Kinetics of Metastable $\text{N}_2(\text{A}^3\Sigma_u^+, v)$ Molecules in High-Pressure Nonequilibrium Plasmas


Department of Mechanical and Aerospace Engineering
The Ohio State University, Columbus, OH 43210

*State Key Laboratory of Electrical Insulation and Power Equipment,
Xi’an Jiaotong University, Xi’an, 710049, People’s Republic of China

Abstract

Absolute, time-resolved populations of $\text{N}_2(\text{A}^3\Sigma_u^+, v=0-5)$ vibrational levels in high-pressure ns pulse discharge plasmas are measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS). The diffuse plasma is generated by a repetitively pulsed, double dielectric barrier, ns discharge across a 10 mm gap in a plane-to-plane geometry, at pressures of up to 400 Torr. The results of TDLAS measurements in nitrogen and in $\text{H}_2$-$\text{N}_2$, $\text{O}_2$-$\text{N}_2$, and $\text{NO}$-$\text{N}_2$ plasmas are compared with kinetic modeling predictions, identifying the mechanisms of $\text{N}_2(\text{A}^3\Sigma_u^+)$ generation and decay during the discharge pulses and in the afterglow. Comparison with the modeling predictions indicates that electron impact dissociation of $\text{N}_2$ from the ground electronic state significantly underpredicts the yield of N atoms. The present data suggest that N$_2$ dissociation in the plasma also occurs during the energy pooling process in collisions of two $\text{N}_2(\text{A}^3\Sigma_u^+)$ molecules. The results also show that high-pressure, high repetition rate, volume-scalable ns pulse discharges can be used for efficient generation of atomic species for plasma chemical and plasma catalysis syntheses. In an NO-$\text{N}_2$ mixture, it is shown that the $\text{N}_2(\text{A}^3\Sigma_u^+)$ decay is controlled by the rapid energy transfer to NO, resulting in its electronic excitation and UV emission (NO γ bands). The diagnostics used in the present work can be used for the accurate characterization of both high-pressure, low-temperature gas discharge plasmas and high-temperature nonequilibrium flows generated in pulsed facilities such as shock tubes and expansion tunnels.
1. Introduction

Energy transfer processes and chemical reactions involving a metastable excited electronic state of molecular nitrogen, N$_2$(A$^3\Sigma_u^+$), are known to play an essential role in low-temperature air plasmas and atmospheric pressure plasma jets [1-3], as well as in electric discharges used for plasma-assisted fuel oxidation and ignition [4,5] and other plasma chemical syntheses [6,7]. In these plasmas, N$_2$(A$^3\Sigma_u^+$) is generated by the direct electron impact, quenching of higher energy electronic states of N$_2$, and energy transfer from other excited metastable species, such as Ar(3p$^4$4s). In high-temperature nonequilibrium reacting flows, such as occurs behind strong shock waves in atmospheric reentry flows, N$_2$(A$^3\Sigma_u^+$) may also be generated in collisions with heavy species, strongly affecting kinetics of NO UV emission due to the rapid energy transfer to nitric oxide [8-10]. Reactive quenching of N$_2$(A$^3\Sigma_u^+$) by molecular oxygen and hydrocarbon species is a major source of O atoms, H atoms, and other reactive radicals in air and fuel-air plasmas [5]. A reaction of N$_2$(A$^3\Sigma_u^+$) with O atoms is also one of the key pathways of NO formation, which leads to generation of other reactive nitrogen species [2]. Finally, quenching of N$_2$(A$^3\Sigma_u^+$) by CO$_2$ is among the dominant sources of CO generation in electric discharges in N$_2$-CO$_2$ mixtures [6].

Low-uncertainty, absolute, time-resolved measurements of metastable electronically excited species such as N$_2$(A$^3\Sigma_u^+$) are critically important for the analysis of high-pressure nonequilibrium reacting plasma kinetics, and for the development of predictive, high-fidelity kinetic models. Such measurements require sustaining a uniform transient plasma with well-defined boundaries and minimal spatial gradients. This greatly simplifies the interpretation of the measurement results and enables straightforward quasi-zero-dimensional kinetic modeling. The approach used in the present work, a repetitive ns pulse discharge sustained between two parallel plate electrodes covered by dielectric plates, has been shown to generate nearly uniform electron impact excitation [11] across the discharge gap. N$_2$(A$^3\Sigma_u^+$,v) vibrational populations are measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) [12], which yields the absolute number density data and does not require additional calibration, unlike Laser Induced Fluorescence (LIF) techniques. Our recent work [13] demonstrated that N$_2$(A$^3\Sigma_u^+$,v) populations decay rapidly after a discharge pulse burst and do not accumulate in the flow through the discharge cell. This makes possible the accurate determination of the absorption path length and inference of the absolute number densities from the absorption data.

The objective of the present work is to use TDLAS and kinetic modeling for N$_2$(A$^3\Sigma_u^+$) measurements and analysis of the energy transfer kinetics in a repetitive ns pulse discharge sustained in high-pressure molecular gas mixtures, at P=100-400 Torr. Comparison of the experimental data with the kinetic modeling predictions is of crucial importance. Specifically, reproducing the peak absolute N$_2$(A$^3\Sigma_u^+$,v) populations during the discharge pulses by kinetic modeling calculations would quantify the accuracy of the predicted input energy partition in the plasma. In addition, reproducing the N$_2$(A$^3\Sigma_u^+$) decay in the afterglow between the pulses would assess the accuracy of predicting the number densities of atomic species generated in the plasma (such as N and H), since they strongly affect the quenching rate [14]. Both of these factors are essential for assessing the overall predictive capability of the kinetic model.

2. Experimental and Data Reduction

Figure 1 displays the schematic of the electric discharge cell and TDLAS diagnostics. The plasma discharge cell is a 22 mm x 10 mm rectangular cross section quartz channel 30 cm long,
fused to 1 inch diameter quartz-to-metal adapters with conflat flanges at both ends. The total length of the cell is 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, through the ¼ inch diameter inlet and exit ports, connected to the gas delivery and exhaust lines by the UltraTorr fittings. Different amounts of hydrogen (up to 10%, 99.999% purity) or medical air (up to 10%) are added to the nitrogen flow. The mixture components are delivered from individual gas cylinders. Some of the measurements have been done in a 1000 ppm NO / N₂ mixture stored in a separate cylinder, at the same flow rate of 1 SLM. The flow rates of the mixture components are regulated and monitored by the mass flow controllers (Sierra Smart-Trak 2). The total pressure in the discharge cell is varied from 100 to 412 Torr, by throttling the flow in the vacuum exhaust line. The combined leak rate of the cell and the gas delivery system is approximately 1.6 × 10^{15} molecules/s, over 5 orders of magnitude lower compared to the flow rate, 5.3 × 10^{20} molecules/s, such that the upper bound oxygen and water vapor impurity level is ~10^{-6} and ~10^{-7} mole fraction, respectively.

The plasma in the cell is generated by a double dielectric barrier discharge between two parallel rectangular plate copper electrodes 60 mm long and 12 mm wide, mounted to the top and bottom walls in the middle of the quartz channel, as shown in Fig. 1. The electrodes are attached to the walls by a silicon rubber adhesive, to prevent corona discharge formation in ambient air near the electrode surfaces, and to ensure the accurate measurement of the energy coupled to the plasma. 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 the pulse voltage and current waveforms using custom-made, high bandwidth capacitive voltage probes and shunt current probes [15].

In the present work, three different continuous wave, tunable diode lasers have been used for the measurements of the N₂(A^3Σ_u⁺,v) vibrational level populations. The first is a 20 mW 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. The second is an external cavity diode laser (Sacher Lasertechnik), tunable from 808 to 880 nm, with the output power of 20 mW and a nominal linewidth of 0.1 MHz. The third is a 20 mW diode laser (New Focus Velocity 6324) with a scan range of 1277 to 1342 nm and a nominal linewidth of less than 0.3 MHz. These lasers provide access to the N₂(A^3Σ_u⁺) vibrational levels v=0;1; v=2; and v=4,5, respectively, using relatively strong absorption transitions in each vibrational band. In all cases, a focused laser beam is directed along the cell, as shown schematically in Fig. 1. The laser wavelength is scanned by varying the voltage on the piezoelectric driver of the laser and is monitored continuously during the experiment by a wavemeter (High Finesse WS6-200-IR), using the laser beam scattering off an anti-reflected coated glass window (see Fig. 1). 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 through a band pass filter to a photodiode detector (Thorlabs DET36A and Thorlabs DET10C), 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. This is critical for measuring weak absorption signals (path integrated absorption below ~10^-3). Some of the TDLAS measurements have been performed using a double-pass absorption set-up, also shown in Fig. 1. In this case, the vertically polarized output of the diode laser is reflected
by a polarizing beamsplitter (PBS) into the discharge cell. On the opposite side of the cell, a Fresnel Rhomb Quarter-Wave prism, acting as a broadband quarter wave plate, and a high reflector mirror, rotate the beam polarization plane to horizontal, before reflecting it back into the cell. After the second pass through the cell, the laser beam is transmitted through the PBS, focused into the optical fiber, and sent to the photodiode detector.

The measurements are controlled by a computer executing 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 at each wavelength. During the experiment, the wavelength of the diode laser 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 preset 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, until the wavelength scan is completed.

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 N₂ first positive emission spectra. Finally, 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).

As discussed in our previous work [12], N₂(A²Σ_u^+, v) absolute populations are inferred from the single-pass or double-pass absorption data as follows,

$$N(v'') = \frac{\alpha(v)}{f_{J''} k_{v_0} g_A(v)},$$

(1)

where \(\alpha(v)\) is the spectral absorption coefficient, \(f_{J''}\) is the relative population of the \(J''\) state (assumed to be in rotational-translational equilibrium at the gas temperature), \(k_{v_0}\) 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 in Section 3. The absorption line positions and absolute line intensities are taken from the computer program Pogopher [16]. 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,

$$\frac{\alpha_1}{\alpha_2} = \frac{\Phi_1 \cdot S_1}{\Phi_2 \cdot S_2} \exp \left\{ \frac{h c}{k_B T} \left( E(N''_2) - E(N''_1) \right) \right\},$$

(2)

where \(\Phi = \frac{1}{3}\) (even \(N''\)) or \(\frac{2}{3}\) (even \(N''\)) 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 Hönig-London factor for each transition. In the present TDLAS measurements, we used absorption transitions R_{11}(6) and P_{33}(14) in the N₂(B^3Π_g, v' = 2 \leftarrow A^3Σ_u^+, v'' = 0) absorption band, separated 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 taken into account Doppler and pressure broadening of the absorption transitions, before comparing the synthetic and experimental spectra.

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, $n$.

$$2\gamma(T) = 2\gamma(T_0) \left(\frac{T_0}{T}\right)^n.$$  \hspace{1cm} (3)

During the pressure broadening measurements, the pressure and the discharge burst duration were varied, to ensure independent variation of pressure and temperature.

3. Kinetic Model

The quasi-zero-dimensional kinetic model used in the present work incorporates the electron impact excitation and dissociation processes in N$_2$-O$_2$, N$_2$-H$_2$, and N$_2$-NO plasmas, quenching of excited electronic states of N$_2$ by N$_2$, O$_2$, H$_2$, NO, N atoms, O atoms, H atoms, and ozone, as well as the chemical reactions among the gas mixture components. Vibrational levels of N$_2$(A$^3\Sigma_u^+$) electronic state, $v=0-7$ (up to the energy of the next triplet electronic state, B$^3\Pi_g$), are treated as separate species. The electron impact rate coefficients are calculated by the Boltzmann equation solver Bolsig+ [17] vs. electron temperature and incorporated into the input plasma chemical reaction set. The cross sections of the electron impact processes are taken from [18,19]. The rates of reactions of excited electronic states of N$_2$ and O atoms, as well as chemical reactions among species in the ground electronic state are taken from [20,21,14]. “Grouping” of the excited electronic states of N$_2$ (10 states listed in the Bolsig+ cross section database [18]) into a smaller number of relatively stable states for which the collisional quenching data are available, such as $a^3\Sigma_u^+$, B$^3\Pi_g$, and C$^3\Pi_u$ [20], is a widely accepted approach in the gas discharge plasma literature. However, comparison of the kinetic modeling predictions with the experimental data, discussed in Section 4, demonstrates a significant overprediction of the peak N$_2$(A$^3\Sigma_u^+$) number density calculated using the experimental discharge input power waveform. Therefore in the present model, N$_2$(A$^3\Sigma_u^+$) after the discharge pulse was assumed to be generated during the collisional quenching of B$^3\Pi_g$ state only, instead of a “group” of the triplet states with similar energies including B$^3\Pi_g$, W$^3\Delta_u$, and B$^3\Sigma_u^-$.

Our recent work [13] indicated that the rate of N$_2$(A$^3\Sigma_u^+$) decay between the discharge pulses in nitrogen is significantly underpredicted, almost certainly due to the underprediction of the number density of N atoms generated by the electron impact dissociation from the ground electronic state of N$_2$. At the present conditions, the role of the “stepwise” electron impact dissociation from the excited electronic states N$_2$, using the cross sections predicted in Ref. [22], was found to be insignificant. This is at variance with the conclusion of the recent study of nitrogen dissociation in a ns pulse discharge in a capillary tube, at a much higher pulse specific energy [23], where it was determined that the stepwise dissociation via the excited electronic states N$_2$(A$^3\Sigma_u^+$,
$B^3\Pi_g$, $C^3\Pi_u$) increases the yield of N atoms by over an order of magnitude. In the present work, we hypothesize that N$_2$ dissociation may also occur in an additional channel of the rapid energy pooling process, i.e.

$$N_2(A^3\Sigma_u^+,v) + N_2(A^3\Sigma_u^+,w) \rightarrow \begin{cases} N_2(B^3\Pi_g) + N_2(X^1\Sigma_g^+) \\ N_2(C^3\Pi_u) + N_2(X^1\Sigma_g^+) \\ N(0) + \Sigma + N_2(X^1\Sigma_g^+) \end{cases} \quad \text{(4)}$$

As mentioned in Ref. [24], N$_2$ dissociation in this process may be possible via the excitation of predissociated electronic states above the dissociation energy. Since the rate coefficient of this dissociation channel is not known, it was treated as an adjustable parameter. As will be shown in Section 4, this assumption results in good agreement with the measured time-resolved N$_2(A^3\Sigma_u^+,v)$ populations.

At the present conditions, the energy fractions going into vibrational excitation of the ground electronic state nitrogen, N$_2(X^1\Sigma_g^+)$, and electronic excitation of the low-energy metastable states of oxygen, O$_2(a^1\Delta)$ and O$_2(b^1\Sigma)$, are very low, and these processes are not taken into account in the present work. As shown in Ref. [13], incorporating vibrational excitation of the ground electronic state of N$_2$, state-specific vibrational kinetics (vibration-vibration and vibration-translation energy transfer processes), and coupling between N$_2(X^1\Sigma_g^+,v)$ and N$_2(A^3\Sigma_u^+,v)$ populations had almost no effect on the N$_2(A^3\Sigma_u^+)$ kinetics. Finally, since H$_2$ does not have the bound electronic states below the dissociation level, electronic excitation of H$_2$ by electron impact is assumed to result in its dissociation.

The vibrational quantum number dependence of the N$_2(A^3\Sigma_u^+,v)$ quenching rates, wherever available, is taken from Ref. [14]. The state-specific rates are one of the critical processes controlling the 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,

$$N_2(A^3\Sigma_u^+,v) + N_2(X^1\Sigma_g^+,w=0) \rightarrow N_2(A^3\Sigma_u^+, v-2) + N_2(X^1\Sigma_g^+, w=I) \quad \text{(5)}$$

are taken from Ref. [25]. For the processes where the vibrational state-specific data is not available, such as the rapid energy pooling process of Eq. (4), the rate coefficients are assumed to be independent of the quantum number. The two notable exceptions are the electron impact excitation of N$_2(A^3\Sigma_u^+,v)$ from the ground electronic state,

$$N_2(X^1\Sigma_g^+) + e \rightarrow N_2(A^3\Sigma_u^+, v) + e \quad \text{(6)}$$

and the collisional quenching of N$_2(B^3\Pi_g)$ state,

$$N_2(B^3\Pi_g) + M \rightarrow N_2(A^3\Sigma_u^+, v) + M . \quad \text{(7)}$$

The process of Eq. (6) is of the secondary importance and predominantly results in the excitation of high vibrational levels, N$_2(A^3\Sigma_u^+, v=5-13)$, which cascade to the lower vibrational levels, v=0-2, by the rapid V-V exchange process of Eq. (5). The vibrational distribution of the N$_2(B^3\Pi_g)$ quenching products in the process of Eq. (7), 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. (7) populated predominantly the high vibrational levels, \( N_2(A^3\Sigma_u^+, v=6,7) \) [26]. 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 the radiative transitions \( N_2(B^3\Pi_g,v') \rightarrow N_2(A^3\Sigma_u^+,v'') \) appears to provide better agreement with the experiment in a pulsed discharge afterglow [25,27]. In the present work, the nascent vibrational distribution of \( N_2(A^3\Sigma_u^+) \) in the process of Eq. (7) is inferred from the comparison of the experimental data and the modeling predictions in pure nitrogen, as discussed in detail in Section 4. We note, however, that this distribution may well vary depending on the reduced electric field during the discharge pulse and on the mixture composition. Determining it in a non-empirical way would require analysis of the quenching reaction dynamics and additional kinetic modeling calculations.

The dominant channels of \( N_2(A^3\Sigma_u^+) \) decay at the conditions of the present experiments are the energy pooling, Eq. (4), and the rapid collisional quenching by the gas mixture components, especially by N, H, and O atoms, ozone, and NO, i.e.

\[
N_2(A^3\Sigma_u^+, v) + M \rightarrow N_2(X^1\Sigma_g^+) + M
\]  

(8)

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 \( O_2 \).

The kinetic model is exercised using ChemKin-Pro software, which solves the electron energy equation predicting the electron temperature (a moment of the Boltzmann equation), the heavy species energy equation, and equations for the species concentrations. The time-resolved repetitive ns pulse discharge power waveform, used as an input in the model, is obtained from the measured discharge voltage and current waveforms, as discussed in Section 4. The estimated effect of associative ionization processes on the electron density between the discharge pulses, using the rate coefficients suggested in Ref. [28], is insignificant compared to the electron-ion recombination. The plasma volume used in the model, 7.2 cm\(^3\), is inferred from the plasma emission images. Effects of diffusion, conduction heat transfer, and convection, are incorporated as quasi-zero-dimensional corrections. The present model was validated in our previous work, showing good agreement with the measurements of \( N_2 \) vibrational temperature in air, as well as H, O, and OH number density measurements in mixtures of \( H_2 \), CH\(_4\), and C\(_2\)H\(_4\) with air and O\(_2\)-Ar [29,11]. The modeling predictions at the present conditions were also compared with a higher-fidelity one-dimensional model predicting the electric field, electron density, and electron temperature distributions in the gap during a ns discharge pulse, also exhibiting good agreement. The 1-D model, which incorporates the equations for the electron and ion number densities, electron energy equation, and the Poisson equation for the electric field, has been validated vs. the measurements of time-resolved electric field distributions in a ns pulse discharge plasma [30].

4. Results and Discussion

Typical discharge voltage, current, power, and coupled energy traces in nitrogen at P=250 Torr are plotted in Fig. 2(a,b). Multiple pulse reflections from the load and the pulse generator are detected, as expected. Figure 2(b) also plots the coupled power waveform used in the kinetic modeling calculations, inferred from the experimental waveform by canceling the power stored / reflected by the capacitive load. Figure 2(c) illustrates the variation of the coupled energy measured at 250 and 150 Torr with the pulse number in the burst, with the uncertainty bars for
each pulse determined over 20 discharge bursts. 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. At quasi-steady-state, the average coupled pulse energy decreases as the pressure is reduced from 250 Torr to 150 Torr, from 6.2 mJ/pulse to 4.8 mJ/pulse.

The discharge reproducibility apparent from Fig. 2(c) is consistent with the single-shot plasma emission images taken at these conditions, shown in Fig. 3. It can be seen that, although multiple plasma filaments are detected during the first pulse in the burst, all subsequent pulses generate a 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. 4,5). Although the discharge filamentation in air-nitrogen mixtures appears more pronounced, as expected, the plasma remains volume-filling and diffuse. At these conditions, the N₂(A³Σ⁺) decay time is much shorter compared to the flow residence time between the electrodes, estimated to be approximately 130 ms (at P=250 Torr) and 80 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, L₀ = 6.0 ± 0.5 cm.

High resolution TDLAS N₂(A³Σ⁺, vʺ=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 6 and 7, plotted on the same scale, compare the experimental and synthetic TDLAS spectra for N₂(B³Π₅, vʹ=2 ← A³Σ⁺, vʺ=0) and N₂(B³Π₅, vʹ=3 ← A³Σ⁺, vʺ=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 R₁₁(6) and P₃₃(14) absorption transitions in the vʹ=2 ← vʺ=0 band. As discussed in Section 2, 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, ΔE₉₂₀ = 303 cm⁻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, the 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. 8. For the pressure broadening measurements at room temperature, TDLAS scans of a N₂(B³Π₅, vʹ=2 ← A³Σ⁺, vʺ=0) Q₁₁(12) transition are taken with the discharge operating 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. 8(a)). For the measurements at different temperatures, the discharge burst duration is varied from 1 to 100 pulses, which corresponds to the temperature variation in the range of T=300 K to 400 K (see Fig. 8(b)). Based on the results of these measurements, the pressure broadening coefficient is 2γ(T) = (4.79 ± 0.10) \left(\frac{300}{T (K)}\right)^{0.61±0.15} GHz atm⁻¹.

For the time-resolved TDLAS measurements, the diode laser wavelength is tuned to the centerline (peak absorption) of specific rotational transitions in N₂(B,vʹ=2 ← A,vʺ=0), N₂(B,vʹ=3 ← A,vʺ=1), N₂(B,vʹ=3 ← A,vʺ=2), N₂(B,vʹ=2 ← A,vʺ=4), and N₂(B,vʹ=3 ← A,vʺ=5) bands, listed in Table 1.
Table 1. Absorption transitions used in TDLAS measurements and their wavelengths

<table>
<thead>
<tr>
<th>Vibrational band</th>
<th>v′=2 ← v″=0</th>
<th>v′=3 ← v″=1</th>
<th>v′=3 ← v″=2</th>
<th>v′=2 ← v″=4</th>
<th>v′=3 ← v″=5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational transition</td>
<td>Q_{11}(12)</td>
<td>O_{12}(9)</td>
<td>Q_{11}(10)</td>
<td>R_{33}(12)</td>
<td>Q_{11}(10)</td>
</tr>
<tr>
<td>Wavelength, nm</td>
<td>773.215</td>
<td>764.291</td>
<td>852.120</td>
<td>1339.672</td>
<td>1300.115</td>
</tr>
<tr>
<td>k_{0}, cm^{-2}Hz</td>
<td>7.40·10^{-6}</td>
<td>3.41·10^{-6}</td>
<td>3.83·10^{-6}</td>
<td>2.63·10^{-6}</td>
<td>1.32·10^{-6}</td>
</tr>
</tbody>
</table>

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 the N_{2}(A^{3}Σ_{u}^{+}) number density during the first 1 μs after the discharge pulse, Fig. 9(a) compares the time-resolved TDLAS data in nitrogen at P=250 Torr with the normalized plasma 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_{2}(A^{3}Σ_{u}^{+}, v=0-2) populations, 2-20 μs, is much longer compared to the decay time of the second positive band emission, N_{2}(C^{3}Π_{u}, v′=0→ B^{3}Π_{g}, v″=0) at 337 nm (~10 ns), and first positive band emission, N_{2}(B^{3}Π_{g}, v′=2→A^{3}Σ_{u}^{+}, v″=0) at 770 nm (~100 ns). On the other hand, the rise time of N_{2}(A^{3}Σ_{u}^{+}, v=4,5) populations is much shorter, 100-300 ns, and comparable to the first positive system emission decay time. The time-resolved N_{2}(A^{3}Σ_{u}^{+}) vibrational populations, plotted on a semi-log time scale in Fig. 9(b), indicate that the low vibrational levels, v=0 and v=1, are populated mainly by the V-V energy transfer “cascade” from the higher vibrational levels, v>2 (the process of Eq. (5)), following their initial population during the collisional quenching of N_{2}(B^{3}Π_{g}), Eq. (7).

To determine the nascent vibrational distribution of N_{2}(A^{3}Σ_{u}^{+}) created by the processes of Eq. (7), the model was exercised for different branching ratio for N_{2}(B^{3}Π_{g}→ A^{3}Σ_{u}^{+}, v) quenching. Assuming that only N_{2}(A^{3}Σ_{u}^{+}, v=6,7) are populated, with equal probabilities [26], resulted in a significantly longer rise time of N_{2}(A^{3}Σ_{u}^{+}, v=1,2) populations compared to the experimental data, as well as overprediction of v=1 and underprediction of v=2 populations. Reducing the predicted rise time would require significantly increasing the rate coefficients of the V-V exchange process of Eq. (5). On the other hand, assuming that the nascent N_{2}(A^{3}Σ_{u}^{+}, v″) vibrational populations are proportional to N_{2}(B^{3}Π_{g}, v′=0) P_{(0→v″)} N_{2}(A^{3}Σ_{u}^{+}, v″) Franck-Condon factors, k_{7}(v″) ~ P(0 → v″), which favors populating the vibrational levels v″=0,1 (see Fig. 10(a)), resulted in a strong overprediction of the peak v″=0 population, higher compared to that v″=1, and at variance with the present results (e.g. see Fig. 9(b)). Using the nascent vibrational populations governed by the sums of the Franck-Condon factors, k_{7}(v″) ~ Σ_{v=0-7} P′(v′ → v″) (see Fig. 10(a)), considerably improves the agreement with the experiment. Finally, employing an empirical fit for the quenching branching ratio (obtained mainly by adjusting the v″=0 and v″=1 fractions, see Fig. 10(a)), provides further moderate improvement and yields the best overall agreement with the present measurements in the pulse-burst discharge in nitrogen, discussed below. This empirical fit was used for the modeling predictions in the remainder of this paper. It may well be possible to obtain a better agreement with the data, in particular for short time delays after the discharge pulse, by adjusting the branching ratio further. However, doing this would be of limited value since the branching ratio does change as the mixture composition is varied, as will be evident from the data.
taken in N₂-H₂, N₂-O₃, and N₂-NO mixtures. Development of a non-empirical, state-specific model of energy transfer during N₂(B⁢3Πg, ν′ → A⁢3Σu⁺, ν″) quenching would be highly desirable.

Figure 10(b) plots the predicted time-resolved N₂(A⁢3Σu⁺, ν=0-5) populations after a single-pulse discharge in nitrogen at P=250 Torr, at the conditions of Fig. 9. It illustrates the cascade evolution of N₂(A⁢3Σu⁺,ν) populations predicted after a single discharge pulse at the conditions of Fig. 9, controlled mainly by the 2-by-1 V-V exchange of Eq. (5). During this process, the odd and even vibrational level populations cascade down independently, “piling up” at ν=1 and ν=0, as discussed in Ref. [25]. Since the ratio of the V-V rate coefficients is greater than 1, k_d(ν=3→1,k=0→1)/k_d(ν=2→0,w=0→1) = 5 [25], and the vibration-translation (V-T) relaxation of molecules in the N₂(A⁢3Σu⁺) state by N₂ is much slower, this leads to the absolute inversion of N₂(A⁢3Σu⁺,ν=1) and N₂(A⁢3Σu⁺,ν=0) populations.

Figure 11 compares the experimental and predicted absolute number densities of N₂(A⁢3Σu⁺, ν) during and after the discharge in nitrogen at 250 Torr, for a 20-pulse burst (a-e) and 100-pulse bursts (f-h). N₂(A⁢3Σu⁺,ν=4,5) number densities, which decay rapidly after each discharge pulse, have only been measured during the 20-pulse burst. Note that panels (d,e), plotting ν=4,5 populations, show only 5 pulses during the burst, on the vertical scale different from the rest of the panels. It can be seen that the measured populations of vibrational levels ν=0-2 increase after each discharge pulse, peaking approximately 20 μs, 7 μs, and 2 μs after the pulse, respectively. This is consistent with the characteristic time for the V-V exchange with the ground electronic state N₂, the process of Eq. (5), based on the rate coefficients suggested in Ref. [25]. Between the discharge pulses, N₂(A⁢3Σu⁺,ν=0,1) populations decay on a ~10 μs time scale (see panels (a,b)). Comparison with the modeling predictions shows that this decay is controlled by the rapid energy pooling process of Eq. (4), with a nearly gas kinetic rate, as well as by N₂(A⁢3Σu⁺) quenching in collisions with N atoms, the process of Eq. (8). In comparison, the N₂(A⁢3Σu⁺,ν=2) population decays between the pulses considerably more rapid than ν=0 and ν=1 (see panel (c)), due to the V-V exchange with the ground electronic state. It can be seen that N₂(A⁢3Σu⁺,ν=4,5) populations decay much faster, on a ~1 μs time scale, and their decay rate is underpredicted by the kinetic model (see panels (d,e)), indicating that the V-V rates for the high vibrational levels may be higher than recommended in Ref. [25].

From the data taken during the 20-pulse and especially 100-pulse bursts, as well as from the modeling predictions, it can be seen that the peak N₂(A⁢3Σu⁺, ν=0-2) populations achieved after each discharge pulse is gradually decreasing during the burst (see Fig. 11(f-h)). The reduction of N₂(A⁢3Σu⁺,ν=4,5) populations over the 20-pulse burst, not plotted in Fig. 11, is comparable to those of ν=0-2. Since the coupled pulse energy during the burst remains nearly the same (see Fig. 2(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 N₂(A⁢3Σu⁺) number density in the plasma and afterglow. Therefore, comparison of the time-resolved N₂(A⁢3Σu⁺) population measurements during the long discharge bursts with the modeling predictions also provides indirect insight in the absolute, time-resolved N atom number density.

As stated in Section 3, in the present modeling calculations we assume that N₂ dissociation in the discharge occurs in an additional channel of the rapid energy pooling process of Eq. (4). Without this process, the baseline kinetic model significantly underpredicts both the N₂(A⁢3Σu⁺) decay rate between the discharge pulses and its gradual reduction during the burst, the latter by about a factor of 3 to 5. Therefore the present data indicate that the net rate of N₂ dissociation in a ns pulse dielectric barrier discharge operated at a high pulse repetition rate is significantly higher.
compared to the rate of electron impact dissociation from the ground electronic state. Allowing the
dissociation channel in the energy pooling of Eq. (4), with the relative weight of 50% (i.e. the
channel branching ratio of 1 : 2 : 3), results in a much better agreement with the N_2(A^3Σ_u^+,v=0-2)
populations measured during the 100-pulse burst, as illustrated in Fig. 11(f-g)). It can be seen that
the model overpredicts the absolute populations of v=0,1, mostly likely due to the uncertainty in
the nascent N_2(A) vibrational distribution. However, both the rapid decay between the discharge
pulses and the gradual decay during the burst are reproduced well by the model. Additional
TDLAS data taken in nitrogen at a lower pressure of P=150 Torr, and their comparison with the
modeling predictions, indicate the same trend. Note that in our previous work [13], where
vibrational levels of the ground electronic state N_2 were excited selectively in a hybrid ns pulse / RF plasma, it was shown that N_2(X^1Σ_g^+) vibrational excitation has almost no effect on the rate of
N_2(A^3Σ_u^+) quenching.

The accumulation of N atoms and the temperature rise during the burst are illustrated in
Fig. 12. The predicted N atom generation at these conditions varies from 1.0·10^{14} cm^{-3} / pulse
(early in the burst, when the N_2(A^3Σ_u^+,v) populations peak), to 2.5·10^{13} cm^{-3} at the end of the burst,
when N_2(A^3Σ_u^+) is quenched more rapidly by the accumulating N atoms. The N atom number
density predicted at the end of a 100-pulse burst is [N] ≈ 5·10^{15} cm^{-3} (see Fig. 12). The flow
temperature rise predicted by the model is ≈ 1 K / pulse, with the net temperature increase over a
100-pulse burst of ΔT ≈ 100 K (see Fig. 12). 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. 12), higher N atom number densities and flow temperatures can be achieved by
further 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 somewhat with the
burst duration (see Fig. 12), 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^3Σ_u^+,v=1) population during the burst, as the number of pulses is increases from 20
to 100, from 9.3·10^{13} cm^{-3} to 7.4·10^{13} cm^{-3} (see Fig. 11(b,g)).

Adding hydrogen or oxygen to the gas mixture results in a dramatic reduction of N_2(A^3Σ_u^+)
populations, as summarized in Figs. 13-16. Fig. 13 plots the N_2(A^3Σ_u^+,v=0-2) populations during a
20-pulse discharge burst in a 5% H_2/N_2 mixture at P=150 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. 11). Comparison with the modeling predictions (see Fig. 13) indicates that
this difference is caused by the rapid (nearly gas kinetic) N_2(A^3Σ_u^+) quenching by H atoms,
generated by electron impact and by the reactive quenching of the excited electronic states of N_2,
including N_2(A^3Σ_g^+) (see Fig. 14). Accumulation of N and H atoms between the pulses also results in
a gradual reduction of the peak N_2(A^3Σ_u^+) populations during the burst, as well as the
acceleration of their decay rate between the pulses (see Fig. 13). Note that, unlike in pure nitrogen,
the peak N_2(A^3Σ_u^+,v=0) population is now significantly lower compared to that of v=2 (compare
Figs. 13(a,c) and 11(a,c)), since now the v=0 quenching rate exceeds that of its population by the
2-by-1 V-V exchange of Eq. (5). Also, it is apparent that the kinetic model is overpredicting the
v=1 population (see Fig. 13(b)), indicating that adding hydrogen to the mixture changes the nascent
N_2(A^3Σ_u^+,v) population branching ratio.
From Fig. 14, it can be seen that the predicted H and N atom number densities at the end of the burst are comparable, [H] \approx 3.5 \cdot 10^{15} \text{ cm}^{-3} and [N] \approx 2.6 \cdot 10^{15} \text{ cm}^{-3}, although the H$_2$ mole fraction in the mixture is only 5%. This is expected, since the hydrogen dissociation energy, 4.5 eV, is significantly lower than that of N$_2$, 9.8 eV. 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 N$_2$-H$_2$ gas mixtures.

Figure 15, which compares the experimental and predicted N$_2$(A$^3\Sigma_u^+$, v=0-2) populations during a 20-pulse discharge burst in a 10% dry air / N$_2$ mixture at P=150 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 O$_2$, although the presence of residual ozone and the gradual accumulation of O atoms during the burst also contribute to the net quenching rate. O atoms are generated both by electron impact and by reactive quenching of N$_2$ excited electronic states, including N$_2$(A$^3\Sigma_u^+$), by O$_2$. From Fig. 16, it can be seen that the predicted O atom number density at the end of the burst, [O] \approx 5.1 \cdot 10^{15} \text{ cm}^{-3}, exceeds that of N atoms, mainly due to the reactive quenching and the lower contribution of the pooling process to N$_2$ dissociation.

Figure 17 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/N$_2$ mixture at P=250 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 that of NO(A$^2\Sigma$, v) emission, which demonstrates the dominant role of a near-resonance state-specific energy transfer process

\[
N_2(A^3\Sigma_u^+) + NO(X^2\Pi) \rightarrow N_2(X^1\Sigma_g^+) + NO(A^2\Sigma)
\]  

in the NO UV emission at these conditions. Finally, Fig. 18 compares the experimental and the predicted N$_2$(A$^3\Sigma_u^+$, v=0-2) populations in a 1000 ppm NO/N$_2$ mixture during a 20-pulse discharge burst at P=150 Torr, using the state-specific quenching rates by NO from Ref. [31]. The use of the quenching rates from Ref. [32], which are significantly faster, especially for v=0,1, results in a noticeable overprediction of their decay rates. The predicted N$_2$(A$^3\Sigma_u^+$, v=0-2) population decay rate somewhat decreases during the discharge burst, due the NO number density reduction by the rapid scavenging of N atoms generated in the plasma,

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

which reduces the combined number density of the rapid quencher species (NO, N, and O). Finally, comparison of the measurement results in N$_2$-O$_2$ and N$_2$-NO provides additional evidence that the mixture composition strongly affects the N$_2$(A$^3\Sigma_u^+$, v) population branching ratio, since the v=1 population is strongly overpredicted in both cases, up to a factor of 2 (see Fig. 15(b), 18(b)).

5. Summary

In the present work, single-pass and double-pass Tunable Diode Laser Absorption Spectroscopy (TDLAS) diagnostics are used for measurements of absolute, time-resolved populations of N$_2$(A$^3\Sigma_u^+$, v=0-5) vibrational levels in ns pulse discharge plasmas in nitrogen-based
molecular gas mixtures. The plasma is generated by the repetitively pulsed, double dielectric
barrier, ns discharge bursts across a 10 mm gap in a plane-to-plane geometry, operated at a pulse
repetition rate of 100 kHz and burst repetition rate of 30 Hz. The discharge exhibits good
reproducibility pulse-to-pulse and burst-to-burst, generating a diffuse plasma with well-defined
boundaries, at pressures of up to at least 400 Torr. Sustaining the plasma at higher pressures is
limited by the pulse peak voltage (up to 30 kV), such that breakdown no longer occurs as the
pressure is increased further. However, a stable plasma in nitrogen is sustained across a smaller
gap of 5 mm up to atmospheric pressure. \( N_2(A^3\Sigma_u^+, v=0-5) \) populations and the gas temperature are
inferred from the comparison of the experimental and synthetic absorption spectra. The detection
limit of the present measurements is approximately \( 0.5 \cdot 10^{12} \text{ cm}^{-3} \) (double-pass absorption of \( 10^{-3} \)).

The results of TDLAS measurements in nitrogen and in \( \text{H}_2-\text{N}_2 \), \( \text{O}_2-\text{N}_2 \), and NO-\( \text{N}_2 \) 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 confirmed that the
dominant process of \( N_2(A^3\Sigma_u^+, v) \) generation during the discharge pulse is the collisional quenching of
\( N_2(B^3\Pi_g) \) electronic state, followed by the cascade population redistribution to the lower
vibrational levels by the vibration-vibration exchange with \( N_2 \) in the ground electronic state. In
nitrogen, the rate of \( N_2(A^3\Sigma_u^+) \) decay is controlled by the energy pooling (rapid decay between the
discharge pulses) and by the collisional quenching by \( \text{N} \) atoms (gradual decay during the entire
discharge burst). Comparison with the modeling predictions indicates that electron impact
dissociation of \( \text{N}_2 \) from the ground electronic state significantly underpredicts the yield of \( \text{N} \) atoms
in pure nitrogen, consistent with our previous work [13]. Since the role of \( \text{N}_2 \) dissociation via the
stepwise excitation of electronic states at the present conditions is insignificant, this suggests that
additional dissociation may occur during the rapid pooling process in collisions of two \( N_2(A^3\Sigma_u^+) \)
molecules. Indeed, adding this process to the kinetic model results in a much better agreement of
the modeling predictions with the time-resolved \( N_2(A^3\Sigma_u^+, v) \) populations measured during a
discharge burst. The rate of this process assumed in the present work is 50% of the total pooling
reaction rate coefficient of \( 4 \cdot 10^{-10} \text{ cm}^{-3} \) [14]. Additional evidence of the existence of this major
dissociation channel in the nitrogen plasma would require absolute, time-resolved measurements
of both \( \text{N} \) atoms and \( N_2(A^3\Sigma_u^+, v) \) populations at the same conditions, and their comparison with
the kinetic modeling predictions. These measurements are currently underway.

In the mixtures of nitrogen with \( \text{H}_2 \) and \( \text{O}_2 \), the decay of \( N_2(A^3\Sigma_u^+, v) \) populations is
significantly faster, mainly due to the collisional quenching by \( \text{H} \) atoms and \( \text{O}_2 \) molecules,
respectively. Again, the present data can be used to infer the \( \text{H} \) atom number density. The present
results indicate that high-pressure, high repetition rate, volume-scalable ns pulse discharges can
be used for efficient generation of atomic species for plasma chemical and plasma catalysis
syntheses. In a 1000 ppm NO-\( \text{N}_2 \) mixture, it is shown that the dominant \( N_2(A^3\Sigma_u^+) \) decay process is the rapid energy transfer to NO, resulting in its electronic excitation and UV emission (NO \( \gamma \) bands). After the discharge pulse, both the time-resolved \( N_2(A^3\Sigma_u^+, v) \) populations and the \( \gamma \) band
emission decay on the same time scale.

The diagnostics used in the present work can be used for the accurate characterization of
both high-pressure, low-temperature gas discharge plasmas and high-temperature nonequilibrium
hypersonic flows generated in shock tubes, expansion tubes, and shock tunnels. Time-resolved
TDLAS measurements in pulsed, short run-time flow facilities are feasible using rapidly tuned
Distributed Feedback (DFB) diode lasers, with the scan time across an absorption line of several
\( \mu \text{s} \) [33]. The sensitivity of the present measurements is estimated to be sufficient for the detection
of N$_2$(A$^3\Sigma_u^+$) in a hypervelocity stagnation flow behind a Mach 7 bow shock in nitrogen and air at the conditions of Ref. [34].

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Figure 1. Schematic of the Tunable Diode Laser Absorption Spectroscopy experimental setup, (a) single-pass, and (b) double-pass.
Figure 2. (a) Voltage and current waveforms, (b) instantaneous power and coupled energy waveforms in a ns pulse discharge in nitrogen at P=250 Torr, pulse repetition rate of 100 kHz, and burst repetition rate of 30 Hz; (c) Coupled pulse energy vs. pulse number in the train at 250 Torr and 150 Torr (error bars indicated standard deviations of multiple measurements).
Figure 3. Single-shot, broadband plasma emission images taken during a 100-pulse discharge burst at the conditions of Fig. 2(a), (a) side view and (b) end view. Nitrogen, P=250 Torr, camera gate 300 ns.
Figure 4. 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% H\textsubscript{2} / N\textsubscript{2} mixture, camera gate 300 ns.

Figure 5. 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 / N\textsubscript{2} mixture, camera gate 300 ns.
Figure 6. TDLAS scans of (a) 5 rotational lines in the $\text{N}_2(B_3\Pi_g, v'=2 \rightarrow A_3^3\Sigma_u^+, v''=0)$ band, and (b) a single rotational line in the $\text{N}_2(B_3\Pi_g, v'=3 \rightarrow A_3^3\Sigma_u^+, v=1)$ 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 7. TDLAS scans of (a) 5 rotational lines in the $\text{N}_2(B_3\Pi_g, v'=2 \rightarrow A_3^3\Sigma_u^+, v''=0)$ band, and (b) a single rotational line in the $\text{N}_2(B_3\Pi_g, v'=3 \rightarrow A_3^3\Sigma_u^+, v''=1)$ 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 8. (a) Variation of the Lorentzian Full Width at Half Maximum (FWHM) with pressure at 300 K; (b) Pressure broadening coefficient vs. temperature for the $N_2(B^3\Pi_g, v'=2 \leftrightarrow A^3\Sigma_u^+, v''=0)$ Q$_{11}(12)$ spectral line. The pressure broadening coefficient inferred from the data is $2\gamma(T) = 4.79 \left( \frac{300}{T(K)} \right)^{0.61} \text{GHz} \text{ atm}^{-1}$.

Figure 9. (a) Comparison of time-resolved Second Positive System (SPS) band, $N_2(C^3\Pi_u, v'=0 \rightarrow B^3\Pi_g, v''=0)$, and First Positive System (FPS) band, $N_2(B^3\Pi_g, v'=2 \rightarrow A^3\Sigma_u^+, v''=0)$, emission intensity with $N_2(A^3\Sigma_u^+, v)$ populations during a single pulse ns discharge. (b) $N_2(A^3\Sigma_u^+, v)$ populations during a ns pulse discharge and the afterglow. Nitrogen, P=250 Torr.
Figure 10. (a) Different $N_2(A^3\Sigma_u^+,v)$ branching ratios tested in the kinetic model; (b) Time-resolved absolute populations of $N_2(A^3\Sigma_u^+,v=0-5)$ vibrational levels and $N$ atoms, predicted using an “empirical fit” branching ratio. Single-pulse ns discharge and the afterglow in nitrogen at $P=250$ Torr.
Figure 11. Time-resolved absolute $N_2(A^3\Sigma_u^+,v)$ populations during a ns discharge burst and the afterglow in nitrogen at P=250 Torr: (a-e) 20-pulse burst, and (f-h) 100-pulse burst.
Figure 11. Time-resolved absolute $N_2(A^3\Sigma_u^+,v)$ populations during a ns discharge burst and the afterglow in nitrogen at $P=250$ Torr: (a-e) 20-pulse burst, and (f-h) 100-pulse burst.

Figure 12. Time-resolved N atom number density and temperature, predicted by the model at the conditions of Fig. 11 (20-pulse and 100-pulse bursts in nitrogen at $P=250$ Torr). Lines, modeling predictions, symbols, experimental data.
Figure 13. Time-resolved absolute $N_2(A^3\Sigma_g^+,v)$ populations during a 20-pulse discharge burst and the afterglow in 5% H$_2$/N$_2$ at P=150 Torr.

Figure 14. Time-resolved N and H atom number densities and temperature, predicted by the model at the conditions of Fig. 13 (20-pulse discharge burst in 5% H$_2$/N$_2$ at P=150 Torr).
Figure 15. Time-resolved absolute $N_2(A^3\Sigma_u^+,v)$ populations during a 20-pulse discharge burst and the afterglow in a 10% dry air / $N_2$ mixture at P=150 Torr.

Figure 16. Time-resolved species number densities and temperature, predicted by the model at the conditions of Fig. 15 (20-pulse discharge burst in a 10% dry air / $N_2$ mixture at P=150 Torr).
Figure 17. Comparison of $N_2(A^3\Sigma_u^+, v=0,1)$ absolute number densities and NO($A^2\Sigma, v=0,1$) relative emission intensities during after a single-pulse ns discharge in 1000 ppm NO/N$_2$ mixture at $P=250$ Torr.

Figure 18. Time-resolved absolute $N_2(A^3\Sigma_u^+, v)$ populations during a 20-pulse discharge burst and the afterglow in a 1000 ppm NO / N$_2$ mixture at $P=150$ Torr.