s$ is the sheath thickness. The analytic model is in very good agreement with numerical modeling of nanosecond pulse discharge in nitrogen [17].
Figure 5.14 Applied electric field (experimental and Gaussian fit), field in the plasma, and electron density in the plasma; nitrogen, $P_0 = 300$ torr.

The calculations have been done for nitrogen at $T = 300$ K and $P_0 = 200 – 370$ torr, for the discharge gap of $L = 5$ mm, electrode surface area of $A = 3.0 \times 3.6$ cm$^2$, and alumina ceramic dielectric thickness of $l = 1.5$ mm ($\varepsilon = 9.1$). The electron mobility was assumed to be constant, $\mu_e = 400 \frac{[760/P(\text{torr})]}{\text{cm}^2/\text{V} \cdot \text{s}}$, and the Townsend ionization coefficient in nitrogen was taken to be the same as in Ref. [17]. The discharge energy fraction going directly into vibrational excitation by electron impact vs. reduced electric field was taken from the numerical solution of the Boltzmann equation for plasma electrons [34]. The initial electron density before the pulse was assumed to be
very low, \( n_{e0} = 10^8 \text{ cm}^{-3} \). It was shown previously that pre-ionization starts affecting the coupled pulse energy at initial electron densities above \( n_{e0} = 10^{11} \text{ cm}^{-3} \) [17].

Figure 5.14 plots the electron density and the field in the plasma during and after breakdown at \( P_0 = 300 \text{ torr} \). It can be seen that after breakdown, the field in the plasma falls rapidly and becomes about an order of magnitude lower than the applied field, as discussed previously. During breakdown, electron density increases by several orders of magnitude and reaches steady state when the field in the plasma becomes too low to produce additional ionization. Figure 5.15 plots the reduced electric field in the plasma during and after breakdown at the conditions of Figure 5.14, as well as energy coupled to the plasma, energy loaded into nitrogen vibrational mode, and total energy in the load (which includes energy coupled to the plasma and electrostatic energy stored in the capacitive load) vs. time. These results are compared to the total energy in the load measured in the experiment [33].

From Figure 5.15, it can be seen that energy coupled to the plasma by the incident pulse and two reflected pulses is close to the experimentally measured value (in the experiment, the coupled energy increases by an additional \( \sim 10\% \) due to additional pulse reflections not shown in Figures 5.14-5.15). It is also apparent that vibrational energy loading occurs primarily after breakdown (during the latter portion of the incident pulse and during reflected pulses), when the reduced electric field in the plasma does not exceed 30 Td (see Figure 5.15). The net energy fraction loaded into nitrogen vibrations, predicted by the model, is fairly significant, approximately 33%. This is in fairly good agreement with the experimental nonequilibrium vibrational and rotational temperatures
inferred from the CARS spectra, N₂ vibrational mode energy ~12-30% of total energy loaded to the flow at $P_0 = 200 – 300$ torr (see Figure 5.13). Thus, comparison of the results of CARS measurements with kinetic modeling demonstrate that fairly significant vibrational excitation can be achieved in repetitive nanosecond pulse discharges, due to energy coupling to the plasma after breakdown.

![Graph](image)

Figure 5.15 Reduced electric field, coupled energy, energy loaded into vibrational mode of nitrogen, and total energy in the load (experimental and predicted); nitrogen, $P_0 = 300$ torr.

5.2.3 Pulser-Sustainer Discharge, with Relaxer Injection

Figure 5.16 shows a pair of N₂ CARS spectra obtained from operation of the pulser-sustainer discharge, with a DC power supply voltage ($V_{PS}$) of 4.5 kV. The dash-
dotted black curve corresponds to a baseline case of pure nitrogen flow at 300 torr and the solid blue curve shows the spectrum when 1 torr partial pressure of CO$_2$ is injected downstream of the discharge, approximately 9 cm (~2 msec) upstream of the CARS measurement location, as shown in Figure 4.1. It is clear that there is a significant difference between the two conditions. For no relaxer injection, the flow is extremely non-equilibrium, with a vibrational temperature (see Eq. 5.1) of nearly 2000 K, while the inferred gas rotational-translation temperature is $T_{rot} \approx 450$ K. With only 1 torr partial pressure of carbon dioxide injected, nearly all the vibrational energy has been removed from the nitrogen, evidenced by the nearly equilibrated $T_{vib} = 815$ K and $T_{rot} = 630$ K.

Figure 5.16 CARS spectra for pulser-sustainer discharge with no relaxer injection (black dash-dotted) and 1 Torr CO$_2$ injection (blue solid).
Five different species: carbon dioxide, nitric oxide, hydrogen, oxygen and nitrogen; were injected over a range of partial pressures. These gases were chosen because their rates for nitrogen vibrational relaxation vary by several orders of magnitude. Figure 5.17 plots both the nitrogen vibrational and rotational-translational temperatures measured simultaneously in these mixtures, versus the partial pressure of the injected species. It can be seen that the addition of oxygen to the discharge-excited nitrogen (solid red curve), up to 20% mole fraction (nearly “synthetic air”), does not cause a significant change in either the vibrational or rotational gas temperature, due to the low vibration-vibration (V-V, see Eq. 5.6) energy transfer rate coefficient, \( k_{VV} = 3 \cdot 10^{-17} \text{ cm}^3/\text{sec} \) at \( T_{rot} = 450 \text{ K} \) [39]. For injection of 60 Torr oxygen, the characteristic time for nitrogen V-V relaxation, \( \tau_{VV} \sim 1/k_{VV} n_{O_2} \sim 17 \text{ msec} \), is significantly longer than the \( \sim 2 \text{ msec} \) flow residence time between the injection location and the CARS measurement region. The characteristic time for V-T relaxation for N\(_2\)-O\(_2\) is even longer.

As can also be seen in Figure 5.17, carbon dioxide (magenta dash-dot curve), which is known to be an extremely rapid relaxer of nitrogen vibrations, exhibits the most rapid rate of relaxation. Even at the lowest injection partial pressure, \( P_{CO_2} = 0.25 \text{ torr} \), a substantial reduction of nitrogen vibrational temperature, by more than 450 K, is observed, as well as a corresponding increase in nitrogen rotational temperature by 50 K. The rate coefficient for V-V energy transfer (see Eq. 5.7), at \( T_{rot} = 450 \text{ K} \), is very high, \( k_{VV} = 4.5 \cdot 10^{-13} \text{ cm}^3/\text{sec} \) [39] (\( \tau_{VV} \sim 1/k_{VV} n_{CO_2} \sim 70 \mu\text{sec} \) for CO\(_2\) partial pressure of only 1 torr). As discussed previously, CO\(_2\) vibrationally excited in collisions with
nitrogen relaxes via rapid intramolecular V-V energy transfer to \( v_2 \) (010) and \( v_1 \) (100) modes, with subsequent rapid V-T relaxation.

Injection of nitric oxide and hydrogen exhibit similar behavior to carbon dioxide, although on a slower time scale. The rate coefficient of V-V energy transfer from nitrogen to nitric oxide (see Eq. 5.8) is \( k_{VV} = 3.4 \cdot 10^{-15} \text{ cm}^3/\text{sec} \) at 450 K [40] \((\tau_{VV} \approx 1/k_{VV}n_{NO} \approx 2 \text{ msec} \) for NO partial pressure of 5 torr, comparable to the flow residence time). The V-T relaxation rate coefficient for N\(_2\)-H\(_2\) (see Eq. 5.9), is \( k_{VT} = 6.1 \cdot 10^{-16} \text{ cm}^3/\text{sec} \) at 450 K [41] \((\tau_{VT} \approx 1/k_{VT}n_{H_2} \approx 6 \text{ msec} \) for H\(_2\) partial pressure of 0.3 torr.

Figure 5.17 Pulser-sustainer discharge, \( V_{PS} = 4.5 \text{ kV} \), various injected species, 300 torr total mixture pressure.
10 torr). Using the temperature dependence suggested in Ref. [42], this rate increases to

\[ k_{VT} = 1.3 \cdot 10^{-15} \text{ cm}^3/\text{sec} \quad \text{at} \quad T = 550 \text{ K} \quad (\tau_{VT} \sim 3 \text{ msec}). \]

Similarly to N\textsubscript{2}-O\textsubscript{2}, the V-V energy transfer for N\textsubscript{2}-H\textsubscript{2} is extremely slow, due to a significant difference in vibrational quanta [43].

Injection of non-excited nitrogen was also performed; although the V-V energy transfer rate coefficient for nitrogen,

\[ N_2(v = 1) + N_2(v = 0) \rightarrow N_2(v = 0) + N_2(v = 1) \quad \text{Eq. 5.14} \]

is relatively high, \( k_{vv} = 1.5 \cdot 10^{-14} \text{ cm}^3/\text{sec} \quad (T = 300 \text{ K}) \) [44] \( \tau_{vv} \sim 1/k_{vv}n_{N_2} \sim 0.5 \text{ msec} \) (for injection of N\textsubscript{2} partial pressure of 5 torr), the resonant energy transfer process simply results in the redistribution of N\textsubscript{2} vibrational energy amongst the discharge loaded “hot” and downstream injected “cold” molecules, but the energy remains “locked” in the nitrogen vibrational mode.

As the results of Figure 5.17 indicate, extraction of energy from the nitrogen vibrational mode results in an increase of the gas temperature, i.e. thermalization of the vibrational energy as the discharge-loaded flow is equilibrated. Figure 5.18 plots the average total nitrogen translational + rotational + vibrational energy per molecule as a function of partial pressure of the injected species for all of the conditions shown previously in Figure 5.17. As Figure 5.18 demonstrates, within the experimental uncertainty, the total nitrogen rotational, translational, and vibrational energy is conserved for all injection cases. This indicates that any inter-species V-V transfer is
followed by rapid V-T relaxation, with a result that there is negligible energy storage in the vibrational modes of injected species.

Figure 5.18 Sum of nitrogen translational + rotational + vibrational energy as a function of relaxant species partial pressure.

5.3 USED-CARS Mach 5 Supersonic Nozzle Studies

The last set of experiments done in the Mach 5 wind tunnel involved measurements performed in the supersonic test area (see Figure 4.1). In this portion of the study, measurements of vibrational temperature in both “cold” nitrogen flows and pulser-sustainer discharge loaded nitrogen flows have been carried out in the supersonic free-stream and around the cylindrical test object. These measurements are especially challenging due to very low free-stream static pressure, $P = 1.2$ torr measured using a wall pressure tap at the end of the nozzle. As mentioned, a 5 mm diameter quartz
cylinder is situated in the supersonic flow which creates a bow shock, as shown previously in Figure 4.6 (a). The CARS spectra in Figure 5.19 (a) are eight-shot averages, collected both in the supersonic free-stream and behind the bow shock for 300 torr pure N\textsubscript{2} in the plenum with no discharge. The difference in signal level results from the very different number densities present in the two measurement locations; the spectra also demonstrate typical signal-to-noise levels for this arrangement.

Figure 5.19 Sample CARS spectra collected in the supersonic flow; (a) eight-shot average spectra collected in the free-stream and behind the shock layer with no discharge present; ten-shot average spectra with the pulser-sustainer discharge operating, collected: (b) in the supersonic free-stream, and (c) behind the bow shock.
The plots in Figure 5.19 (b) and (c) show ten-shot average spectra, collected in the supersonic free-stream and behind the bow shock, respectively, for 300 torr N$_2$ in the plenum, with the pulser-sustainer discharge in operation (sustainer $V_{PS} = 4.5$ kV). Electromagnetic interference (EMI) caused by the nsec pulser can be clearly seen in both spectra, and becomes increasingly problematic as signal levels decrease. The significant reduction in the ground vibrational level signal strengths for both of these spectra (compared to the “no-discharge” data acquired at each location) can be attributed to both a reduction in total number density, due to gas heating from the discharge, as well as significant population loss to excited vibrational states. The ratio of the integrated square-root of peak intensities is used to determine the first-level nitrogen vibrational temperatures, as previously described.

Due to the nearly quadratic scaling of CARS signal intensity to the density, the integrated square-root of the CARS signal gives an estimate of local number density. Because of the significant rise in density as the flow traverses the bow shock, this can be used to determine if the measurement volume location is upstream or downstream of the shock location. Spectra captured without the discharge in operation, such as those seen in Figure 5.19 (a), are collected at various locations upstream of the cylinder, and estimated local number densities are inferred. The results are shown in Figure 5.20 (a), where the black x’s are for pulser-sustainer discharge operating in 300 torr pure N$_2$ flow, and the red +’s are recorded with 0.25 torr CO$_2$ injection, as previously described. As the plot indicates, a sharp rise in density occurs ~1.0 mm upstream of the cylinder surface. The cluster of data points captured at x = -1.00 mm (number density ~10 in arbitrary units),
represent the free-stream position directly adjacent to the shock front. Moving downstream, measurements captured at $x = -0.99$ mm, -0.98 mm, and -0.95 mm, shown as the next three black x’s on the plot, demonstrate much higher densities, indicating the measurement region has moved beyond the shock location.

Figure 5.20 Inferred (a) estimated number density, and (b) vibrational temperature in the supersonic flow free-stream and behind the bow shock.

As mentioned above, shock stand-off distance detected in the present work, ~1.0 mm, is somewhat smaller than measured in our previous experiments using a 4 cm long, 5 mm diameter cylinder, supported at the tunnel sidewalls, 1.2 mm [45]. This may be explained by the effect of finite cylinder length, which has been studied in a Mach 4
flow in a shock tube experiment [46]. In Ref. [46], it was shown that the ratio of stand-off distance to the cylinder diameter, $d/D$, tends to decrease as the cylinder length-to-diameter ratio, $l/D$, is reduced below $l/D = 4$. This effect is primarily due to flow three-dimensionality, i.e. spanwise flow behind the bow shock. At the present conditions, $l/D = 7.5 \text{ mm} / 5 \text{ mm} = 1.25$. The number densities measured behind the shock are nominally 3-4 times higher than those measured in the free-stream, somewhat less than the factor of 5.1 predicted by 3D CFD calculation for the Mach 4.5 flow upstream of the shock location [45]. The density ratio across the shock may be also affected by the three-dimensionality of the flow over the short cylinder.

The plot in Figure 5.20 (b) shows the inferred $T_{\text{vib}}(N_2)$ for several locations both in the free-stream and behind the shock. These data are taken with the pulser-sustainer discharge operating in 300 torr $N_2$ in plenum, with and without 0.25 torr $CO_2$ injection. Both with $CO_2$ injection and without injection, vibrational temperatures inferred behind the shock are very similar to those observed in the free-stream. As the recovery pressure behind the shock is significantly lower than the plenum pressure, vibrational relaxation beyond that present in the relatively high density subsonic flow does not occur. The vibrational temperature inferred for the case of 0.25 torr $CO_2$ injection is close to the value inferred in plenum at the same conditions, $T_{\text{vib}} \sim 1450$ K. The vibrational temperature for pure $N_2$ without injection is $\sim 150$ K less than the value measured in plenum at the same conditions, $T_{\text{vib}} = 1900$ K, a difference of less than 10%. Significant spread in the data is observed, primarily due to the rather low signal-to-noise levels
present due to the EMI effects from the nsec pulser previously mentioned, as well as the
general difficulty of very low CARS signal levels in these extremely low density flows.
Chapter 6: Results and Discussion Part 2 – Elevated Temperature PAC Reactor and Bare-Metal Electrode Single-Pulse Discharge Studies

Beyond the work performed in the Mach 5 wind tunnel, presented in the previous chapter, two additional research efforts were also undertaken for this work. The outcome of these studies will be presented here; first, measurement results from the elevated temperature plasma assisted combustion facility will be discussed, followed by the results of the bare-metal electrode, single pulse discharge studies.

6.1 Elevated Temperature PAC Reactor Studies

Two sets of CARS measurements were performed in the elevated temperature plasma assisted combustion facility which will be presented in the following sections, these are: measurements of nitrogen vibrational loading and decay in air discharges, and measurements of rotational / equilibrium temperature in air and fuel-air mixtures of interest. Modeling of representative cases has also been performed and will be compared with experimental results. All measurements for this work were carried out using the USED-CARS phase matching geometry, with an optical arrangement very similar to the USED-CARS arrangement used in the Mach 5 wind tunnel studies (see Figure 4.8).
6.1.1 Vibrational Non-Equilibrium Measurements in Air Plasmas

As mentioned, a portion of this work investigated the vibrational non-equilibrium generated by diffuse nanosecond discharges in air plasmas at $P_0 = 100$ torr and $T_0 = 300$ K. Bursts of 40-150 discharge pulses were investigated, at pulse repetition rate of 10 kHz. Low-resolution vibrational spectra were captured 4 μsec after the last pulse in the burst. As can be seen in Figure 6.1, small bursts exhibit an approximately linear increase in vibrational energy loaded to the flow versus the number of pulses in the burst. In the region of 100 pulse bursts, vibrational energy loaded per pulse falls off, as the average vibrational energy per molecule appears to be leveling off near $\sim 22$ meV / molec. First level vibrational temperature (see Eq. 5.1), also shown in Figure 6.1, for a burst of 40 pulses is $T_v \sim 900$ K. For bursts larger than 100 pulses, vibrational temperature levels off near $T_v \sim 1250$ K. Modeling predictions for both the vibrational energy loading per molecule and the vibrational temperature are also included. As the plot demonstrates, the trend measured in the experiment matches the model predictions very closely, although the model appears to slightly over predict both the vibrational energy and temperature for long bursts. This over prediction is likely due to nitrogen excited vibrational state quenching processes not entirely captured by the model.
Figure 6.1 Vibrational energy loaded per molecule vs. number of pulses in the discharge; corresponding first level vibrational temperature also plotted; air, $P_0 = 100$ torr, $T_0 = 300$ K.

Figure 6.2 shows the experimentally measured applied voltage waveform for the nsec pulsed discharge, as well as the Gaussian fit of the voltage peaks used for the modeling predictions. The reduced electric field, $E/N$, and electron number density, $n_e$, produced in the plasma discharge are plotted as well. As Figure 6.2 shows, during the initial discharge breakdown, peak reduced electric field is very high,
E/N_{peak} \sim 500-600 \text{Td}. After this however, as electron number density increases drastically, plasma shielding occurs, significantly lowering the field in the plasma, and resulting in the considerably lower reduced field “lobes”, E/N \sim 20-50 \text{Td}. It is believed that the significant portion of energy loaded into nitrogen vibrations arises via these low E/N pulse reflections.

![Electric field diagram](image)

**Figure 6.2** Experimental and fit voltage waveforms, reduced electric field, and electron number density predicted by the model.

In addition to observation of the vibrational loading at the end of the discharge burst, vibrational energy decay in time after the last pulse was also investigated. Figure 6.3 plots the results for P_0 = 100 \text{ torr air}, T_0 = 300, 500 \text{ K}, with burst ranging from
50-125 pulses. Similar to the results shown in Figure 6.1, vibrational temperature immediately after the end of the discharge burst increases with burst size, reaching an apparent maximum value for bursts of 100 pulses. Vibrational temperatures remain approximately constant through the first several hundred microseconds, while beginning to fall off more rapidly after \(\sim 1\) msec. The two curves for \(T_0 = 500\) K show that vibrational temperature falls off much more rapidly at the elevated temperature than for the \(T_0 = 300\) K case (note the log scale of the time axis). Figure 6.4 shows similar data, captured in air at \(P_0 = 300\) torr. At higher pressure, there is less disparity between the behavior observed for the \(T_0 = 300\) K and \(T_0 = 500\) K cases, as well as less difference between the 50 or 100 pulse cases.

![Experimental measurements of vibrational temperature decay with time after discharge bursts of various lengths; \(P_0 = 100\) torr air, \(T_0 = 300, 500\) K.](image)

Figure 6.3 Experimental measurements of vibrational temperature decay with time after discharge bursts of various lengths; \(P_0 = 100\) torr air, \(T_0 = 300, 500\) K.
Figure 6.4 Experimental measurements of vibrational temperature decay with time; $P_0 = 300$ torr, $T_0 = 300, 500$ K.

A representative vibrational energy decay case (burst of 100 pulses, with $P_0 = 100$ torr and $T_0 = 300$ K was modeled. As can be seen in the plot in Figure 6.5, the experimentally measured vibrational energy decay is somewhat more rapid than the model prediction, which is likely due to a vibrational energy quenching process that is not completely captured. A variety of fuel-air mixture cases were investigated, however in the presence of fuel, nonequilibrium vibrational loading was not readily detected and this was not explored further. The lack of observable nitrogen vibrational excitation for these plasma discharges in fuel-air mixtures substantiates the use of a fuel-air chemistry model for these systems which does not consider molecular vibrational nonequilibrium.
Figure 6.5 Vibrational energy loading and decay for a burst of 100 pulses, experimental results and modeling prediction; $P_0 = 100$ torr, $T_0 = 300$ K.

6.1.2 Validation of CARS Low Temperature Thermometry

As discussed previously, the CARS system is capable of high resolution spectroscopy, providing partial resolution of individual rotational lines of the Q-branch spectra. Sample 100-shot average spectra, captured in 100 torr at $T_0 = 300$ K and 500 K, can be seen in Figure 6.6. Along with the experimental data, least-squares fit theoretical spectral produced by the equilibrium Sandia CARSFT code [18] are also plotted.
Figure 6.6 Sample 100-shot average CARS spectra along with best fit theoretical spectra; 100 torr air at 300 K (left) and 500 K (right).

As was previously done for the Mach 5 work, the accuracy and precision of the CARS diagnostic rotational temperature measurement was examined. In this system configuration, 60 100-shot average spectra were captured at both $T_0 = 300$ K and 500 K. Each of the spectra was least-squares fit with the CARSFT code [18], generating 60 best fit equilibrium temperatures for both conditions. The results of this analysis have been plotted in histograms, and are shown in Figure 6.7, along with normal distribution curves of the same mean fit temperature and standard deviation. Fit accuracy is quite good for both conditions, with mean fit temperatures of 310 K and 492 K, for the $T_0 = 300$ K and 500 K conditions respectively. System precision is of the same order with standard deviations in the fit temperatures of 6.5 K and 7.5 K, corresponding to 95% confidence intervals of +/-13 K and 15 K respectively. Overall, this analysis demonstrates CARS
system temperature sensitivity within +/- 3-4% of the temperature values measured directly by thermocouple.

![Histograms of CARS best fit equilibrium temperatures obtained from Sandia CARSFT; 100 torr air, 300 K (left) and 500 K (right).]

**Figure 6.7** Histograms of CARS best fit equilibrium temperatures obtained from Sandia CARSFT; 100 torr air, 300 K (left) and 500 K (right).

### 6.1.3 Air and Fuel-Air Mixtures, \( T_0 = 500 \text{ K}, 50 \text{ Discharge Pulses at 10 kHz} \)

Both air and lean fuel-air mixtures (\( \text{C}_2\text{H}_4, \text{CH}_4, \text{and H}_2 \)) were studied in the discharge section at elevated initial temperature, \( T_0 = 500 \text{ K} \). For this work, 50 pulses of the nanosecond discharge were fired with a pulse repetition frequency of 10 kHz. Air, \( \text{C}_2\text{H}_4 \)-air, and \( \text{CH}_4 \)-air mixtures at \( P_0 = 100, 200 \) and 300 torr, and \( \text{H}_2 \)-air at \( P_0 = 100 \) torr were examined. Equivalence ratios for \( \text{C}_2\text{H}_4 \)-air and \( \text{CH}_4 \)-air mixtures were \( \varphi = 0.09, 0.18, \) and 0.36, while equivalence ratios for \( \text{H}_2 \)-air were \( \varphi = 0.1, 0.2, \) and 0.3.
For each condition, equilibrium temperatures were measured at various delay times after the firing of the last discharge pulse in the burst. For a given condition (i.e. a particular fuel, equivalence ratio, and pressure), no significant variation in temperature was found over the range of 4 μsec to 1 msec after the discharge burst. Similarly, for a given fuel, varying the discharge pressure or mixture equivalence ratio yielded no appreciable effect on temperature. Each of the 4 mixtures yielded slightly different temperatures though, as can be seen in Figure 6.8. In air plasmas with no fuel, a gas temperature rise of ~30 K was observed. The CH₄-air mixtures produced a temperature increase of ~50 K, the C₂H₄-air mixtures resulted in a temperature rise of ~70 K, and the H₂-air mixture effect was in between these.

Figure 6.8 Temperature profiles versus time delay after the end of the discharge burst for air and fuel-air mixtures; T₀ = 500 K, P₀ = 100 torr, 50 pulses at 10 kHz.
Lean equivalence ratio ($\phi = 0.4$), hydrogen-air mixtures at $T_0 = 500$ K and $P_0 = 92$ torr, were examined in the discharge. With a pulse repetition frequency of 10 kHz, measurements were made with bursts of 50, 99, and 120 pulses, at time delays ranging from 4 $\mu$s up to 20 msec after the last pulse. The experimental results of this are plotted as the symbols in Figure 6.9 below. The data from the 50 pulse case agrees quite well with the 50 pulse hydrogen-air data previously plotted in Figure 6.8. As the number of pulses in the burst is increased however, the temperature profile no longer remains constant. For a burst of 99 pulses, temperature just after the burst is ~650 K, increasing slightly to a peak temperature of 690 K after 1 msec and slowly decaying as heat is transferred out of the system.

Increasing the burst size by one pulse, from 99 to 100, a new phenomenon is observed. The discharge emission signature is monitored with a photomultiplier tube (PMT); for a burst of 100 pulses at this pressure, equivalence ratio, and temperature, the characteristic chemiluminescent signature of ignition begins to appear. For bursts of 99 pulses, this signature is completely nonexistent; for 100 pulses it occurs somewhat sporadically, from one discharge burst to the next. At these conditions, the observed intermittent ignition condition occurs for bursts of 100-119 pulses. Bursts of 120 pulses or more produce quite steady and repeatable ignition traces, along with an extremely stable ignition delay time from one burst to the next.
In addition to the experimental data, 0-D modeling results of these conditions are also plotted, shown as the solid lines in Figure 6.9. As can be seen, the model prediction for both the ignition delay time and peak temperature for the 120 pulse ignition case agrees very closely with the experimental data. The model also predicts the slight rise and slow decay in temperature observed in the experimental data for the two non-ignition cases, although for all three conditions, the model somewhat over-predicts the
equilibrium gas temperature immediately after the end of the discharge, where the over-prediction in each case is on the order of 50 K.

An example 100-shot average CARS spectrum captured near the temperature peak, 3.5 msec after the last pulse for the 120 pulse case, is shown in Figure 6.10 below, along with the least-squares fitted theoretical spectrum for a best-fit temperature of 1250 K. As can be seen, the individual rotational lines are fairly well resolved at this temperature, and despite the rather low number density, compounded by the low pressure and high temperature, spectral signal-to-noise is still quite good.

Figure 6.10 Equilibrium CARS spectra, H2-air ignition; $P_0 = 92$ torr, $T_0 = 500$ K, 120 pulses at $v = 10$ kHz, $\Delta t = 3.5$ msec after the last pulse in the burst.
6.2 Bare-Metal Electrode Single-Pulse Discharge Studies

As previously described, the discharges studied in this work are produced between two bare-metal copper spheres, 7.5 mm in diameter, fixed 1 cm apart. Discharges in 100 torr nitrogen and dry air are each examined. As will be demonstrated, in the case of nitrogen or air, the plasma produced is a diffuse single filament, several mm in diameter. CARS spectroscopy has been performed at a variety of input DC voltages (see Table 4.1), with the focus of measuring nitrogen vibrational distribution function (VDF) and rotational-translational temperature ($T_{rot}$) versus time delay after the single nanosecond duration discharge pulse.

6.2.1 Characterization of the Discharge Filament Size

Two methods were used to estimate the discharge filament size, ICCD imaging of the discharge emission, as well as spatially-resolved CARS measurements. The results of the ICCD imaging can be seen on the left in Figure 6.11; the image is a 10 shot average that was taken in 100 torr N$_2$, with the DC voltage into the nsec pulser set to 430 V, and a 100 μsec camera gate. For measurements by CARS, the position of the discharge electrodes were scanned relative to the CARS interrogation volume, with spectra collected each 200 μm. The spectra are processed, as has been described, and the first-level vibrational temperature is measured across the discharge filament. This was done at the same discharge conditions as the ICCD imaging, with a 100 μsec delay between the discharge and laser firing. The results of this analysis can be seen in the plot on the right in Figure 6.11. As can be seen, both the ICCD imaging and the spatially-resolved $T_v$
measurements yield very a similar result, with FWHM of the filament for this condition estimated to be $\sim 2$ mm. While not shown, additional ICCD imaging has been performed, which indicates that the filament diameter increases with increasing discharge energy loading.

![Figure 6.11 Discharge filament size estimated by (left) ICCD imaging, and (right) spatially-resolved measurement of $T_v$; FWHM $\sim 2$ mm.](image)

6.2.2 Vibrational Distribution Function

The plot on the left in Figure 6.12 shows three sample low-resolution vibrational CARS spectra captured in the 100 torr nitrogen discharge, at delays of 100 nsec, 1 $\mu$sec, and 10 $\mu$sec after the beginning of the $\sim 125$ nsec current pulse. The spectra shown are from the “high-current” case, however they represent the typical behavior seen for all conditions; as the spectra show, extreme vibrational excitation is observed, with vibrational levels $v = 0-9$ visible here. The plot on the right in Figure 6.12 shows the same spectra for the 100 nsec and 1 $\mu$sec delays, zoomed in to show that the higher
vibrational levels are populated for these conditions as well. The spectra captured for this portion of the study were 600 shot accumulations.

The time evolution observed in the spectra in Figure 6.12 is typical of that observed in the vibrational spectra for all conditions, which appear to have three distinct phases. The first phase, sample results from which are plotted along with modeling predictions in Figure 6.13 (a) below, is characterized by the initial appearance and steady growth of several excited vibrational levels. Typically the excited levels appear in the spectra within 50-100 nsec after discharge initiation, with somewhat even population growth of all excited vibrational levels continuing up to ~1-2 microseconds after the discharge ends. Modeling predictions over this time scale agree well with the measured
experimental result, indicating that the vibrational excitation by direct electron impact processes are well represented in the model.

Approximately ~1-2 μsec after discharge initiation, the transition into the second phase occurs, the experimental and modeling results of which can be seen in Figure 6.13 (b). This phase is dominated by extensive growth of the low lying excited vibrational states, typically v = 1-3, while the higher states appear to remain relatively unaffected or perhaps decrease slightly. As can be seen, the modeling prediction captures the behavior of the v = 0-1 levels very well, while significantly over predicting the higher vibrational level relaxation. This stage lasts up to a few hundred microseconds, after which the system transitions into the third phase, dominated by vibrational energy decay, which is plotted in Figure 6.13 (c). Because of the very slow rate of V-T energy transfer in pure nitrogen, combined with the fairly small volume of the discharge, it is likely that the “decay” effects observed are simply the result of diffusion. Again in this regime, the model correctly predicts the ground and first excited vibrational state populations while severely over predicting higher vibrational state relaxation.
Figure 6.13 Normalized nitrogen VDFs and modeling predictions from the "medium current" case; (a) phase 1 – vibrational level appearance and steady growth, (b) phase 2 – $v = 1$-2 increase dramatically, higher levels remain relatively unaffected, (c) phase 3 – excited vibrational level decay; $P_0 = 100$ torr N$_2$.

An alternative representation of the evolution of vibrational level populations versus time can be seen in the plot in Figure 6.14, which shows the experimentally measured and model predicted populations of vibrational levels $v = 0$-3, from $\Delta t = 10$ nsec to 10 msec. As previously shown, this plot demonstrates the close agreement between the measured and predicted populations within the initial $\sim$1 $\mu$sec.
After this time, the measured and predicted behavior for the v = 0-1 levels remain quite close, while the modeling predictions for the higher vibrational levels fall severely, failing to capture the dynamics measured for these levels. This plot also demonstrates the scale and timing of the population increases present in vibrational levels v = 1-3 after the end of the discharge, which will be discussed in more detail below.

Figure 6.14 Normalized nitrogen VDFs and modeling predictions plotted versus time for levels v = 0-3; $P_0 = 100$ torr air, “high current” discharge condition.

### 6.2.3 Vibrational Temperature and Vibrational Quanta

The vibrational level populations for levels v = 0-1 are used to infer the “first-level” vibrational temperature, $T_v$ (see Eq. 5.1). Vibrational temperature is a common metric for describing vibrationally nonequilibrium systems, and is shown, for each of the five conditions tested, in Figure 6.15. For the lowest energy loading condition in N$_2$, 130
after 100 nsec, slight vibrational loading is evident, with $T_v \sim 600$ K. The vibrational temperature continues increasing modestly to a maximum of $T_v \sim 1400$ K after 100 μsec. In contrast, the highest loading condition in nitrogen yields $T_v \sim 1000$ K after 100 nsec, and rises to a maximum of $T_v \sim 2700$ K after 50 μsec. Very significant is that for all of the conditions examined, the peak $T_v$ happens between 50 – 100 μsec after the nsec discharge pulse occurs.

Figure 6.15 Nitrogen "first-level" vibrational temperature, $T_{vib}$, as a function of time delay after the pulse; $P_0$ = 100 torr for all conditions.
Model predicted first level vibrational temperature for the highest loading discharge condition in air can be seen in Figure 6.16. As the plot shows, the experimentally measured and model predicted results match quite closely, as expected since the model predictions for the $v = 0$-1 level populations were previously shown to agree very well with the experimentally measured populations.

![Figure 6.16 Comparison between experimentally measured and model predicted rotational-translational temperature and first-level vibrational temperature for the highest loading discharge condition in air; $P_0 = 100$ torr.](image)

While the first level vibrational temperature gives some insight into the vibrational energy picture of the plasma, it is an incomplete picture. At low rotational-translational temperatures, vibrationally nonequilibrium systems like discharge
excited pure nitrogen or dry air typically have very slow V-T energy exchange rates, while the non-resonant V-V exchange processes:

$$N_2(v) + N_2(w + 1) \rightarrow N_2(v + 1) + N_2(w)$$ \hspace{1cm} \text{Eq. 6.1}$$

for \( v \neq w \)

typically happen much more rapidly. The average number of vibrational quanta per molecule in the system, \( Q_v \), is defined as:

$$Q_v = \sum_{v=1}^{n} v \cdot n_v$$ \hspace{1cm} \text{Eq. 6.2}$$

where \( v \) is the vibrational quantum number, \( n_v \) is the normalized number density of molecules in vibrational level \( v \), and \( n \) is the highest measureable vibrational level. In addition to \( T_v \), \( Q_v \) is also an important metric for these vibrationally nonequilibrium systems, as it reveals a broader perspective of the vibrational energy of the system, which is not necessarily captured by \( T_v \) alone.

Figure 6.17 includes a plot of the total vibrational quanta, for each of the five conditions examined, versus time delay after the beginning of the discharge pulse. As the plot shows, similar to the vibrational temperature, the measurable vibrational quanta appears \( \sim 50-100 \) nsec after the discharge pulse begins, and continues to climb until
reaching a maximum value after 50-100 μsec. Moreover, this plot shows that the vibrational quanta per molecule increases drastically long after the discharge pulse ends.

Figure 6.17 Average nitrogen vibrational quanta per molecule, $Q_v$, versus time delay after the initiation of the ~125 nsec discharge pulse, $P_0 = 100$ torr.

For the various conditions, the maximum value of vibrational quanta is typically a factor of 2-4 times greater than the value at the end of the discharge pulse. It is also notable that the significant increase in vibrational quanta occurs for both nitrogen and air discharges. In the low current regime, the air discharge appears to produce ~50% more nitrogen vibrational quanta per molecule, however when the molar fraction of nitrogen in
air is factored in, the difference observed in Figure 6.17 represents an increase of \(~30\%\) compared to pure nitrogen. Recalling from Table 4.1 above, the increased fraction of vibrational quanta is very similar to the ratio of energy loaded into the discharge in the two conditions, \(~4.2\) mJ/pulse in air versus \(~3.1\) mJ/pulse in pure nitrogen.

For the high current loading cases, the maximum average nitrogen vibrational quanta per molecule measured in pure nitrogen is very close to that observed in dry air. Again taking into account the molar fraction of N\(_2\), and the fact that the discharge in air loads \(~15\%\) more energy than the same condition in nitrogen (\(~16.6\) mJ/pulse vs. \(~14.4\) mJ/pulse), this means there is a fairly sizable relative fraction of energy deposited in that air discharge which does not results in N\(_2\) vibrational excitation. This issue will be revisited in the next section. An additional discussion point from the results shown in Figure 6.17 that will be discussed further in the next section is the apparently different rate of vibrational quanta decay for the high-current air discharge, when compared with the other four conditions.

Comparison between the experimentally measured total vibrational quanta versus the value predicted by the model for the high-discharge loading case in air can be seen in Figure 6.18. As the plot shows, the measured total vibrational quanta per molecule immediately after the discharge is fairly close to the model predicted value. As previously described, this agreement results from the well known processes of vibrational excitation via direct electron impact captured by the model. The model predicts maximum vibrational quanta immediately at the end of the discharge, which is clearly not the behavior observed experimentally. It is noted this result is similar to that observed by
Devyatov et al. (1986), who reported CARS measurements of vibrational levels $v = 0-4$ in a 200 nsec duration pulsed discharge in nitrogen at 60 torr. Of particular relevance to this thesis, Devyatov et al. found that an observed rise in relative populations of vibrational levels $v = 2$ and $v = 3$, which reached a maximum $\sim 1-2 \mu$sec after the discharge pulse, could not be explained solely by V-V transfer. This, in combination with an observed rise in the fraction of discharge coupled energy stored in vibrations, from $\sim 30\%$ to a maximum of $40\% \sim 1 \mu$sec after the pulse, led to the conclusion that the energy pooling process $N_2(A^3\Sigma) + N_2(A^3\Sigma) \rightarrow N_2(C^3\Pi) + N_2(X^1\Sigma,v)$ was adding additional vibrational quanta to the nitrogen vibration mode[47].

Figure 6.18 Comparison of experimentally measured and model predicted total vibrational quanta for the highest energy loading condition; $P_0 = 100$ torr, air.
6.2.4 Rotational-Translational Temperature

In addition to the measurement of $N_2$ VDF described above, rotational-translational temperature, $T_{rot}$, measurement was also performed for the same five discharge conditions discussed in the previous section. A typical example of a high-resolution spectrum from which $T_{rot}$ is inferred, captured in 100 torr room temperature dry air, is plotted below in Figure 6.19, along with the least-squares fit synthetic spectrum produced by the CARSFT code [18].

To estimate the accuracy and precision of the rotational-translational temperature measurement capabilities of the system at these low temperatures, 80 spectra like that
shown in Figure 6.19 were collected, pre-processed, and fit with the Sandia CARSFT code. The results of this analysis have been plotted in the histogram shown in Figure 6.20, along with a Gaussian distribution with the same mean value, $\mu = 302$ K, and standard deviation, $\sigma = 4.6$ K as the data set. As the statistics show, both the accuracy and precision of the system at these temperatures is quite good, with both within $\sim 1-2\%$ of the actual temperature.

![Figure 6.20 Fit temperature histogram along with Gaussian distribution with the same mean, $\mu = 302$ K, and standard deviation, $\sigma = 4.6$ K.](image)

The rotational-translational temperature was measured for the same five discharge cases for which $N_2$ VDF measurements were presented above, the results of which are
shown in the plot in Figure 6.21. There are several interesting items to be seen in this plot. All of the $T_{rot}$ profiles exhibit an initial rise, typically occurring within the first 100 nsec – 1 μsec after breakdown, which is followed by something like a plateau region. For all conditions, with the exception of the high energy loading air case, there is an additional modest temperature rise, in the range of 10-40 K depending on condition. The high-current air discharge shows significantly different behavior in that the second temperature rise is quite dramatic. At ~10-20 μsec after the pulse $T_{rot}$ ∼ 500 K, by 500 μsec delay, this value has increased to $T_{rot}$ ∼ 850 K. The time delay at which this drastic increase in $T_{rot}$ begins, $\Delta t$ = 50-100 μsec, corresponds very closely with the time at which the $N_2$ vibrational quanta begin to fall off rapidly in the same discharge condition. As mentioned above, the fall off in $Q_v$ occurs much more rapidly for the high-current air discharge than for any of the other four conditions. This implies that there is some species produced in the high-current air discharge, most likely O atoms, which are V-T quenching the excited vibrational states of nitrogen and releasing that energy to heat the gas.
Another interesting feature, which is visible when comparing $T_{\text{vib}}$, $Q_p$, and $T_{\text{rot}}$ in Figures 6.15, 6.17, and 6.21, is the relatively slow rise of all three quantities for the high-current $N_2$ case, in the time region $0.1 – 1 \ \mu\text{sec}$, as compared with the medium-current $N_2$ discharge. For all three quantities in question, the high-current discharge case ultimately reaches higher maximum values than the medium-current case, however is unclear why the medium-current case exhibits higher values during the $0.1 – 1 \ \mu\text{sec}$ interval. Additionally, considering there is approximately twice the energy loading for the high-current case compared with the medium-current case, it would be expected that
the difference in peak value for $T_{\text{vib}}$, $Q_v$, and $T_{\text{rot}}$ between the medium and high-current discharge conditions should be more drastic. Detailed modeling of each of these discharge conditions, as well as additional diagnostic measurement of other important species, such as N and O atoms, may shed more light on the cause of this behavior.

Returning to Figure 6.16, the comparison between the model prediction for rotational-translational temperature and that measured experimentally shows an interesting discrepancy. The model and the experiment agree on the peak temperature value and time delay for this temperature to occur, as well as agreeing very closely about the temperature decay process. However, the model predicts that the temperature rise should begin immediately after the end of the discharge, rising steadily to this maximum value, while the experimental result indicates slight temperature immediately after the end of the discharge pulse, followed by a long constant plateau, and then a very sudden rise to the peak. This discrepancy reveals that the model is predicting some mechanism for energy thermalization which is not found to be present in the experiment. In other words, there is some significant fraction of energy that remains “locked” in molecular vibrations significantly longer than the model expects, before being released and finally completely thermalized.
Chapter 7: Conclusions and Future Work

This thesis has described the development of a picosecond, modeless, broadband dye laser, its use in the formation of a picosecond Coherent Anti-Stokes Raman Scattering spectroscopy system, and the implementation of this system for the measurement of nitrogen vibrational non-equilibrium level populations and rotational-translational temperatures. As discussed, this work has been carried out in a variety of experimental environments, including the plenum and supersonic nozzle of a nonequilibrium Mach 5 wind tunnel, an elevated temperature plasma assisted combustion reactor, and a bare-metal electrode single-pulse discharge system. Each of these experimental efforts will be reviewed in the following sections.

7.1 Mach 5 Wind Tunnel Plenum

As discussed, a variety of experimental measurements have been carried out in the low-speed, relatively high-pressure Mach 5 wind tunnel plenum, at pressures in the range of 200-370 torr. These efforts have included utilization of both collinear and Unstable-resonator Spatially Enhanced Detection phase matching alignments, and both low and high resolution CARS spectroscopy has been performed. Non-equilibrium first level vibrational temperature as well rotational-translational temperature of nitrogen resulting from both the nanosecond pulsed discharge operating alone and the pulser-sustainer discharge have been measured. With the pulser operating alone, non-
equilibrium vibrational loading has been observed, with $T_{rot} \sim 380 \pm 20$ K, and $T_v \sim 800$ K, despite the relatively high peak reduced electric field of the nanosecond pulser. Modeling of the nsec discharge pulse indicates that the relatively low E/n pulse reflections may be responsible for the vibrational loading observed in this condition.

In the pulser-sustainer discharge, very significant vibrational non-equilibrium is observed, with nitrogen $T_{rot} \sim 450 \pm 20$ K, and $T_v \sim 2000$ K. The effect of injection of various relaxant gas species was also examined. Carbon dioxide was observed to be an extremely fast relaxer of nitrogen vibrational energy, even at extremely low injection partial pressures $\sim0.25/300$ torr, which is as expected based on the extremely high V-V energy transfer rate. Injection of oxygen, up to 20% (nearly “synthetic air”), was observed to have no significant effect, as the V-V and V-T rates for N$_2$-O$_2$ are both very low compared with the $\sim2$ msec flow residence time between the injection and measurement location. Nitric oxide and hydrogen injection were both observed to partially relax the nitrogen vibrations, although each at slower time scales than observed for the case of CO$_2$. Injection of “cold” nitrogen results in no observable change to the vibrational energy; although the V-V exchange rate is quite high, this process results only in a transfer of N$_2$ vibrational quanta, but the energy remains “locked” in the vibrational mode.

Based on the measured vibrational and rotational-translational temperature, total energy in the flow was calculated for each of the injection cases described. Regardless of the degree of vibrational relaxation, in each condition the average total energy per molecule is conserved, within the uncertainty of the measurement. This indicates that
there is no significant storage of energy in the vibrational modes of relaxant species. Future work that could be performed in the Mach 5 plenum would involve high fidelity 3-D CFD modeling of the gas injection and mixing processes, which would enable more thorough comparison of the experimentally obtained results with known energy exchange rate coefficients.

7.2 Mach 5 Wind Tunnel Supersonic Nozzle

Utilization of USED-CARS in the supersonic nozzle for measurement of nitrogen vibrational temperature in both the supersonic free-stream as well as behind a bow shock created in the supersonic flow has been demonstrated. As has been discussed, the spectra captured in these locations demonstrate significant system capability, considering the great difficulty of performing CARS measurements in this very low number density flow (~1% of atmospheric number density at STP). As described, measurements in pure nitrogen, with no discharge actuation, display the ability to resolve the spatial location of the bow shock quite well. Furthermore, it was demonstrated that CARS measurements within ~300 μm of the cylinder surface could be performed.

Measurements in pure nitrogen with the pulser-sustainer discharge in operation reveal very little vibrational relaxation between the plenum measurement location and the supersonic nozzle exit, with vibrational temperatures within ~10% of the values measured in the plenum. Injection of carbon dioxide was also performed, and as for the no injection case, no additional vibrational relaxation is observed in the supersonic freestream than was observed in the subsonic measurement location. For either
condition, no relaxation was found to occur behind the bow shock; this is as expected since the recovery pressure in this location is still quite low.

### 7.3 Elevated Temperature PAC Reactor

As has been described, psec USED-CARS has been used to measure nitrogen first-level vibrational temperature as well as rotational-translational temperature in air and fuel-air mixtures excited in an elevated temperature plasma assisted combustion reactor. Non-equilibrium vibrational loading resulting from a nsec pulsed discharge fired at 10 kHz was examined in dry air at $T_0 = 300$ K and $P_0 = 100$ torr. Bursts of 40 pulses result in $T_v \sim 900$ K; increasing the number of pulses reveals an initial quasi linear vibrational loading regime up to $\sim 100$ pulses, after which vibrational temperature levels off near $T_v \sim 1250$ K.

The very high peak reduced electric field $(E/n)_{peak} \sim 500-600$ Td of the nsec discharge is quite inefficient at loading the nitrogen vibrational mode directly by electron impact. Modeling of the nsec pulsed discharge indicates that pulse reflections, which occur at relatively low $E/n \sim 20-30$ Td, due to plasma shielding, appear to be responsible for the vibrational loading levels observed. Vibrational energy relaxation was also measured for dry air $T_0 = 300$ and 500 K and $P_0 = 100$ and 300 torr. Vibrational temperatures are found to remain fairly constant until a few msec after the last pulse in the discharge, when the vibrational energy decay occurs more dramatically. Vibrational energy decay is found to occur more rapidly in the experiment than predicted by the kinetic modeling results.
Characterization of the rotational-translational temperature measurement capability of the CARS system in this configuration exhibits significant ability; collections of 60 spectra captured at both 300 K and 500 K demonstrate both accuracy and precision within ~3-4% of the temperature values measured directly by thermocouple. Measurement of $T_{\text{rot}}$ of air and fuel-air mixtures excited by bursts of 50 pulses in the nsec discharge was performed for $T_0 = 500$ K, $P_0 = 100$, 200, and 300 torr (for C$_2$H$_4$-air and CH$_4$-air) and $P_0 = 100$ torr (for H$_2$-air). Fuel-air mixtures of ethylene and methane at $\varphi = 0.09$, 0.18, and 0.36, and hydrogen at $\varphi = 0.1$, 0.2, and 0.3 were examined. For a given fuel equivalence ratio and mixture pressure, $T_{\text{rot}}$ was found to remain approximately constant between 4 μsec to 1 msec after the last pulse in the burst. Furthermore, for a given fuel, changing equivalence ratio and pressure had no detectable impact on temperature. Air plasma discharge indicated a temperature rise of ~30 K, while the methane-air and ethylene-air mixtures resulted in ~50 K and ~70 K temperature increases respectively; the hydrogen-air mixture falls between the methane and ethylene mixtures.

Further investigation in hydrogen-air mixtures was performed at $T_0 = 500$ K, $P_0 = 92$ torr, and $\varphi = 0.4$. Bursts of 50, 99, and 120 discharge pulses at 10 kHz were used to excite the mixture. For the first two conditions, increase in the equilibrium temperature is observed, up to peak $T \sim 700$ K for the 99 pulse case, with no ignition occurring. For 120 pulses, ignition is observed with peak temperature of $T \sim 1250$ K. Results for each of these three cases are compared to results from a 0-D fuel-air chemistry model; the measured ignition delay time and peak temperature for the
120 pulse condition are shown to agree quite well with the modeling predictions. The model slightly over-predicts the temperature immediately after the end of the discharge burst for the two non-ignition cases, with a temperature excess of ~50 K for both of these conditions.

7.4 Bare-Metal Electrode Single-Pulse Discharge

CARS diagnostic work, utilizing the BoxCARS phase matching geometry, in the bare-metal electrode single-pulse discharge system was performed at $T_0 \sim 300$ K, $P_0 \sim 100$ torr, in both nitrogen and dry air, at a variety of discharge loading conditions. Nitrogen vibrational distribution function is measured versus time delay after the beginning of the discharge current pulse, and as shown, vibrational levels up to $v = 9$ are detected. From the VDFs, first-level vibrational temperature and total vibrational quanta are inferred. For the high current discharge cases in nitrogen and air, peak vibrational temperatures are $T_v \sim 2700$ K and 2400 K, respectively, significantly higher than the $T_v \sim 1000$ K measured immediately after the end of the discharge pulse. Likewise, the peak value measured for the vibrational quanta is ~2-4 times greater than the value measured immediately after the end of the discharge pulse. In both nitrogen and air, both the vibrational temperature and quanta peak between ~10-100 μsec after the nsec duration pulse, which is unexpected.

Initial nsec discharge modeling has failed to capture this phenomenon, and while additional experiments and modeling need to be performed, it is very likely that the increase in vibrational quanta can be attributed to collisional quenching processes of
electronically excited nitrogen such as $\text{N}_2(\text{A}^3\Sigma) + \text{N}_2(\text{A}^3\Sigma) \rightarrow \text{N}_2(\text{C}^3\Pi) + \text{N}_2(\text{X}^1\Sigma,v)$. It is stressed, however, that additional modeling analysis, and certainly additional experimental studies, will be needed to fully understand this effect. Time resolved measurements of certain important species, such as nitrogen atoms and molecular nitrogen excited electronic states, may indicate where the energy from the discharge pulse exists for the $\sim 10^+ \mu$sec between the end of the discharge and the time at which it begins to appear in the nitrogen molecular vibrations.

The CARS system performance for measurement of rotational-translational temperature was characterized by capturing and fitting 80 spectra in 100 torr room temperature air. System performance for the current configuration is shown to be particularly good, with accuracy and precision within $\sim 2\%$ of the room temperature value. Measurement of rotational-translational temperature was performed versus time delay for the same five discharge loading conditions mentioned above. As the results of this analysis have shown, $T_{\text{rot}}$ values reach their maximum near the same delay times as the vibrational temperature and vibrational quanta. For all cases, except the high loading condition in air, the peak temperature is found to scale approximately linearly with the total discharge pulse energy, up to a peak of $T_{\text{rot}} \sim 550$ K for the high loading condition in pure nitrogen.

For the high loading case in air, peak temperature of $T_{\text{rot}} \sim 850$ K is observed, and it is noted that the time delay at which the temperature begins to climb toward this peak, $\Delta t \sim 100 \mu$sec, corresponds quite closely with the time at which vibrational quanta for this condition begins to fall off sharply. It is clear from this analysis that some species
present in the air discharge at the high pulse energy condition is working to effectively relax the nitrogen vibrational energy. It is suspected that oxygen atoms are responsible for this, however modeling of these discharge conditions will need to be performed to investigate this further. Viewing the visible emission from the discharge, the two high loading pulse conditions (one in N₂ and one in air) clearly exhibit a different characteristic emission spectra than observed in the three lower discharge current conditions (significant orange-yellow glow observed which is not seen in the lower loading cases). Highly recommended future work would be to perform time-resolved emission spectroscopy of these discharge conditions, to examine which species or excited states may be responsible for the behavior observed.
References


[6] Eckbreth, A.C., Laser Diagnostics for Combustion Temperature and Species,


[40] Doyennette, L., and M. Margottin-Maclou, "Vibrational Relaxation of NO(v=1) by
NO, N2, CO, HCl, CO2, and N2O from 300 to 600 K, "J. Chem. Phys.," vol. 84, no. 12, pp. 6668-6678, 1986.


