Complementary Laser Diagnostics of Metastable N$_2$(A$^3\Sigma_u^+$,v) Molecules in Nonequilibrium Plasmas and in High-Speed Flows

E.R. Jans$^1$, I. Gulko$^2$, X. Yang$^3$, T.A. Miller$^4$, and I.V. Adamovich$^5$

Department of Mechanical and Aerospace Engineering

Department of Chemistry

The Ohio State University, Columbus, OH 43210

Abstract

Non-intrusive laser diagnostics of metastable N$_2$ molecules in the lowest excited electronic state, A$^3\Sigma_u^+$, are used for measurements of N$_2$(A$^3\Sigma_u^+$,v) vibrational level populations in ns pulse discharge plasmas in molecular gas mixtures and in a nonequilibrium supersonic flow. In high pressure plasmas, at pressures of 100-400 Torr, time-resolved absolute N$_2$(A$^3\Sigma_u^+$,v=0.1) populations are measured by single-pass, continuous wave Tunable Diode Laser Absorption Spectroscopy (TDLAS). In a supersonic flow, at a pressure of several Torr, absolute N$_2$(A$^3\Sigma_u^+$,v=0.1) populations are determined by Cavity Ring Down Spectroscopy (CRDS). TDLAS measurements are made in nitrogen, H$_2$-N$_2$, O$_2$-N$_2$, and NO-N$_2$ mixtures excited by a double dielectric barrier, repetitively pulsed, ns discharge in a plane-to-plane geometry, operated at a pulse repetition rate of 100 kHz. The results are compared with kinetic modeling predictions, identifying the dominant mechanisms of N$_2$(A$^3\Sigma_u^+$) generation and decay during the discharge pulses and in the afterglow. Temporal evolution of N$_2$(A$^3\Sigma_u^+$,v) populations during the discharge bursts in nitrogen provides an indirect measurement of time-resolved N atom number density, since collisional quenching by N atoms is the dominant process controlling N$_2$(A$^3\Sigma_u^+$) decay. CRDS measurements are made in nitrogen, in the test section of a nonequilibrium flow supersonic wind tunnel with the steady-state run time of approximately 10 seconds. The flow is excited by a 4 kHz repetitive ns pulse discharge in the wind tunnel plenum, at plenum pressures of P$_0$=200-300 Torr, and expands through a two-dimensional contoured nozzle to the Mach number of M=3.6. The cavity ring down time is not affected by the supersonic flow. During each run, 50 single-shot ring down traces are acquired, demonstrating good shot-to-shot reproducibility. N$_2$(A$^3\Sigma_u^+$,v=0.1) populations and the flow temperature are inferred from the single-shot CRDS data. The two diagnostic techniques are complementary and can be used for characterization of both low-temperature plasmas and nonequilibrium reacting flows over a wide range of pressures, as well as at short run time high-enthalpy flow facilities.

1 Graduate Research Fellow, Department of Mechanical and Aerospace Engineering, AIAA Member
2 Graduate Research Assistant, Department of Mechanical and Aerospace Engineering, AIAA Member
3 Visiting Scholar, Department of Mechanical and Aerospace Engineering,
4 Professor Emeritus, Department of Chemistry and Biochemistry
5 Professor, Department of Mechanical and Aerospace Engineering, Associate Fellow AIAA
1. Introduction

Energy transfer processes and reactions involving electronically excited metastable molecules, such as \( \text{N}_2(\text{A}^3\Sigma_u^+) \) and \( \text{O}_2(\text{a}^1\Delta_g) \), are known to play an essential role in low-temperature air and oxygen plasma chemistry [1,2], as well as for plasma assisted combustion and fuel reforming [3]. Along with the electron impact dissociation, reactive quenching of \( \text{N}_2(\text{A}^3\Sigma_u^+) \) and \( \text{O}_2(\text{a}^1\Delta_g) \) by molecular oxygen, hydrogen, and hydrocarbon species is a major source of O atoms, H atoms, and other reactive radicals in air and fuel-air mixtures, which is critical for kinetics of plasma assisted combustion. A reaction of \( \text{N}_2(\text{A}^3\Sigma_u^+) \) with O atoms is one of the key pathways of NO formation, which leads to generation of other reactive nitrogen species in air plasmas. In high-temperature nonequilibrium reacting flows, \( \text{O}_2(\text{a}^1\Delta_g) \) and \( \text{N}_2(\text{A}^3\Sigma_u^+) \) excitation by heavy species impact may also affect kinetics of molecular dissociation [4] and NO emission behind strong shock waves [5,6].

For quantitative insight into kinetics of energy transfer and chemical reactions involving \( \text{N}_2(\text{A}^3\Sigma_u^+) \) and \( \text{O}_2(\text{a}^1\Delta_g) \), it is highly desirable to measure their time-resolved, absolute number densities. Tunable Diode Laser Absorption Spectroscopy (TDLAS) and Cavity Ring Down Spectroscopy (CRDS) yield direct number density measurements and do not require additional calibration, which may introduce additional uncertainty into the measurements. This is a critical advantage compared to the measurements using Laser Induced Fluorescence (LIF) and absolute emission spectroscopy. In addition, both of these techniques may be adapted for measurements at pulsed high-enthalpy test facilities, such as shock tubes and shock tunnels. This would be possible if the laser scan time across an absorption line (for TDLAS) or the ring down time (for CRDS), respectively, are shorter compared to the facility run time and the characteristic transient time (e.g. relaxation time behind the shock wave). Our recent work [7] demonstrated that these two diagnostics are complementary to each other, yielding absolute time-resolved measurements at relatively low pressures ranging from a few Torr to a few tens of Torr (CRDS) as well as at high pressures, above \( \sim 100 \) Torr (TDLAS), at the conditions where the ring down time may become too short.

The objective of the present work is to demonstrate the capabilities of these diagnostics for \( \text{N}_2(\text{A}^3\Sigma_u^+) \) measurements in two nonequilibrium environments, (i) repetitive ns pulse discharge sustained in slow flow molecular gas mixtures at pressures of 100-400 Torr, and (ii) nonequilibrium supersonic flow excited by a ns pulse discharge in the plenum of a blowdown wind tunnel, at the static pressure of several Torr. In both cases, the excitation generates a diffuse, stable, and reproducible plasma, which greatly simplifies the interpretation of absorption measurements and the kinetic modeling analysis.

2. Experimental

2.1. TDLAS Measurements

Figure 1 shows the schematic of the slow flow discharge cell and TDLAS diagnostics. The discharge cell is is a 22 mm x 10 mm rectangular cross section quartz channel 55 cm long, fused to 1.5 inch diameter quartz tubes at both ends, with the total length of 90 cm. Anti-reflection coated BK-7 glass windows at both ends of the cell provide optical access to the TDLAS laser beam. Nitrogen (99.999% purity) flows through the cell at the flow rate of 1 SLM. Different amounts hydrogen (up to 10%, 99.999% purity) or medical air (up to 10%) are added to the nitrogen flow.
Some of the measurements have been done in a 1000 ppm NO / N₂ mixture, also at the flow rate of 1 SLM. The flow rates of the mixture components are regulated by the mass flow controllers (Sierra Smart-Trak 2). The total pressure in the cell is varied from 100 to 412 Torr, by throttling the flow in the vacuum exhaust line. The combined leak rate of the vacuum cell and the gas delivery system is approximately 1.6×10¹⁵ molecules/s, over 5 orders of magnitude lower compared to the flow rate, 5.3×10²⁰ molecules/s, such that the upper bound oxygen and water vapor impurity level is ~10⁻⁶ and ~10⁻⁷ mole fraction, respectively.

The flow in the cell is excited by a double dielectric barrier discharge maintained between two parallel rectangular plate copper electrodes 60 mm long and 12 mm wide, mounted to the top and bottom walls of the quartz channel in the middle of the cavity, as shown in Fig. 1. The electrodes are attached to the walls by a silicon rubber adhesive, which prevents corona discharge formation in ambient air, near the electrode surfaces. The discharge in the cell is sustained by a MegaImpulse NPG-18/100k high-voltage pulse generator, with the pulse peak voltage up to 30 kV and pulse duration of approximately 20 ns FWHM, operated at a pulse repetition rate of 100 kHz and a burst repetition rate of 30 Hz. Energy coupled to the plasma is determined by measuring pulse voltage and current waveforms using custom-made, high bandwidth capacitive voltage probes and shunt current probes [8].

A collimated output beam of a 20 mW continuous wave diode laser (New Focus Velocity 6312), with a scan range from 764 to 781 nm and a nominal linewidth of less than 0.3 MHz, is directed along the cell, as shown in Fig. 1. The beam diameter is approximately 1 mm. The laser wavelength is scanned by varying the voltage on the piezoelectric driver of the laser and is monitored during the experiment by a wavemeter (High Finesse WS6). The transmitted beam is focused into an optical fiber (Thorlabs BFL22-910) 20 m long by a 2.5 cm focal distance lens, which sends the transmitted signal to a silicon photodiode (Thorlabs DET36A), monitored by an oscilloscope (Agilent DSO-X 4032A). The use of the optical fiber allows the data acquisition to be spatially isolated from the electromagnetic noise generated by the electric discharge in the cell, which is critical for measuring weak absorption signals (path integrated absorption below ~10⁻³). The experiment is controlled by a computer running a LabView script, which varies the piezoelectric driver voltage to tune the laser output wavelength, records the wavelength measured by the wavemeter, and saves the time-resolved transmitted signal intensity traces taken by the oscilloscope. During the present experiments, the diode laser was tuned using two different methods. The first method is the so-called “step-and-measure”, where the piezoelectric voltage controlling the wavelength is set to a certain value and is held constant, while the discharge is triggered repeatedly, and the time-resolved absorption signal is acquired by the data acquisition system. After averaging over the desired number of discharge bursts on the oscilloscope, the absorption trace at this wavelength is saved and the piezoelectric voltage is stepped to a new value. The second method is the laser wavelength modulation by rapid scanning of the piezoelectric voltage using a function generator (Keysight 33220A), at the rate of up to 200 MHz/μs, which allows scanning across the individual absorption lines in the N₂(B,ν' ← A, ν") bands over approximately 10 μs.

Optical emission spectra are taken through the side wall of the channel, near the center of the plasma, using the same optical fiber that is used for the TDLAS measurements. The other end of the fiber is positioned near the entrance slit of a 0.5 m spectrometer (Princeton Instrument SpectraPro 500i) with a PI-MAX gated ICCD camera as a detector, as shown in Fig. 1. A 2400 grooves/mm grating blazed at 250 nm is used for taking the N₂ second positive band and NO γ
band emission spectra, and a 600 grooves/mm grating blazed at 500 nm is used for N$_2$ first positive emission spectra. Plasma emission images are taken using a gated PI-MAX 3 ICCD camera with a UV lens (UV-Nikkor 105 mm f/4.5, Nikon).

2.2. CRDS Measurements

A schematic of a nonequilibrium flow blowdown wind tunnel used for CRDS measurements is shown in Fig. 2. Figure 3 shows a cutout view of the tunnel and the CRDS cavity. In the present work, the wind tunnel is operated using nitrogen (99.999% purity), at the plenum pressure of P$_0$=200-300 Torr. The flow expands through an aerodynamically contoured two-dimensional nozzle, with the throat height of 0.8 mm and the area ratio of A$'/A = 25$, designed for the exit flow of M=5. The top and bottom walls of the supersonic test section after the nozzle exit diverge at a 0.5° angle each, to provide boundary layer relief. The static pressure in the supersonic section is measured by two MKS 925 Micro Pirani pressure transducers, using the wall pressure taps at the end of the nozzle and the beginning of the diffuser, as shown in Fig. 2. At the baseline conditions of the plenum pressure of P$_0$=250 torr, the test section static pressures are P=2.8 Torr and 4.0 Torr, corresponding to the Mach number of M=3.6 and 3.4, respectively, with the steady-state run of about 10 s.

Nonequilibrium flow in the supersonic test section tunnel is produced by a transverse ns pulse discharge sustained between two plane electrodes flush mounted in the top and bottom walls of the rectangular cross section plenum, using the same MegaImpulse pulse generator operated at a pulse repetition rate of 4-100 kHz. The electrodes are rectangular copper plates with the length (along the flow) of 25 mm and the width (across the flow) of 34 mm, covered with alumina ceramic dielectric plates 1/16 inch thick. The plenum test section height is 6.4 mm. The estimated flow Mach number in the discharge section is M ≈ 0.07, with the flow residence time of approximately 1 ms. The number density of N$_2$(A$^3\Sigma_u^+$) molecules generated in the discharge in plenum is measured by TDLAS, using two wedged, AR-coated BK-7 glass optical access windows 12.5 mm in diameter, flush mounted in the side walls, as shown in Fig. 2. Plasma images are taken through a 1.5 inch diameter fused silica window in the back (upstream) wall of the discharge section.

The transverse ring-down cavity is formed between two high-reflectivity windows (R=0.99994, Layertec GmbH, 1 m curvature radius) at the ends of stainless steel arms 12.5 cm long each attached to the side walls of the supersonic test section, with the total cavity length of 35.5 cm. The mirrors are placed in adjustable mounts for precision alignment. A pulsed laser system generating a spectrally narrow tunable output for the CRDS measurements is described in detail in our previous work [7]. Briefly, a Nd:YAG laser (Continuum PowerLite Precision II) pumps a narrowband tunable dye laser (Continuum Vista) using a mixture of Rhodamine 590 and Rhodamine 610 dyes. The dye laser output is frequency-shifted using a Raman cell filled with 15 bar of hydrogen. The first Stokes output beam from the Raman cell, used for the CRDS measurements, is separated from the pump beam and higher order Stokes beams using a dichroic mirror and a Pellin-Broca prism. The wavelength and the linewidth of the first Stokes beam, 745 to 770 nm and 2100 MHz, respectively, with the energy of 1-2 mJ/pulse, are monitored continuously during the experiment by a wavemeter (High Finesse WS6). The ring down signal is measured by a silicon avalanche photodiode (Thorlabs APD410A) and acquired by a DAQ card (PCI-DAS4020/12). Once the flow in the wind tunnel reaches the steady state, several delay generators are used to synchronize the repetitively pulse discharge in the plenum with the CRDS
laser system, such that each ring down trace is taken at the same time delay after to the discharge pulse. For all runs, the time delay between the discharge pulse and the laser shot is set to 177 µs. During each run, 50 ring down traces are acquired and saved at the laser pulse repetition rate of 10 Hz.

3. Data Reduction

As discussed in our previous work [7], $N_2(A^3Σ_u^+,v)$ absolute populations are inferred from the single-pass absorption data,

$$N(v'') = \frac{\alpha(v)}{j_{v''} g_A(v)} ,$$

where $\alpha(v)$ is the spectral absorption coefficient, $j_{v''}$ is the relative population of the $J''$ state (assumed to be in rotational-translational equilibrium at the gas temperature), $k_{v0}$ is the line intensity, and $g_A(v)$ is the normalized absorption line shape. The absorption path length used in the Beer-Lambert law is determined from the plasma emission images, as discussed below. The absorption line positions and absolute line intensities are taken from the computer program Pogopher [9]. A synthetic spectrum code for the first positive band system of molecular nitrogen is used to compare the experimental absorption spectra with the theoretical predictions. The translational-rotational temperature is inferred from the intensity ratio of two absorption transitions,

$$\frac{\alpha_1}{\alpha_2} = \frac{\Phi_1 \cdot S_1}{\Phi_2 \cdot S_2} \exp \left( \frac{\hbar c}{k_b T} (E(N_2''') - E(N_1''')) \right) ,$$

where $\Phi = \frac{1}{3}$ (even $N''$) or $\frac{2}{3}$ (odd $N''$) is the nuclear spin statistical weight factor, $k_b$ is the Boltzmann constant, $h$ is the Planck constant, $c$ is the speed of light, and $S$ is the Hön-London factor for each transition. In the present TDLAS measurements, we used absorption transitions $R_{11}(6)$ and $P_{33}(14)$, separated in energy by approximately 303 cm$^{-1}$ (rotational energy difference of 439 K), which provides sufficient sensitivity at near room temperature. At higher temperatures, the use of a different line pair with a larger energy separation would be necessary. Eq. (2) is modified appropriately to take into account Doppler and pressure broadening.

Since the knowledge of the absorption line shape (controlled by the convolution of Doppler and pressure broadening) is critical for the accuracy of the measurements, in the present work the pressure broadening factor has been determined from the TDLAS data. For this, the width of the pressure-broadened (Lorentzian) component of the de-convolved Voigt profile absorption line is measured over a range of pressures and temperatures, to determine the pressure broadening factor at room temperature, $2\gamma(T_0)$, and its temperature dependence coefficient, $n$,

$$2\gamma(T) = 2\gamma(T_0) \left( \frac{T_0}{T} \right)^n ,$$

During the CRDS measurements, the ring down of the light coupled to the cavity on one of the cavity modes, $I(t)$,
\[
\frac{I(t)}{I_0} = \exp \left( -\frac{t}{\tau} \right),
\]

(4)

is measured by the photodiode. In Eq. (4), \( I_0 \) is the incident light intensity, and \( \tau \) is the ring down time,

\[
\tau = \frac{L_c}{c[(1 - R) + \alpha(v)L_c]},
\]

(5)

controlled by the reflectivity of the mirrors, \( R \), cavity length, \( L_c \), absorption path, \( L_a \), and the spectral absorption coefficient, \( \alpha(v) \).

The CRDS data reduction at the conditions when the pulsed laser linewidth is comparable to the absorption linewidth, such that absorption in the cavity occurs on multiple cavity modes, is discussed in detail in our previous work [7]. Briefly, in this case the time-resolved ring down signal becomes

\[
\frac{I(t)}{I_0} = \exp \left( -\frac{ct(1 - R)}{L_c} \right) \sum_m g_L(v_0 - v_m) \exp \left( -\frac{ctg_A(v_0 - v_m)\alpha L_a}{L_c} \right),
\]

(6)

where the sum is over all cavity modes overlapping with the absorption line. In Eq. (6), \( g_L(v) \) and \( g_A(v) \) are the normalized laser and absorption line shapes, \( v_0 \) is the absorption line center, \( v_m \) are cavity mode frequencies, and \( \alpha \) is the line-integrated absorption coefficient. The laser line width is measured directly by the wavemeter, and the laser line shape is inferred by comparing the convolution of the calculated absorption and laser line profiles to the apparent absorption line shape measured in the experiment. The integrated absorption coefficient is inferred by matching the ring down signal predicted by Eq. (6) and the experimental signal on the absorption line center. Finally, the \( N_2(A^3\Sigma_u^+, v) \) absolute populations are obtained as follows,

\[
N(v') = \frac{\alpha}{f^{v'}_{v_0}k_{v_0}}.
\]

(7)

4. Kinetic Model

The quasi-zero-dimensional kinetic model used in the present work incorporates electron impact excitation and dissociation processes in \( N_2-O_2 \) and \( N_2-H_2 \) plasmas, quenching of excited electronic states of \( N_2 \) by \( N_2, O_2, H_2, NO, \text{N atoms, O atoms, and H atoms, and chemical reactions} \) among the gas mixture components. Vibrational levels of \( N_2(A^3\Sigma_u^+) \) electronic state, \( v=0-7 \), are treated as separate species. The time-resolved electric field and electron density in the plasma during the discharge pulses are inferred from the experimental pulse voltage and current waveforms, using a kinetic model of ns pulse breakdown in plane-to-plane geometry [10]. The electron impact rate coefficients are calculated from the experimental cross sections by a Boltzmann equation solver incorporated into the model. The \( N_2(A^3\Sigma_u^+, v) \) quenching rates and their vibrational quantum number dependence are taken from Ref. [11]. The state-specific rates of one of the key processes controlling \( N_2(A^3\Sigma_u^+, v) \) populations between the discharge pulses, the “2-by-1” vibration-vibration (V-V) energy exchange with the ground electronic state nitrogen,

\[
N_2(A^3\Sigma_u^+, v) + N_2(X^1\Sigma_g^+, w=0) \to N_2(A^3\Sigma_u^+, v-2) + N_2(X^1\Sigma_g^+, w=1)
\]

(8)
are taken from Ref. [12]. For the processes where the state-specific data is not available, such as
the energy pooling process
\[
N_2(A^1\Sigma_u^+, v) + N_2(A^3\Sigma_u^+, w) \rightarrow \begin{cases} N_2(B^3\Pi_u^+) + N_2(X^1\Sigma_u^+) \\ N_2(C^3\Pi_u) + N_2(X^1\Sigma_u^+) \end{cases},
\]
(9)
the rate coefficients are assumed to be independent of the quantum number, with two notable
exception, electron impact excitation of \(N_2(A^3\Sigma_u^+, v)\) from the ground electronic state,
\[
N_2(X^1\Sigma_u^+) + e \rightarrow N_2(A^3\Sigma_u^+, v) + e
\]
(10)
and (ii) collisional quenching of \(N_2(B^3\Pi_u)\) state,
\[
N_2(B^3\Pi_u) + M \rightarrow N_2(A^3\Sigma_u^+, v) + M .
\]
(11)

The process of Eq. (10) favors the excitation of high vibrational levels, \(N_2(A^3\Sigma_u^+, v=5-13)\),
such that the direct electron impact population of vibrational levels \(v=0\) and \(v=1\), detected in the
present experiments, is unlikely [12]. The vibrational distribution of the \(N_2(B^3\Pi_u)\) quenching
products in the process of Eq. (11), which is the dominant pathway of \(N_2(A^3\Sigma_u^+)\) generation at the
present conditions, is not known with certainty. In one previous study, it was assumed that the
process of Eq. (1) populates predominantly the high vibrational levels, \(N_2(A^3\Sigma_u^+, v=6,7)\) [13]. On
the other hand, assuming that the nascent vibrational populations of \(N_2(A^3\Sigma_u^+)\) are proportional to
the Franck-Condon factors for radiative transitions \(N_2(B^3\Pi_u,v') \rightarrow N_2(A^3\Sigma_u^+,v'')\) appears to
provide better agreement with the experiment in a pulsed discharge afterglow [12,14]. In the
present work, the nascent vibrational distribution of \(N_2(A^3\Sigma_u^+)\) in the process of Eq. (11) is inferred
from the comparison of the experimental data and the modeling predictions in nitrogen. The
branching ratio of \(k_{11}(v=3)/k_{11}(v=2)/k_{11}(v=1)/k_{11}(v=0) = 0.47 / 0.47 / 0.03 / 0.03\) provides best
agreement with the present data. However, it may well be possible this branching ratio will change,
depending on the reduced electric field during the discharge pulse and the mixture ratio. Determining
it in a non-empirical way will require additional kinetic modeling studies.

The dominant channels of \(N_2(A^3\Sigma_u^+)\) decay at the conditions of the present experiments are
the energy pooling, Eq. (9), and the rapid collisional quenching by the gas mixture components,
especially by N, H, and O atoms, e.g.
\[
N_2(A^3\Sigma_u^+, v) + N \rightarrow N_2(X^1\Sigma_g^+) + N
\]
(12)
The atomic species in the plasma are generated both by electron impact dissociation of \(N_2\), \(H_2\), and
\(O_2\), and during reactive quenching of \(N_2\) excited electronic states by \(H_2\) and \(O_2\).

5. Results and Discussion
5.1. Slow flow discharge cell

Typical discharge voltage, current, and coupled energy traces in the slow flow cell in
nitrogen at \(P=250\) Torr are plotted in Fig. 4(a). Figure 4(b) illustrates the variation of the coupled
energy with the pulse number in the burst, with the uncertainty bars for each pulse are determined
over 20 discharge bursts. The coupled pulse energy decreases with pressure, from 6.2 mJ/pulse to 4.8 mJ/pulse as the pressure is reduced from 250 Torr to 150 Torr. With the exception of the first 2 pulses, the coupled energy remains constant within ~5%, with a few percent uncertainty, illustrating the discharge reproducibility pulse-to-pulse and burst-to-burst. This result is consistent with single-shot plasma emission images taken at these conditions, shown in Fig. 5. Multiple plasma filaments are detected during the first pulse in the burst, however all subsequent pulses generate diffuse and volume-filling plasma, with well-defined boundaries controlled by the length and width of the electrodes. Similar behavior is observed in the mixtures of nitrogen with hydrogen and dry air (see Figs. 6,7). Although the discharge filamentation in air-nitrogen mixtures appears more pronounced, as expected, the plasma remains volume-filling and diffuse. At these conditions, the N\textsubscript{2}(A\textsuperscript{3}Σ\textsubscript{u}\textsuperscript{+}) decay time is much shorter compared to the flow residence time between the electrodes, estimated to be approximately 260 ms (at P=250 Torr) or 160 ms (at P=150 Torr). Therefore the length of the plasma estimated from the emission images is essentially the same as the TDLAS laser absorption path, L\textsubscript{a} = 6.0 ± 0.5 cm.

High resolution TDLAS N\textsubscript{2}(A\textsuperscript{3}Σ\textsubscript{u}\textsuperscript{+}, v"=0,1) spectra in the nitrogen plasma have been taken at pressures of P=100-412 Torr and discharge bursts from 1 to 100 pulses. Varying the number of pulses in the burst, as well as the burst repetition rate, enables taking the spectra at different temperatures. Figures 8 and 9 compare the experimental and synthetic TDLAS spectra for N\textsubscript{2}(B3Π\textsubscript{g},v′=2 ↔ A\textsuperscript{3}Σ\textsubscript{u}\textsuperscript{+}, v"=0) and N\textsubscript{2}(B3Π\textsubscript{g},v′=3 ↔ A\textsuperscript{3}Σ\textsubscript{u}\textsuperscript{+}, v"=1) band transitions, at pressures of 150 and 412 Torr, respectively, illustrating the effect of the pressure broadening. The translational-rotational temperature for these two cases, T = 330 ± 10 K and T = 360 ± 20 K, respectively, is inferred from the intensity ratio of R\textsubscript{11}(6) and P\textsubscript{33}(14) absorption transitions in the v′ = 2 ↔ v" = 0 band. At the present conditions, the use of these two transitions for the temperature inference is optimal, due to their proximity and the difference in the rotational energy, ΔE\textsubscript{rot} = 303 cm\textsuperscript{-1}, being comparable to the temperature (see Eq. (2)).

The knowledge of the pressure broadening parameter is also critical for the accurate temperature inference from the TDLAS spectra. To determine it, FWHM of the Lorentzian component of the absorption line shape Voigt profile was measured over a wide range of pressures and temperatures. The results of these measurements are summarized in Fig. 10. For the pressure broadening measurements at room temperature, TDLAS scans of a N\textsubscript{2}(B\textsuperscript{3}Π\textsubscript{g},v′=2 ↔ A\textsuperscript{3}Σ\textsubscript{u}\textsuperscript{+}, v"=0) Q\textsubscript{11}(12) transition are taken with the discharge operated in a “single pulse” mode (i.e. for the burst duration of 1 pulse), when the temperature inferred from the rotational line intensity ratio is T=300 ± 10 K (see Fig. 10(a)). For the measurements at different temperatures, the discharge burst duration is varied from 1 to 100 pulses, such that the temperature is varied in the range of T=300 K to 400 K (see Fig. 10(b)). Based on the results of these measurements, the pressure broadening coefficient is 2γ(T) = (4.79 ± 0.10) (300\textsuperscript{T}/T (K))\textsuperscript{0.61±0.15} GHz\textsuperscript{1} atm\textsuperscript{-1}.

For time-resolved TDLAS measurements, the diode laser wavelength is tuned to the peak absorption of rotational transitions Q\textsubscript{11}(12) for N\textsubscript{2}(B,v′=2 → A,v"=0) band and O\textsubscript{2}(9) for N\textsubscript{2}(B,v′=3 → A,v"=1) band, and the absorption signal is measured during the entire discharge pulse burst and in the afterglow. The signal is averaged over 100 discharge bursts. To illustrate the initial rise of N\textsubscript{2}(A\textsuperscript{3}Σ\textsubscript{u}\textsuperscript{+}) number density during the first 1 μs after the discharge pulse, Fig. 11 compares the time-resolved TDLAS data in nitrogen at P=250 Torr with the normalized optical emission spectra intensity. The emission spectra are taken every 10 ns, with the camera gate of 5 ns. It is readily apparent that the rise time of N\textsubscript{2}(A\textsuperscript{3}Σ\textsubscript{u}\textsuperscript{+},v=0,1) populations, several microseconds,
is much longer compared to the decay time of the positive band emission, \( N_2(C^3\Pi_u, \nu=0 \rightarrow \beta^3\Pi_g, \nu''=0) \) at 337 nm (~10 ns), and first positive band emission, \( N_2(B^3\Pi_g, \nu'=2 \rightarrow \alpha^3\Sigma_u^+, \nu''=0) \) at 770 nm (~100 ns). The \( N_2(A^3\Sigma_u^+, \nu=0, 1) \) populations 100 ns after the discharge pulse are at least an order of magnitude lower compared to their peak values reached in the afterglow (compare Fig. 11 and Fig. 12(a)). This demonstrates that vibrational levels \( \nu=0 \) and \( \nu=1 \) of \( N_2(A^3\Sigma_u^+) \) are excited mainly by the V-V energy transfer from the higher vibrational levels, \( \nu>1 \) (the process of Eq. (8)), following their initial population during the collisional quenching of \( N_2(B^3\Pi_g) \), Eq. (11). Therefore the assumption that the nascent vibrational populations of \( N_2(A^3\Sigma_u^+) \) are proportional to the \( N_2(B^3\Pi_u, \nu') \rightarrow N_2(A^3\Sigma_u^+, \nu'') \) Franck-Condon factors [12] is not consistent with the present experimental results. In the present kinetic model, it is assumed that the quenching of \( N_2(B^3\Pi_g) \) results is primarily populating the vibrational levels \( N_2(A^3\Sigma_u^+, \nu=2, 3) \), with equal probabilities (see Section 4). Assuming that higher vibrational levels are populated during the \( N_2(B^3\Pi_g) \) quenching would require increasing the rate coefficients of the V-V exchange process of Eq. (8).

Figure 12 compares the experimental and predicted absolute number densities of \( N_2(A^3\Sigma_u^+, \nu=0, 1) \) during and after the discharge in nitrogen at 250 Torr, for a single pulse, 20-pulse burst, and 100-pulse burst, exhibiting good agreement. It can be seen that the populations of vibrational levels \( \nu=0 \) and \( \nu=1 \) increase after each discharge pulse, peaking approximately 5 \( \mu \)s and 15 \( \mu \)s after the pulse, respectively. This is consistent with the characteristic time for the V-V exchange with the ground electronic state \( N_2 \), the process of Eq. (8), based on the rate coefficients suggested in Ref. [12]. Between the discharge pulses, \( N_2(A^3\Sigma_u^+, \nu=0, 1) \) populations decay on the \( \sim 10 \) \( \mu \)s time scale. Comparison with the modeling predictions shows that this occurs due to the rapid energy pooling process of Eq. (9), at a nearly gas kinetic rate. As discussed in Section 4, the present model assumes that the state-specific rates of this process are independent of the vibrational quantum numbers of \( N_2(A^3\Sigma_u^+) \) molecules.

From the data taken during 20-pulse and 100-pulse bursts, as well as from the modeling predictions, it can be seen that the peak \( N_2(A^3\Sigma_u^+, \nu=0, 1) \) density achieved after each discharge pulse is gradually decreasing during the burst (see Fig. 12). Since the coupled pulse energy during the burst remains nearly the same (see Fig. 12(b)), it is evident that this trend is caused by the accumulation of a “rapid quencher” species, which can only be \( N \) atoms. Along with the energy pooling, the accumulation of \( N \) atoms limits the peak \( N_2(A^3\Sigma_u^+) \) number density in the plasma and afterglow. Therefore comparison of the time-resolved \( N_2(A^3\Sigma_u^+) \) population measurements during long discharge bursts with the modeling predictions also provides quantitative data on the absolute, time-resolved \( N \) atom number density. Additional TDLAS data taken in nitrogen at a lower pressure of \( P=150 \) Torr, and their comparison with the modeling predictions, indicate the same trends.

Figure 13 illustrates the cascade evolution of \( N_2(A^3\Sigma_u^+, \nu) \) populations after a single discharge pulse at the conditions of Fig. 12, controlled by the 2-by-1 V-V exchange of Eq. (8). During this process, the odd and even vibrational level populations cascade down independently, “piling up” at \( \nu=1 \) and \( \nu=0 \) independently, as discussed in Ref. [12]. Since the vibration-translation (V-T) relaxation of molecules in the \( N_2(A^3\Sigma_u^+) \) state by \( N_2 \) is much slower, this leads to the absolute inversion of \( N_2(A^3\Sigma_u^+, \nu=1) \) and \( N_2(A^3\Sigma_u^+, \nu=0) \) populations. The accumulation of \( N \) atoms and the temperature rise during the burst are illustrated in Fig. 14. At the present conditions, \( N \) atoms are generated by the electron impact dissociation of \( N_2 \). In the kinetic model, it is assumed that electron impact excitation of all electronic states of \( N_2 \) above \( C^3\Pi_u \) results in dissociation, which provides good agreement with the decay of \( N_2(A^3\Sigma_u^+, \nu=0, 1) \) populations during the discharge burst and
therefore suggests that the N atom number density is predicted fairly accurately. The predicted N atom generation at these conditions is \( \approx 0.8 \times 10^{14} \text{ cm}^{-3} / \text{pulse} \), such that the N atom number density at the end of a 100-pulse burst is \([N] \approx 0.65 \times 10^{16} \text{ cm}^{-3}\) (see Fig. 14). The flow temperature rise predicted by the model is \( \approx 1 \text{ K} / \text{pulse} \), with the net temperature increase over a 100-pulse burst of \( \Delta T \approx 80 \text{ K}\) (see Fig. 14). Between the discharge bursts, the N atom number density decays due to the 3-body recombination and diffusion to the walls of the discharge section. Similarly, the temperature decreases due to conduction to the test section walls. Since the characteristic time for the N atom population decay and conduction heat transfer is relatively slow, ~10 ms (see Fig. 14), higher N atom number densities and flow temperatures can be achieved by increasing the number of discharge pulses in the burst. Note that both the initial N atom number density and the temperature predicted at the beginning of the burst vary with the burst duration (see Fig. 14), due to the residual atom accumulation and gas heating from the previous burst. Quenching by the residual N atoms explains a modest but noticeable reduction of the peak \( N_2(A^3\Sigma_u^+,v=1) \) population after the first pulse in the burst, as the number of pulses is increases from 1 to 100, from \( 5.3 \times 10^{13} \text{ cm}^{-3} \) to \( 3.9 \times 10^{13} \text{ cm}^{-3}\) (see Fig. 12).

Adding hydrogen or oxygen to the gas mixture results in a dramatic reduction of \( N_2(A^3\Sigma_u^+) \) populations, as summarized in Figs. 15-18. Fig. 15(a,b) plots the \( N_2(A^3\Sigma_u^+,v=0,1) \) populations during a 20-pulse discharge burst in a 5% \( \text{H}_2/\text{N}_2 \) mixture at \( P=150 \text{ Torr} \). It is clear that the peak populations are much lower and the decay time between the pulses is much shorter, compared to pure nitrogen (see Fig. 12). Comparison with the modeling predictions (see Fig. 15) indicates that this difference is caused by the rapid (nearly gas kinetic) \( N_2(A^3\Sigma_u^+) \) quenching by \( \text{H} \) atoms, generated by electron impact and by the reactive quenching of the excited electronic states of \( N_2 \), including \( N_2(A^3\Sigma_u^+) \) (see Fig. 16). Accumulation of \( \text{N} \) and \( \text{H} \) atoms between the pulses also results in a gradual reduction of the peak \( N_2(A^3\Sigma_u^+) \) populations during the burst (see Fig. 15). From Fig. 16, it can be seen that the predicted \( \text{H} \) and \( \text{N} \) atom number densities at the end of the burst are comparable, \( [N] \approx 1.8 \times 10^{15} \text{ cm}^{-3} \) and \( [\text{H}] \approx 1.5 \times 10^{15} \text{ cm}^{-3} \), although the \( \text{H}_2 \) mole fraction in the mixture is only 5%. This is as expected, since the hydrogen dissociation energy, 4.5 eV, is significantly lower than that of \( \text{N}_2 \), 9.8 eV. At these conditions, several percent of the coupled pulse energy goes to \( \text{N}_2 \) and \( \text{H}_2 \) dissociation. Relatively high dissociation efficiency and high number densities of atomic species generated in the plasma suggest that a repetitive ns pulse discharge may be used for plasma-catalytic ammonia generation in high-pressure \( \text{N}_2/\text{H}_2 \) gas mixtures.

Figure 17, which compares the experimental and predicted \( N_2(A^3\Sigma_u^+,v=0,1) \) populations during a 10-pulse discharge burst in a 10% dry air / \( \text{N}_2 \) mixture at \( P=150 \text{ Torr} \), exhibits similar trends. In this case, the peak populations and their decay rate between the pulses are controlled mainly by \( N_2(A^3\Sigma_u^+) \) quenching by \( \text{O}_2 \), although the gradual accumulation of \( \text{O} \) atoms during the burst also contributes to the net quenching rate. \( \text{O} \) atoms are generated both by electron impact and by reactive quenching of \( \text{N}_2 \) excited electronic states, including \( N_2(A^3\Sigma_u^+) \), by \( \text{O}_2 \). From Fig. 18, it can be seen that the \( \text{O} \) atom number density at the end of the burst, \( [\text{O}] \approx 1.8 \times 10^{15} \text{ cm}^{-3} \), exceeds that of \( \text{N} \) atoms, mainly due to the contribution of the reactive quenching.

Figure 19 compares the experimental time-resolved \( N_2(A^3\Sigma_u^+,v=0,1) \) number densities with the relative NO(\( A^2\Sigma, v'=0 \rightarrow X^2\Pi, v''=5 \)) and NO(\( A^2\Sigma, v'=1 \rightarrow X^2\Pi, v''=6 \)) emission intensities (NO \( \gamma \) bands) during a single-pulse ns discharge in a 1000 ppm NO/\( \text{N}_2 \) mixture at \( P=250 \text{ Torr} \). The NO emission spectra are taken using the ICCD camera gate of 50 ns and averaged over 500 discharge pulses. It can be seen that the decay of the \( N_2(A^3\Sigma_u^+,v) \) populations approximately
correlates with the NO(A^3Σ_g,v) emission, which demonstrates the dominant role of a near-resonance state-specific energy transfer process

\[ N_2(A^3Σ_g^+) + NO(X^2Π) \rightarrow N_2(X^1Σ_g^+) + NO(A^3Σ) \]  \hspace{1cm} (13) \]

in the NO emission decay at these conditions. Figure 20 compares the experimental and the predicted \( N_2(A^3Σ_g^+, v=0, 1) \) populations in a 1000 ppm NO/N\(_2\) mixture during a 20-pulse discharge burst at \( P=150 \) Torr. It can be seen that the model significantly underpredicts the \( v=0, 1 \) vibrational level populations, most likely due to neglecting the V-T relaxation of the higher vibrational levels, \( v>1 \), by NO.

5.2. Nonequilibrium flow wind tunnel

Figure 21 plots the time-resolved pressure traces measured in the nitrogen flow in the wind tunnel plenum and in the supersonic test section, at the plenum pressure of \( P_0=300 \) Torr. The static pressure is taken at the end of the nozzle and the beginning of the diffuser, as shown schematically in Figs. 2, 3, which indicates the locations of the wall pressure taps. Although the nozzle area ratio is designed for \( M=5 \), the Mach number in the beginning of the test section, inferred from the pressure ratio using a quasi-one-dimensional isentropic flow, is lower, \( M=3.6 \). This may be due to the interaction of the side wall boundary layers with the oblique shocks in the diffuser [15]. This effect can be reduced by increasing the flow cross section and placing the diffuser further downstream of the test section, as has been done in our previous work [16]. In Ref. [16], the test section Mach number of \( M=4.5-5.0 \) has been achieved at plenum pressures of \( P_0=380-760 \) Torr, using a contoured nozzle with the Mach 5 area ratio. The test section pressure remains very nearly constant for approximately 10 s, after which it begins to increase gradually due to the pressure rise in the vacuum system (see Fig. 21). During a typical wind tunnel run, the data are acquired over a 5 s period.

Figures 22 and 23 show the typical discharge pulse waveforms and a plasma emission image, both taken in nitrogen at the plenum pressure of \( P_0=227 \) Torr and the pulse repetition rate of 100 kHz. The pulse peak voltage and current, as well as the coupled energy, are comparable to the data taken in the slow flow discharge section (see Fig. 4). The plasma emission image, taken through the optical access window in the back wall of the plenum section (see Figs. 2, 3), is also similar to the images taken in the slow flow section, demonstrating that the plasma is diffuse and fills nearly the entire cross section of the flow, with no sign of filamentation.

To quantify the \( N_2(A^3Σ_g^+) \) number density generated in the discharge in the wind tunnel plenum, single-pass TDLAS measurements have been made in the discharge section approximately 12 cm upstream of the nozzle throat, with the laser beam directed perpendicular to the flow, as shown in Figs. 2, 3. The TDLAS data are taken at two different discharge pulse repetition rates, 4 kHz and 100 kHz. Figure 24 shows a typical TDLAS scan across two overlapping rotational transitions in the \( N_2(B_3Π_g,v'=2 \leftarrow A^3Σ_g^+, v''=0) \) band, \( Q_{11}(18) \) and \( Q_{33}(8) \). The absorption line profile in Fig. 24 is a composite data set, obtained by tuning the laser during the discharge burst, at the pulse repetition rate of 4 kHz and tuning rate of approximately 90 MHz/ms. Therefore different parts of the composite scan in Fig. 24 are taken during different discharge pulses, over a period of 150 ms, and all the data points are single-pulse data. The
synthetic line profile in Fig. 24 is calculated for T=300 K and P=227 Torr, using the pressure broadening coefficient measured in the slow flow discharge cell (see Fig. 10).

Figure 25 plots the time-resolved \( \text{N}_2(\text{A}^3\Sigma_u^+,v=0) \) number densities in the wind tunnel plenum, measured with the diode laser parked at the center of the overlapping \( Q_{11}(18) \) and \( Q_{33}(8) \) transitions. As expected, at the low discharge pulse repetition rate of 4 kHz, the \( \text{N}_2(\text{A}^3\Sigma_u^+,v=0) \) population nearly fully decays between the pulses, due to the energy pooling process and quenching by N atoms (compare with the single-pulse data in Fig. 12). The data taken at the high pulse repetition rate of 100 kHz are also similar to the measurement results in the slow flow cell (see Fig. 12), exhibiting the same transient \( \text{N}_2(\text{A}^3\Sigma_u^+,v=0) \) population overshoot and gradual reduction due to the N atom accumulation in the flow. These results indicate that the characteristic time for the \( \text{N}_2(\text{A}^3\Sigma_u^+,v) \) population decay in the plenum varies from ~ 100 \( \mu \)s (at 4 kHz) to ~ 10 \( \mu \)s (at 100 kHz), much shorter compared to the flow transit time from the plenum to the supersonic test section, estimated to be about 1 ms. Therefore for the CRDS measurements in the supersonic flow, the discharge section in the plenum was moved closer to the nozzle throat (3 cm away), and the discharge was operated at 4 kHz pulse repetition rate, to limit the N atom accumulation in the flow. As discussed in Section 2.2, the CRDS laser pulses are delayed relative to the discharge pulses, to allow for the excited flow transit from the plenum to the supersonic section.

To assess the effect of the supersonic flow on the results of CRDS measurements (specifically, the possible laser beam steering in the boundary layers on the side walls of the test section), the ring down traces were taken with the flow in the wind tunnel turned off and on. During these measurements, the discharge in the plenum was turned off, such that these traces represent the “empty cavity” ring down. As illustrated in Fig. 26, the results do not exhibit a detectable difference. In both cases, the empty cavity ring down time is \( \tau = 34 \) \( \mu \)s. Figure 26 also compares the ring down traces taken with the plenum discharge operating at 4 kHz, with the laser tuned to the center of the \( ^0Q_{20}(4) \) absorption transition in the \( \text{N}_2(\text{B}^3\Pi_g,v'=2 \leftarrow \text{A}^3\Sigma_u^+,v''=0) \) band and between the absorption transitions, respectively. It is readily apparent that the ring down time measured on the absorption line center is shorter compared to the empty cavity ring down. As expected, the ring down trace taken on the line center exhibits a non-single exponential decay, since the laser line width is comparable to the absorption line width and the light is coupled to the cavity on multiple modes. This effect, discussed in detail in our previous work [7], is taken into account in the CRDS data reduction, Eq. (6).

Figure 27 summarizes the CRDS data taken in the nonequilibrium flow of nitrogen in the supersonic test section, excited by a ns discharge in plenum at the pulse repetition rate of 4 kHz and pressure of \( P_0=250 \) Torr. In this figure, sets of 50 single-shot ring down times measured during the wind tunnel runs with the discharge off (red symbols) and on (blue symbols) are shown for 4 different absorption transitions. Two transitions in the \( \text{N}_2(\text{B}^3\Pi_g,v'=2 \leftarrow \text{A}^3\Sigma_u^+,v''=0) \) band, \( ^0Q_{23}(4) \) and \( Q_{11}(8) \), and two transitions in the \( \text{N}_2(\text{B}^3\Pi_g,v'=3 \leftarrow \text{A}^3\Sigma_u^+,v''=1) \) band, \( Q_{11}(6) \) and \( Q_{11}(8) \), are used for the inference of \( \text{N}_2(\text{A}^3\Sigma_u^+,v=0) \) and \( \text{N}_2(\text{A}^3\Sigma_u^+,v=1) \) populations, respectively. In addition, these two line pairs are used to estimate the temperature in the flow. During these measurements, single-shot ring down traces, as well as the laser wavelengths and line widths, are acquired by the data acquisition system, as discussed in Section 2.2. This enables monitoring the slight drift of the laser wavelength and line shape during the operation. Figure 27 also shows the synthetic apparent absorption line profiles, calculated for the pressure of \( P=2.7 \) Torr and temperature of \( T=80 \) K, for better illustration. It is apparent that the standard deviation of the shot-to-shot laser drift is approximately half of the absorption line FWHM.
From the data in Fig. 27, it can be seen that the shot-to-shot variation of the “empty cavity” (i.e. discharge off) ring down time is very small, with the standard deviation of ±1%. Note that during these measurements the empty cavity ring down time is shorter compared to that in Fig. 26, \( \tau = 23 \) to 26 \( \mu \text{s} \) vs. \( \tau = 34 \) \( \mu \text{s} \). This reduction is caused by the depletion in the reflectivity of the mirrors, which need to be cleaned periodically, as well as by a slight cavity misalignment. With the discharge turned on, the shot-to-shot variation becomes more significant, up to ±10-15% standard deviation. It is readily apparent that the average ring down time with the discharge on is significantly shorter compared with the empty cavity ring time, with the difference well above the statistical uncertainty of the data. As expected, the average ring down times for the absorption transitions in the same vibrational band are close to each other. Finally, the average ring down time for the \( v'=3 \leftarrow v''=1 \) band transitions is considerably shorter compared to the \( v'=2 \leftarrow v''=0 \) band transitions, respectively, indicating that the \( N_2(A^3\Sigma_u^+,v=1) \) population exceeds that of \( N_2(A^3\Sigma_u^+,v=0) \).

Figure 28 compares the \( N_2(A^3\Sigma_u^+,v=0,1) \) absolute populations inferred from the ring down data, using Eq. (6). As expected, these populations, \((3.5\pm1.0)\times10^{10} \) \( \text{cm}^{-3} \) and \((4\pm2)\times10^{11} \) \( \text{cm}^{-3} \), respectively, are two to three orders of magnitude lower compared to the \( N_2(A^3\Sigma_u^+,v=0) \) population measured in the plenum, both due to the lower number density in the supersonic test section and because of the rapid decay of \( N_2(A^3\Sigma_u^+) \) molecules in the discharge afterglow (see Fig. 25). This illustrates the sensitivity of the present CRDS diagnostic.

The ratio of the two populations, \([N_2(A^3\Sigma_u^+,v=1)] / [N_2(A^3\Sigma_u^+,v=0)]\), is approximately an order of magnitude, significantly higher compared to the data taken in the slow flow cell (see Fig. 12). The most significant uncertainty in the \( N_2(A^3\Sigma_u^+) \) number density is the uncertainty in the flow temperature, inferred from the absorption line intensity ratio, \( T=105\pm60 \) K. It can be reduced considerably by increasing the number of ring down traces (laser shots) taken during the run up to 100, which is feasible within the steady-state run time of the wind tunnel (see Fig. 21).

6. Summary

In the present work, Tunable Diode Laser Absorption Spectroscopy (TDLAS) and Cavity Ring Down Absorption Spectroscopy (CRDS) diagnostics are used for measurements of absolute populations of \( N_2(A^3\Sigma_u^+,v=0,1) \) vibrational levels in ns pulse discharge plasmas in nitrogen-based molecular gas mixtures and in a nonequilibrium supersonic flow of nitrogen. In both cases, the flow is excited by a repetitively pulsed ns discharge in a plane-to-plane geometry, operated at a pulse repetition rate of up to 100 kHz. TDLAS measurements using a continuous wave diode laser are most effective in high pressure plasmas, where the number density of \( N_2(A^3\Sigma_u^+) \) molecules are sufficiently high. On the other hand, CRDS measurements using a repetitively pulsed laser system are most effective in low-pressure nonequilibrium flows, where the sensitivity of single-pass absorption techniques is not sufficient. Therefore the two diagnostic techniques are complementary and can be used for the characterization of nonequilibrium plasmas and reacting flows over a wide range of pressures, from below 1 Torr to atmospheric pressure.

The results of TDLAS measurements in nitrogen and in \( \text{H}_2-N_2 \), \( \text{O}_2-N_2 \), and \( \text{NO}-N_2 \) plasmas are compared with kinetic modeling predictions, identifying the mechanisms of \( N_2(A^3\Sigma_u^+) \) generation and decay during the discharge pulses and in the afterglow. It is shown that the dominant process of \( N_2(A^3\Sigma_u^+) \) decay in nitrogen is the collisional quenching by N atoms. Therefore the time-resolved TDLAS data provide an indirect measurement of the N atom number.
density. In the mixtures of nitrogen with H2 and O2, the decay of N2(A3Σu+) is significantly faster, due to the collisional quenching by H and O atoms, and O2 molecules. In the NO-N2 mixture, it is shown that the main N2(A3Σu+) decay process is the rapid energy transfer to NO, resulting in its electronic excitation and subsequent UV emission (NO γ bands). The detection limit of TDLAS measurements is approximately 10^{-12} \text{cm}^{-3}.

CRDS measurements are made in the test section of a nonequilibrium flow supersonic wind tunnel. The nitrogen flow is excited by a repetitive ns pulse discharge in the wind tunnel plenum. The excited flow expands through a two-dimensional contoured nozzle to the Mach number of M=3.6. It is shown that the cavity ring down time is not affected by the supersonic flow. During each run, 50 single-shot ring down traces are acquired, demonstrating good shot-to-shot reproducibility. The ring down time measured on several N2(B3Πg, ν' ← A3Σu, ν'') absorption transitions is significantly shorter compared to the baseline value, measured when the laser is tuned off resonance. N2(A3Σu+,ν=0,1) populations and the flow temperature are inferred from the single-shot CRDS data. The detection limit of CRDS measurements at the present conditions is approximately 10^{-10} \text{cm}^{-3}. To the best of our knowledge, these are the first CRDS measurements in a supersonic wind in a wind tunnel, rather than in a free expansion jet.

Both diagnostics used in the present work can be used for characterization of low-temperature gas discharge plasmas and high-enthalpy nonequilibrium hypersonic flows, potentially at pulsed high-enthalpy flow facilities. TDLAS measurements in short run-time flows are feasible using rapidly tuned Distributed Feedback (DFB) diode lasers, with the scan time across an absorption line of several μs [17]. The detection limit of the present TDLAS measurements is approximately 10^{-12} \text{cm}^{-3} (single-pass absorption of ~10^{-3}). This is comparable to the single-pass absorption for the estimated equilibrium N2(A3Σu+) number density behind a strong shock in nitrogen (T = 5000 K, P = 5 atm), over an absorption path of 8 cm. The present results suggest that single laser shot CRDS measurements, with the ring down time of ~10 μs, are also compatible with the use in short run-time flows. The uncertainty of single-shot CRDS measurements may be reduced considerably by using a pulse-burst laser system operating at a high pulse repetition rate, such that multiple ring down traces may be taken during a single run.

7. Acknowledgments

The support of U.S. Air Force Office of Scientific Research project “Energy Transfer Processes in Nonequilibrium Hypersonic Flows” (technical monitor Dr. Ivett Leyva), US Department of Energy Plasma Science Center “Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems”, and National Science Foundation grant “Nanosecond Pulse Discharges at a Liquid-Vapor Interface and in Liquids: Discharge Dynamics and Plasma Chemistry”, is gratefully acknowledged. The authors also wish to express their gratitude to Dr. Nikolay Popov (Moscow State University, Russia) for helpful discussions.

References


Figure 1. Schematic of the Tunable Diode Laser Absorption Spectroscopy experimental setup.

Figure 2. Schematic of the nonequilibrium flow wind tunnel and Cavity Ring Down Spectroscopy experimental setup. A cross section view of the wind tunnel is shown in the insert.
Figure 3. Cutout view of the tunnel and the CRDS cavity.
Figure 4. (a) Ns pulse discharge voltage, current, and coupled energy waveforms in nitrogen at P=250 Torr, pulse repetition rate of 100 kHz, and burst repetition rate of 30 Hz; (b) coupled pulse energy vs. pulse number in the train at 250 Torr and 150 Torr (error bars indicated standard deviations of multiple measurements).

Figure 5. Single-shot, broadband plasma emission images taken during a 100-pulse discharge burst at the conditions of Fig. 4, (a) side view and (b) end view. Camera gate 300 ns.
Figure 6. Single-shot, broadband nitrogen plasma emission images during a 20-pulse ns discharge burst, (a) side view and (b) end view. P=150 Torr, 5% H₂ / N₂ mixture, camera gate 300 ns.

Figure 7. Single-shot, broadband nitrogen plasma emission images taken during a 10-pulse ns discharge burst, (a) side view and (b) end view. P=150 Torr, 10% air / N₂ mixture, camera gate 300 ns.
Figure 8. TDLAS scans of (a) 5 rotational lines in the $\text{N}_2(B^3\Pi_g, \nu' = 2 \leftarrow A^3\Sigma_u^+, \nu'' = 0)$ band, and (b) a single rotational line in the $\text{N}_2(B^3\Pi_g, \nu' = 3 \leftarrow A^3\Sigma_u^+, \nu'' = 1)$ band. Nitrogen, $P=150$ Torr, single pulse discharge, 20 $\mu$s after the pulse. Inferred rotational-translational temperature is $T = 330 \pm 10$ K.

Figure 9. TDLAS scans of (a) 5 rotational lines in the $\text{N}_2(B^3\Pi_g, \nu' = 2 \leftarrow A^3\Sigma_u^+, \nu'' = 0)$ band, and (b) a single rotational line in the $\text{N}_2(B^3\Pi_g, \nu' = 3 \leftarrow A^3\Sigma_u^+, \nu'' = 1)$ band. Nitrogen, $P=412$ Torr, 11-pulse discharge burst, 4 $\mu$s after the third pulse. Inferred rotational-translational temperature is $T = 360\pm 20$ K.
Figure 10. (a) Variation of the Lorentzian Full Width at Half Maximum (FWHM) with pressure at 300 K, and (b) Pressure broadening coefficient vs. temperature for the $N_2(B^3\Pi_g, \nu' = 2 \leftarrow A^3\Sigma_u^+, \nu'' = 0)$ Q$_{11}(12)$ spectral line. The pressure broadening coefficient inferred from the data is $2\gamma(T) = 4.79 \left(\frac{300}{T(K)}\right)^{0.61}$ GHz/atm.

Figure 11. Comparison of time-resolved second positive band, $N_2(C^3\Pi_u, \nu'=0 \rightarrow B^3\Pi_g, \nu''=0)$, and first positive band, $N_2(B^3\Pi_g, \nu'=2 \rightarrow A^3\Sigma_u^+, \nu''=0)$, emission with $N_2(A^3\Sigma_u^+, \nu=0,1)$ level populations during a single pulse ns discharge in nitrogen at P=250 Torr.
Figure 12. Time-resolved absolute populations of $N_2(A^3\Sigma^+_u,v=0,1)$ vibrational levels during a ns discharge burst and the afterglow in nitrogen at $P=250$ Torr: (a) single pulse, (b) 20-pulse burst, and (c,d) 100-pulse burst.
Figure 13. Predicted Time-resolved absolute populations of $N_2(A^3\Sigma_u^+, v=0-3)$ vibrational levels and N atoms during a single-pulse ns discharge and the afterglow in nitrogen at $P=250$ Torr.

Figure 14. Time-resolved N atom number density and temperature, predicted by the model at the conditions of Fig. 12 (single-pulse discharge, 20-pulse burst, and 100-pulse burst in nitrogen at $P=250$ Torr). Lines, modeling predictions, symbols, experimental data points.
Figure 15. Time-resolved absolute populations of \(N_2(A^3\Sigma_u^+, v=0,1)\) vibrational levels during a 20-pulse discharge burst and the afterglow in 5% \(H_2/N_2\) at \(P=150\) Torr.

Figure 16. Time-resolved N and H atom number densities and temperature, predicted by the model at the conditions of Fig. 15 (20-pulse discharge burst in 5% \(H_2/N_2\) at \(P=150\) Torr).
Figure 17. Time-resolved absolute populations of $N_2(A^3\Sigma_u^+, v=0,1)$ vibrational levels during a 10-pulse discharge burst and the afterglow in a 10% dry air / $N_2$ mixture at $P=150$ Torr. Experimental data: (a), modeling predictions: (b).

Figure 18. Time-resolved species number densities and temperature, predicted by the model at the conditions of Fig. 17 (10-pulse discharge burst in a 10% dry air / $N_2$ mixture at $P=150$ Torr).
Figure 19. Comparison of $N_2(A^3\Sigma_u^+,v=0,1)$ absolute number densities and NO($A^2\Sigma_u,v=0,1$) relative emission intensities during after a single-pulse ns discharge in 1000 ppm NO/N$_2$ mixture at P=250 Torr.

Figure 20. Time-resolved absolute populations of $N_2(A^3\Sigma_u^+,v=0,1)$ vibrational levels during a 20-pulse discharge burst and the afterglow in a 1000 ppm NO / N$_2$ mixture at P=150 Torr.
Figure 21. Plenum pressure and test section pressure traces during the wind tunnel operation.

Figure 22. Typical ns pulse discharge voltage, current, and coupled energy waveforms. Nitrogen, $P_0=227$ Torr, pulse repetition rate 100 kHz.
Figure 23. ICCD camera image of the ns pulse discharge in the plenum taken through the optical access window in the back wall of the plenum (flow into the page). Nitrogen, $P_0=227$ Torr, pulse repetition rate 100 kHz, camera gate 1 $\mu$s.

Figure 24. Composite line shape of overlapping $Q_{11}(18)$ and $Q_{33}(8)$ rotational transitions in the $N_2(B^3Π_g, \nu'=2 \leftarrow A^3Σ_u, \nu''=0)$ band during a ns discharge burst in nitrogen in the wind tunnel plenum at $P_0=227$ Torr, and pulse repetition rate of 4 kHz.
Figure 25. Time-resolved absolute population of N₂(A³Σₙ₊₁,v=0) during the ns discharge burst in nitrogen in the wind tunnel plenum at P₀=227 Torr, at pulse repetition rates of (a) 4 kHz and (b) 100 kHz.

Figure 26. Typical cavity ring down traces: (a) empty cavity without flow and with M=3.6 flow in the cavity; (b) M=3.7 flow with ns discharge in the plenum at P₀=250 Torr, on and off resonance with the absorption transition τQ₂₅(4) in the N₂(B³Π₉, v'=2 ← A³Σ₉, v''= 0) band.
Figure 27. Comparison of the ring down time in the M=3.6 flow with the plenum discharge on and off. $^pQ_{23}(4)$ and $Q_{11}(8)$ absorption transitions in the $N_2(B^3\Sigma_u^+, v'=2 \rightarrow A^3\Sigma_u, v''=0)$ band, and $Q_{11}(6)$ and $Q_{11}(8)$ transitions in the $N_2(B^3\Pi_g, v'=2 \rightarrow A^3\Sigma_u, v''=0)$ band. Nitrogen, $P_0=250$ Torr, discharge pulse repetition rate 4 kHz.

Figure 28. $N_2(A^3\Sigma_u^+, v=0)$ and $N_2(A^3\Sigma_u^+, v=1)$ populations inferred from the ring down data at the conditions of Fig. 25 (nitrogen, $P_0=250$ Torr, discharge pulse repetition rate 4 kHz).