The Development and Characterization of Femtosecond Laser Velocimetry Methods

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Abstract

Measurements in high speed wind tunnels and reactive testing facilities require remote, non-perturbing, high-fidelity diagnostic tools. Femtosecond Laser Electronic Excitation Tagging (FLEET) is a recent addition to ultrafast laser diagnostics for fluid dynamic measurements. FLEET is uniquely suited for making difficult measurements: in its most basic form, it requires only a nitrogen-containing flow, a laser system, focusing optics and a gateable camera. The further development of FLEET as a velocimetry tool is presented in this work.

Three aspects of FLEET velocimetry are examined in this work. The first extends FLEET from primarily nitrogen and air environments to flows with argon, oxygen, helium, carbon dioxide, methane, water vapor and freon mixtures. Time-resolved and time-integrated emission are captured to study the temporal behavior of the signal, and spectra are gathered to study molecular and atomic species present in the dynamics associated with FLEET. A zero-dimensional kinetics model is developed to study excited species decay following femtosecond laser excitation in argon-nitrogen and oxygen-nitrogen mixtures. Argon gas, which is frequently used in arcjet facilities, shock tubes, and plasma experiments, enhances the signal and lifetime of FLEET emission when combined with nitrogen. Oxygen has a non-monotonic quenching effect on the signal when it is combined with nitrogen gas.

Secondly, experiments are performed in well-developed subsonic turbulent flow and acoustic measurements are made of the laser pulse to determine the effects of laser heating on the gas. Turbulence statistics are computed for different sets of optical parameters and compared to expected values. Strong laser focusing and high pulse energies appear to perturb the flow enough to mask small features, and weak magnification also introduced artificial correlations into the flow.

Lastly, outcomes from the previous two efforts are synergized to develop FLEET as a tool for near wall measurements, specifically to resolve the viscous sublayer in supersonic flows for skin friction characterization. To minimize flow perturbation, tagging is performed
using less than a millijoule of energy per pulse at 400 nm, and magnification and gain are chosen to avoid intensity saturation or cutting off any of the measured region.
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The projects in this thesis began in a time when the aerospace industry is renewing its efforts towards enabling efficient super- and hypersonic flight. The study of skin friction, once a periphery topic in the field, now has its own dedicated funding, and laser diagnostics have become more relevant than ever. I was privileged to come to Princeton University at this time to apply laser diagnostics to aerospace problems, and to be under the mentorship of my advisers Dick Miles and Julia Mikhailova.

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Chapter 1

Introduction

Since the 1960s, laser diagnostics have been implemented in a wide range of fields including combustion, fluid dynamics, plasmas, geology and even art history. Their advantages are multifold: laser-based measurements can be conducted in-situ, remotely, are generally non-perturbing, have high temperature capability, good temporal resolution, and are spatially precise. Challenges to obtaining temporally-resolved, spatially precise measurements using laser methods typically fall into the categories of obtaining optical access, achieving good signal strength and cost of equipment. This chapter presents an introduction to different types of fluid diagnostics, motivates the use of laser-based diagnostics, and introduces the femtosecond laser method employed throughout this thesis. Chapter 2 communicates the applicability of femtosecond laser diagnostics to different gas mixtures. Limitations and optimization of the diagnostic is studied in Chapter 3, and wind tunnel experiments are detailed in Chapter 4.

1.1 Motivation for Advanced Fluid Diagnostics

Aerodynamics applications are the primary focus of this work, although it is important to note that fluid diagnostics have a wide variety of applications. Qualitative and quantitative methods for pressure, temperature, velocity, species concentration measurements and
flow visualization are necessary to understand fluid behavior, especially small-scale, rapidly-evolving structures that have an outsized role on the overall fluid dynamics. Computational models, which often face limitations due to processing power, require experimental data for validation. The difficulty of procuring in-flight data has motivated the construction of ground-level test facilities which can mimic the enthalpy and Mach number of flight conditions and allow the installation of aircraft components, model geometries and full-scale structures. Experimental testing is performed in a wide variety of test facilities. Many of the earliest subsonic wind tunnels were built in the 1900s to test aircrafts for World War II, and they continue to be in use. Beyond subsonic flow, transonic tunnels operate in the Mach number range of 0.8 to 1.2. Notable transonic facilities include the National Transonic Facility, a high-pressure, cryogenic, closed-circuit tunnel that flows pure nitrogen gas, and the Transonic Dynamics Tunnel [10, 33, 31, 30], which uses a combination of air and freon to create high Reynolds number flow conditions. Supersonic ($M > 1$) wind tunnels typically come in two varieties: indraft tunnels may use a vacuum chamber downstream of the test section to pull air from the atmosphere, which serves as the gas reservoir, and blowdown tunnels rely on flow from a high-pressure chamber upstream of the test section. Flow speed in the test section is defined by the nozzle’s area ratio and plenum temperature. A great number of super- and hypersonic wind tunnels are situated across the world. Ludwieg Tubes are supersonic-to-hypersonic blowdown tunnels that operate by using a diaphragm to separate a “dump tank”, or supply, from the test section. Flow is started when the diaphragm ruptures and a nonsteady expansion wave propagates upstream into the driver tube and nozzle. The Arnold Engineering Development Complex (AEDC) [91] in Maryland operates the Hypervelocity Wind Tunnel 9, a hypersonic facility that can generate Mach numbers of up to Mach 14. Typical run times in these tunnels range from tens of milliseconds to a couple of seconds, creating challenges for data collection. Access to these facilities, including the installation and operation of sensors, can be difficult. Often, simultaneous measurement of multiple properties are desired but not easily obtained. Traditional methods include pitot
probes for pressure measurements, thermocouples for temperature, hot wire anemometry for velocity, and schlieren imaging for flow visualization. The latter two are elaborated below.

1.1.1 Hot Wire Anemometry

Constant temperature hot wire anemometry (CTA) is a well-established technique for measuring velocities and fluctuations in a wide range of flows. It is characterized by a high frequency response on the order of kilohertz, high signal-to-noise ratio, and an ability to be reliably used in subsonic to supersonic conditions. The simplest sensing element consists of a wire spanned across two prongs and placed orthogonal to the flow direction. The configuration of an anemometer is the Wheatstone bridge circuit, which has a total of four resistors across four arms: two fixed resistors $R_1$ and $R_2$, a variable resistor $R_3$ and the probe, $R_4$ (Figure 1.1). The bridge seeks to balance the ratio between the two sets of resistors. When the sensor is inserted into incoming flows, heat from the wire will be dissipated into the fluid and the resistance of the probe will change. To balance that change in resistance, an amplifier detects the difference and applies feedback control to increase or decrease the current through the sensor, thus heating up the sensor through the Joule effect and causing a change in the bridge voltage. This bridge voltage is directly related to a change in velocity. Hot wire measurements offer the advantage of analog voltage outputs and high temporal resolution, depending on the sensor type. Common industrial anemometers include a network of signal conditioners and amplifiers in addition to the basic Wheatstone circuitry. The simplest probe uses a single sensing element to resolve

![Figure 1.1: Wheatstone bridge circuit for HWA](image-url)
one-dimensional flow. Because a single-wire probe has no directional sensitivity, this particular method is not appropriate for resolving velocity components. Calibration is performed using King’s Law, \( E^2 = A + BU^n \), which is derived by solving for wire heat loss from forced convection into the fluid. Voltage measurements \( E \) are initially taken in well-characterized flows at several different velocities to determine the constants \( A \) and \( B \). The calibration relation can then be used for that particular hot wire to extract velocity from subsequent measured data. More complex hot wire probes have multiple prongs and wires in different orientations in order to resolve different components of flow velocity. Simultaneous spatial measurements can be conducted with multiple probes in an array configuration. Fiber film probes are sturdier than conventional single-sensor wire probes, and used in liquids and gases with large particulates. Hot wires do not allow for Lagrangian streamwise measurements, so Taylor’s hypothesis of frozen turbulence is employed in this thesis to compare FLEET measurements along the transverse direction to hot wire measurements at the pipe axis over time. Taylor’s hypothesis relies on the assumption that a large mean flow exists with respect to the turbulent fluctuations and can therefore be used as the convection velocity [133]. When this is valid, the time derivative of velocity fluctuations in the flow is considered proportional to its spatial derivative in the streamwise direction and a comparison between the two can be made.

1.1.2 Schlieren Imaging

Schlieren and shadowgraphy rely on changing densities in transparent fluids to visualize flow structures. Snell’s Law dictates that a light ray passing through an inhomogeneous medium will be deflected from its original path. Density gradients in the measurement region lead to deflections of light rays, which can then be visualized on a screen. The shadowgraph technique requires only a light source and viewing plane onto which an image will be projected, creating a shadowgram. It is the simplest form of imaging nonuniform densities in a medium. In a basic schlieren setup, a lens first collimates a point light source
to pass through the measurement region and a second lens decollimates the light and focuses it onto a knife edge, which is used to increase the contrast of the image. The placement of the knife edge causes rays refracted onto it to be blocked, and rays deflected in the opposite direction to illuminate a screen placed beyond the knife edge at a location determined by the thin lens equation \(1/f = 1/d_i + 1/d_o\), where \(f\) is the focus of the decollimating lens, \(d_o\) is the distance of the object to the decollimating lens, and \(d_i\) is the distance of the image on screen to the lens. The schlieren image can be related to the gradient of the index of refraction in the direction orthogonal to the knife edge. Figure 1.2 is taken with a USB 2.0 Mightex Monochrome 8/12bi CCD camera and depicts Mach disks at the exit of an aerosol duster jet impinging on a flat surface. A diode light source is used in combination with two D=75 mm, f=400 mm lenses to create this image. Schlieren imaging is used in Chapter 4 to determine the flow Mach number in various setups, and to determine the location of shock/boundary layer interactions reported in [20].

1.2 Optical Diagnostics

While HWA and other probe- and sensor-based diagnostics have been widely utilized in the past and provide much of current fundamental understanding of fluid phenomena, they are intrinsically intrusive and unable to provide accurate measurements of difficult flow features, such as small scale structures and boundary layer fluctuations, without changing the flowfield of interest. The installation of mechanical sensors is not possible in certain cases, due to extreme flow conditions or flow blockage. Recent developments towards less-intrusive fluid diagnostics include pressure- and temperature-sensitive
paints for making surface measurements [87, 138, 47], Rayleigh scattering velocimetry [48], laser-induced thermal acoustics [35], and Laser Doppler anemometry (LDA) [51], the latter which was applied to study freestream velocity fluctuations in the NASA Langley 0.3-meter Transonic Cryogenic Tunnel. A typical LDA experiment requires laser focusing optics, photodetectors, light-scattering seeding particles and signal processing components. Techniques such as LDA and particle image velocimetry (PIV) have and continue to play a large role in quantifying flowfields. PIV obtains two sequential images of velocity vectors in a flow by capturing laser-scattered light off of seeded particles. It can be utilized in stereoscopic and tomographic applications, giving volumetric measurements of the flowfield of interest. Another technique, Doppler optical coherence tomography (DOCT) has been used to characterize velocity profiles using low-coherence interferometry to provide information on the location, density and speed of seed particles in subsonic water [57]. With these seeded techniques, a variety of challenges arise from using seed particles. There is a trade-off between seeding with larger particles, since larger particles scatter more light, and using particles that are small enough to track the flow. Even when they are small, seed particles may not always follow the flow, especially in near-wall regions, near shock waves, or in combustion settings.

Unseeded, laser-based velocimetry methods are becoming increasingly popular as a result of improvements in laser technology and increased demand for more robust gas diagnostics. A number of methods, including scattering techniques and molecular tagging, take advantage of existing particles in the air to produce measurable signals from a standoff distance. These are advantageous compared to their seeded counterparts since homogeneous seeding is difficult to accomplish and the presence of particles may alter the flowfield. Molecular tagging methods are especially desirable in air-breathing testing facilities that mimic flight conditions. Laser-induced fluorescence methods are one class of laser-based velocimetry techniques, and they include vibrationally-excited nitric oxide monitoring (VENOM) [117] and Raman excitation and laser induced electronic fluorescence (RELIEF) [96], both of which require an excitation pulse to create the active molecular tracers, followed by an interrogation
pulse. Stimulated Raman techniques, which include coherent anti-Stokes Raman scattering (CARS) variations and stimulated Raman gain spectroscopy, are frequently employed to measure species concentration and temperature in both mild and harsh environments. Using Boltzmann statistics, it is possible to analyze the rovibrational populations of molecules to determine temperature. When temperature is known, species concentration can be found by measuring the concentration of populations in one energy state. Optical, non-seeded methods range from the simple (NO-LIF, when NO is naturally generated by combustion) to complex setups (hybrid fs-ps CARS).

The advent of ultrafast lasers with pulse durations on the pico- and femtosecond timescale allows for near-instantaneous probing of the flowfield of interest. The unique combination of high power and short pulse duration can excite atoms and molecules without inducing a cascade reaction. This is also advantageous for investigating reactive gases undergoing rapid kinetic processes such as that found around a body in hypersonic flow. The next section introduces one of the simplest, yet most robust non-seeded, ultrafast laser methods for gaseous flows.

1.3 Femtosecond Laser Electronic Excitation Tagging

Femtosecond Laser Electronic Excitation Tagging (FLEET) [94] was originally developed in the Applied Physics Group at Princeton University in 2010. FLEET relies on a multiphoton process to produce long-lived emission from excited nitrogen species for velocimetry and thermometry applications. Focused femtosecond laser pulses dissociate molecular nitrogen into atomic nitrogen, which produces long-lived fluorescence as the atoms recombine into excited electronic states of molecular nitrogen. Ultrafast laser pulses have intensities that are orders of magnitude higher than their nanosecond equal-energy counterparts, and femtosecond pulses in particular have a pulse duration that is much shorter than the collision time at atmospheric conditions. Because of this, avalanche breakdown processes do not need to be
considered in the excitation physics. Modern femtosecond lasers are turn-key systems often composed of a regenerative amplifier coupled with a titanium sapphire (Ti: Sa) oscillator, and the entire system, excluding liquid coolers, fits onto a single optical table unit.

Of primary interest for the FLEET radiation is the first positive system of molecular nitrogen, the transition from the nitrogen B state to the A state. This emission, the Lewis-Rayleigh afterglow, is a visible fluorescence that is swept with the flow and can be tracked with a camera. The detectable nitrogen first positive system \( (B^3\Pi_g - A^3\Sigma_u^+) \) creates emission in the 500-950 nm range, whereas the shorter-lived second positive system \( (C^3\Pi_u^+ - B^3\Pi_g^+) \) emits primarily in the 300-450 nm range and overlaps heavily with the first negative system \( (N_2^+ (B^2\Sigma_u^+ - X^2\Sigma_g^+)) \).

\[
N_2 + h\nu \rightarrow e^- + N_2^+ \quad [1.1]
\]

\[
e^- + N_2^+ \rightarrow N + N \quad [1.2]
\]

\[
N(^4S) + N(^4S) + M \rightarrow N_2(^5\Sigma_g^+) + M \quad [1.3]
\]

\[
N_2(^5\Sigma_g^+) + M \rightarrow N_2(B^3\Pi_g) + M \quad [1.4]
\]

\[
N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) \quad [1.5]
\]

Equations 1.1–1.5 describe the proposed mechanism by which the ionization and dissociation of molecular nitrogen produces the first positive emission through a long-lived recombination process. Evidence for this mechanism is found in the preferential population of the \( v' = 11 \) level. The strong transition lines corresponding to the \( N_2(B^3\Pi_g, v' = 11) \) state lends credence to the theory that \( N(^4S) \) initially recombines into a predissociative state \( N_2(^5\Sigma_g^+) \) [6, 45, 83].
The Lewis-Rayleigh afterglow intensity is found to be proportional to the square of the ground state nitrogen atom density, \( N(^4S) \), using mass spectrometry over a range of temperatures and pressures [16]. Further work concluded that the same excitation mechanism must be responsible for populating the nitrogen B-state, since the relative intensities of all the first positive bands remained constant during their decay over 140 seconds [141]. Possibilities for producing this population also included excitation by metastable nitrogen molecules, but [141]'s work determined that the lifetime of the constant decay far exceeded the lifetime of metastable states, thereby ruling out that mechanism. [12] and [16] proposed a collisional recombination process involving the formation of a \( N_2(5\Sigma_g^+) \) state, as well as other intermediate states such as \( N_2(Y^3\Sigma_u^-) \) that eventually form B-state molecules. Some debate remains as to whether the \( N_2(5\Sigma_g^+) \) state is weakly-bound [12] or stable [16], but there is general agreement that following nitrogen atom recombination into \( N_2(5\Sigma_g^+) \), the predissoociative state undergoes intersystem collisional transfer of excitation to selectively populate certain vibrational levels of the nitrogen B state.

The previously mentioned observations together suggest that the recombination of nitrogen atoms is the rate-limiting step in the FLEET process, and therefore responsible for the long-lived emission. Figure 1.3 shows the electronically excited molecular nitrogen levels, including where the \( N_2(5\Sigma_g^+) \) state crosses \( N_2(B^3\Pi_g) \) at \( v = 11 \). Representative transition lines are drawn to show the first and second positive emission.

Using the nitrogen second positive emission, temperature measurements can also be made. Under atmospheric conditions, rotational-translational relaxation of molecules occurs in about 1 ns, allowing rotational temperature from rotational spectra to be directly related to gas translational temperature [42]. While the prospect for simultaneous velocity, temperature and perhaps even density measurements (using Rayleigh scattering) is alluring, this thesis focuses only on the further development of FLEET velocimetry.

A plethora of applications and variations of this method have since emerged as FLEET was adopted by multiple other facilities across the country. At the time of writing, FLEET
Figure 1.3: Nitrogen potential energy diagram, adapted from [88]. The dashed line corresponds to the $N_2(^5\Sigma_g^+)$ level.
can no longer claim to only use a non-resonant multiphoton excitation process, nor limited to femtosecond excitation pulses. The fundamental wavelength has been frequency doubled and tripled to produce tagging at higher efficiencies. Recently a resonant version of this process, called Selective Two-Photon Absorptive Resonance FLEET (STARFLEET) [68] has been developed. STARFLEET uses over an order of magnitude lower pulse energy at the same laser repetition rate for tagging (1 kHz), at the cost of increasing the optical setup complexity because it relies on producing and transmitting UV wavelengths. Improvements in the frequency response (up to 100 kHz) of these nitrogen tagging velocimetry methods have also been made with the use of a picosecond laser instead of a femtosecond laser, resulting in a technique called Picosecond Laser Electronic Excitation Tagging (PLEET) [69].

1.3.1 Calculation of Velocity

Velocity is determined in a straightforward manner by dividing the measured displacement by the time delay. Two position images are required for each velocity measurement - a initial position and a displaced position. It is recommended to collect both images in the same frame by using the camera’s "burst mode" capability, where the shutter opens multiple times in rapid succession to follow the fluorescence produced by the tagged region as it moves with the flow. Burst mode flow profiles increase the robustness of FLEET in facilities that suffer from rapid perturbations or vibrations, which can affect the beam alignment and position. These multiple-capture images can also serve as a benchmark for other velocity measurements in the case where the existence of significant structural perturbations is unknown. Burst mode imaging is unsuitable if the flow velocity is too low to resolve the displacement between sequential emission frames.

Raw images of FLEET emission typically take the shape of lines or spots. The emission is brightest along the centerline of the laser axis and produces a Gaussian-type profile in the radial direction. In the case of lines, a Gaussian or Lorentzian fit may be applied to each transverse position along the length of the line, and the center of that fit gives the
Figure 1.4: FLEET emission spots in a free jet position. For points, a two-dimensional Gaussian fit is used in combination with a least-squares optimization algorithm to account for elipsoidal emission. The time delay is given by the camera delay, which is typically on the order of several microseconds for this thesis work, plus one half of the camera gate, or exposure time. The camera gate is usually much less than the delay time, between several hundred nanoseconds and one microsecond.

Figure 1.4 gives an example of FLEET images that can be used to calculate velocity. The four panels are taken over a supersonic open-jet flow (600 m/s), where the flow direction is from top to bottom and the delay time is labeled. Each image is the average of over 700 shots, taken at delays of 0, 10, 15, 22 µs respectively, and the gate time is 1 µs. Focusing is performed with a f=25 cm plano-convex lens.
1.3.2 Uncertainty Analysis

Errors in the displacement measurements may stem from three sources: the experimental apparatus, experimental conditions and data processing. Specifically, experimental apparatus error is frequently caused by the amplification of background noise by the intensifier. Intensifier modules may enhance sensitivity variations in a camera sensor and boost signals in a nonlinear fashion. A flat-field correction may be applied by dividing images by a map of sensitivity variations across the CCD and removing voltage bias through background subtraction. Uncertainties in the data processing step can be attributed to the fitting procedure. Because the displacement variation is much larger than any variations in the initial line position and the relative signal-to-noise of the initial line image is high, we approximate the measurement uncertainty only as a function of final line position and timing uncertainty. Jitter from the laser trigger pulse to the camera is less than a nanosecond and can be safely disregarded, while timing errors introduced by the signal generation system has an upper limit of 35 ns due to the length of the cables. The scale factor for the images is calibrated by imaging a ruler. Uncertainties in determining the pixel resolution result in errors of up to several microns per pixel and may be accounted for in the overall displacement error calculation. Error in the velocity calculation can be derived from the general equation for uncertainty propagation for some function $y$ that is dependent on variables $x_1, x_2, ..., x_n$ (Equation 1.6) [80]. Equation 1.7 describes velocity uncertainty from measurement uncertainties in the initial line position $x_0$, final line position $x_f$, and timing $\Delta t$.

\[
y = f(x_1, x_2, ..., x_n)
\]

\[
\delta y = \sqrt{\left(\frac{\partial f}{\partial x_1}\delta x_1\right)^2 + \left(\frac{\partial f}{\partial x_2}\delta x_2\right)^2 + ... + \left(\frac{\partial f}{\partial x_n}\delta x_n\right)^2}
\]  
[1.6]
\[ V = f(\Delta x, \Delta t) = \frac{\Delta x}{\Delta t} \]

\[ \delta V = \sqrt{\left( \frac{\delta(\Delta x)}{\Delta t} \right)^2 + \left( \frac{\Delta x \ast \delta(\Delta t)}{\Delta t} \right)^2} \approx \frac{\delta(\Delta x)}{\Delta t} \]  

[1.7]

\[ \Delta x = x_f - x_0 \]  

[1.8]

\[ \delta(\Delta x) = \sqrt{(\delta(x_f))^2 - (\delta(x_0))^2} \]  

[1.9]

It is important to consider the trade-off between using a longer camera gate width and a shorter one. A longer gate will allow more light to reach the aperture, but at the cost of increased error. Typically for longer delays, the time delay used to calculate velocity is simply the time between the arrival of the pulse and the time corresponding to the middle of the exposure gate time interval, as represented by \( \Delta t = \frac{1}{2}g + d \), where \( g \) is the camera gate and \( d \) is the delay, assuming that the fluorescence intensity is constant during the exposure time. But when that gate is on the order of microseconds, approaching the delay time of the camera, the gate width becomes nontrivial with respect to the delay and methods to evaluate the total delay time should be reevaluated. The timing uncertainty in this thesis is approximated by adding the camera gate width to the overall timing jitter in the measurement apparatus: \( \delta(\Delta t) \approx g + 35 \text{ ns} \).

### 1.4 Motivation for Skin Friction Measurements

Skin friction, or wall shear stress, is critical to the performance of aerodynamic vehicles. Approximately 40-50\% of the total drag on a commercial aircraft flying at cruise conditions can be attributed to shear drag, and this number increases with increasing heat transfer from the boundary layer to the surface [151]. Any fractional reduction of this skin friction drag would
translate directly to substantial fuel savings and contribute to the design of more efficient, capable aircrafts. A knowledge of the skin friction distribution is also useful as an input for flow control. Turbulent shear layers are a ubiquitous but not well understood component of flow around and through high-speed transport vehicles. A thorough understanding of the physics in compressible turbulence and the ability to develop accurate models are necessary for the advancement of high speed aircrafts. It is currently not feasible to simulate turbulent boundary layers in full detail so simplifications, such as incompressible flow assumptions, are made to minimize computational resources. Numerical models furthermore require accurate experimental data for verification and validation. A rich history of skin friction measurement techniques have existed since the 1870s, when Froude [50] created a moveable surface friction measurement device for water. Direct sensors and probes are typically complex to fabricate, sensitive to vibrations and thermal conditions, inherently intrusive, and lacking in the spatial and temporal scales necessary to characterize turbulent behavior. Measuring instantaneous values of streamwise velocity in the shear region can lead to characterization and insight on the drag imposed by near-wall turbulence. The removal of near-wall turbulent fluctuations below $y^+ = 10$ can lead to large drag reductions of up to 35% at $Re_\tau = 10^5$ [67]. Hot wire anemometry, detailed in Section 1.1.1, has been used to resolve the viscous sublayer in a flat plate turbulent boundary layer, but required the sensing element length to be less than 20-25 wall units in order to resolve the turbulence intensity, kurtosis and skewness factor [84]. Furthermore, [84] used subminiature hot wire probes with wire lengths as short as 50 $\mu$m and still observed spatial averaging of higher frequency motions. It is desirable to both avoid the spatial averaging effects of intrusive probes, as well as demonstrate a high-fidelity method that can replicate accepted empirical scaling laws. To study supersonic boundary layers, it is first important to understand scaling laws. In order to collapse the velocity profiles in the classic inner and outer layer coordinates, the data must first undergo a compressibility transformation, specifically a normalization by a velocity scale derived from the wall shear stress and local density [128].
1.4.1 Empirical and Semi-empirical theories

According to Morkovin’s Hypothesis [99], the dynamics of a compressible turbulent boundary layer resemble that of the incompressible for Mach numbers less than 5. It has important consequences for the scaling of flow parameters \(Re, M, t\) and \(L\), the Reynolds number, Mach number, turbulent time scale and length scale, respectively. The hypothesis states that scaling properties such as correlation coefficients and ratios of turbulence quantities to mean flow values are approximately the same for supersonic flows as for slower flows. Compressibility effects are accounted for in the mean density variations since the RMS density fluctuation is assumed to be small compared to the mean density. Departure from the validity regime is expected if compressibility effects are strong. When Morkovin’s Hypothesis is invoked, mean velocity transformations of compressible boundary layers follow the conventional Law of the Wall.

Law of the Wall

The law of the wall is a commonly accepted semi-empirical model for turbulent flows that introduces a non-dimensional velocity \(u^+ = \frac{u}{u^*}\) as a function of dimensionless distance \(y^+ = \frac{u* y}{\nu}\) from the wall. In the viscous sublayer, if the viscous stress dominates, the pressure gradient is typically ignored and the molecular shear stress is large compared to the Reynolds shear stress, then the velocity profile follows the linear law \(u^+ = y^+\) and assumptions in the near-wall region \(\left(\frac{d\nu}{dy}\right) \gg \rho u'v'\)) allow one to write the shear stress in the viscous sublayer as a function of the velocity gradient. A single characteristic Reynolds number is associated with the sublayer and compressibility effects can be ignored if they are taken into account in the density and viscosity terms in the transformation. At the wall, the no-slip condition requires that all velocities are zero. The velocity gradient in the viscous sublayer \(y^+ \leq 5\) can be directly related to shear stress through Equation 1.10, where \(\mu\) is viscosity and \(\tau_w\) is the wall shear stress. There is general agreement that this formula gives an accurate estimate
of skin friction in the region up to Mach 4.5 under zero heat transfer assumptions.

$$\tau_w = \mu \left( \frac{du}{dy} \right)$$  \hspace{1cm} [1.10]

Outside of this region, the buffer layer $5 < y^+ < 30$ transitions the linear law to the region governed by the logarithmic law $u^+ = \frac{1}{\kappa} ln(y^+) + C^+$. The buffer or overlap layer can be logarithmic if the pressure gradient is small, and can also take a power law form. There is no single scaling law that describes the velocity profile in the supersonic boundary layer since a different transformation is required for the inner and outer regions.

A number of theories have been developed to transform the mean flow. These theories are typically based on simplifications introduced by the Prandtl boundary layer equations, which are solutions to the simplified Navier-Stokes equations, the von Karman momentum integral method, and other differential approaches [118]. The Van Driest II theory transforms supersonic compressible turbulent boundary layer velocities into an incompressible logarithmic law [137]. Spalding and Chi established a semi-empirical relationship between the drag coefficient and Reynolds number when both are multiplied by a Mach number- and temperature ratio-dependent factor, $F_C$ and $F_R$, respectively [130, 29]. Sommer and Short examined skin friction with heat transfer between Mach 2.8 to 7.0 [129]. Coles looked at turbulent skin friction in adiabatic flow and devised a transformation, called the law of corresponding stations, to generalize the compressible two-dimensional boundary layer flow over a smooth wall into an incompressible form [32]. He relates two local friction coefficients for compressible ($C_f$) and incompressible ($\overline{C_f}$) flows. Huang and Bradshaw constructed a model for the mean velocity profile for isothermal and adiabatic walls [63]. This non-exaustive list of theories are summarized in Table 1.1.
### Table 1.1: Supersonic Boundary Layer Theory

<table>
<thead>
<tr>
<th>Approach</th>
<th>Algorithm</th>
<th>Validity Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van Driest II [137]</td>
<td>$\tau_w = \frac{D\mu_\infty}{K} \cdot \frac{d}{dx} \left[ J a^2 \exp \left( \frac{a}{A} \sin^{-1} \frac{B}{\sqrt{B^2 + A^2}} \right) \right]$</td>
<td>$D = \exp(-FK)$</td>
</tr>
<tr>
<td></td>
<td>$a = KU_e/\sqrt{\frac{T_w}{\rho_w}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mach 0 - 15, $0.05 \leq \frac{T_w}{T_e} \leq 30$</td>
</tr>
<tr>
<td>Spalding and Chi [130, 29]</td>
<td>$\frac{T_w}{T_e} = 1 + b z - a^2 z^2$</td>
<td>$a^2 = \frac{1}{2} \left( \frac{(\rho - 1)M^2}{\rho} \right)$ - 1</td>
</tr>
<tr>
<td></td>
<td>$b = \left( \frac{1 + \frac{1}{2} \left( \frac{(\rho - 1)M^2}{\rho} \right)}{T_w/T_e} \right) - 1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mach 2.8 - 7.0</td>
</tr>
<tr>
<td>Sommer and Short [129]</td>
<td>$\frac{T_w}{T_e} = 1 + 0.035 M_1^2 + 0.45 \left( \frac{T_w}{T_e} - 1 \right)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>compared with Mach 0 - 15</td>
</tr>
<tr>
<td>Coles [32]</td>
<td>$C_f Re_\theta = \frac{\rho \mu_\infty u_\tau}{\rho u_\tau} C_f Re_\theta$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mach 2 - 4.5</td>
</tr>
<tr>
<td>Huang and Bradshaw [63]</td>
<td>$\frac{U}{u_\tau} = \frac{1}{R} \sin \left( \frac{RU}{u_\tau} \right) - \frac{A}{u_\tau} \left[ 1 - \cos \left( \frac{RU}{u_\tau} \right) \right]$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A = q_w/\tau_w$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$B = 2c_p T_w/Pr_l$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R = u_\tau/\sqrt{B}$</td>
<td></td>
</tr>
</tbody>
</table>

**Curved Surfaces**

The focus of this section is boundary layers over curved surfaces, which has many applications in aerodynamic situations. In general, the effects of curvature on boundary layer flows is small when $\delta/|R| \ll 1$, where $R$ is the radius of curvature of the wall and $\delta$ is the boundary layer thickness. Curvature in the streamwise direction creates pressure variations that lead to instabilities including Tollmien-Schlichting waves and Görtler vortices, which eventually affect laminar-to-turbulent transition within the boundary layer. Streamwise curvature in the concave direction is found to increase the rate of heat transfer in supersonic turbulent boundary layers even when pressure is held constant along the wall [135]. Flows entering a curved wall section can develop new large-eddy structures that were not previously present in the flow, as the curved surface can amplify structures in the wall-normal direction. This leads to amplification of pre-existing turbulence in the flow through inciting and increasing longitudinal vortices in the flow. When the streamwise curvature is in the convex direction, there is a pressure decrease and general attenuation of the pre-existing turbulence [62].
However for the case of transversal curvature, the Navier-Stokes equations can effectively be reduced to a 2D planar case. A Mangler transformation may be used to reduce the axisymmetric boundary-layer equations to plane boundary-layer equations. If a cross section of a body is taken at some point along its rotating axis in the $r-\theta$ plane, the transformation is given by Equation 1.11 where $r_\perp$ denotes the local radius of curvature, $y$ is perpendicular to the curved surface, $x$ is the arc length, $l$ is the reference length [90, 118].

\[
\begin{align*}
\bar{x} &= \frac{1}{l^2} \int_0^x r_\perp^2(x)dx \\
\bar{y} &= \frac{r_\perp(x)}{l} y \\
\sin(\bar{\alpha}) &= \frac{l^2}{r_\perp^2} \sin(\alpha)  \\
\bar{v} &= \frac{l}{r_\perp} \left( v + \frac{1}{r_\perp} yu \right) \\
\bar{u} &= u, \bar{U} = U, \bar{T} = T
\end{align*}
\]

1.5 Summary

FLEET can be a valuable tool to complement existing fluid diagnostic techniques, or serve as a standalone diagnostic in environments where other techniques have been unable to produce high-fidelity measurements. This thesis discusses broad efforts to improve the FLEET method for velocimetry in gas flows, especially for turbulent boundary layers. While other laser-based diagnostics were discussed in this introduction, the experiments presented in this work will only involve FLEET. Limited signal strength and lifetime, in addition to optical access are the main challenges to the deployment of optical diagnostics in ground testing facilities. Chapter 2 presents some suggestions for signal enhancement using testing in non-air and non-pure-nitrogen gas mixtures. Testing is performed in an optically-clear gas cell that. A kinetic model is developed to complement the experiments and to better understand the underlying physics. Chapter 3 discusses how the many parameters in the FLEET experiment, including optics and imaging equipment, can influence the accuracy of
the measurement. Experiments are performed in a subsonic turbulent pipe flow. Chapter 4 describes the application of FLEET to near-wall measurements in supersonic flows. Experiments are conducted in supersonic air flow with different experimental geometries to mitigate the problems of optical access, surface damage and excess flow perturbation. The concluding chapter, Chapter 5 summarizes results from each of the previous chapters. Each chapter includes a short literature review and motivation for the task.
Chapter 2

Gas Mixtures

2.1 Introduction

High enthalpy test facilities often render mechanical fluid diagnostic methods unusable, so there is motivation to develop robust laser diagnostics that can be deployed remotely. Local measurements of off-body flow parameters (pressure, temperature, density, velocity), which are necessary for computational model validation, often cannot be achieved with seeding or probe-based methods. While in-flight testing involves atmospheric air, these tests are often expensive and offer limited data collection opportunities. As a result, ground test facilities have been developed to simulate the enthalpy, Reynolds number, turbulence and Mach numbers of different flight conditions. To do this, different gases and gas mixtures are often used. In this chapter, FLEET viability is extended to non-air gas mixtures to increase the breadth of FLEET applications. Section 2.2 includes experimental and modeling work on FLEET in nitrogen-argon mixtures, Section 2.3 discusses nitrogen-oxygen mixtures, Section 2.4 includes a short discussion of FLEET in helium, methane and carbon dioxide, Section 2.5 describes preliminary work on FLEET in saturated water vapor and Section 2.6 details a study of FLEET applied to freon and air mixtures for application in the NASA Transonic Dynamics Tunnel.
2.2 Nitrogen-Argon Mixtures

Argon gas is an important working gas in aerodynamics studies due to its natural abundance and inert behavior. It is often flowed through supersonic and hypersonic wind tunnels, and shock tubes [5], or used as a plasma medium. Argon has a smaller thermal conductivity and heat content than nitrogen, which results in higher and longer levels of breakdown emission in argon as compared to nitrogen. Argon gas also commonly serves as a buffer gas for plasma experiments. The NASA Ames Arc Jet Complex has several facilities that use air and nitrogen as working gases, and argon is frequently used to stabilize reactive plasmas for ablation experiments. Argon is particularly important for arcjet facilities, which provide dissociated hypersonic flow for model testing, a key step for the characterization of atmospheric reentry. Previous velocimetry studies in these facilities relied on laser-induced fluorescence of atomic oxygen and nitrogen species [9]. These measurements are necessary to better understand flows in arcjet facilities for the validation and refinement of computational models. In plasma jets, velocity measurements have proved to be challenging due to the high jet enthalpies, but necessary to get accurate velocity fields [25]. Cold atmospheric plasmas are additionally interesting for the field of plasma medicine [49, 116]. Enchancement of FLEET with argon may occur through several key mechanisms [144, 15]. Excitation transfer from two-body collisions with ground state atoms and molecules explains some of the phenomena observed with FLEET gas composition experiments. Reactions between metastable argon and molecular nitrogen can lead to both direct excitation of nitrogen molecules and elevation of populations of species, such as atomic nitrogen and electrons, that contribute to the FLEET process. When argon excited into these metastable states is mixed with molecular nitrogen in its vibrational ground state, energy may transfer from argon to nitrogen, exciting nitrogen into one of the vibrational levels of the $C^3\Pi_u$ or $B^3\Pi_g$ states since the energy of the argon metastable states matches the necessary excitation energies between 11.033 and 11.52eV (Equations 2.1-2.2). Since metastable argon possesses more energy than most levels of the nitrogen $B^3\Pi_g$ and $C^3\Pi_u$ states, it is unlikely to de-excite nitrogen and thereby reduce
emission in the first or second positive spectra.

\[ \text{Ar}^*(4^3P_2) + N_2 \rightarrow \text{Ar} + N_2(C^3\Pi_u) \] \[2.1\]

\[ \text{Ar}^*(4^3P_2) + N_2 \rightarrow \text{Ar} + N_2(B^3\Pi_g) \] \[2.2\]

Argon can also induce the dissociation of molecular nitrogen and increase the production of nitrogen atoms (Equation 2.3), which recombine into excited states as previously described in Equations 1.3-1.5. These processes are shown in Figure 2.1.

\[ \text{Ar}^*(4^3P_2) + N_2 \rightarrow \text{Ar} + N + N \] \[2.3\]

In addition to argon directly exciting ground state nitrogen into its \(C^3\Pi_u\) or \(B^3\Pi_g\) states or aiding in the dissociation of molecular nitrogen, the presence of argon in the mixture reduces the strong electron quenching effect and subsequent electron temperature drop caused by nitrogen molecules [65]. The decrease of electron quenching thus leads to a higher sustained electron temperature and a greater rate of subsequent dissociation reactions. Nitrogen’s relatively large collisional cross section makes it one of the most efficient quenchers of its own higher-energy states. In less direct methods, species created through nitrogen-argon reactions contribute to the production of excited nitrogen metastables through pooling processes over time delays longer than tens of nanoseconds (Equations 2.4-2.5).

\[ N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow N_2(C^3\Pi_u) + N_2 \] \[2.4\]

\[ N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow N_2(B^3\Pi_g) + N_2 \] \[2.5\]
2.2.1 Experiment

The laser used in this study is a Spectra Physics Solstice laser with titanium sapphire oscillator and MaiTai regenerative amplifier operating at a fundamental wavelength centered at 800 nm and emitting a beam with a $1/e^2$ intensity half-width of 1.95 mm [85]. Each pulse has a temporal full-width at half maximum duration of 60 fs and a frequency doubling crystal is used to produce second harmonic generation at 400 nm. The second harmonic is used in order to allow collection of nitrogen first positive (visible - infrared) without background interference from the laser, and the 800 nm is used to avoid the same problem while collecting second positive UV and near-UV emission. While both tagging wavelengths produce FLEET emission through a multiphoton excitation process, the second harmonic requires half as many photons to dissociate nitrogen as the fundamental and can therefore produce tagging at lower pulse energies. They both produce relatively long-lived first positive and short-lived second positive spectra, suggesting that the overall FLEET chemistry does not change greatly as one switches between the two. Both the fundamental and its frequency-doubled pulses are focused with a $f=30$ cm lens into a custom-made optically clear gas cell.
that allows for linear flow along the length of the cell. This cylindrical cell has an inner diameter of 47 mm and 3.175 mm thick optical-grade fused quartz windows that allow > 94% transmission at the operating laser wavelengths, 800 nm and 400 nm. The full transmission spectra of the windows can be found in reference [46]. The gas mixing manifold permits up to three independently controlled inputs to be mixed in the cell. A constant flow rate of 0.016 m³/min and atmospheric pressure is maintained, while the gas mixtures and ratios are varied with a resolution of up to 0.001 m³/min. The flow rate corresponds to a linear gas movement of approximately 6 m/s in the center of the cell where the tagged line is located, allowing each incoming laser pulse to come into contact with a fresh tagging volume containing minimal plasma build-up from the previous pulse. A vacuum pump maintains 1 atm pressure in the cell throughout the experiment. Spectroscopic measurements of the tagged line in nitrogen-argon gas mixtures at different times following excitation enable determination of the temporal evolution of atomic and molecular participants in the reactions. Both time-gated and time-integrated spectra are taken with an Acton SpectraPro 300i spectrometer with a resolution of 0.1 ± 0.2 nm. The spectrometer is calibrated before each test using an argon-mercury lamp with known spectral features and checked against known features in the nitrogen emission spectrum for accuracy. Time integrated spectra are taken with a Princeton Instruments PIXIS 512 camera, whereas both direct images of the emission and time-gated spectra are made possible by the use of a gateable image intensifier module in conjunction with a high-speed pco.dimax HD camera. Signal amplification is achieved with a 25 mm diameter, dual stage Quantum Leap gateable image intensifier module with a S25 photocathode (spectral range approximately 350 - 920 nm), Y₃Al₅O₁₂ : Ce type phosphor screen, a reported resolution of > 60 LP/mm and gate repetition rate of 2 MHz. The intensifier serves the dual purpose of signal amplification and high-speed shutter. The observation of atomic lines provides evidence of participating short- and long-lived species. Spectra undergo background subtraction and are integrated both temporally and spatially. Shot-to-shot variation in the spectra is found to be less than a percent, so all the presented spectra are
taken with camera averaging over 100-5000 frames per set of conditions. Argon spectra are calibrated with a pure argon spectrum taken with a fiber-optic sensor over several seconds. While self-focusing and defocusing of the laser beam in the plasma is negligible under low pressure conditions, we must take into account these effects for our experimental conditions. We therefore rely on clamped femtosecond laser intensities that limit initial ionization rates, as presented by [36] and elaborated further in Section 2.2.2.

![Four tagged lines in Ar+N2 mixtures with 6%, 20%, 56%, 94% argon, from left to right respectively. Each panel is averaged over 100 shots. Right: Evolution of total FLEET emission intensity in different nitrogen-argon mixtures over 20 µs. Laser properties: λc = 400 nm, 1 kHz, 0.8 mJ/pulse](image)

Figure 2.2: Left: Four tagged lines in Ar+N2 mixtures with 6%, 20%, 56%, 94% argon, from left to right respectively. Each panel is averaged over 100 shots. Right: Evolution of total FLEET emission intensity in different nitrogen-argon mixtures over 20 µs. Laser properties: λc = 400 nm, 1 kHz, 0.8 mJ/pulse

Even a small amount of argon in a nitrogen mixture significantly affects the amount of visible emission produced, with increasing intensity and duration as the percentage of argon rises. Total emission intensity is plotted in Figures 2.2 and 2.3, and both plots show a strong increase in signal intensity with increasing levels of argon present, up to an order of magnitude stronger at short time delays. Compared to tagging in air, the maximum signal is an order of magnitude stronger for all delays relevant to tagging in near-sonic or supersonic flows (Figure 2.3b). Figures 2.2 and 2.3 both measure averaged emission intensity produced by a 400 nm beam operating at 1 kHz, 0.8 mJ/pulse, and imaged at each delay...
with an exposure time of 1 $\mu$s. The intensity is spatially averaged over a 12 x 150 pixel region centered in the signal area to account for shot-to-shot fluctuations. Small shot-to-shot variations in measured signal intensities (summarized by the error bars) can be attributed to flow fluctuations caused by the rotary displacement pump and background noise amplified by the camera intensifier, and can both be eliminated through averaging. The pump creates a low pressure environment in the inlet connected to the test cell by mechanically trapping and compressing a volume of gas, and venting it through the exhaust outlet. An oil seal separates the inlet and outlet sides, as well as fills the gap between the rotor top and housing. Even at moderate pumping speeds needed for maintaining an atmospheric pressure environment, gas leakage around the seal can increase the signal fluctuations.

The length of the resolvable tagged line increases with increasing levels of argon in the mixture as well, while the line width only increases slightly as seen in Figure 2.4. The growth in fluorescence area is most likely the result of diffused argon stimulating reactions with nitrogen in the tagging area perimeter. Here, length and width are defined as the full-width at half maximum of the fitted longitudinal or transverse profile on the spatially
Figure 2.4: Left: FLEET FWHM longitudinal length as a function of argon and nitrogen ratio, for different delays. Right: FLEET FWHM transverse length as a function of argon and nitrogen ratio, for different delays

averaged line. Width is measured at a location corresponding to the vertical line center, if the emission lines are oriented vertically as in Figure 2.2a. Emission lines in Figure 2.4 are created with a 1 kHz, 800 nm beam with a pulse energy of 2.2 mJ. All line images are averaged over at least 100 shots and emission features being compared are created with the same laser settings and optics. Signal intensity is spatially averaged over approximately a 20x100 pixel (or similar) rectangle in the center of each tagged line. Line length is found using a Gaussian fit through the longitudinal profile of an image spatially averaged over the transverse width of the emission line.

Spectra give clues to which emitting species are present in the reactions. The presence of atomic lines provide evidence of participating short- and long-lived species whose time-resolved behaviors are not well known. Of special interest are the first and second positive, as well as the first negative spectrum which we mention briefly. A correction for quantum efficiency is introduced in the plots by convolving the resulting spectra with the QE curve for the intensifier module. Spectra undergo background subtraction and are integrated both temporally and spatially. A five-term moving average filter is applied to smooth spectra and
enhance key vibrational features in Figures 2.6, 2.8 and 2.9. Argon spectra are calibrated with a pure argon spectrum taken with a fiber-optic sensor over several seconds.

Figure 2.5: Time-gated second positive spectra in a mixture of 94% argon and 6% nitrogen where each line is averaged over 5000 shots at 1 kHz laser repetition rate. An attenuated 800 nm fundamental beam firing at 1 kHz rate with a pulse energy of 2 mJ is used for the excitation process. These spectra are integrated over varying time intervals of 0.1-0.6 µs, 0.5-1 µs, 1-2 µs, 2-5 µs, and 5-10 µs in order to produce the signal necessary to balance the decaying emission. The exponential decay characteristics of the second positive emission can be more clearly seen in Figure 2.7b, where the signal at each time interval is divided by the exposure time. The data are integrated using a trapezoidal method with unit spacing and plotted at the middle of each time interval. Shot-to-shot uncertainty in the spectra is very low: one standard deviation from the mean for each integrated first and second positive spectra point is found to be less than 1% of the mean value in Figure 2.7.

Figure 2.6 sheds more light on the specific processes induced by argon in the flow. By normalizing sets of spectra taken in the same time interval (0.1-0.5 µs) to the 357.7 nm peak ($v' = 0 \rightarrow v'' = 1$), the effects on individual transitions are made more pronounced. The $v' = 0 \rightarrow v'' = 2, v' = 1 \rightarrow v'' = 3$ and $v' = 1 \rightarrow v'' = 4$ features are reduced in strength in the presence of more argon, while the $v' = 0 \rightarrow v'' = 0$ and $v' = 0 \rightarrow v'' = 1$ remain prominent, suggesting that argon assists the population of the $v = 0$ vibrational level of
the C state and selects for particular $C \rightarrow B$ transitions. Figure 2.6 also shows a relative decrease of emission in the nitrogen $v' = 0 \rightarrow v'' = 0$ first negative peak with the increase of argon percentage in the mixture, indicating a faster decrease of $N_2^+$ species with respect to other participants. Meinel band lines $[X^2\Sigma_g^+(v = 0) - A^2\Pi_u(v = 5)]$ in the red and infrared region are visible past 10 $\mu$s in mixtures of over 80% argon, indicating a strong persistence of $N_2^+$. In the interest of applications in air, the introduction of oxygen into any mixture reduces nitrogen first negative spectra.

Figure 2.7 compares the decay of the integrated first and second positive emission systems with the decay of $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_u)$ populations predicted by the zero-dimensional kinetics model detailed in Section 2.2.2. The experimental first positive system is calculated by integrating the entire signal from 550 to 700 nm, and the second positive system from 330 to 400 nm. The measurements are taken in the time intervals of 0.1-0.6 $\mu$s, 0.5-1 $\mu$s, 1-2 $\mu$s, 2-5 $\mu$s, and 5-10 $\mu$s, normalized by each gate width, and plotted at the corresponding center of each temporally-integrated interval. While the intensity of the first positive emission for different mixtures converges to approximately the same level after about 1 $\mu$s, the second positive emission takes about 10 $\mu$s to converge. The exponential decay characteristics of the second positive emission can be seen in Figure 2.7b, where the signal at each time interval is normalized by the exposure time. To estimate emission intensity from the model, the rate
Figure 2.7: The decay of the integrated first positive system emission (550 – 700nm, left) and second positive (330 – 400nm, right) excluding the first negative peak at 391nm, as compared with normalized model predictions from 0 – 10µs. Laser properties (a): λ = 400nm, 0.8mJ per pulse, 1kHz repetition rate. Laser properties (b): λ = 800nm, 2mJ per pulse, 1kHz repetition rate.

of photon production or decay is multiplied by each timestep taken by the solver, giving an instantaneous quantity of emitting photons at each point in time. This curve is smoothed, normalized and compared to the experimental data, which are integrated using a trapezoidal method with unit spacing and normalized by the camera gate interval. The detectable second positive emission in pure nitrogen was previously found to last for about 100 ns, suggesting that reactions with metastable argon are prolonging the lifetime of this emission through reducing the effects of collisional deactivation and/or increasing the production of C-state nitrogen, as suggested previously. The nitrogen electronic transitions are isolated from argon contributions for this plot to highlight the effect on the first positive system. It is found that the ratio of contribution from argon atomic lines to the contribution of the first positive spectrum becomes vanishingly small with time. Atomic argon lines between 700-900 nm diminish in intensity with respect to the first positive spectrum in all mixtures of nitrogen and argon within 1 µs. The overall contribution from argon emission is quite small and the trends are very similar as the time delay approaches 10 µs. Equipment sensitivity at
different wavelengths, the exclusion of spectra arising from transitions outside the measured range, as well as the accidental inclusion of spectra produced through transitions between other electronic states such as the first negative system, may all contribute to discrepancies between model and experiment.

Figure 2.8: Time-gated first positive spectra in a mixture of 20% nitrogen and 80% argon

Figures 2.8 and 2.9 depict the temporal evolution of the first positive spectra in a 20% nitrogen and 80% argon mixture. Varying integration time intervals of 0.1-0.5 µs, 0.5-1 µs, 1-2 µs, 2-5 µs, and 5-10 µs are employed in these images as well. A 400 nm beam operating at 1 kHz with pulse energy of 0.8 mJ is used.

Lastly, in pure argon, femtosecond laser dissociation can create atomic emission that lasts for tens of microseconds due to the long-lived ionization-recombination processes that dominate the reactions. Radiative transitions that contribute heavily to argon atomic lines in the 690-900 nm region are produced as a result of the intense fields created by the laser pulse. A collision between argon metastable atoms can ionize one of the atoms since their ionization energy is 4.2 eV, as compare to 15.76 eV for the ground state atom. The production of argon atomic and molecular ions, $Ar^+$ and $Ar_2^+$, has been previously detected and evidence of increased populations of $Ar^*$, $Ar_2^+$ and $Ar_4^+$ 100 ns following excitation have been qualitatively observed in the kinetic models. Most of the strong lines in Figure 2.11 belong to singly ionized
Figure 2.9: Time-gated first positive spectra in a mixture of 20% nitrogen and 80% argon with key vibrational transitions labeled, where $v'(B^3\Pi_g), v''(C^3\Pi_u)$.

Figure 2.10: Comparing the intensity of emission in pure argon to that of emission in argon-nitrogen mixtures and in air.

argon, or Argon II, and are observed to decay relatively quickly on an absolute scale as well as with respect to the normalized peak at 765 nm. Figure 2.10 shows the time evolution of argon emission intensity as compared to that in argon-nitrogen mixtures, pure nitrogen and air. It is clear that pure argon produces the strongest fluorescence measured in all the gas composition environments below approximately 7 $\mu$s. A strong fluorescence is observed
Figure 2.11: Pure argon time-gated spectra normalized to the 765 nm peak for microseconds before decaying to the level of FLEET emission in air for the next tens of microseconds. It is hypothesized that the presence of nitrogen inhibits some of these argon processes so that the overall emission in the mixture is not equal to the sum of the individuals.

2.2.2 Kinetics Model

The temporal behavior of different concentrations of argon and nitrogen following femtosecond laser dissociation is studied using a zero-dimensional kinetics model with the reactions listed in Table A.1. The creation of 13 different species ($e, N, N^+, N_2^+, N_3^+, N_4^+, N_2(A^3\Sigma_u^+), N_2(B^3\Pi_g), N_2(C^3\Pi_u), Ar^+, Ar_2^+, Ar^+(4^3P_2), ArN^+)$ is taken into account, and the initial vibrational temperature is assumed to be equal to that of the gas ($T_v \approx T_g$). Electronic quenching reactions such as $N_2(A^3\Sigma_u^+) \rightarrow N_2 + h\nu$ are assumed to arrive at the ground electronic state $N_2(1\Sigma_g^+)$. Important processes taken into account include direct ionization, collisional transitions between electronic states of nitrogen, collisionally induced excitation transfer, reactions between positive ions and neutrals, dissociative recombination, formation of cluster ions, and pooling between excited nitrogen states. Reaction rates are found in or derived from literature [113, 59, 124, 77, 1, 110, 61], initial ionization rates of gaseous species are taken from [98], and density-dependent electron-neutral collision frequencies $\nu_{e,N_2}$ and
νe,Ar are obtained from empirical data [54]. Low electron temperature (< 0.1 eV) electron-neutral collision frequencies are computed using BOLSIG+, the Boltzmann equation solver for weakly ionized gases. The rate constant for ArN+ cluster ion dissociation is extrapolated from data with ArXe+ cluster ions [81]. The electron temperature is calculated using an ordinary first order differential equation approximation of the hydrodynamic equation presented by [115] and used by [123], given in Equation 2.6. The zero-dimensional approximation is given in Equation 2.7. Vibrational temperature is found using the Landau-Teller approximation since no additional pumping is added to the system after the initial excitation pulse. Initial excited atom and molecule populations are assumed to be zero. Ionized species are calculated from available rates using femtosecond laser intensity-clamping ranges as a function of the fundamental and second harmonic wavelength [36]. Electron-ion Coulomb collisions are calculated using Equations 2.16-2.17 [64]. The resulting system of differential equations is computed using a variable-order stiff equation solver with a relative error tolerance of 10^{-15}. Mass conservation is fully realized within the tolerance of the solver and charge conservation, within 10^{-17} of the total number of charged particles. Because this investigation deals with an elaborate nonequilibrium plasma, the theoretical approach requires a large computing time that is reduced by simplifying the vibrational kinetics. While individual vibrational states are not analyzed, many of the rate coefficients are the summation of that from each vibrational state. For instance, \( k_{23} \) for \( N_2(B^3\Pi_g) \) formation through pooling is the summation of \( N_2(B^3\Pi_g, v = 1 - 11) \) rate coefficients [110]. No rate coefficients have been modified from literature to fit experimental data in this study. When discrepancies between references were found, preference is given to the source with the more recent publication date or to the most commonly cited values. For example, the rate constant for \( N^+ + N + N_2 \rightarrow N_2^+ + N_2 \) is given as \( k = 10^{-29}[m^6/s] \) [77] and \( k = 10^{-29}\left(\frac{300}{T_\text{eq}}\right)[m^6/s] \) [17], and the latter rate coefficient is implemented in the model. Preference is also given to rate coefficients that are derived from theory, such as for the reaction \( N_2(A^3\Sigma_g^+) \rightarrow N_2 + h\nu \) [26]. Here, the rate coefficient is the Einstein A coefficient derived assuming that the en-
tire population is originating from the $N_2(A^3Σ_u^+, v = 0)$ level. A combination of empirical constants from other studies and computed parameters are used in developing the model, with the former being used whenever possible. Rate coefficients for reactions 40 and 41 ($e + N_4^+ \rightarrow N_2 + N_2(A^3Σ_u^+, B^3Π_g, C^3Π_u)$) are disputed in literature, with strong implications towards predicting a population inversion in nitrogen species. It is found that setting $k_{40} = k_{41}$ has little effect on our results, which are dominated by argon. Diffusion effects are neglected in modeling the pressure conditions in our experiments, but are important for lower $\mathcal{O}(< 10\text{Torr})$ pressures [76]. This model does not take into account the experimental gas convection rate of $6 \times 10^{15}$ particles per cubic centimeter per second, which depletes unrealistic behavior. A convection model that takes into account the system mass and energy balance would need to be developed for accurate studies in faster flows. Assuming a weakly-ionized and quasi-neutral gas at rest, the gas’s state can be described by the electron gas equations. Fluid models are often used to describe low-temperature plasmas if the magnetic field is small and can be neglected. The hydrodynamic equation for electron energy is obtained by evaluating the velocity moment of the Boltzmann equation and multiplying by $mv^2$. Equation 2.6 introduces the hydrodynamic description for electron energy in a weakly ionized gas [115].

$$\frac{\partial}{\partial t} \left( \frac{3}{2} n_e k T_e \right) + \nabla \cdot F =$$

$$-\frac{3}{2} n_e k (T_e - T_v) \nu_{ev} - \frac{3}{2} k n_e (T_e - T_g) \sum_i (\delta_i \nu_{e,i}) - n_e (\nu_i N_2 I_{N_2} + \nu_{ex} I^* + E_{e,ex})$$

[2.6]

$$F = \frac{5}{2} n_e k (T_e v_e - D_e \nabla T_e)$$

Here, $F$ represents the flux density of electron energy, $v_e$ is electron velocity, $D_e$ is the electron diffusion coefficient, and $k$ is Boltzmann’s constant, $E_{e,ex}$ represents energy gained by electrons through collisions with excited atoms, and $\nu_{e,i}$ refers to electron-neutral collision frequencies $\nu_{e,N_2}$ and $\nu_{e,Ar}$. The electron, vibrational and gas temperatures are represented
by $T_e$, $T_v$ and $T_g$, respectively. The first and second terms on the right-hand side represent the electron inelastic energy losses through electron-impact vibrational excitation of ground state nitrogen, and energy loss to other heavy particles, respectively. The third term on the right-hand side represents second-order collisions: $\nu_{ex}$ is the rate of electronic level excitation and $I^*$ is the corresponding excitation energy. Because initial electron temperatures are assumed to be high (> 1eV), excitation energies of nitrogen molecules are released through collisions with electrons in second-order reactions, allowing us to neglect the $n_e\nu_{e,N_2}I_{N_2}$ process in the energy balance. The collision rate $k_e$ is a function of the electron scattering cross section with metastable argon, and is dependent on electron temperature. Its maximum value is $0.2 * 10^{-13}$ m$^3$/s in the range $0.03 < T_e < 1$ eV [150].

Simplifying Equation 2.6 into its zero-dimensional form, we arrive at Equation 2.7, where $k_e$ is the rate of collisions of electrons and excited-state atoms.

$$\frac{dT_e}{dt} = \nu_{ev}(T_v - T_e) - (T_e - T_g) \sum_i (\delta_i \nu_{e,i}) + \frac{2}{3k} k_e Ar^* (4^3 P_2) I^*_{Ar} - \frac{T_e n_e}{n_e}$$

$$\sum_i (\delta_i \nu_{e,i}) = \delta_{N_2}(\nu_{e,N_2} + \nu_{e,N_2^+} + \frac{1}{2}\nu_{e,N_2^{+}}) + \delta_{Ar}(\nu_{e,Ar} + \nu_{e,Ar^+} + \frac{1}{2}\nu_{e,Ar^+_2})$$

[2.7]

For a given electronic state, the vibrational-rotational energy levels in a diatomic molecule are given by Equation 2.8 where $v$ is the vibrational quantum number, $J$ is the rotational quantum number, $w_e, w_e x_e, w_e y_e$ are the vibrational coefficients for the electronic state $e$, and $\alpha_e, \beta_e, \gamma_e$ are the rotational-vibrational interaction coefficients for that same electronic state [121]. The Mayer and Mayer approximation uses only the first term of Equation 2.8 to calculate the vibrational partition function and replaces the sum over available states with a geometrical series. Equation 2.10 is derived from the vibrational partition function evaluated
as a simple geometric series (Equation 2.9).

\[ \varepsilon_e(v, J) = w_e(v + \frac{1}{2}) - w_e x_e(v + \frac{1}{2})^2 + w_e y_e(v + \frac{1}{2})^3 + \ldots \]
\[ + [B_e - \alpha_e(v + \frac{1}{2} + \varepsilon_e(v + \frac{1}{2})^2]J(J + 1) \]
\[ - [D_e + \beta_e(v + \frac{1}{2})]J^2(J + 1)^2 \ldots \]  

\[ Q_v = \sum e^{-\varepsilon(v) / kT} \approx \sum_{v=0}^{\infty} e^{-\omega_e(v + \frac{1}{2}) / kT} \]
\[ = \frac{\frac{e^{-h\nu}}{2kT}}{1 - e^{-h\nu}} \]  

[2.9]

Variables \( E_v, E_{v0}, \frac{dE_v}{dt}, \nu_{ev}, \delta_{N_2}, \delta_{Ar}, \tau_{N_2}, \tau_{Ar} \) are defined in Equations 2.10-2.23 and all temperature values are in units of Kelvin. A vibrational quantum of \( N_2, \varepsilon_v \), is 0.29 eV.

\[ E_v = N_2 \left( \frac{\varepsilon_v}{e^{\frac{\varepsilon_v}{kT}} - 1} \right) \]  

[2.10]

\[ E_{v0} = N_2 \left( \frac{\varepsilon_{v0}}{e^{\frac{\varepsilon_{v0}}{kT}} - 1} \right) \]  

[2.11]

\[ \frac{dE_v}{dt} = Q_eV - Q_{VT} \]
\[ = 3 \frac{n_e k(T_e - T_v) \nu_{ev}}{\tau_{VT} n_{N_2}} - \frac{E_v - E_{v0}}{\tau_{VT} n_{N_2}} \]
\[ - 3 \frac{k A_r}{\tau_{Ar}} (T_v - T_g) \]  

[2.12]

The first term of Equation 2.12 is the molecular vibration excitation energy transfer rate from collisions with electrons and the second term is the rate of vibration-translation energy transfer. A subscript ‘0’ indicates thermal equilibrium values. This model only considers the lower vibrational states. When the harmonic oscillator approximation holds at small
displacements from equilibrium, we can approximate

\[ Q_{VT} = \frac{E_v - E_{v,0}}{\tau_{VT}} \]

\[ T_v = \frac{\varepsilon_v}{\ln \left(1 + \frac{N_2 \varepsilon_v}{E_v}\right)} \]

\[ \frac{dT_v}{dt} = \frac{-\varepsilon_v}{\left(1 + \frac{N_2 \varepsilon_v}{E_v}\right) \left(\ln \left(1 + \frac{N_2 \varepsilon_v}{E_v}\right)\right)^2} \left[ \frac{\varepsilon_v dN_2}{E_v dt} - \frac{\varepsilon_v N_2 dE_v}{E_v^2 dt} \right] \]

\[ \rho c_p \frac{dT_g}{dt} = \frac{E_v - E_{v0}}{\tau_{VT,eff}} + \frac{3}{2} k n_e (T_e - T_g) \sum_i (\nu_{e,i}) \]

Electron-ion Coulomb collision frequencies are calculated using Equation 2.16.

\[ \tau_e = \frac{3 \sqrt{m_e (kT_e)^{3/2}}}{2 \sqrt{2 \pi n_+ \Lambda e^4}} \]

\[ \nu_{ev} = \begin{cases} 3.87 \times 10^{-14} N_2 e^{-17400/T_e} & \text{if } T_e \leq 11600 K \\ A + 7.5 \times 10^{-15} (1 - 3.1 \times 10^{-6} T_e)^{11600N_2/1} & \text{if } T_e > 11600 K \end{cases} \]

\[ A = 2.13 \times 10^{-13} \sqrt{T_e/11600} \left[1 - 0.05(T_e/11600 - 4)\right] e^{-7.86 \times 11600/T_e} \]

\[ \delta_{N_2} = \frac{2m}{M_{N_2}}, m = \text{electron mass}, M = \text{neutral particle mass} \]

\[ \delta_{Ar} = \frac{2m}{M_{Ar}} \]

The general form of the vibrational relaxation time is expressed in Equation 2.20. Using Millikan and While’s constants \( A = 1, B = 221.4, C = 0 \), Equations 2.21 and 2.22 give
the vibrational relaxation times for $N_2 - N_2$ and $N_2 - Ar$ collisions.

$$\tau_V = \frac{A}{P} e^{B/T^{1/3}+C}$$ \hfill [2.20]$$

$$\tau_{N_2} = \frac{1}{N_2} \left( 3.98 \times 10^9 e^{221.46/T^{1/3}} \right)$$ \hfill [2.21]$$

$$\tau_{Ar} = \frac{1}{Ar} \left( 1.73 \times 10^9 e^{239.5/T^{1/3}} \right)$$ \hfill [2.22]$$

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{N_2}} + \frac{Ar}{N_2} \frac{1}{\tau_{Ar}}$$ \hfill [2.23]$$

Figure 2.12: Predicted temporal variation of excited nitrogen number densities $[cm^{-3}]$ as a function of time $[s]$ in different mixtures of nitrogen and argon at 300K and atmospheric pressure. The laser pulse used in this model has a central wavelength of 400nm, duration of 50fs and pulse energy of 0.8mJ/pulse.

The model is computed for a number of mixtures ranging from 1%$Ar + 99%N_2$ to 80%$Ar + 20%N_2$. Populations of excited nitrogen species are plotted, from which the first positive system (FPS) and second positive system (SPS) emission levels can be deduced.
Figure 2.12 predicts the rapid creation of excited nitrogen species 0.1 – 100ns following excitation with the addition of any argon (down to 1% is modeled) in the mixture. This initial spike in populations is reflected in a large production of photons in the visible and infrared regimes within the first microsecond. The first positive system then decays to immeasurable amounts after about 100µs (Figure 2.12a), while emission from the second positive system lasts for several microseconds in the presence of argon (Figure 2.12b). About two orders of magnitude enhancement in \( N_2(C^3\Pi_u) \) populations is observed even at 1 – 5% argon. Previous results[144] showed the B-state nitrogen to be orders of magnitude larger than that at C-state around 1µs, and the current model maintains the dominant role of the first positive system at even longer delays. We also observe an intense emission between \( 10^{-7} \) and \( 10^{-6} \) seconds, corresponding to high levels of B- and C-state populations in the model. Increases of argon in the mixture cause stronger transition lines at shorter timescales for both the first and second positive spectra, but a collapse to lower levels than in pure nitrogen at longer delays after about 10µs (Figure 2.2). The qualitative model of the B- and C-state nitrogen species evolution is in accordance with the measured fluorescence. The rapid decay of electron populations can be attributed to recombination processes with argon and nitrogen ions. Numerical calculations of \( Ar^*(4^3P_2) \) species show a peak which precedes that of \( N_2(B^3\Pi_g) \) and \( N_2(C^3\Pi_u) \), supporting the excitation mechanism \( Ar^*(4^3P_2) + N_2 \rightarrow Ar + (N_2(B^3\Pi_g), N_2(C^3\Pi_u)) \). We investigate the mechanism by which excited states are populated by iterating through the intermediate processes represented in Figure 2.1 to determine the dominating effects. We previously hypothesize that the formation of cluster ion \( ArN^+ \) [136], pooling reactions [75, 114], metastable excitation and dissociation of nitrogen cluster ion \( N_4^+ \) [74] are important contributors to the FLEET enhancement process.

Figure 2.13 depicts results for excitation of a 80%\( \text{N}_2 + 20%\text{Ar} \) gas with a femtosecond laser pulse centered at 400 nm. This simulation shows the rapid creation and decay of ions and electron species, and the relative amounts of these species can be related to the magnitude of their influence on the FLEET process. Higher amounts of nitrogen cluster ions
than metastable argon species appear here, suggesting that collisional excitation of nitrogen by $\text{Ar}^*$ may not be the dominant player in this mixture. $\text{ArN}^+$ formation and dissociation causes a faster decay of excited species, as ions used for other reactions are spent in the production of the cluster ion. The effect is limited as $\text{ArN}^+$ undergoes rapid decay after formation (Figure 2.14).

Figure 2.15 shows that neglecting the nitrogen pooling processes, $\text{N}_2(A^3\Sigma_u^+) + \text{N}_2(A^3\Sigma_u^+) \rightarrow \text{N}_2 + \text{N}_2^*$ where $\text{N}_2^* = \text{N}_2(B^3\Pi_g), \text{N}_2(C^3\Pi_u)$, has minimal effect on the populations of $\text{N}_2(B^3\Pi_g)$ and $\text{N}_2(C^3\Pi_u)$. This is unsurprising because while the metastable A-state has a long lifetime, its low concentrations in the flow are barely affected by the addition of argon. Pathways towards $\text{N}_2(A^3\Sigma_u^+)$ formation remain essentially the same. The model
Figure 2.14: Predicted temporal variation of excited nitrogen number densities [cm$^{-3}$] as a function of time [s] comparing those from Figure 2.12 (solid) to their evolution without cluster ion ArN$^+$ processes (dashed). The x-axis depicts elapsed time in seconds.

Figure 2.15: Predicted temporal variation of excited nitrogen number densities [cm$^{-3}$] as a function of time [s] comparing those from Figure 2.12 (solid) to their evolution without pooling reactions (dashed). The x-axis depicts elapsed time in seconds.

shows that $N_2(A^3\Sigma^+)$ pooling is not a dominant contributor to electronically-excited nitrogen populations at delays of interest.
Figure 2.16: Predicted temporal variation of excited nitrogen number densities \([cm^{-3}]\) as a function of time [s] comparing those from Figure 2.12(solid) to their evolution without \(Ar^*(4^3P_2)\) excitation (dashed). The label \(Ar^*\) indicates the process modeled without metastable \(Ar^*(4^3P_2)\) excitation. The x-axis depicts elapsed time in seconds.

The removal of Equations 2.1 and 2.2 illustrates the role of the metastable energy transfer process. \(Ar^*(4^3P_2)\) has an unequal effect on the two excited states, favoring \(N_2(C^3\Pi_u)\) production and appears to play a larger role in \(N_2(B^3\Pi_g)\) and \(N_2(C^3\Pi_u)\) creation in mixtures with a large percentage of argon. Its elimination had little effect on early concentrations of excited nitrogen species. Metastable argon does not efficiently populate the C-state of nitrogen in mixtures composed of less than 50% argon and cannot account for the orders of magnitude increase in excited nitrogen species. However at higher argon concentrations, the populations of metastable argon are large enough to play a role in sustaining \(N_2(C^3\Pi_u)\) levels at several microseconds. Metastable argon excitation has previously been used to produce C-state nitrogen using resonance-enhanced multiphoton ionization (REMPI) to selectively ionize argon and give rise to metastable excited argon atoms in mixtures where \(P_{Ar} \geq P_{N_2}\) for the purpose of lasing [123]. To effectively use this process for sustained first- and second positive emission in a nitrogen-dominant mixture, we would need to selectively excite argon through a multiphoton process and avoid large levels of impact ionization. Furthermore, the removal of the process \(Ar^*(4^3P_2) + N_2 \rightarrow Ar + N + N\) has little effect on excited nitrogen...
populations during timescales of interest, implying that increased dissociation of nitrogen by metastable argon also plays a minor role in the signal enhancement.

Figure 2.17: Predicted temporal variation of excited nitrogen number densities \([cm^{-3}]\) as a function of time \([s]\) comparing those from Figure 2.12(solid) to their evolution without \(N_4^+\) excitation (dashed). The x-axis depicts elapsed time in seconds.

The formation of the nitrogen cluster ion \(N_4^+\) has a positive effect on \(N_2(B^3\Pi_g)\) and \(N_2(C^3\Pi_u)\) populations in argon-nitrogen mixtures within the first 100 ns. Its removal causes a slower build-up of these species since \(N_4^+\) plays a role in their formation as it dissociates into a number of other ions and neutral particles. The contribution of \(N_4^+\) formation to \(N_2(C^3\Pi_u)\) and \(N_2(B^3\Pi_g)\) is unequal, as expressed in reaction 42 (Table A.1).

Two photon absorption laser induced fluorescence (TALIF) is used to measure the relative densities of ground state nitrogen atoms following excitation by a femtosecond laser pulse (Figure 2.18). In this experiment, photons at 207 nm are used to excite atomic nitrogen in a FLEET tagged region to its \((3p)^4S_{3/2}\) upper state and the subsequent \((3p)^4S_{3/2} \rightarrow (3s)^4P\) transition produces measurable emission at 745nm. Two different laser pulses are used. The first excites nitrogen and produces FLEET emission, while the second is used to probe that emission at varying temporal delays. The measured emission is then normalized by the FLEET emission at each corresponding delay. We observe that the emission increases
Figure 2.18: Comparison between experimentally predicted densities of atomic nitrogen (in pure nitrogen) and model predictions (in pure nitrogen and nitrogen + argon mixtures). Left: TALIF emission showing the evolution of atomic nitrogen densities. Right: Predicted temporal variation of nitrogen atom number densities $[cm^{-3}]$ as a function of time in seconds $[s]$.

...to a maximum at about $0.1\mu s$ and decreases after about a hundred microseconds (Figure 2.18a). We are unable to temporally resolve the signal below $10ns$ so caution should be taken in interpreting the data at earlier timescales. Good agreement between experimentally measured atomic nitrogen levels and predicted populations in pure nitrogen can be seen from the figure. $N$ is predicted to strongly decay around $100\mu s$ for all mixtures (blue line in Figure 2.18b), following the trend observed through the TALIF experiment in pure nitrogen. The inclusion of argon atoms in the mixture bolsters the production of nitrogen atoms at later timescales, which in turn leads to increased populations of excited nitrogen species and emission through the first and second positive systems (Equation 2.24). As previously mentioned, this is not the effect of $Ar^*(4^3P_2)$ alone, but most likely the result of a number of different processes. Atomic nitrogen also reacts with a number of ions and molecules that
indirectly lead to the production of emitting species. The modeled decay rate of argon ions correlates well with measured decay from Figure 2.10.

\[ N + N + N_2 \rightarrow N_2(B^3\Pi_g) + N_2 \]  

[2.24]

Figure 2.19: Left: \( N_2(B^3\Pi_g) \) and \( N_2(C^3\Pi_u) \) with (solid line) and without (dashed) the processes in Equations 1.2-1.4, as a function of time in seconds [s]. Right: Predicted temporal variation of \( T_e, T_v \) and \( T_g \) [K] in pure nitrogen and in a nitrogen-argon mixture at 300K and atmospheric pressure, as a function of time in seconds [s].

Furthermore, the model provides support for Equations 1.1-1.5 as the dominant mechanism behind the FLEET process in nitrogen. Removing Equations 1.2-1.4 leads to a large drop in B and C-state populations to levels unlikely to produce detectable fluorescence at longer delays (Figure 2.19a). This also corresponds with previous experimental work that supports the recombination model for FLEET emission [86]. Studies are performed with a variety of initial conditions, including that taking into account initial excited populations of nitrogen. The single-electron ionization process is more likely than higher order ionization, and the ionization cross section is significantly larger than that for direct dissociation of the neutral nitrogen particle. It has previously been shown that intense femtosecond pulses can be used to create nearly 100% single-ion ionization in complex molecules before dissociation,
multi-ionization or Coulomb explosion, and these results can be projected onto nitrogen, a more stable diatomic molecule[58].

Figure 2.19b depicts the modeled temperature change. Most notable is argon’s effect of slowing the decay of electron temperature, which affects a number of processes that lead to FLEET emission. The model also predicts an overall higher gas temperature rise for FLEET in mixtures with argon, which is important for analyzing the effects of flow perturbations.

**Femtosecond laser filaments**

Under high pressure conditions, self-focusing and defocusing by the laser-generated plasma must be considered when estimating laser beam intensity. Self-focusing is produced by the intensity dependence of the refractive index, a relationship described by the Kerr effect in Equation 2.25, which gives the refractive index as a function of the zero-field refractive index $n_0$ and the Kerr nonlinear index of refraction multiplied by the beam intensity minus a defocusing term. Here $\omega_p$ is the plasma frequency, $n_e$ is the electron density due to ionization, $m_e$ is the electron mass and $\omega_0$ is the laser frequency [119]. The Kerr nonlinear index, $n_2$, is $3 \times 10^{-19} \text{ cm}^2/\text{W}$ for $\lambda = 800 \text{ nm}$ and $4 \times 10^{-19} \text{ cm}^2/\text{W}$ for $\lambda = 400 \text{ nm}$, where the latter is an estimate based on values for $\lambda = 800$ and $\lambda = 248$ nm [34, 36].

$$n = n_0 + n_2 I - \frac{\omega_p^2}{2\omega_0^2} \left[1.25\right]$$

$$\omega_p^2 = \frac{e^2 n_e}{\epsilon_0 m_e}$$

Self-focusing is counteracted by the increased production of electrons through photo-ionization, which modifies the index of refraction opposite to that of the Kerr effect. Laser intensity in FLEET is dependent on wavelength, beam power, beam focusing and gas mixture. At high intensities, ultra-short laser pulses reach an intensity limit due to the opposing effects of Kerr self-focusing and plasma defocusing. This “clamping intensity” varies depending on the Kerr coefficient and multiphoton ionization cross-section of the gas.
mixture. Clamping intensity is typically expressed by Equation 2.26 where \( n_0 \) is number density of particles, \( \sigma_K \) is the multiphoton absorption cross section for \( K \) photons, \( \Delta t \) is the laser pulse length [85]:

\[
I_c \approx \left( \frac{2\eta n_c}{\sigma_K \Delta t n_0} \right)^{K-1}
\]

[2.26]

The laser pulse energy for intensity clamping as a function of nitrogen gas pressure is experimentally determined by looking at fluorescence signal from two major band systems in the molecular nitrogen and nitrogen molecular ion spectra, the transitions \( C^3\Pi_u(v = 0) \rightarrow B^3\Pi_g(v' = 0) \) and \( B^2\Sigma^+_u(v = 0) \rightarrow X^2\Sigma^+_g(v' = 0) \), respectively [14]. The band head of the second positive system is found to be strongly dependent on gas pressure while the first negative system is nearly independent of it. A sharp change in the scaling of signal with input pulse energy is found for different gas pressures, and that change happens at a much lower energy at high pressure than at lower pressure levels. The critical power for self-focusing and intensity clamping is found to have a linear relationship with the inverse gas pressure. Determining this critical power is important for establishing accurate initial conditions for the simulation.

Plasma density inside a femtosecond laser filament is additionally more dependent on the focusing of the lens than on the laser power [134]. Multiple studies show a quick rise of intensity with input laser pulse energy before the slope trends towards a slower increase. In this kinetics study, a theoretical model of clamping intensities at 400 and 800 nm is used. For the fundamental wavelength at 800 nm, the clamping intensity is determined to be between \((3 - 5.5) \times 10^{13} \text{ W/cm}^2\) for \( \lambda = 800 \) nm and \((1 - 2.5) \times 10^{13} \text{ W/cm}^2\) for \( \lambda = 400 \) nm [36]. A chief difference at \( \lambda = 400 \) nm is a larger population of \( N_2^+ \) ions created by the 6.4 times higher inner-shell multiphoton ionization to the \( N_2^+(B^2\Sigma^+_u) \) state.

**Relaxation of Molecules**

Typical relaxation times follow the hierarchy described in Equation 2.27, where \( \tau_{TT}, \tau_{RT}, \tau_{VT}, \tau_{ET} \) are time for achieving equilibrium between translation, rotational, vibrational and
electronic degrees of freedom for atoms, molecules and ions; $\tau \epsilon$ is the energy relaxation time for plasma free electrons and $\tau_{Ch}$ is the time for chemical conversion [27].

$$\tau_{TT} \leq \tau_{RT} \ll \tau_\epsilon \leq \tau_{VT}, \tau_{ET}, \tau_{Ch}$$ [2.27]

Translational relaxation of atoms, molecules and ions is one of the fastest collisional relaxation processes. The characteristic energy relaxation time due to translational-translational energy exchanges can be as low as a single collision at room temperature and is described by Equation 2.28 where $N$ is the density of relaxing particles, $Z$ is the number of collisions per unit time of a particle at rest with other moving particles, and $\Delta E_T$ is the average translational energy transferred in these collisions.

$$\tau = \frac{E_0}{ZN\Delta E_T}$$ [2.28]

Rotational relaxation between rotational and translational degrees of freedom occurs with a characteristic time scale of the same order as for translational relaxation [27]. This is also dependent on the shape of the molecule: elongated molecules such as $CO_2$ achieve equilibrium quickly, whereas spherical molecules such as neopentane may take 10-100 collisions. The Massey parameter ($M$) describes the types of collisions likely to occur for a given set of energy gaps between states and collisional timescales. At low Massey parameters, the transferred energy is almost equally distributed between rotational and translational degrees of freedom of the relaxing molecule. As the Massey parameter increases, the energy transferred to the rotational degrees of freedom decreases. As $M$ increases, the relaxing molecule behaves as a spherically symmetric particle and the energy transferred to the rotational degrees of freedom decreases since rotations are more difficult to excite in the collision. The Massey parameter for vibrational excitation is $\pi \omega L/c \gg 1$. Relative to translational and rotational processes, vibrational relaxation is a slow process at gas temperatures below a few thousand degrees. A linear molecule with $N$ atoms has $3N - 5$ degrees of vibrational modes and a
nonlinear molecule has $3N - 6$, allowing molecules to store a lot of energy in their vibrational levels. The rate at which vibrational-translational energy transfer occurs is dependent on the fraction of transferred energy that can excite vibrational degrees of freedom. Only the most favorable configuration for vibrational energy transfer, that between a harmonic oscillator and atom, is considered in this description. Collisions between an atom and a harmonic oscillator are frequently modeled using semiclassical theory. A simple harmonic oscillator relies on the assumption that all of the vibrational levels are equally spaced and the Boltzmann distribution will be followed. To first order, the oscillator’s equation of motion is described by $\ddot{y} + \omega^2 y = \frac{1}{m} F(t)$, where $y$ is the deviation from equilibrium position, $\omega$ is the oscillator frequency and $m$ is the reduced mass of the oscillator. Assuming a short-range interaction potential between neighboring particles of the form $V = C e^{-r/L}$, the transferred energy can then be rewritten and solved for in Equation 2.29. We assume a Maxwellian velocity distribution for translational and rotational degrees of freedom for heavy particles.

\[
\Delta\varepsilon_{\text{vib}} = \frac{m}{2} \left( \dot{y}^2 + \omega^2 y^2 \right)
= \frac{1}{2m} \left| \int_{-\infty}^{\infty} F(t)e^{-i\omega t} dt \right|^2
= \frac{1}{L^2} \frac{\mu^2 c^4 m_b^2}{8m(m_b + m_c)^2} \left[ \frac{4\pi \omega L^2}{c^2 \sinh (\pi \omega L / c)} \right]^2
\]

Landau and Teller originally derived the energy relaxation equation below. For a constant gas temperature, the solution of the energy relaxation equation corresponds to the second line of Equation 2.30 for harmonic oscillators and the third line for anharmonic oscillators, where $\Delta E$ is the anharmonicity.

\[
\frac{dE_v}{dt} = -\frac{E_v - E_{v0}}{\tau_{VT}}
\]

\[
E_v(t) = E_{v0} + (E_v(0) - E_{v0}) e^{-t/\tau_{VT}}
\]

\[
E_v(t) = \sum [nE_{10} - \Delta En(n - 1)] N_n
\]
2.3 Nitrogen-Oxygen Mixtures

2.3.1 Introduction

The discussion of laser diagnostics in mixtures of nitrogen and oxygen necessitates the mention of several methods that take advantage of long-lived species such as ozone and nitric oxide, or dominant reactive particles such as atomic oxygen. Several of these rely on emission in the $\delta$, $\epsilon$ and $\gamma$ bands from long-lived populations of nitric oxide. Nitric oxide laser-induced fluorescence (NO-LIF) \cite{55} is a popular method for thermometry and velocimetry. In velocimetry, a laser is used to probe NO's ground vibrational state at 226 nm and short-lived ($O(ns)$, where $O$ indicates the order of magnitude) emission from the $\delta$ and $\gamma$ bands are measured with CCD cameras. Vibrational energy exchange with $N_2$, $O_2$, and energy transfer with atomic oxygen can also excite the nitric oxide species. The vibrationally-excited nitric oxide monitoring (VENOM) \cite{117} technique is a modification of NO-LIF that uses a 355 nm laser pulse to tag the flow by photodissociation of $NO_2$ into $NO(v=0,1)$ and $O$. The vibrationally-excited NO is subsequently interrogated with a 226 nm ”read” pulse as it moves with the flow. The ratio of NO at each rotational state can provide insight into the translational temperature of the flow. Air photolysis and recombination tracking (APART) \cite{125} relies on the photosynthesis of $NO$ in air with an ArF excimer laser centered at 193 nm and similarly uses a 226 nm beam for excitation. Ozone tagging velocimetry (OTV) \cite{112} forms ozone by 193 nm photo-dissociation of $O_2$. The ozone is interrogated by a 248 nm laser that dissociates the ozone and images the vibrationally excited $O_2$ fragment through the Schumann-Runge band. Raman excitation and laser induced electronic fluorescence (RELIEF) \cite{96} relies on stimulated Raman scattering to vibrationally excite oxygen, and laser-induced electronic fluorescence by an ArF laser at 183 nm to interrogate the long-lived ($O(ms)$) excited species.

Unseeded, laser-based velocimetry methods with long-lived signals are extremely desirable in compressible flow facilities for aerodynamics and fundamental fluids research. The
discussion of laser diagnostics in mixtures of nitrogen and oxygen necessitates the mention of methods that take advantage of long-lived species such as ozone and nitric oxide, or dominant reactive particles such as atomic oxygen. Several of these methods rely on emission in the $\delta$, $\epsilon$ and $\gamma$ bands from long-lived populations of nitric oxide and are mentioned in Section 1.2. Previous work demonstrated that the FLEET signal is strongest at all delays in pure nitrogen and decreases by about an order of magnitude in air, a phenomenon attributed to the loss of nitrogen atoms to reactions with oxygen species [93]. The main ion species following laser excitation is $O_2^+$, which has an ionization energy of 12.07 eV, compared to 15.58 eV for nitrogen. Thus reactions involving oxygen species, especially odd oxygen species ($O$, $O_3$) at high pressures as suggested in [89], are expected to be dominant. Oxygen is furthermore found to be a more efficient quencher of excited nitrogen states than molecular nitrogen, especially for higher vibrational states [106, 109]. Signal intensity and lifetime become limiting factors when flows, such as in a wind tunnel testing facility, experience large pressure and density drops. The goal is to better understand the main processes that impact FLEET emission levels, which are beneficial to the study of FLEET’s perturbative effects on the flow, and to improving the diagnostic. Insight from these results can prove useful towards enhancing the FLEET signal in air. The rapid incorporation of the FLEET method into fluid diagnostic studies [94, 43, 143] invites a better understanding of these femtosecond laser-produced plasmas at conditions relevant to flow applications. In this section, femtosecond laser excitation in gas mixtures of nitrogen and oxygen, including synthetic air, is investigated in order to determine favorable conditions for flow tagging.

2.3.2 Experiments

The laser used in this study is the same Spectra Physics Solstice laser as used in Section 2.2. Femtosecond laser pulses at both the fundamental and frequency-doubled wavelengths at 1 kHz are focused with 30 cm focal length AR-coated lenses into a custom-made optically clear quartz gas cell containing various mixtures of industrial-grade $N_2$ and $O_2$ at atmospheric gas
temperature, as shown in Figure 2.20. The gases flow through the cell to avoid build-up of NO or other contaminants, and a vacuum pump maintains the pressure at 1 atm in the cell throughout the experiment. Broad spectrum images and time-integrated spectra of the FLEET emission are taken in different mixtures of nitrogen and oxygen. Time-integrated spectra are taken of the FLEET emission with a Princeton Instruments PIXIS 512B camera and an Acton SpectraPro 300i spectrometer with a resolution of 0.1 ± 0.2 nm by collecting 150 shots at each spectral range and stitching them together with a matching algorithm. These spectra are first spatially averaged along the FLEET line and then calibrated by the spectral response of the camera. Shot-to-shot variation in the spectra is found to be less than a percent, so all the presented spectra are taken with camera averaging over 100-5000 frames per set of conditions. The spectrometer is calibrated before each test using an argon-mercury lamp with known spectral features and checked against known features in the nitrogen emission spectrum for accuracy. Emission from the tagged line in nitrogen-oxygen gas mixtures enable identification of key atomic and molecular participants in the reactions and the relative concentrations of prominent species as a function of gas mixture. To obtain broad-spectrum images of FLEET, we use two different camera systems with different spectral responses. The first is an intensified CMOS PCO.dimax HD+ camera system with a 1920x1440 pixel resolution at 11 $\mu$m x 11 $\mu$m pixel size and maximum frame rate of 2128 frames per second. Signal amplification is achieved with a Quantum Leap gateable image intensifier module with a reported resolution > 60 LP/mm and gate repetition of 2 MHz. The intensifier serves the dual purpose of signal amplification and high-speed shutter, and the MCP gain is held constant for the duration of the experiment. The spectral response of the camera-intensifier system is entirely dependent on the intensifier’s quantum efficiency. The second camera is a LaVision PicoStar UF 12 intensified and gated camera system equipped with a S20 photocathode.

Figure 2.21 depicts the spatially-averaged peak emission intensity as a function of nitrogen fraction for several different delays following excitation. For the sake of visual clarity,
errorbars are only shown for the 2 \( \mu s \) and 20 \( \mu s \) delay cases. The camera gate width is fixed at 1 \( \mu s \) for each data point. The introduction of small percentages of oxygen into the nitrogen mixture causes the signal to drop steeply by a factor of two or three, forming a local signal intensity minimum. The signal intensity in air under the same experimental conditions at a 5 \( \mu s \) delay (not shown) falls approximately on the curve indicated by the 5.5 \( \mu s \) delay line at 78% \( N_2 \). At 21% mole fraction, the ratio of oxygen to nitrogen in air unfortunately falls close to that minimum well, affecting FLEET’s attractiveness as a non-seeded diagnostic method for air flows. The signal appears to have a local maximum in a mixture of 50% nitrogen and 50% oxygen before dipping to immeasurable values as the mole fraction of nitrogen in the mixture continues to decrease.

Figures 2.22 and 2.23a depict the second and first positive regimes in detail. These spectra are averaged over 150 individual shots with a pulse energy of 2 and 1 millijoules,
Figure 2.21: FLEET emission intensity as a function of time and mole fraction at 1 atm total pressure. Errorbars are only shown for the $d=2\ \mu s$ and $d=20\ \mu s$ cases. Laser parameters: $\lambda = 800$ nm, 2 mJ/pulse, $f=30$ cm, 1 kHz repetition rate. Camera gate: 1.0 $\mu s$

Figure 2.22: Time-integrated FLEET second positive spectra as a function of mixture. Laser parameters: $\lambda = 800$ nm, 2 mJ/pulse, $f=30$ cm, 1 kHz repetition rate
Figure 2.23: Time-integrated FLEET first positive spectra as a function of mixture. Left and right figures show different wavelength ranges for clarity. Nitrogen first positive transitions are labeled. Laser parameters: $\lambda = 400$ nm, 1 mJ/pulse, f=30 cm, 1 kHz repetition rate respectively. Time integrated spectra taken at the $v' = 0 \rightarrow v'' = 0$ transition at $\lambda = 337$ nm show strong, monotonic quenching behavior with increasing oxygen levels (Figures 2.22). The second positive system typically has a short lifetime of tens of nanoseconds in air or nitrogen [43]. In Figure 2.23, the visible spectrum in oxygen mixtures shows a strong transition near $v' = 8 \rightarrow v'' = 7$ that corresponds to the 777 nm transition of atomic oxygen. No other measurable features were found outside of these spectral ranges. These results suggest that the increase in fluorescence at approximately 50%$O_2 + 50%N_2$ (Figure 2.21) may be a result of increased B-state populations due to $N_2(C^3Π_u)-N_2(B^3Π_g)$ transitions. The time-integrated visible spectra in oxygen mixtures shows a strong transition at the 777 nm line, suggesting a strong contribution from atomic oxygen. This feature at 777 nm is present for both 50%$O_2$ and 20%$O_2$ with no noticeable change in signal strength between the two mixtures. In contrast, the $v' = 11 \rightarrow v'' = 7$ and $v' = 11 \rightarrow v'' = 8$ lines of the first positive system dominate in pure nitrogen, with no additional transitions from other species. Direct
quenching of excited nitrogen states (reactions 81-84) by $O^-$ and $O_2^-$ ions is virtually the same for both the C and B electronic states and also does not explain the spectrally-integrated non-monotonic behavior. Transitions to the lower vibrational levels of the A-state fall in the infrared spectrum, outside the detection limits of our equipment. Further experiments would be necessary to explore the possibility of selective quenching of excited nitrogen states by oxygen.

Previous work [147] suggests that increases in signal levels may be attributed to emission from excited nitric oxide, whose spectrum lies outside the sensitive range of most imaging equipment. Calibration data for equipment often does not include sensitivity measurements in the UV regime unless the equipment is marketed specifically for that purpose. $NO$ can initially be produced through a series of recombination, charge transfer and ion-neutral reactions, followed by continued production from dissociation of the secondary species $NO_2$, and excited through collisions with molecules and atoms. Because neither the Quantum-Leap intensifier nor the PIXIS 512B camera equipment calibration tests show their spectral response below 400 nm, and existing QE data suggest very little sensitivity in those wavelengths, the signal intensity as a function of delay and mixture is measured a second time using a LaVision PicoStar camera system, which has about 10% quantum efficiency between 250 nm and 300 nm. A custom aperture is built using a 50 cm dark tube and a $D = 5$ cm calcium chloride lens, and results are shown in Figure 2.24. A comparison between Figures 2.21 and 2.24 show the signal local maximum to be much more pronounced in the former. It is unlikely that increased UV emission can explain the presence of the local signal maximum. Fast reactions rates, low emission levels and equipment sensitivity currently limit the availability of temporally-resolved full-spectrum analyses in air-like gas mixtures. A kinetic model is able to provide physical insight over the entire time range of interest and spectrum of initial conditions with computation time being the only cost. To minimize computing time without losing important physics, the model incorporates only major species and reactions following validation under experimental conditions presented by other studies.
Seeding argon in nitrogen + oxygen mixtures

Since argon provided signal enhancement in pure nitrogen, an attempt was made to see if argon could offset the quenching effects of oxygen. Figure 2.25 depicts the spatially-averaged, background-subtracted peak emission intensity as a function of mixture for several different delays following excitation. The camera gate is held constant at $0.5 \mu s$ and each data point is the average of 128 individual shots. Low shot-to-shot fluctuations produced errors of less than 2% for most cases, so error bars are excluded. Small percentages of argon seeded in mixtures with large percentages of oxygen (Figure 2.25, top) and synthetic air (Figure 2.25, bottom) appeared to have very little benefit for the signal intensity during timescales of interest. In fact, small decreases in signal intensity are observed at early delays. The middle image in Figure 2.25 investigated the effects of argon on equal ratios of nitrogen to
argon, and the results are largely similar to the other cases. It appears that oxygen’s lower ionization energy, relative to nitrogen and argon, allows oxygen processes to dominate in those mixtures.

### 2.3.3 Kinetics Model

The temporal behavior of different concentrations of oxygen and nitrogen following femtosecond laser dissociation is studied using the zero-dimensional kinetics model outlined in Section 2.2.2. The creation of 24 different species \( (e, N_2(A^3\Sigma_u^+), N_2(B^3\Pi_g), N_2(C^3\Pi_u), N^+, N^+_2, N^+_3, N^+_4, O_2^+, O_2^-, O_3, O_3^-, O, O^+, O^-, NO, NO^+, NO_2, O_2^+(a^1\Delta_g), O_2(b^1\Sigma_g^+)) \) is taken into account, and the initial vibrational temperature is assumed to be equal to that of the ambient gas \( (T_v \approx T_g \approx T_0) \). Reaction rates are primarily taken from [123] and [77],
initial ionization rates of gaseous species from [98], and electron-neutral collision frequencies are approximated from energy losses [66]. Detailed reactions and corresponding rates can be found in Table A.2-A.4. The following processes are included in this model:

- Excitation, ionization and dissociation of neutral particles by electron impact
- Electron attachment and detachment processes for positive and negative ion formation
- Recombination of electrons and positive ions
- Associative detachment processes such as atomic collisions with negative ions
- Cluster ion formation
- Pooling reactions between $N_2(A^3\Sigma_u^+)$ molecules
- Formation of electronically excited molecular nitrogen
- Formation of metastable oxygen states
- Depopulation by electron impact
- Collisional quenching by molecules

Some quenching processes of nitrogen excited electronic states are excluded due to their low probabilities, and the $N_2(a, a')$ states are not modeled, but a comprehensive list of these processes can be found in Table 9.3 of reference [27]. The deexcitation of excited nitrogen by electrons is also excluded. This is justified using a rough approximation: $k_e$, the rate of collisions of electrons and metastable argon, is used to approximate the rate of electron quenching of excited nitrogen. By comparing the quantity $k_e \cdot n_e \cdot N_2(C)$ with $k_{95} \cdot O_2 \cdot N_2(C)$ ($k_{95}$ from Table A.3), we see that the latter is at least 3 times larger at $t = 0$ for most mixtures, and quenching by molecular oxygen dominates since the electron population is constantly decaying. Electron and vibrational temperatures are calculated using Equations 2.7 and 2.13 [123], respectively. The electron temperature is calculated using an ordinary
first order differential equation approximation of the hydrodynamic equation \[115\] in Equations 2.6-2.7 and vibrational temperature is defined in Equations 2.13-2.14. Species formed immediately as a result of multiphoton ionization (\(e, N_2^+\) and \(O_2^+\)) are calculated from available rates using femtosecond laser intensity-clamping ranges for 800 and 400 nm \[36\]. Other initial excited atom and molecule populations are assumed to be zero. Electron-ion Coulomb collisions are computed using Equation 2.35 \[64, 4\]. The resulting system of differential equations is found using a variable-order stiff equation solver and mass and charge conservation are realized. More details about this model can be found in \[148\]. This work extends the models presented in \[143, 148\] by taking into account the rapid vibrational relaxation caused by oxygen atoms in the mixture and heat lost to the gas through vibrational-translational relaxation. The gas temperature is described by Equation 2.15, which takes into account heat production from VT relaxation and recombination processes. The model assumes that most of the gas vibrational energy is assumed to be stored in nitrogen while estimating the VT relaxation time.

\[
\tau_{VT} = \left( (N_2 + O_2)(7 \times 10^{-16} e^{-141/T_1^{1/3}} + X_{O_2} \times 5 \times 10^{-18} e^{-128 \sqrt{T_g}}) \right)^{-1} \tag{2.31}
\]

When the harmonic oscillator approximation holds at small displacements from equilibrium, we can approximate the following:

\[
Q_{VT} = \frac{E_v - E_{v,0}}{\tau_{VT}}
\]

. We neglect anharmonicity in the calculation of the vibrational temperature \(T_v\) because our modeled plasma is continuously decaying after the initial laser excitation and the vibrational temperature remains very close to the gas temperature, which is an order of magnitude smaller than a vibrational quantum of the nitrogen molecule. Rate coefficients (Equation 2.33) and threshold energies are used to obtain the electron energy loss rate as a function of electron temperature [K]. From the sum of energy losses due to vibrational and electronic
excitation, Equation 2.32 [66], we can approximate $\nu_{ev}$ in Equation 2.33. Various rates from [64] and [13] are found in Equations 2.33-2.36. In Equations 2.32-2.36, $T_e$, $\varepsilon$, $I$ are expressed in units of electron volts.

\[ q_v + q_{ex} = 8.917 \times 10^{10} \times T_e^{-3}(9.93 + T_e^5) \times n_e \]  \[ \text{[2.32]} \]

\[ \nu_{ev} \approx \frac{1}{\hbar \omega_0} \left( 8.917 \times 10^{10} \times T_e^{-3}(9.93 + T_e^5) \times n_e e^{-2.36/T_e^3} - \nu_{ex} I \right) \]  \[ \text{[2.33]} \]

\[ \nu_{ex} = 5.53 \times 10^6 \times \left( \frac{N}{N_0} \right) T_e^2 \times (1812.23 + T_e^{-15}) \times e^{-1.7835/T_e^2} \]  \[ \text{[2.34]} \]

\[ \nu_e = 2.907 \times 10^{-12} n_e T_e^{-1.5} \times \ln(\Lambda) \]  \[ \text{[2.35]} \]

\[ \nu_m = 2.91 \times 10^{-14} N_2 \sqrt{T_e} \]  \[ \text{[2.36]} \]

Figure 2.26 depicts the evolution of most of the secondary species created upon excitation of a synthetic air mixture. The relatively long lifetimes of atomic oxygen, ozone and nitric oxide can be contrasted with the rapid consumption of nitrogen ions. The predicted temporal variation of nitric oxide number density as a function of nitrogen fraction in the mixture is lower for all mixtures and the relative behavior changes at lower percentages of nitrogen, as shown in Figure 2.27. Each point on the curve corresponds to the predicted number densities integrated over $t=1-10 \ \mu s$. The model supports the experimental data that nitric oxide, with emission in the UV, does not contribute significantly to emission at the microsecond timescale.

The model is computed for a number of mixtures ranging from 1% $O_2 + 99% \ N_2$ to 80% $O_2 + 20% \ N_2$. Populations of excited nitrogen species are plotted, from which the first positive system (FPS) and second positive system (SPS) emission levels can be deduced. From the
Figure 2.26: Predicted temporal variation of all secondary species in a synthetic air mixture (80% N₂ + 20% O₂) at 300 K and atmospheric pressure. Laser properties: λ ≈ 800 nm, 2 mJ/pulse

population densities, the number density of photons due to spontaneous emission may be computed using the relaxation lifetime τ_{C→B}: n_{ph} = N_{2}(C)/τ_{C→B} where τ_{C→B} is taken from [19]. Einstein coefficients for transitions between C^3Π_u (v = 0 – 4) to B^3Π_g (v' = 0 – 21) are taken from [52] and computed using the r-centroid approximation. Photon densities from both stimulated and spontaneous emission between the nitrogen C and B state are shown in Figure 2.29. The long photon lifetimes can be attributed to several mechanisms: i) the long-lived nitrogen recombination process, ii) creation of N₂(C) from electron-impact dissociation of cluster ions, and iii) indirect processes maintaining a relatively high electron density. Despite the high excitation cross section and low quenching rate of O₂(a¹Δg) in
Figure 2.27: Predicted temporal variation of nitric oxide number densities integrated over $t=1-10 \, \mu s$ as a function of mixture at 300 K and atmospheric pressure. Laser properties: $\lambda_c = 800$ nm, 2 mJ/pulse

oxygen discharge plasmas, the lowest oxygen metastables $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ do not appear to have a large effect on the calculated visible emission or excited nitrogen populations in our mixtures.

This zero-dimensional model is developed to study the contributions from intermediate processes in femtosecond laser excitation of oxygen and nitrogen gas at atmospheric pressure and temperature for velocimetry applications. It captures key observed behaviors that correspond with the experimental study, most notably the decay of the nitrogen first and second positive emissions and the relative populations of atomic nitrogen throughout the FLEET process. Emission from atomic oxygen lies in the visible regime and is strong enough to be spectrally resolved in Figure 2.23, despite the overall quenching effect of oxygen on the signal. It is likely that the emission from atomic oxygen increases as the percentage of oxygen
in the mixture increases, and this effect is counteracted by the overall quenching effect of oxygen on the FLEET signal to produce a local maximum at 50% oxygen. Differences in measured emission and that predicted by the model are partially accounted for by other nitrogen deactivation processes - the modeled photon populations do not translate one-to-one to detectable FPS and SPS radiation. Some variation between our study and those conducted by other groups is expected due to unspecified initial conditions, different processes taken into account, variable rates, temperature models, and unique species considered [17]. Many of the reaction rates used are originally derived in low-pressure discharge environments, so care should be taken when applying these results to higher pressure conditions [53]. The zero-dimensional approximation is reasonable within the accuracy of the solver up to several microseconds. Diffusion, not included in this zero-dimensional study, plays a larger role in lower pressure situations, whereas collisions, nonlinear optical effects and quenching
Figure 2.29: Predicted photon number density \([\text{cm}^{-3}]\) as a function of nitrogen and oxygen mixture at 300 K and atmospheric pressure. Laser properties: \(\lambda_c = 800\ \text{nm}, 2\ \text{mJ/pulse}\)

dominate at higher pressures. The model is unable to capture local gas effects resulting from the expulsion of an acoustic wave from the laser interaction region at several hundred nanoseconds following excitation. A one-dimensional model taking into account the rapid gas expansion and hydrodynamic effects is recommended for a follow-up to this study. This model is most accurate for low temperature plasmas \((T_g \lesssim 10^3\ \text{K})\) and is expected to deviate from experimental conditions at higher gas temperatures or under cryogenic conditions.

Summary

This study uses an experimental and theoretical approach to investigate emission following femtosecond laser excitation of atmospheric pressure mixtures of nitrogen and oxygen gas. A non-monotonic decrease in fluorescence of the interaction region has been experimentally observed at the microsecond timescale. At equal ratios of oxygen to nitrogen, a slight
increase in fluorescence occurs, as compared to slightly less or slightly more oxygen, and this behavior can attributed to emission from atomic oxygen and early emission from the nitrogen C electronic state. These results open possibilities for optimizing the FLEET velocimetry signal in non-air environments, such as in combustion. Excited long-lived species such as nitric oxide and ozone do not appear to have any significant contribution to the emission levels.

2.4 Helium, Methane, Carbon Dioxide Mixtures

The experiment in Section 2.2.1 is conducted in mixtures containing helium, methane and carbon dioxide. Because argon has been found to effectively enhance the FLEET signal, helium is tested see if the effects can be extended to other inert gases. Methane is an important gas for combustion, and tagging in methane-containing reactive flows can reveal new insights. Lastly, carbon dioxide is a readily-available atmospheric gas with implications for climate science and combustion.

2.4.1 Helium

Figure 2.30 depicts the FLEET spatially-integrated signal intensity as a function of delay for various helium-nitrogen mixture ratios. An apparent local maximum is reached at about half helium, half nitrogen, which suggests the existence of enhancement pathways. The signal increase is strongest for smaller amounts of helium, and as the mole fraction of helium in the gas increases beyond that of nitrogen, the signal drops monotonically for all delays. $He_2^*$’s energy levels lie between 10-16 eV, which overlaps with energy levels of the $N_2(C^3Π_u^+)$ states (Figure 1 in [15]). The energy overlap can result in collisional energy transfer between $He_2^*$ and $N_2$ and increased emission through the first or second positive systems. Another source of emission is the nitrogen molecular ion’s first negative system, which occurs in the near-UV spectrum. The charge-transfer reactions in equations 2.37 and 2.38 have rate constants on
The order of $10^{-29} \text{cm}^6/\text{s}$, and may lead to strong lines at 391.4 nm and 427.8 nm as a result of the nitrogen ion laser transition $N_2^+ (B^2\Sigma_u \rightarrow X^2\Sigma_g)$.

$$He_2^+ + N_2 (^1\Sigma_g^+) \rightarrow N_2^+ (^2\Sigma_u^+) + 2He$$ \[2.37\]

$$He_2^+ + N_2 (^1\Sigma_g^+) + He \rightarrow N_2^+ (^2\Sigma_u^+) + 3He$$ \[2.38\]

### 2.4.2 Methane

FLEET has previously been used in a methane-air mixture in the post-flame region of a Hencken burner [38]. Methane gas is found to have a strong quenching effect on FLEET emission. The spectra of various mixtures of methane and nitrogen is measured at atmospheric pressure and temperature, and the only significant detectable features are in the near-UV regime, 300-450 nm. It is likely that femtosecond laser excitation creates a number
of carbon, carbon-hydrogen and carbon-nitrogen radicals, and through a series of reactions, emission is produced in the $CN(B^2\Sigma^+ - X^2\Sigma^+)$ band. The $\Delta v = v' - v'' = 1, 0, -1$ transitions, corresponding to 358 nm, 387 nm and 417 nm, are observed in the time-gated spectra in Figure 2.31. Only the 6% methane and 94% nitrogen case is shown since these features become difficult to resolve at higher mixture fractions of methane, and no signal is observed at later delays. A pure nitrogen spectrum is taken in order to calibrate this spectrum, and it is important to note that the signal in pure nitrogen is 20 times weaker than the $\Delta v = 0$ peak at 387.7 nm. Unfortunately tagging in methane mixtures appears to have a very short detectable lifetime, not longer than a microsecond at atmospheric conditions with our current equipment.

![Figure 2.31: Time-gated spectra in a mixture of 6% methane and 94% nitrogen, integrated from t=0.1-0.6 $\mu$s](image)

2.4.3 Carbon Dioxide

Carbon dioxide is the fifth most abundant gas in our atmosphere and a major byproduct of fermentation, respiration and hydrocarbon combustion. In addition to carbon dioxide's
relevance on Earth, it plays an even larger role in making up approximately 96% of Mars’s atmosphere. The FLEET images in Figure 2.32 are taken in mixtures of $4.7\% N_2 + 1.5\% Ar + 94\% CO_2$ in order to replicate Mars’s atmospheric composition as closely as the equipment would allow. In Figure 2.33, the absolute FLEET intensity in carbon dioxide mixtures is very similar to that in oxygen mixtures, albeit with monotonic behavior as the mixture fraction changes.

Figure 2.32: From left to right: delays of 2 $\mu s$, 5.5 $\mu s$, 15 $\mu s$ and 20 $\mu s$. The gate is held constant at 1 $\mu s$. Laser properties: $\lambda_c = 800$ nm, 1 kHz, 2 mJ/pulse
Figure 2.33: FLEET signal intensity as a function of delay in carbon dioxide and nitrogen mixtures. The gate is held constant at 1 µs. Laser properties: $\lambda_c = 800$ nm, 1 kHz, 2 mJ/pulse.

### 2.5 Humid Conditions

In humid nonthermal air plasmas, a buildup of ozone, higher oxides and hydrides of nitrogen is expected. Loss time for less reactive species such as $H, N, O, OH$ and $NH$ is relatively long, on the order of $10^4 - 10^5$ s [60]. The addition of water molecules to air and nitrogen gases can reduce three-body recombination of nitrogen atoms (Equation 1.3), remove nitrogen atoms and form oxygen atoms (Equations 2.39-2.41), and deactivate excited molecular nitrogen species directly (Equation 2.39) [24]. In Equation 2.39, $N_2^*$ refers to $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g^+)$ and $N_2(C^3\Pi_u^+)$ .

$$N_2^* + H_2O \rightarrow N_2 + H + OH$$  [2.39]
\[ N + OH \rightarrow NO + H \] [2.40]

\[ N + NO \rightarrow N_2 + O \] [2.41]

Figure 2.34: FLEET signal in pure nitrogen, pure air, nitrogen + water vapor, air + water vapor. Note that a logarithmic scale is used on the y-axis. Laser properties: \( \lambda_c = 800 \) nm, 1 kHz, \( f = 30 \) cm

To understand this process, a FLEET experiment is conducted with 15 mL of water inside the horizontally-oriented gas cell described in Section 2.2.1 and industrial-grade nitrogen or air is flowed through the cell. Figure 2.34 depicts the signal intensity in saturated water vapor under atmospheric conditions: 1 atm and 300 K. Emission decay in pure nitrogen and air are plotted for comparison, and it is important to note that the signal persists for much longer (tens to hundreds of microseconds) than shown on the graph. Notable characteristics of this data is that the initial decay of emission is much faster in nitrogen + water vapor mixtures than in air + water vapor, and the signal is about twice as strong in air + water vapor at delays after a microsecond. The collisional deactivation of \( N_2^* \) by oxygen is much
stronger than that by nitrogen, as seen in Section 2.3, so the relative quenching rates in water vapor cannot be attributed to direct quenching by nitrogen, oxygen, or water vapor alone. Explanations for the observations in air may rely on the creation of secondary oxygen species, which help to remove hydrogen byproducts that would otherwise deactivate excited nitrogen. Oxygen can react directly with water to produce long-lived species such as ozone, effectively removing both oxygen and water from the mixture and reducing collisional deactivation by those particles. Oxygen may also react with $OH$ and $NO$ species to reduce the consumption of nitrogen atoms. A full kinetic model for humid nonthermal air or nitrogen plasmas is not included in this work, but can be useful for better understanding these results.

2.6 R134a and Air Mixtures

2.6.1 NASA Transonic Dynamics Tunnel

The Transonic Dynamics Tunnel (TDT) [10, 33, 31, 30] at the NASA Langley Research Center is a large-scale variable pressure closed-circuit wind tunnel capable of using 1,1,1,2-Tetrafluoroethane ($CH_2FCF_3$, R134a) or air at speeds up to Mach 1.12. R134a serves as a high density fluid for aeroelastic model testing. R12, a chlorofluorocarbon (CFC), was formerly used as the heavy gas test medium but ultimately phased out due to the enactment of the Montreal Protocol and U.S. Clean Air Act. In 1995, R134a was chosen as a more environmentally safe alternative to the other candidate gas, sulphurhexafluoride (SF6), and continues to be used today. The TDT Heavy Gas Reclamation System introduces the heavy gas into the tunnel prior to testing and evacuates it after the test through an air-to-heavy gas exchange detailed in [33]. This method typically leaves behind trace percentages of air in the heavy gas flow. The TDT has an octagonal cross section of 16 feet by 16 feet and supports the installation of a variety of mount systems including sting mounts, a sidewall turntable, a floor mounted turntable, a two-cable free-flight support system, helicopter test apparatuses,
tilt-rotor test apparatuses and custom mount systems. A large matrix of observation windows provides optical access to the test section.

The motivations for testing in TDT are closely coupled with the complexities that arise in the transonic flow regime. Transonic flow is a mixture of sub- and supersonic local flow with nonlinear flow features introduced by the presence of oscillating shocks. When the maximum local velocity on an airfoil in the flow becomes supersonic, a shock develops and moves along the surface, leading to rapid variations in drag, lift and pitching as the Mach number changes. Aeroelasticity, the interplay of structural (elastic, inertial) and aerodynamic forces, is responsible for a number of dynamic behaviors such as limit cycle oscillations (LCO), internal resonances and chaotic motion [82], as well as for static phenomena such as deformation of aircraft parts under aerodynamic loads. The unsteady aerodynamics of airfoils and wings in transonic flow create a phenomenon called "flutter", or oscillatory instabilities that can lead to catastrophic failure of the part if not mitigated. Over the past few decades, the TDT has frequently been used for studying flutter trends, nonlinear transonic effects on flutter, aeroelastic characteristics of different wing and rotor concepts and active control methods, as well as for providing CFD model validation. NASA Langley’s TDT has played a large role in the development of active controls technology by providing a facility for testing new concepts and validating models and design methods. In addition to aeroelasticity programs, the TDT has been used for space-related test programs that take advantage of its large test section, variable pressure capabilities and heavy gas medium [30]. These tests address launch vehicle and spacecraft transition through Earth and similar atmospheres, launch vehicle ground-wind loading due to the natural wind environment, launch vehicle dynamics, atmospheric flight, atmospheric reentry, and effects of planetary conditions on instrumentation accuracy during landing.

Critical to the objective of the TDT wind tunnel test program is the validation of flutter suppression techniques [71, 100] and the ability to assess the effectiveness of active controls. The program aims to understand and predict nonlinear dynamic response behaviors of the
aircraft in order to improve overall reliability, safety and performance. To validate these methods and theories, measurements of local flow are required. A robust diagnostic method with high spatial and temporal resolution is needed to measure local flow behaviors under transonic conditions in mixtures of R134a with small percentages of air. This section focuses on a variation of FLEET. FLEET has previously been used to measure the flowfield around a symmetric airfoil in the NASA Langley 0.3-m Transonic Cryogenic Tunnel, a closed-loop fan-driven wind tunnel operating at subsonic conditions with nitrogen working gas [18]. Femtosecond laser excitation for velocimetry has been studied in a number of different gaseous mixtures, including oxygen, argon, carbon dioxide and methane, and notable lifetimes have been measured in all but methane gas [23, 144, 148]. The mechanisms at work are expected to be vastly different for tagging in single-gas species or air versus in pure R134a. Femtosecond laser near-infrared interactions of polyatomic molecules composed of carbon, hydrogen, and halogen group atoms result primarily in dissociation through field ionization and fragmentation. Formation of $CF_4$, $CF_3H$ and secondary product $CF_2$ is expected [7].

2.6.2 Experiment

We investigate the possibility of extending femtosecond laser tagging to flows composed primarily of gaseous R134a for application in the NASA TDT. Tests are conducted in a glass cylindrical gas cell ($D \approx 2''$) with optically clear windows that allow $> 94\%$ transmission at the operating laser wavelengths, 800 nm and 400 nm. Mixtures of R134a and industrial-grade air are supplied from a gas-mixing manifold and flowed through the cell. A rotary vane vacuum pump evacuates the cell and helps to regulate pressure between 0.1 and 1.0 atmospheres. The laser used in this study is a Spectra Physics Solstice laser with titanium sapphire oscillator and MaiTai regenerative amplifier operating at a fundamental wavelength centered at 800 nm with 1 kHz repetition rate. Frequency-doubling to 400 nm is achieved with a SHG BBO crystal at approximately 30\% efficiency. Focusing of the beam is performed with a f=25 cm focusing lens. We use an intensified CMOS PCO.dimax HD+ camera system.
with a 1920x1440 pixel resolution at 11 µm by 11 µm pixel size and maximum frame rate of 2128 frames per second to obtain both broad-spectrum images and spectra of the tagged line. An experimental spatial resolution of 18 µm per pixel is attained through the use of extension tubes. Signal amplification is achieved with a Quantum Leap gateable image intensifier module with a reported resolution of > 60 LP/mm and gate repetition rate of 2 MHz. The intensifier serves the dual purpose of signal amplification and high-speed shutter. The MCP gain is held constant for the duration of the experiment at approximately 8.3/10 to minimize amplification of background noise. Two lenses collimate and focus the diffuse radiating signal into the slit of an Acton SpectraPro 300i spectrometer for spectroscopy. The intensity and lifetime of the visible emission at different mixtures and pressures is measured and reported on in this study. Intensity is determined by summing all the signal counts in a rectangular area enclosing the radiating line, and subtracting the same sum of background counts with no signal present. This process reduces the effect of shot-to-shot fluctuations in the gas flow. The optically clear cylindrical gas cell is depicted in Figure 2.35. It is supported by two sets of clamps and the laser beam is focused into the center of the cell. These two photographs depict the emission as seen by the naked eye (or an ordinary DSLR camera) under different pressure conditions. At low pressures, the emission appears to be bright blue, and as the pressure is increased, it gradually becomes violet before turning white. These changes reflect the strong pressure sensitivity of this tagging process. Time-gated spectra, which are only resolvable within the first several hundred nanoseconds, are taken of the emitting line in order to give insight to the processes responsible for these changes.

Figure 2.36 depicts spectra that are temporally integrated over the first hundred nanoseconds following femtosecond laser excitation for two different pressure conditions. In the presence of small amounts of nitrogen (≈ 20% mole fraction), there are three prominent features between 400 and 550 nm that may be attributed to spectral lines in the $C_2$ Swan band or the $A^2\Delta - X^2\Pi$ and $B^2\Sigma - X^2\Pi$ transitions of the CH radical. Further fluorescence in the UV (from $CF_2$ and $CF$ radicals) may contribute to the overall signal as well, but lie
Figure 2.35: Photographs of femtosecond laser excitation in 15% air + 85% (mole fraction) R134a at different pressures, taken with a Canon DSLR camera. At higher pressure levels (up to atmospheric), the emission appears white. Laser: $\lambda_c = 800\text{nm}, 1.5 \text{ mJ/pulse}, 1 \text{ kHz}$ outside of the resolvable range of our spectroscopy equipment. No other detectable spectra are observed in the experiment. Time-integrated spectra in pure R134a or R134a + 15% air taken with a Princeton Instruments PIXIS 512B camera in combination with the spectrometer offered similar or worse resolution of intensity differences between the same two peaks at different pressures.

Figure 2.37 shows signal decay curves taken at different pressures for 15%Air+85%R134a, which was chosen as the maximum air-to-R134a ratio expected to be encountered in the TDT. The signal is measured as the sum of the averaged intensity over 100 shots in a fixed region, indicated by the red boxes, minus the background levels. Visuals corresponding to 50 and 120 a.u. averaged signal levels are given on the right panel. At $P=0.2 \text{ atm}$, the signal in
Figure 2.36: Spectra taken with 80% R134a and 20% N₂, delay = 0 and 100 ns exposure. Laser: $\lambda_c = 800$ nm, 1.5 mJ/pulse, 1 kHz

Figure 2.37: Signal decay curves for data averaged over 100 shots taken at different pressures, using a 1.5 mJ laser pulse centered at 800 nm. Note that the y-axis (signal intensity) does not begin at zero. On the right are two averaged representations of the signal at approximately 120 a.u. and 50 a.u.
pure R134a is 1/10 the strength of that in air and 1/50 the strength of that in nitrogen under the same laser properties and focusing, a trend also observed at other pressure levels. Together, Figures 2.36 and 2.37 suggest that while air does not seem to have a large effect on the emission process, the displacement of some freon molecules by air reduces the quenching of the radiation and thus allows for overall higher signal levels for most delays and pressure conditions.

![Graph and images showing signal decay and single-shot images.](image)

**Figure 2.38:** Signal at the minimum pulse energy needed for tagging in mixtures of 15%Air + 85%R134a. (a) Intensity at lowest pulse energy, 0.5 mJ, and 0.7 atm. (b) Single shot images of the signal at 0.7 atm. Top row: 800 nm, 1.5 mJ/pulse, \( d = 1, 3, 5 \mu s \). Bottom row: 800 nm, 0.5 mJ/pulse, \( d = 0.5, 1, 3 \mu s \)

Next, we determine that the minimum pulse energy necessary to produce visible emission in the gas cell at 800 nm and 1 kHz repetition rate with a \( f=25 \) cm focusing lens is 0.5 mJ. Figure 2.38a shows the signal decay curve for tagging with the minimum pulse energy at 0.7 atm and the corresponding averaged images. Figure 2.38b depicts single-shot images of the tagged line at 0.7 atm produced using pulse energies of 1.5 mJ and delays of 1, 3, 5 \( \mu s \) (top row) and 0.5 mJ and delays of 0.5, 1, 3 \( \mu s \) (bottom row). The effects of pressure and delay on signal levels are studied in Figure 2.39. Dashed lines link two intensity measurements at
Figure 2.39: Emission intensity in pure R134a at different pressures and delays, where the delay, $t$, is defined by $t = d + \frac{1}{2}g$ and the gate width is 1 $\mu$s. Note that the y-axis (emission intensity) does not begin at zero. Laser: $\lambda_c = 400$ nm, 1.2 mJ/pulse, 1 kHz

arbitrary units (a.u.) to their corresponding signal levels. We observe that at low pressure conditions ($\lesssim 0.2$ atm), the signal strength and lifetime are strongest. Pressure appears to have the strongest effect on the measurable signal, second to delay time. Signals at longer delays and pressures $\gtrsim 0.5$ atm were not measurable with our experimental equipment. Delay time along the x-axis is the sum of the delay after pulse arrival plus half of the gate width. Strong shot-to-shot fluctuations observed at low pressures in Figure 2.40 can be partially attributed to the limitations of our oil-sealed rotary vane pump, as explained in Section 2.2.1.

At the high pumping speeds necessary to maintain a low-pressure environment, gas leakage around the seal can increase the signal fluctuations. These fluctuations are normalized with signal measurements in pure air to isolate and remove the effects of the vacuum pump on our signal. Another source of error comes from the individual gas flow-meters, which can oscillate and lead to slightly varying ratios between air and R134a especially in the third case (5%
Air +95% R134a), which becomes more pronounced at low pressure levels. Measurements are made to show that these oscillations are relatively constant between the two flow-meters and their effects on the mean signal can be removed by averaging over many samples.

### 2.6.3 Single-shot precision in stationary gas

Examining the measurement in low-velocity flows is helpful in evaluating the goodness of the fitting algorithm and overall measurement precision. For this study, 100 single-shot images of tagging in 0.12 atm quiescent gas are fitted with Gaussians along each transverse line position, and corresponding uncertainties are given. The images are taken with a delay of 3 $\mu$s and a gate of 1 $\mu$s. Displacement uncertainty $\delta(\Delta x)$ (Equations 1.8-1.9) includes the standard deviation of the fitted Gaussian centers at each pixel location over 200 shots and a
5% fitting error. Displacement uncertainty is limited by the signal strength, which itself is a function of the delay and any fluctuations in gas properties in the experiment. Figure 2.41 shows one sample shot fitted with Gaussians along its transverse length (top), and the mean velocity and uncertainty at each transverse line position (bottom) measured in a stationary 0.12 atm gas. The velocities are analyzed over a length of 200 pixel rows in the transverse direction and outliers, which make up about 15% of the data, are discarded. In the bottom plot of Figure 2.41, representative error bars are shown for every other point to prevent overcrowding. Note that due to the relatively small sample size, the mean velocity in this flow is nonzero in many locations and strongly influenced by fluctuations and other sources of error. The velocity uncertainty falls within 5 m/s of the mean along the line. For a delay of 1 µs and the same gate, the velocity uncertainty increases to 10 m/s despite the increase of SNR at shorter delays. Increasing the delay time to 5 µs in a 0.01 atm flow reduces the uncertainty even further, to just over 2 m/s. Not every set of experimental conditions can
achieve uncertainty reduction with an increase in delay time, however, as the deterioration of the signal outpaces the decrease in timing uncertainty at high (near-atmospheric) pressures. This particular low-pressure condition is chosen because it represents the lower threshold for pressure conditions expected in the TDT and exemplifies the strongest effects of intensity saturation and fluctuations on the overall measurement.

2.6.4 Single-shot precision in moving flow

Figure 2.42: Gas cell modified with an inlet pipe insertion (2 mm diameter) for velocimetry

Figures 2.43 and 2.44 demonstrate velocimetry in a pipe flow as shown in the gas cell configuration (Figure 2.42). The pipe is long enough relative to its diameter such that the flow is fully-developed before rapidly expanding as it enters the evacuated cell. The laser pulse energy was increased to 3 mJ per pulse in this experiment to overcome losses as the focused beam enters the optical-grade fused silica flat windows on the cell located perpendicular to the cell’s cylindrical axis, and the repetition rate is kept constant at 1 kHz. The laser beam is positioned normal to the pipe axis. The regulated supply pressure and measured gas cell pressure are close to 1 atmosphere, but that value is expected to deviate from the pressure seen by the laser signal at the pipe exit due to the pressure increase in the narrow pipe. $Re_D = 1.7 \times 10^5$, which exceeds the critical Reynolds number for transition to
Figure 2.43: Single-shot images of femtosecond laser velocimetry in pure R134a flow at the pipe exit (230m/s), imaged in burst mode with camera delays at $t = 0, 5, 10\mu s$, gate of $0.5\mu s$. The flow is from right to left and each frame is about 6 mm across, horizontally. Each of the five frames depicts three exposures corresponding to the previously stated delays, $t = 0, 5, 10\mu s$. $t = 0$ corresponds to approximately 200ns following the pulse arrival time in order to temporally filter out Rayleigh scattering from the beam. The laser direction is from bottom to top of each frame. Laser: $\lambda_c = 800$ nm, 1.5 mJ/pulse, 1 kHz

Figure 2.44: Single-shot images of femtosecond laser velocimetry in a mixed R134a + 5% air flow at the pipe exit, imaged in burst mode with camera delays at $t = 0, 5, 10\mu s$, gate of $0.5\mu s$. The optical arrangement and timing are the same as in Figure 2.43.

turbulence in a pipe flow, so the flow is fully-developed and turbulent. Gas flow velocity is maximized so that a clear signal displacement could be measured in the cell. Three positions marked by the displaced emission captured in burst mode can be seen in some of the panels, demonstrating the capability for capturing small fluctuations in the flow with good temporal resolution. The first and longest signal line corresponds to the $t = 0$ delay (approximately 200 ns following the pulse arrival time), imaged right after the Rayleigh scattering of the
laser pulse; some bright scattering from the pipe is visible. In the second "burst" signal lines, we observe some uneven "clumping" of the emission that is not seen in femtosecond laser tagging in diatomic or atomic gas mixtures. The positions of these "clumps" can potentially be used to resolve multiple components of velocity. In this study, no significant difference is observed between tagging in pure R134a or in a mixture with small percentages of air. We also notice that the increase in laser power corresponds to a longer lifetime, but care must be taken to balance the lifetime and strength of the signal with perturbations introduced by the deposited pulse energy. We find that in R134a tagging, the CMOS sensor frequently suffers from negative ghosting where depleted signal count regions occur following a high intensity event. Depleted signal counts typically fall between 5% and 70% of the average background signal. Approximately 2% of the images are strongly affected by this negative ghosting and cannot be fitted, so these images are discarded for the subsequent velocity measurements. About half of the images are missing 40% or more of the signal line, as measured in the transverse direction, due to ghosting. Uncertainty is further complicated by the presence of fully-developed turbulent flow at the pipe exit. For a comprehensive analysis, the parameter \( \delta(\Delta x) \) must be modified to exclude shot-to-shot displacement uncertainties caused by the flow and not the measurement instrument. Figure 2.45b depicts the mean velocity uncertainty (top) and mean velocity with error bars representing uncertainty (bottom) for the data taken in the pure R134a turbulent pipe flow, as calculated using Equation 1.7. This represents an upper bound for the actual measurement precision since it includes variations caused by turbulent flow. No significant difference in velocity uncertainty is found in the R134a + 5% air flow data. A row of fifty pixels, representing approximately 0.9mm at the pipe exit, is fitted. This region indicated by Figure 2.45a is chosen to maximize the area of usable signal and avoid discontinuous signal regions, as seen previously in Figures 2.43 and 2.44. Clumping and signal discontinuity prevent good fits along the entire velocity profile. The uncertainty does not vary significantly across the row of pixels, suggesting that the appearance of "clumps" in the signal does not introduce large errors into the line center fit.
Figure 2.45: (a) The velocity fits are taken over the region indicated by the red box and the flow is going from right to left. From right to left, the fluorescent lines taken in burst mode correspond to $t = 0$ and $t = 5$. (b) This plot shows the mean velocity [m/s] and one standard deviation uncertainty computed with Equation 1.7 using signal lines measured at $t = 0$ and $t = 5\mu s$. Mean velocity is found over 100 shots and uncertainty at each horizontal position reflects the standard deviation over the same dataset. Note that the y-axis (velocity) does not begin at zero.

Figure 2.46 depicts the probability contour plot for different velocities at different y-positions along the tagged line. Images with more than 40% ghosting along the tagged line are discarded for this analysis so out of 200 single-shot images, only 105 are used to create this plot. The range of velocities is divided into nineteen evenly-spaced bins, from 40-220 m/s in increments of 10 m/s, and the number of values in each bin is denoted by the color. The clumping nature of the signal can clearly be seen in this image.
2.6.5 Summary

Femtosecond laser velocimetry has been demonstrated in pure R134a flows and R134a flows with small percentages of air between 0.1 atm and 1 atm. A systematic study of this tagging method is explored through the adjustment of gas pressure, mixture ratio and laser properties. The variable parameter space is chosen to mimic conditions used in the NASA Langley Research Center’s Transonic Dynamics Tunnel. It is found that the signal strength and lifetime are greatest at low pressures for excitation at both the 400 nm and 800 nm laser wavelengths. A time-resolved pressure dependence in the signal is reflected in changing relative intensities of two peaks in the near-UV spectrum. The pressure dependence of this technique is also manifested in the decrease of overall signal intensity as the pressure increases, although even at atmospheric pressure, the signal may be strong enough for a single-shot measurement, or at least an averaged measurement. A minimum energy of 0.5 mJ per pulse at 800 nm and 1 kHz focused with a f=25 cm lens is necessary to produce
a signal lifetime of several microseconds in our gas cell. The signal lifetime increases with increasing power. This technique is shown to be appropriate for measuring mean and instantaneous velocities in a pure R134a flow or in a mixture of R134a with small percentages of air. The single shot precision of this tagging method is demonstrated to be about 18 m/s in a turbulent flow, and 5 m/s in a stationary 0.1 atm gas for a 3 µs delay. Velocity uncertainty scales inversely with delay time up to about six microseconds only in low pressure gas, when the signal-to-noise ratio is above a certain threshold. This non-intrusive and unseeded method should be able to provide quantitative velocity measurements for the TDT facility if practical issues such as optical access and focusing the laser beam through this heavy gas in a large-scale wind tunnel can be addressed. The precision and signal lifetime demonstrate the feasibility of using this technique for measuring flowfields that induce airfoil flutter.
Chapter 3

Optimizing FLEET for Turbulence Measurements

3.1 Introduction

While FLEET shot-to-shot precision has been previously investigated, it is not well understood how the experimental parameters in Table 3.1 affect the overall accuracy of the diagnostic method. Questions arise as to how the energy deposited by the laser could affect the flow, as well as the accuracy of assumptions used for fitting the measured line. The trade-off between the use of higher laser pulse energies and lower f-number lenses for a stronger signal, and the increase of flow perturbations faces particular scrutiny. Spatial resolution can be a limiting factor for resolving small features, but the trade-offs of increasing magnification have yet to be understood. FLEET has been used for tracking high and low velocities, but the velocity error is a function of the flow speed and the mentioned experimental parameters as well. To assess the accuracy and validity of measurements obtained using different configurations, a self-comparison is performed using limitations on spatial scales imposed by constant temperature hot wire anemometry (CTA).
Taylor’s hypothesis is justified for this study because the mean flow is large with respect to velocity fluctuations ($u'/U \approx 0.02 \ll 1$). Under this assumption, the turbulence contribution draws primarily from fluctuations induced by the mean flow and turbulence induced by shear layer vortices is neglected. Additionally, Townsend’s Reynolds number similarity hypothesis proposes that the turbulence structure far from the wall (in the center of the pipe in this experiment) is unaffected by pipe inner-wall roughness.

Previous data taken to quantify FLEET in turbulence showed deviations from expected behaviors measured in [102] at smaller length scales [44], motivating a closer investigation. Since then, we have achieved good conversion to the second and third harmonic, and have access to higher laser pulse energies, which can be useful for larger spatial coverage by splitting the beam into multiple pathways to form a two- or three-dimensional tagging grid. Turbulence statistics are used in order to quantify the limitations of FLEET measurements.

<table>
<thead>
<tr>
<th>Beam Properties</th>
<th>Imaging Properties</th>
<th>Experimental Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse energy density (60 µJ – 4.5 mJ/pulse, focusing)</td>
<td>Camera/Intensifier properties (gain, magnification)</td>
<td>Pressure</td>
</tr>
<tr>
<td>Wavelength (267, 400, 800 nm)</td>
<td>Gating/Delay</td>
<td>Temperature</td>
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<tr>
<td>Pulse duration</td>
<td>Sensor spectral range</td>
<td>Gas Mixture (Air, $N_2$, $Ar$)</td>
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Spatial correlations are integral moments of the joint probability distribution for velocity components separated by some distance $\Delta y$. This correlation function $R$ is introduced in Equation 3.1. $R$ describes how velocity at a point $y$, generally taken to be on the pipe axis, is influenced by the velocity at a location $r$ away at a given time. When $R$ is negative, the time-averaged velocities at those two points have opposite signs.

$$R(y, r) = \frac{\langle u'(y)u'(y + r) \rangle}{u'_{rms}(y)u'_{rms}(y + r)} \quad [3.1]$$
The intersection of a parabola fitted to the correlation function and the separation axis is used to determine the Taylor microscale $\lambda$, which provides a length scale for estimating the velocity gradients of the small eddies. From this, we may determine $Re_\lambda$ of the experiment from the Taylor microscale as determined from the autocorrelation function (Equation 3.2).

$$Re_\lambda = \frac{u'\lambda}{\nu} \quad [3.2]$$

In addition to the autocorrelation function, transverse structure functions of some order $p$ are frequently used to describe small-scale structures of turbulence. They are generally defined as $S_p(r) = \langle [\Delta u(r)]^p \rangle \sim r^{\zeta(p)}$, where Kolmogorov’s predicted scaling is $\zeta(p) = p/3$ not taking into account intermittency. Average kinetic energy fluctuations $\langle (\delta_y u)^2 \rangle$ in the inertial range are proportional to some length scale $r$ raised to the $2/3$ power for $p = 2$. In the dissipation range where inertia effects can be safely neglected, Batchelor and Townsend [11] originally proposed that the longitudinal double-velocity correlation asymptotically approaches $e^{-r^2/8\nu t}$, which when plotted on a log scale for long decay times gives a $-r^2$ scaling. We expect to observe the log plot of the second order structure function approach a slope of 2 in the smallest scales of separation. Following the process outlined in [102], we may normalize the second order structure function such that it approaches unity as separations approach infinity. The Kolmogorov scale can be estimated based on these mean-square transverse velocity gradients (Equations 3.4-3.6).

$$S_p^+(r) = \langle [u(y + r) - u(y)]^p \rangle \propto (\epsilon r)^{p/3}$$

\[ S_p^+ = \frac{S_p^+(r)}{2^{p/2} \gamma_p u_{rms}^2} \]

\[ \gamma_p = \frac{2^{p/2}}{\pi^{1/2}} \Gamma \left( \frac{p + 1}{2} \right) \]

\[ p = 2 \]

\[ \langle (\delta_y u)^2 \rangle = \lim_{r \to 0} \left( \frac{[u(y + r) - u(y)]^2}{r^2} \right) = \lim_{r \to 0} \frac{S_2^+(r)}{r^2} \quad [3.4] \]
Another way to describe turbulence structure is to explore the frequency spectra of the flow, which is mathematically just the Fourier transform of the autocorrelation.

### 3.2 Experiments

We conduct an experiment in a subsonic jet to optimize FLEET parameters for turbulent flows. Turbulent flow is produced at the exit of a circular pipe with an $L/D$ ratio of $\approx 130$ flowing industrial-grade air and nitrogen. Calculations from measured data are taken at small displacements from the center of the pipe where the flow is considered to be isotropic.

A custom pressure transducer - pressure tap array is used to characterize the flow, and the flow rate is varied between 1 cubic foot per minute (CFM) to 4 CFM to determine the transition from laminar to turbulent flow. Measurements are taken at the pipe exit where $Re_D = 3.4 \times 10^4$. Because the mean flow velocity is subsonic with $M \approx 0.15$, we can neglect compressibility effects. FLEET line positions are taken at delays of 0 and 5 $\mu$s after the measured pulse arrival, with gate widths of 0.2 and 0.5 $\mu$s, respectively. This delay is chosen to be slightly less than the eddy rollover time of the flow, yet long enough to produce measurable displacement.

Taylor’s hypothesis of frozen turbulence is employed in this study to compare FLEET measurements along the transverse direction to hot wire measurements at the pipe axis at different temporal locations. A single-wire probe is used to resolve one-dimensional flow in a long pipe. Because a single-wire probe has no directional sensitivity, this particular method is not appropriate for resolving velocity components. One-dimensional flow in the
pipe direction is assumed. Voltage measurements $E$ are initially taken in well-characterized flows at several different velocities to determine the constants $A$ and $B$, as described in Section 1.1. The calibration relation can then be used for that particular hot wire to extract velocity from subsequent measured data. A constant fluid density in the region of interest is assumed in order to measure mean flow. Calibration in this experiment is performed separately for nitrogen gas and air, although the values differed very little between the two.

An intensified CMOS PCO.dimax HD+ camera system with a 1920x1440 pixel resolution, 11 $\mu$m x 11 $\mu$m pixel size and maximum frame rate of 2128 frames per second is used to image the FLEET emission. An experimental spatial resolution of 7.7 to 33 $\mu$m per pixel is achieved through use of extension tubes. Signal amplification is achieved with a Quantum leap gateable image intensifier module with a reported resolution > 60 LP/mm and gate repetition of 2 MHz. The intensifier, or microchannel plate (MCP), serves the dual purpose of signal amplification and high-speed shutter. Its sensitivity is above 10% between approximately 350 nm and 900 nm and no calibration data exists for wavelengths outside this range. In this study, MCP gain is held constant and below maximum gain to minimize amplification of background noise for the duration of the experiment. To achieve statistical conversion, parameters are computed for data sets of 100, 300, 500 and 1000. Approximately 1000 shots are necessary for convergence at the lowest SNR cases, and fewer for higher SNR. Over 2000 individual shots are taken and analyzed at each set of parameters in this study.

### 3.2.1 Magnification

The resolution limit is a function of the optical resolution of the camera + intensifier imaging system. Typically, the limiting resolution is set by the object with the lowest spatial resolution in the system, which is the camera, although it is possible that the image intensifier’s true performance resolution is lower than that measured under factory calibration conditions. At the low light-level limit, image details are obscured by general noise produced by single photons amplified through the MCP. As the brightness of the imaged emission increases, the
speckles disappear and the signal-to-noise level approaches acceptable levels. Increasing the gain of the MCP also causes amplification of electronic noise and may lead to saturation of the signal while still increasing the intensity of noise and reducing overall spatial resolution. Noise amplification, saturation effects, and the non-linearity of the MCP optical response function may all limit the attainable pixel density as advertised by the product manufacturers. Resolution improvements through magnification introduce two types of errors at their extremes. At the lower limit of resolution when the measured object is small with respect to pixel size, targets are biased towards the nearest pixel location, creating unrealistic uniformity and pixelation. Maximizing resolution improves proper detection of emission location at the cost of increased data processing time. At the upper limit when the pixel size becomes very small with respect to the target, errors caused by electronic and ambient noise can begin to dominate, especially when the signal-to-noise ratio is low. The partial Gaussian fitting technique is more likely to suffer from this bias, particularly if the bit depth of the imaging equipment is low. The magnification is limited by the camera’s sensor region and to avoid cutoff of relevant velocity profile regions, we do not increase the magnification level above 7.7 µm per pixel. Four different image resolutions are used during the experiment. For the fundamental and second harmonic beams, FLEET images are captured at pixel resolutions of 33 µm and 12.5 µm. For the third harmonic, images are taken at pixel resolutions of 12.5 µm, 9.5 µm and 7.7 µm. Transverse correlation coefficients plotted in Figures 3.14 and 3.16 highlight the effects of magnification on noise amplification in a low tagging energy density case. Figure 3.2 depicts the normalized second order structure function for FLEET imaged with the low magnification case. The hot wire data shows no well-defined inertial range in this flow, so the 2/3 scaling is not expected for these experiments and any large-scale correlations can be attributed to measurement error or laser-induced perturbations. The low magnification cases depicted in these figures show overcorrelation for almost the entire length of measurement. Increasing the optical magnification leads to more pronounced “spikes” at \( r = 0 \), which were also observed in [44]. At a given wavelength and pulse energy, there is
Figure 3.1: FLEET images taken in pure nitrogen flow, two different magnifications. Laser properties: \( \lambda = 400 \text{ nm}, 1.1 \, \mu \text{J per pulse}, 1 \text{ kHz}, f=30 \text{ cm}. \)

(a) Transverse correlation coefficient, low magnification

(b) Normalized second order structure function, low magnification

Figure 3.2: Right: Normalized second order structure function \( S_p^\perp \) calculated for FLEET data taken in a pure nitrogen flow, comparing the effects of focusing and magnification. Laser properties: \( \lambda_c = 400 \text{ nm}, 1 \text{ kHz}, 1.1 \, \text{mJ per pulse}. \)
no strong difference between perturbations introduced by the $f = 30$ and $f = 50$ cm beam focusing.
3.2.2 Wavelength, gas type and beam energy density

The highest obtainable pulse energy that doesn’t oversaturate the camera intensifier is about 4.5 mJ at 1 kHz. Since focusing with a f=30 cm lens produced emission that spans the diameter of the pipe exit, and the tagged line produced with f=50 cm easily doubled that length, weaker focusing was not considered.

Figure 3.3 shows the transverse correlation coefficient calculated for measurements taken in air using tagging with the 800 nm beam focused with a f=30 cm lens. The $r = 0$ point corresponds to the middle of the FLEET line, which is centered with respect to the pipe axis, but comparable results are gathered for positions offset from the center by up to 2 mm. $R(r)$ has a maximum of 1 at zero separation and decreases in a roughly Gaussian/parabolic manner to 0 as the separation distance increases. The center data point is excluded from both the Gaussian and parabolic fits since it will always be perfectly correlated with itself.

Figure 3.3: Transverse correlation coefficient $R(r)$ calculated for FLEET data taken in a pure air flow with resolution of 12.5 $\mu$m per pixel. Top: 3 mJ per pulse. Bottom: 4.5 mJ per pulse. Laser properties: $\lambda = 800$ nm, 3, 4.5 $\mu$J per pulse, 1 kHz, f=30 cm.
Figure 3.4: Transverse correlation coefficient $R(r)$ calculated for FLEET data taken in a pure nitrogen flow with resolution of 12.5 $\mu$m per pixel. Top: 400 nm, 1.1 mJ. Bottom: 800 nm, 1 mJ. Laser properties: $\lambda = 400, 800$ nm, 1.1, 1 $\mu$J per pulse, 1 kHz, f=30 cm.

Eight data points around the $r = 0$ point are fitted to give the Taylor microscale of the flows. For the high pulse energy case in the lower plot, overcorrelation is observed from scales of 0.07 mm to 1.8 mm. Not shown are turbulence statistics for the 1.1 $\mu$J in air at 800 nm case, which is significantly noisier. Figure 3.5 compares the effects of pulse energy (tagging energy density). Kolmogorov’s predicted scaling for the inertial range and the scaling for the dissipation range are indicated by the dashed gray lines.

Since the FLEET signal is much stronger in pure nitrogen and tagging with $\lambda_c = 400$ nm is more efficient than with the fundamental, data taken in Figure 3.4 have higher signal-to-noise than in air and fewer erroneous fits are observed. Intensifier noise also appears to be higher for this case and the Taylor microscale is obscured by approximately a millimeter of artificial correlation. The pulse energy used for the measurement in the top chart is almost the entirety of the beam converted to the second harmonic, given an upper threshold conversion efficiency of about 30%. Reading left to right on the correlation coefficient plots corresponds
to the laser propagation direction in the experiment, where the separation $r = 3.4$ mm in Figure 3.4 is the closes measured point to the beam dump. For both $\lambda_c = 400$ or $\lambda_c = 800$, the overcorrelation suggests that because the tagging process is stronger in a nitrogen flow, the energy density in the tagging area must be lowered for accurate measurements.

Abrupt spikes at $r = 0$ can be attributed to the intensifier’s effect on the image. The intensifier module is found to enhance the digital count differences among the four quadrants of the camera’s sensor, forming striations in the background image that are not generally visible under normal light conditions, but can nevertheless reduce signal quality. In order to prevent the appearance of these sensor artifacts, the intensifier gain is held constant at approximately $8.5/10$ for the duration of the experiment. Image intensifiers are known to amplify signal in a nonlinear and nonuniform fashion, creating areas of increased contrast between bright and dark areas, and even neighboring pixels as a result of its sensitivity variations. As the camera magnification increases, the number of photons seen by the aperture decreases, increasing the contrast between pixels and reducing the image reproduction fidelity. Thus at very high optical magnifications, deviations from expected correlations are observed near $r = 0$ (Figure 3.16). Corrections for both the flat field and nonlinearity by characterizing the nonlinear response of each pixel across its full dynamic range, which must be performed separately for each instrument, have been suggested [139] but application of that correction on this dataset was not performed due to the laborious nature of the task.

Figure 3.5: $\tilde{S}_{p\perp}^\perp$ in air. Laser properties: $\lambda_c = 800$ nm - 3.4.5 $\mu$J per pulse, 1 kHz, $f = 30$ cm.
3.2.3 Two Point Correlations

Transverse velocity spatial correlations show little change when the focusing lens is changed from \( f=50 \) cm to \( f=30 \) cm. We use a lower f-number lens in this experiment in order to determine the effect of focusing on the accuracy of our results. Focusing is performed here using two \( f=3.5 \) cm lenses in order to form two "points", used frequently in the "boresight" configuration. One lens is stationary while the other is attached to a translation stage such that it may be moved in the transverse direction, either towards or away from the stationary point. Both points are located at the same vertical height with respect to the ground and the camera lens, which is situated above the experiment. The beam is split evenly using a beamsplitter and attenuated to the minimum possible energy for use in a nitrogen flow at atmospheric pressure and temperature.

The two point cross-correlations are in the spanwise \( (x) \) and streamwise \( (y) \) directions. The two-point correlation coefficient \( R_{ij} \) is defined by Equation 3.7. Fitting non-axisymmetric signal distributions is performed by fitting a 2-dimensional Gaussian to the signal and optimizing through an iterative procedure using least-squares curving fitting.

Burn marks on the pipe exterior in Figure 3.6 were produced during alignment and do not affect the inner wall.

\[
R_{ij} = \frac{U_i(x, y)U_j(x + \Delta x, y + \Delta y)}{\sigma_i\sigma_j} \quad [3.7]
\]

Figure 3.7 is produced using the lowest laser pulse energy needed to see a clearly-resolved spot. The color gradient indicates the strength of the correlation. Decreasing the energy further increases the fitting error and decreases SNR drastically. The data shows weak to no correlations in both the streamwise and transverse directions for the resolvable separations in the experiment, which is expected. The effects of the increased focusing and beam energy density appear to have a range smaller than 0.25 mm in this type of experiment.
Figure 3.6: Experimental schematic and photograph of the raw FLEET emission at the pipe exit. Camera is imaging from above.

Figure 3.7: Spatial correlations for the streamwise (top) and spanwise (bottom) velocity components as a function of separation. $R_x$ and $R_y$ are normalized. Laser properties: $\lambda = 400$ nm - 60 $\mu$J per pulse, 1 kHz, $f = 3.5$ cm
3.2.4 Tagging with the Third Harmonic

This chapter section describes the work reported in [146]. Laser-based diagnostics inherently deposit energy into the flow of interest and minimizing perturbation effects from laser heating is crucial for accurate velocimetry measurements. Rayleigh scattering experiments showed the formation of a shock within hundreds of nanoseconds following laser excitation. The invasiveness of the FLEET method has been quantified in flows and temperature uncertainties of up to 100 K and increases of several hundred Kelvin are measured [42], as well as strong deviation from expected turbulence statistics in higher beam energy densities [145]. We seek to reduce the tagging energy from the previous $O(mJ)$ by switching to a more efficient multi-photon excitation process through nonlinear frequency conversion. The second harmonic has been shown to produce a more narrowly focused beam with less diffraction than the fundamental. The relation $n_p = \frac{I\Delta t}{hc}$ shows that about ten photons are needed for the excitation process at the fundamental, and that number scales directly with wavelength. Each laser pulse has a temporal full-width at half maximum duration of 60 fs and is frequency tripled to 267 nm. Third harmonic conversion is achieved using a two-stage interaction. First, the fundamental laser wavelength is frequency-doubled using a SHG BBO crystal. Second, the pump and second harmonic beams are overlapped in a THG BBO crystal to achieve sum frequency generation. A 5.6 mJ pulse at the fundamental wavelength is converted to a 80 $\mu$J pulse at 267 nm.

Emission Characterization

The first experiment seeks to quantify the exact gas mixture in which tagging is performed by using a cylindrical gas cell, as shown in Figure 3.8. Femtosecond laser pulses at 1 kHz are focused with a f=10 cm UV-grade calcium fluoride lens (for 267 nm) or AR-coated f=30 cm (for 400 nm) lens into a custom-made optical-grade fused silica cell containing various mixtures of industrial-grade $N_2$ and Ar gas at atmospheric temperature. The gases flow through the cell to avoid build up of contaminants, and a vacuum pump maintains the
desired pressure in the cell throughout the experiment. We estimate an additional 10% loss of pulse energy as the beam passed through the 3.1 mm thick optical-grade fused silica window, leaving $\lesssim 70 \mu J$ of tagging beam energy. The second harmonic at 400 nm with 0.8 mJ pulse energy is also used in this configuration to provide spectral measurements, which could not be obtained with the low-energy 267 pulses.

Figure 3.11 shows that the 267 nm beam produces a much thinner tagged line than a 400 nm or 800 nm beam (latter not shown). A comparison between time-gated spectra integrated from 700 nm to 900 nm produced using 400 nm laser excitation, and spectrally integrated
Figure 3.9: Time-gated pure argon spectra taken from 5-5.5 µs, excited with a 0.8 mJ at 1 kHz, centered at 400 nm.

Signal intensity produced with 267 nm suggests that similar processes are at effect in pure argon (Figure 3.12). The dashed line represents the signal integrated over all peaks in the range of 700 nm to 900 nm. The 1/e signal lifetime in pure argon under these experimental conditions is approximately 1.5 µs. From Figure 3.12, we observe that the decay curve of the overall emission in argon at atmospheric pressure behaves similarly to that of the integrated time-gated spectra. We hypothesize that the main processes responsible for the signal emit primarily in this range. Any addition of nitrogen causes strong spectral features in the nitrogen second positive regime to appear. [144] showed that the signal in pure argon is stronger than that in mixtures with nitrogen for the first 7 µs following excitation by 400...
Figure 3.10: 267 nm-excited emission in pure argon as a function of delay at 1 atm. Each image is averaged over 100 shots and integrated over a 0.5 \( \mu s \) gate From left to right: 0.5-1 \( \mu s \), 1-1.5 \( \mu s \), 2-2.5 \( \mu s \), 3-3.5 \( \mu s \)

...Figure 3.12 shows that tagging with 267 nm reflects this trend: the signal in pure argon is stronger than that in 96% argon + 4% nitrogen.
Figure 3.11: A comparison of the Gaussian-fitted 267 nm line versus that of the 400 nm line in pure argon. The dark horizontal line indicates the row of pixels fitted in the plots below. The 267 line is temporally integrated from $t = 0.5 \mu s$ to $t = 1 \mu s$, where $t$ indicates time elapsed after excitation.
Demonstration of velocimetry

In the second experiment, we use a subsonic jet to demonstrate velocimetry capability. Well-developed turbulent flow is produced at the exit of a circular pipe with an $L/D$ ratio of $\approx 130$ flowing industrial-grade argon and nitrogen. Tagging with 267 nm is performed only in pure nitrogen and pure argon gas since the beam intensity is not high enough to produce a good signal-to-noise ratio in air. Measurements are taken at small displacements from the centerline of the pipe where the flow is considered to be isotropic. The viscous sublayer thickness is estimated to be 0.3 mm. Measurements are taken at the pipe exit where $Re_D = 3.4 \times 10^4$. Because the mean flow velocity is subsonic with $M \approx 0.15$, we can neglect compressibility effects. FLEET line positions are taken at delays of 0 and 5 $\mu$s after the measured pulse arrival, with gate widths of 0.2 and 0.5 $\mu$s, respectively. Focusing is
Figure 3.13: Sample single-shot images of the FLEET displaced line, centered at the pipe axis. The camera delay and gate width are indicated on the left of each image. The flow is moving upwards in the vertical direction. Gas: nitrogen; Laser properties: $\lambda_c=267$ nm, 60 $\mu$J per pulse, 1 kHz, f=25 cm.

performed with a f=25 cm UV lens. Velocity is calculated by dividing the displacement by the delay time plus half of the gate width. Because the total displacement is typically larger than variations in the initial line position, we approximate the measurement uncertainty only as a function of final line position and timing uncertainty. Timing uncertainty is a combination of jitter from the laser trigger pulse to the camera, which is less than a nanosecond and can be safely disregarded, timing errors introduced by the signal generation system, which has an upper limit of 35 ns, and the camera gate duration, 0.5 $\mu$s. The mean centerline flow velocity is measured to be $45 \pm 4$ m/s, where some of the uncertainty can be attributed to the turbulent nature of the flow. Figure 3.13 shows sample single-shot images of the FLEET line produced using $\lambda=267$ nm pulses. The tagged line is only long enough to resolve some of the flattened profile of the flow. Figures 3.14 and 3.15 show the transverse correlation coefficient calculated for measurements taken in nitrogen and argon gas with the 267 nm beam. The r=0 point corresponds to the middle of the FLEET line, which is centered with
Figure 3.14: Transverse correlation coefficient $R$ calculated for FLEET data taken in a pure nitrogen flow with resolution of 12.5 $\mu$m per pixel. Inset: zoomed in to center of the correlation coefficient to show Gaussian and parabolic fits. Laser properties: $\lambda = 267$ nm, 60 $\mu$J per pulse, 1 kHz, $f=25$ cm.

respect to the pipe axis, but comparable results are gathered for positions offset from the center. As expected, $R(r)$ has a maximum of 1 at zero separation and decreases in a roughly Gaussian manner to 0 as the separation distance increases. The center data point is excluded from both the Gaussian and parabolic fits since it will always be perfectly correlated with itself and includes otherwise uncorrelated noise. Eight data points around the $r=0$ point are fitted to give Taylor microscales of 130 $\mu$m and 150 $\mu$m, respectively. These figures suggest that the gas type does not appear to have a large effect on the behavior of the correlation coefficient, given that FLEET signal levels for short delay times in argon and nitrogen flow are similar. The signal in argon is approximately 1.03 times the signal in nitrogen at a delay of 5 $\mu$s and gate of 0.5 $\mu$s, averaged over 2000 shots.
Figure 3.15: Transverse correlation coefficient $R$ calculated for FLEET data taken in a pure argon flow with resolution of 12.5 $\mu m$ per pixel. Inset: zoomed in to center of the correlation coefficient to show Gaussian and parabolic fits. Laser properties: $\lambda = 267$ nm, 60 $\mu J$ per pulse, 1 kHz, $f=25$ cm.

Figure 3.16 shows that the effects of noise on the correlation coefficient are amplified with increased magnification. The measured Taylor microscale values are also lower, due to the fit being skewed by noise. If only the center data point is excluded from the parabolic fit, $\lambda$ is measured to be 101 $\mu m$ and 93 $\mu m$ for magnifications of 9.5 $\mu m$/pixel and 7.7 $\mu m$/pixel, respectively. However if the entire spike, the three points in the center, were excluded, the measured $\lambda$ values became 126 $\mu m$ and 115.5 $\mu m$ for those two cases.

In summary, tagging is demonstrated in argon and nitrogen gases using a femtosecond laser with pulse energies of approximately 70 $\mu J$ through a nonresonant ionization process at 267 nm. The signal fluorescence lifetime in pure argon and nitrogen-argon mixtures are measured and found to be long enough to make mean velocity and turbulence measurements
Figure 3.16: Transverse correlation coefficient $R$ calculated for FLEET data taken in a pure nitrogen flow and different pixel resolutions. Inset: zoomed in to center of the correlation coefficient to show Gaussian and parabolic fits. Laser properties: $\lambda = 267$ nm, 60 $\mu J$ per pulse, 1 kHz, $f=25$ cm.

in a subsonic flow. In pure argon, the dominating processes involve atomic transitions between 700 and 900 nm. In argon-nitrogen mixtures, nitrogen quenches atomic argon species and the dominant radiating processes are transitions in the nitrogen second positive system. In pure nitrogen, emission on the microsecond timescale comes from the nitrogen first positive system. Lower energy density is needed for tagging and narrower tagged lines are produced using 267 nm as compared to femtosecond laser tagging in argon and nitrogen using 400 nm or 800 nm. Velocimetry using the 267 nm line is demonstrated in a turbulent argon pipe flow and the Taylor microscale of the flow is determined.

### 3.2.5 Summary

Data falling more than two standard deviations outside of the fitting confidence intervals is discarded. Also discarded are data fits in unreliably low SNR areas. This is calculated as a percentage of total points used for the statistical correlations and noted in Table 3.2. Table
Table 3.2: Discarded data due to low SNR

<table>
<thead>
<tr>
<th>Gas</th>
<th>λc (nm) &amp; Pulse energy</th>
<th>f (cm)</th>
<th>Pixel Resolution (µm)</th>
<th>Percentage Discarded (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>267, 60 µJ</td>
<td>25</td>
<td>12.5</td>
<td>1.3</td>
</tr>
<tr>
<td>N₂</td>
<td>267, 60 µJ</td>
<td>25</td>
<td>12.5</td>
<td>0.6</td>
</tr>
<tr>
<td>N₂</td>
<td>267, 60 µJ</td>
<td>25</td>
<td>9.5</td>
<td>2</td>
</tr>
<tr>
<td>N₂</td>
<td>267, 60 µJ</td>
<td>25</td>
<td>7.7</td>
<td>1.4</td>
</tr>
<tr>
<td>N₂</td>
<td>400, 1.1 mJ</td>
<td>30</td>
<td>33.3</td>
<td>12.6</td>
</tr>
<tr>
<td>N₂</td>
<td>400, 1.1 mJ</td>
<td>50</td>
<td>33.3</td>
<td>19.2</td>
</tr>
<tr>
<td>N₂</td>
<td>400, 1.1 mJ</td>
<td>30</td>
<td>12.5</td>
<td>0.51</td>
</tr>
<tr>
<td>Air</td>
<td>800, 4.5 mJ</td>
<td>30</td>
<td>12.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Air</td>
<td>800, 3 mJ</td>
<td>50</td>
<td>12.5</td>
<td>14.8</td>
</tr>
<tr>
<td>N₂</td>
<td>800, 1.0 mJ</td>
<td>30</td>
<td>12.5</td>
<td>3.82</td>
</tr>
</tbody>
</table>

3.3 summarizes the measured turbulence parameters for the different experiments performed in this study.

Table 3.3: Measured Turbulence Parameters

<table>
<thead>
<tr>
<th></th>
<th>Gas</th>
<th>λc (nm) &amp; Pulse energy</th>
<th>f (cm)</th>
<th>Pixel Resolution</th>
<th>u’ (m/s)</th>
<th>λ(µm)</th>
<th>η(µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar</td>
<td>267, 60 µJ</td>
<td>25</td>
<td>12.5 µm</td>
<td>5.0</td>
<td>150</td>
<td>13.21</td>
</tr>
<tr>
<td>2</td>
<td>N₂</td>
<td>267, 60 µJ</td>
<td>25</td>
<td>12.5 µm</td>
<td>2.7</td>
<td>131.3</td>
<td>14.82</td>
</tr>
<tr>
<td>3</td>
<td>N₂</td>
<td>267, 60 µJ</td>
<td>25</td>
<td>9.5 µm</td>
<td>3.2</td>
<td>126</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>N₂</td>
<td>267, 60 µJ</td>
<td>25</td>
<td>7.7 µm</td>
<td>2.9</td>
<td>115.5</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>N₂</td>
<td>400, 1.1 mJ</td>
<td>30</td>
<td>33.3 µm</td>
<td>5.3</td>
<td>470</td>
<td>8.33</td>
</tr>
<tr>
<td>6</td>
<td>N₂</td>
<td>400, 1.1 mJ</td>
<td>50</td>
<td>33.3 µm</td>
<td>12.5</td>
<td>283.5</td>
<td>20.01</td>
</tr>
<tr>
<td>7</td>
<td>N₂</td>
<td>400, 1.1 mJ</td>
<td>30</td>
<td>12.5 µm</td>
<td>6.8</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>Air</td>
<td>800, 4.5 mJ</td>
<td>30</td>
<td>12.5 µm</td>
<td>4.6</td>
<td>232</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>Air</td>
<td>800, 3.0 mJ</td>
<td>50</td>
<td>12.5 µm</td>
<td>4.1</td>
<td>175</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>N₂</td>
<td>800, 1.0 mJ</td>
<td>30</td>
<td>12.5 µm</td>
<td>4.8</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

In Table 3.3, the Taylor microscale λ is that determined from the parabolic fit to the transverse velocity correlation function, and compared to that obtained by the structure function to check that it is within a factor of each other. The frequency response of the hot wire setup is limited by the probe dimensions and higher frequency fluctuations are unable to be captured for comparison with FLEET. The computed transverse correlation
functions for HWA and FLEET do not collapse in the experiment and this may be due to the inapplicability of the initial assumptions. Averaging along the sensing length of the hot wire obscures any small-scale features in the flow so an estimate for $\eta$ was not obtained. Gas mixture corresponds to FLEET signal strength, which has a large effect on what laser parameters produce the least perturbation. For gases that produce high signal strength during the delays of interest, such as pure nitrogen or argon, a lower tagging energy density is required to avoid changing the flow behavior. Tagging efficiency also scales with laser wavelength: whereas tagging with only 60 $\mu$J is possible with $\lambda_c = 267$ nm, at least half a millijoule is required at 800 nm and 400 nm to write a line with reasonable SNR. At the current time, the experimental setup for FLEET “spots” is not sophisticated enough to resolve the smallest features $\eta$ and $\lambda$. The turbulence length scale is estimated to be 380 $\mu$m from $\lambda = 0.038D$. The entrance length in this experiment is slightly shorter than that needed to produce fully-developed turbulent flow, thus producing Taylor microscale values about half of what is theoretically predicted. In summary, FLEET is used for velocimetry in a turbulent subsonic flow and the resulting measurements are compared with those captured using constant temperature hot wire anemometry. This study investigates the effects of optical properties (wavelength, pulse energy, beam focusing), imaging properties (camera delay, magnification) and flow medium (air, argon, pure nitrogen) on small-scale velocity measurements with FLEET. Parameters that contribute to higher emission intensity, such as gas, pulse energy and focusing, tend to decrease velocity error but result in overcorrelation, suggesting perturbations from the laser-deposited energy. Tagging medium (air, nitrogen) also affects emission line thickness and signal-to-noise: lower velocity errors are found with pure nitrogen tagging. At the signal levels produced in this study, higher magnification tends to improve measurements overall, but increased magnification can feasibly introduce bias into measurements conducted at inferior SNRs.
Chapter 4

Near Wall Measurements

There is currently a demand for more robust, reliable methods to obtain highly-resolved near-wall measurements in supersonic flows. It is known that in the viscous sublayer, the velocity profile is linear and can be directly related to the shear stress. From this, the skin friction distribution across a surface may be determined. Several methods for evaluating skin friction on flat surfaces exist. One solution is the development of direct sensors, which measure the force produced by the flow on a flush-mounted device. Challenges include installation and calibration of the device in the presence of very low shear stress. Early attempts at implementing direct sensors include meter-scale floating element sensors installed on the flat underside of boats [73]. Modern methods that measure shear stress directly using a MEMS-based device (e.g. a microfabricated pillar array sensor, monolithic floating plates, are typically complex to fabricate, sensitive to vibrations and thermal conditions, intrusive, and lacking in the spatial and temporal scales necessary to characterize turbulent behavior. It is difficult to make accurate measurements without introducing modifications to the surface itself or precariously perturbing the boundary layer. Other methods rely on thin oil film techniques [40], or calculate shear stress from a measured velocity gradient, the latter of which will be the focus of this document. While oil film interferometry is an attractive method for direct measurement of skin friction, the implementation is temperature sensitive.
and it is not always possible to apply an oil film to surfaces of interest. The surfaces of interest are almost always curved in at least one, but more often, in multiple directions, making it tough to encompass the problem completely with computational tools. Nevertheless, skin friction knowledge is critical for the future of supersonic and hypersonic flight. While a non-intrusive optical diagnostic is generally seen as superior to probes and sensors for this task, obtaining velocity measurements in the laminar sublayer is complicated by limited optical access to the surface, laser damage of the surface, low gas density in the boundary layer, which reduces the signal-to-noise ratio, and a desire to minimize the laser-flow perturbation. Several optical and geometric solutions to optimize FLEET for this task are explored in this chapter, which details two experiments that demonstrate the application of FLEET to this problem.

4.1 Experiments in an In-draft Wind Tunnel

In this experiment, tagging is performed in two air-breathing in-draft wind tunnels operating at roughly Mach 2.5. The accuracy of FLEET in resolving flow velocities is limited by the signal-to-noise ratio. The strength of the visible FLEET signal is a function of environmental parameters, including gas composition, temperature and pressure. Given that the working fluid is air flowing at speeds between Mach 2.3 and Mach 2.8, it is important to consider the effects of pressure variation on the FLEET signal intensity. Near Mach 3, the total pressure corresponds to the minimum of the signal intensity curve at about 30 Torr [95]. To counter the adverse effects of low pressure, the second harmonic at 400 nm is used to generate a more narrowly focused beam with less diffraction than at 800 nm, creating the potential for more efficient, resolved tagging. Additionally, the laser focusing is varied to produce both signal points and lines, where a single, tightly focused spot in the boresight configuration (Figure 4.3) is much brighter. Naturally, a higher pulse energy density also results in a higher signal, at the cost of increased perturbations in the flow as seen in Section
3.2. Thermal diffusion from the high-energy laser pulse results in a symmetric distribution and therefore these effects can be mitigated by fitting a Gaussian profile to the line and using its center. Using a Gaussian fit, images with a resolution of 10 μm/pixel will have error on the order of several tenths of a pixel at a signal-to-noise ratio (SNR) of 1, and this error approaches zero as the SNR improves. A SNR of ≥ 20 is easily achievable in the boresight configuration even in the presence of high speed flow. Velocity is determined by dividing the measured displacement by the time delay, as explained in Section 1.3.1. Using lenses with foci greater than approximately 15 cm results in usable signal lengths of over 1 cm. In the boresight configuration, FLEET is focused down to a signal point rather than a line, which allows for the application of spot-fitting techniques used earlier in Section 3.2.3. In this setup, a short-wavelength reflecting dichroic mirror placed directly in front of the camera to selectively reflect the laser beam while permitting the FLEET emission to be imaged by the camera, thus allowing for a “down the boresight” imaging configuration. A second filter is placed directly in front of the camera to prevent any reflected or scattered laser light from reaching the sensitive intensifier. The advantages of imaging a signal spot include increased SNR and the elimination of projection ambiguity that exists with imaging the movement of a homogeneous line. When the flow is at an angle to the imaging plane, accurate measurements can be difficult. One solution involves using two crossed beams that form an X in the flow, but that requires several additional optical components to split and redirect the beam [22]. This study focuses only on the simplest configurations with one beam. The laser used is an earlier model Spectra Physics Solsticle laser with titanium sapphire oscillator and MaiTai regenerative amplifier operating at a fundamental wavelength centered at 800 nm with Gaussian bandwidth of 50 nm. The beam has a nearly Gaussian spatial mode with an \( \frac{1}{e^2} \) intensity half-width of 1.95 mm, determined through knife-edge characterization [85]. Each pulse has a temporal FWHM duration of 49.5 fs. A frequency-doubling crystal is used to achieve the second harmonic at 400 nm, with pulse energies up to 1.3 mJ, and a repetition rate of 1 kHz is used for both wavelengths. Both the 800 nm
and 400 nm are used in experimental configuration 2, but data taken with the fundamental are ultimately discarded in favor of that taken with the second harmonic because of the latter’s superior SNR. The fundamental wavelength is not used at all in configuration 3 for lack of suitable optics. Data is collected with the intensified PCO.dimax HD camera system described in Sections 2.2.1 and 3.2. Two wind tunnel facilities were used for the experiments: a Mach 2.3 aluminum in-draft tunnel with a measured static pressure of 60 Torr, and a Mach 2.6-2.8 acrylic in-draft tunnel with a measured static pressure of 28 Torr. Both tunnels have rectangular cross-sections. The Mach 2.3 tunnel has optical access on all four sides and the Mach 2.8 has optical access in two. All optically clear windows are made of fused silica, which has almost a 90% transmission rate in the near-UV to near-IR spectrum, allowing transmission of both the FLEET signal and laser beam. All free-stream temperature and density values used are derived from isentropic flow relations. While the acrylic tunnel allows for faster flows, aluminum is shatter-resistant and can support the frequent installation of removable inserts. Pitot tube measurements [142] make it possible to determine the Mach number of boundary layer flow in the acrylic tunnel. Kalra [70] simulated a 4-5 mm thick boundary layer corresponding to the Mach 2.6 tunnel. Additionally, using two tunnels with different core flow velocities allows for the sampling of two pressure conditions with different FLEET signal levels.

A law-of-the-wall analysis approximates a laminar sublayer of 55 $\mu$m in the Mach 2.3 facility where the tests are performed. The spatial length scale, a wall unit $y^+$, is calculated to be 11 $\mu$m, with variations based on pressure, temperature and flow speed. This is based on an approximation itself since the wall shear stress is precisely the value we set out to measure and an empirical friction coefficient is used to estimate the wall unit. The time scale, based on the length scales of observed eddies in turbulent flow, is $t = L/U \approx 10 \mu$s. More precise calculations of the boundary layer thickness are found using a flat plate insert in the wind tunnel. Equation 4.1 is used to calculate the expected turbulent boundary layer thickness over a flat plate in our experiment. The skin friction coefficient $C_f$ is estimated using both
Figure 4.1: Flat plate boundary layer configuration: the purple arrow represents the tagged FLEET line threaded through a D=0.4 mm hole at an angle such that the hole is located downstream of the measured flow. On the right is an image of the FLEET line averaged over 100 shots taken in a stationary flow condition.

the Blasius approximation (Equation 4.2) and using tables for turbulent compressible flows [28]. Measured data from all configurations are collapsed onto the universal logarithmic profile for comparison with the model. Furthermore, velocity can be redefined through the Van Driest transformation (Equation 4.3), where $q_w$ represents the heat transfer per unit area at wall, such that $u^+ = \frac{U_c}{u_w}$. This universal profile can then be compared to near-wall velocity data taken under different experimental conditions.

\[
\delta = \frac{0.382x}{Re_x^{0.2}} \approx 1\text{mm} \tag{4.1}
\]

\[
C_f = 0.664Re_x^{-\frac{1}{2}} \tag{4.2}
\]

\[
U_c = \sqrt{\frac{2c_f T_w}{Pr_t}} \left[ \sin^{-1} \left( \frac{q_w}{\tau_w} + \frac{U}{{\sqrt{\left(\frac{q_w}{\tau_w}\right)^2 + \frac{2c_f T_w}{Pr_t}}}} \right) - \sin^{-1} \left( \frac{q_w}{\tau_w} \right) \right] \tag{4.3}
\]
Figure 4.2: Left: curved plate with sharp leading edge. The beam travels along the curved surface, normal to the direction of the flow, represented by blue arrows. Camera images from above. Right: frontal view of steel curved plate used in experiment

Using a flat plate and measuring the velocity profile at a precise location on the lower side of the flat plate in Figure 4.1 allows for direct characterization of the boundary layer. The beam enters the test section at an angle in order to maximize the number of tagged points in the region of interest, and to ensure that the displaced line will fit within the camera’s sensor region.

The laser beam passes tangential to a curved surface placed in the flow and the displacement of the FLEET signal varies according to its location along the surface. A clear advantage of this set-up is the ability to resolve close to a surface without ablating the wall material, limited only by the thickness of the FLEET line at the beam’s focal region. Measurements have been successfully obtained in an open jet 20 µm from the surface [21]. Additionally, it is important to be able to characterize curved geometries since they are commonplace in aerospace systems. In configurations 1 and 2, 20-50cm focal length lenses
Figure 4.3: Left: Boresight experimental configuration in a supersonic nozzle where the laser is focused down to a small spot size approximately 0.5-2 mm in diameter (FWHM) and the camera is imaging down the boresight of laser propagation. A dichroic mirror selectively reflects the 400 nm laser beam while allowing the FLEET emission to be imaged by the camera. Right: View of the Mach 2.6-2.8 wind tunnel test section at an angle. The arrow points towards the FLEET Emission in boresight configuration, focused down to a 0.5 mm (FWHM) spot. Laser properties: $\lambda = 400$ nm, 1.27 $\mu$J per pulse, 1 kHz, f=3.5, 6 cm

are used to maximize the signal length in the flow. Laser energy transmission through fused silica decreases with beam intensity, and while there is close to 90% transmission of an unfocused beam, it is not possible to create the FLEET tagged lines in the tunnel with any kind of optically clear window located close to the focal region. In order to circumvent this problem, the focused laser beam is threaded through a small hole in the tunnel wall.

This configuration produces an axially symmetric Gaussian spot that can be tracked by a single camera to resolve multiple components of velocity [37] rather than measuring the displacement of a FLEET tagged line in a single direction. Measurements are taken at two positions within the boundary layer of the Mach 2.6-2.8 tunnel, located 2.3 mm and 3.7 mm from the wall, and compared to previous tunnel characterizations [70]. Burst-mode imaging is used to capture successive displacements of a signal spot created by a single laser pulse, allowing for the calculation of the acceleration as well as the velocity of the flow.
Additional pointwise data can be collected by using microtranslators to carefully reposition the optics and laser beam at each new location. The tracking of a single data point is useful in situations where the three components of velocity need to be resolved with good signal-to-noise ratio. In a supersonic tunnel, the boresight measurements are conducted with a similar setup as outlined in Figure 4.3. The fundamental lasing wavelength is frequency-doubled to 400 nm, with 1.27 mJ per pulse, operating at 1 kHz. For tunnel operation, both a 2” diameter plano-convex lens with focal length of 6 cm and a 1” diameter plano-convex lens with focal length 3.5 cm are used to focus the beam down to a small spot (Figure 4.3), and a bandpass filter is used to protect the camera and intensifier module from scattered 400 nm light. The purple/blue light in the figure is from the laser beam, coming in through the spot on the right, focused down in the middle and leaving the tunnel at the bright purple spot on the left. The beam is oriented perpendicular to the tunnel and in line with the camera.

A background subtraction is first performed on the raw images in order to remove intensifier-enhanced on-chip camera amplifier patterns and other camera aberrations. Images are furthermore averaged over at least a hundred shots in order to derive the mean flow behavior and eliminate shot-to-shot fluctuations. Turbulent fluctuations are deferred to a further study. Unusually low signal intensity images are not included in the dataset and account for about 2% of the total dataset. 1D Gaussian centers are found along each FLEET line and used to determine the flow displacement in a given timeframe. 2D Gaussian profiles are fitted to FLEET emission spots taken in the boresight configuration and the displacement between Gaussian centers is used for velocity calculations.

### 4.1.1 Results

Law-of-the-wall models for the experiments rely on using Equation 4.4 to solve for temperature in the boundary layer and Sutherland’s law to determine viscosity as a function of temperature in the boundary layer. Measurements are scaled and plotted against the
Figure 4.4: Images taken in configuration 2. Average of five images, delay of 2.5 $\mu$s between each line, arrow pointing in the direction of flow. The signal line has a FWHM thickness of 100 $\mu$m and length of 14 mm. The center of the line is located approximately 30 $\mu$m above the surface of the plate.

![Figure 4.4: Images taken in configuration 2.](image1)

(a) Flat Plate

(b) Scaled in terms of $u^+$, $y^+$

Figure 4.5: Velocity as a function of distance from the flat plate wall and dimensionless velocity $u^+$ as a function of the wall unit, $y^+$. A small percentage of measured data points are included for comparison with the model. Laser properties: $\lambda = 800$ nm, 5.2 $\mu$J per pulse, 1 kHz, $f=30$ cm

![Figure 4.5: Velocity as a function of distance from the flat plate wall and dimensionless velocity $u^+$ as a function of the wall unit, $y^+$](image2)

Theoretical models.

\[
\frac{T}{T_\infty} = 1 + \frac{\gamma - 1}{2} Pr^{1/3} M_f^2 \left[ 1 - \left( \frac{U}{U_\infty} \right)^2 \right] + \frac{T_w - T_{aw}}{T_\infty} \left( 1 - \frac{U}{U_\infty} \right) \tag{4.4}
\]

Fluctuations in the data taken at the surface of the flat plate can be attributed to the limited distance over which the boundary layer has to develop. A number of investigations on the effects of pressure tap holes on measured static pressure and flow have been performed in the past with general consensus that the presence of a hole in the tunnel has non-negligible
Figure 4.6: Velocity as a function of distance from the curved plate surface and dimensionless velocity $u^+$ as a function of the wall unit, $y^+$. A small percentage of measured data points are included for comparison with the model. Laser properties: $\lambda = 400$ nm, $1.2 \mu J$ per pulse, 1 kHz, f=30 cm

Figure 4.7: FLEET taken in boresight configuration at two different positions in the boundary layer and images from one location are shown here on the left (flow is from left to right). The two left images show different camera exposure times, 0.5$\mu$s and 0.8$\mu$s. Right: dimensionless velocity $u^+$ as a function of the wall unit, $y^+$. Both data points taken at two distances from the wall are plotted against the model. Laser properties: $\lambda_c = 400$ nm, 1.27 mJ/pulse, 1 kHz
effects on the boundary layer [120, 92]. Small vortices are expected to form in the opening, and the no-slip condition at the wall would no longer apply. Configurations 1 and 2 thus allow for measurements to be performed several $\delta$ away from the beam entryway in the tunnel wall. In configuration 1, a smaller hole is bored through the flat plate to allow the focused beam to pass through. Without the 0.4 $\mu$m hole through the flat plate, the near wall FLEET signal would be drowned out by continuous broadband emission created at the steel surface by the focused femtosecond beam. In configuration 2, flow measurements are taken at various vertical displacements from the curved plate. In both experiments, the measurements are taken in the middle of the tunnel where it is reasonable to assume minimal flow effects from the beam entry hole. The pressure differential across the flat plate is approximated using a shock wave model. Because $M_1 = 2.3$ and $M_2 = 1.91$, there is a nominal static pressure differential of about 50 Torr across the flat plate and subsequently causes flow in the small hole through which the laser beam passes. However because this pressure difference is across a 1 mm long channel, calculation of changes in flow velocity using a casual application of Bernoulli would be incorrect. We instead determine the nondimensional hole Reynolds number $d^+$ (Equation 4.5 and corresponding nondimensional pressure error $\Pi$ (Equation 4.6) as defined in [92]. A $D^+ \approx 50$ is found using shear velocities estimated from both a Blasius boundary layer assumption and from empirical fits [28], corresponding to $\Pi < 0.1$, which gives $\Delta P \approx 3.6 Pa$, less than 1% of the dynamic pressure in the test section.

$$d^+ = \frac{u_r d}{\nu}$$  \[4.5\]
The curved plate configuration avoids clipping the laser beam, making it particularly suitable for near-wall measurements. This configuration demonstrates the feasibility of resolving near-wall flows along irregular, curved surfaces by passing a beam tangential to the curve. In this experiment, we are able to achieve measurements within two or three wall units away from the surface, demonstrating the potential for direct interrogation of the viscous sublayer. Subsequent measurements may benefit from taking static pressure measurements both above the plate where measurements are taken and below it to better quantify flow disturbances caused by the presence of the plate. Measurements in Figure 4.6 shows velocity values below that predicted by the model, which may be attributed to the non-ideal flow in the test section, possibly introduced by unexpected normal shocks from the tunnel inserts. While flow behavior in a single direction is explored here, the boresight configuration allows for unambiguous measurement of flow behavior in all three dimensions.

It must be noted that a beam entryway, as implemented in configurations 1 and 2, is not necessary for application of the FLEET method as demonstrated by the boresight experiment. In order to create a reasonable FLEET tagged line, a lens of focal length greater than 15 cm is needed. The physical dimensions of our wind tunnels are relatively small with respect to the Rayleigh range of the beam, and the focused beam would exceed the damage thresholds of the fused silica windows at that distance. This condition is removed when a lens with a faster focus is used, such as the lens with focal length 6 cm implemented in the boresight configuration. The broadening of the FLEET ”spot” seen in Figure 4.7 can be attributed to small tunnel movements during the experimental runs and the defocusing of the image as viewed by the camera through the plano-convex lens. Movement of the FLEET emission spot in supersonic flow causes the image to no longer pass through the center of the lens, thereby creating the defocusing effect. This can be mitigated with lenses of longer
focal length and larger test area. The boresight method is shown to have a wide spatial bandwidth.

The velocity measurement is ultimately limited by the ability to distinguish between two Gaussian centers, that of the initial and displaced FLEET emission line, over a corresponding time delay. To address this resolution issue, both the FLEET emission from the femtosecond laser fundamental beam at 800 nm and the second harmonic at 400 nm are compared. It is important to note that the physical processes for dissociation differ between the fundamental and second harmonic. The former relies primarily on a non-linear multi-photon absorption while the latter favors tunneling, although for practical purposes of this study, we focus only on the resulting signals. Saturation effects have been observed at the center of the laser’s focal region. After a certain level, increasing the laser’s power will increase the width of the saturation region but not affect emission levels, resulting in an undesirably thicker tagged line. Through nonlinear frequency conversion, it is possible to decrease these saturation effects by accessing the laser’s higher harmonics, as seen in Section 3.2.4.

Optical access to measurement locations is necessary in order to perform FLEET velocimetry. This can pose a design challenge for conducting internal measurements. Where external measurements are concerned, focused femtosecond pulses at 1 kHz exceed the damage threshold of most materials and so it is recommended that no crucial components lie in the Rayleigh range of the beam, and best not in the beam path at all. The pressure and density drop in supersonic flow leads to a decrease in FLEET line signal intensity, thus affecting our ability to fit centers to the emission line. This is observed in both wind tunnels and reflected in previous work that characterizes FLEET emission intensity as a function of pressure. The second harmonic showed some improved results. The FLEET spot, which is much more strongly focused, is unaffected by pressure and density conditions at the focusing and power levels we used, but also does not provide the multiple simultaneous closely spaced measurements that the line does.
Table 4.1: Comparison of Experimental Configurations

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Range ($y^+$)</th>
<th>Uncertainty</th>
<th>Reynolds Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat Plate</td>
<td>$y^+ \geq 8$</td>
<td>5%</td>
<td>$3.6 \times 10^5$</td>
</tr>
<tr>
<td>Curved Plate</td>
<td>$y^+ \geq 3$</td>
<td>31%</td>
<td>$2.8 \times 10^5$</td>
</tr>
<tr>
<td>Boresight</td>
<td>$y^+ \geq 12$</td>
<td>1.2%</td>
<td>$6.9 \times 10^5$</td>
</tr>
</tbody>
</table>

4.1.2 Summary

Table 4.1 compares the three different configurations. FLEET velocimetry has been demonstrated to be capable of resolving shear flow measurements within several wall units away from a surface in compressible supersonic flow using a single-laser, single-camera system. We have achieved velocity measurements with less than 5% uncertainty, corresponding to velocity uncertainties on the order of meters per second, with spatial resolutions on the order of single microns. We have demonstrated the ability to acquire closely-spaced, single-dimension near-wall velocity measurements with a tagged line, as well as explored the potential for three-dimensional measurements using a single tagged point.

On-going work explores using FLEET to better understand separation shock unsteadiness in compressible supersonic flows. This study relies on the relationship between shear stress and velocity. We demonstrate the capability of FLEET to resolve velocity measurements in the viscous sublayer for shear stress calculations. In two of the studies, a 100 $\mu m$ thick, 2.5 cm long fluorescent line is written into the flow and the displacement of the line is recorded after a time delay to give velocity measurements in the boundary layer of the flow, forming a velocity gradient that can then be translated into shear stress. In a third study, a single fluorescent point is written into the flow to reduce the projection ambiguity of a displaced line. Measurements are obtained from three different experimental configurations and a comparison of their respective advantages and disadvantages is given. It is shown that FLEET provides the spatial and temporal scales necessary to interrogate the boundary layers in these experiments. This study also sheds light on some difficulties of using a molecular tagging method to visualize supersonic flows in a confined space.
4.2 Experiments in a Vertical Free Jet

Out of the three different configurations tested in Section 4.1, measuring the velocity gradient tangential to a curved surface, where the beam is oriented in the direction normal to the flow, is best able to resolve the laminar sublayer. Measurements using this grazing incidence approach have also been obtained in an open jet down to a reported 20 $\mu$m from the surface[21]. A clear advantage of this set-up is the ability to resolve close to a surface without ablating the wall material, and the distance to the wall is limited only by the thickness of the FLEET line at the beam’s focal region. Turbulent boundary layer structures across curved surfaces have not been studied as frequently as across canonical boundary layers, such as that across a flat plate in zero pressure gradient. Additionally, it is important to be able to characterize curved geometries since they are commonplace in aerospace systems. The curved plate configuration avoids clipping the laser beam, making it particularly suitable for near-wall measurements. In the case of flat and low-curvature surfaces, the law of the wall scaling is obeyed and the zero-pressure gradient assumption in the wall-normal direction holds. Mass-flow continuity causes velocity to increase or decrease according to the changing curvature of the wall relative to that for a flat surface. Viscous drag dominates when the surface is curved in the direction normal to the flow, while pressure losses play a much larger role when there is curvature in the streamwise direction. If the curvature is in the transverse direction, the Reynolds number is large and the boundary layer is thin, the effects of curvature on the flow are small [111]. We can subsequently negate the effects of curvature and treat every streamline as if it were moving along a flat plate. This configuration demonstrates the feasibility of resolving near-wall fluctuations along irregular, curved surfaces by passing a beam tangential to the curve. Both the signal lifetime and potential for wall damage pose challenges for using FLEET for boundary layer measurements.

The femtosecond laser and camera system are the same as those used in previous sections. A neutral density filter is used to attenuate the 400 nm beam and minimize the energy needed for tagging. A pulse energy of 0.6 mJ at 1 kHz and 400 nm is used to balance the trade-offs
of stronger flow perturbations and increased signal-to-noise. The beam is focused with a 
\( f = 30 \) cm lens for all measurements. Velocity measurements are taken in turbulent air flow 
from a \( D = 10 \) mm circular jet opening of a Mach 2 de Laval nozzle with total pressure 
capability up to 150 psi. The operating conditions for this study use a stagnation pressure of 
110 psi, resulting in a plenum air temperature of 260 K and \( Re_D = 3 \times 10^5 \). The momentum 
thickness Reynolds number is estimated from the momentum thickness of the equivalent 
incompressible boundary layer: \( Re_\theta = 1.44 \times 10^3 \). A 1 mm thick brass hollow cylinder with a 
sharp 4° leading edge and 19 mm radius of curvature is placed in the free jet and serves as the 
surface along which the boundary layer forms. \( Tw \approx T_\infty \) since the entire surface is immersed 
in the flow and thermocouple measurements confirm the accuracy of this approximation to 
within 0.3 K after 5 seconds of tunnel operation at the experimental pressure. Because the 
jet diameter is smaller than the cylinder diameter, only part of the cylinder’s circumference 
is placed in the flow. The outer measurement region is limited by the development of the 
free shear layer in the jet. \( \delta/R \ll 1 \) in this experiment, implying low departure from the log 
law. High turbulence intensities prevented the installation of a thin razor-edge surface as was 
used in previous studies [21]. Streamwise velocity profile measurements are made tangential 
to the brass surface at supersonic conditions. To process the FLEET data, each transverse 
position along a signal line is fitted with a Gaussian to determine its center. After fitting the 
FLEET line, the location of the tagged position relative to the wall can be found by tracing 
the distance between any transverse position along the line to its nearest corresponding point 
normal to the surface, as shown in the left pane of Figure 4.9. The shortest distance from 
the beam to the wall is where the beam just barely grazes the surface, and that distance is 
found using methods detailed in the next section. The wall’s full position is known from 
the surface’s radius of curvature and the pixel spatial conversion.
4.2.1 Determination of Wall Position

Accurate determination of the wall position has strong implications for the velocity distribution in the viscous sublayer, although effects diminish around $y^+ = 30$ and further [105]. Previous attempts to determine the exact wall position relied on opto-mechanical tools including microscopes, theodolites and cathetometers, which have inaccuracies of $\delta = 25 \mu m$. Laser methods have also been used to determine distance from the wall. In his wall-bounded hot-wire experiment, Takagi [131] uses optical glass fibers to create emitted spots as small as 50 $\mu m$ for use as an optical trip wire for when the probe crosses the beam’s path, with measurement accuracies up to 10 $\mu m$. Reviews of optical and electro-mechanical techniques for determining sensor distance from the wall conclude that errors of $O(10 \mu m)$ are expected [105]. Post-processing techniques typically involve fitting the linear, buffer and log-law regions of the data to determine the wall position. Additionally, models of error in the absolute wall position (10, 25, 50 $\mu m$) and estimates of the friction velocity ($\pm 2, 5\%$) show widely varying effects on estimates of the other parameter [105]. Errors in the absolute wall position have a larger effect on the
sublayer (Figure 4.10), while errors in estimating the friction velocity influence the overlap and outer layers more heavily. The importance of correctly determining the absolute wall position has direct implications for the shear stress measurement. Previous studies using FLEET to measure the near-wall region have used the radius of the focal region as an approximation of the wall position [21, 143]. The focused laser filament is brought close to the wall until it begins to burn the surface, and backed off until the filament is no longer touching. This method, which relies heavily on the finesse of translation stages and tuning knobs, can introduce errors of tens of microns. We introduce two ways to determine the actual wall location. In the first, we use the damage threshold of the wall material (brass) as a function of maximum laser intensity to determine the distance from the laser axis to the wall. A Gaussian beam has a well-defined intensity distribution along its radial position, 

\[ I = I_0 e^{-r^2/w_0^2} \]

where \( I_0 = \frac{2P_0}{\pi w_0^2} \) and \( w_0 = \frac{2L}{\pi d} \). The intersection between the focused beam’s intensity distribution with the damage threshold of the wall material gives the vertical distance to the wall (Figure 4.11a). Because the damage is visually inspected, uncertainty on the order of a hundred microjoules is expected, which results in uncertainties of about 1.5 \( \mu m \) for the absolute wall position.

The second method takes advantage of self-similarity within the viscous sublayer. Self-similarity of the cumulative streamwise velocity fluctuation distribution within the sublayer may be used to help determine the wall position and friction velocity [3]. For a given value of the cumulative distribution function, the velocity may be plotted as a function of wall-normal distance to give a straight line that crosses the origin. By plotting multiple lines for different values of the CDF, the absolute wall position can be estimated from their intersection (Figure 4.11b). These two methods give estimates within 2 \( \mu m \) of one another, so the wall location determined using the first method is used for all subsequent analysis.
Figure 4.11: (a) Plot of laser intensity and damage threshold of brass surface, to determine distance from wall. (b) Using self-similarity: intersection of two lines (bottom)

4.2.2 Uncertainty Quantification

Displacement uncertainty $\delta(\Delta x)$ (Equations 1.8-1.9) is primarily composed of fitting error, which varies from shot-to-shot. In this study, the 95% confidence interval for each fit in the transverse direction is nominally taken to be the position uncertainty. However this captures only the ability of the algorithm to fit the unfiltered data, and not the true accuracy of the fit. Quantifying instantaneous signal positions in a highly turbulent flow can be better performed using spatial correlations between adjacent pixels, assuming a signal that is continuous in the transverse direction. Non-Gaussian (or Gaussian-like) cross-correlations would imply discontinuity in the signal or flow, neither of which are physical. The shape of the cross-correlation function can then be used to quantify uncertainties in the fitted line centers. This method is currently still being developed for the FLEET diagnostic because at small separation distances, self-correlated measurement noise dominates and causes a "spike" in the function [44, 145]. There is some projection ambiguity in these measurements due to the assumption of purely one-dimensional (streamwise) flow. Flows in the spanwise or wall-normal directions can not be captured by the FLEET line in this configuration. This
Figure 4.12: (a) Measured acoustic signal from pulse-generated shock wave as function of laser pulse energy. Inset: zoomed in on 0-2 mJ range. (b) Oscilloscope trace of microphone signal, channel 1. Channel 2 is the femtosecond laser pulse as seen by a photodetector. Laser properties: \( \lambda = 800, 400 \text{ nm}, 1 \text{ kHz repetition rate} \)

uncertainty quantification also does not include outliers, defined here as velocities outside of \( U_{e}(y) \pm 0.5 \ast U_{e}(y) \) which are removed in the fitting step.

4.2.3 Quantifying the Laser Pulse Perturbation

Perturbations induced by the FLEET filament have been previously observed using planar Rayleigh scattering [86] and deviations from expected turbulent behavior are seen using tagging at high energy densities (Section 3.2). Planar Rayleigh scattering measurements are able to capture shock waves emanating from the focused femtosecond laser pulse down to pulse energies of 0.3 mJ with a \( f=17.5 \) cm focusing lens. These perturbations correspond to temperature increases of several hundred Kelvin within the first few microseconds following excitation. Limbach [85] notes that any audible sound is evidence for 300+ K gas heating. Using Limbach’s findings, the behavior of this acoustic perturbation is mapped for a number of pulse energies for both the fundamental wavelength and second harmonic. An elektret microphone (P1064) with a 20 Hz - 200 kHz frequency response and \(-44 \text{ dB} \pm 2 \text{ dB} \) sensitivity is used in a circuit with a non-inverting operational amplifier (LM318-N) to measure the laser
acoustic perturbations in atmospheric air for a f=30 cm focusing. The elektret microphone’s voltage output is proportional to the changing capacitance caused by the pressure waves produced by the shock coming off of the laser filament. A cylindrical resonator is used to enhance the signal of pulse energies lower than 0.8 mJ for both wavelengths. Figure 4.12b shows an oscilloscope trace of the microphone signal for a 3 mJ pulse centered at 800nm and focused with a f=30 cm lens in air. Figure 4.12a depicts the acoustic signal as a function of pulse energy for the fundamental and second harmonic wavelengths using a f=30 cm focusing lens. Here, the error bars represent the range of values over ten traces at each condition. The lowest resolvable signal for this focusing corresponds to a pulse energy of approximately 0.2 mJ at both 800 and 400 nm. No significant difference in behavior is found at pulse energies below 1 mJ, but the perturbation induced by the second harmonic seems to increase faster than that of the fundamental. Due to second harmonic conversion efficiency limitations, we are unable to make measurements at higher 400 nm energies.

4.2.4 Results

Figure 4.14: (a) Streamwise velocity profile in a Mach 1.5 turbulent boundary layer. (b) Transformed velocity. Laser properties: \( \lambda = 400 \) nm, 0.6 mJ per pulse, 1 kHz repetition rate
Figure 4.14a depicts the normalized mean local streamwise velocity profile as a function of wall normal distance scaled by the boundary layer thickness, $\delta$, as compared to Spalding’s [130] theoretical turbulent boundary layer model. Figure 4.14b shows the transformed velocity as compared to theoretical predictions, where $u_\tau$ is determined from the Clauser Chart method, and $Re_\tau \approx 9200$. Uncertainty in Figure 4.13 is computed using the process described in Section 1.3.2, where the displacement error is primarily reflected in the algorithm’s confidence intervals for each fit, which are heavily skewed by any noise in the unfiltered data. We are confident that further processing of the images can improve the fitting procedure, and implementation of cross-correlations will improve the accuracy of the overall fits. The normalized probability density function as a function of wall-normal distance is shown in Figure 4.15. The red box indicates a cutoff for the closest wall-normal distance measured. The magnitude of the turbulence intensity and streamwise fluctuations are captured in Figures 4.15 and 4.16. The strength of streamwise fluctuations appear to increase closer to the wall, but we are not able to capture the decay of the fluctuations at the surface of the wall.

The goal of this study is to resolve the smallest-possible spatial scales in the near-wall regime of a surface with transverse curvature, and characterize velocity fluctuations in turbulent shear layers using FLEET. FLEET is demonstrated to be a non-intrusive way to resolve the near-wall region to within ten microns from the wall. The optimal tagging parameters for this study include a central wavelength of 400 nm, 1 kHz repetition rate offered by our laser system, 0.6 mJ pulse energy, and focusing

Figure 4.13: Local mean velocity and mean instantaneous velocity uncertainty. Laser properties: $\lambda = 400$ nm, 0.6 mJ per pulse, 1 kHz repetition rate
Figure 4.15: Normalized velocity probability density function. Laser properties: $\lambda = 400$ nm, 0.6 mJ per pulse, 1 kHz repetition rate.

Figure 4.16: (a) Streamwise RMS velocity fluctuations for a Mach 1.15 air flow. (b) RMS velocity fluctuations for a Mach 1.5 air flow. Data for both figures are taken from over 6000 individual shots. Laser properties: $\lambda = 400$ nm, 0.6 mJ per pulse, 1 kHz repetition rate.
with a \( f=30 \text{ cm} \) lens. This set of parameters pose a fundamental limit to resolution in the shear layer since moving the beam closer to the surface will damage it, but the system cannot be easily adapted to decrease the beam waist further. Two different methods are used to determine the absolute wall position with an accuracy of several microns, and measurements are made within ten microns of the absolute wall position. The second method, using self-similarity within the viscous sublayer, makes the assumption that there are data within the shear layer, and may be less reliable in this case. While FLEET measurements are able to capture the increase in velocity fluctuations near the wall, only the edge of the shear layer (from \( y^+ \approx 10 \) onwards) can be resolved in this experiment due to the existence of a very thin boundary layer. Experimental parameters are chosen to minimize flow perturbation while providing an adequate signal-to-noise ratio for fitting purposes.
Chapter 5

Conclusion

5.1 Summary

This work presents efforts to extend FLEET’s capability to new gaseous environments, optimize FLEET parameters for accurate turbulence measurements, and apply FLEET to resolve flow behavior in the near-wall region. The accuracy and effectiveness of FLEET velocimetry is limited by the emission signal intensity and lifetime, which in turn are functions of experimental conditions including optical parameters, imaging equipment and gas mixture. Signal intensity and lifetime become limiting factors when flows, such as in a wind tunnel testing facility, experience large pressure and density drops. In order to develop FLEET as a viable tool for near-wall boundary layer measurements in supersonic flows, three collections of studies are performed.

Chapter 2 discusses femtosecond laser tagging in combinations of common test gases including argon, helium, carbon dioxide, methane and water vapor. The FLEET signal intensity is enhanced by the addition of argon in a nitrogen gas, but the addition of oxygen cancels out the enhancement from argon. Results from modeling suggest that increased signal is primarily attributed to greater emission from the nitrogen second positive system, which traditionally has a much shorter lifetime. Tagging in pure argon at atmospheric
pressure has a lifetime of several microseconds. Two-Photon Absorption Laser-Induced Fluorescence (TALIF) in nitrogen is implemented to validate the model and to better understand the FLEET physics. In oxygen and nitrogen mixtures, the FLEET signal varies non-monotonically with mixture fraction. Modest enhancement is observed in tagging in helium and nitrogen mixtures. Tagging is also feasible in a synthetic Mars atmosphere comprised of $4.7\% \text{N}_2 + 1.5\% \text{Ar} + 94\% \text{CO}_2$. Only modest success is found in methane gas, since the only detectable signal was recorded with less than a microsecond delay. Investigations of FLEET in air and nitrogen flow with saturated water vapor revealed that the signal decay occurs faster in nitrogen. Femtosecond laser tagging has been extended to non-air environments such as R134a, a gas commonly used for refrigeration and cooling, for application in the NASA Transonic Dynamics Tunnel. Tagging in R134a is shown to be pressure sensitive, and have a long enough lifetime for measuring velocity fluctuations in subsonic to transonic flow.

Chapter 3 assesses the accuracy of turbulence measurements using FLEET, and determined its ability to resolve integral length scales such as the Taylor microscale and Kolmogorov scale. FLEET is implemented using different tagging wavelengths ($\lambda_c = 800, 400, 267$ nm), focusing ($f=3.5, 10, 30, 50$ cm) and pulse energy ($60 \mu J - 4.5$ mJ/pulse) in air, nitrogen and argon gas flow at atmospheric temperature. The gas flow affects the signal intensity, which in turn affects the accuracy of the FLEET line fit. In combination with high tagging pulse energy, a signal in nitrogen flow resulted in artificial correlation. Imaging parameters were varied as well. Excess magnification reduces the viewing window of the measurement and amplifies intensifier noise. Low magnification created bias and overcorrelation in the image. The cleanest and most accurate data was taken with $\lambda_c = 267$ nm, which requires an order of magnitude less energy than at higher wavelengths under similar experimental conditions.

Chapter 4 describes two experiments that demonstrate FLEET’s capability of making near-wall measurements in air flow. The first experiment takes place in an in-draft wind tunnel facility and showcases three experimental setups using a flat-plate inset, a curved plate
inset, and FLEET in the boresight configuration. These setups each have their respective advantages and disadvantages. The first two, which use a FLEET line to achieve multiple measurements in the spanwise direction, requires an entrance hole for the beam. While the flat plate boundary layer provides a well-defined problem, the curved plate configuration avoids clipping the laser beam. In the second experiment, a curved surface is placed in a vertical free jet and measurements are taken within 10 $\mu m$ of the wall. Both canonical flat-plate and curved-surface geometries have been explored in the study. In combination with the previous chapter, measurements of the laser acoustic perturbations in atmospheric air with an electret microphone help to prescribe the best laser parameters for the experiment: $\lambda_c = 400$ nm, 1 kHz repetition rate, 0.6 mJ pulse energy, and focusing with a $f=30$ cm lens. Two different methods are implemented to determine the absolute wall position with an accuracy of several microns, and measurements are made within ten microns of the absolute wall position. The second method, using self-similarity within the viscous sublayer, makes the assumption that there are data within the shear layer, and may be less reliable in this case. While FLEET measurements are able to capture the increase in velocity fluctuations near the wall, only the edge of the shear layer (from $y^+ \simeq 10$ onwards) can be resolved in this experiment due to the existence of a very thin boundary layer. Experimental parameters are chosen to minimize flow perturbation while providing an adequate signal-to-noise ratio for fitting purposes. Further efforts are needed to quantify all the contributions to error, including vibrations of the facility during data collection, equipment noise, and data fitting. The feasibility of using FLEET to measure velocity profiles within tens of microns to the wall in an open supersonic jet as well as in an in-draft wind tunnel facility has been demonstrated.

5.2 Future Directions

This thesis touches on only nascent efforts to apply FLEET to modern problems in fluid dynamics and aerospace engineering. At the time of writing, FLEET has already been
adopted by two agencies outside the Applied Physics Group at Princeton, Spectral Energies LLC and NASA Langley. There exists on-going interest in boundary layer measurements for shear stress characterization and transition. A renewed national interest in hypersonic aircraft development provides new opportunities for ultrafast nonintrusive laser diagnostics, including FLEET. There is a pressing need to better understand flow in the wake of a vehicle subject to hypersonic flows. Wake flows, the region of flow separation and recirculation behind a body, are poorly understood and so far, no quantitative measurements have been made in the hypersonic regime. Aft-body vortices are inherently multi-dimensional and require more complex optical setups. Quantitative wake measurements will be useful for designing the next generation of hypersonic vehicles and assessing the validity of computation models. FLEET can be implemented to make nonintrusive spatially- and temporally-resolved measurements of aft-body fluid structures in order to further the understanding of hypersonic flows. Potential solutions to the optical access challenge include the use of plenoptic cameras in order to increase the field of view in a three-dimensional flow, and bundles of fiber-coupled detectors to circumvent geometrical constraints of the test section. Future implementations of FLEET can be advised by the limitations and capabilities demonstrated in this thesis. Only FLEET’s capability as a velocimetry tool has been studied in this work, and much room exists for the development of FLEET as a thermometry or density measurement tool.
# Appendix A

## Rate Coefficients of Chemical Reactions

Table A.1: Relevant $N_2 + Ar$ reactions and their respective rate constants ($m^3/s$ or $m^6/s$, unless otherwise indicated), $T_g, T_e[K]$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e + N_2^+ \rightarrow 2N$</td>
<td>$k_1 = 2 \times 10^{-13} \sqrt{300/T_e}$</td>
<td>[77]</td>
</tr>
<tr>
<td>$N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu$</td>
<td>$\nu_2 = 2.74 \times 10^7 1/s$</td>
<td>[88]</td>
</tr>
<tr>
<td>$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu$</td>
<td>$\nu_3 = 2 \times 10^5 1/s$</td>
<td>[108]</td>
</tr>
<tr>
<td>$N + N + N_2 \rightarrow N_2(B^3\Pi_g) + N_2$</td>
<td>$k_4 = 8.3 \times 10^{-46} * e^{500/T_g}$</td>
<td>[113], [114]</td>
</tr>
<tr>
<td>$e + N_2 \rightarrow N + N + e$</td>
<td>$k_5 = 6.3 \times 10^{-12} T_e^{-1.6} * e^{-1.368 \times 10^5/T_e}$</td>
<td>[132]</td>
</tr>
<tr>
<td>$Ar^*(4^3P_2) + N_2 \rightarrow Ar + N_2(C^3\Pi_u)$</td>
<td>$k_6 = 3 \times 10^{-17}$</td>
<td>[113]</td>
</tr>
<tr>
<td>$Ar^*(4^3P_2) + N_2 \rightarrow Ar + N_2(B^3\Pi_g)$</td>
<td>$k_7 = 9.8 \times 10^{-18}$</td>
<td>[113]</td>
</tr>
<tr>
<td>$e + Ar^+_2 \rightarrow Ar^*(4^3P_2) + Ar$</td>
<td>$k_8 = 9.1 \times 10^{-13} (300/T_g)^{0.6}$</td>
<td>[122]</td>
</tr>
<tr>
<td>$2e + Ar^+ \rightarrow Ar^*(4^3P_2) + e$</td>
<td>$k_9 = 5 \times 10^{-39} (T_e/11600)^{-4.5}$</td>
<td>[113]</td>
</tr>
<tr>
<td>$Ar^+ + 2Ar \rightarrow Ar^+_2 + Ar$</td>
<td>$k_{10} = 2.5 \times 10^{-43} (300/T_g)^{0.75}$</td>
<td>[115]</td>
</tr>
</tbody>
</table>
\[ N_2(B^3\Sigma_g) + N_2 \rightarrow N_2 + N_2 \]
\[ Ar^+ + N_2 \rightarrow Ar + N_2^+ \]
\[ e + Ar^+(4^3P_2) \rightarrow Ar^+ + e + e \]
\[ Ar^+(4^3P_2) + Ar^+(4^3P_2) \rightarrow \]
\[ Ar^+ + Ar + e \]
\[ N_2(B^3\Pi_g) + Ar \rightarrow N_2 + N_2 + Ar \]
\[ N_2(C^3\Pi_u) + Ar \rightarrow N_2(B^3\Pi_g) + Ar \]
\[ N_2(A^3\Sigma_u^+) + N_2 \rightarrow N_2 + N_2 \]
\[ N_2(A^3\Sigma_u^+) + N \rightarrow N_2 + N \]
\[ N_2(C^3\Pi_u) + N_2 \rightarrow N_2 + N_2 \]
\[ e + Ar \rightarrow Ar^+ + e + e \]
\[ e + N_2 \rightarrow N_2^+ + e + e \]
\[ N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow \]
\[ N_2(C^3\Pi_u) + N \]
\[ N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow \]
\[ N_2(B^3\Pi_g) + N \]
\[ N_2^+ + Ar \rightarrow ArN^+ + N \]
\[ N_2 + Ar^+ \rightarrow ArN^+ + N \]
\[ ArN^+ + e \rightarrow Ar + N \]
\[ Ar_2^+ + e \rightarrow Ar^* + Ar \]
\[ Ar^+(4^3P_2) + N_2 \rightarrow Ar + N + N \]
\[ N_2^+ + 2N_2 \rightarrow N_4^+ + N_2 \]
\[ N_2^+ + N_2 + Ar \rightarrow N_4^+ + Ar \]
\[ N_3^+ + e \rightarrow N + N_2 \]
\[ N_3^+ + N \rightarrow N_2^+ + N_2 \]

\[ k_{11} = 3 \times 10^{-17} \]
\[ k_{12} = 4.5 \times 10^{-16} \]
\[ k_{13} = 6.8 \times 10^{-15}(T_e/11600)^{0.67} \]
\[ k_{14} = 5 \times 10^{-16} \]
\[ k_{15} = 8 \times 10^{-18} \]
\[ k_{16} = 8.16 \times 10^{-19} \]
\[ k_{17} = 3 \times 10^{-23} \]
\[ k_{18} = 9.6 \times 10^{-17} \]
\[ k_{19} = 1.4 \times 10^{-17} \]
\[ k_{20} = 4 \times 10^{-18}T_e^{0.5}e^{-1.83 \times 10^5/T_e} \]
\[ k_{21} = 5 \times 10^{-17}(T_e/11600)^{0.5}(1 + 1.1 \times 10^{-5}T_e)e^{-1.82 \times 10^5/T_e} \]
\[ k_{22} = 2 \times 10^{-16} \]
\[ k_{23} = 8 \times 10^{-17} \]
\[ k_{24} = 10^{-19} \]
\[ k_{25} = 10^{-19} \]
\[ k_{26} = 10^{-12} \]
\[ k_{27} = 5 \times 10^{-14}(T_e/11600)^{-0.67} \]
\[ k_{28} = 1.6 \times 10^{-17} \]
\[ k_{29} = 1.9 \times 10^{-35} \]
\[ k_{30} = 5.24 \times 10^{-41}(300/T_g)^{2.2} \]
\[ k_{31} = 2 \times 10^{-13}\sqrt{300/T_e} \]
\[ k_{32} = 6.6 \times 10^{-17} \]
\[
\begin{array}{lll}
N_4^+ + N & \rightarrow & N_3^+ + N_2 \\
N_4^+ + N_2 & \rightarrow & N_2^+ + N_2 + N_2 \\
N^+ + N_2 + e & \rightarrow & N + N_2 \\
N^+ + e + e & \rightarrow & N + e \\
N^+ + e & \rightarrow & N + h\nu \\
N^+ + N_2 & \rightarrow & N + N_2^+ \\
N^+ + N_2 + N_2 & \rightarrow & N_3^+ + N_2 \\
e + N_4^+ & \rightarrow & N_2 + N_2(A^3\Sigma_u^+, B^3\Pi_g) \\
e + N_4^+ & \rightarrow & N_2 + N_2(C^3\Pi_u) \\
N_2^+ + N_2 + N & \rightarrow & N_3^+ + N_2 \\
N_2^+ + N & \rightarrow & N^+ + N_2 \\
N_3^+ + N_2 & \rightarrow & N^+ + N_2 + N_2 \\
N_3^+ + N_2(A^3\Sigma_u^+) & \rightarrow & N^+ + N + N_2 \\
e + N_2 & \rightarrow & N^+ + N + e + e \\
e + e + N_2^+ & \rightarrow & N_2 + e \\
N^+ + N + N_2 & \rightarrow & N_2^+ + N_2 \\
N_2(A^3\Sigma_u^+) & \rightarrow & N_2 + h\nu \\
e + e + N_4^+ & \rightarrow & N_2 + N_2 + e \\
k_{33} = 10^{-15} \\
k_{34} = 2.1 \times 10^{-22} e^7/121 & \text{[72]} \\
k_{35} = 6 \times 10^{-39} (300/T_e)^{1.5} & \text{[26]} \\
k_{36} = 7 \times 10^{-32} (300/T_e)^{4.5} & \text{[26]} \\
k_{37} = 7 \times 10^{-18} & \text{[26]} \\
k_{38} = 10^{-19} & \text{[1]} \\
k_{39} = 1.7 \times 10^{-41} (300/T_g)^2 & \text{[1, 56]} \\
k_{40} = 2.6 \times 10^{-13} \sqrt{300/T_e} & \text{[74]} \\
k_{41} = 2.6 \times 10^{-12} \sqrt{300/T_e} & \text{[74]} \\
k_{42} = 0.9 \times 10^{-41} e^{400/T_g} & \text{[126, 1]} \\
k_{43} = 7.2 \times 10^{-19} e^{300/T_g} & \text{[126, 1]} \\
k_{44} = 10^{-17} & \text{[126, 1]} \\
k_{45} = 5.5 \times 10^{-18} & \text{[126, 1]} \\
k_{46} = 1.2 \times 10^{-17} & \text{[126, 1]} \\
k_{47} = 3 \times 10^{-16} & \text{[126, 1]} \\
k_{48} = 4 \times 10^{-16} & \text{[126, 1]} \\
k_{49} = 6 \times 10^{-16} & \text{[126, 1]} \\
k_{50} = 6 \times 10^{-16} & \text{[126, 1]} \\
k_{51} = 4.3 \times 10^{-16} \sqrt{T_e} (1 + 6.76 \times 10^{-6} T_e) e^{-2.96 \times 10^5/T_e} & \text{[132]} \\
k_{52} = 10^{-25} (T_e/300)^{-4.5} & \text{[77]} \\
k_{53} = 10^{-41} (300/T_g) & \text{[77, 17]} \\
v_{54} = 0.51/s & \text{[61, 26]} \\
k_{55} = 7 \times 10^{-32} (300/T_g)^{4.5} & \text{[74]} \\
\end{array}
\]

Table A.2: Relevant $\text{N}_2$ plasma reactions and their respective rate constants ($m^3/s$ or $m^6/s$, unless otherwise indicated), $T_v, T_e, T_g[K]$
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e + N_2^+ \rightarrow 2N$</td>
<td>$k_1 = 2 \times 10^{-13}(300/T_e)^{0.5}$</td>
<td>[77]</td>
</tr>
<tr>
<td>$N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu$</td>
<td>$k_2 = 2.74 \times 10^7 \text{1/s}$</td>
<td>[88]</td>
</tr>
<tr>
<td>$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu$</td>
<td>$k_3 = 2 \times 10^5 \text{1/s}$</td>
<td>[108]</td>
</tr>
<tr>
<td>$N_4^+ + N \rightarrow N_3^+ + N_2$</td>
<td>$k_4 = 10^{-15}$</td>
<td>[72]</td>
</tr>
<tr>
<td>$N_4^+ + N_2 \rightarrow N_2^+ + 2N_2$</td>
<td>$k_5 = 2.1 \times 10^{-22}e^{T_g/121}$</td>
<td>[126]</td>
</tr>
<tr>
<td>$e + N_2 \rightarrow N + N + e$</td>
<td>$k_6 = 6.3 \times 10^{-12}T_e^{-1.6}e^{-1.1368 \times 10^5/T_e}$</td>
<td>[132]</td>
</tr>
<tr>
<td>$N^+ + N_2 + e \rightarrow N + N_2$</td>
<td>$k_7 = 6 \times 10^{-39}\left(\frac{300}{T_e}\right)^{1.5}$</td>
<td>[26]</td>
</tr>
<tr>
<td>$N^+ + 2e \rightarrow N + e$</td>
<td>$k_8 = 7 \times 10^{-32}\left(\frac{300}{T_e}\right)^{4.5}$</td>
<td>[26]</td>
</tr>
<tr>
<td>$N^+ + e \rightarrow N + h\nu$</td>
<td>$k_9 = 7 \times 10^{-18}$</td>
<td>[26]</td>
</tr>
<tr>
<td>$N^+ + N_2 \rightarrow N + N_2^+$</td>
<td>$k_{10} = 10^{-19}$</td>
<td>[1]</td>
</tr>
<tr>
<td>$N^+ + 2N_2 \rightarrow N_3^+ + N_2$</td>
<td>$k_{11} = 1.7 \times 10^{-41}(300/T_g)^{2.1}$</td>
<td>[1, 56]</td>
</tr>
<tr>
<td>$2N_2(A^3\Sigma_u^+) \rightarrow N_2(C^3\Pi_u) + N_2$</td>
<td>$k_{12} = 2 \times 10^{-16}$</td>
<td>[110]</td>
</tr>
<tr>
<td>$2N_2(A^3\Sigma_u^+) \rightarrow N_2(B^3\Pi_g) + N_2$</td>
<td>$k_{13} = 7 \times 10^{-17}$</td>
<td>[110]</td>
</tr>
<tr>
<td>$N_2(A^3\Sigma_u^+) + N \rightarrow N_2 + N$</td>
<td>$k_{14} = 9.6 \times 10^{-17}$</td>
<td>[113]</td>
</tr>
<tr>
<td>$e + N_2 \rightarrow N_2^+ + 2e$</td>
<td>$k_{15} = 7 \times 10^{-17}$</td>
<td>[110]</td>
</tr>
<tr>
<td>$N_3^+ + e \rightarrow N + N_2$</td>
<td>$k_{16} = 4.7 \times 10^{-19}\left(\frac{T_e}{11600}\right)^{0.5}(1 + \sqrt{300/T_e})$</td>
<td>[132]</td>
</tr>
<tr>
<td>$N_3^+ + N \rightarrow N_2^+ + N_2$</td>
<td>$k_{17} = 2 \times 10^{-13}\sqrt{300/T_e}$</td>
<td>[77]</td>
</tr>
<tr>
<td>$N_2(B^3\Pi_g) + N_2 \rightarrow N_2 + N_2$</td>
<td>$k_{18} = 6.6 \times 10^{-17}$</td>
<td>[126]</td>
</tr>
<tr>
<td>$N_2(C^3\Pi_u) + N_2 \rightarrow N_2 + N_2$</td>
<td>$k_{19} = 3 \times 10^{-17}$</td>
<td>[113]</td>
</tr>
<tr>
<td>$N_2^+ + N_2 + N_2 \rightarrow N_4^+ + N_2$</td>
<td>$k_{20} = 1.4 \times 10^{-17}$</td>
<td>[113]</td>
</tr>
<tr>
<td>$N_2^+ + N_2 + N_2 \rightarrow N_4^+ + N_2$</td>
<td>$k_{21} = 5.24 \times 10^{-41}(300/T_g)^{2.2}$</td>
<td>[56]</td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Source</td>
</tr>
<tr>
<td>----------</td>
<td>--------------</td>
<td>--------</td>
</tr>
<tr>
<td>( e + O_2 + O_2 \rightarrow O_2^- + O_2 )</td>
<td>( k_{36} = 1.4 \times 10^{-41} \left( \frac{300}{T_e} \right) * e^{-600/T_g} e^{700(T_e - T_g)/(T_e T_g)} )</td>
<td>[77]</td>
</tr>
</tbody>
</table>

Table A.3: Relevant reactions and their respective rate constants (\( m^3/s \) or \( m^6/s \), unless otherwise indicated), \( T_g, T_e[K] \)
\[
\begin{align*}
e + O_2 + N_2 & \rightarrow O_2^- + N_2 \\
O_2^+ + O_2 + O_2 & \rightarrow O_4^+ + O_2 \\
N_4^+ + O_2 & \rightarrow O_4^+ + N_2 + N_2 \\
O_4^+ + O_2 & \rightarrow O_2^+ + O_2 + O_2 \\
O_4^+ + e & \rightarrow O_2 + O_2 \\
e + O_2^+ & \rightarrow O + O \\
e + NO^+ & \rightarrow N + O \\
e + O + O_2 & \rightarrow O_2^- + O \\
O_2^- + O & \rightarrow O_3 + e \\
O_2 + N & \rightarrow NO + O \\
O^+ + N + (O_2, N_2) & \rightarrow NO^+ + (O_2, N_2) \\
N^+ + O_2 & \rightarrow O_2^+ + N \\
N^+ + O_2 & \rightarrow NO^+ + O \\
N^+ + O & \rightarrow N + O^+ \\
N^+ + O_3 & \rightarrow NO^+ + O_2 \\
N^+ + NO & \rightarrow N + NO^+ \\
N^+ + NO & \rightarrow N_2^+ + O \\
N^+ + NO & \rightarrow O^+ + N_2 \\
O^+ + N_2 & \rightarrow NO^+ + N \\
N_2^+ + O_2 & \rightarrow O_2^+ + N_2 \\
N_2^+ + O & \rightarrow NO^+ + N \\
N_2^+ + O & \rightarrow O^+ + N_2 \\
N_2^+ + O_3 & \rightarrow O_2^+ + O + N \\
N_2^+ + NO & \rightarrow NO^+ + N_2 \\
O_2^+ + N_2 & \rightarrow NO^+ + NO \\
\end{align*}
\]

\[k_{37} = 1.07 \times 10^{-43} e^{−70/T_g} \left( \frac{300}{T_e} \right)^2 \]

\[e^{1500(T_e−T_g)/(T_e T_g)}\]

\[k_{38} = 2.4 \times 10^{-42} \left( \frac{300}{T_g} \right)^{3.2} \]

\[k_{39} = 2.5 \times 10^{-16} \]

\[k_{40} = 3.3 \times 10^{-12} \left( \frac{300}{T_g} \right)^4 \]

\[e^{−5030/T_g} \]

\[k_{41} = 1.4 \times 10^{-12} \sqrt{\frac{300}{T_e}} \]

\[k_{42} = 2 \times 10^{-13} \left( \frac{300}{T_g} \right) \]

\[k_{43} = 4 \times 10^{-13} \left( \frac{300}{T_g} \right)^{1.5} \]

\[k_{44} = 10^{-43} \]

\[k_{45} = 1.5 \times 10^{-16} \]

\[k_{46} = 1.1 \times 10^{-20} T_g e^{-3150/T_g} \]

\[k_{47} = 10^{-41} \]

\[k_{48} = 2.8 \times 10^{-16} \]

\[k_{49} = 2.5 \times 10^{-16} \]

\[k_{50} = 10^{-18} \]

\[k_{51} = 5 \times 10^{-16} \]

\[k_{52} = 8 \times 10^{-16} \]

\[k_{53} = 3 \times 10^{-18} \]

\[k_{54} = 10^{-18} \]

\[k_{55} = 3 \times 10^{-18} \]

\[k_{56} = 6 \times 10^{-17} \]

\[k_{57} = 1.3 \times 10^{-16} \]

\[k_{58} = 10^{-17} \left( \frac{300}{T_g} \right)^{0.2} \]

\[k_{59} = 10^{-16} \]

\[k_{60} = 3.3 \times 10^{-16} \]

\[k_{61} = 10^{-23} \]
\[
\begin{align*}
O_2^+ + N &\rightarrow NO^+ + O \\
O_2^+ + NO &\rightarrow NO^+ + O_2 \\
N_4^+ + O &\rightarrow O^+ + N_2 + N_2 \\
e + O_3 + O_2 &\rightarrow O_3^- + O_2 \\
N_4^+ + NO &\rightarrow NO^+ + N_2 + N_2 \\
O_4^+ + O &\rightarrow O_2^+ + O_3 \\
O_4^+ + NO &\rightarrow NO^+ + O_2 + O_2 \\
O_2^- + O_2 &\rightarrow e + O_2 + O_2 \\
e + O + O_2 &\rightarrow O^- + O_2 \\
e + O_3 &\rightarrow O + O_2^- \\
e + O_3 &\rightarrow O^- + O_2 \\
O^- + O &\rightarrow O_2 + e \\
O^- + N &\rightarrow NO + e \\
O^- + O_2 &\rightarrow O_3 + e \\
e + O_2 &\rightarrow O_2^+ + e + e \\
e + NO_2 &\rightarrow O^- + NO \\
O_2^- + N_2 &\rightarrow O_2 + N_2 + e \\
O_2^- + O_2 &\rightarrow O_2 + O_2 + e \\
O_3^- + O &\rightarrow O_2 + O_2 + e \\
O_2^- + N_2(A^3\Sigma_u^+) &\rightarrow O_2 + N_2 + e \\
O_2^- + N_2(B^3\Pi_g) &\rightarrow O_2 + N_2 + e \\
O^- + N_2(A^3\Sigma_u^+) &\rightarrow O + N_2 + e \\
O^- + N_2(B^3\Pi_g) &\rightarrow O + N_2 + e \\
\end{align*}
\]

\[
\begin{align*}
k_{62} &= 1.2 \times 10^{-16} \\
k_{63} &= 4.4 \times 10^{-16} \\
k_{64} &= 2.5 \times 10^{-16} \\
k_{65} &= 1.4 \times 10^{-41} \left(\frac{300}{T_e}\right) e^{-600/T_y} \times e^{700(T_e-T_y)/(T_eT_y)} \\
k_{66} &= 4 \times 10^{-16} \\
k_{67} &= 3 \times 10^{-16} \\
k_{68} &= 10^{-16} \\
k_{69} &= 8.6 \times 10^{-16} e^{-6030/T_y} \times (1 - e^{-1570/T_y}) \\
k_{70} &= 10^{-43} \\
k_{71} &= 10^{-15} \\
k_{72} &= 10^{-17} \\
k_{73} &= 5 \times 10^{-16} \\
k_{74} &= 2.6 \times 10^{-16} \\
k_{75} &= 5 \times 10^{-21} \\
k_{76} &= P\left(\frac{10^7}{\sqrt{T_e}}\right) (1.43 + 2.47T_e + 0.456T_e^2)e^{-12.06/T_e} \times 1/s \\
k_{77} &= 10^{-17} \\
k_{78} &= 1.9 \times 10^{-18} \sqrt{\frac{T_y}{300}} e^{-4990/T_y} \\
k_{79} &= 2.7 \times 10^{-16} \sqrt{\frac{T_y}{300}} e^{-5590/T_y} m^3/s \\
k_{80} &= 3 \times 10^{-16} \\
k_{81} &= 2.1 \times 10^{-15} \\
k_{82} &= 2.5 \times 10^{-15} \\
k_{83} &= 2.2 \times 10^{-15} \\
k_{84} &= 1.9 \times 10^{-15} \\
\end{align*}
\]
\begin{align*}
O + O_2 + (O_2, N_2) &\rightarrow O_3 + (O_2, N_2) \\
O_3^- + O &\rightarrow O_2^- + O_2 \\
O_2^- + O &\rightarrow O_2 + O^- \\
O_2^- + O_3 &\rightarrow O_2 + O_3^- \\
O^- + O_3 &\rightarrow O + O_3^- \\
O_2^- + N &\rightarrow NO_2 + e \\
O_2^- + O_2^+ &\rightarrow O_2 + O_2 \\
O_2^- + N_2^+ &\rightarrow O_2 + N_2 \\
O + O_3 &\rightarrow O_2 + O_2 \\
O + NO_2 &\rightarrow NO + O_2 \\
N_2(C^4\Pi_u) + O_2 &\rightarrow N_2 + O + O
\end{align*}

\begin{align*}
k_{85} &= 6.55 \times 10^{-40} \left(\frac{300}{T_g}\right)^2 & [79] \\
k_{86} &= 3.2 \times 10^{-16} & [17] \\
k_{87} &= 3.3 \times 10^{-16} & [17, 101] \\
k_{88} &= 4 \times 10^{-16} & [17, 101] \\
k_{89} &= 5.3 \times 10^{-16} & [17, 101] \\
k_{90} &= 5 \times 10^{-16} & [17, 101] \\
k_{91} &= 2.2 \times 10^{-12} & [77] \\
k_{92} &= 2.2 \times 10^{-12} & [77] \\
k_{93} &= 2 \times 10^{-11} & [79] \\
k_{94} &= 1.13 \times 10^{-11} & [79] \\
k_{95} &= 28 \times 10^{-17} & [107]
\end{align*}

Table A.4: Relevant reactions involving $O_2$ metastables ($O_2(a^1\Delta_g), O_2(b^1\Sigma_g^+)$) and their respective rate constants ($m^3/s$ or $m^6/s$), $T_v, T_e, T_g[K]$
\begin{tabular}{|l|l|}
\hline
\(O_2(b) + O_3 \rightarrow O_2 + O_2 + O\) & \(k_{m9} = 1.8 \times 10^{-17}\) \\
\(O_2(b) + N_2 \rightarrow O_2(a) + N_2\) & \(k_{m10} = 4.9 \times 10^{-21}e^{-253/T_g}\) \\
\(O_2(b) + O_2 \rightarrow O_2(a) + O_2\) & \(k_{m11} = 4.3 \times 10^{-28}T_g^{2.4}e^{-241/T_g}\) \\
\(O_2(b) + O \rightarrow O_2(a) + O\) & \(k_{m12} = 8 \times 10^{-20}\) \\
\(O_2(b) + NO \rightarrow O_2(a) + NO\) & \(k_{m13} = 4 \times 10^{-20}\) \\
\(O + O + N_2 \rightarrow (O_2(a), O_2(b)) + N_2\) & \(k_{m14} = \left(\frac{1}{3}\right) \times 2.76 \times 10^{-46}e^{720/T_g}\) \\
\(O + O + O_2 \rightarrow (O_2(a), O_2(b)) + O_2\) & \(k_{m15} = \left(\frac{1}{3}\right) \times 2.45 \times 10^{-43}T_g^{-0.63}\) \\
\hline
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